Designation: D6581 – 12

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

This standard is issued under the fixed designation D6581; 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.

1. Scope

1.1 These multi-test methods cover the determination of the oxyhalides—chlorite, bromate, and chlorate, and bromide, in raw water, finished drinking water and bottled (non-carbonated) water by chemically and electrolytically suppressed ion chromatography. The ranges tested using these test methods for each analyte were as follows:

	Range	Sections
Test Method A: Chemically Suppressed Ion Chromatography		8 to 20
Chlorite	5 to 500 µg/L	
Bromate	1 to 25 µg/L	
Bromide	5 to 250 µg/L	
Chlorate	5 to 500 µg/L	
Test Method B: Electrolytically Suppressed Ion Chromatography		21 to 31
Chlorite	20 to 1000 µg/L	
Bromate	1 to 30 µg/L	
Bromide	20 to 200 µg/L	
Chlorate	20 to 1000 µg/L	

1.1.1 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 these test methods. However, analysis of these ions is not the object of these test methods.

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

1.3 These test methods are 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 The values stated in either SI or inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

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:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in the test methods, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.2 *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.

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

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

[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 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.

3.2.5 *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.

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

3.2.7 *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.

3.2.7.1 *chemical suppression*—the use of an acid solution to the suppressor in order to suppress the background conductivity.

3.2.7.2 *electrolytic suppressor device*—electrolytic suppression is an ion exchange device that is placed between the analytical column and the conductivity detector. Its purpose is similar to a suppressor device, however, it does not require addition of acid. Instead the electrolytic suppressor generates protons electrolytically and plugs into an electrical power source on typically located on the chromatography device.

4. Significance and Use

4.1 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.

5. Reagents and Materials

5.1 *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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, 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.

6. Precautions

6.1 These test methods address the determination of very low concentrations of selected anions. Accordingly, every precaution should be taken to ensure the cleanliness of sample containers as well as other materials and apparatus that come in contact with the sample.

7. Sampling and Sample Preservation

7.1 Collect the sample in accordance with Practice D3370, as applicable.

7.2 Immediately upon taking the sample, sparge it with an inert gas (for example, nitrogen, argon, or helium) for 5 minutes to remove active gases such as chlorine dioxide or ozone. Add 1.00 mL of EDA Preservation Solution (see 15.3) per 1.000 litre of sample to prevent conversion of residual hypochlorite or hypobromite to chlorate or bromate. This also prevents metal catalyzed conversion of chlorite to chlorate. The oxyhalides in samples preserved in this manner are stable for at least 14 days when stored in amber bottles at 4°C.[5]

Test Method A
Chemically Suppressed Ion Chromatography

8. Scope

8.1 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 test method for each analyte were as follows:

Chlorite	5 to 500 µg/L
Bromate	1 to 25 µg/L
Bromide	5 to 250 µg/L
Chlorate	5 to 500 µg/L

8.1.1 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 test method. However, analysis of these ions is not the object of this test method.

8.2 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8.3 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."

8.4 *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.*

9. Summary of Test Method A

9.1 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

[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."

[5] Hautman, D. P., and Bolyard, M., *Journal of Chromatography*, Vol 602, 1992, p. 65.

column set. Here, anions are separated from the sample matrix according to their retention characteristics, relative to the anions in the eluent.

9.1.1 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.

9.2 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.

10. Interferences

10.1 Positive errors can be caused by progressive oxidation of residual hypochlorite or hypobromite, or both, 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 15.3. Chloride present at >200 mg/L can interfere with bromate determination.

11. Apparatus

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

11.1.1 *Eluent Pump*—Capable of delivering 0.10 to 5.0 mL/min of eluent at a pressure of up to 4000 psi (27600 kPa).

11.1.2 *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 50 µL may be used without compromising the resolution of early eluting peaks, such as chlorite and bromate.

11.1.3 *Guard Column*—Anion exchange column typically packed with the same material used in the analytical column. The purpose of this column is to protect the analytical column from particulate matter and irreversibly retained material.

11.1.4 *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. The separation shall be at least as good as that shown in Fig. 1. Conditions of the eluent may vary by column manufacturer.

NOTE 1—The Analytical Column Set (see 3.2.2) should be able to give baseline resolution of all anions, even for a 50 µL injection containing up to 200 mg/L, each, of common anions, such as chloride, bicarbonate, and sulfate.

11.1.5 *Suppressor Device*—A suppressor device based upon cation exchange principles. In this test method, simultaneously regenerating suppressor device with sequential carbonate remover was used. An equivalent suppressor device may be used provided that comparable method detection limits are achieved and that adequate baseline stability is attained.

11.1.6 *Conductivity Detector*—A low-volume, flow through, temperature stabilized conductivity cell equipped with a meter capable of reading from 0 to 15 000 µS/cm on a linear scale.

11.1.7 *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.

12. Example of Chromatogram—IC Conditions—1

12.1 See Fig. 1, Fig. 2, and Table 1.

13. Example of Chromatogram—IC Conditions—2

13.1 A carbonate removal device is developed to remove the majority of the carbonate from the eluent and allow hydroxide-like performance with improved detection sensitivity. This

Peak No	Component	Concentration mg/L
1	Fluoride	4.0
2	Chlorite	0.002
3	Bromate	0.001
4	Chloride	50.0
5	Nitrite	0.5
6	Bromide	0.010
7	Chlorate	0.010
8	Nitrate	50.0
9	Phosphate	10.0
10	Sulfate	50.0

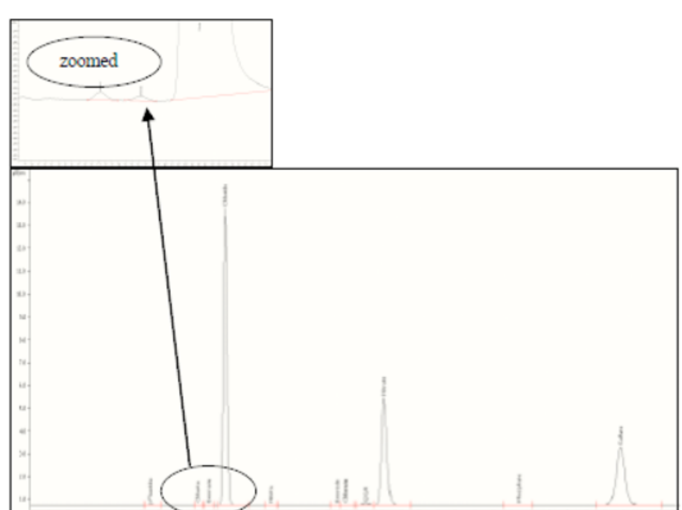


FIG. 1 Chromatogram of a Standard Containing Low µg/L Oxyhalides, and Bromide, in the Presence of Common Inorganic Anions (See Table 1 for Analysis Conditions)

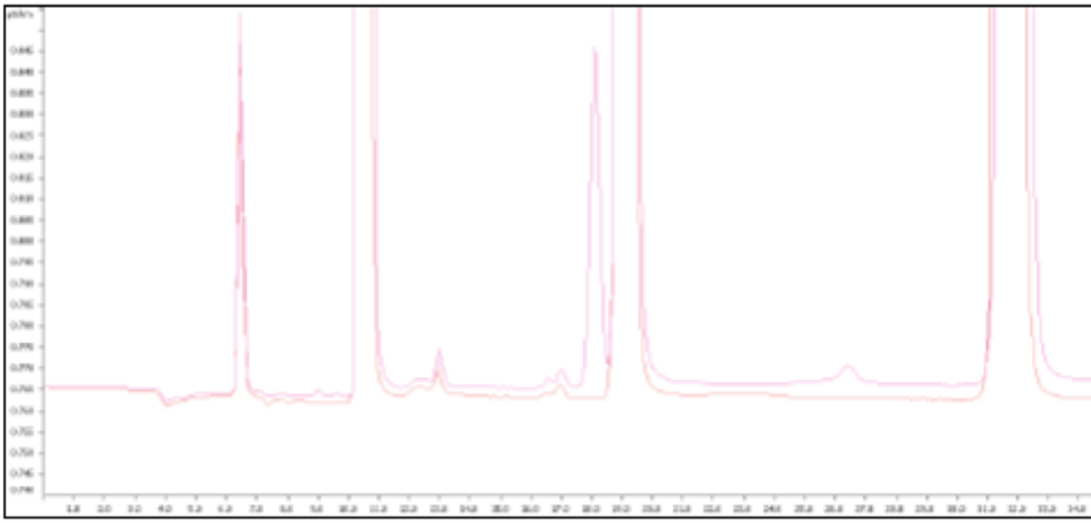


FIG. 2 Overlay Chromatogram Spiked and Unspiked of Low µg/L Oxyhalides, and Bromide, in Houston, TX, Drinking Water (See Table 1 for Analysis Conditions)

TABLE 1 Instrumentation[A] and Operating Conditions for the Determination of Oxyhalides and Bromide and by Ion Chromatography, as shown in Figs. 1 and 2

Ion Chromatograph:	Metrohm 850 Professional IC[A] (or equivalent)
Guard Column:	Metrosep ASUPP4/5[A] (or equivalent)
Analytical Column:	Metrosep ASUPP7[A] (or equivalent)
Eluent:	3.5 mM Sodium carbonate
Flow-Rate:	0.7 mL/min
Injection Volume:	50 µL
Suppressor:	Metrohm MSM-II[A] (Tri-Chamber Micro-packed) or equivalent coupled sequentially with MCS[B]
Detector:	Conductivity Detector stabilized at 40°C

[A] Metrohm AG, Switzerland.
[B] MCS is a carbonate suppressor device that permits use of carbonate/bicarbonate buffer based eluent in ion chromatography to achieve greater sensitivity and better detection limits.

device, the CRD-300, was used with the IonPac AS23 to determine bromate in a bottled mineral water samples. This data shows the improved detection sensitivity when using the CRD-300 compared to chromatography without the CRD-300. Scientists responsible for water analysis can chose the column and eluent chemistry that best meets their needs to reliably determine bromate at concentrations below the common 10 µg/L regulatory limit.

