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. The following compounds have been evaluated using this sample preparation technique:

Compound	CAS No.[a]	Response	Stability
Acetone	67-64-1	pp / ht	hs
Acetonitrile	75-05-8	pp	nd
Acrolein (Propenal)	107-02-8	pp	ms
Acrylonitrile	107-13-1	pp	hs
Allyl alcohol	107-18-6	ht	nd
Allyl chloride	107-05-1	c	ms
t-Amyl alcohol (TAA)	75-85-4	ht	hs
t-Amyl ethyl ether (TAEE)	919-94-8	c / ht	nd
t-Amyl methyl ether (TAME)	994-05-8	c / ht	hs
Benzene	71-43-2	c	hs
Benzyl chloride	100-44-7	c	nd
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd
Bromoacetone	598-31-2	pp	nd
Bromochloromethane	74-97-5	c	hs
Bromodichloromethane	75-27-4	c	ms
Bromoform	75-25-2	c	hs
Bromomethane	74-83-9	c	hvs
n-Butanol	71-36-3	ht	nd
2-Butanone (MEK)	78-93-3	pp	hvs
t-Butyl alcohol (TBA)	75-65-0	ht	nd
Carbon disulfide	75-15-0	pp	hvs
Carbon tetrachloride	56-23-5	c	hvs
Chloral hydrate	302-17-0	pp	nd
Chlorobenzene	108-90-7	c	hvs
Chlorodibromomethane	124-48-1	c	nd
Chloroethane	75-00-3	c	ms
2-Chloroethanol	107-07-3	pp	nd
2-Chloroethyl vinyl ether	110-75-8	c	ls
Chloroform	67-66-3	c	hs

(continued)

Compound	CAS No.[a]	Response	Stability
Chloromethane	74-87-3	c	hvs
Chloroprene	126-99-8	c	nd
Crotonaldehyde	4170-30-3	pp	nd
1,2-Dibromo-3-chloropropane	96-12-8	pp	ms
1,2-Dibromoethane	106-93-4	c	hs
Dibromomethane	74-95-3	c	hs
1,2-Dichlorobenzene	95-50-1	c	hs
1,3-Dichlorobenzene	541-73-1	c	ms
1,4-Dichlorobenzene	106-46-7	c	ms
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd
trans-1,4-Dichloro-2-butene	110-57-6	pp	ls
Dichlorodifluoromethane	75-71-8	c	hs
1,1-Dichloroethane	75-34-3	c	hs
1,2-Dichloroethane	107-06-2	c	hs
1,1-Dichloroethene	75-35-4	c	hvs
cis-1,2-Dichloroethene	156-59-4	c	hs
trans-1,2-Dichloroethene	156-60-5	c	ms
1,2-Dichloropropane	78-87-5	c	hs
1,3-Dichloro-2-propanol	96-23-1	pp	nd
cis-1,3-Dichloropropene	10061-01-5	c	ls
trans-1,3-Dichloropropene	10061-02-6	c	ls
1,2,3,4-Diepoxybutane	1464-53-5	c	nd
Diethyl ether	60-29-7	c	nd
Diisopropyl ether (DIPE)	108-20-3	c / ht	hs
1,4-Dioxane	123-91-1	ht / pp	nd
Ethylbenzene	100-41-4	c	hvs
Ethylene oxide	75-21-8	pp	nd
Ethyl methacrylate	97-63-2	c	ms
Ethyl *tert*-butyl ether (ETBE)	637-92-3	c / ht	hs
Hexachlorobutadiene	87-68-3	c	ms
2-Hexanone	591-78-6	pp	hvs
Iodomethane	74-88-4	c	nd
Isobutyl alcohol	78-83-1	ht / pp	nd
Isopropylbenzene	98-82-8	c	ms
Malononitrile	109-77-3	pp	nd
Methacrylonitrile	126-98-7	pp	hs
Methylene chloride	75-09-2	c	hs
Methyl methacrylate	80-62-6	c	ms
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	ms
Methyl *tert*-butyl ether (MTBE)	1634-04-4	c / ht	hs
Naphthalene	91-20-3	c	ms
Nitrobenzene	98-95-3	c	nd
2-Nitropropane	79-46-9	c	nd
N-Nitroso-di-*n*-butylamine	924-16-3	pp	nd

