

condensed formaldehyde and the rinsate combined with the impinger contents prior to sample analysis.

**6.3 Midget Impingers.** Three midget impingers are required for sample collection. The first impinger serves as a moisture knockout, the second impinger contains 20 mL of reagent water, and the third impinger contains silica gel to remove residual moisture from the sample prior to the dry gas meter.

**6.4 Vacuum Pump.** Vacuum pump capable of delivering a controlled extraction flow rate between 0.2 and 0.4 L/min.

**6.5 Flow Measurement Device.** A rotameter or other flow measurement device is required to indicate consistent sample flow.

**6.6 Dry Gas Meter.** A dry gas meter is used to measure the total sample volume collected. The dry gas meter must be sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).

**6.7 Spectrophotometer.** A spectrophotometer is required for formaldehyde analysis, and must be capable of measuring absorbance at 412 nm.

## 7.0 Reagents and Standards

### 7.1 Sampling Reagents

**7.1.1 Reagent water.** Deionized, distilled, organic-free water. This water is used as the capture solution, for rinsing the sample probe, sample line, and impingers at the completion of the sampling run, in reagent dilutions, and in blanks.

**7.1.2 Ice.** Ice is necessary to pack around the impingers during sampling in order to keep the impingers cold. Ice is also needed for sample transport and storage.

### 7.2 Analysis

**7.2.1 Acetyl acetone Reagent.** Prepare the acetyl acetone reagent by dissolving 15.4 g of ammonium acetate in 50 mL of reagent water in a 100-mL volumetric flask. To this solution, add 0.20 mL of acetyl acetone and 0.30 mL of glacial acetic acid. Mix the solution thoroughly, then dilute to 100 mL with reagent water. The solution can be stored in a brown glass bottle in the refrigerator, and is stable for at least two weeks.

**7.2.2 Formaldehyde.** Reagent grade.

**7.2.3 Ammonium Acetate**

**7.2.4 Glacial Acetic Acid**

## 8.0 Sample Collection, Preservation, Storage, and Transport

### 8.1 Pre-test

**8.1.1** Collect information about the site characteristics such as exhaust pipe diameter, gas flow rates, port location, access to ports, and safety requirements during a pre-test site survey. You should then decide the sample collection period per run and the target sample flow rate based on your best estimate of the formaldehyde concentration likely to be present. You want to assure that sufficient formaldehyde is captured in the impinger solution so that it can be measured precisely by the spectrophotometer. You may use Equation 323-1 to design your test program. As a guideline for optimum performance, if you can, design your test so that the liquid concentration ( $C_l$ ) is approximately 10 times the assumed spectrophotometer detection limit of 0.2 µg/mL. However, since actual detection limits are instrument specific, we also suggest that you confirm that the laboratory equipment can meet or exceed this detection limit.

**8.1.2** Prepare and then weigh the midget impingers prior to configuring the sampling train. The first impinger is initially dry. The second impinger contains 20 mL of reagent water, and the third impinger contains silica gel that is added before weighing the impinger. Each prepared impinger is weighed and the pre-sampling weight is recorded to the nearest 0.5 gm.

**8.1.3** Assemble the sampling train (see Figure 1). Ice is packed around the impingers in order to keep them cold during sample collection. A small amount of water may be added to the ice to improve thermal transfer.

**8.1.4** Perform a sampling system leak check (from the probe tip to the pump outlet) as follows: Connect a rotameter to the outlet of the pump. Close off the inlet to the probe and observe the leak rate. The leak rate must be less than 2 percent of the planned sampling rate of 0.2 or 0.4 L/min.

**8.1.5** Source gas temperature and static pressure should also be considered prior to field sampling to ensure adequate safety precautions during sampling.

### 8.2 Sample Collection

**8.2.1** Set the sample flow rate between 0.2-0.4 L/min, depending upon the anticipated concentration of formaldehyde in the engine exhaust. (You may have to refer to published data for anticipated concentration levels—see References 5 and 6.) If no information is available for the anticipated levels of formaldehyde, use the higher sampling rate of 0.4 L/min.

**8.2.2** Record the sampling flow rate every 5 to 10 minutes during the sample collection period.

NOTE: It is critical that you do not sample at a flow rate higher than 0.4 L/min. Sampling at higher flow rates may reduce formaldehyde collection efficiency resulting in measured formaldehyde concentrations that are less than the actual concentrations.

8.2.3 Monitor the amount of ice surrounding the impingers and add ice as necessary to maintain the proper impinger temperature. Remove excess water as needed to maintain an adequate amount of ice.

8.2.4 Record measured leak rate, beginning and ending times and dry gas meter readings for each sampling run, impinger weights before and after sampling, and sampling flow rates and dry gas meter exhaust temperature every 5 to 10 minutes during the run, in a signed and dated notebook.

8.2.5 If possible, monitor and record the fuel flow rate to the engine and the exhaust oxygen concentration during the sampling period. This data can be used to estimate the engine exhaust flow rate based on the Method 19 approach. This approach, if accurate fuel flow rates can be determined, is preferred for reciprocating IC engine exhaust flow rate estimation due to the pulsating nature of the engine exhaust. The F-Factor procedures described in Method 19 may be used based on measurement of fuel flow rate and exhaust oxygen concentration. One example equation is Equation 323-2.

8.3 Post-test. Perform a sampling system leak-check (from the probe tip to pump outlet). Connect a rotameter to the outlet of the pump. Close off the inlet to the probe and observe the leak rate. The leak rate must be less than 2 percent of the sampling rate. Weigh and record each impinger immediately after sampling to determine the moisture weight gain. The impinger weights are measured before transferring the impinger contents, and before rinsing the sample probe and sample line. The moisture content of the exhaust gas is determined by measuring the weight gain of the impinger solutions and volume of gas sampled as described in Method 4. Rinse the sample probe and sample line with reagent water. Transfer the impinger catch to an amber 40-mL VOA bottle with a Teflon-lined cap. If there is a small amount of liquid in the dropout impinger (<10 mL), the impinger catches can be combined in one 40 mL VOA bottle. If there is a larger amount of liquid in the dropout impinger, use a larger VOA bottle to combine the impinger catches. Rinse the impingers and combine the rinsings from the sample probe, sample line, and impingers with the impinger catch. In general, com-

bined rinse volumes should not exceed 10 mL. However, in cases where a long, flexible extension line must be used to connect the sample probe to the sample box, sufficient water must be used to rinse the connecting line to insure that any sample that may have collected there is recovered. The volume of the rinses during sample recovery should not be excessive as this may result in your having to use a larger VOA bottle. This in turn would raise the detection limit of the method since after combining the rinses with the impinger catches in the VOA bottle, the bottle should be filled with reagent water to eliminate the headspace in the sample vial. Keep the sample bottles over ice until analyzed on-site or received at the laboratory. Samples should be analyzed as soon as possible to minimize possible sample degradation. Based on a limited number of previous analyses, samples held in refrigerated conditions showed some sample degradation over time.

#### 8.4 Quality Control Samples

8.4.1 Field Duplicates. During at least one run, a pair of samples should be collected concurrently and analyzed as separate samples. Results of the field duplicate samples should be identified and reported with the sample results. The percent difference in exhaust (stack) concentration indicated by field duplicates should be within 20 percent of their mean concentration. Data are to be flagged as suspect if the duplicates do not meet the acceptance criteria.

8.4.2 Spiked Samples. An aliquot of one sample from each source sample set should be spiked at 2 to 3 times the formaldehyde level found in the unspiked sample. It is also recommended that a second aliquot of the same sample be spiked at around half the level of the first spike; however, the second spike is not mandatory. The results are acceptable if the measured spike recovery is 80 to 120 percent. Use Equation 323-4. Data are to be flagged as suspect if the spike recovery do not meet the acceptance criteria.

8.4.3 Field Blank. A field blank consisting of reagent water placed in a clean impinger train, taken to the test site but not sampled, then recovered and analyzed in the same manner as the other samples, should be collected with each set of source samples. The field blank results should be less than 50 percent of the lowest calibration standard used in the sample analysis. If this criteria is not met, the data should be flagged as suspect.

#### 9.0 Quality Control



QA/QC	Acceptance	Frequency	Corrective action
Leak-check—Sections 8.1.4, 8.3.	<2% of Sampling rate	Pre- and Post-sampling .....	Pre-sampling: Repair leak and recheck Post-sampling: Flag data and repeat run if for regulatory compliance.
Sample flow rate .....	Between 0.2 and 0.4 L/min	Throughout sampling .....	Adjust.
VOA vial headspace .....	No headspace .....	After sample recovery .....	Flag data.
Sample preservation .....	Maintain on ice .....	After sample recovery .....	Flag data.
Sample hold time .....	14 day maximum .....	After sample recovery .....	Flag data.
Field Duplicates—Section 8.4.1.	Within 20% of mean of original and duplicate sample.	One duplicate per source sample set.	Flag data.
Spiked Sample—Section 8.4.2	Recovery between 80 and 120%.	One spike per source sample set.	Flag data.
Field Blank—Section 8.4.3 .....	<50% of the lowest calibration standard.	One blank per source sample set.	Flag data.
Calibration Linearity—Section 10.1.	Correlation coefficient of 0.99 or higher.	Per source sample set .....	Repeat calibration procedures.
Calibration Check Standard—Section 10.3.	Within 10% of theoretical value.	One calibration check per source sample set.	Repeat check, remake standard and repeat, repeat calibration.
Lab Duplicates—Section 11.2.1.	Within 10% of mean of original and duplicate sample analysis.	One duplicate per 10 samples	Flag data.
Analytical Blanks—Section 11.2.2.	<50% of the lowest calibration standard.	One blank per source sample set.	Clean glassware/analytical equipment and repeat.

#### 10.0 Calibration and Standardization

10.1 Spectrophotometer Calibration. Prepare a stock solution of 10 µg/mL formaldehyde. Prepare a series of calibration standards from the stock solution by adding 0, 0.1, 0.3, 0.7, 1.0, and 1.5 mL of stock solution (corresponding to 0, 1.0, 3.0, 7.0, 10.0, and 15.0 µg formaldehyde, respectively) to screw-capped vials. Adjust each vial's volume to 2.0 mL with reagent water. At this point the concentration of formaldehyde in the standards is 0.0, 0.5, 1.5, 3.5, 5.0, and 7.5 µg/mL, respectively. Add 2.0 mL of acetyl acetone reagent, thoroughly mix the solution, and place the vials in a water bath (or heating block) at 60 °C for 10 minutes. Remove the vials and allow to cool to room temperature. Transfer each solution to a cuvette and measure the absorbance at 412 nm using the spectrophotometer. Develop a calibration curve from the analytical results of these standards. The acceptance criteria for the spectrophotometer calibration is a correlation coefficient of 0.99 or higher. If this criteria is not met, the calibration procedures should be repeated.

10.2 Spectrophotometer Zero. The spectrophotometer should be zeroed with reagent water when analyzing each set of samples.

10.3 Calibration Checks. Calibration checks consisting of analyzing a standard separate from the calibration standards must be performed with each set of samples. The calibration check standard should not be prepared from the calibration stock solution. The result of the check standard must be within 10 percent of the theoretical value to be acceptable. If the acceptance criteria are not met, the standard must be reanalyzed. If

still unacceptable, a new calibration curve must be prepared using freshly prepared standards.

#### 11.0 Analytical Procedure

11.1 Sample Analysis. A 2.0-mL aliquot of the impinger catch/rinsate is transferred to a screw-capped vial. Two mL of the acetyl acetone reagent are added and the solution is thoroughly mixed. Once mixed, the vial is placed in a water bath (or heating block) at 60 °C for 10 minutes. Remove the vial and allow to cool to room temperature. Transfer the solution to a cuvette and measure the absorbance using the spectrophotometer at 412 nm. The quantity of formaldehyde present is determined by comparing the sample response to the calibration curve. Use Equation 323-5. If the sample response is out of the calibration range, the sample must be diluted and reanalyzed. Such dilutions must be performed on another aliquot of the original sample before the addition of the acetyl acetone reagent. The full procedure is repeated with the diluted sample.

#### 11.2 Analytical Quality Control

11.2.1 Laboratory Duplicates. Two aliquots of one sample from each source sample set should be prepared and analyzed (with a minimum of one pair of aliquots for every 10 samples). The percent difference between aliquot analysis should be within 10 percent of their mean. Use Equation 323-3. Data are flagged if the laboratory duplicates do not meet this criteria.

11.2.2 Analytical blanks. Blank samples (reagent water) should be incorporated into each sample set to evaluate the possible presence of any cross-contamination. The acceptance criteria for the analytical blank is

less than 50 percent of the lowest calibration standard. If the analytical blank does not meet this criteria, the glassware/analytical equipment should be cleaned and the analytical blank repeated.

## 12.0 Calculations and Data Analysis

### 12.1 Nomenclature

A = measured absorbance of 2 mL aliquot  
 B = estimated sampling rate, Lpm  
 C<sub>t</sub> = target concentration in liquid, µg/mL  
 D = estimated stack formaldehyde concentration (ppmv)  
 E = estimated liquid volume, normally 40 mL (the size of the VOA used)  
 C<sub>form</sub> = formaldehyde concentration in gas stream, ppmvd  
 C<sub>form @15%O<sub>2</sub></sub> = formaldehyde concentration in gas stream corrected to 15% oxygen, ppmvd  
 C<sub>sm</sub> = measured concentration of formaldehyde in the spiked aliquot  
 C<sub>u</sub> = measured concentration of formaldehyde in the unspiked aliquot of the same sample  
 C<sub>s</sub> = calculated concentration of formaldehyde spiking solution added to the spiked aliquot  
 F = dilution factor, 1 unless dilution of the sample was needed to reduce the absorbance into the calibration range  
 F<sub>d</sub> = dry basis F-factor from Method 19, dscf per million btu GCV<sub>g</sub> = Gross calorific value (or higher heating value), btu per scf  
 K<sub>c</sub> = spectrophotometer calibration factor, slope of the least square regression line, µg/absorbance (Note: Most spreadsheets are capable of calculating a least squares line.)  
 K<sub>1</sub> = 0.3855°K/mm Hg for metric units, (17.65°R/in.Hg for English units.)  
 MW = molecular weight, 30 g/g-mole, for formaldehyde 24.05 = mole specific volume constant, liters per g-mole

m = mass of formaldehyde in liquid sample, mg  
 P<sub>std</sub> = Standard pressure, 760 mm Hg (29.92 in.Hg)  
 P<sub>bar</sub> = Barometric pressure, mm Hg (in.Hg)  
 PD = Percent Difference  
 Q<sub>e</sub> = exhaust flow rate, dscf per minute  
 Q<sub>g</sub> = natural gas fuel flow rate, scf per minute  
 T<sub>m</sub> = Average DGM absolute temperature, °K (°R).  
 T<sub>std</sub> = Standard absolute temperature, 293 °K (528 °R).  
 t = sample time (minutes)  
 V<sub>m</sub> = Dry gas volume as measured by the DGM, dcm (def).  
 V<sub>m(std)</sub> = Dry gas volume measured by the DGM, corrected to standard conditions of 1 atmosphere and 20 °C, dscm (dscf).  
 V<sub>t</sub> = actual total volume of impinger catch/rinsate, mL  
 V<sub>a</sub> = volume (2.0) of aliquot analyzed, mL  
 X<sub>1</sub> = first value  
 X<sub>2</sub> = second value  
 O<sub>2d</sub> = oxygen concentration measured, percent by volume, dry basis  
 %R = percent recovery of spike  
 Z<sub>u</sub> = volume fraction of unspiked (native) sample contained in the final spiked aliquot [e.g., Vu/(Vu + Vs), where Vu + Vs should = 2.0 mL]  
 Z<sub>s</sub> = volume fraction of spike solution contained in the final spiked aliquot [e.g., Vs/(Vu + Vs)]  
 R = 0.02405 dscm per g-mole, for metric units at standard conditions of 1 atmosphere and 20 °C  
 Y = Dry Gas Meter calibration factor

### 12.2 Pretest Design

$$C_1 = \frac{B * t * D * 30}{24.05 * E} \quad \text{Eq. 323-1}$$

### 12.3 Exhaust Flow Rate

$$Q = \frac{F_d Q_g GCV_g}{10^6} \left[ \frac{20.9}{20.9 - O_{2d}} \right] \quad \text{Eq. 323-2}$$

### 12.4 Percent Difference—(Applicable to Field and Lab Duplicates)

$$PD = \frac{(X_1 - X_2)}{\left( \frac{X_1 + X_2}{2} \right)} * 100 \quad \text{Eq. 323-3}$$

### 12.5 Percent Recovery of Spike

$$\%R = \frac{(C_{sm} - Z_u C_u)}{Z_s C_s} * 100 \quad \text{Eq. 323-4}$$

### 12.6 Mass of Formaldehyde in Liquid Sample

$$m = K_c * A * F \left( \frac{V_t}{V_a} \right) \left( \frac{1 \text{ mg}}{1000 \cdot g} \right) \quad \text{Eq. 323-5}$$

12.7 Dry Gas Sample Volume Corrected to Standard Conditions

$$\begin{aligned} V_{m(std)} &= \frac{(V_m Y T_{std} P_{bar})}{T_m P_{std}} \quad \text{Eq. 323-6} \\ &= \frac{K_i Y V_m P_{bar}}{T_m} \end{aligned}$$

12.8 Formaldehyde Concentration in gas Stream

$$c_{form} = \frac{R}{MW} \left( \frac{m}{V_{m(std)}} \right) \left( \frac{1 g}{1000 mg} \right) (1 \times 10^6 \text{ ppmv}) \quad \text{Eq. 323-7}$$

12.9 Formaldehyde Concentration Corrected to 15% Oxygen

$$c_{form@15\%O_2} = c_{form} * \frac{(20.9 - 15)}{(2.9 - O_{2d})} \quad \text{Eq. 323-8}$$

### 13.0 Method Performance

13.1 Precision. Based on a Method 301 validation using quad train arrangement with post sampling spiking study of the method at a natural gas-fired IC engine, the relative standard deviation of six pairs of unspiked samples was 11.2 percent at a mean stack gas concentration of 16.7 ppmvd.

13.2 Bias. No bias correction is allowed. The single Method 301 validation study of the method at a natural gas-fired IC engine, indicated a bias correction factor of 0.91 for that set of data. An earlier spiking study got similar average percent spike recovery when spiking into a blank sample. This data set is too limited to justify using a bias correction factor for future tests at other sources.

13.3 Range. The range of this method for formaldehyde is 0.2 to 7.5 µg/mL in the liquid phase. (This corresponds to a range of 0.27 to 10 ppmv in the engine exhaust if sampling at a rate of 0.4 Lpm for 60 minutes and using a 40-mL VOA bottle.) If the liquid sample concentration is above this range, perform the appropriate dilution for accurate measurement. Any dilutions must be taken from new

aliquots of the original sample before reanalysis.

13.4 Sample Stability. Based on a sample stability study conducted in conjunction with the method validation, sample degradation for 7- and 14-day hold times does not exceed 2.3 and 4.6 percent, respectively, based on a 95 percent level of confidence. Therefore, the recommended maximum sample holding time for the underivatized impinger catch/rinsings is 14 days, where projected sample degradation is below 5 percent.

### 14.0 Pollution Prevention

Sample gas from the combustion source exhaust is vented to the atmosphere after passing through the chilled impinger sampling train. Reagent solutions and samples should be collected for disposal as aqueous waste.

### 15.0 Waste Management

Standards of formaldehyde and the analytical reagents should be handled according to the Material Safety Data Sheets.



## 16.0 References

1. National Council of the Paper Industry for Air and Stream Improvement, Inc. "Volatile Organic Emissions from Pulp and Paper Mill Sources, Part X—Test Methods, Quality Assurance/Quality Control Procedures, and Data Analysis Protocols." Technical Bulletin No. 684, December 1994.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc., "Field Validation of a Source Sampling Method for Formaldehyde, Methanol, and Phenol at Wood Products Mills." 1997 TAPPI International Environmental Conference.
3. Roy F. Weston, Inc. "Formaldehyde Sampling Method Field Evaluation and Emission Test Report for Georgia-Pacific Resins, Inc., Russellville, South Carolina." August 1996.
4. Hoechst Celanese Method CL 8-4. "Standard Test Method for Free Formalde-

hyde in Air Using Acetyl Acetone." Revision 0, September 1986.

