

METHOD 8015D

NONHALOGENATED ORGANICS USING GC/FID

1.0 SCOPE AND APPLICATION

1.1 This method may be used to determine the concentrations of various nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography. The following compounds have been determined quantitatively by this method, using the preparative techniques indicated.

Compound	CAS No. ^a	Appropriate Technique				
		Purge-and-Trap ^b	Head-space ^e	Direct Aqueous Injection	Azeo. Dist. ^c	Vacuum Dist. ^d
Acetone	67-64-1	pp / ht	x	x	x	x
Acetonitrile	75-05-8	pp	ne	x	x	ne
Acrolein	107-02-8	pp	ne	x	x	x
Acrylonitrile	107-13-1	pp	ne	x	x	x
Allyl alcohol	107-18-6	ht	ne	x	x	ne
t-Amyl alcohol (TAA)	75-85-4	ht	x	ne	ne	x
t-Amyl ethyl ether (TAEE)	919-94-8	x/ ht	x	ne	ne	x
t-Amyl methyl ether (TAME)	994-05-8	x/ ht	x	ne	ne	x
Benzene	71-43-2	x	x	ne	ne	x
t-Butyl alcohol (TBA)	75-65-0	ht	x	x	x	x
Crotonaldehyde	123-73-9	pp	ne	x	x	ne
Diethyl ether	60-29-7	x	ne	x	ne	ne
Diisopropyl ether (DIPE)	108-20-3	x/ ht	x	ne	ne	x
Ethanol	64-17-5	l	x	x	x	x
Ethyl acetate	141-78-6	l	x	x	x	ne
Ethyl Benzene	100-41-4	x	x	ne	ne	x
Ethylene oxide	75-21-8	l	ne	x	x	ne
Ethyl <i>tert</i> -butyl ether (ETBE)	637-92-3	x/ ht	x	ne	ne	x
Isopropyl alcohol (2-Propanol)	67-63-0	pp	x	x	x	ne
Methanol	67-56-1	l	x	x	x	ne
Methyl ethyl ketone (MEK, 2-Butanone)	78-93-3	pp	x	x	x	x
Methyl <i>tert</i> -butyl ether (MTBE)	1634-04-4	x/ ht	x	x	ne	x
<i>N</i> -Nitroso-di- <i>n</i> -butylamine	924-16-3	pp	ne	x	x	ne
Paraldehyde	123-63-7	pp	ne	x	x	ne
2-Pentanone	107-87-9	pp	x	x	x	ne
2-Picoline	109-06-8	pp	ne	x	x	ne
1-Propanol (<i>n</i> -Propyl alcohol)	71-23-8	pp	x	x	x	ne
Propionitrile	107-12-0	ht	ne	x	x	ne
Pyridine	110-86-1	l	ne	x	x	ne
Toluene	108-88-3	x	x	ne	ne	x

Compound	CAS No. ^a	Appropriate Technique				
		Purge-and-Trap ^b	Head-space ^e	Direct Aqueous Injection	Azeo. Dist. ^c	Vacuum Dist. ^d
<i>o</i> -Toluidine	95-53-4	l	ne	x	x	ne
<i>o</i> -Xylene	95-47-6	x	x	ne	ne	x
<i>m</i> -Xylene	108-38-3	x	x	ne	ne	x
<i>p</i> -Xylene	106-42-3	x	x	ne	ne	x

a Chemical Abstracts Service Registry Number

b Purge-and-Trap (Methods 5030 or 5035)

c Azeotropic distillation (Method 5031)

d Vacuum distillation (Method 5032)

e Headspace (Method 5021)

x Adequate response using this technique

ht Method analyte only when purged at 80 °C (high temperature purge)

l Inappropriate technique for this analyte

ne Not evaluated

pp Poor purging efficiency, resulting in higher quantitation limits. Use of an alternative sample preparative method is strongly recommended. May be amenable to purging at elevated temperature.

1.2 This method is applicable to the analysis of other analytes, including triethylamine and petroleum hydrocarbons. The petroleum hydrocarbons include gasoline range organics (GRO) and diesel range organics (DRO). The sample preparation techniques are shown in the table below.

Compound	CAS No. ^a	Appropriate Technique			
		Purge-and-Trap	Head-space	Direct Aqueous Injection	Solvent Extraction
Triethylamine	121-44-8	l	ne	x	l
Gasoline range organics (GRO)	--	x	x	x	l
Diesel range organics (DRO)	--	l	x	l	x

a Chemical Abstracts Service Registry Number

x Adequate response using this technique

l Inappropriate technique for this analyte

ne Not evaluated

1.2.1 This method has been applied to the analysis of triethylamine in water samples by direct aqueous injection onto a different GC column than is used for any other analytes. Descriptions of the GC column, temperature program, and performance data for triethylamine are provided in this method (see Secs. 6.2.5 and 11.2.6, and Table 8).

1.2.2 GRO corresponds to the range of alkanes from C₆ to C₁₀ and covering a boiling point range of approximately 60 °C - 170 °C (Reference 6). DRO corresponds to the range of alkanes from C₁₀ to C₂₈ and covering a boiling point range of approximately 170 °C -

430°C (Reference 6). The quantitative analyses of these fuel types are based on the procedures described in Sec. 11.11. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present. Methods from other sources may be more appropriate for GRO and DRO, since these hydrocarbons are not regulated under RCRA. Consult State and local regulatory authorities for specific requirements.

1.2.3 This method may be applicable to classes of analytes and to fuel types and petroleum hydrocarbons other than those listed in Secs. 1.1 and 1.2. However, in order to be used for additional analytes, fuel types, or petroleum hydrocarbons, the analyst must demonstrate that the gas chromatographic conditions, including the GC column, are appropriate for the analytes of interest. The analyst must also perform the initial demonstration of proficiency described in Sec. 9.6 and Method 8000. Expansion of this method to other fuel types or petroleum hydrocarbons will also require that the boiling point range or carbon number range of the material be carefully defined and the quantitation approach be modified to match such ranges. Analysts are advised to consult authoritative sources, such as the American Petroleum Institute (API), for appropriate definitions of other fuel types or petroleum fractions.

NOTE: Mention of the analyses of other fuel types and petroleum fractions does *not* imply a regulatory requirement for such analyses, using this or any other method.

1.3 The method can also be used as a screening tool (for both volatile and semivolatile organics) to obtain semiquantitative data to prevent overloading the GC/MS system during quantitative analysis. This may be accomplished using a purge-and-trap method (e.g., Method 5030), an automated headspace method (e.g., Method 5021), direct aqueous injection, or by direct injection, if a solvent extraction method has been utilized for sample preparation. Single-point calibration is acceptable in this situation. Performance data are not provided for screening.

1.4 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 required 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.

1.5 This method is restricted for use by, or under the supervision of, analysts experienced in the use of a gas chromatograph and skilled in the interpretation of gas chromatograms. In addition, if this method is used for the analysis of petroleum hydrocarbons, it is limited to analysts experienced in the interpretation of hydrocarbon data. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of certain nonhalogenated volatile and semivolatile organic compounds.

2.2 Depending on the analytes of interest, samples may be introduced into the GC by a variety of techniques, including:

- Purge-and-trap (Methods 5030 or 5035)
- Equilibrium headspace (Method 5021)
- Direct injection of aqueous samples
- Injection of the concentrate from azeotropic distillation (Method 5031)
- Vacuum distillation (Method 5032)
- Following solvent extraction (Methods 3510, 3520, 3535, 3540, 3541, 3545, 3546, 3550, 3560, or other appropriate technique)

2.3 Groundwater or surface water samples generally must be analyzed in conjunction with Methods 5021, 5030, 5031, 5032, 3510, 3520, or other appropriate preparatory methods to obtain the necessary quantitation limits. Method 3535 (solid-phase extraction) may also be applicable to some of the target analytes, but has not been validated by EPA in conjunction with this determinative method.

2.4 Samples to be analyzed for diesel range organics may be prepared by an appropriate solvent extraction method.

2.5 Gasoline range organics may be introduced into the GC/FID by purge-and-trap (Methods 5030 and 5035), automated headspace (Method 5021), vacuum distillation (Method 5032), or other appropriate technique.

