METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION TECHNIQUES AND GAS CHROMATOGRAPHY WITH FLAME IONIZATION AND ELECTRON CAPTURE DETECTION

1. Scope

1.1 This document describes a method for the determination of highly volatile compounds having boiling points in the range of -10 to 200°C.

1.2 The methodology detailed in this document is currently employed by numerous laboratories (1-4;8-11). Modifications to this methodology should be accompanied by appropriate documentation of the validity and reliability of these changes.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition 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 (1-4).
U. S. EPA Technical Assistance Document (5).

3. Summary of Method

3.1 Ambient air analyses are performed as follows. A collection trap, as illustrated in Figure 1, is submerged in either liquid oxygen or argon. Liquid argon is highly recommended for use because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position an air sample is then admitted into the trap by a volume measuring apparatus. In the meantime, the column oven is cooled to a sub-ambient temperature (-50°C). Once sample collection is completed, the valve is switched so that the carrier gas sweeps the contents of the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is

removed and the trap is heated to assist the sample transfer process. The GC column is temperature programmed and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternate detectors (e.g., photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function has been described in the literature (8,9).

3.2 Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended. However, when highly selective detectors (such as the electron capture detector) are employed, packed column technology without cryogenic temperature programming can be effectively utilized in some cases.

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 Because these organic species are present at ppb levels or below, some means of sample preconcentration is necessary in order to acquire sufficient material for identification and quantification. The two primary preconcentration techniques are cryogenic collection and the use of solid adsorbents. The method described herein involves the former technique.

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 within this document at the point of use.

6. Interferences/Limitations

6.1 Compounds having similar GC retention times will interfere in the method. Replacing the flame ionization detector with more selective detection systems will help to minimize these interferences. Chlorinated species, in particular, should be determined using the electron capture detector to avoid interference from volatile hydrocarbons.

6.2 An important limitation of the technique is the condensation of moisture in the collection trap. The possibility of ice plugging the trap and stopping the flow is of concern, and water subsequently transferred to the capillary column may also result in flow stoppage and cause deleterious effects to certain column materials. Use of permaselective Nafion® tubing in-line before the cryogenic trap avoids this problem; however, the material must be used with caution because of possible losses of certain compounds. Another potential problem is contamination from the Nafion® tubing. The user should consult the literature (7-12) for details on the use of permeation-type driers.

7.   Apparatus

7.1 Gas chromatograph/Flame Ionization/Electron Capture Detection System - must be capable of subambient temperature programming. A recent publication (8) describes an automated GC system in which the cryogenic sampling and analysis features are combined. This system allows simultaneous flame ionization and electron capture detection.

7.2 Six-port sampling valve - modified to accept a sample collection trap (Figure 1).

7.3 Collection trap - 20 cm x 0.2 cm I.D. stainless steel tubing packed with 60/80 mesh silanized glass beads and sealed with glass wool. For the manual system (Section 9.2) the trap is externally wrapped with 28 gauge (duplex and fiberglass insulated) type "K" thermocouple wire. This wire, beaded at one end, is connected to a powerstat during the heating cycle. A thermocouple is also attached to the trap as shown in Figure 1.

7.4 Powerstat - for heating trap.

7.5 Temperature readout device - for measuring trap temperature during heating cycle.

7.6 Glass dewar flask - for holding cryogen.

7.7 Sample volume measuring apparatus - capable of accurately and precisely measuring a total sample volume up to 500 cc at sampling rates between 10 and 200 cc/minute. See Section 9.

7.8 Stopwatch.

7.9 Dilution container for standards preparation - glass flasks or Teflon (Tedlar) bags, .002 inch film thickness (see Figure 2).

7.10 Liquid microliter syringes - 5-50 μl for injecting liquid standards into dilution container.

7.11 Volumetric flasks - various sizes, 1-10 mL.

7.12 GC column - Hewlett Packard 50 meter methyl silicone cross-linked fused silica column (.3 mm I.D., thick film) or equivalent.

