METHOD TO-2

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METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY CARBON MOLECULAR SIEVE ADSORPTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1. Scope

1.1 This document describes a procedure for collection and determination of selected volatile organic compounds which can be captured on carbon molecular sieve (CMS) adsorbents and determined by thermal desorption GC/MS techniques.

1.2 Compounds which can be determined by this method are nonpolar and nonreactive organics having boiling points in the range -15 to +120°C. However, not all compounds meeting these criteria can be determined. Compounds for which the performance of the method has been documented are listed in Table 1. The method may be extended to other compounds but additional validation by the user is required. This method has been extensively used in a single laboratory. Consequently, its general applicability has not been thoroughly documented.

2. Applicable Documents

2.1 ASTM Standards
D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.
E 355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.2 Other Documents
Ambient Air Studies (1,2).
U.S. EPA Technical Assistance Document (3).

3. Summary of Method

3.1 Ambient air is drawn through a cartridge containing ~0.4 of a carbon molecular sieve (CMS) adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). After sampling, the cartridge is returned to the laboratory for analysis.

3.2 Prior to analysis the cartridge is purged with 2-3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

3.3 For analysis the cartridge is heated to 350°-400°C, under helium purge and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run.

3.4 Due to the complexity of ambient air samples, only high resolution (capillary column) GC techniques are acceptable for most applications of the method.

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 and treatment facilities, etc. Many of these compounds are toxic; hence knowledge of the concentration of such materials in the ambient atmosphere is required in order to determine human health impacts.

4.2 Traditionally air monitoring methods for volatile organic compounds have relied on carbon adsorption followed by solvent desorption and GC analysis. Unfortunately, such methods are not sufficiently sensitive for ambient air monitoring, in most cases, because only a small portion of the sample is injected onto the GC system. Recently on-line thermal desorption methods, using organic polymeric adsorbents such as Tenax® GC, have been used for ambient air monitoring. The current method uses CMS adsorbents (e.g. Spherocarb®) to capture highly volatile organics (e.g., vinyl chloride) which are not collected on Tenax®. The use of on-line thermal desorption GS/MS yields a sensitive, specific analysis procedure.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356 (4). All abbreviations and symbols are defined with this document at the point of use.

6. Interferences

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

6.2 Contamination of the CMS cartridge with the compound(s) of interest can be a problem in the method. The user must be careful in the preparation, storage, and handling of the cartridges through the entire process to minimize contamination.

7. Apparatus

7.1 Gas Chromatograph/Mass Spectrometry system - must be capable of subambient temperature programming. Unit mass resolution to 800 amu. Capable of scanning 30-300 amu region every 0.5-0.8 seconds. Equipped with data system for instrument control as well as data acquisition, processing and storage.

7.2 Thermal Desorption Injection Unit - Designed to accommodate CMS cartridges in use (See Figure 3) and including cryogenic trap (Figure 5) and injection valve (Carle Model 5621 or equivalent).

7.3 Sampling System - Capable of accurately and precisely drawing an air flow of 10-500 ml/minute through the CMS cartridge. (See Figure 2a or b.)

7.4 Dewar flasks - 500 mL and 5 liter.

7.5 Stopwatches.

7.6 Various pressure regulators and valves - for connecting compressed gas cylinders to GC/MS system.

7.7 Calibration gas - In aluminum cylinder. Prepared by user or vendor. For GC/MS calibration.

7.8 High pressure apparatus for preparing calibration gas cylinders (if conducted by user). Alternatively, custom prepared gas mixtures can be purchased from gas supply vendors.

7.9 Friction top can (e.g. one-gallon paint-can) - With layer of activated charcoal to hold clean CMS cartridges.

7.10 Thermometer - to record ambient temperature.

7.11 Barometer (optional).

7.12 Dilution bottle - Two-liter with septum cap for standard preparation.

7.13 Teflon stirbar - 1 inch long.

7.14 Gas tight syringes - 10-500 μl for standard injection onto GC/MS system and CMS cartridges.

7.15 Liquid microliter syringes - 5-50 μL for injecting neat liquid standards into dilution bottle.

7.16 Oven - 60 $\pm$ 5°C for equilibrating dilution bottle.

7.17 Magnetic stirrer.

7.18 Variable voltage transformers - (120 V and 1000 VA) and electrical connectors (or temperature controllers) to heat cartridge and cryogenic loop.

7.19 Digital pyrometer - 30 to 500°C range.

7.20 Soap bubble flow meter - 1, 10 and 100 mL calibration points.

7.21 Copper tubing (1/8 inch) and fittings for gas inlet lines.

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

7.23 Psychrometer (optional).

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

8. Reagents and Materials

8.1 Empty CMS cartridges - Nickel or stainless steel (See Figure 1).

8.2 CMS Adsorbent, 60/80 mesh-Spherocarb® from Analabs Inc., or equivalent.

8.3 Glasswool - silanized.

8.4 Methylene chloride - pesticide quality, or equivalent.

8.5 Gas purifier cartridge for purge and GC carrier gas containing charcoal, molecular sieves, and a drying agent. Available from various chromatography supply houses.