2.6 Triethylamine may be analyzed by direct injection of aqueous samples. This compound has not been found to be amenable to purge-and-trap techniques.

2.7 An appropriate column and temperature program are used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.8 The method allows the use of packed or capillary columns for the analysis and confirmation of the non-halogenated individual analytes. The GC columns and conditions listed have been demonstrated to provide separation of those target analytes. Other columns and conditions may be employed, provided that the analyst demonstrates adequate performance for the intended application.

2.9 The quantitative analyses of GRO and DRO are based on the definitions provided in Sec. 1.2.2 and the procedures described in Sec. 11.11.

2.10 Given the large number of components to be separated, fused-silica capillary columns are necessary for the analysis of petroleum hydrocarbons, including GRO and DRO, and are recommended for all other analytes. A capillary column is also necessary for the analysis of triethylamine.

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 When analyzing for volatile organics, samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling will serve as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be rinsed out between samples with an appropriate solvent. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination.

4.3.1 Clean purging vessels with a detergent solution, rinse with distilled water, and then dry in a 105°C oven between analyses. Clean syringes or autosamplers by flushing all surfaces that contact samples using appropriate solvents.

4.3.2 All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130°C for several hours or rinse it with methanol and drain. Store dry glassware in a clean environment.

4.4 The flame ionization detector (FID) is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis. There is also the potential for analytes to be resolved poorly, especially in samples that contain many analytes. The data user should consider this and may wish to alter the target analyte list accordingly.

5.0 SAFETY

There are no significant safety issues specific to this method. However, SW-846 methods do not purport to address all safety issues associated with their 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 specified 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 Gas chromatograph - Analytical system complete with gas chromatograph suitable for solvent injections, direct aqueous injection, headspace, vacuum distillation sample introduction, or purge-and-trap sample introduction, and equipped with all necessary accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

6.2 Recommended GC columns

The choice of GC column will depend on the analytes of interest, the expected concentrations, and the intended use of the results. The packed columns listed below are generally used for screening analyses. The capillary columns are necessary for petroleum hydrocarbon analyses and for triethylamine analyses and are recommended for all other analyses. Other columns and columns of other diameters may be employed if the analyst can demonstrate acceptable performance for the intended application.

6.2.1 Column 1 - 8-ft x 0.1-in. ID stainless steel or glass column, packed with 1% SP-1000 on Carbopak-B 60/80 mesh or equivalent.

6.2.2 Column 2 - 6-ft x 0.1-in. ID stainless steel or glass column, packed with *n*-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

6.2.3 Column 3 - 30-m x 0.53-mm ID fused-silica capillary column bonded with DB-Wax (or equivalent), 1- μ m film thickness.

6.2.4 Column 4 - 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 5% methyl silicone (DB-5, SPB-5, RTx, or equivalent), 1.5- μ m film thickness.

6.2.5 Column 5 - 30-m x 0.53-mm ID fused-silica capillary column bonded with HP Basic Wax (or equivalent), 1- μ m film thickness. This column is used for triethylamine.

6.2.6 Wide-bore columns should be installed in 1/4-inch injectors, with deactivated liners designed specifically for use with these columns.

6.3 Detector - Flame ionization (FID)

6.4 Sample introduction and preparation apparatus

6.4.1 Refer to the 5000 series sample preparation methods for the appropriate apparatus for purge-and-trap, headspace, azeotropic distillation, and vacuum distillation analyses.

6.4.2 Samples may also be introduced into the GC via injection of solvent extracts or direct injection of aqueous samples.

6.5 Syringes

6.5.1 5-mL Luer-Lok glass hypodermic and 5-mL gas-tight syringe with shutoff valve, for volatile analytes.

6.5.2 Microsyringes - 10- and 25- μ L with a 0.006-in. ID needle (Hamilton 702N or equivalent) and 100- μ L.

6.6 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.

6.7 Analytical balance - 160-g capacity, capable of measuring to 0.0001 g.

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

7.3 Methanol, CH₃OH - Pesticide quality or equivalent. Store away from other solvents.

7.4 Fuels, e.g., gasoline or diesel - Purchase from a commercial source. Low-boiling components in fuel evaporate quickly. If available, obtain fuel from the leaking tank on site.

7.5 Alkane standard - A standard containing a homologous series of *n*-alkanes for establishing retention times (e.g., C₁₀-C₂₈ for diesel).

7.6 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. When methanol is a target analyte or when using azeotropic

distillation for sample preparation, standards should not be prepared in methanol. Standards must be replaced after 6 months or sooner, if comparison with check standards indicates a problem.

7.7 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 7.8 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.8 Calibration standards - Calibration standards at a minimum of five different concentrations are prepared in organic-free reagent water (for purge-and-trap, direct aqueous injection, azeotropic distillation, or vacuum distillation) or in methylene chloride (for solvent injection) from the secondary dilution of the stock standards. For headspace, the standards are prepared as directed in Method 5021. One of the standards should be at or below the concentration equivalent to the appropriate quantitation limit for the project. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte to be determined by this method (e.g., some or all of the compounds listed in Sec. 1.1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

7.8.1 Do not inject more than 20 μL of methanolic standards into 100 mL of water.

7.8.2 Use a 25- μL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

7.8.3 Rapidly inject the primary standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

7.8.4 Mix diluted standards by inverting the flask three times only.

7.8.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

7.8.6 The negative pressure generated by pipettes makes them inappropriate for routine use in the transfer of spiked solutions. As such, use of pipettes to dilute or transfer aqueous standards should be avoided. When sample transfer is absolutely necessary, (such as in the performance of headspace sample preparation for water samples) only high quality, automatic pipettes should be used, and then with extreme care.

7.8.7 Aqueous standards used for purge-and-trap analyses (Method 5030) are not stable and should be discarded after 1 hour, unless held in sealed vials with zero headspace. If so stored, they may be held for up to 24 hours. Aqueous standards used for azeotropic distillation (Method 5031) may be stored for up to a month in polytetrafluoroethylene (PTFE)-sealed screw-cap bottles with minimal headspace, at 4°C, and protected from light.

7.8.8 Standards for direct aqueous injection of triethylamine are prepared by dissolving an appropriate weight of neat triethylamine in organic-free reagent water and diluting to volume in a volumetric flask.

7.9 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The following internal standards are recommended when preparing samples by azeotropic distillation (Method 5031): 2-chloroacrylonitrile, hexafluoro-2-propanol, and hexafluoro-2-methyl-2-propanol.

7.10 Surrogate standards - Whenever possible, the analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with one or two surrogate compounds which are not affected by method interferences.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1 and Method 5035A.

8.2 If the headspace technique is used, also see Method 5021.

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 Refer to Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

9.5 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 9.0, and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

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

9.7 Sample quality control for preparation and analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

9.7.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

9.7.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

9.7.3 See Method 8000, Sec. 9.0, for the details on carrying out sample quality control procedures for preparation and analysis.

9.8 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 9.0, for information on evaluating surrogate data and developing and updating surrogate limits.

9.9 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.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.0 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Introduction/preparation methods

Various techniques are available for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before introduction into the GC/FID system. Consult the applicable sample introduction method regarding when to add standards.

Other sample introduction techniques may be appropriate for specific applications and the techniques described here also may be appropriate for other matrices and analytes. Whatever technique is employed, *including* those specifically listed below, the analyst *must* demonstrate adequate performance for the analytes of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Sec. 9.6, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

11.1.1 Direct aqueous injection - This technique involves direct syringe injection of an aliquot of an aqueous sample into the GC injection port. This technique is applicable to the following groups of analytes in this method.

11.1.1.1 Volatile organics (includes GRO)

This technique may involve injection of an aqueous sample containing a very high concentration of analytes. Direct injection of aqueous samples has very limited application in the analysis of volatile organics. It is only appropriate for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020) to determine if alcohol is present at > 24%.

11.1.1.2 Triethylamine in aqueous samples

Triethylamine may be determined by injecting a portion of an aqueous sample directly into the GC injection port. This technique has been demonstrated to be appropriate for samples containing low µg/L (ppb) concentrations of triethylamine.