7.13 Mass flow controller - 10-200 mL/minute flow control range.

7.14 Permeation drier - PermaPure® - Model MD-125F, or equivalent. Alternate designs described in the literature (7-12) may also be acceptable.

8. Reagents and Materials

8.1 Glass beads - 60/80 mesh, silanized.

8.2 Glasswool - silanized.

8.3 Helium - zero grade compressed gas, 99.9999%.

8.4 Hydrogen - zero grade compressed gas, 99.9999%.

8.5 Air - zero grade compressed gas.

8.6 Liquid argon (or liquid oxygen).

8.7 Liquid nitrogen.

8.8 SRM 1805 - benzene in nitrogen standard. Available from the National Bureau of Standards. Additional such standards will become available in the future.

8.9 Chemical standards - neat compounds of interest, highest purity available.

9. Sampling and Analysis Apparatus

Two systems are described below which allow collection of an accurately known volume of air (100-1000 mL) onto a cryogenically cooled trap. The first system (Section 9.1) is an automated device described in the literature (8,9). The second system (Section 9.2) is a manual device, also described in the literature(2).

9.1 The automated sampling and analysis system is shown in Figure 3. This system is composed of an automated GC system (Hewlett Packard Model 5880A, Level 4, or equivalent) and a sample collection system (Nutech Model 320-01, or equivalent). The overall system is described in the literature (8).

  9.1.1 The electronic console of the sampling unit controls the mechanical operation of the six-port valve and cryogenic trapping components as well as the temperatures in each of the three zones (sample trap, transfer line, and valve).

  9.1.2 The valve (six-port air activated, Seiscor Model 8 or equivalent) and transfer line are constantly maintained at 120°C. During sample collection the trap temperature is maintained at -160 ± 5°C by a flow of liquid nitrogen controlled by a solenoid valve. A cylindrical 250 with heater, held in direct contact with the trap, is used to heat the trap to 120°C in 60 seconds or less during the sample desorption step. The construction of the sample trap is described in Section 7.3.

  9.1.3 The sample flow is controlled by a pump/mass flow controller assembly, as shown in Figure 3. A sample flow of 10-100 mL/minute is generally employed, depending on the desired sampling period. A total volume of 100-1000 mL is commonly collected.

  9.1.4 In many situations a permaselective drier (e.g., Nafion®) may be required to remove moisture from the sample. Such a device is installed at the sample inlet. Two configurations for such devices are available. The first configuration is the tube and shell type in which the sample flow tube is surrounded by an outer shell through which a countercurrent flow of clean, dry air is maintained. The dry air stream must be free from contaminants and its flow rate should be 3-4 times greater than the sample flow to achieve effective drying. A second configuration (7) involves placing a drying agent, e.g., magnesium carbonate, on the outside of the sample flow tube. This approach eliminates the need for a source of clean air in the field. However, contamination from the drying agent can be a problem.

9.2 The manual sampling consists of the sample volume
     measuring apparatus shown in Figure 4 connected to the
     cryogenic trap/GC assembly shown in Figure 1. The
     operation of this assembly is described below.

     9.2.1   Pump-Down Position

               The purpose of the pump-down mode of operation
               is to evacuate the ballast tank in preparation
               for collecting a sample as illustrated in
               Figure 4. (While in this position, helium can
               also be utilized to backflush the sample line,
               trap, etc. However, this cleaning procedure
               is not normally needed during most sampling
               operations). The pump used for evacuating the
               system should be capable of attaining 200 torr
               pressure.

     9.2.2   Volume Measuring Position

               Once the system has been sufficiently
               evacuated, the 4-way ball valve is switched to
               prepare for sample collection. The 3-position
               valve is used to initiate sample flow while
               the needle valve controls the rate of flow.

     9.2.3   Sample Volume Calculation

               The volume of air that has passed through the
               collection trap corresponds to a known change
               in pressure within the ballast tank (as
               measure by the Wallace Tiernan gauge).
               Knowing the volume, pressure change, and
               temperature of the system, the ideal gas law
               can be used to calculate the number of moles
               of air sampled. On a volume basis, this
               converts to the following equation:

$$V_s = \frac{\Delta P}{760} \times \frac{298}{T_A + 273}$$

     where
               V_s = Volume sampled at 760 mm Hg pressure and
                    25°C.
               ΔP = Change in pressure within the ballast
                    tank, mm of Hg.
               V = Volume of ballast tank and gauge.
               T_A = Temperature of ballast tank, °C.

