

SAMPLING METHOD FOR VOLATILE ORGANIC COMPOUNDS (SMVOC)

1.0 SCOPE AND APPLICATION

1.1 Method 0031 is used to determine volatile organic compounds in gaseous emissions from a wide variety of stationary sources including hazardous waste incinerators. The following compounds may be determined by this method:

| Compound | Boiling Point (°C) | CAS No. ^a |
|----------------------------|---------------------|----------------------|
| Acrylonitrile ^b | 77 | 107-13-1 |
| Benzene | 80 | 71-43-2 |
| Bromodichloromethane | 87 | 75-27-4 |
| Carbon disulfide | 46 | 75-15-0 |
| Carbon tetrachloride | 77 | 56-23-5 |
| Chlorodibromomethane | 119-120 @ 748 mm Hg | 124-48-1 |
| Chloroform | 61 | 67-66-3 |
| Chloroprene ^c | 59 | 126-99-8 |
| Dibromomethane | 97 | 74-95-3 |
| 1,1-Dichloroethane | 57 | 75-34-3 |
| 1,2-Dichloroethane | 83 | 107-06-2 |
| 1,1-Dichloroethene | 32 | 75-35-4 |
| trans-1,2-Dichloroethene | 48 | 156-60-5 |
| 1,2-Dichloropropane | 96 | 78-87-5 |
| 1,3-Dichloropropene | 106 @ 730 mm Hg | 542-75-6 |
| Methylene chloride | 39 | 75-09-2 |
| Tetrachloroethene | 121 | 127-18-4 |
| Toluene | 111 | 108-88-3 |
| 1,1,1-Trichloroethane | 75 | 71-55-6 |
| 1,1,2-Trichloroethane | 113 | 79-00-5 |
| Trichloroethene | 87 | 79-01-6 |
| Trichlorofluoromethane | 24 | 75-69-4 |

^a Chemical Abstract Services Registry Number.

^b The water solubility and reactivity of this compound may cause problems with some stationary sources.

^c Reactive compound; may interact with the test matrix.

1.2 Method 0031 may be used to prepare volatile organic compounds that have a boiling point between -15°C and 121°C. Field application for volatile organic compounds with boiling points less than 0°C should be supported by data obtained from laboratory gaseous dynamic spiking and gas chromatographic/mass spectrometric (GC/MS) analysis according to Methods 5041 and 8260 to demonstrate the efficiency of the sampling and analysis method.

1.3 The method is not applicable to particulates or aerosols since isokinetic sampling is not performed. Isokinetic sampling is not required because the volatile organic compounds are in the gas phase when they are sampled.

1.4 Application of Method 0031 is not restricted to those compounds in the target analyte list, however, detection limits have been determined for these compounds and acceptable method performance data have been obtained. Method 0031 may also be applied to the compounds listed in Table 1 if extra care is taken because of the high volatility of these compounds.

1.5 Method 0031 is generally not applicable to polar water-soluble and reactive volatile organic compounds. Examples of polar water-soluble and reactive compounds are shown in Table 2. Other examples where Method 0030 (VOST) sampling and analytical methodology has been used inappropriately include: bromoform (boiling point 137°C, above the maximum limit allowed by the methodology), ethylbenzene (136°C), 1,2,3-trichloropropane (156°C), xylenes (~140°C), styrene (146°C), 1,1,2,2-tetrachloroethane (146°C at 746 mm Hg), and the dichlorobenzenes (~175°C). Although successful analysis for these compounds can be demonstrated by spiking sorbent tubes, the compounds will not be collected quantitatively at the upper temperature limit for the operation of the SMVOC train.

1.6 This method is applicable to the determination of volatile organic compounds in the gaseous effluent of stationary sources such as hazardous waste incinerators with an upper concentration limit per compound in the emissions of approximately 1.5 parts per million (ppm). Method 0031 is not appropriate for gaseous volatile organic compound concentrations above this limit, since saturation of the analytical system or compound breakthrough in the field may occur. Modifications of analytical methods to reduce the concentration of compounds entering the gas chromatograph/mass spectrometer (GC/MS), such as splitters or dilutions, may prevent saturation of the analytical system, but the analytical data are not accurate if breakthrough has occurred during sampling. The analysis of screening samples or distributive volume samples is recommended to prevent analytical system saturation when high analyte concentrations may be encountered.

1.7 The sensitivity of this method is dependent upon the level of interferences in the sample matrix and the presence of detectable levels of volatile organic compounds in the blanks. The target detection limit of this method is 0.1 µg/m³ (ng/L) of gaseous effluent. The upper end of the range of applicability of this method is limited by breakthrough of the volatile organic compounds on the sorbent traps used to collect the sample and the ability of the analytical system to respond within the linear range of the instrumentation. Laboratory method development data have demonstrated a range of 0.1 to 100 µg/m³ (ng/L) for selected volatile organic compounds collected on a set of sorbent traps using a total sample volume of 20 L or less (see Sec. 2.3).

