METHOD 5030B

PURGE-AND-TRAP FOR AQUEOUS SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in Method 5035. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Method 5030, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5030 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Methods 8021 GC/PID) in series with Method 8015.

1.4 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, 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 running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL. These syringes should be equipped with a 20-gauge (0.006 in ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Two 5-mL glass hypodermic syringes with Luer-Lok tip (other sizes are acceptable depending on sample volume used).

4.4 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.5 Vials - 2-mL, for GC autosampler.

4.6 Purge-and-trap device

The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.6.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent or improved performance is demonstrated.

4.6.2 The trap used to develop this method was 25 cm long with an inside diameter of 0.105 in. Starting from the inlet, the trap contains the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.6.3 The desorber must be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.6.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.6.5 Trap Packing Materials

4.6.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.6.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.6.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.6.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.6.5.5 Alternate Trap Materials

A number of hydrophobic carbon molecular sieve and graphitized carbon black materials have been developed. Various combinations of these materials have been shown to provide retention properties similar to the Tenax\Silica gel\Carbon trap. Alternate trap construction with such materials is allowed, provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision in comparison to the performance documented in the Determinative Method.

4.6.5.5.1 The following alternatives have been shown to be viable for most analytes of concern:

7.6-cm Carbopack™ B/1.3-cm Carboseive™ S-III
VOCARB 3000 - 10.0-cm Carbopack™ B/6.0-cm Carboxin ™ 1000/1.0-cm Carboxin™ 1001
VOCARB 4000 - 8.5-cm Carbopack™ C/10.0-cm Carbopack ™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin™ 1001

These combinations require rapid heating to desorption temperatures of 245°C to 270°C (follow manufacturer's instructions). At these increased temperatures, catalytic and thermal decomposition of analytes has been reported. The VOCARB 4000 combination has also been demonstrated to catalytically break down 2-chloroethyl vinyl ether, and to partially decompose 2,2-dichloropropane. Bromoform and bromomethane have shown some thermal decomposition.

4.6.5.5.2 The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of chloromethane and bromomethane. A daily check standard containing surrogates, internal standards, and 20 µg/L bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated.

NOTE: Even newly constructed traps may have become contaminated prior to their first use from airborne vapors. These highly adsorptive materials must be kept tightly sealed in an area of minimum organic vapor contamination.

4.7 Heater or heated oil bath - capable of maintaining the purging chamber to within 1°C, over a temperature range from ambient to 100°C.

4.8 Capillary GC Columns - Any GC column that meets the performance specifications of the determinative method may be used. See the specific determinative method for recommended columns, conditions and retention times.

4.8.1 The wide-bore columns have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface , an all-glass jet

separator, or a cryogenic (Sec. 4.8.2) device are acceptable interfaces. The type of interface and its adjustments can have a significant impact on the method detection limits. Other interfaces can be used if the performance specifications described in this method can be achieved.

4.8.2 A system using a narrow-bore column will require lower gas flows of approximately 2 - 4 mL/minute. Because of these low desorption flows, early eluting analytes need to be refocussed to elute in a narrow band. This refocussing may be carried out by using a cryogenic interface. This type of interface usually uses liquid nitrogen to condense the desorbed sample components in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed form the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by ice caused by desorbing water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution. Low surrogate compound recoveries can be a sign that this is occurring.

5.0 REAGENTS

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

5.2 See the determinative method and Method 5000 for guidance on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Sec. 4.1. Samples should be stored in capped bottles, with minimum headspace, at 4°C or less in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling the sample should not exceed 5 - 6 mm. When a bubble is present, also observe the cap and septum to ensure that a proper seal was made at time of sampling. Is there any evidence of leakage? If the sample was improperly sealed, the sample should be discarded.

6.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values.

7.0 PROCEDURE

7.1 The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and guidance for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

7.2 This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

7.2.1 Initial calibration

Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the specific determinative methods and Method 5000 give details on preparation of standards. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.6. Condition the Tenax trap overnight at 180°C (condition other traps at the manufacturers recommended temperature) in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.1.2 Connect the purge-and-trap device to a gas chromatograph or gas chromatograph/mass spectrometer system.

7.2.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5-mL glass syringe (a 10-mL or 25-mL syringe may be used if preferred) fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-µL or 25-µL micro-syringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10.0 µL of the internal standard solution. Close the 2-way syringe valve at the sample inlet. (The calibration standard, internal standard and surrogate standard may be added directly to the organic free reagent water in the syringe prior to transferring the water to the purging device, see Sec. 7.2.4.7).

