

## Determination of low bromine (Br) and iodine (I) in water with low- to high-salinity content using ICP-MS



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### ABSTRACT

A newly developed method for the determination of bromine (Br) and iodine (I) in low- to high-salinity aqueous samples by ICP-MS was established. Matrix related isobaric interferences ( $^{40}\text{Ar}^{39}\text{K}$  and  $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}$  on  $^{79}\text{Br}$ ) have been quantitatively estimated in the kinetic energy discrimination (KED) operation mode and the standard (STD) mode; it was shown that such interferences can be efficiently eliminated using the KED mode with He as a collision reaction gas. In addition, samples with high salt concentrations were analysed after pre-treatment using H-form cation-exchange resin with low dilution factors (10 or 20), rather than the high dilution factors (>200) reported in previous studies. The values for the total procedure blank of Br and I from this process were 0.784 and 0.015  $\mu\text{g L}^{-1}$ , respectively. The Br and I limits of detection (LOD) and spiked recoveries for this ICP-MS method were 0.1104 and 0.0013  $\mu\text{g L}^{-1}$  and 98.9–100.9% and 98.0–102.9%, respectively. The present method was successfully applied for the rapid and direct determination of Br and I in seawater and other aqueous samples.

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### 1. Introduction

The relative abundances of bromine (Br) and iodine (I) in the continental crust are 1.6 and 1.4  $\mu\text{g g}^{-1}$ , respectively, which are lower than the abundances of most elements, and primarily come from aqueous solutions, specifically seawater [1]. Halogens (e.g., Cl, Br and I) have been used as important geochemical indicators to investigate the history of hydrothermal alterations in geochemical and cosmochemical materials. They represent the source and evolution of ore-forming fluids and changes in environmental circumstances [2–7]. These elements are preferentially retained in the aqueous phase during water/rock interactions or hydrothermal alterations due to their high volatilities and conservative geochemical behaviours. Both Br and I provide primeval sources of information for fluids (e.g., salt lakes, oilfield brines and seawater) and are potential indicators for the exploration of saline resources. In addition, surface fluids are the primary industrial raw material sources for chemical and medicinal halogens (organic and inorganic productions), such as iodine tincture [8]. Hence, the simultaneous

measurement of Br and I for both high- and low-salinity aqueous samples plays an important role in tracking halogen resources and investigating the Br and I principles for certain special geochemical process, such as phase separation in ore-forming fluids.

Currently, Br and I determination is primarily performed using ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS) [9–16]. However, IC is not well suited for highly precise and accurate Br and I analysis at low levels ( $\mu\text{g L}^{-1}$ ) because of its high detection limit. ICP-MS offers several distinct advantages over IC for Br and I analysis, including higher sensitivity, higher selectivity, lower detection limit, smaller sample size and shorter measurement time; these advantages make this method appealing for its application towards the study of sedimentary and igneous rocks, plants, foods and underground waters. Nevertheless, this technique is susceptible to the isobaric interferences of  $^{40}\text{Ar}^{39}\text{K}$  and  $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}$  on  $^{79}\text{Br}$  and of  $^{40}\text{Ar}^{40}\text{Ar}^1\text{H}$  on  $^{81}\text{Br}$ ; memory effect-related background interference; and the matrix effect. It has been suggested that significant Br bias was generated by a certain concentration of potassium (K, >10  $\mu\text{g mL}^{-1}$ ) in MS measurements. Although dilution factors >200 have been used to eliminate the isobaric interferences and matrix effects [14], the sample may be simultaneously diluted, and in view of this, the Br and I concentrations drop below the limit of detection (LOD) of the instrument.

Considering the high importance of Br and I determination in aqueous samples, the goal of this work was to develop a

