METHOD 5032

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 Method 5032 is used to determine volatile organic compounds in a variety of liquid, solid, oily waste matrices, and animal tissues. This method is applicable to nearly all types of matrices regardless of water, soil, sediment, sludge, oil, and biota content. Method 5032 is useful in the determination of the following compounds:

Compound Name	CAS No.[a]
Acetone	67-64-1
Acrolein	107-02-8
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone	78-93-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane	75-00-3
2-Chloroethyl vinyl ether	110-75-8
Chloroform	67-66-3
Chloromethane	74-87-3
Dibromomethane	74-95-3
1,4-Dichloro-2-butene	764-41-0
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-35-4
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-3
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethanol	64-17-5
Ethylbenzene	100-41-4
Ethyl methacrylate	97-63-2
2-Hexanone	591-78-6
Iodomethane	74-88-4
Methylene chloride	75-09-2
4-Methyl-2-pentanone	108-10-1
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	79-34-5

(continued)

Compound Name	CAS No.[a]
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl acetate	108-05-4
Vinyl chloride	75-00-3
m-Xylene	108-38-3
p-Xylene	106-42-3
o-Xylene	95-47-6

[a] Chemical Abstract Service Registry Number.

1.2 This method can be used to quantitate most volatile organic compounds that have a boiling point below 180°C and are insoluble or slightly soluble in water. Reference Method 8260 for a list of compounds, retention times, and their characteristic ions that have been evaluated on the vacuum distillation GC/MS system. Method 8260 also presents a list of compounds that represent a wide range of physical properties. These compounds have been minimally investigated to assist in identifying potential analytes of this method.

1.3 The method detection limits (MDL) determined are identified in tables located in Method 8260. Samples that require dilution will have proportionately higher detection limits.

1.4 Method 5032 is based on a vacuum distillation and cryogenic trapping procedure followed by gas chromatography/mass spectrometry. Alternate columns and detectors may be substituted when appropriate.

1.5 This method is restricted to use by, or under the supervision of, experienced personnel who are familiar with the techniques of vacuum distillation and experienced in the use of gas chromatographs and mass spectrometers as a quantitative tool. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The sample is introduced into a sample flask which is then attached to the apparatus (Figure 1). The sample chamber pressure is reduced using a vacuum pump and remains at approximately 10 torr (vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to a temperature of -10°C or less, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped on a section of 1/8 inch stainless steel tubing chilled to the temperature of liquid nitrogen (-196°C). After an appropriate distillation period which may vary due to matrix or analyte group, the condensate

contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium carrier gas.

2.2 It is emphasized that the apparatus conditions are optimized to remove analyte from the sample matrix and isolate water from the distillate. The conditions may be varied to optimize the method for a given analyte or group of analytes. The length of time required for distillation may vary due to matrix effects or the analyte group of interest. Operating parameters may be varied to achieve optimum analyte recovery.

3.0 INTERFERENCES

3.1 Method interference may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baseline in the chromatograms.

3.1.1 Interferences distilled from the sample will vary from source to source, depending on the particular sample or matrix. The analytical system should be checked to insure freedom from interferences by analyzing method blanks under identical conditions of analysis.

3.1.2 The apparatus can be decontaminated with a ten minute evacuation of the distillation apparatus while the condenser coils are heated to 45^{o}C.

3.2 The laboratory where analysis is to be performed should be completely free of solvents. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratories at low levels. The sample receiving chamber should be loaded in a clean environment to eliminate this problem.

3.3 Samples may be contaminated during shipment. Field and trip blanks should be analyzed to insure integrity of the transported sample. It is recommended that wherever possible, samples aliquots and surrogates are transferred directly to sample flasks in the field, weighed and sealed using O-ring connections.

3.4 Impurities in purge gas and from organic compounds out-gassing from plumbing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by including laboratory reagent blanks. All gas lines should be equipped with hydrocarbon and oxygen removal traps.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1000 µL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle.

4.2 Syringe: 5 mL and 10 mL gas tight, with Luer Lock tip and needles.

4.3 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top loading balance capable of weighing 0.1 g.

