United States Environmental Protection Agency

Air and Radiation (EN-341W)

EPA340/1-91-008
September 1991

EPA

Manual for Coordination of VOC Emissions Testing Using EPA Methods 18, 21, 25, and 25A

EPA 340/1-91-008

MANUAL FOR COORDINATION OF VOC EMISSIONS TESTING USING EPA METHODS 18, 21, 25, AND 25A

U.S. Environmental Protection Agency
Office of Air and Radiation
Stationary Source Compliance Division
Washington, D.C. 20460

September 1991

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

CHAPTER 1
INTRODUCTION

Under current environmental regulations, a plant or facility that emits volatile organic compounds (VOCs) into the atmosphere must maintain emissions at or below certain levels, as set forth in the applicable Federal, State, and local standards. Compliance testing, in which emissions are sampled while the plant operates under those normal maximum operational levels which are expected to produce maximum emissions, is the means by which emissions are documented and permits to operate are obtained. Agency personnel observing the execution of compliance testing, and reviewing the test protocol and compliance test report are "Test Coordinators."*

The purpose of this report is to provide the test coordinator with procedures to (1) identify the data necessary to determine compliance, (2) oversee the compliance test, and (3) review the compliance test report written by the testing firm. This manual is intended to provide guidance to agency representatives with various levels of experience in coordinating VOC compliance tests. A detailed overview of the methods has been provided for the more experienced test coordinator.

While the facility is responsible for the proper conduction of the compliance test, it is the agency representative's responsibility to ascertain that the test is conducted in accordance with established conditions. It is the agency representative's responsibility to ascertain that the test is conducted in accordance with established conditions. The test coordinator determines whether the test protocol, probably prepared by a testing firm and submitted by the facility, will provide the data necessary to determine compliance with a reasonable degree of certainty; conducts a pretest meeting, or other pretest communication, to finalize the test conditions; coordinates the compliance test; and reviews the data submitted in the compliance test report.

A performance test consists of the following steps:

1. The source owner/operator notifies the agency (responsible for determining compliance) of the proposed test.
2. The proposed test plan is submitted to the agency.
3. A pretest meeting, or in some circumstances a pretest teleconference, is held at the affected facility to finalize the test conditions.
4. The conditions established at the pretest meeting are formally documented in writing by the agency, by letter, or a form suitable for this purpose, or other acceptable means.

---

*The use of this terminology (i.e., "Test Coordinators") instead of the more commonly used terminology "observers," reflects the expanded role, in addition to observing the actual test, of EPA representatives in having a test performed in an acceptable manner.

5. The performance tests are conducted as coordinated by the agency representative.
6. Preparation of a report by the agency coordinator to document the events concerning the tests.
7. Receipt and review of the test report and documentation of the official test results.

This manual deals with the coordination of compliance testing for volatile organic compounds. A volatile organic compound (VOC) is defined in 40 CFR Subpart A, General Provisions, 60.2, as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions or which is measured by a reference method, an equivalent method, or an alternative method; or which is determined by procedures specified under any subpart. Negligibly photochemically reactive solvents used in inks to decrease drying time or other purposes do not contribute to the total VOC emissions tally. These materials should not count toward VOC emission levels if they are "exempt" from the applicable regulation. These negligibly-reactive compounds shall not be considered VOC if the amount of such compounds can be and is accurately quantified. The EPA considers the following organic solvents to have negligible photochemical reactivity, and therefore does not consider them to be VOCs.

- Methane
- Ethane
- 1,1,1-Trichloroethane (methyl chloroform)
- Methylene chloride (dichloromethane)
- Trichlorofluoromethane (CFC-11)
- Dichlorodifluoromethane (CFC-12)
- Chlorodifluoromethane (CFC-22)
- Trifluoromethane (CFC-23)
- Trichlorotrifluoroethane (CFC-113)
- Dichlorotetrafluoroethane (CFC-114)
- Chloropentafluoroethane (CFC-115)
- 1,1,1-Trifluoro 2,2-dichloroethane (HCFC-123)
- 1,1,1,2-Tetrafluoroethane (HFC-134a)
- 1,1-Dichloro 1-fluoroethane (HCFC-141b)
- 1-Chloro 1,1-difluoroethane (HCFC-142b)
- 2-Chloro-1,1,1,2-tetrafluoroethane (HCFC-124)
- Pentafluoroethane (HFC-125)
- 1,1,2,2-Tetrafluoroethane (HFC-134)
- 1,1,1-Trifluoroethane (HFC-143a)
- 1,1-Difluoroethane (HFC-152a)

- Perfluorocarbon compounds which fall into these classes: (1) cyclic, branched, or linear, completely fluorinated alkanes, (2) cyclic, branched, or linear, completely fluorinated ethers with no unsaturations, (3) cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations, and (4) sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine

Many States also do not consider some or all these materials to be VOCs.

Chapter 2 of this report provides the coordinator with procedures and references for establishing the test objectives. Chapter 3 discusses the pretest survey and the procedures for coordinating the compliance test. Chapters 4, 5, 6, and 7 present sampling and analysis observation procedures for Methods 18, 21, 25, and 25A, respectively. Chapter 8 presents review procedures for the compliance test report submitted by the facility. The test coordinator must be familiar with the regulations and the test methodology.

CHAPTER 2
ESTABLISHING TEST OBJECTIVES

Under Federal regulations, the facility is required to provide at least thirty days prior notice of the scheduled compliance test. The requirement for submission of a proposal test protocol is usually established by the agency. To develop the test protocol and conduct emissions measurements, the facility usually retains the services of a testing firm. The test protocol is used as a starting point in establishing test conditions. The test coordinator reviews the test protocol, requests changes if necessary, and approves the final test protocol. This chapter provides the procedures for establishing the test objectives and for determining the acceptability of the written test protocol.

2.1 REVIEW OF APPLICABLE REGULATIONS AND BACKGROUND INFORMATION

The test coordinator must be familiar with the regulations which are applicable to the facility to be tested. A more thorough understanding of all applicable regulations and guidelines typically can be obtained through discussions with each of the applicable agency groups. Typical agency groups (agency organizations vary) and types of information needed from these groups are discussed below. The test coordinator generally has copies of the regulations and is usually familiar with them.

Compliance Group - Copies of all applicable regulations should be obtained. Previous compliance history and current compliance problems should be determined.

Permit Group - The test coordinator should obtain a copy of the existing permit to operate, if one exists, and a copy of the permit to construct. These permits are necessary because, depending on the agency, they list process and control equipment operating requirements. All conditions and requirements for an existing permit should be understood. If no previous operating permit exists, the construction permit is used.

Inspection or Enforcement Group - The test coordinator should determine what measurements and other parameters are necessary to establish representative facility operations.

Obtaining Background Information - If needed, the test coordinator may obtain additional background information on testing methodology and process and control equipment operations through State agency personnel, EPA technical manuals, and EPA contact personnel. EPA has a computer bulletin board which agency test coordinators can use to obtain background information. The Emissions Measurement Technical Information Center (EMTIC) computer bulletin board service (BBS) can be reached by calling, on a computer modem, (919) 541-5742. A listing of EPA manuals and contact personnel related to emissions measurement can be found on the EMTIC BBS. The agency emissions test coordinator must be a registered user of the BBS.

The agency contacts and the EMTIC BBS may provide the following types of information:

1. Background information on how the regulation was established and the intent of the regulation.
2. Legal determinations and policy memorandums for facility operations, interpretation of the regulation, and testing methodology.
3. Problems generally associated with facility operation and testing methodology.
4. Process operational procedures and control equipment operation procedures that provide short term emission reductions. These procedures are occasionally used by source personnel to reduce emissions during compliance testing.
5. Compliance test reports from similar sources.
6. Source history information. This will include all permits, compliance test reports, and inspections. If the facility has been cited for noncompliance, it is extremely important that the test coordinator be aware of these actions and their status and that no discussion with facility personnel regarding these problems occur without prior knowledge of the agency.

2.2 DETERMINATION OF COMPLIANCE LIMITS

The compliance limit will be specified in the applicable regulations or permit. It is critical that the test coordinator understand the measurement units of the applicable emission standard or limit and how they are determined. If process rate or weight is used in expressing the limit, then the definitions for process rate or weight must be understood. Many regulations exempt certain compounds from the limits (e.g., methane or ethane may be exempted as VOC). These exemptions should be determined and understood.

For limits expressed as a concentration, the units of the standards are generally parts per million by volume (ppmv). If the emissions are expressed as parts per million by weight (ppmw), significantly different values will be obtained. Also, the standards typically require (1) correction of measurements expressed as parts per million by volume to a dry basis at a standard temperature and pressure and (2) no dilution air.

The EPA Methods for VOC determination produce emission results on several different units of measurement bases. Therefore, results from Methods 18, 21, 24, 25, and 25A may not be directly comparable, unless additional procedures and calibrations are performed. Emission measurements, uncontrolled emissions, and methods for measuring collection efficiency, **must** yield data on the same unit basis. The basis of results for EPA Methods for VOC determination and a comparison of VOC data obtained by the use of different methods are discussed later.

2.3 DETERMINATION OF DATA NECESSARY TO SHOW COMPLIANCE

The test coordinator should determine whether the test protocol submitted to the agency provides the framework to collect data necessary to demonstrate compliance with a reasonable degree of certainty. The test coordinator should: (1) understand the requirements of the compliance test and (2) match requirements of the compliance test to the specifications in the written test protocol.

The test coordinator may also find it helpful to use the pretest survey form, presented and discussed in Chapter 3, to outline the requirements of the compliance test. A partial listing of necessary data requirements is presented in Table 2-1, page 2-4.

2.4 BASIS AND COMPARISON OF RESULTS FOR EPA METHODS 18, 21, 25, AND 25A

When the results from two VOC measurement methods are to be compared, the test coordinator must understand the unit basis of method results (type of calibration standards and emissions correlation to calibration standards) for Methods 18, 21, 25, and 25A. Method 18 identifies only those compounds for which sampling and analysis is specifically conducted; results are expressed in terms of concentration of those specific organic compounds. Method 18 does not identify or quantify unknown compounds.

Methods 21, 25, and 25A do not provide results on an organic compound specific basis (i.e., the exact organic compounds measured cannot be determined from the emission results); measurement results from these methods are expressed in terms of the calibration standard (e.g., ppm as propane or ppm as carbon) or as in the case of Method 24, on a total organic basis (percent volatile organics).

When the facility proposes the use of two different methods for collection efficiency determination, the test coordinator must determine the acceptability of the testing protocol.

The sampling and analytical methods used at each sampling location must provide emission results on the same unit measurement basis.

Ensuring that measurements are obtained on the same unit measurement basis can be complicated. When the test coordinator is uncertain of procedures, the EMTIC representative who is listed as the VOC contact can be consulted.

TABLE 2-1. PARTIAL LISTING OF DATA FOR COMPLIANCE TEST PROTOCOL

1. Safety Considerations

   - Required by EPA
   - Required by plant
   - Recommended by OSHA

2. Process

   - Facility identification and description
   - Parameters to be monitored and recorded (including recording times time intervals)
   - Acceptable range for each parameter monitored
   - Raw materials to be used
   - Fuel
   - Process samples to be taken and analyzed
   - Process rate
   - Mode of operation

     * Manual or automatic operation
     * Cleaning and auxiliary systems
     * Normal period for process cycle
     * Materials processed - coverage and/or shape
     * Diversion or circumvention of pollutants from air pollution control equipment
     * Operational personnel (Must be the same as scheduled for normal day-to-day operations of facility)

   - Instruments to be added and/or calibrated

3. Control Equipment

   - Description of control equipment
   - Parameters to be monitored and recorded (including recording times)
   - Acceptable values for each parameter
   - Control equipment effluent samples to be taken and analyzed

TABLE 2-1. PARTIAL LISTING OF DATA FOR COMPLIANCE TEST PROTOCOL (Concluded)

- Mode of operation
  - Manual or automatic operation
  - Collected pollutant removal cycle
  - Cleaning cycle
  - Auxiliary or gas conditioning systems
- Instruments to be used in monitoring operation
- Instruments used in monitoring operation to be calibrated

4. Measurement Methodology

- Basis of results
- Sample run time
- Portion of the process cycle to be tested
- Portion of the control equipment cycle to be tested
- Sampling locations with drawing showing bends, obstructions, control equipment, etc.
- QA audit samples to be provided by agency
- Fugitive emissions (not discussed in this manual)
- Transfer efficiency (not discussed in this manual)
- Sampling procedures to be used (emission, process and control equipment samples)
- Hood capture efficiency (not discussed in this manual)
- Material balance (not discussed in this manual)
- Sampling procedures not required by method but required by control agency
- Analytical procedures to be used (emission, process and control equipment samples)
- Analytical procedures not required by method but required by control agency
- QA/QC procedures required (e.g., performance audit samples)
- Report format and required data
- Time restrictions for submittal of report

CHAPTER 3
PREPARATION FOR AND OBSERVATION OF COMPLIANCE TEST

This Chapter addresses preparation and procedures for the on-site observation of the compliance test. Preparation for the test observations includes scheduling personnel, scheduling equipment and ordering performance audit gases. A pretest meeting should be conducted at the facility at least 15 days prior to the commencement of testing. This gives the test coordinator the opportunity to inspect the facility, including any air pollution control equipment and test location, determine which operational parameters should be monitored, and obtain information to finalize the test conditions. Preparation also includes conducting a pretest survey when necessary. The sampling procedures common to all EPA VOC Methods are discussed in Section 4 of this chapter. The specific sampling and analytical procedures for Methods 18, 21, 25, and 25A are presented in Chapters 4, 5, 6, and 7, respectively.

Observation of VOC compliance tests is typically more difficult than for tests for other criteria pollutants. Because of the complex nature of compliance testing for VOC, Method 18 recommends that the tester conduct site specific and, if applicable, compound specific pretest preparations. The test coordinator may also find it useful to conduct a pretest survey.

The function of the test coordinator is to ascertain that the test are conducted in accordance with the conditions established at the pretest meeting. The test coordinator has the authority to require changes in the testers' procedures if they are not in accordance with the regulatory requirements or not in agreement with the established conditions.

The test coordinator's principle function is to evaluate the representativeness of compliance testing. In other words, the compliance test results should represent emissions typical of maximum operating conditions which produce maximum emissions. Representativeness is typically evaluated in terms of five criteria; if any of the criteria are not met, the compliance test is considered nonrepresentative:

1. Process and control equipment must be operated in such a manner as to produce representative samples of controlled and uncontrolled emissions. By measuring the emissions before and after control devices, the removal or control efficiency can be determined.
2. Locations of the sampling ports and points must provide samples which are representative of the total uncontrolled (if applicable) and controlled process emissions.
3. Samples collected in a sampling train must be representative of the concentration(s) at the sampling point(s).
4. Samples recovered and analyzed must be representative of samples collected in the sampling train.

5. Reported results must be representative of facility operations and the samples recovered and analyzed.

3.1 NOTIFICATION OF COMPLIANCE TEST

For Federal New Source Performance Standards (NSPS), the general requirements for performance (compliance) testing are presented in Title 40 Part 60.8 of the Code of Federal Regulations. The requirements are as follows:

1. Performance (compliance) testing within 60 days after achieving the maximum production rate at which the facility will operate, but not later than 180 days after initial startup.
2. Performance testing and data reduction in accordance with the test methods and procedures contained in each applicable subpart unless the Administrator allow one of the four options listed.
3. Performance testing conducted under such conditions as the Administrator shall specify to the plant operator based on representative performance of the affected facility.
4. At a least 30 days prior notice of any performance testing to the Administrator.
5. Provision of (1) sampling ports, (2) safe sampling platforms, (3) safe access to sampling platforms, and (4) utilities for sampling by the facility.
6. Three separate runs per compliance test. In the event of the items listed in 60.8(f) the Administrator may accept two sample runs as a test.

The Federal requirements ensure that the agency is notified prior to the test and that the sampling site is acceptable. Many States have developed similar guidelines to ensure proper notification of compliance tests. Testing arrangements and scheduling of staff and equipment for the observation are also facilitated by an agency guideline. A typical State agency guideline requires or includes the following:

1. A testing protocol submitted by the facility.
2. 30 Day notification of testing.
3. Testing to be conducted during normal agency business hours.
4. Operational conditions during testing.
5. Quality assurance requirements for the compliance testing (e.g., performance audit samples).
6. Testing procedures required by the State which are deviations from the EPA Methods.
7. Compliance test report format (see Chapter 8 for example format).
8. Safety and sampling access requirements.

Notification 30 days prior to the test and submission of a written test protocol allows the test coordinator sufficient time to review the test protocol, conduct a pretest

meeting to establish that the requirements for compliance testing will be met, and order performance audit materials.

Performance Audit Materials - The test coordinator must obtain the proper audit materials and/or devices. The testing firm analyzes the audit materials on-site as part of the compliance test. To select the proper audit gas cylinder(s), the test coordinator will consult the applicable method, and written test protocol supplied by the tester to determine the type (specific organic compound) and proper concentration range of the audit gas to order. Table C-1, page C-4, lists audit gases available from EPA for common target organic compounds. Availability and ranges of audit gases can be determined by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance and Technical Support Division
Research Triangle Park, North Carolina 27711
Attention: Audit Cylinder Gas Coordinator

For audit gases obtained from a commercial gas manufacturer, ensure that the manufacturer has (1) certified the gas in a manner similar to the procedure described in 40 CFR Part 61, Appendix A, Method 106, Section 5.2.3.1 and (2) obtained an independent analysis of the audit cylinder to verify that the audit gas concentration is within 5 percent of the manufacturer's stated concentration.

To accurately assess the emission measurements, the performance audit sample concentrations should fall within the range of approximately 50 to 200 percent of the expected emissions concentration. Interpretation of audit results is discussed in Chapter 8. **Performance audit gases with concentrations 5 times greater or 5 times less than the expected emission value or an organic compound different than that being measured should be not used.**

3.2 CONDUCT PRE-TEST SURVEY

Prior to compliance testing, the affected facility is often visited by a representative of the testing firm and the test coordinator. This information gathering visit is referred to as the pretest survey. Agencies should be strongly urged to conduct pretest meetings at the affected facilities well in advance of the test date. During the pretest survey of the process and control equipment, the test coordinator may find it useful to conduct screening measurements to (1) establish some operating baseline values for process and air pollution control equipment and (2) to determine problems with the methods to be applied later in the compliance test. The test coordinator may prepare a form of information to gather during the pretest survey. An example of a general pretest survey checklist is shown in Figure 3.1, page 3-13. Because of the complex nature of most organic processes, the test coordinator may provide the testing firm with the example

checklist to be completed to enhance the probability that the testing will be performed as required.

Since most organic gases are invisible, conducting independent testing to estimate the emission levels and other key parameters using a portable organic analyzer (EPA Method 21 instrumentation) can be extremely useful. Appendix B provides an example of how these instruments can be used.

One of the primary concerns for any organic sampling program must be safety. The test coordinator should always question the facility representative concerning general plant safety requirements and safety in regard to sampling. Every test protocol should address the safety considerations involved in performing the test. There are numerous safety considerations involved in organic sampling, particularly regarding health effects and explosion hazards, however, it is beyond the scope of this manual to discuss each one in detail. It cannot be over-emphasized that the test coordinator must always be aware of the safety hazards.

3.3 FINALIZING COMPLIANCE TEST PROTOCOL

Before the compliance testing, it is recommended that the agency test coordinator meet with a representative of the testing firm, and a facility representative. At this meeting the compliance test protocol can be finalized, the baseline (representative) facility operating conditions can be established, and the testing schedule can be coordinated. The pretest meeting agreements, or conditions established, should be documented in a final letter from the agency test coordinator to the facility owner/operator, or on a form/checklist completed by the test coordinator.

The testing firm representative must know the exact sampling procedures to be used, the minimum data and reporting requirements, and the conditions that constitute an invalid test. If the test coordinator will use a checklist to monitor sampling and analytical procedures, it is beneficial to provide the checklist to the testing firm to ensure that all required steps will be completed. Likewise, the facility representative should explain what process and control equipment data will be recorded, the intervals of data collection, the raw materials to be used, tested, and the conditions that could constitute an invalid test. Since it is the facility representative's responsibility to obtain the baseline operational parameters, it is the agency's responsibility to designate which parameters will be monitored and recorded. Execution of the compliance test in accordance with the established test protocol should constitute a valid test.

The lines of communication for the compliance test should be defined. It is recommended that all official communications regarding facility operations, testing methodology, and agency policy be limited to the test coordinator, facility representative, and testing firm representative. It can be useful to know the names of the supervisors of these individuals in the event of poor cooperation or when requests for information are questioned.

As a minimum for relatively simple processes, a teleconference should be conducted to establish the test conditions, followed by formal documentation. In all cases, whether the process and sampling is simple or complex, it is the test coordinator's responsibility to be certain that all details of the test procedure are understood and accepted before the test begins.

Procedures common to most types of VOC testing and relevant to on-site observation are presented below. The sampling and analytical procedures specific for Methods 18, 21, 25, and 25A are addressed in Chapters 4, 5, 6, and 7, respectively.

3.4 PROCEDURES COMMON TO MOST TYPES OF VOC TESTING

Determination of measurement errors, measurement of flue gas flow rate, moisture determination, organic compound identification by retention time, proper gas chromatography (GC) peak resolution, and application of proper response factors are required for most VOC testing. Each is discussed below.

3.4.1 Measurement Errors

The procedure for determining pollutant emission rates by stack sampling involves measurement of a number of parameters. Errors of measurement associated with each parameter combine to produce an error in the calculated emission rate. Measurement errors are of three types: bias, blunders, and random errors. Bias errors, usually a result of poor sampling and analytical technique, cause the measured value to differ from the true value in one direction. Many bias errors can be eliminated through proper calibration of the equipment. Most blunders occur during sampling, sample transport, and sample preparation for analysis. Elimination of blunders should be a main concern. Random errors (precision), which result from a variety of factors, cause measured values to be either higher or lower than the true value. Such errors result from the inability of sampling personnel to read scales precisely, poor equipment performance, and lack of sensitivity in measurement devices. The usual assumption is that random errors are normally distributed about the mean or true value and can be represented statistically in terms of probabilities. All methods have some inherent random error (precision).

To make on-site decisions based on the significance of error, the test coordinator must know three things to determine the importance of the error.

1. Does the facility have to prove compliance with the standards (Federal regulations) or does the agency have to prove a violation of the standards (State regulations)?
2. What are the direction and magnitude of any biases?
3. What is the acceptable bias that will be allowed before rejecting the results?

If a facility is attempting to prove itself in compliance with most Federal regulations, any magnitude of high bias in an outlet emission measurement (measured emissions higher than actual emissions) conclusively showing compliance would be allowed. However, these high biased results might not be valid for use in emissions trading or banking. A low bias in an outlet emission measurement would be acceptable if it did not cause the reported results to show compliance rather than violation. Since the final results are not generally known during the on-site testing, it is preferable for the test coordinator to have a fixed value to apply in allowing or disallowing a test run while on-site. EPA method development testing reports indicate that most VOC test methods have a precision of about 10 percent. A listing of EPA method development reports and the method's precision are on the EMTIC BBS. Therefore, a good rule of thumb for allowing biases determined on-site is up to 10 percent high bias and 5 percent low bias.

When the State or local agency has the burden of proving that the source is in violation with the applicable regulation, any low bias in a measurement (measured results less than the true value) that still proves the source in violation would be acceptable. The low bias will not be challenged by the facility unless the testing does not comply with legal requirements as stated by the applicable test method. When the agency bears the proof of violation, a good rule of thumb for acceptable bias is up to 5 percent high bias and 10 percent low bias. **Again, it should be stressed that for proof of violation, meeting the requirements of the applicable test method is mandatory.**

Errors from the measurement of most sampling parameters have very little effect on the final data results. The test coordinator or tester may be able to calculate the direction and magnitude of a measurement error.

3.4.2 Determination of Flue Gas Flow Rate

For ducts equal to or greater than 12 inches in diameter, the number of sampling points necessary to determine the flow rate is specified by EPA Method 1, Figure 1-2, "Minimum number of traverse points for velocity (nonparticulate) traverses." For ducts less than 12 inches in diameter, EPA Method 1A should be used to determine the point location for velocity measurements. Sampling port locations upstream of air pollution control equipment do not typically meet Method 1 requirements. If a sampling location does not meet minimum requirements and the system is closed with no air entering or leaving, then the flow rate at the outlet location (after control equipment) can be measured and the standardized flow rate used for the inlet location.

Flow rate is determined by EPA Method 2 for large ducts equal to or greater than 12 inches in diameter. Method 2 uses a "S" type pitot tube to determine the average velocity pressure. The velocity pressure and the stack gas molecular weight (from Method 3) and stack gas moisture content (from Method 4) are used to determine the flue gas flow rate. For ducts less than 12 inches in diameter within the temperature range of 0 to 50°C, Method 2A can be used to measure the gas volume flow rate directly

with a gas meter. Method 2B is used to measure gas volume flow rate from gasoline vapor incinerators. This method determines the flue gas flow rate prior to combustion and then calculates flue gas flow rate after combustion based on a carbon balance. Method 2C applies to ducts less than 12 inches in diameter and measures flue gas flow rate with a standard pitot tube instead of a type S pitot tube. Method 2D also applies to ducts less than 12 inches in diameter and uses the same approach as 2A by measuring flow rate directly with a rotameter or orifice plate.

Flue gas flow rates measured using Methods 1 and 2 are typically within 10 percent of the true flow rate values for all the methods shown above (Methods 2A, 2B, 2C, and 2D). Sections 3.0 and 3.1 of EPA's Quality Assurance Handbook, Volume III, EPA-600/4-77-027b, discusses errors associated with velocity measurements.

3.4.3 Moisture Determination

Stack gas moisture content must be determined when (1) flue gas flow rate is determined or (2) stack gas concentration is measured (container sampling or direct interface sampling). The moisture content is used to correct the emission concentration or mass emission rate to a dry basis. EPA Method 4, Section 3.3 of EPA's Quality Assurance Handbook, Volume III, EPA-600/4-77-027b, is used to measure stack gas moisture content. Section 3.3 of the Quality Assurance Handbook, Volume III, provides detailed information on the application of Method 4.

For flue gas streams at or below 60°C (140°F), flue gas moisture content can be determined using wet bulb/dry bulb thermometers and the partial pressure equation shown below. This is an approximation method, as described in Method 4. Obtain the wet bulb/dry bulb temperatures as follows:

1. Moisten the wet bulb thermometer wick with deionized distilled water.
2. Insert thermometers into flue gas stream and monitor wet bulb temperature.
3. When wet bulb temperature has stabilized, record both wet bulb and dry bulb thermometer temperatures.
4. Calculate flue gas moisture content ($\%H_2O$) using the equations listed below.

$$W_2 = \frac{10^{(6.6911 - (3144/(T_w + 390.86)))}}{P_b + (P_g / 13.6)} \qquad \text{Equation 3-1}$$

$$\%H_{2O} = w_2 - (0.000367 \times (T_d - T_w) \times (1 + (T_w - 32)/1571)) \times 100 \quad \text{Equation 3-2}$$

where:

w_2 = Calculated constant, saturation % H_2O at T_w
T_w = Wet bulb temperature, °F
T_d = Dry bulb temperature, °F
P_b = Barometric pressure, in. Hg
P_s = Static pressure of duct, in. H_2O

3.4.4 Organic Compound Identification and Quantification by Gas Chromatography

When using Method 18, the organic compounds to be measured must be known prior to the test. To identify and quantify the major components of the organic compounds **known** to exist in the sample, the retention time of each component is matched with the retention times of the known compounds (the standard reference material or calibration standard) under identical conditions. Separation of organic compounds is performed with gas chromatographic columns, referred to as GC analysis. The retention time is the time between sample injection into the GC and when the organic compound reaches the detector. If GC conditions remain constant, the retention time for each compound will be constant as well, and will serve as the identifying parameter for each peak. Care must be taken to assure that two compounds do not share the same retention time. **The retention time shall be within 0.5 seconds or 1 percent of the retention time of the known compound's (calibration standard) retention time (whichever is greater) to be considered acceptable.** The retention time will vary with (1) type of column or column material, (2) length of column, (3) temperature of column, (4) organic compound, and (5) several other factors. The exact seconds or minutes of the retention time do not matter, except the longer the retention time, the longer the analysis time.

To obtain proper quantitative values, sample peaks (the result of organic compounds as they reach the detector) must be properly separated to enable the detector to analyze only the compound of interest.

Understanding the use of the response factor is important because (1) different detectors can have a different response factor for the same compound, (2) each detector can have a different response factor for different compounds, and (3) the same detector can give a different response factor for the same compound at different conditions. The response factor for each compound on any detector can be determined by dividing the area units from the integrator printout of the standards by the concentration of the standard (area units/ppm of standard). This is done for all concentrations of standards used to calibrate the detector.

Method 25 was developed to eliminate the reduced response factor problem when the organic compounds are unknown. When the organic compounds in the sample are unknown (e.g., after an incineration process), then proper calibration gases cannot be selected. To minimize this problem, Method 25 removes all the elements that give reduced response factors and analyzes the compound as methane in terms of carbon. The results are then reported as parts per million as carbon. Unfortunately, the true molecular weight of the compound is lost and a concentration or mass emission rate cannot be calculated.

A detailed discussion of organic compound identification and quantification is presented in Appendix A.

3.5 ON-SITE OBSERVATION PROCEDURES

The attitude and behavior of the agency test coordinator during the pretest meeting and compliance test, are of the utmost importance. The test coordinator should conduct his/her duties thoughtfully and thoroughly, not disrupting the testers as they perform the tests. The test coordinator must also avoid appearing meek or reluctant to authoritatively represent the agency's interest. If problems with facility operation or sampling are noted by the test coordinator during the compliance test, it is recommended that the test coordinator deal solely with the designated testing firm representative and facility representative; he/she should have a clear understanding with them if it is necessary to communicate with other testing firm personnel or facility operations personnel. Conversely, it may be advisable to refrain from answering inquiries from the testing firm personnel and facility operations personnel concerning agency enforcement policy.

During the test, the test coordinator should check to ensure representative facility operations and adherence to specified sampling procedures. To eliminate the possibility of overlooking necessary checks and to provide the agency with documentation to use in later enforcement actions, the test coordinator can use checklists covering details of process operations, control equipment operations, and sampling procedures. The pretest survey forms previously discussed in Chapter 3.2 can be used to develop the process and control equipment checklist. Sampling checklists for Methods 18, 25, and 25A are presented in the applicable discussions later in this manual.

Since additional measurements are typically not made by the agency, the recommended procedures for conducting on-site observations do not include use of agency conducted screening measurements. Independent screening measurements conducted by an agency during the compliance test are discussed in Appendix B.

The remainder of this Chapter presents a recommended scheme for the test coordinator to use in conducting the test observation.

3.5.1 First Sampling Run

Applicable methods include Method 18, 25, and 25A. If analyses are to be conducted on-site, acceptable results must be obtained for audit sample(s) prior to any field sample analyses. An inspection of the sample recovery area and observation of the sampling train(s) assembly by the test coordinator may be useful in detecting and eliminating errors before they occur. If only one agency test coordinator is present, the schedule below will make the most effective use of observation time. These procedures are provided to assist less experienced test coordinators in establishing a routine for on-site observations. More experienced test coordinators will follow their established routine.

For the first test run, after determining that the facility operations are as specified in the test protocol, the test coordinator should go to the sampling location to observe the test team recording the initial data. The initial sampling system leak check should be observed. When the test coordinator is satisfied with the sampling train preparation and the facility operation, he should allow the testing to begin. He should observe the sampling procedures for the first 15 minutes of sampling and then conduct a check on the facility operations. If the process and control equipment are operating satisfactorily and the data are being recorded as specified, the test coordinator can return to the sampling location to observe the completion of sampling, giving close attention to the final readings and the final leak check. If conducted on-site, the sample analysis should be observed closely during analysis of the audit gas cylinder and the first field sample. The analyst should be required to conduct all necessary calculations to determine the field results in terms of the units of the allowable emissions standard (e.g., ppmv on a dry, standard condition basis for the specified organic compound). All procedures and calculations should be validated by the test coordinator. The distance between the control room, or area, and the test location may create restrictions, which may be compounded by difficult procedures. The agency coordinator again must use sound judgement in determining his/her activities during the tests.

3.5.2 Second Sampling Run

Applicable methods include Method 18, 25, and 25A. If the test coordinator is satisfied that the sampling procedures applied during the first test run are proper, he should spend most of the second run observing process operations, with intermittent checks on the sampling procedures. At the end of the run, the test coordinator should return to the sampling location and observe recording of the final data, the final leak check, transport of the sampling train to the cleanup area, and sample recovery, as applicable.

3.5.3 Third Sampling Run

Applicable methods include Method 18, 25, and 25A. The focus of observation for the third sampling run is based on observations made during the first and second runs. The test coordinator's attempts to determine which element(s), facility operations, sampling procedures, sample recovery procedures, and/or analytical procedures may introduce the greatest degree of error in the emission measurements. The test coordinator should then place the most emphasis on these elements. However, at least a brief check of each should be included in observations made during the third run.

3.5.4 Sample Recovery and Transport

It is important that sample recovery, sample transport, and analysis are conducted according to applicable method procedures and are well-documented. To reduce the possibility of invalidating the test results, all of the samples should be placed in sealed, nonreactive, properly identified containers. The samples must then be delivered to the laboratory and analyzed within the sample stability time specified by the method or determined by the preliminary evaluations. Each container must be uniquely identified, at the time of sample recovery, to preclude the possibility of interchange. The number of each container must be recorded on the sample recovery form (which documents the chain of custody) and the analytical data sheet.

3.5.5 Analysis

When the analysis is conducted at the testing firm's laboratory or an outside laboratory rather than in the field, the use of performance audit samples is the best method for determining if the sampling and analytical procedures were followed. Consult the applicable Method to determine the allowable error (acceptable results) for the audit sample analysis. Acceptable audit sample results cannot assure acceptable results on the field samples. Acceptable audit sample results only indicate that the method was conducted properly and that the calibration standard values were correct.

Analytical errors are generally difficult to detect by reviewing the compliance test report without the aid of performance audit information. Instrument integrators which record and calculate laboratory data should reduce analytical laboratory error. Computers used to calculate emissions data can greatly reduce calculated analytical errors. The laboratory data, calibrations, and calculations must be well-documented and presented in the compliance test report in such a manner that the test coordinator can evaluate the validity of the data using procedures presented in the chapters on the specific methods (e.g., Chapter 4 for Method 18).

3.5.6 Observation Report

Chapter 8 discusses review of the compliance test report. Information gathered during the pretest survey, if performed by the test coordinator, can be useful in reviewing the compliance test report. The test coordinator may also find it beneficial to organize the on-site observations upon returning from the field. The test coordinator should prepare a formal report concerning the performance tests. This is a narrative report with field notes and forms/checklists attached.

I. General Information

Name of company _____ Date _____
Address _____

_____

Contact _____ Title _____
Phone _____
Process to be tested _____

_____

_____

Source ID No. _____ Permit No. _____ Other ID No. _____
Duct or vent to be sampled _____

_____

Current permit requirements (attach copy of operating or other permit)

II. General Plant Requirements

Plant safety requirements _____

_____

Vehicle traffic rules _____

_____

Plant entry requirements _____

_____

Security agreements _____

_____

Potential problems _____

_____

Safety equipment requirements (glasses, hard hats, shoes, etc.)

_____

_____

Can photographs be taken? _____

III. Process and Product Information

Process description _____

_____

_____

Raw material and fuels that produce the potentially highest emissions _____
Raw materials and fuels for compliance test _____

Figure 3.1. Preliminary survey data forms.

Note: These forms apply to Methods 18, 25, and 25A. Some changes or modifications are necessary to them when applying to Method 21.

Will raw materials be sampled and analyzed? _____ If yes, describe procedures

_____

Estimated precision and accuracy of procedures _____
Methods that the agency will use in analysis of raw materials

_____

_____

Do plant records demonstrate the raw materials used? _____
Are the normal recording intervals satisfactory for test? _____
Should these records be kept on file for future inspections? _____
Remarks: _____

_____

Products that potentially produce the highest emissions

_____

Products selected for compliance test

_____

Products sampled and analyzed by source? _____ If yes, describe procedures

_____

Estimated precision and accuracy of procedures _____
Methods that the agency will use in analysis of the products

_____

_____

Do plant records demonstrate the products produced? _____
Are normal record intervals satisfactory for test? _____
Should these records be kept on file for future inspections? _____
Operating cycle
Check: Batch_____ Continuous_____ Cyclic_____
How is the cycle determined? _____
Timing of batch or cycle (hours and/or minutes) _____
Portion of cycle to be tested _____
Portion of cycle represented by each run _____
Maximum process rate or capacity _____
Method to determine process weight or rate _____
Estimated precision and accuracy of method _____
Do any instruments need calibration? _____ changed for test ? _____
Methods that agency will demonstrate to check rate or weight _____

_____

Do plant records reflect process weight/rate? _____
Are normal record intervals satisfactory for test? _____
Should these records be kept on file for future inspections? _____
Other process parameters to be recorded (e.g., temperatures, air flow rate)

Figure 3.1. (Continued)

Parameter ____________ How determined? ________ Recorded ____________
Estimated precision ___________ accuracy _______ calibrated ____________
Acceptable value for parameter ______________ units ______________
Method that agency will conduct to check parameter________________________
Are normal record intervals satisfactory for test? ____________________
Parameter ____________ How determined? ________ Recorded ____________
Estimated precision ___________ accuracy _______ calibrated ____________
Acceptable value for parameter ______________ units ______________
Method that agency will conduct to check parameter________________________
Are normal record intervals satisfactory for test? ____________________
Parameter ____________ How determined? ________ Recorded ____________
Estimated precision ___________ accuracy _______ calibrated ____________
Acceptable value for parameter ______________ units ______________
Method that agency will conduct to check parameter________________________
Are normal record intervals satisfactory for test? ____________________
Parameter ____________ How determined? ________ Recorded ____________
Estimated precision ___________ accuracy _______ calibrated ____________
Acceptable value for parameter ______________ units ______________
Method that agency will conduct to check parameter________________________
Are normal record intervals satisfactory for test? ____________________
Should these records be kept on file for future inspections? __________
Physical arrangement of process - doors open, hoods on, covers on
____
____
Normal mode of process operation: manual ______ automatic __________
Mode of operation for test: manual ___________ automatic ___________
What constitutes a process malfunction? ___________________________
____
How are malfunctions handled with regard to process operation and notification of agency? ____
____
Description of future, planned changes in operations ______________
____
Normal maintenance schedule ______________________________________
____
List of parameter records which should be retained by facility
____
____

Figure 3.1. (Continued)

IV. Air Pollution Control Equipment

Description of control equipment ______________________________

____

Control equipment operations: continuous ________ cyclic __________
How is the cycle determined? ______ length of cycle __________
Do instruments determine cycle? ___ Are control equipment data recorded? ___
Are these records kept on file for future inspections? __________
Portion of cycle to be tested ______________________
Normal mode of operation: manual __________ automatic __________
Mode of operation for test: manual __________ automatic __________
Control equipment parameters to be recorded (temperatures, air flow rate)
Parameter __________ How determined? ________ Recorded __________
Estimated precision __________ accuracy ______ calibrated __________
Acceptable value for parameter ____________ units __________
Method that agency will conduct to check parameter __________
Are normal record intervals satisfactory for test? __________
Should these records be kept on file for future inspections? __________
Parameter __________ How determined? ________ Recorded __________
Estimated precision __________ accuracy ______ calibrated __________
Acceptable value for parameter ____________ units __________
Method that agency will conduct to check parameter __________
Are normal record intervals satisfactory for test? __________
Should these records be kept on file for future inspections? __________
Parameter __________ How determined? ________ Recorded __________
Estimated precision __________ accuracy ______ calibrated __________
Acceptable value for parameter ____________ units __________
Method that agency will conduct to check parameter __________
Are normal record intervals satisfactory for test? __________
Should these records be kept on file for future inspections? __________
Removal procedure and sequence for collected materials __________

____

Collected materials sampled and analyzed: procedures for
Collected material type ______________________________
Collected material volume or weight ______________________

____

Methods used by agency on collected materials: type and/or volume

____

Physical arrangement of control equipment: auxiliary systems or ducts

____

What constitutes a control equipment malfunction?

____

____

Figure 3.1. (Continued)

How are malfunctions normally handled with regard to keeping the process and control equipment on line? _____

_____

Describe future, planned changes in operations

_____

_____

Normal maintenance schedule _____

_____

V. Sampling Site and Procedures

A. Sampling Site

Site description _____

_____

Duct shape and size _____

Material(s) of construction _____

Wall thickness _____ inches

Upstream distance _____ inches _____ No. of diameters

Downstream distance _____ inches _____ No. of diameters

Size of test port(s) _____

Size of access area for test personnel and equipment _____

Hazards _____ Ambient temp _____ °F

B. Properties of Gas Stream

Temperature _____ °C _____ °F, Data source _____

Velocity _____, Data source _____

Static pressure _____ inches H_2O, Data source _____

Moisture content _____ %, Data source _____

Particulate content _____, Data source _____

Gaseous components

N_2 _____	%	Hydrocarbons (ppm)	Toxics/Acids (ppm)
O_2 _____	%	_____	H_2S _____
CO _____	%	_____	HCl _____
CO_2 _____	%	_____	HF _____
SO_2 _____	%	_____	Other _____

C. Sampling Considerations

Sampling and analytical procedures to be used - attach procedures

Specific procedures - use check lists presented with Methods (i.e., Method 18, Chapter 4; Method 21, Chapter 5; Method 25, Chapter 6 and Method 25A, Chapter 7)

Location to set up GC (when applicable) _____

Figure 3.1. (Continued)

Special hazards to be considered _____

_____

Power available at duct _____

Power available for GC (when applicable) _____

Potential problems _____

_____

Specific safety equipment (glasses, hard hats, shoes, etc.)

_____

_____

D. Other Sampling Considerations

Fugitive emissions: how determined _____

How controlled _____

Attach copy of method to determine fugitive emissions if present

Estimated precision and accuracy of method _____

Screening methods to be conducted by agency _____

Hood capture efficiency: how determined _____

Attach copy of method to determine hood capture efficiency

Estimated precision and accuracy of method _____

Screening methods to be conducted by agency _____

Parameters to show continuing compliance with capture efficiency _____

_____

_____

Interval of recording parameter for test _____

Are test parameters to be recorded in future and kept on file? _____

Transfer efficiency: how determined _____

Attach a copy of method to determine transfer efficiency.

Estimated precision and accuracy of method _____

Screening methods to be conducted by agency _____

Parameters to show continuing compliance with transfer efficiency _____

_____

_____

Interval of recording parameter for test _____

Are test parameters to be recorded in future and kept on file? _____

E. Site Diagrams (attach additional sheets if required)

F. Quality Assurance Performance Audit Samples

Quality assurance audit samples taken? _____

Audit samples: proper compound _____ proper range(s) _____

Figure 3.1. (Continued)

G. Emission Measurement Screening Techniques

Detector tubes or other screening techniques used _____

_____

_____

Screening technique conducted: prior to testing _____

during testing _____ between testing _____

Remarks _____

_____

_____

_____

_____

_____

Figure 3.1. (Concluded)

Note: Some of the information in Figure 3.1 may be presented in tabular format, if desired.

CHAPTER 4
MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY -- METHOD 18

4.1 APPLICABILITY

Method 18 as promulgated on October 8, 1983 and revised on February 19, 1987 is a generic method which is structured to analyze approximately 90 percent of the total gaseous organics emitted from an industrial source. This method is used to measure known organics that are in excess of 1 part per million by volume. It does not include techniques to identify and measure trace amounts (less than 1 ppm) of organic compounds, such as those found in building air and fugitive emission sources. Also, this method will not determine compounds that (1) are polymeric (high molecular weight compounds such as dioxins and furans), (2) polymerize before analysis (such as glues or resins), or (3) have very low vapor pressures at stack or instrument conditions (such as anilines).

4.2 METHOD DESCRIPTION

Method 18 is based on extracting a gas sample from the stack at a rate proportional to the stack gas velocity using one of four techniques: (1) withdrawing the gases directly from the stack into the analyzer (direct interface sampling), (2) collecting gases in a container (integrated bag sampling), (3) dilution interface sampling, or (4) collecting gases on a sorbent tube (adsorption tube sampling). The major gaseous organic components of a gas mixture are then separated by gas chromatography, and measured with a suitable detector.

For the first three techniques, the sample or diluted sample is introduced directly into the sample loop of the gas chromatograph (GC). The measured sample is then carried into the GC column with a carrier gas where the organic compounds are separated. The organic compounds are each quantified by a GC detector such as a flame ionization, photoionization, or electron capture detector. The qualitative analysis is made by comparing the retention times (from injection to detection) of known calibration standards to the retention times of the sample components. The quantitative analysis is made by comparing the detector response for the sample compound to a known quantity of that compound in a corresponding standard. Gas samples collected on adsorption tubes are desorbed from the adsorption media using a solvent. A measured volume of the desorption solution is injected into a heated injection port where the mixture is vaporized and carried into the GC column with a carrier gas. The sample is separated into the individual components, then qualitatively and quantatively analyzed in the same manner as a gas sample.

Gas samples are analyzed immediately as taken from the stack or within a set period of time after being collected in a container or on an adsorption tube. To select

the correct GC column and establish proper GC analytical conditions, the analyst must identify approximate concentrations of organic compounds to be measured beforehand. With this information, the analyst can then prepare or purchase commercially available standard mixtures to calibrate the GC under physical conditions identical to those that are used for the samples. The analyst must also have prior information concerning interferences arising from other compounds present in the emissions, the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of sample loss due to moisture condensation in the sampling apparatus.

4.3 PRECISION, ACCURACY, AND LIMIT OF DETECTION OF THE METHOD

Precision of analytical procedures is quantified based on duplicate sample analysis. All EPA's Method 18 evaluation studies have demonstrated a relative standard deviation of less than 5 percent for the analytical precision which is required by Method 18.

Accuracy of sampling and analysis is quantified based on the required analysis of two audit gas cylinders obtained through the EPA's audit sample repository. Field validations of Method 18 conducted by EPA and numerous compliance test audits have demonstrated, that when proper procedures and checks are conducted, Method 18 is accurate within 10 percent of the true value (as required by the method).

The limit of detection of Method 18 is typically about 1 part per million by volume (ppmv) for most organic compounds. The actual limit of detection will vary for each organic compound and type of detector and is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of 3:1.

4.4 MEASUREMENT AND LOCATION OF SAMPLING POINTS

The agency representative must determine if the final results need to be presented on a concentration basis or a mass emission basis. For data presentation on a concentration basis, only the concentrations of the specified organics and the stack gas moisture content must be measured. If the mass emission rate of any compound is to be presented, the flow rate of the stack gas must also be determined using the velocity traverse. The number and locations velocity traverse points are selected according to Method 1; the traverse is conducted according to Methods 2, 2A, 2C, or 2D, as applicable. Although Method 18 requires sampling at a single point, it may be necessary to perform a velocity traverse to obtain the emission data in the units of the standard.

Method 18 requires that samples are collected proportionally, meaning that the sampling rate must be kept proportional to the stack gas velocity at the sampling point during the sampling period. If the process has a steady state flow (constant), then the

flow rate does not have to be varied during sampling. The majority of sources of organic emissions are of this type because they use constant rate fans. If the testing firm can confirm that the emission source of interest has a steady state flow (e.g., it uses a constant rate fan), then sampling can be conducted at a constant rate and no concurrent velocity measurements need to be made. If it cannot be determined whether the process is steady state, then velocity measurements (based on the velocity head, ΔP) must be made at the point to be sampled. The average velocity head (pitot reading, ΔP) and range of fluctuation is determined and then utilized to establish the proper flow rate settings during sampling.

4.5 OBSERVATION PROCEDURES FOR METHOD 18 TESTING

As previously mentioned, one of the primary concerns for any organic sampling program must be safety. It is beyond the scope of this manual to discuss safety aspects of organic sampling and analysis. However, it cannot be over-emphasized that the test coordinator must always be aware of the safety hazards. The major two hazards are explosion and health effects. For all source performance tests, there may be hazards in gaining access to the test location and in moving about the facility to complete the required activities in observing the tests.