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

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

8.8 Liquid nitrogen or argon (50 liter dewar).

8.9 Compressed air, if required - for operation of GC oven door.

8.10 Perfluorotributylamine (FC-43) for GC/MS calibration.

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

9. Cartridge Construction and Preparation

9.1 A suitable cartridge design is shown in Figure 1. Alternate designs have been reported (1) and are acceptable, provided the user documents their performance. The design shown in Figure 1 has a built-in heater assembly. Many users may choose to replace this heater design with a suitable separate heating block or oven to simplify the cartridge design.

9.2 The cartridge is assembled as shown in Figure 1 using standard 0.25 inch O.D. tubing (stainless steel or nickel), 1/4 inch to 1/8 inch reducing unions, 1/8 inch nuts, ferrules, and endcaps. These parts are rinsed with methylene chloride and heated at 250°C for 1 hour prior to assembly.

9.3 The thermocouple bead is fixed to the cartridge body, and insulated with a layer of Teflon tape. The heater wire (constructed from a length of thermocouple wire) is wound around the length of the cartridge and wrapped with Teflon tape to secure the wire in place. The cartridge is then wrapped with woven silica fiber insulation (Zetex or equivalent). Finally the entire assembly is wrapped with fiber glass tape.

9.4 After assembly one end of the cartridge is marked with a serial number to designate the cartridge inlet during sample collection.

9.5 The cartridges are then packed with ~0.4 grams of CMS adsorbent. Glass wool plugs (~0.5 inches long) are placed at each end of the cartridge to hold the adsorbent firmly in place. Care must be taken to insure that no strands of glasswool extend outside the tubing, thus causing leakage in the compression endfittings. After loading the endfittings (reducing unions and end caps) are tightened onto the cartridge.

9.6 The cartridges are conditioned for initial use by heating at 400°C overnight (at least 16 hours) with a 100 mL/minute purge of pure nitrogen. Reused cartridges need only to be heated for 4 hours and should be reanalyzed before use to ensure complete desorption of impurities.

9.7 For cartridge conditioning ultra-pure nitrogen gas is passed through a gas purifier to remove oxygen, moisture and organic contaminants. The nitrogen supply is connected to the unmarked end of the cartridge and the flow adjusted to ~50 mL/minute using a needle valve. The gas flow from the inlet (marked) end of the cartridge is vented to the atmosphere.

9.8 The cartridge thermocouple lead is connected to a pyrometer and the heater lead is connected to a variable voltage transformer (Variac) set at 0 V. The voltage on the Variac is increased to ~15 V and adjusted over a 3-4 minute period to stabilize the cartridge temperature at 380-400°C.

9.9 After 10-16 hours of heating (for new cartridges) the Variac is turned off and the cartridge is allowed to cool to ~30°C, under continuing nitrogen flow.

9.10 The exit end of the cartridge is capped and then the entire cartridge is removed from the flow line and the other endcap immediately installed. The cartridges are then placed in a metal friction top (paint) can containing ~2 inches of granulated activated charcoal (to prevent contamination of the cartridges during storage) in the bottom, beneath a retaining screen. Clean paper tissues (e.g., Kimwipes) are placed in can to avoid damage to the cartridges during shipment.

9.11 Cartridges are stored in the metal can at all times except when in use. Adhesives initially present in the cartridge insulating materials are "burnt off" during initial conditioning. Therefore, unconditioned cartridges should not be placed in the metal can since they may contaminate the other cartridges.

9.12 Cartridges are conditioned within two weeks of use. A blank from each set of cartridges is analyzed prior to use in field sampling. If an acceptable blank level is achieved, that batch of cartridges (including the cartridge serving as the blank) can be used for field sampling.

10. Sampling

10.1 Flow Rate and Total Volume Selection

10.1.1 Each compound has a characteristic retention volume (liters of air per unit weight of adsorbent). However, all of the compounds listed in Table 1 have retention volumes (at 37°C) in excess of 100 liters/cartridge (0.4 gram CMS cartridge) except vinyl chloride for which the value is ~30 liters/cartridge. Consequently, if vinyl chloride or similarly volatile compounds are of concern the maximum allowable sampling volume is approximately 20 liters. If such highly volatile compounds are not of concern, samples as large as 100 liters can be collected.

10.1.2 To calculate the maximum allowable sampling flow rate the following equation can be used:

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

where

Q_{MAX} is the calculated maximum sampling rate in mL/minute.
t is the desired sampling time in minutes.
V_{MAX} is the maximum allowable total volume based on the discussion in 10.1.1.

10.1.3 For the cartridge design shown in Figure 1 Q_{MAX} should be between 20 and 500 mL/minute. If Q_{MAX} lies outside this range the sampling time or total sampling volume must be adjusted so that this criterion is achieved.

10.1.4 The flow rate calculated in 10.1.3 defines the <u>maximum</u> allowable flow rate. In general, the user should collect additional samples in parallel, at successive 2- to 4-fold lower flow rates. This practice serves as a quality

control procedure to check on component breakthrough and related sampling and adsorption problems, and is further discussed in the literature (5).

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 rates (e.g., less than 100 milliliters/minute). Figure 2a illustrates a sampling system based on mass flow controllers which readily allows for collection of parallel samples. Figure 2b shows a commercially available sampling system based on needle valve flow controllers.

10.2.2 Prior to sample collection the sampling flow rate is calibrated near the value used for sampling, with a "dummy" CMS cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D 3686 (4) 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. Ideally, a rotometer or mass flow meter should be included in the sampling system to allow periodic observation of the 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.

