Determination of Oxyhalide Disinfection By-products in Water by Suppressed Anion Chromatography Coupled with Mass Spectrometry

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1. Introduction

In order to protect public health, drinking water is usually disinfected using chlorine, chlorine dioxide, sodium hypochlorite and ozone. However, disinfection will not only remove microorganisms that cause diseases in humans, but also produce disinfection byproducts (DBPs), including chlorite, chlorate and bromate. It is reported that a significant amount of chlorite and chlorate can be formed during water chlorination and bromate can be produced from water ozonation when water contains high levels of bromide. These DBPs are potentially harmful to humans. For example, bromate has been identified as a potential human carcinogen. Therefore, the Environmental Protection Agency (EPA) of the United States has proposed that the maximum concentration level (MCL) of bromate is 10ppb.

In this study, an IC-MS method was developed using a novel electrolytically regenerated suppressor as a part of a modular IC system coupled with a LC-MS 2020 single quadrupole MS for the determination of oxyhalide anions, including chlorite, chlorate and bromate in drinking water. Both conductivity detection (CDD) and MS with electrospray ionization in negative mode are used in the method. The CDD is used to monitor the column effluent; only the oxyhalides of interest are directed to MS via a divert valve. Quantitative analysis was performed by using the selected ion monitoring (SIM) on two isotopic mass of each compound..

2. Experimental

Experiments were performed using a modular Shimadzu IC system with built-in electrolytically regenerated suppressor and a single quadrupole mass spectrometer detector (LCMS-2020) with electrospray ionization (ESI) interface. The schematic diagram of the IC-MS system used in this study is illustrated in Figure 1. In this method, external fresh D.I water is continuously pumped through the suppressor regeneration channel at 1.2 mL/min flow rate using the second pump, hydronium ions are continuously generated from electrodialysis and exchange with sodium ions, which convert salts to

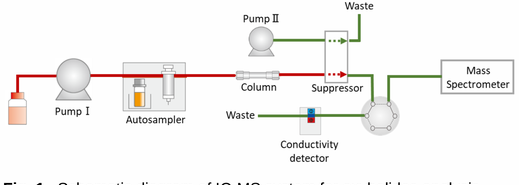

Fig. 1. Schematic diagram of IC-MS system for oxyhalides analysis.

their corresponding acids. The conductivity detector is used to monitor column effluent. Only the oxyhalides of interest are directed to the MS using a divert valve. The desalting of the suppressor not only reduces the conductivity of the eluent, allowing high-sensitivity analysis of anion during conductivity detection, but also protects the MS from a buildup of trace salts from the eluent post-suppressor. Method conditions are listed in Table 1.

Table 1. Method conditions.

IC (Prominence)	
Column	Shodex IC SI-52 E, 4 x 250 mm (P/N 220-91524-04) Guard column, Shodex SI-90G, 4.6 x 10 mm (P/N 220-91524-05)
Eluent	5.4 mM sodium carbonate
Flow rate	0.5 mL/min
Column oven	50 ℃
Injection volume	300 µL
Detection	Suppressed conductivity; 180 mA in external water mode, water flow rate is 1.2 mL/min
Run time	21 min
MS (LCMS-2020)	
Ionization	ESI -
Interface temperature	350 ℃
DL temperature	200 ℃
Nebulizing gas flow	1.5 L/min
Heat block	500 ℃
Drying gas flow	15 L/min
Interface voltage	-5 kv
DL voltage	-20 v
Scan range (m/z)	20-200
Selected ions m/z	66.9, 68.9, 82.9, 84.9, 126.8, 128.8

3. Results and Discussion

Six-point calibration curves were established across the concentration range of 0.5-100 ppb for chlorite and chlorate, and 0.5 -25 ppb for bromate. Triplicate results were obtained and weighing of 1/c was applied on the calibration curve. Correlation coefficients of r^2 > 0.999 with good accuracy (between 82% and 120%) were obtained for all three DBPs at each isotopic mass (shown in Figure 2.

Figure 3 shows that chlorite and chlorate eluted at 10.5 min and 18.8 min, respectively. The 3:1 isotopic mass to charge ratio (m/z) of 66.9 to 68.9 and 82.9 to 84.9 were observed for chlorite and chlorate, respectively. Bromate was eluted at 10.9 min, and around 1:1 isotopic ratio of m/z 126.8 to 128.8 was detected.