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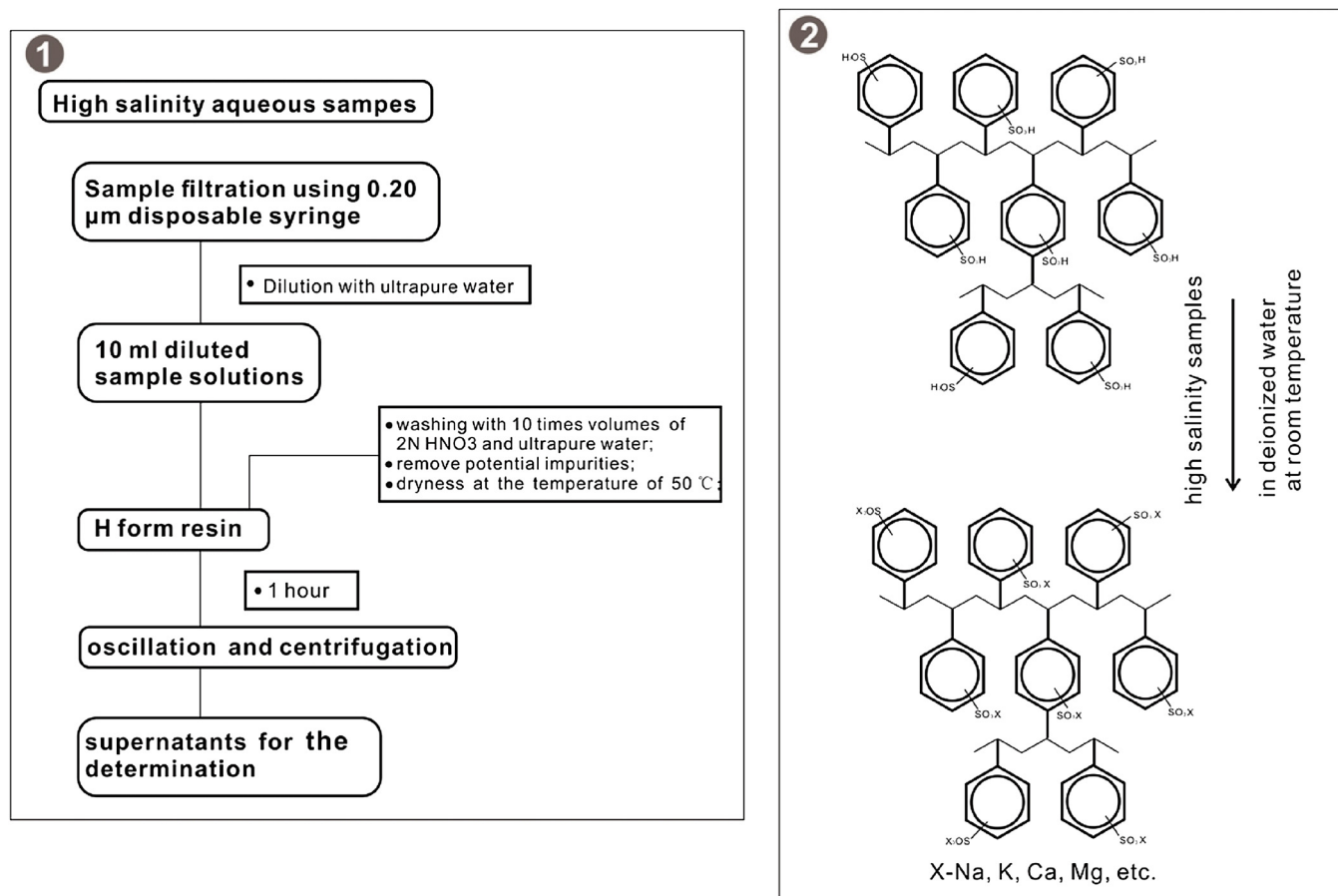


Fig. 1. (1) Flow chart of the pre-treatment process used in this study. (2) Reaction process for the removal of high salinity sample solutions.

pre-treatment method and analytical technique for Br and I determination using ICP-MS. The feasibility of this method and technique was monitored by pre-treatment process recoveries and concentration determinations. Moreover, the results of a seawater standard (CASS-5) were used to evaluate the accuracy of the proposed technique. Finally, a comparison between IC or IC-based techniques and ICP-MS on the determination of Br and I was also performed.

## 2. Experimental

### 2.1. Reagents and solutions

Analytical grade  $\text{HNO}_3$ , purchased from Sinopharm Chemical Reagent Co., Ltd. (China), was purified twice using sub-boiling distillation equipment from Savillex (USA). The 2N  $\text{HNO}_3$  was prepared by dilution with ultra-pure water (resistivity  $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$ ), using laboratory water run through a two-stage purification system (ELGA, England), and titrated by analytical-reagent grade NaOH solutions of known concentrations. Analytical grade ammonia was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. A single-element ( $1000 \text{ g L}^{-1}$ ) standard solution of Br (KBr, BW3063) was obtained from National Research Center for Certified Reference Materials (NRCCRM, China). Approximately 0.5 g of Analytical grade potassium iodide (purchased from Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in 100 mL ultra-pure water. A  $1000 \text{ g L}^{-1}$  I stock solution was obtained by dilution of the above mentioned artificial KI solutions. The Br and I concentrations in the standard solutions used for ICP-MS calibration curves varied from 0 to  $110 \mu\text{g L}^{-1}$ . Standard natural seawater (CASS-5) obtained from

National Research Council Canada (NRCC, Canada) was used as a monitoring sample in laboratory and was employed in evaluating the accuracy of the proposed method.

### 2.2. Sample description and preparation

The main chemical compositions of the samples, including lake water, salt-lake water, oilfield water and seawater, are shown in Table 1. The potassium concentration and total cation concentration of the samples were  $0.16 \text{ g L}^{-1}$  and  $4.83 \text{ g L}^{-1}$  for QH15 (lake water),  $2.87 \text{ g L}^{-1}$  and  $107.31 \text{ g L}^{-1}$  for JH15 (salt-lake water),  $2.10 \text{ g L}^{-1}$  and  $64.30 \text{ g L}^{-1}$  for NLA15-04 (oilfield water), and  $0.33 \text{ g L}^{-1}$  and  $12.87 \text{ g L}^{-1}$  for CASS-5 (seawater), respectively. The total cation concentrations in the above mentioned samples make it difficult to directly measure Br and I concentrations in primary solutions by ICP-MS. Hence, additional pre-treatment was necessary.