11.1.2 Purge-and-trap of volatile organics (includes GRO)

This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030. Normally, purge-and-trap for aqueous samples is performed at ambient temperatures, while soil/solid samples utilize a 40°C purge to improve extraction efficiency. Heated purge may also be used to improve the purging of compounds with high solubilities in water, particularly alcohols associated with fuel oxygenates such as TBA and TAA. Occasionally, there may be a need to perform a heated purge for aqueous samples to lower detection limits; however, a 25-mL sample will often provide the sensitivity needed in most situations.

11.1.3 Azeotropic distillation

This technique exploits the ability of selected water-soluble organic compounds to form binary azeotropes with water during distillation. The organic compounds are removed from the bulk water sample and concentrated in a distillate, as described in Method 5031. An aliquot of the distillate is then injected into the GC/FID.

11.1.4 Vacuum distillation of volatile organics

This technique employs a vacuum distillation apparatus to introduce volatile organics from aqueous, solid, or tissue samples into the GC/FID system, as described in Method 5032.

11.1.5 Automated static headspace

This technique employs a device that collects the volatile organics from the headspace over a sample contained in a sealed vial and introduces them into the GC/FID system, as described in Method 5021.

11.1.6 Solvent injection

This technique involves the syringe injection of solvent extracts of aqueous samples prepared by Methods 3510, 3520, 3535, or other appropriate technique, or extracts of soil/solids prepared by Methods 3540, 3541, 3545, 3546, 3550, 3560, or other appropriate technique. It is applicable to many semivolatile organics, including DRO.

WARNING: Ultrasonic extraction (Method 3550) may not be as rigorous a method as the other extraction methods for soil/solids. This means that it is critical that the method be followed explicitly to achieve an extraction efficiency which approaches that of Soxhlet extraction. Consult Method 3550 for information on the critical aspects of this extraction procedure.

11.2 Suggested chromatographic conditions

Establish the GC operating conditions appropriate for the GC column being utilized and the target analytes specified in the project plan. Optimize the instrumental conditions for resolution of the target analytes and sensitivity. Suggested operating conditions are given below for the columns recommended in Sec. 6.2. The columns listed in this section were the columns used to develop the method performance data and it is not EPA's intent to exclude the use of other columns that may be developed. Laboratories may use these columns or other columns provided that they document method performance data (e.g., chromatographic resolution and sensitivity) that meet the data quality needs of the intended application.

11.2.1 Column 1

Carrier gas (helium) flow rate: 40 mL/min
Temperature program:
Initial temperature: 45 °C, hold for 3 minutes
Program: 45 °C to 220 °C, at 8 °C/min
Final temperature: 220 °C, hold for 15 minutes.

11.2.2 Column 2

Carrier gas (helium) flow rate: 40 mL/min
Temperature program:
Initial temperature: 50 °C, hold for 3 minutes
Program: 50 °C to 170 °C, at 6 °C/min
Final temperature: 170 °C, hold for 4 minutes.

11.2.3 Column 3

Carrier gas (helium) flow rate: 15 mL/min
Temperature program:
Initial temperature: 45 °C, hold for 4 minutes
Program: 45 °C to 220 °C, at 12 °C/min
Final temperature: 220 °C, hold for 3 minutes.

11.2.4 Column 4 (DRO)

Carrier gas (helium) flow rate: 5-7 mL/min
Makeup gas (helium) flow rate: 30 mL/min
Injector temperature: 200 °C
Detector temperature: 340 °C
Temperature program:
Initial temperature: 45 °C, hold for 3 minutes
Program: 45 °C to 275 °C, at 12 °C/min
Final temperature: 275 °C, hold for 12 minutes.

11.2.5 Column 4 (GRO)

Carrier gas (helium) flow rate:	5-7 mL/min
Makeup gas (helium) flow rate:	30 mL/min
Injector temperature:	200 °C
Detector temperature:	340 °C
Temperature program:	
Initial temperature:	45 °C, hold for 1 minute
1st Ramp:	45 °C to 100 °C at 5 °C/min
2nd Ramp:	100 °C to 275 °C, at 8 °C/min
Final temperature:	275 °C, hold for 5 minutes.

11.2.6 Column 5 (triethylamine only)

Carrier gas (helium) flow rate:	5 mL/min
Makeup gas (helium) flow rate:	30 mL/min
Injector temperature:	200 °C
Detector temperature:	250 °C
Temperature program:	
Initial temperature:	110 °C
Program:	110 °C to 175 °C, at 10 °C/min
Final temperature:	175 °C, hold for 3 minutes.

11.3 Initial calibration

11.3.1 Set up the sample introduction system as outlined in the method of choice (see Sec. 11.1). A separate calibration is necessary for each sample introduction mode because of the differences in conditions and equipment. Establish chromatographic operating parameters that provide instrument performance appropriate for the intended application. Prepare calibration standards using the procedures described above (see Sec. 7.8). The external standard technique is described below. Analysts wishing to use the internal standard technique should refer to Sec. 7.9 and to Method 8000.

11.3.2 External standard calibration procedure for single-component analytes

11.3.2.1 For each analyte and surrogate of interest, prepare calibration standards at a minimum of five different concentrations. For headspace analysis, the standards must be prepared in methanol or organic-free reagent water and then spiked into the organic-free water in the headspace vial. The spiking solutions must be at concentrations which will dilute to the desired standard concentrations when added into the organic-free water in the headspace vials. Otherwise, standards should be made by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the standards should be at a concentration at or below the quantitation limit necessary for the project (based on the concentration in the final volume described in the preparation method, with no dilutions). The concentrations of the other standards should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

11.3.2.2 Introduce each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Tabulate peak height or area responses against the mass injected. Calculate the calibration factor (CF) for each single-component analyte as described in Method 8000.

11.3.3 External standard calibration procedure for DRO and GRO

The calibration of DRO and GRO is markedly different from that for single-component analytes. In particular, the response used for calibration must represent the entire area of the chromatogram within the retention time range for the fuel type (DRO or GRO), including the unresolved complex mixture that lies below the individual peaks. See Sec. 11.11 for information on calculating this area.

11.3.3.1 For each fuel type, prepare calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent (for headspace analysis, follow the instructions in Sec. 11.3.2.1, above). One of the standards should be at a concentration at or below the quantitation limit necessary for the project (based on the concentration in the final volume described in the preparation method, with no dilutions). The concentrations of the other standards should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

NOTE: Whenever possible, the calibration should be performed using the specific fuel that is contaminating the site (e.g., a sample of the fuel remaining in the tank suspected of leaking). Where such samples are not available or not known, use recently purchased commercially-available fuel. A qualitative screening injection and GC run may be performed to identify unknown fuels.

11.3.3.2 Introduce each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Determine the area of the response as described in Sec. 11.10. Calculate the calibration factor (CF) for each fuel type as shown below:

$$\text{Calibration Factor} = \frac{\text{Total Area within Retention Time Range}}{\text{Mass injected (nanograms)}}$$

11.3.4 Calibration linearity

The linearity of the calibration must be assessed. This applies to both the single-component analytes and the fuel types.

11.3.4.1 If the percent relative standard deviation (%RSD) of the calibration factors is less than 20% over the working range, then linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

11.3.4.2 If the % RSD is more than 20% over the working range, linearity through the origin cannot be assumed. See Method 8000 for other calibration options that may be employed, which may include: a linear calibration not through the origin or a non-linear calibration model (e.g., a polynomial equation).

11.4 Retention time windows

Single-component target analytes (see Sec. 1.1) are identified on the basis of retention time windows. GRO and DRO are distinguished on the basis of the ranges of retention times for characteristic components in each type of fuel.

11.4.1 Before establishing retention time windows, make sure that the chromatographic system is functioning reliably and that the operating parameters have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Establish the retention time windows for single component target analytes using the procedure described in Sec. 11.0 of Method 8000.

