**METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS
IN AMBIENT AIR USING TENAX® ADSORPTION AND
GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)**

1.   Scope

   1.1   The document describes a generalized protocol for collection and determination of certain volatile organic compounds which can be captured on Tenax® GC (poly(2,6-Diphenyl phenylene oxide)) and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).

   1.2   This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e., documentation of method performance within each laboratory situation is required). Types of documentation required are described elsewhere in this method.

   1.3   Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80° - 200°C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

2.   Applicable Documents

   2.1   ASTM Standards:

      D1356   Definitions of Terms Related to Atmospheric Sampling and Analysis.
      E355   Recommended Practice for Gas Chromatography Terms and Relationships.

   2.2   Other documents:

      Existing procedures (1-3).

U. S. EPA Technical Assistance Document (4).

3. Summary of Protocol

   3.1 Ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

   3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g., $-70°C$). the GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophisticated detectors (e.g., electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

   3.3 Due to the complexity of ambient air samples only high resolution (i.e., capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance

   4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.

   4.2 Conventional air monitoring methods (e.g., for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5% of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal

desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.

5.   Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). All abbreviations and symbols are defined with this document at the point of use.

6.   Interferences

6.1   Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interface in the method. The most commonly encountered interferences are structural isomers.

6.2   Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

7.   Apparatus

7.1   Gas Chromatograph/Mass Spectrometry system - should be capable of subambient temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-400 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2   Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figure 2a or b.

7.3   Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the Tenax cartridge. (See Figure 3a or b.)

7.4   Vacuum oven - connected to water aspirator vacuum supply.

7.5   Stopwatch.

7.6   Pyrex disks - for drying Tenax.

7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.

7.8 Powder funnel - for delivery of Tenax into cartridges.

7.9 Culture tubes - to hold individual glass Tenax cartridges.

7.10 Friction top can (paint can) - to hold clean Tenax cartridges.

7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired. (optional)

7.12 Thermometer - to record ambient temperature.

7.13 Barometer (optional).

7.14 Dilution bottle - Two-liter with septum cap for standards preparation.

7.15 Teflon stirbar - 1 inch long.

7.16 Gas-tight glass syringes with stainless steel needles - 10-500 µl for standard injection onto GC/MS system.

7.17 Liquid microliter syringes - 5.50 µL for injecting neat liquid standards into dilution bottle.

7.18 Oven - $60 \pm 5°C$ for equilibrating dilution flasks.

7.19 Magnetic stirrer.

7.20 Heating mantel.

7.21 Variac

7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.

7.23 Infrared lamp - for drying Tenax.

7.24 GC column - SE-30 or alternative coating, glass capillary or fused silica.

7.25 Psychrometer - to determine ambient relative humidity. (optional)

8.   Reagents and Materials

    8.1 Empty Tenax cartridges - glass or stainless steel (see Figure 1a or b).

    8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).

    8.3 Glasswool - silanized.

    8.4 Acetone - Pesticide quality or equivalent.

    8.5 Methanol - Pesticide quality or equivalent.

    8.6 Pentane - Pesticide quality or equivalent.

    8.7 Helium - Ultra pure, compressed gas. (99.9999%)

    8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)

    8.9 Liquid nitrogen.

    8.10 Polyester gloves - for handling glass Tenax cartridges.

    8.11 Glass Fiber Filter - one inch diameter, to fit in filter holder. (optional)

    8.12 Perfluorotributylamine (FC-43).

    8.13 Chemical Standards - Neat compounds of interest. Highest purity available.

    8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage.

9.   Cartridge Construction and Preparation

    9.1 Cartridge Design

        9.1.1   Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption process. Clean polyester gloves must be worn at all

times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

9.1.2   A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

9.1.3   The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figure 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and b, respectively.

9.2   Tenax Purification

9.2.1   Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.

9.2.2   All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

9.2.3   Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartridge preparation should be cleaned in the same manner as Tenax.

9.2.4   The extracted Tenax is immediately placed in an open glass dish and heated under an infrared lamp for two hours in a hood. Care must be exercised to avoid over heating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a

water aspirator) without heating for one hour. An inert gas (helium or nitrogen) purge of 2-3 ml/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110°C, maintaining inert gas flow and held for one hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

9.3   Cartridge Preparation and Pretreatment

9.3.1   All cartridge materials are pre-cleaned as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.

9.3.2   The cartridge is packed by placing a 0.5-1cm glasswool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5-1cm glasswool plug is placed in the top of the cartridge.

9.3.3   The cartridges are then thermally conditioned by heating for four hours at 270°C under an inert gas (helium) purge (100 - 200 ml/min).