4.5.1 Selection of Proper Sampling and Analytical Technique

Because of the number of different combinations of sampling procedures, sample preparation procedures, calibration procedures, GC column packing materials, GC operating conditions, and GC detectors covered under this method, a set of tables has been developed to assist the tester in selecting (and the test coordinator in evaluating) acceptable sampling and analytical techniques. The organic compounds included in these tables were selected based on their current status as either presently regulated or being evaluated for future regulation by the EPA and State and local agencies. Table C-1, page C-2, provides the user with the following information for the selected compounds: (1) the International Union of Pure and Applied Chemistry (IUPAC) name, any synonyms, the chemical formula, the Chemical Abstracts Service (CAS) number; (2) method, classification and corresponding references for more information; and (3) information on whether EPA currently has an audit cylinder for this compound. Also, detailed discussions on how to select the proper sampling and analytical techniques are presented in Appendix C.

4.5.2 Preliminary Measurements and Setup

Method 18 recommends that a pretest survey and/or laboratory evaluation be conducted by the testing firm prior to sampling and analysis. The pretest survey measurements are needed to properly design the emission test protocol. The primary objective of the preliminary survey is to collect a pretest survey sample for (1) determining which sampling procedure is most appropriate and (2) optimizing the

analytical procedures. Using the pretest survey sample, estimates of the emission concentration(s) are made and the organic compounds in the gas stream are identified. Also, any compounds that may interfere with the quantification of the target analyte(s) are identified and appropriate modifications can be made to the analytical procedures.

Table C-1, page C-2, provides data on availability and ranges of EPA audit gases for the target organic compounds. Further information can be obtained by contacting EPA.

For audit gases obtained from a commercial gas manufacturer, check that the manufacturer has (1) certified the gas in a manner similar to the procedure described in 40 CFR Part 61, Appendix B, Method 106, Section 5.2.3.1 and (2) obtained an independent analysis of the audit cylinder that verifies that the audit gas concentration is within 5 percent of the manufacturer's stated concentration.

4.5.3 Observation of On-site Testing

The on-site observation techniques and reference tables provided in Appendix C should assist the test coordinator in determining if the testing firm has selected an acceptable sampling and analysis technique. Data quality should be enhanced if the testing firm conducts the recommended quality assurance/control checks and procedures provided in this chapter and Appendix C. At some facilities, the testing firm may need to use two or more sampling trains (different sampling techniques) to accurately measure all the organic compounds of interest.

Because of the large number of approaches to the three different sampling techniques (container sampling, adsorption tube sampling, and direct interface sampling), only the most commonly used (evaluated container or Tedlar bag sampling) is discussed in this chapter. The other sampling approaches are addressed in Appendix C in the locations shown below. The test coordinator can use listing below to locate and review the sampling approach of interest.

Evacuated Container Sampling (Heated and Unheated) - In this sampling technique, sample bags are filled by evacuating rigid air-tight containers that hold them. The suitability of the bags for sampling is confirmed by permeation and retention checks using the specific organic compounds of interest during the pretest survey operations. The permeation and retention checks (discussed later) must be performed on the field samples to ensure that the container sampling technique is acceptable.

On-site sampling includes the following steps:

1. Conducting preliminary measurements and setup.
2. Preparing and setup of sampling system.
3. Preparing of the probe.
4. Connecting electrical service and conducting leak check of sampling system.
5. Inserting probe into duct and sealing port.
6. Purging sampling system.
7. Conducting proportional sampling.
8. Recording data.
9. Recovering sample and transporting to laboratory.

The "On-site Checklist" (Figure C.2, page C-17) includes checks for each of the steps above and can be used by the test coordinator as an instructional guide. **To assist the test coordinator, the most critical items are printed in bold lettering.**

It is the responsibility of the testing firm to ensure that the sampling and analytical procedures are performed correctly. The following detailed information is given only as training guide for the less experienced test coordinator and does **not** imply mandatory actions by the test coordinator except when the discussions state that the test coordinator "**shall**" conduct a given procedure.

Method 18 requires that samples be collected proportionally, meaning that the sampling rate must be kept proportional to the stack gas velocity at the sampling point during the sampling period. If the process has a steady state flow (constant), then the flow rate does not have to be varied during sampling. The average velocity head (pitot

reading) and range of fluctuation is determined and then utilized to establish the proper flow rate settings during sampling. If it is found that the process is not steady state, then the velocity head must be monitored during sampling to maintain a constant proportion between the sample flow rate and the flow rate in the duct.

A total sampling time greater than or equal to the minimum total sampling time specified in the applicable emission standard must be selected. The number of minutes between readings while sampling should be recorded as an integer. It is desirable for the time between readings to be such that the flow rate does not change more than 20 percent during this period.

If the sampling system must be heated during sample collection and analysis, the system temperature should not decrease below the specified temperature. The average stack temperature is used as the reference temperature for initial heating of the system and should be determined. Then, the stack temperature at the sampling point is measured and recorded during sampling to adjust the heating system just above the stack temperature or above the dew point. The use of a heated sampling system requires on-site analysis.

A. Sampling System Preparation - The test coordinator should observe the preparation of the probe and sampling train in the laboratory area (see Figure 4.1, page 4-16). The sampling apparatus must meet the following criteria (on-site measurements checklist, Figure C.2, page C-17):

1. The probe must be constructed of stainless steel, glass or Teflon.
2. All connections must be either stainless steel or Teflon.
3. The probe, if required, must be capable of keeping the stack gases at or just above the stack temperature.
4. The sample line must be Teflon.
5. The sample bags must be Tedlar or Teflon, leak checked and blank checked.
6. A permeation check and retention check should have been conducted prior to testing. If these checks have not been made, then they should be conducted on the field samples.
7. The flowmeter must be calibrated, be in the proper range, and heated, if applicable.
8. If located between the probe and bag, the pump must be of the Teflon coated diaphragm type and heated, if applicable. If the pump is after the rigid container, it may be any type of pump that provides the proper flow rate.
9. If a dilution system is used and the probe must be heated, the dilution system must be in a heated box.

B. Proportional Sampling - Sampling must be conducted at a rate in constant proportion to the stack gas flow at the sampling point. Thus, for a steady state operation, the sampling flow rate is not varied during the run. For a nonsteady state process, the sampling flow rate is varied in proportion to the changing velocity. The velocity is monitored by measuring the velocity head (ΔP) which is linearly related to the square of the velocity. A recommended method for determining proportional sampling rates is as follows:

1. Conduct a single point velocity check as previously specified, and determine the average velocity head (ΔP_{avg}) to be sampled.
2. The average sampling flow rate for the test is determined prior to the start of the run. Typically, the average sampling flow rate is about 0.5 l/min yielding approximately 30 liters of sample. The flow rate chosen in the laboratory should fill the bag to about three-fourths of its capacity during the sample run. The average flow rate chosen is then assigned to the average velocity head measured.
3. The flow rate to be used during sampling when the velocity head varies from the average is calculated using the following equation.

$$Q_s = Q_m \frac{\Delta P^{1/2}}{\Delta P_{avg}} \qquad \text{Equation 4-1}$$

where:

Q_m = Average sampling rate, l/min (ft^3/min),
Q_s = Calculated sampling rate, l/min (ft^3/min),
ΔP = Actual velocity head, mm (in.) H_2O, and
ΔP_{avg} = Average velocity head, mm (in.) H_2O.

4. Determine the rotameter setting for the sampling rate (Q_s) from the rotameter calibration curve, and adjust the rotameter accordingly.

C. Tedlar Bag Sampling Procedures using an Indirect Pumping Technique - Use of proportional sampling will provide for the correct sampling rate and the proper filling of the sample bag. The tester should follow the procedure below to obtain an integrated sample when the pump is located after a rigid container (Figure 4.1, page 4-16).

1. If a heating system is required, turn on the heating system and set container temperature at the average stack temperature determined from the pretest measurements. **If probe heating is required, then bag heating would also likely be required.**
2. Leak check the sampling train just prior to sampling by connecting a U-tube, inclined manometer, or equivalent at the probe inlet and pulling a

vacuum of ≥ 10 in. H_2O. Close the needle valve and then turn the pump off. The vacuum should remain stable for at least 30 seconds. If a leak is found, repair before proceeding; if not, slowly release the vacuum gauge. This leak check is optional. **The most critical place for a leak is between the probe and the bag. Air inleakage into the sample bag will produce low results. If the rigid sample container develops a small leak which only effects the pumping rate, this should not cause a significant bias in the results.**

3. If the system is being heated, wait for it to come to the proper temperature. Place the probe in the stack at the sampling point: centroid of the stack or no closer to the walls than 1 meter. Seal the sampling port to prevent dilution of the stack gas by inleakage of ambient air. **It can be important that the port is sealed to prevent air inleakage. Also, if the system must be heated, a significant loss of organics can result from poor heating. It is better to heat the system above than below the specified temperature.**
4. Disconnect the flexible bag. Purge the system by turning on the pump and drawing at least 5 times the sampling system volume through the train, or purge for 10 minutes, whichever is greater. **The system is purged to equilibrate and remove ambient air. If the system is not purged, then a negative error may be introduced.**
5. Adjust the flow rate to the proper setting based on the velocity pressure (measured during the purging, for nonsteady state processes). **Proportional sampling should be conducted for nonsteady state systems, but constant rate sampling generally will not cause a significant bias unless the concentration and flow rate are changing significantly.**
6. Connect the flexible bag to the sampling train (the connections should ensure a leakfree system), and begin sampling. The sampling rate must remain proportional to the stack gas velocity for the total sampling time specified by the applicable standard. **Although Method 18 recommends a rate of about 1 lpm be used, slower sampling rates and smaller sample bags have been shown to be as accurate and precise.**
7. Record all data required (at 5 minute intervals, minimum) on the field sampling data form similar to Figure 4.2, page 4-17. The flow rate and sampling train heating system should be adjusted after every pitot and temperature reading to the correct level. **A shorter sampling time for each point is typically used when the flow rate is changing significantly. For emission sources with small changes in the flow rate, the sampling time per point may be longer.**
8. Disconnect and seal the flexible bag upon completion of sampling. Take care not to dilute the contents with ambient air. **The bag should be sealed well to prevent leakage.**

9. Label each bag clearly and uniquely to identify it with its corresponding data form and/or run. If the sampling system was heated, the sample bag must be maintained at the stack temperature through sample analysis.

D. Sample Recovery and Transport to Laboratory - Sample recovery should be performed so as to prevent contamination of the bag sample and maintain sample integrity. The bag should remain leakfree, be protected from direct sunlight, be maintained at a temperature that will prevent condensation of any of the gases, and be stored in a safe place to prevent damage or tampering prior to analysis. **It is recommended that bag samples be analyzed within two hours of sample collection; however, many of the organic compounds are stable enough to allow a few days prior to analysis. Upon completion of the testing and sample recovery, all the data forms should be checked for completeness and the sample bags re-examined for proper identification. It is important to check the bags for problems with permeation and retention of the sample.**

E. Common Problems - The most common problems encountered with bag sampling techniques are (1) adsorption of the gases on the bag, (2) permeation of the gases through the bag, (3) reaction of gases in the bag, (4) condensation of the gases or water vapor in the bag, and (5) leaks developing in the bag during testing, transport, and/or analysis. The bags must be checked for stability and retention of the target compound.

F. Stability Check - To assess the stability of the gas sample in Tedlar bags, perform a second analysis after a time period equalling the period between sample collection and the first analysis. **If the concentration of the sample collected in a Tedlar bag decreases by more than 10 percent between the first and second analyses, then an accepted sampling method other than Tedlar bags should be considered.**

G. Retention Check - Perform a retention check on the bag sample by successively evacuating the bag and refilling it with hydrocarbon-free air or nitrogen one or more times. Analyze the bag contents for the target compound(s), then allow the gas to sit in the bag overnight and reanalyze bag contents for the target compound(s). **If any target compound is detected in the bag at a concentration greater than 5 percent of the original concentration, then an accepted sampling method other than Tedlar bags should be considered.**

One technique that can be used to reduce both retention and/or condensation in the bag is addition of a heating system. Heating is generally applied during sample collection and maintained through analysis. However, heating may increase the permeation rate. Another option is the use of heat lamps applied to the sample bags after sample collection and during sample analysis. Two other techniques that have been used to prevent condensation are (1) addition of a knockout trap to remove water vapor and heavy organics from the sample stream, and (2) use of sorbents such as Tenax to remove the high boiling point organics. In these cases, the testing firm must demonstrate

that the organic compound(s) of interest are not removed. Alternatively, sample and/or water vapor condensation may be reduced by the use of the prefilled bag technique. The prefilling of the bag lowers the concentrations of the organic and/or water vapor, thereby eliminating condensation.

If gases are reacting in the bag, then the bag material can be changed, the time between sample collection and analysis reduced, or a different sampling technique used such as direct interface sampling. Methods to reduce bag leak problems are proper construction of the sample bags, conducting additional runs, using a backup sample collection technique such as an another bag sampling system or an adsorption tube sampling system, and care in handling the sampling bags. Also, steel canisters can be used in place of bags. If the organic compounds are stable with time, the use of steel canisters may improve preservation of the samples especially if they must be air freighted to the laboratory for analysis.

4.6 OBSERVATION PROCEDURES FOR METHOD 18 ANALYSIS

Unless it is conducted on-site, the test coordinator will not typically have an opportunity to observe the analysis. The test coordinator should therefore check the data and other documentation in the compliance test report for:

1. Audit sample results within 10 percent of true value (see Chapter 4.7 for more details).
2. Proper preparation of calibration standards.
3. Proper resolution of compounds.
4. Additional unidentified peaks.
5. Proper analytical precision.
6. Acceptable collection efficiency for adsorption tube sampling.
7. Acceptable desorption efficiency for adsorption tube sampling.
8. Proper calculation of analytical data results.

A test coordinator's postsampling operations checklist (Figure C.10, page C-37) is provided to assist in the review of the procedures for on-site analysis and the compliance test report for off-site analysis.

4.6.1 Preparation of Calibration Standards

Calibration standards are prepared prior to sample analysis following the procedures described in the following chapters. Refer to Table C-4, page C-8, for recommendations on the procedures suitable for selected compounds. Note that there are two basic types of standards, gaseous or liquid; the type prepared depends on the type of sample collected. Gaseous calibration standards are needed for analysis of pretest survey samples collected in glass flasks or bags, and final samples collected in bags, by direct, or by dilution interface sampling. There are three techniques for

preparing gaseous standards, depending on availability and the chemical characteristics of the standard compound(s); gas cylinder standards may also be used directly, if the proper concentration ranges are available. Liquid calibration standards are required for the analysis of adsorption tube samples from the pretest survey and/or the final sampling, as well as to determine the desorption efficiency; there are two techniques for preparing liquid calibration standards. The concentrations of the calibration standards should bracket the expected concentrations of the target compound(s) in the emissions being sampled. Specific procedures for preparing and analyzing each type of standard are described in Appendix C.3.

4.6.2 Sample Analysis

After the GC has been calibrated and the analysis of the audit sample(s) has been conducted successfully, the samples are analyzed. The following are the key procedures used to analyze emission samples collected in Tedlar bags using a GC calibrated with gaseous calibration standards. The analytical procedures for adsorption tube sampling and direct interface sampling are presented in Appendix C.3.

1. **Note the time of injection on the strip chart recorder and/or actuate the electronic integrator. Record the sample identity, detector attenuation factor, chart speed, sample loop temperature, column temperature and identity, and the carrier gas type and flow rate on a data form.** It is also recommended that the same information be recorded directly on the chromatogram and on an analytical data sheet similar to Figure 4.3, page 4-18. Record the operating parameters for the particular detector being used.
2. **Examine the chromatogram to ensure that adequate resolution is being achieved for the major components of the sample. If adequate resolution is not being achieved, vary the GC conditions until resolution is achieved, and reanalyze the standards to recalibrate the GC at the new conditions.**
3. After conducting the analysis with acceptable peak resolution, determine the retention time of the sample components and compare them to the retention times for the standard compounds. **To qualitatively identify an individual sample component as a target compound, the retention time for the component must match within 0.5 seconds or 1 percent, whichever is greater, of the retention time of the target compound determined with the calibration standards.**
4. **Repeat injection of the first sample until the area counts for each identified target compound from two consecutive injections are within 5 percent of their average.**
5. **Multiply the average area count of the consecutive injections by the attenuation factor to get the area value for that sample, and record the area value on the data form.**

6. Immediately following the analysis of the last sample, reanalyze the calibration standards, and compare the area values for each standard to the corresponding area values from the first calibration analysis. If the individual area values are within 5 percent of their mean value, use the mean values to generate a final calibration curve for determining the sample concentrations. If the individual values are not within 5 percent of their mean values, generate a calibration curve using the results of the second analysis of the calibration standards, and report the sample results compared to both standard curves.

Determine the bag sample moisture content by measuring the temperature and the barometric pressure near the bag. Use water saturation vapor pressure chart, assuming the relative humidity of the bag to be 100 percent unless a lower value is known, to determine the water vapor content as a decimal figure (percent divided by 100). If the bag has been heated during sampling and analysis, the flue gas or duct moisture content should be determined using Method 4.

4.7 USE OF AUDIT MATERIALS AND INTERPRETATION OF DATA

An audit is an independent assessment of data quality. Based on the requirements of Method 18 and the results of collaborative testing of other EPA Methods, two specific performance audits are recommended:

1. An audit of the sampling and analysis procedures of Method 18 is required under NSPS and recommended for other purposes.
2. An audit of the data processing is recommended.

A systems audit may be conducted by the test coordinator in addition to these performance audits. Performance audits are described in detail in Chapter 4.7.1 and the systems audit is explained in Chapter 4.7.2.

4.7.1 Performance Audits

Performance audits are conducted to evaluate quantitatively the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). It is required that cylinder gas performance audits be performed once during every NSPS compliance test utilizing Method 18, and it is recommended that a cylinder gas audit be performed once during any compliance test utilizing Method 18 conducted under regulations other than NSPS.

Performance Audit of the Field Test - As stated in Section 6.5 of 40 CFR 60, Appendix A, Method 18, immediately after the preparation of the calibration curves and prior to the sample analysis, the analysis audit described in 40 CFR 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis," should be performed. The

information required to document the analysis of the audit sample(s) has been included on the example data sheet shown in Figure 4.4, page 4-19. The audit analyses shall agree within 10 percent (or other specified value, as explained below) of the true values. The test coordinator may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance and Technical Support Division, Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided that (1) the gas manufacturer certifies the audit cylinder in a manner similar to the procedure described in 40 CFR 61, Appendix B, Method 106, Section 5.2.3.1, and (2) the gas manufacturer obtains an independent analysis. Independent analysis is defined as an analysis performed by an individual other than the individual who performs the gas manufacturer's analysis, using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is completed and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

Responsibilities of the Test Coordinator - The primary responsibilities of the test coordinator are to ensure that the proper audit gas cylinder(s) are ordered and safeguarded, and to interpret the results obtained by the analyst.

When auditing sampling systems that do not dilute the stack gas during sampling, the audit gases ordered must consist of the same organic compound(s) that are being measured; for emission standards on a concentration basis, the audit gas concentration(s) must be in the range of 25 percent to 250 percent of the applicable standard. The audit should include analysis of two concentration levels. If two cylinders are not available, then one cylinder can be used. It is strongly recommended that audit cylinder values below 5 ppm not be used. For emission standards which specify a control efficiency, the concentration of the audit gases should be in the range of 25 percent to 250 percent of the expected stack gas concentration. The audit should include analysis of two concentration levels. If two cylinders are not available, the audit can be conducted using one cylinder.

The test coordinator must ensure that the audit gas cylinder(s) are shipped to the correct address, and to prevent vandalism, verify that they are stored in a safe location both before and after the audit. Audit cylinders should not be analyzed when their pressure drops below 200 psi because the cylinder gas value may be unreliable.

The audit results must agree within 10 percent of the stated audit cylinder value or true value. Agreement within 15 percent is allowed for cylinders between 5 and 20 ppm. When the measured value agrees within these limits, the test coordinator directs the analyst to begin analyzing the field samples. For on-site analysis, when the measured concentration does not agree, the analyst should first recheck the analytical system and calculations, and then repeat the audit. When the results of the repeat audit are within the limits, the analyst may conduct the field sample analysis. If the analyst

fails the second audit, the agency may reject the compliance test results. Method 18 states "Audit supervisor judgement and/or supervisor policy determine action when agreement in not within ±10 percent." "When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time." The test coordinator should therefore know the policy of the agency related to audit failure.

During the audit, the test coordinator should record the appropriate cylinder number(s), cylinder pressure(s) (at the end of the audit), and the calculated concentrations on the "Field audit report form," Figure 4.4, page 4-19. The individual being audited must not, under any circumstances, be told the actual audit concentration(s) until the calculated concentration(s) have been submitted to the test coordinator and are considered acceptable.

When auditing sampling systems that dilute the emissions during collection, the audit gas concentration value used in the calculations can either be based on (1) the undiluted concentration using the criteria discussed above or (2) the expected concentration of the gases following dilution during collection using the same dilution factor as used for the emission samples.

The audit procedures that follow are used for the evacuated container sampling approach with either on-site or off-site analysis. Auditing procedures for the other sampling techniques are presented in Appendix C according to the sampling approach used to collect the organic emissions and whether the samples are analyzed on-site or off-site.

Container (Bag, Syringe, and Canister) Sampling with On-site Analysis - The cylinder gas performance audit for bag, syringe, or canister sampling with on-site analysis is conducted on-site just prior to the analysis of the field samples. The recommended procedures for conducting the audit are:

1. The audit samples should be collected in the type of container used during sample collection. However, to conserve audit gas, it is usually not necessary to involve the rest of the sampling system in audit sample collection for unheated container sampling. Problems related to the reaction or retention of the organic compounds will occur in the container. Interferents in the stack gas such as water vapor and other organics are not present in the audit cylinders and thus, related problems are not assessed by the audit. For heated container systems, it may be necessary to use the whole sampling system to collect the audit gas. However, if a gas must be heated to prevent its condensation in the sampling system, it is likely that audit gas cylinders are not available for this compound or level of compound.

2. Prior to analysis, the audit samples should remain in the appropriate container approximately the same length of time as the field samples. After the preparation of the calibration curve, a minimum of two consecutive analyses of each audit cylinder gas should be conducted. The analyses must agree within 5 percent of the average. The audit results should be calculated by the analyst (or his representative) and given to the test coordinator. The test coordinator will record all the information and data on the "Field Audit Report Form" and then inform the analyst of the status of the audit. The equations for calculation of error are included on the form.

Container (Bag and Canister) Sampling with Off-site Analysis - For cylinder gas performance audits associated with container samples analyzed off-site, it is recommended that the audit be conducted off-site just prior to the compliance test (if the agency desires) and then repeated during the off-site sample analysis as a quality control measure. The use of the pretest audit will help ensure that the analytical system will be acceptable prior to testing. Alternatively, the audit gases can be collected in the appropriate containers on-site or off-site, and then analyzed just prior to the field samples analysis. It is recommended that the tester fill at least two containers with the audit gas to guard against a container leak causing a failed audit. Since the use of the performance audit is to both assess and improve the data quality, the use of the pretest audit will provide the tester/analyst with a better chance of obtaining acceptable data. The recommended procedure for conducting the audit is the same as described above for the on-site audit with the exception that the test coordinator will likely not be present and the data will have to be reported by telephone.

Performance Audit of Data Processing - Calculation errors are prevalent in processing data. Data processing errors can be determined by auditing the recorded data on the field and laboratory forms. The original and audit (check) calculations should agree within round-off error; if not, all of the remaining data should be checked. The data processing may also be audited by providing the testing laboratory with specific data sets (exactly as would appear in the field), and by requesting that the data calculation be completed and that the results be returned to the agency. This audit is useful in checking both computer programs and manual methods of data processing.

4.7.2 Systems Audit

A systems audit involves checking to ensure that the proper equipment and procedures are used. The observation of the sampling and analytical procedures by the test coordinator described in Chapters 4.5 and 4.6 constitutes a systems audit for Method 18. The systems audit results may be recorded on the sampling and analytical checklists referenced in Chapters 4.5 and 4.6.

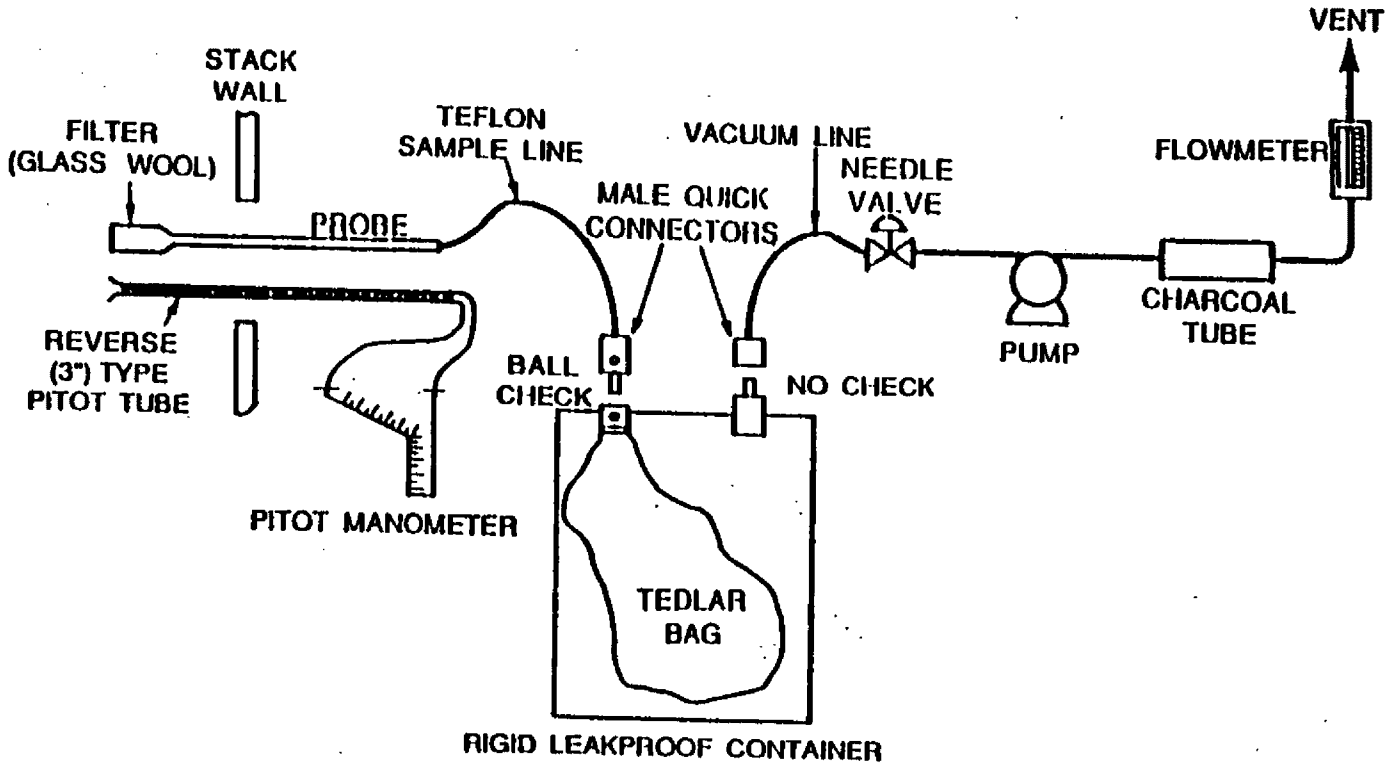


Figure 4.1. Integrated bag sampling system.

Plant _____
City _____
Operator _____
Date _____
Run number _____
Stack dia, mm (in.) _____
_____
Sample box number _____
Pitot tube (C_p) _____
Static press ____ mm (in.) H2O

Flowmeter calib.(Y) _____
Container type: bag _____
syringe _____
canister _____
Container volume, _____ liters
Container number _____
Average (P) _____ mm (in.) H2O
Initial flowmeter setting _____
Average stack temp _____ °C (°F)
Barometric press _____ mm (in.) Hg

Dilution system: (dynamic)
emission flowsetting _____
diluent flowsetting _____
Dilution system: (static)
emission flowsetting _____
Final leak check ____ m^3/min (cfm)
Vacuum during leak check _____
_____ mm (in.) H_2O
Sampling point location _____
_____

Sampling time, min	Clock time, 24 h	Velocity head mm (in.) H2O, (ΔP)	Flowmeter setting L/min (ft3/min)	Temperature readings: stack °C (°F)	probe °C (°F)	sample line °C (°F)	flowmeter box °C (°F)	container °C (°F)
Total		Avg	Avg	Avg	Avg	Avg	Avg	Avg

Figure 4.2. Field sampling data form for container sampling.

Date: _____ Analyst: _____ Plant: _____
Location: _____ Sample Type: _____
Type of Calibration Standard: _____ Target Compound: _____
Number of Standards: ___ Date Prepared: _____ Prepared By: _____

GC Used: _____ Column Used: _____
Carrier Gas Used: _____ Carrier Gas Flow Rate: _____
Column Temperatures, Initial: _____ Program Rate: _____ Final: _____
Sample Loop Volume: ___ Loop Temperature: _____ Inject. Port Temp.: _____
Detector Temp.: ___ Auxiliary Gases: _____

Calibration Data	Standard 1	Standard 2	Standard 3
First analysis/second analysis			
Standard concentration (C_{act})			
Flow rate through loop(ml/min)	/	/	/
Liquid injection volume (tubes)	/	/	/
Injection time (24-hr clock)			
Chart speed (cm/min)	/	/	/
Detector attenuation	/	/	/
Peak retention time (min)	/	/	/
Peak retention time range (min)			
Peak area	/	/	/
Peak area x attenuation factor	/	/	/
Average peak area value (Y)			
Percent deviation from average			
Calculated concentration (C_{std})			
% deviation from actual ($\%D_{act}$)			
Linear regression equation; slope (m): _____		y-intercept (b): _____	

Sample Analysis Data	Sample 1	Sample 2	Sample 3
First analysis/second analysis			
Sample identification			
Interface dilution factor			
Flow rate through loop (ml/min)	/	/	/
Liquid injection volume (tubes)	/	/	/
Injection time (24-hr clock)	/	/	/
Chart speed (cm/min)	/	/	/
Detector attenuation	/	/	/
Peak retention time	/	/	/
Peak retention time range			
Peak area	/	/	/
Peak area x atten. factor (A_1/A_2)	/	/	/
Average peak area value (Y)			
% deviation from average ($\%D_{avg}$)			
Calculated concentration (C_s)			

$$C_{std} \text{ or } C_s = \frac{(Y - b)}{m} \qquad \%D_{avg} = \left| \frac{A_1 - Y}{Y} \right| \times 100\% \qquad \%D_{act} = \frac{C_{std} - C_{act}}{C_{act}} \times 100\%$$

Figure 4.3. Data form for analysis of Method 18 field samples.

Part A. - To be filled out using information from organization supplying audit cylinders.

1. Organization supplying audit sample(s) and shipping address _____
2. Audit supervisor, organization, and phone number _____
3. Shipping instructions: Name, Address, Attention _____
4. Guaranteed arrival date for cylinders - _____
5. Planned shipping date for cylinders - _____
6. Details on audit cylinders from last analysis

	Low conc.	High conc.
a. Date of last analysis.....	.....	.....
b. Cylinder number.....	.....	.....
c. Cylinder pressure, psi.....	.....	.....
d. Audit gas(es)/balance gas.	.....	.....
e. Audit gas(es), ppm.....	.....	.....
f. Cylinder construction.....	.....	.....

Part B. - To be filled out for audit analysis.

1. Process sampled _____
2. Audit location _____
3. Name of individual audit _____
4. Audit date _____
5. Audit Results:

	Low cylinder	High cylinder
a. Cylinder number.....	.....	.....
b. Cylinder pressure before audit, psi.....	.....	.....
c. Cylinder pressure after audit, psi.....	.....	.....
d. Measured concentration, ppm		
Injection #1* Injection #2* Average.....	.....	.....
e. Actual audit concentration, ppm		
f. Audit accuracy:*		
Low Conc. Cylinder.....	.....	.....
High Conc. Cylinder.....	.....	.....
Percent accuracy* = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$		
g. Problems detected (if any).....	.....	.....

*Results of two consecutive injections that meet the criteria.

Figure 4.4. Field audit report form.

CHAPTER 5
DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS -- METHOD 21*

5.1 APPLICABILITY

Method 21 applies to the determination of volatile organic compound (VOC) leaks from process equipment that is in VOC service. *In VOC service* includes any fugitive emission source that contains or contacts a fluid composed of equal to or greater than 10 percent VOC by weight. For the benzene fugitive emission regulation, *in benzene service* includes any source that contains or contacts a fluid equal to or greater than 10 percent benzene by weight.

VOC service can further be divided into light liquid or heavy liquid service. *Light liquid* VOC service is defined as one or more of the stream components having a vapor pressure greater than 0.3 Kpa (0.04 psia) at 20° (68°F). All VOC sources with a stream component vapor pressure equal to or less than 0.3 Kpa at 20°C are in *heavy liquid* service. The NSPS (New Source Performance Standard) for "Refinery Leaks" defines *heavy liquid* as kerosene or heavier liquid.

Leaks are classified as fugitive emissions. Sources of fugitive emissions include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor sealing systems, degassing vents, accumulator vessel vents, agitator seals, and access door seals.

5.2 METHOD DESCRIPTION

A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet certain specifications and performance criteria contained in EPA Method 21, Section 3. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

5.2.1 Regulations and Leak Definition

Industries that emit fugitive VOCs and are affected by federal regulations are shown in Table 5-1. The sources of fugitive emissions, methods by which emissions are detected and repaired, and control procedures are very similar for each of these industries.

---

*The majority of this Chapter is taken directly from EPA-340/1-86-015, "Portable Instruments User's Manual for Monitoring VOC Sources." To reduce the references to the cited manual, reference markings have been left out.

TABLE 5-1. SOURCE CATEGORIES THAT EMIT FUGITIVE VOCs

Source Category	Type of Control Guidance*
Petroleum refineries	CTG, NSPS
Synthetic organic chemicals manufacturing industry	CTG, NSPS
Polymers and resin manufacturing	CTG, NSPS
Natural gas and natural gasoline processing plants	CTG, NSPS
Benzene in coke ovens/by-products plants	NESHAPs
Vinyl chloride sources	NESHAPs
Benzene fugitive sources	NESHAPs

*CTG: Control Technique Guideline
NSPS: New Source Performance Standard
NESHAPs: National Emission Standard for Hazardous Air Pollutants

A leak definition can be based on either a concentration value or a "no detectable emissions." The "no detectable emission" standard is applied to sources designed to operate in a leakless manner, such as pressure-relief devices with rupture or sealless pumps. The concentration-based value most often used to define a leak is a concentration equal to or greater than 10,000 ppmv. The "no detectable emission" standard is not an absolute zero reading. A violation of the "no detectable emission" limit is defined in Method 21 as a concentration greater than five percent of the concentration-based leak definition. For example, based on the 10,000 ppmv definition of a leak, a concentration greater the 500 ppmv would be in violation of the "no detectable emission" standard.

5.2.2 Portable Instrument Operating Principles

Various types of instruments are available for detecting organic vapors. These operate on different principles. Each detector has its own advantages, disadvantages, and sensitivity.

In addition to the portable VOC detectors, other portable equipment used during Method 21 testing includes temperature sensors, flow monitors, and pressure gauges. This equipment is much smaller, less expensive, and easier to use than the portable VOC detectors.

Several types of portable VOC detectors can be used either as screening tools or to meet the requirements of EPA Method 21. These include:

- Flame ionization detector (FID)
- Photoionization (ultraviolet) detector (PID)
- Catalytic combustion or hot wire detector
- Nondispersive infrared detector (NDIR)

The specifications of these instruments vary significantly with regard to sensitivity, range, and responsiveness. Table 5-2 lists the most common instruments currently in use and the associated detection principle, range, sensitivity, and response time.

Flame Ionization Detector - In an FID, the sample is introduced into a hydrogen flame. A concentration of as little as 0.1 ppm of hydrocarbon produces measurable ionization, which is a function of the number of carbon ions present. A positively charged collector surrounds the flame, and the ion current between the flame and the collector is measured electronically. Pure hydrogen burning in air produces very little ionization, so background effects are essentially masked by the hydrogen flame. The calibration output current is read on a panel meter or chart recorder.

Organic compounds containing nitrogen, oxygen, or halogen atoms give a reduced response in a FID when compared to compounds without these atoms. The FID hydrocarbon analyzers are usually calibrated in terms of a gas such as methane or hexane, and the output is read in parts per million of carbon measured as methane or hexane.

Although nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), and water vapor (H_2O) do not produce significant interferences, condensed water vapor can block the sample entry tube and cause erratic readings. Also, when the oxygen (O_2) concentration exceeds 4 percent, it can significantly reduce the detector output. The relative response of the FID to various organic compounds, including those with attached oxygen, chlorine, and nitrogen atoms, varies from compound to compound.

Photoionization Detector - In the photoionization detector, ultraviolet light ionizes a molecule as follows: $R + h\nu^- > R^+ + e^-$, where R^+ is the ionized species and hv represents a photon with energy less than or equal to the ionization potential of the molecule. Generally, all species with an ionization potential less than the ionization energy of the lamp are detected. Because the ionization potential of all major components of air (O_2, N_2, CO, CO_2, and H_2O) is greater than the ionization energy of the lamps in general use, they are not detected.

The detector consists of an argon-filled, ultraviolet (UV) light source that emits photons. A chamber adjacent to the sensor contains a pair of electrodes. When a positive potential is applied to one electrode, the field that is created drives any ions formed by the absorption of UV light to the collector electrode, where the current (proportional to the concentration) is measured.

TABLE 5-2. PORTABLE INSTRUMENTS RANGE, SENSITIVITY, AND RESPONSE TIME

Instrument Trade Names	Detection Principle	Range, ppm	Sensitivity	Response Times
550, 551, 555 (AID, Inc.)	FID	0-200 0-2,000 0-10,000	0.1 ppm at 0-200 ppm	5
OVA 108, 128 Century Systems (Foxboro)	FID	0-10 0-100 0-1,000	0.2 ppm (Model 128) 0.5 ppm (Model 108)	2 2
PI - 101 (Hnu Systems, Inc.)	PID	0-20 0-200 0-2,000	1 ppm	5
TLV Sniffer (Bacharach)	Catalytic combustion	0-500 0-5,000 0-50,000	2 ppm	
Ecolyzer 400 (Energetics Science)	Catayltic combustion	0-100% LEL	1% LEL	15
Miran 1A (Foxboro)	NDIR	ppm to %	1 ppm	1, 4, 10 and 40*

* Response times for different ranges.

Nondispersive Infrared Detector - Nondispersive infrared (NDIR) spectrometry is a technique based on the broadband absorption characteristics of certain gases. Infrared radiation is typically directed through two separate absorption cells: a reference cell and a sample cell. The sealed reference cell is filled with nonabsorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of the gas being analyzed. When a particular hydrocarbon is present, the IR absorption is proportional to the molecular concentration of that gas. The detector consists of a double chamber separated by an impermeable diaphragm. Radiant energy passing through the two absorption cells heats the two portions of the detector chamber differentially. The pressure difference causes the diaphragm between the cells in a capacitor to distend and vary. This variation in capacitance, which is proportional to the concentration of the component of gas present, is measured electronically.

Interferences in NDIR measurements are usually a result of other gases in the sample absorbing at the same wavelength as the gas of interest. Efforts to eliminate these interferences by use of reference cells or optical filters are only partially successful. For hydrocarbon (HC) monitoring, the detector is filled with one or several different hydrocarbons, which may be different from the HC contained in the sample; this causes a disproportionate response. Other sources of errors include gas leaks in the detector and reference cells, inaccurate zero and span gases, nonlinear response, and electronic drift.

Catalytic Combustion or Hot Wire Detector - The heat of combustion of a gas is sometimes used for quantitative detection of that gas. Suffering the same limitations as thermal conductivity, this method is nonspecific, and satisfactory results depend on sampling and measurement conditions.

One type of thermal combustion cell uses a resistance bridge containing arms that are heated filaments. The combustible gas is ignited in a gas cell upon contact with a heated filament; the resulting heat release changes the filament resistance, which is measured and related to the gas concentration.

Another combustion method uses catalytic heated filaments or oxidation catalysts. Filament temperature change or resistance is measured and related to gas concentrations.

Thermocouple - The temperature sensor most commonly used is the direct-readout hand-held thermocouple. The thermocouple is composed of two wires of dissimilar metals that are joined at one end. When the joined end is heated, a voltage flow can be observed. A voltmeter is attached to the thermocouple, and the observed voltage is proportional to the measured temperature. A portable thermocouple assembly consists of a shielded probe, a connecting wire, and a voltmeter. The voltmeter may be a temperature conversion unit on a multimeter or a dedicated direct readout temperature unit. The voltmeter is battery-operated, small, and easily portable.

Static Pressure Gauges - Among the several different available static pressure gauges, the most commonly used for this type of field work are the inclined manometer and the diaphragm gauge. A pressure tap is necessary for use of a portable static pressure gauge. The primary feature of the pressure tap is a small opening in the wall of a duct, which can be fitted with a connection and a hose to make pressure measurements. The tap should be far enough away from such disturbances as elbows and internal obstructions to make the effects of such disturbances negligible.

The appropriate side, positive or negative, of the manometer or pressure gauge is connected by a rubber hose at the tap, and a pressure reading can be taken. It is often advantageous to disconnect a permanent pressure gauge and take a pressure reading at that point to compare it with the facility's instrumentation.

5.3 CALIBRATION PRECISION

Calibration precision is the degree of agreement between measurements of the same known value. To ensure that the readings obtained are repeatable, a calibration precision test must be completed before placing the analyzer in service, and at 3 month intervals, or at the next use, whichever is later. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

To perform the calibration precision test, a total of three test runs are required. Measurements are made by first introducing zero gas and adjusting the analyzer to zero. The specified calibration gas (reference) is then introduced and the meter reading is recorded. The average algebraic difference between the meter reading and the known value of the calibration gas is then computed. This average difference is then divided by the known calibration value and multiplied by 100 to express the resulting calibration precision in percentages.

5.3.1 Calibration of VOC Analyzers

Calibration requirements for VOC instrumentation are specified in Method 21 and in the specific NSPS applicable to sources of fugitive VOC emissions. The requirements pertaining to calibration are briefly summarized here.

- The instrument should be calibrated daily.
- The gas concentrations used for calibration should be close to the leak definition concentration.
- The calibrant gas should be either methane or hexane.
- A calibration precision test should be conducted every 3 months.
- If gas blending is used to prepare gas standards, it should provide a known concentration with an accuracy of ± 2 percent.

The daily calibration requirement specified in Method 21 and in the various NSPS gives individual instrument operators some flexibility. The calibration could consist of a multipoint calibration in the lab, or it could be a single-point "span-check."

Neither Method 21 nor the applicable NSPS specifies where the calibration must take place. It is simpler to conduct the calibration in the laboratory than at the facility being tested; however, there is the possibility that the calibration may shift sufficiently to affect the accuracy of the leak detection measurements. The degree of shift has not yet been documented for the various commercially available instruments. Because of the potential for calibration shift, one should consider conducting, at a minimum, a single-point span check after the instrument arrives on-site. It is also suggested that a span test be run at the midpoint of the day and at the conclusion of the field work.

Although the span checks discussed above would in most cases qualify as the daily calibrations required by the NSPS, a separate calibration test for organic vapor analyzers should be conducted whenever possible. Because uniform day-to-day calibration gas temperatures and calibration gas flow rates can be maintained in the laboratory, calibrations performed in the regulatory agency laboratory are conducted under more controlled conditions than those conducted in the field. Furthermore, the initial calibration test provides an excellent opportunity to confirm that the entire instrument system is working properly before it is taken in the field. The laboratory calibration data should be carefully recorded in the instrument calibration/maintenance notebook. This calibration should be considered the official calibration required by the regulations.

5.3.2 Laboratory Calibrations

As specified in the EPA-promulgated NSPS, the instruments used in accordance with Method 21 must be calibrated by using either methane or hexane at concentrations that are close to the leak-detection limits. In most cases, the leak-detection limit is 10,000 ppmv, however, for certain sources, it is 500 ppmv above the background levels.

Methane-in-air is generally the preferred calibrant gas for the high concentration range. A hexane-in-air concentration of 10,000 ppmv should not be prepared because it is too close to the lower explosive limit. Also, hexane may condense on the calibration bag surface at this high concentration. If hexane-in-air calibrations are necessary, the chosen concentration should reflect a compromise between the need for adequate calibration of leak detection levels and the practical safety and reproducibility problems inherent in the use of hexane. The EPA's position is that the choice of calibrant gas does not affect the ability of the instruments to detect fugitive leaks.

When charcoal beds are used to provide the VOC-free air, a routine check should be made to assess breakthrough of organic compounds. This is done by passing a low-hydrocarbon-concentration gas stream (approximately 10 to 50 ppmv) through the bed for a period of 5 to 10 minutes. If the bed has not become saturated, the outlet hydrocarbon concentration should be low. Methane should not be used as the hydrocarbon because charcoal is ineffective in adsorbing methane.

5.3.3 Field Span Check Procedure

The following are some of the various ways to calibrate the portable instrument in the field:

- Use large pressurized gas cylinders transported to inspection site.
- Use certified gas cylinders provided by the facility being inspected.
- Use disposable gas cylinders with the appropriate gas composition and concentration.
- Use a gas sampling cylinder with a gas blending system.

Transporting large pressurized gas cylinders is generally impractical because most agencies do not have the necessary vehicles. It is not safe to transport unsecured, pressurized gas cylinders in personal or State-owned cars. Furthermore, there are specific Department of Transportation (DOT) regulations governing the shipping of compressed gases.

Using the facility's gas cylinders is certainly the least expensive approach for a regulatory agency; however, the appropriate gas cylinders are not always available. Also, use of the facility's cylinders prevents the agency from making a completely independent assessment of the VOC fugitive leaks and from evaluating the adequacy of the facility's leak-detection program.

Using disposable cylinders of certified calibration gas mixtures is relatively simple because no on-site blending is necessary and the cylinders are easily transported. The calibration gas mixture may be fed to the instrument directly by using a preset regulator that provides constant gas flow and pressure; or the gas can be fed into a Tedlar or Teflon bag, from which it is drawn into the portable instrument.

A fourth approach involves the use of a stainless steel gas sample cylinder with a small Tedlar sample bag. A small quantity of calibration gas is drawn from a large cylinder of certified gas mixture (at the agency's main laboratory) into the small transportable gas sample cylinder. The calibration gas is kept at a relatively low pressure to minimize safety problems during transport of the material to the job site. The compressed gas is transferred to the Tedlar bag through a regulator and needle valve. At a pressure of 325 psig, a 1 liter sample cylinder should provide enough span check gas for two field checks. Zero air can be supplied by drawing ambient air through a small

charcoal filter. This approach is very inexpensive because the agency is using small quantities of the certified calibration gas mixture from the main cylinder at the laboratory and they are not purchasing any disposable cylinders. Some additional development work on this simple approach is necessary to ensure that a regulator is available to transfer the gas from the main cylinder to the sample cylinder at pressures reaching several hundred psig. Most regulators have a delivery pressure limit of 100 psig. It is also necessary to confirm that the compressed gas can be transferred safely. It should be noted, however, that this is the same approach used to fill the hydrogen fuel cylinders on the portable flame ionization analyzers.

The field span check should be performed at the greater distance possible from potential sources of fugitive VOC. It should also be performed in an area where there is no large AC motors or other equipment that generate strong electrical fields, as such equipment can have an adverse effect on certain types of instruments (e.g., photoionization analyzers). The charcoal filter used in the "clean air" supply should be routinely regenerated to avoid the possibility of saturation. It should be checked occasionally for saturation by supplying a moderate, known concentration of VOC and then checking the measured exit concentration after several minutes.

Data concerning the span checks should be recorded in the field notes. If gauges are provided with the instrument, the tester also should occasionally note the instrument sample gas flow rate.

5.3.4 Thermocouple

Thermocouples may be calibrated in several ways. The simplest method is immersion in an ice bath and boiling distilled water. Electronic "ice point" reference circuits are also commercially available to check thermocouple operation. An isothermal zone box may be used to test the thermocouple in a different range.

There are several suggestions for thermocouple operations. These include:

1. Use the largest wire possible that will not shunt heat away from the measurement area.
2. Avoid mechanical stress and vibration that could strain the wires.
3. Avoid steep temperature gradients.
4. Use the thermocouple wire well within its temperature rating.
5. Use the proper sheathing materials in hostile environments.