11.4.2 The retention time range for GRO is defined during initial calibration. Two specific gasoline components are used to establish the range, 2-methylpentane and 1,2,4-trimethylbenzene. Use the procedure described in Sec. 11.0 of Method 8000 to establish the retention time windows for these two components. The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

11.4.3 The retention time range for DRO is defined during initial calibration. The range is established from the retention times of the C₁₀ and C₂₈ alkanes. Use the procedure described in Sec. 11.0 of Method 8000 to establish the retention time windows for these two components. The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

11.4.4 If this method is expanded to address other fuel types or petroleum fractions, then the analyst must establish appropriate retention time ranges for the boiling point range or carbon number range used to define each additional fuel type or petroleum fraction. Use the procedure described in Sec. 11.0 of Method 8000 to establish the retention time windows.

11.5 Calibration verification

11.5.1 The initial calibration and retention times must be verified at the beginning of each 12-hour work shift, at a minimum. When individual target analytes are being analyzed, verification is accomplished by the analysis of one or more calibration standards (normally mid-concentration, but a concentration at or near the action level may be more appropriate) that contain all of the target analytes and surrogates. When petroleum hydrocarbons are being analyzed, verification is accomplished by the measurement of the fuel standard and the hydrocarbon retention time standard. Additional analyses of the verification standard(s) throughout a 12-hour shift are strongly recommended, especially for samples that contain visible concentrations of oily material. See Sec. 11.0 of Method 8000 for more detailed information on calibration verification.

11.5.2 Calculate the % difference as detailed in Sec. 11.0 of Method 8000. If the response for any analyte is within $\pm 20\%$ of the response obtained during the initial calibration, then the initial calibration is considered still valid, and the analyst may continue to use the mean CF or RF values from the initial calibration to quantitate sample results. If the response for any analyte varies from the predicted response by more than $\pm 20\%$, corrective action must be taken to restore the system or a new calibration curve must be prepared for that compound.

11.5.3 All target analytes, surrogates, and/or *n*-alkanes in the calibration verification analyses must fall within previously established retention time windows. If the retention time of any analyte does not fall within the established window, then corrective action must be taken to restore the system or a new calibration curve must be prepared for that compound.

11.5.4 Solvent blanks and any method blanks should be run with calibration verification analyses to confirm that laboratory contamination does not cause false positive results.

11.6 Gas chromatographic analysis

11.6.1 Samples are analyzed in a set referred to as an analytical sequence. The sequence begins with calibration verification followed by sample extract analyses. Additional analyses of the verification standard(s) throughout a 12-hour shift are strongly recommended, especially for samples that contain visible concentrations of oily material. A verification standard is also necessary at the end of a set (unless internal standard calibration is used). The sequence ends when the set of samples has been injected or when retention time and/or % difference QC criteria are exceeded.

If the criteria are exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All sample analyses performed using external standard calibration must be bracketed with acceptable data quality analyses (e.g., calibration and retention time criteria). Therefore, all samples that fall between the standard that failed to meet the acceptance criteria and the preceding standard that met the acceptance criteria must be reanalyzed. Samples analyzed using internal standard calibration need not be bracketed (see Method 8000).

11.6.2 Samples are analyzed with the same instrument configuration as is used during calibration. When using Method 5030 for sample introduction, analysts are cautioned that opening a sample vial or drawing an aliquot from a sealed vial (thus creating headspace) will compromise samples analyzed for volatiles. Therefore, it is recommended that analysts prepare two aliquots for purge-and-trap analysis. The second aliquot can be stored for 24 hours to ensure that an uncompromised sample is available for analysis or dilution, if the analysis of the first aliquot is unsuccessful or if results exceed the calibration range of the instrument. Distillates from Method 5031 may be split into two aliquots and held at 4 °C prior to analysis. It is recommended that the distillate be analyzed within 24 hours of distillation. Distillates must be analyzed within 7 days of distillation.

11.6.3 Sample concentrations are calculated by comparing the sample response with the response from the initial calibration of the system (see Sec. 11.3). Therefore, if the sample response exceeds the limits of the initial calibration range, a dilution of the sample or sample extract must be analyzed. For volatile organic analyses of aqueous samples, the dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use and reanalysis. Samples and/or sample extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, is acceptable as long as calibration limits are not exceeded. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

11.6.4 Tentative identification of a single-component analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation may be necessary on a second column or by GC/MS. Since the flame ionization detector is non-specific, it is highly recommended that GC/MS confirmation be performed on single-component analytes unless historical data are available to support the identification(s). See Method 8000 for additional information on confirmation.

11.6.5 Second-column confirmation is generally not necessary for petroleum hydrocarbon analysis. However, if analytical interferences are indicated, analysis using the second GC column may be necessary. Also, the analyst must ensure that the sample hydrocarbons fall within the retention time range established during the initial calibration.

NOTE: The identification of fuels, especially gasoline, is complicated by their inherent volatility. The early eluting compounds in fuels are obviously the most volatile and the most likely to have weathered unless the samples were taken immediately following a spill. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is the least likely to be present in an environmental sample or may be present at only very low concentration in relation to the remainder of a gasoline chromatogram.

11.6.6 The performance of the entire analytical system should be checked every 12 hours, using data gathered from analyses of blanks, standards, and samples. Significant peak tailing must be corrected. Tailing problems are generally traceable to active sites on the column, cold spots in a GC, the detector operation, or leaks in the system. See Sec. 11.8 for GC/FID system maintenance. Follow manufacturer's instructions for maintenance of the introduction device.

11.7 Screening

11.7.1 This method can be used with a single-point calibration for screening samples prior to GC/MS analyses (e.g., Methods 8260 and 8270). Such screening can reduce GC/MS down-time when highly-contaminated samples are analyzed.

11.7.2 When this method is used for screening, it is recommended that the same sample introduction device (e.g., purge-and-trap versus direct injection) that is used for the subsequent GC/MS analyses also be used for the screening analysis. This will improve the correlation between the results and make the screening results more useful in predicting those samples that may overload the GC/MS system. However, other sample introduction techniques may be employed as well.

11.7.3 Establish that the system response and chromatographic retention times are stable. Analyze the high-point GC/MS calibration standard.

11.7.4 Analyze samples or sample extracts. Compare peak heights in the sample chromatograms with the high-point standard to establish that no compound with the same retention time as a target analyte exceeds the calibration range of the GC/MS system.

NOTE: The FID is much less sensitive to halogenated compounds than the MS detector. As a result, a simple peak height comparison for such compounds in the GC/MS standard may underestimate the actual concentration of halogenated compounds. When using this method as a screening tool, such an underestimate could lead to GC/MS results over the calibration range or result in contamination of the GC/MS system. Therefore, the analyst should exercise caution when screening samples that also contain halogenated compounds.

11.7.5 There are no formal QC requirements applied to screening analyses using this method. However, it is recommended that the high-point standard be run at least once every 12 hours to confirm the stability of the instrument response and chromatographic retention times. The analyst should consider the costs associated with making the wrong decision from the screening results (e.g., GC/MS instrument down-time and maintenance) and use appropriate judgment.

11.8 Instrument Maintenance

11.8.1 Injection of sample extracts from waste sites often leaves a high boiling residue in the injection port area, splitters (when used), and the injection port end of the chromatographic column. This residue affects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is necessary.

11.8.2 Recommended chromatograph maintenance

Corrective measures may require any one or more of the following remedial actions. Also see Sec. 11.0 in Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

11.8.2.1 Splitter connections - For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

11.8.2.2 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a satisfactory final rinse and in some cases may be the only solvent necessary. The column should then be filled with methylene chloride and allowed to remain flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

11.9 Calculations and data handling

Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

11.10 The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the mean CF or RF from the initial calibration, or another appropriate calibration model (see Method 8000).

11.11 While both diesel fuel and gasoline contain a large number of compounds that will produce well-resolved peaks in a GC/FID chromatogram, both fuels contain many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of these fuels. In addition, although the resolved peaks are important for the identification of the specific fuel type, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

11.11.1 For the analysis of DRO, sum the area of all peaks eluting between C_{10} and C_{28} . This area is generated by projecting a horizontal baseline between the retention times of C_{10} and C_{28} .

