METHOD 5021A

VOLATILE ORGANIC COMPOUNDS IN VARIOUS SAMPLE MATRICES
USING EQUILIBRIUM HEADSPACE ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 This method is a general purpose method for the 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). The method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from samples using an equilibrium headspace procedure. The following compounds have been evaluated using this sample preparation technique:

Compound	CAS No.[a]	Stability
Acetone	67-64-1	hs
t-Amyl alcohol (TAA)	75-85-4	hs
t-Amyl ethyl ether (TAEE)	919-94-8	nd
t-Amyl methyl ether (TAME)	994-05-8	hs
Benzene	71-43-2	hs
Bromochloromethane	74-97-5	hs
Bromodichloromethane	75-27-4	ms
Bromoform	75-25-2	hs
Bromomethane	74-83-9	hvs
t-Butyl alcohol (TBA)	75-65-0	nd
Carbon tetrachloride	56-23-5	hvs
Chlorobenzene	108-90-7	hvs
Chloroethane	75-00-3	ms
Chloroform	67-66-3	hs
Chloromethane	74-87-3	hvs
Dibromochloromethane	124-48-1	nd
1,2-Dibromo-3-chloropropane	96-12-8	ms
1,2-Dibromoethane	106-93-4	hs
Dibromomethane	74-95-3	hs
1,2-Dichlorobenzene	95-50-1	hs
1,3-Dichlorobenzene	541-73-1	ms
1,4-Dichlorobenzene	106-46-7	ms
Dichlorodifluoromethane	75-71-8	hs
1,1-Dichloroethane	75-34-3	hs
1,2-Dichloroethane	107-06-2	hs
1,1-Dichloroethene	75-35-4	hvs
trans-1,2-Dichloroethene	156-60-5	ms
1,2-Dichloropropane	78-87-5	hs
Diisopropyl ether (DIPE)	108-20-3	hs
Ethanol	64-17-5	nd
Ethylbenzene	100-41-4	hvs

Compound	CAS No.[a]	Stability
Ethyl *tert*-butyl ether (ETBE)	637-92-3	hs
Hexachlorobutadiene	87-68-3	ms
Isopropanol	67-63-0	nd
Methyl *tert*-butyl ether (MTBE)	1634-04-4	hs
Methylene chloride	75-09-2	hs
Naphthalene	91-20-3	ms
Styrene	100-42-5	hvs
1,1,1,2-Tetrachloroethane	630-20-6	hs
1,1,2,2-Tetrachloroethane	79-34-5	nd
Tetrachloroethene	127-18-4	ms
Toluene	108-88-3	hs
1,2,4-Trichlorobenzene	120-82-1	hs
1,1,1-Trichloroethane	71-55-6	ms
1,1,2-Trichloroethane	79-00-5	hs
Trichloroethene	79-01-6	ms
Trichlorofluoromethane	75-69-4	ls
1,2,3-Trichloropropane	96-18-4	ls
Vinyl chloride	75-01-4	hvs
o-Xylene	95-47-6	hvs
m-Xylene	108-38-3	hvs
p-Xylene	106-42-3	hvs
Gasoline Range Organics		

[a] Chemical Abstract Service Registry Number

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 lower limits of detection are compound-, matrix-, and instrument-dependent. As an example, with a soil matrix and using Method 8260 for measurement, quantitation levels varied from approximately 0.1 to 3.4 µg/kg. The applicable concentration range of this method is dependent upon the determinative method used. Analytes that are inefficiently extracted from the soil will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient concentrations.

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

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

[a] Chemical Abstract Service Registry Number

1.4 When exercised with care and appropriate quality control, this technique can be used to produce quantitative data. This preparation method must be combined with a determinative method such as Methods 8015, 8021 or 8260. If quantitative data is to be produced, all of the quality control criteria in the determinative method and/or Method 8000 should be followed. Alternatively, this method may be utilized as an automated sample introduction protocol for screening samples for volatile organics. If used for screening, a suggested configuration is to employ it with Method 8021 but use very minimal calibration and quality control, i.e., a reagent blank and a single calibration standard, to obtain semi-quantitative or estimated sample results.

As with any preparative method for volatiles, samples should be screened to avoid contamination of the headspace system by samples that contain very high concentrations of volatiles above the calibration range of the determinative method. In addition, because the sealed sample container should only be opened once 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 This method may be applicable to other compounds that have sufficient volatility to be removed from the sample matrix using the conditions described in this method. It may also be applicable to both listed and non-listed target analytes in other matrices. For solid samples that contain more than 1% organic matter or for compounds with high octanol/water partitioning coefficients, the equilibrium headspace technique may yield slightly lower results then either dynamic purging or methanol extraction followed by dynamic purging.

1.6 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.

1.7 Use of 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 VOA vial is filled with water. The water sample can be fixed by addition of a chemical preservative to the vial. When the vial is headspace free, it is capped. At the laboratory, that vial is sub-sampled into a headspace vial. A matrix modifier is added to the headspace vial, along with internal standards and surrogates, and the headspace vial is then capped. The matrix modifier acts to partition the volatile organic compounds into the headspace.

2.1.2 Soil samples - at least 2 g of a soil sample are placed into a crimp-seal or screw-top glass headspace vial, along with a matrix modifier and any chemical preservative, at time of sampling. For soils, the matrix modifier also acts as a chemical preservative, so it must be added to the soil during sampling. The headspace vial is then sealed. Surrogates and internal standards can be added to the vial upon sampling, or at the laboratory by injection.

NOTE: If ethers are present, the pH of the matrix modified sample should be checked and adjusted to pH >10, if necessary (See Sec. 7.8.1).