(continued)

Compound	CAS No.[a]	Response	Stability
Paraldehyde	123-63-7	pp	nd
2-Pentanone	107-87-9	pp	nd
2-Picoline	109-06-8	pp	nd
1-Propanol	71-23-8	ht / pp	nd
2-Propanol	67-63-0	ht / pp	nd
β-Propiolactone	57-57-8	pp	nd
Propionitrile (ethyl cyanide)	107-12-0	ht	nd
n-Propylamine	107-10-8	c	nd
Styrene	100-42-5	c	hvs
1,1,1,2-Tetrachloroethane	630-20-6	c	hs
1,1,2,2-Tetrachloroethane	79-34-5	c	nd
Tetrachloroethene	127-18-4	c	ms
Toluene	108-88-3	c	hs
o-Toluidine	95-53-4	pp	nd
1,2,4-Trichlorobenzene	120-82-1	c	hs
1,1,1-Trichloroethane	71-55-6	c	ms
1,1,2-Trichloroethane	79-00-5	c	hs
Trichloroethene	79-01-6	c	ms
Trichlorofluoromethane	75-69-4	c	ls
1,2,3-Trichloropropane	96-18-4	c	ls
Vinyl acetate	108-05-4	c	ls
Vinyl chloride	75-01-4	c	hvs
o-Xylene	95-47-6	c	hvs
m-Xylene	108-38-3	c	hvs
p-Xylene	106-42-3	c	hvs

[a] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at elevated temperature, e.g., 80°C
pp = Poor purging efficiency resulting in high quantitation limits. Use of an alternative sample preparative method is strongly recommended. May be amenable to purging at elevated temperature.
nd = Not determined
hs = High stability in preserved water samples (> 60 days). Longer holding times may be appropriate, see Method 5035, Appendix A, Table A.1 footnote and ref. 47 for additional information
ms = Medium stability in preserved water samples (15 - 60 days). Longer holding times may be appropriate, see Method 5035, Appendix A, Table A.1 footnote and ref. 47 for additional information
ls = Low stability in preserved water samples (< 14 days), analyses should be performed as soon as possible. May be degraded if acid preserved.
hvs = Highly variable stability in preserved water samples. Longer holding times may be appropriate, see Method 5035, Appendix A, Table A.1 footnote and ref. 47 for additional information.

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) in some cases are approximately ten times higher with erratic precision because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. The purging efficiency can be improved for water soluble analytes, e.g. ketones and alcohols, when purging at an elevated temperature of 80°C as compared to 20° or 40°C.

Problems are often encountered with the analysis of methyl *t*-butyl ether (MTBE) and related fuel oxygenated compounds, both with the effectiveness of the analytical methods, and the evaluation of the resulting data. These fuel oxygenated compounds generally include: methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME), diisopropyl ether (DIPE), *t*-amyl ethyl ether (TAEE), *t*-amyl alcohol (TAA) and *t*-butyl alcohol (TBA) and can be classified as volatile organics based on their boiling points and vapor pressures. However, the major analytical problem is a result of the high solubility of some of these compounds in water, which makes it more difficult to use purge-and-trap (P&T) techniques for removing the compounds from the environmental samples and introducing them into the analytical instrumentation (e.g., a GC or GC/MS system). Thus, using procedures that have been optimized for other, less water-soluble volatiles can potentially lead to significantly underestimating the concentrations of the oxygenates in the same samples.