     The internal volume of the ballast tank and gauge can be
     determined either by H_2O displacement or by injecting
     calibrated volumes of air into the system using large
     volume syringes, etc.

10. Sampling and Analysis Procedure - Manual Device

10.1 This procedure assumes the use of the manual sampling system described in Section 9.2.

10.2 Prior to sample collection, the entire assembly should be leak-checked. This task is accomplished by sealing the sampling inlet line, pumping the unit down and placing the unit in the flow measuring mode of operation. An initial reading on the absolute pressure gauge is taken and rechecked after 10 minutes. No apparent change should be detected.

10.3 Preparation for sample collection is carried out by switching the 6-port valve to the "fill" position and connecting the heated sample line to the sample source. Meanwhile the collection trap is heated to 150°C (or other appropriate temperature). The volume measuring apparatus is pumped-down and switched to the flow measuring mode. The 3-position valve is opened and a known volume of sample is then passed through the heated sample line and trap to purge the system.

10.4 After the system purge is completed, the 3-position valve is closed and the corresponding gauge pressure is recorded. The collection trap is then immersed into a dewar of liquid argon (or liquid oxygen) and the 3-position valve is temporarily opened to draw in a known volume of air, i.e. a change in pressure corresponds to a specific volume of air (see Section 9). Liquid nitrogen cannot be used as the cryogen since it will also condense oxygen from the air. Liquid oxygen represents a potential fire hazard and should not be employed unless absolutely necessary.

10.5 After sample collection is completed, the 6-port valve is switched to the inject position, the dewar is removed and the trap is heated to 150°C to transfer the sample components to the head of the GC column which is initially maintained at -50°C. Temperature programming is initiated to elute the compounds of interest.

10.6 A GC integrator (or data system if available) is activated during the injection cycle to provide component identification and quantification.

11.   Sampling and Analysis Procedure - Automated Device

11.1 This procedure assumes the use of the automated system shown in Figure 3. The components of this system are discussed in Section 9.1.

11.2 Prior to initial sample collection the entire assembly should be leak-checked. This task is completed by sealing the sample inlet line and noting that the flow indication or the mass flow controller drops to zero (less than 1 mL/minute).

11.3 The sample trap, valve, and transfer line are heated to 120°C and ambient air is drawn through the apparatus (~60mL/minute) for a period of time 5-10 minutes to flush the system, with the sample valve in the inject position. During this time the GC column is maintained at 150°C to condition the column.

11.4 The sample trap is then cooled to -160 $\pm$ 5°C using a controlled flow of liquid nitrogen. Once the trap temperature has stabilized, sample flow through the trap is initiated by placing the valve in the <u>inject</u> position and the desired volume of air is collected.

11.5 During the sample collection period the GC column is stabilized at -50°C to allow for immediate injection of the sample after collection.

11.6 At the end of the collection period the valve is immediately placed in the inject position, and the cryogenic trap is rapidly heated to 120°C to desorb the components onto GC column. The GC temperature program and data acquisition are initiated at this time.

11.7 At the desired time the cryogenic trap is cooled to -160°C, the valve is returned to the collect position and the next sample collection is initiated (to coincide with the completion of the GC analysis of the previous sample).

12.   Calibration Procedure

Prior to sample analysis, and approximately every 4-6 hours thereafter, a calibration standard must be analyzed, using the identical procedure employed for ambient air samples (either Section 10 or 11). This section describes three alternative approaches for preparing suitable standards.

12.1 Teflon® (or Tedlar®) Bags

12.1.1   The bag (nominal size; 20L) is filled with zero air and leak checked. This can be easily accomplished by placing a moderate weight (text book) on the inflated bag and leaving overnight. No visible change in bag volume indicates a good seal. The bag should also be equipped with a quick-connect fitting for sample withdrawal and an insertion port for liquid injections (Figure 2).