5. Shareef, G.S., *et al.* "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities." Report No. GRI-96/0009.1, Gas Research Institute, Chicago, Illinois, February 1996.

6. Gundappa, M., *et al.* "Characteristics of Formaldehyde Emissions from Natural Gas-Fired Reciprocating Internal Combustion Engines in Gas Transmission. Volume I: Phase I Predictive Model for Estimating Formaldehyde Emissions from 2-Stroke Engines." Report No. GRI-97/0376.1, Gas Research Institute, Chicago, Illinois, September 1997.

## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

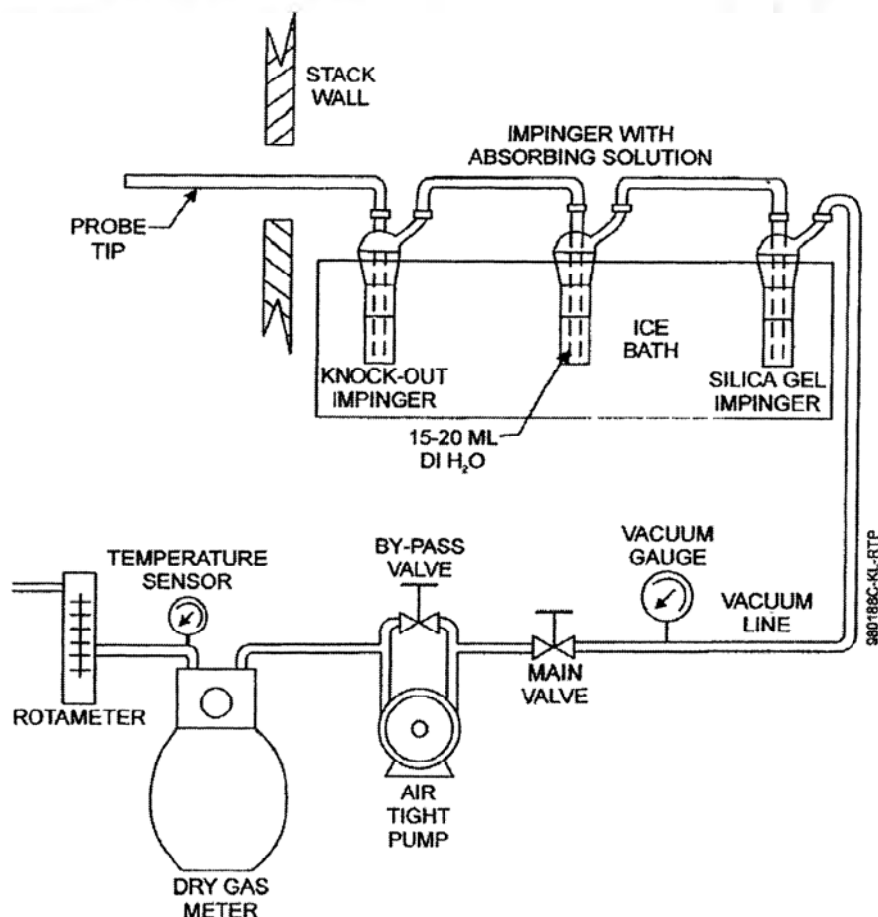


Figure 323-1. Chilled Impinger Train Sampling System

**METHOD 325A—VOLATILE ORGANIC COMPOUNDS  
FROM FUGITIVE AND AREA SOURCES:**

**Sampler Deployment and VOC Sample  
Collection**

**1.0 SCOPE AND APPLICATION**

1.1 This method describes collection of volatile organic compounds (VOCs) at or inside a facility property boundary or from fugitive and area emission sources using passive (diffusive) tube samplers (PS). The concentration of airborne VOCs at or near these potential fugitive- or area-emission sources may be determined using this method in

combination with Method 325B. Companion Method 325B (Sampler Preparation and Analysis) describes preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes collected using either this passive sampling procedure or alternative active (pumped) sampling methods.

1.2 This method may be used to determine the average concentration of the select VOCs using the corresponding uptake rates listed in Method 325B, Table 12.1. Additional compounds or alternative sorbents must be evaluated as described in Addendum A of Method 325B or by one of the following national/

international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in the peer-reviewed open literature.

1.3 Methods 325A and 325B are valid for the measurement of benzene. Supporting literature (References 1-8) indicates that benzene can be measured by flame ionization detection or mass spectrometry over a concentration range of approximately 0.5 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) to at least 500  $\mu\text{g}/\text{m}^3$  when industry standard (3.5 inch long  $\times$  0.25 inch outside diameter (o.d.)  $\times$  5 mm inner diameter (i.d.)) inert-coated stainless steel sorbent tubes packed with Carbagraph™ I TD, Carbopack™ B, or Carbopack™ X or equivalent are used and when samples are accumulated over a period of 14 days.

1.4 This method may be applied to screening average airborne VOC concentrations at facility property boundaries or monitoring perimeters over an extended period of time using multiple sampling periods (*e.g.*, 26  $\times$  14-day sampling periods). The duration of each sampling period is normally 14 days.

1.5 This method requires the collection of local meteorological data (wind speed and direction, temperature, and barometric pressure). Although local meteorology is a component of this method, non-regulatory applications of this method may use regional meteorological data. Such applications risk that the results may not identify the precise source of the emissions.

## 2.0 SUMMARY OF THE METHOD

### 2.1 PRINCIPLE OF THE METHOD

The diffusive passive sampler collects VOC from air for a measured time period at a rate that is proportional to the concentration of vapor in the air at that location.

2.1.1 This method describes the deployment of prepared passive samplers, including determination of the number of passive samplers needed for each survey and placement of samplers along or inside the facility property boundary depending on the size and shape of the site or linear length of the boundary.

2.1.2 The rate of sampling is specific to each compound and depends on the diffusion constants of that VOC and the sampler dimensions/characteristics as determined by prior calibration in a standard atmosphere (Reference 1).

2.1.3 The gaseous VOC target compounds migrate through a constant diffusion barrier (*e.g.*, an air gap of fixed dimensions) at the sampling end of the diffusion sampling tube and adsorb onto the sorbent.

2.1.4 Heat and a flow of inert carrier gas are then used to extract (desorb) the retained VOCs back from the sampling end of the tube and transport/transfer them to a gas

chromatograph (GC) equipped with a chromatographic column to separate the VOCs and a detector to determine the quantity of target VOCs.

2.1.5 Gaseous or liquid calibration standards loaded onto the sampling ends of clean sorbent tubes must be used to calibrate the analytical equipment.

2.1.6 This method requires the use of field blanks to ensure sample integrity associated with shipment, collection, and storage of the passive samples. It also requires the use of field duplicates to validate the sampling process.

2.1.7 At the end of each sampling period, the passive samples are collected, sealed, and shipped to a laboratory for analysis of target VOCs by thermal desorption gas chromatography, as described in Method 325B.

## 2.2 APPLICATION OF DIFFUSIVE SAMPLING

2.2.1 This method requires deployment of passive sampling tubes on a monitoring perimeter encompassing all known emission sources at a facility and collection of local meteorological data. It may be used to determine average concentration of VOC at a facility's "fenceline" using time integrated passive sampling (Reference 2).

2.2.2 Collecting samples and meteorological data at progressively higher frequencies may be employed to resolve shorter term concentration fluctuations and wind conditions that could introduce interfering emissions from other sources.

2.2.3 This passive sampling method provides a low cost approach to screening of fugitive or area emissions compared to active sampling methods that are based on pumped sorbent tubes or time weighted average canister sampling.

2.2.3.1 Additional passive sampling tubes may be deployed at different distances from the facility property boundary or from the geometric center of the fugitive emission source.

2.2.3.2 Additional meteorological measurements may also be collected as needed to perform preliminary gradient-based assessment of the extent of the pollution plume at ground level and the effect of "background" sources contributing to airborne VOC concentrations at the location.

2.2.4 Time-resolved concentration measurements coupled with time-resolved meteorological monitoring may be used to generate data needed for source apportionment procedures and mass flux calculations.

## 3.0 DEFINITIONS

(See also Section 3.0 of Method 325B.)

3.1 *Fenceline* means the property boundary of a facility or internal monitoring perimeter established in accordance with the requirements in Section 8.2 of this method.



3.2 *Passive sampler (PS)* means a specific type of sorbent tube (defined in this method) that has a fixed dimension air (diffusion) gap at the sampling end and is sealed at the other end.

3.3 *Passive sampling* refers to the activity of quantitatively collecting VOC on sorbent tubes using the process of diffusion.

3.4  $PS_i$  is the annual average for all PS concentration results from location  $i$ .

3.5  $PS_{ij}$  is the set of annual average concentration results for  $PS_i$  and two sorbent tubes nearest to the PS location  $i$ .

3.6  $PS_{ip}$  is the concentration from the sorbent tube at location  $i$  for the test period or episode  $p$ .

3.7 *Sampling period* is the length of time each passive sampler is exposed during field monitoring. The sampling period for this method is 14 days.

3.8 *Sorbent tube* (Also referred to as tube, PS tube, adsorbent tube, and sampling tube) is an inert coated stainless steel tube. Standard PS tube dimensions for this method are 3.5-inch (89 mm) long  $\times$  0.25-inch (6.4 mm) o.d. with an i.d. of 5 mm, a cross-sectional area of 19.6 mm<sup>2</sup> and an air gap of 15 mm. The central portion of the tube is packed with solid adsorbent material contained between 2  $\times$  100-mesh stainless steel gauzes and terminated with a diffusion cap at the sampling end of the tube. These axial passive samplers are installed under a protective hood during field deployment.

NOTE: Glass and glass- (or fused silica-) lined stainless steel sorbent tubes (typically 4 mm i.d.) are also available in various lengths to suit different makes of thermal desorption equipment, but these are rarely used for passive sampling because it is more difficult to adequately define the diffusive air gap in glass or glass-line tubing. Such tubes are not recommended for this method.

#### 4.0 SAMPLING INTERFERENCES

##### 4.1 GENERAL INTERFERENCES

Passive tube samplers should be sited at a distance beyond the influence of possible obstructions such as trees, walls, or buildings at the monitoring site. Complex topography and physical site obstructions, such as bodies of water, hills, buildings, and other structures that may prevent access to a planned PS location must be taken into consideration. You must document and report siting interference with the results of this method.

##### 4.2 BACKGROUND INTERFERENCE

Nearby or upwind sources of target emissions outside the facility being tested can contribute to background concentrations. Moreover, because passive samplers measure continuously, changes in wind direction can cause variation in the level of background concentrations from interfering sources during the monitoring period. This is why local

meteorological information, particularly wind direction and speed, is required to be collected throughout the monitoring period. Interfering sources can include neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, and nearby highways or roads. As PS data are evaluated, the location of potential interferences with respect to PS locations and local wind conditions should be considered, especially when high PS concentration values are observed.

##### 4.3 TUBE HANDLING

You must protect the PS tubes from gross external contamination during field sampling. Analytical thermal desorption equipment used to analyze PS tubes must desorb organic compounds from the interior of PS tubes and exclude contamination from external sampler surfaces in the analytical/sample flow path. If the analytical equipment does not comply with this requirement, you must wear clean, white, cotton or powder-free nitrile gloves to handle sampling tubes to prevent contamination of the external sampler surfaces. Sampling tubes must be capped with two-piece, brass, 0.25 inch, long-term storage caps fitted with combined polytetrafluoroethylene ferrules (see Section 6.1 and Method 325B) to prevent ingress of airborne contaminants outside the sampling period. When not being used for field monitoring, the capped tubes must be stored in a clean, air-tight, shipping container to prevent the collection of VOCs (see Section 6.4.2 of Method 325B).

##### 4.4 LOCAL WEATHER CONDITIONS AND AIRBORNE PARTICULATES

Although air speeds are a constraint for many forms of passive samplers, axial tube PS devices have such a slow inherent uptake rate that they are largely immune to these effects (References 4,5). Passive samplers must nevertheless be deployed under non-emitting weatherproof hoods to moderate the effect of local weather conditions such as solar heating and rain. The cover must not impede the ingress of ambient air. Sampling tubes should also be orientated vertically and pointing downwards, to minimize accumulation of particulates.

##### 4.5 TEMPERATURE

The normal working range for field sampling for sorbent packing is 0–40 °C (References 6,7). Note that most published passive uptake rate data for sorbent tubes is quoted at 20 °C. Note also that, as a rough guide, an increase in temperature of 10 °C will reduce the collection capacity for a given analyte on a given sorbent packing by a factor of 2, but the uptake rate will not change significantly (Reference 4).

## 5.0 SAFETY

This method does not purport to include all safety issues or procedures needed when deploying or collecting passive sampling tubes. Precautions typical of field air sampling projects are required. Tripping, falling, electrical, and weather safety considerations must all be included in plans to deploy and collect passive sampling tubes.

## 6.0 SAMPLING EQUIPMENT AND SUPPLIES, AND PRE-DEPLOYMENT PLANNING

This section describes the equipment and supplies needed to deploy passive sampling monitoring equipment at a facility property boundary. Details of the passive sampling tubes themselves and equipment required for subsequent analysis are described in Method 325B.

## 6.1 PASSIVE SAMPLING TUBES

The industry standard PS tubes used in this method must meet the specific configuration and preparation requirements described in Section 3.0 of this method and Section 6.1 of Method 325B.

**NOTE:** The use of PS tubes packed with various sorbent materials for monitoring a wide variety of organic compounds in ambient air has been documented in the literature (References 4–10). Other sorbents may be used in

standard passive sampling tubes for monitoring additional target compound(s) once their uptake rate and performance has been demonstrated following procedures in Addendum A to Method 325B. Guidance on sorbent selection can also be obtained from relevant national and international standard methods such as ASTM D6196–03 (Reapproved 2009) (Reference 14) and ISO 16017-2:2003(E) (Reference 13) (both incorporated by reference—see §63.14).

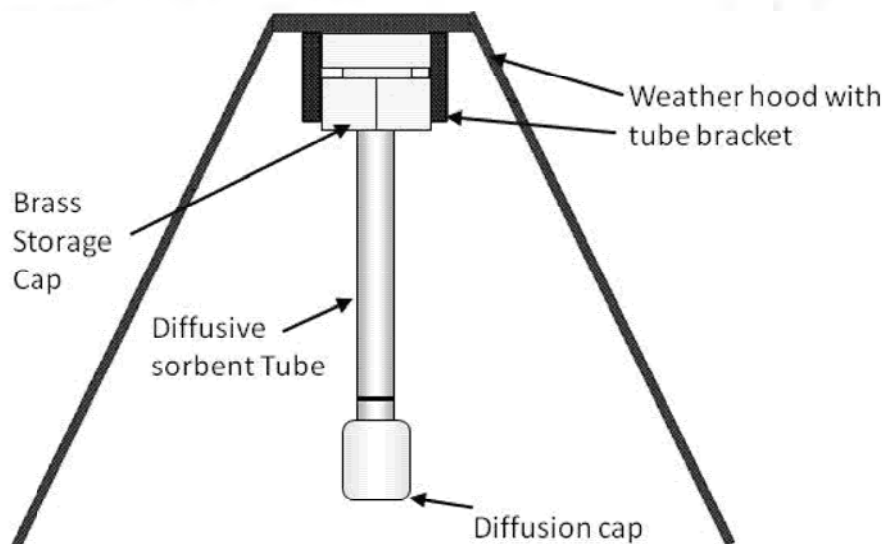
## 6.2 PASSIVE OR DIFFUSIVE SAMPLING CAP

One diffusive sampling cap is required per PS tube. The cap fits onto the sampling end of the tube during air monitoring. The other end of the tube remains sealed with the long-term storage cap. Each diffusive sampling cap is fitted with a stainless steel gauze, which defines the outer limit of the diffusion air gap.

## 6.3 SORBENT TUBE PROTECTION COVER

A simple weatherproof hood, suitable for protecting passive sampling tubes from the worst of the weather (see Section 4.4) consists of an inverted cone/funnel constructed of an inert, non-outgassing material that fits over the diffusive tube, with the open (sampling) end of the tube projecting just below the cone opening. An example is shown in Figure 6.1 (Adapted from Reference 13).





**Figure 6.1. PS Tube with Weather Protector**

#### 6.4 THERMAL DESORPTION APPARATUS

If the analytical thermal desorber that will subsequently be used to analyze the passive sampling tubes does not meet the requirement to exclude outer surface contaminants from the sample flow path (see Section 6.6 of Method 325B), then clean, white, cotton or powder-free nitrile gloves must be used for handling the passive sampling tubes during field deployment.

#### 6.5 SORBENT SELECTION

Sorbent tube configurations, sorbents or other VOC not listed in this method must be evaluated according to Method 325B, Addendum A or ISO 16017-2:2003(E) (Reference 13) (incorporated by reference—see §63.14). The supporting evaluation and verification data described in Method 325B, Addendum A for configurations or compounds different from the ones described in this method must meet the performance requirements of Method 325A/B and must be submitted with the test plan for your measurement program.

#### 7.0 REAGENTS AND STANDARDS

No reagents or standards are needed for the field deployment and collection of passive sampling tubes. Specifications for

sorbents, gas and liquid phase standards, preloaded standard tubes, and carrier gases are covered in Section 7 of Method 325B.

#### 8.0 SAMPLE DEPLOYMENT, RECOVERY, AND STORAGE

Pre-deployment and planning steps are required before field deployment of passive sampling tubes. These activities include but are not limited to conducting a site visit, determining suitable and required monitoring locations, and determining the monitoring frequency to be used.

#### 8.1 CONDUCTING THE SITE VISIT

8.1.1 Determine the size and shape of the facility footprint in order to determine the required number of monitoring locations.

8.1.2 Identify obstacles or obstructions (buildings, roads, fences), hills and other terrain issues (*e.g.*, bodies of water or swamp land) that could interfere with air parcel flow to the sampler or that prevent reasonable access to the location. You may use the general guidance in Section 4.1 of this method during the site visit to identify sampling locations. You must evaluate the placement of each passive sampler to determine if the conditions in this section are met.

8.1.3 Identify to the extent possible and record potential off-site source interferences (*e.g.*, neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, nearby highways).

8.1.4 Identify the closest available meteorological station. Identify potential locations for one or more on-site or near-site meteorological station(s) following the guidance in EPA-454/B-08-002 (Reference 11) (incorporated by reference—see §63.14).

## 8.2 DETERMINING SAMPLING LOCATIONS (REFERENCES 2, 3)

8.2.1 The number and placement of the passive samplers depends on the size, the shape of the facility footprint or the linear distance around the facility, and the proximity of emission sources near the property boundaries. Aerial photographs or site maps may be used to determine the size (acreage) and shape of the facility or the length of the monitoring perimeter. Place passive samplers on an internal monitoring perimeter on or inside the facility boundary encompassing all emission sources at the facility at different angles circling the geometric center of the facility or at different distances based on the monitoring perimeter length of the facility.

NOTE: In some instances, permanent air monitoring stations may already be located in close proximity to the facility. These stations may be operated and maintained by the

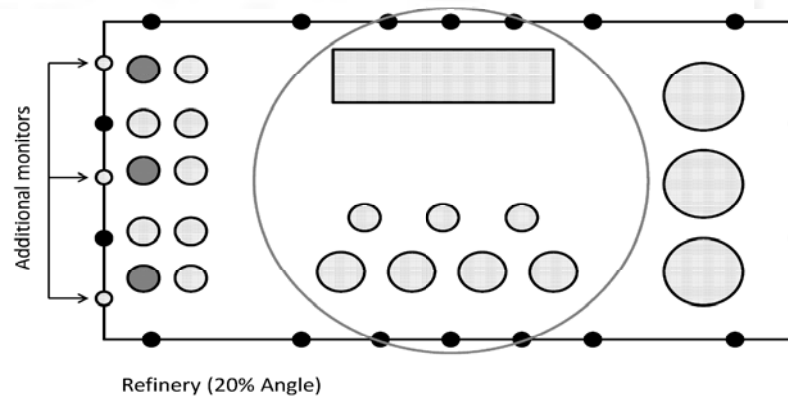
site, or local or state regulatory agencies. If access to the station is possible, a PS may be deployed adjacent to other air monitoring instrumentation. A comparison of the pollutant concentrations measured with the PS to concentrations measured by site instrumentation may be used as an optional data quality indicator to assess the accuracy of PS results.

