Designation: D 6581 – 00 (Reapproved 2005)

Standard Test Method for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Chemically Suppressed Ion Chromatography[1]

This standard is issued under the fixed designation D 6581; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the determination of the oxyhalides - chlorite, bromate, and chlorate, and bromide, in raw water, finished drinking water and bottled (non-carbonated) water by chemically suppressed ion chromatography. The ranges tested using this method for each analyte were as follows:

Chlorite	20 to 500 µg/L
Bromate	5 to 30 µg/L
Bromide	20 to 200 µg/L
Chlorate	20 to 500 µg/L

The upper limits may be extended by appropriate sample dilution or by the use of a smaller injection volume. Other ions of interest, such as fluoride, chloride, nitrite, nitrate, phosphate, and sulfate may also be determined using this method. However, analysis of these ions is not the object of this test method.

1.2 It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 This test method is technically equivalent with Part B of U.S. EPA Method 300.1[2], titled "The Determination of Inorganic Anions in Drinking Water by Ion Chromatography".

1.4 *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:* [3]

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2777 Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water

D 5810 Standard Guide for Spiking into Aqueous Samples

D 5847 Standard Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions*—For definition of terms used in the test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *ion chromatography*—a form of liquid chromatography in which ionic constituents are separated by ion exchange then detected by an appropriate detection means, typically conductance.

3.2.2 *eluent*—the ionic mobile phase used to transport the sample through the chromatographic system.

3.2.3 *analytical column*—the ion exchange column used to separate the ions of interest according to their retention characteristics prior to detection.

3.2.4 *guard column*—a column used before the analytical column to protect it from contaminants, such as particulates or irreversibly retained material.

3.2.5 *analytical column set*—a combination of one or more guard columns, followed by one or more analytical columns used to separate the ions of interest. All of the columns in series then contribute to the overall capacity and resolution of the analytical column set.

3.2.6 *suppressor device*—an ion exchange based device that is placed between the analytical column set and the conductivity detector. Its purpose is to minimize detector response to the ionic constituents in the eluent, in order to lower background conductance; and at the same time enhance the conductivity detector response of the ions of interest.

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[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] U.S. EPA Method 300.1, Cincinnati, OH, 1997.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.7 *resolution*—the ability of an analytical column to separate the method analytes under specific test conditions.

4. Summary of Test Method

4.1 Oxyhalides (chlorite, bromate, and chlorate) and bromide in raw water, finished drinking water and bottled water are determined by ion chromatography. A sample (200 µL) is injected into an ion chromatograph and the pumped eluent (sodium carbonate) sweeps the sample through the analytical column set. Here, anions are separated from the sample matrix according to their retention characteristics, relative to the anions in the eluent.

The separated anions in the eluent stream then pass through a suppressor device, where all cations are exchanged for hydronium ions. This converts the eluent to carbonic acid, thus reducing the background conductivity. This process also converts the sample anions to their acid form, thus enhancing their conductivity. The eluent stream then passes through a conductivity cell, where they are detected. A chromatographic integrator or appropriate computer-based data system is typically used for data presentation.

4.2 The anions are identified based on their retention times compared to known standards. Quantification is accomplished by measuring anion peak areas and comparing them to the areas generated from known standards.

5. Significance and Use

5.1 The oxyhalides chlorite, chlorate, and bromate are inorganic disinfection by-products (DBPs) of considerable health risk concern worldwide. The occurrence of chlorite and chlorate is associated with the use of chlorine dioxide, as well as hypochlorite solutions used for drinking water disinfection. The occurrence of bromate is associated with the use of ozone for disinfection, wherein naturally occurring bromide is oxidized to bromate. Bromide is a naturally occurring precursor to the formation of bromate.

6. Interferences

6.1 Positive errors can be caused by progressive oxidation of residual hypochlorite and/or hypobromite in the sample to the corresponding chlorate and bromate. Furthermore, chlorite can also be oxidized to chlorate, causing negative errors for chlorite and positive errors for chlorate. These interferences are eliminated by the sample preservation steps outlined in 8.5. Chloride present at > 200 mg/L and carbonate present at > 300 mg/L can interfere with bromate determination. These interferences can be minimized, or eliminated, by the sample pretreatment steps outlined in 8.6. Fluoride and low molecular weight monocarboxylic acids, present at mg/L concentrations, may interfere with the quantitation of chlorite and bromate.

7. Apparatus

7.1 *Ion Chromatography Apparatus*—Analytical system complete with all required accessories, including eluent pump, injector, syringes, columns, suppressor, conductivity detector, data system and compressed gasses.

7.1.1 *Eluent Pump*—capable of delivering 0.25 to 5 mL/min of eluent at a pressure of up to 4000 psi.

7.1.2 *Injection Valve*—A low dead-volume switching valve that will allow the loading of a sample into a sample loop and subsequent injection of the loop contents into the eluent stream. A loop size of up to 200 µL may be used without compromising the resolution of early eluting peaks, such as chlorite and bromate.

7.1.3 *Guard Column*—Anion exchange column typically packed with the same material used in the analytical column, e.g., Dionex IonPac AG9-HC, or equivalent. The purpose of this column is to protect the analytical column from particulate matter and irreversibly retained material.

7.1.4 *Analytical Column*—Anion exchange column capable of separating the ions of interest from each other, as well as from other ions which commonly occur in the sample matrix, e.g., Dionex IonPac AS9-HC (4 mm ID), or equivalent. The separation shall be at least as good as that shown in Fig. 2. The use of 2 mm ID AS9-HC column, in conjunction with a 50 µL sample loop, may improve the peak shape for early eluting anions, such as chlorite and bromate.

NOTE 1—The Analytical Column Set (see 3.2.3) should be able to give baseline resolution of all anions, even for a 200 µL injection containing up to 200 mg/L, each, of common anions, such as chloride, bicarbonate, and sulfate.

7.1.5 *Suppressor Device*—A suppressor device based upon cation exchange principles. In this method, a membrane-based self regenerating suppressor device, Dionex ASRS-ULTRA, was used. An equivalent suppressor device may be used provided that comparable method detection limits are achieved and that adequate baseline stability is attained.

7.1.6 *Conductivity Detector*—A low-volume, flow through, temperaturestabilized conductivity cell equipped with a meter capable of reading from 0 to 1000 µS/cm on a linear scale.

7.1.7 *Data System*—A chromatographic integrator or computer-based data system capable of graphically presenting the detector output signal versus time, as well as presenting the integrated peak areas.

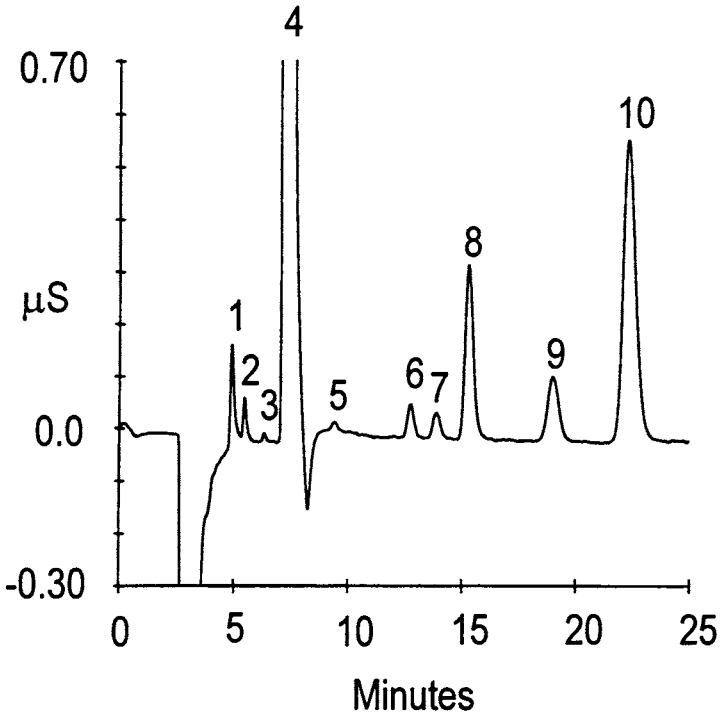
8. Reagents and Materials

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.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without reducing 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. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the determination.

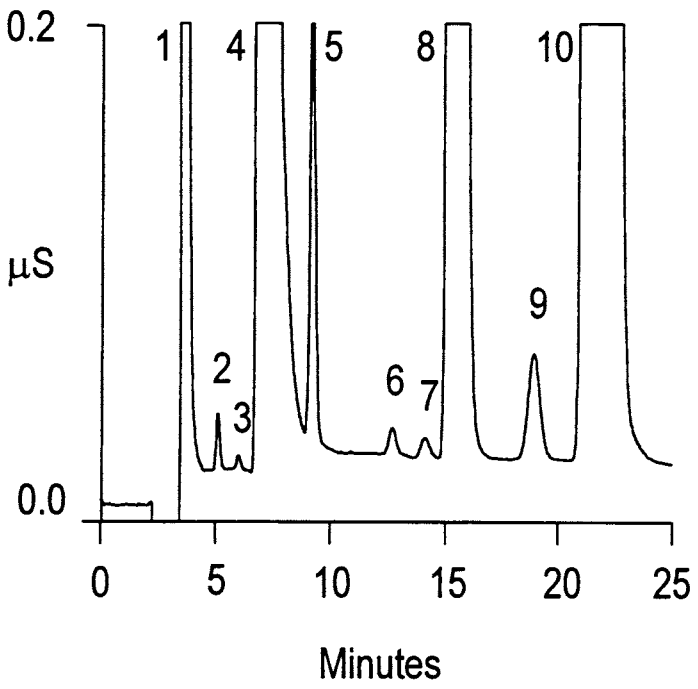
8.3 *Eluent, Concentrate (90.0 mM Sodium Carbonate)*—Dissolve 9.540 g of sodium carbonate in 1000 mL of water.

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory Chemicals," by BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopoeia."



	Peaks	mg/L
1.	Fluoride	-
2.	Chlorite	0.025
3.	Bromate	0.01
4.	Chloride	1.0
5.	Nitrite	-
6.	Bromide	0.04
7.	Chlorate	0.04
8.	Nitrate	0.2
9.	Phosphate	0.2
10.	Sulfate	0.4

FIG. 1 Chromatogram of a Standard Containing Low µg/L Oxyhalides, and Bromide, in the Presence of Common Inorganic Anions. See Table 1 for Analysis Conditions.



	Peaks	mg/L
1.	Fluoride	1.0
2.	Chlorite	0.01
3.	Bromate	0.005
4.	Chloride	50
5.	Nitrite	0.1
6.	Bromide	0.01
7.	Chlorate	0.01
8.	Nitrate	10
9.	Phosphate	0.1
10.	Sulfate	50

FIG. 2 Chromatogram of Low µg/L Oxyhalides, and Bromide, in Simulated Drinking Water. See Table 1 for Analysis Conditions.

8.4 *Eluent, Analysis (9.0 mM Sodium Carbonate)*—Dilute 100.0 mL of Eluent Concentrate (8.3) to 1.000 L with water.

8.4.1 The Eluent Analysis solution (9.0 mM Sodium Carbonate) must be purged for 10 minutes with helium prior to use to remove dissolved gasses in order to ensure optimal system performance.

8.5 *Ethylenediamine (EDA) Preservation Solution (50.0 g/L)*—Dilute 11.2 mL of ethylenediamine (99%) to 200 mL with reagent water. Prepare this solution fresh monthly. Add 1.00 mL of this solution per 1.000 L of blank, standard or sample to produce a final EDA concentration of 50 mg/L.