METHOD 0040

SAMPLING OF PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS FROM COMBUSTION SOURCES USING TEDLAR® BAGS

1.0 SCOPE AND APPLICATION

1.1 This method establishes standardized test conditions and sample handling procedures for the collection of volatile organic compounds collected from effluent gas samples from stationary sources, such as hazardous waste incinerators and other combustion sources, using time-integrated evacuated Tedlar® bags. As indicated, the first group of compounds listed below have met Method 301 (Ref. 6) acceptance criteria in a field method evaluation study. The second group of compounds did not meet Method 301 criteria, and the third group of compounds have been identified as candidate analytes from the literature but have not been tested. This is a sample collection method and does not directly address the analysis of these samples. Gas chromatography/mass spectrometry (GC/MS) (Method 8260) is the recommended analytical technique because of its ability to provide positive identification of compounds in complex mixtures such as stack gas.

Compound	CAS Registry No.
Compounds that Met Method 301 Acceptance Criteria in a Field Method Evaluation	
1,1,1-Trichloroethane	71-55-6
Trichloroethene	79-01-6
1,1-Dichloroethane	75-34-3
1,1-Dichloroethene	75-35-4
2,2,4-Trimethylpentane	540-84-1
Allyl chloride	107-05-1
Benzene	71-43-2
Carbon tetrachloride	56-23-5
Methyl chloride	74-87-3
n-Hexane	110-54-3
Methylene chloride	75-09-2
Toluene	108-88-3
Trichlorofluoromethane	353-54-8
Vinyl bromide	593-60-2
Vinyl chloride	75-01-4
Compounds that Did Not Meet Method 301 Acceptance Criteria in a Field Method Evaluation	
Methyl bromide	74-83-9
1,3-Butadiene	106-99-0
Dichlorodifluoromethane	75-71-8
Appropriate Candidate Compounds Not Tested in the Field	
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2
1,1,2-Trichlorotrifluoroethane	76-13-1
Chloroform	67-66-3
1,2-Dichloropropane	78-87-5
Tetrachloroethene	127-18-4

1.2 This method is not applicable to the collection of samples in areas where there is an explosion hazard. Substitution of intrinsically safe equipment or procedures for the equipment or procedures described in this method will not be sufficient to adapt this method for use in areas where there is an explosion hazard. Additional modifications to the sampling and analytical protocols may be required.

1.3 This method does not employ isokinetic sampling and therefore is not applicable to the collection of highly water soluble volatile organic compounds contained in an aerosol of water. This method uses either a constant or proportional rate sampling, depending upon the extent of the variability of the emission flow rate.

1.4 This method is restricted to use by, or under the close supervision of, trained analytical personnel experienced in sampling organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Each compound for which this method can be considered shall meet the criteria listed in Secs. 1.5.1 - 1.5.3, below. Table 1 provides boiling points, condensation points (calculated from vapor pressure) at 20°C (72°F), and estimated instrument detection limits for compounds for which applicability of the method has been demonstrated. This method is not limited to the compounds in the target analyte list, however, stability and recovery shall be demonstrated when compounds other than those listed in Sec. 1.1 are to be sampled.

1.5.1 The compound must have a boiling point < 121°C.

1.5.2 The compound must have a concentration in the stack gas below the condensation point.

1.5.3 During validation studies, the loss of the compound from a Tedlar® bag must be less than 20% over a 72-hour storage time at temperatures above 0°C.

1.5.4 This method is not applicable to sources that are under vacuum. Under conditions of sufficiently high positive pressure, it may be possible to force sample gas into the Tedlar® bag causing the gas volume in the bag to be biased high versus the actual meter reading.

2.0 SUMMARY OF METHOD

2.1 A representative sample is drawn from a source through a heated sample probe and filter.

2.2 The sample then passes through a heated 3-way valve and into a condenser where the moisture and condensable components are removed from the gas stream and collected in a trap.

2.3 The sample is collected in a Tedlar® bag held in a rigid, air-tight opaque container.

2.4 The dry gas sample and the corresponding condensate are then transported together to a GC/MS. A mass spectrometer is most suited for the analysis and quantitation of complex mixtures of volatile organic compounds. The total amount of the analyte in the sample is determined by summing the individual amounts in the bag and condensate. A flow chart of the procedure is given at the end of this method.

3.0 INTERFERENCES

3.1 The materials from which the Tedlar® bag is constructed may contribute background hydrocarbon contamination. Purging the bag with air or N_2 may reduce the concentration of these hydrocarbons. Exposure of the bag to direct sunlight may increase the concentration of these hydrocarbons. Therefore, the bag must be protected from exposure to sunlight by using an opaque container to house the bag during sampling and shipping.

3.2 Components of the source emissions other than the target compounds may interfere. Interferents may be differentiated from the target compounds during mass spectrometric analysis.

3.3 Common problems that can invalidate Tedlar® bag sampling data and techniques to remedy these problems are listed in Table 2.

3.4 Available stability data suggest that this method may not perform well in sampling streams containing polar and reactive compounds like methyl ethyl ketone, formaldehyde, methanol, 1-butene, and acetone. The use of this method to sample these compounds needs to be evaluated before sampling.

4.0 APPARATUS AND MATERIALS

4.1 Tedlar® bag sampling train - A detailed schematic of the principal components of the sampling train is shown in Figure 1.

4.1.1 The sampling train (Figure 1) consists of a glass-lined probe, a heated glass or Teflon® filter holder and quartz filter attached to one of two inlets of a glass and Teflon® 3-way isolation valve (Figures 2 and 3). The purge line is connected to a charcoal trap and a silica gel trap, which filters incoming air. The outlet of the isolation valve is connected to a glass, water-cooled coil-type condenser and a glass condensate trap for removal and collection of condensable liquids present in the gas stream. A 1/4-in. OD x 1/8-in. ID Teflon® transfer line connects the condensate trap to a second 3-way isolation valve and the isolation valve to a Tedlar® bag contained in a rigid, air-tight container for sampling, storage, and shipping. The bag container is connected to a control console with 1/4-in. OD x 1/8-in. ID vacuum line by means of 1/4-in. Teflon® connectors at each end. A silica gel trap is placed in the vacuum line between the bag container and the control console to protect the console from moisture during sampling.

4.1.2 The vacuum required to operate this system is provided by a leak-free diaphragm pump contained in the control console (Figure 4). When the pump is turned on, the space between the inner walls of the bag container and the Tedlar® bag is evacuated, placing the system under negative pressure, which pulls the sample through the sampling train and into the Tedlar® bag. The sampling train vacuum is monitored with a vacuum gauge installed in-line between the vacuum line and the coarse adjustment valve mounted in the control console.

4.1.3 Sample flow rate is regulated by adjusting the coarse and fine valves on the control console. The coarse adjustment valve controls the sample inlet volume and rate and isolates the vacuum line, vacuum gauge, and sample train from the pump and other console components during leak checks. Sample volume is monitored by a rotameter, contained in the control console and installed on the outlet side of the dry gas meter.

4.1.4 The source, probe, filter, and condenser temperatures are monitored by Type J or K thermocouples using the temperature readout in the control console. Probe heater temperature is regulated by the temperature controller provided in the control console.

4.1.5 The velocity pressure and temperature of the source gases are measured using a standard or S-type pitot tube connected to a manometer with 1/4-in. OD x 1/8-in. ID tubing, in accordance with Method 2 (see Ref. 9). The source velocity pressure and temperature must be monitored during sampling and the sampling rate adjusted proportionally to changes in the flue gas velocity (Sec. 7.5.2.1).

4.2 Sample train components

4.2.1 Probe assembly - The probe assembly consists of a length of heated and insulated borosilicate glass tube inside a length of stainless steel tubing. The probe temperature shall be maintained between 130°C and 140°C (266°F and 284°F) in order to prevent damage to Teflon® lines and to facilitate efficient cooling of the gases in the condenser. The stainless steel sheath must be cooled with water when the source temperature approaches or exceeds 140°C (284°F).

4.2.2 Particulate filter - Particulate matter from the sample gas stream exiting the probe is collected on a quartz filter substrate in a heated 47-mm Teflon® or glass filter holder. Use clean filters in order to prevent sample contamination. The particulate matter itself is not analyzed or archived. However, removal of the particulate matter provides a cleaner sample for analysis. All connections between the probe and particulate filter shall be heated to maintain the temperature between 130°C and 140°C (266°F and 284°F) so that the compounds remain in the volatile phase. Heat-wrapped Teflon® unions with stainless steel nuts and Teflon® ferrules are recommended for all heated connections.

4.2.3 Isolation valves - A typical isolation valve is shown in Figure 2. The isolation valves shall be constructed of Teflon® or glass with Teflon® stopcocks to provide gas-tight seals without the use of sealing greases. The probe and bag isolation valves are of identical design and materials and are therefore interchangeable. The probe isolation valve provides for the attachment of a charcoal or similar purge trap to allow filtered ambient air to enter the train when returning the train to ambient pressure after leak checks. This valve directly connects the probe and filter assembly to the condenser inlet and must be heated to between 130°C and 140°C (266°F and 284°F). The bag isolation valve allows the bag to be opened for sampling or evacuation and isolated and sealed for leak checks or system purges.

4.2.4 Condenser - Use a jacketed, water-cooled, coil-type glass condenser with a jacket volume of at least 125 mL. The condenser shall have sufficient capacity to maintain the temperature of the sample gas stream between 20°C and 4°C (68°F and 39.2°F) to ensure proper removal and collection of condensable moisture in the effluent gas stream. The cooled sample gas stream temperature should not exceed the coldest temperature to be encountered during sampling, transport and storage prior to analysis. All condenser connections must form a leak-free, vacuum-tight seal without using sealing greases. Stainless steel fittings are not permitted, and Teflon® unions or washers with screw caps are recommended.

4.2.5 Condensate trap - A glass Erlenmeyer distilling flask with threaded screw cap connections, Teflon® seals, and a minimum volume of 125 mL may be used to collect condensate. All connections on the condenser and trap shall be sized to accept 1/4-in. OD x 1/8-in. ID Teflon® or glass fittings. The stem from the condenser must be positioned to within 0.5-in from the bottom of the condensate trap.