1.8 The SMVOC is designed to be operated at a sampling rate of 1 L/min with traps being replaced every 20 min for a total sampling time of 2 hrs. Analysis of the traps is carried out by thermal desorption purge-and-trap gas chromatography/mass spectrometry (see Methods 5041 and 8260). Traps may be analyzed separately or combined onto one trap to improve detection limits. Additional flow rates and sampling times are acceptable. For example, when less than maximum detection ability is needed, it is acceptable to operate the SMVOC at 0.5 L/min for a total of three 40-minute periods (two-hour total sampling time). In this example, a two-hour sampling time is maintained, but the number of sampling tubes which must be changed in the field is minimized, as is the number of analyses which must be performed.

NOTE: The SMVOC sampling train may be operated no slower than 0.25 L/min, and no faster than 1 L/min.

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

2.0 SUMMARY OF METHOD

2.1 This method employs a sampling module and meter box to withdraw a 20-L sample of effluent gas containing volatile organic compounds from a stationary source at a flow rate of 1 L/min, using a glass-lined probe heated to $130 \pm 5^\circ\text{C}$ and a sampling method for volatile organic compounds (SMVOC) train.

2.2 The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile organic compounds are collected on a set of sorbent traps (Tenax®-GC/Tenax®-GC/Anasorb®-747). Liquid condensate is collected in an impinger placed between the two Tenax®-GC traps and the Anasorb®-747 trap. The first and second traps contain 1.6 g of Tenax®-GC each and the third trap (back trap) contains 5.0 g of Anasorb®-747. A total number of sorbent tube sets to encompass a total sampling time of 2 hrs is collected: i.e., if a sampling rate of 1 L/min for 20 minutes is used, a total of six sorbent tube sets will be collected in 2 hr of sampling.

2.3 Alternative conditions for sample collection may be used, collecting a sample volume of 20 L or less at a flow rate reduced from 1 L/min. (Operation of the SMVOC under these conditions is referred to as SLO-SMVOC.) The SLO-SMVOC may be used to collect 5 L of sample (0.25 mL/min for 20 min) or 20 L of sample (0.5 L/min for 40 min) on each set of sorbent tubes. These smaller sample volumes collected at lower flow rates should be considered when the boiling points of the volatile organic compounds of interest are below 0°C (see Table 1) to prevent breakthrough. Refer to Sec. 2.2 for the total number of tube sets collected per run.

3.0 INTERFERENCES

3.1 Interferences are encountered in the analytical methodology and arise primarily from background contamination of sorbent traps prior to or after sample collection. Other interferences may arise from exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile organic compounds in the ambient air at a stationary source site. To avoid or minimize the low-level contamination of train components with volatile organic compounds, care should be taken to avoid contact of all interior surfaces or train components with synthetic organic materials such as organic solvents, and lubricating and sealing greases. Train components should be carefully cleaned and conditioned according to the procedures described in this protocol. The use of a sealed/enclosed sampling train is suggested but not required (for example, a purged glove bag may be used). The use of blanks (Sec. 6.6) is essential to assess the extent of any contamination. Refer to Method 5041 for additional information on analytical interferences.

3.2 If the emission source has a high level of organic compounds in the emissions matrix (for example, hydrocarbons present at levels of hundreds of ppm), the presence of these volatile organic compounds may interfere with the performance of the SMVOC analytical methodology. If the probability of saturation of the analytical instrumentation exists, preliminary SMVOC screening samples with distributive volumes may be necessary to help ensure that valid and usable data will be obtained. To perform sampling according to distributive volumes, samples of different volumes are collected (typically 5 L, 10 L, and 20 L) to verify that analyte concentrations are 1X, 2X, and 4X.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train - A schematic of the principal components of the SMVOC is shown in Figure 1. The SMVOC consists of a heated glass-lined probe, followed by an isolation valve and charcoal trap, a water-cooled glass condenser, two sorbent tubes containing Tenax®-GC (1.6 ± 0.1 g each), an empty knock-out trap for condensate removal, a second water-cooled glass condenser, a third sorbent tube containing Anasorb®-747 (5.0 g ± 0.1 g), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The vacuum during sampling and for leak-checking is monitored by pressure gauges which are in-line with and downstream from the silica gel drying tube. The components of the sampling train are described below.

4.1.1 Probe - The probe is made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is maintained at 130°C ± 5°C or higher, but not so high that the sorbent temperature exceeds 20°C. A water-cooled probe may be necessary at elevated source temperatures to protect the probe and meet the required sorbent temperature maximum. Isokinetic sample collection is not a requirement for the use of SMVOC since the compounds of interest are in the vapor phase at the point of sample collection. No nozzle is required, but a plug of clean quartz wool (approximately 2.5 cm. (1 in.)) is inserted in the probe to remove particulate matter.

NOTE: No stainless steel components should be in contact with the sample stream.

4.1.2 Isolation valve - The isolation valve is a greaseless stopcock (0.25 in. outer diameter stem is recommended) with a glass bore and sliding Teflon® plug with Teflon® washers (Ace Glass 8193 or equivalent).