7.2.1.4 Follow the purge-and-trap analysis as outlined in Sec. 7.2.4.

7.2.1.5 Calculate response factors (RF) or calibration factors (CF) for each analyte of interest using the procedure described in Method 8000.

7.2.1.6 The average CF (external standards) or RF (internal standards) must be calculated for each compound. For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.6.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.7 The analytes in Method 8021 normally are not as strongly affected by small changes in purge flow or system contamination. When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross contamination and memory effects from a high concentration sample or even the standard are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification: Refer to Method 8000 for details on calibration verification.

7.2.2.1 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard to an aliquot of organic free reagent water in a volumetric flask, a gas tight syringe, or to a purge device, and inject an appropriate amount of internal standard to the organic free reagent water. Be sure the same amount of internal standard is added to each standard and sample. The volume of organic free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Assemble the purge-and-trap device as outlined in 4.6. Follow the guidance for the purge-and-trap procedure in Sec. 7.2.4. Ongoing GC or GC/MS calibration criteria must be met as specified in Method 8000 before analyzing samples.

7.2.3 Sample screening

7.2.3.1 Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.3.2 SW-846 contains two screening techniques that may be utilized: the automated headspace sampler (Method 5021) connected to a gas chromatograph equipped with a photoionization detector in series with an electrolytic conductivity detector; and extraction of the samples with hexadecane (Method 3820) and analysis of the extract on a gas chromatograph equipped with a flame ionization detector and/or electron capture detector. In addition, other appropriate screening techniques may be employed at the discretion of the analyst.

7.2.4 Sample introduction and purging

7.2.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.2.4.2 Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in Sec. 7.0 of the specific determinative method to be employed. Whole oven cooling may be needed for certain GC columns and/or certain GC/MS systems to achieve adequate resolution of the gases. Normally a 30 meter wide-bore column will require cooling the GC oven to 25°C or below for resolution of the gases.

7.2.4.3 GC or GC/MS calibration verification criteria must be met (Method 8000) before analyzing samples.

7.2.4.4 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min (also see Table 1 for guidance on specific analyte groups), on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. Alternatively, carefully transfer the remaining sample into a 20-mL VOA vial. Seal the vial with zero headspace. The second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 10- or 25-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hrs. Care must be taken to prevent air from leaking into the syringe.

7.2.4.6 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.2.4.6.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.2.4.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.2.4.6.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.2.4.5 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.2.4.6.4 Fill a 5-mL syringe with the diluted sample as in Sec. 7.2.4.5.

7.2.4.7 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Sec. 5.0) and, if applicable, 10.0 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10.0 µL) to the sample at this time.

7.2.4.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.2.4.9 Close both valves and purge the sample for the time and at the temperature specified in Table 1. For GC/MS analysis using Method 8260, purge time is 11 minutes at ambient temperature.

7.2.5 Sample desorption

The procedures employed for sample desorption depend on the type of GC interface used. Procedures for non-cryogenic and cryogenic interfaces are described below. Analysts should also consult the instructions from the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

7.2.5.1 Non-cryogenic interface - After the recommended 11-minute purge (see Table 1 for guidance on purge times for specific analyte groups), place the purge-and-trap system in the desorb mode and preheat the trap to 180°C (or other temperature recommended for the specific trap packing material) without a flow of carrier gas passing through the trap.

NOTE: Some purge-and-trap systems are capable of performing a moisture removal step (e.g., dry purge) which can eliminate excess moisture from the trap and gas lines by purging the trap just prior to the desorption step. However, the utility of a moisture removal step depends on the nature of the trap packing material. In general, when using a carbon-based, hydrophobic trap packing, this step may prevent moisture from entering the GC system and affecting chromatography, but may require that the trap be cooled to keep the temperature at or below 25°C. However, for packings that are less hydrophobic or hydrophilic (such as silica gel), a moisture removal step may actually create more significant problems, including loss of sensitivity, poor chromatography, and premature failure of the trap packing material, through the release of increasing amounts of water into the GC system during the course of an analytical shift. The problem may be evident as erratic responses for the early-eluting internal standards and surrogates over the course of the day. Optimum results may be achieved through the proper choices of: the moisture control device, the trap packing material, trap temperature during moisture removal, and carrier gas flow. The use of trap back pressure control may also be necessary. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material before employing a moisture removal step.

Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition. The carrier gas flow rate will depend on the trap employed. A flow rate of 15 mL/min is used for the standard silica gel trap (Sec. 4.6.2), while 10 mL/min may

be adequate for other traps. Continue the carrier gas flow for about 4 min, or as recommended by the manufacturer. Desorption times as low as 1.5 min may be adequate for analytes in Method 8015.