9.3.4   After the four hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glasswool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.

9.3.5   The cartridges are labeled and placed in a tightly sealed metal can (e.g., paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge, is labeled.

9.3.6   Cartridges should be used for sampling within 2 weeks after preparation and analyzed within two weeks after sampling. If possible the cartridges should be stored at -20°C in a clean freezer (i.e., no solvent extracts or other sources of volatile organics contained in the freezer).

10. Sampling

10.1 Flow Rate and Total Volume Selection

10.1.1   Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard areprovided in a recent report (5). Approximate breakthrough volumes at 38°C (100°F) in liters/gram of Tenax are provided in Table 1. These retention volume data are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2   To calculate the maximum total volume of air which can be sampled use the following equation:

$$V_{MAX} = \frac{V_b xW}{1.5}$$

where

     V_{MAX} is the calculated maximum total volume in liters.

     V_b is the breakthrough volume for the least retained compound of interest (Table 1) in liters per gram of Tenax.

     W   is the weight of Tenax in the cartridge, in grams.

1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e. maximum total volume decreased).

10.1.3   To calculate maximum flow rate use the following equation:

$$Q_{MAX} = \frac{V_{MAX}}{t} x 1000$$

where

Q_{MAX} is the calculated maximum flow rate in milliliters per minute.
t   is the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained.

10.1.4   The maximum flow rate Q_{MAX} should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = \frac{Q_{MAX}}{\mathbf{B}r^2}$$

where

B   is the calculated linear flow velocity in centimeters per minute.
r   is the internal radius of the cartridge in centimeters.

If B is greater then 500 centimeters per minute either the total sample flow rate (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less then 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample value (V_{MAX}) cannot be increased due to component breakthrough.

10.1.5   The flow rate calculated as described above
          defines the maximum flow rate allowed. In
          general, one should collect additional samples
          in parallel, for the same time period but at
          lower flow rates. This practice yields a
          measure of quality control and is further
          discussed in the literature (5). In general,
          flow rates 2 to 4 fold lower than the maximum
          flow rate should be employed for the parallel
          samples. In all cases a constant flow rate
          should be achieved for each cartridge since
          accurate   integration   of   the   analyte
          concentration requires that the flow be
          constant over the sampling period.

10.2 Sample Collection

10.2.1   Collection of an accurately known volume of
          air is critical to the accuracy of the
          results. For this reason the use of mass flow
          controllers, rather than conventional needle
          valves or orifices is highly recommended,
          especially at low flow velocities (e.g., less
          than 100 milliliters/minute.   Figure 3a
          illustrates a sampling system utilizing mass
          flow controllers. This system readily allows
          for collection of parallel samples. Figure 3b
          shows a commercially available system based on
          needle valve flow controllers.

10.2.2   Prior to sample collection insure that the
          sampling flow rate has been calibrated over a
          range including the rate to be used for
          sampling, with a "dummy" Tenax cartridge in
          place. Generally calibration is accomplished
          using a soap bubble flow meter or calibrated
          wet test meter. The flow calibration device
          is connected to the flow exit, assuming the
          entire flow system is sealed. ASTM Method
          D3686 describes an appropriate calibration
          scheme, not requiring a sealed flow system
          downstream of the pump.

10.2.3   The flow rate should be checked before and
          after each sample collection. If the sampling
          interval exceeds four hours the flow rate
          should be checked at an intermediate point
          during sampling as well. In general, a
          rotameter should be included, as shown in
          Figure 3b, to allow observation of the
          sampling flow rate without disrupting the
          sampling process.

10.2.4   To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.

10.2.5   A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.

10.2.6   Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours. At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect.

10.2.7   Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g., $-20°C$) before analysis if possible to maximize storage stability.

10.2.8   Calculate and record the average sample rate
          for each cartridge according to the following
          equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where

          Q_A = Average flow rate in ml/minute.
          Q_1, Q_2, $\ldots Q_N$ = Flow rates determined at
          beginning, end, and intermediate points during
          sampling.
          N = Number of points averaged.

10.2.9   Calculate and record the total volumetric flow
          for   each   cartridge   using   the   following
          equation:

$$V_m = \frac{T \times Q_A}{1000}$$

where

          V_m = Total   volume   sampled   in   liters   at
                measured temperature and pressure.
          T_2 = Stop time.
          T_1 = Start time.
          T = Sampling time = T_2 = T_1, minutes

10.2.10   The total volume (V_s) at standard conditions,
          25°C and 760 mmHg, is calculated from the
          following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where

          P_A = Average barometric pressure, mmHg
          t_A = Average ambient temperature, °C.