8.2.1.1 The monitoring perimeter may be located between the property boundary and any potential emission source near the property boundary, as long as the distance from the source to the monitoring perimeter is at least 50 meters (162 feet). If a potential emissions source is within 50 meters (162 feet) of the property boundary, the property boundary shall be used as the monitoring perimeter near that source.

8.2.1.2 Samplers need only be placed around the monitoring perimeter and not along internal roads or other right of ways that may bisect the facility.

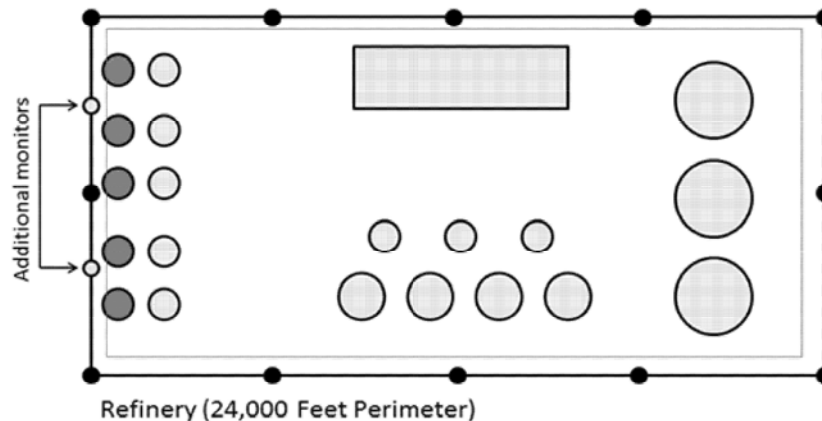
8.2.1.3 Extra samplers must be placed near known sources of VOCs if the potential emission source is within 50 meters (162 feet) of the boundary and the source location is between two monitors. Measure the distance ( $x$ ) between the two monitors and place another monitor halfway between ( $x/2$ ) the two monitors. For example, in Figure 8.1, the facility added three additional monitors (*i.e.*, light shaded sampler locations) and in Figure 8.2, the facility added two additional monitors to provide sufficient coverage of all area sources.





Note: Shaded sources are within 50 meters of the property boundary and are located between two monitors. Additional coverage required by this method was accomplished by placing the monitors halfway between two existing monitors.

**Figure 8.1. Facility with a Regular Shape Between 750 and 1,500 Acres in Area**



Note: Shaded sources are within 50 meters of the property boundary and are located between two monitors. Additional coverage required by this method was accomplished by placing the monitors halfway between two existing monitors.

**Figure 8.2. Facility with a Boundary Length of 24,000 feet**

8.2.2 Option 1 for Determining Sampling Locations.

8.2.2.1 For facilities with a regular (circular, triangular, rectangular, or square)

shape, determine the geographic center of the facility.

8.2.2.1.1 For facilities with an area of less than or equal to 750 acres, measure angles of

30 degrees from the center point for a total of twelve 30 degree measurements evenly spaced ( $\pm 1$  degree).

8.2.2.1.2 For facilities covering an area greater than 750 acres but less than or equal to 1,500 acres, measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements evenly spaced ( $\pm 1$  degree). Figure 8.1 shows the monitor placement around the property boundary of a facility with an area between 750 and 1,500 acres. Monitor placements are represented with black dots along the property boundary.

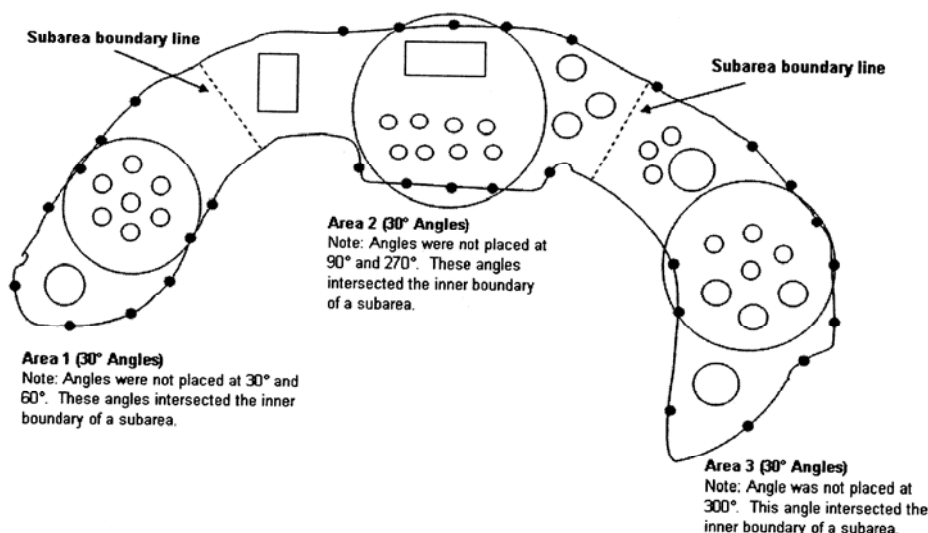
8.2.2.1.3 For facilities covering an area greater than 1,500 acres, measure angles of 15 degrees from the center point for a total of

twenty-four 15 degree measurements evenly spaced ( $\pm 1$  degree).

8.2.2.1.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter.

8.2.2.2 For irregularly shaped facilities, divide the area into a set of connecting sub-area circles, triangles or rectangles to determine sampling locations. The subareas must be defined such that a circle can reasonably encompass the subarea. Then determine the geometric center point of each of the subareas.

8.2.2.2.1 If a subarea is less than or equal to 750 acres (e.g., Figure 8.3), measure angles of 30 degrees from the center point for a total of twelve 30 degree measurements ( $\pm 1$  degree).



**Figure 8.3. Facility Divided into Three Subareas**

8.2.2.2.2 If a subarea is greater than 750 acres but less than or equal to 1,500 acres (e.g., Figure 8.4), measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements ( $\pm 1$  degree).

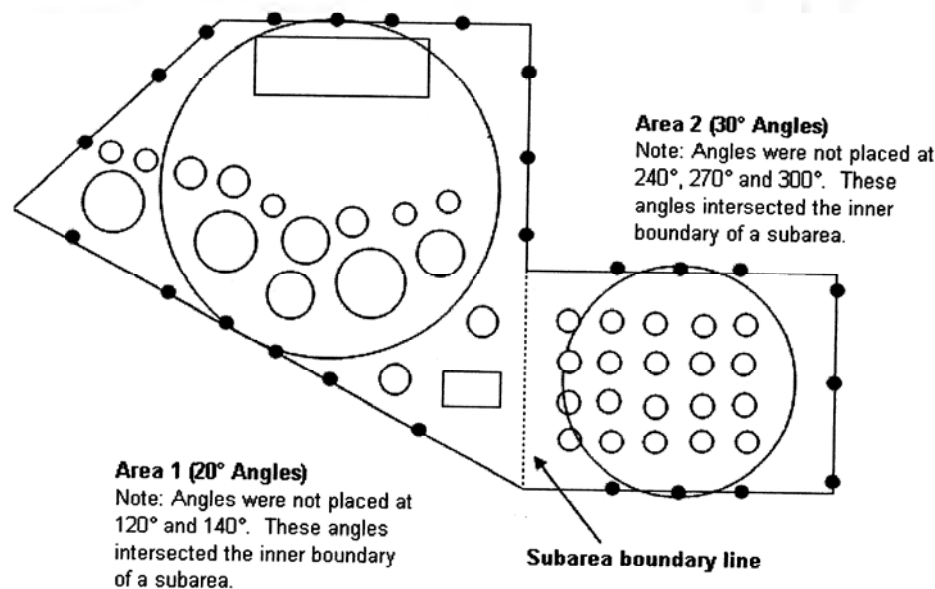
8.2.2.2.3 If a subarea is greater than 1,500 acres, measure angles of 15 degrees from the center for a total of twenty-four 15 degree measurements ( $\pm 1$  degree).

8.2.2.2.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter. Sampling points need not be placed closer than 152 meters (500 feet)

apart (or 76 meters (250 feet) if known sources are within 50 meters (162 feet) of the monitoring perimeter), as long as a minimum of 3 monitoring locations are used for each subarea.

8.2.2.2.5 Sampling sites are not needed at the intersection of an inner boundary with an adjacent subarea. The sampling location must be sited where the measured angle intersects the subarea's outer monitoring perimeter.





**Figure 8.4. Facility Divided into Two Subareas**

#### 8.2.3 Option 2 for Determining Sampling Locations.

8.2.3.1 For facilities with a monitoring perimeter length of less than 7,315 meters (24,000 feet), a minimum of twelve sampling locations evenly spaced  $\pm 10$  percent of the location interval is required.

8.2.3.2 For facilities with a monitoring perimeter length greater than 7,315 meters (24,000 feet), sampling locations are spaced  $610 \pm 75$  meters ( $2,000 \pm 250$  feet) apart.

#### 8.3 SITING A METEOROLOGICAL STATION

A meteorological station is required at or near the facility you are monitoring. A number of commercially available meteorological stations can be used. Information on meteorological instruments can be found in EPA-454/R-99-005 (Reference 11) (incorporated by reference—see §63.14). Some important considerations for siting of meteorological stations are detailed below.

8.3.1 Place meteorological stations in locations that represent conditions affecting the transport and dispersion of pollutants in the area of interest. Complex terrain may require the use of more than one meteorological station.

8.3.2 Deploy wind instruments over level, open terrain at a height of 10 meters (33 feet). If possible, locate wind instruments at a distance away from nearby structures that

is equal to at least 10 times the height of the structure.

8.3.3 Protect meteorological instruments from thermal radiation and adequately ventilate them using aspirated shields. The temperature sensor must be located at a distance away from any nearby structures that is equal to at least four times the height of the structure. Temperature sensors must be located at least 30 meters (98 feet) from large paved areas.

8.3.4 Collect and record meteorological data, including wind speed, wind direction, temperature and barometric pressure on an hourly basis. Calculate average unit vector wind direction, sigma theta, temperature and barometric pressure per sampling period to enable calculation of concentrations at standard conditions. Supply this information to the laboratory.

8.3.5 Identify and record the location of the meteorological station by its GPS coordinate.

#### 8.4 MONITORING FREQUENCY

8.4.1 Sample collection may be performed for periods up to 14 days.

8.4.2 A site screening protocol that meets method requirements may be performed by collecting samples for a year where each PS accumulates VOC for a 14-day sampling period. Study results are accumulated for the sampling periods (typically 26) over the

course of one calendar year. To the extent practical, sampling tubes should be changed at approximately the same time of day at each of the monitoring sites.

#### 8.5 PASSIVE SAMPLER DEPLOYMENT

8.5.1 Clean (conditioned) sorbent tubes must be prepared and packaged by the laboratory as described in Method 325B and must be deployed for sampling within 30 days of conditioning.

8.5.2 Allow the tubes to equilibrate with ambient temperature (approximately 30 minutes to 1 hour) at the monitoring location before removing them from their storage/shipping container for sample collection.

8.5.3 If there is any risk that the analytical equipment will not meet the requirement to exclude contamination on outer tube surfaces from the sample flow path (see Section 6.6 of Method 325B), sample handlers must wear clean, white, cotton or powder-free nitrile gloves during PS deployment and collection and throughout any other tube handling operations.

8.5.4 Inspect the sampling tubes immediately prior to deployment. Ensure that they are intact, securely capped, and in good condition. Any suspect tubes (*e.g.*, tubes that appear to have leaked sorbent) should be removed from the sampling set.

8.5.5 Secure passive samplers so the bottom of the diffusive sampling cap is 1.5 to 3 meters (4.9 to 9.8 feet) above ground using a pole or other secure structure at each sampling location. Orient the PS vertically and with the sampling end pointing downward to avoid ingress of particulates.

NOTE: Duplicate sampling assemblies must be deployed in at least one monitoring location for every 10 monitoring locations during each field monitoring period.

8.5.6 Protect the PS from rain and excessive wind velocity by placing them under the type of protective hood described in Section 6.1.3 or equivalent.

8.5.7 Remove the storage cap on the sampling end of the tube and replace it with a diffusive sampling cap at the start of the sampling period. Make sure the diffusion cap is properly seated and store the removed storage caps in the empty tube shipping container.

8.5.8 Record the start time and location details for each sampler on the field sample data sheet (see example in Section 17.0.).

8.5.9 Expose the sampling tubes for the required sampling period—normally 14-days.

8.5.10 Field blank tubes (see Section 9.3 of Method 325B) are stored outside the shipping container at representative sampling locations around the site, but with both long-term storage caps kept in place throughout the monitoring exercise. Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment, collection, and storage.

#### 8.6 SORBENT TUBE RECOVERY AND METEOROLOGICAL DATA COLLECTION

Recover deployed sampling tubes and field blanks as follows:

8.6.1 After the sampling period is complete, immediately replace the diffusion end cap on each sampled tube with a long-term storage end cap. Tighten the seal securely by hand and then tighten an additional quarter turn with an appropriate tool. Record the stop date and time and any additional relevant information on the sample data sheet.

8.6.2 Place the sampled tubes, together with the field blanks, in the storage/shipping container. Label the storage container, but do not use paints, markers, or adhesive labels to identify the tubes. TD-compatible electronic (radio frequency identification (RFID)) tube labels are available commercially and are compatible with some brands of thermal desorber. If used, these may be programmed with relevant tube and sample information, which can be read and automatically transcribed into the sequence report by the TD system.

NOTE: Sampled tubes must not be placed in the same shipping container as clean conditioned sampling tubes.

8.6.3 Sampled tubes may be shipped at ambient temperature to a laboratory for sample analysis.

8.6.4 Specify whether the tubes are field blanks or were used for sampling and document relevant information for each tube using a Chain of Custody form (see example in Section 17.0) that accompanies the samples from preparation of the tubes through receipt for analysis, including the following information: Unique tube identification numbers for each sampled tube; the date, time, and location code for each PS placement; the date, time, and location code for each PS recovery; the GPS reference for each sampling location; the unique identification number of the duplicate sample (if applicable); and problems or anomalies encountered.

8.6.5 If the sorbent tubes are supplied with electronic (*e.g.*, RFID) tags, it is also possible to allocate a sample identifier to each PS tube. In this case, the recommended format for the identification number of each sampled tube is AA-BB-CC-DD-VOC, where:

AA = Sequence number of placement on route (01, 02, 03 . . .)

BB = Sampling location code (01, 02, 03 . . .)

CC = 14-day sample period number (01 to 26)

DD = Sample code (SA = sample, DU = duplicate, FB = field blank)

VOC = 3-letter code for target compound(s) (*e.g.*, BNZ for benzene or BTX for benzene, toluene, and xylenes)

NOTE: Sampling start and end times/dates can also be logged using RFID tube tags.



## 9.0 QUALITY CONTROL

9.1 Most quality control checks are carried out by the laboratory and associated requirements are in Section 9.0 of Method 325B, including requirements for laboratory blanks, field blanks, and duplicate samples.

9.2 Evaluate for potential outliers the laboratory results for neighboring sampling tubes collected over the same time period. A potential outlier is a result for which one or more PS tube does not agree with the trend in results shown by neighboring PS tubes—particularly when data from those locations have been more consistent during previous sampling periods. Accidental contamination by the sample handler must be documented before any result can be eliminated as an outlier. Rare but possible examples of contamination include loose or missing storage caps or contaminated storage/shipping containers. Review data from the same and neighboring monitoring locations for the subsequent sampling periods. If the anomalous result is not repeated for that monitoring location, the episode can be ascribed to transient contamination and the data in question must be flagged for potential elimination from the dataset.

## 9.3 DUPLICATES AND FIELD BLANKS

9.3.1 Collect at least one co-located/duplicate sample for every 10 field samples to determine precision of the measurements.

9.3.2 Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment,

collection, and storage. You must use the entire sampling apparatus for field blanks including unopened sorbent tubes mounted in protective sampling hoods. The tube closures must not be removed. Field blanks must be placed in two different quadrants (*e.g.*, 90° and 270°) and remain at the sampling location for the sampling period.

## 10.0 CALIBRATION AND STANDARDIZATION

Follow the calibration and standardization procedures for meteorological measurements in EPA-454/B-08-002 March 2008 (Reference 11) (incorporated by reference—see §63.14). Refer to Method 325B for calibration and standardization procedures for analysis of the passive sampling tubes.

## 11.0 ANALYTICAL PROCEDURES

Refer to Method 325B, which provides details for the preparation and analysis of sampled passive monitoring tubes (preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes).

## 12.0 DATA ANALYSIS, CALCULATIONS AND DOCUMENTATION

## 12.1 CALCULATE ANNUAL AVERAGE FENCELINE CONCENTRATION.

After a year's worth of sampling at the facility fence line (for example, 26 14-day samples), the average ( $PS_i$ ) may be calculated for any specified period at each PS location using Equation 12.1.

$$PS_i = \frac{\sum PS_{ip}}{N} \quad \text{Eq. 12.1}$$

Where:

$PS_i$  = Annual average for location  $i$ .

$PS_{ip}$  = Sampling period specific concentration from Method 325B.

$i$  = Location of passive sampler (0 to 360°).

$p$  = The sampling period.

$N$  = The number of sampling periods in the year (*e.g.*, for 14-day sampling periods, from 1 to 26).

NOTE:  $PS_{ip}$  is a function of sampling location-specific factors such as the contribution from facility sources, unusual localized meteorological conditions, contribution from nearby interfering sources, the background caused by integrated far-field sources and measurement error due to deployment, handling, siting, or analytical errors.

## 12.2 IDENTIFY SAMPLING LOCATIONS OF INTEREST

If data from neighboring sampling locations are significantly different, then you may add extra sampling points to isolate background contributions or identify facility-specific "hot spots."

## 12.3 EVALUATE TRENDS

You may evaluate trends and patterns in the PS data over multiple sampling periods to determine if elevated concentrations of target compounds are due to operations on the facility or if contributions from background sources are significant.

12.3.1 Obtain meteorological data including wind speed and wind direction or unit vector wind data from the on-site meteorological station. Use this meteorological data to determine the prevailing wind direction

and speed during the periods of elevated concentrations.

12.3.2 As an option you may perform preliminary back trajectory calculations (<http://ready.url.noaa.gov/HYSPLIT.php>) to aid in identifying the source of the background contribution to elevated target compound concentrations.

12.3.3 Information on published or documented events on- and off-site may also be included in the associated sampling period report to explain elevated concentrations if relevant. For example, you would describe if there was a chemical spill on site, or an accident on an adjacent road.

12.3.4 Additional monitoring for shorter periods (See section 8.4) may be necessary to allow better discrimination/resolution of contributing emission sources if the measured trends and associated meteorology do not provide a clear assessment of facility contribution to the measured fence-line concentration.

12.3.5 Additional records necessary to calculate sampling period average target compound concentration can be found in Section 12.1 of Method 325B.

### 13.0 METHOD PERFORMANCE

Method performance requirements are described in Method 325B.

