Application note | 003449

Environmental

Fast determination of chlorite, bromate, chlorate, dichloroacetic acid, and trichloroacetic acid in drinking water

Authors

Chunxia Han, Hongguo Zheng

Application Development Center,
Thermo Fisher Scientific (China) Co., Ltd.
Shanghai, 201203

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Introduction

During the disinfection of drinking water, disinfection by-products (DBPs) are produced when the disinfectant (such as chlorine, chloramine, chlorine dioxide and ozone) reacts with inorganic or organic substances. Some DBPs are carcinogenic and toxic to reproduction and development, creating a risk to human health.[1] In the Chinese regulation "GB 5749-2022 Standards for Drinking Water Quality," the limits for five DBPs are specified for drinking water (Table 1). There is a lot of variation in DBP regulatory limits from one country to the next.[2] If we focus on Haloacetic Acids (HAAs), China and Malaysia, for example, regulate two of these, while the United States (US) has set limits for five (HAA5). To monitor all HAA5, the recommended method uses ion chromatography (IC) coupled to a triple quadrupole mass spectrometer.[3] This application note describes a method that determines two of the HAAs, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) using anion exchange ion chromatography with suppressed conductivity detection.

Table 1. Maximum concentration limits specified in GB 5749-2022

Analyte	Concentration limit (µg/L)
Bromate (BrO_3^-)	10
Chlorite (ClO_2^-)	700
Chlorate (ClO_3^-)	700
Dichloroacetic acid (DCAA)	50
Trichloroacetic acid (TCAA)	100

In addition to DBPs, drinking water also contains a variety of common ions, such as chloride, nitrate, carbonate, and sulfate, with concentrations reaching several hundred parts-per-million (ppm), creating potential interference in the separation and detection of DBPs. "GBT 5750.10-2023 Standard Examination Methods for Drinking Water-Part 10: Disinfection by-products indices" provides recommended chromatographic conditions, in which KOH is utilized as the eluent, with gradient elution and analysis time of approximately 40 min.

In the past 10 years, several high-pressure ion chromatography (HPIC) products, along with a variety of small particle-size chromatography columns, have been introduced that use enhanced column efficiencies with higher back pressure tolerance to enable development of more rapid separation methods. In this application note, the Thermo Scientific™ Dionex™ Inuvion™ IC system, combined with the Thermo Scientific™ Dionex™ IonPac™ AS19-4µm column (4 x 150 mm), was used to develop a fast separation method that assays chlorite, bromide, chlorate, DCAA, and TCAA in drinking water in under 21 minutes. Using a column with smaller particles (4 µm vs 8 µm) provided greater peak resolution and allowed the use of a shorter column (150 mm vs 250 mm) to obtain sufficient separation in a much shorter run time. The outstanding performance of the Dionex Inuvion IC system enabled method detection limits that were much lower than the Chinese standard limit requirements and provided the needed resolution, accuracy, and stability to determine DBPs in drinking water in almost half the time when compared to the method described in GBT 5750.10-2023.

Experimental

IC system setup

Instrumentation, reagents and materials

- Dionex Inuvion IC system with RFIC (P/N 22185-60108)
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 07492)
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3.2
- Dionex IonPac AS19-4µm analytical column, 4 × 150 mm, (P/N SP6931*)
- Thermo Scientific™ Dionex™ IonPac™ AG19-4µm Guard Column, 4 × 30 mm, (P/N SP6932*)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor (4 mm), (P/N 088666)
- Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge, (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column, (P/N 088662)
- Thermo Scientific™ Dionex™ RFIC Eluent Degasser (P/N 106-60001)
- Ultrapure water (18.2 MΩ·cm)
- Disinfection by-products standards
  - Separate 1000 mg/L solutions of each of the following: chlorite, chlorate, bromate, DCAA, TCAA (o2si smart solutions)

Method

Chromatographic conditions

Columns: Dionex IonPac AG19-4µm (4 × 30 mm) + Dionex IonPac AS19-4 µm (4 × 150 mm)

Eluent: KOH gradient elution; See Table 2 for the gradient parameters

Flow rate: 1.2 mL/min

Injection volume: 250 µL

Column temperature: 25° C

Detection: Suppressed conductivity, Dionex ADRS 600, 149 mA, recycle mode

Background conductance: 0.4 µS/min

System backpressure: 2,800 psi

Run time: 21 min

Table 2. Gradient elution procedure

Time (min)	KOH concentration (mM)
0 - 6.0	6
6.1 - 14.0	6 - 20
14.0 - 15.0	20
15.1 - 18.0	50
18.1 - 21.0	6

Pre-treatment conditions

Drinking water samples were filtered using a 0.22 µm syringe filter (Tianjin Jinteng Experiment Equipment Co. Ltd.) prior to analysis.