11. GC/MS Analysis

11.1 Instrument Set-up

11.1.1   Considerable variation from one laboratory to
another is expected in terms of instrument
configuration. Therefore each laboratory must
be responsible for verifying that their
particular system yields satisfactory results.
Section 14 discusses specific performance
criteria which should be met.

11.1.2   A block diagram of the typical GC/MS system
required for analysis of Tenax cartridges is
depicted in Figure 5. The operation of such
devices is described in 11.2.4. The thermal
desorption module must be designed to
accommodate the particular cartridge
configuration. Exposure of the sample to
metal surfaces should be minimized and only
stainless steel, or nickel metal surfaces
should be employed. The volume of tubing and
fittings leading from the cartridge to the GC
column must be minimized and all areas must be
well-swept by helium carrier gas.

11.1.3   The GC column inlet should be capable of being
cooled to -70°C and subsequently increased
rapidly to approximately 30°C. This can be
most readily accomplished using a GC equipped
with subambient cooling capability (liquid
nitrogen) although other approaches such as
manually cooling the inlet of the column in
liquid nitrogen may be acceptable.

11.1.4   The specific GC column and temperature program
employed will be dependent on the specific
compounds of interest. Appropriate conditions
are described in the literature (1-3). In
general a nonpolar stationary phase (e.g., SE-
30, OV-1) temperature programmed from 30°C to
200°C at 8°/minute will be suitable. Fused
silica bonded phase columns are preferable to
glass columns since they are more rugged and
can be inserted directly into the MS ion
source, thereby eliminating the need for a
GC/MS transfer line.

11.1.5   Capillary column dimensions of 0.3 mm ID and
50 meters long are generally appropriate
although shorter lengths may be sufficient in
many cases.

11.1.6   Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 ml/minute and 1-2 ml/minute respectively. If applicable, the injector sweep flow is set at 2-4 ml/minute.

11.1.7   Once the column and other system components are assembled and the various flows established the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

11.1.8   The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately 5×10^4 should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1   Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source though a molecular leak. The instrumental parameters (e.g., lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these alternate values must be repeatable on a day-to-day basis.

11.2.2   After the mass standardization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) injection of dilute vapor phase standards into a carrier gas stream directed through the Tenax cartridge, and 3) introduction of permeation or diffusion tube standards onto a Tenax cartridge. The standards preparation procedures for each of these approaches are described in Section 13. The following paragraphs describe the instrument calibration process for each of these approaches.

11.2.3   If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 ml) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe. The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g., 30°C). The temperature program is started at a consistent time (e.g., four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted acquisition is terminated and the data is processed as described in Section 11.2.5. The standard injection process is repeated using different standard volumes as desired.

11.2.4   If the system is to be calibrated by analysis of spiked Tenax cartridges a set of cartridges is prepared as described in Sections 13.2 or 13.3.   Prior to analysis the cartridges are stored as described in Section 9.3.   If glass cartridges (Figure 1a) are employed care must be taken to avoid direct contact, as described earlier.   The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C.   The inlet valve is placed in the <u>desorb</u> mode and the standard cartridge is placed in the desorption module, making certain that no leakage or purge gas occurs.   The cartridge is purged for 10 minutes and then the inlet valve is placed in the <u>inject</u> mode and the liquid nitrogen source removed from the collection trap.   The GC column is maintained at -70°C for two minutes and subsequent steps are as described in 11.2.3.   After the process is complete the cartridge is removed from the desorption module and stored for subsequent use as described in Section 9.3.

11.2.5   Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest.   In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance.   Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use.   Overall performance criteria for instrument calibration are provided in Section 14.   If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

11.3 Sample Analysis

11.3.1   The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2   Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine.   As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

12. Calculations

12.1 Calibration Response Factors

12.1.1   Data from calibration standards is used to calculate a response factor for each component of interest.   Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected versus area (for the characteristic ion).   In general quantities of component greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2   In practice the daily routine may not always allow analysis of three such calibration standards.   In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3   If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area
X = quantity of component, nanograms
A, B, and C are coefficients in the equation

12.2 Analyte Concentrations

12.2.1   Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A$$

where

Y_A is the area of the analyte characteristic ion for the sample cartridge.
X_A is the calculated quantity of analyte on the sample cartridge, in nanograms.
A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.3.

12.2.2   If instrumental response is essentially linear over the concentration range of interest a linear equation (C=O in the equation above) can be employed.

12.2.3   Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte in nanograms per liter.
V_S and X_A are as previously defined in Section 10.2.10 and 12.2.1, respectively.