5.4 LOCATION OF SAMPLING POINTS

There are many potential sources of fugitive VOC emissions in a given facility. The sources that will be considered here include: pump seals, compressor seals, process valves, pressure relief devices, and agitator seals.

Pumps are used extensively by the target industries to move organic liquid. The most widely used pump is the centrifugal pump. Other pumps used are the positive displacement, reciprocating and rotary action, canned-motor, and diaphragm pumps. Most pumps have a moving shaft which is exposed to the atmosphere. The fluid being moved inside the pump must be isolated from the atmosphere. This requires a seal. Leaks can occur at the point of contact between the moving shaft and the stationary casing. The canned-motor and the diaphragm pumps do not have seals; therefore, they more effectively prevent leaks.

Compressors are, basically, pumps that are used in gas service. Gas compressors used in process units can be driven by rotary or reciprocating shafts and therefore need shaft seals to isolate the process gas from the atmosphere. Rotary shafts may use either packed or mechanical seals, while reciprocating shafts must use packed seals. As with the seals in pumps, the seals in compressors are the most likely source of fugitive emissions from these units.

One of the most common pieces of equipment in an industrial plant is the valve. Individually, process valves have a low emission rate. However, because of the large number of valves present in most plants, as a group they usually constitute the largest percentage of fugitive VOC emissions. For example, in a 100,000 gallon per day petroleum refinery, there are usually 25,000 process valves as compared to about 250 pump seals. In some instances, valves may make up 90 percent of the process components that must be checked for leaks.

Many different types of valves exist, such as globe, gate, plug, ball and check valves. However, they can be grouped into three functional categories:

- Block: used for on/off control. Generally, these valves are used only occasionally, such as when there is a process change (i.e., unit shutdown).
- Control: used for flow rate control.
- Check: used for directional control. Since check valves are enclosed within process piping, they have no stem or packing gland and are not considered to be a potential source of fugitive emissions.

The most common valves in use are the gate valve and the globe valve. These valves can be found either in-line or at the end of a process line.

Engineering codes require that pressure-relieving devices or systems be used in applications where the process pressure may exceed the maximum allowable working pressure of the vessel. The most common pressure-relieving device used in process units is the *pressure relief valve*. Typically, a relief valve is spring loaded. It is designed to open when the process exceeds a set pressure. This allows the release of vapors or liquids until the system pressure is reduced to a normal operating level. When the normal pressure is retained, the valve reseats and a seal is again formed. There are two

potential causes of leakage from relief valves. Simmering occurs when the operating pressure is similar to the set pressure of the valve, while popping occurs when the operating pressure exceeds the set pressure, generally for an extremely short period of time. The other cause of leakage is improper valve reseating after a relieving operation.

Agitators are commonly used to stir or blend chemicals. Like pumps and compressors, agitators may leak organic chemicals at the point where the shaft penetrates the casing. Consequently, seals are required to minimize fugitive emissions from agitators.

Flanges are bolted, gasket-sealed junctions between sections of pipe and pieces of equipment. They are used whenever pipe or equipment components (vessels, pumps, valves, heat exchangers, etc.) may require isolation or removal. The possibility of a leak through the gasket seal makes flanges a potential source of fugitive emissions. However, the results of EPA's refinery sampling programs have shown that flanges have a very low emission factor. Even though there are many of them in any refinery or chemical plant, their overall contribution to fugitive emissions is small.

5.5 OBSERVATION PROCEDURES AND CHECKLISTS FOR VOC TESTING

5.5.1 Performance Criteria and Evaluation Procedures for Portable VOC Detectors

As previously stated, any portable VOC detector may be used as long as it meets the performance criteria specified in Method 21. The performance criteria and detector evaluation procedure is summarized in Table 5-5.

In addition to the performance criteria, Method 21 also requires that the analyzer meet the following specifications:

- The VOC detector shall respond to those organic compounds processed at the facility (determined by the response factor).
- The analyzer shall be capable of measuring the leak definition specified in the regulation (i.e., 10,000 ppmv or "no detectable limit").
- The scale of the analyzer shall be readable to ± 5 percent of the specified leak definition concentration.
- The analyzer shall be equipped with a pump so that a continuous sample is provided at a nominal flow rate of between 0.5 and 3 liters per minute.
- The analyzer shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable standards.

TABLE 5-5. PERFORMANCE CRITERIA FOR PORTABLE VOC DETECTORS

Criteria	Requirement	Time Interval
Response factor	Must be <10	One time, before detector is put in service
Response time	Must be ≤ 30 seconds	One time, before detector is put in service; if modification to sample pumping or flow configuration is made, a new test is required
Calibration precision	Must be $\leq 10\%$ of calibration gas value	Before detector is put in service and at 3 month intervals or next, use, whichever is later

Also, criteria for the calibration gases to be used are specified in Method 21. Two calibration gases are required for both monitoring and analyzer performance evaluation. One is a zero gas which is air with less than 10 ppmv VOC. The other calibration gas uses a reference compound/air mixture. This calibration gas is also referred to as the reference gas. The concentration of the reference gas is approximately equal to the leak definition. The leak definition and the reference compound are both specified in the applicable regulations. Calibration may be performed using a compound other than the reference compound if a conversion factor is determined for the alternate compound. The resulting meter readings during source surveys can be converted to reference compound results. Often instrument manufacturers list conversion factors for other gases in their operator's manuals. Because of the nonlinear responses, however, care must be taken to use the conversion factor at the action level.

Selection of the Necessary Types of Instruments - Selection of the types of instruments needed for source evaluation is based primarily on a review of the types of industrial facilities within the agency's jurisdiction and an evaluation of the measurement requirements inherent in the promulgated VOC regulations. Agencies should also determine if it is possible to select instruments that can be used for future air toxic control requirements as well as the already existing VOC regulations.

Organic Vapor Analyzers - One important criterion in the selection of organic vapor detectors is the response of the instrument to the specific chemical or chemicals present in the gas stream. The abilities of the major classes of organic vapor analyzers to detect different organic chemicals differ substantially. The response factor provides a

convenient index of this property. The response factor (RF) is defined by:

$$\text{Response factor} = \frac{\text{Actual concentration of compound}}{\text{Observed concentration from detector}} \qquad \text{Equation 5-1}$$

A response factor must be determined for each compound that is to be measured, either by testing of from reference sources. The analyzer response factor for individual compounds to be measured must be less than 10.0. The response factor tests are required before placing the analyzer in service, but do not have to be repeated at subsequent intervals.

Response factors can be determined by the following method. First the analyzer is calibrated using the reference gas. Then, for each organic species that is to be measured, a known standard in air is obtained or prepared. The standard should be at a concentration of approximately 80 percent of the leak definition unless limited by volatility or explosivity. In these cases, a standard at either 90 percent of the saturation concentration or 70 percent of the lower explosive limit (LEL) is prepared. This mixture is then injected into the analyzer and the observed meter reading is recorded. The analyzer is then zeroed by injecting zero air until a stable reading is obtained. The procedure is repeated by alternating between the mixture and zero air until a total of three measurements have been obtained. A response factor is calculated for each repetition and then averaged over three runs.

Alternately, if response factors have been published for the compounds of interest for the type of detector, the response factor determination is not required, and existing results may be referenced. When published response factors of the organic compound being monitored are greater than 1 (approaching 10) or much smaller than 1 (approaching 0.1), it is prudent to measure the response factor for these specific compounds. When screening for leaks from a source containing cumene, and FID can be used (RF=1.87), while the catalytic oxidation detector cannot (no RF value). The same data shows that neither of these devices would be capable of detecting leaks from a source containing carbon tetrachloride.

The concept of using response factors as a general guide to analyzer applicability is especially important when dealing with chemical mixtures. Since many process streams in industrial plants are composed of a mixture of compounds, having a simple method to determine the response factor for a given detector type is important. One EPA study has concluded that analyzer response factors for a mixture fall between the responses expected for the pure components. Therefore, if desired, an interpolated or weighted average can be used to predict the response for mixtures based on known responses for individual compounds. For further information see EPA 600/2-81-110, "Response of Portable VOC Analyzers to Chemical Mixtures."

Range and Accuracy - The ability of an instrument to measure 10,000 ppmv should be carefully considered if the instrument will be used to determine compliance with EPA Method 21 regulations. As indicated in Table 5-1, only a few of the currently available units can operate at 10,000 ppmv or above. Other units can operate at this concentration only by using dilution probes. Although dilution probes can be used accurately, they can also be a large source of error. Both changes in flow rate through the dilution probe and saturation of the charcoal tubes used to remove organic vapors from the dilution air can lead to large errors in the indicated organic vapor concentration. Dilution probes also complicate calibration and field span checks. For these reasons, they should be avoided whenever possible.

Generally, an instrument should have the desired accuracy at the concentration of interest. It should be noted that an accuracy of ± 5 percent is required for Method 21 work.

Response Time - The response time of an analyzer is defined as the time interval from a step change in VOC concentration at the input of a sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the analyzer readout meter. The response time must be equal to or less than 30 seconds. The response time must be determined for the analyzer configuration that will be used during testing. The response time test is required before placing and analyzer in service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

The response time of an analyzer is determined by first introducing zero gas into the sample probe. When the meter has stabilized, the system is quickly switched to the specified calibration gas. The time, from the switching to when 90 percent of the final stable reading is reached, is noted and recorded. This test sequence must be performed three times. The reported response time is the average of the three tests.

Safety - All instruments used during field inspections of VOC emission sources and air toxics emission sources must be intrinsically safe if they are to be used in potentially explosive atmospheres. Localized pockets of gas (and even particulates) within the explosive range can result from fugitive leaks and malfunctioning control devices. Intrinsically safe means that the instrument will not provide a source of ignition for the explosive materials when used properly. Instrument designs are certified as intrinsically safe for certain types of atmospheres by organizations such as the Factory Mutual Research Corporation.

The large majority of the organic vapor analyzers are designed to be intrinsically safe in Class I areas. Factory Mutual, however, has certified only a few of the currently available commercial instruments to be intrinsically safe for Class II areas.

It should also be noted that battery-powered thermocouple are not designed as intrinsically safe for either Class I or Class II atmospheres. Therefore, these instruments cannot be taken into or through areas where there is a possibility of encountering explosive mixtures of organic vapors and/or dust. Conventional flashlights are also not intrinsically safe, and they should be replaced by explosion-proof flashlights.

5.5.2 Laboratory And Shop Support Facilities

Because of their level of sophistication, organic vapor analyzers require laboratory and instrument shop support facilities. Regulatory agency inspectors should not attempt to store and calibrate the instruments in their offices, as this practice can lead to significant safety problems and complicate the routine maintenance of the instruments.

Gas Flow Evaluation - Many of the organic vapor analyzers, especially the flame ionization detectors, are sensitive to the sample flow rate. Routine confirmation of proper flow rate is important, especially for those instruments that do not include a flow sensor. Flow rates are normally measured by use of a rotameter designed for flow rates between 0.5 and 5.0 liters per minute. The rotameter should be calibrated against a soap bubble flow meter.

Electrical Diagnostic Equipment - The extent to which malfunctioning organic vapor analyzers can be serviced by agency personnel is limited because the intrinsic safety of the instrument can be voided inadvertently. Nevertheless, qualified agency instrument technicians should be equipped to check such operating parameters as the lamp voltage of photoionization units and the battery output voltage of all portable instruments.

Thermocouple Calibration Equipment - The thermocouple readout device and thermocouple probes should be calibrated at least twice a year. For convenience, the calibrations should be performed in-house with a conventional tube furnace. The field instrument and probes are compared against National Institute of Standards and Technology (NIST) traceable thermocouple probes.

Static Pressure Calibration Equipment - All diaphragm-type static pressure gauges must be calibrated on at least a weekly basis. A relatively large U-tube manometer can be permanently mounted in the agency laboratory for calibration of 0 to 10 inch W.C. and 0 to 60 inch W.C. gauges. An inclined manometer is needed for calibration of the 0 to 2 inch W.C. gauges.

5.5.3 Routine Field-Oriented Evaluations of Instrument Conditions and Performance

Several instrument performance checks should be made before the inspector leaves for the job site and during the routine screening of possible fugitive VOC sources. The field-check procedures are in addition to, not a replacement for, the calibration

procedures discussed earlier. The daily calibration, the field span check, and the routine field performance checks are necessary to confirm that the instrument is operating properly. Preferably, the initial instrument checks should be made by the agency's instrument specialist assigned responsibility for the analyzers. Brief notes concerning each day's initial instrument checks should be included in the main instrument evaluation/maintenance notebook kept in the instrument laboratory. The inspectors make the field checks by using the instruments at the job site and documentation of these field checks should be a part of the inspectors' field notes.

Initial Instrument Checks - It is very important that a few simple instrument checks be made before the inspector leaves for the job site. The appropriate field checks for each instrument can be found in the instruction manual supplied by the instrument manufacturer. The following common factors, however, should be checked regardless of the type of instrument:

- Leak checks including integrity of sample line and adequacy of pump operation
- Probe condition
- Battery pack status
- Detector conditions
- Spare parts and supplies

These checks can be made in a period of 5 to 15 minutes. Repairs to the detectors, batteries, and probes usually can be accomplished quickly if a set of spare parts is kept on hand. Some of the checks that should be made before field work is begun are discussed in the following discussions.

Leak Checks - To leak check the probes on units with flow meters, the probe outlet should be plugged for 1 to 2 seconds while the sample pump is running. If the sample flow rate drops to zero, there are no significant leaks in the entire sampling line. If any detectable sample flow rate is noted, further leak checks will be necessary to prevent dilution of the VOC sample gas during sampling. The leak checks involve a step-by-step disassembly of the probe/sample line starting at the probe inlet and working back toward the instrument. At each step, the probe/sample line is briefly plugged to determine if inleakage is still occurring at an upstream location. Once the site of leakage has been determined, the probe/sample line is repaired and reassembled. To confirm that the probe/sample line is now free of air infiltration, the probe is again briefly plugged at the inlet to demonstrate that the sample flow rate drops to zero.

When leaks are detected, there is sometimes a tendency to over-tighten the fittings, especially those between the instrument body and the end of the sample line. With some types of fittings (e.g., Swagelok fittings) over-tightening can damage the fitting and even lead to persistent leaks.

Units that do not have flow monitors should be leak-tested by installing a rotameter on the sample line as close as possible to the inlet to the instrument body. The leak-testing procedure described above can then be followed. Also, the sound of the pump should be noted, as this provides one qualitative means of identifying clogs. It should be noted, however, that pump noise is useless for identification of probe leakage because the pump continues to receive air due to the infiltration.

Some catalytic combustion units should not be leak tested by plugging the probe. Short-term loss of sample flow would reportedly lead to high detector temperatures.

When more than one probe can be attached to the same instrument body, each probe should be tested. Only those that can be sealed properly should be packed for field use.

Probe Condition - The probes for some instruments can contain a number of independent components, especially those that dilute the sample before analysis. The physical condition of the probe should be checked visually before use. These checks include, but are not limited to, an examination for:

- Presence of any organic deposits on the inside of the probe
- Presence of clean a particulate filter in the probe
- Condition of orifice

5.6 TYPICAL SAMPLING PROBLEMS AND SOLUTIONS

One of the main problems in monitoring organic vapors is locating or pinpointing the leaking source. Organic vapors are dispersed by the wind, sometimes making it difficult to determine their source. It is important that the probe be moved slowly; the slower the instrument response time, the slower the probe must be moved. Placing a notebook or something similar (to block the wind) on the upward side of the suspected leaking source may help locate the leak, but is not required by Method 21.

In some cases, it may be difficult to determine whether a meter response is caused by high ambient air hydrocarbons or by a source leak, particularly when the ambient reading is highly variable. This problem is commonly experienced in enclosed areas. One method to determine if a source is leaking is to place the probe at the leak source and then remove it from the leak source. This operation is repeated at regular intervals. If the movement of the needle corresponds to the placement and removal of the probe (keeping in mind the analyzer response time), the source is probably leaking. The screening value is then determined by subtracting the ambient reading from the measured screening results. A variety of such situations may be encountered and judgement on the part of the operator may be required to obtain a representative reading.

Occasionally, a source may be encountered which has a highly variable leak rate. In general, the maximum sustained reading or the maximum repeatable reading should be recorded. Again, judgement on the part of the operator may be required to obtain a representative reading.

Further difficulty may arise when emission sources contain heavier hydrocarbon streams, particularly hot sources. When these sources are sampled, some of the organic vapor tends to condense on the internal surfaces of the probe or sample hoses. The response of the meter is considerably slower for the heavier hydrocarbons than for the lighter ones. And, the meter may require more time to return to zero. When sampling heavier hydrocarbons, the meter should be allowed to stabilize before reading the results. Before sampling the next source, sufficient time should be allowed for the meter to stabilize or return to zero. Often the meter will not return completely to zero and a considerable adjustment may be required.

Under no circumstances should the end of the probe be placed in contact with liquid. If liquid is drawn into the system through the sample hose, it may damage the analyzer. A liquid trap, connected between the analyzer and the sample probe, can be used. In addition, the equipment being sampling may be covered with a film of grease or dirt. If the probe touches these components, the grease may plug the probe. The inspector can carry a package of pipe cleaners to clean out the probe. Alternatively, a Teflon probe extension can be used and the end cut off if it becomes clogged.

When using a portable VOC detector, the following safety practices are suggested:

1. Do not place a rigid probe in contact with a moving part such as a rotating pump shaft. A short, flexible probe extension may be used.
2. Do not place the umbilical cord from the detector on a heated surface such as a pipe, valve, heat exchanger, or furnace.

CHAPTER 6
TOTAL GASEOUS NON-METHANE ORGANICS AS CARBON -- METHOD 25

6.1 APPLICABILITY

Method 25 is designed to measure Total Gaseous Non-Methane Organics (TGNMO's). Organic compounds which exist as a gas or which have significant vapor pressure at or below 250°F are subject to measurement by this method. Methane is excepted from regulation and is not included in the reported organic emissions. During analysis of the samples, all organics are catalyzed to methane. With proper analytical procedures methane in the sample does not bias the TGNMO result. The catalyzed methane generated during sample analysis corresponds one-to-one with the carbon content of the sample, therefore the TGNMO results are reported in ***"ppm as carbon."***

Method 25 exhibits a 1:1 response for all carbon present in the sample and therefore shows no bias due to differing response factors for different compounds. Method 25 should be used when multiple organics are present or when the make-up of the gas stream is not known. Products of incomplete combustion can be present at any combustion source, therefore the make-up of the exhaust gas cannot be known with certainty. For this reason Method 25 should be used for most combustion sources.

During Method 25 analysis, all carbon present is catalyzed to methane. Because of this, the relative contribution to the total carbon content from different compounds cannot be determined. If specific organic compounds are to be identified and quantified, EPA Method 18 or some other method must employed, as Method 25 is not a compound specific method.

Method 25 is applicable to sources with VOC concentrations of 100 ppm to several percent by volume as carbon. The general application of the method allows detection of concentrations as low as 100 ppmv, but with modifications cited in Section 3.17 of EPA's "Quality Assurance Handbook, Volume III" (EPA-600/4-77-027b) and prior approval of these modification by the Administrator, a lower detectable limit of 50 ppmv can be achieved.

Organic compound concentrations are expressed as carbon by adjusting the ppm values for the number of carbon atoms per molecule. For example, an audit cylinder containing 50 ppmv of toluene would have a concentration of 350 ppm as carbon because toluene has seven carbons per molecule. A mixture of 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm propane would have an organic concentration of 60 ppm as carbon. The 50 ppm CH_4 is not counted because Method 25 excludes methane, 20 ppm propane is counted three times because there are three carbons per molecule in propane. CO and CO_2 are not counted because they are not organic constituents.

6.2 METHOD DESCRIPTION

6.2.1 Sampling Procedures

EPA Method 25 uses an evacuated cylinder or tank to draw gas from the emission source at a constant rate from a single point in the gas stream. The sample is integrated evenly over the period of the test run. The sample is withdrawn from the source through a heated probe, passed through a heated particulate filter and cold condensate trap, and drawn into the evacuated cylinder. Heavy molecular weight organics are condensed out of the sample into the chilled trap, and lighter organics are trapped in the evacuated cylinder. The contents of both the condensate trap and the evacuated cylinder are analyzed for organics following the test run.

A gaseous organic is defined as any organic which is in the gaseous state at standard pressure and 121°C (250°F). Therefore, the probe is kept at a temperature above 121°C at 129°C (265°F) and the filter housing is kept at 121±3°C (250±5°F). The filter ensures that only gaseous organics and no organic particulate matter or mist passes through to the sample. Particulate matter or mist could significantly bias the results high. A thermocouple well should be placed at the probe exit and the filter housing. The temperatures at these locations are monitored every 5 minutes during testing.

After passing through the filter, "heavy" organics condense in the chilled condensate trap. The trap is kept on dry ice to maintain the coldest possible temperature. The dry ice should be kept in an insulated container to ensure that it does not sublime during the run. The dry ice level should be checked periodically during the run. After the condensate trap, the remaining sample flows through a rotameter and fine metering valve used to control the sampling rate, then into the evacuated tank or cylinder. Method 25 states that the sample flow rate shall be between 60 cc/min and 100 cc/min. For a one hour run at a sampling rate of 60 cc/min, a sample volume of 3600 cc or 3.6 liters will be collected. At a flow rate of 100 cc/min, the sample volume will be 6 liters. The evacuated tank should have a volume of at least 4.5 liters to allow for a minimum of 3.6 liters sample with room for error. The tank should not exceed 12 liters unless the sampling time is planned to be greater than one hour. If the volume of the tank is too large, the sample becomes diluted when the tank is pressurized, and the sensitivity of the analysis is decreased. A diagram of the Method 25 sampling train is shown in Figure 6.1 at the end of the chapter, page 6-22. All other figures and tables are also presented at the end of the chapter.

6.2.2 Sampling Equipment

The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, sample purge pump, and evacuated sample tank. Complete systems are commercially available, however a system can be fabricated from easily obtained materials. Any system should meet the specifications listed below. Table 6-1, page 6-23,

lists the calibration specifications and frequencies for the sampling system. Specifications for the sampling equipment are presented in Table D-1, page D-2. Figure 6.2, page 6-24, is an example of an acceptable filter housing. Figure 6.3, page 6-25, is an example of an acceptable condensate trap design.

6.2.3 Analytical Procedures

Both the condensate trap and the sample tank are analyzed for nonmethane organics (NMO's). The condensible organics are recovered from the trap by volatilizing the organics and catalytically oxidizing them to carbon dioxide and collecting the CO_2 in an intermediate collection vessel (ICV). The carbon dioxide concentration in the ICV is then measured. The non-condensible NMO's are recovered from the sample tank by pressurizing the tank and analyzing the contents by using a flame ionization detector (FID).

Both the CO_2 evolved from the condensibles recovery and the non-condensible NMO's are analyzed by using a gas chromatograph with an FID. This analysis differs from other VOC methods because the sample is first conditioned such that all organics are reduced to methane before being introduced to the FID. A separation column is used tc separate methane, carbon monoxide, carbon dioxide, and NMO's. As each compound elutes from the separation column, it is catalytically oxidized to CO_2. The CO_2 is then passed over a reduction catalyst in the presence of hydrogen. The CO_2 is reduced to methane. In this process, only methane is passed to the detector. The FID response is assigned to CO, CO_2, methane and NMO's by the elution time in the cycle. Figure 6.4, page 6-26, is a schematic of the analysis cycle, and Figure 6.5, page 6-27, is a schematic of the sample delivery valve and flow path for the analysis.

The condensible organics are recovered by "burning " the trap, i.e., heating the trap in an oven to 200°C. After burning the trap, the CO2 generated by catalytic oxidation is measured. Any CO2 present in the trap prior to burning will bias the results high. To eliminate this bias, a "cold purge " is done. The cold purge consists of purging the trap with pure air while the trap is immersed in dry ice to drive off any CO2 present. The purge effluent is monitored with a non-dispersive infrared (NDIR) analyzer to assure that all the CO2 is gone before ending the purge. The NDIR analysis is non-destructive, and the purge effluent is collected at the exit of the NDIR in a second ICV. As the NDIR response approaches zero, a 10 ml syringe is used to extract a sample from an injection port located before the NDIR. The 10 ml sample is analyzed using the NMO analyzer for CO2 concentration. The purge is considered complete when the CO2 concentration is below 10 ppm. This ICV is analyzed for NMO's as some organics may volatilize during the purge.

After the cold purge, the trap burn is done. The trap is placed in the oven at room temperature. Then it is heated to 200°C. During the burn, the trap is purged with pure oxygen. As the trap is heated, organics are carried by the purge to the catalyst bed

where they are oxidized to CO_2. The purge is again monitored for end-point using the NDIR, and 10 ml samples are withdrawn from the injection port and checked until the CO_2 concentration is less than 1 ppm. The purge gas is collected in the ICV and analyzed for CO_2 and NMO's (in case some organics passed through the catalyst). Care must be taken that the organics are not volatilized too fast or the catalyst may become saturated. If this happens, some organics will pass through to the ICV. They might not be accounted for by NMO analysis. However, if the organics have high boiling points, they may condense on the side of the ICV and bias the results low. This can be avoided by heating the trap slowly or by adding auxiliary oxygen to the system through a tap between the oven and the oxidation catalyst. Each analytical system should be equipped with such a tap for handling samples with high organic catches. High NMO concentrations in the ICV vessel may indicate breakthrough of unoxidized hydrocarbons.

The NMO concentrations from the sample tank, the ICV from the cold purge, and the ICV from the trap burn, as well as the CO_2 concentration from the trap burn are weighted according to the vessel volume associated with each concentration to determine the carbon content of the original sample.

6.2.4 Analytical Equipment

Since most Method 25 analyses are done post-test in a laboratory, it will be difficult to observe the equipment and procedures. A list of the major equipment components needed for analysis is presented in Appendix D.2, page D-4. Table 6-2, page 6-28, contains the major components of the analytical system and the calibration schedule for each.

6.3 PRECISION AND ACCURACY

Very little data is available concerning the precision and accuracy of Method 25. A limited number of laboratories actively perform the NMO analysis and interlaboratory studies are not complete as of this writing. The generally accepted limits for precision and accuracy are both 20 percent of the mean value. Preliminary results of interlaboratory studies indicate that at lower concentrations, less than 200 ppm, the accuracy limit becomes much higher than 20 percent. At high concentrations, greater than 1000 ppm, the accuracy limit should be less than 20 percent. High concentrations of CO_2 and water will further increase the limits of the accuracy and precision, especially at low organic concentrations.

6.4 LOCATION OF SAMPLING POINTS

Method 25 sampling is performed at a constant rate from a single point in the duct. No traversing or isokinetic sampling is required. The nozzle on the sample probe

can be of any size, but should be constructed such that it can be turned away from the direction of flow in the stack to avoid collecting particulate matter. The nozzle should be placed at the point in the stack or duct with average velocity.

A velocity traverse should be done prior to sampling, and the average impact pressure differential of the gas stream should be determined. The nozzle should be placed at the point where the *delta P* (ΔP) is closest to the average ΔP. If the velocity profile across the duct is level, place the nozzle at the center of the duct.

6.5 OBSERVATION PROCEDURES FOR METHOD 25 TESTING

It is the responsibility of the testing firm to ensure that the sampling and analytical procedures are performed correctly. The following detailed information is given only as training guide for the less experienced test coordinator and does **not** imply mandatory actions by the test coordinator except when the discussions state that the test coordinator "**shall**" conduct a given procedure.

6.5.1 Equipment Specifications

All equipment used during sampling should be checked to ensure that it conforms to the requirements of Method 25. Table D-1, page D-2, is a checklist for sampling equipment specifications and calibration which may be completed or used as a guide by the test coordinator or testing firm. Thermocouples and rotameters should be calibrated and the calibration values and last date of calibration should be noted. Rotameters should have a gamma between 0.9 and 1.1, and thermocouples must agree with the calibration standard within 3°C (5°F). The sample tanks should have been calibrated for standard volume and tagged with a unique identification code. The volume and tag number for each tank should be recorded by the testing firm.

6.5.2 Pre-test Leak Checks

A leak check must be conducted on the entire sampling system prior to sampling. Table D-2, page D-4, is for sampling operations checklist which may be completed or used as a guide by the test coordinator. The allowable leak rate is 1 percent of the sample flow rate. The system is assembled and the probe and filter housing are heated to their respective set-points. A system which is leak tight when cold may not be leak tight when hot, so leak checks should be conducted with the system heated. The condensate trap is placed in the container of dry ice. The top of the trap should be 2.5 to 5 cm above the top of the dry ice. If the 1/8 inch tubing connecting the trap to the filter is covered with dry ice, water and CO_2 will freeze in the tubing and block the flow during sampling. As the trap temperature reaches equilibrium with the dry ice, frost will form on the trap. The frost line should not extend onto the connecting tubing. The inlet tubing to the condensate trap should extend into the filter housing so that organics don't condense in the tubing, but condense in the packing of the trap.

The leak rate is determined by attaching a mercury manometer to the inlet of the probe and evacuating the system to within 10 mm Hg of absolute. The metering valve used to control sample flow rate should be wide open to allow the system to evacuate as quickly as possible. Each sampling system will allow diversion of sample flow to a purge pump. This is usually done with a 3-way valve. Be sure that the 3-way valve is turned toward the sampling position.

As the system is evacuated, the air moving from the sampling train to the evacuated tank can be monitored with the rotameter. The flow through the rotameter should drop to zero, indicating that all the air is out of the system, before the leak check is started. If no flow is initially seen on the rotameter, the flow control valve may be closed or the sample/purge valve might be at the neutral or purge position. The sample valve at the sample tank is switched off to isolate the system from the tank. The system should maintain the same vacuum, as read on the Hg manometer, for 5 or 10 minutes. The allowable leak rate is based on a check time of 10 minutes, so if 5 minutes is used, divide the allowable leak rate by 2. A tank other than the one intended for sample should be used for the leak check because the air initially present in the sampling system is drawn into the leak check tank. The allowable leak rate is calculated by the following equation:

$$\Delta P = 0.01 \times F \times P_b \times t / V_t \qquad \text{Equation 6-1}$$

where:

ΔP = allowable pressure change, mm Hg
F = sample flow rate, cc/min
P_b = barometric pressure, mm Hg
t = leak check time, minutes
V_t = volume of the sampling train, cc

For example, if the sampling train volume were 30 cc's, the intended flow rate 60 cc/min, and 760 mm Hg and 10 minutes are used for barometric pressure and leak check time. Then the maximum allowable pressure change over the 10 minute period is:

$$\Delta P = 0.01 \times 60 \text{ cc/min} \times 760 \text{ mm Hg} \times 10 \text{ mins}/30 \text{ cc} \qquad \text{Equation 6-2}$$
$$= 152 \text{ mm Hg} = 5.98 \text{ in. Hg}$$

After the leak check, the sample/purge valve is turned to the neutral position to prevent in-leakage of ambient air. The flow control valve is closed all the way so that the sample flow rate can be accurately controlled when the run is started. The leak check tank is replaced with a fresh sample tank. When the probe exit temperature and filter housing temperature are at their set points ±3°C (±5°F), remove the manometer fitting from the tip of the probe and place the probe in the stack at the previously determined sampling point.

Each sample tank should also be leak checked. This is most easily accomplished by evacuating the sample tanks one day prior to the test date. The absolute pressure in each tank as well as the barometric pressure and tank temperature are recorded. On the day of testing, the tank pressure and temperature are measured again. After allowing for differences in barometric pressure and tank temperature, the tank absolute pressure should be identical to the previous day's reading. If the sample tanks cannot be evacuated on the day preceding testing, they should be evacuated and left for at least one hour. The absolute pressure in the tank should not change in that hour. If the tank leak checks are started the day prior to testing, the absolute pressure change should be no more than 5 mm Hg. For a one hour leak check, the pressure change should be no more than 1 mm Hg.

6.5.3 Pre-test Sampling Train Purge

A minimum of 10 minutes before the start of the run, the sample/purge valve is turned to purge, and the purge pump is turned on. The purge rate should be set at 60 to 100 cc/min. The purge pump draws stack gas through the probe and filter, but not the condensate trap or sample tank. Just before sampling starts, the purge pump is turned off and the sample/purge valve is returned to the neutral position.

6.5.4 Sampling Procedures

To start the run, the sampler needs to perform the next four steps nearly simultaneously:

1. Start the run timer.
2. Open the sample/purge valve to the sample position
3. Open the valve to the sample tank. If a sealing quick connect is used, push the quick connect to the "locked-in" position.
4. Open the flow control valve to the desired flow rate.

The pressure differential between the duct and the sample tank is the driving force in the sampling train. As the sample tank vacuum decreases, the flow rate will decrease if left unattended. The sample flow rate, probe exit temperature, and filter housing temperature should be monitored and recorded every 5 minutes during the run. The flow control valve should be used to adjust the sample flow rate such that it stays constant to ±10 percent of the intended flow rate.

If the vacuum in the sample tank decreases to the point that the flow rate can no longer be maintained, the following procedure should be followed: Turn off the tank sample valve. Disconnect the tank from the system without disconnecting any other part of the system. Take another leak check and evacuate the sample tank. Record the tank vacuum and temperature. Attach it to the sampling train and resume sampling until the required run time has been met or exceeded.

To end the sampling run, the sample/purge valve is moved to the neutral position and the sample tank valve is turned off. Before the train is taken apart, the condensate trap and sample tank should be tagged with the date, run number, facility and sampling location designations, and the reference number assigned to the project by the testing company. This will assure that no mix-up or confusion arises over sample identity during analysis. The condensate trap and sample tank identification numbers must be recorded on the data sheet for that run.

A post-test leak check is not required by Method 25. Under no circumstances should a leak check be done using a fresh sample tank or a leak check tank, or the purge pump. Since sampling is completed at a vacuum much lower than that of a completely evacuated sample tank, organics will volatilize and be carried from the cold trap to the leak check tank or purge pump. An alternative that is acceptable to verify the integrity of the sampling system at the end of the run is as follows:

Turn the sample/purge valve to the neutral position. Reconnect the sample tank or open the sample tank valve. Wait for the rotameter to drop to zero. Record the system vacuum on the gauge installed in the system (this may be close to zero, but is usually 10 mm Hg). Turn off the sample tank valve and remove the sample tank from the system. Wait 5 minutes and check the system vacuum again. The vacuum should not decrease by more than 2 mm Hg.

This procedure is not required and is at the option of the test coordinator. This procedure will not cause sample loss because it is conducted at the lowest vacuum in the system during the run. If any lighter organics are drawn from the trap to the sample tank, they will be recorded in the non-condensible NMO analysis.

6.5.5 Post Sampling Procedures

Proper procedures must be followed on-site to insure the samples are recovered for analysis. The sample tank is removed from the train and the final tank absolute pressure is recorded to the nearest mm Hg. The condensate trap is removed from the sampling system promptly and both the inlet and outlet are plugged to prevent leakage into or out of the trap. The trap must be kept cold until condensate recovery. To accomplish this, sufficient dry ice must be available to keep the traps cold until they are transported to the analytical lab. The dry ice should be kept in specially designed coolers which will maintain dry ice for several days. The sample tanks may be pressurized on-site. If they are, the final positive pressure must be recorded as well as the tank temperature at that time.

Pressurizing the sample tanks is done by using a "Y" connector to attach the sample tank to both a cylinder of carrier grade air, and the mercury manometer. An on/off valve is located in the leg of the "Y" between the sample tank and the air cylinder. The on/off valve must be closed at this point. The tank pressure is read on

the manometer and the tank temperature is measured and recorded. The on/off valve is opened and air is pushed into the sample tank until approximately 300 mm Hg pressure is indicated by the manometer. The on/off valve is closed again to isolate the sample tank from the air cylinder and the new tank temperature and pressure are measured and recorded. The sample tank is removed from the "Y" and prepared for shipment to the laboratory.

Inspection of the test data sheets before leaving the site may disclose omissions or problems which can easily be remedied now, but which could cause the data to be unacceptable if undetected until later. A copy of an acceptable data sheet is included in Figure D.1, page D-8. Items which must be recorded are:

- Date
- Company Name
- Test Start Time
- Operator
- Sample Tank I.D.
- Trap I.D.
- Train Volume
- Run Number
- Source Designation
- Test Finish Time
- Sample Train I.D.
- Sample Tank Nominal Volume
- System Leak Check Rate
- Tank Temperatures & Pressures - pre-test and post-test

Some missing data may be filled in at the end of the test run with the correct values. Failure to record other values at the appropriate time may be cause for repeating a run. One such item is the pre-test or post-test tank pressure and temperature. If the tank was pressurized before this data was recorded, the run must be repeated, because the sample volume cannot be calculated without it. A missing tank I.D. or trap I.D. may be recovered from the tags on the tanks and traps, but if the traps and tanks were not tagged and no other way exists to assign the proper tanks or traps to the proper runs, the runs must be repeated.

6.6 SAMPLING PROBLEMS, ERRORS, SOLUTIONS, AND ACTION REQUIRED

Because of the large number and variety of organic processes, it is not possible to discuss all of the sampling problems related to Method 25 sampling. Only the most common problems will be addressed.

6.6.1 High Gas Sample Moisture Content and Freezing of Trap

Due to the condensate trap temperature maintained by the dry ice, any moisture and some CO_2 present in the sample will freeze in the trap. If the tubing leading to the trap becomes too cold, water will freeze in the tubing causing a plug. This condition is indicated by a sudden loss of flow during sampling or by difficulty in maintaining proper flow with the flow control valve entirely open. If a plug develops, the timer should be stopped. The purge/sample valve is turned to the neutral position and the

sample tank valve is closed. Any simultaneous trains must also be stopped. The trap is then raised out of the dry ice until the connecting tubing is 2.5 to 5 cm above the dry ice. When the frost film on the connecting tubing melts, sampling can be resumed.

If the sample gas has a high moisture content, the freezing problem at the inlet to the trap may become chronic. If raising the trap out of the dry ice bath does not alleviate the problem, the inlet line can be insulated. Also, a second trap may be placed in front of the condensate trap. The second trap should be kept in an ice water bath. The water will condense out in this trap without freezing and the condensate trap will not collect as much moisture. This second trap must be analyzed in the same manner as the condensate trap. Both traps are kept on dry ice during shipping and storage.

6.6.2 Use of Electrical Service Not Permitted for Probe and Filter

If for safety reasons, the plant cannot allow the use of electrical service at the sampling site, sampling should be conducted using an in-stack filter. The filter should consist of a stainless steel tube packed with quartz wool. The condensate trap is then connected directly to the in-stack filter.

6.6.3 Probe Exit or Filter Temperatures Not Within Specification

The temperature at the probe exit and the filter housing are measured every 5 minutes during the test run. Method 25 requires that these temperatures be maintained above 129°C and at 121 ±3°C, respectively. If specifications, the test coordinator may allow or disallow the run. Since an NMO is defined as a non-methane organic existing at or below 121°C, a probe temperature or filter temperature significantly below 121°C may allow some organics to condense in the sampling train. Therefore, if the probe exit or filter temperature is maintained at or falls below 121°C for an appreciable length of time, the run should be considered invalid. If, however, the probe exit or filter temperature exceeds the limits, organics which have higher boiling points may pass through the filter. If the temperature specifications are exceeded, the bias will be toward higher organic concentrations and the agency may choose to accept the runs.

6.6.4 Non-constant Sample Flow Rate

Method 25 sampling requires a constant flow rate. The flow rate is monitored every 5 minutes throughout the run. However, because of the variable driving force from the sample tank, the flow may not have been maintained at the proper setting ±10 percent. This can be detected at the end of the run by examining the vacuum gauge readings for each five minute point. The difference between readings should be constant over the course of the run. For instance, if a 4.5 liter tank is used for a 1 hour run, the vacuum change over each 5 minute period should be between 3 and 5 cm Hg. If the flow rate falls below the set point the vacuum change would be less than 3 cm Hg. If

the flow is higher than the set point the vacuum change will be greater than 5 cm Hg. Vacuum gauges normally have increments of 1 cm Hg. So, a vacuum reading is only accurate to within about 1 cm Hg, and this should be considered when reviewing the data. A difference of greater than 2 cm Hg from the normal vacuum change for any 5 minute period would indicate a problem with that reading.

The appropriate response when inconsistent flow is detected is dependent on the emission source characteristics. If the emission source is a batch operation where one full batch comprises one test run, the flow problems would weight the results toward the period of highest flow and away from the period of lowest flow. This could be significant depending on process conditions. If the source operates in a steady state condition, then each 5 minute sampling period would be fairly equivalent in terms of the emission rate, and the inconsistent flow would have little effect on the results.

One situation which is serious regardless of process conditions is very high flow. The condensate trap is designed for a flow rate of 60 to 100 cc/min. If the flow is much higher, then breakthrough of heavy organics may occur. The heavy organics would then condense on the sides of the sample tank and not be included in the NMO analysis. If the vacuum change for any period indicates that the flow rate during that period was greater than 200 cc/min, the run should be repeated. High flows are commonly seen at the start of sampling. If the flow control valve is not closed after being wide open during sampling a large amount of gas will be drawn through the system before the flow can be set properly.

6.6.5 Use of Method 25 for Measuring Low Levels of Organics

The lower detectable limit of Method 25 is 100 ppm as carbon. Due to the large number of factors contributing to imprecision in both sampling and analysis, the accuracy of the results is questionable at concentrations near the lower limit. A simple way to increase the accuracy at lower concentrations is to extend the sampling time from 1 to 2 hours. This will require that the vacuum in the sample tank be sufficient to draw sample for twice as long. This can be accomplished by using a larger sample tank (>9 liters) or by changing sample tanks halfway through the run. When the vacuum in the first sample tank becomes too low to maintain the proper flow rate, stop sampling and disconnect the sample tank. The condensate trap should not be disconnected. The same condensate trap is used for the entire test run. The tester should then install a new sample tank and record its volume and I.D. number on the data sheet. Do not perform a leak check with the new sample tank in place. Organics will be drawn from the condensate trap to the sample tank by the higher vacuum. Proceed with the extended test run.

If the source emissions have a high moisture content, the extended test period may cause the condensate trap to fill up with water or ice. This can be avoided by using an auxiliary trap placed in an ice water bath prior to the condensate trap (see

Section 6.6.1). Both traps must be analyzed. The NMO contribution from both tanks and traps is summed.

Method 25 was not intended to measure organics at levels below 100 ppm as carbon. However, if the tester has no other options, Method 25 can be used under the following conditions: (1) extreme caution must be used in preparing the traps and tanks and (2) two traps and two tanks should be set aside as field blanks with the analytical results subtracted from the field sample values. This approach will improve measurements at low level sources, but the accuracy and precision will be poor.

6.6.6 Sampling and Analysis by Different Companies

Because of the small number of laboratories that conduct Method 25 analysis, a large portion of the Method 25 sampling and analysis is conducted by two different companies. This creates problems in assigning responsibility when audit sample results are not acceptable. If the sampling company wants to check the consistency of the analytical results, they should obtain extra traps and cylinders from the laboratory. These clean traps and cylinders should not be opened, marked as if they were a sample, and submitted for analysis.

6.6.7 Measurement in Ducts Containing Organic Droplets

If the gas stream to be sampled contains organic droplets, Method 25 results can be significantly biased-high. The testing firm should first try to find another sampling location. If this is not possible, an in-stack filter may be added to the sampling system with both the in-stack and out-of-stack filters being replaced after each run. The addition of an in-stack filter should help collect organic droplets and will reduce the loading on the out-of-stack filter.

6.7 ANALYSIS

6.7.1 Analytical System Performance Checks

Method 25 analysis is rarely conducted on-site. Therefore, direct observation of the analytical procedures is seldom possible. However, documentation of the quality control checks required by Method 25 should be included in the compliance test report. Method 25 requires the following checks to be done at system start-up or after any period where the analytical system has been unused for 6 months or longer:

- Oxidation Catalyst Efficiency Test
- Reduction Catalyst Efficiency Test
- NMO Response Linearity Test
- CO_2 Response Linearity Test
- NMO Analyzer Performance Check

- Condensible Organic Recovery System Check

Although these tests and checks are only required at system start-up, documentation showing each test to be within the specifications of the method should be included with each report. The checks are described below.

The last portion of this chapter addresses performance checks that should be conducted each day that the system is used for NMO analysis.

Oxidation Catalyst Efficiency Test - With both the oxidation and reduction catalysts unheated, analyze the high level methane standard (nominal 1 percent CH_4 in air) in triplicate. With only the oxidation catalyst heated to its operating temperature, reanalyze the high level methane standard in triplicate. Record data and calculate the oxidation catalyst efficiency using the following equation:

$$\text{Oxidation Catalyst Efficiency} = (R1 - R2)/R1 \times 100 \qquad \text{Equation 6-2}$$

where:

R1 = response with both catalysts unheated
R2 = response with only oxidation catalyst heated

If the oxidation catalyst is working properly, the methane is all oxidized to CO_2 when the catalyst is heated. The system response would then be zero during condition R2. The average response with the oxidation catalyst heated should be less than 1 percent of the average response obtained with both catalysts unheated.

Reduction Catalyst Efficiency Test - With the oxidation catalyst unheated and the reduction catalyst heated to its operating temperature, analyze the high level methane standard in triplicate. Repeat the analysis in triplicate with both catalysts heated to their operating temperatures. Record the data and calculate the reduction catalyst efficiency using the equation below:

$$\text{Reduction Catalyst Efficiency} = R4/R3 \times 100 \qquad \text{Equation 6-3}$$

where:

R3 = response with reduction catalyst only heated
R4 = response with both catalysts heated

When the oxidation catalyst is heated (condition R4), the methane is oxidized to CO_2 and the reduction catalyst must then reduce the CO_2 back to methane. If the reduction catalyst is not 100 percent efficient, then the CO_2 will pass through to the FID and the response will be lower than the response at condition R3. The responses observed under these two conditions should agree within 5 percent.

NMO Response Linearity Test and Initial Calibration - With both catalysts at their operating temperatures, perform triplicate injections of each of the following propane standards: 20 ppm, 200 ppm, and 3,000 ppm in air nominal. Convert certified concentrations in ppm to ppm C by multiplying the ppm concentrations by 3. Record these concentrations on a data sheet, along with the area responses observed for each injection. Calculate the mean response factor as ppm C/mean area for each standard and the overall mean response factor for all three standards. The NMO response linearity is acceptable if the average response factor of each calibration gas standard is within 2.5 percent of the overall mean response factor and if the relative standard deviation for each set of triplicate injections is less than 2 percent. The overall mean response factor is used as the initial NMO calibration response factor (RF_{NMO}).

CO_2 Response Linearity Test and Initial Calibration - Perform the linearity test as described above, except use CO_2 calibration standards of 50 ppm, 500 ppm, and 1 percent in air. The overall mean response factor is used as the initial CO_2 calibration response factor (RF_{CO2}). The CO_2 calibration response factor (RF_{CO2}) should be within 10 percent of the NMO calibration response factor (RF_{NMO}).

NMO Analyzer Performance Test - After calibration of the NMO response as described above, analyze each of the following four gas standard mixtures in triplicate. Standard 1 is nominally 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm propane in air; Standard 2 is nominally 50 ppm hexane in air; Standard 3 is nominally 20 ppm toluene in air; and Standard 4 is nominally 100 ppm methanol in air. Record the NMO area responses for each standard on the data sheet. Convert the certified organic compound concentrations of the standards to ppm C by multiplying by the carbon number of the compound (3 for propane, 6 for hexane, and 7 for toluene). Record these concentrations on the data sheet as the expected concentrations. Calculate the mean NMO concentration of the test gas. The analyzer performance is acceptable if the average measured NMO concentration for each mixture or standard is within 5 percent of the expected value.

Condensible Organic Recovery System Check - This check is conducted in three stages. First, the carrier gas is checked for its blank concentration. The carrier gas blank value should be less than 5 ppm. Second, the oxidation catalyst is checked, then the system is checked by spiking with a known organic concentration. A schematic of the condensate recovery system is shown in Figure 6.6, page 6-29.

The oxidation catalyst efficiency is tested by the following sequence.

1. The system is set-up as normal using a clean condensate trap, and clean immediate collection vessel (ICV) which has been evacuated.
2. The recovery valve is set to the vent position, and the carrier gas is replaced with the 1 percent methane in air cylinder.
3. Set the flow from the 1 percent methane standard equal to the normal

carrier gas flow rate. Allow the NDIR response to stabilize, then turn the recovery valve to the ICV. Using the flow control valve on the ICV, maintain the system pressure near atmospheric. Continue flow until the ICV has been pressurized to 300 mm Hg.