12.1.2   Before preparing a standard mixture, the bag is sequentially filled and evacuated with zero air (5 times). After the 5th filling, a sample blank is obtained using the sampling procedure outlined in Section 10.

12.1.3   In order to prepare a standard mixture, the bag is filled with a known volume of zero air. This flow should be measured via a calibrated mass flow controller or equivalent flow measuring device. A measured aliquot of each analyte of interest is injected into the bag through the insertion port using a microliter syringe. For those compounds with vapor pressures lower than benzene or for strongly adsorbed species, the bag should be heated (60° C oven) during the entire calibration period.

12.1.4   To withdraw a sample for analysis, the sampling line is directly connected to the bag. Quick connect fittings allow this hook-up to be easily accomplished and also minimizes bag contamination from laboratory air. Sample collection is initiated as described.

12.2 Glass Flasks

12.2.1   If a glass flask is employed (Figure 2) the exact volume is determined by weighing the flask before and after filling with deionized water. The flask is dried by heating at 200°C.

12.2.2   To prepare a standard, the dried flask is flushed with zero air until cleaned (i.e., a blank run is made). An appropriate aliquot of

each analyte is injected using the same procedures as described for preparing bag standards.

12.2.3   To withdraw a standard for analysis, the GC sampling line is directly connected to the flask and a sample obtained. However, because the flask is a rigid container, it will not remain at atmospheric pressure after sampling has commenced. In order to prevent room air leakage into the flask, it is recommended that no more than 10% of the initial volume be exhausted during the calibration period (i.e., 200cc if a 2 liter flask is used).

12.3 Pressurized Gas Cylinders

12.3.1   Pressurized gas cylinders containing selected analytes at ppb concentrations in air can be prepared or purchased. A limited number of analytes (e.g., benzene, propane) are available from NBS.

12.3.2   Specialty gas suppliers will prepare custom gas mixtures, and will cross reference the analyte concentrations to an NBS standard for an additional charge. In general, the user should purchase such custom mixtures, ratherthan attempting to prepare them because of the special high pressure filling apparatus required. However, the concentrations should be checked, either by the supplier or the user using NBS reference materials.

12.3.3   Generally, aluminum cylinders are suitable since most analytes of potential interest in this method have been shown to be stable for at least several months in such cylinders. Regulators constructed of stainless steel and Teflon® (no silicon or neoprene rubber).

12.3.4   Before use the tank regulator should be flushed by alternately pressuring with the tank mixture, closing the tank valve, and venting the regulator contents to the atmosphere several times.

12.3.5   For calibration, a continuous flow of the gas mixture should be maintained through a glass or Teflon® manifold from which the calibration

standard is drawn. To generate various
calibration concentrations, the pressurized
gas mixture can be diluted, as desired, with
zero grade air using a dynamic dilution system
(e.g., CSI Model 1700).

13. Calibration Strategy

13.1 Vapor phase standards can be prepared with either neat
liquids or diluted liquid mixtures depending upon the
concentration levels desired. It is recommended that
benzene also be included in this preparation scheme so
that flame ionization detector response factors, relative
to benzene, can be determined for the other compounds.
The benzene concentration generated in this fashion
should be cross-checked with an NBS (e.g., SRM 1805) for
accuracy determinations.

13.2 Under normal conditions, weekly multipoint calibrations
should be conducted. Each multipoint calibration should
include a blank run and four concentration levels for the
target species. The generated concentrations should
bracket the expected concentration of ambient air
samples.

13.3 A plot of nanograms injected versus area using a linear
least squares fit of the calibration data will yield the
following equation:

$$Y = A + BX$$

where

Y = quantity of component, nanograms
A = intercept
B = slope (response factor)

If substantial nonlinearity is present in the calibration
curve a quadratic fit of the data can be used:

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

where
C = constant

Alternatively, a stepwise multilevel calibration scheme may be
used if more convenient for the data system in use.

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.