4.4 Balance weights: Stainless steel S-class weights ranging from 5 mg to 100 g.

4.5 Sample Flask: 100 mL Pyrex® bulb joined to a 15 mm ID Pyrex® O-ring connector. The flask must be capable of being pumped down to a pressure of 10 mtorr without implosion. The flask is sealed for sample storage with a Buna-N O-ring, a 15 mm ID O-ring connector cap, and a pinch clamp.

4.6 Vacuum distillation apparatus (see Figure 1): The basic apparatus consists of a sample chamber connected to a condenser which is attached to a heated six port valve (V4). The sampling valve is connected to the following;

1) condenser (by way of Vacuum Pump Valve - V3)
2) vacuum pump
3) cryotrap
4) gas chromatograph/mass spectrometer

The sampling valve (V4) is heated to prevent condensation and potential carryover.

The circulating system which supplies the condenser coils consists of a cryogenic cooler with reservoir and an elevated temperature bath (45°C). The coolant reservoir may be filled with isopropyl alcohol or other appropriate fluid such as salt water. The fluid is circulated through the condenser coils with a peristaltic pump and the alternating of bath fluids are accomplished by the circulating fluid valve (V3).

The apparatus is heated to a temperature sufficient to prevent condensation of analytes onto condenser walls, valves, and connections. The temperature of the transfer line from the sampling valve to the gas chromatograph should be heated to the upper temperature utilized by the GC program.

Pirani gauges are recommended at the sample chamber, condenser and vacuum pump for distillation monitoring. Edwards Pirani gauge model 1001 with Pirani gauge head model PRH10K or equivalent.

The dimensions of the various parts of the apparatus are as follows:

1) The loop on which the sample is condensed is an 8 inch by 1/8 inch stainless steel piece of tubing.

2) The condenser is 12 inches long and 2 inches in diameter. The ends are made of ½ inch ground glass and are secured to all stainless steel joints by the use of ½ inch Buna rubber O-rings. The cooling coils within the condenser are made of 3/16 inch glass which terminate as 1/4 inch tubing fittings on the exterior of the condensers.

3) The cooling liquid passing through the condenser is routed from the refrigerant reservoir using 1/4 inch pure silicone tubing.

4) The tubing between the GC inlet and the six port valve is made of 1/16 inch capillary fused silica lined stainless steel.

5) The sampling chamber valve (V1) and the vacuum pump valve V3) are made of ½ inch stainless steel.

6) The circulating fluid valve (V2) is made of 1/4 inch brass.

7) The six port sampling valve (V4) is made of stainless steel with polytetrafluoroethylene (PTFE) internal parts.

4.7 Gas chromatograph/mass spectrometer system:

4.7.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.7.2 Column: 30 m by 0.7 mm ID fused silica capillary column chemically bonded with methylphenyl cyanopropyl silicone J&W DB-624, or equivalent, 3.0 µm film thickness.

4.7.3 Mass spectrometer: Capable of scanning from 35-350 amu every 2 sec. or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria listed in Method 8260 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

4.7.4 Gas chromatograph/mass spectrometer heated jet separator interface: A heated glass jet separator interface capable of removing from 10 to 40 mL/min of helium from the exit end of the wide bore capillary column. The interface should have the ability to be heated through a range of 100 to 220^{o}C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

5.3 Methanol: CH_3OH, purge and trap grade or equivalent. Store apart from other solvents.

5.4 Standard solutions: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared, ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids: Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas onto the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at -10 to -20°C and protect from light.

5.4.5 Prepare fresh gas standards every two months. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standards: The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 25 µg/mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.7 Internal Standards: It is recommended that one or more internal standards be selected from: bromochloromethane, 1,4-difluorobenzene, vinyl chloride-d_3, chlorobenzene-d . $_5$ The compound(s) selected should demonstrate minimal matrix effects. Other compounds maybe used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Method 8260 should be reviewed to select compounds appropriate for the matrix being tested. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 µg/mL of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.8 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/µL of BFB in methanol should be prepared.