4.1.3 Condensers - The condensers (Ace Glass 5979-14 or equivalent) must be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent tube. The top connection of the condenser must form a leak-free, vacuum-tight seal without using sealing greases. Solverall® tube fittings and screw caps with Solverall® washers (¼ in. OD, or equivalent) are recommended.

4.1.4 Sorbent tubes - See Figure 2 for a diagram of a SMVOC tube.

4.1.4.1 The first and second tubes of a three-tube set of sorbent tubes should each be packed with 1.6 ± 0.1 g of Tenax®-GC resin and the third tube of the set should be packed with 5.0 ± 0.1 g of Anasorb®-747. The tubes should be marked with an arrow to indicate the direction of flow during sampling.

4.1.4.2 The sorbent tubes are glass tubes with approximate dimensions of 10 cm x 1.6 cm ID. The tube is a single glass tube which has the ends reduced in size to accommodate a ¼-in. Swagelok® fitting. The sorbent is held in place by unsilanized clean glass wool at each end of the sorbent layer. Threaded end caps are placed on the sorbent tube after packing with sorbent to protect the sorbent from contamination during storage and transport. In order to minimize tube breakage, fittings are finger-tight plus an additional quarter of a turn. Ceramic-filled Teflon® ferrules (Supeltex M2A or equivalent) are used for tubes. Graphite ferrules (Supeltex M4 or equivalent) are used if reconditioning of the tubes is necessary. The Swagelok® end caps should be finger-tightened with the ferrules in place so that the entire cap assembly may be turned as a unit. In order to seal the assembly and avoid glass breakage, the cap assembly should be pushed to the end of the glass and then backed off slightly before tightening.

the cap with a wrench one quarter of a turn. Backing the cap assembly off from the end of the tube will prevent chipping, cracking, or breaking of the glass.

4.1.4.3 The sorbent tubes are placed in transport tubes (capped culture tubes with glass wool and charcoal) for shipment. A layer of clean charcoal is placed in the bottom of the transport tube to absorb any volatile organics in the air in the transport tube. A plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed above the charcoal. The SMVOC tube, with both ends capped, is placed in the transport tube, and a plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed on top of the SMVOC tube. The two glass wool plugs cushion the SMVOC tube during shipping. The transport tube is then sealed tightly with a Teflon®-lined screw cap. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

4.1.5 Metering system - The metering system for SMVOC consists of a vacuum gauge, a pump, a calibrated rotameter for monitoring the sampling flow rate, a dry gas meter (2% accuracy, with a minimum resolution of 0.01 L) at the required sampling rate, needle valves, and a temperature readout device. Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and the first sorbent tube, since this temperature should not exceed 20°C. The temperature can be monitored by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20°C. If the cooling is not sufficient, an alternative condenser providing the necessary cooling capacity must be used.

4.1.6 Sample transfer lines - All sample transfer lines connecting the probe to the SMVOC shall be less than 1.52 m. (5 ft.) in length. All sample transfer lines ahead of the first condenser shall be heat-traced Teflon® or glass maintained at $130 \pm 5^\circ\text{C}$. Connecting fittings must be capable of forming leak-free, vacuum-tight connections without the use of sealing grease. All other sample transfer lines used with the SMVOC shall be Teflon® with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease. These sample transfer lines should not be reused at other emission sources.

4.2 Solverall® washers - All washers or gaskets used in SMVOC shall be Teflon®-coated (Solverall® washers or equivalent; ¼ in. stainless steel Swagelok® fittings with Supeltex M2A ferrules may also be used). Prior to use, these gaskets should be ultrasonically-cleaned with methanol and air-dried in a contained/isolated organic vapor-free area. Gaskets should be stored in clean, screw-capped containers prior to use.

4.3 Glass wool - Glass wool shall be Soxhlet-extracted for 8 to 16 hours using methanol, and oven dried at 110°C before use. Glass wool should not be silanized to prevent contamination of samples with siloxanes. Quartz wool is recommended for high temperature applications.

4.4 Cold packs/ice - Ice or any commercially-available reusable liquids or gels that can be frozen repeatedly are acceptable. These reusable liquids are typically sold in plastic containers as "Blue Ice" or "Ice-Packs". Enough cold packs or ice should be used to maintain tubes less than 10°C. If ice is used as a coolant for the tubes, the tubes should be shielded from direct contact with the ice so they will not become wet when the ice melts. Use of dry ice (solid CO₂) for cooling tubes should be avoided; the sorbent tubes take up carbon dioxide as the solid coolant vaporizes and the analytical system is vented when the tubes are desorbed and analyzed. The tubes should not be stored at freezing temperatures, since the seal between the glass and Teflon® fittings will be compromised and diffusion of volatile organic compounds into the sorbent may occur.

4.5 VOA vials - 40-mL glass vials with Teflon®-lined screw caps are required for recovery of condensate.

4.6 Teflon® squeeze bottles -Teflon® squeeze bottles should be washed with a solution of a laboratory detergent, rinsed with hot tap water, then with distilled water, then rinsed with clean purged water prior to use.