4.2.6 Sample transfer lines and connection fittings - All sample transfer lines connecting components shall be less than 5 ft long and constructed of 1/4-in. OD x 1/8-in. ID Teflon® tubing or glass. All sample lines upstream of the condenser and condensate trap must be heated and the temperature maintained between 130°C and 140°C (266°F and 284°F). Use Teflon® fittings for connections between various train components to provide leak-free, vacuum-tight connections without the use of sealing greases. New tubing, which has been cleaned according to Sec. 6.1.2, should be used for each separate test series to prevent cross contamination. Care should be used in the application of excessive heat to Teflon® fittings in order to avoid damage and subsequent failure.

4.2.7 Tedlar® storage bag - Choose a bag size according to the guidelines provided in Sec. 7.2.4. In order to minimize wall effects, the sample volume must fill at least 80% of the bag capacity. The recommended size range for bags is 25 L to 35 L. Small bags (< 25 L) are easier to store and transport but may have insufficient volume for proportional sampling. In addition, accurate volumetric measurement is difficult with smaller bags. Large bags (> 50 L) lack portability, but may be required under certain conditions, such as during proportional sampling and for sampling sources requiring high sample rates.

4.2.8 Evacuated container (bag container) - Use any rigid, air-tight metal or plastic (e.g., PVC®/Polyethylene®/Nalgene®) drums to house the Tedlar® bag during sampling, storage, and transport. The container must be constructed so that it can easily be assembled and disassembled (for bag removal). The container must be able to hold a negative pressure of at least 10 in. H_2O. The bag container must be at least 20% smaller than the Tedlar® bag being used but must be large enough to hold the volume of sample required (e.g., for a sample size of 20 L, a 25-L Tedlar® bag inside a 20-L container provides sufficient volume without danger of overinflating the bag).

Containers must not have staples, sharp edges, or metal closures which might damage bags. The container should also be constructed of a material that shields the sample from exposure to sunlight to protect the bag and its contents from ultra-violet light. A viewing port or other means of observing the flexible bag during sampling is desirable. During storage and transport, the viewing port shall be covered with opaque material.

4.2.9 Vacuum lines - Use Tygon®, Poly®, Nylon®, or similar tubing capable of maintaining at least 10-in. H_2O negative pressure without collapse as vacuum lines. Tubing should be 1/4-in. OD x 1/8 in. ID size to minimize volume and ensure compatibility of connection fittings throughout the train. Stainless steel fittings and valves may be used for vacuum line connections but may not be used in the sampling line.

4.2.10 Control console (meter system) - The metering system required for this method is readily available in the form of the control console/meter box from a Volatile Organic Sampling Train (VOST, Method 0030), and shall consist of the components pictured in Figure 4.

4.2.10.1 Vacuum gauge (meter pressure) - Use a direct reading, mechanical vacuum gauge capable of measuring a vacuum of at least 15 in. Hg with 1-in. or smaller increments to monitor the system vacuum during sampling and leak checking the bag, the container, and the sampling train.

4.2.10.2 Sample flow rate adjustment valves - Coarse and fine adjustment valves are provided. The coarse adjustment valve controls volume and rate of sample flow and isolates the control console from the sampling train and vacuum line during leak checks. The fine adjustment valve controls sample rate and system vacuum. Closing the valve increases train vacuum and sample flow rate. Opening the valve decreases train vacuum and sample flow rate.

4.2.10.3 Pump - Use a leak-free diaphragm pump or equivalent that is capable of pulling and maintaining a vacuum of at least 15 in. Hg and a flow rate of at least 1 liter per minute (Lpm).

4.2.10.4 Calibrated dry gas meter - The control console contains a calibrated dry gas meter capable of reading 1 L per revolution with 0.1-L increments, and provides accurate measurement of the volume of the sample collected.

4.2.10.5 Flow meter - Use a rotameter with a glass tube and a glass, Teflon®, or sapphire float ball of suitable range to measure the sample flow rate. A range of ± 25% of the desired sampling rate is suggested to ensure greater accuracy of readings and a better range for adjustment of the sampling rate (proportional to the source gas stream velocity). The flow meter shall be accurate to within 5% over the selected range. The rotameter is installed at the outlet of the dry gas meter in the console.

4.2.10.6 Thermocouples and temperature read-out device - Use a sufficient number and length of Type J or K thermocouples. A multi-channel digital thermocouple read-out should be provided in the control console to display the source, probe, filter, condenser, and dry gas meter temperatures.

4.2.10.7 Heat controller - Use a rheostat or digital temperature controller (e.g., Fuji PYZ4 or equivalent) to regulate probe heat temperatures.

4.2.11 Pitot tube probe - A standard or S-type pitot tube must be used for pretest and post-test velocity traverses and to monitor flow so that the sampling rate can be regulated proportionally to the source gas velocity throughout the length of the sampling run.

4.2.12 Pressure gauge (manometer) - Use a water- or oil-filled U-tube or inclined manometer capable of measuring to at least 10 in. H_2O and accurate to within 0.1 in. H_2O for monitoring and measuring the source gas velocity.

4.2.13 Barometer - Use an aneroid or other barometer capable of measuring atmospheric pressure to within 0.1 in. Hg of actual barometric pressure.

4.2.14 Charcoal and silica gel absorbent traps - Use charcoal traps to absorb organic compounds in the atmosphere at the site and an indicating silica gel trap to absorb water. One charcoal trap is attached to the probe isolation valve and filters incoming air when releasing vacuum to prevent contamination of the train during leak checks. Any readily available, ready-made charcoal tube similar to a VOST tube may be used. The silica gel trap is used in the vacuum line to protect the pump from water.

4.2.15 Stopwatch - Use any stopwatch capable of measuring 1 second, to time sample collection.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Water - Water used for sample train preparation shall be distilled and deionized. Water used for rinses during recovery of condensate shall be prepurged high performance liquid chromatography (HPLC)-grade. Clean, clear tap water may be used as condenser cooling water.

5.3 Nitric acid, HNO_3 (10%) - reagent grade.

5.4 Charcoal - SKC petroleum-based charcoal, or equivalent. A mesh size of 6-14 is recommended. New or reused charcoal may be used for each run series or test condition. Reused charcoal must be reconditioned using the same criteria specified in VOST (Method 0030).

5.5 Silica gel - Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

5.6 Methanol - Spectrometric-grade, or equivalent.

5.7 Field spiking standards - Appropriate gas cylinders containing the target components of interest in known concentrations (highest purity available) for field spiking.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Pretest preparation

6.1.1 Glassware - Before sampling, prepare the glass components of the train by cleaning with non-ionic detergent (e.g., Alconox) and hot water in an ultrasonic bath. Rinse each component three times with distilled, deionized water, then rinse three times with 10% HNO_3, followed by an additional three rinses with distilled, deionized water. Dry in an oven at 130°C (266°F) for 2 hours.

6.1.2 Sample lines and rigid containers - Treat all Teflon® lines, fittings, and the sample bag containers as outlined in Sec. 6.1.1, but air dry these components in an area free of organic compounds rather than in an oven. Use clean Teflon® tubing for each test series or condition. Hand wash the rigid containers.

6.1.3 Bag cleaning procedure - Ensure that all bags are clean before using them for sampling. First, flush each bag three times with high-purity nitrogen (N_2; 99.998%). Then fill each bag with N_2 and analyze the bag contents at the highest sensitivity setting using the same analytical technique that will be used for analyzing samples. Before constructing the calibration curve, analyze one analytical system blank each day by taking the gas chromatograph through its analytical program with no sample injection. Analyze an analytical system blank again if carryover between samples is indicated. Other, less stringent, methods of cleaning and analysis may be used at the risk of overlooking important contaminants. An acceptable level of contamination will be a response less than five times the instrument detection limit or half of the level of concern, whichever is less. Repeat the nitrogen flush as necessary until the acceptable level has been reached. No bag shall be used until it has been satisfactorily cleaned.

6.2 Sample bag storage and transport procedures - To ensure sampling integrity, perform sample recovery in a manner that prevents contamination of the bag sample. Protect the bag from sharp objects, direct sunlight and low ambient temperatures (below 0°C [32°F]) that could cause condensation of any of the analytes. Store the bags in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Analyze the bag samples within 72 hours of sample collection unless it can be shown that significant (> 20%) sample degradation does not occur over a longer period of sample storage. Upon completion of the testing and sample recovery, check all the data forms for completeness and the sample bags for proper identification. Store the bags in rigid, opaque containers during all sampling, storage and transport procedures. Ship the bags using ground transportation. Follow all hazardous materials shipping procedures.

6.3 Condensate storage and transport procedures - To ensure sample integrity, perform sample recovery in a manner that prevents the contamination of the condensate (Sec. 7.6.5). Store the condensate in 40-mL vials with no headspace. Place the vials in ice or in a refrigerated container at 4°C (± 2°C) [39.2°F (±7.2°F)] immediately following recovery and during transport for analysis. In addition, store the vials in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Upon completion of the testing and sample recovery, check all the data forms for completeness and the condensate samples for proper identification. Follow all hazardous materials shipping procedures.

6.4 The time lapse between sampling and analysis shall not exceed 72 hours unless it can be justified by specific sample matrix stability data that meet the criteria of Sec. 1.5.3. Stability in a Tedlar® bag shall be demonstrated by spiking analytes into inert gas in the laboratory and into stack gas in the field. The spiking level must be at least at the level found in the samples of the emissions matrix obtained during the pre-site survey. Compound recovery in both laboratory and field studies must be $\geq$ 80% after 72 hours for consideration of applicability.

7.0 PROCEDURE

The overall sampling procedure involves a pretest survey of the source to establish sampling parameters, a series of pretest checks of the sampling system and the source conditions, and the actual sample collection. These steps are described in Secs. 7.1 - 7.5. Following the actual sample collection step, sampling data are recorded and a post-test leak check is performed (Sec. 7.6). As noted in Sec. 1.0, this method does not include sample analysis procedures, but general guidelines for sample analysis are given in Sec. 7.7. Sec. 7.8 provides an extensive set of calculations associated with the sample collection and analysis procedures.

7.1 Pretest survey

7.1.1 Perform a pretest survey for each source to be tested. The purpose of the survey is to obtain source information to select the appropriate sampling and analysis parameters for that source. Potential interferences may be detected and resolved during the survey. When necessary information about the source cannot be obtained, collection and analysis of actual source samples may be required.

Use the pretest survey data form (Figure 5) to record information gathered during the pretest survey.