4. Analyze the CO_2 concentration in the ICV using the NMO analyzer. The CO_2 concentration should agree with the certified concentration of the 1 percent methane standard within 2 percent.

The condensible organic recovery efficiency is checked by setting the recovery system up as normal, except the condensate trap is replaced with a liquid sample injection unit similar to that shown in Figure 6.7, page 6-30. The recovery valve is turned to the collect position, then 50 μl of hexane is injected into the liquid sample injection unit. The liquid organic is collected by the normal procedures of the method. Hexane has six carbons and the percent recovery is calculated using the following equation:

$$\textit{Percent Recovery} = 1.604 \times \frac{M x V_v x P_f x C_{cm}}{L x \rho x T_f x N} \qquad \text{Equation 6-4}$$

where:

M	=	molecular weight of compound injected, g/g-mole
V_v	=	volume of ICV tank, m^3
P_f	=	final pressure of ICV tank, mm Hg absolute
C_{cm}	=	measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2
L	=	volume of liquid injected, μl
ρ	=	density of liquid injected, g/cc
T_f	=	final temperature of ICV, °K
N	=	carbon number of liquid compound injected (N = 12 for decane, N = 6 for hexane).

The recovery efficiency should be checked in triplicate with 50 μl hexane, then in triplicate with 10 μl hexane, 50 μl decane, and 10 μl decane. The percent recovery is acceptable if the average percent recovery is 100 ±10 percent with a relative standard deviation of less than 5 percent for each set of triplicate injections.

The following set of performance checks should be performed each day that the system is used for NMO analysis.

Leak Test of Condensibles Recovery System - A clean trap should be installed in the system, then the vacuum pump is used to evacuate the system to 10 mm Hg absolute.

The system is closed off and the system pressure is monitored for 10 minutes. The system pressure should change by no more than 2 mm Hg over this time period.

System Background Check for Condensibles Recovery System - The carrier air and auxiliary air are set to their normal operating parameters. The recovery valve is set to the vent position and a 10 ml syringe is used to extract a sample from the injection port upstream of the NDIR. The 10 ml sample is injected into the NMO analyzer and the CO_2 concentration is recorded. The CO_2 concentration should be less than 10 ppm.

Oxidation Catalyst Efficiency - This test is performed in the same manner as described previously for system start-up.

CO_2 Analyzer Response - The highest level CO_2 calibration gas is analyzed in triplicate. The average peak area is used to calculate a daily response factor for CO_2. The daily CO_2 response factor should agree with the system CO_2 response factor determined during system start-up.

NMO Response Check - The gas mixture containing nominally 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm propane in air is analyzed in triplicate. The average area count value is used to calculate a daily response factor as carbon. The daily response factor should be within 5 percent of the initial NMO response factor.

If audit cylinder samples are included with the field samples to be analyzed, the test results may be accepted or rejected on the basis of the audit results, and the performance check documentation may be optional. However, if no audit is performed, the test results cannot be evaluated without proper documentation of system performance and calibration.

6.7.2 Calculations

The calculations required to compute the TGNMO concentration of the original sample from the sampling and analytical data recorded are reproduced in Appendix D.3, page D-4. The number of variables is large and some of the equations are complex. It is recommended that a computer program or spreadsheet software be used to handle all calculations. A copy of the program used for calculations should be included with the test results. Also, example calculations using data from one of the test runs for each test series should be included. The run number of the example calculation must be stated. Check to be sure that the example calculation agrees with the reported concentration within reasonable round-off error. Choose a different test run and perform the calculations yourself. The answer should again agree with the reported result to within reasonable round-off error.

Calculations should be carried out to at least one extra decimal place beyond that of the acquired data and should be rounded off after final calculation to two significant

digits for each run or sample. All rounding of numbers should conform to ASTM 380-76 procedures.

6.8 AUDIT PROCEDURES

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) administering the audit and their standards and equipment are different from the regular field team and their standards and equipment. Routine quality assurance checks by a field team are necessary to generate good quality data, but they are not part of the auditing procedure. Table 6.3, page 6-31, summarizes the quality assurance functions for auditing.

Based on the requirements of Method 25 and the results of collaborative testing of other EPA Test Methods, one performance audit is required when testing for compliance for Standards of New Source Performance and is recommended when testing for other purposes; and a second performance audit is recommended. The 2 performance audits are:

1. An audit of the sampling and analysis of Method 25 is required for NSPS and recommended for other purposes.
2. An audit of the data processing is recommended.

It is suggested that a systems audit be conducted as specified by the test coordinator in addition to these performance audits. The two performance audits and the systems audit are described in detail in Chapters 6.8.1 and 6.8.2, respectively.

6.8.1 Performance Audits

Performance audits are conducted to evaluate quantitatively the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). It is required that a cylinder gas performance audit be performed once during every NSPS compliance test utilizing Method 25 and it is recommended that a cylinder gas audit be performed once during any test utilizing Method 25 conducted under regulations other than NSPS.

Performance Audit of the Field Test - As stated in Section 4.5 of Method 25 (40 CFR 60, Appendix A) and the "Instructions for the Sampling and Analysis of Total Gaseous Nonmethane Organics from Quality Assurance Audit Cylinders using EPA Method 25 Procedures" (supplied with the EPA audit gas cylinders), a set of two audit samples are to be collected in the field (not laboratory) from **two different concentration** gas cylinders at the same time the compliance test samples are being collected. The two audit samples are then analyzed concurrently and in exactly the same manner as the compliance samples to evaluate the tester's and analyst's technique and the instrument calibration. The information required to document the collection and analysis of the

audit samples has been included on the example data sheet shown in Figure 6.8, page 6-32. The audit analyses shall agree within 20 percent of the actual cylinder concentrations. The testing firm may obtain audit cylinders by contacting the agency responsible for observing and/or evaluating the compliance test and informing the agency the time and location of the compliance test. The test coordinator will then contact: U.S. Environmental Protection Agency, Atmospheric Research and Exposure Laboratory, Quality Assurance and Technical Support Division, Research Triangle Park, North Carolina 27711 and have the cylinders shipped to the specified site.

Responsibilities of the Test Coordinator - The primary responsibilities of the observer are to ensure that the proper audit gas cylinders are ordered and safe-guarded, and to interpret the results obtained by the analyst.

When notified by the testing firm that a compliance test is to be conducted, the test coorinator orders the proper cylinders from the EPA's Quality Assurance Division. Generally the audit cylinders will be shipped (at EPA's expense) directly to the specified test site. However, if the test coordinator will be on-site during the compliance test, the audit cylinders may be shipped to the testing firm for transport to the sampling site. Since the audit cylinders are sealed by EPA, the testing firm will not be allowed to collect any audit gas without breaking the seal.

The audit gas concentration(s) should be in the range of 50 percent below to 100 percent above the applicable standard. If two cylinders are not available, then one cylinder can be used. If the applicable regulation is based on removal efficiency rather than emission limits, an audit cylinder should be provided near the expected concentration of both the inlet and outlet of the control system. The testing firm should provide the test coordinator with the best available information to approximate the concentration at the control system inlet. The expected concentration at the control system outlet can be calculated using the regulated removal efficiency.

The test coordinator must ensure that the audit gas cylinder(s) are shipped to the correct address, and to prevent vandalism, verify that they are stored in a safe location both before and after the audit. Also, audit cylinders should not be analyzed when the pressure drops below 200 psi. The test coordinator ensures that the audits are conducted as described below. At the conclusion of the collection of the audit samples, if the testing firm will transport the audit cylinders to the home laboratory for shipment back to the EPA/QAD contractor, the test coordinator seals both cylinders to ensure that additional audit sample gas cannot be collected without breaking the seal.

The test coordinator must interpret the audit results. Indication of acceptable results may be obtained by the testing firm immediately following analysis by telephoning the responsible agency with the audit and compliance test results in ppm C. The testing firm must include the results of both audit samples, their identification numbers, and the analyst's name along with the results of the compliance test samples in the appropriate

reports to the EPA regional office or other appropriate agency during the 30 day period following the test.

When the measured audit concentration agrees within 20 percent of the true value, the audit results are considered acceptable. Failure to meet the 20 percent specification may require reanalysis of the audit samples and compliance test samples, reauditing, or retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the agency may waive the reanalysis, further audits, or retest requirements and accept the results of the compliance test. For example, if the audit results average 38.6 percent low, the compliance results would be divided by (1 - 0.386) to determine the correlated effect. If the audit results average 58.3 percent high, the compliance sample results would be divided by (1 + 0.583) to determine the effect. When the compliance status of the facility is the same with and without the correlated value, then the responsible agency may accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the agency may also choose to use the test data to determine the compliance or noncompliance of the affected facility.

The same analyst, analytical reagents, and analytical system shall be used for analysis of the compliance test samples and the EPA audit samples; if this condition is met, and the same testing firm is collecting other sets of compliance test samples, auditing of subsequent compliance analyses for the same agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance test samples under the jurisdiction of different agencies, unless prior arrangements are made with both agencies.

During the audit, the test coordinator should record the coded cylinder number(s) and cylinder pressure(s) on the "Field Audit Report Form," Figure 6.8, page 6-32. The individual being audited must not be told the actual audit concentrations or the calculated audit percent accuracy.

On-site Collection of Audit Sample(s) - The cylinder gas performance audit sample collection must be conducted in the field (not laboratory) at the same time the compliance test samples are being taken. A maximum of 5 liters of audit gas is to be used for each test run unless multiple sample tanks are required for sampling. The testing firm is required to supply a 2 stage regulator (CGA - 350), a glass manifold or Teflon tee connection, and other suitable Swagelok fittings (they are not supplied) for use with the audit gas cylinder. The recommended procedures for conducting the on-site audit sample collection are as follows:

1. The test coordinator should verify that the seal affixed to the audit cylinder by the shipping laboratory is still intact. After the seal has been checked by the test coordinator, the testing firm may break the seal. However, if the test coordinator is not present at the time of the audit, the testing firm may break the seal and proceed with the audit.

2. The tester should set up the Method 25 sampling train and perform the leak check.
3. The audit gas from the cylinder has to be sampled at atmospheric pressure either from a glass manifold or through a Teflon tee connection. This can be done by attaching both the cylinder and the probe of the Method 25 sampling train to two of the manifold or tee connections while excess gas flows out through the remaining connection as shown in Figure 6.9, page 6-33. This can be accomplished by starting the cylinder gas flow into the manifold or tee with the sampling train flow turned off. Then, turn on the sampling train flow while adjusting the flow from the audit cylinder to ensure excess audit gas flows from the manifold or tee. After the proper sampling flow rate has been obtained in the sampling train, adjust the audit cylinder so only a few cubic centimeters of excess gas is discharged from the manifold or tee. The testing firm must ensure that the audit gas is conserved.
4. Use the same sampling flow rate and sample volume as used for the field test samples. When a constant flow rate can no longer be maintained by the sampling train, it should be turned off and then the audit cylinder shut off. Ensure that the audit cylinder is closed tight to prevent leakage. If the compliance test requires more than one sample tank to complete a run, each audit sample should use the same number of tanks required by the average run.
5. The same procedures are repeated for the second audit cylinder using a separate sampling train.
6. The sampling trains containing the audit samples should be recovered and shipped in the same manner as and along with the field test samples.
7. In all cases, it is recommended that the test coordinator reseal the audit cylinders to ensure against tampering. However, if the testing firm is to return the cylinder to the EPA/QAD contractor, it is mandatory that the audit cylinders are resealed by the test coordinator.
8. The audit cylinders are to be shipped back immediately after the test to the EPA/QAD contractor at the cost of the responsible agency or the testing firm either by ground transportation or air cargo. They are <u>not</u> to be shipped collect.

Analysis of Audit Sample(s) - The collected audit sample fractions (condensate trap and evacuated tank) are analyzed at the same time as the Method 25 compliance test samples. Follow the procedures described in Method 25 for sample analysis, calibration, and calculations. The same analysts, analytical reagents, and analytical system shall be used for both the compliance test samples and the EPA audit samples.

Reporting of Audit Sample(s) Results - The audit sample results are to be reported to the responsible agency by the testing firm in terms of condensibles (condensate trap fraction), noncondensibles (tank fraction), and total (sum of both

fractions) as ppm C. The agency will in turn report the results to the EPA/QAD contractor for continuing evaluation of the Method 25 audit program. The testing firm must also supply the agency with the results of both audit samples as described above, their identification numbers, and the analyst's name along with the results of the compliance test samples in written reports to the EPA regional office or the appropriate agency during the 30 day period.

Performance Audit of Data Processing - Calculation errors are prevalent in processing data. Data processing errors can be identified by auditing the recorded data on the field and laboratory forms. The original and audit (check) calculations should agree within round-off error; if not, all of the remaining data should be checked. The data processing may also be audited by providing the testing firm with specific data sets (exactly as would appear in the field), and by requesting that the data calculation be completed and that the results be returned to the agency. This audit is useful in checking both computer programs and manual methods of data processing.

6.8.2 Systems Audit

A systems audit is an on-site, qualitative inspection and review of the total measurement system (sample collection, sample analysis, etc.). Initially, a systems audit is recommended for each compliance test, defined here as a series of three runs at one facility. After the testing firm gains experience with the method, the frequency of auditing may be reduced -- for example, to once every four tests.

While on site, the auditor observes the testing firm's overall performance, including the following specific operations:

1. Setting up and leak testing the sampling train.
2. Collecting the sample at a constant rate at the specified flow rate.
3. Conducting the final leak check and recovery of the samples.
4. Sample documentation procedures, sample recovery, and preparation of samples for shipment.

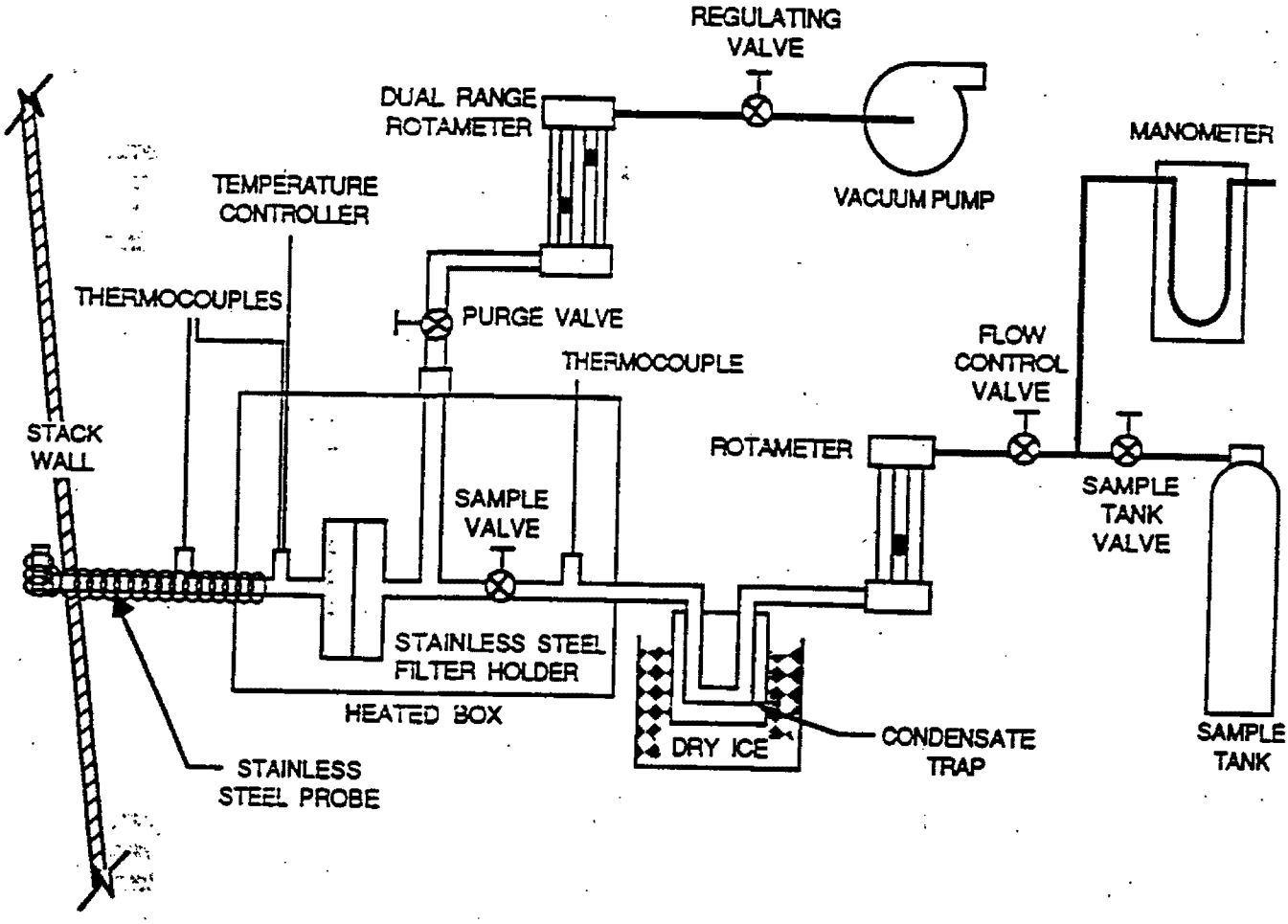


Figure 6.1. Method 25 sampling train.

TABLE 6-1. METHOD 25 SAMPLING EQUIPMENT COMPONENT AND CALIBRATION SPECIFICATIONS

Apparatus	Limits	Frequency and Method
Sample Tank Volume	±5 cc or 5 g	Initially
Sampling Train Volume	No Limit (suggest ±2 cc)	Initially and after replacing any component; should have condensate trap installed during calibration.
Rotameters	r = 0.9 to 1.1	Initially and whenever calculated sample volume does not match volume expected from sample flow rate (deviation of > 10%)
Thermometers	Within 3°C (5.4°F)	Calibrate against mercury-in-glass thermometer and in boiling water; check at ambient temp before each test; recalibrate if ambient check is outside limit
Barometer	Within 2.5 mm Hg (0.1 in Hg)	Check against mercury-in-glass barometer or National Weather Service value. Check before and after each test.

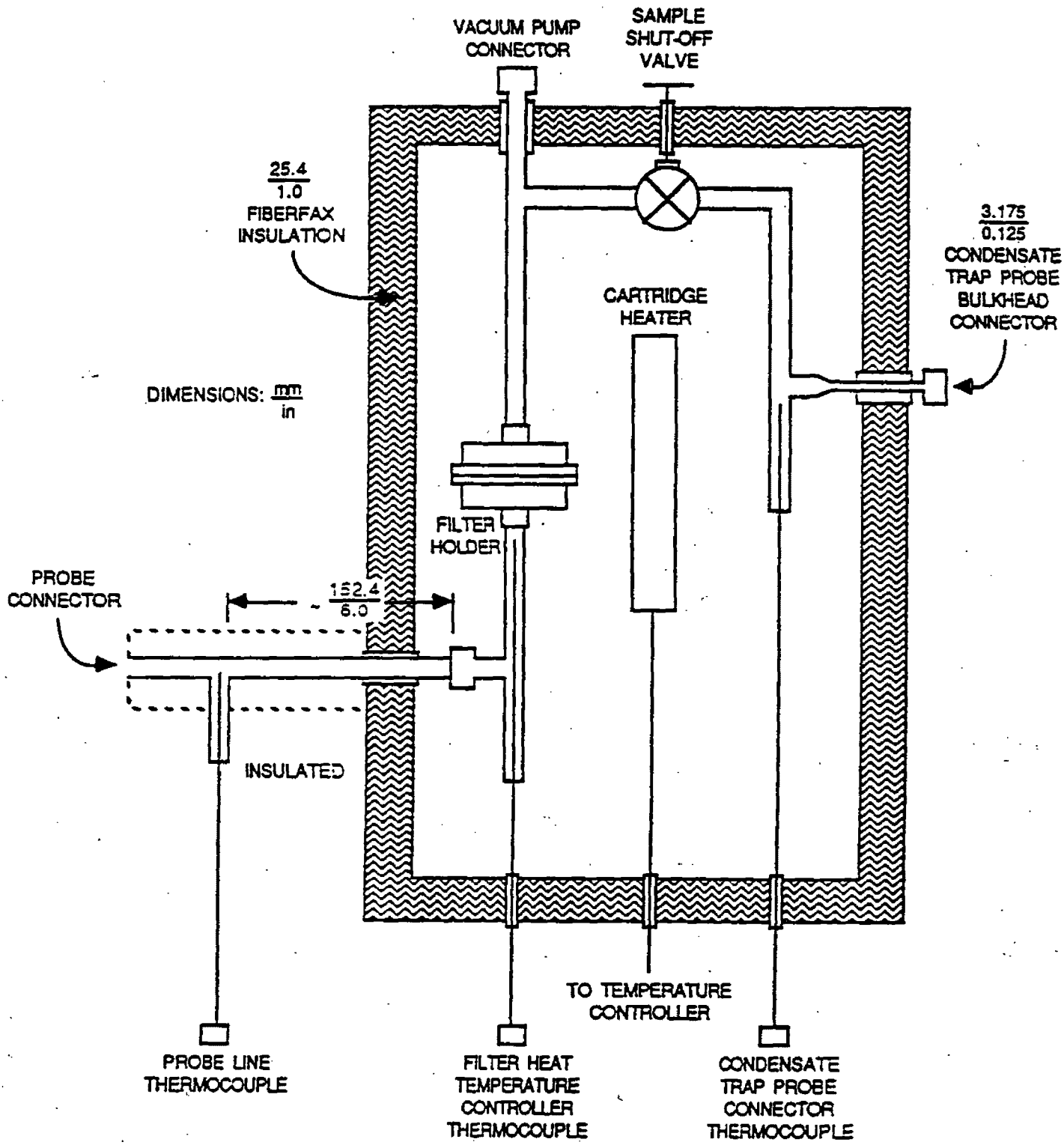


Figure 6.2. Method 25 filter housing.

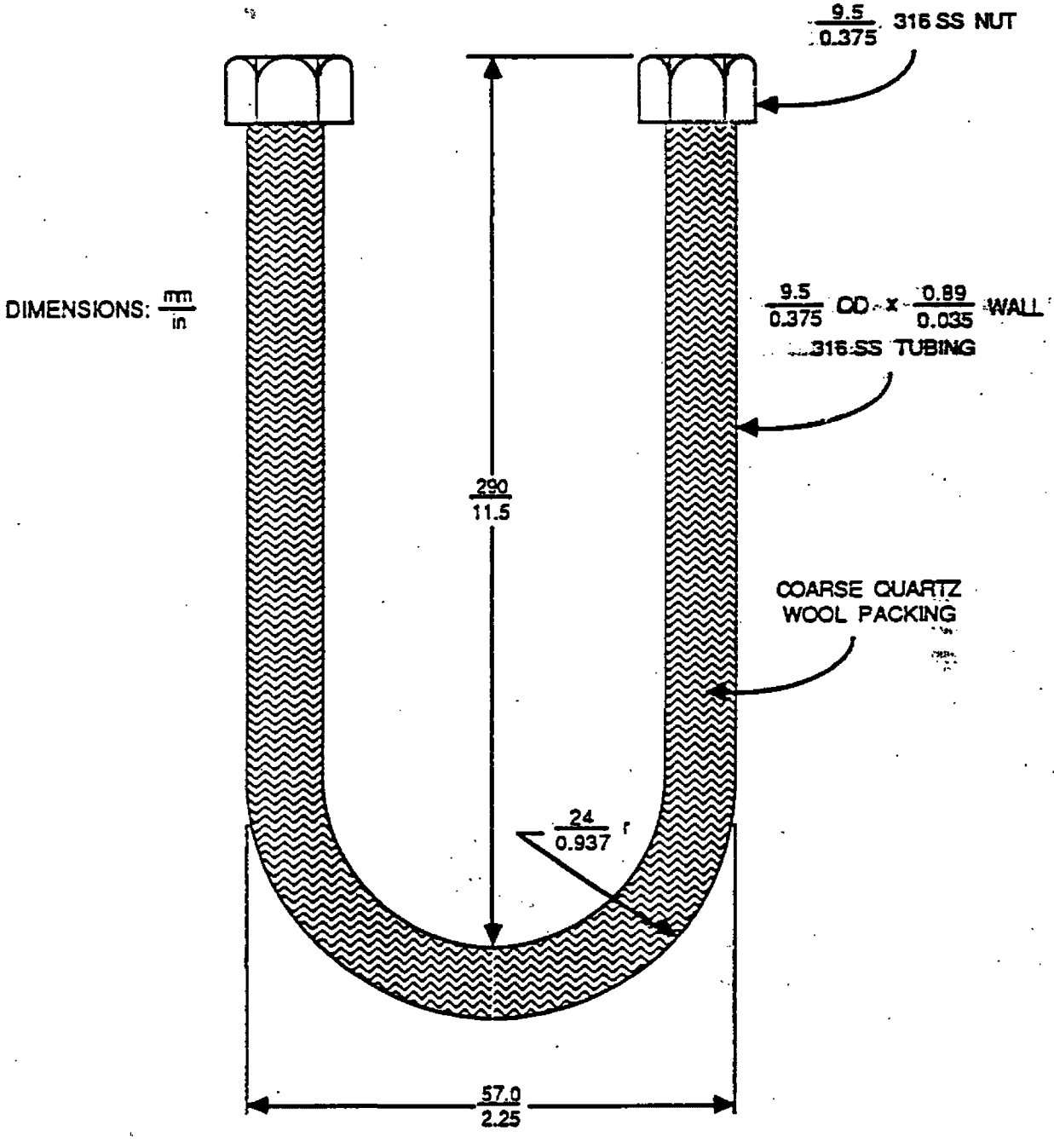


Figure 6.3. Method 25 condensate trap.

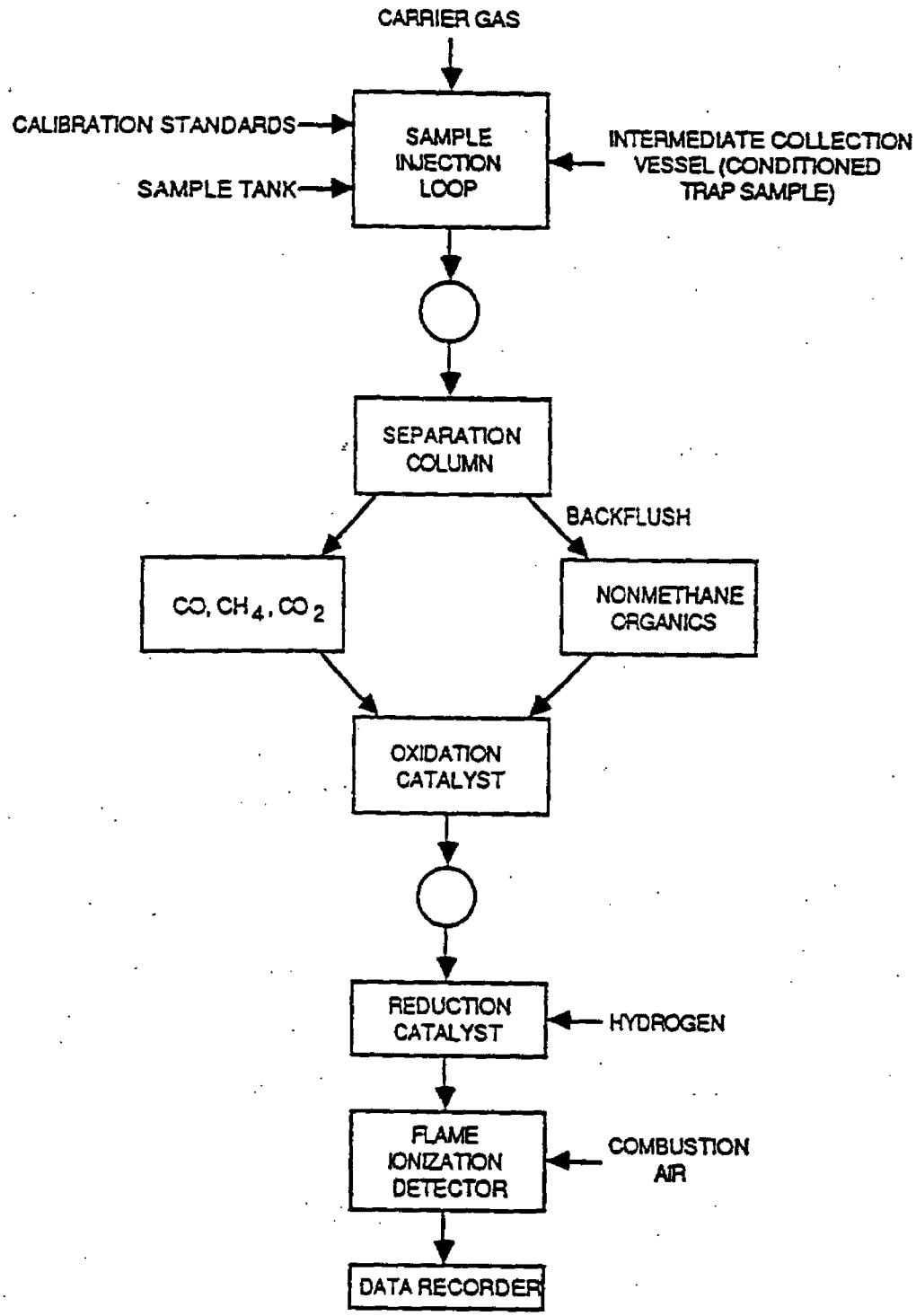


Figure 6.4. NMO analytical cycle.

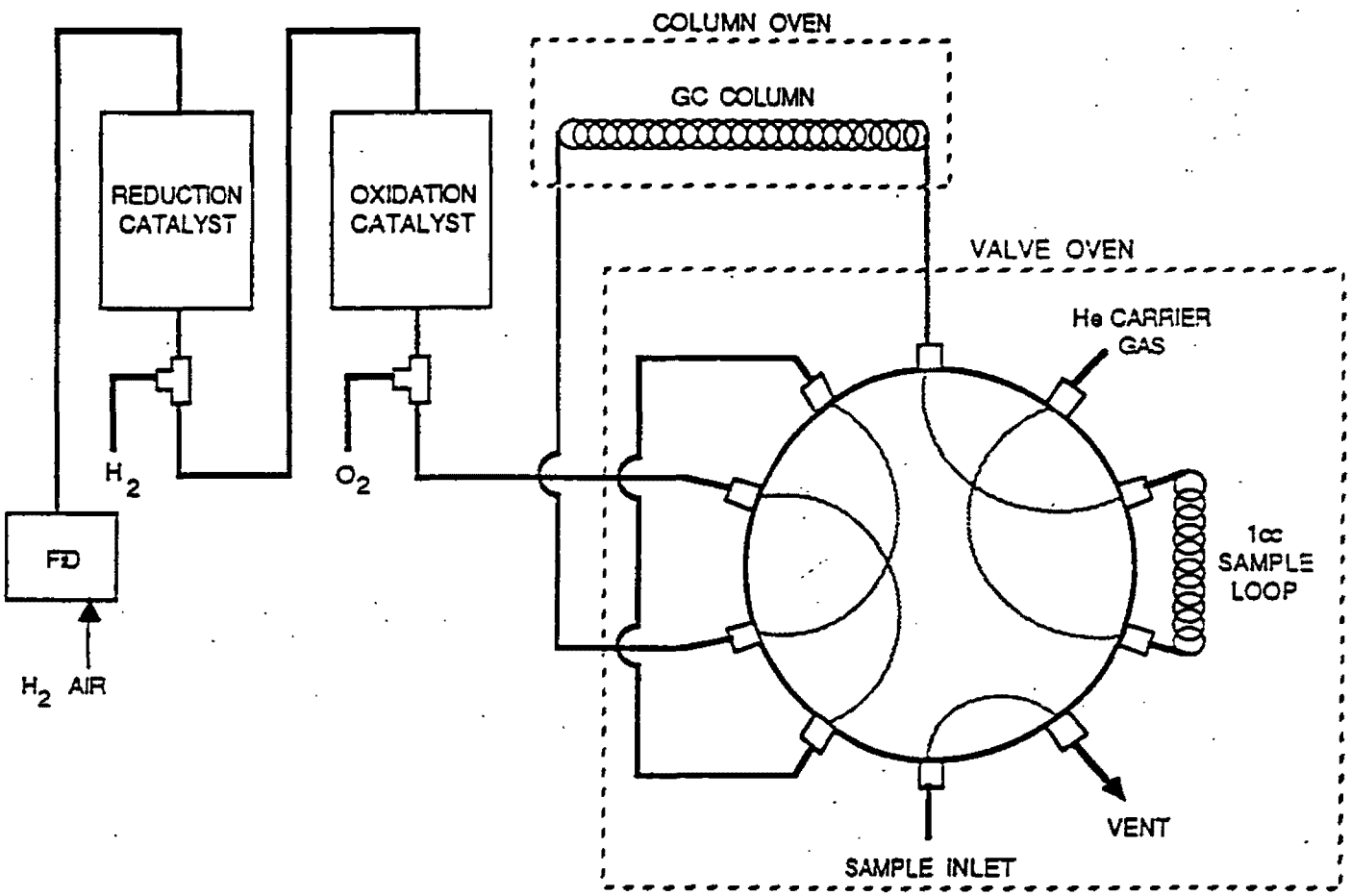


Figure 6.5. NMO sample delivery schematic.

TABLE 6-2. ANALYTICAL COMPONENT AND CALIBRATION SCHEDULE

Component	Limits	Calibration Check	Frequency
Condensate Recovery System			
NDIR	±2% of span	3 point linearity check	Each day used for analysis
Catalytic Oxidizer	≥ 99%	Oxidation efficiency	In triplicate each day of analysis
System (overall)	≥ 95%	Recovery efficiency	@ system start up or after 6 month shutdown
NM0 Analyzer			
FID	±2.5% of tag	3 point linearity check	@ system start up or after 6 month shutdown
FID	±5% of tag	Response test	Each day used for analysis
Catalytic Oxidizer	≥ 99%	Oxidation efficiency	@ system start up or after 6 month shutdown
Reduction Catalyst	≥ 95%	Reduction efficiency	@ system start up or after 6 month shutdown
System (overall)	±5%	4 point performance check	@ system start up or after 6 month shutdown

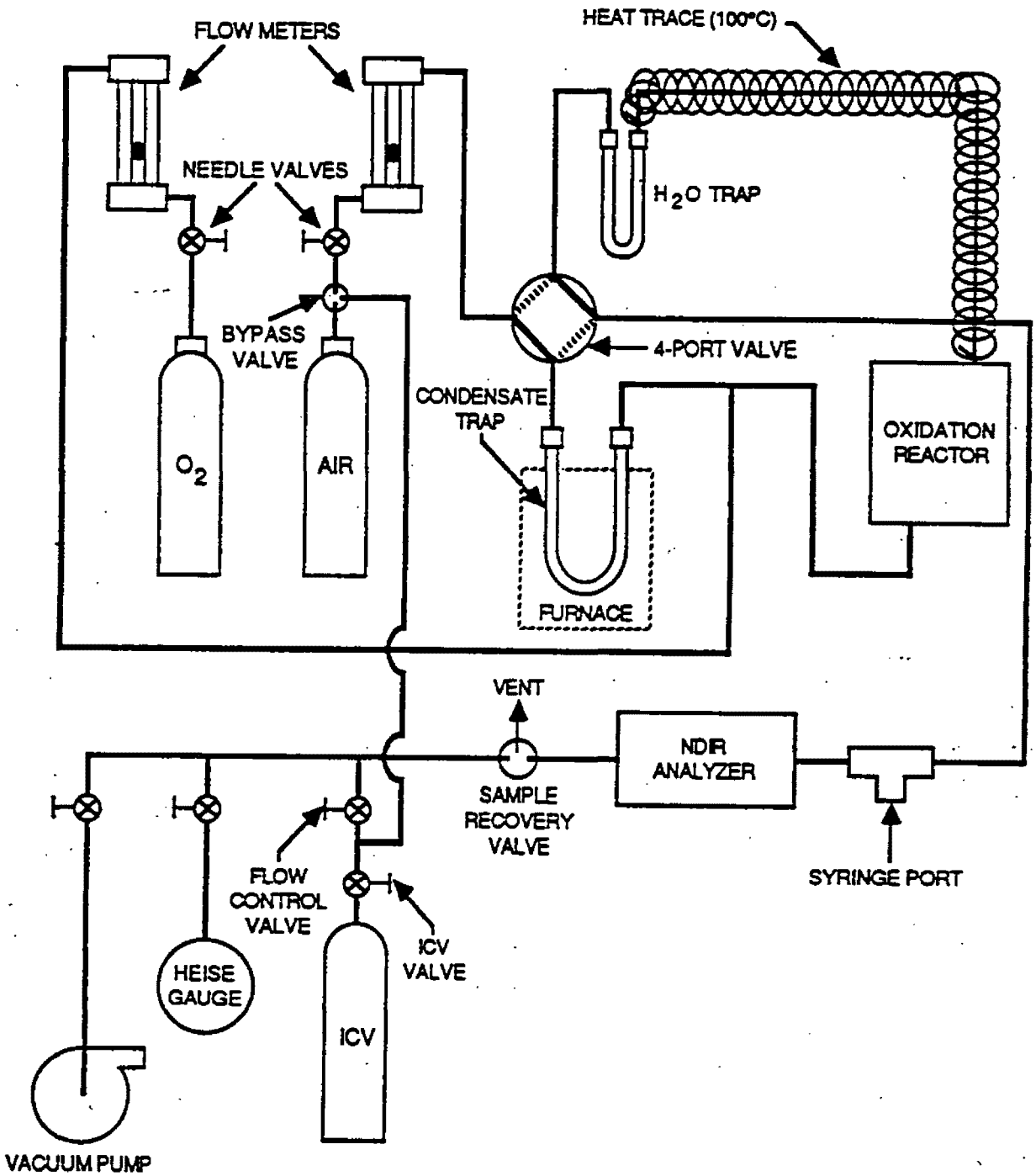


Figure 6.6. Condensate recovery system.

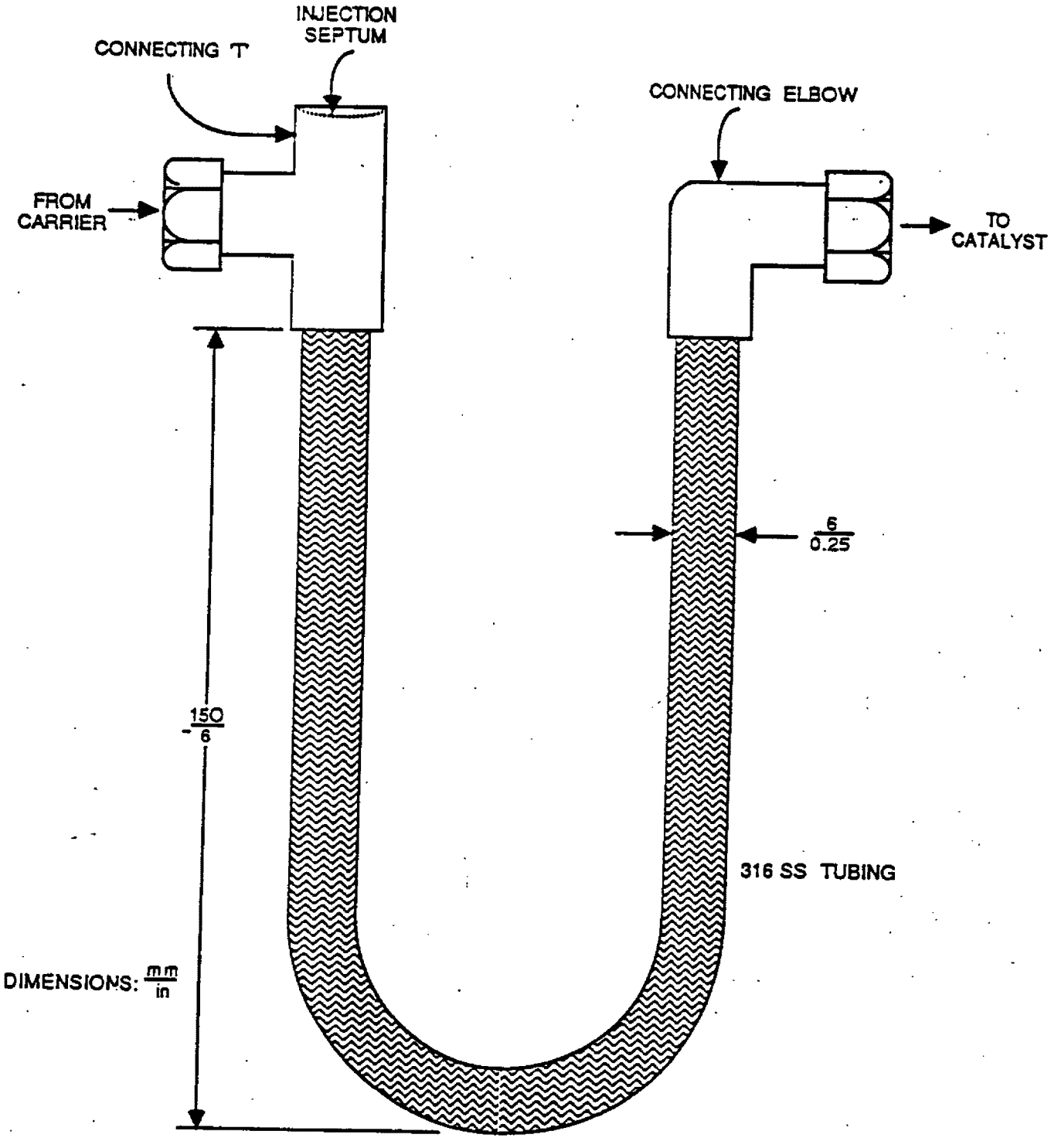


Figure 6.7. Liquid sample injection unit.

TABLE 6-3. ACTIVITY MATRIX FOR METHOD 25 AUDITING PROCEDURES

Apparatus	Acceptance Limits	Frequency and Method of Measurement	Action If Requirements Are Not Met
Performance Audit of Analytical Phase	Measured relative error of audit samples less than 20% for both samples	Frequency: Once during every enforcement source test* Method: Measure audit samples and compare results to true values	Review operating technique and repeat audit, repeat test, reject test, or accept results
Data Processing Errors	Original and checked calculations agree within round-off error	Frequency: Once during every enforcement source test* Method: Independent calculations starting with recorded data	Check and correct all data from the audit period represented by the checked data
Systems Audit--observance of technique	Operational technique as described in this chapter	Frequency: Once during every enforcement source test* until experience gained, then every fourth test Method: Observation of techniques assisted by audit checklist, Figure 6.8	Explain to test team their deviations from recommended techniques and note on Figure 6.8

*As defined here, a source test for enforcement of the NSPS comprises a series of runs at one source. Source tests for purposes other than enforcement of NSPS may be audited at the frequency determined by the applicable group.

Part A. - To be filled out using information from organization supplying audit cylinders.

1. Company supplying audit sample(s) and shipping address

_____

2. Test coordinator, organization, and phone number

_____

3. Shipping instructions: Name, Address, Attention

_____

4. Guaranteed arrival date for cylinders - _____
5. Planned shipping date for cylinders - _____
6. Details on audit cylinders from last analysis

	Low conc.	High conc.
a. Date of last analysis.....	.....	.....
b. Cylinder number.....	.....	.....
c. Cylinder pressure, psi.....	.....	.....
d. Audit gas(es)/balance gas..	N2	N2
e. Audit gas(es), ppm.....	.....	.....
f. Cylinder construction.....	Aluminum	Aluminum

Part B. - To be filled out by test coordinator.

1. Process sampled _____
2. Audit location _____
3. Name of individual audit _____
4. Audit date _____
5. Audit cylinders sealed _____
6. Audit results:

	Low conc. cylinder	High conc. cylinder
a. Cylinder number.....	.....	.....
b. Cylinder pressure before audit, psi.....	.....	.....
c. Cylinder pressure after audit, psi.....	.....	.....
d. Measured concentration, ppm C		
U-tube fraction	.....	.....
Tank fraction	.....	.....
Total concentration	.....	.....
e. Actual audit concentration, ppm C		
f. Audit accuracy:[1]		
Low conc. cylinder.....	.....	.....
High conc. cylinder.....	.....	.....
Percent accuracy = $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$		
g. Problems detected (if any).....	.....	.....

[1]The audit accuracy is calculated on the total concentration.

Figure 6.8. Field audit report form.

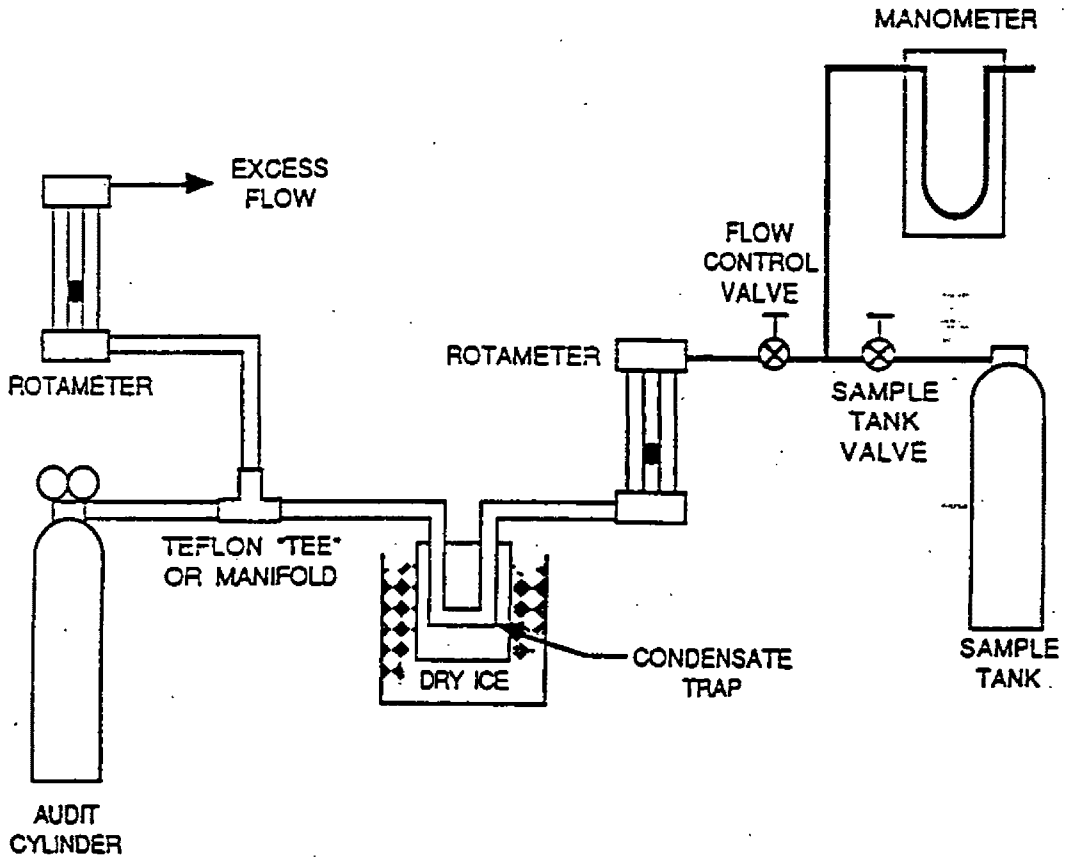


Figure 6.9. Schematic of Method 25 audit system.

CHAPTER 7
TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER - METHOD 25A

7.1 APPLICABILITY

Method 25A is designed to measure Total Hydrocarbon (THC) concentrations in flue gas streams. Total hydrocarbons are measured by a flame ionization detector (FID) on a continuous, real-time basis. No compound separation takes place, so Method 25A is noncompound specific, like Method 25. Not all hydrocarbons are suitable for analysis by FID. Highly substituted or halogenated hydrocarbons, in particular, are not amenable to FID analysis. In general alkanes, alkenes, and aromatics are the most appropriate compound groups for Method 25A sampling and analysis. Method 25A results are measured on a wet basis and the concentrations must be adjusted for the percent moisture in the sample gas stream for the purpose of emissions calculations.

Method 25A has some advantages over other methods used for measuring organic compounds. Specifically, the data is generated continuously in real time. Method 25A can only be used in situations where an appropriate response factor for the stack gas can be determined. In gas streams that cannot be characterized or which have changing composition, the response factor for the stream cannot be determined; Method 25A is not applicable for such a gas stream.

