NONHALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

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

Compound Name	CAS No.[a]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Diethyl ether	60-29-7	b	b
Ethanol	64-17-5	i	b
Methyl ethyl ketone (MEK)	78-93-3	pp	b
Methyl isobutyl ketone (MIBK)	108-10-1	pp	b

a Chemical Abstract Services Registry Number.
b Adequate response using this technique
i Inappropriate technique for this analyte
pp Poor purging efficiency, resulting in high EQLs

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile organic compounds. Samples may be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed by Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 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 can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column 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 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.

4.1.3 Detector - Flame ionization (FID).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

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

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

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall 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.

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 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared, ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.4.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards - Using stock standard solutions, prepare in methanol 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 Section 5.5 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.

5.6 Calibration standards - Calibration standards at a minimum of five concentrations are prepared in water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. 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 Section 1.1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

5.6.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.6.2 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).

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

5.6.4 Mix aqueous standards by inverting the flask three times only.

5.6.5 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).

5.6.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.6.7 Aqueous standards are not stable and should be discarded after 1 hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 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.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.6.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ng/µL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

5.7.3 Analyze each calibration standard according to Section 7.0, adding 10 µL of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - 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 water blank with one or two surrogate compounds recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.4, add a volume to give 750 µg of each surrogate to 45 mL of water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.7.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For high-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis. Method 5030 also provides guidance on the analysis of aqueous miscible and non-aqueous miscible liquid wastes (see Section 7.4.1.1).

7.2 Chromatographic conditions (Recommended)

7.2.1 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.

7.2.2 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.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L);

therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

Non-aqueous miscible wastes may also be analyzed by direct injection if the concentration of target analytes in the sample falls within the calibration range. If dilution of the sample is necessary, follow the guidance for High Concentration samples in Method 5030, Section 7.3.3.2.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Calculation of concentration is covered in Method 8000.

7.4.5 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.6 If the response for a peak is off-scale, prepare a dilution of the sample with water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000, Section 8.6.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required:

- Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and calibration procedures used.

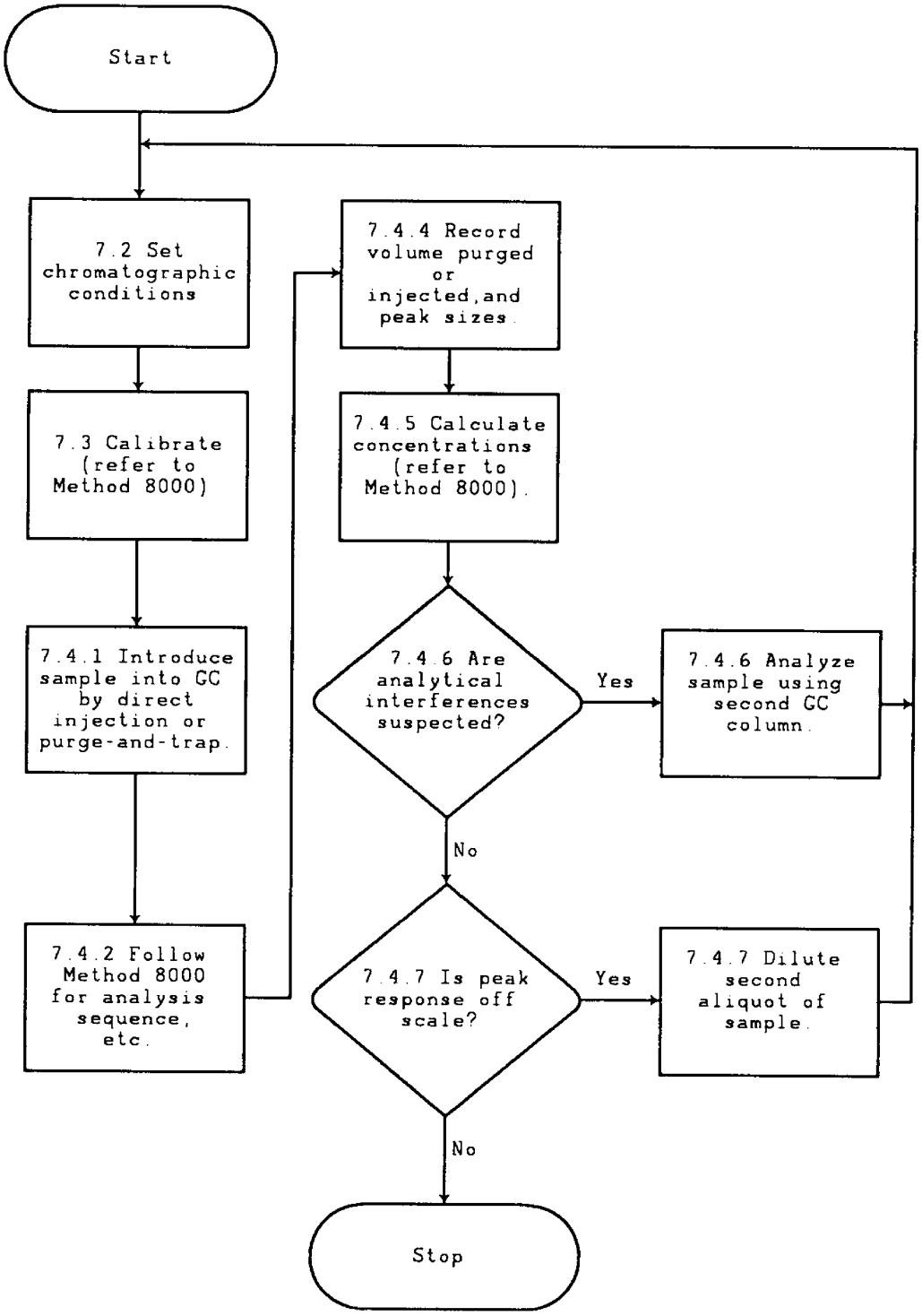
9.2 Specific method performance information will be provided as it becomes available.

10.0 REFERENCES

1. Bellar, T.A., 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. Bellar, T.A., 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 (in preparation).


Start
7.2 Set chromatographic conditions
7.3 Calibrate (refer to Method 8000)
7.4.1 Introduce sample into GC by direct injection or purge-and-trap.
7.4.2 Follow Method 8000 for analysis sequence, etc.
7.4.4 Record volume purged or injected, and peak sizes.
7.4.5 Calculate concentrations (refer to Method 8000).
7.4.6 Are analytical interferences suspected?
Yes
7.4.6 Analyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
7.4.7 Dilute second aliquot of sample.
No
Stop