EPA evaluated the performance of commonly used analytical methods in order to determine the appropriate analytical conditions for measuring MTBE and other target oxygenates in aqueous samples. (Method 5035, Appendix A, Refs. 49,50) With a minimal Method 5030 modification (heated 80°C rather than ambient temperature purge) and the choice of analytical column for the commonly used volatiles Method 8260, the low-level concentration recoveries of MTBE and related oxygenates can be improved. The EPA study performance data indicated that using an RTX-Volatile capillary column with a heated rather than ambient temperature purge significantly improved the overall recovery of the alcohols, and consistent oxygenate recoveries were obtained using a heated purge and a DB-WAX capillary column. It is therefore recommended to use the heated at 80°C purge conditions along with a DB-WAX capillary column for optimum oxygenate recovery in aqueous samples containing low-level concentrations, if alcohols, e.g., TBA and TAA are target analytes

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.

As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without

compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.5 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained laboratory 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 or an elevated temperature depending on the desired target analytes, 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 methanol 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 DEFINITIONS

Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 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 may 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.

4.2 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 an appropriate organic-free matrix and sample container, and carried through sampling and handling protocols, serves as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary. 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.

4.4 The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken when analyzing for methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels can result. Since methylene chloride can 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 can also lead to random background levels and the same precautions must be taken.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals included in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 Sample containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 6.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain the minimum

sample volume and can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices. Additional information on sample containers can be found in Method 5035, Appendix A.

6.2 Purge-and-trap system

The purge-and- trap system consists of a unit that either manually or automatically samples an appropriate volume, e.g., 5 mL or 25 mL from the vial, adds surrogates, matrix spikes and internal standards (if applicable) to the sample and transfers the sample to the purge device, which purges the VOCs using an inert gas stream and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

6.2.1 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 appropriate performance is demonstrated.

6.2.2 The trap used to develop this method was 25 cm long with an inside diameter of 0.267 cm. 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.

6.2.3 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.

6.2.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

6.2.5 Trap Packing Materials

6.2.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

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

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

6.2.5.5 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 method sensitivity and precision in comparison to the performance appropriate for the intended application.

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

7.6-cm Carbopack™ B/1.3-cm Carbosieve™ 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.

6.2.5.5.2 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.

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

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

6.4.1 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. 6.4.2) device are acceptable interfaces. The type of interface and its adjustments can have a significant impact on the detection limits of the method. Other interfaces can be used if the performance criteria described in this method can be achieved.

6.4.2 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 refocused to elute in a narrow band. This refocusing 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 from 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.

6.5 Syringe and syringe valves

6.5.1 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.

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

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

6.6 Miscellaneous

6.6.1 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

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

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

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

7.3 Sample preservative

7.3.1 For determination as to whether sample preservation is necessary and for selection of appropriate preservation options, see Method 5035, Appendix A.

7.3.2 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

7.3.3 Hydrochloric acid, concentrated, HCl - ACS reagent grade or equivalent.

CAUTION: If samples containing MTBE, TAME, ETBE or other fuel ethers have been acid preserved with either sodium bisulfate (Sec. 7.3.2) or hydrochloric acid (Sec. 7.3.3), and will be analyzed by purging at elevated temperatures, these samples must be adjusted to pH >10 with trisodium phosphate dodecahydrate (TSP) (Sec. 7.3.4) prior to initiation of the analysis.

7.3.4 Trisodium phosphate dodecahydrate (TSP), $Na_3PO_4 \bullet 12H_2O$ - ACS reagent grade or equivalent (for fuel oxygenates) (Ref. 5).

7.3.5 The preservative, if necessary, should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

CAUTION: If a dechlorinating agent and acid are both added as preservatives, the samples must be dechlorinated first and then acidified.

7.4 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure. The recommended surrogates are 4-bromofluorobenzene, 1,4-difluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8. Other compounds may be used as surrogates, depending upon the analysis requirements and the specific target analytes. The recommended internal standards are chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, and fluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the target analytes being detected.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, and Method 5035, Appendix A for general sample collection information. Samples should be stored in capped vials, 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.

8.2 Preparation of sample vials

The specific preparation procedures for sample vials will depend on the desired target analytes as specified in the project planning documents. Depending on the desired class of target analytes sample preservation may or may not be necessary and the analytical holding time will be based on whether a preservative is present. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps. More detailed information on additional options for the preparation of sample vials can be found in Method 5035, Appendix A.