10.2.5 The exit (unmarked) end of the cartridge is connected to the sampling apparatus. The endcap is left on the sample inlet and the entire system is leak checked by activating the sampling pump and observing that no flow is obtained over a 1 minute period. The sampling pump is then shut off.

10.2.6 The endcap is removed from the cartridge, a particulate filter and holder are placed on the inlet end of the cartridge, and the sampling pump is started. In many situations a particulate filter is not necessary since the compounds of interest are in the vapor state. However, if large amounts of particulate matter are encountered, the filter may be useful to prevent contamination of the cartridge. The following parameters are recorded on an appropriate data sheet (Figure 4): date, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotometer reading (if applicable), cartridge number, pump, and dry gas meter serial number.

10.2.7 The samples are collected for the desired time, periodically recording the variables listed above. At the end of the sampling period the parameters listed in 10.2.6 are recorded and the flow rate is checked. If the flows at the beginning and end of the sampling period differ by more than 10%, the cartridge should be marked as suspect.

10.2.8 The cartridges are removed (one at a time), the endcaps are replaced, and the cartridges are placed into the original container. The friction top can is sealed and packaged for immediate shipment to the analytical laboratory.

10.2.9 The average sample rate is calculated and recorded 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 is ml/minute
Q_1, Q_2 ....Q_N = Flow rates determined at beginning, end, and immediate points during sampling.

N = Number of points averaged.

10.2.10 The total volumetric flow is obtained directly from the dry gas meter or calculated and recorded 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 = Sampling time = T_2-T_1, minutes.

10.2.11 The total volume sampled (V_s) at standard conditions, 760 mm Hg and 25°C, is calculated from the following equation:

$$V_s = V_m \times \frac{Pa}{760} \times \frac{298}{273 + ta}$$

where

Pa = Average barometric pressure, mm Hg
ta = Average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Purging

11.1.1 Prior to analysis all samples are purged at room temperature with pure, dry air or nitrogen to remove water vapor. Purging is accomplished as described in 9.7 except that the gas flow is in the same direction as sample flow (i.e. marked end of cartridge is connected to the flow system).

11.1.2 The sample is purged at 500 mL/minute for 5 minutes. After purging the endcaps are immediately replaced. The cartridges are returned to the metal can or analyzed immediately.

11.1.3 If very humid air is being sampled the purge time may be increased to more efficiently remove water vapor. However, the sum of sample volume and purge volume must be less than 75% of the retention volume for the most volatile component of interest.

11.2 GC/MS Setup

11.2.1 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.

11.2.2 A block diagram of the analytical system required for analysis of CMS cartridges is depicted in Figure 3. The thermal desorption system must be designed to accommodate the particular cartridge configuration. For the CMS cartridge design shown in Figure 1, the cartridge heating is accomplished as described in 9.8. The use of a desorption oven, in conjunction with a simpler cartridge design is also acceptable. Exposure of the sample to metal surfaces should be minimized and only stainless steel or nickel should be employed. The volume of tubing leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

11.2.3 The GC column oven must be capable of being cooled to -70°C and subsequently temperature programmed to 150°C.

11.2.4 The specific GC column and temperature program employed will be dependent on the compounds of interest. Appropriate conditions are described in the literature (2). In general, a nonpolar stationary phase (e.g., SE-30, OV-1) temperature programmed from -70 to 150°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. Fused silica columns are also more readily connected to the GC injection valve (Figure 3). A drawback of fused silica, bonded-phase columns is the lower capacity compared to coated, glass capillary columns. In most cases the column capacity will be less than 1 microgram injected for fused silica columns.

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

11.2.6 Prior to instrument calibration or sample analysis the GC/MS system is assembled as shown in Figure 3. Helium purge flow (through the cartridge) and carrier flow are set at approximately 50 mL/minute and 2-3 mL/minute respectively. When a cartridge is not in place a union is placed in the helium purge line to ensure a continuous inert gas flow through the injection loop.

11.2.7 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.

11.2.8 The MS and data system are set up 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 11.3. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.3 GC/MS Calibration

11.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant user prepared SOPs. Perfluorotributylamine (FC-43) should generally be employed as the reference compound. The material is introduced directly into the ion source through 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.

11.3.2 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 GC/MS system by introducing known quantities of the components of interest into the system. Three alternate procedures may be employed for the calibration process including 1) direct injection of dilute vapor phase standards, prepared in a dilution bottle or compressed gas cylinder, onto the GC column, 2) injection or dilute vapor phase standards into a flowing inert gas stream directed onto a CMS cartridge, and 3) introduction of permeation or diffusion tube standards onto a CMS cartridge. Direct injection of a compressed gas cylinder (aluminum) standard containing trace levels of the compounds of interest has been found to be the most convenient practice since such standards are stable over a several month period. The standards preparation processes for the various approaches are described in Section 13. The following paragraphs describe the instrument calibration process for these approaches.

11.3.3 If the system is to be calibrated by direct injection of a vapor phase standard, the standard, in either a compressed gas cylinder or dilution flask, is obtained as described in Section 13. The MS and data system are setup for acquisition, but the ionizer filament is shut off. The GC column oven is cooled to -70°C, the injection valve is placed in the load mode, and the cryogenic loop is immersed in liquid nitrogen or liquid argon. Liquid argon is required for standards prepared in nitrogen or air, but not for standards prepared in helium. A known volume of the standard (10-1000 mL) is injected through the cryogenic loop at a rate of 10-100 mL/minute.