7.1.2 The following information must be collected during a survey before a test can be conducted. The information can be collected from literature surveys and source personnel, but an actual on-site inspection is recommended. A copy of the survey results must be forwarded to the staff performing the sample analyses.

7.1.2.1 Determine whether the sampling site is in a potentially explosive atmosphere. If the sample site is located in an explosive atmosphere, use other, intrinsically safe test methods. This method is never to be used in a potentially explosive atmosphere (Sec. 1.2).

7.1.2.2 Measure and record the stack dimensions. Select the sampling site and the gaseous sampling points according to Method 1 (Reference 9) or as specified by the regulatory personnel.

7.1.2.3 Determine the stack pressure, temperature, and the range of velocity pressures using Method 2 (Reference 9). A source with a negative pressure is not suitable for this method.

7.1.2.4 Determine the stack gas moisture content (Sec. 7.2.3) using Approximation Method 4 (Reference 9) or its alternatives. Perform the determination when process operations are as they will be during final sampling. If the process uses and emits ambient air, use a sling psychrometer to measure the moisture content of the ambient air in the area of process air uptake.

7.1.2.5 In accordance with Method 1, select a suitable probe liner and probe length as determined by the temperature and dimensions of the source. Determine the point within the stack that represents an average flow and temperature of the stack. Mark the probe at the determined distance to provide a reference point. For sample collection, insert the probe into the duct to the predetermined point to ensure proper probe placement and collection of a representative sample.

7.1.2.6 Determine whether the source has a constant or variable gas flow rate. The flow rate may be considered constant if the variation over the sampling period is no more than 20%. If the process is constant, use a constant sampling rate (Sec. 7.5.1). If the process is not constant, use proportional sampling (Sec. 7.5.2).

7.1.2.7 Determine approximate levels of target compounds by collecting a pretest bag sample for analysis. This information is needed to establish parameters for the analytical system.

7.1.2.8 Check the sampling site to ensure that adequate electrical service is available.

7.1.2.9 Follow all guidelines in the health and safety plan for the test. Use appropriate safety equipment as required by conditions at the sampling site (e.g., respirator, ear and eye protection, and a safety belt).

7.2 Pretest procedures

7.2.1 Assemble the train according to the diagram in Figure 1. Adjust the probe, filter, and valve heater controls to maintain a temperature between 130°C and 140°C (266°F and 284°F). Circulate cooling water from an ice bath to the condenser until the temperature is stabilized at or below 20°C (68°F). Allow the probe, filter, valve, and condenser temperatures to stabilize before sampling. Mark the probe, pitot tube, and thermocouple assembly with the proper sampling points as determined in accordance with Method 1. Before sampling, insert the pitot tube and thermocouple probe into the stack, to allow the thermocouple readings to stabilize.

7.2.2 Preliminary velocity and temperature traverse - While the probe, filter, valve, and condenser temperatures are stabilizing, perform a preliminary velocity/temperature traverse in accordance with Methods 1 and 2. Record the velocity (ΔP) and temperature (T, °C) at each point to determine a point of average flow and velocity and measure the static pressure at that point. Determine the average velocity head (ΔP_{avg}) and range of fluctuation.

7.2.3 Determination of moisture content - Determine the moisture content of the gas stream being sampled before (Sec. 7.1.2.4) or during actual sampling. For combustion of water controlled processes (wet electrostatic precipitators and scrubbers), obtain moisture content of the flue gas during test conditions from plant personnel or by direct measurement using Method 4.

7.2.4 Criteria for selection of sample volume and flow rate - The flow rate should fill the bag to at least 80% of its capacity during the sampling period. The following criteria should be met:

7.2.4.1 Minimum stack sampling time for each run should be 1 hr. Data from less than 1 hr of sample collection would be an invalid test run. Two hours of stack sampling time is recommended as optimal.

7.2.4.2 The minimum sample volume shall be at least 15 L.

7.2.4.3 The minimum sample flow rate shall be 250 mL/min.

7.2.4.4 Typically, the average sampling flow rate is about 0.5 L/min, which will collect approximately 30 L of sample per hour.

7.2.4.5 Mass emission rate determination - Determine whether the final result will be presented on a concentration or mass emission basis before sampling. If results will be presented on a concentration basis, only the concentrations of the target analytes and the stack gas moisture content need to be measured. If the mass emission rate of any compound is to be presented, the volumetric flow rate of the stack gas must also be determined. The volumetric flow rate may be determined by performing a temperature and velocity traverse in accordance with Methods 1 and 2, with actual sample collection.

7.3 Leak check procedures

7.3.1 Bag evacuation and bag leak check procedure - Before sampling, ensure that the Tedlar® bag is fully evacuated and leak free.

7.3.1.1 Assemble the sampling train as illustrated in Figure 1 and described in Sec. 4.1.1, ensuring that all connections are tight.

7.3.1.2 Disconnect the vacuum line from the bag container and attach this quick connect fitting to the quick connect fitting on the outlet of the bag isolation valve (Figure

1) and turn on the pump in the control console (Figure 1). Turn bag isolation valve to position 1(Figure 3) and turn on the pump in the control console (Figure 4).

7.3.1.3 Open the coarse adjustment valve and adjust the fine adjustment valve on the control console (Figure 4) until the vacuum gauge reads 5 in. Hg.

7.3.1.4 Observe the dry gas meter and rotameter on the control console as the bag is evacuated. The bag is completely evacuated when no flow is indicated on the dry gas meter and the vacuum rises to 5 in. Hg.

7.3.1.5 Allow the rotameter float ball to drop to zero. Time and record the leak rate using the following procedure.

7.3.1.5.1 Timed leak rate - Observe the leak rate indicated on the vacuum gauge and time for 1 min. The leak rate must be less than 0.1 in. Hg.

7.3.1.6 If all connections are found to be leak tight and the leak rate cannot meet the set criteria, discard the bag and test another clean bag.

7.3.1.7 Turn the bag isolation valve to position 3 (Figure 3) to seal the evacuated bag.

7.3.1.8 Turn off the pump.

7.3.2 Pretest leak check

7.3.2.1 Before sampling and immediately after evacuating and leak checking the bag, perform a pretest leak check of the sampling train.

7.3.2.2 Ensure that the bag isolation valve is in position 3 (Figure 3) and the end of the probe is sealed.

7.3.2.3 Turn the probe isolation valve to position 2 (Figure 3), turn the pump on, and open the coarse adjustment valve(Figure 4).

7.3.2.4 Allow the sampling train to evacuate and adjust the fine adjustment valve to increase the vacuum to 5 in. Hg.

7.3.2.5 When the rotameter drops to zero and the dry gas meter slows to a stop, time and record the leak rate following the procedure outlined in Sec. 7.3.1.5.

7.3.2.6 If the leak rate is greater than 0.1 in Hg/min, check all connections, valves, and the probe seal for tightness. Any leak found must be corrected and the leak check repeated before sample collection begins. It is suggested that new fittings and connections be used when the train is assembled. During the testing, replace as necessary.

7.3.2.7 After completing a satisfactory leak check, return the sampling train to ambient pressure by turning the probe isolation valve to position 3 and turning off the pump.

7.3.2.8 When the vacuum gauge drops to zero, immediately turn the probe isolation valve to position 1. Disconnect the vacuum line from the bag isolation exit quick connect fitting, then attach the vacuum line to the bag container to return the system to the initial state described in Sec. 4.1.1 (Figures 1 and 3).

7.3.3 Post-test leak check

7.3.3.1 A post-test leak check must be performed after each bag sample is collected, before changing the bag and container for the next sample.

7.3.3.2 Ensure that the bag isolation valve is in position 1 (Figure 3) and and the probe isolation valve is in position 1 and the pump is turned off when sample collection is completed.

7.3.3.3 Remove the probe from the stack and seal the end of the probe with a leak-tight seal. Check all connections and train components for looseness or breakage. Do not tighten any connections. Record any abnormal conditions.

7.3.3.4 Disconnect the vacuum line from the container and attach to the outlet of the big isolation valve. Turn the probe isolation valve to position 2. Turn on the pump and adjust the fine adjustment valve until the train vacuum reaches at least 1 in. Hg above the highest vacuum attained during sample collection. Time and record the leak rate as previously outlined in Sec. 7.3.1.5.

7.3.3.5 If the leak rate is less than 0.1 in. Hg/min., the sample is considered valid (Secs. 7.3.1.5.1).

7.3.3.6 Return the sample train to ambient pressure (Secs. 7.3.2.7 and 7.3.2.8) and disconnect the sample and vacuum lines from the bag and container to prepare the train for the next sample.

7.3.3.7 If the post-test leak check proves invalid, discard the invalid sample. Attach a new Tedlar® bag, evacuate and leak check the bag, and repeat the sample collection.

7.4 Preparation for sample collection

7.4.1 Perform the pretest leak checks outlined in Sec. 7.3.

7.4.2 Remove the seal from the end of the probe and insert the probe into the stack to the point of average velocity and temperature and constant flow.

7.4.3 Purge the sampling train (probe, valve, and filter assembly ONLY) using the following procedures.

7.4.3.1 Disconnect the vacuum line quick connect fitting from the rigid bag container (the quick connect fitting has a valve to seal the line).

7.4.3.2 Connect the purge line from the probe isolation valve tee to the vacuum line using the quick connect fittings (Figure 1).

7.4.3.3 Ensure that the probe isolation valve is in position 1 (Figure 3), and turn on the pump.

7.4.3.4 Draw at least eight times the sample volume of flue gas, or purge for at least 10 minutes, whichever is greater.

7.4.4 Adjust the sample flow rate to the desired setting and check all temperature and flow readings during the purge to ensure proper settings.

7.4.5 Purge the sampling train before and between the collection of each sample during the test run.

7.4.6 Label each bag/container and VOA vial clearly, uniquely, and consistently with its corresponding data form and run. Follow appropriate traceability requirements as defined by the regulatory personnel. Return the train to the initial configuration described in Section 4.1.1 (Figure 1) before collecting a sample. First, disconnect the vacuum line quick connect fitting from the purge line quick connect fitting, then reconnect the vacuum line quick connect fitting to the bag container.