Method 25A can be used in other situations which require a response factor to be established or estimated, for instance, a surface coating operation which uses which four solvents. The amount of each solvent used as a percentage of the total solvent usage is known. A standard is prepared using the weighted percent of each solvent used in the coating operation. The concentration in ppm as carbon is calculated for the standard. The standard is introduced to the sampling system and the response factor is calculated. The analyzed concentrations from the emission source are then adjusted by dividing by the response factor.

7.2 METHOD DESCRIPTION

Method 25A sampling is performed continuously using a THC monitor. Sample gas is extracted from the emission source from a single point in the duct and pumped to the monitor at a constant rate. The sample is analyzed by an FID detector and the resulting electrical signal is proportional to the carbon content of the sample stream passing through the detector.

The sample gas is pumped through a Teflon line 1/4 inches to 3/8 inches in diameter from the sampling point to the analyzer. The line and the sample pump are heated to prevent condensation of water vapor or hydrocarbons. The analyzer and the detector are also heated. All parts of the sampling system are kept above 121°C (250°F).

The sample is pumped to the detector at a constant pressure, which is monitored by a gauge on the analyzer. The analyzer is calibrated and operated at the same sample delivery pressure to insure equivalent instrument response for the same concentration.

The FID consists of a flame, fed by hydrogen and air, a collection ring, and an amplifier for the electrical signal. A small portion of the sample gas extracted from the duct is passed through the flame using a capillary tube to restrict the flow. If the sample delivery pressure is not kept constant, the flow rate through the capillary is not constant, and the instrument response will vary accordingly. As the sample passes through the flame, the organic molecules are burned. The flame and the collector ring are maintained with a very high electrical potential between them. As the molecules are burned, the gas between the collector ring and the jet becomes conductive due to the presence of ions given off during combustion. The ions carry a small current from the jet to the collector ring. The current is proportional to the amount of organics being combusted in the flame. The current is amplified and output as a 0 to 1 volt signal.

An FID is capable of measuring hydrocarbons in ranges varying from 0 to 10 ppm to 100,000 ppm. The analyzer is calibrated in the range applicable to the emission limit, given flow rate estimates. Calibration gases are prepared and the concentrations certified by National Institute of Standards and Technology (NIST) methods or EPA Protocol 1. The gases should be prepared such that three gas concentrations, high, mid-, and low range, are used for each instrument range. The concentrations should correspond to 80 to 90 percent of range limit, 45 to 55 percent of range limit, and 25 to 35 percent of range limit. The range selected (e.g., 0 to 100 ppm) should correspond to 100 percent of full scale response at one of the available signal amplifier settings. The highest available response on each range is the range **span**. The high range calibration standard is introduced to the analyzer and the analyzer output is adjusted so that the output matches the standard concentration. If the analyzer response is linear, the mid- and low range gases should give responses equal to their certified concentrations.

The analyzer can be calibrated by introducing the calibration gasses directly to the instrument (direct cal), or by introducing the gases to the inlet of the sampling system (system cal). If a direct cal is done, a **performance check** must be conducted to validate the sampling system. After calibration, the mid-level gas is introduced at the sampling system inlet and the response is recorded at the analyzer. The instrument response should match the calibration gas concentration. To allow calibration gases to be introduced into the sampling system as close as possible to the sample gas inlet, a three-way valve is installed at the back of the sample probe. The three-way valve is used to allow either stack gas or calibration gas to be drawn through the sampling system. A diagram of the Method 25A sampling system is shown in Figure 7.1, page 7-14. The major components of the sampling system are listed below:

Probe - 1/4 inch or 3/8 inch in diameter. Constructed of Teflon or stainless steel.

Cal/Sample Valve - A three-way valve which allows the analyzer to draw from either the sampling probe or the calibration line. This should be located at the rear of the probe and must be heated to 250°F.

Particulate Filter - A 25-mm glass mat filter with a cut size of 2 microns or less. It must be heated to 250°F.

Sample Line - 1/4-inch or 3/8-inch Teflon line encased in an insulated shell with heat tracing. It must be capable of maintaining 250°F along the entire length of the line.

Sample Pump - Teflon-sealed diaphragm pump capable of pulling at least 1 liter/minute and attaining 10 inch Hg vacuum. The pump heads must be heated to at least 250°F.

THC Analyzer - Hydrocarbon analyzer equipped a flame ionization detector. The analyzer should keep the sample stream above 250°F until delivered to the FID. The FID must be equipped with an output amplifier compatible with a strip chart recorder or data acquisition system.

Recorder - A strip chart recorder or data acquisition system capable of recording the analyzer output continuously or recording the analyzer output average response at intervals of no greater than 1 minute. The instrument output voltage should represent full scale deflection of the strip chart.

7.3 PRECISION AND ACCURACY

The precision and accuracy of Method 25A are defined by the calibration parameters imposed on the tester before and after the run. **Calibration error** is defined as the deviation of the analyzer response from the true value of a calibration gas. Method accuracy is commonly determined in this manner. Therefore, the calibration error can be used to assess the accuracy of Method 25A. The specification for calibration error is ±5 percent of the true value of the calibration gas.

Calibration drift is defined as the deviation between the value determined for a calibration gas measured before the test run and the value determined for the same gas after the test run. This is a measure of the reproducibility of the analysis and represents the precision of the method. The limit for calibration drift is ±3 percent of the span used for analysis.

The precision of the method should remain the same for all volatile organic compounds introduced to the system. However, the accuracy determination is based on use of a single compound calibration gas. In situations that require a response factor to be used to adjust the analyzed concentrations, the accuracy is only as good as the response factor. If the response factor is generated for a specific compound, the

accuracy of the response factor is determined by the care taken in preparing the compound standard, and the accuracy of the analyzer when used to generate the response factor. A standard of a different concentration can be used to check the response factor by comparing the actual reading to the predicted response using the response factor. The cumulative accuracy limits can be estimated as the square root of the sum of the squares of contributing limits. If the analyzer accuracy is ±5 percent and the response factor accuracy is ±10 percent, the cumulative accuracy limit is $(0.05^2 + 0.10^2)^{1/2}$ = 11 percent. For emission sources where the response factor is estimated, the accuracy is no better than the estimate of the response factor.

7.4 SAMPLING POINT LOCATION

Method 25A sampling is conducted nonisokinetically at a constant rate. A sampling point is selected in one of three ways: (1) the probe can be placed at a single point in the center of the duct, (2) the probe can be placed at a single point at a position in the duct with average gas velocity, (3) or a rake-type probe may be used. If no stratification is expected in the duct, a single point sample can be extracted. If the test location is immediately downstream of the inlet of an auxiliary gas stream or ambient intake, the concentration may not be constant across the duct. If this might be the case, a rake-type probe should be used. The probe is sized to be the same length as the stack diameter. Several holes of equal size are drilled in the side of the probe such that the spacing between the holes is equal. No holes should be placed within an inch of the duct walls, and it is most important that no holes extend into the port nipple or out of the duct. The end of the probe should be blocked, or the majority of sample will enter the probe through the end. If particulate matter is expected to be present, the holes should be turned away from the direction of flow to minimize plugging.

7.5 OBSERVATION PROCEDURES FOR METHOD 25A SAMPLING

7.5.1 Leak Check

A leak check of the sampling system is recommended prior to testing. The method does not require a leak check, but it is a good idea to verify the integrity of the sampling system before starting a test run. If the tester can show that the system calibration has a calibration error of less than ±5 percent of the certified value of the cal gas, he may decline to perform a leak check. If a leak check is performed, it can be done in one of two manners. The first method is to place a vacuum gauge at the probe tip and draw a vacuum on the system of 10 inch Hg. A valve is used to isolate the system from the sample pump. The system vacuum should remain constant for a period of 5 minutes. The second method is to plug the probe tip and place a rotameter or water bubbler at the pump exhaust. The pump should evacuate the system until there is no flow through the pump. One disadvantage to this approach is that the system vacuum will be as high as the pulling capacity of the sample pump, while sampling should never exceed 10 inch Hg.

The leak check and other sampling procedures are summarized in a sampling checklist (Figure 7.2, page 7-15) to be completed or used a guide by the test coordinator.

7.5.2 Calibration

Prior to the start of testing, the hydrocarbon analyzer must be calibrated. The calibration is done by introducing the high, mid-, and low range calibration gases to the analyzer to show that the analyzer response reflects the true concentration of the gases. The analyzer range must be chosen so that the source THC limit is 10 to 100 percent of the range. Preliminary traverses may be done to determine the emission source flow rate so that the allowable concentration limit can be calculated from the mass emission limits. The allowable concentration limit should be higher than 10 percent of the analyzer range. If not, a lower range should be selected until the limit is above 10 percent of the range or the lowest range of the analyzer is reached. The allowable concentration limit should not be above 100 percent of the analyzer range unless the source concentration is expected to be less than 10 percent of the allowable concentration limit.

The calibration gases are usually propane in air or propane in nitrogen. Some regulatory agencies may require that the calibration gases be methane in air or nitrogen. If the calibration gases are propane, the propane concentrations should be multiplied by three to represent the concentration as carbon in the cylinder. If the calibration cylinder concentrations are not adjusted to carbon concentration, the test results must later be multiplied by a K factor of 3.0 to adjust for the number of carbons in the calibration gas. Any gas standard may be used as a calibration standard if it is National Institute of Standards and Technology traceable and the K factor is known. The K factor for methane is 1.0.

The calibration gas may be introduced directly into the analyzer or through the sampling system. A cylinder of carrier grade purity zero air containing no hydrocarbons is introduced to the analyzer and the back pressure to the FID is set. The zero offset adjustment of the analyzer is set such that the analyzer output is 0 ppm ±3 percent of the span. The high range calibration gas is then introduced to the analyzer. The amplifier gain adjustment is set such that the analyzer output matches the calibration gas certified value within 5 percent of that value. The actual analyzer response is recorded and a **calibration factor** is calculated. The calibration factor is equal to the certified cylinder concentration divided by the analyzer response in divisions:

$$CF = \frac{\text{Certified Cylinder Value}}{\text{\# Divisions Analyzer Response}} \qquad \text{Equation 7-1}$$

If the high range cylinder value is 85.7 ppm and the instrument response is 84.6 divisions, the calibration factor is:

$$CF = \frac{85.7\ ppm}{84.6\ Divisions} = \frac{1/013\ ppm}{Division}$$ Equation 7-2

Since the amplifier gain is set such that the recorded value is ±5 percent of the true value, the calibration factor should always fall in the range of 0.95 to 1.05. If higher instrument ranges are used, the factor will be some factor of ten, e.g., 9.5 to 10.5 (for a factor of ten) or 950 to 1050 (for a factor of one-thousand).

The calibration factor is used to predict the response for the mid- and low range gases using the following equation:

$$\text{Analyzer Response} = \frac{\text{Cylinder Concentration}}{\text{Calibration Factor}}$$ Equation 7-3

The actual response must be within 5 percent of the predicted response. This procedure is a **linearity check** on the analyzer. A linearity check must be done once for each set of test runs. If any range is to be used other than the one in which the linearity check is performed then a mid-level gas in that range is introduced to confirm the multiplier for that range. The analyzer response for the mid-level gas in each range must agree with the cylinder value within 5 percent.

When the linearity check is done through the sampling system using the cal sample valve at the rear of the sample probe, the integrity of the sampling system is not in question. However, if the calibration is done directly through the analyzer, a performance check must be conducted using the high range gas. The high range gas is purged through the calibration line to the cal/sample valve. A "T" with a rotameter on the tap leg is placed in the calibration line before the cal/sample valve. The rotameter allows excess calibration gas to dump to the atmosphere. The flow rate through the calibration valve is set such that, with the sample pump on, the dump rate at the rotameter is less than 2 liters per minute. If no dump were provided in the system, the calibration gas would pressurize the system and system leaks would not affect the performance check results. When the cal/sample valve is switched to sample, the system is under negative pressure and system leaks will be indicated by the test results. If the dump rate falls to zero flow, ambient air will be drawn in through the rotameter and the performance check results will be low. If the dump rate is too high, the ability of the rotameter to relieve the delivery pressure of the calibration gas will be exceeded and the sampling system will still be under positive pressure. A diagram of the calibration/sample valve with an ambient dump is included in Figure 7.3, page 7-16.

7.5.3 Response Time Test

Response time is defined as the time required for a step change in system conditions to show a response at the analyzer equal to 95 percent of the step change. The response time of the sampling system must be checked to assure that the sample is delivered from the emission source to the analyzer in an acceptable period of time. No limit for response time is set in Method 25A. A typical response time is less than one minute, and should not be over two minutes. A long response time indicates that the flow rate of sample being drawn by the sample pump is not high enough for the test conditions. Any test which requires more than 100 feet of sample line will probably require a pump that can pull at least 1 liter per minute to keep the response time down to an acceptable limit.

The response time test is accomplished by first purging the sampling system with zero air with the calibration/sample valve turned to calibration. The zero air flow is stopped and replaced as quickly as possible with the high level calibration gas. A stopwatch is used to record the time taken for the instrument response to equal 95 percent of the high level cal gas value. This procedure is repeated until three step changes have been measured. The three response times are averaged and recorded as the response time for the test series.

7.5.4 Sampling Procedures

Sampling is initiated by turning the cal/sample valve to the sample position and starting the sample pump and data recorder. A period of time longer than the response time of the system must be allowed to purge the system with sample gas. The start time for the test run is marked on the data recorder. If a strip chart is used for recording data, a separate data sheet should be used to record one-minute averages from the strip chart trace. The delivery back pressure to the FID must be maintained at the same value used for calibrations. The analyzer and recorder are allowed to operate with no adjustments except those needed to maintain FID delivery pressure for the required test duration. Any process changes or interruptions should be recorded on the strip chart or in a test log.

For test runs longer than one hour, it may become necessary to interrupt the test run to check the calibration drift and zero drift of the analyzer. No adjustments to the output multiplier may be made between the pretest calibration and the calibration drift check. The drift check is also performed immediately following completion of the test run. On longer test runs, the drift check may be performed as often as every hour. If a drift check is done and the drift exceeds 3 percent of the span value or the zero drift exceeds 3 percent of the span value, the data collected prior to the drift check are invalid. The system must be adjusted and recalibrated and the testing repeated. For example, if a four-hour test run is in progress with a drift check performed every hour, and the drift check after the third hour is outside the specifications, the data recorded

between the second-hour drift check and the third-hour drift check is considered invalid. The analyzer is recalibrated and the testing is resumed. The third-hour of testing is repeated and if the hourly drift check is acceptable, the fourth hour of testing is then completed.

Alternately, the sampling system may be recalibrated without adjustments. The calibration factor from the new calibration is recorded and the results are reported using both the pretest calibration factor and the post-test calibration factor. The agency will accept the data showing worst case results.

7.5.5 Establishing Response Factors

Response factors can be established in three ways: (1) using a gas standard of known concentration, (2) using a liquid standard of known concentration, and (3) using a liquid standard of unknown concentration. The proper approach will be determined by the specifics of each test for which Method 25A is applied. The testing firm should insure that the procedures for establishing response factors have been approved by the appropriate regulatory agency prior to testing. The three methods are described below.

Gas Standard - If the molar fraction of each compound present in the emissions is known before testing, a gas standard in the same ratio of mole fractions can be prepared for the response factor test. The concentration as carbon is calculated for the gas standard. The gas standard is introduced to the calibrated analyzer and the analyzer response is recorded. The response factor is equal to the predicted response divided by the actual response.

The response factor should be established on the day of testing. An FID uses a flame to oxidize hydrocarbons. The response factor is a function of the efficiency of the flame to perform this oxidation. Each time the flame is extinguished and relit, its efficiency may change. Therefore, the same flame should be used to establish the response factor as is used for testing. If multiple days of testing are planned, the response factor should be reestablished each day. An alternative to establishing the response factor on the day of testing is to determine the response factor in the lab before testing. The flame must then be extinguished and the system allowed to cool. The analyzer is then relit from a cold start. The response factor test is performed again, and the results compared to the previous test. If the deviation between the two response factors is <5 percent of the first response factor, the two are averaged and the average response factor is used for the test.

Liquid Standard of Known Composition - A liquid standard of known composition can be used to make a gaseous standard by volatilizing a small amount of liquid into a gas cylinder or Tedlar bag. A heated injection port is recommended to assure that all of the liquid is volatilized. The cylinder or Tedlar bag should be filled with a metered amount of zero grade air or nitrogen. The composition of the liquid,

volume of liquid injected, molecular weight of each component, density of the liquid, and volume of diluent gas used must be known to calculate the concentration of the resulting gas standard. The response factor determination is then done exactly as for a gas standard. Polar compounds such as alcohols are not stable in Tedlar bags; it is recommended that cylinders be used for alcohols or that the response factor be determined immediately after the standard is prepared in a Tedlar bag.

Liquid Standard of Unknown Composition - If the test program entails measuring the emissions from a process which uses a solvent which is a complex mixture that remains constant in composition, a known mass of the solvent can be used to generate a response factor. This is not truly a response factor since there is no predicted response. Normally the response factor has no units. A response factor produced from a liquid of unknown concentration has the units of divisions response/mass/volume. Since the carbon content of the liquid is never determined, this response factor cannot be used when the emission limit is expressed as lbs carbon, but may be used for mass balance determination such as a capture efficiency test.

The solvent is used to make a gas sample in the same manner as described for the liquid of known concentration. The mass of solvent used must be measured or can be calculated if the density of the solvent is known. The total volume of the air or nitrogen introduced into to the cylinder or bag is also measured. The mass concentration of the gas standard is calculated by dividing the mass of solvent injected by the volume in the container. The concentration units are mass/volume (e.g., mg/liter). When the gas standard is introduced into the analyzer, the response is recorded and the response factor is calculated by dividing the divisions of response by the standard concentrations. Since the composition of the liquid is unknown, the boiling point of the liquid is also unknown, therefore, a heated injection port must be used to make the gas standard. The container should be checked for condensation and the injection port temperature should be kept above 250°F.

An example of this technique follows: The exhaust over a countercurrent solvent rinsing station is sampled. As long as the operation remains steady state, the concentration in the dip tank remains constant, but it is difficult to estimate the composition in the tank. A sample is taken from the tank and 10 ml is weighed to establish the density of the solvent. 50 μl of solvent at a specific gravity of 0.88 are used to make a gas standard in a bag containing 10.5 liters of nitrogen. The resulting gas standard is introduced to the analyzer and the response is 54.5 divs.

$$\text{Gas Concentration} = \frac{(50\ \mu l \times 0.88\ mg/\mu l}{10.5\ \text{liter}} = 4.19\ mg/l \qquad \text{Equation 7-4}$$

$$\text{Response Factor} = \frac{54.5\ \text{divs}}{4.19\ mg/l} = 13.01\ \text{divs/mg/l} \qquad \text{Equation 7-5}$$

The first test run resulted in an average instrument response of 41 divisions and the flow rate through the exhaust was calculated to be 1000 scfm which translates to 28320 standard liters per minute. The emission rate of solvent through the exhaust is:

Concentration of Exhaust = $\frac{41 \text{ divs}}{13.01 \text{ divs/mg/l}}$ Equation 7-6

= 3.15 mg/l

Mass Emissions = 3.15 mg/l x 28320 liters/min x 60 min/hr
= 5352480 mg/hr x 1 lb/454000 mg
= 11.79 lb/hr Equation 7-7

7.6 SAMPLING PROBLEMS AND SOLUTIONS

7.6.1 Cold Spots in Sampling System

The sampling system is heated to 250°F for two reasons: first to prevent condensation of hydrocarbons in the sampling system. Second, to prevent condensation of moisture in the system. Some organics are soluble in water, and water condensed in the sampling system could act as a scrubber causing sample loss. Also, water droplets carried into the analyzer can cause malfunction of the gauge reading the back pressure to the FID. Although the FID will still be functional, the faulty back pressure reading could cause the flow to the FID to change and result in incorrect readings.

No part of the sampling system may drop below 121°C (250°F). Any part of the system found to be less than 121°C (250°F) must be heated or replaced. Since heated lines are insulated, it is hard to tell how hot the sample line is at any one point. One quick check is to disconnect the sampling system at the entrance to the analyzer. With the lines heated and the sample pump operating at its normal flow rate, the exit temperature from the pump is measured and should be ≥121°C (250°F). Some other things to look for are: (1) temperature drop in unions between two lengths of sample line, (2) unheated or uninsulated Teflon showing anywhere in the system, (3) sudden concentration spikes from what should be a steady state process, and (4) an inadequately heated filter or calibration/sample assembly.

Two inches of unheated stainless steel or four inches of unheated Teflon is enough to cause condensation in a sample line. Unions between lines should be too hot to touch or they should be wrapped with a heat tape to keep them above 121°C (250°F). The filter and calibration/sample assembly should also be wrapped in heat tape. Sudden concentration spikes which cannot be explained by process changes may indicate moisture condensation in the line which is passing through the back pressure regulator in droplets.

7.6.2 Sampling System Leaks

Anytime a performance check or calibration drift check is conducted and the results are lower than expected, the cause could be a sampling system leak. If the cause of the low value cannot be found, a leak check should be done on the system. If a leak is found, the results from the preceding test run should be invalidated. A leak cannot be considered constant, and the results of the preceding test should not be reported using either the pretest or post-test calibration.

7.6.3 High Moisture

Because the THC analyzer operates under positive pressure and because the back pressure gauge is mounted on the front of the analyzer and acts as a cold sink, a high moisture content in the sample gas can cause problems using Method 25A. The oven temperature of the analyzer can be turned up to help alleviate the problem. However, the oven temperature should be set before the calibration. Moisture condensing in the pressure gauge would be part of the bypass stream and would not be considered a loss of sample. However, this moisture will affect the reading on the gauge. The gauge may be replaced by running a line to a mercury manometer. The line to the manometer should be heated. A small amount of condensation in the manometer will not greatly affect the reading due to the difference in density between mercury and water. A column of 13.6 inches of water would have to collect in the manometer before affecting the manometer reading by one inch of Hg.

Method 25A may not be applicable for testing emissions containing more than 40 percent by volume of moisture. These situations should be reviewed on a case-by-case basis to determine the most appropriate method of testing.

7.6.4 Adjustments to Gain or Zero Offset

When multiple test runs are being done, the calibration drift is checked after each run. If the calibration has drifted, but is still within the limits, the run data is acceptable. The tester may want to readjust the output gain to eliminate the drift. If the pot is not reset, the drift may exceed the limit by the end of the following run. This may also be true for the zero offset.

The gain or offset may be adjusted by the following sequence:

1. The results of the calibration drift check and zero drift check performed prior to adjustment are recorded as the post-test drift check for the preceding run.
2. The gain and offset may then be adjusted.
3. The analyzer calibration and zero offset are checked again. The results are recorded as the calibration and zero offset pretest check for the next run.

7.6.5 High THC Concentrations

Some hydrocarbon analyzers can be used to measure concentrations up to 10 percent by volume as carbon. Many, however, are not linear above concentrations of 4 to 6 percent carbon by volume. When emission concentrations at a facility are higher than this, two strategies may be used.

The first strategy is to dilute the sample before introducing it to the analyzer. Any of a variety of dilution techniques may be used. The dilution ratio of the sampling system must be calibrated after the analyzer calibration is completed. A high range calibration gas of the same compound used for the analyzer calibration is introduced to the system through the calibration position of the calibration/sample valve. The dilution ratio is the ratio of the known calibration concentration and the analyzer response. Propane standards are available at concentrations as high as 8 percent (24 percent as carbon), or liquid propane tanks can be used to provide 100 percent propane gas. If 8 percent propane is used as the dilution standard and the instrument response were 5300 ppm as carbon, then the dilution ratio is:

$$\text{Dilution Ratio} = \frac{240{,}000 \text{ ppm C}}{5{,}300 \text{ ppm C}} = 45.3 \qquad \text{Equation 7-8}$$

The second strategy is to reduce the flow rate of the sample to the FID. This will extend the range in which the FID is linear. Conversely, the sensitivity of the FID will be reduced. The flow rate can be changed most easily by installing a smaller capillary to the FID. Using the same back pressure, the flow change through the capillary is proportional to the ratio of the square of the capillary diameter. The analyzer must be calibrated after changing the capillary. The calibration gases must bracket the expected concentrations from the emission source. Since propane standard upper concentrations are limited, methane or ethane would provide a more appropriate calibration standard.

7.7 AUDITS

A performance evaluation audit is not required by Method 25A because the calibration gases must be NIST traceable and serve as an audit each time a system calibration is performed. The testing firm should not, however, refuse an audit if the test coordinator deems one necessary.

The audit material must be limited to the gas compound in the calibration standard(s). Also, the audit sample concentration must be in the range used for the test runs. In order to assure that the audit samples are appropriate, the test coordinator must contact the testing firm prior to the test and inform them that an audit will be performed. The compound used in the standards and the calibration ranges expected to be used during testing must be identified.

The audit gases must be prepared according to NIST guidelines or EPA Protocol 1 guidelines. The cylinder concentrations should be certified to ±2 percent of the tag value. Three to six weeks should be allowed for preparation and shipment of the audit cylinders.

The audit gas is introduced into the sampling system in the same manner as the calibration gas used for calibration drift checks.

No limit is specified for audit accuracy, however, the audit accuracy should fall within the 5 percent limit imposed on calibration error. The tester may be allowed to reset the output gain and zero offset before the audit if the calibration drift and zero drift checks have been performed and recorded for the previous runs.

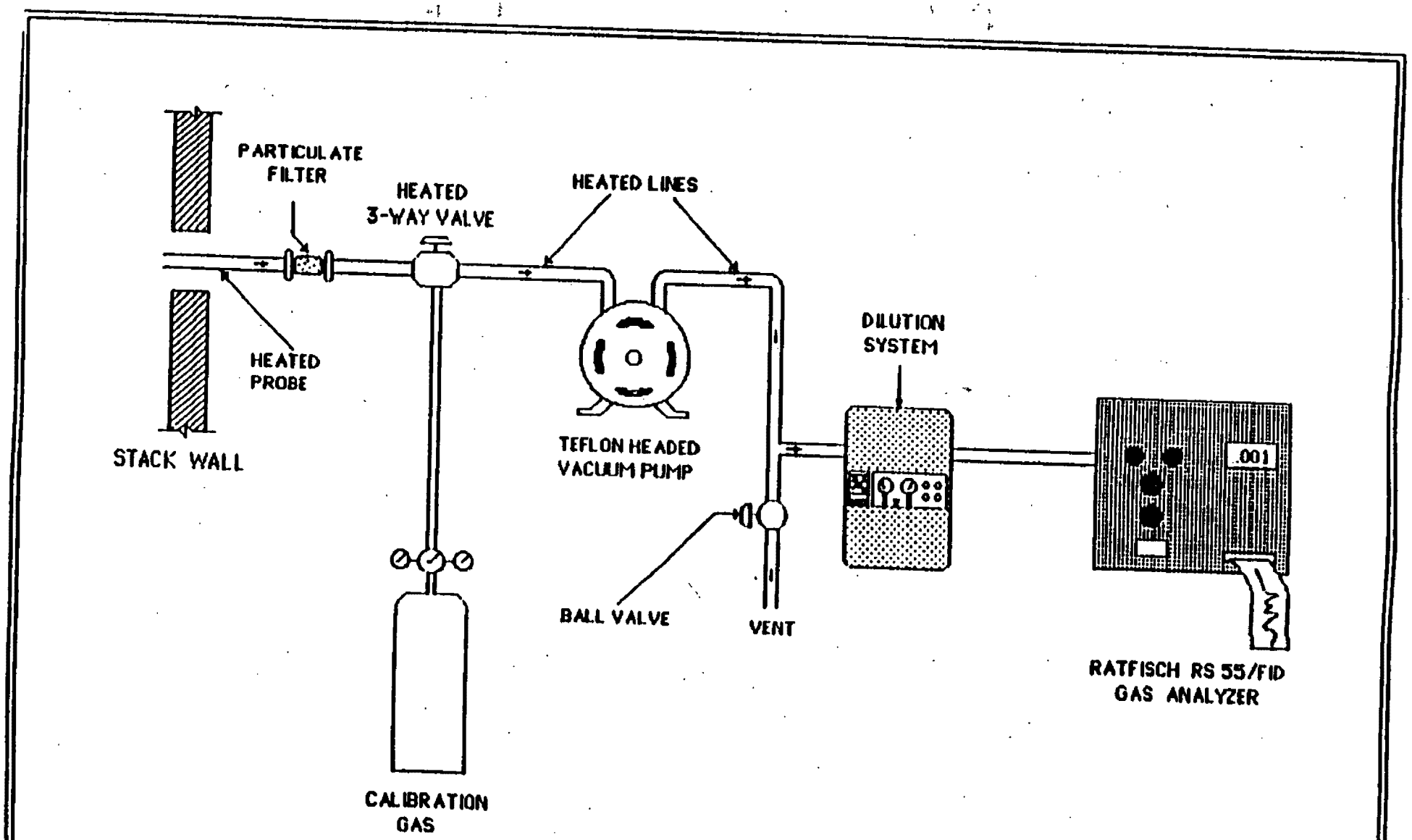


Figure 7.1. Method 25A sampling train.

Test coordinator complete once per test series.
Check if acceptable; "X" if not acceptable.

Leak Test
Was a Leak Check done _____
YES _____ What was the Leak Rate _____ Intended Flow Rate _____
NO _____ See Performance Check

Calibration
Is applicable limit >10% of analyzer range _____ <100% analyzer range _____
Are calibration gasses NBS traceable or EPA Protocol 1 _____
What gas is used as Calibration Standard _____
What is the K factor _____ Methane = 1 Propane = 3
Ethane = 2 Butane = 4
Was calibration direct or system cal _____
High Range Calibration Gas Tag Value _____ Analyzer response _____ ±5% _____
Mid-Range Gas Tag _____ Predicted Response _____ Analyzer Response ±5% _____
Low Range Gas Tag _____ Predicted Response _____ Analyzer Response ±5% _____

Performance Check - Not Necessary if Calibration was done Through System
Tag Value of Calibration Gas _____
Analyzer Response _____
Analyzer Response ± 5% of Tag Value _____

Response Time Test
Three repetitions performed _____
Average Response Time < 2 mins _____

Post-test Calibration Checks
Calibration Drift Check - Pretest Response _____ Post-test Response _____
Deviation ≤ 3% of Span _____
Zero Drift Check - Pretest Response _____ Post-test Response _____
Deviation ≤ 3% of Span _____

Response Factor
Was a response factor used _____
How was the Response Factor Generated Gas Standard _____
Known Liquid Standard _____
Unknown Liquid Standard _____
What is the Response Factor _____ Units of Response Factor _____
Unitless if Gas Standard or Liquid Standard used.
Units of mass/volume/division if Unknown Liquid Standard used.

Figure 7.2. Method 25A sampling checklist.

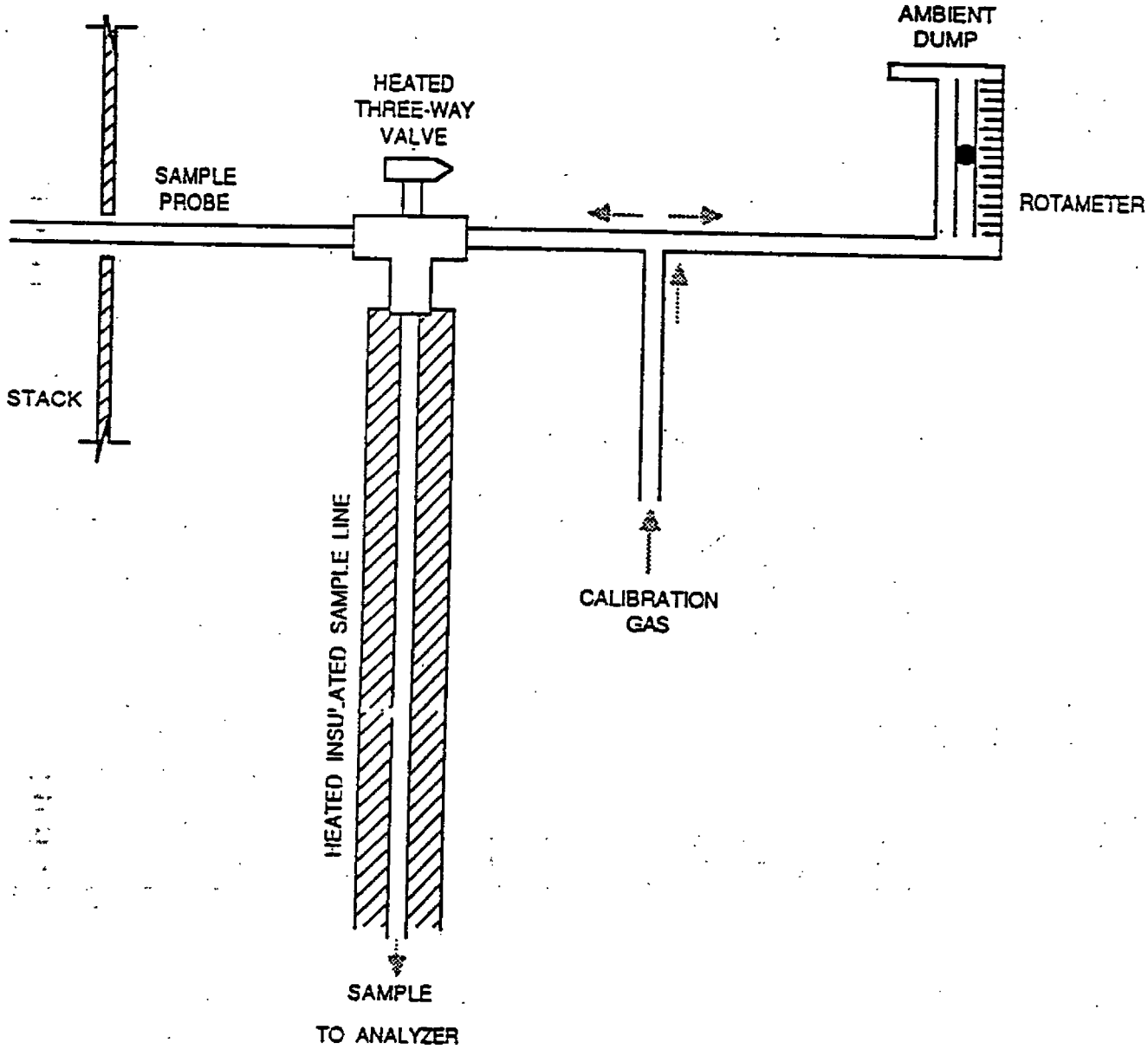


Figure 7.3. Calibration/sample valve assembly with ambient dump.

CHAPTER 8
REVIEW PROCEDURES FOR VOC TEST REPORTS

The compliance test report is written by the testing firm and submitted by the facility. It is typically the test coordinator's responsibility to review the report. Some states lack written guidelines that specify the compliance test report format and minimum data reporting requirements. This chapter provides a standardized report format that can be used by the testing firm in the preparation of the compliance test report and instructions on compliance test report review for the test coordinator.

8.1 VOC COMPLIANCE TESTING REPORT FORMAT

EPA's NSPS does not have or need a deadline for submission of the report after completion of the compliance testing, since there is a deadline for submission of the report without regard to timing of the compliance test. Unless the state and local agencies have a deadline for VOC compliance test results to be submitted to the responsible agency by the facility representative, it is recommended that a sixty (60) day limit from completion of the field work is recommended. The report should include, but is not limited to, the following:

1. Basis format and information shown in Figure 8.1, Page 8-8.
2. Certification by testing firm representative stating that sampling procedures, analytical procedures, and data presented in the report are authentic and accurate.
3. Certification by testing firm representative (preferably by a professional engineer) that all testing details and conclusions are accurate and valid.
4. Certification by a facility representative that the facility process data are correct to the best of his/her knowledge.
5. Calculations made using applicable equations shown in the applicable method. An example calculation should be shown for one run.
6. Final results presented in English and metric units and containing two significant digits for each run. Values may be rounded off to three significant digits after calculation of each equation and two digits for the final results or all digits may be carried in the computer and rounded to two significant digits only for the final results. All rounding of numbers should be performed in accordance with the ASTM 380-76 procedures.

8.2 REPORT REVIEW

The following discussion of report review procedures assumes that the test coordinator has (1) reviewed a written test protocol, (2) stated the requirements of the compliance test to the testing firm and facility, (3) conducted a pretest survey of the facility, (4) observed facility operations during the test, (5) observed the sampling procedures during the test, and (6) required the testing firm to conduct a performance audit.

Figure 8.2, page 8-10, is an example compliance test report review form. The test coordinator may complete the form or use it as a guide for the report review. This report review form contains three sections: "Report Contents," "Report Comments," and "Summary of Results." The first section of the form is presented in order of the report format. The test coordinator should verify whether each item was included by checking "yes," "no," or "OK." "OK" means the information is not complete, but it does not effect the report review. When the "no" or "OK" column is marked, the test coordinator should state the reason for that mark. Deficiencies should be noted and specific recommendations and conclusions made in the "Report Comments" Section. **The test report should be reviewed in its entirety.**

The following subsections provide some discussion of the content and review of specific parts of the compliance test report.

8.2.1 Cover, Certification, and Introduction

The cover and certifications are self explanatory. The following items should be in the Introduction of the report.

Test Purpose - The purpose for testing will typically be to comply with one or more of the state or federal regulations. A complete description of purpose(s) and/or applicable regulation numbers should be given, for example: state regulation (list regulation No.), federal regulation (list regulation No.), obtain a permit, certify a monitor, establish an alternative emission limit, or establish a control or transfer efficiency.

Test Location - The test location description should provide sufficient information to ensure that there is no confusion as to which process and control equipment emissions were tested.

Source Identification No. - Many agencies assign a source identification number to each facility and each process or emission point in the facility. If an ID number exists, the correct number should be used.

Test Dates, Pollutants Tested, Plant Representative Name, and Any Other Background Information - This is self-explanatory.

8.2.2 Emission Results and Performance Audit Results

A quick review of the results, including appendices, to assure completeness of the reported results and determine if the values seem reasonable (i.e., correct moisture, temperature, and pressure corrections) may be helpful. Report revisions should be made by the testing firm.

Comparison of compliance test emission results with screening method emission results, if performed, should reveal obvious errors.

The performance audit results should be compared to the EPA audit sample values. For Method 18, audit results should fall within 10 percent of EPA audit sample values. This method allows for discretionary acceptance for any audit value which does not fall within the 10 percent range based on the effect on the facility's compliance status.

The is another consideration in interpreting results form analysis of EPA audit gases. Acceptable results on EPA performance audit gases does not ensure correct field sample results. The atmosphere surrounding any compound of interest is referred to as a "sample matrix." The sample matrix for audit gases is typically pure nitrogen. The target compound in a stack gas will have a more complicated matrix. Occasionally there is a component in the stack gas matrix which causes an analytical interference. If this interferant has the same retention time as the target compound (the volatile organic compound found in the audit gas cylinder), then the analyzed audit gas concentration could be correct, while the additive effect of the interferant compound would cause the analyzed concentration of the compound in the stack gas to be biased high. The target compound and the interferant compound would create a single peak. The concentration value supplied by the area of this peak, would not be representative of the true concentration of either component.

EPA audit gas "true value" results are accurate to about ±5 percent. EPA audit materials are obtained from and analyzed by an EPA contractor. Yearly audits of these contractors and their audit materials have shown error and variance as great as 5 percent. EPA audit reports issued annually summarize all audits conducted, and when necessary, assign new values to each audit cylinder. The test coordinator can use the EPA audit summary report to assess the variation in the reported audit value for the actual cylinder used. The test coordinator may make the acceptability criteria the 10 percent allowable error plus the deviation in EPA audit values for that cylinder.

Audit sample results should never be used to correct field data results. To determine the effect the audit results have on the compliance status of the facility, the test coordinator should mathematically adjust the field results to determine if the compliance status would change. For example: the allowable emissions were 100 ppm, the average emission results were 80 ppm, and the audit results were 25 percent low (75 percent of the true value). Corrected, the 80 ppm emission (results which are in compliance) would become (80 divided by 0.75) 107 ppm, which shows noncompliance. The test data, for this example, should be rejected because the audit results were outside of the acceptable range and the results of the audit samples affect the compliance status of the facility. Use of the same values with audit results with 25 percent high would yield adjusted data showing the facility in compliance, but by a greater margin. The test coordinator could accept the results, if desired.

Process and Control Equipment Data - The test coordinator can review his field observation notes to ensure that the reported process data are consistent with agency observations. If data regarding raw materials, product, or collected materials are related to determination of compliance, they should also be presented.

Allowable Emissions - The facility should restate the emissions standards. This demonstrates an understanding of the applicable regulation(s). It is beneficial for the test coordinator to make an independent assessment of the allowable emissions. Any differences should be noted and the report corrected accordingly.

Discussion of Errors (real and apparent) - This discussion is important to the future validity of the data. If the testing firm and the facility state that the data is valid, then they will not be able to easily discredit the data at a later time. Testing firms do not like to admit errors. However, when they do state that the data is invalid, the agency typically requires a retest. If no errors were noted by the testing firm or facility, it should be recorded in the report that "no errors were noted." If errors are noted, the test coordinator writes his observations regarding these errors on the review form.

8.2.3 Facility Operations

Facility operations may be critical in establishing compliance with the emission standard(s). The following items should be evaluated.

Description of Process and Control Equipment - The process and control equipment descriptions in the test report must be sufficient to (1) identify the process and control equipment in comparison to the permit to operate and (2) allow the agency enforcement inspector to determine if the facility does make major modification to process or control equipment.

Process and Control Equipment Flow Diagrams - The report should include a flow diagram which shows all ducts leading in and out of the process and control equipment of interest and any auxiliary systems that can be enabled or disabled. The diagram will allow the test coordinator to determine whether the system has been modified since it was last tested.

Process Parameter, Materials and Product Results (with example calculations) - The process operating parameter, raw materials, and product results should be presented as required to determine compliance with applicable regulation(s). Some facilities cannot directly determine process rates and use indirect measurements with assumed factors to calculate process rates. For example, if a facility assumes that the final product contains 5 percent of the organics input as residues, then they must state whether they consider this to be a constant factor or a variable factor. The effect on the compliance status may be small, but it is to the advantage of the agency that the facility not be allowed to change their assumptions to fit their needs at a later date.

Calculations should be checked to ensure that reported values include the proper assumptions, are based on the correct equations, and are mathematically correct. The test coordinator may wish to assign a confidence limit to each value.

Describe Process Operations Tested - If the process is cyclic or a batch operation, the report should describe the portion(s) of process cycle covered by the testing and the rationale for selecting them. This is important because facility could stretch out a cycle to reduce emissions during sampling. When cycles of operation or batches are compressed or reduced, emissions are typically higher. The portion of the process cycle tested should be approved by the agency prior to sampling.

Representativeness of Process Parameters, Raw Material, and Products - It is preferable if the facility representative or testing firm state that the process parameters, raw materials, and products were representative. If this information is not stated in a report showing noncompliance, facility representative may later claim that the facility was tested under conditions of upset or malfunction.

Two items not typically presented in a compliance test report that should be determined during the pretest survey are (1) the normal process maintenance schedule and (2) how malfunctions are handled. These may be specified in the permit to operate and should be checked by inspectors in the future.

Describe Control Equipment Operations Tested - Many VOC control systems involve cyclic operations. For example, two carbon bed absorbers in parallel may be used as a control device. One is cleaned while the other is collecting emissions. Depending on the methods of bed cleaning and switching from one bed to the other, emission rates may be the highest at the beginning or end of the cycle. Removal or recycling of the collected material is another area of concern. The facility should not be allowed to change their cycle of operation or method of removing collected material for the compliance test.

Representativeness of Control Equipment Parameters and Collected Materials - The same concerns apply here as for the process parameters.

8.2.4 Sampling and Analytical Procedures

Sampling Port Location(s) and Dimensions of Cross-section - Ensure that the sampling location drawings are accurate and that the mass emission rates are directly related to the area of the stack.

Sampling Point Description (including labeling) - Check on the accuracy of the description.

Brief Description of Sampling Procedures (including equipment and diagram of the sampling train) - The EPA Methods include many options regarding equipment and procedures. For example, Method 18 sampling can be performed by at least six approaches. A detailed and accurate diagram of sampling equipment and a description of the sampling procedures used should be included in the compliance test report.

Deviations of Sampling Procedures from Method - The compliance test report should address any deviations (planned or not) from the standard method including an explanation justifying the deviation(s). Planned deviations to the standard test method should obtain pretest approval from the agency.

For accidental deviations, the report should provide a description of the deviation and expected effect. When appropriate, the test coordinator should comment on what effect the accidental deviation had on the validity of and the degree of confidence in the emission results. If the test coordinator does not feel qualified to make this determination, the VOC emission measurement contact for the agency can be consulted.

Brief Description of Analytical Procedures (including calibration) - The analytical equipment (e.g., the detector and column), analytical conditions (e.g., oven temperatures, isothermal analysis, program temperature ramping analysis, gases, and fuels), calibration procedures, and calibration materials should be described. The report cannot simply state that Method 18 allows at least five approaches for preparing the calibration gases.

Analytical Deviations from Standard Method - See the discussion above on sampling procedure deviations.

8.2.5 Compliance Report Appendices

As previously noted, the test coordinator may find it more productive to review appendix material first. The essential elements of the appendices are discussed below.

Complete Results with Example Calculations - Example calculations should be provided in the report showing the individual equations and input data. These calculations should be checked, with special attention given to all assumed values or factors used to determine emissions presented in the test report (e.g., molecular weight, moisture content, and correction factors). The testing firm should include raw data, equations, and calculations for all measurement and calibration procedures in the report.

Raw Field Data - Check the field data for completeness. It is a good policy for the test coordinator to sign all completed field data forms while in the field. This practice discourages the alteration of raw data by the testing firm.

Laboratory Reports, Signed Chain-of-Custody Sheets - Acceptable audit sample results ensure that the proper detector was used and that the calibration gases were prepared correctly. When acceptable audit sample results are obtained, errors in compliance sample results are generally biased positive to positive interferences.

The test coordinator should refer to the appropriate chapter in this manual (e.g., Chapter 4 for Method 18) to determine exact procedures for validating the analytical results for a specific method. Although it is the responsibility of the analyst to identify and eliminate interferences, the test coordinator may wish to compare the retention times, peak resolution, and peak shapes for the calibration standards, audit samples, and field samples.

When performance audit samples are not used in the test program, the test coordinator will need to conduct a evaluation of the calibration standards used. When no audit samples are analyzed, all test results are based on the value assigned to the calibration standards. Therefore, it is critical that the calibration standards are assigned the correct values.

Calibration Procedures and Results - Calibration results are used to calculate emission concentrations and mass emission results. Complete documentation of sampling equipment and analytical instrumentation calibration, including complete presentation of results and calculations should be included in the compliance test report. All calculated values must be within round off error of the true value.

Raw Process and Control Equipment Data (signed by plant representative) - The test coordinator and facility representative should sign process and control equipment data sheets.

Test Logs, Project Participants and Titles, and Related Correspondence - Self-explanatory.

Cover

1. Plant name and location
2. Emission source sampled
3. Dates of testing
4. Testing company name and address

Certification

1. Certification by team leader
2. Certification by reviewer (Professional Engineer preferred)

Introduction

1. Test purpose
2. Test location, type of process and control equipment
3. Any source identification numbers, if applicable
4. Test dates
5. Pollutants tested
6. Name of plant representative
7. Other important background information

Summary of Results

1. Emission(s) results and performance audit results
2. Process and control equipment data, related to determination of compliance
3. Allowable emissions
4. Discussion of errors, both real and apparent

Facility Operations

1. Description of the process and control equipment
2. Process and control equipment flow diagrams
3. Process parameter, material, and product results, with example calculations
4. Describe portions of process operation tested
5. Representativeness of process parameters, raw materials, and products
6. Describe portions of control equipment operation tested
7. Representativeness of control equipment parameters, and collected materials

Sampling and Analytical Procedures

1. Sampling port location(s) and dimensions of cross-section
2. Sampling point description, including labeling system
3. Brief description of sampling procedures, including equipment and diagram of sampling train

Figure 8.1. VOC compliance test report format.

