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Standard Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling[1]

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1. Scope

1.1 This test method covers the determination of most purgeable organic compounds that boil below 200°C and are less than 2 % soluble in water. It covers the low µg/L to low mg/L concentration range (see Section 15 and Appendix X1).

1.2 This test method was developed for the analysis of drinking water. It is also applicable to many environmental and waste waters when validation, consisting of recovering known concentrations of compounds of interest added to representative matrices, is included.

1.3 Volatile organic compounds in water at concentrations above 1000 µg/L may be determined by direct aqueous injection in accordance with Practice D 2908.

1.4 It is the user's responsibility to assure the validity of the test method for untested matrices.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.5.5.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[3]

E 355 Practice for Gas Chromatography Terms and Relationships[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practice E 355.

3.2 *Description of Term Specific to This Standard:*

3.2.1 *purgeable organic*—any organic material that is removed from aqueous solution under the purging conditions described in this test method (10.1.1).

4. Summary of Test Method

4.1 An inert gas is bubbled through the sample to purge volatile compounds from the aqueous phase. These compounds are then trapped in a column containing a suitable sorbent. After purging is complete, trapped components are thermally desorbed onto the head of a gas chromatographic column for separation and analysis. Measurement is accomplished with an appropriate detector.

5. Significance and Use

5.1 Purgeable organic compounds, including organohalides, have been identified as contaminants in raw and drinking water. These contaminants may be harmful to the environment and man. Dynamic headspace sampling is a generally applicable method for concentrating these components prior to gas chromatographic analysis **(1 to 5).**[5] This test method can be used to quantitatively determine purgeable organic compounds in raw source water, drinking water, and treated effluent water.

6. Interferences

6.1 Purgeable compounds that coelute with components of interest and respond to the detector will interfere with the chromatographic measurement. Likelihood of interference may be decreased by using dissimilar columns or a more selective detector for the chromatographic step.

7. Apparatus

7.1 *Purging Device*—Commercial devices are available for this analysis. Either commercial apparatus or the equipment described below may be used for this analysis. Devices used shall be capable of meeting the precision and bias statements given in 15.1.

7.1.1 *Glass Purging Device* having a capacity of 5 mL is shown in Fig. A1.1. Construction details are given in Annex A1. A glass frit is installed at the base of the sample reservoir to allow finely divided gas bubbles to pass through the aqueous

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] *Annual Book of ASTM Standards,* Vol 11.01.

[3] *Annual Book of ASTM Standards,* Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] The boldface numbers in parentheses refer to the references at the end of this test method.

sample while the sample is restrained above the frit. The sample reservoir is designed to provide maximum bubble contact time and efficient mixing.

7.1.2 Gaseous volumes above the sample reservoir are kept to a minimum to provide efficient transfer and yet large enough to allow sufficient space for foams to disperse. Inlet and exit ports are constructed from 6.4-mm (¼-in.) outside diameter medium-wall tubing so that leak-free removable connections can be made using" finger-tight" compression fittings containing plastic ferrules. The optional foam trap is used to control occasional samples that foam excessively.

7.2 *Trap*—A short section of stainless steel or glass tubing is packed with a suitable sorbent. Traps should be conditioned before use (Section 11). While other trap designs and sorbent materials may be used (see Section 12), the trap and sorbent described here are recommended and were used to collect precision and bias data. If another trap design or sorbent material is used, these precision and bias statements should be verified. A suitable trap design is 150 mm long by 3.17-mm outside diameter (2.54-mm inside diameter). The front 100 mm is packed with 60 to 80 mesh 2,6-diphenyl-*p*-phenylene oxide followed by 50 mm of 35 to 60-mesh silica gel. One trap design is shown in Fig. A1.2, with details in Annex A1. The body assembly acts as a seal for the exit end of the trap. The modified stem assembly is used to seal the inlet end of the trap when it is not in use.

7.3 *Desorber* consists of a trap heater and an auxiliary carrier gas source to backflush the trap at elevated temperatures directly onto the gas-chromatographic column. Desorber 1 (Fig. A1.3 and Annex A1) is dedicated to one gas chromatograph, but Desorber 2 can be used as a universal desorber for many gas chromatographs with a septum-type liquid-inlet system.

7.3.1 *Desorber 1* is attached directly onto the gas-chromatograph liquid-inlet system after removing the septum nut, the septum, and the internal injector parts. The modified body assembly is screwed onto the inlet system using the PTFE gasket as a seal. A plug is attached to one of the stem assemblies.