7.5 Sample Collection

Start sample collection after the pretest leak check (Sec. 7.3.2) and the system purge (Sec. 7.4). Collect the sample using proportional rate sampling if the pretest survey measurements (Sec. 7.1.2.7) show that the emission flow rate varies by more than 20% over the sampling period. Otherwise, use constant rate sampling. Prepare for sample collection for either method by turning the probe isolation valve to position 2 for sampling and the bag isolation valve to position 2 while the pump is still running from the system purge.

If a viewing port has been incorporated in the bag container design, visually inspect the Tedlar® bag frequently during the sampling run to ensure that it is filling properly and that a sufficient sample volume is collected. This frequent inspection will also help prevent overfilling and bursting the bag during sampling. Use the field sampling data form (Figure 6) to record sample collection data.

7.5.1 Constant rate sampling

7.5.1.1 Place the end of the probe at a point within the duct determined to have the average velocity and temperature and a constant flow rate.

7.5.1.2 Record the start volume from the dry gas meter and begin timing the sample period.

7.5.1.3 Take flue gas velocity and temperature readings using either Method 2A for smaller ducts (< 24 inches) with a remote pitot tube and thermocouple or Method 2 for larger ducts (> 24 inches). Utilizing a sample probe with pitot tubes and thermocouples attached will generally ease sampling and will provide a direct means to monitor flue gas velocity and temperature at the sample probe inlet.

7.5.1.4 Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form.

7.5.1.5 Adjust the sample flow rate and sampling train heating systems to the correct levels, after every velocity and temperature reading. The tester must closely monitor the sample train and control console to ensure that the sample flow rate does not vary by more than 20% during any 5-minute period.

7.5.2 Proportional sampling

7.5.2.1 Position the probe in the center of the stack.

7.5.2.2 Record the start volume from the dry gas meter and begin timing the sample period.

7.5.2.3 Monitor the velocity head during sampling as described in Sec. 4.1.5 and maintain a constant proportion between the sample flow rate and the flow rate in the duct. The flow rate to be used during sampling (Sec. 7.2.2) is calculated using the proportional sample rate equation in Sec. 7.8.4. With this equation and the sample rate assigned to the average flow rate, the rotameter setting can be determined after each velocity reading and the sample rate set accordingly.

7.5.2.4 Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form.

7.5.3 Single-point sampling

Collect samples from a single point within the duct as described in Secs. 7.5.1.1 and 7.5.1.2, unless multipoint sampling has been determined necessary (Sec. 7.5.4).

7.5.4 Multipoint sampling

Perform multipoint integrated sampling only in a case where there is a possibility of effluent stratification. Stratification of gases is less likely than of particulates. If however, multipoint sampling is required, determine the necessary number of sample points in accordance with Methods 1 and 2.

7.6 Post-test procedures

7.6.1 Record the final volume from the dry gas meter at the end of each sample collection period.

7.6.2 Perform a post-test leak check as described in Sec. 7.3.3.

7.6.3 Inspect the field sampling data form and sample identification labels for accuracy and completeness.

7.6.4 Replace the particulate filter after each sample.

7.6.5 Condensate Recovery - The condensate collected during sampling must be recovered separately for each individual bag sample collected, using the following procedures.

7.6.5.1 Carefully remove the condensate trap, the condenser and the sample line (from the trap to the bag) from the sample train. Pour the contents of the condensate trap into a clean measuring cylinder.

7.6.5.2 Rinse the condenser, the condensate trap and the sample line three times with 10 mL of HPLC grade water and add the rinsings to the measuring cylinder containing the condensate. Record the final volume of the condensate and rinse mixture on the field sampling data form. High moisture sources (such as those with wet control devices) may require a 150-mL or 200-mL measuring cylinder while low moisture sources (such as some rotary kilns and pyrolytic incinerators) may require only a 100-mL size.

7.6.5.3 Pour the contents of the measuring cylinder into a 20- or 40-mL amber glass VOA vial with a Teflon® septum screw cap. Fill the vial until the liquid level rises above the top of the vial and cap tightly. The vial should contain zero void volume (i.e., no air bubbles). Discard any excess condensate into a separate container for storage and transport for proper disposal.

7.6.5.4 Label each vial by using wrap-around labels. Labels can be preprinted or can be filled out on site.

7.7 Analytical Approach

The following description provides general guidelines to the analytical approach rather than a comprehensive analytical approach. The primary analytical tool recommended for the measurement of volatile organic compounds in source emissions is GC/MS using fused-silica capillary GC columns such as described in Method 8260. Prescreening of the sample by gas chromatography with either flame ionization (GC/FID) or, for electronegative compounds, electron capture detection (GC/ECD) is recommended because it may not only be cost effective, but will also yield information regarding the complexity and concentration of the sample. If the smallest feasible injection loop saturates the analytical system, dilutions of the sample can be made into Tedlar® bags using pure N_2 (99.998%) as diluent. Calculate the concentration of the volatile organic compounds in the gaseous emissions by using the equations (13-17) in Sec. 7.8.

7.7.1 Analysis of gaseous components - Introduce the gases into the gas chromatograph through the use of a sample loop. Use a cryogenic trap if sample concentration before analysis if necessary.

For most purposes, electron ionization (EI) mass spectra will be collected because a majority of the volatile organic compounds give characteristic EI spectra. Also, EI spectra are compatible with the NIST Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions can be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. For descriptions of GC conditions, MS conditions, internal standard usage, and qualitative and quantitative identification, refer to Method 8260.

7.7.2 Analysis of condensates - Refer to Method 5030 to analyze condensate samples by using the purge and trap technique or by direct aqueous injection. Use direct solvent injection if an organic phase is present distinct from the aqueous phase. Use dilution as necessary to prevent saturation of the analytical system.

7.8 Calculations

7.8.1 Carry out all calculations for determining the concentrations and emission rates of the target compounds. Round off figures after final calculations to three significant figures.

7.8.2 Nomenclature

A = Stack/source cross sectional area, m^2 (ft^2)

A_B = Amount of volatile organic compound in bag (ng)

A_c = Amount of volatile organic compound in condensate (ng)

A_{vol} = Amount of volatile organic compound in analytical sample (ng)

A_T = Total amount of volatile organic compound (ng), $A_B + A_C$

B_{ws} = Water vapor in the gas stream, proportion by volume (x100=% H_2O)

C_P = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

$C_{Emission}$ = Concentration of volatile organic compound in emissions (ng/mL)

C_{vol} = Concentration of volatile organic compound per volume sampled (ng/mL)

C_{spike} = Concentration of spiking standard in the Tedlar® bag (ng/mL or µg/L)

C_{stock} = Concentration of spike standard in the stack/audit cylinder.

$DV_{eff(std)}$ = Volumetric flow rate of exhaust gas, m^3/min, ft^3/min.

K_p = Pitot tube constant,

$$34.97\,\text{m/sec}\left[\frac{\left(\frac{\text{g}}{\text{gmole}}\right)(\text{mmHg})}{(\text{K})(\text{mmH}_2\text{O})}\right]^{1/2}$$

$$85.49\,\text{ft/sec}\left[\frac{\left(\frac{\text{lb}}{\text{lbmole}}\right)(\text{inHg})}{(^{\text{O}}\text{R})(\text{inH}_2\text{O})}\right]^{1/2}$$

L_a = Maximum acceptable leakage rate for a leak check following a component change; less than or equal to 0.1 in. Hg.

LDL_{vol} = Lower detectable amount of volatile organic compound in entire sampling train.

L_i = Individual leakage rate observed during the leak check conducted before to the "ith" component change (i = 1, 2, 3...n), L/min.

L_p = Leakage rate observed during the post-test leak check,in. Hg/min.

Max $Mass_{vol}$ = Maximum allowable mass flow rate (g/hr [lb/hr]) of volatile organic compound emitted from the combustion source.

Max $Conc_{vol}$ = Maximum anticipated concentration of the volatile organic compound in the exhaust gas stream, g/m^3 (lb ft^3).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_{fd} = Dry mole fraction of the flue gas.

M_s = Wet molecular weight of the flue gas, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_g = Flue gas static pressure, mm H_2O (in. H_2O).

P_k = Specific gravity of mercury (13.6)

P_m = Dry gas meter pressure, inches H_2O

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

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

Q_m = Average sampling rate, L/min.

Q_s = Calculated sampling rate, L/min.

Q_{sd} = Volumetric air flow rate, (m^3/min, ft^3/min).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature, K (°R).

T_s = Absolute average stack gas temperature, K (°R).

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

V_A = Analytical sample volume (mL).

V_B = Bag volume (mL).

V_i = Concentration of volatile organic compound (wt %) introduced into the combustion process.

V_i conc = Anticipated concentration of the volatile organic compound in the exhaust gas stream, g/L (lb/ft^3).

V_{lc} = Total volume of liquid collected in the condensate knockout trap.

V_m = Volume of gas sample as measured by dry gas meter, L.

$V_{m(std)}$ = Volume of gas sample measured by dry gas meter, corrected to standard conditions, L.

V_{spike} = Volume of gaseous or liquid spiking standard (mL)

V_{TBC} = Minimum dry standard volume to be collected at dry gas meter.

V_T = Train sample volume (mL)

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, L (ft^3).

V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 4, m/sec (ft/sec).

WF = Mass flow rate of waste feed per hour, g/hr (lb/hr).

γ = Dry gas meter calibration factor, dimensionless.

ΔP = Actual velocity pressure, mm (in.) H_2O.

ΔP_{avg} = Average velocity pressure, mm (in.) H_2O.

ρw = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_i = Sampling time interval of each successive component change, beginning with the interval between the start of the run and the first component change, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

60 = Second/minute conversion.

100 = Conversion to percent.

7.8.3 Conversion factors

From	To	Multiply by
ft^3	L	0.02832

7.8.4 Proportional sample rate calculation. The flow rate to be used during sampling when the velocity head varies from the average is calculated using the following equation:

$$Q_s = Q_m \frac{\sqrt{\Delta P}}{\sqrt{\Delta P_{Avg}}} \tag{1}$$

7.8.5 Dry gas volume: Correct the sample measured by the dry gas meter to standard conditions (20°C, 760 mm Hg [68°C, 29.92 in. Hg]) by using the following equation:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + P_M/13.6}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + P_M/13.6}{T_m} \tag{2}$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or

K_1 = 17.64°R/in. Hg for English units.