14.1 Standard Operating Procedures (SOPs)

    14.1.1   Each user should generate SOPs describing the following activities as accomplished in their laboratories:

        1)   assembly, calibration and operation of the sampling system.
        2)   preparation and handling of calibration standards.
        3)   assembly, calibration and operation of the GC/FID 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 Method Sensitivity, Precision and Accuracy

    14.2.1   System sensitivity (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 = calculated detection limit in nanograms injected.
    A = intercept calculated in Section 13.
    S = standard deviation of replicate determination of the lowest level standard (at least three determinations are required).

For many compounds detection limits of 1 to 5 nanograms are found using the flame ionization detection. Lower detection limits can be obtained for chlorinated hydrocarbons using the electron capture detector.

14.2.2   A precision of $\pm$ 5% (relative standard deviation) can be readily achieved at concentrations 10 times the detection limit. Typical performance data are included in Table 1.

14.2.3   Method accuracy is estimated to be within $\pm$ 10%, based on National Bureau of Standard calibrated mixtures.

REFERENCES

1. Holdren, M., Spicer, C., Sticksel, P., Nepsund, K., Ward, G., and Smith, R., "Implementation and Analysis of Hydrocarbon Grab Samples from Cleveland and Cincinnati 1981 Ozone Monitoring Study", EPA-905/4-82-001. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1982.

2. Westberg, H., Rasmussen, R., and Holdren, M., "Gas Chromatographic Analysis of Ambient Air for Light Hydrocarbons Using a Chemically Bonded Stationary Phase", Anal. Chem. 46, 1852-1854, 1974.

3. Lonneman, W. A., "Ozone and Hydrocarbon Measurements in Recent Oxidant Transport Studies", in Int. Conf. on Photochemical Oxidant Pollutant and Its Control Proceedings, EPA-600/3-77-001a, 1977.

4. Singh, H., "Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies", EPA-450/4-80-008. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1980.

5. 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.

6. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis", American Society for Testing and Materials, Philadelphia, Pennsylvania, 1983.

7. Foulger, B. E. and P. G. Sinamouds, "Drier for Field Use in the Determination of Trace Atmospheric Gases", Anal. Chem., 51, 1089-1090, 1979.

8. Pheil, J. D. and W. A. McClenney, "Reduced Temperature Preconcentration Gas Chromatographic Analysis of Ambient Vapor-Phase Organic Compounds: System Automation", Anal. Chem., submitted, 1984.

9. Holdren, M. W., W. A. McClenney, and R. N. Smith "Reduced Temperature Preconcentration and Gas Chromatographic Analysis of Ambient Vapor-Phase Organic Compounds: System Performance", Anal. Chem., submitted, 1984.

10. Holdren, M., S. Rust, R. Smith, and J. Koetz, "Evaluation of Cryogenic Trapping as a Means for Collecting Organic Compounds in Ambient Air", Draft Final Report on Contract No. 68-02-3487, 1984.

11. Cox, R. D. and R. E. Earp, "Determination of Trace Level Organics in Ambient Air by High-Resolution Gas Chromatography with Simultaneous Photoionization and Flame Ionization Detection", Anal. Chem. <u>54</u>, 2265-2270, 1982.