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. It is recommended that blanks be taken of all reagents used in testing.

5.2 2,6-Diphenyl-p-phenylene oxide polymer (Tenax®-GC, 35/60 mesh, or equivalent).

5.2.1 New Tenax®-GC is Soxhlet-extracted for 24 hours with methanol. The Tenax®-GC is dried for 6 hours in a vacuum oven at 50°C before use. Thermal conditioning (Sec. 7.1.1) of the Tenax®-GC should be done prior to blanking.

5.2.2 If reuse of Tenax®-GC is necessary, the polymer may be extracted sequentially with methanol and pentane, dried in a vacuum oven, and thermally reconditioned as described above. However, reused tubes must meet the same criteria for cleanliness as new tubes. Reuse of sorbents is not recommended. Common practice in laboratories where SMVOC tubes are prepared commercially or where SMVOC sampling and analysis are done extensively is not to reuse sorbents.

5.3 Anasorb®-747 - New Anasorb®-747 is used as it is received from the manufacturer without preparation other than thermal conditioning pending a Quality Control check (Sec. 7.1.1). Anasorb®-747 must not be reused. The Anasorb®-747 should not be extracted with organic solvent prior to use as a sorbent in the SMVOC.

5.4 Silica gel - Indicating type, 6-16 mesh. New silica gel may be used as received from the vendor. Silica gel should not be reused for SMVOC.

5.5 Methanol, CH₃OH - The methanol used for extracting the Tenax®-GC and glass wool should be pesticide grade or equivalent.

5.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 SMVOC glassware cleaning- All glass components of the train should be cleaned thoroughly. The following procedure has been found to be effective, but any protocol which consistently results in contamination-free glassware is acceptable.

6.1.1 Sonicate for 1 hour in a solution of a laboratory detergent such as Alconox®.

- 6.1.2 Rinse with copious amounts of hot tap water to remove all detergent residue.
- 6.1.3 Rinse three times with HPLC grade water.
- 6.1.4 Oven dry at 110°C.
- 6.1.5 Cap for shipment using Teflon® tape or aluminum foil.

6.2 Assembly

The assembly and packing of the sorbent tubes should be carried out in an area free of volatile organic material, such as a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, an air-tight sealed glove box is suggested.

6.3 Tenax®-GC tubes

6.3.1 The Tenax®-GC glass tubes and metal tube parts are cleaned and stored (see Sec. 6.1). Ferrules are discarded but the metal unions are cleaned by sonication in methanol. Tenax®-GC (1.6 ± 0.1 g) is weighed and packed into each of the first two sorbent tubes which have unsilanized cleaned glass wool in the downstream end. The Tenax®-GC is held in place by inserting unsilanized cleaned glass wool. Each tube should be marked, using an engraving tool, permanent marker or diamond-tipped pencil, with an arrow to indicate the direction of sample flow during sampling, and a serial number.

6.3.2 Conditioned sorbent tubes are capped and placed on cold packs or ice for storage and transport. The temperature of the tubes during storage and transport is maintained at a temperature of less than 10°C. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

6.4 Anasorb®-747 tubes - Anasorb®-747 (5.0 ± 0.1 g) is weighed and packed into the third sorbent tube which also has unsilanized cleaned glass wool in the downstream end. The Anasorb®-747 is held in place by inserting unsilanized cleaned glass wool. Special care should be taken to conspicuously mark the Anasorb®-747 tube with an arrow to indicate the direction of flow during sampling, and a serial number.

6.5 Sample collection

6.5.1 For sample collection, place the inlet of the probe at the centroid of the stack or at a point no closer to the walls than 1 meter. After leak checking (see Sec. 6.5.3) but before the initiation of sample collection, the probe shall be purged with stack gas. This purge can be accomplished by attaching a pump to the isolation valve upstream of the first condenser and drawing stack gas through the probe via the isolation valve, so that the probe is purged of ambient air at the initiation of sample collection.

6.5.2 Sample collection is accomplished by opening the valve at the inlet to the first condenser (see Figure 1), turning on the pump, and sampling at a rate of 1 L/min (or slower rate, if desired, according to the guidelines for SLO-SMVOC) for 20 minutes (or an appropriately longer period, if slower sampling rates are used). The volume of sample for any

set of traps should not exceed 20 liters. The end caps of the sorbent tubes should be placed in a clean screw-capped glass container during sample collection to prevent contamination.

6.5.3 Following completion of sample collection, the SMVOC is leak-checked a second time at the highest vacuum encountered during the sampling run to minimize the chance of vacuum desorption of volatile organic compounds from Tenax®-GC. The sample is considered invalid if the leak test does not meet specifications. The train is returned to atmospheric pressure and the set of sorbent tubes is removed. The end caps are replaced and the tubes are placed in an organic-free environment and maintained at a temperature less than 10°C for storage and transport. The set of tubes and any condensate collected (see Sec. 6.5.4) are placed in self-sealing plastic storage bags.