### 14.0 POLLUTION PREVENTION

[Reserved]

### 15.0 WASTE MANAGEMENT

[Reserved]

### 16.0 REFERENCES

1. Ambient air quality—Standard method for measurement of benzene concentrations—Part 4: Diffusive sampling followed by thermal desorption and gas chromatography. BS EN 14662-4:2005.
2. Thoma, E.D., Miller, C.M., Chung, K.C., Parsons, N.L. and Shine, B.C. Facility Fence Line Monitoring using Passive Samplers. J. Air & Waste Manage. Assoc. 2011, 61:834–842.
3. Quality Assurance Handbook for Air Pollution C Systems. Volume II: Ambient Air Quality Monitoring Program, EPA-454/B-13-003, May 2013. Available at <http://www.epa.gov/ttnamtl1/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf>.
4. Brown, R.H., Charlton, J. and Saunders, K.J.: The development of an improved diffusive sampler. Am. Ind. Hyg. Assoc. J. 1981, 42(12): 865–869.
5. Brown, R. H. Environmental use of diffusive samplers: evaluation of reliable diffusive uptake rates for benzene, toluene and xylene. J. Environ. Monit. 1999, 1 (1), 115–116.
6. Ballach, J.; Greuter, B.; Schultz, E.; Jaeschke, W. Variations of uptake rates in benzene diffusive sampling as a function of ambient conditions. Sci. Total Environ. 1999, 244, 203–217.
7. Brown, R. H. Monitoring the ambient environment with diffusive samplers: theory and practical considerations. J Environ. Monit. 2000, 2 (1), 1–9.
8. Buzica, D.; Gerboles, M.; Plaisance, H. The equivalence of diffusive samplers to reference methods for monitoring O<sub>3</sub>, benzene and NO<sub>2</sub> in ambient air. J. Environ. Monit. 2008, 10 (9), 1052–1059.
9. Woolfenden, E. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. J. Chromatogr. A 2010, 1217, (16), 2685–94.
10. Pfeffer, H. U.; Breuer, L. BTX measurements with diffusive samplers in the vicinity of a cokery: Comparison between ORSA-type samplers and pumped sampling. J. Environ. Monit. 2000, 2 (5), 483–486.
11. US EPA. 2000. Meteorological Monitoring Guidance for Regulatory Modeling Applications. EPA-454/R-99-005. Office of Air Quality Planning and Standards, Research Triangle Park, NC. February 2000. Available at <http://www.epa.gov/scram001/guidance/met/mmgrma.pdf>.
12. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV: Meteorological Measurements Version 2.0 Final. EPA-454/B-08-002 March 2008. Available at [http://www.epa.gov/ttnamtl1/files/ambient/met/Volume%20IV\\_Meteorological\\_Measurements.pdf](http://www.epa.gov/ttnamtl1/files/ambient/met/Volume%20IV_Meteorological_Measurements.pdf).
13. ISO 16017-2:2003(E). Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling.
14. ASTM D6196-03 (Reapproved 2009): Standard practice for selection of sorbents, sampling, and thermal desorption analysis procedures for volatile organic compounds in air.

### 17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

Environmental Protection Agency

Pt. 63, App. A

Method 325 A/B

EXAMPLE FIELD TEST DATA SHEET (FTDS)  
AND  
CHAIN OF CUSTODY

I. GENERAL INFORMATION

SITE NAME: \_\_\_\_\_

SITE LOCATION ADDRESS: \_\_\_\_\_

CITY: \_\_\_\_\_ STATE: \_\_\_\_\_ ZIP: \_\_\_\_\_

II. SAMPLING DATA

Sample ID (Tube) #	Sorbent	Sample or blank	Start Date	Start Time	Stop Date	Stop Time	Location (gps)	Ambient Temp. (°F)	Barometric Pressure (in. Hg)

III. CUSTODY INFORMATION

COLLECTED BY: \_\_\_\_\_

Relinquished to Shipper -

Name: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Received by Laboratory -

Name: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Sample condition upon receipt: \_\_\_\_\_

Analysis Required: \_\_\_\_\_

Comments: \_\_\_\_\_

Figure 17.1. Example Field Data Form and Chain of Custody



METHOD 325B—VOLATILE ORGANIC COMPOUNDS  
FROM FUGITIVE AND AREA SOURCES:

## SAMPLER PREPARATION AND ANALYSIS

## 1.0 SCOPE AND APPLICATION

1.1 This method describes thermal desorption/gas chromatography (TD/GC) analysis of volatile organic compounds (VOCs) from fugitive and area emission sources collected onto sorbent tubes using passive sampling. It could also be applied to the TD/GC analysis of VOCs collected using active (pumped) sampling onto sorbent tubes. The concentration of airborne VOCs at or near potential fugitive- or area-emission sources may be determined using this method in combination with Method 325A. Companion Method 325A (Sampler Deployment and VOC Sample Collection) describes procedures for deploying the sorbent tubes and passively collecting VOCs.

1.2 The preferred GC detector for this method is a mass spectrometer (MS), but flame ionization detectors (FID) may also be used. Other conventional GC detectors such as electron capture (ECD), photoionization (PID), or flame photometric (FPD) may also be used if they are selective and sensitive to the target compound(s) and if they meet the method performance criteria provided in this method.

1.3 There are 97 VOCs listed as hazardous air pollutants in Title III of the Clean Air Act Amendments of 1990. Many of these VOC are candidate compounds for this method. Compounds with known uptake rates for Carbigraph™ 1 TD, Carbopack™ B, or Carbopack™ X are listed in Table 12.1. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring one or more of the compounds listed Table 12.1. If standard passive sampling tubes are packed with other sorbents or used for other analytes than those listed in Table 12.1, then method performance and relevant uptake rates should be verified according to Addendum A to this method or by one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see § 63.14), or reported in the peer-reviewed open literature.

1.4 The analytical approach using TD/GC/MS is based on previously published EPA guidance in Compendium Method TO-17 (<http://www.epa.gov/ttnamti1/airtox.html#compendium>) (Reference 1), which describes active (pumped) sampling of VOCs from ambient air onto tubes packed with thermally stable adsorbents.

1.5 Inorganic gases not suitable for analysis by this method include oxides of carbon, nitrogen and sulfur, ozone (O<sub>3</sub>), and other diatomic permanent gases. Other pollutants

not suitable for this analysis method include particulate pollutants, (i.e., fumes, aerosols, and dusts), compounds too labile (reactive) for conventional GC analysis, and VOCs that are more volatile than propane.

## 2.0 SUMMARY OF METHOD

2.1 This method provides procedures for the preparation, conditioning, blanking, and shipping of sorbent tubes prior to sample collection.

2.2 Laboratory and field personnel must have experience of sampling trace-level VOCs using sorbent tubes (References 2,5) and must have experience operating thermal desorption/GC/multi-detector instrumentation.

2.3 Key steps of this method as implemented for each sample tube include: Stringent leak testing under stop flow, recording ambient temperature conditions, adding internal standards, purging the tube, thermally desorbing the sampling tube, refocusing on a focusing trap, desorbing and transferring/injecting the VOCs from the secondary trap into the capillary GC column for separation and analysis.

2.4 Water management steps incorporated into this method include: (a) Selection of hydrophobic sorbents in the sampling tube; (b) optional dry purging of sample tubes prior to analysis; and (c) additional selective elimination of water during primary (tube) desorption (if required) by selecting trapping sorbents and temperatures such that target compounds are quantitatively retained while water is purged to vent.

## 3.0 DEFINITIONS

(See also Section 3.0 of Method 325A).

3.1 Blanking is the desorption and confirmatory analysis of conditioned sorbent tubes before they are sent for field sampling.

3.2 *Breakthrough volume and associated relation to passive sampling.* Breakthrough volumes, as applied to active sorbent tube sampling, equate to the volume of air containing a constant concentration of analyte that may be passed through a sorbent tube at a given temperature before a detectable level (5 percent) of the input analyte concentration elutes from the tube. Although breakthrough volumes are directly related to active rather than passive sampling, they provide a measure of the strength of the sorbent-sorbate interaction and therefore also relate to the efficiency of the passive sampling process. The best direct measure of passive sampling efficiency is the stability of the uptake rate. Quantitative passive sampling is compromised when the sorbent no longer acts as a perfect sink—i.e., when the concentration of a target analyte immediately above the sorbent sampling surface no longer approximates to zero. This causes a reduction in the uptake rate over time. If

the uptake rate for a given analyte on a given sorbent tube remains relatively constant—i.e., if the uptake rate determined for 48 hours is similar to that determined for 7 or 14 days—the user can be confident that passive sampling is occurring at a constant rate. As a general rule of thumb, such ideal passive sampling conditions typically exist for analyte:sorbent combinations where the breakthrough volume exceeds 100 L (Reference 4).

3.3 *Continuing calibration verification sample (CCV).* Single level calibration samples run periodically to confirm that the analytical system continues to generate sample results within acceptable agreement to the current calibration curve.

3.4 *Focusing trap* is a cooled, secondary sorbent trap integrated into the analytical thermal desorber. It typically has a smaller i.d. and lower thermal mass than the original sample tube allowing it to effectively refocus desorbed analytes and then heat rapidly to ensure efficient transfer/injection into the capillary GC analytical column.

3.5 *High Resolution Capillary Column Chromatography* uses fused silica capillary columns with an inner diameter of 320  $\mu\text{m}$  or less and with a stationary phase film thickness of 5  $\mu\text{m}$  or less.

3.6 *h* is time in hours.

3.7 *i.d.* is inner diameter.

3.8 *min* is time in minutes.

3.9 *Method Detection Limit* is the lowest level of analyte that can be detected in the sample matrix with 99% confidence.

3.10 *MS-SCAN* is the mode of operation of a GC quadrupole mass spectrometer detector that measures all ions over a given mass range over a given period of time.

3.11 *MS-SIM* is the mode of operation of a GC quadrupole mass spectrometer detector that measures only a single ion or a selected number of discrete ions for each analyte.

3.12 *o.d.* is outer diameter.

3.13 *ppbv* is parts per billion by volume.

3.14 *Thermal desorption* is the use of heat and a flow of inert (carrier) gas to extract volatiles from a solid matrix. No solvent is required.

3.15 *Total ion chromatogram* is the chromatogram produced from a mass spectrometer detector collecting full spectral information.

3.16 *Two-stage thermal desorption* is the process of thermally desorbing analytes from a sorbent tube, reconcentrating them on a focusing trap (see Section 3.4), which is then itself rapidly heated to "inject" the concentrated compounds into the GC analyzer.

3.17 *VOC* is volatile organic compound.

#### 4.0 ANALYTICAL INTERFERENCES

4.1 *Interference from Sorbent Artifacts.* Artifacts may include target analytes as well as other VOC that co-elute chromatographically with the compounds of

interest or otherwise interfere with the identification or quantitation of target analytes.

4.1.1 *Sorbent decomposition artifacts* are VOCs that form when sorbents degenerate, e.g., when exposed to reactive species during sampling. For example, benzaldehyde, phenol, and acetophenone artifacts are reported to be formed via oxidation of the polymeric sorbent Tenax® when sampling high concentration (100–500 ppb) ozone atmospheres (Reference 5).

4.1.2 *Preparation and storage artifacts* are VOCs that were not completely cleaned from the sorbent tube during conditioning or that are an inherent feature of that sorbent at a given temperature.

4.2 *Humidity.* Moisture captured during sampling can interfere with VOC analysis. Passive sampling using tubes packed with hydrophobic sorbents, like those described in this method, minimizes water retention. However, if water interference is found to be an issue under extreme conditions, one or more of the water management steps described in Section 2.4 can be applied.

4.3 *Contamination from Sample Handling.* The type of analytical thermal desorption equipment selected should exclude the possibility of outer tube surface contamination entering the sample flow path (see Section 6.6). If the available system does not meet this requirement, sampling tubes and caps must be handled only while wearing clean, white cotton or powder free nitrile gloves to prevent contamination with body oils, hand lotions, perfumes, etc.

#### 5.0 SAFETY

5.1 This method does not address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate field and laboratory safety and health practices prior to use.

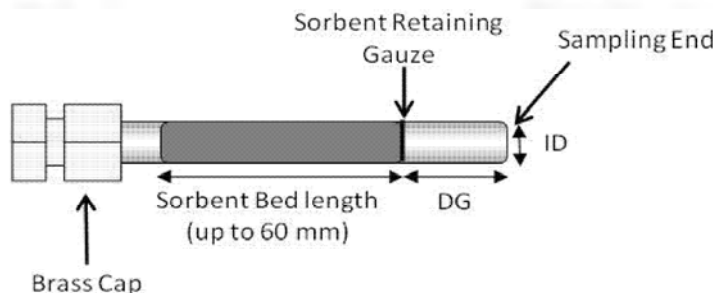
5.2 Laboratory analysts must exercise extreme care in working with high-pressure gas cylinders.

5.3 Due to the high temperatures involved, operators must use caution when conditioning and analyzing tubes.

#### 6.0 EQUIPMENT AND SUPPLIES

6.1 *Tube Dimensions and Materials.* The sampling tubes for this method are 3.5-inches (89 mm) long, 1/4 inch (6.4 mm) o.d., and 5 mm i.d. passive sampling tubes (see Figure 6.1). The tubes are made of inert-coated stainless steel with the central section (up to 60 mm) packed with sorbent, typically supported between two 100 mesh stainless steel gauze. The tubes have a cross sectional area of 19.6 square mm (5 mm i.d.). When used for passive sampling, these tubes have an internal diffusion (air) gap (DG) of 1.5 cm between the sorbent retaining gauze at the sampling end of the tube, and the gauze in the diffusion cap.





**Figure 6.1. Cross Section View of Passive Sorbent Tube**

#### 6.2 TUBE CONDITIONING APPARATUS

6.2.1 Freshly packed or newly purchased tubes must be conditioned as described in Section 9 using an appropriate dedicated tube conditioning unit or the thermal desorber. Note that the analytical TD system should be used for tube conditioning if it supports a dedicated tube conditioning mode in which effluent from contaminated tubes is directed to vent without passing through key parts of the sample flow path such as the focusing trap.

6.2.2 Dedicated tube conditioning units must be leak-tight to prevent air ingress, allow precise and reproducible temperature selection ( $\pm 5^\circ\text{C}$ ), offer a temperature range at least as great as that of the thermal desorber, and support inert gas flows in the range up to 100 mL/min.

NOTE: For safety and to avoid laboratory contamination, effluent gases from freshly packed or highly contaminated tubes should be passed through a charcoal filter during the conditioning process to prevent desorbed VOCs from polluting the laboratory atmosphere.

#### 6.3 TUBE LABELING

6.3.1 Label the sample tubes with a unique permanent identification number and an indication of the sampling end of the tube. Labeling options include etching and TD-compatible electronic (radio frequency identification (RFID)) tube labels.

6.3.2 To avoid contamination, do not make ink markings of any kind on clean sorbent tubes or apply adhesive labels.

NOTE: TD-compatible electronic (RFID) tube labels are available commercially and are compatible with some brands of thermal desorber. If used, these may be programmed with relevant tube and sample information, which can be read and automatically transcribed into the sequence report by the TD system (see Section 8.6 of Method 325A).

#### 6.4 BLANK AND SAMPLED TUBE STORAGE APPARATUS

6.4.1 Long-term storage caps. Seal clean, blank and sampled sorbent tubes using inert, long-term tube storage caps comprising non-greased, 2-piece, 0.25-inch, metal SwageLok®-type screw caps fitted with combined polytetrafluoroethylene ferrules.

6.4.2 Storage and transportation containers. Use clean glass jars, metal cans or rigid, non-emitting polymer boxes.

NOTE: You may add a small packet of new activated charcoal or charcoal/silica gel to the shipping container for storage and transportation of batches of conditioned sorbent tubes prior to use. Coolers without ice packs make suitable shipping boxes for containers of tubes because the coolers help to insulate the samples from extreme temperatures (*e.g.*, if left in a parked vehicle).

#### 6.5 UNHEATED GC INJECTION UNIT FOR LOADING STANDARDS ONTO BLANK TUBES

A suitable device has a simple push fit or finger-tightening connector for attaching the sampling end of blank sorbent tubes without damaging the tube. It also has a means of controlling carrier gas flow through the injector and attached sorbent tube at 50-100 mL/min and includes a low emission septum cap that allows the introduction of gas or liquid standards via appropriate syringes. Reproducible and quantitative transfer of higher boiling compounds in liquid standards is facilitated if the injection unit allows the tip of the syringe to just touch the sorbent retaining gauze inside the tube.

#### 6.6 THERMAL DESORPTION APPARATUS

The manual or automated thermal desorption system must heat sorbent tubes while a controlled flow of inert (carrier) gas passes through the tube and out of the sampling end. The apparatus must also incorporate a focusing trap to quantitatively



refocus compounds desorbed from the tube. Secondary desorption of the focusing trap should be fast/efficient enough to transfer the compounds into the high resolution capillary GC column without band broadening and without any need for further pre- or on-column focusing. Typical TD focusing traps comprise small sorbent traps (Reference 16) that are electrically-cooled using multistage Peltier cells (References 17, 18). The direction of gas flow during trap desorption should be the reverse of that used for focusing to extend the compatible analyte volatility range. Closed cycle coolers offer another cryogen-free trap cooling option. Other TD system requirements and operational stages are described in Section 11 and in Figures 17-2 through 17-4.

#### 6.7 THERMAL DESORBER—GC INTERFACE

6.7.1 The interface between the thermal desorber and the GC must be heated uniformly and the connection between the transfer line insert and the capillary GC analytical column itself must be leak tight.

6.7.2 A portion of capillary column can alternatively be threaded through the heated transfer line/TD interface and connected directly to the thermal desorber.

NOTE: Use of a metal syringe-type needle or unheated length of fused silica pushed through the septum of a conventional GC injector is not permitted as a means of interfacing the thermal desorber to the chromatograph. Such connections result in cold spots, cause band broadening and are prone to leaks.

#### 6.8 GC/MS ANALYTICAL COMPONENTS

6.8.1 The GC system must be capable of temperature programming and operation of a high resolution capillary column. Depending on the choice of column (*e.g.*, film thickness) and the volatility of the target compounds, it may be necessary to cool the GC oven to subambient temperatures (*e.g.*, -50 °C) at the start of the run to allow resolution of very volatile organic compounds.

6.8.2 All carrier gas lines supplying the GC must be constructed from clean stainless steel or copper tubing. Non-polytetrafluoroethylene thread sealants, flow controllers, cylinder regulators, or other pneumatic components fitted with rubber components are not suitable.

#### 6.9 CHROMATOGRAPHIC COLUMNS

High-resolution, fused silica or equivalent capillary columns that provide adequate separation of sample components to permit identification and quantitation of target compounds must be used.

NOTE: 100-percent methyl silicone or 5-percent phenyl, 95-percent methyl silicone fused silica capillary columns of 0.25- to 0.32-mm i.d. of varying lengths and with varying

thicknesses of stationary phase have been used successfully for non-polar and moderately polar compounds. However, given the diversity of potential target lists, GC column choice is left to the operator, subject to the performance criteria of this method.

#### 6.10 MASS SPECTROMETER

Linear quadrupole, magnetic sector, ion trap or time-of-flight mass spectrometers may be used provided they meet specified performance criteria. The mass detector must be capable of collecting data from 35 to 300 atomic mass units (amu) every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode, and producing a mass spectrum that meets all the instrument performance acceptance criteria in Section 9 when 50 ng or less of p-bromofluorobenzene is analyzed.

#### 7.0 REAGENTS AND STANDARDS

##### 7.1 SORBENT SELECTION

7.1.1 Use commercially packed tubes meeting the requirements of this method or prepare tubes in the laboratory using sieved sorbents of particle size in the range 20 to 80 mesh that meet the retention and quality control requirements of this method.

7.1.2 This passive air monitoring method can be used without the evaluation specified in Addendum A if the type of tubes described in Section 6.1 are packed with 4-6 cm (typically 400-650 mg) of the sorbents listed in Table 12.1 and used for the respective target analytes.

NOTE: Although Carboxpack™ X is the optimum sorbent choice for passive sampling of 1,3-butadiene, recovery of compounds with vapor pressure lower than benzene may be difficult to achieve without exceeding sorbent maximum temperature limitations (see Table 8.1). See ISO 16017-2:2003(E) or ASTM D6196-03 (Reapproved 2009) (both incorporated by reference—see §63.14) for more details on sorbent choice for air monitoring using passive sampling tubes.

7.1.3 If standard passive sampling tubes are packed with other sorbents or used for analytes other than those tabulated in Section 12.0, method performance and relevant uptake rates should be verified according to Addendum A to this method or by following the techniques described in one of the following national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14)—or reported in the peer-reviewed open literature. A summary table and the supporting evaluation data demonstrating the selected sorbent meets the requirements in Addendum A to this method must be submitted to the regulatory authority as part of a request to use an alternative sorbent.