Equation 2 can be used as written, unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted before component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 2 must be modified as follows (with the approval of the appropriate regulatory personnel):

7.8.5.1 Case I (no component change made during sampling run)

Replace V_m in Equation 2 with the expression:

$$V_m - \left[(L_p - L_a)\right] \theta \tag{3}$$

7.8.5.2 Case II (one or more component changes made during the sampling run)

Replace V_m in Equation 2 with the expression:

$$V_m - \left(\sum_{i=1}^{n} (L_i - L_a) \theta_1 \right) - (L_P - L_a) \theta_p \tag{4}$$

and substitute only for those leakage rates (L_i or L_p) that exceed L_a.

7.8.6 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 \; V_{1c} \tag{5}$$

where:

K_2 = 0.001333 m^3/mL for metric units, or

K_2 = 0.04707 ft^3/mL for English units.

7.8.7 Moisture content

$$B_{ws} = \frac{V_{w\ (std)}}{V_{m\ (std)} + V_{w\ (std)}} \tag{6}$$

7.8.8 Volumetric flow rate equations

7.8.8.1 Static pressure

$$P_s = P_{Bar} + \left(\frac{P_g}{P_k} \right) \tag{7}$$

7.8.8.2 Dry molecular weight

$$M_d = (\%\ CO_2\ x\ 0.44) + (\%\ O_2\ x\ 0.32) + [(\%\ CO + \%\ N_2)\ x\ 0.28] \tag{8}$$

7.8.8.3 Dry mole fraction

$$M_{fd} = 1 - B_{ws} \tag{9}$$

7.8.8.4 Wet molecular weight

$$M_s = (M_d\ x\ M_{fd}) + (18\ x\ B_{ws}) \tag{10}$$

7.8.8.5 Flue gas velocity

$$V_s = k_P \ C_P \ \left(\sqrt{\Delta P}\right)_{avg} \left(\frac{T_{s(avg)}s}{M_s P_s} \right)^{½} \qquad (11)$$

7.8.8.6 Volumetric flow rate

$$DV_{eff(std)} = 60 \ V_s \ M_{fd} \ A \left(\frac{T_{std}}{T_{s(avg)}} \right) \ x \left(\frac{P_s}{P_{std}} \right) \qquad (12)$$

7.8.9 Concentration of a volatile organic compound in the gaseous emissions of a combustion process.

7.8.9.1 Divide the amount of volatile organic compound determined through analysis by the volume of sample introduced into the analytical system to obtain concentration of the volatile organic compound in the bag or the condensate.

$$C_{vol} = \frac{A_{vol}}{V_A} \qquad (13)$$

7.8.9.2 Multiply the concentration of the volatile organic compound (ng/mL) by the sample volume (bag or condensate) to determine the amount of the volatile organic compound in the bag or condensate.

$$A_B = C_{vol} \ x \ V_B \qquad (14)$$

or

$$A_C = C_{vol} \ x \ V_{lc} \qquad (15)$$

7.8.9.3 Sum the amount of volatile organic compound found in all samples associated with a single train.

$$A_T = A_B + A_C \qquad (16)$$

The mass of each compound from the A fraction is added to that from the B fraction to obtain a train total before further calculation. If a measurable amount of the compound is found in one fraction, but the amount in the second fraction is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "nondetect" as zero if the detection limit is less than 10% of the total of the detected amount from the other fraction, but in cases where the detection limit in the second fraction is greater than 10% of the amount detected in the first fraction, then report the total as greater than the detected amount but less than the detected amount plus the second fraction detection limit.

7.8.9.4 Divide the total amount found by the volume of stack gas sampled to determine the concentration of the volatile organic compound in the gaseous emissions.

$$\frac{A_T}{V_T} = C_{Emission} \qquad (17)$$

7.8.10 Concentration of the spiking standard in the Tedlar® bag

$$C_{spike} = \frac{V_{spike} \ X \ C_{stock}}{V_B} \qquad (18)$$

7.8.11 Recovery of the spiking standard from the Tedlar® bag sample

$$\% \ Recovery = \frac{C_{vol}}{C_{spike}} \ X \ 100 \qquad (19)$$

8.0 QUALITY CONTROL

8.1 Quality assurance/quality control requirements before sampling

8.1.1 Pitot tube probe - Before sampling, assemble and calibrate the pitot tube probe (described in Sec. 4.2.11) in accordance with Method 2. Leak check above the static stack pressure. The pitot tube assembly must be leak free (0.00 in. H_2O in 1 minute).

8.1.2 Pressure gauge (manometer) - Calibrate the pressure gauge (described in Sec. 4.2.12) in accordance with Method 2. Leak check the pitot tubes, pressure gauge, and pitot tube lines simultaneously, as a unit, before the velocity traverse.

8.1.3 Thermocouple and temperature read-out device - Calibrate these devices (described in Sec. 4.2.10.6) within 30 days of sampling and in accordance with Method 2. The thermocouple and temperature read out must be accurate to ± 1°C.

8.1.4 Metering system - Calibrate the dry gas meter contained in the control console in accordance with the procedures outlined in Method 5. Calibrate the meter at a flow rate appropriate for the sampling rate used during the test.

8.1.5 Probe heater - Calibrate the probe heater before sample collection following procedures outlined in Method 5.

8.1.6 Barometer - Record the barometric pressure at the test site before each test. Alternatively, obtain the barometric pressure from a local weather service and correct it to the altitude of the test site if the reporting center is at a different altitude.

8.2 Blanks and field spikes

Field, trip and laboratory blanks, contamination checks and field spiked samples are required to monitor the performance of the sampling method and to provide the required information to take corrective action if problems are observed in the laboratory operations or in field sampling activities.

8.2.1 Field blanks - Take at least one field blank sample daily and per source. Collect high purity air or N_2 (99.998%) from a compressed gas cylinder in the same manner as source emissions. Draw the air or nitrogen gas through the sampling system and into the bag. Field blank samples shall consist of the condensate and a bag sample. Transport and analyze this blank sample along with the stack gas samples. When the field blank values are greater than 20% of the stack values, flag the data. Report the field blank values with the stack gas results. A condensate blank is prepared by filling a vial with HPLC-grade water. The condensate blank is transported and analyzed with the stack gas condensate samples. When the field condensate blank values are greater than 20% of the stack values, flag the data.

8.2.2 Trip blanks - Take at least two Tedlar® bags labeled “trip blanks” and filled with an inert gas to the sampling site. These bags will be treated like any other samples except that they will not be opened during storage at the site. These bags will be subsequently analyzed to monitor potential contamination which may occur during storage and shipment.

8.2.3 Laboratory blanks - Leave two Tedlar® bags labeled “laboratory blanks” in the laboratory using the method of storage that is used for the field samples. If the field and trip blanks contain high concentrations of contaminants (i.e., greater than five times the detection limit of particular analyte), the laboratory blank shall be analyzed to identify the source of contamination.

8.2.4 Tedlar® bag contamination checks - The use of new bags for each test series is recommended. All bags must be cleaned and checked for contamination before being used for sampling (Sec. 6.1.3).

8.2.5 Field spike samples - Take at least one field spike per 10 field samples, or a minimum of one field spike per test. Spike the chosen bag sample with a known mixture (gaseous or liquid) of isotopically labeled analogs of all the target pollutants using either gaseous or liquid injection into the bag. Transport and analyze the spiked sample with the stack gas samples. Report the spike sample recoveries with the source test results. The compound recoveries in the spiked sample must be 80 - 120%. Use Equation 19 in Sec. 7.8.11 to calculate spiking compound recovery.

The spiking concentration should be at least twice the concentration anticipated in the emissions matrix. Use Equation 18 in Sec. 7.8.10 to calculate the spiking concentration. The syringe volume for the gaseous injection should not exceed 200 mL to minimize leakage through the septum after injection. For liquid injections, the volume injected must not exceed 1 mL to ensure complete volatilization. The final volume of the spiked gas must not exceed 1% of the total sample volume. Use the ideal gas equation to calculate the volume of gas generated by a liquid injection into the bag.

8.2.5.1 Obtain spiking stock that is sufficiently concentrated to spike a Tedlar® sample without exceeding the 1% volume limit. Select appropriate analytes, analyte homologs, or isotopically labeled analogs in cylinders or SUMMA® canisters for gaseous injections or neat liquids or methanol solutions for liquid injections.

8.2.5.2 Install an injection port that consists of a Swagelok® tee fitting with a septum in the sample line just before the 1/4-in. Quick connector on the Tedlar® bag (Figure 1). Locate this port as close to the bag as possible to minimize wall effects. Use a new septum for each sampling run that involves spiking.

8.2.5.3 Perform a leak test as described in Sec. 7.3 with the injection port in line.

8.2.5.4 Start sampling the stack as described in Secs. 7.4 and 7.5.

8.2.5.5 In preparation for injection, clean the syringe by flushing three times with an inert gas (high purity N_2, 99.998%) for gaseous injections, or with methanol for liquid injections. Then flush the syringe three times with the gaseous or liquid spiking standard.

8.2.5.6 After half an hour of sample collection, take up the desired volume of the spiking standard into the syringe (for gases, allow the standard to equilibrate to atmospheric pressure) and inject it through the septum into the bag without interrupting the sampling procedure. All apparatus upstream of the bag should be under slight negative pressure.

8.3 An EPA performance audit shall be completed during a trial burn as a check on the entire Tedlar® bag sampling system. The audit results should agree within 50% to 150% of the expected value for each specific compound of interest. This audit consists of collecting a gas sample containing one or more volatile organic compounds in the Tedlar® bag sampling system from an EPA audit gas cylinder. Collection of the audit sample in the Tedlar® bag sampling system may be conducted either in the laboratory or at the field test site. Analysis of the Tedlar® bag audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular Tedlar® bag samples from the field test.

8.4 Evaluation of analytical procedures for a selected series of compounds shall include the sample preparation procedures and each associated analytical determination. Challenge the analytical procedures by spiking the test compounds at appropriate levels carried through the procedures.

8.5 Determine the overall method detection limits (lower and upper) on a compound-by-compound basis according to the 40 CFR Part 136b for the determination of the detection limit. Different compounds may exhibit different collection efficiencies as well as instrumental minimum detection limit.

8.6 During the sampling planning stage, determine whether each compound on the analyte list has been validated for this method at a similar source. For all compounds which have not, either plan to determine the method precision and bias by dynamic spiking ahead of the filter in accordance with Method 301 (Reference 6) or present a justification for not running Method 301 to appropriate regulatory personnel. The justification may be based on previous validation of one or more compounds very similar to those in question, or on other technical issues as appropriate.

