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Determining haloacetic acids in drinking water by one-pump column-switching ion chromatography: An online and cost-effective tool for matrix removal and sample enrichment

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ABSTRACT

Haloacetic acids (HAAs) are a group of disinfection byproducts ubiquitously found in disinfected drinking water and they are currently regulated by some governments. Conventional HAAs analytic methods employ either gas chromatography (GC), two-dimensional ion chromatography (2D-IC), or ion chromatography with electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS) to reduce the effect of interfering compounds and enhance detection resolution; however, they are either laborious in sample preparation procedures or too expensive to be used by common laboratories. To bypass these problems, this study proposes to analyze HAAs by employing a one-pump column-switching ion chromatography (OPCS-IC) that allows direct sample injection without requiring extraction and derivatization pretreatments. Unlike 2D-IC method, which uses two pumps and two parallel sets of IC columns, this method applies only one pump and one column. The tailored OPCS-IC removes coexisting anions from water and enriches HAAs simultaneously, thereby distinguishing HAAs from interfering anions and magnifying the signals of HAAs. For example, when HAAs were enriched by five times, the coexisting F^-, Cl^-, Br^-, NO_3^-, and SO_4^{2-} were removed by 62.4%, 93.9%, 99.7%, 99.9%, and 98.9%, respectively. Meanwhile, the recoveries of HAAs dosed into real samples ranged from 84% to 102%, similar to those obtained from conventional GC method, meaning that the convenience of this method did not compromise its performance. The study hence proves an easy-to-use and relatively cheaper method for measuring HAAs in drinking water.

1. Introduction

During drinking water treatment process, disinfectants (e.g., chlorine, ozone, and chlorine dioxide) can react with aqueous organic matter and bromide/iodide to produce disinfection byproducts (DBPs) [1,2]. To date, over 700 chlorinated DBPs have been identified in water, and haloacetic acids (HAAs) are the second most abundant DBP group in drinking water, ranking just after trihalomethanes [3,4]. The average concentration of five major HAAs (HAA_5) in finished drinking waters was found to be 23 $\mu g \cdot L^{-1}$ in the United States [5], 10 $\mu g \cdot L^{-1}$ in Korea [6], 17 $\mu g \cdot L^{-1}$ in Spain [7], and 45 $\mu g \cdot L^{-1}$ in the United Kingdom [8]. Due to their widespread occurrence and potential health risks [5], some authorities have issued limits on HAA_5 concentrations in drinking water, such as 60 $\mu g \cdot L^{-1}$ in the United States [9] and 80 $\mu g \cdot L^{-1}$ in Health Canada [10]. Thus, it is necessary to analyze HAAs routinely in drinking water to safeguard consumers' health.

Currently, the United States Environmental Protection Agency (USEPA) has issued a series of standard methods (i.e., Method 552, Method 552.1 Method 552.2, and Method 552.3) to determine HAAs by using gas chromatography (GC) tandem electron capture detector (ECD) [11–14]. These GC-based methods generally take three steps during sample preparation process prior to GC analysis, including sample acidification, liquid–liquid extraction, and esterification derivatization [15], which are labor-intensive and time-consuming (e.g., 2 h is needed for derivatization only). Meanwhile, high-performance liquid chromatography (HPLC) with ultraviolet detector (UV) was once used to detect HAAs [16]. However, it is difficult to quantify trace levels of HAAs nor separate HAAs from coexisting compounds well in water, because HAAs are highly hydrophilic and do not have characteristic UV absorbing wavelengths. Given that HAAs normally exist in ionic forms in neutral water because their acid-dissociation coefficients (pK_a) are low (ranging from 0.6 to 2.9 for HAA_5) [17], the use of ion chromatography (IC)

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tandem conductivity (CD) detector has been already brought about to determine HAAs as it can distinguish HAAs without requiring any sample pretreatment [18].

However, a major challenge for HAAs determination via IC-based methods derives from the interference of abundant coexisting components in water, which may have either similar elution time as HAAs or huge chromatographic peaks that overlap HAAs' peaks. For example, the chromatographic peak of chloride (Cl^-) may interfere with the detections of monobromoacetic acid (MBAA) and dichloroacetic acid (DCAA), while the presence of abundant sulfate (SO_4^{2-}) may conceal the chromatographic peak of trichloroacetic acid (TCAA) [19]. To overcome this issue, USEPA issued another standard method (i.e., Method 557) to analyze HAAs by equipping IC with electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS) [20]. Despite so, coexisting salts in water may disturb the ionization performance of MS, thus affecting the accuracy of HAAs quantification. Now that the MS method may not adequately quantify HAAs in the presence of interferents, a two-dimensional ion chromatography (2D-IC) method [21–23] was developed to detect HAAs and remove interferents by placing divert valves in eluent flow path [19,24,25]. Although this approach has been adopted as a standard USEPA method in 2017 (i.e., Method 557.1) [26], two sets of IC systems (i.e., two pumps, two sets of columns, two detectors, two suppressors, etc.) are needed, making it expensive and hard to be accepted by common laboratories.