7.1.4 Passive (diffusive) sampling and thermal desorption methods that have been evaluated at relatively high atmospheric concentrations (*i.e.*, mid-ppb to ppm) and published for use in workplace air and industrial/mobile source emissions testing (References 9-20) may be applied to this procedure. However, the validity of any shorter term uptake rates must be verified and adjusted if necessary for the longer monitoring periods required by this method by following procedures described in Addendum A to this method or those presented in national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14).

7.1.5 Suitable sorbents for passive sampling must have breakthrough volumes of at least 20 L (preferably >100 L) for the compounds of interest and must quantitatively release the analytes during desorption without exceeding maximum temperatures for the sorbent or instrumentation.

7.1.6 Repack/replace the sorbent tubes or demonstrate tube performance following the requirements in Addendum A to this method at least every 2 years or every 50 uses, whichever occurs first.

## 7.2 GAS PHASE STANDARDS

7.2.1 Static or dynamic standard atmospheres may be used to prepare calibration tubes and/or to validate passive sampling uptake rates and can be generated from pure chemicals or by diluting concentrated gas standards. The standard atmosphere must be stable at ambient pressure and accurate to  $\pm 10$  percent of the target gas concentration. It must be possible to maintain standard atmosphere concentrations at the same or lower levels than the target compound concentration objectives of the test. Test atmospheres used for validation of uptake rates must also contain at least 35 percent relative humidity.

NOTE: Accurate, low-(ppb-) level gas-phase VOC standards are difficult to generate from pure materials and may be unstable depending on analyte polarity and volatility. Parallel monitoring of vapor concentrations with alternative methods, such as pumped sorbent tubes or sensitive/selective on-line detectors, may be necessary to minimize uncertainty. For these reasons, standard atmospheres are rarely used for routine calibration.

7.2.2 Concentrated, pressurized gas phase standards. Accurate ( $\pm 5$  percent or better), concentrated gas phase standards supplied in pressurized cylinders may also be used for calibration. The concentration of the standard should be such that a 0.5–5.0 mL volume contains approximately the same mass of analytes as will be collected from a typical air sample.

7.2.3 Follow manufacturer's guidelines concerning storage conditions and recertification of the concentrated gas phase standard. Gas standards must be recertified a minimum of once every 12 months.

## 7.3 LIQUID STANDARDS

Target analytes can also be introduced to the sampling end of sorbent tubes in the form of liquid calibration standards.

7.3.1 The concentration of liquid standards must be such that an injection of 0.5–2  $\mu$ L of the solution introduces the same mass of target analyte that is expected to be collected during the passive air sampling period.

7.3.2 Solvent Selection. The solvent selected for the liquid standard must be pure (contaminants <10 percent of minimum analyte levels) and must not interfere chromatographically with the compounds of interest.

7.3.3 If liquid standards are sourced commercially, follow manufacturer's guidelines concerning storage conditions and shelf life of unopened and opened liquid stock standards.

NOTE: Commercial VOC standards are typically supplied in volatile or non-interfering solvents such as methanol.

7.3.4 Working standards must be stored at 6 °C or less and used or discarded within two weeks of preparation.

## 7.4 GAS PHASE INTERNAL STANDARDS

7.4.1 Gas-phase deuterated or fluorinated organic compounds may be used as internal standards for MS-based systems.

7.4.2 Typical compounds include deuterated toluene, perfluorobenzene and perfluorotoluene.

7.4.3 Use multiple internal standards to cover the volatility range of the target analytes.

7.4.4 Gas-phase standards must be obtained in pressurized cylinders and containing vendor certified gas concentrations accurate to  $\pm 5$  percent. The concentration should be such that the mass of internal standard components introduced is similar to those of the target analytes collected during field monitoring.

## 7.5 PRELOADED STANDARD TUBES

Certified, preloaded standard tubes, accurate within  $\pm 5$  percent for each analyte at the microgram level and  $\pm 10$  percent at the nanogram level, are available commercially and may be used for auditing and quality control purposes. (See Section 9.5 for audit accuracy evaluation criteria.) Certified preloaded tubes may also be used for routine calibration.

NOTE: Proficiency testing schemes are also available for TD/GC/MS analysis of sorbent



tubes preloaded with common analytes such as benzene, toluene, and xylene.

#### 7.6 CARRIER GASES

Use inert, 99.999-percent or higher purity helium as carrier gas. Oxygen and organic filters must be installed in the carrier gas lines supplying the analytical system according to the manufacturer's instructions. Keep records of filter and oxygen scrubber replacement.

#### 8.0 SORBENT TUBE HANDLING (BEFORE AND AFTER SAMPLING)

##### 8.1 SAMPLE TUBE CONDITIONING

8.1.1 Sampling tubes must be conditioned using the apparatus described in Section 6.2.

8.1.2 New tubes should be conditioned for 2 hours to supplement the vendor's conditioning procedure. Recommended temperatures for tube conditioning are given in Table 8.1.

8.1.3 After conditioning, the blank must be verified on each new sorbent tube and on 10 percent of each batch of reconditioned tubes. See Section 9.0 for acceptance criteria.

TABLE 8.1—EXAMPLE SORBENT TUBE CONDITIONING PARAMETERS

Sampling sorbent	Maximum temperature (°C)	Conditioning temperature (°C)	Carrier gas flow rate
Carbotrap® C Carbopack™ C Anasorb® GCB2 Carbograph™ 1 TD Carbotrap® Carbopack™ B Anasorb® GCB1 Tenax® TA Carbopack™ X	>400        350	350        330	100 mL/min        100 mL/min

#### 8.2 CAPPING, STORAGE AND SHIPMENT OF CONDITIONED TUBES

8.2.1 Conditioned tubes must be sealed using long-term storage caps (see Section 6.4) pushed fully down onto both ends of the PS sorbent tube, tightened by hand and then tighten an additional quarter turn using an appropriate tool.

8.2.2 The capped tubes must be kept in appropriate containers for storage and transportation (see Section 6.4.2). Containers of sorbent tubes may be stored and shipped at ambient temperature and must be kept in a clean environment.

8.2.3 You must keep batches of capped tubes in their shipping boxes or wrap them in uncoated aluminum foil before placing them in their storage container, especially before air freight, because the packaging helps hold caps in position if the tubes get very cold.

#### 8.3 CALCULATING THE NUMBER OF TUBES REQUIRED FOR A MONITORING EXERCISE

8.3.1 Follow guidance given in Method 325A to determine the number of tubes required for site monitoring.

8.3.2 The following additional samples will also be required: Laboratory blanks as specified in Section 9.1.2 (one per analytical sequence minimum), field blanks as specified in Section 9.3.2 (two per sampling period minimum), CCV tubes as specified in Section

10.9.4. (at least one per analysis sequence or every 24 hours), and duplicate samples as specified in Section 9.4 (at least one duplicate sample is required for every 10 sampling locations during each monitoring period).

#### 8.4 SAMPLE COLLECTION

8.4.1 Allow the tubes to equilibrate with ambient temperature (approximately 30 minutes to 1 hour) at the monitoring location before removing them from their storage/shipping container for sample collection.

8.4.2 Tubes must be used for sampling within 30 days of conditioning (Reference 4).

8.4.3 During field monitoring, the long-term storage cap at the sampling end of the tube is replaced with a diffusion cap and the whole assembly is arranged vertically, with the sampling end pointing downward, under a protective hood or shield—See Section 6.1 of Method 325A for more details.

#### 8.5 SAMPLE STORAGE

8.5.1 After sampling, tubes must be immediately resealed with long-term storage caps and placed back inside the type of storage container described in Section 6.4.2.

8.5.2 Exposed tubes may not be placed in the same container as clean tubes. They should not be taken back out of the container until ready for analysis and after they have had time to equilibrate with ambient temperature in the laboratory.



8.5.3 Sampled tubes must be inspected before analysis to identify problems such as loose or missing caps, damaged tubes, tubes that appear to be leaking sorbent or container contamination. Any and all such problems must be documented together with the unique identification number of the tube or tubes concerned. Affected tubes must not be analyzed but must be set aside.

8.5.4 Intact tubes must be analyzed within 30 days of the end of sample collection (within one week for limonene, carene, bis-chloromethyl ether, labile sulfur or nitrogen-containing compounds, and other reactive VOCs).

NOTE: Ensure ambient temperatures stay below 23 °C during transportation and storage. Refrigeration is not normally required unless the samples contain reactive compounds or cannot be analyzed within 30 days. If refrigeration is used, the atmosphere inside the refrigerator must be clean and free of organic solvents.

## 9.0 QUALITY CONTROL

### 9.1 LABORATORY BLANK

The analytical system must be demonstrated to be contaminant free by performing a blank analysis at the beginning of each analytical sequence to demonstrate that the secondary trap and TD/GC/MS analytical equipment are free of any significant interferences.

9.1.1 Laboratory blank tubes must be prepared from tubes that are identical to those used for field sampling.

9.1.2 Analysis of at least one laboratory blank is required per analytical sequence. The laboratory blank must be stored in the laboratory under clean, controlled ambient temperature conditions.

9.1.3 Laboratory blank/artifact levels must meet the requirements of Section 9.2.2 (see also Table 17.1). If the laboratory blank does not meet requirements, stop and perform corrective actions and then re-analyze laboratory blank to ensure it meets requirements.

### 9.2 TUBE CONDITIONING

9.2.1 Conditioned tubes must be demonstrated to be free of contaminants and interference by running 10 percent of the blank tubes selected at random from each conditioned batch under standard sample analysis conditions (see Section 8.1).

9.2.2 Confirm that artifacts and background contamination are  $\leq 0.2$  ppbv or less than three times the detection limit of the procedure or less than 10 percent of the target compound(s) mass that would be collected if airborne concentrations were at the regulated limit value, whichever is larger. Only tubes that meet these criteria can be used for field monitoring, field or laboratory blanks, or for system calibration.

9.2.3 If unacceptable levels of VOCs are observed in the tube blanks, then the processes of tube conditioning and checking the blanks must be repeated.

## 9.3 FIELD BLANKS

9.3.1 Field blank tubes must be prepared from tubes that are identical to those used for field sampling—i.e., they should be from the same batch, have a similar history, and be conditioned at the same time.

9.3.2 Field blanks must be shipped to the monitoring site with the sampling tubes and must be stored at the sampling location throughout the monitoring exercise. The field blanks must be installed under a protective hood/cover at the sampling location, but the long-term storage caps must remain in place throughout the monitoring period (see Method 325A). The field blanks are then shipped back to the laboratory in the same container as the sampled tubes. One field blank tube is required for every 10 sampled tubes on a monitoring exercise and no less than two field blanks should be collected, regardless of the size of the monitoring study.

9.3.3 Field blanks must contain no greater than one-third of the measured target analyte or compliance limit for field samples (see Table 17.1). If either field blank fails, flag all data that do not meet this criterion with a note that the associated results are estimated and likely to be biased high due to field blank background.

## 9.4 DUPLICATE SAMPLES

Duplicate (co-located) samples collected must be analyzed and reported as part of method quality control. They are used to evaluate sampling and analysis precision. Relevant performance criteria are given in Section 9.9.

## 9.5 METHOD PERFORMANCE CRITERIA

Unless otherwise noted, monitoring method performance specifications must be demonstrated for the target compounds using the procedures described in Addendum A to this method and the statistical approach presented in Method 301.

## 9.6 METHOD DETECTION LIMIT

Determine the method detection limit under the analytical conditions selected (see Section 11.3) using the procedure in Section 15 of Method 301. The method detection limit is defined for each system by making seven replicate measurements of a concentration of the compound of interest within a factor of five of the detection limit. Compute the standard deviation for the seven replicate concentrations, and multiply this value by three. The results should demonstrate that the method is able to detect analytes such as benzene at concentrations as low as 50 ppt or

1/3rd (preferably 1/10th) of the lowest concentration of interest, whichever is larger.

NOTE: Determining the detection limit may be an iterative process as described in 40 CFR part 136, Appendix B.

#### 9.7 ANALYTICAL BIAS

Analytical bias must be demonstrated to be within  $\pm 30$  percent using Equation 9.1. An-

alytical bias must be demonstrated during initial setup of this method and as part of the CCV carried out with every sequence of 10 samples or less (see Section 9.14). Calibration standard tubes (see Section 10.0) may be used for this purpose.

$$\text{Analytical Bias} = \frac{(\text{Spiked Value} - \text{Measured Value})}{\text{Spiked Value}} \times 100 \quad \text{Eq. 9.1}$$

Eq. 9.1

Where:

Spiked Value = A known mass of VOCs added to the tube.

Measured Value = Mass determined from analysis of the tube.

#### 9.8 ANALYTICAL PRECISION

Demonstrate an analytical precision within  $\pm 20$  percent using Equation 9.2. Analytical precision must be demonstrated during initial setup of this method and at least once per year. Calibration standard tubes may be used (see Section 10.0) and data from CCV may also be applied for this purpose.

$$\text{Analytical Precision} = \frac{(|A1 - A2|)}{\bar{A}} \times 100 \quad \text{Eq. 9.2}$$

Eq. 9.2

Where:

A1 = A measurement value taken from one spiked tube.

A2 = A measurement value taken from a second spiked tube.

$\bar{A}$  = The average of A1 and A2.

#### 9.9 FIELD REPLICATE PRECISION

Use Equation 9.3 to determine and report replicate precision for duplicate field samples (see Section 9.4). The level of agreement between duplicate field samples is a measure of the precision achievable for the entire sampling and analysis procedure. Flag data sets for which the duplicate samples do not agree within 30 percent.

$$\text{Field Precision} = \frac{(|F1 - F2|)}{\bar{F}} \times 100 \quad \text{Eq. 9.3}$$

Eq. 9.3

Where:

F1 = A measurement value (mass) taken from one of the two field replicate tubes used in sampling.

F2 = A measurement value (mass) taken from the second of two field replicate tubes used in sampling.

$\bar{F}$  = The average of F1 and F2.

#### 9.10 DESORPTION EFFICIENCY AND COMPOUND RECOVERY

The efficiency of the thermal desorption method must be determined.

9.10.1 Quantitative (>95 percent) compound recovery must be demonstrated by repeat analyses on a same standard tube.

9.10.2 Compound recovery through the TD system can also be demonstrated by comparing the calibration check sample response factor obtained from direct GC injection of



liquid standards with that obtained from thermal desorption analysis response factor using the same column under identical conditions.

9.10.3 If the relative response factors obtained for one or more target compounds introduced to the column via thermal desorption fail to meet the criteria in Section 9.10.1, you must adjust the TD parameters to meet the criteria and repeat the experiment. Once the thermal desorption conditions have been optimized, you must repeat this test each time the analytical system is recalibrated to demonstrate continued method performance.

#### 9.11 AUDIT SAMPLES

Certified reference standard samples must be used to audit this procedure (if available). Accuracy within 30 percent must be demonstrated for relevant ambient air concentrations (0.5 to 25 ppb).

#### 9.12 MASS SPECTROMETER TUNING CRITERIA

Tune the mass spectrometer (if used) according to manufacturer's specifications. Verify the instrument performance by analyzing a 50 ng injection of bromofluorobenzene. Prior to the beginning of each analytical sequence or every 24 hours during continuous GC/MS operation for this method demonstrate that the bromofluorobenzene tuning performance criteria in Table 9.1 have been met.

TABLE 9.1—GC/MS TUNING CRITERIA<sup>1</sup>

Target mass	Rel. to mass	Lower limit %	Upper limit %
50 .....	95	8	40
75 .....	95	30	66
95 .....	95	100	100
96 .....	95	5	9
173 .....	174	0	2
174 .....	95	50	120
175 .....	174	4	9
176 .....	174	93	101
177 .....	176	5	9

<sup>1</sup> All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

#### 9.13 ROUTINE CCV AT THE START OF A SEQUENCE

Run CCV before each sequence of analyses and after every tenth sample to ensure that the previous multi-level calibration (see Section 10.6.3) is still valid.

9.13.1 The sample concentration used for the CCV should be near the mid-point of the multi-level calibration range.

9.13.2 Quantitation software must be updated with response factors determined from the CCV standard. The percent deviation between the initial calibration and the CCV for all compounds must be within 30 percent.

#### 9.14 CCV AT THE END OF A SEQUENCE

Run another CCV after running each sequence of samples. The initial CCV for a subsequent set of samples may be used as the final CCV for a previous analytical sequence, provided the same analytical method is used and the subsequent set of samples is analyzed immediately (within 4 hours) after the last CCV.

#### 9.15 ADDITIONAL VERIFICATION

Use a calibration check standard from a second, separate source to verify the original calibration at least once every three months.

#### 9.16 INTEGRATION METHOD

Document the procedure used for integration of analytical data including field samples, calibration standards and blanks.

#### 9.17 QC RECORDS

Maintain all QC reports/records for each TD/GC/MS analytical system used for application of this method. Routine quality control requirements for this method are listed below and summarized in Table 17.1.

### 10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibrate the analytical system using standards covering the range of analyte masses expected from field samples.

10.2 Analytical results for field samples must fall within the calibrated range of the analytical system to be valid.

10.3 Calibration standard preparation must be fully traceable to primary standards of mass and/or volume, and/or be confirmed using an independent certified reference method.

10.3.1 Preparation of calibration standard tubes from standard atmospheres.

10.3.1.1 Subject to the requirements in Section 7.2.1, low-level standard atmospheres may be introduced to clean, conditioned sorbent tubes in order to produce calibration standards.

10.3.1.2 The standard atmosphere generator or system must be capable of producing sufficient flow at a constant rate to allow the required analyte mass to be introduced within a reasonable time frame and without affecting the concentration of the standard atmosphere itself.

10.3.1.3 The sampling manifold may be heated to minimize risk of condensation but the temperature of the gas delivered to the sorbent tubes may not exceed 100 °F.

10.3.1.4 The flow rates passed through the tube should be in the order of 50–100 mL/min and the volume of standard atmosphere sampled from the manifold or chamber must not exceed the breakthrough volume of the sorbent at the given temperature.

10.4 Preparation of calibration standard tubes from concentrated gas standards.



10.4.1 If a suitable concentrated gas standard (see Section 7.2.2) can be obtained, follow the manufacturer's recommendations relating to suitable storage conditions and product lifetime.

10.4.2 Introduce precise 0.5 to 500.0 mL aliquots of the standard to the sampling end of conditioned sorbent tubes in a 50-100 mL/min flow of pure carrier gas.

NOTE: This can be achieved by connecting the sampling end of the tube to an unheated GC injector (see Section 6.6) and introducing the aliquot of gas using a suitable gas syringe. Gas sample valves could alternatively be used to meter the standard gas volume.

10.4.3 Each sorbent tube should be left connected to the flow of gas for 2 minutes after standard introduction. As soon as each spiked tube is removed from the injection unit, seal it with long-term storage caps and place it in an appropriate tube storage/transportation container if it is not to be analyzed within 24 hours.

10.5 Preparation of calibration standard tubes from liquid standards.

10.5.1 Suitable standards are described in Section 7.3.

10.5.2 Introduce precise 0.5 to 2  $\mu$ L aliquots of liquid standards to the sampling end of sorbent tubes in a flow (50-100 mL/min) of carrier gas using a precision syringe and an unheated injector (Section 6.5). The flow of gas should be sufficient to completely vaporize the liquid standard.

NOTE: If the analytes of interest are higher boiling than n-decane, reproducible analyte transfer to the sorbent bed is optimized by allowing the tip of the syringe to gently touch the sorbent retaining gauze at the sampling end of the tube.

10.5.3 Each sorbent tube is left connected to the flow of gas for 5 minutes after liquid standard introduction.

10.5.3.1 As soon as each spiked tube is removed from the injection unit, seal it with long-term storage caps and place it in an appropriate tube storage container if it is not to be analyzed within 24 hours.