12. Burns, W. F., O. T. Tingy, R. C. Evans and E. H. Bates, "Problems with a Nafion® Membrane Dryer for Chromatographic Samples", J. Chrom. <u>269</u>, 1-9, 1983.
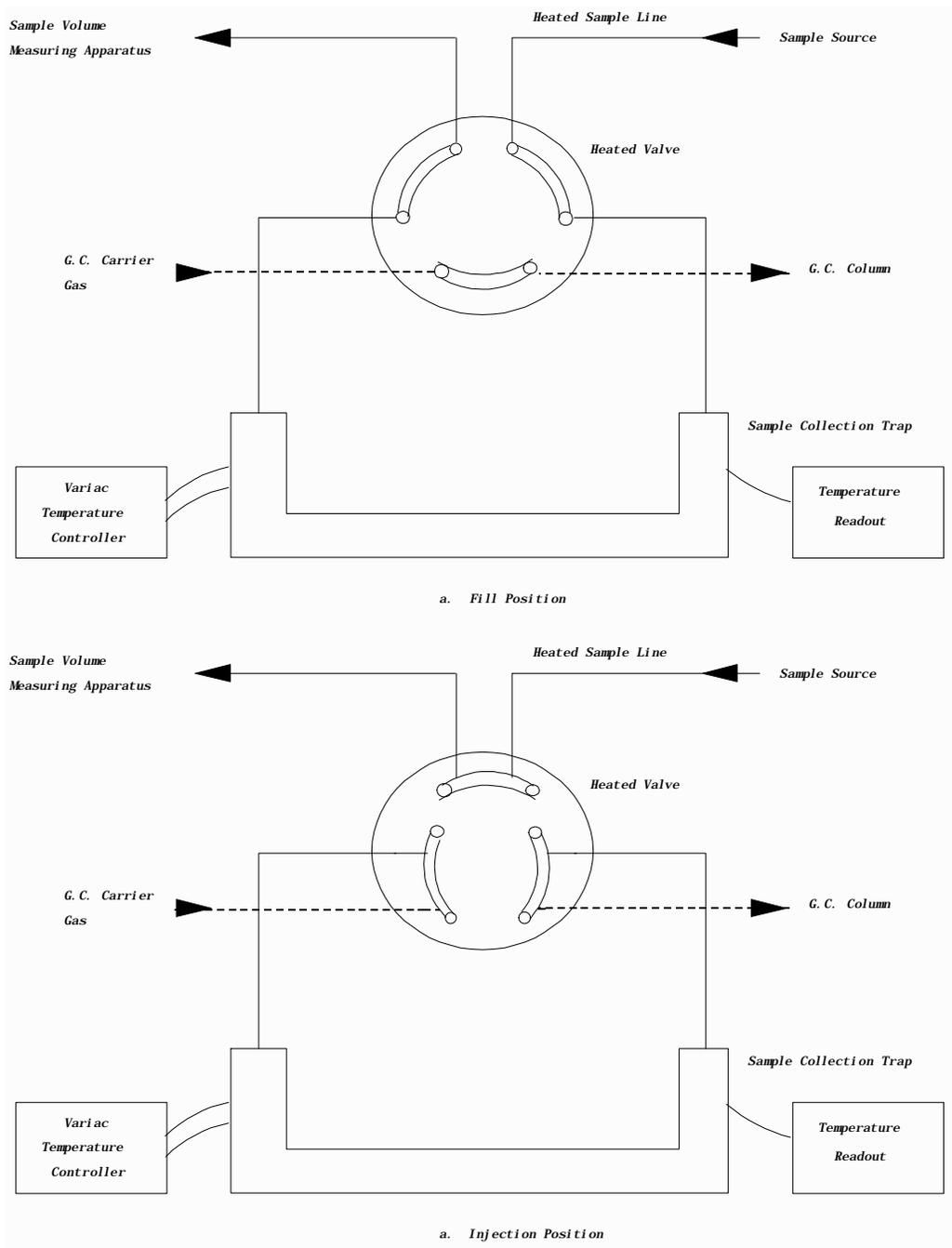
Figure 1. Schematic of Six-Port Valve Used for Sample Collection.