11.11.2 Because the chromatographic conditions employed for DRO analysis can result in significant column bleed and a resulting rise in the baseline, it is appropriate to perform a subtraction of the column bleed from the area of the DRO chromatogram. In order to accomplish this subtraction, a methylene chloride blank should be analyzed during each 12-hour analytical shift during which samples are analyzed for DRO. The area of this chromatogram is measured in the same fashion as is used for samples (see Sec. 12.3.1), by projecting a horizontal baseline across the retention time range for DRO. This area is then subtracted from the area measured for the sample and the difference in areas is used to calculate the DRO concentration, using the equations in Method 8000.

11.11.3 For the analysis of GRO, sum the areas of all peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene. This area is used to calculate the GRO concentration, using the equations in Method 8000. Column bleed subtraction is not generally necessary for GRO analysis.

11.12 Refer to Method 8000, Sec. 11.0, for the calculation formulae. The formulae cover external and internal standard calibration, aqueous and non-aqueous samples, and linear and non-linear calibrations.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.0 for information on data analysis and calibration.

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 Example method performance data for non-purgeable volatiles prepared using the azeotropic microdistillation technique from Method 5031 are included in Tables 1, 3 and 4 for aqueous matrices and in Tables 2 and 5 for solid matrices. Typical chromatograms are included in Figs. 4 and 5. These data are for illustrative purposes only.

13.3 Example method performance information are provided in Tables 6 and 7 for diesel fuel spiked into soil as are chromatograms of GRO and DRO standards in Figures 1 to 3.. These data are for illustrative purposes only.

13.4 Table 8 contains example precision and bias data for the analysis of triethylamine. Reagent water was spiked with triethylamine at $1.0 \mu\text{g/L}$ and analyzed by direct aqueous injection in a GC/FID equipped with an HP Basic Wax column (30-m x 0.53-mm ID). These data are for illustrative purposes only.

13.5 Table 9 contains example single-laboratory data on the pressurized fluid extraction of diesel range organics (DRO) from three types of soil (sand, loam, and clay). The soils were spiked at two levels of DRO, approximately 5 mg/kg each and approximately 2000 mg/kg. Seven replicates of each level and soil type were extracted using pressurized fluid extraction (Method 3545), using a mixture of methylene chloride and acetone (1:1). The data are taken from Reference 8 and are for illustrative purposes only. This extraction technique may be applicable to other analyte classes, fuel types, or petroleum fractions (see Sec. 1.2.3).

13.6 This method was the determinative technique used by one of the three laboratories participating in the study of headspace analysis of oxygenated gasoline contaminated groundwater samples. Please refer to Secs. 13.0 and 17.0 of Method 5021 for discussion and the results of that study.

13.7 This method was used in combination with Method 5021 to analyze a standard with several gasoline components, including MTBE and 2-methylpentane. As can be seen from the chromatogram in Figure 6, the two analytes can be resolved quite well (column: Restek 502.2 105m x 0.53 μm , 3 df).

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. T.A. Bellar, and J.J. Lichtenberg. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography", J. Amer. Water Works Assoc., 66(12), pp. 739-744 (1974).
2. T.A. Bellar, and J.J. Lichtenberg. "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall, ed., *Measurement of Organic Pollutants in Water and Wastewater*, ASTM STP 686, pp. 108-129, 1979.
3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635.
4. M.L. Bruce, R.P. Lee, and M.W. Stevens. "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environ. Sci. Technol. 1992, 26, 160-163.
5. S.F. Tsang, N. Chau, P.J. Marsden, and K.R. Carter. "Evaluation of the EnSys PETRO RIS_c kit for TPH", Report for Ensys, Inc., Research Triangle Park, NC, 27709, 1992.
6. "Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils," API Publication Number 4599, American Petroleum Institute, March 1994.
7. "Carbamates Method Evaluation Report," Science Applications International Corporation, Report for EPA Contract No. 68-W6-0068, August 1998.
8. B. E. Richter, "Single Laboratory Method Validation Report. Extraction of Diesel Range Organics (DRO), Waste Oil Organics (WOO), and Total Petroleum Hydrocarbons (TPH) using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC," Document 118357, Dionex Corporation, June 21, 1999.
9. R.J. Pirkle, and P.W. 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.
10. USEPA OUST, *Environmental Fact Sheet: Analytical Methods for Fuel Oxygenates*, EPA510-F-03-001, April, 2003, <http://www.epa.gov/OUST/mtbe/omethods.pdf>.

11. 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

EXAMPLE LOWER LIMITS OF DETECTION FOR NON-PURGEABLE VOLATILE
COMPOUNDS IN AQUEOUS MATRICES BY AZEOTROPIC MICRODISTILLATION
(METHOD 5031)

Analyte	Lower Quantitation Limit ($\mu\text{g/L}$) ^a		
	Reagent Water	Ground Water	TCLP Leachate
Acetone ^b	48	16	63
Acetonitrile	15	6	14
Acrolein	13	15	7
Acrylonitrile	8	9	14
1-Butanol	14	8	7
<i>t</i> -Butyl alcohol	8	7	17
1,4-Dioxane	12	15	16
Ethanol	18	12	13
Ethyl acetate	9	8	16
Ethylene oxide	8	9	10
Isobutyl alcohol	11	8	4
Isopropyl alcohol	18	17	7
Methanol	21	21	22
Methyl ethyl ketone	4	5	9
Methyl isobutyl ketone	4	2	8
2-Pentanone	2	2	7
1-Propanol	--	7	--
Propionitrile	10	6	13
Pyridine	11	9	21

^a Derived from analysis of seven aliquots of water spiked at 25 $\mu\text{g/L}$, using internal standard calibration. **Lower quantitation limits provided in SW-846 are for illustrative purposes and may not always be achievable.** Laboratories should establish their own in-house lower quantitation limits, if necessary to document method performance

^b Problematic due to transient laboratory contamination.

TABLE 2

EXAMPLE LOWER LIMITS OF DETECTION FOR NON-PURGEABLE VOLATILE
COMPOUNDS IN SOLID MATRICES BY AZEOTROPIC MICRODISTILLATION
(METHOD 5031)

Analyte	Lower Quantitation Limit (mg/kg)	
	Incinerator Ash	Kaolin
Acrylonitrile	0.42	0.09
1-Butanol	0.23	0.09
<i>t</i> -Butyl alcohol	0.34	0.13
1,4-Dioxane	0.31	0.16
Ethanol	0.47	0.19
Ethyl acetate	0.18	0.07
Isopropyl alcohol	0.40	0.19
Methanol	0.46	0.31
Methyl ethyl ketone	0.27	0.12
Methyl isobutyl ketone	0.12	0.05
2-Pentanone	0.16	0.07
Pyridine	0.20	0.08

Derived from analysis of seven aliquots of incinerator ash and kaolin spiked at 0.50 mg/kg, using internal standard calibration. **Lower quantitation limits provided in SW-846 are for illustrative purposes and may not always be achievable.** Laboratories should establish their own in-house lower quantitation limits, if necessary to document method performance

TABLE 3

EXAMPLE METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILES IN GROUND WATER BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Analyte	<u>Low</u> Concentration ^a		<u>Med.</u> Concentration ^b		<u>High</u> Concentration ^c	
	Mean Rec ^d	%RSD	Mean Rec ^d	%RSD	Mean Rec ^d	%RSD
Acetone ^e	126	17	N/A	--	N/A	--
Acetonitrile	147	5	105	8	92	9
Acrolein	146	13	120	27	80	20
Acrylonitrile	179	7	143	28	94	21
1-Butanol	127	8	86	8	90	9
<i>t</i> -Butyl alcohol	122	7	N/A	--	N/A	--
1,4-Dioxane	124	16	96	10	99	8
Ethanol	152	10	N/A	--	N/A	--
Ethyl Acetate	142	7	135	33	92	25
Ethylene oxide	114	10	N/A	--	N/A	--
Isobutyl alcohol	122	8	87	13	89	13
Isopropyl alcohol	167	13	N/A	--	N/A	--
Methanol	166	14	94	9	95	7
Methyl ethyl ketone	105	6	N/A	--	N/A	--
Methyl isobutyl ketone	66	4	N/A	--	N/A	--
2-Pentanone	94	3	N/A	--	N/A	--
1-Propanol	N/A	--	91	7	91	7
Propionitrile	135	5	102	14	90	14
Pyridine	92	12	N/A	--	N/A	--

^a 25 µg/L spikes, using internal standard calibration.