13. Standard Preparation

13.1 Direct Injection

13.1.1   This process involves preparation of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.

13.1.2   Fifteen three-millimeter diameter glass beads and a one-inch Teflon stirbar are placed in a clean two-liter glass septum capped bottle and the exact volume is determined by weighing the bottle before and after filling with deionized water. The bottle is then rinsed with acetone and dried at 200°C.

13.1.3   The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$W_T = \frac{W_I}{V_I} \times V_B$$

where

W$_T$ is the total quantity of analyte to be injected into the bottle in milligrams
W$_I$ is the desired weight of analyte to be injected onto the GC/MS system or spiked cartridge in nanograms
V$_I$ is the desired GC/MS or cartridge injection volume (should not exceed 500) in microliters.
V$_B$ is total volume of dilution bottle determined in 13.1.1, in liters.

13.1.4   The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$V_T = \frac{W_T}{d}$$

where

V$_T$ is the total volume of neat liquid to be injected in microliters.
d   is the density of the neat standard in grams per milliliter.

13.1.6   The bottle is placed in a 60°C oven for at least 30 minutes prior to removal of a vapor phase standard.

13.1.7   To withdraw a standard for GC/MS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight microber syringe, warmed to 60°C, is inserted through the septum cap and pumped three times slowly. The appropriate volume of sample (approximately 25% larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GC/MS system as described in Section 11.2.3.

13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1   This process involves preparation of a dilution bottle containing the desired concentrations of the compound(s) of interest as described in 13.1 and injecting the desired volume of vapor into a flowing inert gas stream directed through a clean Tenax cartridge.

13.2.2   A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel Tee fitted with a septum injector. The clean Tenax cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas stream the appropriate volume vapor standard, in the dilution bottle, is injected through the septum as described in 13.1.6. The syringe is flushed several times by alternately filling the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintained through the cartridge for approximately 5 minutes after injection.

13.3 Preparation of Spiked Traps Using Permeation or Diffusion Tubes

13.3.1   A flowing stream of inert gas containing known amounts of each compound of interest is generated according to ASTM Method D3609(6).

Note that a method of accuracy maintaining temperature within $\pm$ 0.1°C is required and the system generally must be equilibrated for at least 48 hours before use.

13.3.2   An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean Tenax cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section

13.3.1   (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.

13.3.3   The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

14.   Performance Criteria and Quality Assurance

This section summarizes quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate section describing the particular activity (e.g., parallel sampling).

14.1 Standard Operating Procedures (SOPs)

14.1.1   Each user should generate SOPs describing the following activities as they are performed in their laboratory:
1)   assembly, calibration, and operation of the sampling system,
2)   preparation, handling and storage of Tenax cartridges,
3)   assembly and operation of GC/MS system including the thermal desorption apparatus and data system, and
4)   all aspects of data recording and processing.

14.1.2   SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

14.2 Tenax Cartridges Preparation

14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may choose to use GC/FID due to logistical and cost considerations.

14.2.2. Analysis by GC/FID is accomplished as described for GC/MS (Section 11) except for use of FID detection.

14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

14.3 Sample Collection

14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within $\pm$ 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow

rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

14.3.3   Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

14.4 GC/MS Analysis

14.4.1   Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

14.4.2   Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 6) should be between 0.8 and 2.0. The asymmetry factor for

any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and are necessary. Some laboratories may choose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g., acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

14.4.3   The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL   is the calculated detection limit in nanograms injected.
A   is the intercept calculated in Section 12.1.1 or 12.1.3.
S   is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required).

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

14.4.4   The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

14.4.5   A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g., perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than $\pm$ 2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX

COMPOUND	ESTIMATED RETENTION VOLUME AT 100°F (38°C)–LITERS/GRAM
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene(s)	~200
Cumene	440
n-Heptane	20
l-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

