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Trace Analysis of Bromate, Chlorate, Iodate, and Perchlorate in Natural and Bottled Waters

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A simple and rapid method has been developed to simultaneously measure sub- $\mu\text{g/L}$ quantities of the oxyhalide anions bromate, chlorate, iodate, and perchlorate in water samples. Water samples (10 mL) are passed through barium and hydronium cartridges to remove sulfate and carbonate, respectively. The method utilizes the direct injection of 10 μL volumes of water samples into a liquid chromatography–tandem triple-quadrupole mass spectrometry (LC–MS/MS) system. Ionization is accomplished using electrospray ionization in negative mode. The method detection limits were 0.021 $\mu\text{g/L}$ for perchlorate, 0.045 $\mu\text{g/L}$ for bromate, 0.070 $\mu\text{g/L}$ for iodate, and 0.045 $\mu\text{g/L}$ for chlorate anions in water. The LC–MS/MS method described here was compared to established EPA methods 300.1 and 317.1 for bromate analysis and EPA method 314.0 for perchlorate analysis. Samples collected from sites with known contamination were split and sent to certified laboratories utilizing EPA methods for bromate and perchlorate analysis. At concentrations above the reporting limits for EPA methods, the method described here was always within 20% of the established methods, and generally within 10%. Twenty-one commercially available bottled waters were analyzed for oxyhalides. The majority of bottled waters contained detectable levels of oxyhalides, with perchlorate $\leq 0.74 \mu\text{g/L}$, bromate $\leq 76 \mu\text{g/L}$, iodate $\leq 25 \mu\text{g/L}$, and chlorate $\leq 5.8 \mu\text{g/L}$. Perchlorate, iodate, and chlorate were detectable in nearly all natural waters tested, while bromate was only detected in treated waters. Perchlorate was found in several rivers and reservoirs where it was not found previously using EPA 314.0 (reporting limit of 4 $\mu\text{g/L}$). This method was also applied to common detergents used for cleaning laboratory glassware and equipment to evaluate the potential for sample contamination. Only chlorate appeared as a major oxyhalide in the detergents evaluated, with concentrations up to 517 $\mu\text{g/g}$. Drinking water treatment plants were also evaluated using this method. Significant formations of chlorate and bromate are demonstrated from hypochlorite generation and ozonation. From the limited data set provided here, it appears that perchlorate is a ubiquitous contaminant of natural waters at trace levels.

Introduction

The presence of certain oxyhalides in drinking water has become a major issue for the water industry. Most important

are the perchlorate and bromate anions, which have become focal issues for regulatory agencies. The U.S. EPA originally published a reference dose for perchlorate, which would suggest a drinking water equivalent level of approximately 1 $\mu\text{g/L}$ (1). More recently, the National Academy of Sciences and the U.S. EPA have suggested reference doses with a drinking water equivalent level of 24.5 $\mu\text{g/L}$ (2, 3). However, the state of Massachusetts requires public notification of drinking water containing perchlorate at 1 $\mu\text{g/L}$ or greater (4), while California has established a public health goal of 6.0 $\mu\text{g/L}$ (5). Bromate, a disinfection byproduct, is currently regulated in U.S. drinking waters with a maximum contaminant limit (MCL) of 10 $\mu\text{g/L}$ in drinking water (6). Chlorate and iodate are not currently regulated in drinking water; however, they occur naturally and as byproducts of certain water treatment processes (e.g., hypochlorite generation, chlorine dioxide disinfection, and ozonation). The state of California has set an action level of 800 $\mu\text{g/L}$ for chlorate in drinking water (7), and an action level of 200 $\mu\text{g/L}$ has been suggested (8). The perchlorate anion is well-known for having direct action on the thyroid gland by inhibiting the production of thyroid hormones (9–12). Bromate has been reported to be a carcinogen in mammalian studies (13, 14). Toxicological reports have shown that chlorate has toxic modes of action similar to those of perchlorate (15–17). Iodate is generally considered to be an important component of the human diet as iodate is rapidly reduced to iodide in the body, and iodide is essential for thyroid function (18). However, high levels of iodate (>600 mg/day) have been shown to cause ocular toxicity by damaging the retina (18). Bromate, chlorate, and iodate are known disinfection byproducts (DBPs) of drinking water treatment, namely, ozone and chlorine dioxide processes. Environmental contamination of perchlorate has primarily been associated with industrial and military activities; however, perchlorate has also been shown to occur naturally (10, 19, 20). The bromate MCL and the draft reference dose for perchlorate have led to the need for more robust and sensitive analytical methods.

The most commonly applied analytical technique for measurement of oxyhalide anions is ion chromatography with conductivity detection (IC–CD). Conductivity detection is of low specificity as many compounds are ionic and thus would be detected by conductivity. EPA methods 300.1 and 314.0 using IC–CD are the most commonly used methods for the analysis of bromate and perchlorate, and typically have reporting limits of 5 and 4 $\mu\text{g/L}$, respectively. While IC–CD can be applied successfully to many drinking waters, obtaining reliable results in higher conductivity waters (i.e., membrane brine streams and saline groundwater) when accurate quantification is desired is challenging. Furthermore, these methods suffer from potential matrix interferences when applied to environmental mixtures (21–23). For instance, a recent report has shown that *p*-chlorobenzene-sulfonate, a compound often found in paints and chemical manufacturing, coelutes with perchlorate when analyzed by EPA method 314.0 (IC–CD method) (24). Some investigators have used preconcentration steps, such as solid-phase extraction (SPE) and ion-exchange columns, to obtain more concentrated solutions prior to IC–CD analysis (25–27). Another development in ion chromatography is the advent of postcolumn reactions (derivatizations) followed by UV measurement (IC–PCR) (28–32). A more recent EPA method uses IC–PCR for bromate analyses (EPA method 317.1); however, it is not applicable to other oxyhalides and has a reporting limit around 1 $\mu\text{g/L}$. Mass spectrometry has also been applied for the detection of oxyhalide anions, most

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TABLE 1. Compound-Dependent Parameters

compound	retention time (min)	precursor ion mass	product ion mass (loss of oxygen)	declustering potential (V)	collision energy (eV)	collision cell exit potential (V)
iodate	5.3	174.616	158.650	-15	-40	-25
[⁷⁹ Br]bromate	5.9	126.852	110.859	-50	-30	-17
[⁸¹ Br]bromate	5.9	128.852	112.859	-50	-30	-17
[³⁵ Cl]chlorate	7.1	83.010	66.950	-45	-26	-9
[³⁷ Cl]chlorate	7.1	85.010	68.950	-45	-26	-9
[³⁵ Cl]perchlorate	8.2	98.872	82.776	-50	-36	-17
[³⁷ Cl]perchlorate	8.2	100.872	84.776	-50	-36	-17

commonly in tandem with ion chromatography (IC-MS) or liquid chromatography (LC-MS) (33-39). The use of mass spectrometry for the detection of ionic compounds has increased dramatically with the development of commercially available IC-MS systems (40). While ion chromatography is able to separate multiple anions in a single chromatographic analysis, liquid chromatography generally relies on ion-pairing techniques. Unfortunately, liquid-phase mass spectrometric methods are often hindered by ion-suppression and ion-enhancement effects, where nontarget species interfere with accurate quantification. To obtain accurate quantitation using IC-MS or LC-MS techniques, many investigators used cleanup techniques to minimize interfering compounds (21) or standard addition to compensate for suppression/enhancement artifacts (36, 37, 41).

In this study we sought to develop and apply an extremely sensitive and robust method for four major oxyhalides in a variety of water matrixes using LC-MS/MS technology. Experiments were designed to show that the proposed method compares favorably to established IC-CD and IC-postcolumn derivatization (IC-PCD) methods, yet with much improved sensitivity and selectivity. The method was applied to a variety of matrixes, including challenging salt solutions and detergents.

Experimental Section

Materials. Bromate and perchlorate standards were obtained from Ultra Scientific (North Kingstown, RI). Chlorate and iodate standards were purchased as sodium salts from J.T. Baker (Phillipsburg, NJ) and EM Science (Gibbstown, NJ), respectively, at >99.5% purity. Stock and calibration standards were made by dissolving neat standards into deionized water, which had been previously determined free of the compounds of interest at the method detection limits. Trace analysis grade methanol was obtained from Burdick and Jackson (Muskegon, MI). Formic acid was purchased from EM Science.

Sample Collection and Preservation. Bottled water samples were purchased from local merchants, and surface water samples were collected in 125 mL plastic bottles (Nalge Nunc, Rochester, NY). Both were stored at 4 °C until analysis.

Sample Preparation. All water samples were prepared by elution through one OnGuard II Ba cartridge and one OnGuard II H cartridge (Dionex, Sunnyvale, CA) in series. The in-series cartridges were prepared by flushing with 10 mL of deionized water. Samples were eluted at a flow rate of 2.0 mL/min, with the first 6 mL being discarded. The following 2 mL was collected in an autosampler vial and saved for analysis. Detergent samples were prepared by diluting approximately 1 g in 100 mL of deionized water.

Liquid Chromatography. An Agilent (Palo Alto, CA) G1312A binary pump and an HTC-PAL autosampler (CTC Analytics, Zwingen, Switzerland) were used for all analyses. All analytes were separated using a 250 × 4.6 mm Synergi Max-RP C12 column with a 4 μm pore size (Phenomenex, Torrance, CA). A binary gradient consisting of 0.1% formic

TABLE 2. Source-Dependent Parameters

collision gas (psig)	10
curtain gas (psig)	10
ion source gas 1, nebulizer gas (psig)	50
ion source gas 2, turbo gas (psig)	50
ionspray voltage (V)	-4200
temperature (°C)	550
probe x-axis position (mm)	5
probe y-axis position (mm)	5
entrance potential (V)	-10

acid (v/v) in water (A) and 100% methanol (B) at a flow rate of 700 μL/min was used. The gradient was as follows: 5% B held for 3.5 min, increased linearly to 80% by 10 min, and held for 3 min. A 9 min equilibration step at 5% B was used at the beginning of each run to bring the total run time per sample to 22 min. An injection volume of 10 μL was used for all analyses.

Mass Spectrometry. Mass spectrometry was performed using an API 4000 triple-quadrupole mass spectrometer (Applied Biosystems, Foster City, CA). The process of optimization of the mass spectrometer has been previously published (42) and, therefore, will not be covered in detail in this work. Briefly, ESI negative was found to be the most sensitive and selective of the various ionization techniques/polarities. Once this was established, the optimal compound-dependent parameters were determined and are shown in Table 1. Subsequently, source-dependent parameters were optimized, and the results are shown in Table 2.

To ensure the quality of the data, transitions containing isotopes of chlorine and bromine were used to qualitatively confirm peaks obtained using the most abundant isotopes. Iodine has no nonradioactive, naturally occurring isotopes and therefore was not confirmed in this manner. Chlorine-37 was used to confirm both perchlorate and chlorate peaks, and bromine-81 was used to confirm bromate peaks. Only peaks showing confirmation isotopic transitions from chlorine or bromine were reported.

Detection Limit Studies and Calibration. The method detection limit (MDL) was determined by consecutively injecting 1.0 pg on column eight times. The MDL was then calculated by multiplying the standard deviation of the replicate measurements by the appropriate Student's *t* value for 7 degrees of freedom (Table 3). Since water samples were injected directly after pretreatment and no concentration/dilution steps were performed, the MDL is synonymous with the instrument detection limit (IDL). A conservative lowest calibration point was chosen as the method reporting limit (MRL). For perchlorate, this MRL was 0.050 μg/L, while for all other analytes the MRL was set at 0.100 μg/L. The remaining calibration points were at 0.25, 0.50, 1.0, 5.0, and 10 μg/L. All analytes were calibrated externally using linear or quadratic regression with 1/*x*² weighting. Correlation coefficients were required to be at least 0.990 and typically exceeded 0.995.

TABLE 3. Method Detection Limit Studies at 0.100 $\mu\text{g/L}^a$

	perchlorate	bromate	iodate	chlorate
replicate no. 1	0.0992	0.0929	0.148	0.110
replicate no. 2	0.105	0.113	0.112	0.0882
replicate no. 3	0.114	0.0980	0.118	0.101
replicate no. 4	0.115	0.0860	0.127	0.113
replicate no. 5	0.105	0.0909	0.166	0.137
replicate no. 6	0.118	0.121	0.127	0.111
replicate no. 7	0.112	0.0864	0.169	0.102
replicate no. 8	0.0992	0.128	0.164	0.125
std dev	0.00729	0.0164	0.0231	0.0150
Student's <i>t</i> value	2.998	2.998	2.998	2.998
MDL	0.0219	0.0491	0.0694	0.0450
MRL/lowest calibration point	0.050	0.100	0.100	0.100

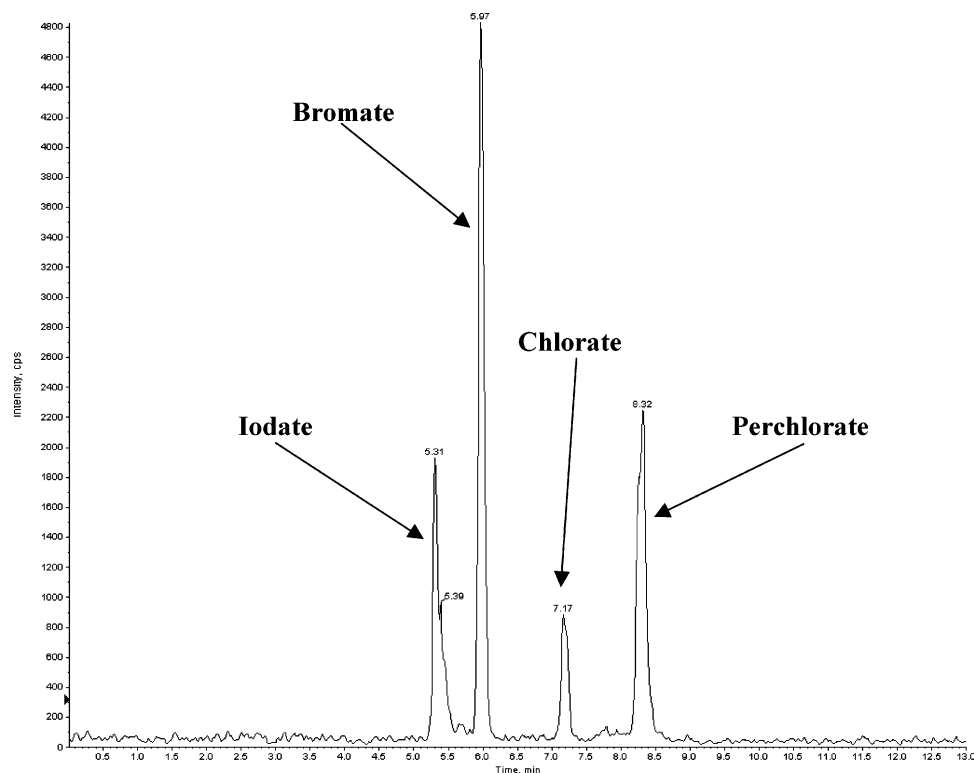
^a All values in $\mu\text{g/L}$.

FIGURE 1. Total ion chromatogram from a bottled water sample.

Results and Discussion

Analytical Observations. The four oxyhalide species investigated were completely resolved using the HPLC separation described (Figure 1). Initial testing of high-conductivity ($>1000 \mu\text{S/cm}$) water without sample pretreatment showed significant matrix interferences. Figure 2 shows LC-MS/MS chromatograms of a natural water sample before and after the removal of sulfate and carbonate. The primary sulfate ion transition is the loss of one oxygen atom (from m/z 97 to m/z 81). While this transition does not show a direct interference with either perchlorate transition (from m/z 99 to m/z 83 for ^{35}Cl and from m/z 101 to m/z 85 for ^{37}Cl), two isotopic forms of sulfate ($\text{H}^{34}\text{S}^{16}\text{O}_4$ and $\text{H}^{32}\text{S}^{16}\text{O}_3^{18}\text{O}$) both exhibit the same mass transition as the ^{37}Cl perchlorate transition. In most natural waters, sulfate will be present at concentrations much higher than those of the oxyhalide anions studied here. To further confirm the presence and impact of sulfate, the ion transition of sulfate was verified using standards and then monitored along with the target oxyhalides (Figure 3). Pretreatment of water samples using hydronium and barium cartridges for carbonate and sulfate

removal, respectively, eliminated the matrix interferences and provided more reliable quantitation. Furthermore, these pretreatment steps also reduced instrument contamination and maintenance.

Since these data were produced, an ^{18}O -labeled perchlorate (Icon Isotopes, New Jersey) was made commercially available and was obtained for use as an internal standard. Preliminary results using Cl^{18}O_4 as an internal standard have been favorable. Infusion into the mass spectrometer revealed a precursor ion of m/z 107 and a product ion of m/z 89. This corresponds to a loss of one ^{18}O atom and correlates with our precursor/product transitions for unlabeled perchlorate. Although Cl^{18}O_4 is now available, no stable isotopically labeled bromate, chlorate, or iodate standards exist, to the knowledge of the authors. Even though this standard was not used for the data presented in this paper, quality control procedures were used to ensure the stability of the instrument and the integrity of the data. This included requirements for calibration curves and continuing calibration verifications that bracketed all non-quality-control samples and spike/recovery data for each matrix encountered.

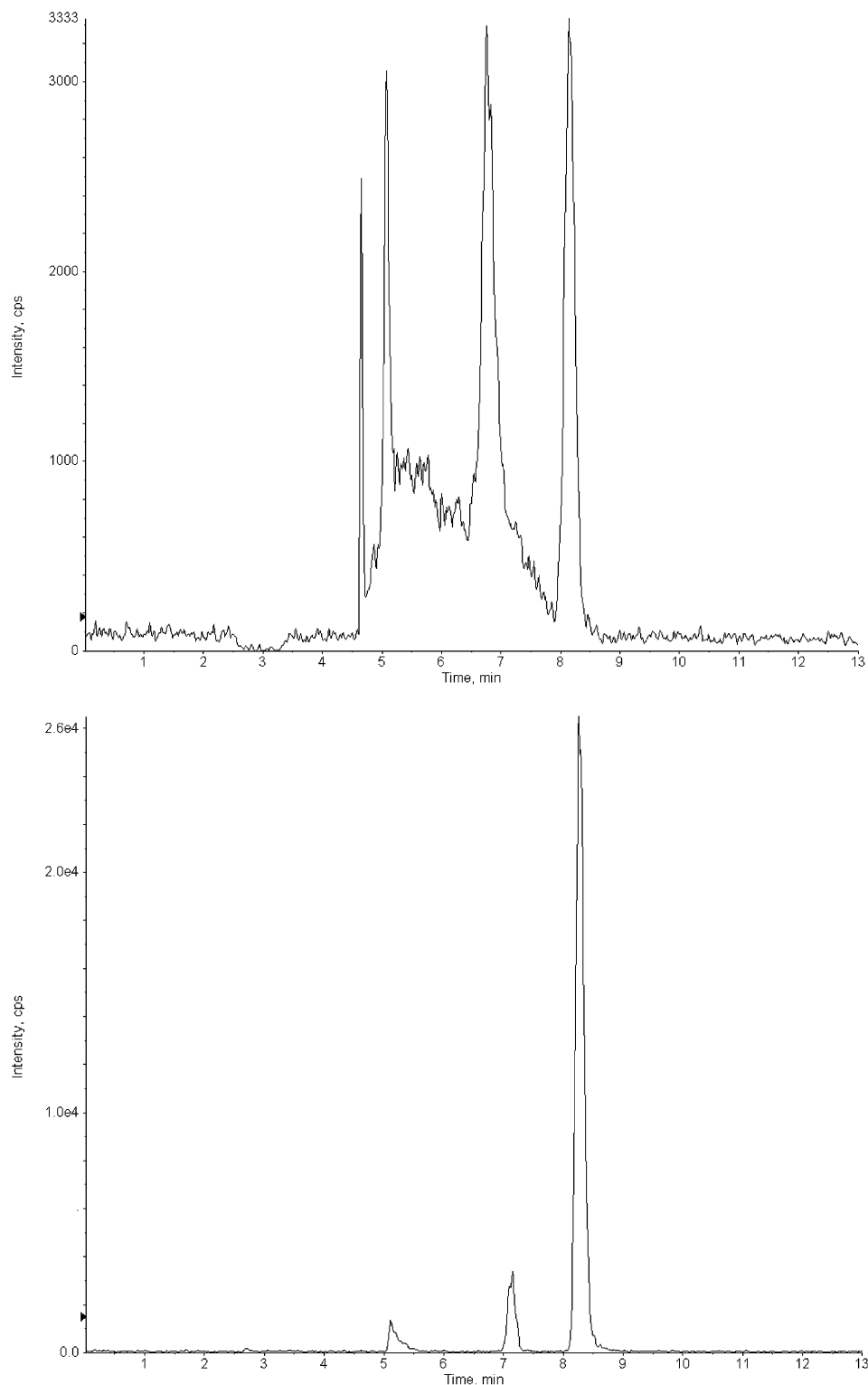


FIGURE 2. Chromatograms of a natural water before (a, top) and after (b, bottom) elution through hydronium and barium cartridges. Note the large increase in perchlorate intensity due to removal of matrix interference.

Comparison to Established Analytical Methods. To demonstrate the performance of the proposed LC-MS/MS against an established IC-CD method, water samples previously reported to have perchlorate and bromate contamination were split and analyzed by both the proposed LC-MS/MS method and EPA standard methods 314.0 and 317.1 using IC-CD and IC-PCD, respectively, in a double-blind experiment. Table 4 shows the comparative results for perchlorate analyzed in seven natural waters using the method described here and EPA method 314.0. Table 5 shows

comparative results for bromate in five ozonated waters and two hypochlorite solutions. Both methods showed good agreement among the samples analyzed with deviation always less than 20% and generally less than 10%. In several waters, the proposed LC-MS/MS method detected perchlorate and bromate at levels below the MRL for EPA 314.0 and 317.1, respectively, while the EPA methods employed were unable to detect either compound; examples are provided in Tables 4 and 5. None of the oxyhalides investigated were detected in any blanks.

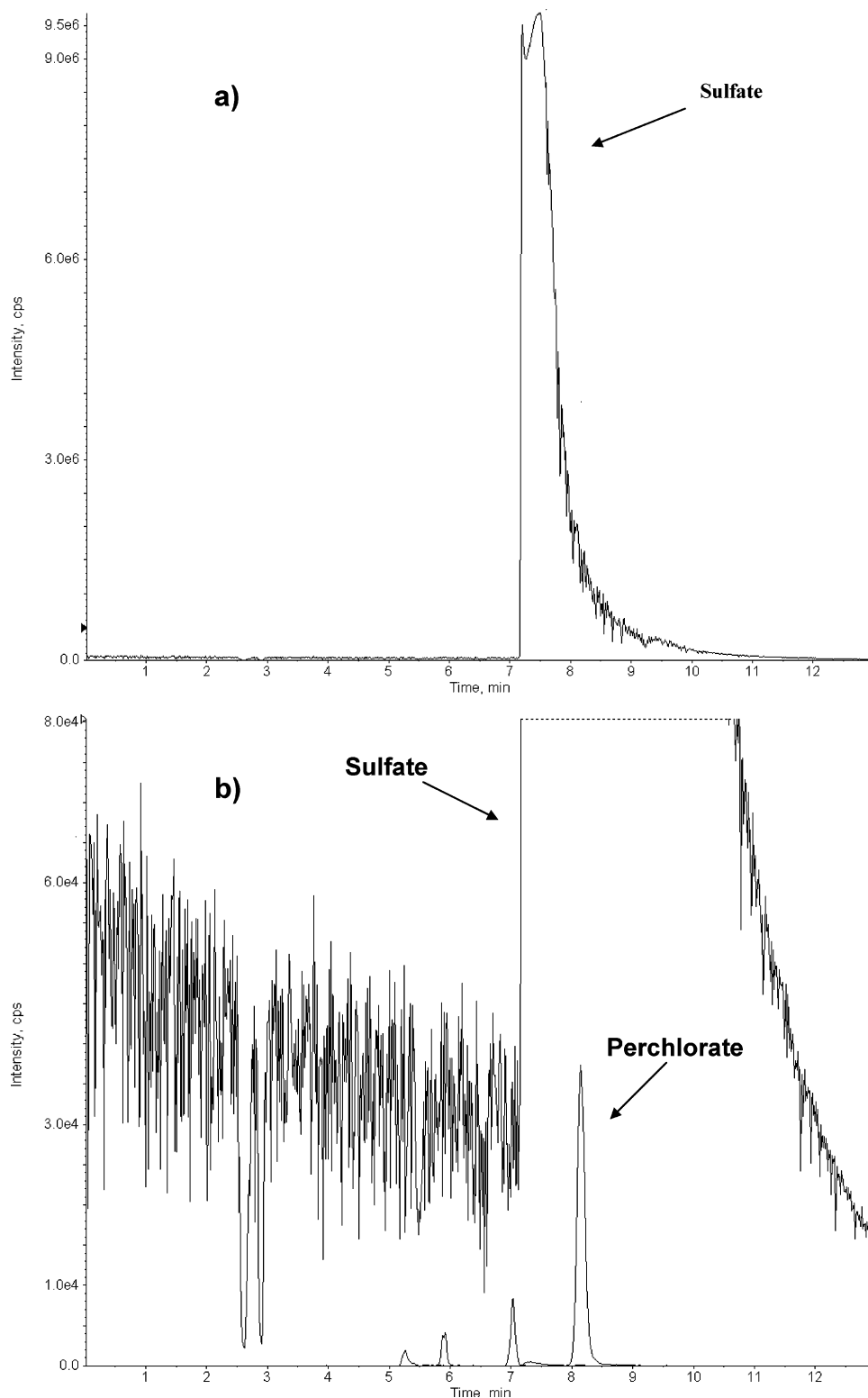


FIGURE 3. Chromatogram from a 1/10 dilution of a natural water sample: (a) extremely large sulfate peak, (b) magnification revealing perchlorate and other oxyhalides (unlabeled).

