

METHOD 5021A

VOLATILE ORGANIC COMPOUNDS IN VARIOUS SAMPLE MATRICES USING EQUILIBRIUM HEADSPACE ANALYSIS

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria or for the purpose of laboratory accreditation.

1.0 SCOPE AND APPLICATION

Please see Appendix A at the end of this document for a summary of changes from the previous version.

1.1 This method describes equilibrium-based static headspace preparation of volatile organic compounds (VOCs) in soil/sediment, solid waste, aqueous and water-miscible liquid samples for determination by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). This method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from samples using the described conditions. While the method is designed for use on samples containing low levels of VOCs or aqueous dilutions thereof to be analyzed by direct vapor partitioning, a solvent extraction and extract introduction procedure is also described for solid samples containing high concentrations of VOCs or for oily materials that may not be appropriate for the low level technique. This preparation method is intended to be combined with a determinative method such as Methods 8015, 8021 or 8260. This preparation method is appropriate for the compounds listed below, and it may also be appropriate for other VOCs included in the determinative method (e.g., Sec. 1.1 of 8260), provided method performance is demonstrated to be acceptable for the intended use of the data.

Compound	CAS No. ^a	Response	Stability
Acetone	67-64-1	ws	hs
<i>t</i> -Amyl alcohol (TAA)	75-85-4	nd	hs
<i>t</i> -Amyl ethyl ether (TAEE)	919-94-8	nd	nd
<i>t</i> -Amyl methyl ether (TAME)	994-05-8	nd	hs
Benzene	71-43-2	c	hs
Bromochloromethane	74-97-5	p	hs
Bromodichloromethane	75-27-4	c	ms
Bromoform	75-25-2	p	hs
Bromomethane	74-83-9	c	hvs

Compound	CAS No. ^a	Response	Stability
<i>t</i> -Butyl alcohol (TBA)	75-65-0	ws	nd
Carbon tetrachloride	56-23-5	c	hvs
Chlorobenzene	108-90-7	c	hvs
Chloroethane	75-00-3	c	ms
Chloroform	67-66-3	c	hs
Chloromethane	74-87-3	c	hvs
Dibromochloromethane	124-48-1	p	nd
1,2-Dibromo-3-chloropropane	96-12-8	p	ms
1,2-Dibromoethane	106-93-4	p	hs
Dibromomethane	74-95-3	p	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
Dichlorodifluoromethane	75-71-8	c	hs
1,1-Dichloroethane	75-34-3	c	hs
1,2-Dichloroethane	107-06-2	p	hs
1,1-Dichloroethene	75-35-4	c	hvs
<i>trans</i> -1,2-Dichloroethene	156-60-5	c	ms
1,2-Dichloropropane	78-87-5	c	hs
Diisopropyl ether (DIPE)	108-20-3	c	hs
Ethanol	64-17-5	ws	nd
Ethylbenzene	100-41-4	c	hvs
Ethyl <i>tert</i> -butyl ether (ETBE)	637-92-3	c	hs
Hexachlorobutadiene	87-68-3	c	ms
Isopropanol	67-63-0	ws	nd
Methyl <i>tert</i> -butyl ether (MTBE)	1634-04-4	c	hs
Methylene chloride	75-09-2	c	hs
Naphthalene	91-20-3	p	ms
Styrene	100-42-5	c	hvs
1,1,1,2-Tetrachloroethane	630-20-6	c	hs
1,1,2,2-Tetrachloroethane	79-34-5	p	nd
Tetrachloroethene	127-18-4	c	ms
Toluene	108-88-3	c	hs
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	p	hs
Trichloroethene	79-01-6	c	ms
Trichlorofluoromethane	75-69-4	c	ls
1,2,3-Trichloropropane	96-18-4	p	ls
Vinyl chloride	75-01-4	c	hvs
<i>o</i> -Xylene	95-47-6	c	hvs
<i>m</i> -Xylene	108-38-3	c	hvs
<i>p</i> -Xylene	106-42-3	c	hvs

Gasoline range organics

^a Chemical Abstracts Service Registry Number

- c = Response in reagent water is acceptable; similar response expected in matrix modifier solution (< 50% improvement).
- p = Response in matrix modifier solution expected to improve >50% compared to reagent water; Use of matrix modifier is recommended.
- ws = Highly water soluble analyte. Method sensitivity expected to be poorer than for other analytes due to poor partitioning into headspace; matrix modifier expected to be critical for acceptable method performance.
- 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 depending on the sample matrix. Longer holding times may be appropriate, see Method 5035, Appendix A, Table A.1 footnote and Ref. 47 for additional information.

1.2 The following compounds may also be analyzed by this procedure or may be used as surrogates:

Compound	CAS No. ^a	Response	Stability
Bromobenzene	108-86-1	c	nd
<i>n</i> -Butylbenzene	104-51-8	c	nd
<i>sec</i> -Butylbenzene	135-98-8	c	nd
<i>tert</i> -Butylbenzene	98-06-6	c	nd
2-Chlorotoluene	95-49-8	c	nd
4-Chlorotoluene	106-43-4	c	nd
<i>cis</i> -1,2-Dichloroethene	156-59-4	c	hs
1,3-Dichloropropane	142-28-9	c	nd
2,2-Dichloropropane	590-20-7	c	nd
1,1-Dichloropropene	563-58-6	c	nd
Isopropylbenzene	98-82-8	c	nd
4-Isopropyltoluene	99-87-6	c	nd
<i>n</i> -Propylbenzene	103-65-1	c	nd
1,2,3-Trichlorobenzene	87-61-6	c	nd
α,α,α -Trifluorotoluene	98-08-8	nd	nd
1,2,4-Trimethylbenzene	95-63-6	c	nd
1,3,5-Trimethylbenzene	108-67-8	c	nd

^a Chemical Abstracts Service Registry Number

1.3 In order to produce quantitative data with this technique, all of the quality control criteria described in the determinative method and/or Method 8000 should be met. Alternatively, this method may be utilized as a screening protocol. If used for screening, semi-quantitative or estimated sample results may be obtained with minimal calibration and quality control, such as a reagent blank and a single calibration standard.

As with any preparative method for volatiles, screening samples prior to low level analysis may help minimize problems associated with carryover contamination from samples that contain very high concentrations of volatiles above the calibration range of the determinative method. In addition, because removing a sample aliquot from a container may compromise the integrity of the sample, multiple sample aliquots should be collected to allow for screening and re-analysis.

1.4 In order to accommodate analysis of a variety of sample matrices and VOCs, a matrix modifier (Sec. 7.7) is generally recommended to be used with this method. The matrix modifier is a water soluble salt solution that is added to each sample and standard vial prior to analysis. The matrix modifier solution acts to increase the VOCs mass transfer into the headspace of the vial. The principal benefits of using the matrix modifier are:

- 1) better response and reproducibility of the VOCs that do not otherwise partition efficiently into the headspace of the vial from the aqueous phase (identified with 'p' or 'ws' in the response column in the table in Sec. 1.1); and
- 2) less potential for measurement bias resulting from aqueous activity differences between standards and samples.

Measurement bias results from VOCs partitioning into the vial headspace differently in a sample than in the calibration standards. Some potential sources of measurement bias and the anticipated effects of the matrix modifier on these sources of bias are described below.

1.4.1 Aqueous field samples containing high dissolved solute concentrations:

At higher solute concentrations substantially larger fractions of some VOCs partition into the headspace leading to high bias in the determined concentration. The VOCs most prone to high bias measurement at higher dissolved solute concentrations are also the VOCs whose responses are most substantially improved in the matrix modifier solution relative to reagent water (identified with 'p' or 'ws' in the response column in the tables in Sec. 1.1). The VOCs identified with 'c' in the response column in the analytes table in Secs. 1.1 and 1.2 are not as subject to this source of measurement bias. The matrix modifier is used to normalize the solute concentration between samples and calibration standards, thereby minimizing this source of bias.

1.4.2 Aqueous field samples containing water miscible organic component:

The presence of a water miscible organic component (e.g., cosolvent or surfactant) may result in low bias measurement of VOCs with high octanol-water partitioning coefficients (e.g., C3 and C4 alkylbenzenes, trichlorobenzenes and naphthalene), while recovery of the lighter and more highly water soluble VOCs is unlikely to be strongly affected unless the proportion of the water miscible organic component in the sample is high. The matrix modifier helps improve the recovery of VOCs whose partitioning into the headspace is most strongly affected by this source of measurement bias.

1.4.3 Field samples containing a water immiscible component:

For samples with a separate water immiscible phase, partitioning of VOCs into the headspace competes with the water immiscible phase. While addition of the matrix modifier has a favorable effect on partitioning of VOCs into the headspace from the aqueous phase, it may also increase partitioning into the water immiscible phase(s) (e.g., soils with >1% organic matter, oily materials), potentially exaggerating matrix effects relative to the calibration standards. This matrix effect is more pronounced for VOCs with higher octanol-water partitioning coefficients when the matrix modifier is used for the analysis. Recovery of the lighter and more water soluble VOCs is expected to be less affected.

For complex samples, more than one of these types of matrix effects may be relevant, and a compromise may have to be made for data quality of some analytes in order to obtain reliable data for the analytes deemed most critical for the project. For simple sample matrices and VOCs

not expected to subject to measurement bias (e.g., analysis of BTEX and other alkylbenzenes in surface water samples) the matrix modifier solution may be omitted.