9.0 METHOD PERFORMANCE

Method evaluation data are available from testing at a coal-fired power plant (Reference 10). Compounds which met method validation criteria are shown in Sec. 1; compounds which were tested and failed to meet method validation criteria are also shown in Sec. 1.

10.0 REFERENCES

1. Howe, G.B., B.A. Pate, and R.K.M. Jayanty, "Stability of Volatile Principal Organic Hazardous Constituents (POHCs) in Tedlar® Bags", Research Triangle Institute Report to the EPA, Contract No. 68-02-4550, 1991.

2. Andino, J.M., and J.W. Butler, "A Study of the Stability of Methanol-Fueled Vehicle Emissions in Tedlar® Bags", *Environ. Sci. Technol.* 1991, 25(9), 1644-1646.

3. Posner, J.C., and W.J. Woodfin, "Sampling with Gas Bags I: Loses of Analyte with Time", Appendix L Industrial Hygiene, 1986, (4), 163-168.

4. Seila, R.L., W.A. Lonneman, and S.A. Meeks, "Evaluation of Polyvinyl Fluoride as a Container Material for Air Pollution Samples", J. Environ. Sci. Health., 1976, 2, 121-130.

5. U.S. Environmental Protection Agency, Hazardous Waste Incineration Measurement Guidance Manual, Volume III of the Hazardous Waste Incineration Guidance Series, EPA/625/6-89/021.

6. U.S. Environmental Protection Agency, Method 301, "Protocol for the Field Validation of Emission Concentrations from Stationary Sources", EPA 450/4-90-015, February 1991.

7. 40 CFR Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit".

8. Kanniganti, R., Moreno, R.L., and J.T. Bursey, Radian Corporation, Research Triangle Park, North Carolina, "Method 0040: Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags", EPA Contract No. 68-D1-0010.

9. 40 CFR Part 60, Appendix A, Methods 1, 2, 3, 4, 5, 18 and 25.

10. U. S. Environmental Protection Agency, Contract No. 68-D4-0022, Work Assignment 34 to Eastern Research Group, Incorporated, “Field Evaluation of EPA Method 0040 (Volatiles Using Bags) at a Coal-Fired Power Plant,” September 30, 1996.

TABLE 1

COMPOUNDS FOR WHICH APPLICABILITY OF THE METHOD HAS BEEN DEMONSTRATED

Compound	CAS No.	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Instrument Detection Limit[a] (ppm)
Dichlorodifluoromethane	75-71-8	-30	Gas	0.20
Vinyl chloride	75-01-4	-19	Gas	0.11
1,3-Butadiene	106-99-0	-4	Gas	0.90
1,2-Dichlor-1,1,2,2-tetrafluoroethane	76-14-2	4	Gas	0.14
Methyl bromide	74-83-9	4	Gas	0.14
Trichlorofluoromethane	353-54-8	24	88	0.18
1,1-Dichloroethene	75354	31	22	0.07
Methylene chloride	75-09-2	40	44	0.05
1,1,2-Trichlorotrifluoroethane	76-13-1	48	37	0.13
Chloroform	67-66-3	61	21	0.04
1,1,1-Trichloroethane	71-55-6	75	13	0.03
Carbon tetrachloride	56-23-5	77	11	0.03
Benzene	71-43-2	80	10	0.16
Trichloroethene	79-01-6	87	8	0.04
1,2-Dichloropropane	78-87-5	96	5	0.05
Toluene	108-88-3	111	3	0.08
Tetrachloroethylene	127-18-4	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits

TABLE 2

PROBLEMS THAT CAN INVALIDATE TEDLAR® BAG SAMPLING DATA AND SUGGESTED REMEDIES

Problem	Remedy
1. Condensation of the gases or water vapor in the bag	Sample below the condensation point of the analytes; lower the temperature in the condensate trap.
2. Leaks developing in the bag during testing, transport, and/or analysis	Use double sealed bags; perform additional sampling runs; protect the bags from sharp objects by sampling and shipping in rigid, opaque containers; ship the bags in the same containers used during sampling.
3. Hydrocarbon contamination	Minimize exposure of the bag to heat and direct light, by sampling and shipping in rigid, opaque containers; purge the bags with ultrapure N_2 in the laboratory and establish through analysis that the hydrocarbon levels are acceptable; use the bags only once.

FIGURE 1
SCHEMATIC OF THE METHOD 0040 SAMPLING TRAIN

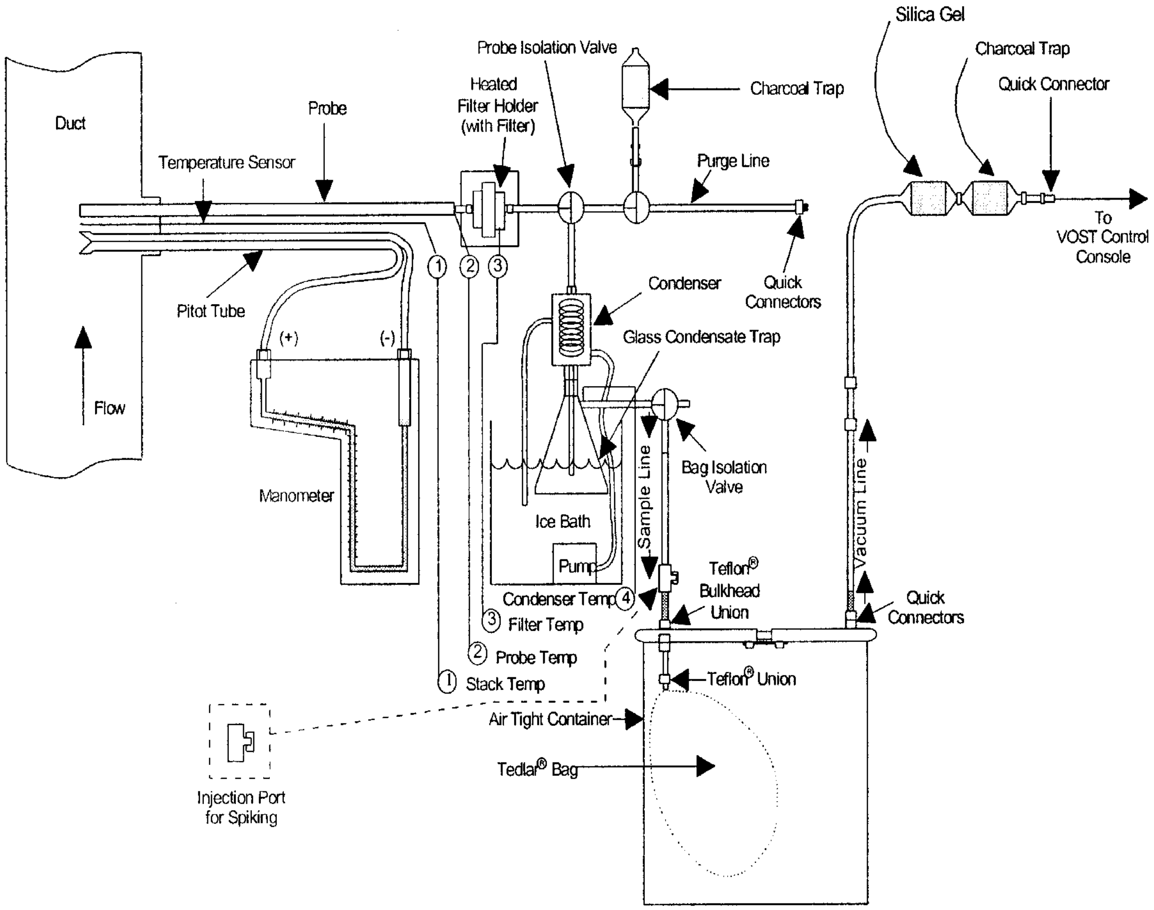


FIGURE 2
ISOLATION VALVE DESIGN

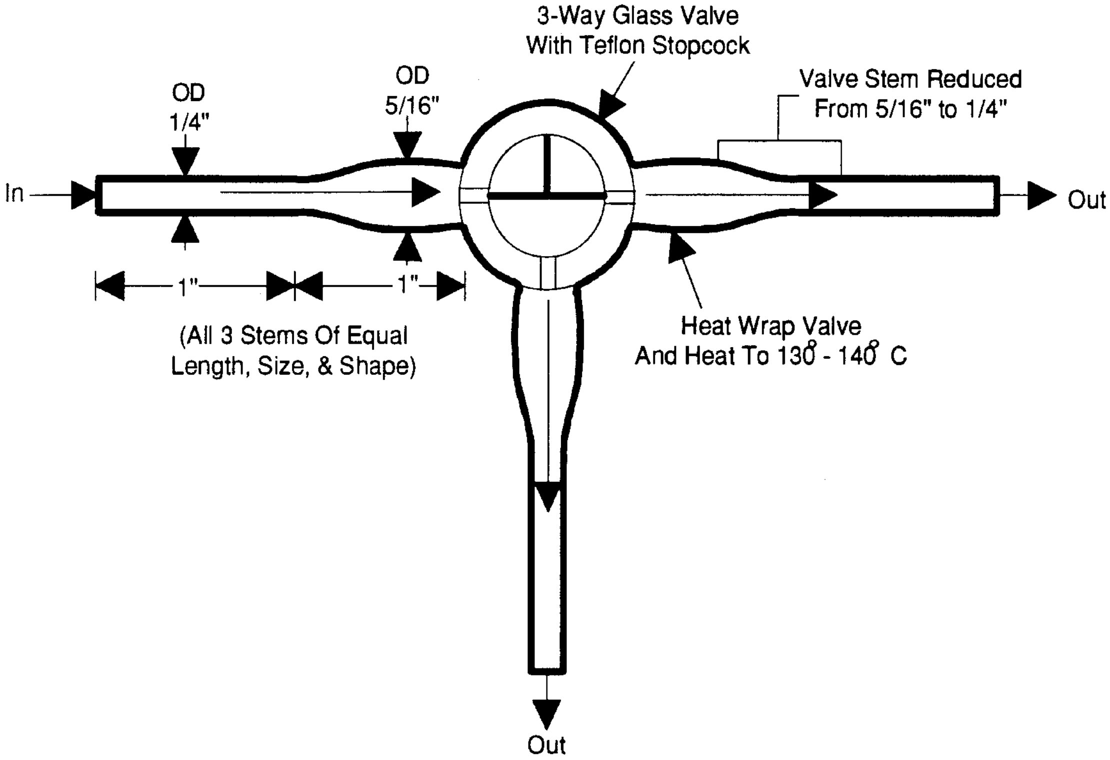
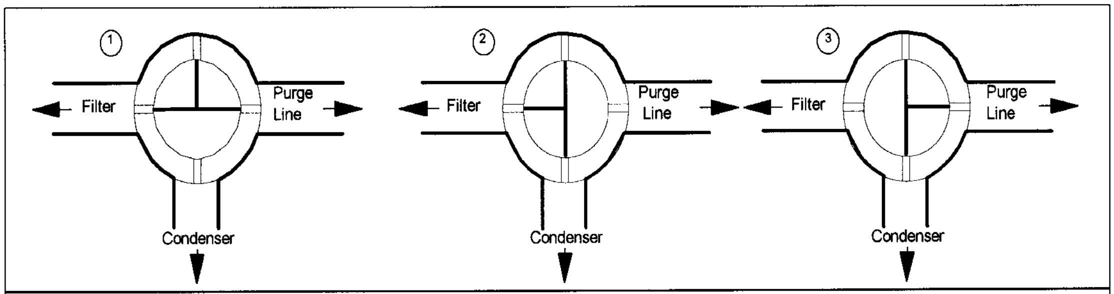