Conditions
Condition A with and without CRD-300

Column:	IonPac AS23 (4 × 250 mm)
	IonPac AG23 (4 × 50 mm)
Eluent:	4.5 mM K_2CO_3 / 0.8 mM $KHCO_3$
Flow rate:	1.0 mL/min
Suppressor:	Suppressed conductivity ASRS-300, 4 mm External water mode,
	CRD-300 4 mm, Vacuum mode
Background:	<1.5 µS
Noise:	~0.3 nS

13.2 See Fig. 3, Fig. 4, Table 2, Table 3, and Table 4.

14. Preparation of Apparatus

14.1 Set up the ion chromatograph according to the manufacturer's instructions. If an Anion Self Regenerating Suppressor is used, operate the device at 100 mA in the external water mode. The conductivity detector cell should be thermally stabilized at 35°C.

14.2 The recommended operating conditions for the ion chromatograph are summarized in Table 1.

14.3 The detector ranges are variable. Normal operating ranges for quantifying the low level of oxyhalides encountered in treated drinking water are in the 0.2 to 2 µS/cm full scale range. Choose a range consistent with the concentration range in the expected samples and with the operating requirements of the chromatographic system used.

14.4 Equilibrate the chromatographic system by pumping the analysis eluent (see 15.2) through the system until a stable baseline is obtained (approximately 20 minutes). Typical baseline characteristics necessary to obtain the method detection limits required for this analysis are: *(1)* a background conductance of 20 to 25 µS/cm and *(2)* a peak-to-peak (noise) variation of no greater than 5 nS/cm per minute of monitored baseline response.

15. Reagents and Materials

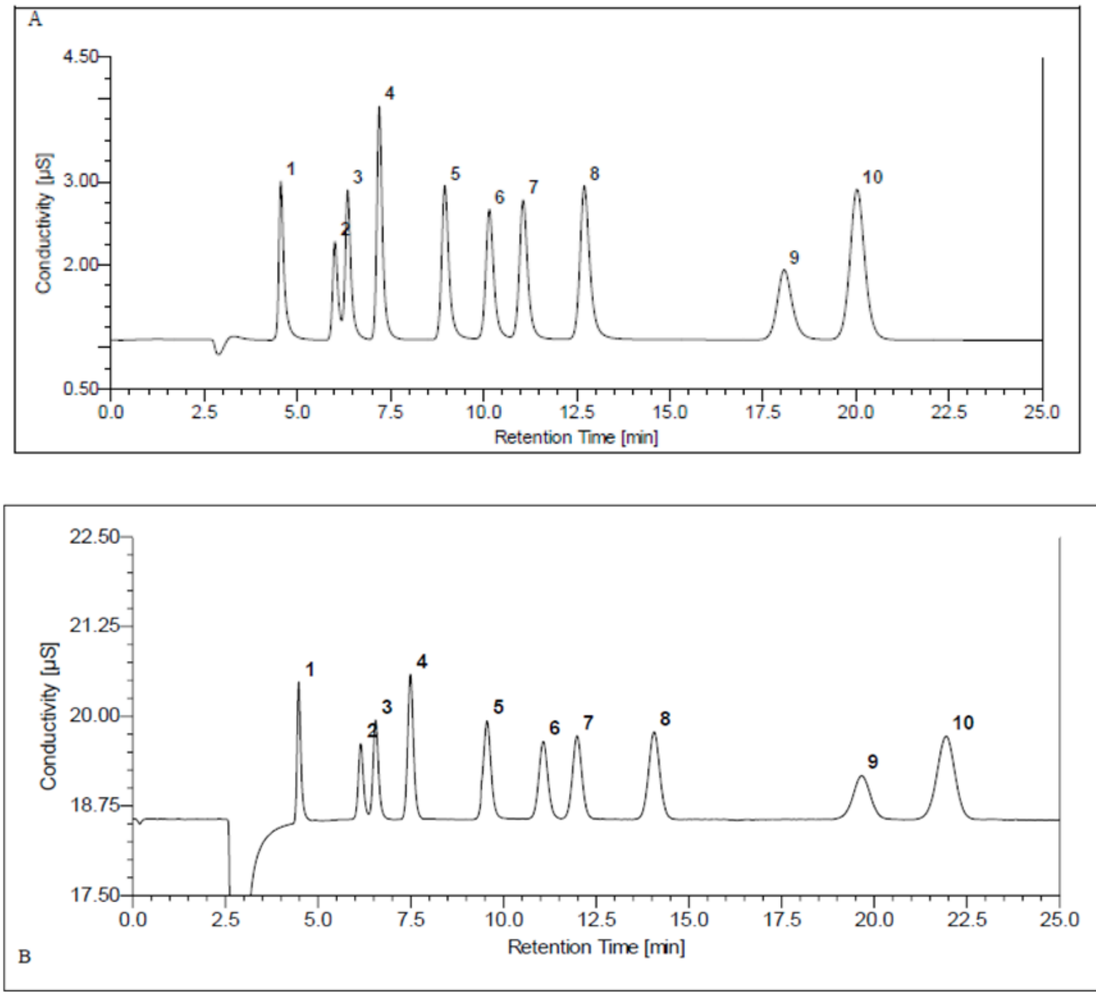
15.1 *Eluent, Concentrate (90.0 mM Sodium Carbonate)*—Dissolve 9.540 g of sodium carbonate in 1000 mL of water.

15.2 *Eluent, Analysis (9.0 mM Sodium Carbonate)*—Dilute 100.0 mL of Eluent Concentrate (see 15.1) to 1.000 L with water.

15.2.1 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.

15.3 *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.

15.4 *SPE Sample Pretreatment Cartridges*—Chloride present at >200 mg/L and carbonate present at >300 mg/L can



NOTE 1—Peaks:

1. Fluoride (0.1 mg/L)
2. Chlorite (0.3 mg/L)
3. Bromate (0.6 mg/L)
4. Chloride (0.2 mg/L)
5. Nitrite (0.3 mg/L)
6. Chlorate (0.5 mg/L)
7. Bromide (0.5 mg/L)
8. Nitrate (0.5 mg/L)
9. Phosphate (0.8 mg/L)
10. Sulfate (0.6 mg/L)

FIG. 3 Chromatography of a Mixed Anion Standard with a CRD-300 (A) and without a CRD-300 (B)

interfere with bromate determination. H^+ form and Ag^+ form cation exchange SPE cartridges can be used to minimize the carbonate and chloride interferences, respectively, if required. OnGuard-H and OnGuard-Ag cartridges have been shown to be suitable for this application.[6] The use of these pretreatment cartridges will effect recoveries for bromide, requiring that it be analyzed in a separate run.

15.5 *Suppressor Regenerant Solution*—If a suppressor requiring chemical regeneration is used, the regenerant solution is prepared by cautiously adding 3.00 mL of concentrated sulfuric acid (sp. gr. 1.84) to 4.000 L of water. If an Anion Self Regenerating Suppressor is used, it should be operated in the external water mode.

[6] Joyce, R. J., and Dhillon, H. J., *Chromatography*, Vol 671, 1994, p. 165.

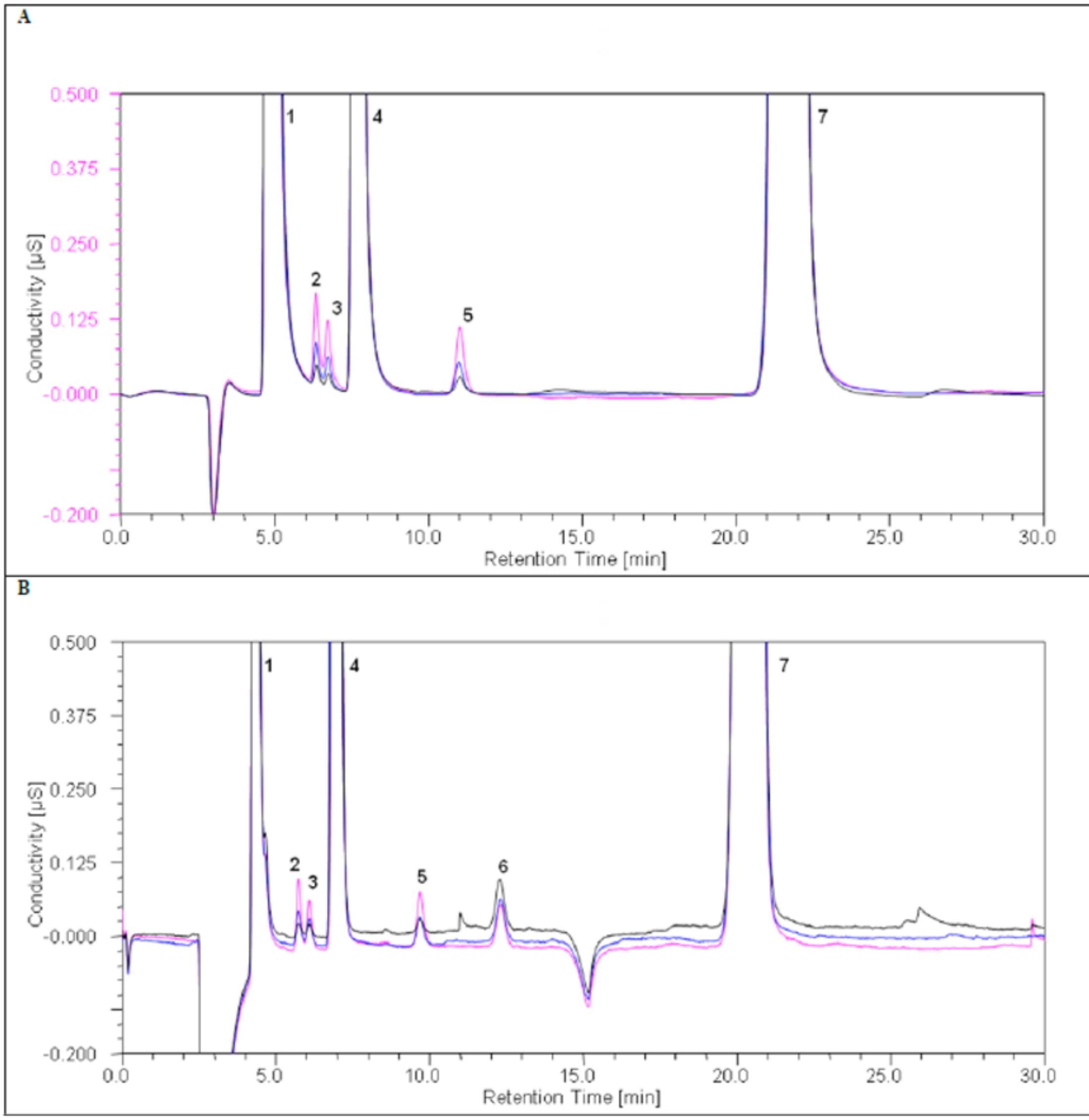
15.6 *Standard Solutions, Stock (1.00 mL = 1.00 mg)*—Purchase certified solutions or prepare stock standard solutions from the following salts, as described below:

15.6.1 *Bromate (BrO_3^-) Solution, Stock (1.00 mL = 1.00 mg BrO_3^-)*—Dissolve 1.180 g of sodium bromate ($NaBrO_3$) in water and dilute to 1.000 L.