2.2 For soil samples, additional sample volume is collected in a VOA vial for dry weight determination and for high concentration determination if the sample concentration requires it.

2.3 In the laboratory, the vials are rotated to allow for diffusion of the internal standards, surrogates, and matrix modifier throughout the matrix. The vials are placed in the autosampler carousel of the headspace analyzer and maintained at room temperature. Approximately 1 hour prior to analysis, the individual vials are moved to a heated zone and allowed to equilibrate. The sample is then mixed by mechanical vibration while the elevated temperature is maintained.

2.4 The autosampler then pressurizes the vial with helium which forces a portion of the headspace gas mixture through a heated transfer line onto the GC column.

2.5 Determinative analysis is performed using the appropriate GC or GC/MS method.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All 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 in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

4.2 Volatile organic analyses are subject to major interference problems because of the prevalence of volatile organics in a laboratory. See Method 5000, Sec. 3.0, 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 oily material and organic sludge wastes inhibit the partitioning of the volatile target analytes into the headspace, therefore, recoveries will be low. This so- called "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 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 <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

4.6 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.

4.7 Ethers in acidic samples (i.e., samples with a pH less than 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. Alternately, strong bases may catalyze substitution and elimination reactions that can occur if halogenated compounds are present. Accordingly, acidic preservatives may be necessary if the target analytes are halogenated compounds. The chemical reactivity introduced by the preservative should be monitored with the percent recovery of a laboratory spike of a field sample. 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.

6.1 Headspace Containers - Clear glass, 22-mL soil vials, that are equipped with a polytetrafluoroethylene (PTFE)-lined septum and are compatible with the analytical system. Ideally, the vials and septa should have a uniform tare weight. Prior to use, wash the vials and septa with detergent solution, then rinse with tap water followed by distilled water. Dry the vials and septa in an oven at 105°C for 1 hour, then remove and allow to cool. Store in an area free of organic solvents. Vials of other sizes may be employed, provided that they can be hermetically sealed and equipped with a suitable septum.

6.2 Headspace System - This method was developed using a totally automated equilibrium headspace analyzer, the Tekmar Model 7000 Equilibrium Headspace Autosampler and a Tekmar 7050 Carousel (Tekmar-Dohrmann, 4736 Socialville Foster Road, Mason, OH 45040). Similar systems are available from several commercial sources. 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. This must be accomplished without adversely affecting the chromatography or the detector.

6.2.3 The operating conditions listed in Sec. 11.0 are those selected for the equipment used in developing this method. 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.

6.3 Field Sampling Equipment

6.3.1 Water Samples - Clear or amber 40 mL vials with screw-cap PTFE lined vials (for water samples only).

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 10.0 mL of matrix modifier solution, e.g., Automatic Vaccinator Model C1377SN (NASCO, 901 Jamesville Ave., P.O. Box 901, Fort Atkinson, WI 53538), or equivalent.

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

6.3.2.4 VOA vials - 40- or 60-mL VOA vials 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.

6.4 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 An automatic syringe calibrated to deliver internal standards and surrogate analytes and fitted with a #21 (or smaller) needle.

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.

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

7.3 Methanol, CH_3OH - Pesticide quality or equivalent. Store away from other solvents. Purchase in small quantities (½ Liter or 1 Liter size) to minimize 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 and the surrogate standards. The concentrations of the calibration solutions should be such that the addition of 1.0 µL of each to the 22 mL vials will bracket the analytical range of the detector.

7.4.2 Internal and surrogate standards - Follow the recommendations of the determinative methods for the selection of internal and surrogate standards. A concentration of 20 mg/L in methanol for both internal and surrogate standards will be needed for spiking each sample. If determination is by GC, external standard calibration may be preferred and the internal standard is omitted. The concentration may vary depending on the relative sensitivity of the GC/MS system or any other determinative method that is utilized.

7.5 Blank Preparation - Transfer 10.0 mL (Sec. 7.7) of matrix modifying solution to a sample vial. Inject the necessary amounts of the internal standards and surrogate compounds under the surface of the water in the headspace vial, and seal the vial. Place it in the autosampler and analyze in the same manner as an unknown sample. Analyzing the blank in this way will indicate possible problems with the autosampler as well as the headspace device.

7.6 Preparation of Calibration Standards - Prepare calibration standards in the same manner as the blanks (Sec. 7.5), adding the standard spiking solutions prepared in Sec. 7.4.1 in the same manner that the internal standards and surrogates are added.

7.7 Preparation of Matrix Modifying Solution - Add 180 g of ACS grade sodium chloride (NaCl, other salts may be used at equivalent concentrations provided they do not alter the matrix modifier pH) to 500 mL of reagent water. Mix well until all components are dissolved. Analyze a 10.0 mL portion from each batch per Sec. 7.5 to verify that the solution is free of contaminants. Store in a sealed bottle in an area free of organic chemicals, at 4°C.

7.8 Preparation of Chemical Preservative - The procedure in 7.7 produces a neutral matrix modifier. It does not contain a pH adjusting chemical preservative. The preservative should be chosen based on the analytes of interest, and it should be mixed with the sample at the time of sampling.

CAUTION: The matrix modifying solution may not be appropriate for soil samples having high carbon content.

7.8.1 If a basic preservative is chosen, the addition of 100 mg of ACS grade tri-sodium phosphate dodecahydrate ($Na_3PO_4 \bullet 12H_2O$) to either a 22 mL headspace vial or a 40 mL water sample vial will 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 gram 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 (Sec. 7.8.2), 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 HANDLING

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. All samples should be stored in capped vials at 4 °C or less in an area free of solvent fumes. Water samples are collected and stored with minimum headspace and the diameter 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. If any evidence of leakage is found, the sample can be considered corrupted and should be discarded.