1.5 This method, in conjunction with determinative Method 8015 (GC/FID), may be used for analysis of the aliphatic hydrocarbon fraction in the light ends of petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use this method and Method 8021 (GC/PID). A total determinative analysis of gasoline and other volatile petroleum hydrocarbon fractions may be obtained using Method 8021 in series with Method 8015. If MS detection is desired for these target analytes, Method 8260 (Volatile Organic Chemicals by GC/MS) may be used.

1.6 Measurements of VOCs using this method may be subject to bias from several sources, including differences in partitioning of VOCs between the aqueous phase and headspace in samples relative to standards, differences in headspace volume in samples relative to standards, and adsorption of VOCs to surfaces or absorption into compatible phases (e.g., soil organic matter). Measurement bias is monitored through internal standard, surrogate, and matrix spike recovery when appropriate for the project and determinative method. Use of the matrix modifier (Sec. 7.7) will help minimize measurement bias resulting from differences in partitioning behavior of VOCs in samples relative to standards. Measurement bias resulting from adding solid material to the vial, which changes the headspace volume in the sample relative to the calibration standards, is expected to be negligible as long as the volume of material is small relative to the headspace volume. The magnitude of this bias may be reduced by adding a similar volume of solid organic-free control material to calibration standards as the volume of the bulk material being tested. Measurement bias related to sorption of VOCs to solid samples with fine particle size distributions and/or significant organic content may be substantial. The magnitude of this bias may be reduced by analyzing a smaller amount of material or by solvent extraction (Sec. 11.4).

1.7 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also 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 (DQOs) for the intended application.

1.8 This method is restricted to use by, or under supervision of, appropriately experienced and trained analysts for volatile organic analysis in general and specifically the use of equilibrium headspace devices interfaced to the determinative method selected by the analyst. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Sample collection and headspace vial preparation

2.1.1 Water samples – A 40-mL volatile organic analyte (VOA) vial is filled to capacity and capped so no headspace remains in the vial. The water sample may be preserved at the time of sampling by addition of a chemical preservative (e.g., hydrochloric acid solution, solid sodium bisulfate or solid trisodium phosphate) to the vial. At the laboratory, that vial is sub-sampled into a headspace vial, and internal standards and surrogates are added, if used. The matrix modifying solution (Sec. 7.7) should be added to the headspace vial during subsampling if used for the analysis.

2.1.2 Low concentration soil samples -- Approximately 2 g of soil is collected with an appropriately sized coring tool and placed in a pre-weighed crimp seal or screw top glass headspace vial, and then the vial is sealed. Depending on the analytes of interest, the soil sample may be preserved by addition of a pH modifying chemical preservative (e.g., sodium bisulfate, trisodium phosphate) prior to sealing the sample vial, and the matrix modifying solution (Sec. 7.7) should also be added prior to capping the vial if used for the analysis. Sec. 8.3.3 also describes the use of a sealable coring device as an alternative sampling technique, which may simplify collection and handling of soils in the field.

Surrogates and internal standards may be added to the vials during sampling or at the laboratory. If the matrix modifying solution is used for the analysis and was not added to sample vials in the field, it should be added when any surrogates and internal standards are added at the laboratory. Adding the matrix modifying solution or reagent water to a vial after adding the sample may cause loss of gas phase VOCs from the container due to displacement of a portion of the vial headspace. Adding the matrix modifying solution (Sec. 7.7) to the vial prior to adding the sample and sealing quickly will help to limit loss of VOCs from the sample container and maintain sample representativeness.

NOTE: The choice of chemical preservative(s) will depend on the VOCs that will be measured in the samples and to some extent on the sample matrix. The matrix modifying solution acts as a chemical preservative, but it does not otherwise alter the sample pH and may not protect against degradation of some classes of VOCs, including hydrolysis of ethers or dehydrohalogenation of chlorinated aliphatics (Sec. 4.7). Sodium bisulfate has also been identified as inappropriate for use as a preservative for calcareous soils, which may off-gas CO₂ when exposed to acid due to chemical reaction with any carbonate salts, which may cause loss of VOCs from the container or build up pressure once the container is sealed, potentially leading to rupture.

2.1.3 High concentration soils or other solid materials – A representative portion of soil is collected with an appropriately sized coring tool and placed in a pre-weighed glass VOA vial, and then the vial is sealed. The soil sample may be preserved by addition of extraction solvent (e.g., methanol) at the time of sampling or upon receipt by the laboratory. At the laboratory, the methanol extract is then diluted with the matrix used for the calibration standards (organic-free reagent water or the matrix modifying solution) and analyzed as an aqueous sample. Sec. 8.3.3 also describes the use of an air-tight sealable coring device as an alternative sample collection technique that may be useful, and Sec. A.6 of SW-846 method 5035A provides additional information pertaining to methanol extraction of soils.

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or into reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to

when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

2.2 For soil samples, additional aliquot(s) are collected in VOA vials for dry weight determination.

2.3 In the laboratory, the vials are rotated to allow for diffusion of internal standards and surrogates throughout the matrix. The vials are placed in the autosampler carousel of the headspace analyzer and maintained at room temperature. Approximately 1 hr prior to analysis, the individual vials are moved to a heated zone and mechanically agitated while the elevated temperature is maintained, allowing the VOCs to equilibrate between the headspace, liquid and any solid phases in the vial.

2.4 The autosampler then pressurizes the vial with helium and forces a portion of the headspace gas mixture into the gas chromatograph through a heated transfer line, either passing through the GC inlet or directly connected to the analytical column via an inert, low dead volume connector.

2.5 Determinative analysis is performed using the appropriate GC or GC/MS method. Any chemical preservative and matrix modifier added to the field samples should also be added to the calibration standards and other QC samples.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to the determinative methods to be used for information regarding potential interferences.

4.2 Volatile organic analyses are subject to major interference problems because of the prevalence of volatile organics in a laboratory. See Method 5000 for common problems and precautions to be followed.

4.3 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.

4.4 The sample matrix itself can cause severe interferences by one of several processes or a combination of these processes. These include, but are not necessarily limited to, the absorption potential of the soil, the biological activity of the soil, and the actual composition of the soil. Soils high in organic matter or oily material and organic sludge wastes inhibit the

partitioning of the volatile target analytes into the headspace. Therefore, analyte recovery by direct vapor partitioning may be low and will depend on the properties of the particular chemical. This matrix effect can be difficult, if not impossible, to overcome. It is recommended that surrogates or additional deuterated compounds (for GC/MS methods) be added to a matrix and analyzed to determine the percent recovery of these compounds. The calculated percent recovery can give some indication of the degree of the matrix effect, but not necessarily correct for it. Alternatively, the use of the high-concentration procedure in this method should minimize the problem with oily waste and other organic sludge wastes.

4.5 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 one or more method blanks or instrument blanks to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in subsequent samples, the analyst must demonstrate that the compounds are not affected by carryover contamination. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of a blank is not necessary.

4.6 The laboratory where volatiles analysis is performed should be free of any solvents that may interfere with the analysis. 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 polytetrafluoroethylene (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.

4.7 Ethers in acidic samples (*i.e.*, samples with a $\text{pH} < 7$) will hydrolyze at the higher temperatures used in this method. As such, basic preservatives should be used if the target analytes are ethers or the alcohols that those ethers would form if hydrolyzed. Strong bases may catalyze substitution and elimination reactions that can occur if halogenated compounds are present. Halogenated aliphatic VOCs are particularly susceptible to dehydrohalogenation reactions in neutral to basic conditions at elevated temperature such as with a heated sample preparation procedure as is described here. Accordingly, acidic preservatives may be necessary to prevent dehydrohalogenation if halogenated aliphatic VOCs are analytes of interest or their presence is suspected and their transformation products are of interest. Acetone has also been observed to form in high organic content soils preserved with sodium bisulfate (Sec. A.8 in the Appendix of method 5035A provides more information). The chemical reactivity introduced by the preservative should be monitored by analyzing a matrix spike of a field sample with each batch. The spiking solution should contain all analytes which the client intends to monitor.

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.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Headspace containers - Clear glass, 22-mL vials equipped with PTFE-lined septa that are compatible with the analytical system. Vials of other sizes may be employed, provided that they can be hermetically sealed and equipped with suitable septa. Ideally, the vials and septa should have a uniform tare weight. The septa should be unpunctured, as piercing the PTFE face may allow target analytes to diffuse into and adsorb to the silicone backing material. New, disposable vials may be used without pretreatment provided they are demonstrated to be clean through method blank analysis. Store the vials in an area free of organic solvents. If vials are suspected of being a source of contamination, first wash the vials in a detergent solution, then thoroughly rinse with tap water followed by distilled water, and finally dry the vials in an oven at 105 °C for 1 hour. Allow vials to cool prior to use.

6.2 Headspace system - The operating conditions listed in Sec. 11.0 are those selected for the equipment used in developing this method. See Reference #1 in Sec. 16 for more detail. Other equipment and conditions may be employed, provided that the laboratory demonstrates performance for the analytes of interest using the determinative method appropriate for the intended application. The system used must meet the following specifications:

6.2.1 The system must be capable of holding samples at elevated temperatures and establishing a reproducible equilibrium between a wide variety of sample types and the headspace.