Recently, a one-pump column-switching ion chromatography (OPCS-IC) technique has been developed to detect trace anions in the presence of coexisting components, such as trace chlorate and iodate in water enriched with salts [27,28], to distinguish selected anions and pharmaceutical drugs in the presence of other organics [29,30], and to determine selected anions in water containing abundant weak acids or surfactants [31–35]. The principle of OPCS-IC method is to enrich and separate aqueous analytes by switching valve ports and aligning the positions of analytical column and concentrator column alternatively [21]. By heart-cutting interfering compounds and delivering them into waste, target components were selectively and temporarily retained at the concentrator column [35]. So, the analytes of interest can be enriched for subsequent analysis in the second run. Compared to conventional IC, the OPCS-IC method is more robust in reducing coexisting interferents and therefore enabling better quantification of target analytes. Compared to 2D-IC, the OPCS-IC requires fewer instruments. However, this technique has yet been applied to analyze HAAs before, because it is more challenging than before as it needs to carry out multiple column-switching actions to reduce the interferences of multiple anions.

In addition to matrix removal, online analytes enrichment is another merit of OPCS-IC method. In most of earlier 2D-IC and OPCS-IC studies, the concentrator column was only used to enrich analytes by only once. In theory, the concentrator column can be used multiple times for further enrichments by successive injections, as well as simultaneous matrix removal. Compared to conventional HAAs enrichment and matrix removal methods, such as liquid–liquid extraction [36], solid-phase extraction [37], and liquid extraction/back extraction [38,39], the online OPCS-IC method is not only labor-saving in sample pretreatments but also easy to automate. However, there are few studies employing OPCS-IC method to enrich HAAs now, probably because interfering anions are likely enriched too in the meantime of HAAs enrichment. So, both analytes enrichment and matrix removal are necessary to detect trace HAAs in drinking water.

In this context, we for the first time tested and optimized the OPCS-IC method in analyzing HAA_5 in drinking water. The recovery of HAAs and removal of interferents are the two major prerequisites guarantying its practical application. In sequence, we assessed the performance of this method on HAA_5 enrichment first. Then, we checked the performance of HAA_5 enrichments and interferents removals. Next, we explored the applicability of the method in terms of its method detection limit (MDL), calibration curve, analytical accuracy, and precision. Lastly, we compared the detections of HAA_5 in several real water samples between this method and a conventional GC-based method (i.e., USEPA standard method 552.3).

2. Materials and methods

2.1. Chemicals and samples

The HAA_5 stock solutions including monochloroacetic acid (MCAA), MBAA, DCAA, dibromoacetic acid (DBAA), and TCAA were prepared by dilution of 97 % or higher purity reagents (Aladdin Inc., China) in ultrapure water. Ultrapure water with an electric resistance of 18.2 $M\Omega \cdot cm^{-1}$ was used for preparing synthetic samples. KOH (purity $\geq$ 95 %, Aladdin Inc., China) was used as mobile phase of IC. The reagents used in the USEPA 552.3 method, including sodium sulfate, sodium bicarbonate, methyl *tert*-butyl ether, 1,2,3-trichloropropene, and methyl alcohol were chromatographic grade and purchased from Aladdin Inc., China. Sodium hydroxide and sulfuric acid were used to adjust water pH whenever needed. In addition, four typical drinking water samples were collected from laboratory faucets and public drinking water facilities. The contents of anions in these samples are provided in Table S1.

2.2. Apparatus

The proposed OPCS-IC consists of a host engine (RPIC-2017, Qingdao Reepo Analytic Instrument Co., ltd., China), an automatic electrodialytic eluent generator (RPEG-1-A, Qingdao Reepo Analytic Instrument Co., ltd., China), an automatic eluent suppressor (WLK-8A, Qingdao Reepo Analytical Instrument Co., ltd, China), a CD detector, and a UV detector (SPD 20A, Shimadzu, Japan). The IC engine contains a high-pressure peek pump, an injection loop (500 μL), an eluent purification column (RPTC, 40 μm × 100 mm × 4 mm), two valves (one six-port and another ten-port valve), and a temperature-maintaining oven (set to 30 °C in this study). In this system, an IonPac AG 19 guard column (Thermo Fisher, USA, 11 μm × 50 mm × 4 mm) was used as the concentrator column and an IonPac AS 19 (Thermo Fisher, USA, 7.5 μm × 250 mm × 4 mm) was used for compounds separation (Fig. S1). The working pressure in this system was 1552 psi. The setups of the IC are provided in Fig. 1.

USEPA method 552.3 was also carried out to analyze HAA_5. For this method, a GC equipped with an ECD (GC-9720, Fuli, China) was used. In brief, 3.0 μL sample was introduced into the GC under splitless injection mode and the compounds were separated by a capillary column (ZB-624, Phenomenex, USA, 1.40 μm × 30 m × 0.25 mm). The flow of carrier gas (nitrogen) was set at 1.0 $mL \cdot min^{-1}$. The oven temperature was held at 50 °C for 1 min and then ramped to 190 °C at a rate of 10 $°C \cdot min^{-1}$ and held for 16 min, further to 250 °C at a rate of 20 $°C \cdot min^{-1}$ for 20 min. The injector temperature was 220 °C, and the temperature in the electron capture detector was maintained at 280 °C. The UV spectra of HAA_5 were obtained by using a UV–vis spectrophotometer (S-3100, Scinco, Korea). The detailed descriptions of its acidification, liquid–liquid extraction, and derivatization procedures are described elsewhere [14].

2.3. Operation procedures

Firstly, sample was loaded into the IC sampling loop (Fig. 1a). During the injection period, IC eluent flew stepwise through the six-port valve, concentrator column, ten-port valve, analytical column, suppressor, detector, and finally to the waste. Secondly, the sample was carried by IC eluent and moved from the sample loop to the analytical column for primary separation, during which most of interfering components were delivered to waste by adjusting the positions of valve ports (Fig. 1b). Thirdly, the concentrator column was shifted behind the CD detector and the target compounds were selectively retained on the concentrator column (Fig. 1c). For those interferents (e.g., Cl^-) with elution time right

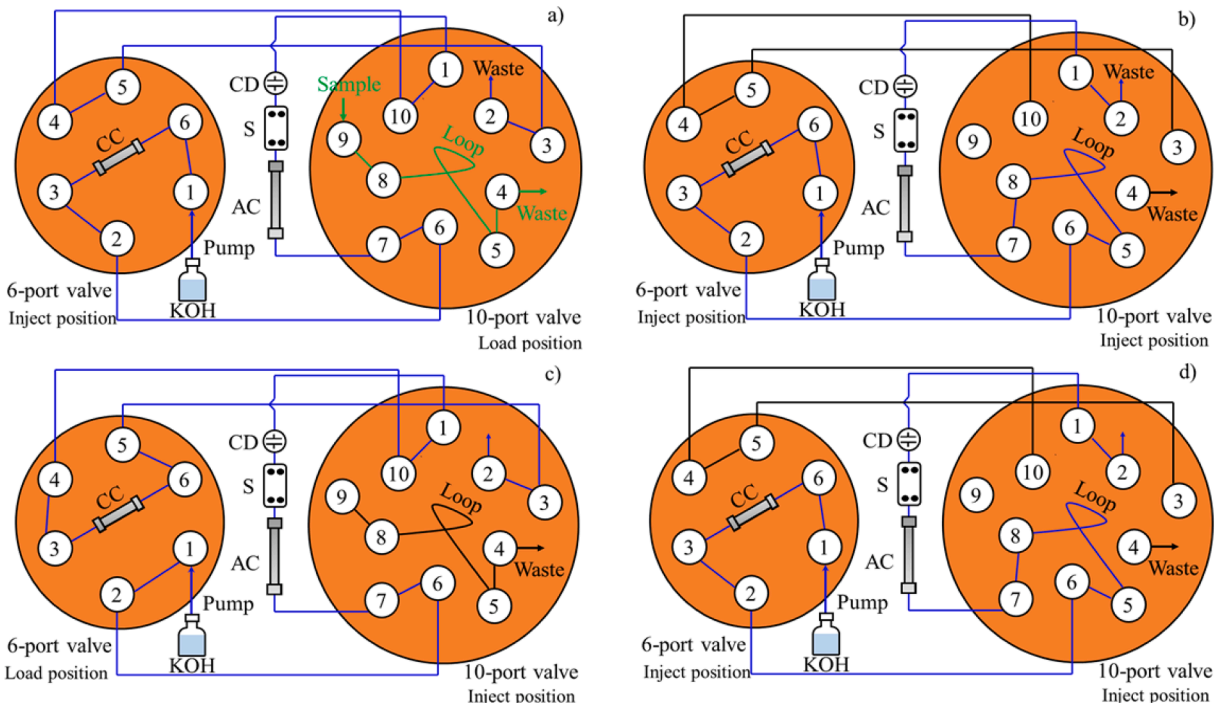

Fig. 1. Chromatographic instrument configuration for the analysis of HAA_5 in drinking water: a) loading the sample loop; b) analyzing HAA_5 in the sample and eliminating interferents; c) collecting HAA_5; d) analyzing the concentrated HAA_5. Green line: sample injection; blue line: pipeline in operation; black line: pipeline without operation. Abbreviations: (CC) concentrator column; (AC) analytical column; (S) suppressor; (CD) conductivity detector.

after target analytes (e.g., MBAA), we first collected target analytes and then delivered interferents into waste. Since samples contained not only HAAs but also interfering anions, the second and third steps need to be repeated several times until HAAs were all collected in the concentrator column and most of potential interfering anions were removed. The criteria for selection of column-switching time for HAAs collection was described in Fig. S2. Finally, the concentrator column was shifted in front of the separation column, and the initially concentrated HAAs in the concentrator column were further separated (Fig. 1d).

3. Results and discussion

3.1. HAA_5 preconcentration

Fig. 2 shows the comparison between five successive injections at 0.2 $mg{\cdot}L^{-1}$ and a single injection at 1.0 $mg{\cdot}L^{-1}$. The peaks of HAA_5 and interfering anions between these two concentrations overlapped well, indicating that online preconcentration was successfully achieved. In theory, components can be enriched by many times as long as their concentrations do not outweigh the capacity of the concentrator column. However, considering analysis time, this study only evaluated fivefold enrichment at most. To prevent excessive backpressure for the suppressor, this OPCS-IC only used a set of guard and analytical column, a pump, a detector, and a suppressor, so it required less instrumental cost than that of 2D-IC. The separation result between HAA_5 and interfering anions in this system is similar to that obtained by combining an analytical column and a capillary column in an earlier 2D-IC system [19]. However, the elution time of HAAs in a 2D-IC system is theoretically longer than that of this method because eluent flows much slowly in a capillary column than that in an anion analytical column. Therefore, compared with 2D-IC, OPCS-IC not only decreases the test cost of HAA_5 but also improves the analytical efficiency.

To further assess the enrichment performance, we compared the HAA_5′ calibration curves (ranging from 2.0 ~ 100.0 $\mu g{\cdot}L^{-1}$) between online preconcentration (at low concentrations) and calibrations without preconcentration (at high concentrations). As seen in Fig. S3,

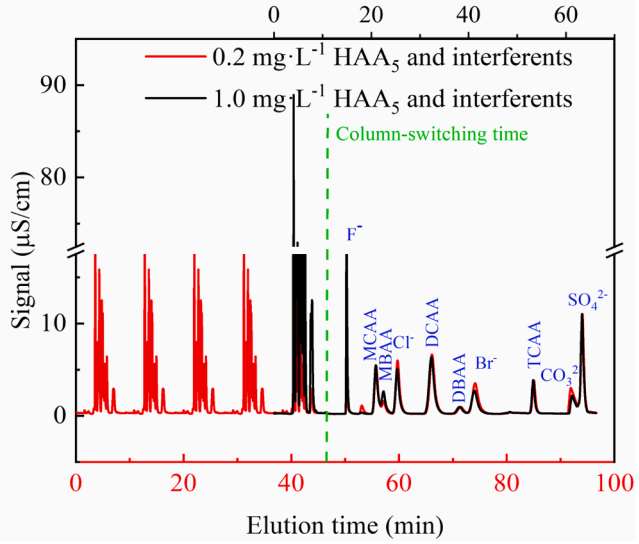

Fig. 2. A chromatogram comparison between a 0.2 $mg{\cdot}L^{-1}$ solution (containing 0.2 $mg{\cdot}L^{-1}$ HAA_5, F^-, Cl^-, Br^-, and SO_4^{2-}) after preconcentration by fivefold and a 1.0 $mg{\cdot}L^{-1}$ solution (containing 1.0 $mg{\cdot}L^{-1}$ HAA_5, F^-, Cl^-, Br^-, and SO_4^{2-}) without preconcentration (eluent gradient of KOH: 0–6.0 min: 30 mM, 6.1–10 min 8 mM, 10.1–40 min: 2 mM, 40.1–45 min: 8 mM, 45.1–60 min: 12 mM, elution time of preconcentration: 8.0 min).

the enrichment and non-enrichment calibration curves of MCAA, DCAA, DBAA, and TCAA were very close (their slopes and correlation coefficients were provided in Table S2). These phenomena indicate that MCAA, DCAA, DBAA, and TCAA were not lost throughout the column-switching processes. However, there was an exception between MBAA's enrichment and non-enrichment calibration curves, which suggests a loss of MBAA during the enrichment process. To verify this distinction, we checked the effect of retention time on the integrity of

MCAA and MBAA. As seen in Fig. S4, the concentration of MCAA remained stable as the retention time increased, whereas the concentration of MBAA first decreased and then remained stable. The loss of MBAA in the concentrator column is probably attributed to its hydrolysis at low concentrations. Despite the drawback, preconcentration of HAA_5 through the OPCS-IC still enhanced their detection signals.

3.2. Matrix removal

In addition to analytes enrichment, another virtue of column-switching IC is matrix removal. Fig. 3 compares the HAA_5 analyses in simulated drinking water with and without matrix removal by the OPCS-IC. Without matrix removal, the chromatographic peaks of Cl^- and SO_4^{2-} clearly interfered with the chromatographic peaks of DCAA and TCAA, respectively. In contrast, HAA_5 were differentiated and quantified well after matrix removal via this method. Although the peaks of MCAA and MBAA were close, their resolutions are clear enough to quantify their concentrations, and their resolutions were similar to those of 2D-IC method [15]. In other methods, the analysis time for HAA_5 by IC-ESI-MS/MS [20] and 2D-IC [19] methods were 55 min and 100 min, respectively. Both are similar to or greater than the method used in this study, which was ≤ 60 min. The detailed gradient elution and operation procedures for matrix removal and HAA_5 enrichment are provided in Table S3.

Specifically, Table 1 shows the HAA_5 recoveries and matrix removals after the whole operation. The HAA_5 recoveries ranged from 98 % to 105 % with relative standard deviations (RSDs) being less than 2 %. Meanwhile, the interferents were removed by 62.4 % for F^-, 93.9 % for Cl^-, 99.7 % for Br^-, 99.9 % for NO_3^-, and 98.9 % for SO_4^{2-}. The average matrix removal was 90.9 % with an average RSD of 1 %. These results indicate that the separation of HAA_5 from coexisting interferents in drinking water by the OPCS-IC technique is feasible and stable.

During the removals of coexisting interferents, HAA_5 and a few interfering anions were temporarily retained and concentrated in the concentrator column. Once we enriched the HAA_5 by 5 times, they were eluted out, resulting in simultaneous matrix removal and HAA_5 enrichment (Fig. 4). Although a portion of interfering anions was also enhanced, their signals did not pose a significant interference on the resolution of HAA_5. Compared with earlier online matrix removal for HAA_5 analyses, which require multiple pretreatment columns (e.g., silver column for Cl^-, hydrogen column for CO_3^{2-}, barium column for SO_4^{2-}) [40,41], this method can easily remove a series of coexisting interferents with only one column. So, the OPCS-IC method is a promising alternative for HAA_5 determination in drinking water.

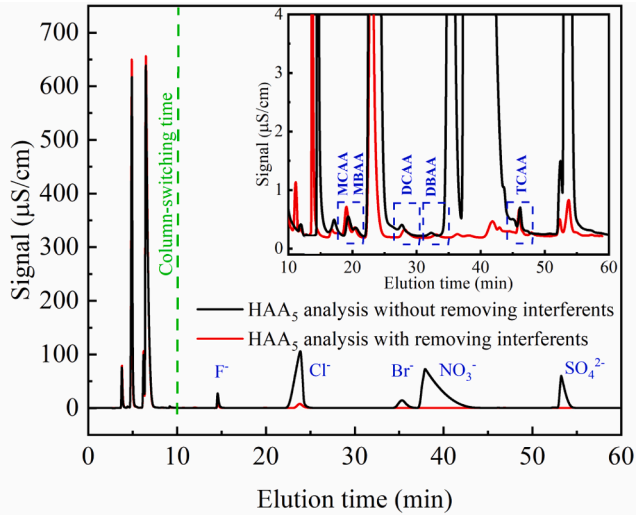

Fig. 3. The chromatograms of HAA_5 in samples with and without removing interfering anions by column-switching technique (eluent gradient of KOH: 0–7.0 min: 20 mM, 7.1–11 min 8 mM, 11.1–40 min: 2 mM, 40.1–45 min: 8 mM, 45.1–60 min: 12 mM, elution time of preconcentration column: 9.3 min; initial HAA_5 = 50 μg·L^{-1}, F^- = 1 mg·L^{-1}, Cl^- =15 mg·L^{-1}, Br^- = 5 mg·L^{-1}, NO_3^- = 10 mg-N·L^{-1}, SO_4^{2-} =10 mg·L^{-1}).

Table 1
The recoveries of HAA_5 and interferents removal after switching columns.

HAA_5	Recovery		Interferents	Removal	
	Spiked 50.0 μg·L^{-1}	RSD		Removal	RSD
MCAA	105 %	1 %	F^-	62.4 %	3 %
MBAA	98 %	2 %	Cl^-	93.9 %	1 %
DCAA	103 %	1 %	Br^-	99.7 %	0.01 %
DBAA	98 %	2 %	NO_3^-	99.9 %	0.01 %
TCAA	102 %	1 %	SO_4^{2-}	98.9 %	1 %

Initial F^- =1 mg·L^{-1}, Cl^- =15 mg·L^{-1}, Br^- = 5 mg·L^{-1}, NO_3^-=10 mg-N·L^{-1}, SO_4^{2-} =10 mg·L^{-1} (replicate ≥ 2).
HAA, haloacetic acid; MCAA, monochloroacetic acid; MBAA, monobromoacetic acid; DCAA, dichloroacetic acid; DBAA, dibromoacetic acid; TCAA, trichloroacetic acid; RSD, relative standard deviations.

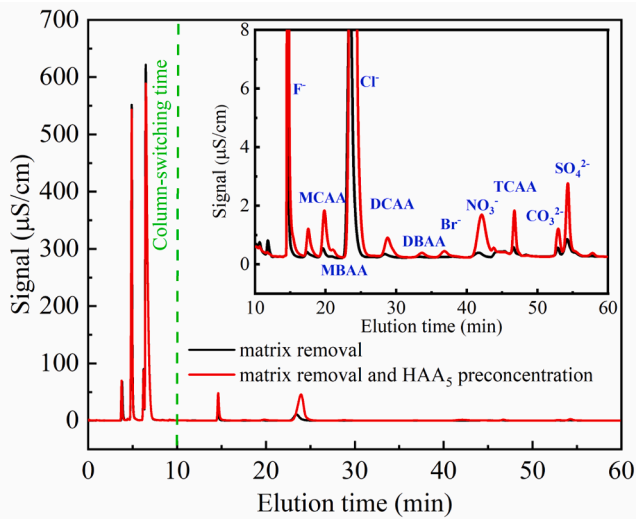

Fig. 4. The chromatograms of HAA_5 with matrix removal only and with both matrix removal and HAA_5 preconcentration (by 5 times) by using OPCS-IC (eluent gradient of KOH: 0–7.0 min: 20 mM, 7.1–11 min 8 mM, 11.1–40 min: 2 mM, 40.1–45 min: 8 mM, 45.1–60 min: 12 mM, elution time of preconcentration column: 9.3 min; initial HAA_5 = 50 μg·L^{-1}, F^- = 1 mg·L^{-1}, Cl^- =15 mg·L^{-1}, Br^- = mg·L^{-1}, NO_3^- = 10 mg-N·L^{-1}, SO_4^{2-} =10 mg·L^{-1}).

Since OPCS-IC was often used to detect trace anions in seawater where the interfering anions contents are much higher than those in drinking water, [27,31], there is no upper limits of interfering anions as long as they do not exceed the column capacity. In case the signals of coexisting anions still interfere with the analysis of certain HAA_5 species after switching columns (e.g., HAAs determination in coastal seawater), a cycling-column-switching mode is recommended to be used [27,28]. That is, the separated HAA_5 with undesired interferents may be separated again by repeating the process abovementioned until interferents do not affect HAA_5 quantification any more.

3.3. Limits of quantitation and MDLs

Given that earlier studies used UV detector to quantify HAAs [16,36], we herein compared CD detector and UV detector in their HAA_5′ limits of quantitation (LOQ) and MDLs. The data presented in Table S4 were obtained by measuring at least seven replicate samples according to the USEPA method [42], in which LOQs and MDLs were estimated by the product of standard deviation and a statistic coefficient when the RSDs of these replicates fell within a recommended range (i.e.,

10 % < RSD < 40 %) [43]. As seen, the LOQs and MDLs obtained from the CD detector were obviously lower than those from the UV detector, meaning that the CD detector is more sensitive to HAA_5 detection than the UV detector. In addition, we tested the effect of online preconcentration on LOQs and MDLs of HAA_5. The results show that fivefold preconcentration of MCAA, MBAA, DCAA, DBAA, and TCAA successfully decreased their MDLs from 0.4 $\mu g{\cdot}L^{-1}$ to 0.1 $\mu g{\cdot}L^{-1}$, 0.5 $\mu g{\cdot}L^{-1}$ to 0.2 $\mu g{\cdot}L^{-1}$, 3 $\mu g{\cdot}L^{-1}$ to 0.7 $\mu g{\cdot}L^{-1}$, 10 $\mu g{\cdot}L^{-1}$ to 2 $\mu g{\cdot}L^{-1}$, and 2 $\mu g{\cdot}L^{-1}$ to 0.3 $\mu g{\cdot}L^{-1}$, respectively. The average MDL drops of four HAAs correlated well with their enrichment factors except for MBAA (i.e., 2 vs 5). In terms of the effect of UV wavelengths on HAAs' LOQs and MDLs, the relevant results and explanations are provided in Supporting Information.

3.4. Methods comparison

To evaluate the applicability of the OPCS-IC method for HAA_5 analyses, we compared the IC method with the USEPA method 552.3, which is a GC-based method featuring little interference from coexisting anions because most of anions were eliminated by liquid–liquid extraction process. The detailed anion contents of these samples are provided in Table S1. The average ion strengths of the drinking water samples were ranked as: reverse osmosis treated water (ROW) > drinking facility water (DFW) > tap water (TW) > boiled tap water (BTW). Table 2 presents a comparison of HAA_5' recoveries and RSDs under two different HAA_5 spiking levels (i.e., 1.0 $\mu g{\cdot}L^{-1}$and 10.0 $\mu g{\cdot}L^{-1}$). The samples containing 1.0 $\mu g{\cdot}L^{-1}$ HAA_5 were analyzed through a sequential injection and matrix removal mode (i.e., Fig. 4), while the samples containing 10.0 $\mu g{\cdot}L^{-1}$ HAA_5 were analyzed through a single injection and matrix removal mode (i.e., Fig. 3).

In general, the recoveries and RSDs of 1.0 $\mu g{\cdot}L^{-1}$ of HAA_5 between the two methods are summarized as follows: 1) for the BTW water: 95 % ~ 100 % recoveries and 3 % ~ 10 % RSDs were obtained by the OPCS-IC method, while 95 % ~ 110 % recoveries and 2 % ~ 4 % RSDs were obtained by the GC method; 2) for the TW water: 90 % ~ 100 % recoveries and 2 % ~ 6 % RSDs were obtained by the OPCS-IC method, while 90 % ~ 99 % recoveries and 1 % ~ 4 % RSDs were obtained by the GC method; 3) for the DFW water: 98 % ~ 102 % recoveries and 3 % ~ 6 % RSDs were achieved by the OPCS-IC method, while 97 % ~ 105 % recoveries and 1 % ~ 6 % RSDs were obtained by the GC method; 4) for the ROW water: 90 % ~ 100 % recoveries 3 % ~ 9 % RSDs were obtained by the OPCS-IC method, while 85 %~ 96 % recoveries and 2 % ~ 6 % RSDs were achieved by the GC method. Similar to the samples spiked with 1.0 $\mu g{\cdot}L^{-1}$, the HAA_5' recoveries in samples dosed with 10.0 $\mu g{\cdot}L^{-1}$ HAA_5 all exceeded 82 % in both OPCS-IC and GC methods along with lower RSDs. These results indicate that the OPCS-IC method can maintain HAA_5' integrities well in real samples, which is comparable to the GC method

Specifically, the worst recoveries of HAA_5 in the GC method were found in the ROW sample among four real water samples, which may attribute to the abundance of organic matrix contents in the ROW sample. Although coexisting anions cannot interfere with the GC method for HAA_5' recoveries, the presence of various organic matrix still posed an influence on the quantification of HAA_5. In contrast, those organic components had little influence on the RSDs of the OPCS-IC method because they have distinctive anion-exchanging properties. Therefore, the OPCS-IC method is a promising alternative for HAA_5 determination in drinking water.

Table 2
The recovery of HAA_5 in four real water samples (n ≥ 2).

HAA_5 in DFW	OPCS-IC method				GC method (EPA 552.3)			
	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD
MCAA	102 %	3 %	99 %	2 %	105 %	3 %	104 %	2 %
MBAA	98 %	3 %	98 %	2 %	99 %	2 %	99 %	1 %
DCAA	100 %	4 %	99 %	4 %	101 %	1 %	99 %	2 %
DBAA	101 %	6 %	98 %	4 %	97 %	6 %	94 %	3 %
TCAA	99 %	3 %	97 %	3 %	98 %	4 %	96 %	2 %
HAA_5 in BTW	OPCS-IC method				GC method (EPA 552.3)			
	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD
MCAA	99 %	6 %	96 %	2 %	110 %	3 %	98 %	2 %
MBAA	95 %	4 %	92 %	3 %	96 %	3 %	93 %	2 %
DCAA	98 %	3 %	98 %	2 %	103 %	2 %	99 %	2 %
DBAA	100 %	4 %	99 %	1 %	95 %	4 %	96 %	5 %
TCAA	99 %	10 %	97 %	8 %	102 %	2 %	101 %	2 %
HAA_5 in TW	OPCS-IC method				GC method (EPA 552.3)			
	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0$\mu g{\cdot}L^{-1}$	RSD
MCAA	100%	2%	99%	2%	99%	2%	99%	1%
MBAA	90%	3%	87%	2%	91%	2%	89%	3%
DCAA	98%	5%	96%	2%	99%	4%	93%	2%
DBAA	96%	6%	94%	2%	90%	1%	90%	1%
TCAA	100%	3%	98%	2%	93%	1%	92%	1%
HAA_5 in ROW	OPCS-IC method				GC method (EPA 552.3)			
	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 1.0 $\mu g{\cdot}L^{-1}$	RSD	Recovery Spiked 10.0 $\mu g{\cdot}L^{-1}$	RSD
MCAA	100%	3%	99%	2%	96%	1.55%	97%	2%
MBAA	91%	9%	84%	4%	90%	5.32%	84%	1%
DCAA	90%	7%	88%	6%	89%	1.20%	96%	1%
DBAA	92%	3%	90%	3%	89%	1.04%	88%	1%
TCAA	96%	5%	91%	4%	85%	0.49%	82%	1%

TW, tap water; BTW, boiled tap water; ROW, reverse osmosis treated water; DFW, drinking facility water.
OPCS IC, one pump column-switching ion chromatography; GC, gas chromatography; RSD, relative standard deviations.
HAA, haloacetic acid; MCAA, monochloroacetic acid; MBAA, monobromoacetic acid; DCAA, dichloroacetic acid; DBAA, dibromoacetic acid; TCAA, trichloroacetic acid.

4. Conclusions

In this study, we proposed and verified the OPCS-IC method for HAA_5 determination in drinking water. Under optimal operation conditions, the method achieved a clear resolution between HAA_5 and interfering anions, which features similar virtues as 2D-IC technique but requires fewer equipments. This method presented a wonderful online preconcentration effect for HAA_5 analysis, with the calibration slopes (at 0.2 $mg{\cdot}L^{-1}$) similar to those without enrichment pretreatment (at 1.0 $mg{\cdot}L^{-1}$). The average MDLs of MCAA, DCAA, DBAA, and TCAA were well correlated with enrichment factors, with an exception for MBAA (i.e., 2 vs 5). The average removal for interfering anions was over 90 % while the recoveries of HAA_5 ranged within 98 % ~ 105 % by the column-switching process. The recoveries of 1.0 $\mu g{\cdot}L^{-1}$ and 10.0 $\mu g{\cdot}L^{-1}$ HAA_5 dosed into real samples with varying salinity and organics were over 82 % for both the OPCS-IC method and the GC-based method (USEPA method 552.3), proving that the new method can obtain similar performance as the standard method. Thus, the OPCS-IC method is likely to be a promising alternative for HAA_5 determination in drinking water. Once automated, it is feasible to use it to determine trace HAA_5 in water with high-level salts and/or interfering organics.

CRediT authorship contribution statement

Yang Yang: Conceptualization, Investigation, Data curation, Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Wei Ma:** Writing – review & editing. **Baiyang Chen:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **Chong Peng:** Writing – review & editing. **Wang Luo:** Writing – review & editing. **Huan He:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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