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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Organic Halides in Water by Carbon AdsorptionMicrocoulometric Detection [1]

This standard is issued under the fixed designation D 4744; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Section 15 was added editorially in June 1995.

1. Scope

1.1 This test method covers the determination of the organic halides in water in concentrations from 5 to 1000 µg/L. Higher halide concentrations may be determined by making an appropriate dilution.

1.2 This test method is applicable only for those organic halides that can be adsorbed by granular activated carbon (GAC).[2,3,4]

1.3 This test method is applicable to samples whose inorganic halide concentration does not exceed the organic halide concentration by more than 20 000 times. Chloride ion may be determined by Test Methods D 512. See Section 6.

1.4 This test method was used successfully with several waters (see 14.3). It is the user's responsibility to ensure the validity of this test method for waters of 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 512 Test Methods for Chloride Ion in Water [5]
D 1129 Terminology Relating to Water [5]
D 1193 Specification for Reagent Water [5]
D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water [5]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *organic halides*—all organic species containing chlorine, bromine, and iodine that are adsorbed by granular activated carbon and produce titratable species under the conditions of the test method. See Section 6.

3.2.2 Since the description of organic halides is method-dependent, the following descriptions are provided to simplify communications.

3.2.3 *total organic halides (TOX)*—when a sample is run unpurged and unfiltered, the result is called total organic halides (TOX).

3.2.4 *nonpurgeable organic halides (NPOX)*—when a sample is purged before running, the result is called nonpurgeable organic halides (NPOX).

3.2.5 *purgeable organic halides (POX)*—the difference between the TOX and the NPOX is the purgeable organic halides (POX). The POX fraction may also be determined directly by a variation of this test method.

3.2.6 *dissolved organic halides (DOX)*—when a sample containing some solid material is filtered or centrifuged and the liquid portion is analyzed, the result is called dissolved organic halides (DOX).

3.2.7 *suspended organic halides (SOX or SX)*—when the solid material is resuspended in TOX-free water and analyzed, the result is called suspended organic halides (SOX). Since this test method is not designed to specifically remove inorganic halides from suspended matter, this measurement may more properly be called suspended halides (SX). It should be noted that DOX and SX results are highly dependent upon the type of filtration or centrifugation process used.

4. Summary of Test Method

4.1 This test method consists of three steps. These are the following:

4.1.1 Adsorption of organics from water onto granular activated carbon (GAC) packed in microcolumns,

4.1.2 Desorption of inorganic halides by washing the GAC with nitrate solution, and

4.1.3 Combustion of sorbed organics along with the GAC,

[1] This test method is under the jurisdiction of ASTM Committee D-19 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] Belford, G., "Absorption on Carbon: Theoretical Considerations,'' *Environmental Science and Technology*, August 1980, p. 910.

[3] Dobbs, R., and Cohen, J., "Carbon Adsorption Isotherms for Toxic Organics," *EPA600/8-80-023*, April 1980, National Technical Information Center, Springfield, VA 22161.

[4] Fochtman, E., and Dobbs, R., *Adsorption of Carcinogenic Compounds by Activated Carbon, Activated Carbon Adsorption of Organics from the Aqueous Phase*, Vol 1, Ann Arbor Science, Ann Arbor, MI, p. 157.

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

followed by microcoulometric titration against silver ion of halides thus produced.

4.2 The procedure may be further detailed as follows:

4.2.1 First, sodium sulfite is added to a water sample to reduce any residual chlorine to chloride. The sample is then acidified to pH 2 with nitric acid to improve the adsorption of organics. Then, 100 mL of the acidified sample is forced at 3 mL/min through two glass columns in series. Each column contains 40 mg of granular activated carbon (100/200 mesh).

4.2.2 Second, the two GAC columns are washed with 2 mL of a reagent containing 5000 mg/L of nitrate ion in water. This reagent removes inorganic halides from GAC.

4.2.3 Third, after the adsorption and wash steps, each GAC portion is analyzed for halides using controlled atmosphere combustion and microcoulometric detection.