11.3.4 Immediately after loading the vapor phase standard, the injection valve is placed in the inject mode, the GC program and system clock are started, and the cryogenic loop is heated to 60°C by applying voltage (15-20 volts) to the thermocouple wire heater surrounding the loop. The voltage is adjusted to maintain a loop temperature of 60°C. An automatic temperature controller can be used in place of the manual control system. After elution of unretained components (~3 minutes after injection) the ionizer filament is turned on and data acquisition is initiated. The helium purge line (set at 50 mL/minute) is connected to the injection valve and the valve is returned to the load mode. The loop temperature is increased to 150°C, with helium purge, and held at this temperature until the next sample is to be loaded.

11.3.5 After the last component of interest has eluted, acquisition is terminated and the data is processed as described in Section 11.3.8. The standard injection process is repeated using different standard concentrations and/or volumes to cover the analytical range of interest.

11.3.6 If the system is to be calibrated by analysis of standard CMS cartridges, a series of cartridges is prepared as described in Sections 13.2 or 13.3. Prior to analysis the cartridges are stored (no longer than 48 hours) as described in Section 9.10. For analysis the injection valve is placed in the load mode and the cryogenic loop is immersed in liquid nitrogen (or liquid argon if desired). The CMS cartridge is installed in the helium purge line (set at 50 mL/minute) so that the helium flow through the cartridge is opposite to the direction of sample flow and the purge gas is directed through the cryogenic loop and vented to the atmosphere. The CMS cartridge is heated to 370-400°C and maintained at this temperature for 10 minutes (using the temperature control process described in Section 9.8). During the desorption period, the GC column oven is cooled to -70°C and the MS and data system are setup for acquisition, but the ionizer filament is turned off.

11.3.7 At the end of the 10 minute desorption period, the analytical process described in Sections 11.3.4 and 11.3.5 is conducted. During the GC/MS analysis heating of the CMS cartridge is discontinued. Helium flow is maintained through the CMS cartridge and cryogenic loop until the cartridge has cooled to room temperature. At that time, the cryogenic loop is allowed to cool to room temperature and the system is ready for further cartridge analysis. Helium flow is maintained through the cryogenic loop at all times, except during the installation or removal of a CMS cartridge, to minimize contamination of the loop.

11.3.8 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.

11.4 Sample Analysis

11.4.1 The sample analysis is identical to that described in Sections 11.3.6 and 11.3.7 for the analysis of standard CMS cartridges.

11.4.2 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 reversed-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 components greater than 1,000 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. In all cases one given standard concentration, near the midpoint of the analytical range of interest, should be injected at least once each day to determine day-to-day precision of response factors.

12.1.3 Since substantial nonlinearity may be 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 injected 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:

$$Y_A = A + BX_A + CX^2$$

where

Y_A is the area of the analyte characteristics 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 ng/L.

V_s and X_A are as previously defined in Section 10.2.11 and 12.2.1, respectively.

13. Standard Preparation

13.1 Standards for Direct Injection

13.1.1 Standards for direct injection can be prepared in compressed gas cylinders or in dilution vessels. The dilution flask protocol has been described in detail in another method and is not repeated here (6). For the CMS method where only volatile compounds (boiling point <120°C) are of concern, the preparation of dilute standards in 15 liter aluminum

compressed gas cylinders has been found to be most convenient. These standards are generally stable over at least a 3-4 month period and in some cases can be purchased from commercial suppliers on a custom prepared basis.

13.1.2 Preparation of compressed gas cylinders requires working with high pressure tubing and fittings, thus requiring a user prepared SOP which ensures that adequate safety precautions are taken. Basically, the preparation process involves injecting a predetermined amount of neat liquid or gas into an empty high pressure cylinder of known volume, using gas flow into the cylinder to complete the transfer. The cylinder is then pressurized to a given value (500-1000 psi). The final cylinder pressure must be determined using a high precision gauge after the cylinder has thermally equilibrated for a 1-2 hour period after filling.

13.1.3 The concentration of components in the cylinger standard should be determined by comparison with National Bureau of Standards reference standards (e.g., SRM 1805-benzene in nitrogen) when available.

13.1.4 The theoretical concentration (at 25°C and 760 mm pressure) for preparation of cylinder standards can be calculated using the following equation:

$$C_T = \frac{V_I \times d}{V_c} \times \frac{14.7}{P_c + 14.7} \times 24.4 \times 1000$$

where

C_T is the component concentration, in ng/mL at 25°C and 760 mm Hg pressure.

V_I is the volume of neat liquid component injected in μL.

V_c is the internal volume of the cylinder, in L.

d is the density of the neat liquid component, in g/mL.

P_c is the final pressure of the cylinder standards, in pounds per square inch gauge (psig).

13.2 Preparation of Spiked Traps by Vapor Phase Injection

This process involves preparation of dilution flask or compressed gas cylinder containing the desired concentrations of the compound(s) of interest and injecting the desired volume of vapor into a flowing gas stream which is directed onto a clean CMS cartridge. The procedure is described in detail in another method within the Compendium (6) and will not be repeated here.

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 (4). Note that a method of accurately 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 liters) is drawn through a clean CMS 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 traps are then stored or immediately analyzed as in Sections 11.3.6 and 11.3.7.