*Contact your local sales representative for ordering information

Results and discussion

Linearity and stability

Chlorite, chlorate, bromate, DCAA, and TCAA standard solutions were prepared by dilution of standard concentrates with deionized (DI) water at the concentrations shown in Table 3. Analysis was performed using the chromatographic conditions described in the method section above, and a typical chromatogram is shown in Figure 1. As can be seen, peaks were all baseline resolved, except for a small amount of overlap between chlorite and bromate, although this did not impact quantification within the concentration range analyzed. All the analytes monitored eluted in less than 15 min with a total run time of 21 min, an almost 50% reduction in overall run time compared to the 40 min of the standard method. This reduction resulted from a combination of a shorter column (150 mm vs 250 mm) and smaller stationary phase particles (4 um vs 8 um). The greater column efficiency from the reduced particle size allowed sufficient resolution to be achieved with a shorter column length.

Table 4 shows the linear ranges, linear equations, and correlation coefficients of the standard curves. All DBPs had linear correlation coefficients (R) > 0.999. When standard solution 3 was run 6 times in succession (as per the recommendation of method GBT 5750.10-2023 for precision testing), the relative standard deviation (RSD) of the DBP retention times was < 0.3%, and for the peak areas it was < 0.90%, demonstrating the method repeatability.

Table 3. Standard solutions of chlorite, bromate, DCAA, chlorate, and TCAA

	Standard solution (µg/L)					
Analyte	**1**	**2**	**3**	**4**	**5**	**6**
Chlorite	25	50	100	200	500	1000
Bromate	5	10	20	40	100	200
DCAA	12	25	50	100	250	500
Chlorate	25	50	100	200	500	1000
TCAA	12	25	50	100	250	500

Table 4. Linear equations, linear ranges and correlation coefficients of chlorite, bromate, DCAA, chlorate, and TCAA

Analyte	Linear equation	Linear range (µg/L)	Correlation coefficient (R)
Chlorite	y = 0.0012x + 0.0100	50 - 1000	1.000
Bromate	y= 0.0006x - 0.0024	5 - 200	0.9995
DCAA	y = 0.0010x - 0.0083	25 - 500	0.9998
Chlorite	y = 0.0010x - 0.0123	50 - 1000	0.9999
TCAA	y = 0.0005x - 0.0053	25 - 500	0.9994

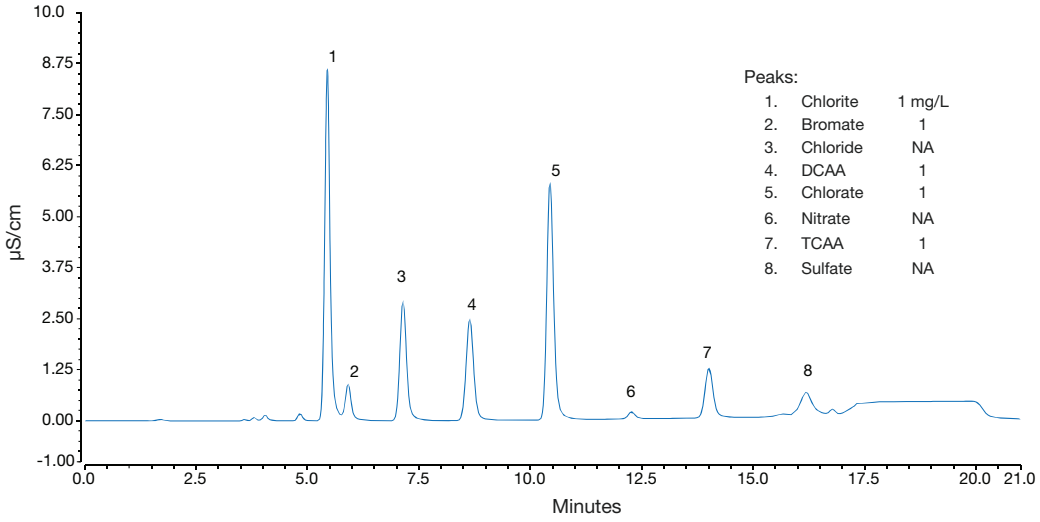


Figure 1. DBP standards separation. NA = Not assayed.

Limit of detection and limit of quantification

The target concentrations corresponding to a three times signal-to-noise ratio (S/N=3) and 10 times signal-to-noise ratio (S/N=10) were utilized as the detection limit and instrumental limit of quantification, respectively. The limit of detection and limit of quantification for the 5 DBPs are shown in Table 5.