7.2.5.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure the cryogenic interface is -150°C or lower, and rapidly heat the trap to 180°C (temperature may vary depending on the trap material) while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Method 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C; simultaneously begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.6 Trap Reconditioning

7.2.6.1 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C for Methods 8021 and 8260, and 210°C for Method 8015. Trap temperatures up to 220°C may be employed. However, the higher temperatures will shorten the useful life of the trap. (Trap temperatures may vary depending on the trap material). After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.2.6.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic free reagent water (or methanol followed by organic free reagent water) to avoid carryover of volatile organics into subsequent analyses.

7.2.7 Interpretation and calculation of data

7.2.7.1 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by the analysis of organic free reagent water. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can meet the organic-free reagent water criteria specified in Chapter One.

7.2.7.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.2.8 Analysis of water-miscible liquids

7.2.8.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

7.2.8.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample into a 100-mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.2.8.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with organic-free reagent water by adding at least 20.0 µL, but not more than 100.0 µL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3 This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1 The GC or GC/MS system should be set up as in Sec. 7.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.3.2 Table 2 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100.0 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3 Remove the plunger from a 5.0-mL Luer-lok type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10.0 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.3.2 and a volume of the same solvent used in Method 5035 to total 100.0 µL (excluding methanol in standards).

7.3.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.5 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100.0 µL of methanol to simulate the sample conditions.

7.4 Sample analysis

The samples prepared by this method may be analyzed by Methods 8015, 8021, and 8260. Refer to these methods for appropriate analysis conditions. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be

processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when specified in the appropriate determinative method

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

TABLE 1

PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method	
	8015	8021/8260
Purge gas	N_2 or He	N_2 or He
Purge gas flow rate (mL/min)	20	40
Purge time (min)	15.0 ±0.1	11.0 ±0.1
Purge temperature (°C)	85 ±2	Ambient
Desorb temperature (°C)	180	180
Backflush inert gas flow (mL/min)	20-60	20-60[1]
Desorb time (min)	1.5	4

[1] The desorption flow rate for Method 8021 with a wide bore capillary column will optimize at approximately 10 to 15 mL/minute.