8.2 Water Samples - Collection of a water sample is fairly straightforward. Fill the 40 mL vial and, according to the site quality assurance program, chemically preserve the sample if necessary, ensure that there is no headspace in the vial, and seal. At least two vials should be collected per sample, and more may be necessary for duplicate analyses and MS/MSD analyses. The transfer of the sample into a headspace vial and the addition of matrix modifier and standards shall be performed in the laboratory.

8.3 Soil Samples - Three alternative procedures are presented for the collection of low concentration samples in special headspace sample vials. Two procedures include the addition of a matrix modifying solution in the field while the third procedure does not. The standards should be added in the laboratory by injection through the septum of the sealed headspace vial. 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 of interest, and the intended use of the analytical results. Whichever alternative is used, collect 3 or 4 vials of sample from each sampling point to allow for sample reanalyses if necessary. In addition, separate portions of sample are taken for dry weight determination and for high concentration analysis (if necessary).

8.3.1 The addition of the matrix modifying solution at the time of sampling is the preferred option unless high concentrations of volatile organics are expected. The addition of the matrix modifying solution eliminates the need to open the sample vial in the laboratory, minimizing the loss of volatilized analytes. The matrix modifier also facilitates the mixing of any chemical preservative with the sample, reduces the potential for biodegradation of the analytes, and reduces the possibility for the analytes to be affected by abiotic reactions. The downside is increased opportunity for contamination of the matrix modifier in a field sampling situation. Also, skilled personnel are desirable to precisely and accurately add the matrix modifying solution. These problems are minimized when these solutions are not added in the field (Sec. 8.3.2), however, there is an increased likelihood of significant losses of volatile analytes when the vial is reopened in the laboratory.

8.3.2 Sample collection without the addition of modifying solution and standards - If high concentrations of volatile organics are expected (greater than 200 µg/kg), collection of the sample in the 22-mL vial without the addition of the matrix modifying solution allows direct addition of methanol to the vial, as described in the high concentration procedure 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 tared 22-mL headspace vial and seal immediately with the PTFE side of the septum facing toward the sample. The samples should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

8.3.3 The third alternative is to add the soil sample to a vial containing 10.0 mL of the matrix modifier (if the matrix modifier is not available, organic-free reagent water may be used, but the analyzing laboratory must be made aware that this was done). This may be added to the vial either in the field or in the laboratory prior to shipping the vials to the field. In either case, the laboratory should tare the vial and cap, and record the mass, prior to sending the vials to the field.

8.3.3.1 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).

8.3.3.2 Using the soil sampler (Sec. 6.3.2.1), add 2-3 cm (approximately 2 g) of the soil sample to a tared 22-mL headspace vial containing 10.0 mL of matrix modifier or reagent water. 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.

CAUTION: Preliminary indications are that soil samples containing over 1% organic carbon may yield low recoveries when the matrix modifying solution is used. The matrix modifying solution may not be appropriate for these samples.

8.4 Field blanks should be prepared, regardless of which alternative is employed for the soil sample collection. If the matrix modifying solution is not added in the field, then the field blank should be prepared by adding 10.0 mL of organic-free reagent water to a clean vial and immediately sealing the vial. If the matrix modifying solution is to be added in the field, then prepare a field blank by adding 10.0 mL of matrix modifying solution plus internal standards to a clean vial.

8.5 Fill a 40- or 60-mL VOA vial with soil from each sampling point to use for dry weight determination, sample screening, and for high concentration analysis (if necessary). Sample screening is optional since there is no danger of contaminating the headspace device because of carryover from a high concentration sample.

8.6 Sample Storage

8.6.1 Store samples at 4°C until analysis. The vials should be stored at 4°C to eliminate 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. The sample storage area should be free of organic solvent vapors.

8.6.2 All samples should be analyzed within 14 days of collection or sooner if labile compounds are target analytes. 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. Samples not analyzed within this period should be identified to the data user and the results are 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. 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 demonstration 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.

9.8 The heating of 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 must contain all desired target analytes. The acceptance criteria shall be those recommended in the determinative method or specified by a properly executed systematic planning document. If these criteria can not be met, the analyst can try adjusting the pH of the mixture through the addition of the solid ACS grade $NaHSO_4$ to excessively basic mixtures or solid $Na_3PO_4 \bullet 12H_2O$ 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.

11.1.1 Water Samples – The preparation of the water sample inevitably involves some sample manipulation and exposure of the sample 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 the analytes' volatility, and the benefits of this are substantially greater than the inaccuracies introduced by measuring sample volume at lower temperatures.

11.1.1.2 Pipette 5mL of the matrix modifier solution into a headspace vial (Sec. 6.2). Set the septum and crimp top onto the vial, tare and record the weight. Set the septum, crimp top and crimping tool in a readily available position.

11.1.1.3 insert the tip of a 5-mL gas tight syringe through the septum of the vial to withdraw the sample. Fill the syringe, remove the syringe from the sample and place it underneath the top level of the matrix modifier in the headspace vial. Inject the entire aliquot into the headspace vial 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 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.

11.1.2 Soil samples – If the sample was sealed into a headspace vial, the vial simply must be injected with applicable internal standards and surrogates, so proceed to Sec. 11.1.3. Otherwise, two options exist.

11.1.2.1 If the sample is expected to contain high concentrations of analytes, proceed to Sec.11.4.

11.1.2.2 If the soil sample is not expected to contain high concentrations of analytes, but was placed into a headspace vial with neither water nor matrix modifier, unseal the vial, rapidly add 10.0 mL of matrix modifying solution, and immediately reseal the vial. As noted in the introductory text in Sec. 8.0, volatilization losses will occur as a result of opening the vial and displacing 10 mL of headspace.

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

11.1.3 Using the syringe (Sec. 6.4.2), inject each headspace vial with internal standards and surrogates. 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 the 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). Mix the samples (on a rotator or shaker) for at least 5 min.

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 for BTEX in series with Method 8015 with the GC/FID 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 method for water, soil/sediment and solid waste amenable to the equilibrium headspace method. (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

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 22-mL vial containing reagent water and the amount of BFB listed in the determinative method.

11.3.1.2 Initial calibration

Prepare five 22-mL vials, 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 eliminated since no soil is present in the vial.

11.3.1.3 Calibration verification

Prepare a 22-mL 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 22-mL vial containing reagent water and the amount of BFB listed in the determinative method.

11.3.2 Headspace operating conditions

The conditions described throughout Sec. 11.3 were experimentally optimized using the equipment described in Sec. 6.2 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. Place the vials in the autosampler carrousel at room temperature. The individual vials are heated to 85°C and allowed to equilibrate for 50 min. Each sample is mixed by mechanical vibration for at least 10 min. 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.

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 matrix modifying solution or organic-free reagent water to the vial, then weigh the sample to the nearest 0.01 g, add 10.0 mL of methanol to the sample in the tared 22-mL vial, and immediately reseal the vial. Open only one vial at a time to minimize the loss of volatile organics.

11.4.2 If the procedures in either Sec. 8.3.1 or 8.3.3 were employed for sample collection and either the matrix modifying solution or organic-free reagent water were added to the vial, then the sample for high concentration analysis should be taken from the separate 40- or 60-mL VOA vial collected without matrix modifying solution or reagent water as described in Sec. 8.3.2. Transfer approximately 2 g of sample from the 40- or 60-mL VOA vial into a tared 22-mL sample vial. Immediately add 10.0 mL of methanol to the 22-mL vial and seal both the 22-mL and the VOA vials. Open only one vial at a time to minimize the loss of volatile organics.

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 µL, or appropriate volume of extract noted in Table 1, and inject into a 22 mL vial containing 10.0 mL of matrix modifying solution and internal standards (if necessary) and surrogates. 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 volatile organic compounds 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 not 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: sand and a surface garden soil. These data are found in tables in Method 8260.

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. P. Flores, and T. Bellar, "Determination of Volatile Organic Compounds in Soils using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry," U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

2. B.V. Ioffe, and A.G. Vitenberg, "Headspace Analysis and Related Methods in Gas Chromatography," John Wiley and Sons, 1984.

3. R.J. Pirkle, and R.P. McLoughlin, "The Analysis of Selected Components of Reformulated Gasoline in Environmental Samples" *from* MTBE Handbook, *ed*. Kostecki, P. and Moyer, E. Amherst Scientific Publishers, 2002.

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

TABLE 1

QUANTITY OF METHANOL EXTRACT NEEDED 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 RESULTS FOR SITE A STUDY OF ETHYL *TERT*-BUTYL ETHER

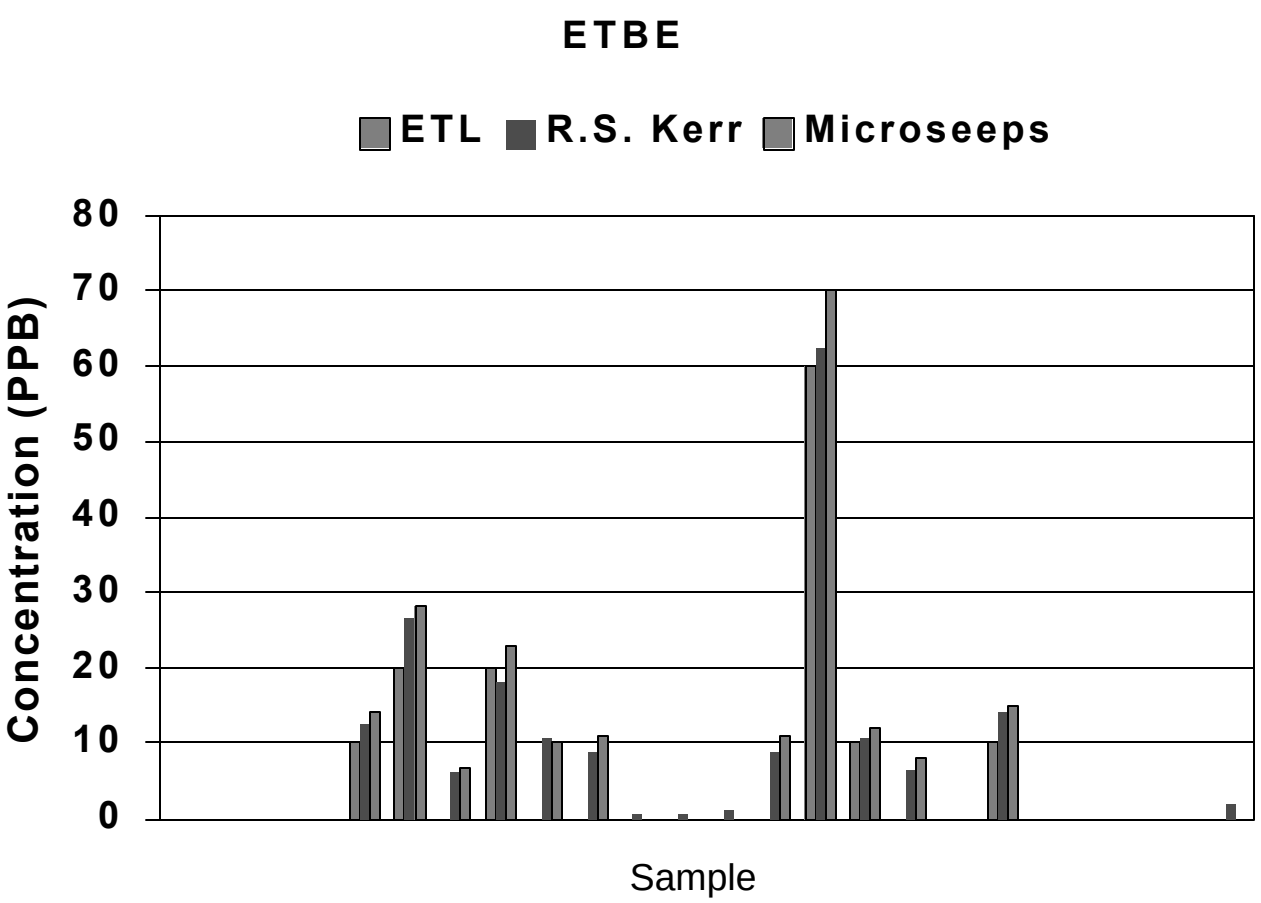

FIGURE 2

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

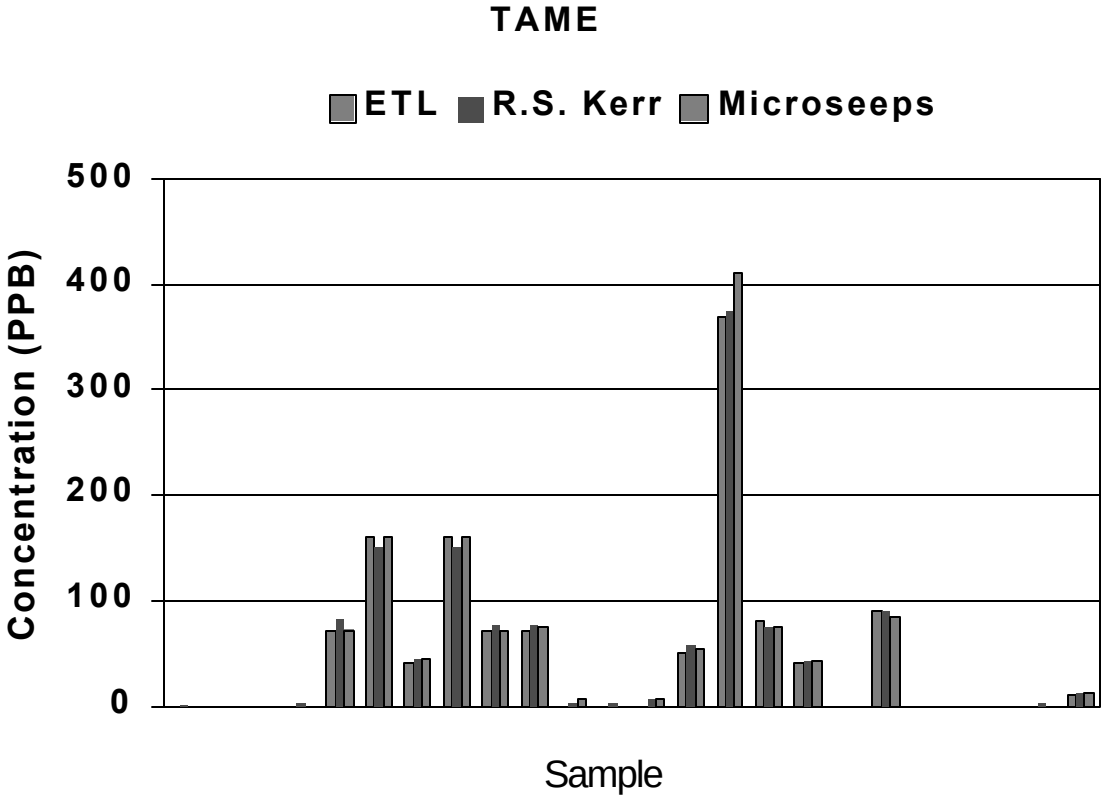

FIGURE 3

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

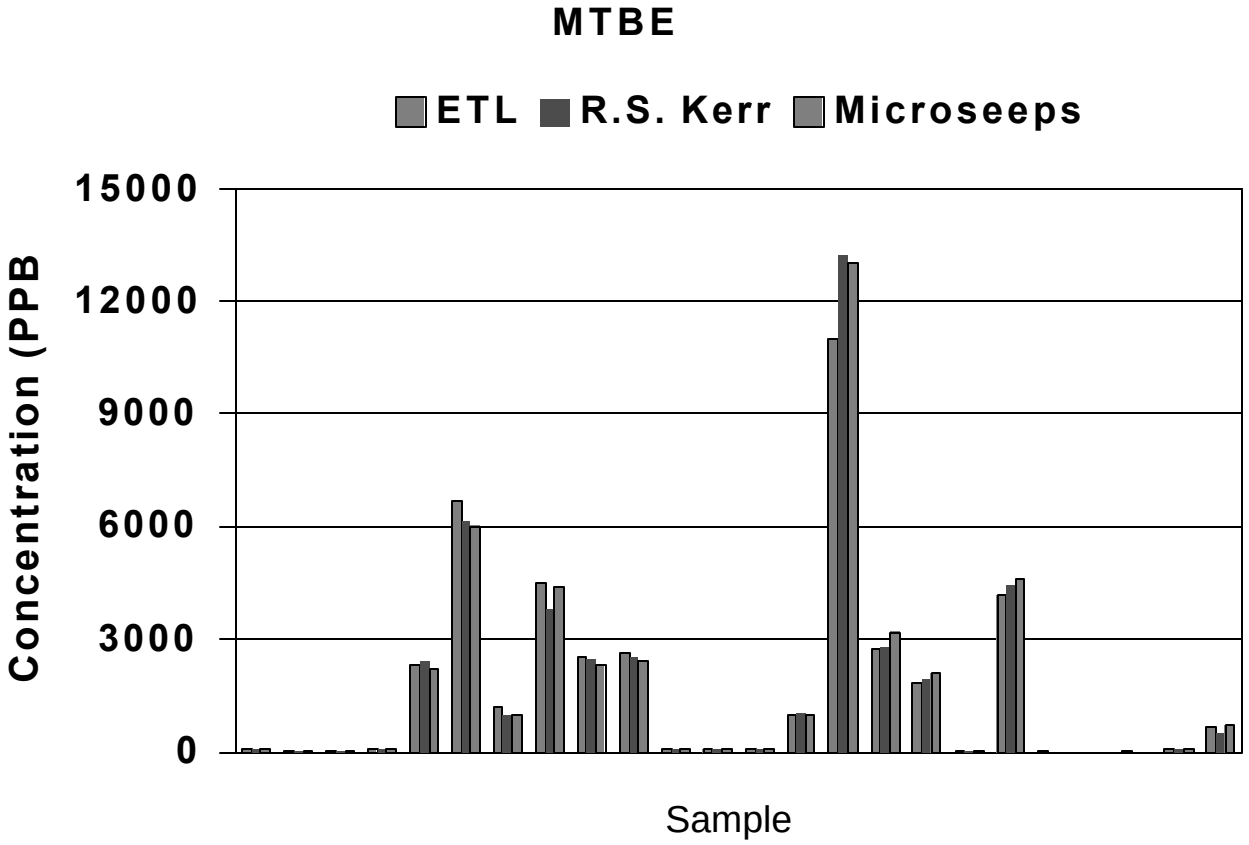

FIGURE 4

EXAMPLE RESULTS FROM SITE B STUDY FOR BENZENE

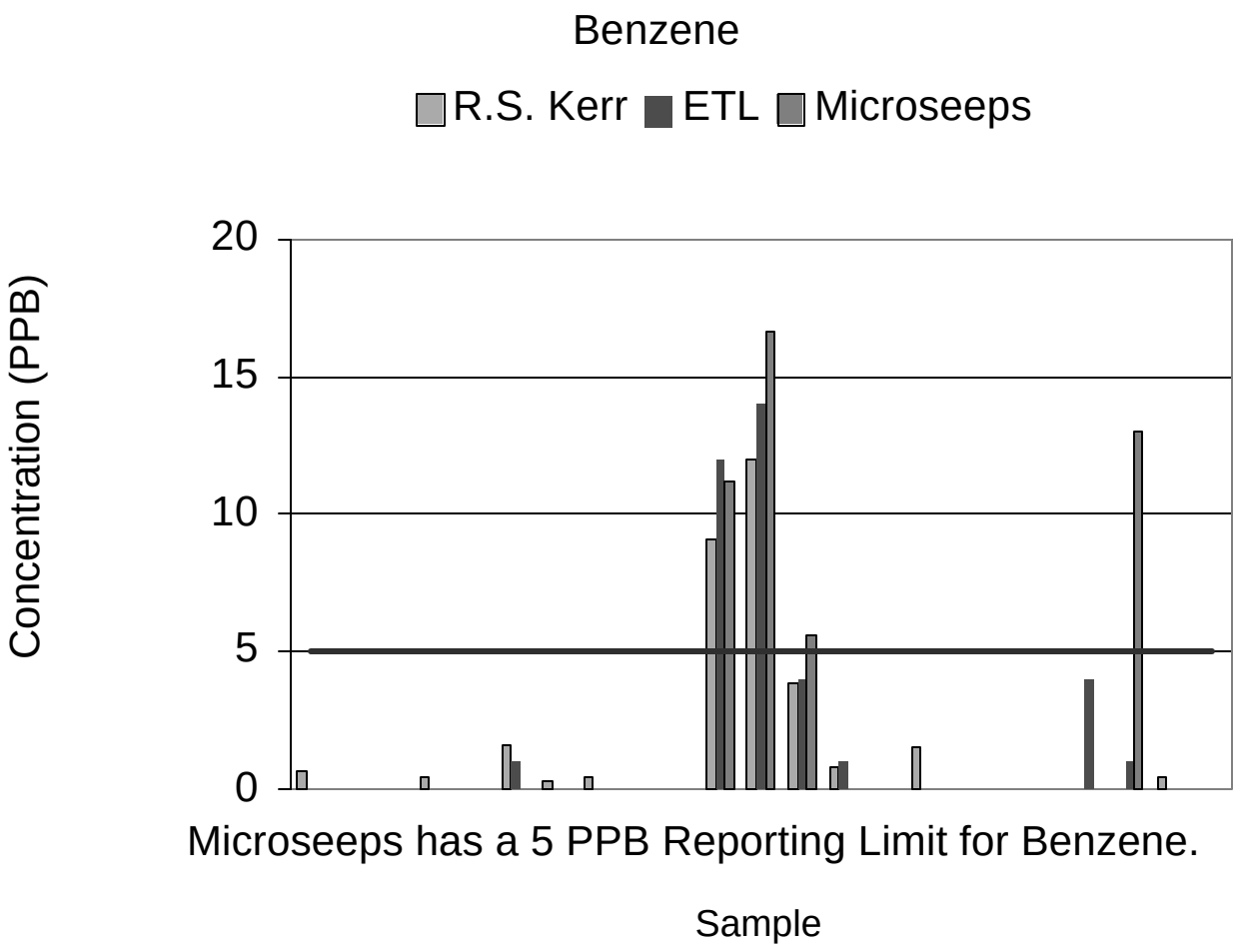

FIGURE 5

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

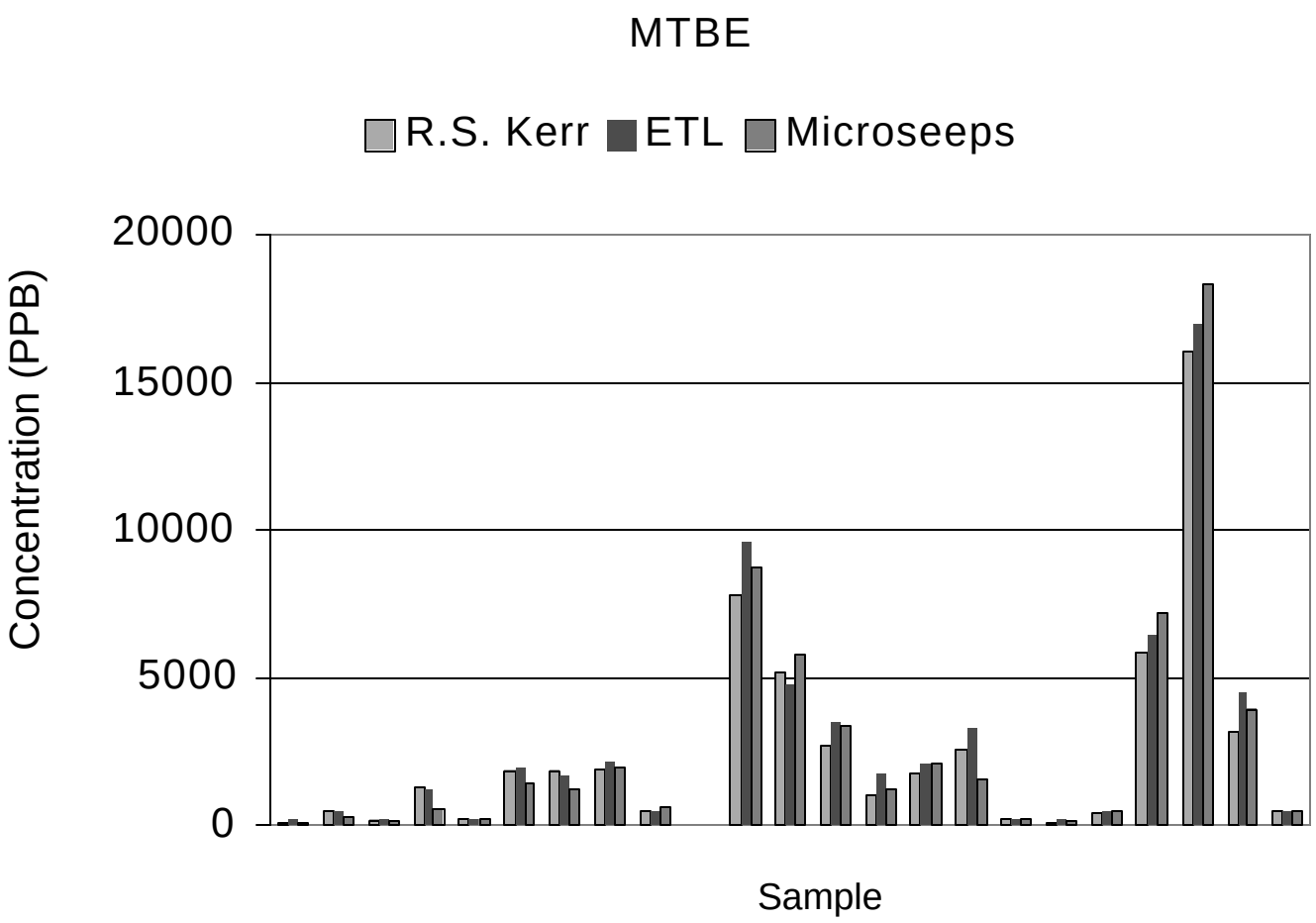

FIGURE 6

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

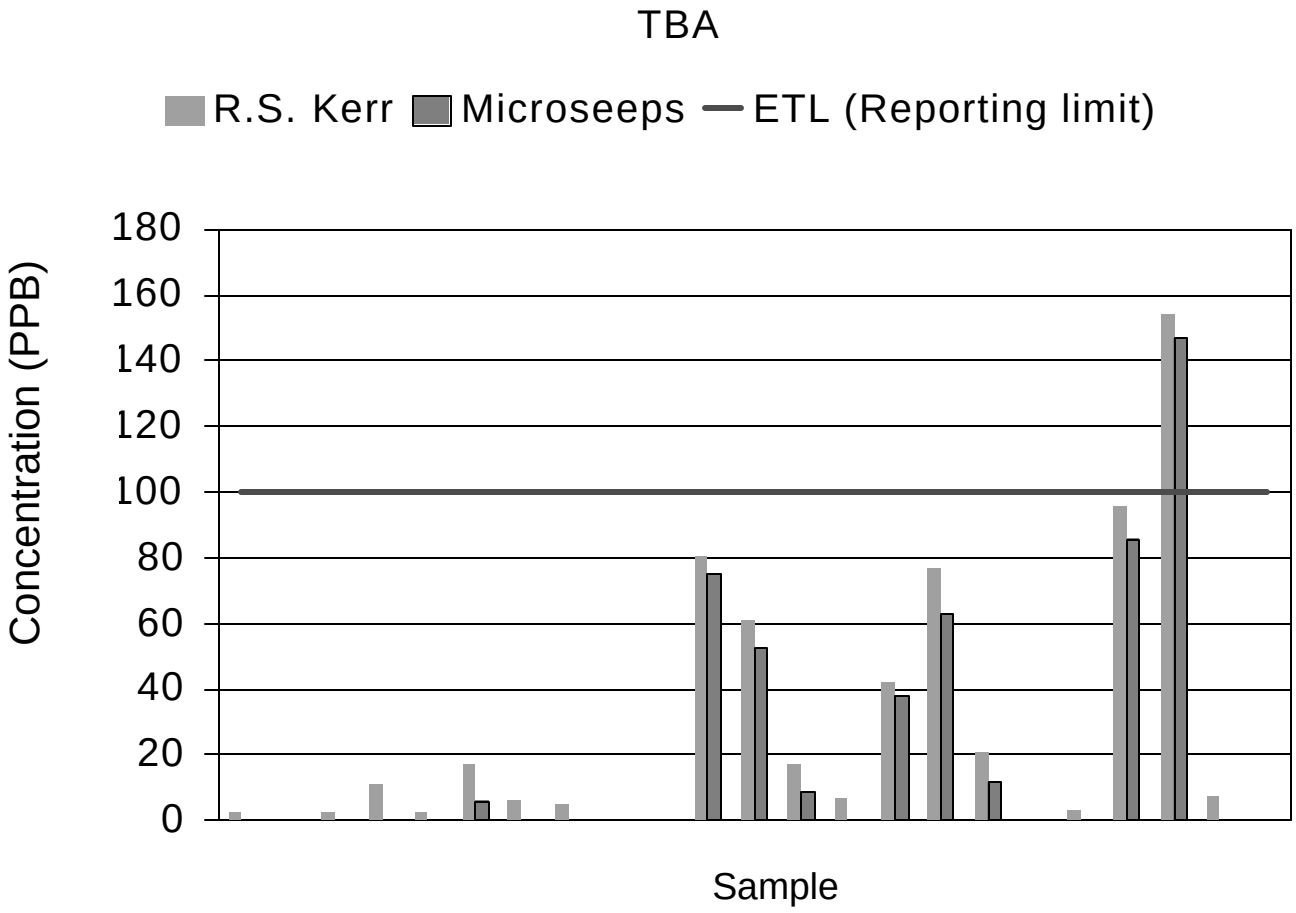