Occurrence in Bottled Waters. Twenty-one commercially available bottled waters were purchased from various local merchants, representing a variety of sources and treatment processes. Results for the four oxyhalide anions are presented in Table 6. Perchlorate was detected in 10 of the 21 (48%) waters investigated with detectable concentrations ranging from 0.07 to 0.74 $\mu\text{g/L}$. Bromate was detected in 12 of the 21 (57%) waters with detectable concentrations ranging from 0.57 to 76 $\mu\text{g/L}$. Iodate was detected in 15 of 21 (71%) samples

with detectable concentrations ranging 0.14 to 25 $\mu\text{g/L}$. Chlorate was also detected in 15 of the 21 (71%) samples analyzed with detectable concentrations ranging from 0.21 to 5.8 $\mu\text{g/L}$.

Occurrence in Natural and Treated Waters. Thirteen waters were collected from various sources throughout the U.S. These samples include seven surface waters, one groundwater, one spring water, and four treated waters. The results are presented in Table 7. Samples 1b, 2b, 3, and 4 are

TABLE 4. Comparison of Methods—Perchlorate ($\mu\text{g/L}$)^a

sample	proposed method	EPA 314.0	% dev
1	7.8	7.5	2.8
2	7.3	5.8	16.2
3	6.9	5.4	17.2
4	17	16	4.3
5	16	14	9.4
6	16	14	9.4
7	11	10	6.7
8	2.4	ND	NA
9	0.8	ND	NA
10	1.5	ND	NA

^a NA = not applicable. ND = not detected.

TABLE 5. Comparison of Methods—Bromate ($\mu\text{g/L}$)^a

sample	proposed method	EPA 317.1	% dev
1	38	37	1.9
2	14	14	0.0
3	18	19	3.8
4	13	17	18.9
5	19	25	19.3
6	0.45	ND	NA
hypochlorite no. 1	2700	2700	0.0
hypochlorite no. 2	1900	2000	3.6

^a NA = not applicable. ND = not detected.

treated drinking water originating from surface water sources. Utilities providing samples 1b, 3, and 4 utilize chlorine gas, while sample 2b was provided by a utility using on-site hypochlorite generation. Perchlorate was reported in 12 of the 13 samples (92%) tested with detectable concentrations ranging from 0.06 to 6.8 $\mu\text{g/L}$. In the single sample that is listed as less than detection, perchlorate was clearly visible yet at less than the reporting limit of 0.05 $\mu\text{g/L}$. Bromate was detected in only 2 of the 13 samples analyzed, with both detections in treated drinking water. Samples 2a,b show the production of 4.6 $\mu\text{g/L}$ bromate through ozonation of natural water. Iodate was detected in 12 of the 13 samples analyzed with detectable concentrations ranging from 0.2 to 6.2 $\mu\text{g/L}$.

The data suggest that iodate is produced during drinking water treatment, as would be expected for processes such as ozonation and hypochlorite generation. All untreated water samples contained 1.2 $\mu\text{g/L}$ or less iodate, while waters posttreatment contained >2.8 $\mu\text{g/L}$. Chlorate was detected in 10 of the 13 waters tested with detectable concentrations ranging from 1.2 to 270 $\mu\text{g/L}$. Of particular interest are samples 1a,b and 2a,b, which show the raw water and subsequent treated water. In each case of treated water investigated, the concentration of chlorate increases after treatment. Samples 2a,b show a dramatic increase in chlorate concentration (+238 $\mu\text{g/L}$). Upon further investigation, it was determined that the source of chlorate within the treatment system was the result of on-site electrolytic hypochlorite generation, which produces hypochlorite from salt. The hypochlorite generator produces a concentrated hypochlorite solution, which is then metered into the water. We determined the hypochlorite solution to contain 9.7, 133, 143, and 950000 $\mu\text{g/L}$ perchlorate, bromate, iodate, and chlorate, respectively.

Occurrence in Detergents. Seven commercially available detergents were purchased from various vendors. Reporting limits for detergents were calculated in the same manner as for the water samples except that the mass of the sample dissolved had to be accounted for in the reporting limit (Table 8). Perchlorate, bromate, and iodate were detected in only one of the seven samples at 0.71, 2.6, and 1100 $\mu\text{g/g}$, respectively. Conversely, chlorate was detected in every sample tested at concentrations ranging from 2 to 571 $\mu\text{g/g}$.