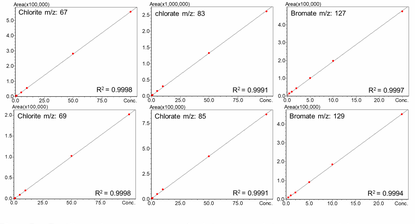

Fig. 2. Calibration curves of chlorite, chlorate and bromate.

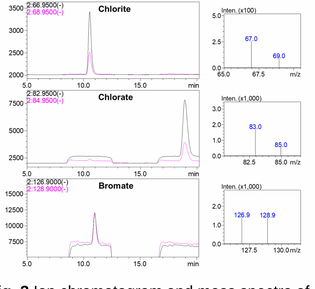

Fig. 3 Ion chromatogram and mass spectra of standard (chlorite, chlorate and bromate; 5 ppb for each compound).

Method precision was performed using three mixed standards with concentrations of 0.5, 1 and 10 ppb, respectively. Table 2 shows the percent RSD of the concentration from seven replicate injections of the three mixed standards for each compound. Excellent reproducibility (< 3%) was achieved for the samples at concentration of 10 ppb. Although the RSD is slightly increased at the concentration of 0.5 ppb, it is still less than 6.5% for each compound.

Table 2 . Method precision (n=7).

Compounds	m/z	Standard (ppb)	Conc. (% RSD)	Standard (ppb)	Conc. (% RSD)	Standard (ppb)	Conc. (% RSD)
Chlorite ($^{35}ClO_2^-$)	66.9	0.5	4.6	1	3.7	10	0.69
Chlorite ($^{37}ClO_2^-$)	68.9	0.5	4.0	1	3.2	10	0.95
Chlorate ($^{35}ClO_3^-$)	82.9	0.5	5.3	1	3.3	10	0.41
Chlorate ($^{37}ClO_3^-$)	84.9	0.5	5.4	1	3.7	10	0.44
Bromate ($^{79}BrO_3^-$)	126.8	0.5	6.5	1	3.8	10	0.74
Bromate ($^{81}BrO_3^-$)	128.8	0.5	4.4	1	2.8	10	2.78

The recovery of the method were investigated by spiking a mixed standard with a concentration of 10 ppb into the six water samples. A good recovery range of 84.1%-113.6 for all three oxyhalides was obtained as shown in Table 3.

Table 3. Recovery of chlorite, chlorate and bromate in different water samples (n=3).

Compounds	m/z	Added concentration (ppb)	Bottle water recovery (%)	Tap water Recovery (%)	Dispenser water recovery (%)	Well water 1 Recovery (%)	Well water 2 Recovery (%)	Well water 3 Recovery (%)
Chlorite ($^{35}ClO_2^-$)	66.9	10	105.0	104.4	104.5	100.1	89.0	99.2
Chlorite ($^{37}ClO_2^-$)	68.9	10	106.6	105.8	105.1	99.8	91.6	100.0
Chlorate ($^{35}ClO_3^-$)	82.9	10	104.6	100.8	84.5	105.8	96.0	101.6
Chlorate ($^{37}ClO_3^-$)	84.9	10	104.0	98.0	84.1	105.3	89.4	102.2
Bromate ($^{79}BrO_3^-$)	126.8	10	106.8	113.6	107.5	107.2	99.7	110.7
Bromate ($^{81}BrO_3^-$)	128.8	10	97.4	98.5	96.1	97.2	85.0	97.0

4. Conclusion

A sensitive and simple quantitative IC-MS method for determination of three oxyhalides, including chlorite, chlorate and bromate, was developed using a Shimadzu Prominence IC coupled with a single quadruple MS (LCMS-2020). All three oxyhalide anions can be simultaneously quantified at < 0.5 ppb without using any laborious sample preparation or post-column additions to increase sensitivity. With mass identification, more specific and confident results can be obtained using this method, especially in complex matrices. This study demonstrated robust and reliable performance of the novel modular IC-MS for the determination of oxyhalides in drinking and bottled water.