NOTE: In cases where it is possible to selectively purge the solvent from the tube while all target analytes are quantitatively retained, a larger 2  $\mu$ L injection may be made for optimum accuracy. However, if the solvent cannot be selectively purged and will be present during analysis, the injection volume should be as small as possible (*e.g.*, 0.5  $\mu$ L) to minimize solvent interference.

NOTE: This standard preparation technique requires the entire liquid plug including the tip volume be brought into the syringe barrel. The volume in the barrel is recorded, the syringe is inserted into the septum of the spiking apparatus. The liquid is then quickly injected. Any remaining liquid in the syringe tip is brought back into the syringe barrel. The volume in the barrel is recorded and the amount spiked onto the tube is the dif-

ference between the before spiking volume and the after spiking volume. A bias occurs with this method when sample is drawn continuously up into the syringe to the specified volume and the calibration solution in the syringe tip is ignored.

10.6 Preparation of calibration standard tubes from multiple standards.

10.6.1 If it is not possible to prepare one standard containing all the compounds of interest (*e.g.*, because of chemical reactivity or the breadth of the volatility range), standard tubes can be prepared from multiple gas or liquid standards.

10.6.2 Follow the procedures described in Sections 10.4 and 10.5, respectively, for introducing each gas and/or liquid standard to the tube and load those containing the highest boiling compounds of interest first and the lightest species last.

10.7 Additional requirements for preparation of calibration tubes.

10.7.1 Storage of Calibration Standard Tubes

10.7.1.1 Seal tubes with long-term storage caps immediately after they have been disconnected from the standard loading manifold or injection apparatus.

10.7.1.2 Calibration standard tubes may be stored for no longer than 30 days and should be refrigerated if there is any risk of chemical interaction or degradation. Audit standards (see section 9.11) are exempt from this criteria and may be stored for the shelf-life specified on their certificates.

10.8 Keep records for calibration standard tubes to include the following:

10.8.1 The stock number of any commercial liquid or gas standards used.

10.8.2 A chromatogram of the most recent blank for each tube used as a calibration standard together with the associated analytical conditions and date of cleaning.

10.8.3 Date of standard loading.

10.8.4 List of standard components, approximate masses and associated confidence levels.

10.8.5 Example analysis of an identical standard with associated analytical conditions.

10.8.6 A brief description of the method used for standard preparation.

10.8.7 The standard's expiration date.

10.9 TD/GC/MS using standard tubes to calibrate system response.

10.9.1 Verify that the TD/GC/MS analytical system meets the instrument performance criteria given in Section 9.1.

10.9.2 The prepared calibration standard tubes must be analyzed using the analytical conditions applied to field samples (see Section 11.0) and must be selected to ensure quantitative transfer and adequate chromatographic resolution of target compounds, surrogates, and internal standards in order to enable reliable identification and quantitation of compounds of interest. The

analytical conditions should also be sufficiently stringent to prevent buildup of higher boiling, non-target contaminants that may be collected on the tubes during field monitoring.

10.9.3 Calibration range. Each TD/GC/MS system must be calibrated at five concentrations that span the monitoring range of interest before being used for sample analysis. This initial multi-level calibration determines instrument sensitivity under the analytical conditions selected and the linearity of GC/MS response for the target compounds. One of the calibration points must be within a factor of five of the detection limit for the compounds of interest.

10.9.4 One of the calibration points from the initial calibration curve must be at the

same concentration as the daily CCV standard (e.g., the mass collected when sampling air at typical concentrations).

10.9.5 Calibration frequency. Each GC/MS system must be recalibrated with a full 5-point calibration curve following corrective action (e.g., ion source cleaning or repair, column replacement) or if the instrument fails the daily calibration acceptance criteria.

10.9.5.1 CCV checks must be carried out on a regular routine basis as described in Section 9.14.

10.9.5.2 Quantitation ions for the target compounds are shown in Table 10.1. Use the primary ion unless interferences are present, in which case you should use a secondary ion.

TABLE 10.1—CLEAN AIR ACT VOLATILE ORGANIC COMPOUNDS FOR PASSIVE SORBENT SAMPLING

Compound	CAS No.	BP (°C)	Vapor pressure (mmHg) <sup>a</sup>	MW <sup>b</sup>	Characteristic ion(s)	
					Primary	Secondary
1,1-Dichloroethane	75-35-4	32	500	96.9	61	96
3-Chloropropene	107-05-1	44.5	340	76.5	76	41, 39, 78
1,1,2-Trichloro-1,2,2-trifluoroethane-1,1-Dichloroethane	75-34-3	57.0	230	99	63	65, 83, 85, 98, 100
1,2-Dichloroethane	107-06-2	83.5	61.5	99	52	98
1,1,1-Trichloroethane	71-55-6	74.1	100	133.4	97	98, 61
Benzene	71-43-2	80.1	76.0	78	78	
Carbon tetrachloride	56-23-5	76.7	90.0	153.8	117	119
1,2-Dichloropropane	78-87-5	97.0	42.0	113	63	112
Trichloroethene	79-01-6	87.0	20.0	131.4	95	97, 130, 132
1,1,2-Trichloroethane	79-00-5	114	19.0	133.4	83	97, 85
Toluene	108-88-3	111	22.0	92	92	91
Tetrachloroethene	127-18-4	121	14.0	165.8	164	129, 131, 166
Chlorobenzene	108-90-7	132	8.8	112.6	112	77, 114
Ethylbenzene	100-41-4	136	7.0	106	91	106
m,p-Xylene	108-38-3, 106-42-3	138	6.5	106.2	106	91
Styrene	100-42-5	145	6.6	104	104	78
o-Xylene	95-47-6	144	5.0	106.2	106	91
p-Dichlorobenzene	106-46-7	173	0.60	147	146	111, 148

<sup>a</sup> Pressure in millimeters of mercury.<sup>b</sup> Molecular weight.



## 11.0 ANALYTICAL PROCEDURE

## 11.1 PREPARATION FOR SAMPLE ANALYSIS

11.1.1 Each sequence of analyses must be ordered as follows:

- 11.1.1.1 CCV.
- 11.1.1.2 A laboratory blank.
- 11.1.1.3 Field blank.
- 11.1.1.4 Sample(s).
- 11.1.1.5 Field blank.
- 11.1.1.6 CCV after 10 field samples.
- 11.1.1.7 CCV at the end of the sample batch.

## 11.2 PRE-DESORPTION SYSTEM CHECKS AND PROCEDURES

11.2.1 Ensure all sample tubes and field blanks are at ambient temperature before removing them from the storage container.

11.2.2 If using an automated TD/GC/MS analyzer, remove the long-term storage caps from the tubes, replace them with appropriate analytical caps, and load them into the system in the sequence described in Section 11.1. Alternatively, if using a manual system, uncap and analyze each tube, one at a time, in the sequence described in Section 11.1.

11.2.3 The following thermal desorption system integrity checks and procedures are required before each tube is analyzed.

NOTE: Commercial thermal desorbers should implement these steps automatically.

11.2.3.1 Tube leak test: Each tube must be leak tested as soon as it is loaded into the carrier gas flow path before analysis to ensure data integrity.

11.2.3.2 Conduct the leak test at the GC carrier gas pressure, without heat or gas flow applied. Tubes that fail the leak test should not be analyzed, but should be resealed and stored intact. On automated systems, the instrument should continue to leak test and analyze subsequent tubes after a given tube has failed. Automated systems must also store and record which tubes in a sequence have failed the leak test. Information on failed tubes should be downloaded with the batch of sequence information from the analytical system.

11.2.3.3 Leak test the sample flow path. Leak check the sample flow path of the thermal desorber before each analysis without heat or gas flow applied to the sample tube. Stop the automatic sequence of tube desorption and GC analysis if any leak is detected in the main sample flow path. This process may be carried out as a separate step or as part of Section 11.2.3.2.

## 11.2.4 OPTIONAL DRY PURGE

11.2.4.1 Tubes may be dry purged with a flow of pure dry gas passing into the tube from the sampling end, to remove water vapor and other very volatile interferents if required.

## 11.2.5 INTERNAL STANDARD (IS) ADDITION

11.2.5.1 Use the internal standard addition function of the automated thermal desorber (if available) to introduce a precise aliquot of the internal standard to the sampling end of each tube after the leak test and shortly before primary (tube) desorption.

NOTE: This step can be combined with dry purging the tube (Section 11.2.4) if required.

11.2.5.2 If the analyzer does not have a facility for automatic IS addition, gas or liquid internal standard can be manually introduced to the sampling end of tubes in a flow of carrier gas using the types of procedure described in Sections 10.3 and 10.4, respectively.

11.2.6 Pre-purge. Each tube should be purged to vent with carrier gas flowing in the desorption direction (*i.e.*, flowing into the tube from the non-sampling end) to remove oxygen before heat is applied. This is to prevent analyte and sorbent oxidation and to prevent deterioration of key analyzer components such as the GC column and mass spectrometer (if applicable). A series of schematics illustrating these steps is presented in Figures 17.2 and 17.3.

## 11.3 ANALYTICAL PROCEDURE

## 11.3.1 STEPS REQUIRED FOR THERMAL DESORPTION

11.3.1.1 Ensure that the pressure and purity of purge and carrier gases supplying the TD/GC/MS system, meet manufacturer specifications and the requirements of this method.

11.3.1.2 Ensure also that the analytical method selected meets the QC requirements of this method (Section 9) and that all the analytical parameters are at set point.

11.3.1.3 Conduct predesorption system checks (see Section 11.2).

11.3.1.4 Desorb the sorbent tube under conditions demonstrated to achieve >95 percent recovery of target compounds (see Section 9.5.2).

NOTE: Typical tube desorption conditions range from 280-350 °C for 5-15 minutes with a carrier gas flow of 30-100 mL/min passing through the tube from the non-sampling end such that analytes are flushed out of the tube from the sampling end. Desorbed VOCs are concentrated (refocused) on a secondary, cooled sorbent trap integrated into the analytical equipment (see Figure 17.4). The focusing trap is typically maintained at a temperature between -30 and +30 °C during focusing. Selection of hydrophobic sorbents for focusing and setting a trapping temperature of +25 to 27 °C aid analysis of humid samples because these settings allow selective elimination of any residual water from the system, prior to GC/MS analysis.

NOTE: The transfer of analytes from the tube to the focusing trap during primary

(tube) desorption can be carried out splitless or under controlled split conditions (see Figure 17.4) depending on the masses of target compounds sampled and the requirements of the system—sensitivity, required calibration range, column overload limitations, etc. Instrument controlled sample splits must be demonstrated by showing the reproducibility using calibration standards. Field and laboratory blank samples must be analyzed at the same split as the lowest calibration standard. During secondary (trap) desorption the focusing trap is heated rapidly (typically at rates  $>40$  °C/s) with inert (carrier) gas flowing through the trap (3–100 mL/min) in the reverse direction to that used during focusing.

11.3.1.5 The split conditions selected for optimum field sample analysis must also be demonstrated on representative standards.

NOTE: Typical trap desorption temperatures are in the range 250–360 °C, with a “hold” time of 1–3 minutes at the highest temperature. Trap desorption automatically triggers the start of GC analysis. The trap desorption can also be carried out under splitless conditions (*i.e.*, with everything desorbed from the trap being transferred to the analytical column and GC detector) or, more commonly, under controlled split conditions (see Figure 17.4). The selected split ratio depends on the masses of target compounds sampled and the requirements of the system—sensitivity, required calibration range, column overload limitations, etc. If a split is selected during both primary (trap) desorption and secondary (trap) desorption, the overall split ratio is the product of the two. Such “double” split capability gives optimum flexibility for accommodating concentrated samples as well as trace-level samples on the TD/GC/MS analytical system. High resolution capillary columns and most GC/MS detectors tend to work best with approximately 20–200 ng per compound per tube to avoid saturation. The overall split ratio must be adjusted such that, when it is applied to the sample mass that is expected to be collected during field monitoring, the amount reaching the column will be attenuated to fall within this range. As a rule of thumb this means that ~20 ng samples will require splitless or very low split analysis, ~2 µg samples will require a split ratio in the order of ~50:1 and 200 µg samples will require a double split method with an overall split ratio in the order of 2,000:1.

11.3.1.6 Analyzed tubes must be resealed with long-term storage caps immediately after analysis (manual systems) or after completion of a sequence (automated systems). This prevents contamination, minimizing the extent of tube reconditioning required before subsequent reuse.

## 11.3.2 GC/MS ANALYTICAL PROCEDURE

11.3.2.1 Heat/cool the GC oven to its starting set point.

11.3.2.2 If using a GC/MS system, it can be operated in either MS-Scan or MS-SIM mode (depending on required sensitivity levels and the type of mass spectrometer selected). As soon as trap desorption and transfer of analytes into the GC column triggers the start of the GC/MS analysis, collect mass spectral data over a range of masses from 35 to 300 amu. Collect at least 10 data points per eluting chromatographic peak in order to adequately integrate and quantify target compounds.

11.3.2.3 Use secondary ion quantitation only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, flag the data and document the reasons for the alternative quantitation procedure.

11.3.2.4 Data reduction is performed by the instruments post processing program that is automatically accessed after data acquisition is completed at the end of the GC run. The concentration of each target compound is calculated using the previously established response factors for the CCV analyzed in Section 11.1.1.6.

11.3.2.5 Whenever the thermal desorption—GC/MS analytical method is changed or major equipment maintenance is performed, you must conduct a new five-level calibration (see Section 10.6.3). System calibration remains valid as long as results from subsequent CCV are within 30 percent of the most recent 5-point calibration (see Section 10.9.5). Include relevant CCV data in the supporting information in the data report for each set of samples.

11.3.2.6 Document, flag and explain all sample results that exceed the calibration range. Report flags and provide documentation in the analytical results for the affected sample(s).

## 12.0 DATA ANALYSIS, CALCULATIONS, AND REPORTING

### 12.1 RECORDKEEPING PROCEDURES FOR SORBENT TUBES

12.1.1 Label sample tubes with a unique identification number as described in Section 6.3.

12.1.2 Keep records of the tube numbers and sorbent lots used for each sampling period.

12.1.3 Keep records of sorbent tube packing if tubes are manually prepared in the laboratory and not supplied commercially. These records must include the masses and/or bed lengths of sorbent(s) contained in each tube, the maximum allowable temperature for that tube and the date each tube was packed. If a tube is repacked at any stage, record the date of tube repacking and any



other relevant information required in Section 12.1.

12.1.4 Keep records of the conditioning and blanking of tubes. These records must include, but are not limited to, the unique identification number and measured background resulting from the tube conditioning.

12.1.5 Record the location, dates, tube identification and times associated with each sample collection. Record this information on a Chain of Custody form that is sent to the analytical laboratory.

12.1.6 Field sampling personnel must complete and send a Chain of Custody to the analysis laboratory (see Section 8.6.4 of Method 325A for what information to include and Section 17.0 of this method for an example form). Duplicate copies of the Chain of Custody must be included with the sample report and stored with the field test data archive.

12.1.7 Field sampling personnel must also keep records of the unit vector wind direction, sigma theta, temperature and barometric pressure averages for the sampling period. See Section 8.3.4 of Method 325A.

12.1.8 Laboratory personnel must record the sample receipt date, and analysis date.

12.1.9 Laboratory personnel must maintain records of the analytical method and sample results in electronic or hardcopy in sufficient detail to reconstruct the calibration, sample, and quality control results from each sampling period.

## 12.2 CALCULATIONS

12.2.1 Complete the calculations in this section to determine compliance with calibration quality control criteria (see also Table 17.1).

12.2.1.1 Response factor (RF). Calculate the RF using Equation 12.1:

$$RF = \frac{[A_s \times M_{is}]}{[A_{is} \times M_s]} \quad \text{Eq. 12.1}$$

Where:

$A_s$  = Peak area for the characteristic ion of the analyte.

$A_{is}$  = Peak area for the characteristic ion of the internal standard.

$M_s$  = Mass of the analyte.

$M_{is}$  = Mass of the internal standard.

12.2.1.2 Standard deviation of the response factors ( $SD_{RF}$ ). Calculate the SDRF using Equation 12.2:

$$SD_{RF} = \sqrt{\frac{\sum_{i=1}^n (RF_i - \overline{RF})^2}{(n-1)}} \quad \text{Eq. 12.2}$$

Where:

$RF_i$  = RF for each of the calibration compounds.

$\overline{RF}$  = Mean RF for each compound from the initial calibration.

$n$  = Number of calibration standards.

12.2.1.3 Percent deviation (%DEV). Calculate the %DEV using Equation 12.3:

$$\%DEV = SD_{RF} \div \overline{RF} \times 100 \quad \text{Eq. 12.3}$$

Where:

$SD_{RF}$  = Standard deviation.

$\overline{RF}$  = Mean RF for each compound from the initial calibration.

12.2.1.4 Relative percent difference (RPD). Calculate the RPD using Equation 12.4:

$$RPD = \frac{R1 - R2}{[(R1 + R2)/2]} \times 100 \quad \text{Eq. 12.4}$$

Where:

R1, R2 = Values that are being compared (*i.e.*, response factors in CCV).

12.2.2 Determine the equivalent concentration of compounds in atmospheres as follows.

12.2.3 Correct target concentrations determined at the sampling site temperature and atmospheric pressure to standard conditions (25 °C and 760 mm mercury) using Equation 12.5 (Reference 21).

$$U_{NTP} = U \times \left( \frac{298.2}{t_{ss}} \right)^{\frac{3}{2}} \times \left( \frac{P_{ss}}{760} \right) \quad \text{Eq. 12.5}$$

Where:

$t_{ss}$  = The average temperature during the collection period at the sampling site (K).

$P_{ss}$  = The average pressure at the sampling site during the collection period (mm Hg).

U = The diffusive uptake rate (sampling rate) (mL/min).

12.2.4 For passive sorbent tube samples, calculate the concentration of the target compound(s) in the sampled air, in  $\mu\text{g}/\text{m}^3$  by using Equation 12.6 (Reference 22).

$$C_m = \frac{m_{meas}}{U_{NTP} \times t} \times 10^6 \quad \text{Eq. 12.6}$$

Where:

$C_m$  = The concentration of target compound in the air sampled ( $\mu\text{g}/\text{m}^3$ ).

$m_{meas}$  = The mass of the compound as measured in the sorbent tube ( $\mu\text{g}$ ).

$U_{NTP}$  = The diffusive uptake rate corrected for local conditions (sampling rate) (mL/min).

t = The exposure time (minutes).

NOTE: Diffusive uptake rates for common VOCs, using carbon sorbents packed into sor-

bent tubes of the dimensions specified in Section 6.1, are listed in Table 12.1. Adjust analytical conditions to keep expected sampled masses within range (see Sections 11.3.1.3 to 11.3.1.5). Best possible method detection limits are typically in the order of 0.1 ppb for 1,3-butadiene and 0.05 ppb for volatile aromatics such as benzene for 14-day monitoring. However, actual detection limits will depend upon the analytical conditions selected.

TABLE 12.1—VALIDATED SORBENTS AND UPTAKE RATES (ML/MIN) FOR SELECTED CLEAN AIR ACT COMPOUNDS

Compound	Carbopack™ X <sup>a</sup>	Carbograph™1 TD	Carbopack™ B
1,1-Dichloroethene .....	0.57 ±0.14	not available .....	not available .....
3-Chloropropene .....	0.51 ±0.3	not available .....	not available .....
1,1-Dichloroethane .....	0.57 ±0.1	not available .....	not available .....
1,2-Dichloroethane .....	0.57 ±0.08	not available .....	not available .....
1,1,1-Trichloroethane .....	0.51 ±0.1	not available .....	not available .....
Benzene .....	0.67 ±0.06	0.63 ±0.07 <sup>b</sup> .....	0.63 ±0.07 <sup>b</sup> .....
Carbon tetrachloride .....	0.51 ±0.06	not available .....	not available .....
1,2-Dichloropropane .....	0.52 ±0.1	not available .....	not available .....
Trichloroethene .....	0.5 ±0.05	not available .....	not available .....
1,1,2-Trichloroethane .....	0.49 ±0.13	not available .....	not available .....
Toluene .....	0.52 ±0.14	0.56 ±0.06 <sup>c</sup> .....	0.56 ±0.06 <sup>c</sup> .....
Tetrachloroethene .....	0.48 ±0.05	not available .....	not available .....
Chlorotoluene .....	0.51 ±0.06	not available .....	not available .....