TABLE 2

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

FIGURE 1
EXAMPLE OF PURGING DEVICE

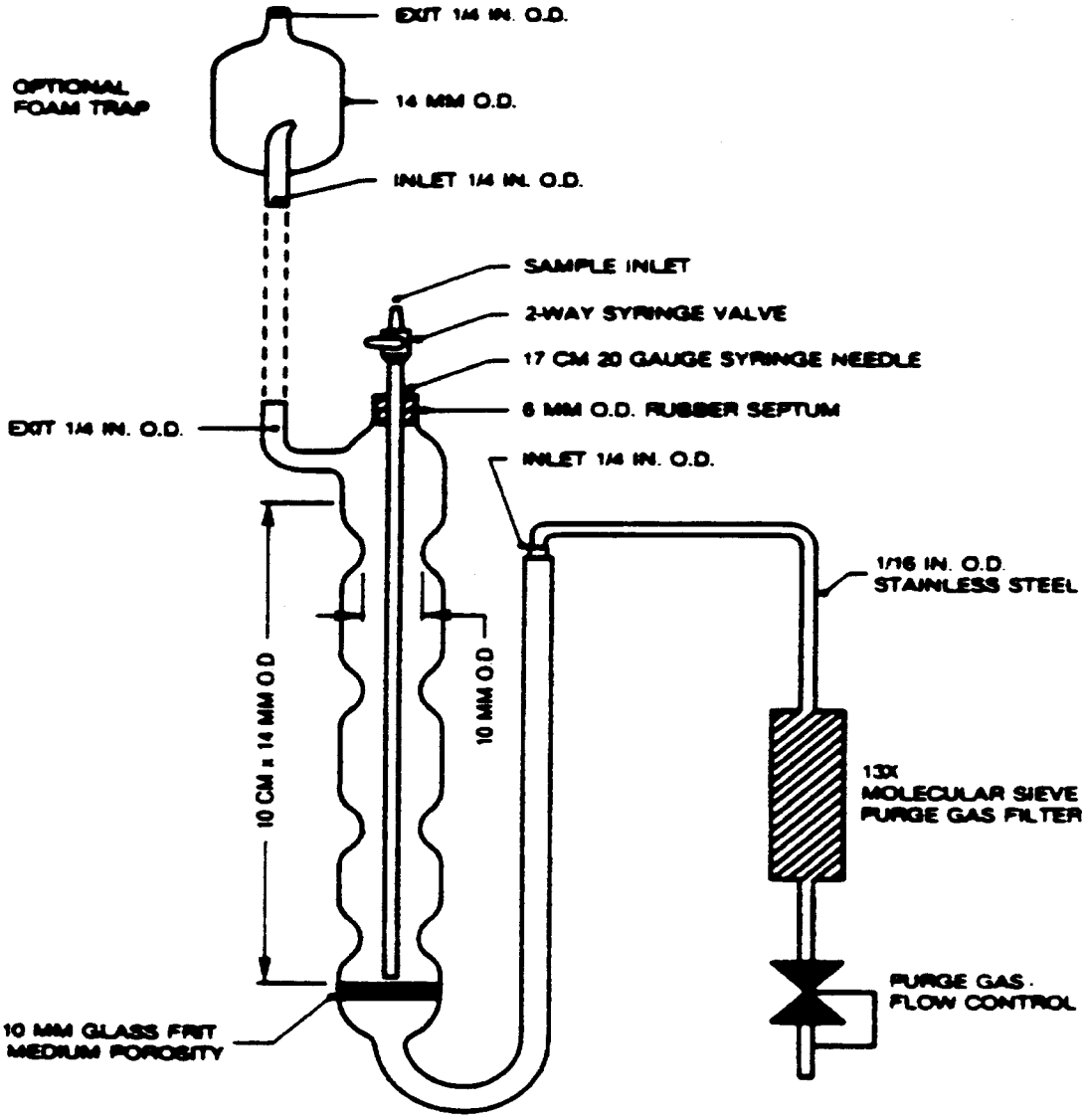