8.3 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Since only one analysis can be peformed on one sample vial, multiple vials should be collected especially for those samples designated for screening and QC analyses. For some specific project situations, VOA compositing can be used to achieve the project's data quality objectives. Samples may only be composited if the laboratory's quantitation and detection levels are adequate for the number of samples being composited (up to a maximum of five). The compositing must be done in the laboratory (See Note after Sec. 11.2.4.5). Always wear gloves whenever handling vials prior to and during sample collection. More detailed information and additional sample collection options can be found in Method 5035, Appendix A.

8.4 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan. See Method 5035, Appendix A for additional sample handling options.

8.5 Sample storage

8.5.1 Once in the laboratory, store samples at the recommended temperature until analysis (refer to Method 5035, Appendix A for additional sample storage information). The sample storage area should be free of organic solvent vapors.

8.5.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Generally, a holding time of 14 days from sample collection will apply to most applications. However, see the cautionary notes in Method 5035, Appendix A, Table A-1 and the Table of Analytes in Sec. 1.1 of this method pertaining to certain compound classes and applicable preservation options that may affect target analyte stability and analytical holding times. A longer holding time may be appropriate if it can be demonstrated that the reported VOC concentrations are not adversely affected by preservation, storage and analyses performed outside the recommended holding times. Otherwise without this performance demonstration, samples not analyzed within the recommended holding time must be noted and the data should be considered as minimum values.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. Each laboratory should maintain a formal quality assurance program. The laboratory

should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

9.2 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.3 Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.4 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Methods 5000 and 8000 for information on how to accomplish this demonstration.

9.5 Sample Quality Control for Preparation and Analysis - See Methods 5000 and 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. This includes the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS) and the addition of surrogates to each sample and QC sample.

9.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.7 The laboratory should have quality control procedures to make sure that sample integrity is not compromised during the sample collection and sample handling process, e.g., making sure that septa and vial caps do not leak, etc. In addition, it would be advisable for the laboratory to monitor the internal standard (IS) area counts for all samples, since leaks attributed to a poor seal with the vial caps and septa will be evident by low IS area counts. Sample containers and data results for instances where low IS area counts are observed and leaks are suspected, should be discarded.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.0 for information on calibration and standardization and refer to the appropriate determinative method for additional calibration and standardization procedures.

11.0 PROCEDURE

11.1 The purge-and-trap technique for aqueous samples is found in Sec. 11.2 and guidance for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 11.3. 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.

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

11.2.1 Initial set-up

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed. The GC/MS methods require instrument tuning prior to proceeding with calibration.

11.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 6.2. 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.

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

11.2.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards and internal standards, and transfer 5 mL to the purge device using either an automated sampler (Sec. 11.2.1.3.1) or manually using a syringe (Sec. 11.2.1.3.2)

NOTE: If sample volumes other than 5 mL are being used, e.g., 25-mL samples, then the calibration standards used must be of the same corresponding volume.

11.2.1.3.1 When using an autosampler, prepare the calibration standard in a volumetric flask and transfer it to a vial and seal it. Place the sample vial in the instrument carousel according to the manufacturer's instructions. Without disturbing the hermetic seal on the sample vial, a specific sample volume is withdrawn (usually 5 or 25 mL) and placed into the purging vessel along with the addition of internal standards and surrogate compounds using an automated sampler.

11.2.1.3.2 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. 6.5.1), 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. 11.2.4.7).

11.2.1.4 Follow the purge-and-trap analysis as outlined in Sec. 11.2.4.

11.2.1.5 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

11.2.1.6 If the purge-and-trap procedure is used with either Method 8021 or Method 8260, 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.

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

11.2.1.6.2 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.

11.2.1.6.3 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.

11.2.1.7 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 vessel after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bake-out of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

11.2.2 Calibration verification (see appropriate determinative method)

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range or the action level is used for verification. This standard may be prepared using either an automated sampler or manually using a syringe.

11.2.2.1 When using an autosampler, prepare the calibration standard in a volumetric flask and transfer it to a vial and seal it. Place the sample vial in the instrument carousel according to the manufacturer's instructions. Without disturbing the hermetic seal on the sample vial, a specific sample volume is withdrawn (usually 5 or 25 mL) and placed into the purging vessel along with the addition of internal standards and surrogate compounds using an automated sampler.

11.2.2.2 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 that is 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 6.2. Follow the guidance for the purge-and-trap procedure in Sec. 11.2.4. Ongoing GC or GC/MS calibration criteria must be met as specified in Method 8000 before analyzing samples.

11.2.3 Sample screening

11.2.3.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system**,** thereby requiring extensive cleanup and instrument maintenance. Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary.

11.2.3.2 SW-846 contains three 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; screening with a portable photoionization detector (PID) (Method 3815) or; 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 using the analyst’s professional judgment.

11.2.4 Sample introduction and purging

11.2.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Suspended particulates in volatile organic samples should be allowed to settle and are not subsampled.

11.2.4.2 Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in Sec. 11.0 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.

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

11.2.4.4 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min (also see Table 1 for guidance on specific analyte groups), and the operating temperature (if other than ambient) 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. All samples and standards should be run using the same purge gas flow rate and at the same temperature.

11.2.4.5 Introduction of the sample into the purging vessel can be done using either an automated sampler (Sec. 11.2.4.5.1) or a manual procedure using a syringe (Sec. 11.2.4.5.2).

11.2.4.5.1 Place the sample vial in the instrument carousel according to the manufacturer's instructions. Without disturbing the hermetic seal on the sample vial, a specific sample volume is withdrawn (usually 5 or 25 mL) and placed into the purging vessel along with the addition of internal standards and surrogate compounds using an automated sampler.

11.2.4.5.2 Alternatively, a gas tight syringe may be inserted through the septum of the vial to withdraw the sample. Or when the sample size taken is greater than 5 mL, remove the plunger from an appropriately sized syringe and attach a closed syringe valve. If lower detection limits are required, use a 25-mL syringe. Open the sample vial, 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 or 25.0 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. This second sample is maintained only until the analyst has determined that the first sample has been analyzed properly. If a second analysis is needed, it should be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

NOTE: Compositing Samples: VOA compositing must be performed in a closed system using an air-tight syringe. This is accomplished by withdrawing equal volumes of water from each discrete sample utilizing a syringe large enough to hold the exact volume to be used for sample analysis. For example, using a small needle to vent the sample vial, withdraw 1.25 mL through the septum from each of 4 sample vials thus collecting 5 mLs of water in the syringe to be analyzed for a 1:4 composite.

11.2.4.6 For the sample selected for matrix spiking, add the matrix spiking solution described in the Reagents Section of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in the Quality Control Section of Method 8000.

11.2.4.7 When sample dilution is necessary, samples can be diluted before purging using the autosampler device. Alternatively, manual dilutions can be performed directly in the 5-mL syringe that has been filled with reagent water through the use of appropriate microliter syringes, or with volumetric glassware, as appropriate. All sample dilution steps must be performed without delays until the diluted sample is in a gas-tight syringe.

11.2.4.7.1 For dilutions prepared in volumetric flasks, 10-mL to 100-mL volumes are recommended. Select the volumetric flask that will allow for the necessary dilution of the desired target analytes within the upper limit of the calibration curve. Intermediate dilutions may be necessary for extremely large dilutions.

11.2.4.7.2 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.

11.2.4.7.3 Inject the proper volume of sample from the syringe prepared in Sec. 11.2.4.5 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.

11.2.4.7.4 Fill a 5-mL syringe with the diluted sample as in Sec. 11.2.4.5.

11.2.4.8 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Sec. 11.0) 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.

11.2.4.9 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.

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

11.2.5 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.

11.2.5.1 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.

11.2.5.2 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.

11.2.6 Trap Reconditioning

11.2.6.1 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.

11.2.6.2 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.

11.2.7 Interpretation and calculation of data

11.2.7.1 Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. 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 should not resume until a blank can meet the organic-free reagent water criteria described in Chapter One.