4. Description of sampling procedures (planned and accidental) that deviated from standard method
5. Brief description of analytical procedures, including calibration
6. Description of analytical procedures (planned and accidental) that deviated from standard method

Appendices

1. Complete results with example calculations
2. Raw field data (original, not computer printouts)
3. Laboratory report, with signed chain-of-custody forms
4. Calibration procedures and results
5. Raw process and control equipment data, signed by plant representative
6. Test log
7. Project participants and titles
8. Related correspondence

Figure 8.1. (Concluded)

Compliance Test Report Review Form - Report Contents

Page _____ of _____

PLANT NAME _____ PLANT ADDRESS _____

SOURCE ID NO. _____ DATE REPORT RECEIVED _____

TEST CO. _____ DATES OF TEST _____

REVIEWER _____ DATE REVIEWED _____

	YES	NO	OK	COMMENTS
Cover				
1. Plant name and location	____	____	____	_____
2. Source sampled	____	____	____	_____
3. Dates of testing	____	____	____	_____
4. Testing company name and address	____	____	____	_____
				_____
Certification				
1. Certification by team leader	____	____	____	_____
2. Certification by reviewer (e.g., P.E.)	____	____	____	_____
				_____
Introduction				
1. Test purpose	____	____	____	_____
2. Test location, type of process and control equipment	____	____	____	_____
				_____
3. Any source identification numbers, if applicable	____	____	____	_____
				_____
4. Test dates	____	____	____	_____
5. Pollutants tested	____	____	____	_____
6. Name of plant representative	____	____	____	_____
7. Other important background information	____	____	____	_____
				_____
Summary of Results				
1. Emission results and performance audit results	____	____	____	_____
				_____
2. Process and control equipment data related to determination of compliance	____	____	____	_____
				_____
3. Allowable emissions	____	____	____	_____
4. Discussion of errors, both real and apparent	____	____	____	_____
				_____

Figure 8.2. Compliance test report review form.

Compliance Test Report Review Form - Report Contents

Page ____ of ____

	YES	NO	OK	Comments
Facility Operations				
1. Description of the process and control equipment	____	____	____	_____
2. Process and control equipment flow diagrams	____	____	____	_____
3. Process parameter, material, and products result, with example calculation	____	____	____	_____
4. Describe portions of process operation tested	____	____	____	_____
5. Representativeness of process parameters, raw materials, and products	____	____	____	_____
6. Describe portions of control equipment operation tested	____	____	____	_____
7. Representativeness of control equipment parameters, and collected materials	____	____	____	_____
Sampling and Analytical Procedures				
1. Sampling port location(s) and dimensions of cross-section	____	____	____	_____
2. Sampling point description, including labeling system	____	____	____	_____
3. Brief description of sampling procedures, including equipment and diagram of sampling train	____	____	____	_____
4. Description of sampling procedures (planned and accidental) that deviated from standard method	____	____	____	_____
5. Brief description of analytical procedures, including calibration	____	____	____	_____
6. Description of analytical procedures (planned and accidental) that deviated from standard method	____	____	____	_____

Additional Comments on Body of Report _____

_____

_____

Figure 8.2. (Continued)

Compliance Test Report Review Form - Report Contents

Page ____ of ____

Appendix

	YES	NO	OK	Comments
1. Complete results with example calculations	____	____	____	_____
2. Raw field data (original, not computer printouts)	____	____	____	_____
3. Laboratory report, with signed chain-of-custody forms	____	____	____	_____
4. Calibration procedures and results	____	____	____	_____
5. Raw process and control equipment data, signed by plant representative	____	____	____	_____
6. Test log	____	____	____	_____
7. Project participants and titles	____	____	____	_____
8. Related correspondence	____	____	____	_____

Additional Comments on Appendix Material _____

Signature of Reviewer _____

Figure 8.2. (Continued)

Compliance Test Report Review Form - Report comments

Page ____ of ____

Were audits results in acceptable range _____ yes _____ no
If no, were audit results acceptable for compliance determination ___ yes ___ no
If no, is it recommended that the test be rejected _____ yes _____ no
Explanation and recommended action _____

Were emission results on correct basis, units and organic compound___ yes ___ no
If no, explain _____

Were emission calculations validated _____ yes ___ no
If yes, were results within normal round-off error _____ yes ____ no

Agency's screening VOC measurement method agree with audit gases ___ % accuracy
Did agency's measurement method agree with compliance results _____ yes ____ no

Were process operations representative _____ yes _____ no
If no, explain problems _____
If yes, list key parameters to establish operating permit and future inspections

Were control equipment operations representative ____ yes _____ no
If no, explain problems _____
If yes, list key parameters to establish operating permit and future inspections

Figure 8.2. (Continued)

Compliance Test Report Review Form - Report comments

Page ____ of ____

Were sampling procedures acceptable _____ yes _____ no
If no, explain problems _____

Were analytical procedures acceptable _____ yes _____ no
If no, explain problems _____

List additional items requested for the source or test firm and changes that need to be made to the report _____

This report is _____ acceptable _____ unacceptable
If unacceptable, list reasons _____

If retested required, list changes for retest _____

Comments reviewed by _____

Figure 8.2. (Continued)

Compliance Test Report Review Form - Summary of Results

Page ____ of ____

	Source Data					Agency Data				
	Run 1	Run 2	Run 3	Avg.	Units	Run 1	Run 2	Run 3	Avg.	Units
Outlet Emissions										
Pollutant _____										
Pollutant _____										
Comments _____										
Inlet Emissions										
Pollutant _____										
Pollutant _____										
Comments _____										
Process Operations										
Parameter _____										
Parameter _____										
Parameter _____										
Parameter _____										
Comments _____										
Control Equipment Operation										
Parameter _____										
Parameter _____										
Comments _____										

Screening methods recommended for inspectors on future inspections _____

Figure 8.2. (Concluded)

APPENDIX A
ORGANIC COMPOUND IDENTIFICATION AND QUANTIFICATION

A.1 Organic Compound Identification by Retention Time
A.2 Adequate Peak Resolution
A.3 Proper Response Factors

A.1 ORGANIC COMPOUND IDENTIFICATION BY RETENTION TIME

For Method 18, the organic compounds to be measured must be known prior to the test. To identify and quantify the major components of the organic compounds **known** to exist in the sample, the retention time of each component is matched with the retention times of known compounds (standard reference materials or calibration standards) under identical conditions. Separation of organic compounds is performed with gas chromatographic columns, referred to as GC analysis. The retention time is the time between sample injection into the gas chromatograph (GC) until the organic compound reaches the detector. If conditions are maintained constant, the retention time for each compound will be constant as well, and will serve as the identifying parameter for each peak. Care must be taken to assure that two compounds do not share the same retention time. **The retention time shall be within 0.5 seconds or 1 percent of the retention time of the known compound's (calibration standard) retention time (whichever is greater) to be considered acceptable.** The retention time will vary with (1) type of column or column material, (2) length of column, (3) temperature of column, (4) organic compound and several other factors (e.g., other organics present). The exact seconds or minutes of the retention time do not matter, although the longer the retention time is, the longer the analysis time will be.

The major problem with the use of retention time in identifying organic compounds is that other organic compounds could share the same retention time. Compound identification is often achieved by using two GC columns with greatly different packing materials which have differing physical properties used for separation. If the proper retention time for a given organic compound is obtained for both columns, then the analyst would assume that the compound has been identified. A listing of organic compounds and their retention times, with respect to certain analytical conditions, is presented in Section 3.16 of the **QA Handbook, Volume III** titled, "Kovats Retention Indices." The Kovats Retention Indices are generally used to help the analyst select the proper column for separating the organic compounds known to be present in the sample. When the analyst only uses a single column at a set condition, there will always be some doubt as to whether other organic compounds have the same retention time and are being reported as the compound of interest. It is not uncommon to have as many as three compounds share the same retention time.

It is the responsibility of the analyst to ensure that the proper column has been selected. When additional compounds share the same retention time, the reported value will be higher than the true value.

To select the correct GC column or establish appropriate GC conditions, the analyst must identify approximate concentrations of organic emission components. With this information, the analyst can prepare or purchase commercially available standard mixtures to calibrate the GC under physical conditions identical to those that will be used for the samples. The analyst must also have presurvey information concerning

interferences arising from other compounds present in the sample matrix and indicating whether there is need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and/or prevention of sample loss by moisture condensation in the sampling apparatus.

Most analysts today use an integrator to determine retention times and sample peak areas. The integrator will print out the retention time for all peaks and the integrated area of all peaks. The observer should confirm that the peaks match within the specified time of 0.5 seconds or 1 percent of the retention time, whichever is greater. The first peak on the printout immediately after injection of the sample is typically not an organic compound from the source. It is usually the air peak or solvent peak and is not counted.

A.2 ADEQUATE PEAK RESOLUTION

To obtain proper quantitative values, sample peaks (organic compounds as they reach the analyzer) must be properly separated. As previously mentioned, compounds must be separated to enable the detector to analyze only the compound of interest. The analyst will perform initial tests using the calibration standards to determine the optimum GC conditions for minimizing analysis time while still maintaining sufficient resolution. **Sufficient resolution shall be determined following the procedure described by Knoll or in EPA Method 625 where the baseline to valley height (V) between two adjacent peaks must be less than 25 percent of the sum of the two peak heights (P1+P2). The equation is shown in Figure A.1.** Both methods for determining peak resolution give about the same results. EPA Method 625 is easier to calculate and understand.

Most integrators will show where they are starting and stopping the peak area integration by placing tick marks on the integrator printout. It is important that the integrator is set properly to determine the proper area. The observer may wish to check where the start and stop marks are placed.

A.3 PROPER RESPONSE FACTORS

Understanding the use of the response factor is important because (1) different detectors can have a different response factor for the same compound, (2) each detector can have a different response factor for different compounds, and (3) the same detector can give a different response factor for the same compound at different conditions. The response factor for each compound on any detector can be determined by dividing the area units from the integrator printout from the standard by the concentration of the standard (area units/ppm of standard). This is done for all concentrations of the standard used to calibrate the detector. A best fit line, which is not forced through zero, is typically calculated for these different response factors. This line is then used to calculate the ppm from each sample's peak area based on the number of area Figure

A.1. Adequate peak resolution. units (area units of sample divided by response factor which is area units per ppm). Today's integrators often make this calculation for the analyst.

A.3.1 Different Response Factors for Different Detectors

It is important to note that different detectors are more or less sensitive to different types of organic compounds. For example, the most commonly used detector, the flame ionization detector, has the highest response factor for organic compounds that are straight chain molecules and contain only carbon and hydrogen. The flame ionization detector's response factor for compounds that contain chlorine or oxygen is reduced. Therefore, if it is calibrated with a compound that contains only carbon and hydrogen like methane, propane, or butane, its measured values for chlorinated or oxygenated compounds would be low.

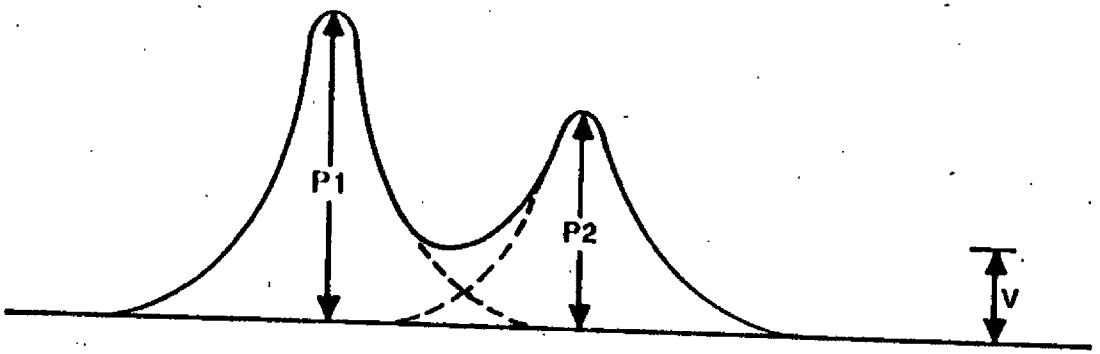
The electron capture detector has the highest response for chlorinated compounds. Its response to methane, propane, and butane would be lower than if they were chlorinated. Selection of a detector with a high response for the compound(s) being measured is desirable, but is not critical unless the organic compound will not be adequately measured by the detector.

A.3.2 Different Response Factors for Different Compounds

After a suitable detector has been selected, the observer should be aware, as mentioned above, that the same detector may have a different response factor for each compound analyzed. Therefore, a corresponding calibration gas must be used for each compound. If the test is conducted for four compounds, the method may require that four different calibration gases be used.

Method 25A is designed to measure emissions consisting of organic compounds with only carbon and hydrogen and therefore requires instrument calibration with propane. Method 25A can provide accurate measurement of organic compounds containing elements other than carbon and hydrogen if the detector is calibrated with a mixture of organic gases that closely represents gases in the stack. Response factors are published for measurement of different organic compounds on each detector. These may not be accurate, but they are a good indication of the variation in response. For the flame ionization detector, most compounds will give at least a 50 percent response when compared to methane, propane, and butane.

Method 25 was developed to eliminate the reduced response factor problem when the organic compounds are unknown. When the organic compounds in the sample are unknown (like after an incineration process), proper calibration gases cannot be selected. To minimize this problem, Method 25 converts all the elements that give reduced response factors and analyzes the compound as methane in terms of carbon. The results



$$V < \frac{P_1 + P_2}{4}$$

Figure A.1. Adequate peak resolution.

are then reported as parts per million as carbon. Unfortunately, the true molecular weights of the compounds are lost and a true concentration or mass emission rate cannot be calculated.

Although it may not always be desirable, there are cases when the use of a surrogate calibration compound has been allowed. For example, if the regulations require that all compounds be analyzed, the use of a calibration standard (specific organic compound can be selected by the tester) for unknown compounds that consists of less than 20 percent of the total area of all peaks (total response) for all compounds in the sample would produce only a small error in the total emissions measured.

A surrogate calibration gas may also be allowed when (1) appropriate calibration gases are not available, or (2) calibrating with multiple gases in the field is anticipated to be too inconvenient. The agency may allow the tester to use a single calibration gas (as a surrogate standard) and correct the measured values based on the response factors obtained in the laboratory.

A.3.3 Different Response Factors for the Same Compound

Manufacturers of GC detectors have published response factors of the organic compounds for their detector. These values should serve as estimates. The exact response factor will vary with sample composition and conditions of the detector. The response factor should be similar from day-to-day on a laboratory instrument analyzing the same compound and composition of gas under the same conditions. However, the repeatability of response factors is not sufficient to eliminate the requirement for calibration. It is important to conduct single point response factor checks every couple of hours or when the environment or sample conditions change significantly.

APPENDIX B
VOC OBSERVATION PROCEDURES

B.1 Agency Use of Screening Measurement Methods During Compliance Test

B.2 On-site Observation Procedures Coupled with the Use of Agency Screening Methods

B.1 AGENCY USE OF SCREENING MEASUREMENT METHODS DURING COMPLIANCE TEST

As previously stated, most organic gases are invisible. Therefore, it can be beneficial for the agency to conduct independent testing to determine the emission levels and other key parameters. The agency's portable organic analyzer (EPA Method 21 instrumentation) can be extremely useful. The discussion below provides a example of how these instruments can be used.

A printing or coating bed operation with a carbon adsorber as the control equipment is to be tested. The same principles apply to other types of processes and control equipment. The procedures are as follows:

1. Determine which organic compounds are used in the process.
2. Obtain the proper calibration gases or determine the correct response factor (see Chapter 5) and use a common calibration gas (e.g., methane). The analytical instrument must accurately measure low concentrations of volatile organic compound emissions (i.e., 0 to 100 ppm or 0 to 500 ppm). The observer may determine the organic materials process during the pretest survey. An instrument recorder or other device which provides continuous recording of the emission data is highly recommended. An external pump may also be required.
3. Prepare instruments and calibration gas(es) for the pretest (presite) survey. Often pretest surveys are conducted before compliance testing. Typically the testing firm representative performs the pretest survey. Agency personnel should participate if the compliance test is expected to be unusual or difficult.
4. During the pretest survey, use the portable VOC analyzer to determine the concentration levels at the edge of any hoods, points of possible fugitive leaks, at the inlet sampling location, and at the outlet sampling location. If problems exist, such as poor hood capture efficiency or fugitive leaks, the facility should be informed and the problems corrected prior to the compliance test. The facility should also be informed that inspectors will use the same procedures and instrumentation during future inspections to determine if the problems still exist.
5. During the compliance test, the same problem areas should be checked for fugitive emissions, and concentrations around the edge of the hood should be determined. Once the observer is satisfied that all problems have been corrected, the test program may start. If only one VOC analyzer is available to the observer, it should be used at the outlet sampling location. The emissions to the atmosphere should be determined before the first run, during the first run, between the first and second runs, during the second run, between the second and third runs, and during the third run. When two analyzers are available, periodic checks for fugitive emissions

should be made before, during, and between runs. Determining the emissions before and between runs will prevent the facility from conducting testing during portions of the process and control equipment operations that have reduced emissions. If emissions increase between the runs, then the observer may have to double the testing time and require testing to be conducted on a continuous basis. The second run starts immediately after the first run is completed. If temperature sensors or other screening instruments are used, it is best to have a primary standard (i.e., ASTM mercury-in-glass thermometer) available to check the measured results.

B.2 ON-SITE OBSERVATION PROCEDURES COUPLED WITH THE USE OF AGENCY SCREENING METHODS

It can be beneficial for the agency to conduct independent screening measurements during the compliance test. An approach to conducting independent screening measurements during the compliance test is presented below. VOC screening instruments (EPA Method 21) can be used for either spot checks or equipped with pumps and continuous recorders to provide continuous emissions measurements. The discussions of on-site observation presented in Chapter 3 will still apply. **The concerns about safety are even more critical when the agency is conducting their own screening measurements. The observer will be in closer contact with the VOC's thereby increasing the health and explosion risk. All instruments and methods of using these instrument must be intrinsically safe. For using these portable instruments, the EPA manual EPA-340/1-86-015, "Portable Instruments User's Manual for Monitoring VOC Sources" should be read.**

B.2.1 First Sampling Run

The observer's emission results should be compared with the testing firm's emission results. On-site analysis by the test team does not diminish the need for the agency to conduct independent on-site measurements; it improves the chances of eliminating errors and obtaining a valid test. If only one agency observer is present, the schedule below will make the most effective use of observation time. These procedures are provided for less experienced observers to help establish a routine for on-site observations. More experienced observers will follow their established routine.

For the first test run, after determining that the facility operations are as specified in the protocol, the observer should go to the sampling location to observe the test team as they record the initial data. If a post test leak check is required, the initial sampling system leak check need not be observed. When the observer is satisfied with the sampling train preparation, he should allow the testing to begin. The agency's analyzer (VOC screening method) should also be started. The observer should observe the test team's sampling procedures for the first 15 minutes of sampling. When satisfied with the test team performance and the agency's emissions results, the observer will note the

average emissions for the last 10-minute period and then conduct a check on the facility operations.

If the process and control equipment are operating satisfactorily and the data are being recorded as specified, the time of the process and control equipment observation is noted and the observer returns to the sampling site. The observer should determine the emissions during the time that the facility operations were being verified by the observer (assuming that a pump and recorder are on the analyzer) or take 10 minutes of emission readings if the analyzer does not have a pump and recorder and must be operated manually. If the observer is satisfied with the emission results, the analyzer probe should be removed from the stack and audit gas should be drawn through the probe and analyzer. The value for the audit sample should be recorded and the appropriate calculation made to determine the relative accuracy. If any major problems exist with the analyzer, they should be corrected.

The observer should observe the completion of the test team's sampling, particularly the final readings and the final leak check. He should then observe transport of the samples and sample recovery. If the test team's analysis is to be conducted on-site, the analysis should be closely observed during the audit gas cylinder analysis and the analysis of the first test run sample(s). The tester's analyst should be required to conduct all necessary calculations to determine the field results in terms of units of allowable emissions standard (e.g., ppmv on a dry, standard condition basis for the specified organic compound). All procedures and calculations should be validated by the observer.

If the agency's organic analyzer is equipped for continuous analysis, it should continue to run and record the emissions between completion of the first run and start of the second run. If the emissions increase significantly during this period, the process and control equipment parameters should be checked to determine the reason for the increase. As previously stated, many VOC process and control equipment operations can be altered to provide short term emission reductions. If the observer feels that this has happened, it may be necessary to require an additional sampling run (total of four runs), informing the source that the emissions will not be allowed to increase between sampling runs. Another option is to double the sampling time and require that subsequent run to be started immediately after the prior run.

B.2.2 Second Sampling Run

If the observer is satisfied with all sampling procedures during the first test run, he should spend most of the second run observing process operations with intermediate checks on the emission levels. During the second run, the observer should record the emissions during two 10-minute periods, conduct one check with the audit gas, and monitor the facility operations between emission readings. Ideally, the emissions will be recorded continuously, so the observer can correlate the emission levels with facility operations.

The observer should observe the test team recording final data of the second test run, final leak check, transport of the sampling train to the cleanup area, and recovery of the second run samples. The observer should determine what his emphasis will be for the third run by considering the facility operations, emission levels measured by the test firm, agency measured emissions, and observation of the sampling procedures. If the analysis is conducted on-site, these results will also be taken into account. The observer's analyzer should continue to monitor the emissions between the second and third run to ensure that they do not increase between runs.

B.2.3 Third Sampling Run

The observer should use available information to determine which procedures need the most attention for the third run by assessing the observations of the facility operations, measured emissions (if applicable), and observation of sampling procedures. If the analysis is being conducted on-site, these results must also be taken into account. All these elements should be used to determine which procedures may have the greatest degree of error. The observer should then focus on these procedures. A check of facility operations, sampling procedures, sample recovery, and sample analysis (if applicable) should be included in the observation procedures of the third run.

APPENDIX C
METHOD 18 OBSERVATION PROCEDURES

C.1 SELECTION OF PROPER SAMPLING AND ANALYTICAL TECHNIQUE FOR METHOD 18

Because of the number of different combinations of sampling, sample preparation, calibration procedures, GC columns packing material and operating procedures, and GC detectors covered under this method, a set of tables has been developed to assist the tester in selecting (and the observer in evaluating) an acceptable sampling and analytical technique. The compounds listed in these tables were selected based on their current status as either presently regulated or being evaluated for future regulations by the EPA and state and local agencies. The selected organic compounds for Method 18 presented in Table C-1 provide the user with: (1) the International Union of Pure and Applied Chemistry (IUPAC) name, any synonyms, the chemical formula, the Chemical Abstracts Service (CAS) number; (2) method, classification and corresponding references for more information; and (3) information on whether EPA currently has an audit cylinder for this compound.

For a given compound, the sampling or analytical techniques described in Tables C-2, C-3, and C-4 are classified into one of five categories as follows:

1. Reference. This is a method promulgated by EPA as the compliance test method for one or more EPA emission regulations.
2. Tentative. This is a method where EPA method development is completed and documented, but the method has not been promulgated.
3. Development. This is a method currently under development by EPA.
4. Other. A method developed and documented by an organization other than EPA.
5. None. This is a sampling or analytical technique that has not been developed or validated but based on experience with similar situations, this may work.

Table C-2 shows all the sampling techniques allowed for Method 18: (1) direct interface, (2) Tedlar bag, and (3) adsorption tube sampling. For each compound, each of the allowed sampling techniques is rated either: (1) recommended, (2) acceptable, (3) not recommended or (4) unknown. A particular sampling technique is rated first based on current EPA methodology. Where EPA methodology does not exist, methodology provided by organizations other than the EPA is used for rating. As an example on how to use Table C-2, the rating for benzene is R-2 for Tedlar bags and A-15,16 with carbon disulfide for adsorbent tubes. This means that for sampling, a Tedlar bag is recommended as a sampling technique and Reference 2 (Appendix C.5) provides further description, while charcoal tubes using carbon disulfide as the desorption liquid are acceptable and Reference 15 and 16 (Appendix C.5) provide further description.

Before a final sampling technique is selected, the observer and source tester will need to consider the general strengths and weaknesses of each technique in addition to

TABLE C-1. STATUS OF SELECTED ORGANIC COMPOUNDS FOR METHOD 18 SAMPLING AND ANALYSIS TECHNIQUES

Chemical Abstracts Name	Synonyms	Formula	CAS No.	Method Class	EPA Audit Cylinder(ppm)*
Alcohols					
Methanol	Methyl Alcohol	CH_4O	(67-56-1)	O-6	30-80
Ethanol	Ethyl Alcohol	C_2H_6O	(64-17-5)	O-7	No
Isopropyl Alcohol	2-Propanol	C_3H_8O	(67-63-0)	O-7	No
n-Propyl Alcohol	1-Propanol	C_3H_8O	(71-23-8)	O-8	No
n-Butyl Alcohol	1-Butanol	$C_4H_{10}O$	(71-36-3)	O-8	No
Alkanes					
Cyclohexane		C_6H_{12}	(110-82-7)	O-9	80-200
Hexane		C_6H_{14}	(110-54-3)	O-9	20-90,1000-3000
Alkenes					
Ethylene	Ethene	C_2H_4	(74-85-1)	N	5-20,300-700
Propylene	Propene	C_3H_6	(115-07-1)	N	5-20,300-700
Dienes					
1,3-Butadiene	Butadiene	C_4H_6	(106-99-0)	O-10	5-60
Hexachlorocyclopentadiene	Perchlorocyclopentadiene	C_5Cl_6	(77-47-4)	O-11	No
Aromatic					
Benzene	Benzol	C_6H_6	(71-43-2)	T-12	5-20,60-400
Mesitylene	1,3,5-Trimethylbenzene	C_9H_{12}	(108-67-8)	N	No
Ethylbenzene		C_8H_{10}	(100-41-4)	O-13	No
Cumene	1-Methylethylbenzene	C_9H_{12}	(98-82-8)	O-13	No
Xylene (m-,o-,p-)	Dimethylbenzene	C_8H_{10}	(1330-20-7)	O-13	5-20,300-700
Toluene	Methylbenzene	C_7H_8	(108-88-3)	O-9,13	5-20,100-700
Styrene	Ethenylbenzene	C_8H_8	(100-42-5)	O-13	No
2-Naphthylamine	2-Naphthylenamine	$C_{10}H_9N$	(91-59-8)	O-14	No
Ketones					
Acetone	2-Propanone	C_3H_6O	(67-64-1)	O-15	No
Methyl Ethyl Ketone	2-Butanone	C_4H_8O	(78-93-3)	O-16	30-80
Methyl Isobutyl Ketone	4-Methyl-2-pentanone	$C_6H_{12}O$	(108-10-1)	O-15	5-20
Epoxides					
Ethylene Oxide	Epoxy Ethane	C_2H_4O	(75-21-8)	O-17	5-20
Propylene Oxide	1,2-Epoxy Propane	C_3H_6O	(75-56-9)	O-18	5-20,75-200
Sulfides					
bis(2-Chloroethyl) Sulfide	Mustard Gas	$C_4H_8Cl_2S$	(505-60-2)	N	No

TABLE C-1. (Concluded)

Chemical Abstracts Name	Synonyms	Formula	CAS No.	Method Class	EPA Audit Cylinder(ppm)*
		Halogenated			
Ethylidene Chloride	1,1-Dichloroethane	$C_2H_4Cl_2$	(5-34-3)	O-19	No
Ethylene Dibromide	1,2-Dibromoethane	$C_2H_4Br_2$	(106-93-4)	O-20	5-20,50-300
Ethylene Dichloride	1,2-Dichloroethane	$C_2H_4Cl_2$	(107-06-2)	T-21	5-20,100-600
Propylene Dichloride	1,2-Dichloropropane	$C_3H_6Cl_2$	(78-87-5)	O-22	3-20,300-700
1,1,1-Trichloroethane	Methylchloroform	$C_2H_3Cl_3$	(71-55-6)	T-21	5-20
Bromodichloromethane		$CHBrCl_2$	(75-27-4)	N	No
Chlorodibromomethane		$CHBr_2Cl$	(124-48-1)	N	No
Chloroform	Trichloromethane	$CHCl_3$	(67-66-3)	T-23	5-20,300-700
Carbon Tetrachloride	Tetrachloromethane	CCl_4	(56-23-5)	T-23	5-20
Dichlorodifluoromethane	Freon 12	CCl_2F_2	(75-71-8)	O-24	No
Methyl Bromide	Bromomethane	CH_3Br	(74-83-9)	O-25	No
Methyl Chloride	Chloromethane	CH_3Cl	(74-87-3)	O-26	No
Methylene Chloride	Dichloromethane	CH_2Cl_2	(75-09-2)	T-27	1-20
Tetrachloroethylene	Perchloroethylene	C_2Cl_4	(127-18-4)	T-21	5-20,300-700
Bromoform	Tribromomethane	$CHBr_3$	(75-25-2)	O-19	No
Trichloroethylene	Trichloroethene	C_2HCl_3	(79-01-6)	T-21	5-20,100-600
Trichlorotrifluoroethane	Freon 113	$C_2Cl_3F_3$	(76-13-1)	T-21	5-20
Vinylidene Chloride	1,1-Dichloroethene	$C_2H_2Cl_2$	(75-35-4)	O-28	5-20,100-600
Ethyl Chloride	Chloroethane	C_2H_5Cl	(75-00-3)	O-29	No
Chlorobenzene	Monochlorobenzene	C_6H_5Cl	(108-90-7)	O-19	5-20
Vinyl Chloride	Chloroethylene	C_2H_3Cl	(75-01-4)	R-30	5-30
1,2-Dibromo-3-chloropropane	DBCP	$C_3H_5Br_2Cl$	(96-12-8)	O-37	No

Method Classification Code
- R = Reference - EPA promulgated method.
- T = Tentative - EPA method development complete; EPA reference available.
- D = Development - EPA method currently under development.
- O = Other - Method development completed by organizations other than EPA; reference available.
- N = None - No reference available; recommendation based on experience.

The codes in the method classification column describe the current status of a sampling and analysis method for each selected compound. For example, the method classification code for benzene is: T-12. This means the current method for benzene is a tentative EPA method with development complete and the reference for the method is citation number 12 in Appendix C.5

The availability of EPA audit cylinders is shown in this column where:

( ) = Audit cylinders for this particular compound are available from EPA in the concentration ranges indicated (Reference 4).

No = Audit cylinders for this particular compound are not available from EPA. The source tester must obtain audit gas cylinders from commercial gas vendors certified by independent analysis to be within 5 percent of the concentration claimed by the vendor.

TABLE C-2. METHOD 18 SAMPLING TECHNIQUES FOR SELECTED VOLATILE ORGANIC COMPOUNDS

Selected Compounds	Direct Interface	Tedlar Bag*	Adsorbent Tubes and Desorption Liquid		
			Charcoal*	Other **	Desorption Liquid***
Alcohols					
Methanol	T	N	N	A-6; Silica Gel	Distilled Water
Ethanol	T	N	T-7	-	1% 2-Butanol in CS2
Isopropyl Alcohol	T	N	T-7	-	1% 2-Butanol in CS2
n-Propyl Alcohol	T	N	T-8	-	Carbon Disulfide
n-Butyl Alcohol	T	N	T-8	-	Carbon Disulfide
Alkanes					
Cyclohexane	T	U	T-9	-	Carbon Disulfide
Hexane	T	U	T-9	-	Carbon Disulfide
Alkenes					
Ethylene	T	N	U	U	U
Propylene	T	U	U	U	U
Dienes					
1,3-Butadiene	T	A-10	A-41	U	Carbon Disulfide
Hexachlorocyclopentadiene	T	U	N	A-11; Porapak	Hexane
Aromatic					
Benzene	T	R-12	T-9,13	-	Carbon Disulfide
Mesitylene	T	U	U	-	U
Ethylbenzene	T	U	T-13	-	Carbon Disulfide
Cumene	T	U	T-13	-	Carbon Disulfide
Xylene (m-,o-,p-)	T	U	T-13	-	Carbon Disulfide
Toluene	T	U	T-9,13	-	Carbon Disulfide
Styrene	T	U	T-13	-	Carbon Disulfide
2-Napthylamine	T	U	T-14	-	Carbon Disulfide
Ketones					
Acetone	T	N	T-15	-	Carbon Disulfide
Methyl Ethyl Ketone	T	N	N	A-16; Ambersorb	Carbon Disulfide
Methyl Isobutyl Ketone	T	N	T-15	-	Carbon Disulfide
Epoxides					
Ethylene Oxide	T	A	T-17	-	99:1 Benzene:CS2
Propylene Oxide	T	U	T-18	-	Carbon Disulfide
Sulfides					
bis(2-Chloroethyl) Sulfide	T	U	U	U	U

Table C-2. (Concluded)

Selected Compounds	Direct Interface	Tedlar Bag*	Adsorbent Tubes and Desorption Liquid		
			Charcoal*	Other **	Desorption Liquid***
Halogenated					
Ethylidene Chloride	T	U	T-19	-	Carbon Disulfide
Ethylene Dibromide	T	N-31	T-20	-	99:1 Benzene:MeOH
Ethylene Dichloride	T	R-21	T-19	-	Carbon Disulfide
Propylene Dichloride	T	U	T-22	-	15% Acetone in Cyclohexane
1,1,1-Trichloroethane	T	R-21	T-19	-	Carbon Disulfide
Bromodichloromethane	T	U	U	-	U
Chlorodibromomethane	T	U	U	-	U
Chloroform	T	R-23	T-19	-	Carbon Disulfide
Carbon Tetrachloride	T	R-23	T-19	-	Carbon Disulfide
Dichlorodifluoromethane	T	U	T-24	-	Methylene Chloride
Methyl Bromide	T	U	T-25	-	Carbon Disulfide
Methyl Chloride	T	U	T-26	-	Methanol
Methylene Chloride	T	R-27	T-32	-	Carbon Disulfide
Tetrachloroethylene	T	R-21	T-33	-	Carbon Disulfide
Bromoform	T	U	T-19	-	Carbon Disulfide
Trichloroethylene	T	R-21	T-34	-	Carbon Disulfide
Trichlorotrifluoroethane	T	R-21	T-35	-	Carbon Disulfide
Vinylidene Chloride	T	U	T-28	-	Carbon Disulfide
Ethyl Chloride	T	U	T-29	-	Carbon Disulfide
Chlorobenzene	T	U	T-19	-	Carbon Disulfide
Vinyl Chloride	T	R-30	T-36	-	Carbon Disulfide
1,2-Dibromo-3-chloropropane	T	U	T-37	-	Carbon Disulfide

Rating Code

R = Recommended. Based on actual source tests experience (sampling and analysis) this method is valid and is the method of choice among Method 18 users.

A = Acceptable. Based on actual source tests or similar source test experience (sampling and analysis), this method is valid. The tester must evaluate for specific test.

T = Theoretical. Method has no documented experience, but in theory could be valid.

N = Not Recommended. Based on actual source tests or similar source test experience and/or theory, this method is invalid.

U = Unknown. Method has no documented experience and the theoretical aspects of sampling by this method are inconclusive. The tester must demonstrate that this sampling method is valid.

The rating codes for sampling are based on the extent of method validation. For example, the rating code for benzene is: T; R-12; A-9,13. This means that direct interface is theoretically possible for benzene, but no documented experience has been found; Tedlar bags are the recommended sampling method for benzene by the tentative EPA method referenced in citation 12 in Appendix C.5; and sampling with charcoal adsorption tubes is acceptable following the two methods referenced in citations 9 and 13 in Appendix .5.

* = If condensibles exist, use the procedure described in Section 3.16.4 of the EPA Quality Assurance Handbook Volume III.

** = Solid sorbents other than charcoal recommended.

*** = The recommended desorption solution is given in this column. Analyst should consult the appropriate reference for details.

TABLE C-3. GC DETECTORS FOR SELECTED VOLATILE ORGANIC COMPOUNDS BY METHOD 18

Selected Compounds	Gas Chromatograph Detector *			
	FID	ECD	PID	ELCD
Alcohols				
Methanol	R-4,6	N	T-38	N
Ethanol	R-7	N	T-38	N
Isopropyl Alcohol	R-7	N	T-38	N
n-Propyl Alcohol	R-8	N	T-38	N
n-Butyl Alcohol	R-8	N	T-38	N
Alkanes				
Cyclohexane	R-4,9	N	T-38	N
Hexane	R-4,9	N	T-38	N
Alkenes				
Ethylene	A-4	N	T-38	N
Propylene	A-4	N	T-38	N
Dienes				
1,3-Butadiene	R-4,10,41	N	T-38	N
Hexachlorocyclopentadiene	R-11	T	U	T
Aromatic				
Benzene	R-4,12	N	T-38	N
Mesitylene	T	N	T-38	N
Ethylbenzene	R-13	N	T-38	N
Cumene	R-13	N	T-38	N
Xylene (o-,m-,p-)	R-4,13	N	T-38	N
Toluene	R-4,9,13	N	T-38	N
Styrene	R-13	N	T-38	N
2-Napthylamine	R-14	N	U	N
Ketones				
Acetone	R-15	N	T-38	N
Methyl Ethyl Ketone	R-4,16	N	T-38	N
Methyl Isobutyl Ketone	R-4,15	N	T-38	N
Epoxides				
Ethylene Oxide	R-4,17	N	T-38	N
Propylene Oxide	R-4,18	N	T-38	N
Sulfides				
bis(2-Chloroethyl) Sulfide	U	U	U	U

TABLE C-3. (Concluded)

Selected Compounds	Gas Chromatograph Detector *			
	FID	ECD	PID	ELCD
Halogenated				
Ethylidene Chloride	R-19	T	U	T
Ethylene Dibromide	A-4	R-20	U	T
Ethylene Dichloride	R-4,21	T	T-38	T
Propylene Dichloride	A-4	T	T-38	R-22
1,1,1-Trichloroethane	R-4,21	T	U	T
Bromodichloromethane	U	T	U	T
Chlorodibromomethane	U	T	U	T
Chloroform	R-4,23	T	T-38	A-23
Carbon Tetrachloride	R-4,23	T	T-38	A-23
Dichlorodifluoromethane	R-24	T	N-38	T
Methyl Bromide	R-25	T	T-38	T
Methyl Chloride	R-26	T	T-38	T
Methylene Chloride	R-4,27,32	T	T-38	T
Tetrachloroethylene	R-4,21	T	T-38	T
Bromoform	R-19	T	T-38	T
Trichloroethylene	R-4,21	T	T-38	T
Trichlorotrifluoroethane	R-4,21	T	N-38	T
Vinylidene Chloride	R-4,28	T	T-38	T
Ethyl Chloride	R-29	T	T-38	T
Chlorobenzene	R-4,19	T	T-38	T
Vinyl Chloride	R-4,30	T	T-38	T
1,2-Dibromo-3-chloropropane	U	R-37	U	T

Rating Code

R = Recommended. Based on actual source test experiences (sampling and analysis) this method is valid and is the method of choice among Method 18 users.

A = Acceptable. Based on actual source tests or similar source test experience (sampling and analysis), this method is valid. The tester must evaluate for specific test.

T = Theoretical. Method has no documented experience, but in theory could be valid.

N = Not Recommended. Based on actual source tests or similar source test experience and/or theory, this method is invalid.

U = Unknown. Method has no documented experience and the theoretical aspects are not conclusive. The tester must demonstrate that this detection method is valid.

The rating codes for GC detectors are based on the detector specified in the method that is referenced. For example, the rating code for benzene is: R-4,12; N; T-38; N. This means that the FID is recommended for detection of benzene by both references 4 and 12 cited in Appendix C.5; the ECD and the ELCD are not recommended for benzene; and detection of benzene with a PID is theoretically possible based on the ionization potential found in reference 38.

* The following abbreviations are used for the gas chromatography detectors:

FID = Flame Ionization Detector
ELCD = Electroconductivity Detector (Hall Detector)
ECD = Electron Capture Detector
PID = Photoionization Detector (with lamps up to 11.7 electron volts)

TABLE C-4. RECOMMENDED CALIBRATION TECHNIQUES FOR SELECTED VOLATILE ORGANIC COMPOUNDS BY METHOD 18

Selected Compounds	Methods for Direct Interface and Tedlar Bag Samples			Methods for Adsorption Tube Samples	
	Gas Cylinders	Gas Injection into Tedlar Bag	Liquid Injection into Tedlar Bag	Prepare Standard in Desorption Liquid	Prepare Standard on Tube and Desorb
Alcohols					
Methanol	T-4	N	U	R-6	T
Ethanol	U	N	U	R-7	T
Isopropyl Alcohol	U	N	U	R-7	T
n-Propyl Alcohol	U	N	U	R-8	T
n-Butyl Alcohol	U	N	U	R-8	T
Alkanes					
Cyclohexane	T-4	N	U	R-9	T
Hexane	T-4	N	U	R-9	T
Alkenes					
Ethylene	T-4	U	N	U	U
Propylene	T-4	U	N	U	U
Dienes					
1,3-Butadiene	A-10	R-10	N	R-41	U
Hexachlorocyclopentadiene	U	N	U	R-11	T
Aromatics					
Benzene	R-12(SRM 1806)	N	A-12	R-9,13	T
Mesitylene	U	N	U	U	U
Ethylbenzene	U	N	U	R-13	T
Cumene	U	N	U	R-13	T
Xylene (m-,o-,p-)	T-4	N	U	R-13	T
Toluene	T-4	N	U	R-9,13	T
Styrene	U	N	U	R-13	T
2-Napthylamine	U	U	U	R-14	T
Ketones					
Acetone	U	N	U	R-15	T
Methyl Ethyl Ketone	T-4	N	U	R-16	T
Methyl Isobutyl Ketone	T-4	N	U	R-15	T
Epoxides					
Ethylene Oxide	T-4	U	N	R-17	T
Propylene Oxide	T-4	U	N	R-18	T
Sulfides					
bis(2-Chloroethyl) Sulfide	U	U	U	U	U

TABLE C-4. (Concluded)

Selected Compounds	Methods or Direct Interface and Tedlar Bag Samples			Methods for Adsorption Tube Samples	
	Gas Cylinders	Gas Injection into Tedlar Bag	Liquid Injection into Tedlar Bag	Prepare Standard in Desorption Liquid	Prepare Standard on Tube and Desorb
			Halogenated		
Ethylidene Chloride	U	N	U	R-19	T
Ethylene Dibromide	T-4	N	N-31	R-20	T
Ethylene Dichloride	R-21	N	A-21	R-19	T
Propylene Dichloride	T-4	N	U	R-22	T
1,1,1-Trichloroethane	R-21	N	A-21	R-19	T
Bromodichloromethane	U	U	U	U	U
Chlorodibromomethane	U	U	U	U	U
Chloroform	R-23	N	A-23	R-19	T
Carbon Tetrachloride	R-23	N	A-23	R-19	T
Dichlorodifluoromethane	U	U	N	R-24	T
Methyl Bromide	U	U	N	R-25	T
Methyl Chloride	U	U	N	R-26	T
Methylene Chloride	R-21	N	A-21	R-32	T
Tetrachloroethylene	R-21(SRM 1809)	N	A-21	R-33	T
Bromoform	U	N	U	R-19	T
Trichloroethylene	R-21	N	A-21	R-34	T
Trichlorotrifluoroethane	R-21	N	A-21	R-35	T
Vinylidene Chloride	T-4	N	U	R-28	T
Ethyl Chloride	U	N	U	R-29	T
Chlorobenzene	T-4	N	U	R-19	T
Vinyl Chloride	R-30	A-30	N	R-36	T
1,2-Dibromo-3-chloropropane	U	N	U	R-37	T

Rating Code

R = Recommended. Based on actual source test experience (sampling and analysis) this method is valid and is the method of choice among Method 18 users.

A = Acceptable. Based on actual source tests or similar source test experience (sampling and analysis), this method is valid. The tester must evaluate for specific test.

T = Theoretical. Method has no documented sampling and analysis experience, but in theory could be valid.

N = Not Recommended. Based on actual source tests or similar source test experience and/or theory, this method is invalid.

U = Unknown. Method has no documented experience and the theoretical aspects are not conclusive. The tester must demonstrate that this calibration method is valid.

The rating codes for calibration procedures are based on procedures specified in applicable sampling and/or analytical methods. For example, the rating code for benzene is: R-12(SRM 1806); N; A-12; R-9,13; T. This means that for benzene, the recommended calibration procedure for direct interface and Tedlar bag samples involves the use of gas cylinders with the procedures described in citation 12 in Appendix C.5 and Standard Reference Material 1806 (available from the National Bureau of Standards, Gaithersburg, MD); calibration standards for benzene prepared by gas injection into Tedlar bags is not recommended; calibration standards prepared by liquid injection into Tedlar bags is acceptable following the procedures described in citation 12 in Appendix .5; preparation of calibration standards in desorption liquid is the recommended procedure for the adsorption tube methods described in citations 9 and 13 in Appendix .5; preparation of calibration standards on adsorption tubes followed by desorption is theoretically valid for use with adsorption tube samples.

the guidance provided in Table C-2. The strengths and weaknesses for the allowed sampling techniques are as follows:

Direct Interface or Dilution Interface

Strengths:

1. Samples are collected in a manner that retain the same compounds and concentrations as the stack emissions.
2. No loss or alteration in compounds due to sampling since a sample collection media (bag or adsorbent) is not used.
3. Method of choice for steady state sources when duct temperature is below 100°C and organic concentrations are suitable for the GC detector.

Weaknesses:

1. GC must be located at the sampling site.
2. GC cannot be operated at a sampling site if the presence of the H_2 flame will be hazardous.
3. Cannot sample proportionally or obtain a time integrated sample.
4. Results represent only grab samples and should not be used for non steady state processes.

Tedlar Bag

Strengths:

1. Samples are collected in a manner that retains the same compounds and concentrations as the stack emissions.
2. Samples may be returned to the laboratory for GC analysis.
3. Multiple analyses, if necessary, may be performed on each collected sample.
4. Samples can be collected proportionally.

Weaknesses:

1. Unless protected, Tedlar bags are awkward and bulky for shipping back to the laboratory. Caution must be taken to prevent bag leaks.
2. Stability of compound(s) of interest in Tedlar bags must be known and sample storage time is generally less than 24 hours.
3. Polar compounds should not be collected due to bag absorption. Direct interface or dilution interface is the method of choice for polar compounds.

Adsorbent Tubes

Strengths:

1. Samples collected are compact and easy to return to the laboratory for analysis.
2. Samples may be returned to the laboratory for GC analysis.
3. Sample storage time generally can be extended to a week by keeping samples at O°C.

Weaknesses:

1. Quantitative recovery of organic compounds from the adsorbent material must be known.
2. Breakthrough sample gas volume for organic compounds for the adsorbent material must be known.
3. Any effect of moisture (in the stack gas) on the adsorbent material collection capacity must be known. Moisture in the sample above 2 to 3 percent may severely reduce the adsorptive capacity.
4. Generally, samples are collected at a constant rate.

Table C-3 shows the GC detectors commonly used with Method 18. For each compound, each GC detector is rated as: (1) recommended, (2) acceptable, (3) not recommended, or (4) unknown. A particular GC detector is rated first based on current EPA methodology. Where EPA methodology does not exist, methodology provided by organizations other than the EPA is used for rating. As an example on how to use Table C-3, the rating for benzene is R-2 for FID. This means FID is recommended as the GC detector and References 4 and 12 (Appendix C.5) provide further description.

Table C-4 shows the GC calibration preference for each compound based on the technique used for sampling. Where appropriate, the source of calibration standards is also shown. For each compound, the calibration technique shown is rated either: (1) recommended, (2) acceptable, (3) not recommended, or (4) unknown. A particular calibration technique is rated first based on current EPA methodology. Where EPA methodology does not exist, methodology provided by organizations other than the EPA is used for rating. As an example on how to use Table C-4, the rating for benzene is R-12 (SRM 1806) for gas cylinders. This means gas cylinders assayed and certified against a National Institute of Standards (NIST) gaseous Standard Reference Material (SRM) using EPA Traceability Protocol No. 1 (Reference 4) are recommended as the calibration standard. Reference 12 provides further description on the source of the calibration standard. NIST SRM 1806 would be used to assay and certify the calibration standard.

For those compounds not listed in the tables, a general approach of classifying compounds and then selecting the method typically used for that classification is provided (Figure C.1, page C-13). The first classification in this general approach is sample concentration. Method 18 can generally be used for samples having a concentration of greater than approximately one part per million by volume. For samples in the part per billion volatile organic compounds range, typically the volatile organic sampling train is used. For samples in the part per billion semivolatile compounds, generally the modified method 5 sample train is used. The discussions on the volatile organic sampling train (VOST) and modified method 5 (MM5) trains is beyond the scope of this manual but can be found in the *Solid Waste Sampling Handbook* SW-896. Method 18 can be used for most gaseous organic compounds with a concentration greater than 1 ppm.

The second classification of compounds depends on stack temperature and moisture content. In general, higher stack temperatures are obtained through direct combustion which means higher moisture. The temperature/moisture are classified as low temperature and moisture, medium temperature and moisture, and high moisture and temperature.

