Designation: D 6581 – 00

An American National Standard

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:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]

D 3370 Practices for Sampling Water[3]

D 3856 Guide for Good Laboratory Practices[3]

D 5810 Standard Guide for Spiking into Aqueous Samples[3]

D 5847 Standard Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

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.

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

[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.

Current edition approved July 10, 2000. Published October 2000.

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

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

(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.

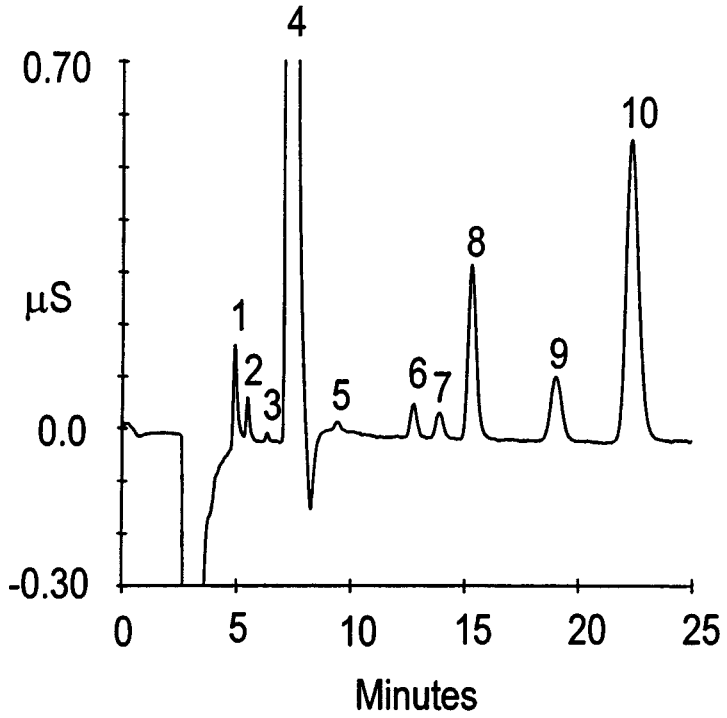
8.3 *Eluent, Concentrate (90.0 mM Sodium Carbonate)*—Dissolve 9.540 g of sodium carbonate in 1000 mL of water.

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.

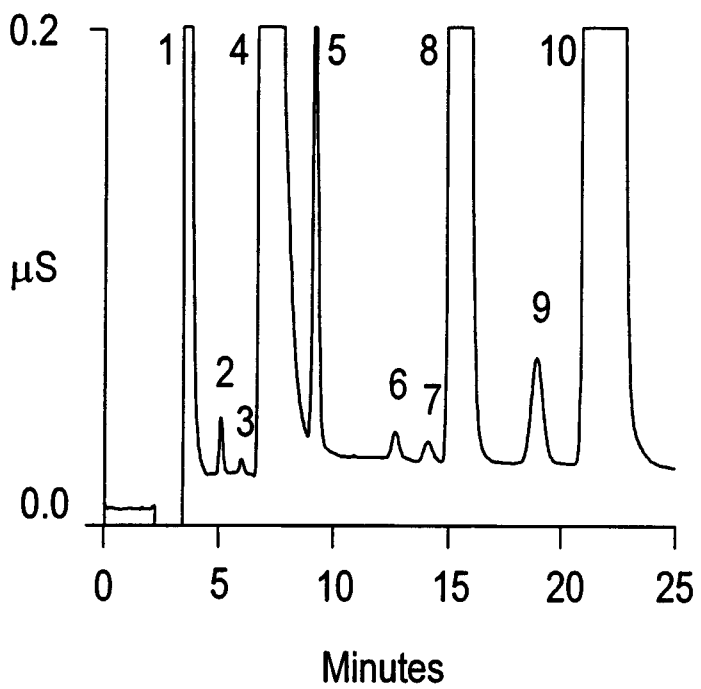
8.5 *Ethylenediamine (EDA) Preservation Solution (50.0 g/L)*—Dilute 11.2 mL of ethylenediamine (99%) to 200 mL

[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.

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.

8.6 *SPE Sample Preatment 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. Dionex OnGuard-H and OnGuard-Ag cartridges have been

shown to be suitable for this application.[5] The use of these pretreatment cartridges will effect recoveries for bromide, requiring that it be analyzed in a separate run.

8.7 *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.

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

8.8.1 *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.

8.8.2 *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.

8.8.3 *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.

8.8.4 *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.[2,6]

8.9 *Reagent Blank*—Add 1.00 mL of EDA Preservation Solution (8.5) to 1.000 L of reagent water.

9. Precautions

9.1 These 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.

10. Sampling and Sample Preservation

10.1 Collect the sample in accordance with Practice D 3370, as applicable.

10.2 Immediately upon taking the sample, sparge it with an inert gas (e.g., 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 (8.5) 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.[7]

11. Quality Control

11.1 Before this test is applied to analyzing unknown samples, the analyst should establish quality control procedures as recommended in Guide D 3856.

11.2 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 (8.5). 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.

The mean and standard deviation of the seven values should then be calculated and compared, according to Standard D 5847, 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:

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

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 6. 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.

11.3 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 (i.e.,

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	DX-500 (or equivalent)
Guard Column	IonPac AG9-HC, (or equivalent)
Analytical Column	IonPac AS9-HC, (or equivalent)
Eluent	9.0 mM Sodium carbonate
Flow-Rate	1.0 mL/min.
Injection volume	200 µL
Suppressor	ASRS-ULTRA, (or equivalent), 100mA in external water mode at 10 mL/min.
Detector	CD20 Conductivity Detector (or equivalent), stabilized at 35°C

[A] Dionex Corporation, Sunnyvale, CA.

[5] R.J. Joyce and H. Dhillon, J. Chromatography, 671 (1994) 165.

[6] 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).

[7] D.P. Hautman and M. Bolyard, J. Chromatography, 602 (1992) 65.

TABLE 2 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 3 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

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 (8.5). 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.

11.4 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 11.4, 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.

11.5 A reagent blank (8.9) 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.

11.6 One Laboratory Control Sample (LCS) should be mn 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 (8.5) per 1.000 L of solution).

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

TABLE 4 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 5 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

TABLE 6 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

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

11.7 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 D 5810. 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 Standard D 5847, 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 %

11.8 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

TABLE 7 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 8 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

analyzed, a Matrix Spike Duplicate should be run instead. The precision of the duplicate analysis should be compared, according to Standard D 5847, to the nearest tabulated S_o value established from the interlaboratory precision and bias study data for each analyte.

11.9 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 within the limits specified by the outside source.

11.10 The laboratory may perform additional quality control as desired or appropriate, for instance the use of a surrogate as outlined in Sect. 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 16.6, before using this test method.

12. Preparation of Apparatus

12.1 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.

12.2 The recommended operating conditions for the ion chromatograph are sumarized in Table 1.

12.3 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.

12.4 Equilibrate the chromatographic system by pumping the analysis eluent (8.4) 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.

13. Calibration and Standardization

13.1 *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.

13.2 *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 (8.8) to a volumetric flask(s). Add 50 mg/L of EDA (the equivalent of 1.00 mL of EDA Preservation Solution (8.5) 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.

13.3 *Calibration Curve*—To establish the calibration curve, analyze a reagent blank and the calibration standards in accordance to the procedure in Section 14, 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 $\geq$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 11.4 and 11.5.

14. Procedure

14.1 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.

15. Calculation

15.1 Compare the peak areas for the anions in the sample to the calibration curves prepared in 13.3 to calculate and report the anion concentration in µg/L:

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

where:

A = reading from the appropriate calibration plot, in µg/L, and

F = dilution factor if the sample was diluted prior to analysis

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

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

16. Precision and Bias

16.1 The precision and bias data presented in this test method meets the requirements of Practice D 2777-98. The full research report can be obtained from ASTM Headquarters.[8]

16.2 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 10 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 (x3), B1-2 (x3), C1-2 (x3) into volumetric flasks (18 total); adding 50 mg/L EDA preservation solution, as detailed in 10.2, and diluting to a total of 100 mL with reagent water (x6), bottled water (x6) and drinking water (x6), as appropriate.

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.

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

16.4 The precision and bias of this test method for each analyte for reagent, drinking and bottled water are shown in Tables 2-5.

16.5 The results of the interlaboratory study can also be summarized as regression equations, as shown in Table 6 for reagent water and in Table 7 for a typical sample matrix - drinking water.

16.6 In addition to performing the analyses required to generate the precision and bias data shown in Tables 2-5, 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[9]

The true amounts injected, mean value determined, and pooled MDL values (10 laboratories × 7 replicates) are shown in Table 8.

17. Keywords

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

[8] Supporting data are available from ASTM Headquarters. Request RR: D19–1164.

[9] Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.