FIGURE 2
EXAMPLE OF TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

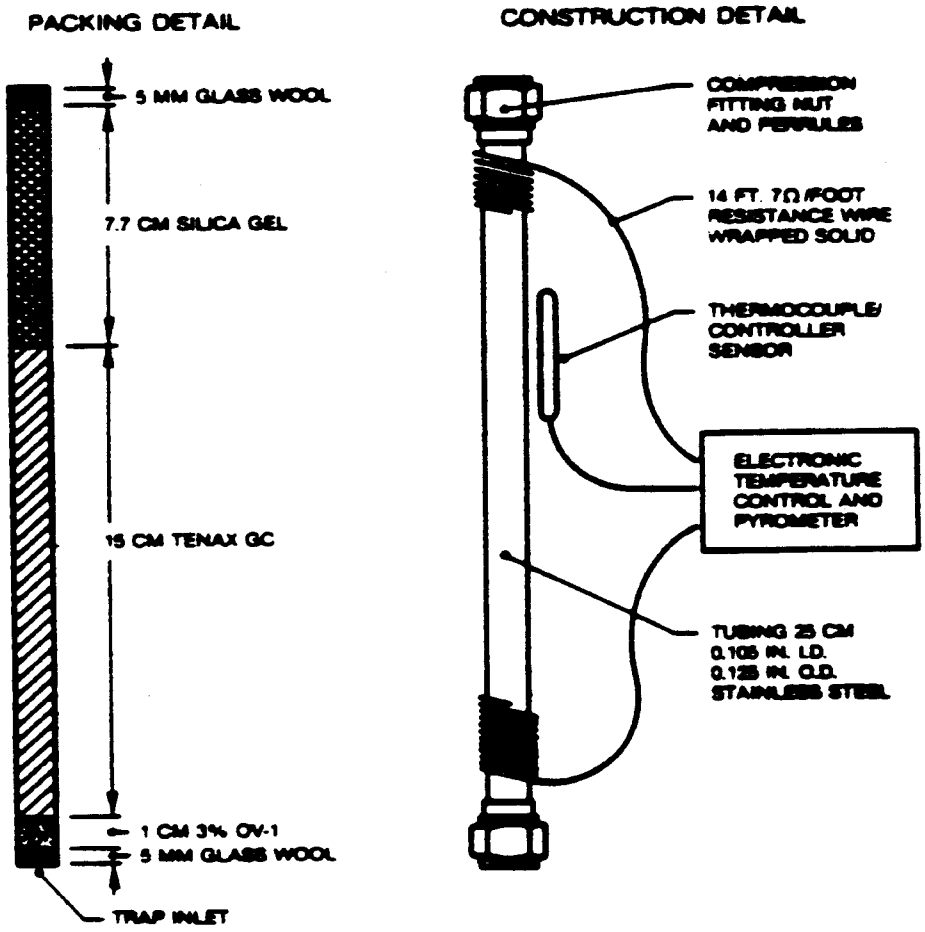


FIGURE 3
