METHOD 8015B

NONHALOGENATED ORGANICS USING GC/FID

1.0 SCOPE AND APPLICATION

1.1 Method 8015 is used to determine the concentration of various nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography. The following compounds can be determined quantitatively by this method:

Compound Name	CAS No.[a]	Appropriate Technique: Purge-and-Trap	Direct Injection	Solvent Extraction
Acetone	67-64-1	pp	b,d	I
Acetonitrile	75-05-8	pp	b,d	I
Acrolein	107-02-8	pp	b,d	I
Acrylonitrile	107-13-1	pp	b,d	I
Allyl alcohol	107-18-6	ht	b,d	I
1-Butanol (n-Butyl alcohol)	71-36-3	ht	b,d	I
t-Butyl alcohol	75-65-0	pp	b,d	I
2-Chloroacrylonitrile (I.S.)	920-37-6	NA	d	NA
Crotonaldehyde	123-73-9	pp	b,d	I
Diethyl ether	60-29-7	b	b	I
1,4-Dioxane	123-91-1	pp	b,d	I
Ethanol	64-17-5	I	b,d	I
Ethyl acetate	141-78-6	I	b,d	I
Ethylene glycol	107-21-1	I	b	I
Ethylene oxide	75-21-8	I	b,d	I
Hexafluoro-2-propanol (I.S.)	920-66-1	NA	d	NA
Hexafluoro-2-methyl-2-propanol (I.S.)	515-14-6	NA	d	NA
Isobutyl alcohol	78-83-1	pp	b,d	I
Isopropyl alcohol	67-63-0	pp	b,d	I
Methanol	67-56-1	I	b,d	I
Methyl ethyl ketone (MEK)	78-93-3	pp	b,d	I
Methyl isobutyl ketone (MIBK)	108-10-1	pp	b,d	I
N-Nitroso-di-n-butylamine	924-16-3	pp	b,d	b
Paraldehyde	123-63-7	pp	b,d	I
2-Pentanone	107-87-9	pp	b,d	I
2-Picoline	109-06-8	pp	b,d	I
1-Propanol	71-23-8	pp	b,d	I
Propionitrile	107-12-0	ht	d	I

Compound Name	CAS No.[a]	Appropriate Technique: Purge-and-Trap	Direct Injection	Solvent Extraction
Pyridine	110-86-1	I	b,d	b
o-Toluidine	95-53-4	I	b,d	b

[a] Chemical Abstract Services Registry Number.
b Adequate response using this technique
d Amenable to concentration by azeotropic distillation (Method 5031)
ht Method analyte only when purged at 80°C
I *Inappropriate technique for this analyte*
pp Poor purging efficiency, resulting in high EQLs
NA Not available
I.S. Internal standard appropriate for Method 5031

1.2 This method may also be applicable to the analysis of petroleum hydrocarbons, including gasoline range organics (GROs) and diesel range organics (DROs). GROs correspond to the range of alkanes from C_6 to C_{10} and covering a boiling point range of approximately 60°C - 170°C (Reference 6). DROs correspond to the range of alkanes from C_{10} to C_{28} and covering a boiling point range of approximately 170°C - 430°C (Reference 6). 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 GROs and DROs, since these hydrocarbons are not regulated under RCRA. Consult State and local regulatory authorities for specific requirements.

1.3 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs 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.

1.4 The method can also be used as a screening tool (for both volatile and semivolatile organics) to obtain semiquantitative data for the prevention of sample overload during quantitative analysis on a GC/MS system. This may be accomplished using an automated (Method 5021) headspace method or by direct injection if a solvent extraction method has been utilized for sample preparation. Single point calibration would be acceptable in this situation. Performance data are not provided for screening.

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile and semivolatile organic compounds.

2.1.1 Samples may be introduced into the GC:

- following solvent extraction (Methods 3510, 3520, 3540, 3541, 3545, 3550, or 3560)

- by direct injection (aqueous samples) including the concentration of analytes by azeotropic distillation (Method 5031)

- by purge-and-trap (Methods 5030 or 5035), or

- by vacuum distillation (Method 5032)

2.1.2 Ground or surface water samples must generally be analyzed in conjunction with Methods 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 the target analytes, but has not yet been validated by EPA in conjunction with Method 8015.

2.1.3 Diesel range organics (DROs) may be prepared by an appropriate solvent extraction method.

2.1.4 Gasoline range organics (GROs) may be introduced into the GC/FID by purge-and-trap, automated headspace, vacuum distillation, or other appropriate technique.

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

2.3 The method allows the use of packed or capillary columns for the analysis and confirmation of the non-halogenated individual analytes. Columns and conditions listed have been demonstrated to provide separation of those target analytes. Analysts may change these conditions as long as they demonstrate adequate performance.

2.4 Fused silica capillary columns are necessary for the analysis of petroleum hydrocarbons.

3.0 INTERFERENCES

3.1 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 must serve as a check on such contamination.

3.2 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.

3.2.1 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.

3.2.2 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 in an oven at 130°C for several hours or rinse with methanol and drain. Store dry glassware in a clean environment.

3.3 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.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for solvent injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Recommended GC Columns

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

4.1.2.2 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.

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

4.1.2.4 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-µm film thickness.

4.1.2.4.1 Capillary columns are needed for petroleum hydrocarbon analyses. Laboratories may use other capillary columns (e.g. 0.25-0.32 mm ID capillary columns) if they document method performance data (e.g. chromatographic resolution and MDLs) if appropriate for the intended use of the data.

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

4.1.3 Detector - Flame ionization (FID)

4.2 Sample introduction and preparation apparatus

4.2.1 Refer to the 5000 series sample preparation methods for the appropriate apparatus.

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

4.3 Syringes

4.3.1 A 5-mL Luer-Lok glass hypodermic and a 5-mL gas-tight syringe with shutoff valve for volatile analytes.

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

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

4.5 Analytical balance - 0 - 160 g capacity, capable of measuring differences of 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used whenever possible. 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.

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

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 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.

5.5 Alkane standard. A standard containing a homologous series of n-alkanes for establishing retention times (e.g., C_{10}-C_{32} for diesel).

5.6 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.

5.7 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. 5.8 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.

5.8 Calibration standards - Calibration standards at a minimum of five different concentrations are prepared in water (purge-and-trap or direct injection) or in methylene chloride (solvent injection) from the secondary dilution of the stock standards. 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 for detection by this method (e.g., some or all of the compounds listed in Sec. 1.1 may be included). Volatile organic standards are prepared in organic-free reagent water. In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

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

5.8.2 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).

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

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

5.8.5 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).

5.8.6 Never use pipets to dilute or transfer samples or aqueous standards when diluting volatile organic standards.

5.8.7 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.

5.9 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: 2-chloroacrylonitrile, hexafluoro-2-propanol and hexafluoro-2-methyl-2-propanol.

5.10 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.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Introduction/preparation methods

Various alternate methods are provided for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before introduction into the GC/FID system. Follow the introduction method on when to add standards.