15.6.2 *Bromide (Br^-) Solution, Stock (1.00 mL = 1.00 mg Br^-)*—Dissolve 1.288 g of sodium bromide (NaBr) in water and dilute to 1.000 L.

15.6.3 *Chlorate (ClO_3^-) Solution, Stock (1.00 mL = 1.00 mg $C1O_3^-$)*—Dissolve 1.275 g of sodium chlorate ($NaClO_3$) in water and dilute to 1.000 L.

15.6.4 *Chlorite (ClO_2^-) Solution, Stock (1.00 mL = 1.00 mg ClO_2^-)*—Dissolve 1.680 g of sodium chlorite ($NaClO_2$) in water and dilute to 1.000 L. Note that as sodium chlorite is



NOTE 1—Peaks:

1. Fluoride (0.5 mg/L)
2. Chlorite (10, 20 and 40 µg/L)
3. Bromate (10, 20 and 40 µg/L)
4. Chloride (50 mg/L)
5. Chlorate (10, 20 and 40 µg/L)
6. Unknown
7. Sulfate (100 mg/L)

FIG. 4 Overlay of Chromatograms of Three Concentration Levels of Chlorite, Bromate, and Chlorate in a Mixed Anion Standard with a CRD-300 (A) and without a CRD-300 (B)

TABLE 2 Calibration Report for Chlorite, Bromate, and Chlorate with a CRD-300 (A) and without a CRD-300 (B)

Peak Name	Points	R-Square (%)	
		A	
Chlorite	3	99.9961	99.9748
Bromate	3	100.0000	99.9986
Chlorate	3	99.9995	99.9637

usually available only as an 80 % technical grade salt, the 80 % purity is accounted for in the 1.680 g weight cited above. If an alternate purity is used, make an appropriate adjustment in the weight of salt used after determining the exact percentage of $NaClO_2$, which can be done using an iodometric titration procedure.[2,7]

15.7 *Reagent Blank*—Add 1.00 mL of EDA Preservation Solution (see 15.3) to 1.000 L of reagent water.

[7] Method 4500–ClO_2.C in A. E. Greenberg, L. S. Clesceri, A. D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., APHA, Washington, DC, 1992.

TABLE 3 Determination of Bromate and Chlorate in a Bottled Mineral Water Sample

Injection No.	A (µg/L)		B (µg/L)	
	Bromate	Chlorate	Bromate	Chlorate
1	11.0	1.52	5.33	ND
2	10.9	1.55	6.23	ND
3	10.9	1.35	5.02	ND
4	10.1	1.91	6.25	ND
5	11.3	1.48	5.89	ND
Average	10.8	1.56	5.74	—
RSD	4.34	13.42	9.61	—

TABLE 4 Spike Recovery of Bromate, Chlorate, and Chlorite in Mineral Water Using a System with a CRD-300 (A) and without a CRD-300 (B)

Injection No.	A (µg/L)			B (µg/L)		
	Chlorite	Bromate	Chlorate	Chlorite	Bromate	Chlorate
Sample	ND[A]	10.83	1.56	ND	5.74	ND
Spike	10	10	10	10	10	10
Measured[B] Amount	9.88	20.51	12.02	8.58	15.30	8.50
RSD	2.39	1.60	2.45	2.39	1.60	2.45
Recovery (%)	98.8	98.5	104	85.8	97.2	85.0

[A] ND = Not Detected
[B] The average of five injections.

16. Calibration and Standardization

16.1 *Typical Range of Applicability*—This test method is applicable to the determination of bromate, bromide, chlorate, and chlorite in raw water, finished drinking water and bottled (non-carbonated) water. The application ranges tested for each analyte are as follows: bromate; 5–30 µg/L, bromide; 20–200 µg/L, chlorite; 20–500 µg/L, and chlorate; 20–500 µg/L.

16.2 *Calibration Standards*—For each individual calibration curve, prepare calibration standards, at a minimum of three concentration levels, by accurately adding measured volumes of the stock standards (see 15.6) to a volumetric flask(s). Add 50 mg/L of EDA (the equivalent of 1.00 mL of EDA Preservation Solution (see 15.3) per 1.000 L of solution) to the volumetric flask(s) and dilute to volume with reagent water. A minimum of five concentration levels is recommended if the curve covers two orders of magnitude.

16.3 *Calibration Curve*—To establish the calibration curve, analyze a reagent blank and the calibration standards in accordance to the procedure in Section 17, using a 200 µL injection (with a 4 mm ID column) or a 50 µL injection (with a 2 mm ID column). Tabulate peak area responses against concentration. These results are used to prepare a calibration curve using a linear least squares fit for each analyte. The squared correlation coefficient of the regression (r^2) should be ≥ 0.995 for accurate results. Once the calibration curves have been established, verification must be performed on each analysis day, whenever fresh eluent is prepared, and twice each batch of samples, as outlined in 20.4 and 20.5.

17. Procedure

17.1 Inject the reagent blank, calibration standard or sample into the eluent stream and record the chromatogram. In the case of a manual injector, flush an excess of the sample (minimum of 5x loop volume) through the sample injection port using a syringe prior to injection. A 200-µL injection is required when using a 4 mm ID column, a 50 µL injection is required when using a 2 mm ID column, in order to achieve the required detection limits for this analysis. An example of a chromatogram of low level oxyhalides and bromide is shown in Fig. 1. An example chromatogram of low level oxyhalides and bromide in a modest ionic strength, simulated drinking water is shown in Fig. 2.

18. Calculation

18.1 Compare the peak areas for the anions in the sample to the calibration curves prepared in 16.3 to calculate and report the anion concentration in µg/L:

$$\text{Anion concentration, } \mu g/L = A \times F \quad (1)$$

where:

A = reading from the appropriate calibration plot, in µg/L, and
F = dilution factor if the sample was diluted prior to analysis.

18.1.1 Computing integrators and computer based chromatographic data systems can be programmed to perform these calculations automatically.

18.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

19. Precision and Bias

19.1 The precision and bias data presented in this test method meets the requirements of Practice D2777 – 98, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 06, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods. The full research report can be obtained from ASTM Headquarters.[8]

19.2 The interlaboratory study that generated the precision and bias data in this test method was performed in reagent water, municipal drinking water, and bottled (non-carbonated) water by ten laboratories using one operator each. Six levels of concentration were used for four analytes, producing three Youden pairs. The Youden pair data was used to calculate the single operator precision (S_o). The analytes were supplied separately as six (mixed) concentrates. The reagent water, municipal drinking water and bottled water were supplied by the participating laboratories. Six reagent water samples, six bottled water samples, and six municipal drinking water samples (for a total of 18 samples) were prepared by pipetting 1.0 mL aliquots of the concentrates labeled A1-2 (×3), B1-2 (×3), C1-2 (×3) into volumetric flasks (18 total); adding 50 mg/L EDA preservation solution, as detailed in 7.2, and diluting to a total of 100 mL with reagent water (×6), bottled water (×6), and drinking water (×6), as appropriate.

19.2.1 A quality control (QC) sample was supplied (as a concentrate) to serve as initial, and on-going, calibration verification. A separate method detection limit (MDL) sample was supplied (as a concentrate) for the determination of the pooled MDL values. The QC sample was prepared by pipetting a 1.0 mL aliquot of the QC concentrate into a clean volumetric flask; adding 50 mg/L EDA, and diluting to a total of 100 mL with reagent water. The MDL sample was prepared by pipetting a 1.0 mL aliquot of the MDL concentrate into a clean volumetric flask; adding 50 mg/L EDA, and diluting to a total of 100 mL with reagent water.

19.3 All the precision and bias data presented in this test method was obtained using the IonPac AS9-HC column listed in Table 1.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1164. Contact ASTM Customer Service at service@astm.org.

19.4 The precision and bias of this test method for each analyte for reagent, drinking, and bottled water are shown in Tables 5-8.

19.5 The results of the interlaboratory study can also be summarized as regression equations, as shown in Table 9 for reagent water and in Table 10 for a typical sample matrix of drinking water.

19.6 In addition to performing the analyses required to generate the precision and bias data shown in Tables 5-8, the participating laboratories each analyzed seven replicates of an MDL sample. The MDLs were derived for each laboratory using the students *t*-test at six degrees of freedom, as follows:

$$MDL = (t) \times (S) \quad (2)$$

where:

t = students t value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates], and

S = standard deviation of the replicate analysis.[8]

19.6.1 True amounts injected, mean value determined, and pooled MDL values (10 laboratories × 7 replicates) are shown in Table 11.

20. Quality Control

20.1 Before this test method is applied to analyzing unknown samples, the analyst should establish quality control procedures as recommended in Guide D3856.

20.2 The laboratory using this test should perform an initial demonstration of laboratory capability. Analyze seven replicates of an Initial Demonstration of Performance (IDP) solution. The IDP solution contains method analytes of known concentration, prepared from a different source to the calibration standards, used to fortify reagent water, which also contains a final EDA concentration of 50 mg/L (see 15.3). Ideally, the IPD solution should be prepared by an independent source from reference materials. The level 3 standard used for the method precision and bias study is recommended as an IDP solution.

TABLE 5 Determination of Precision and Bias for Chlorite

Water	Amount Added (µg/L)	Amount Found (µg/L)	Number Retained Parts	S_o (µg/L)	S_t (µg/L)	Bias (%)
Reagent	20	19.94	8	1.40	1.25	–0.3
	25	25.06			1.05	0.2
	180	178.29	8	4.37	5.64	–1.0
	220	214.73			6.18	–2.4
	400	394.36	8	19.39	21.81	–1.4
	450	440.53			8.29	–2.1
Drinking	20	19.19	8	1.52	6.58	–4.1
	25	23.77			6.17	–4.9
	180	174.30	8	5.06	9.29	–3.2
	220	216.89			14.76	–1.4
	400	398.30	8	4.42	15.56	–0.4
	450	439.85			19.59	–2.3
Bottled	20	20.94	8	4.41	3.65	4.7
	25	22.74			4.64	–9.0
	180	177.71	8	2.95	8.76	–1.3
	220	216.16			8.74	–1.7
	400	390.14	8	9.53	13.65	–2.5
	450	433.72			15.30	–3.6

TABLE 6 Determination of Precision and Bias for Bromate

Water	Amount Added (µg/L)	Amount Found (µg/L)	Number Retained Parts	S_o (µg/L)	S_t (µg/L)	Bias (%)
Reagent	5	4.95	9	0.99	1.19	–0.9
	7	7.84			1.29	12.0
	10	9.98	9	0.66	0.99	–0.2
	12	11.76			0.55	–2.0
	20	19.56	9	2.17	2.37	–2.2
	25	24.18			1.53	–3.3
Drinking	5	4.41	6	0.62	1.20	–11.8
	7	6.44			0.78	–8.0
	10	8.54	8	0.72	2.88	–14.6
	12	10.20			2.88	–15.0
	20	17.31	8	2.80	2.85	–13.4
	25	20.51			4.77	–17.9
Bottled	5	4.95	6	1.09	1.51	–1.1
	7	7.21			1.80	3.0
	10	9.07	6	1.67	4.83	–9.3
	12	10.35			3.41	–13.7
	20	20.16	6	4.34	3.91	0.8
	25	20.99			7.75	–16.0

TABLE 7 Determination of Precision and Bias for Bromide

Water	Amount Added (µg/L)	Amount Found (µg/L)	Number Retained Parts	S_o (µg/L)	S_t (µg/L)	Bias (%)
Reagent	20	20.75	9	1.94	1.91	3.8
	25	25.51			2.32	2.1
	75	74.52	9	3.80	2.94	–0.6
	100	99.42			4.84	–0.6
	150	143.50	9	5.79	5.82	–4.3
	180	176.38			5.24	–2.0
Drinking	20	20.68	8	1.30	4.39	3.4
	25	25.49			3.31	2.0
	75	71.89	8	4.67	5.67	–4.2
	100	97.05			6.90	–3.0
	150	145.81	8	1.23	8.39	–2.8
	180	173.40			9.12	–3.7
Bottled	20	20.25	7	2.21	1.79	1.3
	25	26.23			1.11	4.9
	75	74.35	8	6.45	4.69	–0.9
	100	98.49			5.00	–1.5
	150	142.67	8	6.57	6.08	–4.9
	180	172.71			9.24	–4.1

TABLE 8 Determination of Precision and Bias for Chlorate

Water	Amount Added (µg/L)	Amount Found (µg/L)	Number Retained Parts	S_o (µg/L)	S_t (µg/L)	Bias (%)
Reagent	20	20.69	7	2.73	2.43	3.5
	25	26.64			3.79	6.6
	180	176.05	8	11.96	3.70	–2.2
	220	215.39			7.47	–2.1
	400	393.00	7	18.27	5.85	–1.7
	450	443.47			16.50	–1.5
Drinking	20	19.94	9	1.81	3.95	–0.3
	25	23.93			5.13	–4.3
	180	175.10	9	6.92	9.05	–2.7
	220	216.14			7.02	–1.8
	400	396.74	9	4.74	16.55	–0.8
	450	441.69			16.55	–1.8
Bottled	20	21.72	8	2.86	3.88	8.6
	25	25.75			3.21	3.0
	180	179.82	8	3.59	5.37	–0.1
	220	217.58			9.26	–1.1
	400	389.51	7	6.72	15.83	–2.6
	450	443.70			10.00	–1.4

20.2.1 The mean and standard deviation of the seven values should then be calculated and compared, according to Practice D5847, to the single operator precision and recovery established for this test method. The upper limit for acceptable precision and the range of acceptable recoveries are detailed below:

TABLE 9 Summary of Precision and Bias Results for Reagent Water

	Chlorite Precision and Bias Summary	Bromate Precision and Bias Summary	Bromide Precision and Bias Summary	Chlorate Precision and Bias Summary
Number of Laboratories	10	10	10	10
Range Tested	20–450 µg/L	5–25 µg/L	20–180 µg/L	20–450 µg/L
Mean Recovery	y = 0.9805x + 0.5261	y = 0.9432x + 0.6272	y = 0.9629x + 1.7475	y = 0.9809x + 0.8245
S_o	y = 0.0465x – 1.4801	y = 0.0878x + 0.1281	y = 0.0282x + 1.3087	y = 0.0389x + 2.7278
S_t	y = 0.0332x + 0.3294	y = 0.046x + 0.721	y = 0.0246x + 1.6352	y = 0.0226x + 1.8244

TABLE 10 Summary of Precision and Bias Results for Drinking Water

	Chlorite Precision and Bias Summary	Bromate Precision and Bias Summary	Bromide Precision and Bias Summary	Chlorate Precision and Bias Summary
Number of Laboratories	10	10	10	10
Range Tested	20–450 µg/L	5–25 µg/L	20–180 µg/L	20–450 µg/L
Mean Recovery	y = 0.9872x – 1.0243	y = 0.9432x + 0.6272	y = 0.9583x + 1.2113	y = 0.9868x – 0.7347
S_o	y = 0.0068x + 2.2164	y = 0.1721x – 0.5532	y = –0.0022x + 2.6	y = 0.0066x + 3.0956
S_t	y = 0.0289x + 5.8552	y = 0.1934x + 0.3866	y = 0.0357x + 3.1189	y = 0.03x + 3.3368

TABLE 11 Pooled MDL Values Obtained for This Test Method

Analyte	Injected Amount	Mean Value	Pooled MDL
Chlorite	3.0 µg/L	3.32 µg/L	2.39 µg/L
Bromate	4.0 µg/L	3.98 µg/L	2.73 µg/L
Bromide	4.0 µg/L	3.96 µg/L	2.91 µg/L
Chlorate	4.0 µg/L	3.74 µg/L	3.49 µg/L

Analyte	IDP Solution Amount	Method S_o	Acceptable IDP Precision, n = 7
Chlorite	180 µg/L	4.4 µg/L	≤ 11.8 µg/L
Bromate	10 µg/L	0.66 µg/L	≤ 1.67 µg/L
Bromide	75 µg/L	3.8 µg/L	≤ 9.6 µg/L
Chlorate	180 µg/L	12.0 µg/L	≤ 32.1 µg/L

Analyte	Method Mean Recovery	Lower Acceptable IDP Recovery	Upper Acceptable IDP Recovery
Chlorite	178.3 µg/L	164.6 µg/L	191.7 µg/L
Bromate	9.98 µg/L	7.37 µg/L	12.59 µg/L
Bromide	74.5 µg/L	70.8 µg/L	78.2 µg/L
Chlorate	176.1 µg/L	171.2 µg/L	181.0 µg/L

20.2.2 The S_o and mean recovery values can be calculated for different IDP solution concentrations using the regression equations for each analyte shown in Table 9. If the values obtained for the IDP precision and recovery do not meet the criteria described above, initial demonstration of performance must be repeated until the results fall within these criteria.

20.3 When beginning use of this method, an initial Calibration Verification Standard (CVS) should be used to verify the calibration standards and acceptable instrument performance. This verification should be performed on each analysis day or whenever fresh eluent has been prepared. As this method is intended for use at trace levels, a low level CVS (that is, equivalent to the lowest calibration standard) should initially be analyzed before beginning use of this method. The CVS is a solution of method analytes of known concentration used to fortify reagent water, which also contains a final EDA concentration of 50 mg/L (see 15.3). If the determined low level CVS values are not within ±25 % of the known amounts, the low level CVS should be reanalyzed. If the values still fall outside acceptable limits, a new calibration curve is required which must be confirmed by a successful low level CVS before continuing with on-going analyses.

20.4 A continuing CVS should be analyzed after every tenth field sample and an end CVS should analyzed at the end of the sample batch (maximum of 20 samples) to verify the previously established calibration curves. After initially meeting the requirements of 20.3, the levels selected for the continuing and end CVS should be varied between a middle calibration level and the highest calibration level standard. If the continuing and end CVS values are not within ±15 % of the known amounts, the analyst should reanalyze the CVS. If the analyte concentrations still fall outside acceptable limits (±15 %) that analyte is judged out of control, and the source of the problem should be identified before continuing with on-going analyses. All samples following the last acceptable CVS should be reanalyzed.

20.5 A reagent blank (see 15.7) should be run when generating the initial calibration curves. A blank should also be run with each sample batch (maximum of 20 samples) to check for sample or system contamination.

20.6 One Laboratory Control Sample (LCS) should be used with each sample batch (maximum of 20 samples). The LCS is a solution of method analytes of known concentration added to a matrix which sufficiently challenges the Test Method. A synthetic drinking water matrix, containing fluoride at 1.0 mg/L, chloride at 50 mg/L, nitrite at 0.1 mg/L, nitrate at 10 mg/L, phosphate at 0.1 mg/L and sulfate at 50 mg/L, spiked with the four method analytes at the level of the IDP solution would be an example of an appropriate LCS. The LCS shall also contain 50 mg/L of EDA (the equivalent of 1.00 mL of EDA Preservation Solution (see 15.3) per 1.000 L of solution).

20.6.1 The analyte recoveries for the LCS should fall within the control limits of x ± 3S, where x is the mean recovery and (S) is the standard deviation of the mean recovery established from the interlaboratory precision and bias study data at the IDP levels, as shown below:

Analyte	LCS Amount	Lower Recovery Limit	Upper Recovery Limit
Chlorite	180 µg/L	165 µg/L	191 µg/L
Bromate	10 µg/L	8.0 µg/L	12.0 µg/L
Bromide	75 µg/L	63 µg/L	86 µg/L
Chlorate	180 µg/L	140 µg/L	219 µg/L

20.7 One Matrix Spike (MS) should be run with each sample batch (maximum of 20 samples) to test method recovery. The MS should be prepared in accordance with Guide D5810. Spike a portion of a drinking water (or other) sample from each batch with the four method analytes at the level of the IDP solution. The % recovery of the spike should fall within limits established from the interlaboratory precision and bias study data (assuming a background level of zero), according to Practice D5847, as shown below:

Analyte	MS Amount	Lower Recovery Limit (%)	Upper Recovery Limit (%)
Chlorite	180 µg/L	90.9 %	109.1 %
Bromate	10 µg/L	73.1 %	126.9 %
Bromide	75 µg/L	80.8 %	119.2 %
Chlorate	180 µg/L	88.3 %	111.7 %

20.8 One Matrix Duplicate (MD) should be run with each sample batch (maximum of 20 samples) to test method precision. If non-detects are expected in all the samples to be analyzed, a Matrix Spike Duplicate should be run instead. The precision of the duplicate analysis should be compared, according to Practice D5847, to the nearest tabulated S_o value established from the interlaboratory precision and bias study data for each analyte.

20.9 In order to verify the quantitative values produced by the test method, an Independent Reference Material (IRM), submitted to the laboratory as a regular sample (if practical), should be analyzed once per quarter. The concentration of the IRM should be within the scope of the method, as defined in 1.1. The values obtained must fall within the limits specified by the outside source.

20.10 The laboratory may perform additional quality control as desired or appropriate, for instance the use of a surrogate as outlined in Section 9.4.2 of U.S. EPA Method 300.1. In addition, it is recommended that a laboratory determine the method detection limits, as discussed in 19.6, before using this test method.

Test Method B
Electrolytically Suppressed Ion Chromatography

21. Scope

21.1 This test method is technically consistent with US EPA Method 300.1 (Part B), as cited above, except that it uses analyte separation on a hydroxide-selective anion exchange column, using a hydroxide eluent followed by electrolytically suppressed conductivity detection of the analytes in a deionized water matrix, thus improving method detection limits. The range tested for each analyte were as follows:

Chlorite	20 to 1,000 µg/L
Bromate	1 to 30 µg/L
Chlorate	20 to 1,000 µg/L
Bromide	20 to 200 µg/L

21.1.1 It should be noted that the U.S. EPA maintains that the use of hydroxide-based separation is consistent with Method 300.1 (Parts A and B) for compliance monitoring.

22. Summary of Test Method B

22.1 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 hydroxide eluent 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.

22.1.1 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 water, 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. An appropriate computer-based data system is typically used for data presentation.

22.2 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.

23. Interferences

23.1 Positive errors can be caused by progressive oxidation of residual hypochlorite or hypobromite, or both, 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 26.3. 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 26.4. Fluoride and low molecular weight monocarboxylic acids, present at mg/L concentrations, may interfere with the quantitation of chlorite and bromate.

24. Apparatus

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

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

24.1.2 *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 250 µL may be used without compromising the resolution of early eluting peaks, such as chlorite and bromate.

24.1.3 *Guard Column*—Anion exchange column typically packed with the same material used in the analytical column, for example, AG19, or equivalent. The purpose of this column is to protect the analytical column from particulate matter and irreversibly retained material.

24.1.4 *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, for example, IonPac AS19 (4 mm ID), or equivalent. The separation shall be at least as good as that shown in Fig. 5. The use of 2 mm ID AS19 column, in conjunction with a 50 µL sample loop, may improve the peak shape for early eluting anions, such as chlorite and bromate.

NOTE 2—The Analytical Column Set (24.1.4) should be able to give

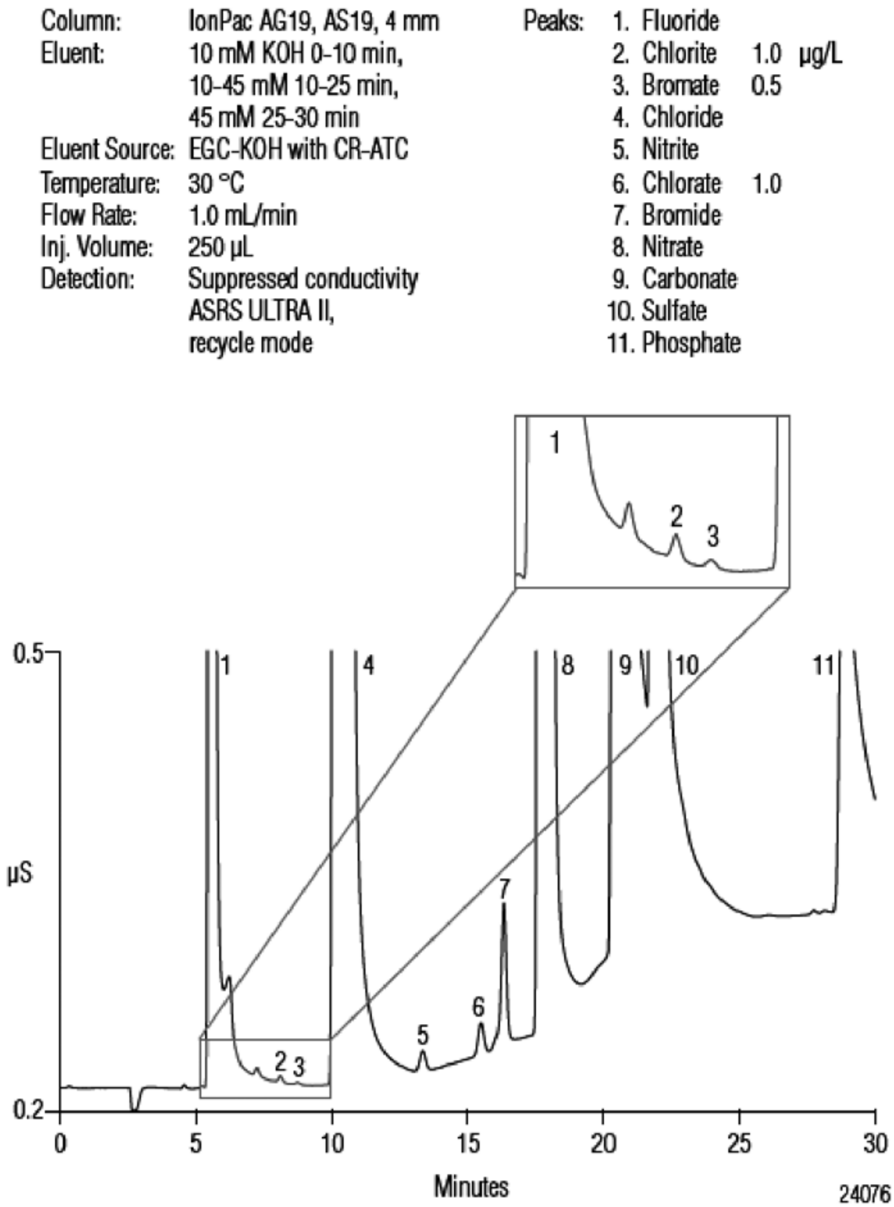


FIG. 5 Chromatogram of Mineral Water A Spiked with 1 µg/L Each Chlorite and Chlorate and 0.5 µg/L Bromate

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.

24.1.5 *Suppressor Device*—A suppressor device based upon cation exchange principles. An ASRA ULTRA II (4 mm) electrolytic suppressor device was used that does not require the addition of an acid but is a plug in electrolytic device. The suppressed eluent (water) is simply recirculated from the conductivity cell back to the electrolytic suppressor to back flush the suppressor device. Alternative pumps are also typically not required.

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

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

25. Preparation of Apparatus

25.1 Set up the ion chromatograph according to the manufacturer's instructions. If an Anion Self Regenerating Suppressor is used, operate the at the appropriate current setting. The conductivity detector cell should be thermally stabilized at 35°C.

25.2 The recommended operating conditions for the ion chromatograph are summarized in Table 12.

TABLE 12 Instrumentation[A] and Operating Conditions for the Determination of Oxyhalides and Bromide by Ion Chromatography, as shown in Fig. 5

Ion Chromatograph	ICS-2000 (or equivalent)
Guard Column	IonPac AG19 (or equivalent)
Analytical Column	IonPac AS19 (or equivalent)
Eluent	Hydroxide
Flow-Rate	1.0 mL/min
Injection Volume	250 µL
Suppressor	ASRS-ULTRA II (or equivalent)
Detector	Conductivity Detector (or equivalent), stabilized at 35°C

[A] Dionex Corporation, Sunnyvale, CA.

25.3 The detector ranges are variable. Normal operating ranges for quantifying the low level of oxyhalides encountered in treated drinking water are in the 0.2 to 2 µS/cm full scale range.

25.4 Equilibrate the chromatographic system by pumping the analysis eluent (see 26.1) through the system until a stable baseline is obtained (approximately 20 minutes). Typical baseline characteristics necessary to obtain the method detection limits required for this analysis are: *(1)* a background conductance of 0 to 2 µS/cm and *(2)* a peak-to-peak (noise) variation of no greater than 5 nS/cm per minute of monitored baseline response.

26. Reagents and Materials

26.1 *Hydroxide Eluent*—If NaOH is manually prepared us 50 % (w/w) NaOH using degassed, deionized water (18.2 megaohm-cm) to a final volume of 1000 µL using a volumetric flask. Avoid the introduction of carbon dioxide from the air into the 50 % NaOH or the distilled water being used to make the eluent. Do not shake the 50 % NaOH or pipette the required aliquot from the top of the solution where sodium carbonate may have formed. Eight grams or 5.25 mL of 50 % NaOH makes a 100 mM solution. A positive pressure of an inert gas should be maintained over the headspace to avoid carbon dioxide contamination. The used of electrolytically generated hydroxide by Reagent Free Ion Chromatography® to generate carbonate free hydroxide is also acceptable.[9]

26.2 *Test Method B Eluent Conditions*—10 mM Hydroxide from 0 to 10 minutes and 45 mM from 10 to 25 minutes at 1 mL/min, 30°C (see Fig. 5).

26.3 *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.

26.4 *SPE Sample Pretreatment Cartridges*—Chloride present at > 200 mg/L and carbonate present at > 300 mg/L can interfere with bromate determination. H^+ form and Ag^+ form cation exchange SPE cartridges can be used to minimize the carbonate and chloride interferences, respectively, if required. OnGuard-H and OnGuard-Ag cartridges have been shown to be suitable for this application. The use of these pretreatment cartridges will effect recoveries for bromide, requiring that it be analyzed in a separate run.[6]

26.5 *Suppressor Regenerant Solution*—Not required if using electrolytic suppression. Refer to 24.1.5, if a suppressor requiring chemical regeneration is used.

26.6 *Standard Solutions, Stock (1.00 mL = 1.00 mg)*—Purchase certified solutions or prepare stock standard solutions from the following salts, as described below:

26.6.1 *Bromate (BrO_3^-) Solution, Stock (1.00 mL = 1.00 mg BrO_3^-)*—Dissolve 1.180 g of sodium bromate ($NaBrO_3$) in water and dilute to 1.000 L.

26.6.2 *Bromide (Br^-) Solution, Stock (1.00 mL = 1.00 mg Br^-)*—Dissolve 1.288 g of sodium bromide (NaBr) in water and dilute to 1.000 L.

26.6.3 *Chlorate (ClO_3^-) Solution, Stock (1.00 mL = 1.00 mg ClO_3^-)*—Dissolve 1.275 g of sodium chlorate ($NaClO_3$) in water and dilute to 1.000 L.

26.6.4 *Chlorite (ClO_2^-) Solution, Stock (1.00 mL = 1.00 mg ClO_2^-)*—Dissolve 1.680 g of sodium chlorite ($NaClO_2$) in water and dilute to 1.000 L. Note that as sodium chlorite is usually available only as an 80 % technical grade salt, the 80 % purity is accounted for in the 1.680 g weight cited above. If an alternate purity is used, make an appropriate adjustment in the weight of salt used after determining the exact percentage of $NaClO_2$, which can be done using an iodometric titration procedure.[2,10]

26.7 *Reagent Blank*—Add 1.00 mL of EDA Preservation Solution (see 26.3) to 1.000 L of reagent water.

27. Calibration and Standardization

27.1 *Typical Range of Applicability*—This test method is applicable to the determination of bromate, bromide, chlorate, and chlorite in raw water, finished drinking water, and bottled (non-carbonated) water. The application ranges tested for each analyte are as follows: bromate; 1–30 µg/L, bromide; 20–200 µg/L, chlorite; 2–500 µg/L, and chlorate; 2–500 µg/L.

27.2 *Calibration Standards*—For each individual calibration curve, prepare calibration standards, at a minimum of three concentration levels, by accurately adding measured volumes of the stock standards (see 26.6) to a volumetric flask(s). Add 50 mg/L of EDA (the equivalent of 1.00 mL of EDA Preservation Solution (see 26.3) per 1.000 L of solution) to the volumetric flask(s) and dilute to volume with reagent water. A minimum of five concentration levels is recommended if the curve covers two orders of magnitude.

27.3 *Calibration Curve*—To establish the calibration curve, analyze a reagent blank and the calibration standards in accordance to the procedure in Section 28, using a 250 µL injection (with a 4 mm ID column) or a 50 µL injection (with a 2 mm ID column). Tabulate peak area responses against

[9] The sole source of supply of the apparatus known to the committee at this time is Reagent Free Ion Chromatography® Systems available from Dionex Corporation. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[10] Method 4500–ClO_2.C in A. E. Greenberg, L. S. Clesceri, A. D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., APHA, Washington, DC, 1992.

concentration. These results are used to prepare a calibration curve using a linear least squares fit for each analyte. The squared correlation coefficient of the regression (r^2) should be ≥ 0.995 for accurate results. Once the calibration curves have been established, verification must be performed on each analysis day, whenever fresh eluent is prepared, and twice each batch of samples.

28. Procedure

28.1 Inject the reagent blank, calibration standard or sample into the eluent stream and record the chromatogram. In the case of a manual injector, flush an excess of the sample (minimum of 5x loop volume) through the sample injection port using a syringe prior to injection. A 250-µL injection is required when using a 4 mm ID column, a 50-µL injection is required when using a 2 mm ID column, in order to achieve the required detection limits for this analysis. An example chromatogram of low level oxyhalides and bromide in a modest ionic strength, drinking water is shown in Fig. 5.

29. Calculations

29.1 Compare the peak areas for the anions in the sample to the calibration curves prepared in 27.3 to calculate and report the anion concentration in µg/L:

$$\text{Anion concentration, } \mu g/L = A \times F \quad (3)$$

where:

A = reading from the appropriate calibration plot, in µg/L, and
F = dilution factor if the sample was diluted prior to analysis.

29.1.1 Computing integrators and computer based chromatographic data systems can be programmed to perform these calculations automatically.

29.2 Recoveries were determined in drinking and bottled waters using the following equation:

$$R = \frac{Cs - C}{S} \times 100 \quad (4)$$

where:

R = percent recovery,
Cs = sample concentration,
C = background concentration, and
S = concentration added.

30. Precision and Bias

30.1 Standard test methods under the jurisdiction of the ASTM committee D19 may be published for a maximum of five years to the completion of a full collaborative study validation. Such standards are deemed to have met all other D19 qualifying requirements but have not completed the required validation studies to fully characterize the performance of the test methods across multiple laboratories and matrices. Publication of standards that have not been fully validated is done to make current technology accessible to users of standards and to solicit additional input from the user community.

30.2 A quality control (QC) sample served as initial, and on-going, calibration verification. A separate method detection limit (MDL) sample was used for the determination of MDL values. The MDL sample was prepared by pipetting a 1.0 mL aliquot of the MDL concentrate into a clean volumetric flask; adding 50 mg/L EDA, and diluting to a total of 100 mL with reagent water.

30.3 All the single operator precision and bias data presented in this test method was obtained using the IonPac AS19 column listed in Table 12.

30.4 The single operator precision and bias of this test method for each analyte for reagent, drinking and bottled water are shown in Tables 13-19.

30.5 In addition to performing the analyses required to generate the precision and bias data shown in Tables 13-19, the participating laboratory analyzed seven replicates of an MDL sample from reagent water and drinking water. The MDLs were derived using the students *t*-test at six degrees of freedom, as follows:

$$MDL = (t) \times (S) \quad (5)$$

where:

t = students t value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates], and
S = standard deviation of the replicate analysis.[8]

30.5.1 True amounts injected, mean value determined, and pooled MDL values (10 laboratories × 7 replicates) are shown in Tables 16 and 17.

31. Quality Control

31.1 Before this test is applied to analyzing unknown samples, the analyst should establish quality control procedures as recommended in Guide D3856.

31.2 The laboratory should repeat the test chromatogram in accordance with the column manufacturer's instructions as an Initial Demonstration of Performance (IDP) using the recommended analytes and concentrations. The user should perform at least 7 replicate injections showing retention time and peak area % RSD's below 5 %.

31.3 When beginning use of this test method, an initial Calibration Verification Standard (CVS) should be used to verify the calibration standards and acceptable instrument performance. This verification should be performed on each analysis day or whenever fresh eluent has been prepared. As this test method is intended for use at trace levels, a low level CVS (that is, equivalent to the lowest calibration standard)

TABLE 13

Analyte	Range	Linearity r^2	Retention Time Precision % RSD[A]	Peak Area Precision % RSD
Chlorite	20–1000	0.9997	< 0.03	0.44
Bromate	1–30	0.9995	< 0.03	1.09
Chlorate	20–1000	0.9996	< 0.03	0.12
Bromide	20–200	0.9997	< 0.03	0.11

[A] n = 10 injections.

TABLE 14 Recoveries of Chlorite, Chlorate, Bromate and Bromide from Drinking Waters

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
Drinking Water 1				
ClO_2	8.765	9.993	18.1983	94.39908
			18.4371	96.78875
			18.2464	94.88042
				95.35608
BrO_3	0	4.88	4.1483	85.00615
			4.7173	96.66598
			4.6325	94.92828
				92.20014
ClO_3	81.93	105.7	184.0871	96.64816
			184.3314	96.87928
			184.6171	97.14957
				96.89234
Br	26.26	29.86	55.7069	98.61654
			56.219	100.3315
			56.0772	99.85666
				99.60159
Drinking Water 2				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.983	21.7133	103.480437
			21.6218	103.044369
			21.548	102.692656
				103.072487
BrO_3	7.98	9.867	17.4425	95.9004763
			17.92	100.73984
			18.2182	103.762035
				100.134117
ClO_3	26.81	28.668	53.3068	92.4263988
			53.5405	93.2415934
			53.5761	93.3657737
				93.0112553
Br	190.3	198.34	396.6508	104.038923
			396.1512	103.787032
			396.6626	104.044872
				103.956943
Drinking Water 3				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.946	22.1486	105.7414
			22.0941	105.4812
			22.0861	105.443
				105.5552
BrO_3	0	5.124	5.0348	98.25917
			4.7266	92.24434
			4.9299	96.21194
				95.57182
ClO_3	119.6	143.92	269.3937	104.0812
			269.7678	104.3412
			270.4989	104.8492
				104.4238
Br	201.5	199.14	401.3183	100.3406
			399.9261	99.64151
			399.4704	99.41267
				99.79827
Drinking Water 4				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	19.982	20.0213	100.196677
			20.2444	101.313182
			20.1344	100.762686
				100.757515
BrO_3	0	4.979	3.3573	67.4292027
			3.3558	67.3990761
			3.1668	63.6031332
				66.143804
ClO_3	10.6	10.282	19.2819	84.4378526
			19.0115	81.808014
			19.2987	84.6012449
				83.6157038
Br	451.9	398.04	853.1127	100.797081
			850.6708	100.1836
			851.8068	100.468998
				100.483226

TABLE 14 *Continued*

Drinking Water 5				
Analyte	Amount Found (μg/L)	Amount Added (μg/L)	Final Concentration (μg/L)	%Recovery
ClO_2	11.6	9.99	20.9888	93.98198
			21.1907	96.003
			21.314	97.23724
				95.74074
BrO_3	0	4.982	4.679	93.91811
			4.7584	95.51184
			5.0302	100.9675
				96.79914
ClO_3	85.3	90.668	173.5636	97.34813
			173.5467	97.32949
			174.2912	98.15062
				97.60941
Br	1.23	24.892	25.1916	96.26225
			24.3046	92.69886
			24.5128	93.53527
				94.16546
Drinking Water 6				
Analyte	Amount Found (μg/L)	Amount Added (μg/L)	Final Concentration (μg/L)	%Recovery
ClO_2	0	20.754	20.9891	101.132794
			21.1041	101.686904
			21.0476	101.414667
				101.411455
BrO_3	0	4.827	4.1992	86.9939921
			4.1658	86.302051
			4.1592	86.1653201
				86.4871211
ClO_3	4.83	20.646	24.653	96.0137557
			24.2799	94.206626
			24.2464	94.0443669
				94.7549162
Br	206.1	229.68	437.5857	100.786181
			436.8931	100.484631
			437.7055	100.83834
				100.703051
Drinking Water 7				
Analyte	Amount Found (μg/L)	Amount Added (μg/L)	Final Concentration (μg/L)	%Recovery
ClO_2	0	19.695	21.6019	109.6822
			21.4894	109.1109
			20.7189	105.1988
				107.9973
BrO_3	1.29	4.907	5.8527	92.98349
			6.0023	96.0322
			5.839	92.7043
				93.90666
ClO_3	73.62	79.387	151.6691	98.31471
			151.596	98.22263
			151.4981	98.09931
				98.21222
Br	9.74	9.79	19.9167	103.9499
			20.2736	107.5955
			20.5738	110.6619
				107.4025
Drinking Water 8				
Analyte	Amount Found (μg/L)	Amount Added (μg/L)	Final Concentration (μg/L)	%Recovery
ClO_2	4.56	13.99	17.7194	94.0629
			17.8656	95.10793
			17.3008	91.07076
				93.41387
BrO_3	0	4.98	4.927	98.93574
			4.9493	99.38353
			5.1358	103.1285
				100.4826
ClO_3	136.36	151.04	285.7773	98.92565
			285.6934	98.8701
			286.1799	99.1922
				98.99598
Br	0	20.304	5.3299	26.25049
			4.3673	21.50955
			5.4314	26.75039
				24.83681

TABLE 14 *Continued*

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
		Drinking Water 9		
ClO_2	0	18.992	18.5731	97.79433
			18.406	96.91449
			18.3725	96.7381
				97.14898
BrO_3	0	4.982	4.7743	95.83099
			4.7031	94.40185
			4.6853	94.04456
				94.75913
ClO_3	0	20.146	21.3346	105.8999
			21.3523	105.9878
			21.888	108.6469
				106.8449
Br	0	19.912	20.5743	103.3261
			20.78	104.3592
			20.3922	102.4116
				103.3656

TABLE 15 Summary of Table 14 Recoveries of Chlorite, Chlorate, Bromate and Bromide from Drinking Waters

Analyte	Tap H_2O Source	Amount Found	Amount Added	Mean % Recovery
Chlorite	Sunnyvale	8.8	10	95.3
	Union City	< MDL	20.9	105.6
	Palo Alto	11.6	10	95.7
	Vacaville	< MDL	19.7	108
	Twain Heart Valley	4.6	14	93.4
	surface water	< MDL	19	97.1
	shallow well water	< MDL	21	103.1
	well water	< MDL	20	101.4
Bromate	Sunnyvale	< MDL	4.9	92.2
	Union City	< MDL	5.1	95.6
	Palo Alto	< MDL	5	96.8
	Vacaville	1.3	4.9	93.9
	Twain Heart Valley	< MDL	5	100.5
	surface water	< MDL	5	94.7
	shallow well water	16	9.8	100.1
	well water	< MDL	5	86.5
Chlorate	Sunnyvale	81.9	105.7	96.9
	Union City	119.6	143.9	104.4
	Palo Alto	85.3	90.7	97.6
	Vacaville	73.6	79.4	98.2
	Twain Heart Valley	136.4	151	99
	surface water	< MDL	20	106.8
	shallow well water	53.6	28.7	93
	well water	4.8	20	94.8
Bromide	Sunnyvale	26.3	29.9	99.6
	Union City	201.5	199	99.8
	Palo Alto	1.2	24.9	94.2
	Vacaville	9.7	9.8	107.4
	Twain Heart Valley	< MDL	20.3	24.8
	surface water	< MDL	20	103.3
	shallow well water	380.6	198.3	104
	well water	206	230	100.7

TABLE 16 Calculated MDL Results Using the Standards Indicated from Reagent Water

# Injection	Chlorite (1 ppb std)	Bromate (1.5 ppb std)	Chlorate (1.3 ppb std)	Bromide (2 ppb std)
1	0.8816	1.1983	1.0774	2.2766
2	0.7794	0.9713	1.0293	2.1381
3	0.7161	0.9511	1.0428	2.1113
4	0.7881	0.8846	1.0766	1.9853
5	0.7557	0.8962	1.0222	2.0751
6	0.7156	0.9069	1.2095	1.7211
7	0.8961	0.9170	0.8636	2.0353
Avg	0.7903	0.9607	1.0459	2.0489
SD	0.0729	0.1090	0.1022	0.1713
MDL (ppb)	0.2290	0.3425	0.3211	0.5378

TABLE 17 Calculated MDL Results Using the Standards Indicated from Drinking Water

# Injection	Chlorite (1 ppb std)	Bromate (1.5 ppb std)	Chlorate (1.3 ppb std)	Bromide (2 ppb std)
1	0.5662	0.6833	1.3809	3.6176
2	0.4475	1.044	1.2177	3.6838
3	0.6901	0.7641	1.4476	3.7967
4	0.6665	0.7189	1.3978	4.0928
5	0.6247	0.6235	1.4755	3.7301
6	0.5612	0.7254	1.4513	3.602
7	0.6325	0.7539	1.2782	3.6958
Avg	0.5983	0.7590	1.3784	3.7455
SD	0.0817	0.1342	0.0964	0.1666
MDL (ppb)	0.2566	0.4214	0.3027	0.5233

should initially be analyzed before beginning use of this test method. The CVS is a solution of method analytes of known concentration used to fortify reagent water, which also contains a final EDA concentration of 50 mg/L (see 26.3). If the determined low level CVS values are not within ±25 % of the known amounts, the low level CVS should be reanalyzed. If the values still fall outside acceptable limits, a new calibration curve is required which must be confirmed by a successful low level CVS before continuing with on-going analyses.

31.4 A continuing CVS should be analyzed after every tenth field sample and an end CVS should analyzed at the end of the sample batch (maximum of 20 samples) to verify the previously established calibration curves. After initially meeting the requirements of 31.3, the levels selected for the continuing and end CVS should be varied between a middle calibration level and the highest calibration level standard. If the continuing and end CVS values are not within ±15 % of the known amounts, the analyst should reanalyze the CVS. If the analyte concentrations still fall outside acceptable limits (±15 %) that analyte is judged out of control, and the source of the problem should be identified before continuing with on-going analyses. All samples following the last acceptable CVS should be reanalyzed.

31.5 A reagent blank (see 26.7) should be run when generating the initial calibration curves. A blank should also be run with each sample batch (maximum of 20 samples) to check for sample or system contamination.

31.6 One Laboratory Control Sample (LCS) should be used with each sample batch (maximum of 20 samples). The LCS is a solution of method analytes of known concentration added to a matrix which sufficiently challenges the test method. A synthetic drinking water matrix, containing fluoride at 1.0 mg/L, chloride at 50 mg/L, nitrite at 0.1 mg/L, nitrate at 10 mg/L, phosphate at 0.1 mg/L and sulfate at 50 mg/L, spiked with the four method analytes at the level of the IDP solution would be an example of an appropriate LCS. The LCS shall also contain 50 mg/L of EDA (the equivalent of 1.00 mL of EDA Preservation Solution (see 26.3) per 1.000 L of solution).

31.6.1 The analyte recoveries for the LCS should fall within the control limits of $x \pm 3S$, where x is the mean recovery and (S) is the standard deviation of the mean recovery established from the single operator precision and bias study data.

31.7 One Matrix Spike (MS) should be run with each sample batch (maximum of 20 samples) to test method recovery. The MS should be prepared in accordance with Guide D5810. Spike a portion of a drinking water (or other) sample from each batch with the four method analytes at the level of the IDP solution. The % recovery of the spike should fall within limits established from the interlaboratory precision and bias study data (assuming a background level of zero), according to Practice D5847.