5. Significance and Use

5.1 Organic halides typically do not occur in natural waters at concentrations greater than 5 µg/L. A TOX level of greater than 5 µg/L is generally indicative of contamination by synthetic organics. Accordingly, this test method may be used to follow the occurrence, production, and removal of halogenated organic contaminants in water and wastewater.

5.2 When applied to chlorinated drinking water, this test method can be used to follow the production of TOX, which results from the chlorination of naturally occurring organics. The majority of these halogenated organics are not determined by gas chromatography.

5.3 When applied to wastewater, this test method can be used to follow the occurrence and removal of organic halides, many of which have been determined to be toxic.

5.4 When applied to waters from monitoring wells around hazardous waste dump sites, the measurement of dissolved organic halides (DOX) can be used to follow the movement of this class of contaminant through the groundwater system.

6. Interferences and Limitations

6.1 *Chloride Ion*—The nitrate wash step is effective for removing inorganic halide from the activated carbon. However, to minimize the impact of unremoved inorganics on the TOX results, the ratio of inorganic to organic halide concentration in the sample should not exceed 20 000.

6.2 *Halogens Other than Chlorine*—Fluorinated compounds are not detected by this test method, since they do not produce species titratable against silver ion.

6.2.1 Brominated and iodinated compounds make a contribution that is affected by two considerations:

6.2.1.1 The instrument is calibrated with a chlorinated compound, so no allowance is made for the different atomic mass of bromine and iodine;

6.2.1.2 Not all of these two elements are converted to titratable species. The combination of these effects results in about 25 % of the bromine and about 15 % of the iodine appearing as "chlorine.'' Brominated and iodinated organics are rarely found in water, so this recovery level is not usually of significance.

7. Apparatus

7.1 *Adsorption Apparatus*[6]—Arrange components of the adsorption apparatus in accordance with the schematic diagram in Fig. 1. The sample reservoir and the nitrate wash reservoir can be made from 25.4 mm outside diameter by 300-mm long standard wall stainless steel tubing. Interconnection of components can be made with swage-type tube fittings using O-ring ferrules and stainless steel or fluorocarbon tubing.

7.2 *Analyzer Apparatus*[7]—Analyzer apparatus consists of a boat inlet, high-temperature furnace capable of operating at 800°C and a microcoulometric titrator capable of measuring at least 100 ng of halide as hydrogen halide (HX) by silver ion titration, as shown schematically in Fig. 2.

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, where such specifications are available. [8] 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, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I.

NOTE 1—**Caution:** Water that conforms to this specification may still contain significant amounts of TOX (for example, 10 to 30 µg Cl/L). Accordingly, the TOX of the reagent water should be determined. This value should be taken into consideration when preparing standards and making sample dilutions.

[6] Adsorption Apparatus (Model AD-2) available from Dohrmann, Santa Clara, CA, has been found suitable. Also an equivalent may be used.

[7] Analyzer Apparatus (Model MC-1) available from Dohrmann, Santa Clara, CA, has been found suitable. Also an equivalent may be used.

[8] *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.

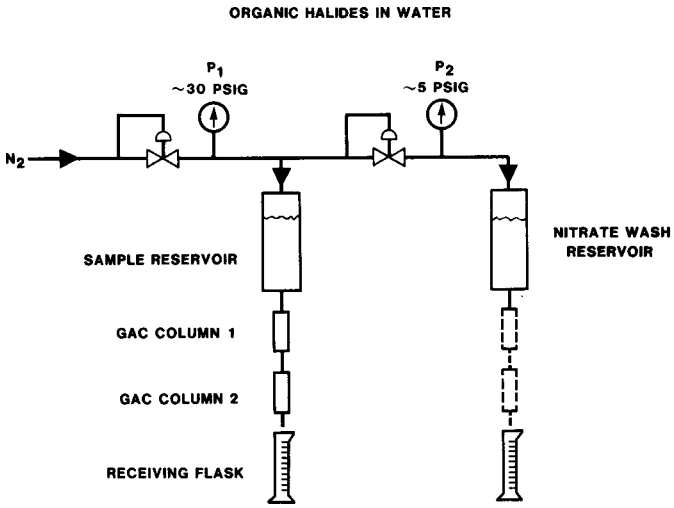

FIG. 1 Schematic of Adsorption Apparatus