Septum Seal

Glass/Teflon Valve

2 Liter
Glass Flask

Quick Connect
Sampling Port

20 Liter
Teflon Bag

Pinhole Insertion
Port or Septum
Injection Port
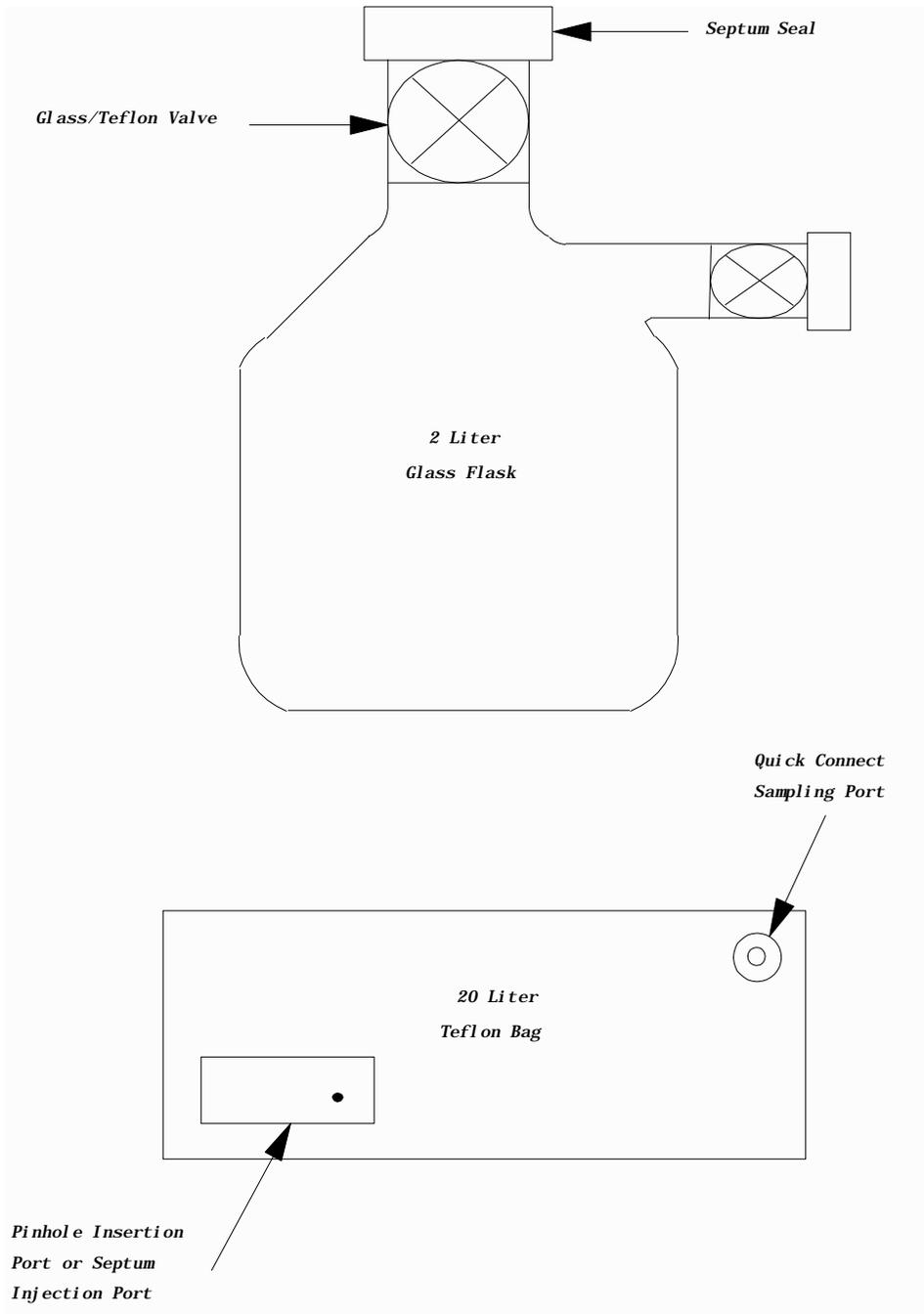
Figure 2. Dilution Containers for Standard Mixtures
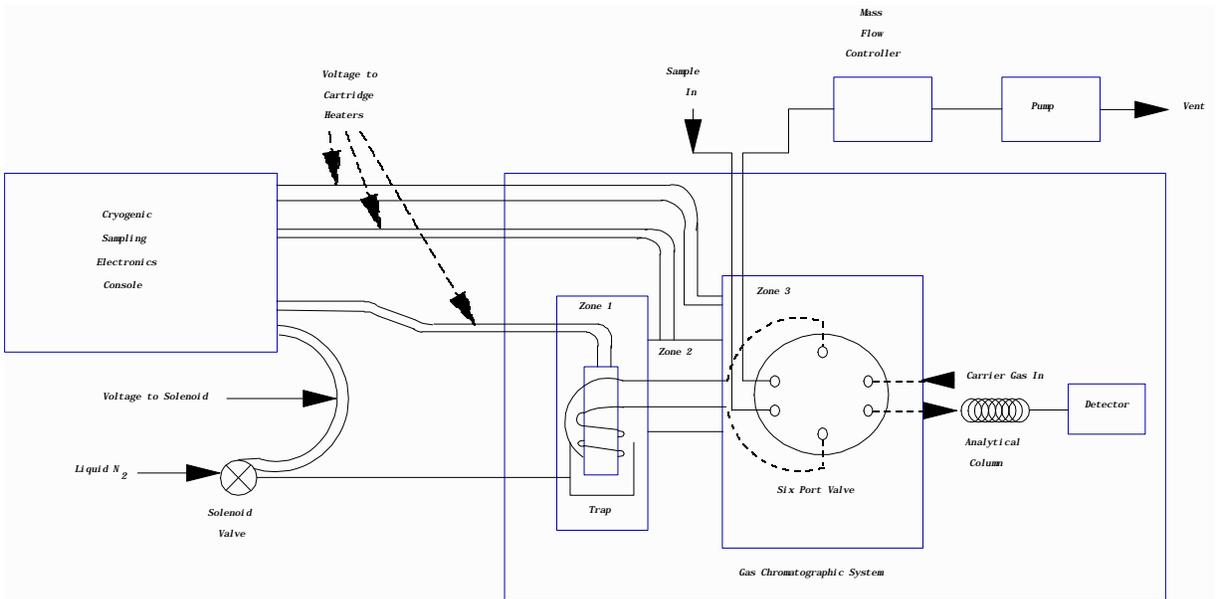
Figure 3. Automated Sampling and Analysis System for Cryogenic Trapping