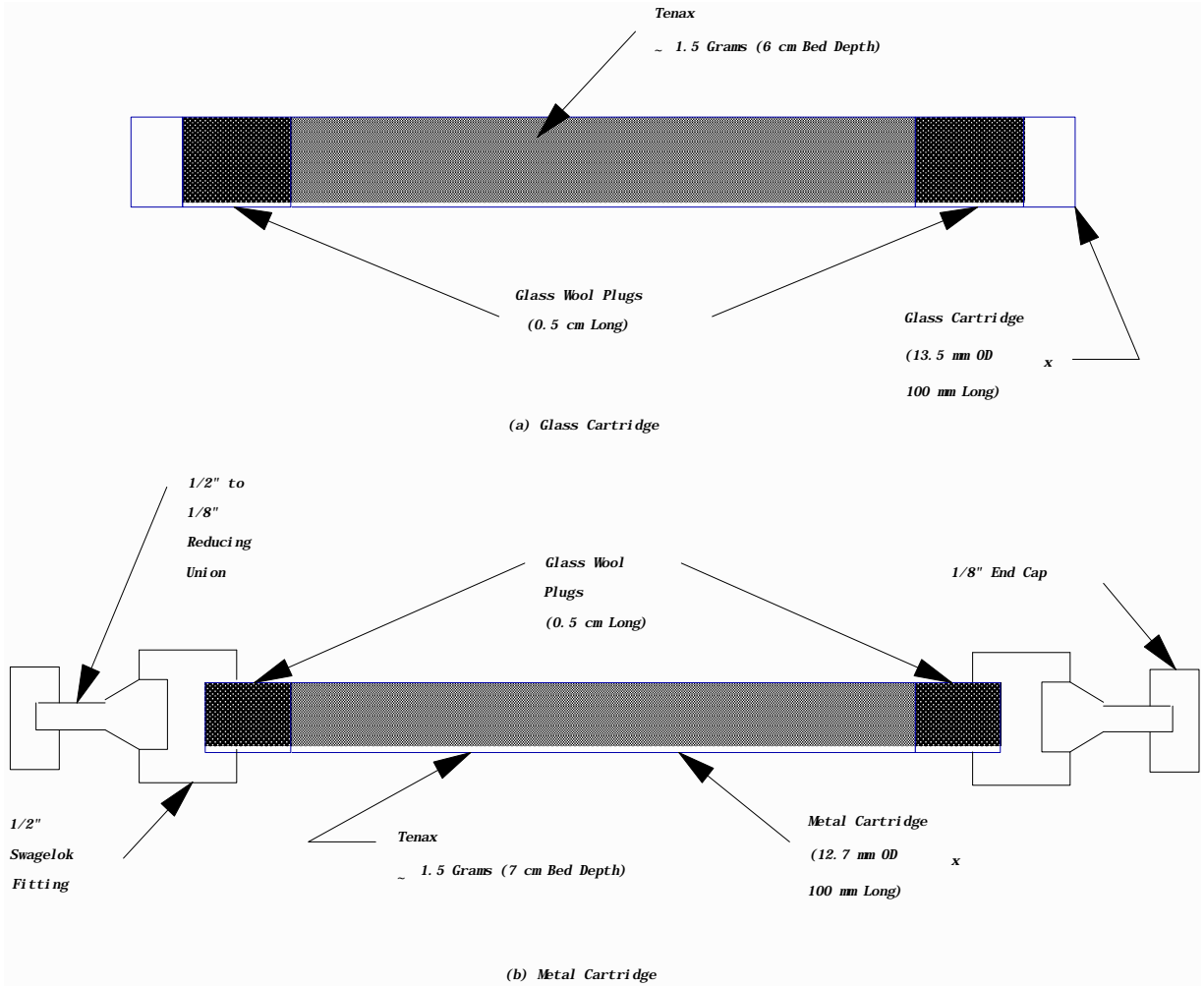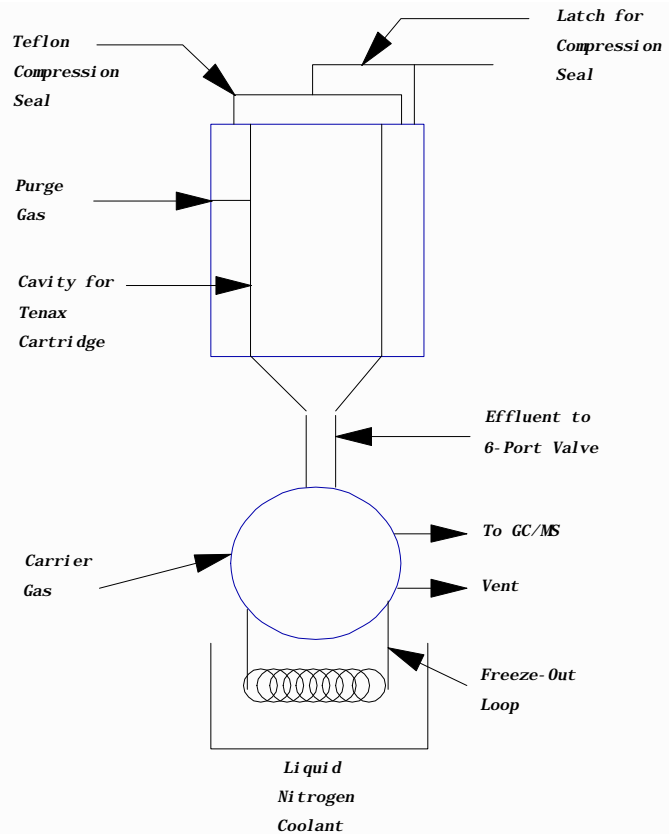**TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION**