^b 100 µg/L spikes, using internal standard calibration.

^c 750 µg/L spikes, using internal standard calibration.

^d Mean of 7 replicates.

^e Problematic, due to transient laboratory contamination.

N/A = Data not available

TABLE 4

EXAMPLE METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILES
IN TCLP LEACHATE BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Analyte	<u>Low</u> <u>Concentration</u> ^a		<u>Med.</u> <u>Concentration</u> ^b		<u>High</u> <u>Concentration</u> ^c	
	Mean Rec ^d	%RSD	Mean Rec ^d	%RSD	Mean Rec ^d	%RSD
Acetone ^e	99	91	N/A	--	N/A	--
Acetonitrile	107	17	111	10	95	11
Acrolein	88	10	109	29	87	41
Acrylonitrile	133	13	123	29	103	38
1-Butanol	119	7	89	12	86	8
<i>t</i> -Butyl alcohol	70	31	N/A	--	N/A	--
1,4-Dioxane	103	20	103	16	102	7
Ethanol	122	13	N/A	--	N/A	--
Ethyl Acetate	164	12	119	29	107	41
Ethylene oxide	111	12	N/A	--	N/A	--
Isobutyl alcohol	115	4	86	13	82	13
Isopropyl alcohol	114	8	N/A	--	N/A	--
Methanol	107	10	102	6	N/A	--
Methyl ethyl ketone	87	13	N/A	--	N/A	--
Methyl isobutyl ketone	78	13	N/A	--	N/A	--
2-Pentanone	101	8	N/A	--	N/A	--
1-Propanol	N/A	--	98	10	89	7
Propionitrile	100	16	100	11	90	17
Pyridine	46	59	N/A	--	N/A	--

^a 25 µg/L spikes, using internal standard calibration.

^b 100 µg/L spikes, using internal standard calibration.

^c 750 µg/L spikes, using internal standard calibration.

^d Mean of 7 replicates.

^e Problematic, due to transient laboratory contamination.

N/A = Data not available

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILE
COMPOUNDS IN SOLID MATRICES BY AZEOTROPIC MICRODISTILLATION
(METHOD 5031)

	<u>Incinerator Ash</u>				<u>Kaolin</u>			
	<u>Low Conc.^a</u>		<u>High Conc.^b</u>		<u>Low Conc.^a</u>		<u>High Conc.^b</u>	
	Mea n Rec ^c	%RSD	Mea n Rec ^c	%RSD	Mea n Rec ^c	%RSD	Mea n Rec ^c	%RSD
Acrylonitrile	50	53	10	31	102	6	12	52
1-Butanol	105	14	61	12	108	5	58	25
<i>t</i> -Butyl alcohol	101	21	60	13	97	9	59	23
1,4-Dioxane	106	19	48	18	105	10	48	25
Ethanol	117	25	52	20	108	11	48	24
Ethyl acetate	62	19	39	12	90	5	41	25
Isopropyl alcohol	119	21	61	15	108	11	58	24
Methanol	55	53	33	28	117	17	37	22
Methyl ethyl ketone	81	21	40	12	91	8	42	20
Methyl isobutyl ketone	68	11	57	14	71	5	55	23
2-Pentanone	79	13	54	10	91	5	54	19
Pyridine	52	24	44	20	50	10	49	31

^a 0.5 mg/kg spikes, using internal standard calibration.

^b 25 mg/kg spikes, using internal standard calibration.

^c Mean of seven replicates.

TABLE 6

EXAMPLE RESULTS FROM ANALYSIS OF LOW AROMATIC DIESEL BY GC/FID
(5 replicates per test)

Spike Concentration	Analysis Results
12.5 ppm	ND
75 ppm	54 ± 7 ppm
105 ppm	90 ± 15 ppm
150 ppm	125 ± 12 ppm
1000 ppm	960 ± 105 ppm

ND = Not detected

Samples were prepared using 2-g aliquots of sandy loam soil spiked with known amounts of low aromatic diesel. Low aromatic diesel is sold in California. It was purchased for this study at a gas station in San Diego, California. Extractions were accomplished using methylene chloride as a solvent (Method 3550, high concentration option).

TABLE 7

EXAMPLE RESULTS FROM ANALYSIS OF DIESEL BY GC/FID
(5 replicates per test)

Spike Concentration	Analysis Results
25 ppm	51 ± 6 ppm
75 ppm	76 ± 8 ppm
125 ppm	99 ± 5 ppm
150 ppm	160 ± 10 ppm

Samples were prepared using 10-g aliquots of sandy loam soil spiked with known amounts of regular #2 diesel purchased at a gas station in Northern Virginia. Extractions were accomplished using methylene chloride as a solvent (Method 3550).

TABLE 8

EXAMPLE TRIETHYLAMINE PERFORMANCE DATA FOR SPIKED REAGENT WATER
(Analyses by Direct Aqueous Injection)

Spike Conc.	Triethylamine Concentration ($\mu\text{g/L}$)							Mean
	Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	
1.00	1.12	1.17	1.14	1.20	1.19	1.18	1.18	1.169
Mean Recovery	117%	S.D.	0.0288 $\mu\text{g/L}$					

The estimated quantitation limit was derived from the analyses of seven aliquots of water spiked at 1.00 $\mu\text{g/L}$, using external standard calibration, on a 30-m, 0.53-mm ID, HP Basic Wax GC column. A 1- μL injection volume was used. **Lower quantitation limits provided in SW-846 are for illustrative purposes and may not always be achievable.** Laboratories should establish their own in-house lower quantitation limits, if necessary to document method performance.

Data are taken from Reference 7.

TABLE 9

SINGLE-LABORATORY DATA FOR PRESSURIZED FLUID EXTRACTION (METHOD 3545)
OF DIESEL RANGE ORGANICS FROM THREE SOIL MATRICES

Matrix and Spiking Level	DRO Concentration in mg/kg								Mean Recovery (%)	%RSD
	Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Mean n		
Low Sand	3.2	8.2	5.9	6.3	7.0	7.7	6.4	6.4	127	25.4
Low Loam	6.5	6.0	7.9	5.1	6.9	9.5	6.4	6.9	138	20.7
Low Clay	4.3	5.8	5.7	8.6	5.4	7.5	7.6	6.4	128	23.6
High Sand	1850	1970	2030	2390	2210	2400	2430	2183	108	10.8
High Loam	1790	1870	1860	1970	1790	1990	1990	1894	94	4.7
High Clay	1910	1890	1990	2860	2880	2150	2040	2246	112	19.4

Low level samples were spiked with approximately 5 mg/kg of DRO.

High level samples were spiked with approximately 2000 mg/kg of DRO.

Seven replicates of each sample were extracted and analyzed by GC/FID.

Data are taken from Reference 8.