TABLE 12.1—VALIDATED SORBENTS AND UPTAKE RATES (ML/MIN) FOR SELECTED CLEAN AIR ACT COMPOUNDS—Continued

Compound	Carbopack™ X <sup>a</sup>	Carbograph™1 TD	Carbopack™ B
Ethylbenzene .....	0.46 ±0.07	not available .....	0.50 <sup>c</sup>
m,p-Xylene .....	0.46 ±0.09	0.47 ±0.04 <sup>c</sup> .....	0.47 ±0.04 <sup>c</sup>
Styrene .....	0.5 ±0.14	not available .....	not available
o-Xylene .....	0.46 ±0.12	0.47 ±0.04 <sup>c</sup> .....	0.47 ±0.04 <sup>c</sup>
p-Dichlorobenzene .....	0.45 ±0.05	not available .....	not available

<sup>a</sup> Reference 3, McClelleny, J. Environ. Monit. 7:248–256. Based on 24-hour duration.

<sup>b</sup> Reference 24, BS EN 14662–4:2005 (incorporated by reference—see § 63.14). Based on 14-day duration.

<sup>c</sup> Reference 25, ISO 16017–2:2003(E) (incorporated by reference—see § 63.14). Based on 14-day duration.

### 13.0 METHOD PERFORMANCE

The performance of this procedure for VOC not listed in Table 12.1 is determined using the procedure in Addendum A of this Method or by one of the following national/international standard methods: ISO 16017–2:2003(E), ASTM D6196–03 (Reapproved 2009), or BS EN 14662–4:2005 (all incorporated by reference—see § 63.14).

13.1 The valid range for measurement of VOC is approximately 0.5 µg/m<sup>3</sup> to 5 mg/m<sup>3</sup> in air, collected over a 14-day sampling period. The upper limit of the useful range depends on the split ratio selected (Section 11.3.1) and the dynamic range of the analytical system. The lower limit of the useful range depends on the noise from the analytical instrument detector and on the blank level of target compounds or interfering compounds on the sorbent tube (see Section 13.3).

13.2 Diffusive sorbent tubes compatible with passive sampling and thermal desorption methods have been evaluated at relatively high atmospheric concentrations (*i.e.*, mid-ppb to ppm) and published for use in workplace air and industrial/mobile source emissions (References 15–16, 21–22).

13.3 Best possible detection limits and maximum quantifiable concentrations of air pollutants range from sub-part-per-trillion (sub-ppt) for halogenated species such as CCl<sub>4</sub> and the freons using an electron capture detector (ECD), SIM Mode GC/MS, triple quad MS or GC/TOF MS to sub-ppb for volatile hydrocarbons collected over 72 hours followed by analysis using GC with quadrupole MS operated in the full SCAN mode.

13.3.1 Actual detection limits for atmospheric monitoring vary depending on several key factors. These factors are:

- Minimum artifact levels.
- GC detector selection.
- Time of exposure for passive sorbent tubes.
- Selected analytical conditions, particularly column resolution and split ratio.

### 14.0 POLLUTION PREVENTION

This method involves the use of ambient concentrations of gaseous compounds that

post little or no danger of pollution to the environment.

### 15.0 WASTE MANAGEMENT

Dispose of expired calibration solutions as hazardous materials. Exercise standard laboratory environmental practices to minimize the use and disposal of laboratory solvents.

### 16.0 REFERENCES

1. Winberry, W. T. Jr., *et al.*, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes: Method TO-17r, Second Edition, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, January 1999. <http://www.epa.gov/ttnamtl/airtox.html#compendium>
2. Ciccioli, P., Brancaleoni, E., Cecinato, A., Sparapini, R., and Frattoni, M., "Identification and Determination of Biogenic and Anthropogenic VOCs in Forest Areas of Northern and Southern Europe and a Remote Site of the Himalaya Region by High-resolution GC-MS," *J. of Chrom.*, 643, pp 55–69, 1993.
3. McClelleny, W.A., K.D. Oliver, H.H. Jacumin, Jr., E.H. Daughtrey, Jr., D.A. Whitaker, 2005. 24 h diffusive sampling of toxic VOCs in air onto Carbopack™ X solid adsorbent followed by thermal desorption/GC/MS analysis—laboratory studies. *J. Environ. Monit.* 7:248–256.
4. Markes International ([www.markes.com/publications](http://www.markes.com/publications)): Thermal desorption Technical Support Note 2: Prediction of uptake rates for diffusive tubes.
5. Ciccioli, P., Brancaleoni, E., Cecinato, A., DiPalo, C., Brachetti, A., and Liberti, A., "GC Evaluation of the Organic Components Present in the Atmosphere at Trace Levels with the Aid of Carbopack™ B for Preconcentration of the Sample," *J. of Chrom.*, 351, pp 433–449, 1986.
6. Broadway, G. M., and Trewern, T., "Design Considerations for the Optimization of a Packed Thermal Desorption Cold Trap for Capillary Gas Chromatography," *Proc. 13th Int'l Symposium on Capil. Chrom.*, Baltimore, MD, pp 310–320, 1991.

7. Broadway, G. M., "An Automated System for use Without Liquid Cryogen for the Determination of VOC's in Ambient Air." Proc. 14th Int'l. Symposium on Capil. Chrom., Baltimore, MD, 1992.
8. Gibitch, J., Ogle, L., and Radenheimer, P., "Analysis of Ozone Precursor Compounds in Houston, Texas Using Automated Continuous GCs," in Proceedings of the Air and Waste Management Association Conference: Measurement of Toxic and Related Air Pollutants, Air and Waste Management Association, Pittsburgh, PA, May 1995.
9. Vandendriessche, S., and Griepink, B., "The Certification of Benzene, Toluene and m-Xylene Sorbed on Tenax® TA in Tubes," CRM-112 CEC, BCR, EUR12308 EN, 1989.
10. MDHS 2 (Acrylonitrile in Air), "Laboratory Method Using Porous Polymer Adsorption Tubes, and Thermal Desorption with Gas Chromatographic Analysis," Methods for the Determination of Hazardous Substances (MDHS), UK Health and Safety Executive, Sheffield, UK.
11. MDHS 22 (Benzene in Air), "Laboratory Method Using Porous Polymer Adsorbent Tubes, Thermal Desorption and Gas Chromatography," Method for the Determination of Hazardous Substances (MDHS), UK Health and Safety Executive, Sheffield, UK.
12. MDHS 23 (Glycol Ether and Glycol Acetate Vapors in Air), "Laboratory Method Using Tenax® Sorbent Tubes, Thermal Desorption and Gas Chromatography," Method for the Determination of Hazardous Substances (MDHS), UK Health and Safety Executive, Sheffield, UK.
13. MDHS 40 (Toluene in air), "Laboratory Method Using Pumped Porous Polymer Adsorbent Tubes, Thermal Desorption and Gas Chromatography," Method for the Determination of Hazardous Substances (MDHS), UK Health and Safety Executive, Sheffield, UK.
14. MDHS 60 (Mixed Hydrocarbons (C to C) in Air), "Laboratory Method Using Pumped Porous Polymer 3 10 and Carbon Sorbent Tubes, Thermal Desorption and Gas Chromatography," Method for the Determination of Hazardous Substances (MDHS), UK Health and Safety Executive, Sheffield, UK.
15. Price, J. A., and Saunders, K. J., "Determination of Airborne Methyl tert-Butyl Ether in Gasoline Atmospheres," Analyst, Vol. 109, pp. 829-834, July 1984.
16. Coker, D. T., van den Hoed, N., Saunders, K. J., and Tindle, P. E., "A Monitoring Method for Gasoline Vapour Giving Detailed Composition," Ann. Occup. Hyg., Vol 33, No. 11, pp 15-26, 1989.
17. DFG, "Analytische Methoden zur prüfung gesundheitsschädlicher Arbeitsstoffe," Deutsche Forschungsgemeinschaft, Verlag Chemie, Weinheim FRG, 1985.
18. NNI, "Methods in NVN Series (Luchtkwaliteit; Werkplekatmasfeer)," Nederlands Normalsatie-Institut, Delft, The Netherlands, 1986-88.
19. "Sampling by Solid Adsorption Techniques," Standards Association of Australia Organic Vapours, Australian Standard 2976, 1987.
20. Woolfenden, E. A., "Monitoring VOCs in Air Using Pumped Sampling onto Sorbent Tubes Followed by Thermal Desorption-capillary GC Analysis: Summary of Reported Data and Practical Guidelines for Successful Application," J. Air & Waste Manage. Assoc., Vol. 47, 1997, pp. 20-36.
21. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, OSHA T-005, Version 3.0, May 2010. <http://www.osha.gov/dts/slc/methods/chromguide/chromguide.pdf>.
22. ASTM D4597-10, Standard Practice for Sampling Workplace Atmospheres to collect Gases or Vapors with Solid Sorbent Diffusive Samplers.
23. Martin, <http://www.hsl.gov.uk/media/1619/issue14.pdf>.
24. BS EN 14662-4:2005, Ambient air quality—Standard method for the measurement of benzene concentrations—Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
25. ISO 16017-2:2003(E): Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography—Part 2: Diffusive sampling.

#### 17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 17.1—SUMMARY OF GC/MS ANALYSIS QUALITY CONTROL PROCEDURES

Parameter	Frequency	Acceptance criteria	Corrective action
Bromofluorobenzene Instrument Tune Performance Check.	Daily <sup>a</sup> prior to sample analysis.	Evaluation criteria presented in Section 9.5 and Table 9.2.	(1) Retune and or (2) Perform Maintenance.



TABLE 17.1—SUMMARY OF GC/MS ANALYSIS QUALITY CONTROL PROCEDURES—Continued

Parameter	Frequency	Acceptance criteria	Corrective action
Five point calibration bracketing the expected sample concentration.	Following any major change, repair or maintenance or if daily CCV does not meet method requirements. Re-calibration not to exceed three months.	(1) Percent Deviation (%DEV) of response factors $\pm 30\%$ . (2) Relative Retention Times (RRTs) for target peaks $\pm 0.06$ units from mean RRT.	(1) Repeat calibration sample analysis. (2) Repeat linearity check. (3) Prepare new calibration standards as necessary and repeat analysis.
Calibration Verification (CCV Second source calibration verification check).	Following the calibration curve.	The response factor $\pm 30\%$ DEV from calibration curve average response factor.	(1) Repeat calibration check. (2) Repeat calibration curve.
Laboratory Blank Analysis .....	Daily <sup>a</sup> following bromofluorobenzene and calibration check; prior to sample analysis.	(1) $\leq 0.2$ ppbv per analyte or $\leq 3$ times the LOD, whichever is greater. (2) Internal Standard (IS) area response $\pm 40\%$ and IS Retention Time (RT) $\pm 0.33$ min. of most recent calibration check.	(1) Repeat analysis with new blank tube. (2) Check system for leaks, contamination. (3) Analyze additional blank.
Blank Sorbent Tube Certification.	One tube analyzed for each batch of tubes cleaned or 10 percent of tubes whichever is greater.	$< 0.2$ ppbv per VOC targeted compound or 3 times the LOD, whichever is greater.	Reclean all tubes in batch and reanalyze.
Samples—Internal Standards ..	All samples .....	IS area response $\pm 40\%$ and IS RT $\pm 0.33$ min. of most recent calibration validation.	Flag Data for possible invalidation.

<sup>a</sup> Every 24 hours.

Environmental Protection Agency

Pt. 63, App. A

Method 325 A/B

EXAMPLE FIELD TEST DATA SHEET (FTDS)  
AND  
CHAIN OF CUSTODY

I. GENERAL INFORMATION

SITE NAME: \_\_\_\_\_

SITE LOCATION ADDRESS: \_\_\_\_\_

CITY: \_\_\_\_\_ STATE: \_\_\_\_\_ ZIP: \_\_\_\_\_

II. SAMPLING DATA

Sample ID (Tube) #	Sorbent	Sample or blank	Start Date	Start Time	Stop Date	Stop Time	Location (gps)	Ambient Temp. (°F)	Barometric Pressure (in. Hg)

III. CUSTODY INFORMATION

COLLECTED BY: \_\_\_\_\_

Relinquished to Shipper -

Name: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Received by Laboratory -

Name: \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Sample condition upon receipt: \_\_\_\_\_

Analysis Required: \_\_\_\_\_

Comments: \_\_\_\_\_

Figure 17.1. Example Field Data Form and Chain of Custody



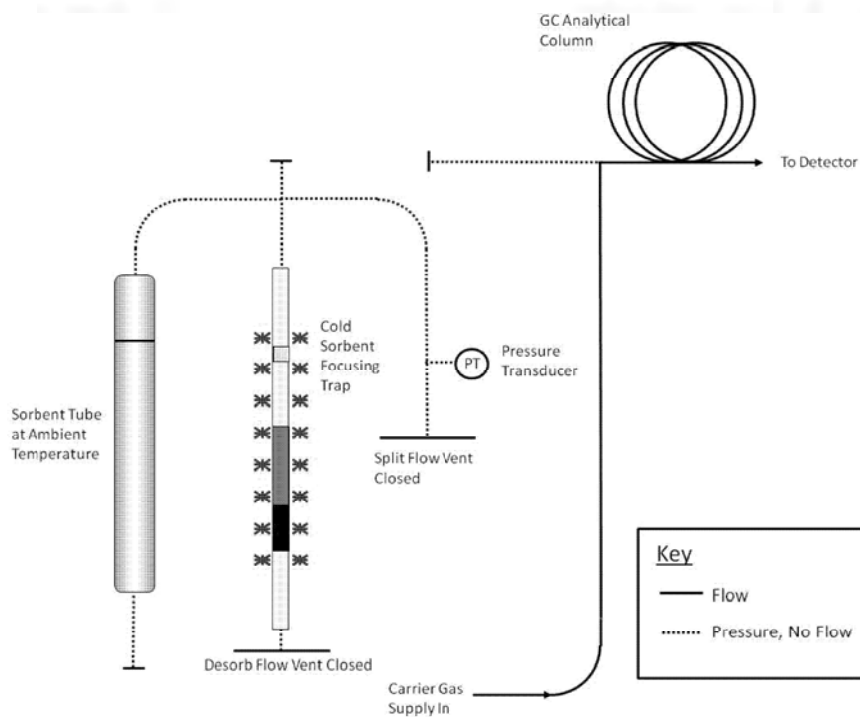


Figure 17.2. Schematic of Thermal Desorption Flow Path During Leak Testing

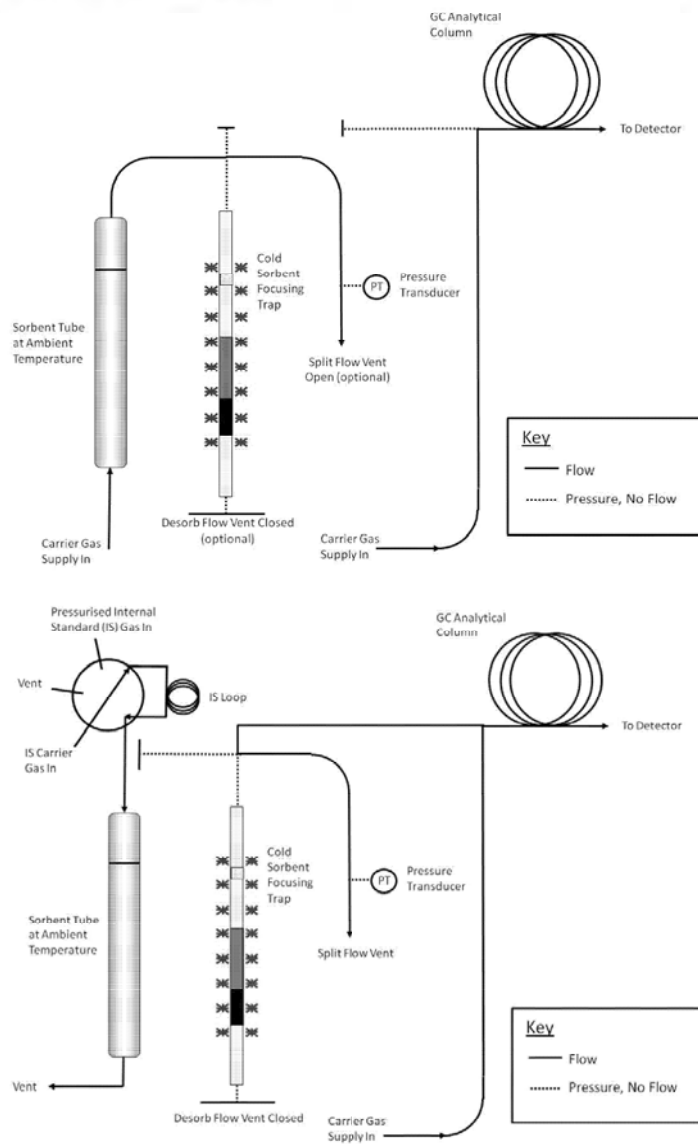
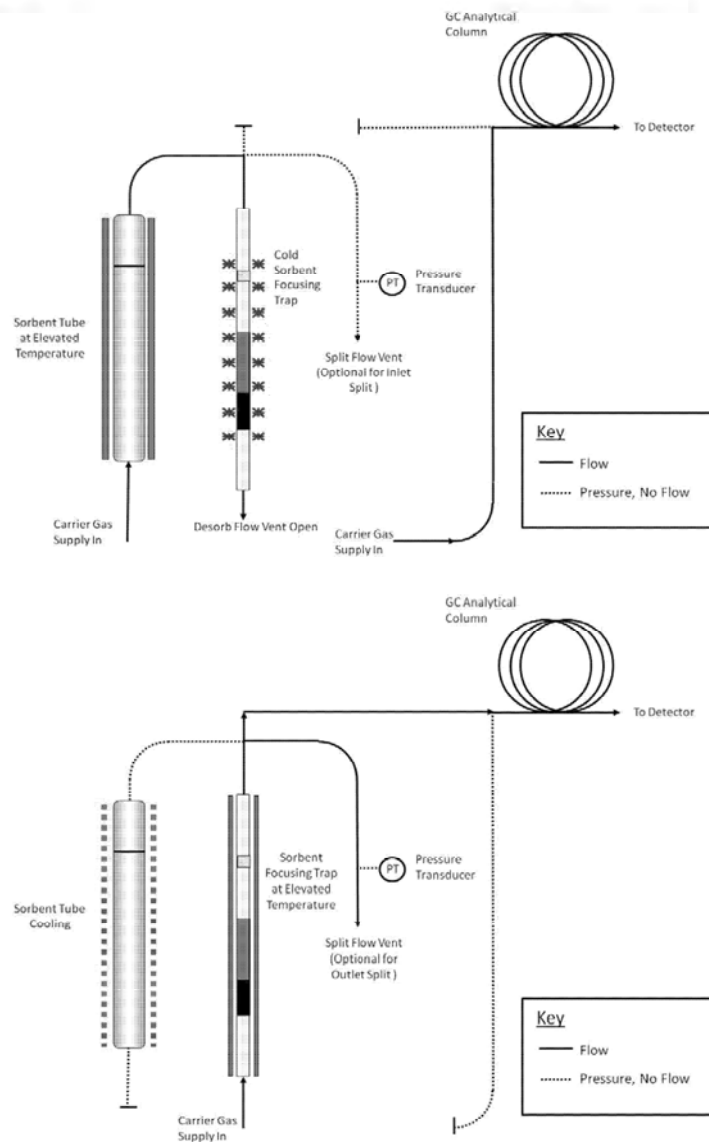


Figure 17.3. Schematic of Thermal Desorption Flow During Purge of Air (Top) and Addition of IS Gas to the Sorbent Tube (Bottom)





**Figure 17.4. Schematic of Thermal Desorption Flow Path During Primary (Tube) Desorption (Top) and Secondary (Trap) Desorption and Transfer to the GC (Bottom)**

ADDENDUM A to Method 325B—Method  
325 Performance Evaluation

#### A.1 SCOPE AND APPLICATION

A.1.1 To be measured by Methods 325A and 325B, each new target volatile organic compound (VOC) or sorbent that is not listed

in Table 12.1 must be evaluated by exposing the selected sorbent tube to a known concentration of the target compound(s) in an exposure chamber following the procedure in this Addendum or by following the procedures in the national/international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in peer-reviewed open literature.