The first temperature/moisture classification is low moisture and temperature. Low moisture is defined as less than 1 percent. The second temperature/moisture category is medium temperature and moisture (3 to 10 percent). The significance of 3 percent to 10 percent moisture is:

1. If the container sample is allowed to sit at room temperature moisture will condense.
2. At between 3 to 10 percent moisture, techniques of heating the containers can be used to keep the water in a vapor form.

The final temperature/moisture category is for moisture content greater than 10 percent. This moisture content renders most of the heating techniques impractical because the moisture is more easily condensed and therefore eliminates most of the standard sampling analytical techniques.

After the sampling conditions have been selected according to temperature and moisture, the next classification deals with the polarity of the organic compound. Polar compounds are generally those compounds that mix with water, such as alcohols, and act as water since water is a polar compound. Silica is a good sorbent for both water and alcohols. The nonpolar compounds, such as the chlorinated organics, typically do not mix with water and can therefore be easily purged out of water.

For nonpolar compounds at low levels or ambient temperatures and moisture content all the collection techniques would work which include: Tedlar bags, adsorption tubes, and direct and dilution interface. Charcoal as we know is the most widely used sorbent for nonpolar compounds.

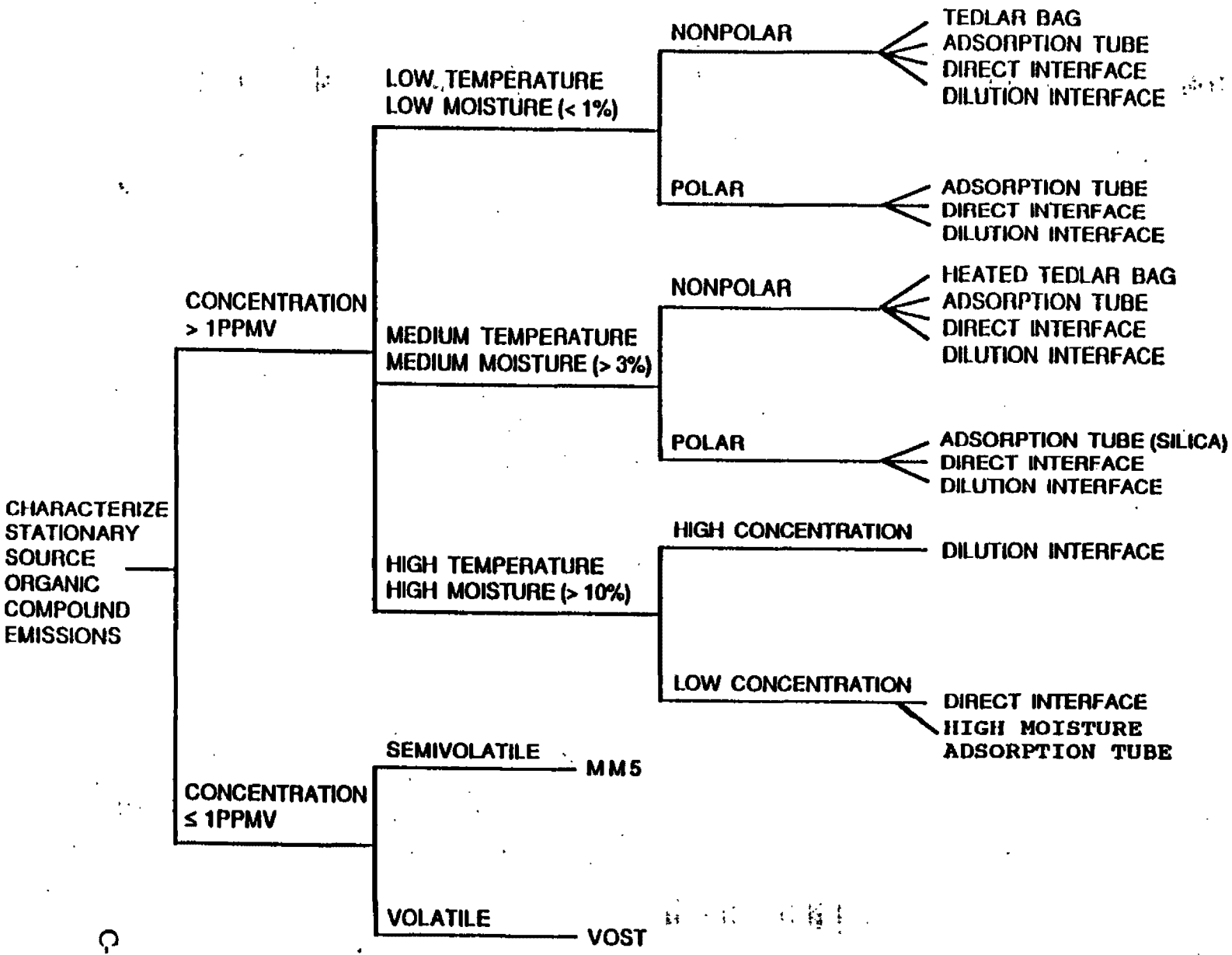


Figure C.1. General scheme for selection of appropriate sampling techniques.

For collection of polar compounds at ambient temperatures and moistures (Figure C.1, page C-13), all sampling techniques with the exception of Tedlar bags work. Bags tend to adsorb polar compounds. Silica is the sorbent most commonly used for polar compounds. Direct and dilution interface will work for all cases of polar and nonpolar compounds in steady state emissions and where the compounds can be separated quickly.

Sampling under medium temperature and moisture conditions (Figure C.1, page C-13) is the same as under low temperature and moisture condition with the exception that containers must be heated to prevent moisture and organic condensation. Therefore, nonpolar compound sampling would include heated container, adsorption tube, direct and dilution interface methods. The polar compounds would best utilize adsorption tube, direct and dilution interface techniques.

It should be noted that the adsorption tubes must be kept cool and that sorbent collection efficiency may be severely affected by water. One approach when moisture is present is to sacrifice the first adsorption tube for collection of water and then have a third collection tube as the backup tube.

The high temperature/high moisture conditions (Figure C.1, page C-13) necessitate direct and dilution interface sampling or the recently EPA developed adsorption tube sampling technique for nonpolar compounds such as chlorinated organics that are not soluble in water. This technique will **not** work for compounds that are soluble in water.

C.2 OBSERVATION OF ON-SITE TESTING

The test coordinator should use the techniques and tables provided above in Appendix C.1 to ensure that the sampling and analytical techniques selected by the tester are acceptable. Because of the complexity involved in sampling organic compounds from the variety of potential source types, only the more common problems are addressed for each sampling method. The observer should have the tester conduct the recommended quality assurance/control checks and procedures provided in this Chapter to assess the suitability of the sampling technique.

Specific sampling system descriptions and observers checklists are provided below. The procedures are presented by sampling techniques as shown. The observer can therefore read only the material of interest.

C.2.1 Evacuated Container Sampling (Heated and Unheated)

In this sampling technique, sample bags are filled by evacuating the rigid air-tight containers that hold them. The suitability of the bags for sampling should have been confirmed by permeation and retention checks using the specific organic compounds of interest during the presurvey operations. The permeation and retention checks must be performed on the field samples to ensure that the container sampling technique is acceptable.

The means of transporting the bags to the laboratory for analysis within the specified time should also have been determined. Delays in shipping and/or analysis can result in significant changes in concentration for many compounds. EPA has conducted several field evaluations of Method 18 bag sampling techniques on a variety of organic compounds. In the EPA Field validation reports the specified time between sample collection and analysis is shown. The permeation and retention checks are not required by Method 18 but are highly recommended for compounds and source categories that have not been validated by EPA.

On-site sampling includes the following steps:

1. Conducting preliminary measurements and setup.
2. Preparation and setup of sampling system.
3. Preparation of the probe.
4. Connection of electrical service and leak check of sampling system.
5. Insertion of probe into duct and sealing of port.
6. Purging of sampling system.
7. Proportional sampling.

8. Recording data.
9. Recovering sample and transportation to laboratory.

The "On-site Checklist" (Figure C.2, page C-17) includes checks for each of the following procedures and should be completed by the observer.

To assist the observer in noting the most critical items to observe, the key points are printed in bold lettering.

Method 18 requires that samples be collected proportionally, meaning that the sampling rate must be kept proportional to the stack gas velocity at the sampling point during the sampling period. If the process has a steady state flow (constant), then the flow rate does not have to be varied during sampling. The average velocity head (pitot reading) and range of fluctuation is determined and then utilized to establish the proper flow rate settings during sampling. If it is found that the process is <u>not</u> steady state, then the velocity head must be monitored during sampling to maintain a constant proportion between the sample flow rate and the flow rate in the duct.

A total sampling time greater than or equal to the minimum total sampling time specified in the applicable emission standard must be selected. The number of minutes between readings while sampling should be an integer. It is desirable for the time between readings to be such that the flow rate does not change more than 20 percent during this period.

If it was determined from the literature or the preliminary survey laboratory work that the sampling system must be heated during sample collection and analysis, the observer must ensure that the sample system does not go below the specified temperature. The average stack temperature is used as the reference temperature for the initial heating of the system and should be determined. Then, the stack temperature at the sampling point is measured and recorded during sampling to adjust the heating system just above the stack temperature or the dew point. In addition, the use of a heated sampling system typically requires that the analysis be conducted on-site since it is not practical to maintain the sample bag at elevated temperatures for long periods of time.

A. **Sampling System Preparation** - See Chapter 4.5

B. **Proportional Sampling** - See Chapter 4.5

C. **Indirect Pump Bag Sampling** - See Chapter 4.5

D. **Sample Recovery and Transport to Laboratory** - See Chapter 4.5

E. **Common Problems** - See Chapter 4.5

EQUIPMENT SETUP

Flue Gas Flowrate _____ constant, _____ variable
Sampling rate _____ constant, _____ proportional
Sample time _____ required, _____ actual
Time per point _____ minutes, probe heat required __ yes ___ no

DIRECT OR DILUTION BAG SAMPLING

Apparatus

Pitot tube: Type S _____ Other _____, Properly attached _____
Pressure gauge: Manometer _____ Other _____, Sensitivity _____
Probe liner: Borosilicate _____ Stainless steel _____ Teflon _____
Clean _____, Probe heater (if applicable) on _____ Glass wool filter (if applicable) in place _____ Stainless steel or Teflon unions used to connect to sample line _____
Sample line: Teflon ____, Cleaned _____, Heated (if applicable) _____
Bag: Tedlar _____ Other _____, Blank checked _____, Leak checked _____
Reactivity check _____, Retention check _____
Flowmeter: Proper range _____, Heated (if applicable) _____, Calibrated ___
Pump: Teflon coated diaphragm _____, Positive displacement pump _____, Evacuated canister _____, Personnel pump _____
Heated box with temperature control system: Maintained at proper temperature ____
Charcoal adsorption tube to adsorb organic vapors: Sufficient capacity _____
Dilution equipment: N_2 gas _____, Hydrocarbon-free air _____, Cleaned and dried ambient air _____, Dry gas meter _____
Barometer: Mercury _____, Aneroid _____, Other _____
Stack and ambient temperature: Thermometer _____, Thermocouple _____, Calibrated _____

Procedures

Recent calibration (if applicable): Pitot tube ____, Flowmeter _____, Positive displacement pump* ____, Dry gas meter* _____, Thermometer _____, Thermocouple _____, Barometer _____
Sampling technique: Indirect bag ___, Direct bag ___, Explosion risk bag ____, Dilution bag _____, Heated syringe _____, Adsorption tube _____, Proportional rate _____, Constant rate _____, Direct interface _____, Dilution interface _____
Filter end of probe and pitot tube placed at centroid of duct (or no closer than 1 meter to stack wall) and sample purged through the probe and sample lines*

Figure C.2. On-site measurements checklist.

Vacuum line attached to sample bag and system evacuated until the flowmeter indicates no flow (leakless)* _____

Heated box (if applicable) same temperature as duct* _____

Velocity pressure recorded and sample flow set _____

Proportional rate sampling maintained during run* _____

Stack temperature, barometric pressure, ambient temperature, velocity pressure at regular intervals, sampling flow rate at regular intervals, and initial and final sampling times recorded* _____

At conclusion of run, pump shut off, sample line and vacuum line disconnected and valve on bag closed _____

Heated box (if applicable) maintained at same temperature as duct until analysis conducted _____

No condensation visible in bag* _____

Sample bag and its container protected from the sunlight _____

Audit gases collected in bags using sampling system* _____

Explosive area bag sampling: (with following exceptions same as above) _____

Pump is replaced with an evacuated canister or sufficient additional line is added between the sample bag container and the pump to remove the pump from the explosive area _____

Audit gases collected in bags using sampling system* _____

Prefilled bag: Proportional rate _____ Constant rate _____

Dilution factor determined to prevent condensation* _____

Proper amount of inert gas metered into bag through a properly calibrated dry gas meter* _____

Filter end of probe (if applicable) and pitot tube placed at centroid of duct (or no closer than 1 meter to stack wall) and sample purged through the heated probe, heated sample line, and heated flowmeter or positive displacement pump* _____

Leak checked and partially filled bag attached to sample line _____

Stack temperature, barometric pressure, ambient temperature, velocity pressure at regular intervals, sampling rate at regular intervals, and initial and final sampling times recorded* _____

Probe, sample line, and properly calibrated flowmeter or positive displacement pump maintained at the stack temperature* _____

Sampling conducted at the predetermined rate, proportionally or constant for entire run* _____

No condensation visible in probe, sample lines, or bag* _____

At conclusion of run, pump shut off, sample line disconnected and valve on bag closed _____

Sample bag and its container protected from sunlight _____

Audit gases collected in bags using dilution system* _____

Figure C.2. (Continued)

Sample Recovery and Analysis

(As described in "Post sampling operations checklist," Figure C.10, page C-37)

DIRECT AND DILUTION INTERFACE

Apparatus

Probe: Stainless steel _____, Glass _____, Teflon _____, Heated system (if applicable) _____, Checked _____
Heated sample line: Checked* _____
Thermocouple readout devise for stack and sample line: Checked* _____
Heated gas sample valve: Checked* _____
Leakless Teflon-coated diaphragm pump: Checked* _____
Flowmeter: Suitable range _____
Charcoal adsorber to adsorb organic vapors _____
Gas chromatograph and calibration standards (as shown in "Post sampling operations checklist," Figure C.10)* _____

For dilution interface sampling only:
Dilution pump: Positive displacement pump or calibrated flowmeter with Teflon-coated diaphragm pump checked* _____
Valves: Two three-way attached to dilution system _____
Flowmeters: Two to measure dilution gas, checked* _____
Heated box: Capable of maintaining 120°C and contains three pumps, three-way valves, and connections, checked* _____
Diluent gas and regulators: N_2 gas ___, Hydrocarbon-free air ___, Cleaned air _, Checked _____

Procedures

All gas chromatograph procedures shown in "Post sampling operations checklist" (Figure C.10)
Recent calibration: Thermocouples _____, Flowmeter _____, Dilution system (for dilution system only)* _____
Filter end of heated probe placed at centroid of duct (or no closer than 1 meter to stack wall), probe and sample line heat turned on and maintained at a temperature of 0°C to 3°C above the source temperature while purging stack gas _____
Gas chromatograph calibrated while sample line purged* _____
After calibration, performance audit conducted and acceptable* _____
Sample line attached to GC and sample analyzed after thorough flushing* _____

Figure C.2. (Continued)

With probe removed from stack for 5 min, ambient air or cleaned air analysis is less than 5% of the emission results* _____

Probe placed back in duct and duplicate analysis of next calibration conducted until acceptable agreement obtained* _____

All samples, calibration mixtures, and audits are analyzed at the same pressure through the sample loop* _____

Sample Analysis

(As shown in "Post sampling operations checklist," Figure C.10.)

If a dilution system is used, check the following:

With the sample probe, sample line, and dilution box heating systems on, probe and source thermocouple inserted into stack and all heating systems adjusted to a temperature of 0°C to 3°C above the stack temperature _____

The dilution system's dilution factor is verified with a high concentration gas of known concentration (within 10%) _____

The gas chromatograph operation verified by diverting a low concentration gas into sample loop _____

The same dilution setting used throughout the run _____

The analysis criteria is the same shown as for the direct interface and in the "Post sampling operations checklist," (Figure C.10.)

ADSORPTION TUBES

Apparatus

Probe: Stainless steel _____, Glass _____, Teflon _____, Heated system and filter (if applicable) _____

Silica gel tube or extra adsorption tube used prior to adsorption tube when moisture content is greater than 3 percent _____

Leakless sample pump calibrated with limiting (sonic) orifice or flowmeter _____

Rotameter to detect changes in flow _____

Adsorption tube: Charcoal (800/200 mg), Silica gel (1040/260 mg) _____

Stopwatch to accurately measure sample time _____

Figure C.2. (Continued)

Procedures

Recent calibration of pump and flowmeter with bubble meter _____
Extreme care is taken to ensure that no sample is lost in the probe or sample line prior to the adsorption tube _____
Pretest leak check is acceptable (no flow indicated on meter) _____
Total sample time, sample flow rate, barometric pressure, and ambient temperature recorded _____
Total sample volume commensurate with expected concentration and recommended sample loading factors _____
Silica gel tube or extra adsorption tube used prior to adsorption tube when moisture content is greater than 3 percent _____
Post-test leak check and volume rate meter check is acceptable (no flow indicated on meter, post-test calculated flow rate within 5 percent of pretest flow rate)

Sample Analysis

(As shown in the "Post sampling operations checklist," Figure C.10, page C-37.)

---

*Most significant items/parameters to be checked.

Figure C.2. (Concluded)

F. **Stability Check** - See Chapter 4.5

G. **Retention Check** - See Chapter 4.5

H. **Direct Pump Bag Sampling** - Direct pump sampling is conducted in a manner similar to evacuated container sampling, **with the exception that the needle valve and the pump are located between the probe and sample bag and the sample exposed surfaces of both must be constructed of stainless steel, Teflon or other material not affected by the stack gas (Figure C.3, page C-23). Due to the additional likelihood that sample may be lost in the needle valve and pump, it is recommended that the probe, sample line, needle valve, and pump be heated.** If it has or can be shown that this not a concern, then the heating may be eliminated. All precautions, procedures, data forms and criteria can be applied. Ensure that the system has been adequately purged before attaching the bag and sampling.

I. **Explosion Risk Area Bag Sampling** - Explosion risk area bag sampling is also similar to evacuated container sampling. The major difference is that no electrical components can be used in the explosion risk area. The first option of the tester is to locate the electrical equipment (e.g., the pump) outside the explosion risk area and run a long flexible line to the container. If that option is not possible, an evacuated steel container may be used as shown in Figure C.4, page C-24. This option may involve a potential spark hazard and must be checked through the plant safety officer. It is unlikely that electrical heating of the system will likely be allowed. If an evacuated steel container is used, the leak check can be conducted outside the explosion risk area and the probe can be purged with a hand squeeze pump. The tester may wish to consider an alternative method of sampling such as adsorption tubes and an intrinsically safe personnel sampling pump or the syringe method. **The primary concern must be safety in an explosion risk area and all operations must be outlined in writing and cleared through the Plant Safety Officer.** The same criteria as described above for suitability of the bag will apply and must be met.

J. **Prefilled Bag Sampling** - The prefilled bag sampling technique is similar to the heated direct pump sampling method. **The major difference is that the sample bag is prefilled with a known volume of nitrogen, hydrocarbon-free air, or cleaned, dried ambient air prior to sampling and the volume of gas sampled must be accurately determined (Figure C.3, page C-23). When using a flowmeter or metering pump, the maximum dilution that should be attempted is 10 to 1. Alternatively, a heated, gas tight syringe may be used to collect** the source and inject it into the sample bag. A heated, gas tight syringe can be used for dilutions of 5 to 1 when the dilution is performed in the syringe and 50 to 1 when performed in the bag. The use of a heated, gas tight syringe should follow the procedures shown below. Both techniques should be verified in the laboratory

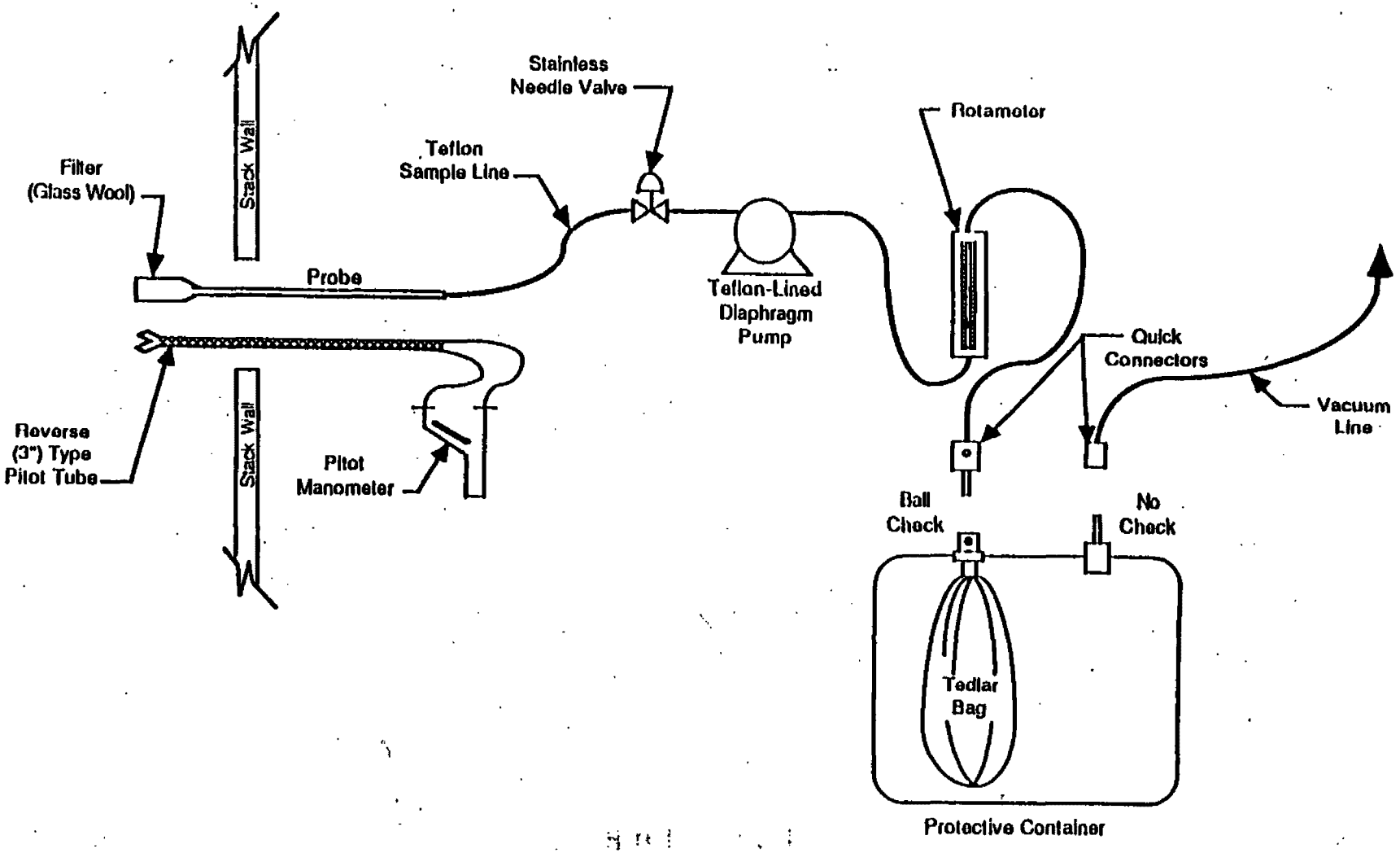


Figure C.3. Direct pump sampling system.

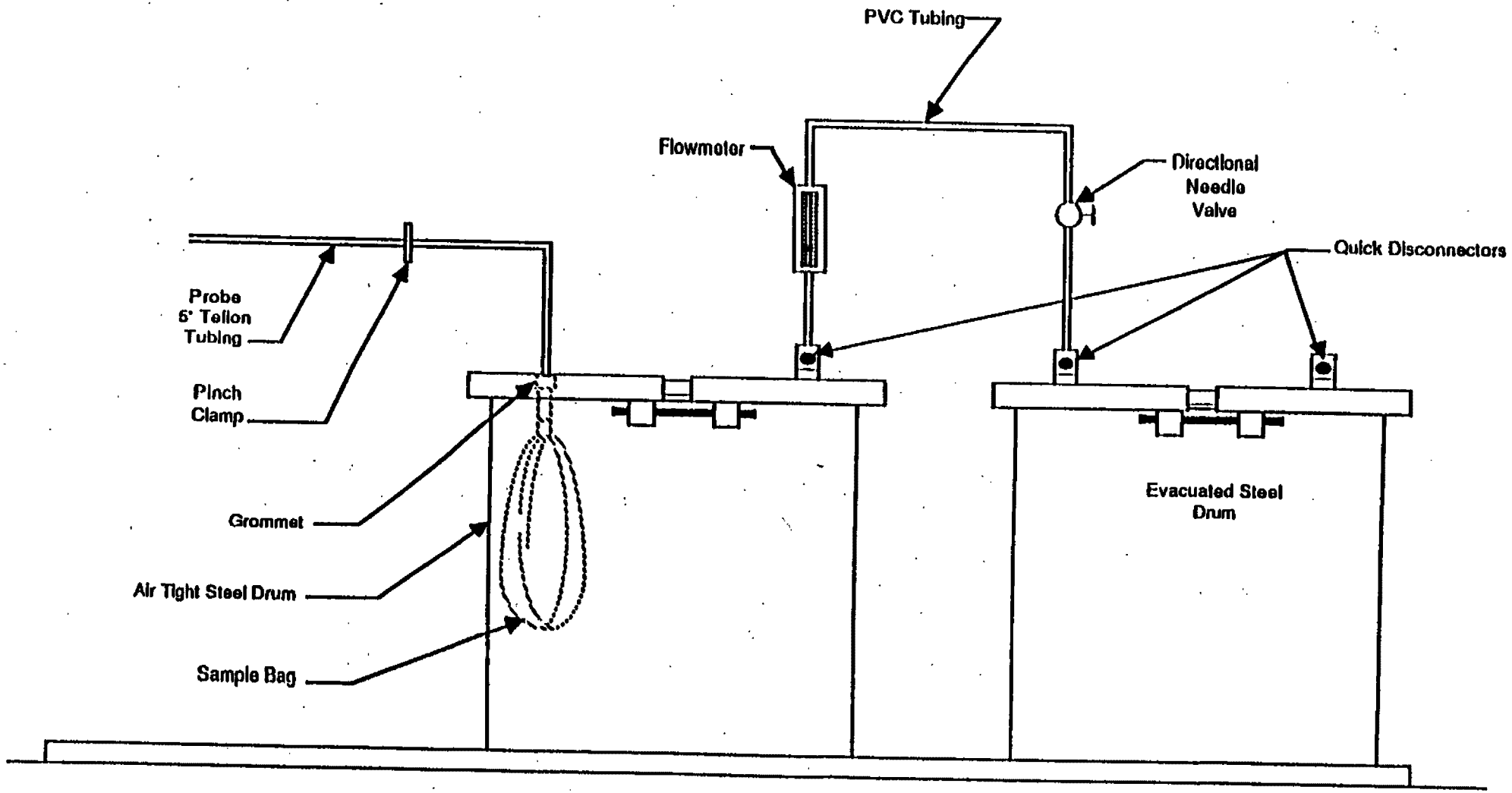


Figure C.4. Explosion risk area sampling system option using an evacuated steel container

using higher concentrations of calibration gases and must be within 10 percent of the calculated value. The technique is verified in the field by diluting the audit gases in the same manner as the stack gases (see Chapter 4.7 for auditing procedures).

Following are the recommended steps to conduct prefilled bag sampling:

1. **The sampling should be conducted proportionally as described above in Appendix C.2.1. Calculation of the average sampling rate versus the average ΔP will be the same with the exception that the volume of the prefilled inert gas must be taken into account.**
2. The suitability of the prefilled bag sampling technique should have been checked in the laboratory. This would include calculating the dilution factor required to obtain an acceptable sample concentration. **The dilution factor must be properly calculated since the concentration of the sample will be corrected for the inert gas volume.**
3. In the laboratory area, fill the sample bag (previously leak checked) with the calculated volume of inert gas. Because of the potential for leaks, bags should be filled the same day they are used. The inert gas volume must be determined with a calibrated dry gas meter or mass flowmeter. The bag should be sealed and taken to the sampling site.
4. At the sampling site, the sampling system is leak checked without the sampling bag attached. Turn on the heating system and heat the system to the stack temperature. Connect a U-tube H_2O manometer or equivalent to the inlet of the probe. After the system comes to the desired temperature, turn on the pump and pull a vacuum of about 10 in. of H_2O. Turn off the needle valve and shut off the pump. If there is no noticeable leak within 30 seconds, then the system is leak free. **The heating and leak check are again important.**
5. Place the probe in the stack at the sampling point (centroid or no less than 1 meter from the wall) and seal the port so there will be no in-leakage of ambient air. Turn on the pump and purge the system for 10 minutes. While the system is purging, determine and set the proper flow rate based on the ΔP.
6. Turn off the pump and attach the sample bag. Compare the heating system.
7. The sampling will be conducted proportionally. The stack temperature and heating system temperature should be monitored and recorded. Record the data on the sampling data form.
8. At the conclusion of the run, turn off the pump and remove the probe from the duct. Remove the bag and seal it.
9. Conduct a final leak check. The system should pass the leak check; if it does not pass, repeat the run.

K. **Heated Syringe Sampling** - The heated syringe technique can be used with the prior approval of the Administrator. This technique should only be used when other techniques are impractical. The heated syringe technique requires on-site analysis with three syringes collected and analyzed for each run. The requirements for the use of the syringes are the same as for the bag with regard to the reaction of the gases with time and the retention of the gases in the syringe.

Following are the procedures recommended for the syringe sampling technique:

1. If heating is required, then the syringe must be encased in material that has a high density to maintain the proper temperature. Alternatively, an external heating system can be used that keeps the syringe at the proper temperature until just before use and to which the syringe can be immediately returned. **The syringe must be properly heated. A check can be made on the heating system by filling the syringe with inert gas after the sample injection, reheating it and then inject the inert gas. If the system give a concentration of 10 percent or more of the original sample concentration, then the sampling system is unacceptable.**
2. The access port should be extremely small to prevent in-leakage of ambient air. The port may be covered with Teflon or other nonreactive material that will allow the syringe to penetrate the material for sampling.
3. For the direct injection method (no dilution), place the syringe needle into the stack and fill and discharge the full volume that will be sampled three times. Then, draw the emission sample into the syringe, immediately seal the syringe and return to the heating system, if applicable. The second and third syringes are sampled at equal time intervals spanning the required sample (run) time. The syringe samples must not be taken one immediately after another.
4. For the diluted syringe method, the inert gas is introduced into the syringe three times and discharged. Following this, the proper volume of inert gas is pulled into the syringe. The syringe is then placed into the duct and the proper volume of stack gas is added. Immediately remove the syringe needle from the duct, seal the syringe, and return to the heating system, if applicable. **If a dilution approach is used it should be checked as shown in Item 1 and the dilution factor should be checked using calibration gases.**
5. For the bag diluted syringe method, the bag should be prefilled with the proper volume of inert gas. The sampling is conducted as described above and the sample injected into the bag through a septum.
6. Record the data on a field sampling data form.
7. Since the method requires that a proportional sample collected, the velocity head (ΔP) should be recorded at about the same time that each sample is collected. The concentrations can then be mathematically corrected to provide an integrated value. If the process is a constant source operation (less than 10 percent change in flow over the sampling period), it is not necessary to correct the measured values.

C.2.2 Direct Interface Sampling - The direct interface procedure can be used provided that the moisture content of the stack gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements when using this method. Because of the amount of time the GC takes to resolve the organic compounds prior to their analysis, the GC can only typically make three analyses in a one-hour period. Therefore, the number of injections in the direct interface method is greatly limited by the resolution time. At least three injections must be conducted per sample run.

Following are the procedures recommended for extracting a sample from the stack, transporting the sample through a heated sample line, and introducing it to the heated sample loop and the GC. The analysis of the sample is described in Appendix C.3.

1. Assemble the system as shown Figure C.5, making all connections tight.
2. Turn on the sampling system heaters. Set the heaters to maintain the stack temperature as indicated by the stack thermocouple. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating system to maintain a temperature adequate to prevent condensation of water and organic compounds.
3. Turn on the sampling pumps and set the flow rate at the proper setting. Typically 1 l/min is used. **The sample rate may vary for the type of system used. The system may use either an internal pump or external pump.**
4. After the system reaches the same temperature as the stack, connect a U-tube H_2O manometer or equivalent to the inlet of the probe. Pull a vacuum of about 10 in. of H_2O, and shut off the needle valve and then the pump. The vacuum should remain stable for 30 seconds. If the system leaks, repair and then recheck the system.
5. Calibrate the system as described in Appendix C.3. Repeat until duplicate analyses are within 5 percent of their mean value (Appendix C.3). **The calibration of the system is critical.**
6. Conduct the analyses of the two audit samples as described in Chapter 4.8. The results must agree within 10 percent of the true value (or greater, if specified on the cylinder). If the results do not agree, repair the system and repeat the analyses until agreement is met or until approval is given by the representative of the Administrator. **The performance audit is critical.**
7. After the audit has been successfully completed, place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 meter, and draw stack gas into the probe, heated line, and sample loop. Purge the system for a least 10 minutes.
8. Record the field sampling data on a form such as the form shown in Figure C.6.
9. Conduct the analysis of the sample as described in Appendix C.3. Record the data on the applicable data form. Ensure that the probe and sample lines are maintained at 0°C to 3°C above the stack temperature (or a temperature which

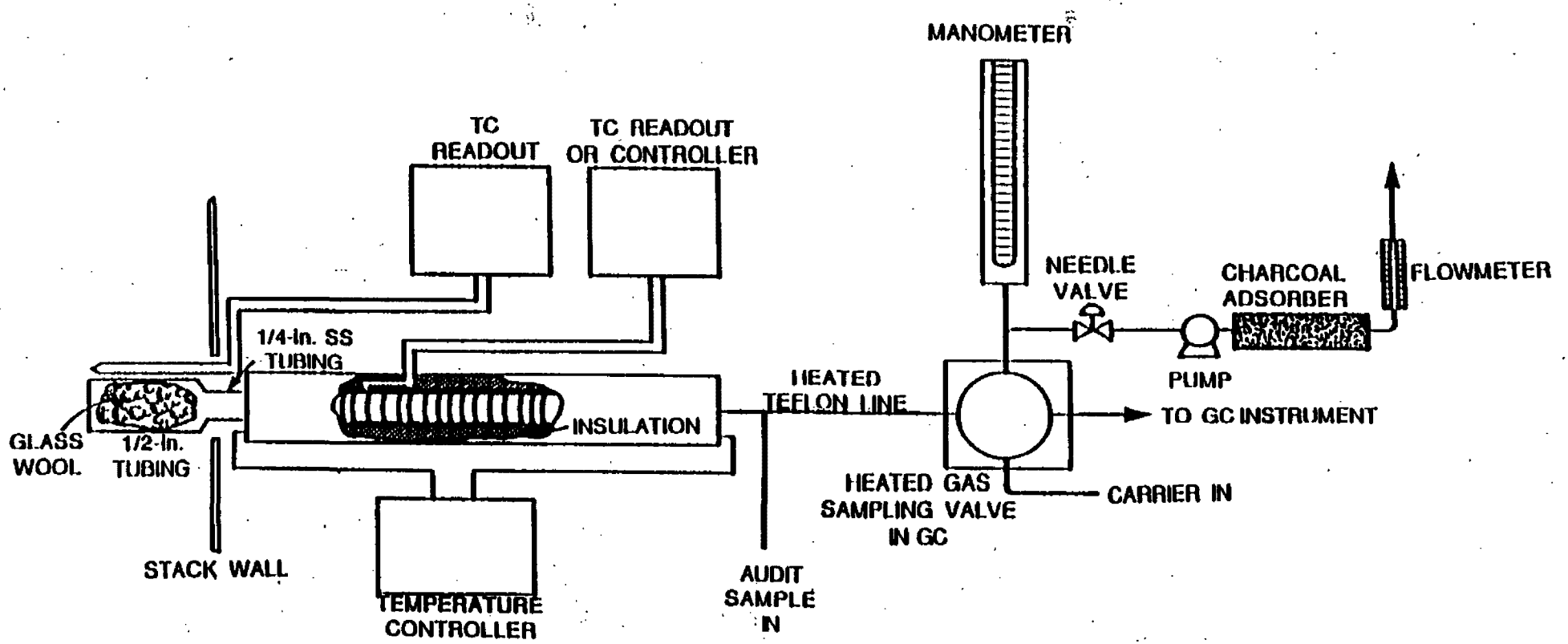


Figure C.5. Direct interface sampling system.

Plant _____
City _____
Operator _____
Date _____
Run number _____
Stack dia, mm (in.) _____
_____
Meter box number _____
Stack temp _____ °C (°F)
Static press ____ mm (in.) H_2O

Barometric press _____ mm (in.) Hg
Initial probe setting _____ °C (°F)
Sampling rate _____ l/min (cfm)
Sampling point location _____
_____
Dilution system:
source flow rate _____ l/min (cfm)
diluent flow rate ____ l/min (cfm)
diluent flow rate ____ l/min (cfm)
Dilution ratio _____

Sample loop volume _____ ml
Sample loop temp _____ °C (°F)
Column temperature:
initial _____/_____ °C/min
program rate _____/_____ °C/min
final _____/_____ °C/min
Carrier gas flow _____ ml/min
Dilution system check _____
Final leak check _____
Vacuum @ check ____ mm (in.) H_2O

Time of injection 24 h	Injection number	Flowmeter(s) settings			Temperature readings			
		source ml/min	diluent ml/min	diluent ml/min	stack °C (°F)	probe °C (°F)	sample line °C (°F)	injection port °C (°F)

Figure C.6. Direct interface sampling form.

prevents condensation). **The sample lines must be properly heated and equilibrated. A good check on the system is to pull the sample probe out of the stack at the conclusion of a sample run. The system should return to less than about 5 percent of the sample concentration within about 5 minutes.**

10. Conduct the post-test calibration as described in Appendix C.3. **System calibrations are critical.**

C.2.3 Dilution Interface Sampling - Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as described above, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph.

Following are the procedures recommended for extracting a sample from the stack, diluting the gas to the proper level, transporting the sample through a heated sample line, and introducing it to the heated sample loop and the GC. The analysis of the sample is described in Appendix C.3.

1. Assemble the apparatus by connecting the heated box, as shown in Figure C.7, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter.
2. Measure the stack temperature, and adjust all heating units to a temperature 0°C to 3°C above this temperature. If the temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds. **Heating is typically more critical for stacks that require dilution. The check of removing the probe from the stack as recommended above should be demonstrated.**
3. After the heaters have come to the proper temperature, connect a U-tube H_2O manometer or equivalent to the inlet of the probe. Turn on the pump and pull a vacuum of about 10 in. of H_2O. Shut off the needle valve and then turn off the pump. The vacuum reading should remain stable for 30 seconds. If a leak is present, repair and then recheck the system.
4. Verify operation of the dilution system by introducing a calibration gas at the inlet of the probe. The diluted calibration gas should be within 10 percent of the calculated value. If the results for the diluted calibration gas are not within 10 percent of the expected values, determine whether the GC and/or the dilution system is in error. If the analyses are not within acceptable limits because of the dilution system, correct it to provide the proper dilution factors. Make this correction by diluting a high concentration standard gas mixture to adjust the dilution ratio as required. **The dilution factor must be correct to obtain the true value. A dilution system can give proper results, but it can also provide very poor results when improperly conducted.**

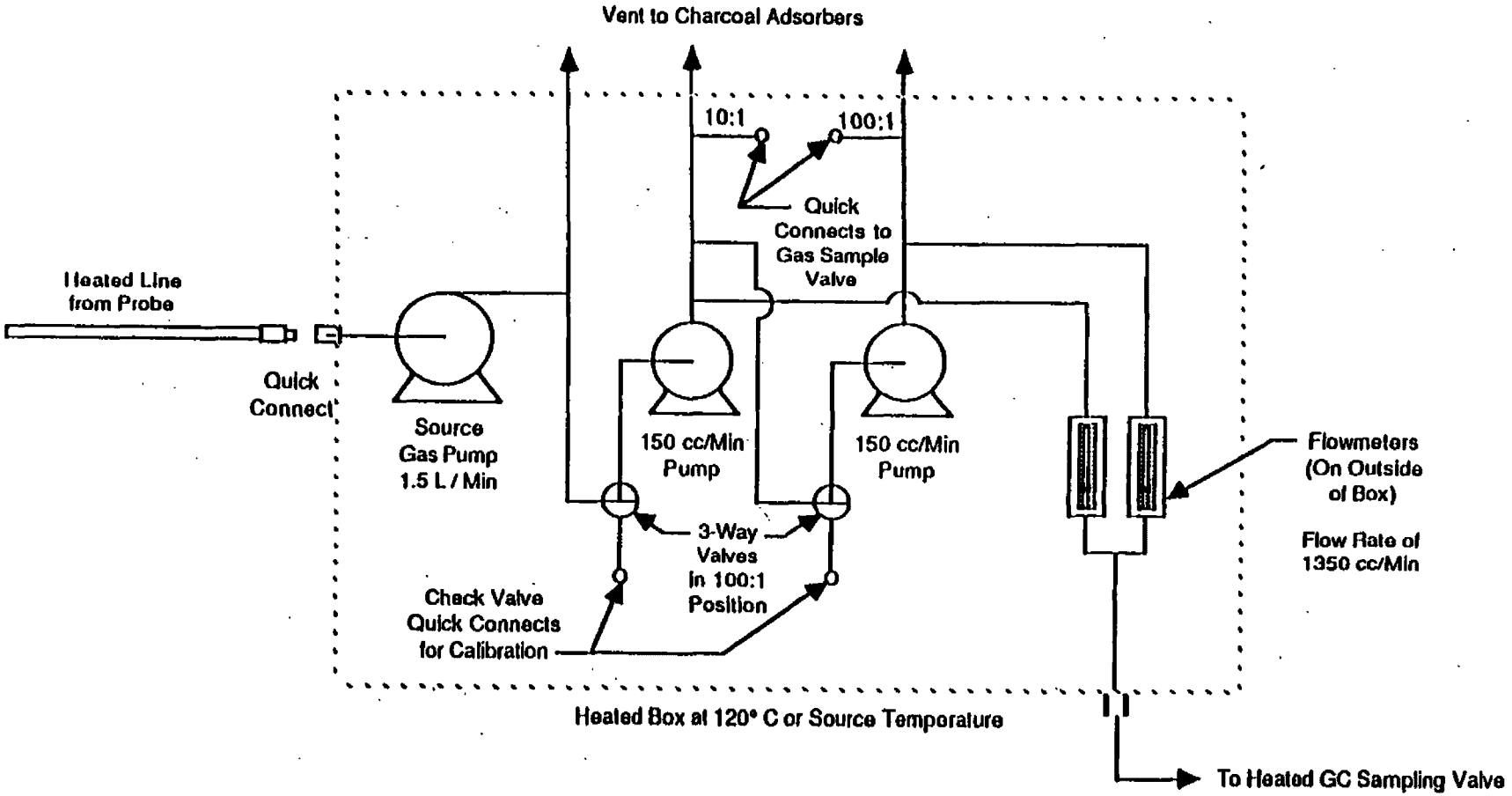


Figure C.7. Dilution interface sampling system.

5. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop and bypassing the dilution system. If these analyses are not within acceptable limits, correct the GC by recalibration, etc. **The test coordinator should verify these calculations.**
6. Conduct the analyses of the two audit samples as described in Appendix C.3 using either the dilution system or directly connect the gas sampling valve as required. The results must agree within 10 percent of the true value or greater value if specified on the cylinder. If the results do not agree, repair the system and repeat the analyses until agreement is met or until approval is given by the representative of the Administrator. **The performance audit is critical and should go through the dilution system when possible.**
7. After the dilution system and GC operations are properly verified and the audit successfully completed, place the probe at the centroid of the duct or at a point no closer to the walls than 1 meter, and purge the sampling system for at least 10 minutes at the proper flow rate. Conduct the analysis of the sample as described in Appendix C.3. Record the field and analytical data on the applicable data forms. Ensure that the probe, dilution system, and sample lines are maintained at 0°C to 3°C above the stack temperature (or a temperature which prevents condensation).
8. Conduct the post-test calibration and verification of the dilution system as described in Appendix C.3. **Check the calibration calculations.**

If the dilution system is used for bag sampling, the procedures for verifying operation of the dilution system will be the same as shown above. The diluted calibration gas will be collected in a bag and then verified. Also the audit samples will be collected in a bag and analyzed. **Acceptable results must be obtained for the audit samples prior to analysis of the field samples.**

C.2.4 Adsorption Tube Sampling - Adsorption tube sampling can be used for those organics specified in Table C-2, page C-4, and for other compounds as specified in the National Institute of Occupational Safety and Health (NIOSH) methods. The selection and use of adsorption tubes must be validated in the laboratory or through the use of the literature. **This check will include selecting the proper adsorption material, and then checking the capacity, breakthrough volume, adsorption efficiency, and desorption efficiency. The adsorption efficiency can be greatly affected by the presence of water vapor and other organics in, and temperature of, the stack gas. If sampling is conducted for more than one organic compound, the adsorption and desorption efficiency checks must consider each.** Because changes in process and control equipment conditions can greatly affect all of the parameters stated above, it is recommended as a standard operating procedure that more than one adsorption tube be used. The first tube is analyzed as described in Appendix C.3. If no problems are found, then the second tube can be discarded. If problems with the first tube's adsorption efficiency are discovered, then the primary section of the second tube can still be analyzed and the results included with those of the primary portion of the first tube.