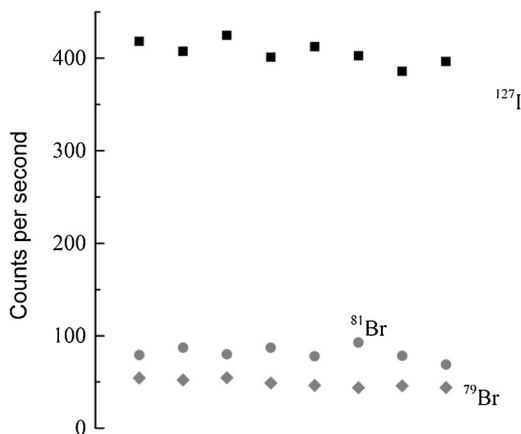
Suspended solids were excluded from the sample solutions using 0.20- $\mu\text{m}$  disposable syringe filters purchased from Tianjin Fuji Science&Technology Co., Ltd. (China). The removal of the sample matrix in high-salinity aqueous samples was performed in a class-1000 clean lab using prepared Dowex 50W-X8 cation exchange resin (H form, 200–400 mesh). Analytically pure resin obtained from Alfa Aesar (China) was passed into a glass column and eluted by nearly 10 times volumes of 2N  $\text{HNO}_3$  followed by ultrapure water to remove trace metals and organic contaminants and produced the H form of the resin. The obtained resin was evaporated to dryness at  $55 \text{ }^\circ\text{C}$  in an oven. Subsequently, 0.5 or 1 mL of the high-salinity solutions were diluted to 10 mL, and approximately 3 g of the H form resin (5.4 meq) was introduced into the

**Table 1**  
Sample chemical compositions.

Sample	Type	unit	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	pH	State
QH15	Lake water	g L <sup>-1</sup>	3.91	0.16	0.76	.bld.	5.75	2.36	8.83	Before pretreatment
		mg L <sup>-1</sup>	2.74	0.02	.bld.	0.37			1.93	After pretreatment
JH15	Salt lake	g L <sup>-1</sup>	82.50	2.87	19.47	2.48	187.50	3.94	6.89	Before pretreatment
		mg L <sup>-1</sup>	216.65	10.29	15.68	0.85			0.74	After pretreatment
NLA15-04	Oilfield water	g L <sup>-1</sup>	61.09	2.10	0.07	1.05	91.83	4.41	5.34	Before pretreatment
		mg L <sup>-1</sup>	123.5	43.32	124.4	63.68			0.60	After pretreatment
CASS-5	Seawater	g L <sup>-1</sup>	10.77	0.399	1.29	0.412	19.354	2.74	7	Before pretreatment
		mg L <sup>-1</sup>	43.72	0.33	.bld.	0.2			2.30	After pretreatment

.bld. below limit detection.

QH15, JH15 and NLA15-04 were collected from northwest of China; Analyte determination of these samples before pretreatment was as follows: K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> was determined by weighting method; Ca<sup>2+</sup> and Mg<sup>2+</sup> by EDTA volumetric method; Cl<sup>-</sup> by mercurimetry; Na<sup>+</sup> by subtraction method; The information of CASS-5 before pretreatment was from references composition; Analyte determination of all samples after pretreatment were determined by ICP-OES.

**Fig. 2.** Counts per second of Br and I in the ICP-MS blank.

solutions to distribute the metal cation matrix between the resin and the solutions.

It takes approximately 1 h for a sufficient distribution interaction to occur. After centrifugation and filtration, the supernatants were extracted for measurement. The general scheme of the preparation and the interaction are displayed in Fig. 1.

### 2.3. Measurement

The measurement was performed using a quadrupole inductively coupled plasma-mass spectrometry (NEXION300X, America) at the State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Before the analytical runs, the instrument was optimized with a tuning solution that contained Be, Th and In and was stabilized in rising mode with a 2% v/v HNO<sub>3</sub> for at least three hours. The KED (kinetic energy discrimination) operation mode was applied to decrease the isobaric interferences of <sup>40</sup>Ar<sup>38</sup>Ar<sup>1</sup>H and <sup>40</sup>Ar<sup>39</sup>K on <sup>79</sup>Br using He as a collision reaction gas at a flow rate of 3 mL min<sup>-1</sup>. Due to the higher counts per second (cps) of <sup>81</sup>Br in the blank, isotopic <sup>79</sup>Br was selected for Br determination (Fig. 2). The higher cps of <sup>81</sup>Br in the instrument might be due to the presence of a larger amount of <sup>40</sup>Ar<sup>40</sup>Ar<sup>1</sup>H in the instrument. The background signal of Br in the KED mode is evidently lower than previously reported values, at 700 cps for <sup>79</sup>Br and 17,000 cps for <sup>81</sup>Br in the blank [9]. The unique stable isotope of iodine, <sup>127</sup>I, was also scanned. The operational conditions are listed in Table 2.