M/E	% RELATIVE ABUNDANCE
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

Tenax

~ 1.5 Grams (6 cm Bed Depth)

Glass Wool Plugs

(0.5 cm Long)

Glass Cartridge

(13.5 mm OD

100 mm Long)

x

(a) Glass Cartridge

1/2" to

1/8"

Reducing

Union

Glass Wool

Plugs

(0.5 cm Long)

1/8" End Cap

1/2"

Swagelok

Fitting

Tenax

~ 1.5 Grams (7 cm Bed Depth)

Metal Cartridge

(12.7 mm OD

100 mm Long)

x

(b) Metal Cartridge

FIGURE 1. TENAX CARTRIDGE DESIGNS

Teflon Compression Seal

Latch for Compression Seal

Purge Gas

Cavity for Tenax Cartridge

Effluent to 6-Port Valve

To GC/MS

Carrier Gas

Vent

Freeze-Out Loop

Liquid Nitrogen Coolant

(a) Glass Cartridges (Compression Fit)

Purge Gas

Tenax Trap

Effluent to 6-Port Valve

To GC/MS

Vent

Heated Block

Carrier Gas

Swagelok End Fittings

Liquid Nitrogen Coolant
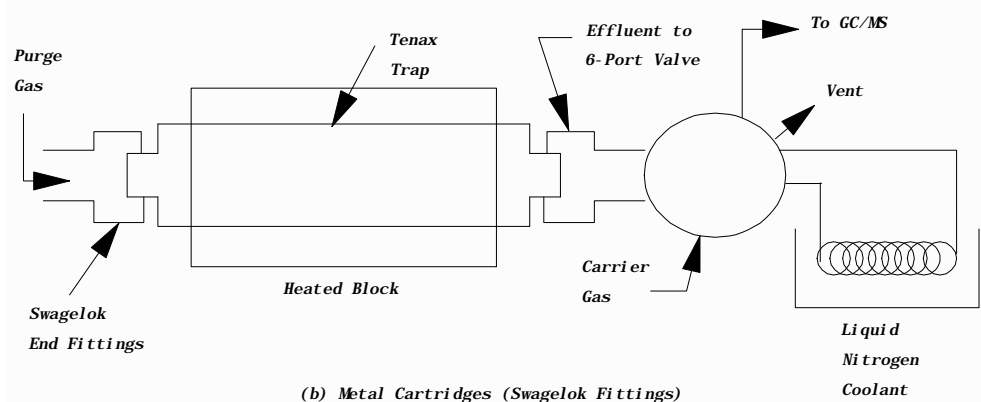
(b) Metal Cartridges (Swagelok Fittings)