FIGURE 1

EXAMPLE CHROMATOGRAM OF A 300 PPM GASOLINE STANDARD

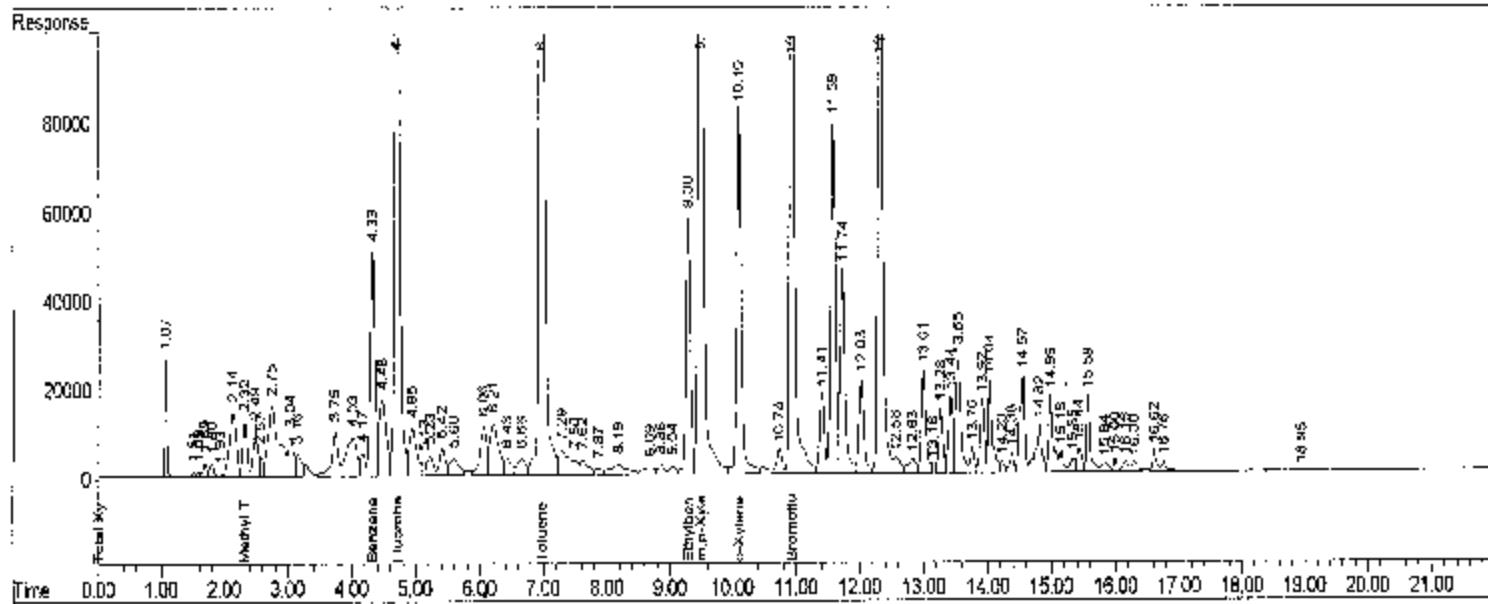


FIGURE 2

EXAMPLE CHROMATOGRAM OF A 30 PPM DIESEL STANDARD

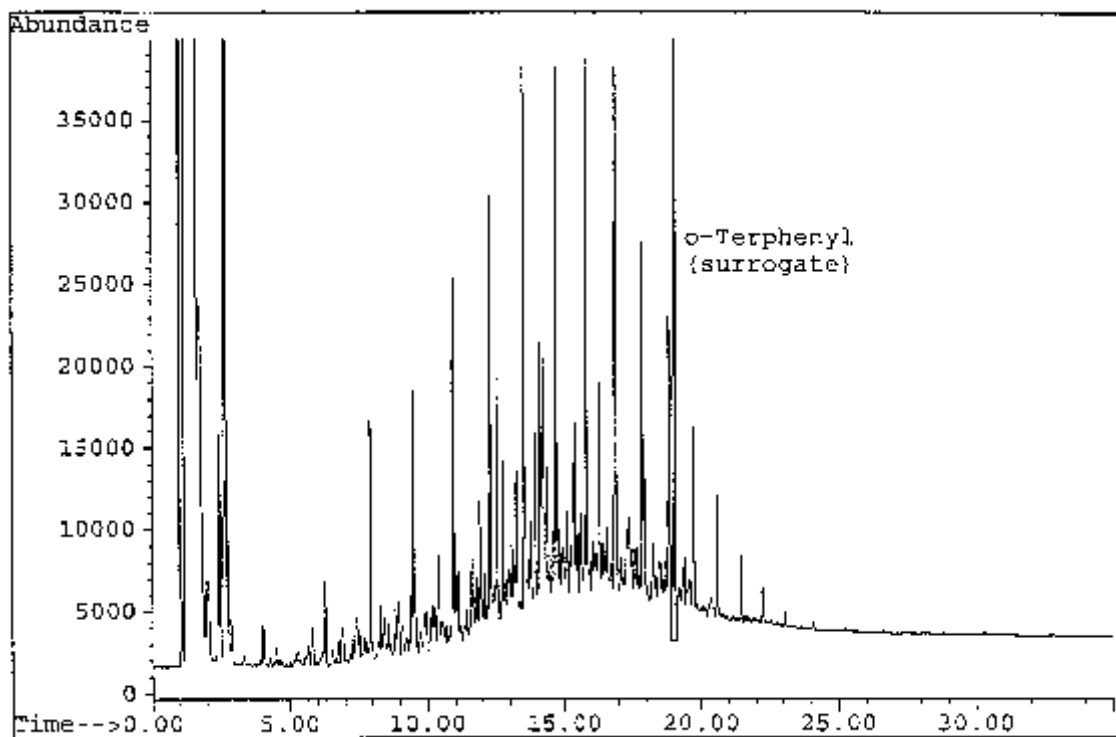


FIGURE 3

EXAMPLE CHROMATOGRAM OF A 30 PPM DIESEL STANDARD WITH THE
BASELINE PROJECTED BETWEEN C₁₀ AND C₂₈

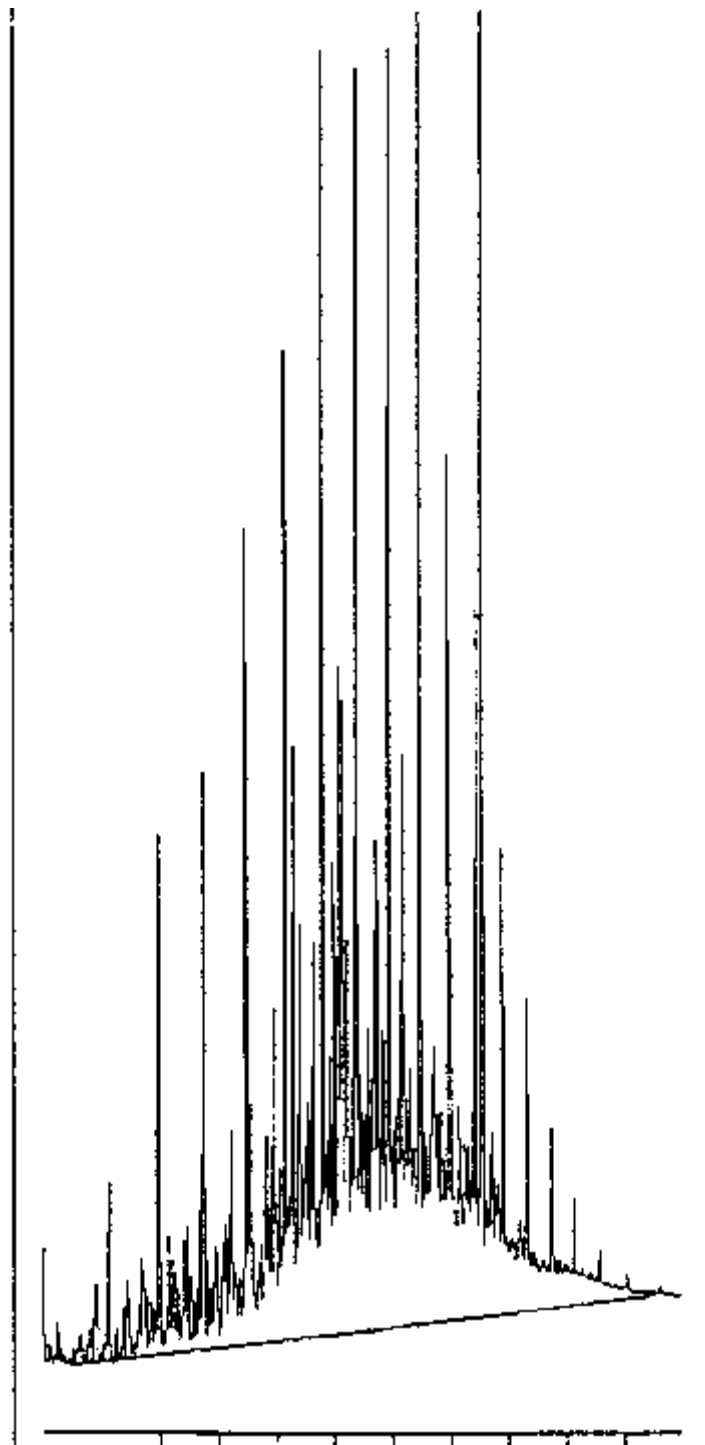
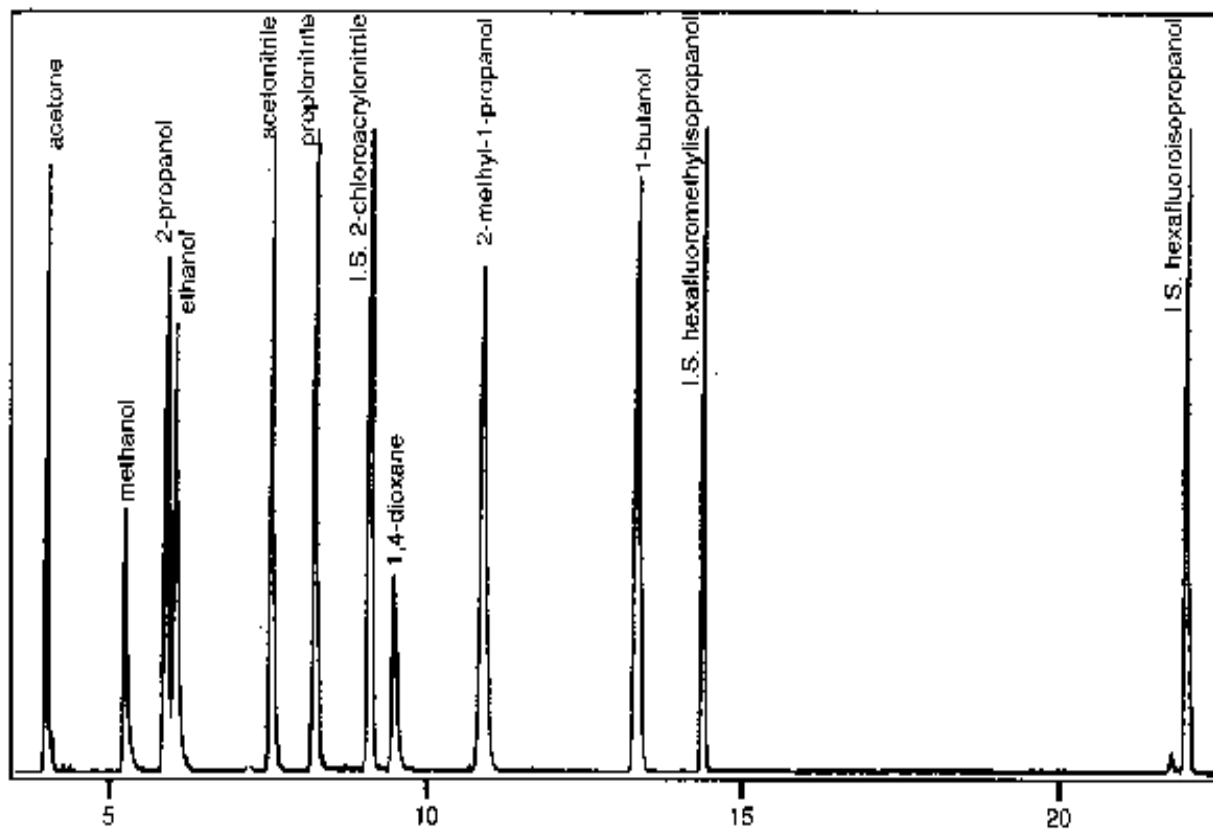