FIGURE 3
VALVE OPERATION

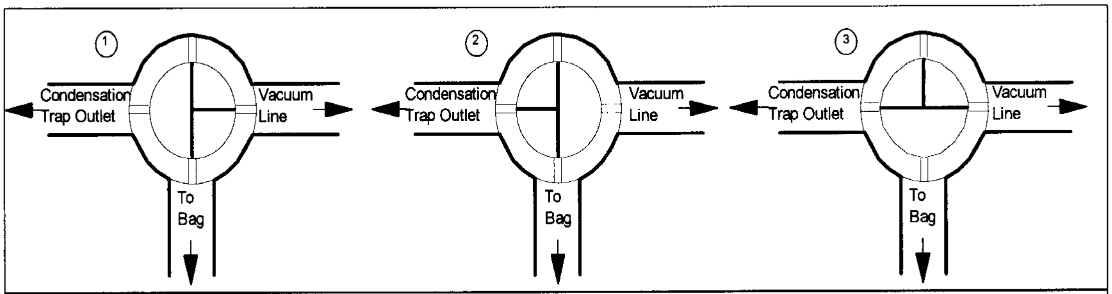


Probe Isolation Valve Positions (a)

① Isolation Position
System Purge Position

② Sample
Position

③ Vacuum Purge Position
(Release System Pressure
After Leak Checks)

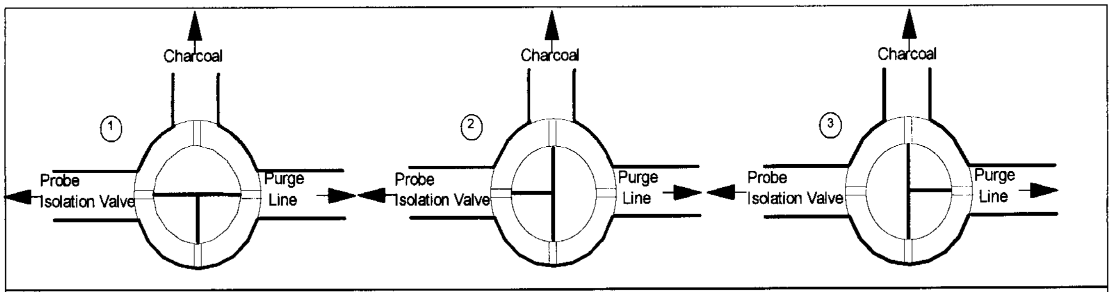


Bag Isolation Valve Positions (b)

① Bag Evacuation and
Leak Check Position (Post Test)

② Sample
Position

③ Bag Isolation Position and
System Purge



Vacuum Release Valve Positions (c)

① Probe Purge
Position

② Vacuum
Release

③ Sample
Position

FIGURE 4
DIAGRAM OF CONTROL CONSOLE

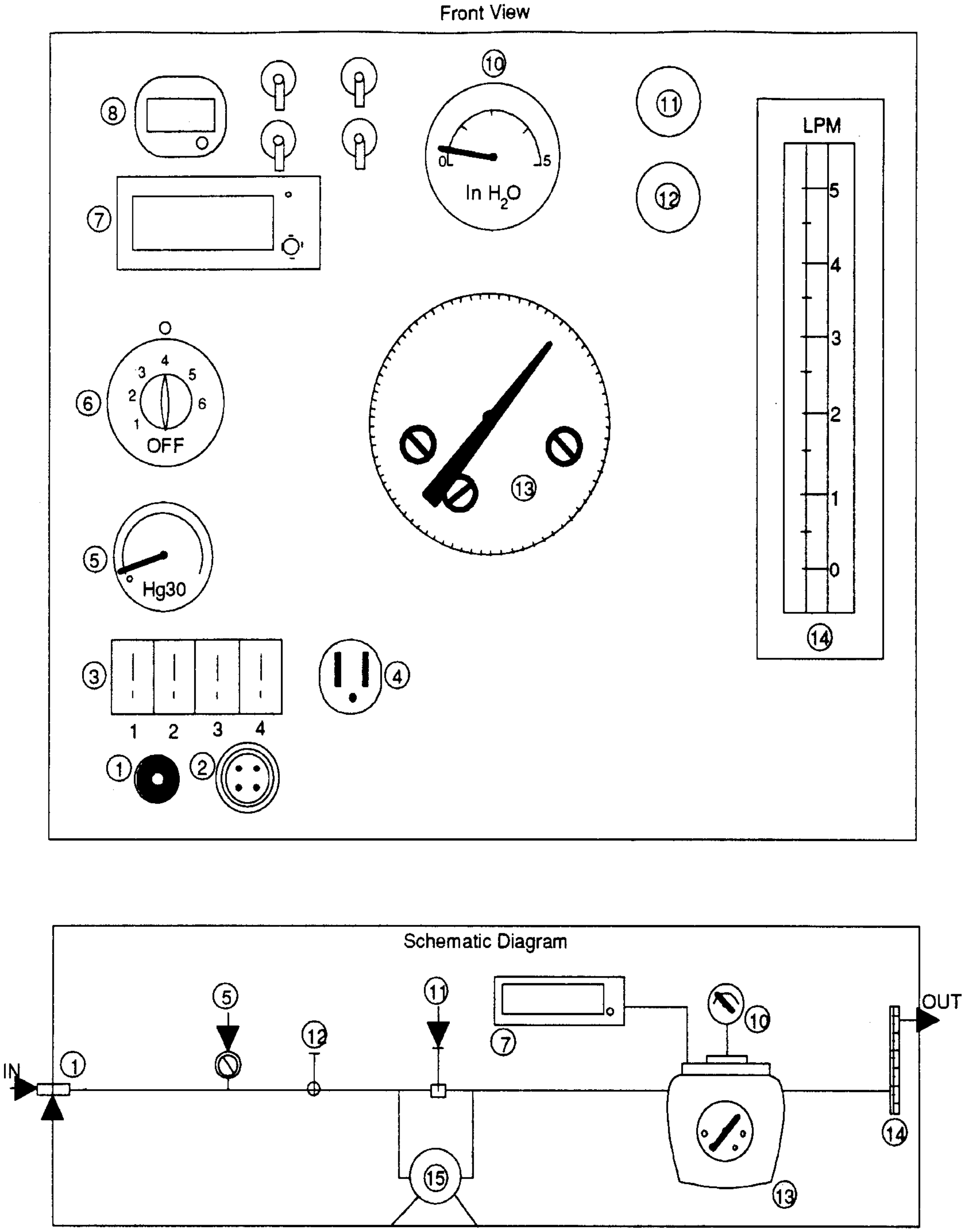


FIGURE 4 (Continued)
CONTROL CONSOLE COMPONENTS

1. 1/4 in. S.S. Quick Connect - Vacuum line inlet from sample train (to bag container).

2. Amphenol Receptacle - provides power through umbilical to probe heat & water pump.

3. Thermocouple Receptacles - 4 thermocouple inlets for:
    1. Stack Temperature
    2. Probe Temperature
    3. Condenser Temperature
    4. Ambient Temperature

4. 110 VAC Receptacle - auxiliary power for isolation valve heat.

5. Vacuum Gauge - 0-30 in. Hg.

6. Heat Controller

7. Digital Thermocouple Read Out - 10 channel (displays temperature readings during sampling)
    - (1-4 remote as listed above)
    - (5 dry gas meter temperature)
    - (6-10 spares)

8. Timer (optional)

9. Power Switches - control (on/off)
    1. Main power - with separate switches for each.
    2. Sample pump
    3. Water pump
    4. Timer

10. Meter pressure Gauge - (inches water column)

11. Fine Adjustment (Bypass) Valve

12. Coarse Adjustment (on/off) Valve

13. Dry Gas Meter

14. Rotometer (Flow Meter)

15. Pump

FIGURE 5
PRETEST SURVEY DATA FORM

1. Name of Company ______________________________ Date __________

Address ______________________________

____

____

Contacts ______________________________

Phone Numbers ______________________________

Process to be sampled ______________________________

____

Duct or vent to be sampled ______________________________

____

II. Process description ______________________________

____

Raw Material ______________________________

____

Products ______________________________

____

Operating cycle

Check: Batch ________Continuous ________ Cyclic ________

Timing of batch or cycle ______________________________

Best time to test ______________________________

III. Sampling site

A. Description

Site description ______________________________

Duct shape and size ______________________________

Materials ______________________________

Wall thickness ______________________________inches

Upstream distance ____________ inches ____________diameter

Downstream distance ____________ inches ____________diameter

Size of port ______________________________

FIGURE 5 (Continued)

Temperature ___________ °C   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

O_2 ___________%   _____________ ____________ ppm

CO ___________%   _____________ ____________ ppm

CO_2 ___________%   _____________ ____________ ppm

SO_2 ___________%   _____________ ____________ ppm

Hydrocarbon components

____   _____________ ppm

____   _____________ ppm

____   _____________ ppm

____   _____________ ppm

____   _____________ ppm

____   _____________ ppm

B. Sampling considerations

Location to set up GC ____

____

Power available at duct ____

____

Plant entry requirements ____

____

Security agreements ____

____

Potential problems ____

____

Site diagrams (Attach additional sheets if required).