FIGURE 7

EXAMPLE PERCENT RECOVERIES FROM THE MATRIX SPIKE STUDIES OF SITE A

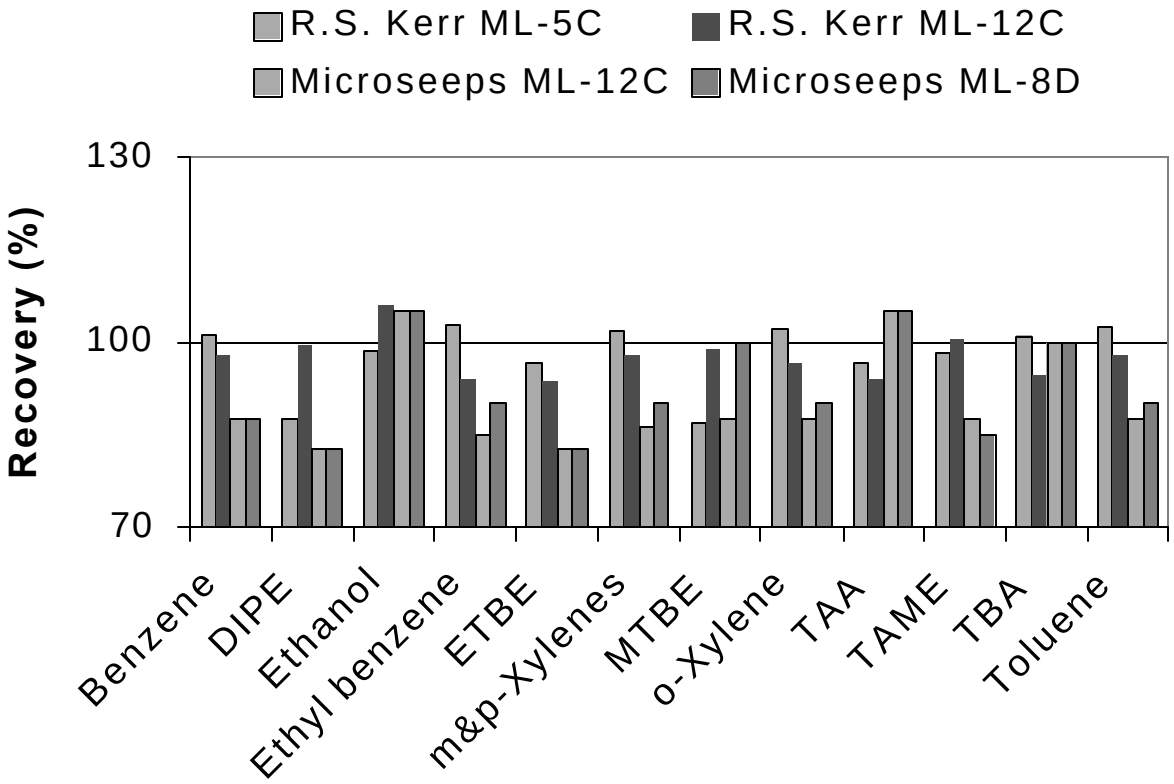

FIGURE 8

EXAMPLE PERCENT RECOVERIES FROM THE MATRIX SPIKE STUDIES OF SITE B