FIGURE 4

EXAMPLE CHROMATOGRAM OF SEVERAL NONPURGEABLE VOLATILE COMPOUNDS IN SPIKED REAGENT WATER USING AZEOTROPIC MICRODISTILLATION (METHOD 5031)



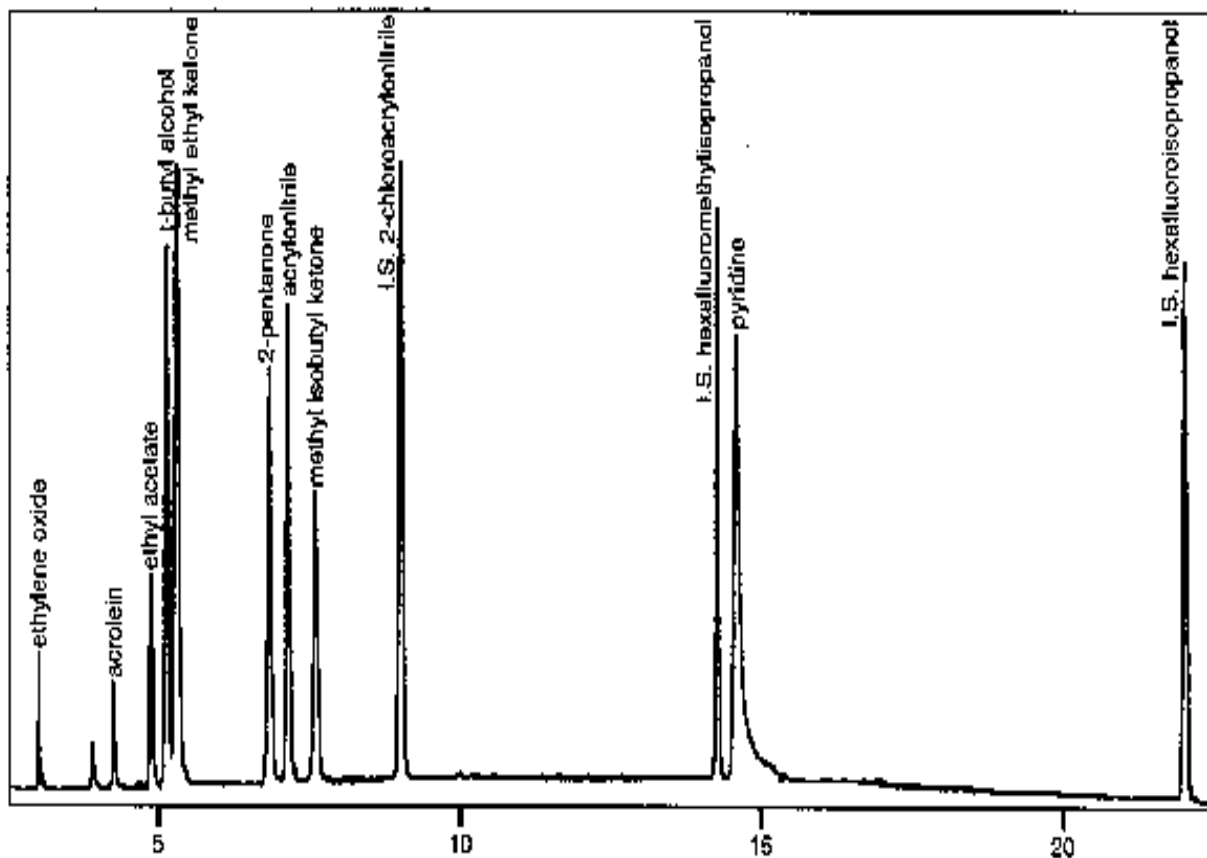
Mix 1: Analytes distilled at 0.25 mg/L, internal standards at 2.5 mg/L

GC Column: J&W DB-Wax column with 0.53-mm ID

Temperature program: 30 °C for 2 min.
3 °C/min. to 100 °C and held for 0 min.
25 °C/min. to 200 °C and held for 4 min.

FIGURE 5

EXAMPLE CHROMATOGRAM OF SEVERAL NONPURGEABLE VOLATILE COMPOUNDS IN SPIKED REAGENT WATER USING AZEOTROPIC MICRODISTILLATION (METHOD 5031)



Mix 2: Analytes distilled at 0.25 mg/L, internal standards at 2.5 mg/L

GC Column: J&W DB-Wax column with 0.53-mm ID

Temperature program: 30 °C for 2 min.
3 °C/min. to 100 °C and held for 0 min.
25 °C/min. to 200 °C and held for 4 min.

FIGURE 6

EXAMPLE CHROMATOGRAM OF MULTI-COMPONENT MIXTURE

File=C:\CP\108\W108A2.54R Sample name=BLEND (CALC) Date printed= 07-26-2002 Time= 15:19:05
10.00 to 26.00 min. Low Y = 0.00000 mv High Y = 12.00000 mv Span = 12.00000 mv