7.3.1.1 The assembled parts, simply called "the plug," are used to seal the desorber whenever the trap is removed to maintain the flow of carrier gas through the gas-chromatographic column.

7.3.1.2 The flow controller, PTFE tubing, and stem assembly are used to provide the trap-backflush flow. This entire assembly also provides gas flow to operate the purging device.

7.3.2 *Desorber 2* (Fig. A1.4 and Annex A1) may be attached to any gas chromatograph by piercing the gas-chromatographic liquid-inlet septum with the needle.

7.3.2.1 The desorber is assembled in accordance with Fig. A1.4 with internal volumes and dead-volume areas held to a minimum. The heat source is concentrated near the base of the desorber so that the internal seals of the body assembly do not become damaged by heat. The use of a detachable needle assembly from a microsyringe makes it easy to replace plugged or dulled needles.

7.3.2.2 The flow controller, PTFE tubing, and stem assembly are used to provide the trap-backflush flow. This entire assembly is also used to provide gas flow to operate the purging device.

7.4 *Gas Chromatograph* equipped with a suitable detector, such as flame ionization, electrolytic conductivity, microcoulometric (halide mode), flame photometric, electron capture, or mass spectrometer.

7.4.1 The gas chromatographic conditions described below are recommended and were used to obtain precision and bias data (Section 15). If other column conditions are used, the analyst must demonstrate that the precision and bias achieved are at least as good as that presented in Section 15.

7.4.2 *Column* is 2.4 m by 2.4-mm inside diameter stainless steel packed with a suitable packing. Glass or nickel columns may be required for certain applications. Helium carrier gas flow is 33 mL/min and a flame ionization detector is used.

7.4.3 *Chromatograph Oven* is held at room temperature during trap desorption, then rapidly heated to 60°C and held for 4 min. Finally, the temperature is programmed to 170°C at 8°C/min and held for 12 min or until all compounds have eluted.

7.5 *Sampling Vials*, glass, 45-mL, sealed with PTFE-faced septa. [6] Vial caps must be open-top screw caps to prevent vial breakage. The vials, septa, and caps are washed with detergent and hot water and rinsed with tap water and organic free water. The vials and septa are then heated to 105°C for 1 h and allowed to cool to room temperature in a contaminant-free area. When cool, the vials are sealed with septa, PTFE side down, and screw capped. Aluminum foil disks may be placed between the septa and screw cap to help minimize contamination. Vials are maintained in this capped condition until just prior to filling with water.

7.6 *Glass Syringe*, 5-mL with two-way syringe valve and 150 to 200 mm, 20-gage syringe needle.

8. Reagents and Materials

8.1 *Purity of Reagents*—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.[7] 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.

8.2 *Purity of Water*—Unless otherwise indicated, Specification D 1193, Type II, will be used in this test method. Analyze a 5-mL aliquot of this water as described in Section 12 before preparing standard solutions. If the blank sample produces interferences for the compounds of interest, purge it free of volatile contaminants with purge gas (8.9) before using.

[6] Pierce No. 13075 Screw Cap System Vials and 12722 Tuf-Bond Discs, Pierce Chemical Co., Rockford, IL, have been found satisfactory for this application.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8.3 *Dechlorinating Agent*—Granular sodium thiosulfate or ascorbic acid.

8.4 *Trap Packings*[8]—60/80 mesh chromatographic grade 2,6-diphenyl-*p*-phenylene oxide and 35 to 60 mesh silica gel. [9] Other packings may be needed for specific determinations.

8.5 *Stock Solutions*—Prepare a stock solution (approximately 2 mg/mL) for each material being measured, as follows:

8.5.1 Fill a 10.0-mL ground glass-stoppered volumetric flask with approximately 9.8 mL of methyl alcohol.

8.5.2 Allow the flask to stand unstoppered about 10 min or until all alcohol wetted surfaces dry.

8.5.3 Weigh the unstoppered flask to the nearest 0.1 mg.

8.5.4 Using a 100-µL syringe, immediately add 6 drops of one reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

8.5.5 Dilute to volume, stopper, then mix by inverting the flask several times.

8.5.5.1 **Warning**—Because the reference materials are likely to be toxic and volatile, prepare concentrated solutions in a hood. It is advisable to wear rubber gloves and use an approved respirator when handling volatile toxic materials.