Following are the recommended procedures for adsorption tube sampling:

1. The sampling system is assembled as shown in Figure C.8, page C-34. **The adsorption tube(s) must be maintained in a vertical direction for sampling.** This is done to prevent channeling of the gases along the side of a tube. It is recommended that the sampling probe be eliminated when possible. **If a sample probe is used, it should be cleaned prior to its initial use with the extraction solvent.** Teflon tubing should be used for the probe and sample line.
2. Just prior to sampling, break off the ends of the adsorption tubes to provide an opening at least one-half of the internal diameter. **Audit samples must be collected on the adsorption tubes during the test program as described in Chapter 4.8.** Since on-site analysis is typically not conducted when using adsorption tubes, it is recommended that two samples be collected from each of the two audit cylinders. This allows the tester a second chance to obtain the proper value for each audit cylinder.
3. Prior to sampling and the collection of the audit samples, the sampling system must be leak checked by connecting a U-tube H_2O manometer or equivalent to the inlet of the sample probe or adsorption tube. Turn the pump on and pull a vacuum of about 10 in. of H_2O. Shut off the needle valve and then turn off the pump. The vacuum must remain stable for 30 seconds. If a leak is present, repair and recheck the system. **The leak check must be passed.**
4. If the flow rate in the duct varies by more than 10 percent during the sampling period, the sample should be collected proportionally. The proportional sampling procedures will be the same as described for the bag sampling. The only difference is that instead of using the volume of the bag as the limiting factor to determine the average sampling rate, the breakthrough volume is the limiting factor. If the source is a constant rate source (less than a 10 percent change in flow rate for the sampling period), the samples can be collected at a constant rate.
5. Prepare the field blank just prior to sampling. The field blank will be handled in be same manner as the field samples and should be from the same lot as the other adsorption tubes. **Blank correction can be allowed.**
6. The flow rate meter must have been calibrated in the laboratory prior to the field trip. **The volume of sample collected must be accurately known for adsorption tube sampling. The calibration data should be checked.**
7. The sample run time must be equal to or greater than that specified by the applicable regulation. During each sample run, the data should be recorded on the sample data form as shown in Figure C.9, page C-35.
8. At the conclusion of each run, conduct another leak check as described above. **If the system does not pass the leak check, the run should be rejected, the leak located and repaired, and another run conducted.**

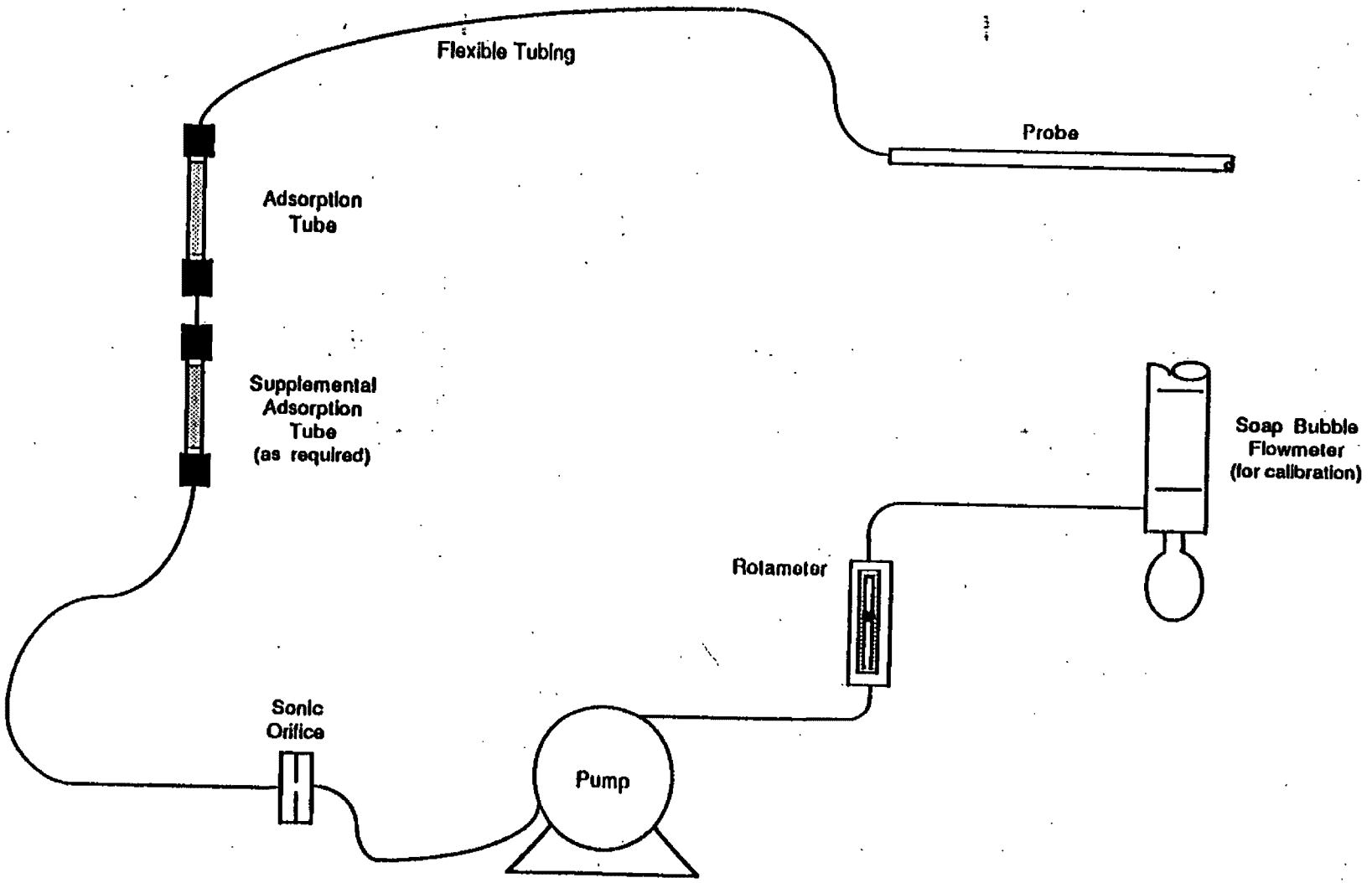


Figure C.8. Adsorption tube sampling system.

Plant _____
City _____
Operator _____
Date _____
Run number _____
Stack dia, mm (in.) _____
_____
Meter box number _____
Pitot tube (C_p) _____
Static press ____ mm (in.) H2O

Flowmeter calib.(Y) _____
Adsorption tube type:
charcoal tube _____
silica gel _____
other _____
Adsorption tube number _____
Average (ΔP) _____ mm (in.) H2O
Initial flowmeter setting _____
Average stack temp _____ °C (°F)
Barometric press _____ mm (in.) Hg

Dilution system: (dynamic)
emission flowsetting _____
diluent flowsetting _____
Dilution system: (static)
emission flowsetting _____
Final leak check ____ m^3/min (cfm)
Vacuum during leak check _____
_____ mm (in.) H_2O
Sampling point location _____
_____

Sampling time, min	Clock time, 24 h	Velocity head mm (in.) H2O, (ΔP)	Flowmeter setting L/min (ft3/min)	Temperature readings: stack °C (°F)	probe, line °C (°F)	adsorp. tube °C (°F)	meter °C (°F)	Vacuum mm (in.) Hg
Total		Avg	Avg	Avg	Avg	Avg	Avg	Avg

Figure C.9. Field sampling data form for adsorption tube sampling.

9. After completing a successful leak check, remove the adsorption tube from the holder and seal both ends with plastic caps. The tubes should be packed lightly with padding to minimize the chance of breakage. **If the samples are to be held for an extended period of time, they should be kept cool to reduce the amount of migration of the organic from the primary section to the secondary section. Note: Pack the tubes separately from bulk samples to avoid possible contamination.**
10. **It is recommended, that at the conclusion of the test, the sample probe (if used) be rinsed into a 20-ml glass scintillation vial with about 5 to 10 ml of the desorption solvent. This sample will be analyzed as a check on the loss of the organic in the probe during sampling. If more than 10 percent of the total sample collected in the adsorption tubes is present in the probe, the samples should be rejected or the sample catch adjusted to account for the loss. Alternatively, the probe can be rinsed after each run and the rinse added to the desorption solvent prior to analysis.**
11. At the conclusion of the test program, check all samples to ensure that they are uniquely identified and check all data sheets to ensure that all data has been recorded.

C.3 VOC SAMPLE ANALYSIS

Figure C.10, page C-37, post sampling operations checklist can be used as a guide by the testing firm for sample analysis or by the observer for observation of the sample analysis.

C.3.1 Preparation of Calibration Standards

Calibration standards are to be prepared prior to sample analysis following the procedures described below. Refer to Table C-4, page C-8, for recommendations on the procedures suitable for selected compounds. Note that there are two basic types of standards, gaseous or liquid; the type prepared depends on the type of sample collected. Gaseous calibration standards will be needed prior to the analysis of preliminary survey samples collected in glass flasks or bags, and final samples collected in bags or by direct and dilution interface sampling. **There are three techniques for preparing gaseous standards, depending on availability and the chemical characteristics of the standard compound(s); gas cylinder standards may also be used directly, if the proper concentration ranges are available. Liquid calibration standards are required for the analysis of adsorption tube samples from the preliminary survey and/or the final sampling, as well as to determine the desorption efficiency; there are two techniques for preparing liquid calibration standards. The concentrations of the calibration standards should bracket the expected concentrations of the target compound(s) at the source being tested.** Specific procedures for preparing and analyzing each type of standard are described below.

Date_____ Plant Name _____
Sampling Location _____

Checks for Analysis of All Calibration Standards

A minimum of three concentration levels used for each target compound?
____ Yes ____ No (The concentration used should bracket the expected concentrations of the actual field samples.)
Proper GC conditions established prior to standard analysis? ____ Yes ____ No
(For initial conditions use analytical conditions found to be acceptable during preliminary survey sample analysis.)
Individual peak areas for consecutive injections within 5 percent of their mean for each target compound? ____ Yes ____ No
(Repeat analysis of standards until 5 percent criteria is met.)
Second analysis of standards after sample analysis completed? ____ Yes ____ No
Peak areas for repeat analysis of each standard within 5 percent of their mean peak area? ____ Yes ____ No
(If no, then report sample results compared to both standard curves.)

Checks for Calibrations using Commercial Cylinder Gases

Vendor concentration verified by direct analysis? _____ Yes ____ No
Sample loop purged for 30 seconds at 100 ml/min prior to injection of calibration standards? ____ Yes ____ No

Checks for Preparation and Use of Calibration Standards Prepared by Dilution

Dilution system flowmeters calibrated? _____ Yes ____ No
(Calibrate following procedure described in Appendix C.3.)
Sample loop purged for 30 seconds at 100 ml/min prior to injection of calibration standards? ____ Yes ____ No
Dilution ratio for dilution system verified? ____ Yes ____ No
(Analysis of low concentration cylinder gas after establishing calibration curve recommended to verify dilution procedure, but not required since audit sample will also verify dilution ratio.)

Figure C.10. Post sampling operations checklist.

Checks for Preparation and Use of Calibration Standards by Direct Injection of Gaseous Compounds or Liquid Injection

Tedlar bag used to contain prepared standard leak and contamination free?
Yes ____ No ____
Dry gas meter used to fill bag calibrated? ____ Yes ____ No
(Calibrate meter following procedure described in Appendix C.3)
Organic standard material used for injection 99.9 percent pure? ____ Yes ____ No
(If no, then determine purity and use to correct calculated calibration standard concentration.)
Prepared standard allowed to equilibrate prior to injection? ____ Yes ____ No
(Massage bag by alternately depressing opposite ends 50 times.)
Sample loop purged for 30 seconds at 100 ml/min prior to injection of calibration standards? ____ Yes ____ No

Development of Relative Response Factors and Retention Times

Suitable target organic or surrogate compound selected? ____ Yes ____ No
(Select compound that is stable, easy to prepare in the field, and has a retention time similar to the target organic compounds.)
Relative response factors and retention times verified in the laboratory prior to actual field use? ____ Yes ____ No
(If no, verify following the procedure described in Appendix C.3.)

Checks for Preparation, Use, and Determination of Desorption Efficiency for Adsorption Tube Standards

Organic standard material used for injection 99.9 percent pure? ____ Yes ____ No
(If no, then determine purity and use to correct calculated calibration standard concentration.)
Correct adsorbent material and desorption solvent selected? ____ Yes ____ No
(Refer to Table C-2 for proper adsorbent material and desorption solvent.)
Desorption efficiency determined for adsorbent to be used for field sampling?
____ Yes ____ No

Figure C.10. (Continued)

Checks for All GC Analysis of Field Samples

Check type of carrier gas used: Helium ____ Nitrogen ____ Other _____
Carrier gas flow rate and pressure set correctly? ____ Yes ____ No
(Carrier gas flow rate and pressure set according to conditions developed during presurvey sample analysis and within limitations of the GC as specified by GC manufacturer.)
Oxygen and hydrogen flow rate and pressure for FID correct? ____ Yes ____ No
(Oxygen and hydrogen gas flow rate and pressure for FID set according to conditions developed during presurvey sample analysis and within limitations of the GC as specified by GC manufacturer.)
Individual peak areas for consecutive injections within 5 percent of their mean for each target compound? ____ Yes ____ No
(Repeat analysis of standards until 5 percent criteria is met.)
Audit sample analyzed and results within 10 percent of actual value? ____ Yes ____ No
(If no, recalibrate GC and/or reanalyze audit sample.)

Checks Type of Standard Used for Tedlar Bag Sample Analysis

Gas cylinders ____ dilution of gas cylinders ____ direct gas injection ____
direct liquid injection ____ and/or relative response factors and retention times ____

Checks For GC Analysis Of Tedlar Bag Samples

Sample loop purged for 30 sec. at 100 ml/min prior to injection of calibration standards? ____ Yes ____ No

Stability of gas sample in Tedlar bag determined? ____ Yes ____ No
(Determine stability by conducting a second analysis after the first at a time period equal to the time between collection and the first analysis. The change in concentration between the first and second analysis should be less than 10 percent.)
Retention of target compounds in Tedlar bag determined? ____ Yes ____ No

Figure C.10. (Continued)

Check GC Interface Technique Used

Direct Interface ____ 10:1 Dilution Interface ____ 100:1 Dilution Interface ____

Checks For Suitability of GC Interface Technique

Analytical interference due to moisture content of source gas? ____ Yes ____ No
(Moisture in the source gas must not interfere with analysis in regard to peak resolution according to EPA Method 625 criterion where the baseline-to-valley height between adjacent peaks is less than 25 percent of the sum of the two adjacent peaks.)

Physical requirements for equipment met on-site? ____ Yes ____ No
(The physical requirements for the equipment include sheltered environment, "clean", uninterrupted power source suited for equipment, and adherence to safety aspects related to explosion risk areas.)

Source gas concentration below level of GC detector saturation? ____Yes ____ No
(Concentrations delivered to the detector can be reduced by using smaller gas sample loops and/or dilution interface.)

Sampling systems purged with 7 changes of system volume prior to sample analysis? ____ Yes ____ No

Check Type(s) of Standards Used for Interface Techniques

Gas Cylinders ____ Dilution of Gas Cylinders ____ Direct Gas Injection ____ Direct Liquid Injection ____ and/or Relative Response Factors and Retention Times ____

Checks For Dilution Interface Analytical Apparatus

Dilution rate verified (within 10 percent) by introducing high concentration gas through dilution system and analyzing diluted gas? ____ Yes ____ No
(If dilution rate not verified, then first check calibration of GC by reanalyzing a calibration standard and then adjust dilution system to give desired ratio.)

Sampling systems purged with 7 changes of system volume prior to sample analysis? ____ Yes ____ No

Figure C.10. (Continued.)

Check Type of Standard Used for Adsorption Tube Analysis

Prepared directly in Desorption Solvent ____ and/or Prepared on adsorbent and desorbed ____

Checks for GC Analysis of Adsorption Tube Samples

Desorption procedure used identical to procedure used to determine the desorption efficiency? ____ Yes ____ No

Collection efficiency determined for adsorption tubes used for actual field sampling? ____ Yes ____ No
(If no, then determine collection efficiency following the procedures described in Appendix C.3.)

Check Type of Standard Used for Analysis of Heated Syringe Samples

Gas Cylinders ____ Dilution of Gas Cylinders ____ Direct Gas Injection ____ Direct Liquid Injection ____ and/or Relative Response Factors and Retention Times ____

Figure C.10. (Concluded)

For each target compound, a minimum of three different standard concentrations are required to calibrate the GC. An exception to this requirement involves developing **relative response factors for each compound to be tested as compared to a single organic compound. Once in the field, the GC is calibrated for all target compounds using the single organic. The validity of this procedure must be first be proven in the laboratory prior to the test. To save time, multiple component standards can be prepared and analyzed provided the elution order of the components is known.**

It is recommended that the linearity of the calibration curve be checked comparing the actual concentration of the calibration standards to the concentration of the standards calculated using the standard peak areas and the linear regression equation. The recommended criteria for linearity is for the calculated concentration for each standard be within 7 percent of the actual concentration.

After establishing the GC calibration curve, an analysis of the audit cylinder is performed as described in Chapter 4.7. For an instrument drift check, a second analysis of the calibration standards and generation of a second calibration curve is required following sample analysis. The area values for the first and second analyses of each standard must be within 5 percent of their average. If this criterion cannot be met, then the sample values obtained using the first and second calibration curves should be averaged. In addition, if reporting such average values for the samples is warranted, an additional analysis of the **audit cylinder should be performed. The average of the audit values obtained using the two calibration curves should be reported.**

C.3.2 Analysis of Direct Interface Samples

Prior to analysis of the direct interface sample, the GC should be calibrated using a set of gaseous standards prepared by one of the techniques described above and **a successful analysis of an audit sample should be completed.** If possible, the audit samples should be introduced directly into the probe. Otherwise, the audit samples are introduced into the sample line immediately following the probe. The calibration is done by disconnecting the sample line coming from the probe, from the gas sampling valve sample loop inlet, and connecting the calibration standards to the loop for analysis. During the analysis of the calibration standards and the audit sample(s), make certain that the sample loop pressure immediately prior to the injection of the standards is at the same pressure that will be used for sample analysis. To analyze the direct interface samples after GC calibration, use the following procedures:

1. **Record the sample identity, detector attenuation factor, chart speed, sample loop temperature, column temperature and identity, and the carrier gas type and flow rate on a form. It is also recommended that the same information be recorded directly on the chromatogram. Record the operating parameters for the particular detector being used.**

2. **Examine the chromatogram to ensure that adequate resolution is being achieved for the major components of the sample. If adequate resolution is not being achieved, vary the GC conditions until resolution is achieved, and reanalyze the standards to recalibrate the GC at the new conditions.**
3. Immediately after the first analysis is complete, repeat steps 2 and 3 to begin the analysis of the second sample.
4. After conducting the analysis of the first sample with acceptable peak resolution, determine the retention time of the sample components and compare them to the retention times for the standard compounds. **To qualitatively identify an individual sample component as a target compound, the retention time for the component must match, within 0.5 seconds or 1 percent, whichever is greater, the retention time of the target compound determined with the calibration standards.**
5. **At the completion of the analysis of the second sample, determine if the area counts for the two consecutive injections give area counts within 5 percent of their average.** If this criterion cannot be met due to the length of the analysis, and the emissions are known to vary because of a cyclic or batch process, then the analysis results can still be used with the prior approval of the Administrator. **If the sample time is extended and the number of injections increased, the agency can accept the data that does not meet the above requirements.**
6. Analyze a minimum of three samples collected by direct interface to constitute an emissions test. **More will be required if the source is variable and the 10 percent requirement is not met.**
7. Immediately following the analysis of the last sample, reanalyze the calibration standards, and compare the area values for each standard to the corresponding area values from the first calibration analysis. **If the individual area values are within 5 percent of their mean value, use the mean values to generate a final calibration curve to determine the sample concentrations. If the individual values are not within 5 percent of their mean values, generate a calibration curve using the results of the second analysis of the calibration standards, and report the sample results compared to both standard curves.**

C.3.3 Analysis of Dilution Interface Samples

For the analysis of dilution interface samples, the procedures described for direct interface sampling shown above, with the addition of a check of the dilution system. Prior to any sample analysis, the GC must first be calibrated, followed by the dilution system check and an analysis of the audit sample(s). The audit sample(s) are introduced preferably into the inlet to the dilution system or directly into the gas

sampling valve. Use the following procedures to conduct the check of the dilution system:

1. Heat the dilution system to the desired temperature (0° to 3°C above the source temperature) or, if the dilution system components can not tolerate that temperature, to a temperature high enough to prevent condensation. **Heating is typically very critical; the gases must be kept at or above the stack temperature at all points through the system. Many systems have an internal pump which is not well heated. Conduct the check on the system as described above by pulling the probe from the stack at the conclusion of the first run.**
2. Adjust the dilution system to achieve the desired dilution rate, and introduce a high concentration target gas into the inlet of the dilution system. After dilution through the stage(s) to be used for actual samples, the target gas should be at a concentration that is within the calibration range.
3. Purge the gas sample loop with diluted high concentration target gas at a rate of 100 cc/min for 1 minute. Adjust the loop pressure measured by a water manometer connected to a tee at the outlet of the loop, to the loop pressure that was used during calibration and will be used during sample analysis. The procedure for pressure adjustment for the sample loop will vary with the type of dilution system that is used. In general, the loop pressure can be lowered by reducing the flow into the loop and raised by restricting the flow from the loop.
4. After achieving the proper loop pressure, immediately switch the gas sample valve to the inject position.
5. Note the time of the injection on the strip chart recorder and/or actuate the electronic integrator. Also, record the sample identity, detector attenuation factor, chart speed, sample loop temperature, column temperature and identity, and the carrier gas type and flow rate on a form. It is also recommended that the same information be recorded directly on the chromatogram. Record the operating parameters for the particular detector being used.
6. Determine the peak area and retention time for the target compound used for the dilution check, and calculate the area value using the detector attenuation. Compare the retention time to the retention time of the target compound calibration standard. **The retention times should agree within 0.5 seconds or 1 percent, whichever is greater. If the retention times do not agree, identify the problem and repeat the dilution check.**
7. Calculate the concentration of the dilution check gas (C_d) using the following formula.

$$C_d = \frac{Y-b}{S} x d \qquad \text{Equation C-1}$$

where:

Y = Dilution check target compound peak area, area counts,
b = y-intercept of the calibration curve, area counts,
S = Slope of the calibration curve, area counts/ppm$_v$, and
d = Dilution rate of the dilution system, dimensionless.

8. If the calculated value for the dilution check gas is not within 10 percent of the actual dilution check gas, then determine if the GC or the dilution system is in error. Check the calibration of the GC by analyzing one of the calibration samples directly bypassing the dilution system. **If the GC is properly calibrated, then adjust the dilution system, and repeat the analysis of the dilution check gas until the calculated results are within 10 percent of the actual concentration.**

Once the dilution system and the GC are operating properly, analyze the audit sample(s). Upon completion of a successful audit, the system is ready to analyze samples. To load the sample from the dilution system may not require a pump on the outlet of the sample loop, but calibration of the GC using standards prepared in Tedlar bags will require a pump. The system should be configured so that the pump can be taken off line when it is not needed.

C.3.4 Analysis of Adsorption Tube Samples

Prior to the analysis of adsorption tube samples, the target compounds adsorbed on the adsorption material must be desorbed. The procedures for the analysis of the sample desorption solutions are the same as those used for the standards. During sample analysis, the sample collection efficiency must be determined. Use the following procedures to determine the collection efficiency:

1. **Desorb the primary and backup sections of the tubes separately using the procedures found to give acceptable (50 percent) desorption efficiency for the spiked adsorption material. Use the same final volume of desorption solution for the samples as was used for the standard solutions.** If more than one adsorption tube was used in series per test run, delay desorbing the additional tubes until the analysis of the primary and backup section of the first tube is complete, and the collection efficiency for the first tube determined. Select the samples from the sampling run when the flue gas or duct moisture was the highest and, if known, when the target compound concentrations were the highest and analyze them first.
2. **Calibrate the GC using standards prepared directly in desorption solvent or**

prepared on adsorbent and desorbed.

3. Select a suitably sized injection syringe (5 or 10 ul), and flush the syringe with acetone (or some other suitable solvent if acetone is a target compound) to clean the syringe.
4. Flush the syringe with the desorption solution from the tube's backup section by withdrawing a syringe full of the solution from the septum vial, and dispensing the solution into a beaker containing charcoal adsorbent.
5. Refill the syringe with the backup section desorption solution, withdraw the syringe from the vial, and wipe the syringe needle with a laboratory tissue.
6. Adjust the syringe volume down to the amount used for injecting standards and inject the sample into the GC. Note the time of the injection on the strip chart recorder and/or actuate the electronic integrator. Also, record the sample identity, detector attenuation factor, chart speed, injection port temperature, column temperature and identity, and the carrier gas type and flow rate on the data form. It is also recommended that the same information be recorded directly on the chromatogram. Record the operating parameters for the particular detector being used.
7. After the analysis, determine the retention time of the major sample components, and compare these retention times to the retention times determined for the target compounds during analysis of the standards. **To qualitatively identify an individual sample component as a target compound, the retention time for the component must match, within 0.5 seconds or 1 percent, whichever is greater, the retention time of the target compound determined with the calibration standards. Determine the peak area for each target compound identified in the sample.**
8. **Repeat the injection of the first sample until the area counts for each identified target compound from two consecutive injections are within 5 percent of their average.**
9. **Multiply the average area count of the consecutive injections by the attenuation factor to get the area value for that sample.**
10. Next analyze the desorption solution from the primary section of the same adsorption tube following steps 4 through 9 above.
11. For each target compound, calculate the total weight (W), in ug, present in each section, taking into account the desorption efficiency using the following formula below.

$$W_p \quad W_b = \frac{Y-B}{S} \times \frac{1}{DE}$$ Equation C-2

where:

W_p = Weight of primary tube,
W_b = Weight of backup tube,
Y = Average value for the target compound in the section (primary or backup), area counts,
b = y-intercept from the three-point calibration curve for the target compound, area counts,
S = Slope from the three-point calibration curve for the target compound, area/ug, and
DE = Desorption efficiency (if standards prepared directly in desorption solvent are used for calibration).

12. Determine the percent of the total catch found in the primary section for each target compound identified using the following formula.

$$E_{cx} = \frac{m_{px}}{(m_{px}+m_{bx})} x100$$ Equation C-3

where:

E_{cx} = Collection efficiency of the primary section for target compound x, percent,
m_{px} = Catch of compound x in the primary section, ug, and
m_{bx} = Catch of compound x in the backup section, ug.

If the collection efficiency for the primary section for each target compound identified is ≥ 90 percent, then the collection efficiency for that compound is acceptable. If the collection efficiency for all the target compounds identified in the sample is acceptable, then the analysis of any additional tubes used in series behind the first tube will not be necessary. Proceed with the analysis of the other adsorption tube samples.

13. If the collection efficiency for any identified target compound is not acceptable, then analyze the second tube (if used) connected in series and determine the collection efficiency for that tube using the steps described above. If the second tube does not exhibit acceptable collection and a third tube was used, analyze the third tube. **If acceptable collection efficiency cannot be demonstrated for the sampling system, then the emission test using adsorption tubes will not be acceptable.**

14. Immediately following the analysis of the last sample, reanalyze the calibration standards, and compare the area values for each standard to the corresponding area values from the first calibration analysis. If the individual area values are within 5 percent of their mean value, use the mean values to generate a final calibration curve for determining the sample concentrations. If the individual values are not within 5 percent of their mean values, generate a calibration curve using the results of the second analysis of the calibration standards, and report the sample results compared to both standard curves.

C.4 AUDITING PROCEDURES

Direct Interface Sampling - Since direct interface sampling involves on-site analysis, the performance audit is conducted on-site after the calibration of the GC and prior to sampling. The audit gas cylinder is attached to the inlet of the sampling probe. Two consecutive analyses of the audit gas must be within 5 percent of the average of the two analyses. The tester/analyst then calculates the results and informs the audit supervisor. The observer records all information and results on the "Field audit report form" and then informs the tester/analyst as to the acceptability of the results.

Dilution Interface Sampling - Since dilution interface sampling involves on-site analysis, the performance audit is conducted on-site after the calibration of the GC and prior to sampling. If the audit gas cylinder obtained has a concentration near the diluted sample concentration, the audit gas is introduced directly into the sample port on the GC. If the audit gas cylinder obtained has a concentration close to the expected sample concentration, then the audit gas is introduced into the dilution system. The observer may wish to order one cylinder to assess both the dilution system and the analytical system and another cylinder to assess only the analytical system. Follow the same procedures described above for recording the information and reporting the results.

Adsorption Tube Sampling - The analysis for adsorption tube sampling is usually conducted off-site. Therefore, the audit analysis is conducted off-site. The recommended procedure is to conduct the audit once prior to the test and again following the test. Though the audit sample could be analyzed by direct injection, the inclusion of the chromatogram printout in the report will prove that the audit results were obtained through adsorption tube sampling and a solvent extraction. Alternatively, the audit samples can be collected on-site or off-site and then analyzed just prior to the analysis of the field samples. Since the observer will likely not be present during the analysis, the results are reported by telephone.

To collect the audit gas with the adsorption tube sampling train, connect a sample "T" to the line from the audit gas cylinder. Place the adsorption tube sampling system on one leg of the "T"; connect a rotameter to the other leg. With the sampling system off, turn on the audit gas flow until the rotameter reads 2 lpm. Turn on the sampling system and sample the audit gas for the specified run time. Approximately 1 lpm should be discharged through the rotameter.

C.5 REFERENCES

1. Method 18 - Measurement of Gaseous Organic Compound, Emissions by Gas Chromatography. Federal Register, Volume 48, No. 202, October 18, 1983, page 48344.

2. Amendments to Method 18. Federal Register, Volume 49, No. 105, May 30, 1984, page 22608.

3. Miscellaneous Clarifications and Addition of Concentration Equations to Method 18. Federal Register, Volume 52, No. 33, February 19, 1987, page 5105.

4. Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits, Status Report #8. U.S. Environmental Protection Agency Publication No. EPA-600/2-86-117, January 1987. Also available form NTIS as Publication No. PB 87-141461.

5. Traceability Protocol for Establishing True Concentration of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). Section 3.0.4, Quality Assurance Handbook, Volume III, Stationary Source Specific Methods, U.S. Environmental Protection Agency Publication No. EPA-600/4-77-027b, June 15, 1978.

6. Methanol, Method 2000. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

7. Alcohols, Method 1400. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

8. Alcohols II, Method 1401. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

9. Hydrocarbons, BP 36 - 126°C, Method 1500. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

10. Development of Methods for Sampling 1,3-Butadiene. Interim Report prepared under U.S. Environmental Protection Agency Contract Number 68-02-3993, March 1987.

11. Hexachlorocyclopentadiene, Method 2518, NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

12. Method 110 - Determination of Benzene from Stationary Sources, Proposed Rule. Federal Register, Volume 45, No. 77, April 18, 1980, page 26677.

13. Hydrocarbons, Aromatic, Method 1501. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

14. Naphthylamines, Method 264. NIOSH Manual of Analytical Methods, Volume 4, Second Edition, U.S. Department of Health and Human Services, August 1978.

15. Ketones I, Method 1300. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

16. 2-Butanone, Method 2500. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

17. Ethylene Oxide, Method 1612. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

18. Propylene Oxide, Method 1612. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

19. Hydrocarbons, Halogenated, Method 1003. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

20. Ethylene Dibromide, Method 1008. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

21. Proposed Method 23 - Determination of Halogenated Organics from Stationary Sources. Federal Register, Volume 45, No. 114, June 11, 1980, page 39766.

22. 1,2-Dichloropropane, Method 1013. NIOSH Manual of Analytical Methods, Volume 1, Third Edition, U.S. Department of Health and Human Services, February 1984.

23. Development of Methods for Sampling Chloroform and Carbon Tetrachloride. Interim Report prepared for U.S. Environmental Protection Agency under EPA Contract Number 68-02-3993, November 1986.

24. Dichlorodifluoromethane, Method 111. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

25. Methyl Bromide, Method 2520. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

26. Methyl Chloride, Method 99. NIOSH Manual of Analytical Methods, Volume 4,

Second Edition, U.S. Department of Health and Human Services, August 1978.

27. Butler, F. E., E. A. Coppedge, J. C. Suggs, J. E. Knoll, M. R. Midgett, A. L. Sykes, M. W. Hartman, and J. L. Steger. Development of a Method for Determination of Methylene Chloride Emissions at Stationary Sources. Association, New York, NY, June 1987.

28. Vinylidene Chloride, Method 266. NIOSH Manual of Analytical Methods, Volume 4, Second Edition, U.S. Department of Health and Human Services, August 1978.

29. Ethyl Chloride, Method 1005. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

30. Method 106 - Determination of Vinyl Chloride from Stationary Sources. Federal Register, Volume 47, No. 173, September 7, 1982, page 39168.

31. Knoll, J. E., M. A. Smith, and M. R. Midgett. Evaluation of Emission Test Methods for Halogenated Hydrocarbons, Volume II, U.S. Environmental Protection Agency Publication No. EPA-600/4-80-003, January 1980.

32. Methylene Chloride, Method 1005. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

33. Tetrachloroethylene, Method 335. NIOSH Manual of Analytical Methods, Volume 3, Second Edition, U.S. Department of Health and Human Services, April 1977.

34. Trichloroethylene, Method 336. NIOSH Manual of Analytical Methods, Volume 3, Second Edition, U.S. Department of Health and Human Services, April 1977.

35. 1,1,2-Trichlorotrifluoroethane, Method 129. NIOSH Manual of Analytical Methods, Volume 3, Second Edition, U.S. Department of Health and Human Services, April 1977.

36. Vinyl Chloride, Method 1007. NIOSH Manual of Analytical Methods, Volume 2, Third Edition, U.S. Department of Health and Human Services, February 1984.

37. Mann, J. B., J. J. Freal, H. F. Enos, and J. X. Danauskas. Development and Application of Methodology for Determining 1,2 Dibromo-2-Chloropropane (DBCP) in Ambient Air. Journal of Environmental Science and Health, B15(5), 519-528 (1980).

38. VOC Sampling and Analysis Workshop. Volume III. U.S. Environmental Protection Agency Publications No. EPA-340/1-001C, September 1984.

39. Knoll, J.E., M. A. Smith, and M. R. Midgett. Evaluation of Emission Test Methods for Halogenated Hydrocarbons, Volume I. U.S. Environmental Protection Agency Publication No. EPA-600/4-79-025, March 1979.

40. Binetti, R. et al.. Headspace Gas Chromatographic Detection of Ethylene Oxide in Air. Chromatographic, Vol. 21. December 1986.

41. Butadiene, Method 591. NIOSH Manual of Analytical Methods, Volume 2, Second Edition, U.S. Department of Health and Human Services, April 1977.

42. Knoll, J. E., Estimation of the Limit of Detection in Chromatography. Journal of Chromatographic Science, Vol. 23, September 1985.

43. Procedure 1 - Determination of Adequate Chromatographic Peak Resolution. Code of Federal Regulations, Title 40, Part 61, Appendix C, July 1, 1987.

44. Method 625 - Base/Neutral Acids. Code of Federal Regulation, Title 40, Part 136, Appendix A, July 1, 1987.

45. C1 through C5 Hydrocarbons in the Atmosphere by Gas Chromatography, ASTM D 2820-72, Part 23. American Society for Testing and Materials, Philadelphia, PA, 23:950-958, 1973.

46. Corazon, V. V. Methodology for Collecting and Analyzing Organic Air Pollutants. U.S. Environmental Protection Agency Publication No. EPA-600/2-79-042, February 1979.

47. Dravnieks, A., B. K. Krotoszynski, J. Whitfield, A. O'Donnel, and T. Burgwald. Environmental Science and Technology, 5(12):1200-1222, 1971.

48. Eggertsen, F. T., and F. M. Nelson. Gas Chromatographic Analysis of Engine Exhaust and Atmosphere. Analytical Chemistry, 30(6): 1040-1043, 1958.

49. Feairheller, W. R., P. J. Marn, D. H. Harris, and D. L. Harris. Technical Manual for Process Sampling Strategies for Organic Materials, U.S. Environmental Protection Agency Publication No. EPA-600/2-76-122, April 1976.

50. FR, 39 FR 9319-9323, 1974.

51. FR, 39 FR 32857-32860, 1974.

52. FR, 41 FR 23069-23072 and 23076-23090, 1976.

53. FR, 41 FR 46569-46571, 1976.

54. FR, 42 FR 41771-41776, 1977.

APPENDIX D
METHOD 25 OBSERVATION PROCEDURES

D.1 Specifications for Method 25 Sampling Equipment
D.2 Specifications for Method 25 Analytical Equipment
D.3 Method 25 Nomenclature and Equations

D.1 SPECIFICATIONS FOR METHOD 25 SAMPLING EQUIPMENT

Heated Probe - Heat-traced and capable of maintaining 269°F ±5°F (129°C ±3°C). An elbow or nozzle is attached to the tip to allow the tip to be turned away from the direction of flow. The probe exit should be equipped with a "T" and thermocouple well so that the exit temperature can be monitored.

Filter and Housing - 25 mm glass mat filter with 0.5 micron cut size and a heated container capable of maintaining the filter temperature at 250°F ±5°F (121°C ±3°C). Must be equipped with a thermocouple well to monitor the filter temperature during sampling. The housing should be large enough to keep the sample/purge valve hot along with the connecting tubing going to the condensate trap.

Sample/Purge Valve - Three-way valve to allow the stack gas to be sampled through the condensate trap and sample tank or diverted to a purge pump. The valve should also have a neutral position to seal the sampling train from either the stack or purge pump.

Condensate Trap - 3/8 inch diameter 316 stainless tubing bent to a "U" shape and packed with quartz wool.

Metering Valve - Stainless steel fine metering valve for regulating the sample flow rate through the train.

On/Off Valve or Sealing Quick Connect - For sealing the train to prevent ambient air leakage and for doing leak checks.

Sample Tank - Rigid vessel at least 4 liters in volume with on/off valve or sealing quick connect. Should be stainless steel or aluminum in construction.

Purge Pump and Switching Valve - Capable of purging the probe and filter housing for 10 minutes at 60 to 100 cc/min.

Other equipment needed:

Mercury Manometer or absolute pressure gauge - Capable of measuring pressure to the nearest 1 mm Hg in the range of 0 - 900 mm Hg.

Vacuum Pump - Capable of evacuating a sample tank to within 10 mm Hg of absolute zero pressure.

Table D-1 is a checklist for sampling equipment specifications and calibration which may be completed or used as a guide by the observer. Table D-2 is sampling operations checklist which may be completed or used as a guide by the observer.

TABLE D-1. METHOD 25 EQUIPMENT CHECKLIST

Observer complete once for each test series.
Check if acceptable; "X" if not acceptable.

Probe
- Capable of maintaining 269°F ±5°F _____
- Movable nozzle at tip to turn away from flow _____
- Theromcouple well at probe exit _____
- Last thermocouple calibration date _____
- T/C reading @ ambient _____ Reference temp ____ Dev ____

Filter
- Housing capable of keeping filter @ 250°F ±5°F _____
- Thermocouple well in filter housing _____
- Last thermocouple calibration date _____
- T/C reading @ ambient _____ Reference temp _____ Dev _____

Purge Sample Valve
- Three positions: Sample _____ Purge _____ Neutral _____
- Located between filter and condensate trap _____

Condensate Trap
- Stainless steel and inconel construction _____
- Capable of sealing ends after sampling _____
- Quartz wool packing instead of porasil or S/S shot _____
- Each has unique identification code _____

Rotameter
- Last calibration date _____
- Gamma _____ gamma between 0.9 and 1.1 _____

Sample Tank
- Rigid construction _____
- Greater than or equal to 4.5 liter capacity _____
- On/off valve or quick connect _____
- Unique identification code _____

Purge Pump
- Capable of purging probe and filter (60 - 100 cc/min) _____

Vacuum Gauge -
- 0 to 30 in Hg vacuum to measure sample tank vacuum _____

Mercury Manometer or Pressure Gauge -
- 1 mm Hg graduations capable of 0-900 mm Hg absolute _____

Sample Train Volume Calibrated _____
Each Sample Tank Volume Calibrated ± 5 cc. _____

TABLE D-2. METHOD 25 SAMPLING CHECKLIST

Observer complete for each test run.
Check if Acceptable "X" if not acceptable.

Sample Tank Leak Check

Pretest Temp (T_i) _____ Pressure (P_i) _____
Post-test Temp (T_f) _____ Pressure (P_f) _____

Post-test Pressure Adjusted for Temperature Change (P_a)
$P_a = P_i * T_f/T_i$ P≈ absolute pressure T≈ °K or °R

P_a = _____ * _____/ _____

Is P_a acceptable (± 5 mm Hg of pretest) _____

Sample Train Leak Check

Sample Flow Rate (F cc/min)_____ Bar. Press (P_b mm Hg) _____
Leak Check Time (t min) _____ Train's Volume (V_t cc) _____

Allowable Leak Rate
delta P = .01 * F * t / V_t
delta P = .01 * _____ * _____/ _____ = _____ mm Hg

Actual delta P _____ Is Actual less than allowable ? _____

Sample point at average stack delta P _____
System Purge by sample pump with stack gas 10 minutes _____

Start of Sampling

Smooth start concurrent with timer _____
Desired sample flow rate achieved quickly _____
Flow rate maintained at ± 10% of mean _____
Probe exit temperature maintained at 269°F ±5°F _____
Filter temperature maintained at 250°F ±5°F _____
Condensate trap labelled with run # etc. _____
Sample tank labelled with run #, etc. _____

Data Sheet Review

Company Name _____ Source ID _____
Run Number _____ Date _____
Condensate Trap ID _____ Sample Tank ID _____
Sample Tank: final press. _____, final temperature _____
Sample Tank Pressurization - press. _____ Temperature _____

Dry ice available for sample transport to lab _____
Chain of custody sheet filled out for condensate trap and sample tank _____

D.2 SPECIFICATIONS FOR METHOD 25 ANALYTICAL EQUIPMENT

Gas chromatograph - Equipped with a sample switching valve and flame ionization detector.

Oxidation Catalyst - Catalytic oxidizer with 19 percent chromia catalyst on alumina pellets. Must be able to heat the catalyst to 650°C.

Reduction Catalyst - 100 mesh pure nickel powder mounted in a tube furnace capable of reaching 400°C.

Trap Oven - Specifically built to hold one condensate trap. Capable of maintaining 200°C for the trap burn and 300°C for conditioning traps for reuse after analysis.

NDIR analyzer - 0 to 5 percent range for monitoring trap burn progress.

Intermediate Collection Vessels (ICV's) - Should be greater in volume than sample tank. Should have volume calibrated to ±5 cc.

Hg manometer - Scaled to 1 mm Hg for reading the tank evacuation and pressurization parameters of the ICV's.

D.3 METHOD 25 NOMENCLATURE AND EQUATIONS

The following nomenclature is used in the calculations:

C = TGNMO concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cb} = Calculated condensible organic (condensate trap) blank concentration of the sampling equipment, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO2.
C_{cmb} = Measured blank concentration (NMO analyzer) for the condensate trap ICV, ppm CO2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tb} = Calculated noncondensible organic blank concentration (sample tank) of the sampling equipment, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
C_{tm} = Measured blank concentration (NMO analyzer) for the sample tank, ppm NMO.

F = Sampling flow rate, cc/min.
L = Volume of liquid injected, ul.
M = Molecular weight of the liquid injected, g/g-mole.
m_c = TGNMO mass concentration of the effluent, mg C/dsm3.
N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_b = Barometric pressure, cm Hg.
P_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m^3.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m^3.
V_s = Gas volume sampled, dsm^3.
n = Number of data points.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 ... q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 ... r).
x_i = Individual measurements.
$\bar{x}$ = Mean value.
ρ = Density of liquid injected, g/cc.
Θ = Leak check period, min.
ΔP = Allowable pressure change, cm Hg.

The following are the equations used to calculate the concentration of TGNMO, the allowable limit for the pretest leak check, and to assess the efficiency of the condensate recovery system.

Allowable Pressure Change - Calculate the allowable pressure change, in cm Hg, for the pretest leak check using the following equation. This value is then compared to the actual pressure change, in cm Hg, to determine if the train is suitable for sampling.

$$\Delta P = 0.01 \frac{(F)(P_b)}{V_t}$$ Equation D-1

Sample Volume - For each test run, calculate the gas volume sampled using the following equation.

$$V_s = 0.3857\ V \left[\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right] \qquad \text{Equation D-2}$$

Noncondensible Organics Concentration - For each sample tank, determine the concentration of nonmethane organics, in ppm C, using Equation D-3.

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tmj} \right] \qquad \text{Equation D-3}$$

Noncondensible Organics Blank Concentration - For blank sample tank, determine the concentration of nonmethane organics, in ppm C, using Equation D-3 and the values for C_{tmb}. The blank value may not exceed 5 ppm. If the blank value exceeds 5 ppm C, then the value of 5 ppm C may be used as the blank value. The calculated blank value is C_b^t.

Condensible Organics Concentration - For each condensate trap, determine the concentration of organics, in ppm C, using Equation D-4.

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cmk} \right] \qquad \text{Equation D-4}$$

Condensible Organics Concentration - For each condensate trap, determine the concentration of organics, in ppm C, using Equation 6-4 and the values for C_{cmb}. The blank value, C_{cmb}, may not exceed 15 ppm. If the blank value exceeds 15 ppm C, then the value of 15 ppm C may be used as the blank value. The calculated blank value is C_{cb}.

TGNMO Concentration - To determine the TGNMO concentration for each test run, use Equation D-5.

$$C = C_t - C_{tb} + C_c - C_{cb} - C_{cmb} \qquad \text{Equation D-5}$$

TGNMO Mass Concentration - To determine the TGNMO mass concentration as carbon for each test run, use Equation D-6.

$$m_c = 0.4993\ C \qquad \text{Equation D-6}$$

Percent Recovery - Calculate the percent recovery for the liquid organic injections used to assess the efficiency of the condensate recovery and conditioning system using Equation D-7. The average recovery for triplicate injections should fall within 10 percent (90 to 110 percent of the injected amount).

$$\textit{Percent Recovery} = 1.604\ \frac{M}{L}\ x\ \frac{V_v}{\rho}\ x\ \frac{P_f}{T_f}\ x\ \frac{C_{cm}}{N} \qquad \text{Equation D-7}$$

Relative Standard Deviation - Calculate the relative standard deviation (RSD) for the percent recoveries for triplicate injections of liquid organics using Equation D-8. The RSD should be less than 5% for each set of triplicate analyses.

$$RSD = \frac{100}{x}\ x\ \sqrt{\frac{\Sigma\ (x_i - x)^2}{n - 1}} \qquad \text{Equation D-8}$$

It is recommended that a computer program or spreadsheet software be used to handle all calculations. The output of the computer program provided by the tester in the emission test report should be in a standardized form containing all of the information listed in Figure D.1. A copy of the program used for calculations should be included with the test results.

FIELD DATA AND RESULTS TABULATION

Plant: _____ Sampling Location: _____

	Run 1	Run 2	Run 3	Blank	Audit 1	Audit 2
Date						
Run Start Time						
Run Finish Time						
Field Data						
Sample Trap I.D.						
Sample Tank I.D.						
Sample Tank Volume, V (m^3)						
Actual Volume Sampled, V_s (dsm^{3*})						
Field Initial Barometric Pressure, P_b (cm Hg)						
Field Final Barometric Pressure (cm Hg)						
Field Initial Gauge Pressure of Tank, P_{gi} (mm Hg absolute)						
Field Final Gauge Pressure of Tank, P_t (mm Hg absolute)						
Field Initial Temperature of Tank, T_{gi} (°K)						
Field Final Temperature of Tank, T_t (°K)						
Laboratory Data						
Final Tank Pressure, P_{tf} (mm Hg absolute)						
Final Tank Temperature, T_{tf} (°K)						
Noncondensible (tank) Portion - Injection #1 (area units)						
Noncondensible (tank) Portion - Injection #2 (area units)						
Noncondensible (tank) Portion - Injection #3 (area units)						
Instrument Blank (area units)						
NMO Response Factor (area units/ppm C)						

*68°F -- 29.92 in. Hg (760 mm Hg)

Figure D.1. Recommended standard format for reporting Method 25 data and results.

	Run 1	Run 2	Run 3	Blank	Audit 1	Audit 2
Laboratory Data (Continued)						
Volume of ICV, V_v (m^3)						
Final ICV Pressure, P_f (mm Hg absolute)						
Final ICV Temperature, T_f (°K)						
Condensible (trap) Portion - Injection #1 (area units)						
Condensible (trap) Portion - Injection #2 (area units)						
Condensible (trap) Portion - Injection #3 (area units)						
Instrument Blank (area units)						
NMO Response Factor (area units/ppm C)						
Results						
Measured Concentration for Sample Tank, C_{tm} (ppm NMO)						
Measured Concentration for Condensate Trap, C_{cm} (ppm CO_2)						
Noncondensible Organic Concentration (tank), C_t (ppm C)						
Condensible Organic Concentration (trap), C_c (ppm C)						
TGNMO Concentration, C (ppm C)						
Flue Gas Flow Rate (dsm^3/h)**						
Emission Rate (mg/h)						

**From EPA Method __ testing.

Figure D.1. (Concluded).

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
340/1-91-008		

4. TITLE AND SUBTITLE	5. REPORT DATE
MANUAL FOR COORDINATION OF VOC EMISSIONS TESTING USING EPA METHODS 18, 21, 25, AND 25A	Final Report: Sept. 1991
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Bill DeWees, Steve Eckard, Cheryl Davis-Eckard	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Entropy Environmentalists, Inc. Research Triangle Park North Carolina, 27709	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. Contract No. 68-02-4462 Work Assignment No. 90-117
12. SPONSORING AGENCY NAME AND ADDRESS Stationary Source Compliance Division Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Washington, DC 20460	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
EPA Technical Contact: Vishnu Katari (703) 308-8717, FTS: 382-8717

16. ABSTRACT

This manual deals with observation of compliance testing for volatile organic compounds. A volatile organic compound (VOC) is defined in 40 CFR Subpart A, General Provisions, 60.2, as any organic compound which participates in atmospheric photochemical reactions or which is measured by a reference method, an equivalent method, or an alternative method; or which is determined by procedures specified under any subpart. The purpose of this report is to provide the observer with procedures to (1) identify the data necessary to determine compliance, (2) oversee the compliance test, and (3) review the compliance test report written by the testing team. A detailed overview of the methods have been provided for the more experienced observer. Chapter 2 of this report provides the observer with procedures and references for establishing the test objectives. Chapter 3 discusses the pretest survey and the procedures for observing the compliance test. Chapters 4, 5, 6, and 7 present sampling and analysis observation procedures for Methods 18, 21, 25, and 25A, respectively. Chapter 8 presents review procedures for the compliance test report submitted by the facility.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE