Designation: D 4744 – 89 (Reapproved 1995)$^{\epsilon 1}$

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

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,

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[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.

Current edition approved Nov. 24, 1989. Published March 1990. Originally published as D 4744 – 87. Last previous edition D 4744 – 87.

[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.

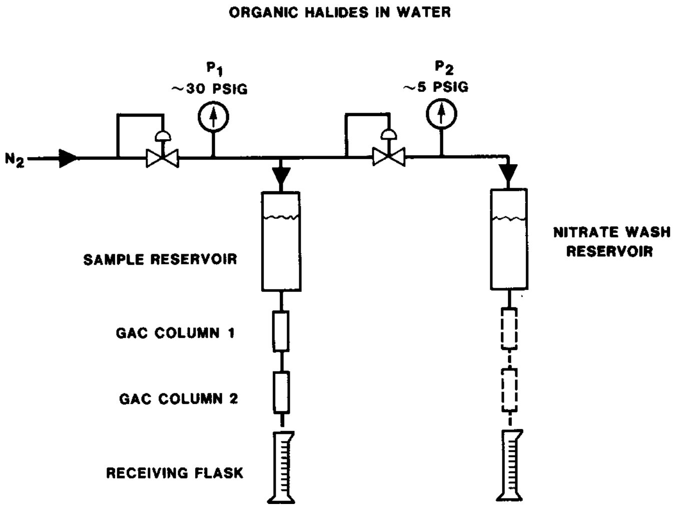

FIG. 1 Schematic of Adsorption Apparatus

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[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.

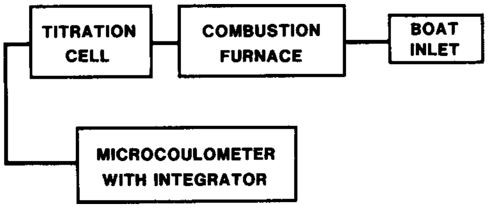

FIG. 2 Analyzer Apparatus

8.3 *Acetic Acid in Water,* 70 %—Dilute 7 volumes of acetic acid with 3 volumes of water.

8.4 *Carbon Dioxide*, purity 99.99 %.

8.5 *Cerafelt* [9] *Refractory Fiber Felt*—Form this material into plugs to hold the GAC in the adsorption columns.

NOTE 2—**Caution:** Be sure to rinse fingers of excess chlorides before forming plugs.

8.6 *Granular Activated Carbon* (100 to 200 mesh)[10]—The GAC used should meet the performance criteria outlined in Annex A1. The carbon as received should be ground and sieved. A100- to 200-mesh cut should be selected for use.

NOTE 3—**Caution:** Grind and sieve carbon in an area free of halogenated organic vapors. Also, protect the ground GAC from all sources of halogenated organic vapors.

8.7 *Granular Activated Carbon (GAC) Columns*—Place 40 mg of GAC (100 to 200 mesh) into each of two glass columns that are 2-mm inside diameter by 6-mm outside diameter by 50-mm long. Hold the GAC in place with plugs of refractory fiber felt.

NOTE 4—**Caution:** Protect these columns from all sources of halogenated organic vapors. Storage in TOX-free water is a good way to accomplish this.

8.8 *Nitrate Wash Solution* (5000 mg/L NO_3)—Prepare a nitrate wash solution by transferring approximately 8.2 g of potassium nitrate into a 1-L volumetric flask. Dilute to volume with water.

8.9 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid.

8.10 *Oxygen*, purity 99.99 %.

8.11 *Reagent Water*—Reserve a portion of the water used to prepare the calibration standard and any sample dilutions. The background TOX in this water should be determined and used in subsequent calculations.

8.12 *Sodium Sulfite Solution* (0.1 *M*)—Prepare a sodium sulfite solution by transferring approximately 10.3 g of sodium sulfite to a 1-L volumetric flask. Dilute to volume with water.

8.13 *Trichlorophenol Solution, Stock* (10 g Cl/L)—Prepare a stock solution by weighing accurately 1.856 g of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

8.14 *Trichlorophenol Calibration Standard* (1000 µg Cl/L)—Prepare a calibration standard by injecting 10 µL of stock solution into 1 L of reagent water.

9. Sampling and Sample Preservation

9.1 This sampling procedure assumes that both purgeable organic halides and residual chlorine may be present. Keep in mind that more than 100 mL (for example, 125 mL) of sample may be required for each replicate analysis.

9.2 Add to a suitably sized clean glass container a sufficient amount of nitric acid to bring the sample to an approximate pH of 2. Also, add sufficient sulfite solution to reduce any residual chlorine that may be present in the sample. This will typically be in the range of 0.2 mL/100 mL of sample. Collect a representative sample in the glass container, being careful to completely fill it. Cap the container with a screw cap that is lined either with aluminum foil or TFE-fluorocarbon to reduce sorption of slightly soluble organic halides.

9.3 If the sample cannot be analyzed within a few days, store it at 2 to 4°C to further ensure sample integrity. Maximum holding time should be 7 days.

10. Apparatus Adjustments

10.1 *Adsorption Apparatus*—Adjust gas pressures such that a water sample will move through the GAC adsorption columns at approximately 3 mL/min and that nitrate wash will flow through the GAC columns at approximately 0.5 mL/min.

10.2 *Analyzer Apparatus*—Follow manufacturer's instructions for operation of the analyzer apparatus.

11. Calibration Check

11.1 *TOX Blank*—Since the reagent water used may contain significant amounts of TOX it should not be depended upon to establish method blank. It has been found that the TOX of the GAC taken through the nitrate wash and halide determination steps can be used as a reliable measure of method blank. Accordingly, make replicate TOX measurements on 40-mg portions of GAC that have been put through the nitrate wash step. The average of these values should be used as C_3 in the calculation section. This procedure must be performed at least once a day, and preferably also at the end of a group of sample runs. If experience shows a substantial variation over this time interval, the blank determination must be made more often. The two pairs of blanks bracketing a set of samples should be averaged, and that value for C_3 applied to the sample set.

11.2 Make duplicate determinations of TOX in the calibration standard and the reagent water used to prepare the calibration standard. The net response to the calibration standard (TOX of calibration standard-TOX of reagent water) should be within 5 % of the prepared value of the calibration standard.

12. Procedure

12.1 Adjust pH of the sample to approximately 2 with concentrated nitric acid if not already done during sampling.

12.2 Add 0.2 mL of sulfite solution to every 100 mL of the sample to be analyzed if not already done during sampling.

12.3 Transfer more than 100 mL of treated sample to the sample reservoir and adjust P_1 to cause sample to flow at 3 mL/min through two GAC adsorption columns arranged in series. Continue until the required volume of the sample has flowed through the columns. Consult Table 1 for volume/range

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[9] Cerafelt supplied by Johns Manville Corp., Denver, CO 80217, has been found satisfactory. Also an equivalent may be used.

[10] Material (Catalog No. APC) supplied by Calgon Corp., Pittsburgh, PA, has been found suitable. Also an equivalent may be used.

TABLE 1 Volume/Range Recomendations

Volume Passed, mL	Optimum Range, µg/L	Workable Range,µ g/L
100	10 – 250	5 – 500
50	20 – 500	10– 1000
25	40 – 1000	20 – 2000

recommendations. Note the exact volume that has passed through the columns.

12.4 Fill the nitrate wash reservoir with nitrate wash solution and wash two GAC columns from 12.3 with 2 mL of nitrate wash solution. Adjust P_2 to cause nitrate wash to flow at approximately 0.5 mL/min.

12.5 Transfer the GAC in the first column contacted by the sample to the boat inlet and determine its halide content. Call this value C_1. Transfer the GAC in the second column contacted by the sample to the boat inlet and determine its halide content. Call this value C_2.

13. Calculation

13.1 Calculate the total organic halide (TOX) concentration of the sample as follows:

$$\text{TOX, µg/L} = (C_1 - C_3)/V + (C_2 - C_3)/V$$

where:

C_1 = halide content of first GAC column, µg Cl,
C_2 = halide content of second GAC column, µg Cl,
C_3 = average halide content of 40 mg of nitrate-washed GAC, and
V = volume of sample adsorbed, L.

13.1.1 Results may also be reported in terms of micromoles of halide per litre (µmol X/L) as follows:

$$\text{TOX, µmol X/L} = \text{TOX (µg Cl/L)}/35.46$$

NOTE 5—If $(C_2 - C_3)/V$ exceeds 10 % of $(C_1 - C_3)/V$, then the adsorption capacity of the first column has been exceeded. Repeat the determination with a smaller sample volume.

14. Precision and Bias [11]

14.1 *Precision*—A cooperative interlaboratory test of the test method was performed using concentrated stock solutions sent to 11 participating laboratories; inorganic halide was not added. The stock solutions consisted of methanol spiked with: (*1*) trichlorophenol plus Lindane; (*2*) trichlorophenol plus bromophenol; (*3*) trichlorophenol alone; and (*4*) chloroform alone. The laboratorties were directed to dilute 10 µL of the stock solutions to 1.00 L using laboratory reagent water, resulting in working solutions of strengths 11.0, 80.0, 210, and 899 µg Cl/L. These solutions were analyzed once on each of three successive days, by one analyst on one instrument. Not all results from all laboratories were acceptable by the criteria of Practice D 2777 – 86. The test yielded the following precisions (Fig. 3):

$$S_t = 0.08x + 1.9 \text{ for overall standard deviation}$$

$$S_o = 0.06x + 1.4 \text{ for single-operator standard deviation}$$

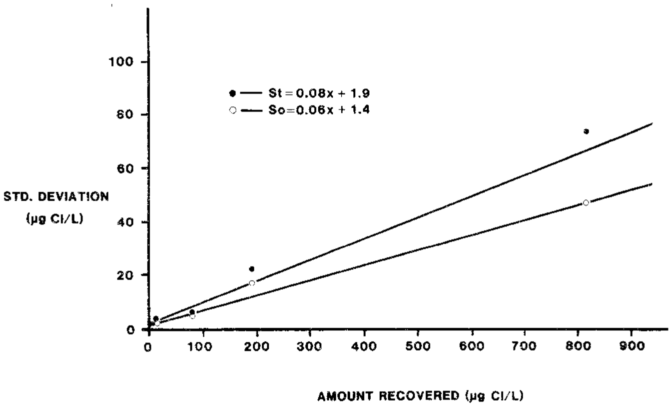

FIG. 3 Interlaboratory and Intralaboratory Precision

where:

x = average amount recovered.

14.2 *Bias*—The test method showed a bias of + 21 % at 10 µg Cl/L, insignificant bias at 80 µg Cl/L, and − 10 % bias at both 210 and 899 µg Cl/L (Fig. 4). This trend can be attributed to contamination from atmosphere or glassware in the low-level case, and to loss of relatively volatile spiking components during sample handling, at the higher levels.

14.3 *Matrix Effects*—Participants were asked to select a water of interest, analyze it, and then spike it to a level of 80 µg Cl/L with the concentrated solution supplied, and reanalyze. The samples varied from tap to waste to groundwater, with TOX levels ranging from 10 to 200 µg Cl/L. Average recovery was 76 µg Cl/L. No pattern emerged from the results. For other matrices, these data may not apply.

14.4 The QA/QC portion of this test method has not been completely established at this time. It is the intent of the ASTM subcommittee responsible for this test method that procedures be incorporated into this test method that require a minimum level of QC. These procedures will require, at a minimum, a method startup check and ongoing performance checks. The analysts performing the test method will be required to measure their performance against the performance level achieved by the laboratories that participated in the ASTM round robin study done on the method. These formal QC procedures will be incorporated at such time as they have been officially accepted by the Society.

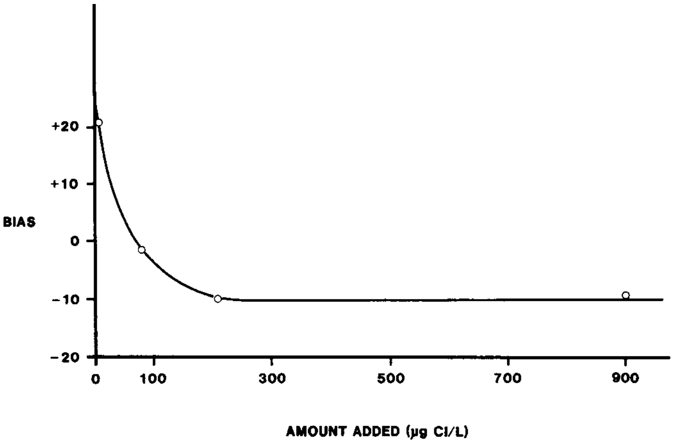

FIG. 4 Bias from TOX Interlaboratory Study

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[11] Supporting data are available from ASTM Headquarters. Request RR:D19 – 1028.

15. Keywords

15.1 activated carbon; adsorption; dissolved organic halides; DOX; microcoulometric; nonpurgeable organic halides; NPOX; organic halides; purgeable organic halides; POX; suspended organic halides; SOX; SX; total organic halides; TOX

ANNEX

(Mandatory Information)

A1. GRANULATED ACTIVATED CARBON

A1.1 The GAC required for this test method is probably one of the greatest sources of variability. Ideally, it should have very low apparent halide background, readily release any adsorbed inorganic halides upon nitrate washing, and reliably adsorb organic halides even in the presence of a large excess of other organics. Accordingly, check each new batch of GAC to be sure that it meets the following performance criteria:

A1.1.1 Upon combustion of 40 mg of GAC the apparent halide background should be less than 1.0 µg Cl equivalent or less.

A1.1.2 After flushing 40 mg of GAC with 2 mL of a 5000 mg/L nitrate solution, combustion of the GAC should yield an apparent halide background increase of less than 0.1 µg Cl equivalent over that determined in A1.1.1.

A1.1.3 After contacting 40 mg of GAC with 100 mL of water containing 100 mg/L of chloride ion and flushing the GAC with 2 mL of a 5000 mg/L nitrate solution, combustion of the GAC should yield an apparent halide background increase of less than 0.1 µg Cl equivalent over that determined in A1.1.2.

A1.1.4 Upon analyzing 100 mL of a water sample containing 5 mg/L of organic carbon from humic acids and 100 µg/L of chlorine from 2,4,6-trichlorophenol, more than 90 % (±2 %) of the organic halide should be recovered on the first 40-mg portion of GAC contacted and remaining 10 % recovered on the second 40-mg portion of GAC contacted.

A1.2 *Test Method Validation*—The following validation procedure should be carried out to confirm test method applicability to samples other than raw or finished drinking water:

A1.2.1 *Equivalent Recovery, Synthetic Standards*—Prepare a standard containing 5 mg/L organic carbon as the organic compounds normally occurring in the water to be analyzed, and 100 µg/L of halogen from the principal halogenated organics occurring in the water. The organic halide measured should be equal to the organic halide added, ±5 %, and more than 90 % of this should be recovered on the first 40-mg portion of GAC contacted.

A1.2.2 *Equivalent Recovery, Spiked Samples*—Spike samples of interest with standard solutions of the principal halogenated organics occurring in the water. Measured organic halide should be higher than that of the unspiked samples by the amount of standard added, ±5%, and more than 90 % of the total organic halides should be recovered on the first 40-mg portion of GAC contacted.

APPENDIX

(Nonmandatory Information)

X1. PRECISION AND BIAS STUDY OF U.S. EPA METHOD 450.1

X1.1 The U.S. Environmental Protection Agency has funded an independent, ten-laboratory study[12] of its Method 450.1, which is essentially the same as this test method. Data were analyzed according to ASTM principles. The study used four different matrix waters, and a mixture of four spiking compounds, for a TOX concentration range of about 40 to about 440 µg/L. For reagent water, the results were:

$$\textit{Bias:}\ 0.807c + 14.1$$

$$\textit{Overall Precision:}\ -0.0128x + 14.2$$

$$\textit{Single-Operator Precision:} -0.0092x + 12.7$$

where:

c = amount added, µg/L, and

x = amount recovered, µg/L.

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[12] *EPA Method Study 32: Method 450.1—Total Organic Halides*, prepared for Environmental Monitoring and Support Laboratory, by U.S. Environmental Protection Agency, Cincinnati, OH 45268, and available from U.S. National Technical Information Service, Springfield, VA 22161 as document PB86-136538.