11.2.7.2 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.

11.2.8 Analysis of water-miscible liquids

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

11.2.8.2 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.

11.2.8.3 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.

11.2.9 Analysis of water soluble analytes

11.2.9.1 Many highly water soluble analytes, e.g., ketones, alcohols, aldehydes, and 1,4-dioxane, which are listed as poor purgers (pp) or high temperature purgers (ht) in the table in Sec. 1.1 can be analyzed using this method, if the purge-and-trap procedure is performed at an elevated temperature, usually at 80°C.

11.2.9.2 If aqueous samples need to be analyzed for fuel oxygenates including the alcohols, e.g. *t*-butyl alcohol (TBA) and *t*-amyl alcohol (TAA), they must be

adjusted to pH >10 with trisodium phosphate dodecahydrate (TSP) (Sec. 7.3.4) prior to initiation of the purge cycle.

11.2.9.3 the following purge-and-trap cycle conditions are a recommended starting point for method optimization:

Use hydrophobic trapping materials to prevent excessive moisture collection in the trap

Varian Archon autosampler (or equivalent) preheated to 80°C for 3 minutes.

Tekmar 3000 purge-and-trap concentrator (or equivalent)
Purge time: 7min.
Dry purge time: 3 min.
Desorb time: 3 min.
Bake time: 3min.

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

11.3.1 The GC or GC/MS system should be set up as in Sec. 11.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to organic-free reagent water.

11.3.2 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.

11.3.3 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. 11.3.2 and a volume of the same solvent used in Method 5035 to total 100.0 µL (excluding methanol in standards).

11.3.4 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.

11.3.5 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.

11.4 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.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no data analysis and calculation steps directly associated with this procedure. Follow the directions given in the determinative method.

13.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data examples and guidance.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 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.
3. USEPA OSW, "Development and Evaluation of Methods for the Analysis of MTBE," September 17, 2001.

4. USEPA OUST, *Environmental Fact Sheet: Analytical Methods for Fuel Oxygenates,* EPA 510-F-03-001, April, 2003, http://www.epa.gov/OUST/mtbe/omethods.pdf.

5. White, H., Lesnik, B., and Wilson, J. T., "Analytical Methods for Fuel Oxygenates", *LUSTLine* (Bulletin #42), October, 2002, http://www.epa.gov/oust/mtbe/LL42Analytical.pdf

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain the tables and figures referenced by this method.

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)	Ambient[2]	Ambient[2]
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.

[2] Purge temperature is 80°C for Methods 8015 and 8260 when analyzing for TBA, TAA or other fuel oxygenate alcohols.