14. Performance Criteria and Quality Assurance

This section summarizes the 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 accomplished in their laboratory: 1) assembly, calibration and operation of the sampling system, (2) preparation, handling and storage of CMS 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 CMS Cartridge Preparation

14.2.1 Each batch of CMS 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 then 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, having been placed in the sampler but without sampling

air, to serve as field blank. The average amount of material found on the field blank cartridges 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) should be collected, preferably at different flow rates as described in Section 10.1.4. 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 sampling 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 might be required.

14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

14.4 GC/MS Analysis

14.4.1 Performance criteria for MS tuning and mass standardization have been discussed in Section 11.2 and Table 2. Additional criteria can 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 daily by the injection of calibration standards. A reference compound(s) should be chosen from the calibration standard and plotted on an expanded time scale so that its

width at 10% of the peak height 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 user should also evaluate chromatographic performance for any polar or reactive compounds of interest, 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 or tubing and/or if replacement of the GC column is required. Some laboratories may choose to evaluate column performance separate by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7).

14.4.3 The 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 12.1.3.
S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are 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 for replicate cartridges 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). Spiking is readily accomplished using the procedure outlined in Section 13.2, using a compressed gas standard. 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.

14.5 Method Precision and Recovery

14.5.1 Recovery and precision data for selected volatile organic compounds are presented in Table 1. These data were obtained using ambient air, spiked with known amounts of the compounds in a dynamic mixing system(2).

14.5.2 The data in Table 1 indicate that in general recoveries better than 75% and precision (relative standard deviations) of 15-20% can be obtained. However, selected compounds (e.g. carbon tetrachloride and benzene) will have poorer precision and/or recovery. The user must check recovery and precision for any compounds for which quantitative data are needed.

References

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2. Riggin, R. M. and L. E. Slivon. Determination of Volatile Organic Compounds in Ambient Air Using Carbon Molecular Sieve Adsorbents, Special Report on Contract 68-02-3745 (WA-7), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September, 1983.

3. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

4. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis: Occupational Health and Safety", American Society for Testing and Materials, 1983.

5. Walling, J. F., Berkley, R. E., Swanson, D. H., and Toth, F. J. "Sampling Air for Gaseous Organic Chemical-Applications to Tenax", EPA-600/7-54-82-059, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

6. This Methods Compendium - Tenax Method (T0 1).

7. Grob, K., Jr., Grob, G., and Grob, K., "Comprehensive Standardized Quality Test for Glass Capillary Columns", J. Chromatog., 156 1-20, 1978.

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CMS ADSORPTION METHOD HAS BEEN EVALUATED

Compound	Retention Time, Minutes[a]	Characteristic Mass Fragment Used for Quantification	Method Performance Data[b] Concentration, ng/L	Percent Recovery	Standard Deviation
Vinyl Chloride	6.3	62	17	74	19
Acrylonitrile	10.8	53	20	85	18
Vinylidene Chloride	10.9	96	36	94	19
Methylene Chloride	11.3	84	28	93	16
Allyl Chloride	11.4	76	32	72	19
Chloroform	13.8	83	89	91	12
1,2-Dichloroethane	14.5	62	37	85	11
1,1,1-Trichloroethane	14.7	97	100	75	9.1
Benzene	15.4	78	15	140	37
Carbon Tetrachloride	15.5	117	86	55	2.9
Toluene	18.0	91	4.1	98	5.4

[a] GC conditions as follows:

Column - Hewlett Packard, crosslinked methyl silicone, 0.32 mm ID x 50 m long, thick film, fused silica.

Temperature Program - 70°C for 2 minutes then increased at 8°C/minute to 120°C.

[b] From Reference 2. For spiked ambient air.