The sample solutions were introduced through a PFA concentric nebulizer with a gas flow rate of 0.92 mL min<sup>-1</sup>, which is mounted onto a quartz impact bead spray chamber. A delay of 51 s was required for the stability of signals after the introduction. The analytical protocol involves data acquisition through peak jump mode

**Table 2**  
Operating parameters of ICP-MS for Br and I determination.

Operating specification	Parameters
RF power (W)	1300
Nebulizer Gas Flow (ml min <sup>-1</sup> )	0.91
Auxiliary Gas Flow (min L <sup>-1</sup> )	0.90
Cell Gas A (min ml <sup>-1</sup> )	3.8
Plasma Gas Flow (min L <sup>-1</sup> )	18
Sample uptake (min ml <sup>-1</sup> )	0.5
Peristaltic pump rotation speed (rpm)	20
Scan Mode	Peak hopping
Isotopes	<sup>79</sup> Br, <sup>127</sup> I

with three runs of 40 sweeps per run for each sample. The Br and I analysis for one sample takes approximately 3 min. A 120 s rinsing time followed each analysis to avoid small memory effect. Severe memory effects of iodine frequently occur during long-term measurements, which were associated with the instability of the signal intensity from IO<sub>4</sub><sup>-</sup> or IO<sub>3</sub><sup>-</sup> formed by oxidation of I<sup>-</sup> [17]. Compared with ultrapure water, weak alkaline solutions (TMAH or ammonia) presented high efficiency in the removal of memory background from iodine [17]. A 4% v/v ammonia solution was used to rinse out residual I and Br.

## 3. Results and discussion

### 3.1. Detection limit, total procedure blank and calibration

The limit of detection (LOD) of the proposed method was evaluated by analysing the standard deviation of 8 consecutive measurements of the ultra-pure water blank solution. The obtained LODs for Br and I determination were calculated using the following equation: LODs (Br or I) = 3 \* SD/sensitivity. The calculated results were 0.1104 and 0.0013 μg L<sup>-1</sup>, respectively (Table 3). In addition, evaluation of the blank was necessary for accuracy because the cation exchange resin and reagents could generate a higher background. Thus, a 1 mL ultra-pure water solution was regarded as a sample solution, and those results indicated that the mean Br and I values for three consecutive measurements of the blank were 0.784 and 0.015 μg L<sup>-1</sup> (Table 3); this finding suggested that negligible Br and I were added to sample solutions during preparation.

Calibration curves from the external standard method by ICP-MS showed good linearity ( $y = 116.6x - 27.68$  ( $R^2 = 0.999$ ) for Br and  $y = 27925x + 1440$  ( $R^2 = 1$ ) for I;  $R^2 = 1$ ) from 0 to 110 μg L<sup>-1</sup> for Br and I. There is no internal standard obtained from other metal elements (e.g., Ce, In, Te and Th) to monitor the variation in the counting efficiency of Br and I because previous research has suggested that the normal internal standards were not optimized for the determination of Br and I by ICP-MS compared with the external standard method [17].

**Table 3**  
Detection limit and total procedure blank for Br and I.

Element	Isotope	Background (cps)	SD	LODs ( $\mu\text{g L}^{-1}$ )	Total procedure blank ( $\mu\text{g L}^{-1}$ )
Br	$^{79}\text{Br}$	48.8	4.4	0.1104	0.784
I	$^{127}\text{I}$	721.9	12.5	0.0013	0.015

### 3.2. Interferences and removal of matrix

Br and I determinations by ICP-MS suffered from polyatomic interferences derived from the sample matrix, especially K (a major element in aqueous samples) [9]. To quantitatively evaluate these interferences, both high and low concentrations of K were added to artificial  $10 \mu\text{g L}^{-1}$  Br and I solutions. There was a significant positive correlation between K and Br in the standard mode (Fig. 3(a)), suggesting that a large amount of  $^{40}\text{Ar}^{39}\text{K}$  occurs during the measurement. Obviously, 100% Br deviation was achieved from the standard mode when the K concentration in the test solution was  $50 \text{ mg L}^{-1}$ . Moreover, it is common for K concentrations to reach hundreds of  $\text{mg L}^{-1}$  to  $\text{g L}^{-1}$  K in high-salinity aqueous samples. Sample solutions containing K and target elements are introduced by the nebulizer for ionization. The signal collector of the instrument for different elements is based on the deflection driven by Lorentz force of the different  $m/z$  ions. Thus, elements or polyatomic groups, such as  $^{40}\text{Ar}^{39}\text{K}$  and  $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}$  for  $^{79}\text{Br}$  in this work, that has the same  $m/z$  of ions as a target element would not be separated during the deflection. The interferences from such polyatomic groups resulted in the Br deviation in the standard mode. However, a negligible Br deviation was observed in the KED mode using He as a cell gas, as shown in Fig. 3. Helium was introduced as a collision gas to prohibit the formation of the polyatomic groups between K and Ar, and those results showed that the variation fell within an acceptable range, even the  $200 \text{ mg L}^{-1}$  K concentration that was in the test solution. This method effectively reduced the interferences from K during Br and I determinations by KED.

As seen in Fig. 3(b), measured Br and I values by KED were slightly lower as the amount of K increased, which could be caused by the matrix effect. Although the decrease has negligible disturbance within the uncertainty for analytical results, the matrix effect must be accounted for, especially for high-salinity samples containing low levels of Br and I. Generally, the total dissolved solids (TDS) in the final solutions should be required to be lower than 2% in ICP-MS. Thus, it is improper to directly analyse the high-salinity samples (salt-lake water, oilfield water and seawater) without additional treatment because such samples may clog the atomizing system as materials accumulate in sampling and/or skimmer cone; this consequently results in the instability of analytical signals.

To minimize the interference induced by the matrix effect, additional purification was carried out for high-salinity samples (details described in Section 2). The prepared cation exchange resin is added to the sample solutions to distribute the cation components between the resin and solution according to relative cation affinities (generally,  $\text{Na} < \text{K} < \text{Mg} < \text{Ca}$ ). In this study, a prepared, strongly acidic cation exchange resin (H form) was added to sample solutions to interact with a large number of cations, giving rise to the occurrence of the substitution between H position in resin and other cations in the sample solution (Fig. 1). As anions, Br and I are theoretically preserved in the mobile phase and do not interact with the stationary phase. The sample solutions—0.5 mL salt-lake water (JH15), 0.5 mL oilfield water (NAL15-04) and 1 mL seawater (CASS-5)—contain 2.70, 2.01, 0.61 total meq, respectively (shown in Table 1), which are lower than the capacity of 5.4 meq for 3 g of cation exchange resin. Although these samples have different pH values (from 5.34 to 8.83 in primary solutions), it was determined that the solutions after the pre-treatment have total dissolved solids (TDS, Na, K, Mg and Ca) lower than  $400 \text{ mg L}^{-1}$  and

K concentration values lower than  $45 \text{ mg L}^{-1}$ . The pH of the primary solutions has no obvious influence on the isolation efficiency for the cation matrix. Moreover, the dilution factor of the primary solution is lower than 20. Gao et al. have demonstrated that the influence from the matrix is negligible when the total ionic concentration in final solution is lower than  $600 \text{ mg L}^{-1}$  [18]. Thus, the determination of high-salinity samples with low levels of Br and I was free from the sample matrix effect and isobaric interferences from K.

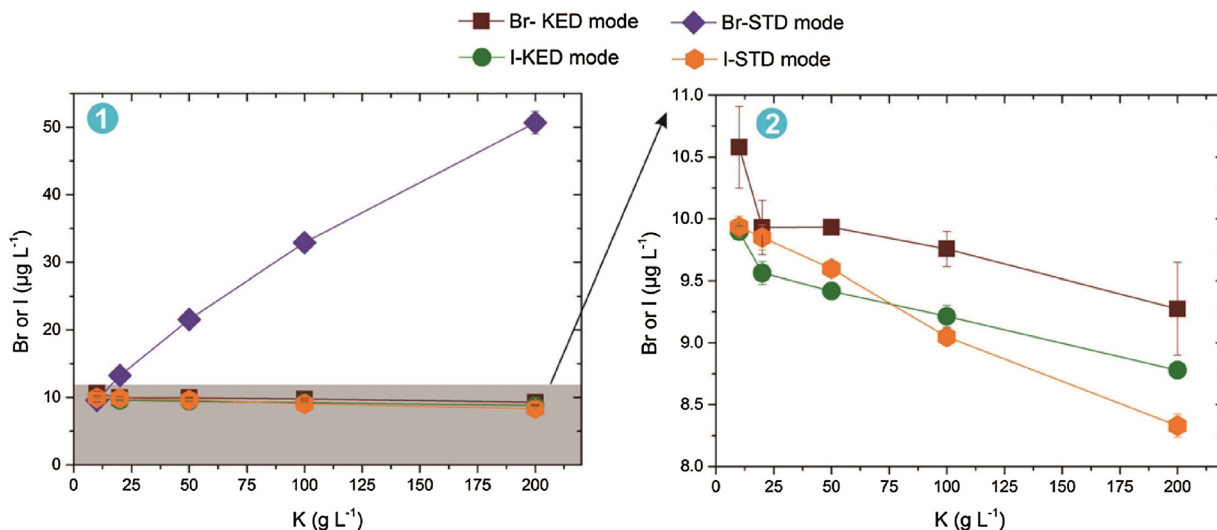
It is essential to monitor the recoveries of Br and I during the pre-treatment, even though Br and I are theoretically free from any loss. An artificial solution (approximately  $5 \mu\text{g}$  Br and I) and seawater were used to monitor the quantitative recovery and the overall recoveries of Br and I after the separation procedures were more than 90%, as shown in Table 4. The formula used to calculate the Br or I recovery =  $\{[\text{Br or I in the solution before pre-treatment} / \text{Br or I in the solution after pre-treatment}] * 100\%$ . Interestingly, the values of Br (93.14%) and I (90.26%) in the final solutions were slightly lower than 100%. Empirical research showed that there could be significant Br and I loss in solutions due to atmospheric oxidation, requiring that the solutions were set aside for long periods and improperly stored. Since that the final solutions after the pre-treatment were preserved in the absence of light and used within two days, we suggested that the minor loss of Br and I may be due to the slight adsorption of  $\text{Br}^-$  and  $\text{I}^-$  in the solutions when combined with the H form of the cation resin rather than loss through oxidation. Consequently, the analytical results were sufficient, as the determined values were within the required uncertainty level.

### 3.3. Spiked recovery of the method

To evaluate the feasibility of analysis method during the determination, a series of samples with added artificial Br and I solutions were continuously analysed three times during the experimental period, and then, the results were compared. As shown in Table 5, the recovery of Br and I, calculated by  $\text{Br or I spiked recovery} = \{[\text{measured Br or I in the solution} - \text{primary Br or I in the solution}] / \text{added Br and I in the solution}\} * 100\%$ , varied from 98.9 to 106.2% and 98.0 to 102.9%, respectively. The pH of the final solutions was found to have no relationship with the spiked recoveries (Table 5), which further demonstrated that the analytical results of Br and I would not be affected by the pre-treatment.

### 3.4. Geological samples

The Br and I concentrations in this study (Table 6) were on the  $\text{mg L}^{-1}$  and  $\mu\text{g L}^{-1}$  levels, respectively. The reliability of the techniques was further evaluated by the comparison of Br and I in seawater using different techniques (Fig. 4) [10,13,19–22]. Choosing seawater as a natural Br and I reference sample has the following several advantages: (1) seawater samples are readily available to everyone; (2) bromine and iodine behave as conservative elements in seawater and it can be assumed that Br and I homogeneity are in the ocean away from coastline; (3) because the Br concentration in seawater is relatively high (approximately  $65 \text{ mg L}^{-1}$ ), there is no need to consume large volumes of sample even if using low sensitivity techniques; and (4) Br and I in seawater are primarily monoatomic anions with a little bromate and iodate present, which favour comparison studies of different methods.



**Fig. 3.** The measured values for approximately  $10 \mu\text{g L}^{-1}$  Br and I with different K concentration using the KED mode and standard (STD) mode of ICP-MS. (1) Obvious interference from K for Br determination using the STD mode. (2) Negligible influence for Br and I determination using the KED mode.

**Table 4**  
Pre-treatment recovery.

Sample	Type	Br ( $\mu\text{g L}^{-1}$ )	I ( $\mu\text{g L}^{-1}$ )	State	Br ( $\mu\text{g L}^{-1}$ )	I ( $\mu\text{g L}^{-1}$ )	State	Description	Recovery of Br and I (%)
H1	Artificial solution	50.036	52.831	Before pretreatment	46.462	47.687	After pretreatment	The dilution factor of about 100 in the final solution	92.86 90.26
CASS-5-1	Seawater	41.508	.bld.	Before pretreatment	38.628	.bld.	After pretreatment	The dilution factor of about 1500 in the final solution	93.06 -
CASS-5-2	Seawater	42.341	.bld.	After pretreatment	39.583	.bld.	After pretreatment	The dilution factor of about 1500 in the final solution	93.49 -

**Table 5**  
Spiked recovery.

Sample	Br ( $\mu\text{g L}^{-1}$ )	Mean	Added standard	Recovery (%)	I ( $\mu\text{g L}^{-1}$ )	Mean	Added standard	Recovery (%)	pH
CASS-5	8.641 8.492 8.348	8.494	0		0.022 0.023 0.022	0.022	0		
CASS-5	18.531 18.875 18.580	18.662	10	100.9	10.409 10.264 10.258	10.310	10	102.9	2.30
CASS-5	30.186 29.369 29.484	29.680	20	104.2	20.210 20.093 20.048	20.117	20	100.5	
CASS-5	40.503 40.348 40.076	40.309	30	104.8	30.462 30.333 30.207	30.334	30	101.0	
CASS-5	62.330 61.598 62.494	62.140	50	106.2	49.561 51.728 49.873	50.387	50	100.7	
JH15	12.974 13.488 13.698	13.386	0		0.039 0.068 0.051	0.053	0		6.89
JH15	25.486 24.923 24.936	25.115	10	107.4	10.254 10.223 10.194	10.224	10	98.3	0.74
QH15	4.937 4.737 4.540	2.369	0		0.085 0.070 0.063	0.073	0		8.83
QH15	12.592 12.306 12.633	12.510	10	98.9	9.721 9.710 9.624	9.69	10	104.0	1.93
NLA15-04	101.638 103.951 103.749	103.113	0		0.073 0.070 0.065	0.069	0		5.34
NLA15-04	116.908 116.053 115.229	116.063	10	102.6	10.356 10.212 10.265	10.278	10	98.0	0.60

The dilution factors in test solutions for CASS-5, JH-5, QH15 and NLA15-04 are about 6000, 1500, 680 and 580.