6.2.2 The system must be capable of accurately transferring a representative portion of the headspace into a gas chromatograph fitted with a capillary column without adversely affecting the chromatography or the detector.

6.3 Field sampling equipment

6.3.1 Water samples - Clear or amber 40 mL volatile organic analysis (VOA) vials with screw-cap PTFE lined vials.

6.3.2 Soil samples

6.3.2.1 A soil sampler which delivers at least 2 g of soil is necessary, e.g., Purge and Trap Soil Sampler Model 3780SPT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

6.3.2.2 An automatic syringe or bottle top dispenser calibrated to deliver a 10.0 mL liquid volume.

6.3.2.3 Crimping tool for headspace vials - If using screw-top vials, this is not needed.

6.3.2.4 VOA vials (22, 40 or 60 mL) with PTFE faced septa and crimp-seal caps or screw-top caps. These vials will be used for sample screening, high concentration analysis (if needed) and dry weight determination.

6.3.2.5 Sealable, air-tight coring device – A soil coring device with an internal volume appropriate for approximately 2 g of sample for direct vapor partitioning analysis, or other size as appropriate for high level analysis, equipped with an o-ring seal or equivalent air-tight sealing mechanism, constructed of materials that will not absorb or react with the target chemicals of interest and with a cross-sectional diameter appropriate for a VOA vial compatible with the headspace analyzer or for use with methanol extraction.

6.4 Miscellaneous equipment

6.4.1 For the preparation of blanks, standards and water samples, it is necessary to have the crimping tool addressed in 6.3.2.3 available in the laboratory.

6.4.2 Graduated microsyringes for standard preparation and for addition of internal standard and surrogate spiking solutions.

6.4.3 5-mL glass hypodermic syringes with Luer-Lok™ tip (other sizes are acceptable depending on sample volume used).

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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Organic-free reagent water - Reagent water must be interference free. All references to water in this method refer to organic-free reagent water, unless otherwise specified.

7.3 Methanol - Pesticide quality or equivalent. Store away from other solvents. Purchase in small quantities (1 Liter size or less) to minimize shelf life to reduce potential for contamination.

7.4 See the determinative method and Method 5000 for guidance on the preparation of stock standards and a secondary standard for internal standards, calibration standards, and surrogates.

7.4.1 Calibration spiking solutions - Prepare five or more spiking solutions in methanol or water that contain all the target analytes. The concentrations of the calibration solutions should be such that the addition of 1.0 μL of each to the headspace vials will bracket the analytical range of the detector. Alternatively, calibration standards may be prepared by adding different volumes of one or more stock solutions provided that the

linearity of the calibration is not affected by the methanol content. For analysis of methanol extracts, it may be appropriate to calibrate surrogates at multiple concentration levels as well to demonstrate calibration linearity at the surrogate level measured in diluted extracts.

7.4.2 Internal and surrogate standards – Follow the recommendations of the determinative method for the selection of internal and surrogate standards. Selection and use of surrogates with physical properties similar to the classes of target analytes that are of interest for the project will provide more meaningful sample-specific quality assurance information. A concentration of 20 mg/L in methanol for both internal and surrogate standards may be used for spiking each sample. The concentration may vary depending on the relative sensitivity of the detector used in the determinative method. If determination is by GC, external standard calibration may be preferred and the internal standard omitted.

7.5 Blank preparation - Transfer 10.0 mL of matrix modifying solution (Sec. 7.7) or reagent water to a sample vial. Inject the necessary amounts of internal standards and surrogate compounds under the surface of the water in the headspace vial, and seal the vial. Place in the autosampler and analyze in the same manner as an unknown sample. Any chemical preservative and/or matrix modifier added to the field samples must also be included in the blank(s).

7.6 Preparation of calibration standards - Prepare calibration standards in the same manner as blanks (Sec. 7.5), adding the standard spiking solution(s) prepared in Sec. 7.4.1 in the same manner that internal standards and surrogates are added. Any chemical preservative and/or matrix modifier added to the field samples should also be included in the calibration standards.

7.7 Preparation of matrix-modifying solution - Add 180 g of ACS-grade sodium chloride (NaCl) to 500 mL of reagent water. Mix well until all components are dissolved. Other water soluble salts may be appropriate. The matrix modifier solution should not affect the pH of the sample to the extent that preservation or analyte stability is compromised. Analyze a 10.0-mL portion from each batch according to Sec. 7.5 to verify that the solution is free of contaminants. Store the prepared matrix-modifying solution in a sealed bottle in an area free of organic chemicals at ≤ 6 °C.

CAUTION: The matrix modifying solution may not be appropriate for analysis of some VOCs in soil samples having high organic matter content.

7.8 Preparation of chemical preservative for low level (vapor partitioning) analysis - The preservative should be chosen based on the analytes of interest and should be mixed with the sample at the time of sampling.

7.8.1 If a basic preservative is chosen, 100 mg of ACS-grade trisodium phosphate dodecahydrate (TSP; $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) should be added to either a 22-mL headspace vial or a 40-mL water sample vial to raise the pH above 10.

7.8.2 If an acidic preservative is chosen, 2-3 drops of 6N hydrochloric acid (HCl) should be added to a 40-mL water sample vial. The HCl solution should be prepared by the 1:1 dilution of ACS-grade concentrated HCl. For acid preservation of a soil sample, 1 g of solid, ACS-grade sodium bisulfate (NaHSO_4) should be added to each 22-mL vial.

CAUTION: If samples containing MTBE, TAME, ETBE or other fuel ethers have been acid preserved with either sodium bisulfate or hydrochloric acid, these samples must be adjusted to pH >10 with trisodium phosphate

dodecahydrate (TSP) (Sec. 7.8.1) prior to initiation of the headspace analysis.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining an appropriate plan for sample collection, preservation and storage prior to sample collection and analysis.

8.1 Refer to Chapter Four and Method 5035A or general sample collection information. All samples should be stored in capped vials at ≤ 6 °C in an area free of solvent fumes. If any evidence of leakage is found, the sample can be considered corrupted and should be discarded.

Pre-testing of a representative soil or aqueous sample, prior to collection, with acid or bisulfate may show effervescence if carbonaceous materials are present. If bubbling occurs during chemical preservation, an increased potential for loss of volatile constituents exists and samples should therefore be collected without preserving with acid or bisulfate.

8.2 Water samples - Fill the 40-mL vial and, according to the analyte list to be analyzed, chemically preserve the sample (Sec. 7.8) as necessary. Ensure that there is no headspace in the vial and seal it. At least two vials should be collected per sample and more may be necessary for duplicate and MS/MSD analyses, if desired. Transfer of the sample into a headspace vial and the addition of the matrix modifier and standards should be performed at the laboratory.

In general, liquid samples should be poured into the vial without introducing any air bubbles into the sample as the vial is being filled. Should bubbling occur as a result of violent pouring, the sample should be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial inverted, no headspace is visible. The sample should be hermetically sealed in the vial at the time of sampling, and not opened prior to analysis to preserve its integrity.

Due to differing solubility and diffusion properties of gases in liquid matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles and should not invalidate a sample for volatiles analysis. The diameter of any bubble caused by degassing upon cooling the sample should not exceed 5 - 6 mm. When a bubble is present, also inspect the cap and septum to ensure that a proper seal was made at the time of sampling. The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-sized" bubbles (i.e., bubbles not exceeding 1/4 inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

8.3 Soil samples - Three alternative procedures are presented below for collection of soil samples in headspace sample vials. Sec. A.7 in the appendix of method 5035A describes some additional alternatives that may also be appropriate. The choice between these alternatives should be based on knowledge of the field conditions, the organic carbon content of

the soil, the specific volatile analytes and concentration levels of interest, and the intended use of the analytical results. For low level analysis by direct vapor partitioning, 3 or 4 replicate samples should be collected from each sampling point to allow for reanalysis, while duplicate samples may be sufficient for high level analysis because the solvent extract can be diluted and reanalyzed. Additional sample replicates should also be collected for duplicate and MS/MSD analyses, as well as separate portions for dry weight determination. If samples will be analyzed by the low level method but have the potential to contain high levels of VOCs, samples may be collected for both low level and high level analysis. This is due to the difficulty of diluting samples prepared for low level analysis once they are sealed in the vials.

8.3.1 Sampling directly into prepared headspace vials for low level analysis:

Soil may be sampled by addition to a prepared vial that contains 10.0 mL of matrix modifier or reagent water, plus any necessary pH altering chemical preservative. The preservative and matrix modifier or water are added to the vial prior to sampling in order to prevent displacing a portion of the headspace from the vial, along with any associated VOCs. The matrix modifying solution has the additional benefits of reducing the biodegradation potential of the sample matrix and increasing partitioning of the VOCs into the vial headspace from water. Problems related to contamination of the aqueous solution in a field sampling situation and incorrect measurement and transfer into the sample vials can be minimized by adding it to the vials at the laboratory and sealing them prior to sending them to the field. Samples should be obtained and transferred to a vial rapidly after sampling (<10 seconds) to minimize volatilization losses. In order to estimate the sample mass added, the vial, cap and any added solutions should be tared and the masses recorded prior to and after adding a soil sample to the vial. If the vials were not prepared in the laboratory prior to sampling, the analyzing laboratory must be made aware of the identities and amounts of any reagents added to each vial in the field.