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

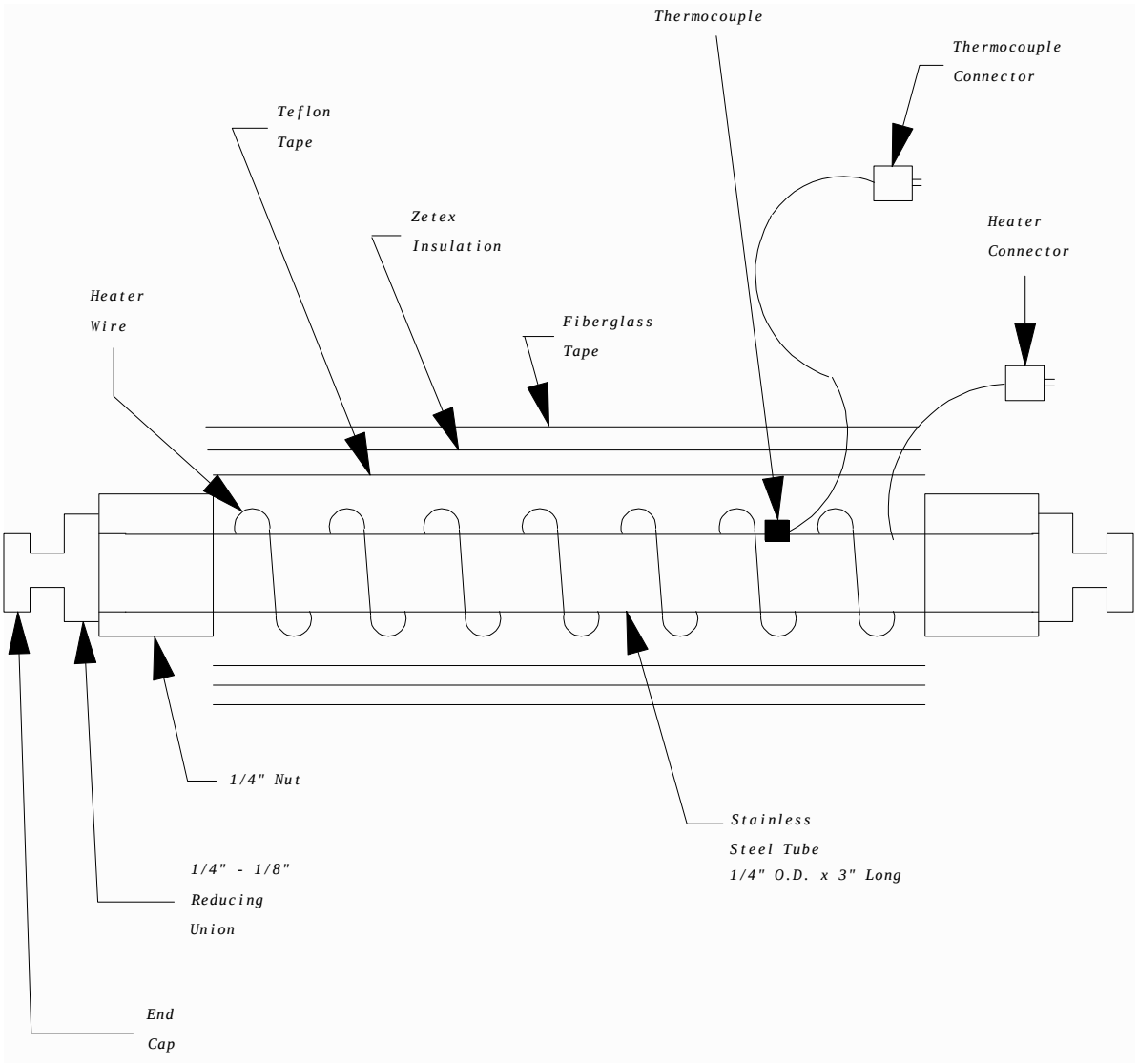


FIGURE 1. DIAGRAM SHOWING CARBON MOLECULAR SIEVE TRAP (CMS) CONSTRUCTION

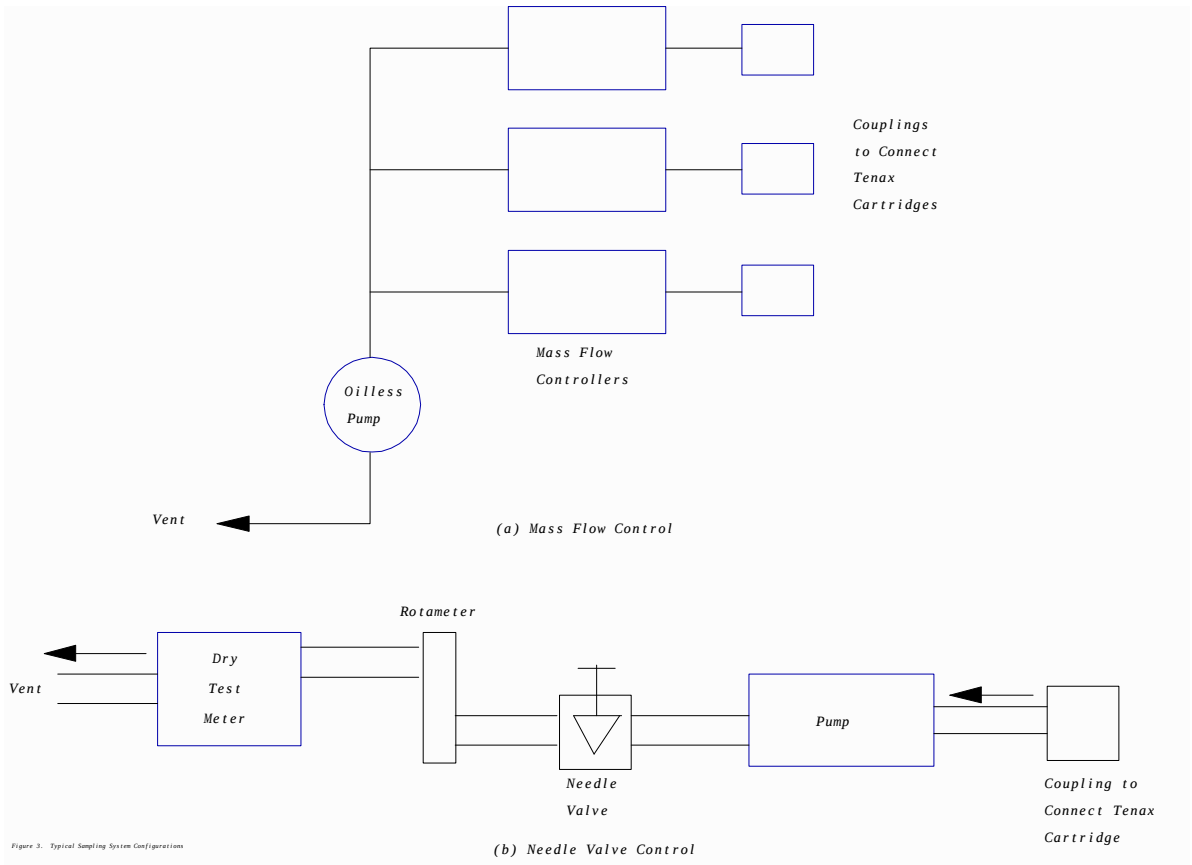


Figure 3. Typical Sampling System Configurations