Method accuracy

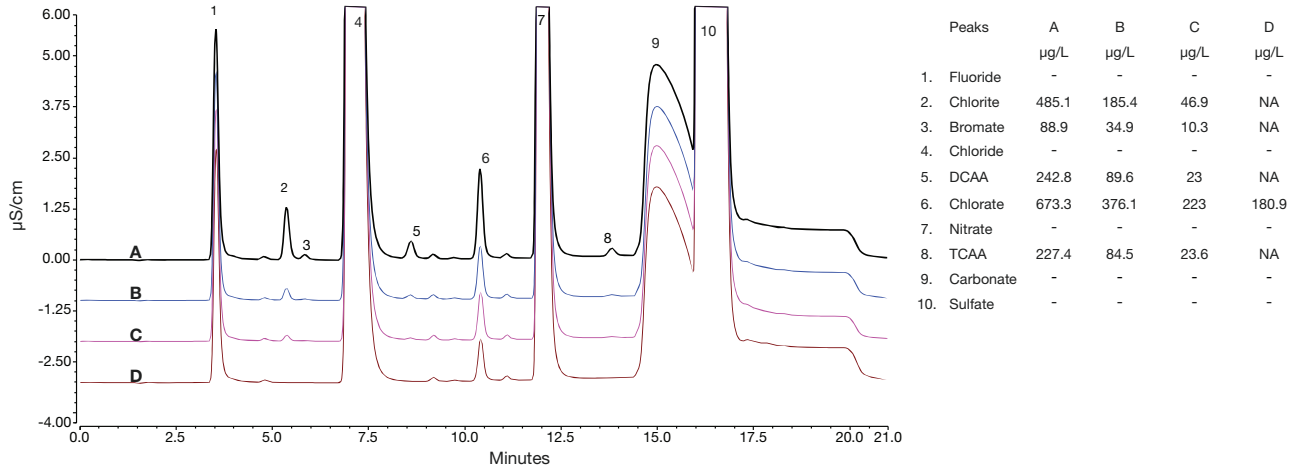
Triplicate samples of Shanghai drinking water were spiked with three concentrations of five DBPs (Figure 2). Recoveries were all between 90% and 107%, demonstrating high method accuracy. Additionally, RSDs were all within 2.0%, demonstrating high method reproducibility (Table 6).

Table 5. Detection limits and limits of quantification

Target	Detection limit (µg/L)	Limit of quantification (µg/L)
Chlorite	0.26	0.87
Bromate	0.34	1.13
DCAA	0.44	1.45
Chlorate	0.46	1.52
TCAA	1.23	4.09

Table 6. Spike recovery and RSDs of DBPs in drinking water

	Spiked concentration (µg/L)	Average recovery	RSD (n=3)
Chlorate	50	96.2%	0.6%
	200	93.2%	0.1%
	500	97.1%	0.0%
Bromate	10	106.7%	1.9%
	40	90.3%	0.4%
	100	90.8%	0.4%
DCAA	25	101.3%	0.5%
	100	91.6%	0.4%
	250	97.2%	0.2%
Chlorite	200	96.0%	1.1%
	500	98.0%	0.1%
	1000	95.5%	1.4%
TCAA	25	106.5%	1.0%
	100	91.8%	0.1%
	250	91.4%	0.1%



	Peaks	A µg/L	B µg/L	C µg/L	D µg/L
1.	Fluoride	-	-	-	-
2.	Chlorite	485.1	185.4	46.9	NA
3.	Bromate	88.9	34.9	10.3	NA
4.	Chloride	-	-	-	-
5.	DCAA	242.8	89.6	23	NA
6.	Chlorate	673.3	376.1	223	180.9
7.	Nitrate	-	-	-	-
8.	TCAA	227.4	84.5	23.6	NA
9.	Carbonate	-	-	-	-
10.	Sulfate	-	-	-	-

Figure 2. DBPs spiked into drinking water (D) at three different concentrations (A-C).

Determination of DBPs in drinking water

Under the conditions described above, a drinking water sample was analyzed to determine the concentrations of DBPs (Table 7). Chlorate, observed at 181 µg/L, was the only analyte determined to be above the detection limit for this method. It was well below the 700 µg/L limit specified in GB 5749-2022.

Table 7. Determination of DBPs in drinking water

Concentration (µg/L)					
Sample	**Chlorite**	**Bromate**	**DCAA**	**Chlorate**	**TCAA**
Shanghai drinking water	×	×	×	181.0	×

×: indicates not detected.

Conclusion

This application note describes the determination of five DBPs in drinking water in 21 min utilizing the Dionex Inuvion IC system and the Dionex IonPac AS19-4µm (4 x 150 mm) column. Compared with methods that use larger-particle size chromatography columns (6-8 µm), the analysis time was decreased from 40 to 21 min while being stable, accurate, and repeatable. This method, which requires multi-step gradients and operates at pressures near the upper limit for older IC systems (3000 psi), is ideally suited to the capabilities of the Dionex Inuvion IC system. This system offers a fast and economical solution for determining DBPs in drinking water.

References

1. Xinyuan Yi, Xinlu Qu, Xin Long, et al. Research progress on chemical properties, transformation, and toxicity of typical disinfection by-products in drinking water [J]. Asian Journal of Ecotoxicology, 2023, 18 (02): 97- 110.
2. Sandhya Rao Poleneni. Chapter 13 - Global disinfection by-products regulatory compliance framework overview, disinfection by-products in drinking water: detection and treatment. Editor(s): Majeti Narasimha Vara Prasad, Disinfection By-products in Drinking Water, Butterworth-Heinemann, 2020.
3. Xin Zhang, Charanjit Saini, Chris Pohl, and Yan Li,. Thermo Scientific Application Note AN73343: Fast Determination of Nine Haloacetic Acids, Bromate, and Dalapon at Trace Levels in Drinking Water Samples by Tandem IC-MS/MS, 2020, Sunnyvale, CA, USA (AN73343).

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