Pump

Wallace
Tiernan
Gauge

Vent

4 Way Ball
Valve

Shut Off
Valve

Helium Tank

Ballast Tank

Needle Valve

3 Position Valve

(1) Gas Chromatograph 6-Port Valve

(2) (Optional 2nd GC System)

(3) Off

1   2

(a) Volume Measuring Position

Pump

Wallace
Tiernan
Gauge

Vent

4 Way Ball
Valve

Shut Off
Valve

Helium Tank

Ballast Tank

Needle Valve

3 Position Valve

(1) Gas Chromatograph 6-Port Valve

(2) (Optional 2nd GC System)

(3) Off

1   2

(b) Pump - Down Position

Figure 4.   Sample Volume Measuring Apparatus

TABLE 1. VOLATILE ORGANIC COMPOUNDS FOR WHICH THE CRYOGENIC SAMPLING METHOD HAS BEEN EVALUATED[a]

4444444444444444444444444444444444444444444444444444444444444444444444444444

Compound	Retention Time, Minutes[b]	Test 1 (4 runs, 200cc samples) Mean (ppb)	%RSD	Test 2 (8 runs, 200-cc samples) Mean (ppb)	%RSD
Vinylidene Chloride	9.26	144	4.4	6.1	3.9
Chloroform	12.16	84	3.8	3.5	5.8
1,2-Dichloroethane	12.80	44	3.7	1.9	5.1
Methylchloroform	13.00	63	4.5	2.7	4.9
Benzene	13.41	93	4.0	3.9	5.1
Trichloroethylene	14.48	84	3.7	3.5	4.1
Tetrachloroethylene	17.37	69	3.7	2.9	4.3
Chlorobenzene	18.09	46	3.3	1.9	3.2

4444444444444444444444444444444444444444444444444444444444444444444444444444

[a] Recovery efficiencies were 100 $\pm$ 5% as determined by comparing direct sample loop (5cc) injections with cryogenic collection techniques (using test 1 data). Data from reference 10.

[b] GC conditions as follows:

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

>   Temperature Program - 50°C for 2 minutes, then increased at 8°C/minute to 150°C.