8.3.1.1 Use standard glass headspace vials with PTFE faced septa.

8.3.1.2 Using the soil sampler (Sec. 6.3.2.1), add 2-3 cm (approximately 2 g) of the soil sample to a tared headspace vial containing 10.0 mL of matrix modifier or reagent water and any pH modifying chemical preservative used. The samples should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. Seal immediately with the PTFE side of the septum facing toward the sample.

8.3.2 Sampling directly into empty or prepared headspace vials for high level analysis:

If high concentrations of VOCs are expected (greater than 200 µg/kg), collection of the sample in an empty headspace vial or a vial containing methanol is appropriate for use with the high concentration procedure described in Sec. 11.4.

8.3.2.1 Use standard 22-mL crimp-cap or screw-top glass headspace vials with PTFE faced septa (other vials may be used, as described in Sec. 6.1).

8.3.2.2 Using the soil sampler (Sec. 6.3.2.1), add 2-3 cm (approximately 2 g) of the soil sample to a headspace vial and seal immediately with the PTFE side of the septum facing toward the sample. The samples should be obtained and transferred to a vial rapidly after sampling (<10 seconds) to minimize volatilization losses, and they should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. If methanol is added to the vial

prior to the sample, the vial, cap and methanol should be tared and the masses recorded prior to and after adding a soil sample to the vial. The recorded mass should be checked by the analyzing laboratory to verify that solvent was not lost during shipping and/or storage.

8.3.3 Sampling with a sealable, air-tight coring device for low or high level analysis:

For cohesive soils, soil samples can be taken in appropriately sized air-tight sealable coring devices for refrigeration and shipping to the laboratory, where the samples are further preserved or immediately prepared for analysis.

8.3.3.1 Insert a clean coring device into a fresh surface for sample collection and ensure that no air is trapped between the coring tool and the sample. The volume of material collected should not cause excessive stress on the coring tool during intrusion into the material. Just before capping, a visual inspection of the lip and threads of the sample vessel should be made and any foreign debris should be wiped clean, allowing an airtight seal to form.

8.3.3.2 Upon laboratory receipt, the soil plug in each sealable coring device is extruded into individual tared headspace VOA vials containing the appropriate solution (either matrix modifier or reagent water for low level analysis, with pH modifying preservative as appropriate, or methanol for high level analysis). The coring device must fit into the mouth of the headspace vial or other VOA vial into which the sample is extruded, or losses of VOCs will result. In order to estimate the sample mass added, the vial, cap and any added solutions should be tared and the mass recorded prior to and after adding a soil sample to the vial.

8.4 Field blanks should be prepared, regardless of which alternative is employed for soil sample collection. If the matrix modifying solution is not added in the field, then the field blank(s) should be prepared by adding any reagents used in the field (e.g., 10.0 mL of organic-free reagent water, methanol, or matrix modifying solution, plus any other chemical preservatives) to a clean vial and immediately sealing the vial.

8.5 Sample storage

8.5.1 Samples should be stored at ≤ 6 °C until analysis in order to limit diffusion of the analytes out of the water, reduce the ability of the analytes to react with the glass walls of the sampling container and further hinder sample biodegradation. Water samples in VOA vials with no headspace should not be frozen, but subsamples added to prepared headspace vials may be frozen, provided the integrity of the container seal is maintained. Freezing of soil samples is also appropriate provided the storage temperature is not lower than the minimum temperature recommended by the manufacturer for maintaining integrity of the container seal. Freezing in this temperature range may be used to extend the holding time of soils in sealed air-tight coring devices and in sealed headspace vials with reagent water, even if no other chemical preservative is added. See Table A1 in the Appendix of method 5035A for more details. The sample storage area should be free of organic solvent vapors.

8.5.2 All samples should be analyzed within 14 days of collection or sooner if labile compounds are target analytes. See the cautionary notes in Table 4-1 of Chapter Four, Method 5035, Appendix A, Table A-1, and the list 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. Samples not analyzed within this period should be identified to the data user and the results considered minimum values unless it can be demonstrated that the reported VOC concentrations are not adversely affected by preservation, storage and analyses performed outside the recommended holding times.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. It should be noted that several methods (e.g., Method 8000) also contain general QC criteria and guidance that pertain to the individual methods referenced therein (e.g., Methods 8081, 8082, 8260 and 8270). Individual methods may also contain QC criteria specific only to that method. The QC criteria in the general methods take precedence over chapter QC criteria. Method-specific QC criteria take precedence over general method QC criteria.

Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. 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.

9.2 Initial Demonstration of Proficiency (IDP)

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 demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000D, Sec. 9.3 for information on how to accomplish a demonstration of proficiency.

9.3 Lower Limit of Quantitation (LLOQ) check standard

The laboratory shall establish the LLOQ as the lowest point of quantitation, which in most cases, is the lowest concentration in the calibration curve. LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. This verification may be accomplished with either clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix, free of target compounds. Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated DQOs.

In order to demonstrate the entire sample preparation and analysis process at the lower limit of quantitation (LLOQ), a LLOQ check standard (not part of an initial calibration) is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. The LLOQ check is carried through the same preparation procedures as environmental samples and other QC samples.

Recovery of target analytes in the LLOQ check standard should be within established in-house limits, or other such project-specific acceptance limits, to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine

acceptance limits, the LCS criteria $\pm 20\%$ may be used for the LLOQ acceptance criteria. This acknowledges the poorer overall response at the low end of the calibration curve. Historically-based LLOQ acceptance criteria should be determined as soon as practical once sufficient data points have been acquired. Additional information on LLOQ can be found in 8000D, Sec. 9.7.

9.4 Initially, 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. As a continuing check, 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. If a peak is observed within the retention time window of any analyte that would interfere with measurement of that analyte, determine the source and eliminate it, if possible, before analyzing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor method and/or instrument blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks must be prepared for each set of reagents.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.5 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, bias, method sensitivity). At a minimum, each batch of 20 or fewer field samples should include at least one method blank, a laboratory control sample (LCS), and either a matrix spike/matrix spike duplicate (MS/MSD) pair or a matrix spike and duplicate analysis of one field sample. When used, surrogates may be added to each field sample and QC sample and their recovery monitored to evaluate the effect of the sample matrix. Any method blanks, matrix spike samples, and duplicate QC samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

See Methods 5000 and 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed.

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., through analysis of trip blanks, method blanks, etc. In addition, it would be advisable for the laboratory to monitor the internal standard (IS) area counts for all samples; 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. Low area counts of the less volatile internal standards may also be attributed to matrix effects and should not be confused with a leaking vial.

9.8 Heating the sample/chemical preservative/matrix modifier mixture can exacerbate chemical interferences such as those introduced by acid catalyzed hydrolysis or base catalyzed substitution and elimination reactions. This can only be monitored through a matrix spike of a sample from every project analytical batch. The spiking solution should be the same as that used to prepare the calibration standards in order to minimize sources of variability in evaluating spike recovery. The acceptance criteria shall be those recommended in the determinative method or specified by a properly executed systematic planning document. If these criteria cannot be met, the analyst may adjust the pH of the mixture through the addition of solid NaHSO_4 to excessively basic mixtures or solid $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ to excessively acidic mixtures. After this is done, the matrix spike analysis should be repeated with an unanalyzed vial. If the results are acceptable, this pH adjustment should be made to all samples in the appropriate analytical batch. Even if the pH-adjusted matrix spike analysis is acceptable, the data user must be made aware that the initial matrix spike failed and the pH adjustment was necessary. The results from the pH adjusted samples should be reported, and the data user must be made aware that the results for the analytes for which the initial matrix spike failed are questionable.

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 Sample preparation - Sample preparation in the laboratory will be necessary except when a soil sample is collected and used only for screening purposes. The procedure for sample preparation depends upon the matrix of the sample and the target analyte concentration range. To minimize loss of VOCs from the samples or exchange of the vial headspace with the room air, add spiking solutions quickly to cold sample vials soon after removing from refrigerated storage and either reseal or place a new cap on top of the vial and apply slight pressure in between preparation steps.

CAUTION: Adding standard solutions (e.g., internal standards) to a sealed vial by puncturing the PTFE septum face with a microsyringe exposes the gas phase contents of the vial to the silicone material backing the septum. This material may absorb some of the gas phase VOCs in the vial, causing problems with calibration, measurement in samples, spike recovery, *etc.*, as a function of exposure time. This problem is generally worse for the higher molecular weight VOCs with high octanol-water partition coefficients, and this practice should be avoided or the vial caps should be exchanged for caps with un-punctured septa soon after spiking if these VOCs are analytes of interest.

11.1.1 Water samples - The preparation of water samples inevitably involves some sample manipulation and exposure to the laboratory atmosphere. Extreme caution should be exercised to minimize any volatilization of analytes out of the sample contents and into the laboratory atmosphere. The first precaution is to prepare the water samples immediately after removal from cold storage. The decreased temperature reduces analyte volatility, and the benefits of this are substantially greater than the inaccuracies introduced by measuring sample volume at lower temperatures.

11.1.1.1 Add 5 mL of the matrix modifier solution to a headspace vial (Sec. 6.0), if used. Otherwise, add 5 mL reagent water. Set the septum and crimp top onto the vial and move the crimping tool to a readily available position.

11.1.1.2 Insert the tip of a 5-mL gas tight syringe through the septum of the vial to withdraw the sample. Fill the syringe, taking care to prevent air from leaking into the syringe while filling it, then remove the syringe from the sample and place it in the liquid phase in the headspace vial. Inject the entire aliquot into the headspace vial, then quickly add the internal standard and/or surrogate standard solution, if used, and immediately seal the vial. 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 prepare a second sample in the same manner as the first at this time to protect against possible loss of sample integrity. This second sample is stored at 6°C until the analyst has determined that the first sample has been analyzed properly. If a second analysis is needed, it should be completed within 24 hr.

11.1.2 Soil samples - If the sample will be analyzed by direct vapor partitioning for low level analysis, follow the instructions in this section. If the sample will be extracted with solvent and the extract diluted for high level analysis, proceed to Sec. 11.4.

11.1.2.1 If the soil sample was placed into a headspace vial with neither water nor matrix modifier and the sample mass was not recorded in the field, estimate the sample mass by weighing the vial plus soil and subtract the mass of an empty vial and cap. Then, unseal the vial, add 10.0 mL of matrix modifying solution, if used, or reagent water, along with any internal standard and/or surrogate standard used, and immediately reseal the vial. As noted in Sec. 8.0, VOC losses may occur as a result of opening the vial and displacing 10 mL of headspace.

CAUTION: Only open and prepare one vial at a time to minimize loss of volatile organics.

11.1.2.2 If the soil sample was placed into a headspace vial with reagent water or the matrix modifier solution at the time of sampling, first weigh the sealed vial and its contents to 0.01 g. If the matrix modifying solution was added at the time of sampling (Sec. 8.3.1), the tare weight does not include 10 mL of matrix modifying solution. Therefore, weigh the field blank associated with those samples and subtract from it the tare weight of the vial in which the field blank was prepared. Use the difference as the weight of the matrix modifying solution in the samples. (Although this approach may introduce some error into the sample results, that error should be much less than the changes that will occur in an unpreserved sample shipped to the laboratory without the modifier). If surrogates and/or internal standards were not added at the time of sampling, they should be added at this time.

11.2 The low-concentration method utilizing an equilibrium headspace technique is found in Sec. 11.3 and sample preparation for the high-concentration method is found in Sec. 11.4. The high-concentration method is recommended for samples that obviously contain oily material or organic sludge waste (see Sec. 4.4). See Method 8000 for guidance on the selection of a GC or GC/MS determinative method. For the analysis of gasoline, use Method 8021 with GC/PID (photoionization detector) for BTEX (benzene, toluene, ethylbenzene, and xylenes) in series with Method 8015 with the GC/FID (flame ionization detector) detector for other gasoline components. If GC/MS analysis is preferred, follow Method 8260. For the analysis of MTBE and

the other fuel oxygenates, use either Method 8015 with the GC/FID detector or Method 8260 using GC/MS.

11.3 Low-concentration (direct vapor partitioning) method for water, soil/sediment and solid waste amenable to the equilibrium headspace method.

11.3.1 Calibration

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 because of possible interference problems with internal standards. If interferences are not a problem, based on historical data, internal standard calibration is acceptable. The GC/MS methods normally utilize internal standard calibration. The GC/MS methods require instrument tuning prior to proceeding with calibration.

11.3.1.1 GC/MS tuning

If a GC/MS determinative method is employed, prepare a headspace vial containing reagent water and the amount of 4-bromofluorobenzene (BFB) listed in the determinative method.

11.3.1.2 Initial calibration

Prepare a minimum of five headspace vials for calibration standards, as described in Sec. 7.6, and a reagent blank (Sec. 7.5), and proceed according to Sec. 11.3.2 and the determinative method selected. The mixing step is unnecessary, because no soil is present in the vial. See method 8000D for the minimum number of calibration standards recommended for each type of calibration model.

11.3.1.3 Calibration verification

Prepare a headspace vial, as described in Sec. 7.6, by spiking with the mid-concentration calibration standard. Proceed according to Sec. 11.3.2.1 (beginning by placing the vial into the autosampler) and the determinative method. If a GC/MS determinative method is employed, prepare a second headspace vial containing reagent water and the amount of BFB listed in the determinative method.

11.3.2 Headspace analyzer operating conditions

The conditions described throughout Sec. 11.3 were experimentally optimized using the equipment described in Reference #1 in Sec. 16 and employing Method 8260 as the determinative method. If other headspace systems and determinative methods are utilized, it is recommended that the manufacturer's headspace operating conditions be followed, provided that they are appropriate for the determinative method to be employed.

11.3.2.1 Mix the samples (on a rotator or shaker) for at least 2 min. For samples that contain water insoluble materials, care must be exercised during mixing to prevent this material from adhering to the inner surface of the vial seal; otherwise the sampling needle can become contaminated with this material upon puncturing the seal. Care must also be exercised to avoid over filling the vial to prevent contaminating the needle with aqueous sample.

Place the vials in the autosampler carousel at room temperature. The individual vials are heated to 85 °C and allowed to equilibrate for 50 min. Each sample is mixed by mechanical agitation during this equilibrium period. Each vial is pressurized with helium carrier gas to a minimum pressure of 10 psi.

11.3.2.2 A representative and reproducible sample of the pressurized headspace is transferred to the GC column through a heated transfer line according to the manufacturer's instructions.

11.3.2.3 Proceed with the analysis as per the determinative method of choice.

NOTE: If maintaining a specified pH is critical to quality assured measurement of the analyte(s) of concern (Sec. 4.7), the pH of each sample should be verified. If basic preservation is necessary, the pH of the sample should be verified to be ≥ 10 (see Sec. 7.8.1). If acid preservation is necessary, the pH should be verified to be ≤ 2 , (see Sec. 7.8.2). This check may be performed after analysis of the sample in order to avoid compromising sample integrity. Wide-range pH paper should provide sufficient information to verify efficacy of the preservative.

11.4 High-concentration soil method

11.4.1 If the sample was collected as described in Sec. 8.3.2 without the addition of methanol to the vial, then weigh the sample to the nearest 0.01 g. Add twice the volume of methanol as the nominal sample mass to a tared VOA vial and immediately reseal the vial. Open only one vial at a time to minimize loss of VOCs. If the sample was collected in a sealable coring device as described in Sec. 8.3.3, add the methanol to a vial first, weigh the vial with the methanol and the cap together to obtain the tare mass, and then add the soil plug, seal immediately, reweigh, and calculate the sample mass.

11.4.2 If the procedure in Sec. 8.3.1 was employed for sample collection and either the matrix modifying solution or organic-free reagent water was added to the sample vials, subsamples for high concentration analysis should be taken from the separate VOA vials collected without matrix modifying solution or reagent water as described in Sec. 8.3.2 or from the vials collected for dry solids determination. Transfer approximately 5 g of sample from the 40 or 60 mL VOA vial into a tared VOA vial containing 10.0 mL of methanol, seal the vial, and reweigh to estimate the mass of sample transferred. Open only one vial at a time to minimize the loss of volatile organics. Substantial VOC losses may occur as a result of transferring a subsample from one vial to another using this procedure. See Sec. A.5 in the Appendix of Method 5035A for more details.

11.4.3 Mix by shaking for 10 min at room temperature. Decant 2 mL of the methanol extract to a screw-top vial with PTFE-faced septa and seal. Withdraw 10 μ L and inject into a headspace vial containing 10.0 mL of matrix modifying solution or organic free reagent water. A larger volume of methanol may be added provided the methanol content does not adversely affect the analyte responses (refer to Sec. 7.4.1). Add internal standards and/or surrogates as appropriate, and analyze by the headspace procedure by placing the vial into the autosampler and proceeding with Sec. 11.3.2.1.

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

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method.

13.2 Water samples

This method was used to measure several VOCs in groundwater samples. The samples were collected from two sites: twenty-four samples were collected from the first site (site A) and twenty-three samples were collected from the second site (site B). Using a basic preservative to prevent the hydrolysis of ethers such as MTBE, multiple groundwater vials were collected at each sampling point. The samples were analyzed by three independent laboratories. All of the laboratories used this method for sample preparation, and each laboratory used a different determinative method. One laboratory used a GC/MS technique with a quadrupole mass spectrometer (Method 8260), another used a GC/MS technique with an ion-trap mass spectrometer (Method 8260), and the third used a GC/FID technique (Method 8015). The example results of the analyses are shown in Figures 1 through 6. Since all three laboratories followed the same project plan and the same data quality objectives, the data generated by the three laboratories is mutually comparable, even though they used different techniques. As recommended in Sec. 9.8, matrix spike studies were done at each site. The example percent recoveries from the site A studies are shown in Figure 7, while those from site B are shown in Figure 8. Figure 8 shows that one of the labs had poor recovery for MTBE. However, the recovery of the other ethers was acceptable, indicating that hydrolysis was unlikely to be the source of the problem. The effect was attributed to sample matrix interference.

13.3 Soil samples - Single-laboratory accuracy and precision data were obtained for the method analytes in two soil matrices, i.e., sand and garden soil. These data are found in Tables 26-28 of Method 8260C.

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*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

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 ACS publication listed in Sec. 14.2.

16.0 REFERENCES

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6. RCRA Organic Methods Workgroup Meeting Minutes, March 20, 2012.
7. RCRA Organic Methods Workgroup Meeting Minutes, March 22, 2012.
8. RCRA Organic Methods Workgroup Meeting presentation describing changes to Method 5021, "Proposed Changes to SW-846 Method 5021A, VOCs by Static Headspace", March 1, 2012.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

FIGURE 1

EXAMPLE RESULTS FOR SITE A STUDY OF ETHYL *TERT*-BUTYL ETHER

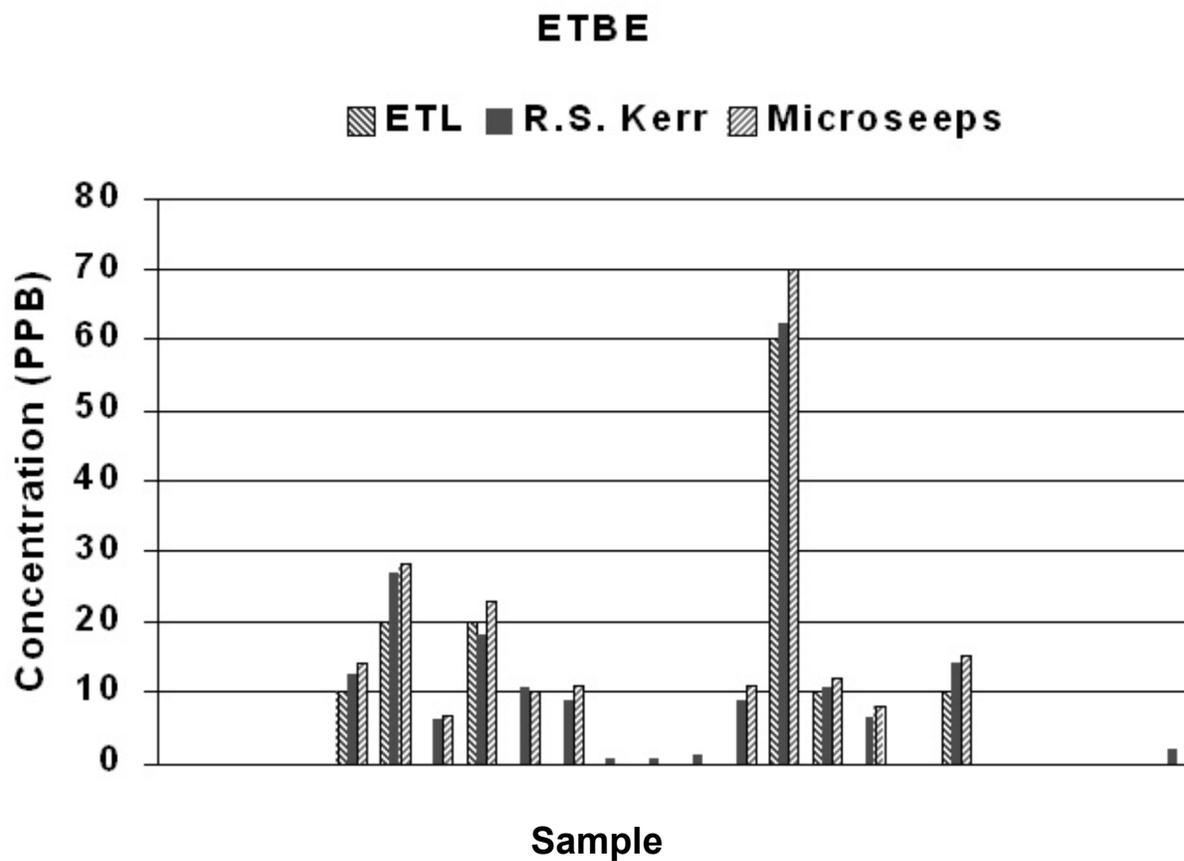


FIGURE 2

EXAMPLE RESULTS FROM SITE A STUDY FOR *TERT* AMYL METHYL ETHER

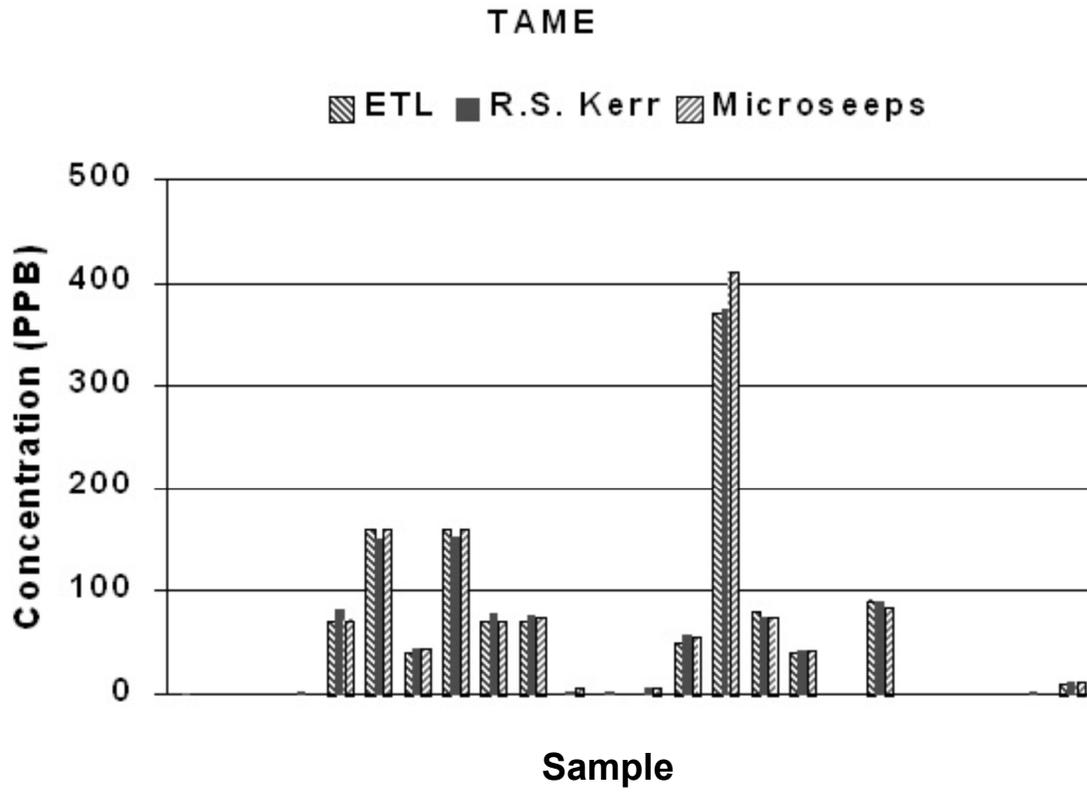


FIGURE 3

EXAMPLE RESULTS FROM SITE A STUDY FOR METHYL *TERT*-BUTYL ETHER

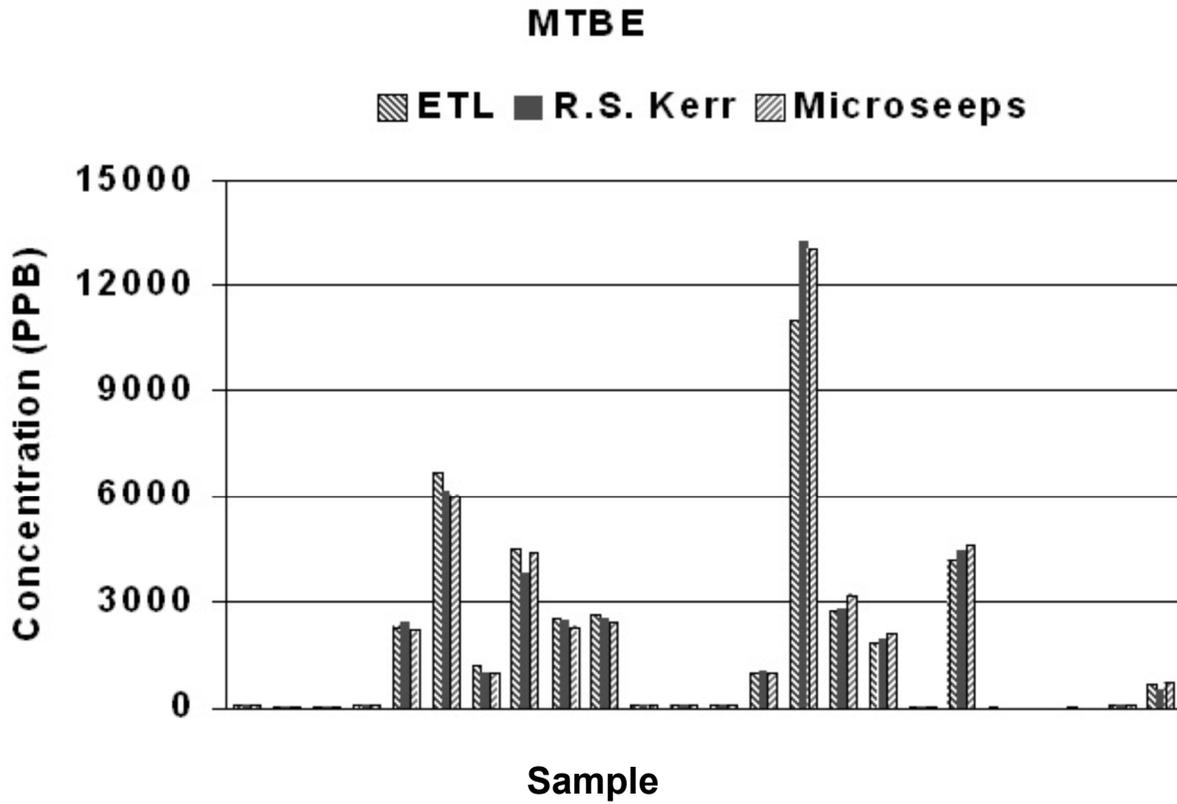


FIGURE 4

EXAMPLE RESULTS FROM SITE B STUDY FOR BENZENE