31.8 One Matrix Duplicate (MD) should be run with each sample batch (maximum of 20 samples) to test method precision. If non-detects are expected in all the samples to be analyzed, a Matrix Spike Duplicate should be run instead.

31.9 In order to verify the quantitative values produced by the test method, an Independent Reference Material (IRM), submitted to the laboratory as a regular sample (if practical), should be analyzed once per quarter. The concentration of the IRM should be within the scope of the test method, as defined in 21.1. The values obtained must fall within the limits specified by the outside source.

31.10 The laboratory may perform additional quality control as desired or appropriate, for instance the use of a surrogate as outlined in Section 9.4.2 of U.S. EPA Method 300.1 or as recommended by the manufacturer. In addition, it is recommended that a laboratory determine the method detection limits, as discussed in 30.5, before using this test method.

32. Keywords

32.1 bottled and finished drinking water; bromate; bromide; chemical suppression; chlorate; chlorite; ion chromatography; raw water; sample preservation

TABLE 18 Recoveries of Chlorite, Chlorate, Bromate, and Bromide from Bottled Waters

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
Bottled Water 1				
ClO_2	0	19.92	21.5416	108.1406
			21.5525	108.1953
			21.5296	108.0803
				108.1387
BrO_3	0	4.983	4.6816	93.95143
			4.6958	94.2364
			4.982	99.97993
				96.05592
ClO_3	2.4	20.072	23.932	107.2738
			23.8838	107.0337
			24.2592	108.9039
				107.7371
Br	7.5	19.992	28.6255	105.6698
			28.3698	104.3908
			28.5085	105.0845
				105.0484
Bottled Water 2				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	19.93	20.9161	104.9478
			20.3823	102.2694
			20.2116	101.4129
				102.8767
BrO_3	0	4.985	4.902	98.33501
			5.0747	101.7994
			5.0815	101.9358
				100.6901
ClO_3	0	20.08	21.3216	106.1833
			21.7464	108.2988
			21.072	104.9402
				106.4741
Br	0	20.002	21.2098	106.0384
			21.2935	106.4569
			21.3975	106.9768
				106.4907
Bottled Water 3				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.929	20.7492	99.1409
			21.0457	100.5576
			20.8743	99.73864
				99.81238
BrO_3	10.2	9.872	20.4379	103.7064
			20.4159	103.4836
			20.718	106.5438
				104.5779
ClO_3	0	21.088	21.7205	102.9993
			21.618	102.5133
			21.6927	102.8675
				102.7934
Br	19.37	21.004	38.9859	93.39126
			38.7882	92.45001
			38.8527	92.75709
				92.86612
Bottled Water 4				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.983	19.0318	90.70104
			19.1275	91.15713
			18.6043	88.66368
				90.17395
BrO_3	0	4.97	4.272	85.95573
			4.2707	85.92958
			3.9144	78.76056
				83.54863
ClO_3	10.16	20.138	30.442	100.7151
			30.9605	103.2898
			31.2967	104.9593
				102.988
Br	95.49	104.5	198.2911	98.37426
			197.7618	97.86775
			196.7893	96.93713
				97.72638

TABLE 18 *Continued*

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
Bottled Water 5				
ClO_2	0	19.952	20.3706	102.098
			20.195	101.2179
			20.0104	100.2927
				101.2029
BrO_3	0	4.872	4.7786	98.08292
			4.5397	93.17939
			4.692	96.30542
				95.85591
ClO_3	1.55	20.106	23.3528	108.4393
			23.3969	108.6586
			23.438	108.863
				108.6536
Br	1.21	19.862	20.0039	94.62239
			20.2719	95.9717
			20.3306	96.26724
				95.62045
Bottled Water 6				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	19.841	20.0341	100.9732
			20.1373	101.4934
			20.2725	102.1748
				101.5471
BrO_3	9.23	9.789	19.3462	103.3425
			19.7821	107.7955
			19.8557	108.5473
				106.5618
ClO_3	374.5	149.96	520.2669	97.20385
			520.7441	97.52207
			520.3303	97.24613
				97.32402
Br	2.49	19.762	22.3591	100.5419
			22.4557	101.0308
			22.4863	101.1856
				100.9194
Bottled Water 7				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	19.978	21.1067	105.6497
			21.4455	107.3456
			21.4251	107.2435
				106.7463
BrO_3	0	4.978	4.5736	91.87626
			4.6553	93.51748
			4.56	91.60305
				92.33226
ClO_3	0	25.165	22.6989	90.20028
			22.6964	90.19034
			23.0201	91.47665
				90.62243
Br	31.8	29.847	61.2379	98.62934
			61.0686	98.06212
			61.6879	100.137
				98.94283
Bottled Water 8				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	19.99	20.3662	101.8819
			20.3674	101.8879
			20.5673	102.8879
				102.2193
BrO_3	0	4.981	4.7302	94.96487
			4.5656	91.66031
			4.7116	94.59145
				93.73887
ClO_3	0	20.146	21.2721	105.5897
			21.2247	105.3544
			21.1961	105.2124
				105.3855
Br	18.67	19.912	37.3404	93.76456
			37.3579	93.85245
			37.3659	93.89263
				93.83655

TABLE 18 *Continued*

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
Bottled Water 9				
ClO_2	0	19.94	21.1555	106.0958
			20.9677	105.154
			21.3584	107.1133
				106.121
BrO_3	0	4.87	4.5977	94.40862
			4.5697	93.83368
			5.2069	106.9179
				98.38672
ClO_3	0	20.094	21.2774	105.8893
			21.3351	106.1765
			21.1095	105.0537
				105.7065
Br	2.66	19.86	23.2262	103.5559
			23.0562	102.6999
			23.6949	105.9159
				104.0572
Bottled Water 10				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.985	20.5197	97.7827
			20.6457	98.38313
			20.6274	98.29593
				98.15392
BrO_3	4.4	4.98	9.388	100.1606
			9.5339	103.0904
			9.3899	100.1988
				101.1499
ClO_3	0	20.14	21.501	106.7577
			21.7981	108.2329
			21.787	108.1778
				107.7228
Br	0	19.906	20.8241	104.6122
			21.0055	105.5235
			21.0659	105.8269
				105.3208
Bottled Water 11				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	20.494	21.3516	104.1846
			21.5828	105.3128
			21.5015	104.9161
				104.8045
BrO_3	0	5.107	5.0536	98.95438
			4.7337	92.69042
			4.9806	97.52497
				96.38992
ClO_3	0	22.947	22.7441	99.11579
			22.1578	96.56077
			22.7628	99.19728
				98.29128
Br	6.34	22.68	27.9533	95.29674
			27.5945	93.71473
			27.7531	94.41402
				94.47516
Bottled Water 12				
Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Final Concentration (µg/L)	%Recovery
ClO_2	0	21.905	20.9851	95.8005
			20.7819	94.87286
			20.8136	95.01758
				95.23031
BrO_3	0.984	4.882	5.7522	97.66899
			6.1172	105.1454
			6.0343	103.4474
				102.0873
ClO_3	4.19	22.072	25.9114	98.41156
			25.9705	98.67932
			25.9366	98.52573
				98.53887
Br	0	21.985	21.8261	99.27723
			21.8205	99.25176
			21.7536	98.94746
				99.15882

TABLE 19 Summary of Table 18 Recoveries of Chlorite, Chlorate, Bromate and Bromide from Bottled Waters

Analyte	Bottled H_2O Source	Amount Found	Amount Added	Mean % Recovery
Chlorite	1	< MDL	19.9	108.1
	2	< MDL	19.9	102.9
	3	< MDL	20.9	99.8
	4	< MDL	21	90.2
	5	< MDL	20	101.2
	6	< MDL	19.8	101.5
	7	< MDL	20	106.7
	8	< MDL	20	102.2
	9	< MDL	19.9	106.1
	10	< MDL	21	98.2
	11	< MDL	20.5	104.8
	12	< MDL	21.9	95.2
Bromate	1	< MDL	5	96.1
	2	< MDL	5	100.7
	3	10.2	9.8	104.6
	4	< MDL	5	83.5
	5	< MDL	4.9	95.9
	6	9.2	9.8	106.6
	7	< MDL	5	92.3
	8	< MDL	5	93.7
	9	< MDL	4.9	98.4
	10	4.4	5	101.1
	11	< MDL	5.1	96.4
	12	0.98	4.89	102.1
Chlorate	1	2.4	20.1	107.7
	2	< MDL	20.1	106.5
	3	< MDL	21.1	102.8
	4	10.2	20	103
	5	1.6	20.1	108.6
	6	374.5	150	97.3
	7	< MDL	25.2	90.6
	8	< MDL	20.1	105.4
	9	< MDL	20.1	105.7
	10	< MDL	20.1	107.7
	11	< MDL	22.9	98.3
	12	4.2	22.1	98.5
Bromide	1	7.5	20	105
	2	< MDL	20	106.5
	3	19.4	21	92.9
	4	95.5	104.5	97.7
	5	1.2	19.9	95.6
	6	2.5	19.8	100.9
	7	31.8	29.8	98.9
	8	18.7	19.9	93.8
	9	2.7	19.9	104.1
	10	< MDL	19.9	105.3
	11	6.3	22.7	94.5
	12	< MDL	22	99.2

TABLE 20 Disinfection Procedure for the Bottled Water Sources Used in This Study

Bottled Water Source	Disinfection Procedure Used for Bottled Waters
1	natural spring water, no treatment
2	UV light, reverse osmosis, ozonation
3	ozonation
4	natural mineral water
5	filtered by reverse osmosis, minerals added
6	micro-filtration, ozonation, UV light treatment
7	filtration
8	microfiltration, ozonation
9	natural spring water
10	microfiltered, ozonated
11	microfiltration, reverse osmosis, deionization, ozonation
12	ozonation