Figure 2. Tenax Cartridge Desorption Modules
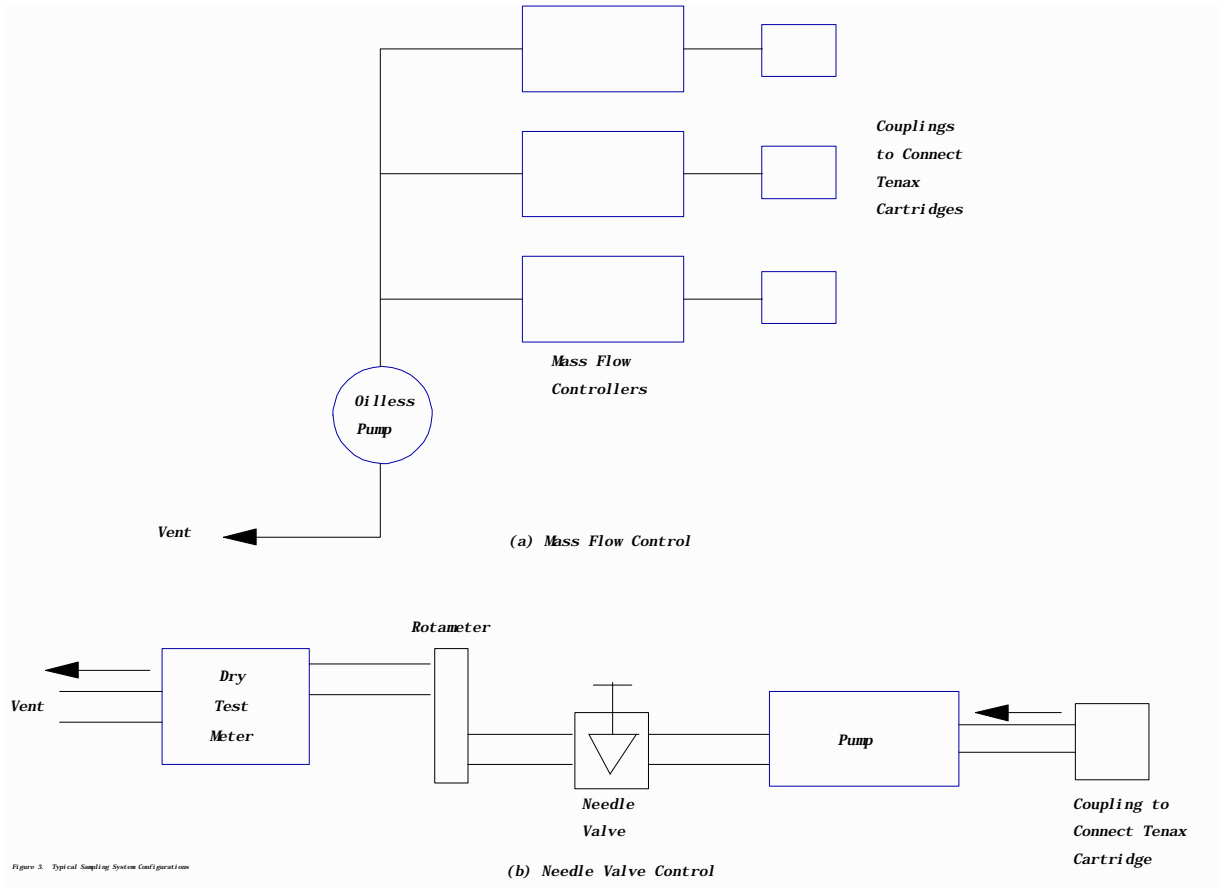
FIGURE 2.   TENAX CARTRIDGE DESORPTION MODULES

Couplings
to Connect
Tenax
Cartridges

Mass Flow
Controllers

Oilless
Pump

Vent

(a) Mass Flow Control

Rotameter

Dry
Test
Meter

Vent

Needle
Valve

Pump

Coupling to
Connect Tenax
Cartridge

Figure 3. Typical Sampling System Configurations

(b) Needle Valve Control

FIGURE 3. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

PROJECT: _____   DATE(S) SAMPLED: _____

SITE: _____   TIME PERIOD SAMPLED: _____

LOCATION: _____   OPERATOR: _____

INSTRUMENT MODEL NO: _____   CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____
Start Time: _____   Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate, Q ml/Min	Ambient Temp. °C	Barometric Pressure, mmHg	Relative Humidity,%	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final – Initial) Dry Gas Meter Reading, or   = _____ Liters

$$= \frac{Q_1 + Q_2 + Q_3 ... Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \underline{\quad} \text{ Liters}$$

* Flowrate from rotameter or soap bubble calibrator (specify which).
** Use data from dry gas meter if available.