Summary. The method presented here represents a rapid and sensitive technique to monitor four prevalent oxyhalides in a variety of aqueous matrixes simultaneously. To the best of the authors' knowledge, no other method has been published that monitors these oxyhalides simultaneously. Therefore, total sample preparation and analysis can be completed in less than 30 min, compared to much longer times to run multiple existing methods. This method requires sample volumes of less than 1 mL for direct injection, which is suitable for most drinking waters. With minimal preparation using barium and hydronium cartridges and sample volumes of 1–2 mL, sulfate and carbonate, respectively, can be removed from more challenging matrixes. Since only 10 μL of pretreated sample is actually injected into the LC–MS/MS, matrix interferences are minimal or eliminated completely. From the limited data shown here, it appears that

TABLE 6. Bottled Water Results ($\mu\text{g/L}$)

sample ID	water source	treatment ^a	perchlorate	bromate	iodate	chlorate
1	unknown	CF, RO	<0.05	0.57	<0.1	1.1
2	unknown	CF, O, RO	<0.05	0.70	0.14	0.21
3	unknown	unknown	<0.05	76	<0.1	3.1
4	unknown	MF, O, RO	<0.05	0.71	<0.1	0.36
5	municipal	unknown	<0.05	<0.1	<0.1	<0.1
6	municipal	RO	<0.05	1.7	<0.1	0.44
7	municipal	CL, O, RO	<0.05	0.80	<0.1	2.1
8	artesian	unknown	<0.067	<0.1	18	0.21
9	artesian	MF, O, UV	0.096	28	3.6	1.5
10	mineral	MF, O, UV	<0.05	<0.1	25	0.29
11	mineral	MF	0.34	<0.1	1.8	5.8
12	mineral	MF	<0.05	<0.1	3.6	0.56
13	spring	unknown	0.13	7.1	3.2	4.8
14	spring	CF, UV	0.15	<0.1	3.3	<0.1
15	spring	MF, O, UV, RO	0.74	2.3	18	<0.1
16	spring	unknown	0.60	2.2	16	<0.1
17	spring	MF, O, UV	0.11	1.2	4.0	0.31
18	spring	MF, UV	<0.05	<0.1	1.1	<0.1
19	spring	unknown	<0.05	<0.1	0.24	<0.1
20	spring	unknown	0.073	14	1.7	5.4
21	spring	unknown	0.11	<0.1	1.2	2.7

^a CF = carbon filtration, RO = reverse osmosis, O = ozonation, MF = microfiltration, CL = chlorination, UV = ultraviolet.

TABLE 7. Natural Water Results ($\mu\text{g/L}$)

sample ID	water source	treatment ^a	perchlorate	bromate	iodate	chlorate
1a	surface	none	6.4	<0.1	0.33	25
1b	municipal	CL	6.6	<0.1	6.2	48
2a	surface	none	6.5	<0.1	0.35	32
2b	municipal	CL, O	6.8	4.6	4.9	270
3	municipal	CL	0.29	0.23	2.8	3.6
4	municipal	CL	0.11	<0.1	4.4	1.2
5	surface	none	1.4	<0.1	<0.1	1.9
6	surface	none	0.14	<0.1	0.29	2.0
7	surface	none	0.06	<0.1	0.33	<0.1
8	surface	none	2.3	<0.1	0.34	9.7
9	surface	none	0.49	<0.1	0.20	1.7
10	ground	none	0.30	<0.1	1.2	<0.1
11	spring	none	<0.05	<0.1	0.26	<0.1

^a O = ozonation, CL = chlorination.

TABLE 8. Various Commercial Soap Solutions ($\mu\text{g/g}$)

sample ID	perchlorate	chlorate	bromate	iodate
A	<0.56	41	<1.1	<1.1
B	0.71	570	2.6	<0.86
C	<0.43	21	<0.86	<0.86
D	<0.26	9.3	<0.52	1100
E	<0.39	23	<0.78	<0.78
F	<0.43	16	<0.86	<0.86
G	<0.38	2.0	<0.76	<0.76

perchlorate is a ubiquitous component of natural waters at trace levels (ng/L). Hypochlorite generation was shown to produce high levels of chlorate, resulting in a greater than 200 $\mu\text{g/L}$ increase in chlorate concentration of finished drinking water. Due to the highly sensitive method applied here, bottled waters were found to contain detectable levels of perchlorate, in contrast to previous data to the contrary using a less sensitive method (26). It is interesting to note that three bottled waters exceed the EPA bromate regulation of 10 $\mu\text{g/L}$, with one sample at nearly 8-fold greater than the bromate MCL. Detergents were not a significant source of perchlorate, but did contain appreciable levels of chlorate. With increasing analytical sensitivity, it is now possible to discover contaminants previously considered absent in a variety of water types.

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