In the laboratory, tubes are maintained in a clean, organic vapor-free environment at a temperature less than 10°C until analysis. The maximum storage time between sampling and analysis of the tubes should be 14 days. The rate of loss of sorbed volatile organic compounds from the tubes is both compound-specific and source-specific. A 14-day period is chosen for the holding time before analysis to provide a reasonably conservative guideline for quantitative analysis of the volatile organic compounds which have been sampled.

NOTE: To prevent breakage and/or loosening of the seals at the end of the tubes, SMVOC tubes should not be stored in a freezer or over dry ice. A solvent-free refrigerator (no cooler than 4°C) is appropriate for storage of the tubes until analysis.

6.5.4 Depending upon condensate volume collected, recovery may be performed with each tube change, or at the end of each run (nominally 2 hrs). Collection of a single composite sample for the run may be especially appropriate when minimal condensate is being collected. If not all the sorbent tubes are analyzed, the total amount of analyte in the composite condensate should be added to the total amount for the run. The condensate is recovered by transferring any liquid contained in the knock-out trap to a 40-mL VOA vial and rinsing the knock-out trap three times with a minimum volume of organic-free reagent water (Sec. 5.6) and adding the rinses to the VOA vial. If necessary, water should be added to eliminate headspace in the vial. If there is sufficient condensate to fill more than one vial, two vials should be used. The VOA vials containing the condensate are placed, with the set of tubes, in a self-sealing plastic storage bag and maintained at a temperature less than 10°C for storage and transport until analysis. The condensate is analyzed by Method 8260. Refer to Method 8260 for details on analytical procedures. Condensate samples, like the sorbent tubes, must be analyzed within 14 days.

6.5.5 A new set of tubes is placed in the SMVOC, the SMVOC is leak-checked, and the sample collection process repeated as described above. To avoid removing the probe from the stack, it is sufficient to perform a glassware leak check using the three way valve just downstream of the probe. Sample collection continues until sufficient samples to encompass a two-hour sampling period have been collected. If samples are taken at a sampling rate of 1 L/minute, a two hour sampling period will result in the collection of six sets of tubes. If SLO-SMVOC procedures are used, fewer than six sets of tubes will be sampled over a two-hour period.

6.6 Blanks

6.6.1 Field blanks - Blank Tenax®-GC and Anasorb®-747 tubes are attached to the sampling train while the train is leak-checked. The tubes are removed and stored with the sample tubes. At least one field blank should be collected for every two-hour sampling period.

6.6.2 Trip blanks - At least one set of blank tubes (two Tenax®-GC, one Anasorb®-747) should be included with each shipment of tubes to a stationary source sampling site. These trip blanks should be treated like any other tubes except that the end caps will not be removed during storage at the site. This set of tubes should be analyzed to assess contamination which may occur during storage and shipment.

6.6.3 Laboratory blanks - One set of blank tubes (two Tenax®-GC, one Anasorb®-747) should remain in the laboratory using the method of storage which is used for field samples. These laboratory blanks should be from the same batch of sorbent as used for the field blanks, trip blanks and collected samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular volatile organic compound), the laboratory blank should be analyzed in order to identify the source of contamination.

7.0 PROCEDURE

7.1 Tube conditioning

7.1.1 In a desorption oven, the sorbent tubes are connected to a source of organic-free nitrogen. Nitrogen is passed through each tube at a flow rate of 80-100 mL/min while the tubes are heated. Anasorb®-747 is thermally conditioned for 18-24 hours at 300°C, under a nitrogen flow rate of 80-100 mL/min. Tenax®-GC is thermally conditioned at 220°C for 8-12 hours at a nitrogen flow rate of 80-100 mL/min. The actual length of time required for the conditioning period may be determined based on the adequacy of the resulting blank checks of the conditioned tubes. Method 5041 (modified to use a sorbent desorption temperature of 250°C) and Method 8260 may be used to perform a blank check of each set of sampling tubes to ensure cleanliness.

7.1.2 An acceptable blank level is less than or equal to (\leq) Method Detection Limits for Method 5041/8260 (see Method 8260 for Method Detection Limits). A general guideline of analyte values less than 2 ng for any volatile organic compound may be used as a criterion of cleanliness.

7.1.3 After conditioning, tubes are sealed and placed on cold packs or ice (maintained at a temperature less than 10°C) until sampling is completed. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination.

7.2 Pretest preparation

7.2.1 All train components should be cleaned and assembled as previously described. A dry gas meter should be calibrated within 30 days prior to use, using a standard orifice, or other approved calibration device/meter.

7.2.2 The SMVOC is assembled according to the schematic diagram in Figure 1. Cooling water should be circulated to the condensers and the temperature of the cooling water must be low enough to maintain the temperature of the gas entering the sorbent below 20°C.

7.3 Leak-checking

7.3.1 To leak-check the entire train, it is necessary to leak-check from the probe to the pump. In order to adequately represent actual sampling conditions, a leak-check should be performed with the pump on and the leak rate measured in liters per minute (Lpm) on the dry gas meter. After the desired vacuum is reached, the pump is isolated from the train to check for leaks.