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

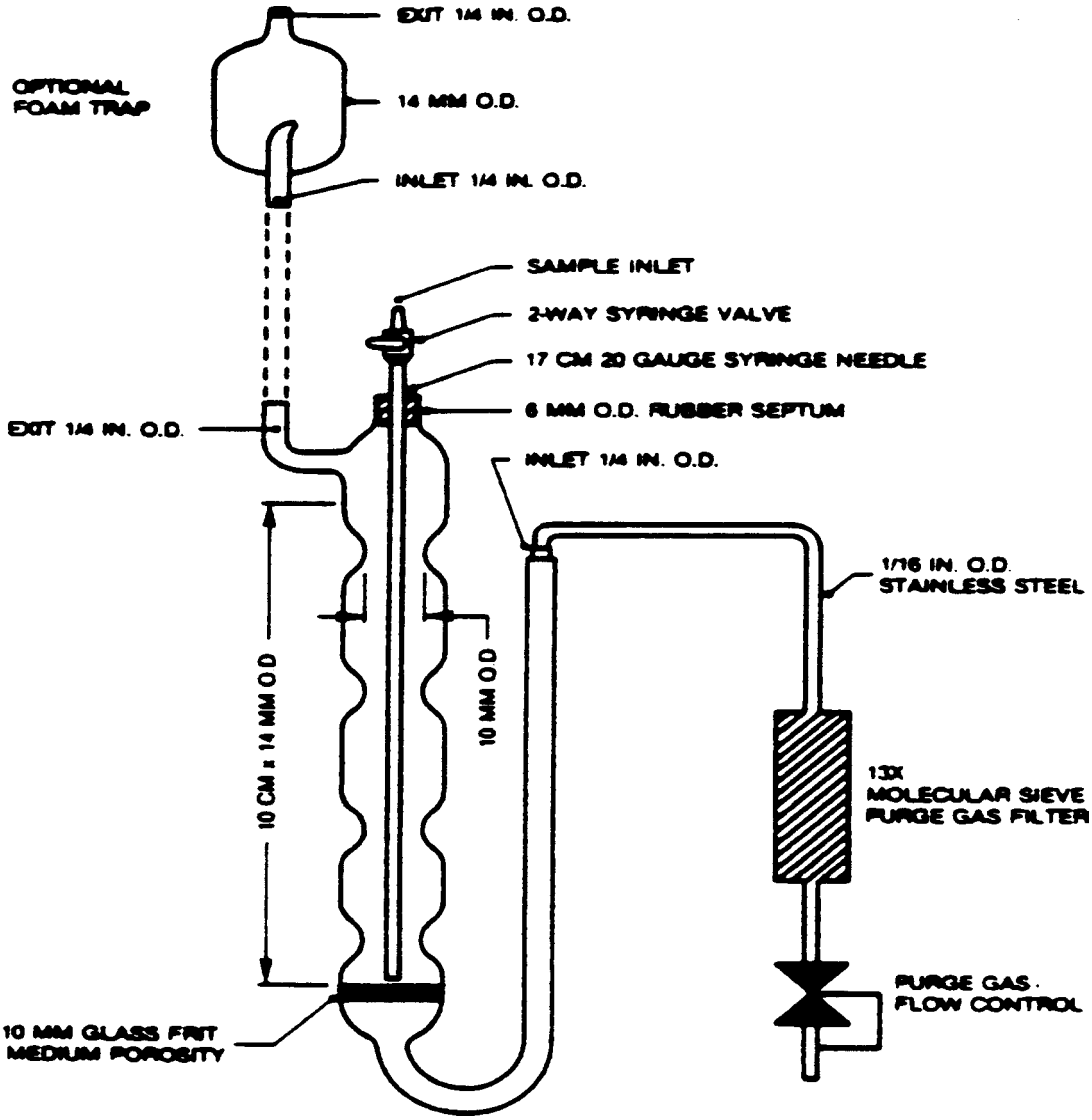

FIGURE 2
EXAMPLE OF TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

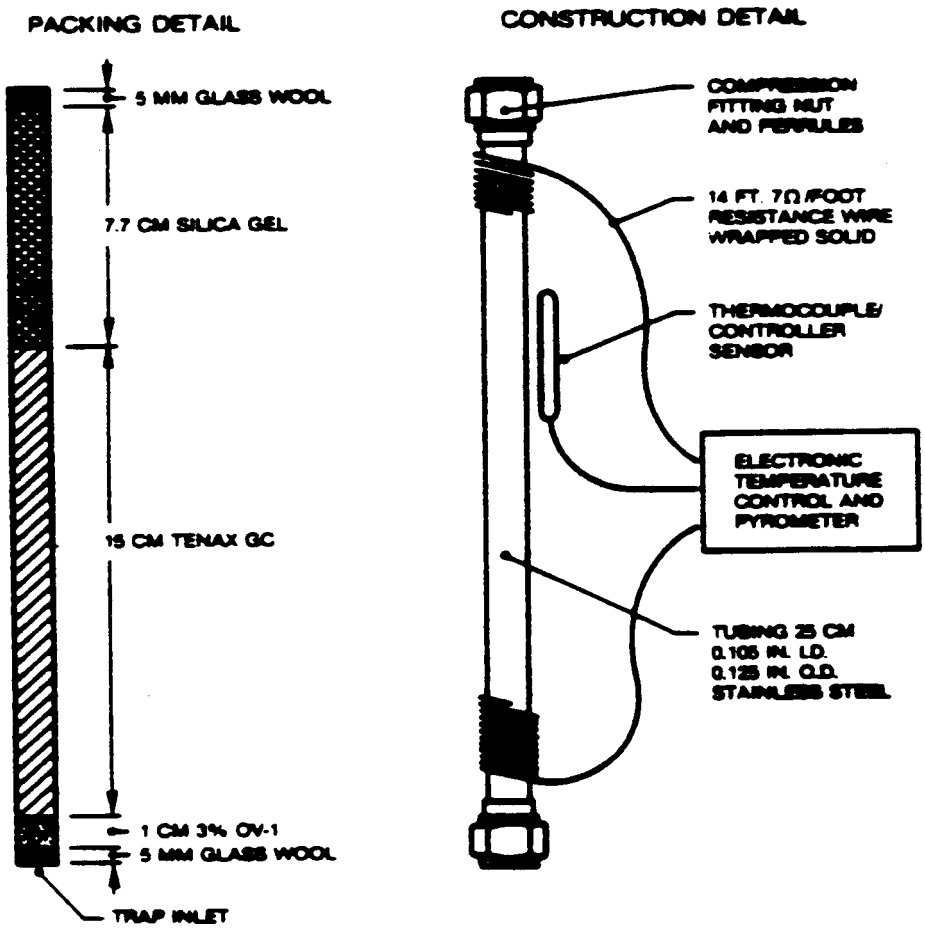