FIGURE 6
FIELD SAMPLING DATA FORM

Plant ______________

City ______________

Operator ______________

Date ______________

Run number ______________

Stack dia. (in.) ______________

Sample box number ______________

Pitot tube (C_p) ______________

Static press ________ (in. H_2O)

Flowmeter calib (Y) ______________

Average (ΔP) ________ (in. H_2O)

Initial flowmeter setting ______________

Average stack temperature ____________ °C

Barometric pressure ______________

Dilution system: (dynamic) ______________

emission flowsetting ______________

diluent flowsetting __________ (in. Hg)

Dilution system (statis) ______________

emission flowsetting ______________

Final Leak Check ___________ (cfm)

Vacuum during leak check _________ (in. H_2O)

Sampling point location ______________

Total condensate volume ______________ mL

VOA vial size ______________ mL

VOA vial number ______________

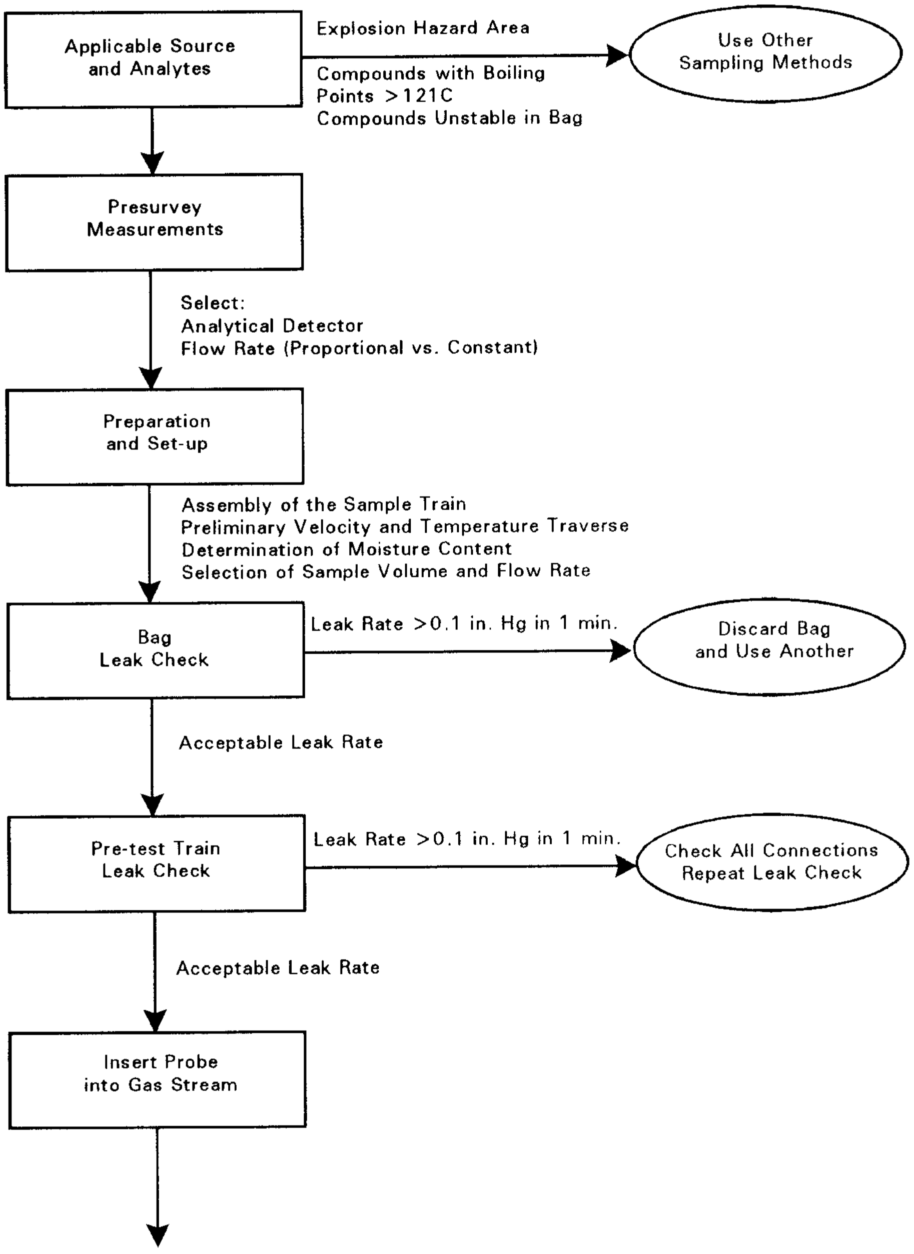
Tedlar® bag volume ____________ liters

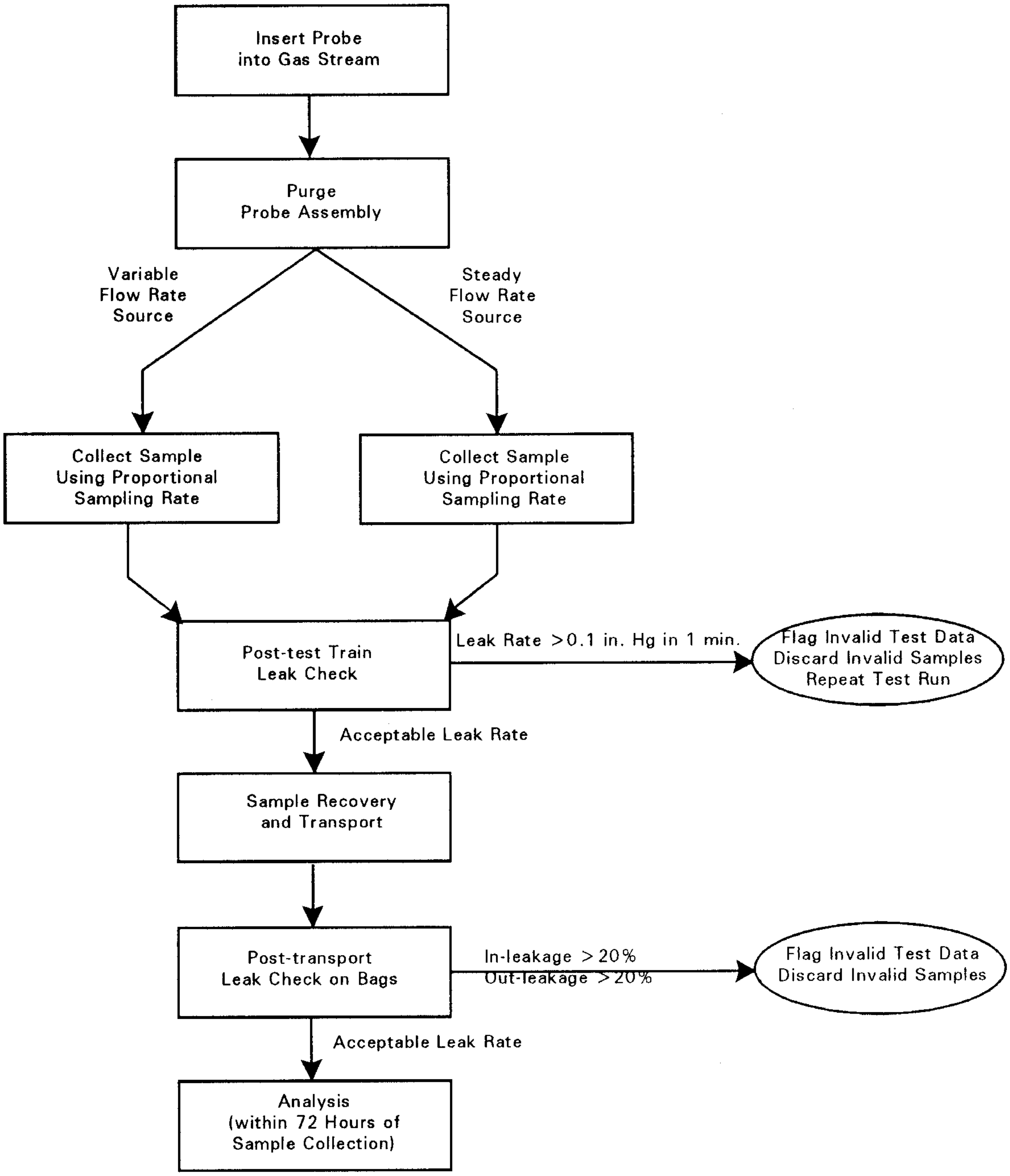
Container volume ____________ liters

Container number ______________

FIGURE 6 (Continued)

Sampling, time, min.	Clock time, 24 hr.	Velocity head (in.) (H_2O) (ΔP)	Flowmeter setting (ft^3/min)	Temperature Readings			
				Stack (°C)	Probe (°C)	Sample Line (°C)	Flowmeter Box (°C)
Total		Avg	Avg	Avg	Avg	Avg	Avg


Applicable Source and Analytes
Explosion Hazard Area
Compounds with Boiling Points >121C
Compounds Unstable in Bag
Use Other Sampling Methods
Presurvey Measurements
Select:
Analytical Detector
Flow Rate (Proportional vs. Constant)
Preparation and Set-up
Assembly of the Sample Train
Preliminary Velocity and Temperature Traverse
Determination of Moisture Content
Selection of Sample Volume and Flow Rate
Bag Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Discard Bag and Use Another
Acceptable Leak Rate
Pre-test Train Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Check All Connections Repeat Leak Check
Acceptable Leak Rate
Insert Probe into Gas Stream


Insert Probe into Gas Stream
Purge Probe Assembly
Variable Flow Rate Source
Steady Flow Rate Source
Collect Sample Using Proportional Sampling Rate
Collect Sample Using Proportional Sampling Rate
Post-test Train Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Flag Invalid Test Data Discard Invalid Samples Repeat Test Run
Acceptable Leak Rate
Sample Recovery and Transport
Post-transport Leak Check on Bags
In-leakage >20%
Out-leakage >20%
Flag Invalid Test Data Discard Invalid Samples
Acceptable Leak Rate
Analysis (within 72 Hours of Sample Collection)