



Designation: D6581 – 18

Standard Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography¹

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 SI units are to be regarded as standard. The values given in parentheses are mathematical

conversions to inch-pound units that are provided for information only and are not considered standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analytical column, n*—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, n*—a combination of one or more guard columns, followed by one or more analytical

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.

*A Summary of Changes section appears at the end of this standard

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, n*—the ionic mobile phase used to transport the sample through the chromatographic system.

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

3.2.5 *ion chromatography, n*—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, n*—the ability of an analytical column to separate the method analytes under specific test conditions.

3.2.7 *suppressor device, n*—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, n*—the use of an acid solution to the suppressor in order to suppress the background conductivity.

3.2.7.2 *electrolytic suppressor device, n*—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 Practices 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.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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.”

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 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 27 600 kPa (4000 psi).

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 $\mu\text{S}/\text{cm}$ on a linear scale.

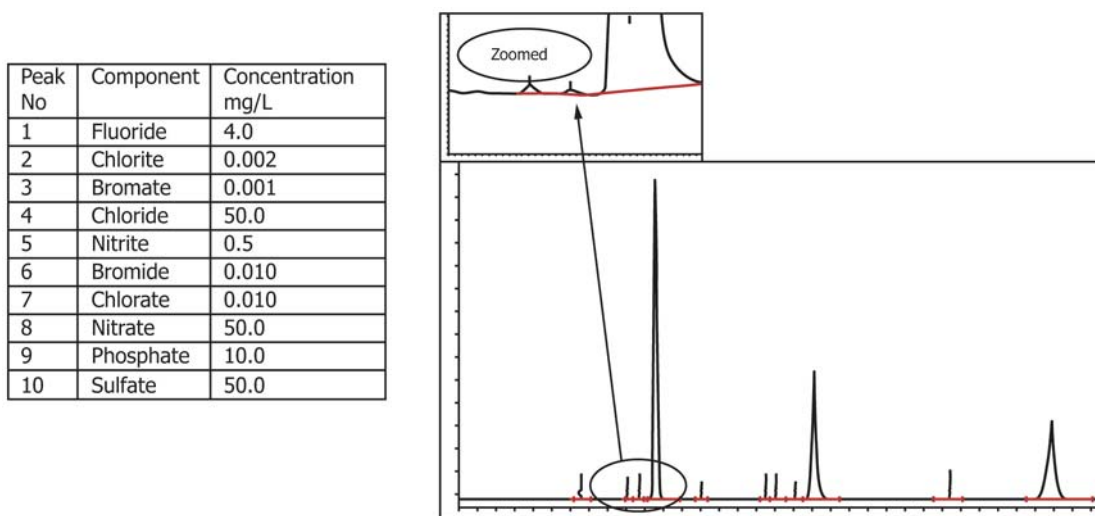


FIG. 1 Chromatogram of a Standard Containing Low $\mu\text{g}/\text{L}$ Oxyhalides, and Bromide, in the Presence of Common Inorganic Anions (See Table 1 for Analysis Conditions)

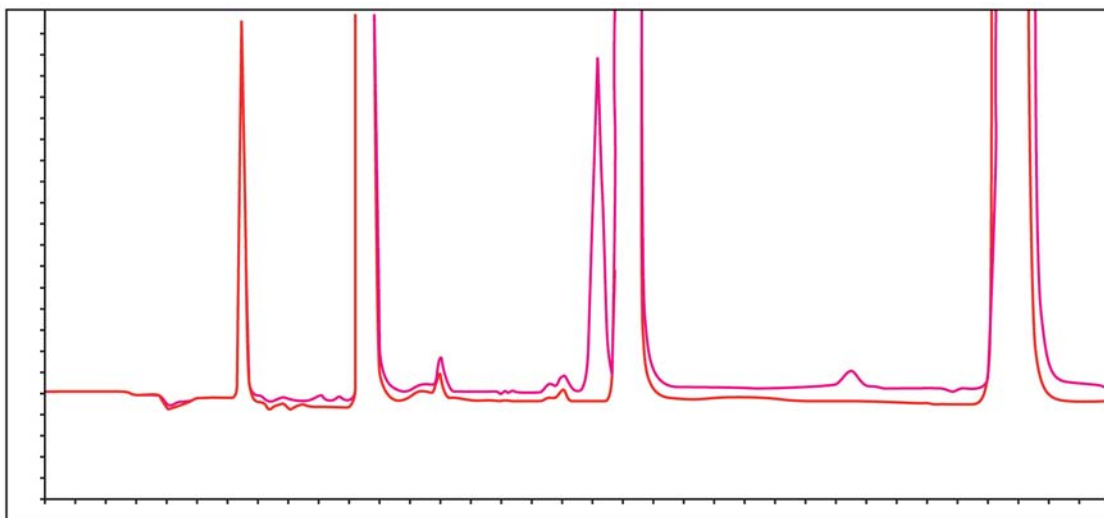


FIG. 2 Overlay Chromatogram Spiked and Unspiked of Low µg/L Oxyhalides, and Bromide, in Houston, TX, Drinking Water (See Table 1 for Analysis Conditions)

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 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.

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 A trademark of 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.

Conditions

Condition A with and without CRD-300

Column:	IonPac AS23 (4 × 250 mm) IonPac AG23 (4 × 50 mm)
Eluent:	4.5 mM K ₂ CO 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.

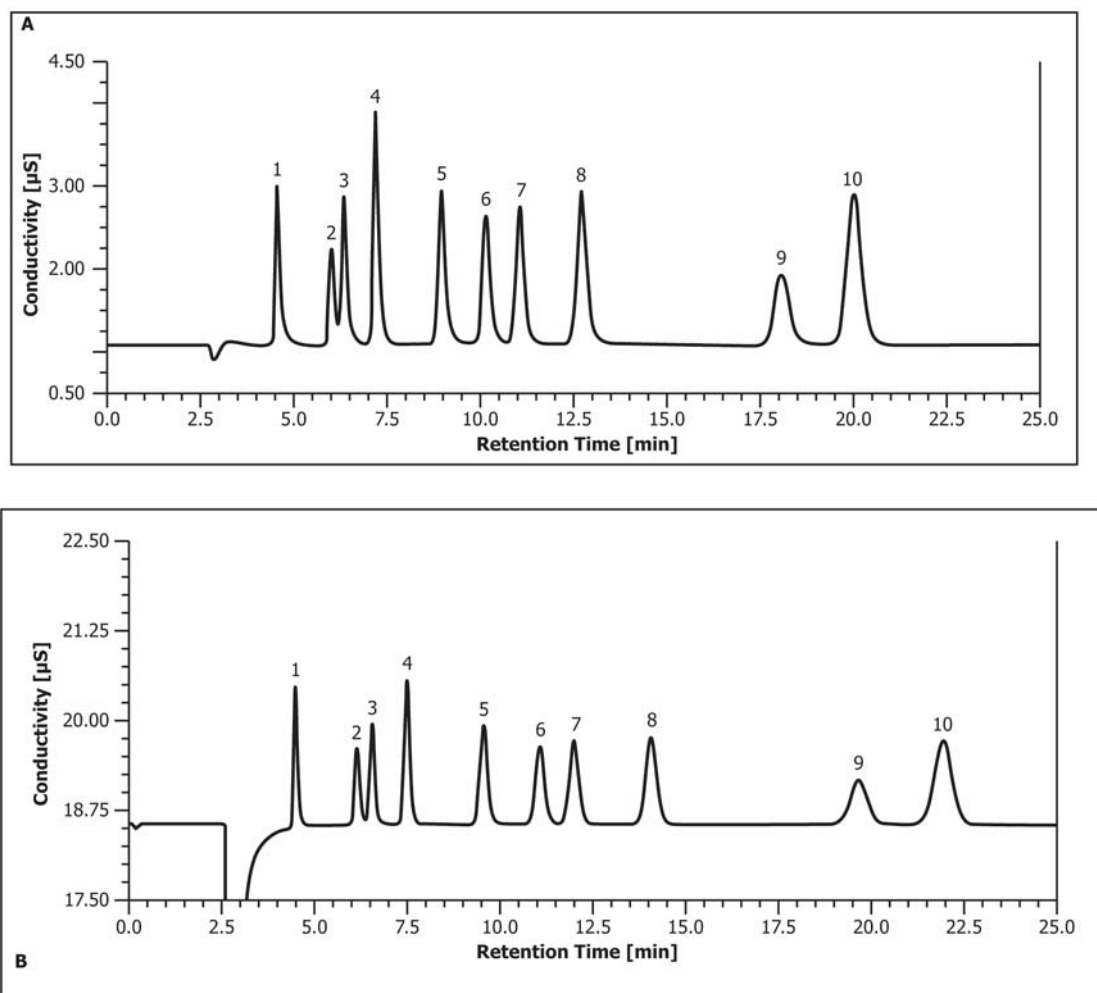
14. Preparation of Apparatus

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.



NOTE 1—Peaks:

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

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

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.

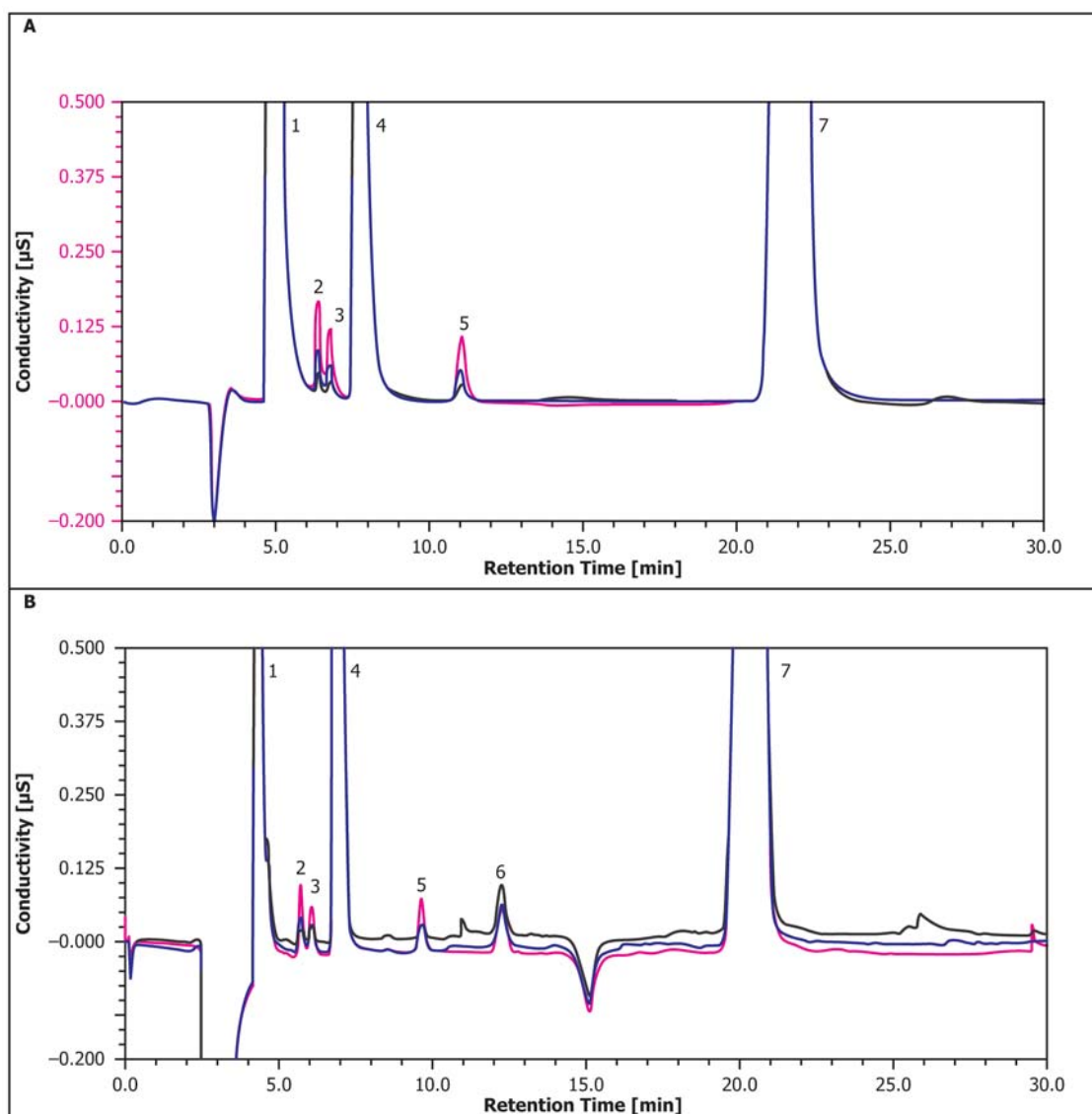
15.2.1 The Eluent Analysis Solution (9.0-mM sodium carbonate) must be purged for 10 minutes with helium prior to use to remove dissolved gasses in order to ensure optimal system performance.

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 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

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



NOTE 1—Peaks:

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

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.

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 ClO_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 usually available only as an 80 % technical grade salt, the 80 % purity is accounted for in the 1.680-g weight.

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.

alternate purity is used, make an appropriate adjustment in the weight of salt used after determining the exact percentage of NaClO₂, 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.

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 5× 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:

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

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.

⁷ Method 4500-ClO₂-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.