7.3.2 Ensure that all connections are tight and that the train is assembled correctly with sorbent cartridges properly assembled and in the right direction for sampling. Seal the end of the probe and turn the isolation valve to the sample open position. Turn on the pump and adjust the vacuum to 25.4 cm above normal operating pressure (38 cm Hg should be sufficient as 12.7 cm or less is normal). Prior to leak-checking, verify that both the coarse and fine adjust valves on the meter box are partially opened to prevent backflushing of any condensate during final leak checks as the fine adjust valve will need to be adjusted to increase vacuum rather than decrease vacuum. Allow the rotameter on the meter box to drop to zero, allow the dry gas meter to stop, and the pressure on the water column gauge (represents the pressure inside the dry gas meter) to stabilize. The pump is isolated from the train by shutting off the coarse adjust valve. Record the leak rate directly from the vacuum gauge and time for one minute. The leak rate must be less than 0.02 Lpm for 1 Lpm sampling and 0.01 Lpm for sampling at a lower rate.

7.3.3 Upon completion of the leak check, turn off the pump and release the pressure/vacuum in the train by turning the isolation valve to the vacuum release position and allowing ambient air (filtered with charcoal or equivalent) to enter the train. The initial leak check should be above normal operating pressure. The final leak check (following collection of 20 L of sample) should be at least at the highest vacuum encountered during the run.

NOTE: The volume of air pulled through the SMVOC during leak-checking procedures prior to sampling should be less than 2.5% of the total volume sampled. If a volume greater than 2.5% of the total sampling volume is pulled through the SMVOC in obtaining a successful leak check, the sorbent tubes used during this leak check must be discarded and a successful leak check with a minimum volume of gas pulled through the train must be obtained with a new set of sampling tubes in place.

7.4 Sample collection - Sample collection procedures are described in Sec. 6.5.

7.5 Analytical procedure - Samples are analyzed by Methods 5041 and 8260. In these methods, adapted for a three-tube SMVOC, the Tenax® sorbent tubes are spiked with surrogates, internal standards are spiked into the purge water, and the tube(s) thermally desorbed at 250°C under a purge of organic-free helium. The tubes may all be analyzed individually, or the Tenax® tubes may be analyzed as a pair with the Anasorb® tube analyzed separately, or multiple tubes may be combined on one trap for analysis in order to decrease detection limits. The gaseous effluent from the tubes is bubbled through purged organic-free reagent water (Sec. 5.6) and trapped on an analytical sorbent trap in a purge-and-trap unit. After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore capillary column (Method 5041) under subambient conditions. The volatile organic compounds desorbed

from the analytical trap are separated by temperature-programmed gas chromatography and detected by continuously-scanning low resolution mass spectrometry (Method 8260). Concentrations of volatile organic compounds are calculated from a multipoint calibration curve, using the method of response factors. Refer to Method 8260 for details.

7.6 Calculations

7.6.1 The following nomenclature is used in the calculation of sample volume:

| | | |
|-----------------------|---|---|
| P_{bar} | = | Barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg. |
| P_{std} | = | Standard absolute pressure, 760 mm Hg. |
| T_m | = | Dry gas meter average absolute temperature, °K (°R) |
| T_{std} | = | Standard absolute temperature, 293°K (528°R) |
| V_m | = | Dry gas volume measured by dry gas meter, dcm (dcf) |
| γ | = | Dry gas meter calibration factor |
| $V_{m_{\text{corr}}}$ | = | Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf) |

7.6.2 The volume of gas sampled is calculated as follows:

$$V_{m_{\text{std}}} = V_m \gamma \frac{T_{\text{std}} P_{\text{bar}}}{T_m P_{\text{std}}} = K_1 \gamma \frac{V_m P_{\text{bar}}}{T_m}$$

where:

$K_1 = 0.3858^\circ\text{K}/\text{mm Hg}$ for metric units or

$K_1 = 17.64^\circ\text{R}/\text{in. Hg}$ for English units.

7.6.3 The concentration of volatile organic compound (CPD) in the stack sample (C_g) is calculated as follows:

$$C_g = \frac{\text{Total weight of CPD in sample, } \mu\text{g (i.e., VOST tubes + condensate)}}{\text{Volume of sample at standard conditions, dscm}}$$

If all three sorbent tubes and the condensate are analyzed separately, four sample results (fewer if some tubes are analyzed together) must be added together to obtain the total weight of CPD. If a measurable amount of the compound is found in one or more fractions of the sample, but the amount in one or more of the other fractions is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "sum of the nondetects" as zero if the sum of the detection limits (in nondetect fractions) is less than 10% of the total of the detected amount from the other fractions. In

cases where the sum of the detection limits in the nondetect fractions is greater than 10% of the amount quantitated in the other fractions, then report the total CPD as greater than the detected amount but less than the detected amount plus the sum of nondetect fraction detection limits.

8.0 QUALITY CONTROL

8.1 Prior to actual sampling on-site, all of the applicable sampling equipment should be thoroughly checked to ensure that each component is clean and operable. Each of the equipment calibration data forms should be reviewed for completeness and adequacy to ensure the acceptability of the equipment. Each component of the sampling system should be carefully packed for shipment. Upon arrival on-site, the equipment should be unloaded, inspected for possible damage, and then assembled for use.