A.1.2 You must determine the uptake rate and the relative standard deviation compared to the theoretical concentration of volatile material in the exposure chamber for each of the tests required in this method. If data that meet the requirement of this Addendum are available in the peer reviewed open literature for VOCs of interest collected on your passive sorbent tube configuration, then such data may be submitted in lieu of the testing required in this Addendum.

A.1.3 You must expose sorbent tubes in a test chamber to parts per trillion by volume (pptv) and low parts per billion by volume (ppbv) concentrations of VOCs in humid atmospheres to determine the sorbent tube uptake rate and to confirm compound capture and recovery.

#### A.2 SUMMARY OF METHOD

NOTE: The technique described here is one approach for determining uptake rates for new sorbent/sorbate pairs. It is equally valid to follow the techniques described in any one of the following national/international standards methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14).

A.2.1 Known concentrations of VOC are metered into an exposure chamber containing sorbent tubes filled with media selected to capture the volatile organic compounds of interest (see Figure A.1 and A.2 for an example of the exposure chamber and sorbent tube retaining rack). VOC are diluted with humid air and the chamber is allowed to equilibrate for 6 hours. Clean passive sampling devices are placed into the chamber and exposed for a measured period of time. The passive uptake rate of the passive sampling devices is determined using the standard and dilution gas flow rates. Chamber concentrations are confirmed with whole gas sample collection and analysis or direct interface volatile organic compound measurement methods.

A.2.2 An exposure chamber and known gas concentrations must be used to challenge and evaluate the collection and recovery of target compounds from the sorbent and tube selected to perform passive measurements of VOC in atmospheres.

#### A.3 DEFINITIONS

A.3.1 cc is cubic centimeter.

A.3.2 ECD is electron capture detector.

A.3.3 FID is flame ionization detector.

A.3.4 LED is light-emitting diode.

A.3.5 MFC is mass flow controller.

A.3.6 MFM is mass flow meter.

A.3.7 min is minute.

A.3.8 ppbv is parts per billion by volume.

A.3.9 ppmv is parts per million by volume.

A.3.10 PSD is passive sampling device.

A.3.11 psig is pounds per square inch gauge.

A.3.12 RH is relative humidity.

A.3.13 VOC is volatile organic compound.

#### A.4 INTERFERENCES

A.4.1 VOC contaminants in water can contribute interference or bias results high. Use only distilled, organic-free water for dilution gas humidification.

A.4.2 Solvents and other VOC-containing liquids can contaminate the exposure chamber. Store and use solvents and other VOC-containing liquids in the exhaust hood when exposure experiments are in progress to prevent the possibility of contamination of VOCs into the chamber through the chamber's exhaust vent.

NOTE: Whenever possible, passive sorbent evaluation should be performed in a VOC free laboratory.

A.4.3 PSDs should be handled by personnel wearing only clean, white cotton or powder free nitrile gloves to prevent contamination of the PSDs with oils from the hands.

A.4.4 This performance evaluation procedure is applicable to only volatile materials that can be measured accurately with direct interface gas chromatography or whole gas sample collection, concentration and analysis. Alternative methods to confirm the concentration of volatile materials in exposure chambers are subject to Administrator approval.

#### A.5 SAFETY

A.5.1 This procedure does not address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate field and laboratory safety and health practices and determine the applicability of regulatory limitations prior to use.

A.5.2 Laboratory analysts must exercise appropriate care in working with high-pressure gas cylinders.

#### A.6 EQUIPMENT AND SUPPLIES

A.6.1 You must use an exposure chamber of sufficient size to simultaneously expose a minimum of eight sorbent tubes.

A.6.2 Your exposure chamber must not contain VOC that interfere with the compound under evaluation. Chambers made of glass and/or stainless steel have been used



successfully for measurement of known concentration of selected VOC compounds.

A.6.3 The following equipment and supplies are needed:

- Clean, white cotton or nitrile gloves;
- Conditioned passive sampling device tubes and diffusion caps; and
- NIST traceable high resolution digital gas mass flow meters (MFMs) or flow controllers (MFCs).

#### A.7 REAGENTS AND STANDARDS

A.7.1 You must generate an exposure gas that contains between 35 and 75 percent relative humidity and a concentration of target compound(s) within 2 to 5 times the concentration to be measured in the field.

A.7.2 Target gas concentrations must be generated with certified gas standards and diluted with humid clean air. Dilution to reach the desired concentration must be done with zero grade air or better.

A.7.3 The following reagents and standards are needed:

- Distilled water for the humidification;
- VOC standards mixtures in high-pressure cylinder certified by the supplier (NOTE: The accuracy of the certified standards has a direct bearing on the accuracy of the measurement results. Typical vendor accuracy is  $\pm 5$  percent accuracy but some VOC may only be available at lower accuracy (e.g., acrolein at 10 percent)); and
- Purified dilution air containing less than 0.2 ppbv of the target VOC.

#### A.8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

A.8.1 You must use certified gas standards diluted with humid air. Generate humidified air by adding distilled organic free water to purified or zero grade air. Humidification may be accomplished by quantitative addition of water to the air dilution gas stream in a heated chamber or by passing purified air through a humidifying bubbler. You must control the relative humidity in the test gas throughout the period of passive sampler exposure.

NOTE: The RH in the exposure chamber is directly proportional to the fraction of the purified air that passes through the water in the bubbler before entering the exposure chamber. Achieving uniform humidification in the proper range is a trial-and-error process with a humidifying bubbler. You may need to heat the bubbler to achieve sufficient humidity. An equilibration period of approximately 15 minutes is required following each adjustment of the air flow through the humidifier. Several adjustments or equilibration cycles may be required to achieve the desired RH level.

NOTE: You will need to determine both the dilution rate and the humidification rate for your design of the exposure chamber by trial

and error before performing method evaluation tests.

A.8.2 Prepare and condition sorbent tubes following the procedures in Method 325B Section 7.0.

A.8.3 You must verify that the exposure chamber does not leak.

A.8.4 You must complete two evaluation tests using a minimum of eight passive sampling tubes in each test with less than 5-percent depletion of test analyte by the samplers.

A.8.4.1 Perform at least one evaluation at two to five times the estimated analytical detection limit or less.

A.8.4.2 Perform second evaluation at a concentration equivalent to the middle of the analysis calibration range.

A.8.5 You must evaluate the samplers in the test chamber operating between 35 percent and 75 percent RH, and at  $25 \pm 5$  °C. Allow the exposure chamber to equilibrate for 6 hours before starting an evaluation.

A.8.6 The flow rate through the chamber must be  $\leq 0.5$  meter per second face velocity across the sampler face.

A.8.7 Place clean, ready to use sorbent tubes into the exposure chamber for predetermined amounts of time to evaluate collection and recovery from the tubes. The exposure time depends on the concentration of volatile test material in the chamber and the detection limit required for the sorbent tube sampling application. Exposure time should match sample collection time. The sorbent tube exposure chamber time may not be less than 24 hours and should not be longer than 2 weeks.

A.8.7.1 To start the exposure, place the clean PSDs equipped with diffusion caps on the tube inlet into a retaining rack.

A.8.7.2 Place the entire retaining rack inside the exposure chamber with the diffusive sampling end of the tubes facing into the chamber flow. Seal the chamber and record the exposure start time, chamber RH, chamber temperature, PSD types and numbers, orientation of PSDs, and volatile material mixture composition (see Figure A.2).

A.8.7.3 Diluted, humidified target gas must be continuously fed into the exposure chamber during cartridge exposure. Measure the flow rate of target compound standard gas and dilution air to an accuracy of 5 percent.

A.8.7.4 Record the time, temperature, and RH at the beginning, middle, and end of the exposure time.

A.8.7.5 At the end of the exposure time, remove the PSDs from the exposure chamber. Record the exposure end time, chamber RH, and temperature.

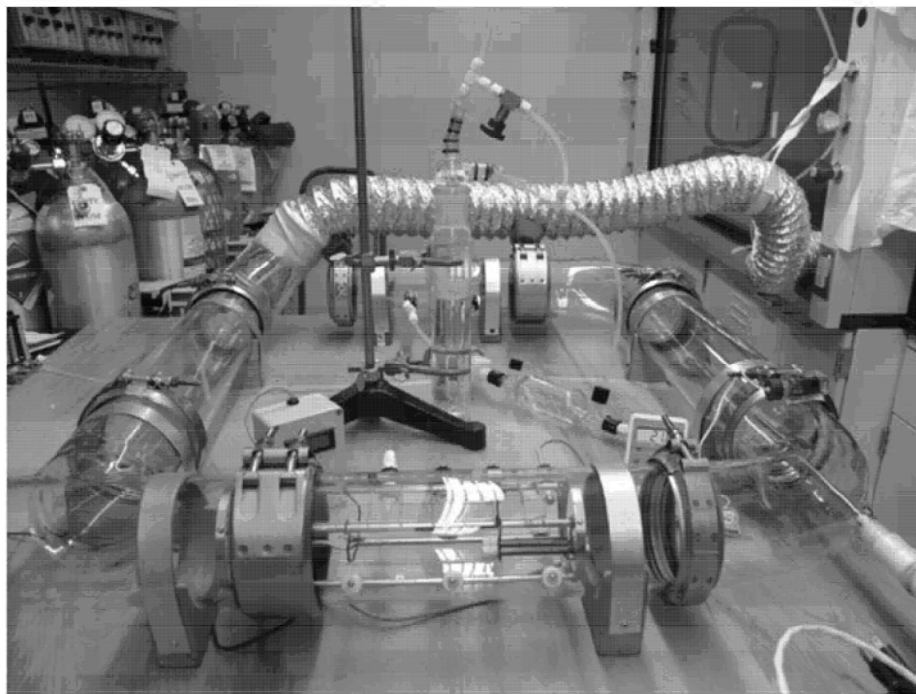
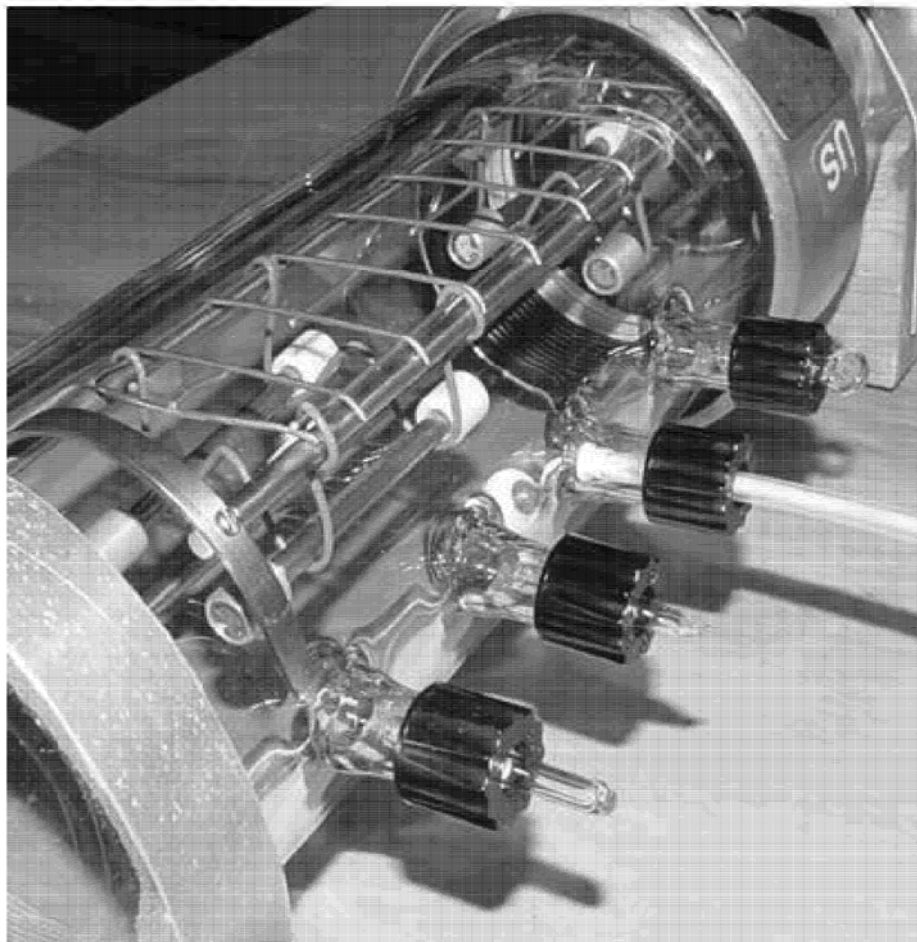
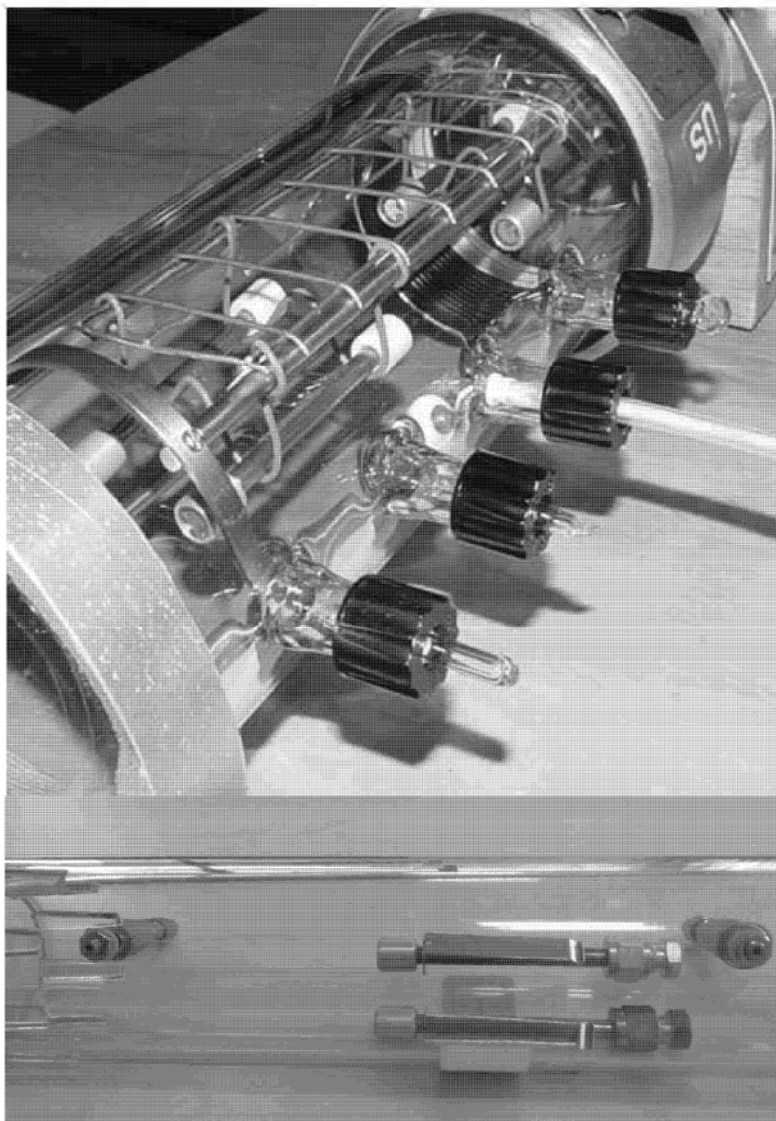


Figure A.1. Example Sorbent Tube Exposure Chamber







**Figure A.2. Example Tube Retaining Rack in Exposure Chamber**

#### A.9 QUALITY CONTROL

A.9.1 Monitor and record the exposure chamber temperature and RH during PSD exposures.

A.9.2 Measure the flow rates of standards and purified humidified air immediately following PSD exposures.

#### A.10 CALIBRATION AND STANDARDIZATION

A.10.1 Follow the procedures described in Method 325B Section 10.0 for calibration.

A.10.2 Verify chamber concentration by direct injection into a gas chromatograph calibrated for the target compound(s) or by collection of an integrated SUMMA canister followed by analysis using a

preconcentration gas chromatographic method such as EPA Compendium Method TO-15, Determination of VOCs in Air Collected in Specially-Prepared Canisters and Analyzed By GC/MS.

A.10.2.1 To use direct injection gas chromatography to verify the exposure chamber concentration, follow the procedures in Method 18 of 40 CFR part 60, Appendix A-6. The method ASTM D6420-99 (Reapproved 2010) (incorporated by reference—see §63.14) is an acceptable alternative to EPA Method 18 of 40 CFR part 60).

NOTE: Direct injection gas chromatography may not be sufficiently sensitive for all compounds. Therefore, the whole gas preconcentration sample and analysis method may be required to measure at low concentrations.

A.10.2.2 To verify exposure chamber concentrations using SUMMA canisters, prepare clean canister(s) and measure the concentration of VOC collected in an integrated SUMMA canister over the period used for the evaluation (minimum 24 hours). Analyze the TO-15 canister sample following EPA Compendium Method TO-15.

A.10.2.3 Compare the theoretical concentration of volatile material added to the test chamber to the measured concentration to confirm the chamber operation. Theoretical concentration must agree with the measured concentration within 30 percent.

#### A.11 ANALYSIS PROCEDURE

Analyze the sorbent tubes following the procedures described in Section 11.0 of Method 325B.

	1,3-butadiene uptake rate mL/min	Estimated detection limit (2 week)	Benzene uptake rates mL/min	Estimated detection limit (2 week)
Carbopack™ X (2 week) .....	0.61 ±0.11 <sup>a</sup>	0.1 ppbv	0.67 <sup>a</sup>	0.05 ppbv

<sup>a</sup>McClenny, W.A., K.D. Oliver, H.H. Jacumin, Jr., E.H. Daughtrey, Jr., D.A. Whitaker. 2005. 24 h diffusive sampling of toxic VOCs in air onto Carbopack™ X solid adsorbent followed by thermal desorption/GC/MS analysis—laboratory studies. J. Environ. Monit. 7:248–256.

#### A.13.2 Data Analysis and Calculations for Method Evaluation

#### A.12 RECORDKEEPING PROCEDURES FOR SORBENT TUBE EVALUATION

Keep records for the sorbent tube evaluation to include at a minimum the following information:

A.12.1 Sorbent tube description and specifications.

A.12.2 Sorbent material description and specifications.

A.12.3 Volatile analytes used in the sampler test.

A.12.4 Chamber conditions including flow rate, temperature, and relative humidity.

A.12.5 Relative standard deviation of the sampler results at the conditions tested.

A.12.6 95 percent confidence limit on the sampler overall accuracy.

A.12.7 The relative accuracy of the sorbent tube results compared to the direct chamber measurement by direct gas chromatography or SUMMA canister analysis.

#### A.13 METHOD PERFORMANCE

A.13.1 Sorbent tube performance is acceptable if the relative accuracy of the passive sorbent sampler agrees with the active measurement method by ±10 percent at the 95 percent confidence limit and the uptake ratio is equal to greater than 0.5 mL/min (1 ng/ppm-min).

NOTE: For example, there is a maximum deviation comparing Perkin-Elmer passive type sorbent tubes packed with Carbopack™ X of 1.3 to 10 percent compared to active sampling using the following uptake rates.

#### A.13.2.1 Calculate the theoretical concentration of VOC standards using Equation A.1.

$$C_f = \left[ \frac{FR_i}{FR_i + FR_a} \right] \times C_s \quad \text{Eq. A.1}$$

Where:

C<sub>f</sub> = The final concentration of standard in the exposure chamber (ppbv).

FR<sub>i</sub> = The flow rate of the target compound I (mL/min).

FR<sub>i</sub> = The flow rate of all target compounds from separate if multiple cylinders are used (mL/min).

FR<sub>a</sub> = The flow rate of dilution air plus moisture (mL/min).