5.9 Calibration standards: Calibration standards at minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Secs. 5.1 and 5.2). Prepare these solutions in reagent water or purge and trap grade methanol. For each analyte, at least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project, which may include establishing compliance with a regulatory or action limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples and should not exceed the working range of the GC/MS system. Each standard should contain each analyte to be determined by this method (e.g., some or all of the compounds listed in Method 8260 may be included). Store for one week or less at -10°C in a vial with minimal headspace.

5.10 Matrix spiking standards: matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,2-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 25 µg/mL.

5.11 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10 to -20°C in screw-cap amber bottles with PTFE liners.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Samples to be analyzed for volatile compounds should be stored separately from standards and other samples.

6.3 Holding times for oil and tissue samples have not been established. Tissue samples should be stored frozen (-20 °C) until analysis. Water and soil samples should be stored consistent with established procedures (see Chapter Two).

7.0 PROCEDURE

7.1 Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal)
Mass range:	35-350 amu
Scan time:	To give 8 scans/peak but not to exceed 3 sec/scan
Initial column temperature:	10°C
Initial hold time:	3.0 min
Column ramp rate:	5.0°C/min
Final column temperature:	230°C
Final hold time:	1.0 min

7.2 Initial calibration for vacuum distillation procedure:

7.2.1 Turn the six port sampling valve (V4) handle to the load position.

7.2.2 Place a styrofoam cup under the sample loop and secure in place. Fill the cup with liquid N_2. Recharge the styrofoam cup under the sample loop throughout the distillation with liquid N_2 as necessary.

7.2.3 Turn the sample chamber valve (V1) to the off position and remove the sample container.

7.2.4 Load the standard, containing surrogates and internal standards, into the sample flask and attach to the apparatus.

7.2.5 Turn the coolant/heat valve (V2) to circulate coolant through the condenser coils. Be sure all connections are complete and sealed properly. Open the sample chamber valve to begin the distillation. Continue distillation for 10 minutes.

NOTE: IF PIRANI GAUGES ARE USED: After five minutes of distillation the Pirani gauge at the vacuum pump should indicate about 0.1 torr, and the Pirani gauge at the condenser and should indicate 250 torr or less. After ten minutes of distillation the Pirani gauge at the sample chamber should read approximately 10 torr. If these pressures are not attained a leak may be present and the distillation may not be successful. Distillation performance surrogates should be evaluated for acceptability of distillation.

7.2.6 Setup the data system for acquisition of the data file. This may be done prior to the beginning of step 1. While distillation times may be variable depending on sample matrix, the data system should be ready and the GC oven at equilibrium by the time the distillation is complete.

7.2.7 Once the distillation is complete GC/MS analyses may be performed. Turn the sampling valve handle to the inject position while maintaining the styrofoam cup with liquid N_2 in place. Rapidly remove the styrofoam cup and replace with the beaker of (90°C) hot tap water and commence GC/MS data acquisition.

7.2.8 Once acquisition has begun the sample chamber valve may be closed and the sample flask removed.

7.2.9 The distillation apparatus can then be readied for the next analyses. This is performed by switching the vacuum pump valve (V3) to the vacuum pump position which disconnects the vacuum stream to the sampling valve (V4). The condenser circulating fluid is then switched to the heated fluid (45°C) by switching valve V2. Evacuate the distillation system for 10 minutes. It is recommended that a liquid nitrogen cooling trap be placed between valve V3 and the vacuum pump to prevent degradation of the vacuum due to overload of moisture in the vacuum pump oil.

7.3 Calibration response factors: Calculate according to Method 8260.

7.4 Sample preparation:

7.4.1 Liquid samples should be stored with minimal or no headspace to minimize the loss of more volatile analytes. Aqueous samples may be preserved with ascorbic acid to stop biological degradation which may occur in water samples. The recommended sample size for water is 5 mL. Other sample sizes may be employed, provided that the sensitivity is adequate to meet the project objectives.