FIGURE 3
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
PURGE MODE

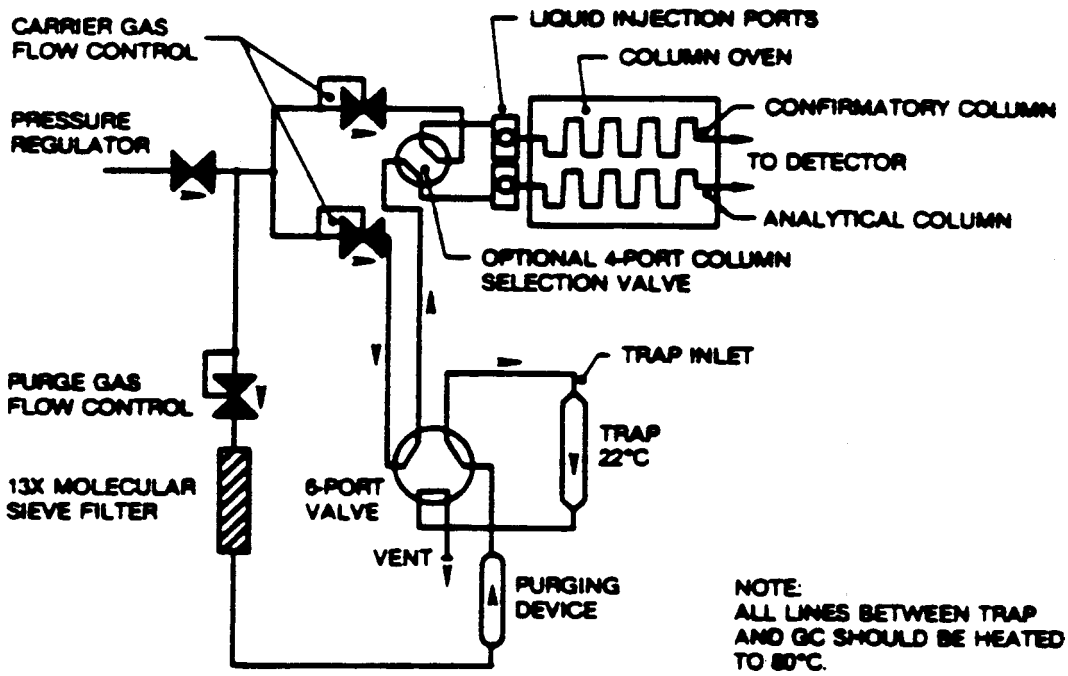

FIGURE 4
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
DESORB MODE