FIGURE 2. TYPICAL SAMPLING SYSTEM CONFIGURATIONS

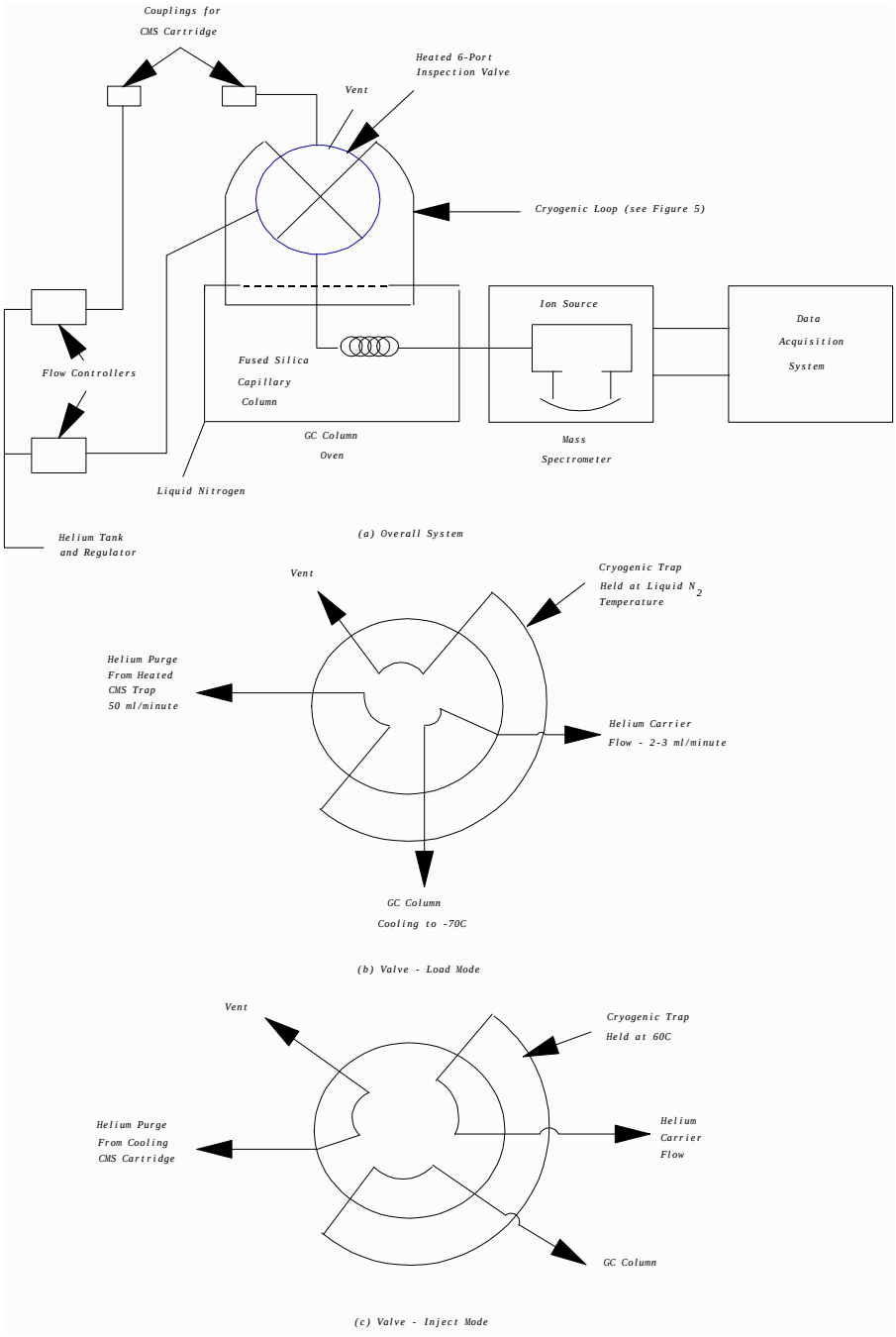


FIGURE 3. GC/MS ANALYSIS SYSTEM FOR CMS CARTRIDGES

SAMPLING DATA SHEET
(One Sample Per Data Sheet)

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 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