7.4.2 Solid and soil samples should be rapidly withdrawn from their sample container and weighed while still cold. The sample is then rapidly transferred to the sample chamber and secured to prevent loss of analytes. The recommended sample size for solid samples is 5 g. Other sample sizes may be employed, provided that the sensitivity is adequate to meet the project objectives.

7.4.3 Tissue samples which are fleshy may have to be minced into smaller pieces to get them through the neck of the sample chamber. This is best accomplished by freezing the sample in liquid nitrogen before any additional processing takes place. Biota samples containing leaves and other softer samples may be minced using clean scissors. The sample size is a function of the sensitivity necessary to meet the project objectives. Samples as large as 10 g can be analyzed with this method, but smaller samples may be more appropriate.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is analyzed, or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 To establish the ability to generate data of acceptable accuracy and precision refer to Method 8000 and the determinative method to be used.

8.4 Matrix and distillation performance surrogates.

8.4.1 Matrix effects and distillation performance may be monitored separately through the use of surrogates. Compounds that have demonstrated minimal matrix effects such as vinyl chloride-d_3 and bromochloromethane may be added directly to the matrix and used as an internal standard. Tables located in Method 8260 present recovery data from water, soil and oil matrices that should be considered when selecting surrogates. Compounds that have demonstrated matrix effects and/or distillation losses (i.e., pyridine-d_5, 2-fluorophenol for matrix effects and 1,2-dichlorobenzene-d_4 for distillation performance) are recommended as surrogates.

8.4.2 The use of multiple matrix surrogates and multiple distillation performance surrogates are recommended. It is recommended that distillation effect surrogates be relatively insoluble in water. Matrix monitoring compounds should be selected to bracket the physical properties of the analytes of interest. If matrix effects have been shown or are suspected for a chosen distillation surrogate compound, the distillation surrogates should be added to the sample flask in an open mini-vial suspended above the sample by a wire stand. Multiple surrogates for monitoring one or more classes of compounds are recommended for evaluating matrix effects.

8.5 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the

sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect <1 µg/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or a larger amount of the sample should be used.

9.0 METHOD PERFORMANCE

9.1 Performance data for Method 5032 are provided in tables in Method 8260.

10.0 REFERENCES

1. Hiatt, M.H. "Analysis of Fish and Sediment For Volatile Priority Pollutants", Analytical Chemistry 1981, 53 (9), 1541.

2. Hiatt, M.H. "Determination of Volatile Organic Compounds in Fish Samples by Vacuum Distillation and Fused Silica Capillary Gas Chromatography/Mass Spectrometry"; Analytical Chemistry 1983, 55 (3), 506.

3. United States Patent 4,600,559. "Vacuum Extractor with Cryogenic Concentration and Capillary Interface", held by the U.S. EPA.