8.5.6 Calculate the concentration in micrograms per millilitre from the net gain in weight.

8.5.7 Store the solutions at 4°C. Warm to room temperature before use.

NOTE 1—Standard solutions prepared in methyl alcohol are generally stable up to 4 weeks when stored under these conditions. Discard them after that time has elapsed.

8.6 *Working Standard* (approximately 100 µg/mL)—Prepare a working standard containing each compound to be tested, as follows.

8.6.1 Fill a 100-mL volumetric flask approximately three fourths full of methanol or acetone.

8.6.2 Pipet 1 mL of the stock solution (8.5) of each compound of interest into the flask, using subsurface addition. Stopper the flask except when actually transferring solutions.

8.6.3 After adding standard stock solutions, dilute to the mark with solvent and mix thoroughly. Immediately transfer this solution to a clean vial (7.5) by filling to overflowing and sealing with a septum, PTFE side down, and screw cap.

8.7 *Quality Check Sample (approximately 20 µg/L)*—Just prior to calibration, prepare a quality check sample by dosing 20.0 µL of the working standard solution (8.6) into 100.0 mL of water.

8.8 *Internal Standard Dosing Solution*—From stock standard solutions prepared as in 8.5, add a volume to provide 1000 µg of each standard to 45 mL of water contained in a 50-mL volumetric flask, dilute to volume, and mix. Prepare a fresh internal standard dosing solution daily. Dose the internal standard solution into every sample and reference standard analyzed. It is up to the analyst to choose internal standard compounds appropriate to the analysis.

8.9 *Purge Gas–Nitrogen or Helium*—Take precautions to prevent organic materials that may be present in the purge gas or laboratory air from contaminating the sample. High-purity purge gases (99.99 %) are desirable. Lower quality gases may be used if impurities are removed, for example by molecular sieve or low-temperature cold traps, or both.

9. Sampling

9.1 If the water has been chlorinated, add 1 to 2 mg of dechlorinating agent to the sampling vial (7.5) before sampling. Whether chlorinated or not, fill the vial to overflowing so that a convex meniscus forms at the top. Place a septum, PTFE side down, carefully on the opening of the vial, displacing the excess water. If an aluminum foil disk is to be used, place it over the septum. Then seal the vial with the screw cap and invert to verify the seal by demonstrating the absence of air bubbles.

NOTE 2—The sample should be headspace-free at this time. A small bubble may form if the vial is stored more than a few hours. *Analyze the sample within a few hours if possible.* If storage is necessary, maintain the sample temperature at 0 to 4°C until analyzed. Retighten the screw cap after the sample is chilled. Storage over charcoal will minimize contamination. Data on compounds tested showed them to be stable for at least 15 days.

10. Calibration and Standardization

10.1 Calibrate the system by analyzing replicate aliquots of the quality check sample (8.7), to which 5 µL of the internal standard dosing solution (8.8) have been added, as described in Section 12. Replicate analyses permit the analyst to determine precision for each component.

10.1.1 Quantitative purging of each component, although desirable, is not required for successful analyses using this procedure. However, purging must be sufficiently reproducible to permit correction for incomplete recovery within the desired overall accuracy.

10.1.2 For each component, the percent recovery is calculated by comparing the gas chromatographic peak area response of the purged and trapped sample to the corresponding response of the same quantity of component injected directly into the chromatograph.

NOTE 3—Either incomplete purging or breakthrough of the trap will result in nonquantitative recovery by this test method. If the former is suspected, analyze a fresh aliquot of the quality check sample (8.7) using a longer purge time or an elevated sample temperature. If this increases the recovery, continue increasing the purge time or sample temperature until a recovery that satisfies the precision and bias statement (15.1) is obtained. If increasing the purge time decreases the recovery, the retention volume of the trap may have been exceeded, and try a shorter purge time. It is up to the analyst to demonstrate that the purge time and temperature are adequate for the specific analysis. In general, maintain the sample temperature constant to within ± 2°C throughout an experiment.

11. Conditioning Traps

11.1 Condition newly packed traps with one of the desorbers (7.3) at 200°C for 16 to 24 h with a carrier flow of 20 mL/min, venting into the atmosphere. Condition used traps just before use (same day) by placing them in a desorber and

[8] 60 to 80 mesh Carbopack C coated with 0.2 % Carbowax 1500 proceded by 0.3 m of 60 to 80 mesh Chromsorb W-H.P., coated with 3 % Carbowax 1500, available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823, has been found satisfactory for this application.

[9] Tenax GC, a registered trademark of Enka, N.V., The Netherlands, and Davidson Type 15 silica gel has been found satisfactory for this application.