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

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

FIGURE 4. EXAMPLE SAMPLING DATA SHEET

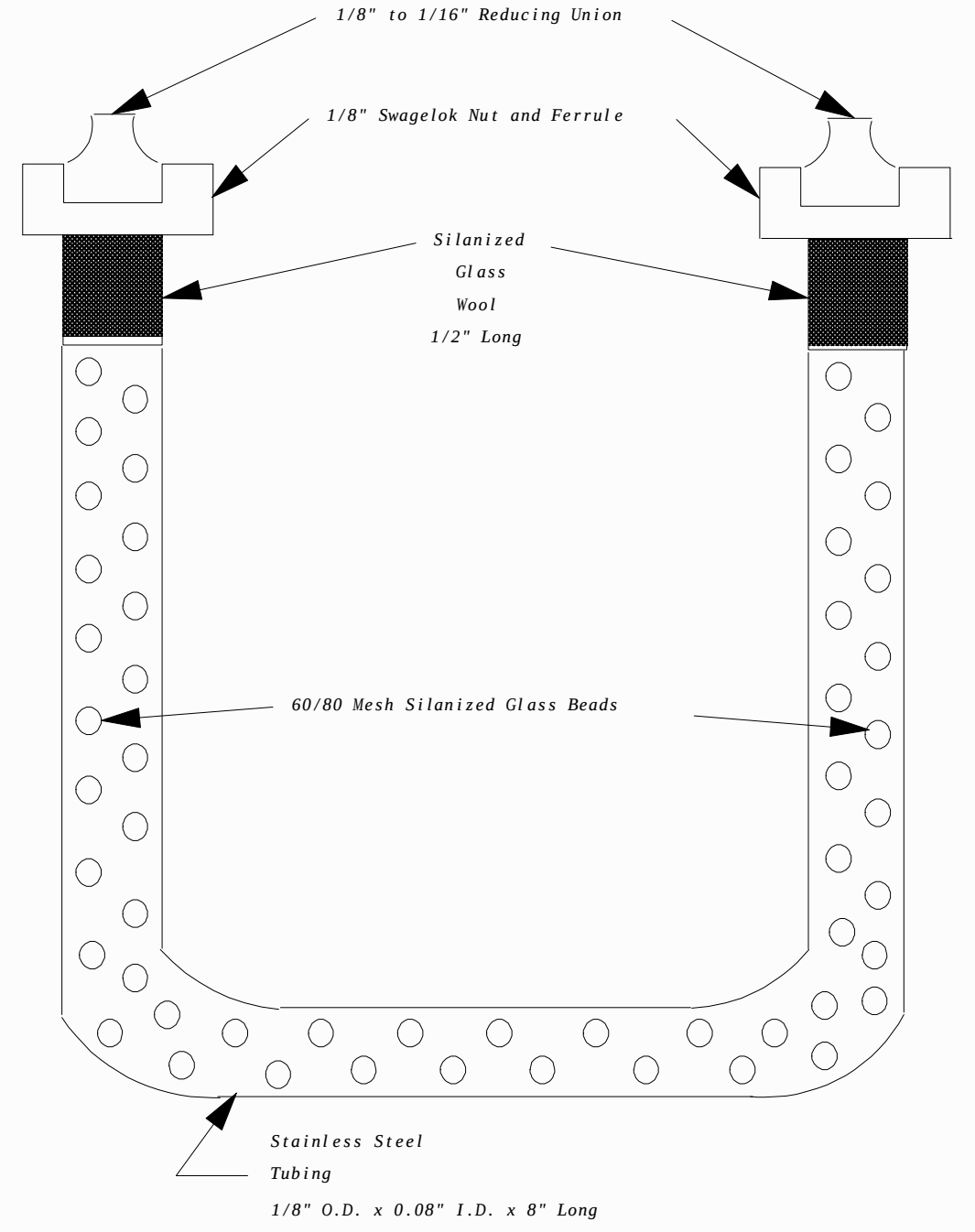
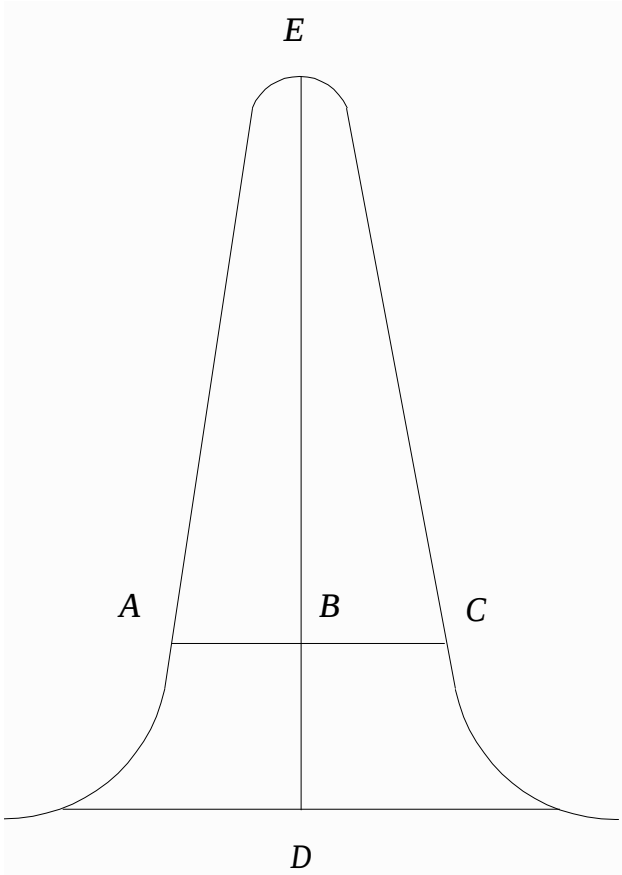


FIGURE 5. CRYOGENIC TRAP DESIGN



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm

10% Peak Height = BD = 10 mm

Peak Width at 10% Peak Height = AC = 23 mm

AB = 11 mm

BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11} = 1.1$

FIGURE 6. PEAK ASYMMETRY CALCULATION