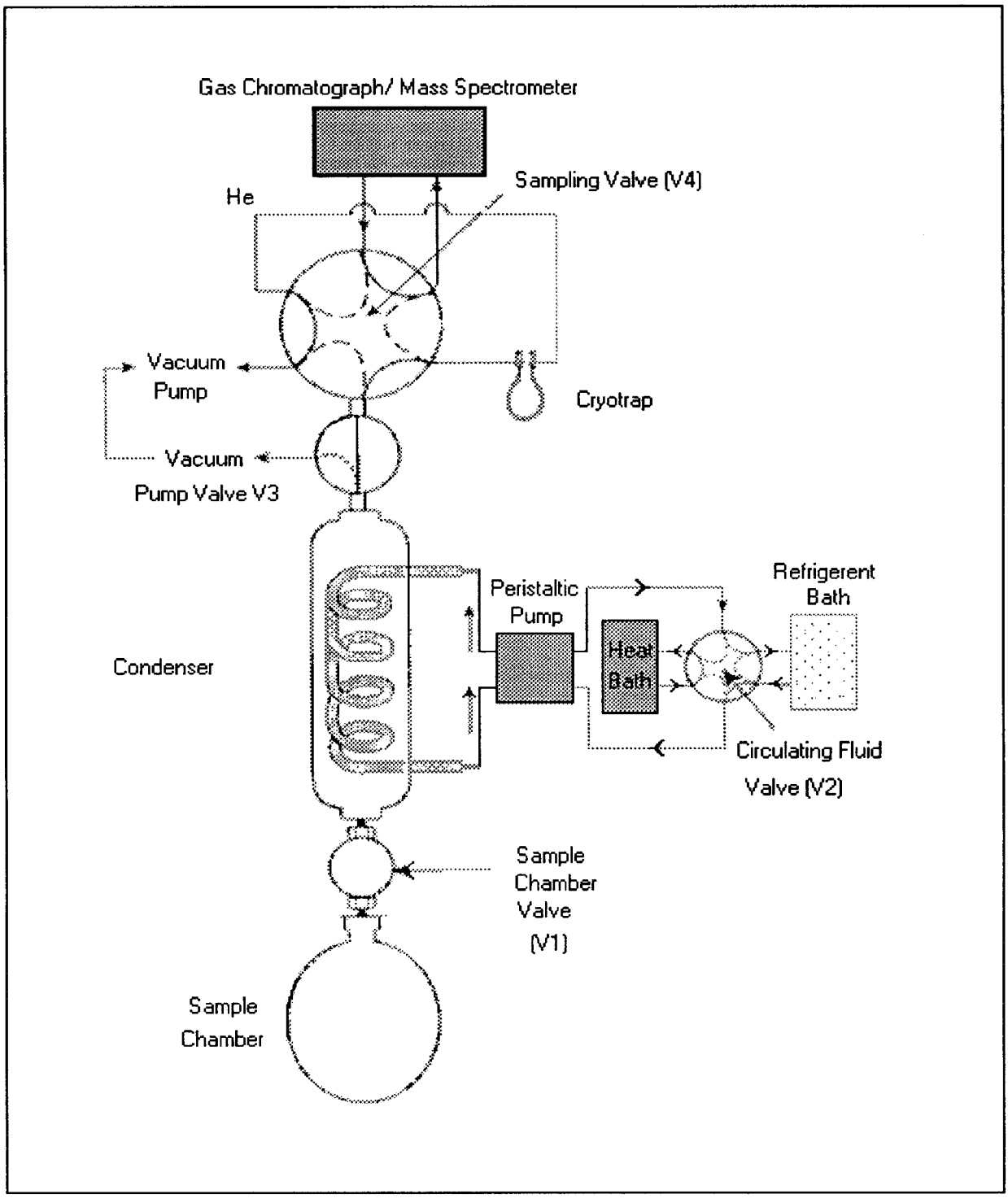
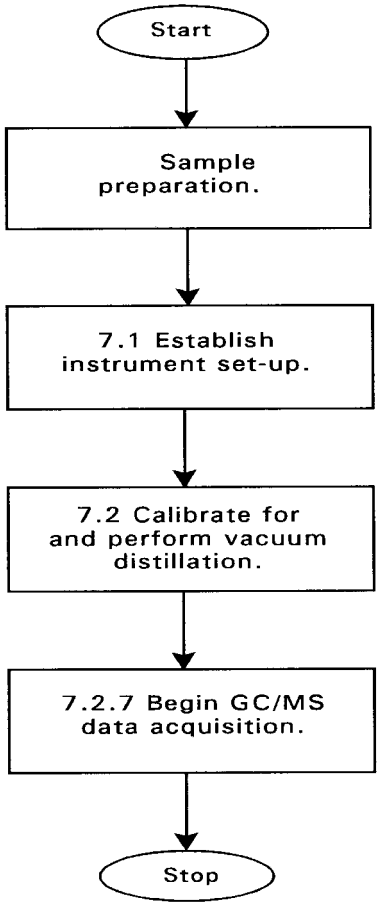


Figure 1
Vacuum Distillation Configuration


Start
Sample preparation.
7.1 Establish instrument set-up.
7.2 Calibrate for and perform vacuum distillation.
7.2.7 Begin GC/MS data acquisition.
Stop