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
PURGE MODE

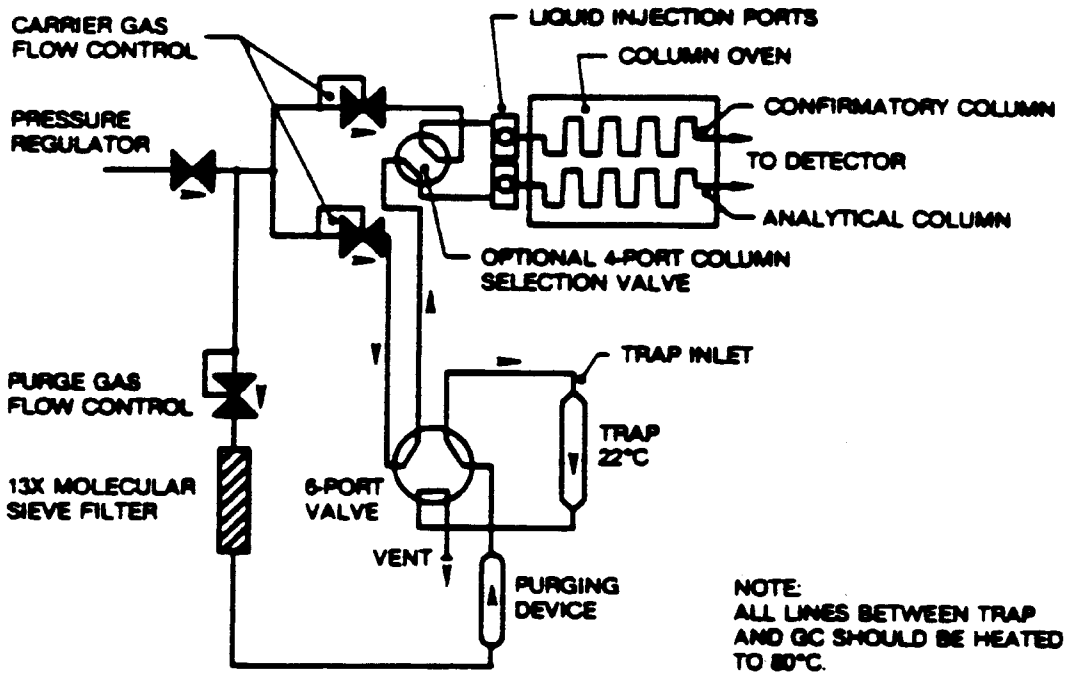
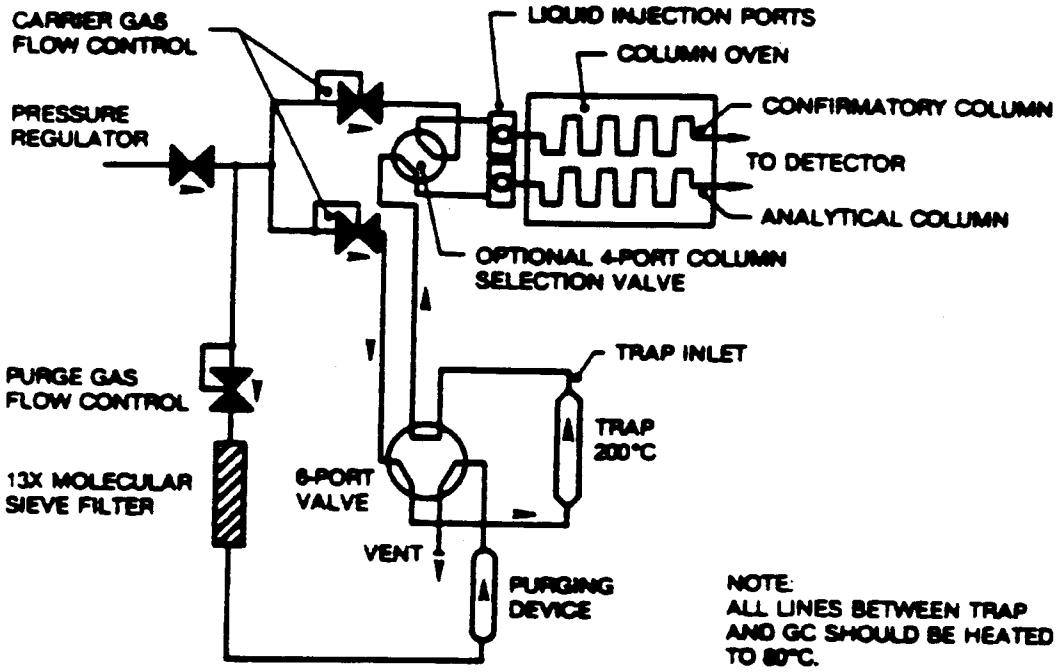