**Table 6**  
Determination of Br and I in aqueous natural waters.

Sample	Type	Br ( $\text{mg L}^{-1}$ )	SD	I ( $\mu\text{g L}^{-1}$ )	SD	n	Method
QH15	Lake water	3.54	0.5	1.69	0.48	3	ICP-MS
JH15	Saline lake	9.13	0.7	5.04	0.52	3	ICP-MS
NLA15	Oilfield water	59.90	1.6	18.95	0.13	3	ICP-MS
CASS-5	Seawater	62.24	2.5	7.17	0.73	4	ICP-MS
CASS-5	Seawater	60	0	.bld.	.bld.	1	IC

.bld. below limit detection.

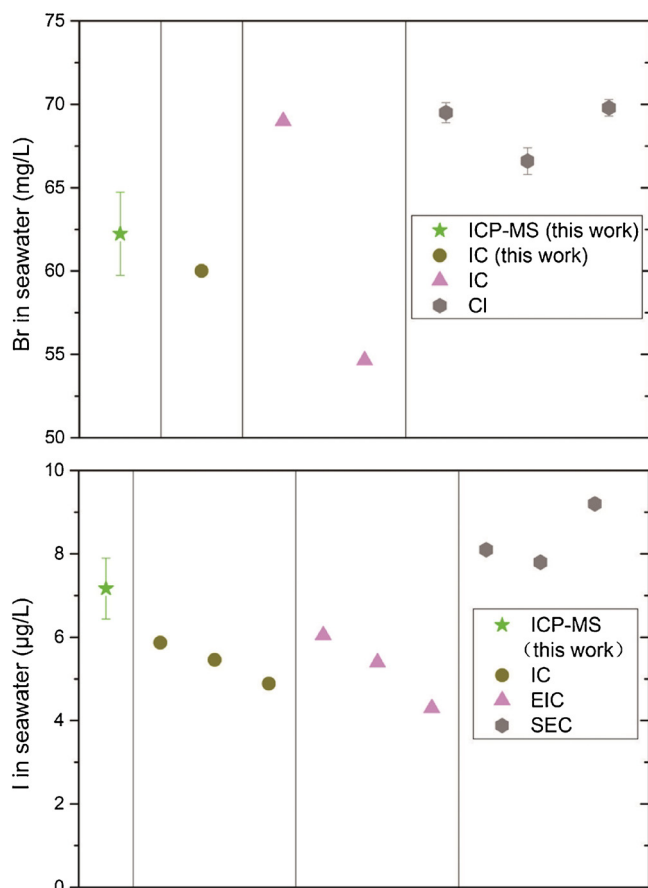
The Br concentrations in seawater determined by different methods showed a relatively narrow variation range ( $57\text{--}72 \text{ mg L}^{-1}$ ), possibly due to instrumental error, disposal by dilution or artificial data processing work. As shown in Table 6, it was clearly shown that the Br data of CASS-5 (standard seawater)

measured by ICP-MS were in good agreement with that measured by IC. The data agreed well with previous reports obtained for IC ( $59\text{--}69 \text{ mg L}^{-1}$ ) and Cl ( $57\text{--}72 \text{ mg L}^{-1}$ ). Table 6 and Fig. 4 show that the concentration of I in CASS-5 was  $7.17 \mu\text{g L}^{-1}$  with a relative standard deviation ( $n=4$ ) of 0.73. However, these values measured

**Table 7**  
Comparative data of methods for the determination of Br and I in aqueous solutions.

Sample	Analytes	Method	LOD	Sample Volume	Recovery	Linear range	Time	Ref
Seawater	bromide	IC with cycling-column-switching	2.3 $\mu\text{g L}^{-1}$	25 $\mu\text{L}$ (DS)	97–101 %	0.05–25 $\text{mg L}^{-1}$	8 min (RT)	13
Seawater	bromide	IC using amperometry and absorbance detectors	20 $\mu\text{g L}^{-1}$	25 $\mu\text{L}$ (DS)	93–119 %	0.1–25 $\text{mg L}^{-1}$	10 min (RT)	22
Seawater	bromide	IC using silica columns	0.26 $\mu\text{g L}^{-1}$	20 $\mu\text{L}$ (DS)	–	–	10 min (RT)	10
Seawater	bromide	Flow system with chemiluminescence detection	0.5 $\text{mg L}^{-1}$	–	94–102 %	0–100 $\text{mg L}^{-1}$	–	21
Seawater	bromide	IC	$\sim 10 \mu\text{g L}^{-1}$	25 $\mu\text{L}$ (DS)	–	0–5 $\text{mg L}^{-1}$	14 min (RT)	This work
Seawater	iodine	Microcolumn liquid chromatography with poly (ethylene glycol) stationary phase	9 $\mu\text{g L}^{-1}$	0.2 $\mu\text{L}$ (DS)	–	30 $\mu\text{g L}^{-1}$ –2.5 $\text{mg L}^{-1}$	4.5 min (RT)	23
Seawater	iodine	Size exclusion chromatography	0.2 $\mu\text{g L}^{-1}$	20 $\mu\text{L}$ (DS)	92–103 %	1–100 $\mu\text{g L}^{-1}$	8 min (RT)	19
Seawater	iodine	Electrostatic ion chromatographic (IC)	1.397 $\mu\text{g L}^{-1}$	400 $\mu\text{L}$ (DS)	99.1–100.9 %	0–571.5 $\mu\text{g L}^{-1}$	6 min (RT)	20
Salt lake water	bromide, iodine	IC	0.9428 $\mu\text{g L}^{-1}$ 4.2720 $\mu\text{g L}^{-1}$	25 $\mu\text{L}$ (DS)	98.63–109.80 % 96.00–103.42 %	0.01–10 $\text{mg L}^{-1}$ 0.01–20 $\text{mg L}^{-1}$	8 min (RT) 23 min (RT)	24
Seawater	bromide, iodine	ICP-MS	0.1104 $\mu\text{g L}^{-1}$ , 0.0013 $\mu\text{g L}^{-1}$	$\sim 400 \mu\text{L}$	98.9–100.9 % 98–102.9 %	0–110 $\mu\text{g L}^{-1}$ , 0–110 $\mu\text{g L}^{-1}$	3 min	This work