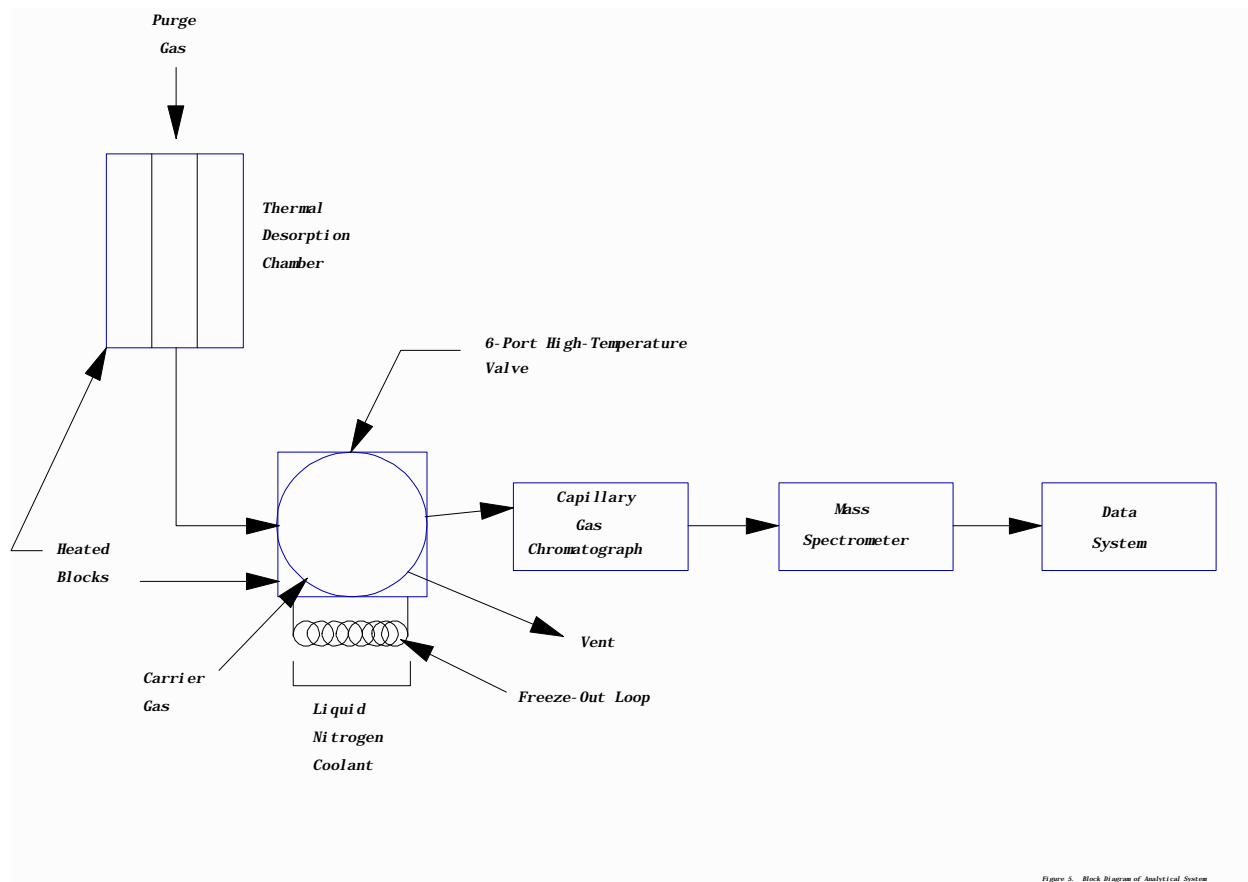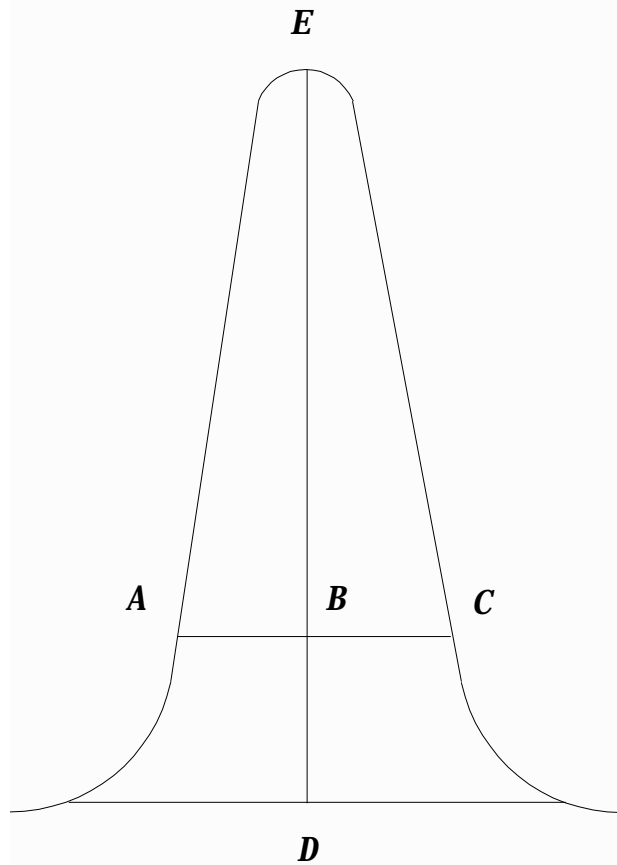**FIGURE 4. EXAMPLE SAMPLING DATA SHEET**

Purge
Gas

Thermal
Desorption
Chamber

6-Port High-Temperature
Valve

Heated
Blocks

Capillary
Gas
Chromatograph

Mass
Spectrometer

Data
System

Vent

Carrier
Gas

Freeze-Out Loop

Liquid
Nitrogen
Coolant

Figure 5. Block Diagram of Analytical System

FIGURE 5.   BLOCK DIAGRAM OF ANALYTICAL SYSTEM

FIGURE 6. PEAK ASYMMETRY CALCULATION