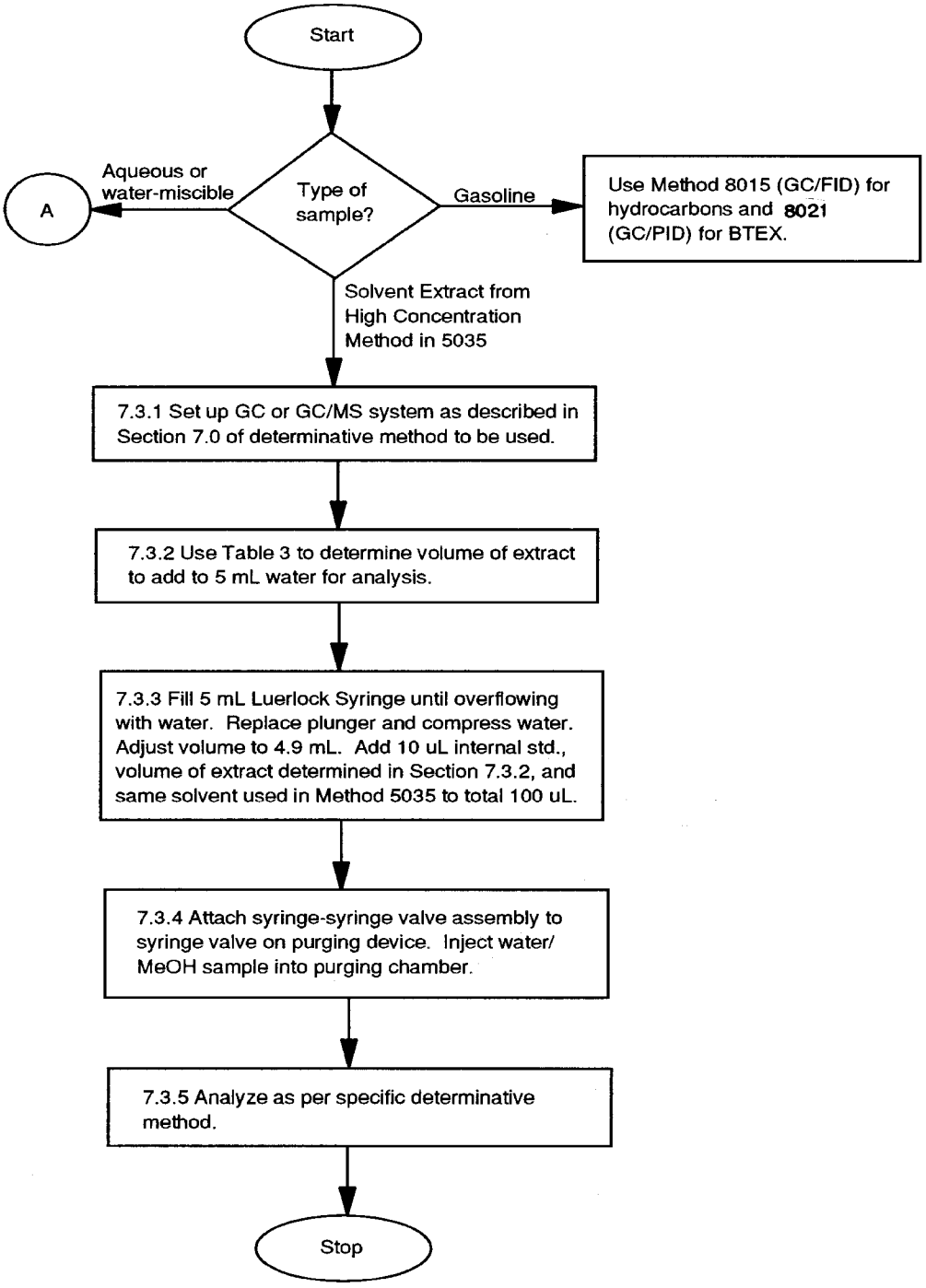
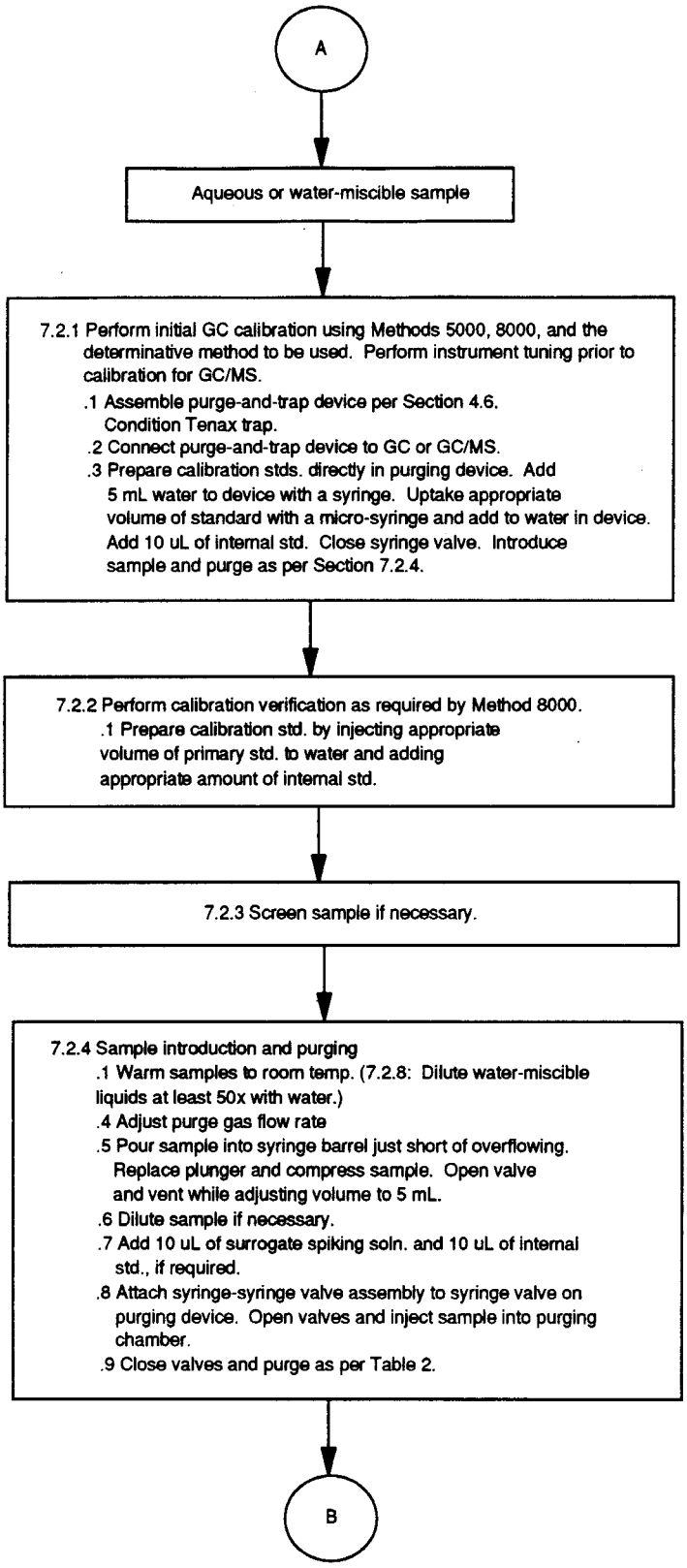
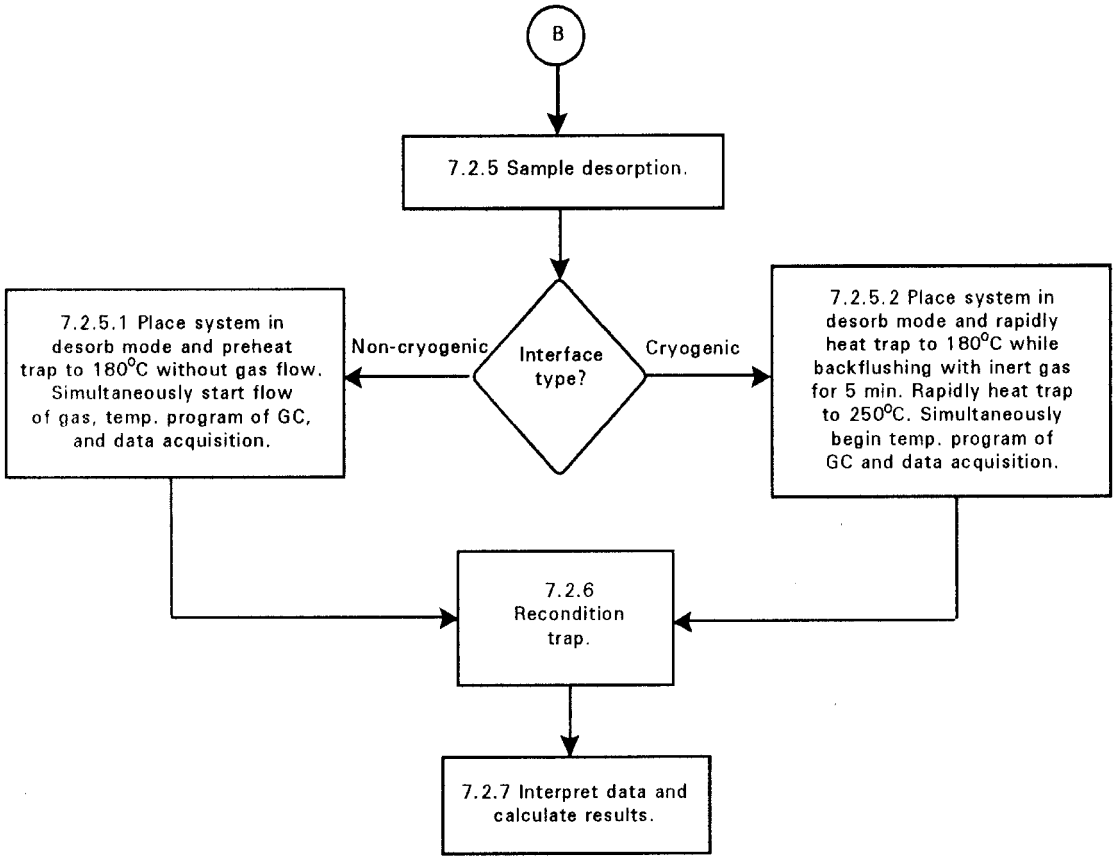