RT is retention time for IC (ion chromatography).  
DS is dosing ring for IC.



**Fig. 4.** Comparisons of Br and I seawater concentrations using other methods. Br data: IC (Ion Chromatography) from [10,13] and CI (chemiluminescence) from [21]. I data: IC from [19], EIC (electrostatic ion chromatography) from [19], and SEC (size exclusion chromatography) from [20].

by ICP-MS cannot be compared with that by IC in this work because of the detection limit. However, the published data for seawater using other methods (IC, EIC and SEC) were comparable with our data, showing the reliability of our method. From the comparison

and above descriptions, our method provided reliable and satisfactory results for the accurate and precise measurement of Br and I.

### 3.5. Comparison with other methods

The run time for simultaneous Br and I determination by IC or methods modified from IC depends on the iodine retention time because iodine is released from the chromatography column after bromide under the same operating conditions (e.g., the eluant concentration, flow rates and curbing current). For example, Wei et al., (2015) determined the anions in salt-lake water using IC and found that bromide had an 8 min retention time while iodine took approximately 23 min using 22  $\text{mmol L}^{-1}$  KOH as the eluant [23]. As shown in Table 7, at least 4 min was needed for I determination by IC. However, it takes less time (approximately 3 min) for Br and I determination by ICP-MS. Although it seems that small sample volumes (20–25  $\mu\text{L}$ ) were used for the dosing ring of IC, larger volumes were needed for the inlet system, e.g., at least 5 mL sample solutions were used for the automatic sampler of IC in our laboratory. Compared with that volume, a 1 mL sample solution was suitable for our proposed method.

The significant advantages for Br and I determination by ICP-MS were the low LOD and accurate determination at the  $\mu\text{g L}^{-1}$  level. Table 7 shows the LOD summary for IC or methods modified from IC- Br: 2.3  $\mu\text{g L}^{-1}$  in [13], 20  $\mu\text{g L}^{-1}$  in [22], 0.26  $\mu\text{g L}^{-1}$  in [10] and 0.9428  $\mu\text{g L}^{-1}$  in [24]; I: 1.397  $\mu\text{g L}^{-1}$  in [20] and 4.2720  $\mu\text{g L}^{-1}$  in [24]. However, the LOD values from this study (using ICP-MS) have LOD values of 0.1104  $\mu\text{g L}^{-1}$  for Br and 0.0013  $\mu\text{g L}^{-1}$  for I. Some detection methods based on IC, such as electrostatic ion chromatography (in Fig. 4 and Table 7), had the capacity to detect low levels of I in seawater. On the whole, IC was used to measure anions (e.g., Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) at levels from 0 to 50  $\text{mg L}^{-1}$ . Moreover, empirical data showed that the sensibility of IC was insufficient for Br and I determination at  $\mu\text{g L}^{-1}$  levels. As mentioned above, our proposed method (with a linear range from 0 to 110  $\mu\text{g L}^{-1}$ ) had more accurately determined the levels of Br and I on the  $\mu\text{g L}^{-1}$  scale than IC.

## 4. Conclusion

The present analytical technique makes it possible to simultaneously determine Br and I in water with high- or low-salinity

contents with satisfactory analytical precision and accuracy. The kinetic energy discrimination model of ICP-MS coupled with He as a collision reaction gas has been utilized to minimize the interference caused by potassium in the samples. High-salinity aqueous samples were further purified to eliminate the matrix effect using Dowex 50WX8 cation exchange resin. The Br and I concentrations of natural seawater were consistent with reported values, and this method was subsequently applied to samples with different salinities, such as lake water, salt-lake water and seawater. Compared with IC, the proposed method has a much lower LOD, less run time, smaller sample size and higher sensibility. Minimizing potassium interference and a low sample dilution factor make this method ideal for samples with high salinity but low Br and I concentrations.

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