8.2 The following quality control (QC) checks are applicable to the sampling procedures:

8.2.1 Each sampling train must be visually inspected for proper assembly before every use.

8.2.2 All sampling data should be recorded on standard data forms which may serve as a pretest checklist.

8.2.3 The temperature measurement system should be visually checked for damage and operability by measuring the ambient temperature.

8.2.4 All sampling data and calculations should be recorded on preformatted data sheets.

8.2.5 All glassware for SMVOC should be cleaned according to the procedure in Sec. 6.1.

8.2.6 Ten percent of the SMVOC tubes should be subjected to GC/MS QC measurements. No analytes should be detected at concentrations above method detection limits in unused SMVOC tubes. If these quality control tests are performed by the manufacturer, documentation should be obtained from the commercial supplier and retained.

8.2.7 All cleaned glassware, hardware, and prepared sorbent traps should be kept closed with ground-glass caps or Teflon® tape until assembly of the sampling train in the field. The sorbent traps should be recapped immediately after each set of samples is collected.

8.2.8 Prior to sampling, the Tenax®-GC and Anasorb®-747 tubes should be spiked with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. This spiking is necessary but not sufficient. The compound must still be sampled from the source.

8.2.9 Assembly and recovery of the sampling trains must be performed in an environment as free from uncontrolled dust and solvent vapors as possible.

8.2.10 Blanks (field, trip, laboratory) must be collected.

8.2.11 The entire sampling train should be leak-checked before and after each run. If the sampling train is moved from one sampling port to another during a run, the train should be leak-checked before and after the move.

8.2.12 Dry gas meter readings, temperature readings, and pump vacuum readings should be made during sampling and recorded in intervals no greater than 5 minutes.

8.2.13 Sorbent traps should be used for sampling within two weeks of preparation.

8.2.14 During sample collection, the gas stream temperature at the inlet to the first sorbent trap must be maintained at or below 20°C.

8.2.15 All sample traps should be stored under refrigeration or on ice or cold packs (temperature maintained less than 10°C) until ready for analysis.

8.3 QC for analytical procedures

8.3.1 Calibration standards should be prepared at five different concentration levels for each analyte of interest. Compounds of interest, surrogate compounds, and internal standards are spiked into the purge water for generation of a multipoint calibration curve. When samples are analyzed, surrogate compounds are spiked onto the sampling tubes using flash vaporization techniques (Method 5041), but internal standards are spiked into the purge water. Response factors for each compound are calculated and these response factors are used for the calculation of analytical results. Refer to Methods 5041 and 8260 for detailed analytical QC procedures for analysis of samples.

8.3.2 To establish the precision and accuracy of the analysis, triplicate paired Tenax®-GC tubes should be spiked with analytical surrogate volatile organic compounds using flash evaporation and analyzed immediately following the initial calibration and before sample analysis. The spiking level should be at the expected level of volatile organic compounds in the stationary source. The spiking standard must be prepared from stock standards separate from those used for calibration. Recovery for each volatile organic compound and surrogate should be within 50% to 150% of spiked value. The relative standard deviation associated with each analyte should be less than 25 percent.

8.3.3 The average recovery from the initial precision and accuracy determinations should be used as an acceptance criterion for sample results. The surrogate recovery in each sample should be within three standard deviations of the average recovery obtained from the initial precision and accuracy determinations.

8.3.4 An EPA performance audit should be completed during a trial burn as a check on the entire SMVOC 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 SMVOC from an EPA audit gas cylinder. Collection of the audit sample in the SMVOC may be conducted either in the laboratory or at the field test site. Analysis of the SMVOC audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular SMVOC samples from the field test.

9.0 METHOD PERFORMANCE

See Method 8260.

10.0 REFERENCES

1. McGaughey, J.F., Bursey, J.T., Merrill, R. G., "Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method", EPA-600/R-94/130, PB95-142055, U.S. EPA, Research Triangle Park, NC, July 1994,
2. Johnson, L.D., Fuerst, R.G., Foster, A.L. and Bursey, J.T., "Replacement of Charcoal Sorbent in the Sampling of Volatile Organics from Stationary Sources," Intern. J. Environ. Anal. Chem., Vol 62, pp. 231-244 (1996).
3. Foster, A.L. and Bursey, J.T., VOST Charcoal Specification Study, EPA-600/R-96/051, PB96-175252, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1996.

TABLE 1
HIGH VOLATILITY ORGANIC COMPOUNDS^a

| Compound | Boiling Point |
|----------------|-----------------|
| Bromomethane | 4°C |
| Chloroethane | 12°C |
| Vinyl bromide | 16°C, at 750 mm |
| Vinyl chloride | -13.4°C |

^aUse of SLO-SMVOC may be helpful.

TABLE 2

COMPOUNDS FOR WHICH METHOD 0031 IS NOT APPLICABLE

| Compounds | Boiling Point | Comment |
|---------------------------|---------------|--|
| Allyl chloride | 45°C | Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility |
| Acetone | 56°C | Polar, water soluble |
| Methyl ethyl ketone | 80°C | Polar, water soluble |
| Chloromethane | -24°C | Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility |
| Epichlorohydrin | 116°C | Not amenable to SMVOC analytical procedure |
| Chloromethyl methyl ether | 56°C | Not amenable to SMVOC analytical procedure |
| Bis(chloromethyl) ether | 106°C | Not amenable to SMVOC analytical procedure |
| Acetonitrile | 82°C | Polar, water soluble |
| Acetaldehyde | 21°C | Polar, water soluble, reactive |
| Acrolein | 53°C | Polar, water soluble, reactive |
| Methanol | 65°C | Polar, water soluble |
| Ethanol | 78°C | Polar, water soluble |
| Isopropyl alcohol | 82°C | Polar, water soluble |

FIGURE 1
 SCHEMATIC OF SAMPLING METHOD FOR VOLATILE
 ORGANIC COMPOUNDS (SMVOC) TRAIN

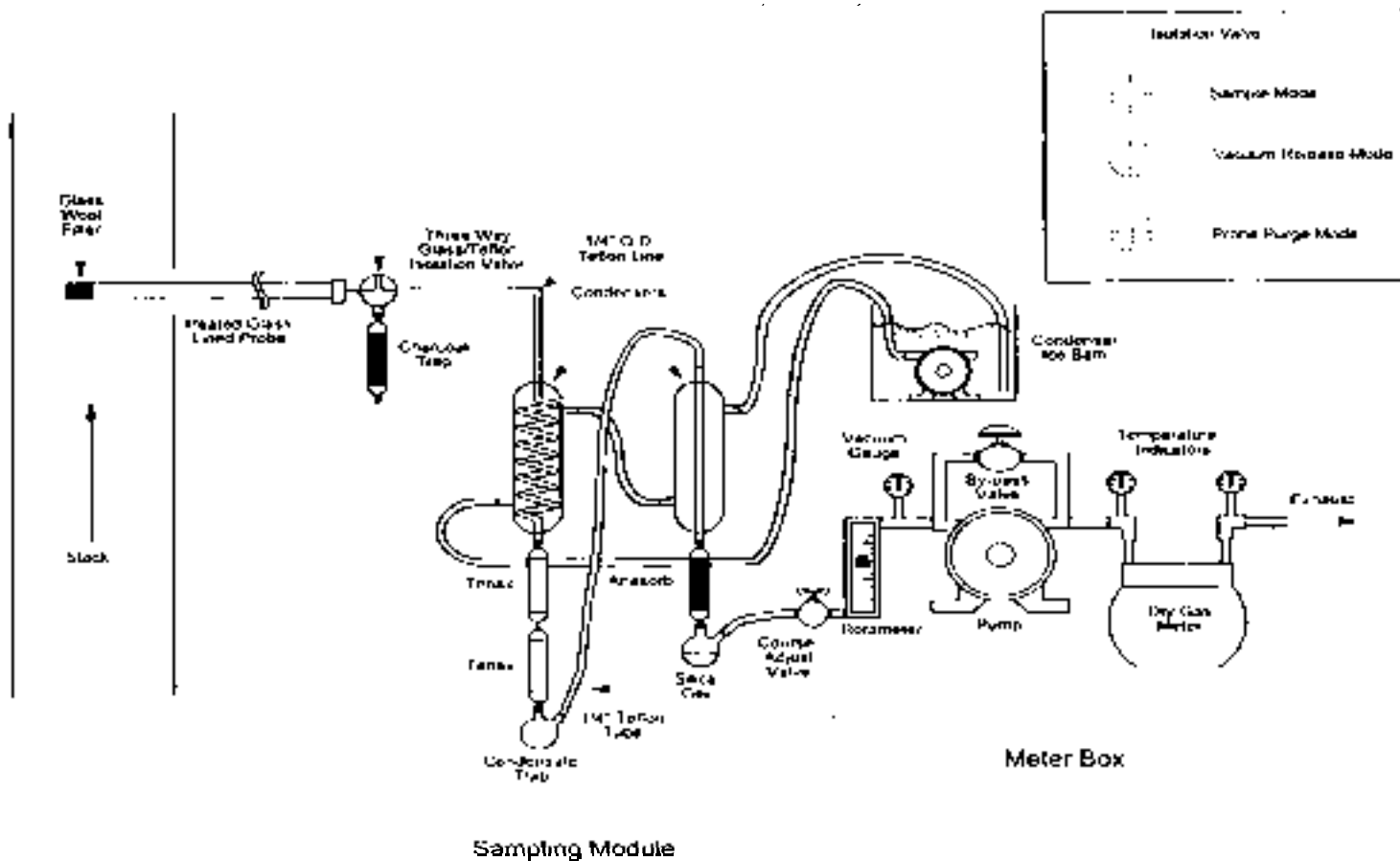


FIGURE 2
SMVOC TUBE