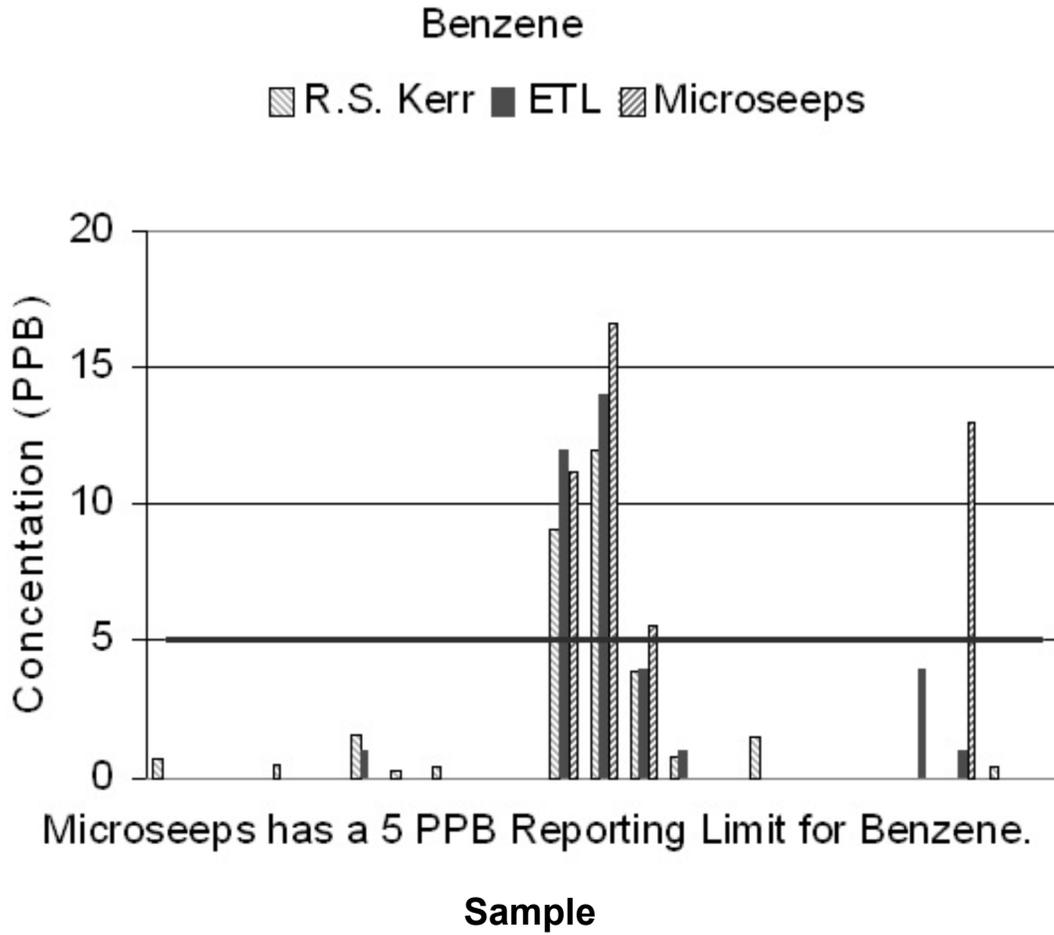


FIGURE 5

EXAMPLE RESULTS FROM SITE B STUDY FOR METHYL *TERT*-BUTYL ETHER

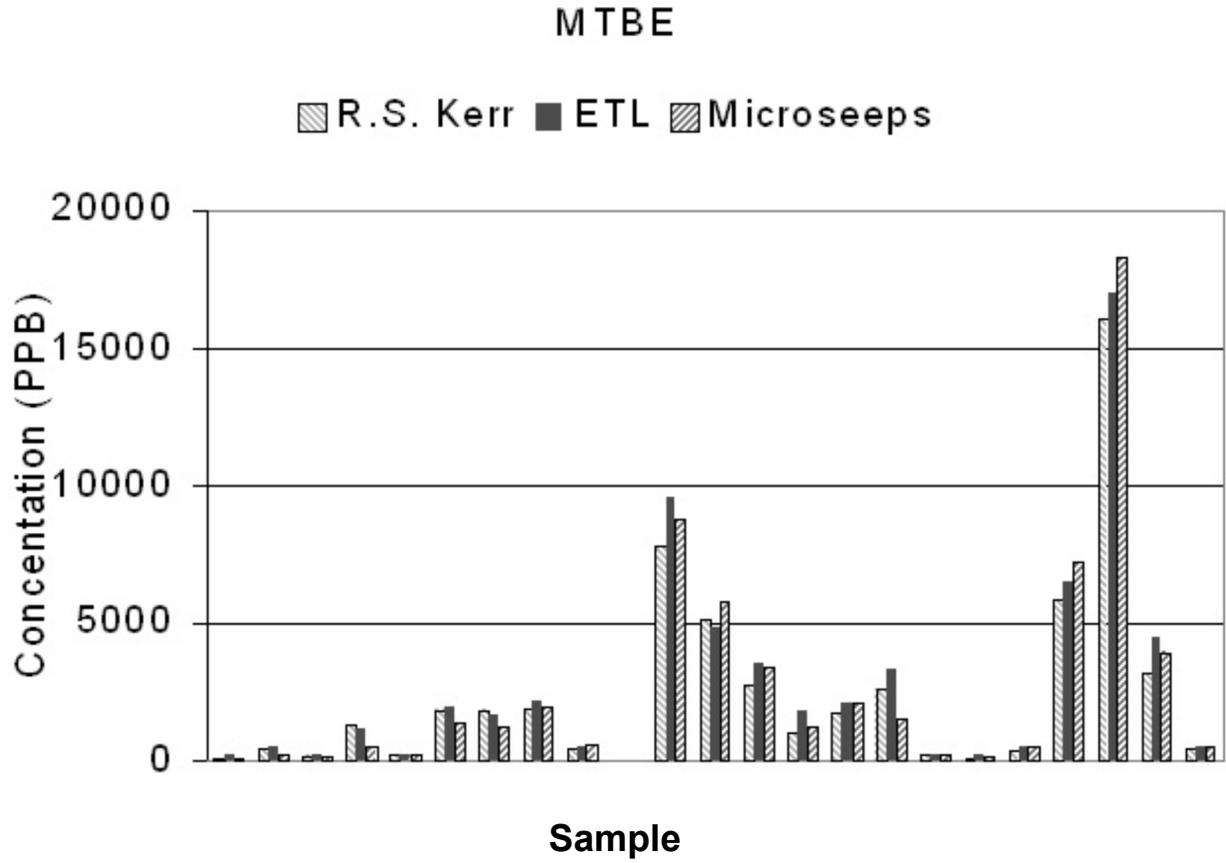


FIGURE 6

EXAMPLE RESULTS FROM SITE B STUDY FOR *TERT*-BUTYL ALCOHOL

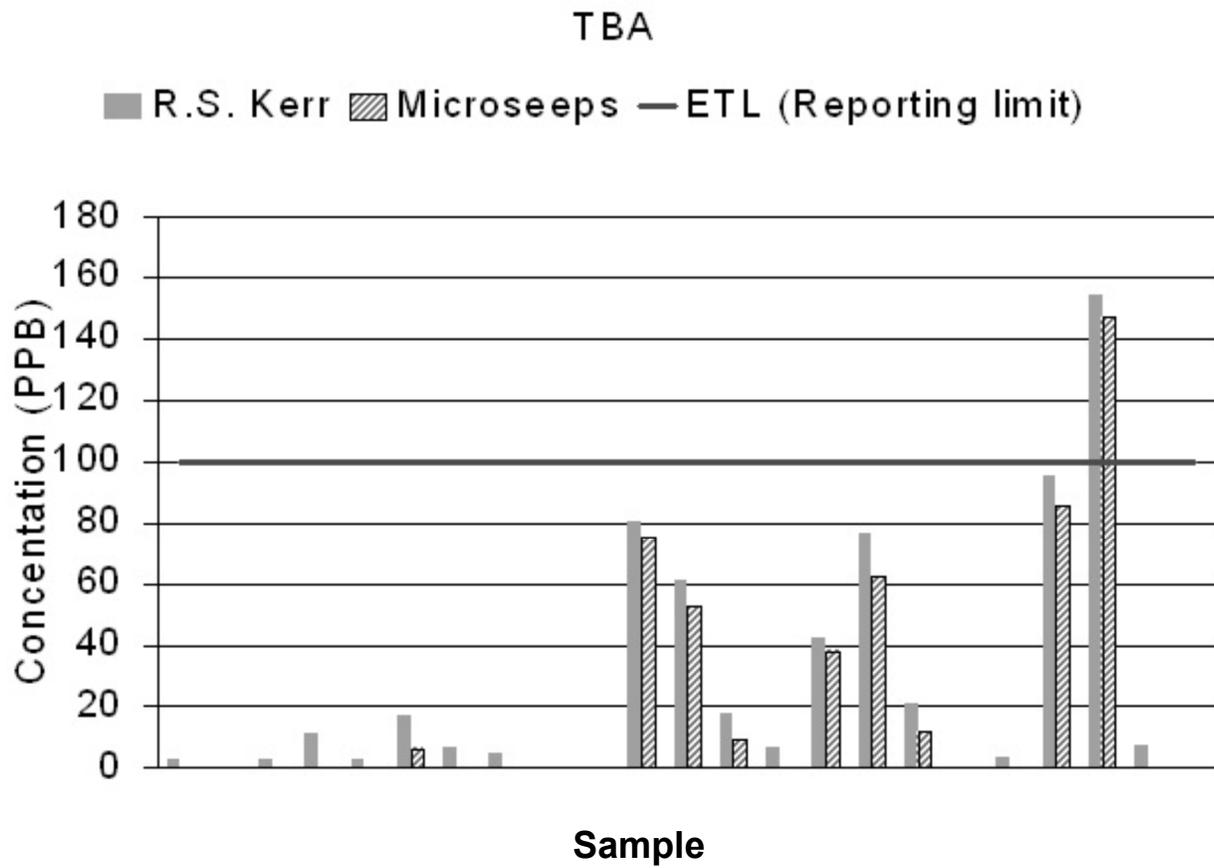


FIGURE 7

EXAMPLE PERCENT RECOVERIES FROM THE MATRIX SPIKE STUDIES OF SITE A

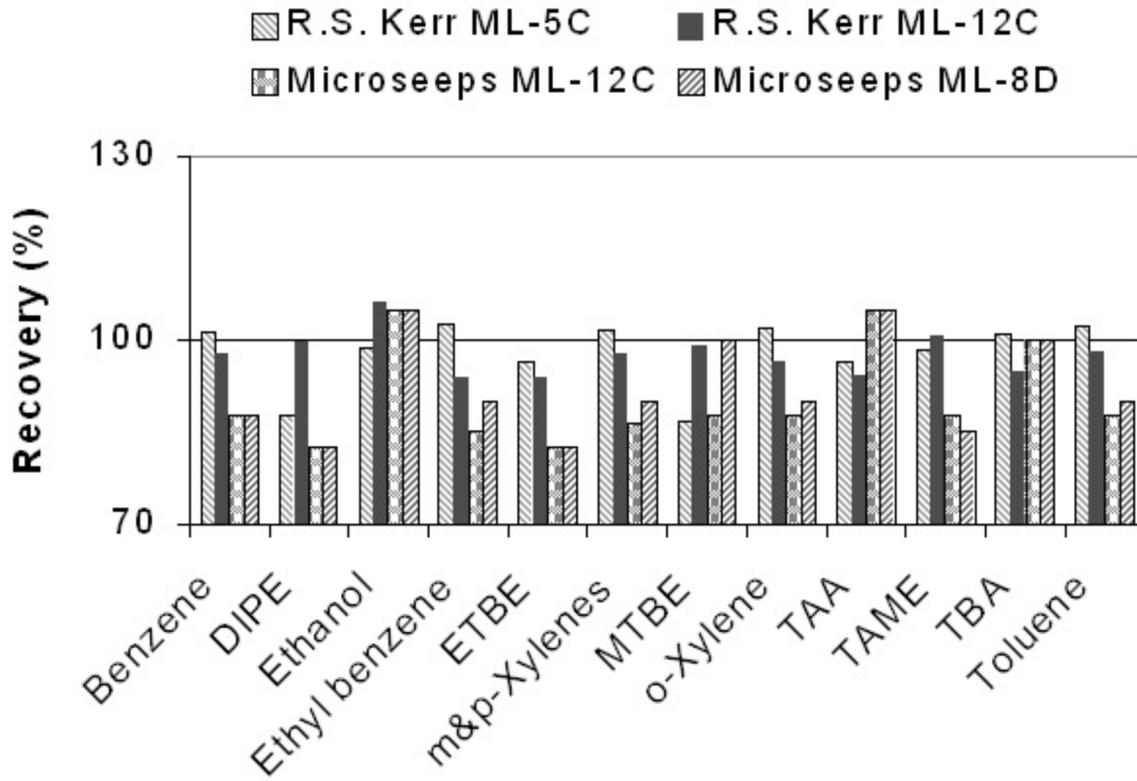
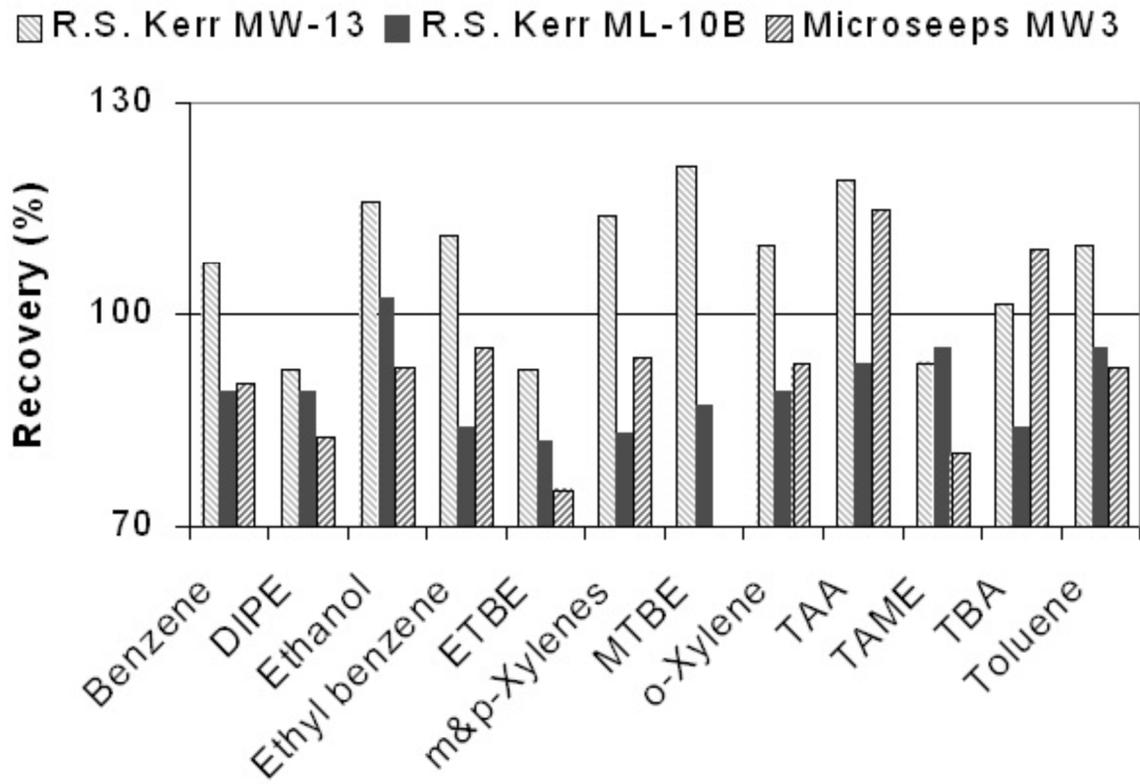


FIGURE 8

EXAMPLE PERCENT RECOVERIES FROM THE MATRIX SPIKE STUDIES OF SITE B



Appendix A:

Summary of Revisions to Method 5021A (as compared to previous Revision 1, June 2003)

1. Improved overall method formatting for consistency with new SW-846 methods style guidance. The format was updated to Microsoft Word .docx.
2. Minor editorial and technical revisions were made throughout to improve method clarity.
3. The revision number was changed to 2 and the date published was changed to July 2014.
4. This appendix was added showing changes from the previous revision.
5. Added updated IDP language and LLOQ verification standard language to Sections 9.2 and 9.3.
6. Included response column and a classification system for analytes in Secs. 1.1 and 1.2 to provide an indication of which VOC responses were improved by the matrix modifier.
7. Added a sealable, air-tight coring device as an alternative sample collection option for soils to Sec. 8.3.3.
8. Added an alternative for calibration standard preparation to Sec. 7.4.1 that allowed for multiple calibration levels prepared by adding different volumes of one or more stock solutions.
9. Clarified in Sec. 1.4 the major sources of measurement bias expected for sample analysis using this method, as well as which sources of measurement bias the matrix modifier may improve, which sources of measurement bias may be made worse by the matrix modifier, and under what other circumstances not adding the matrix modifier may be appropriate.
10. Added a caution after Sec. 11.1 regarding the expected effect of compromising the PTFE face of a vial seal on recovery of oil soluble target analytes.