FIGURE 4
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
DESORB MODE




Start
Type of sample?
Aqueous or water-miscible
A
Gasoline
Use Method 8015 (GC/FID) for hydrocarbons and 8021 (GC/PID) for BTEX.
Solvent Extract from High Concentration Method in 5035
7.3.1 Set up GC or GC/MS system as described in Section 7.0 of determinative method to be used.
7.3.2 Use Table 3 to determine volume of extract to add to 5 mL water for analysis.
7.3.3 Fill 5 mL Luerlock Syringe until overflowing with water. Replace plunger and compress water. Adjust volume to 4.9 mL. Add 10 uL internal std., volume of extract determined in Section 7.3.2, and same solvent used in Method 5035 to total 100 uL.
7.3.4 Attach syringe-syringe valve assembly to syringe valve on purging device. Inject water/ MeOH sample into purging chamber.
7.3.5 Analyze as per specific determinative method.
Stop


A
Aqueous or water-miscible sample
7.2.1 Perform initial GC calibration using Methods 5000, 8000, and the determinative method to be used. Perform instrument tuning prior to calibration for GC/MS.
.1 Assemble purge-and-trap device per Section 4.6. Condition Tenax trap.
.2 Connect purge-and-trap device to GC or GC/MS.
.3 Prepare calibration stds. directly in purging device. Add 5 mL water to device with a syringe. Uptake appropriate volume of standard with a micro-syringe and add to water in device. Add 10 uL of internal std. Close syringe valve. Introduce sample and purge as per Section 7.2.4.
7.2.2 Perform calibration verification as required by Method 8000.
.1 Prepare calibration std. by injecting appropriate volume of primary std. to water and adding appropriate amount of internal std.
7.2.3 Screen sample if necessary.
7.2.4 Sample introduction and purging
.1 Warm samples to room temp. (7.2.8: Dilute water-miscible liquids at least 50x with water.)
.4 Adjust purge gas flow rate
.5 Pour sample into syringe barrel just short of overflowing. Replace plunger and compress sample. Open valve and vent while adjusting volume to 5 mL.
.6 Dilute sample if necessary.
.7 Add 10 uL of surrogate spiking soln. and 10 uL of internal std., if required.
.8 Attach syringe-syringe valve assembly to syringe valve on purging device. Open valves and inject sample into purging chamber.
.9 Close valves and purge as per Table 2.
B


B
7.2.5 Sample desorption.
Interface type?
Non-cryogenic
Cryogenic
7.2.5.1 Place system in desorb mode and preheat trap to 180°C without gas flow. Simultaneously start flow of gas, temp. program of GC, and data acquisition.
7.2.5.2 Place system in desorb mode and rapidly heat trap to 180°C while backflushing with inert gas for 5 min. Rapidly heat trap to 250°C. Simultaneously begin temp. program of GC and data acquisition.
7.2.6 Recondition trap.
7.2.7 Interpret data and calculate results.