

Rapid and Sensitive Speciation of Inorganic Iodine in Groundwater by IC-ICP-MS With Ar-CH₄ Mixed Plasma

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INTRODUCTION

Iodine (I) is one of the most important trace elements in human nutrition, with its main physiological function as a constituent of thyroxine, the hormone secreted by the thyroid gland (1). Iodine deficiency can cause serious delays in neurologic development. However, excess iodine can also produce goiter, hypothyroidism, and hyperthyroidism (2). In some high-iodine areas (e.g., Datong basin, P.R. China), simultaneous consumption of high-iodine groundwater and iodized salt causes an iodine intake several times higher than regulatory levels, negatively affecting the thyroid gland (3). Since 2004, the Chinese government has adopted 150 and 300 $\mu\text{g L}^{-1}$ I as the amounts of iodine in groundwater to be the toxic exposure level and disease-inducing concentration, respectively. Like other elements, iodine toxicity is species-dependent: iodate (IO_3^-) is less toxic than iodide (I^-) and organically bound iodine (4). Hence, it is necessary to determine the iodine species in groundwater samples instead of total iodine.

Several liquid chromatography (LC), size-exclusion chromatography (SEC), capillary electrophoresis (CE), and ion chromatography (IC) methods coupled with different detection techniques for iodine or other element speciation have been reported. These include UV spectrophotometry, inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry

ABSTRACT

Investigation of the iodine species is important to better understand the sources and mobilization processes of high-iodine groundwater. A fast and sensitive method for the determination of iodate (IO_3^-) and iodide (I^-) in groundwater using an improved ion chromatography method coupled with inductively coupled plasma mass spectrometry (IC-ICP-MS) is described. To shorten the separation time of iodine species, a short anion-exchange column, Dionex AG-19, was examined as the analytical column. Isocratic elution using 30 mM KOH facilitated the chromatographic separation of IO_3^- and I^- within one minute, reducing the time in comparison to previous IC-ICP-MS methods with conventional long IC columns (i.e., Hamilton X-100 or Dionex AS-16) by 90%. Moreover, the low analytical sensitivity of iodine, due to its high ionization potential (10.08 eV), was improved five-fold by addition of small amounts of CH_4 to the Ar plasma. The detection limit was 0.005 $\mu\text{g L}^{-1}$ for IO_3^- and 0.006 $\mu\text{g L}^{-1}$ for I^- , while the relative standard deviation for five injections of 0.2 $\mu\text{g L}^{-1}$ I^- or IO_3^- was 1.2–3.3%. The analytical results for three water standard reference materials were in agreement with the certified values. The proposed method was successfully applied to the determination of I^- and IO_3^- in seven shallow groundwater samples collected from the Datong Basin, Northern China. The distributions of the iodine species, differing from mountain front plains to flat alluvial plain regions, indicate that the mobilization process of iodine is associated with complex redox conditions.

(ICP-MS) (5–11). Among these techniques, IC-ICP-MS could be a promising analytical technique for iodine speciation due to high sensitivity and element specificity of the ICP-MS detector (12–21). Recently, ICP-MS has been used for various environmental and biological samples for iodine speciation studies, including water, seaweeds, urine, human serum, and milk (4, 22–25). However, the low analytical sensitivity and lengthy processing times of previous IC-ICP-MS applications are major drawbacks. Generally, the total run time of one injection is between 10–20 minutes in IC-ICP-MS analysis with typical IC analytical columns, such as the Hamilton PRP-X100 and Dionex AG-16 (4, 26, 27). A long elution time not only affects the throughput, but also leads to errors in the results. This is due to the continuous introduction of a high salt mobile phase deposited onto the orifice of the MS interface, which influences the transmission of the target ions (28). Like other non-metallic elements (e.g., As, Se, Hg), the iodine sensitivity in ICP-MS is only 10–30% that of most metal elements (e.g., Li, In, Pb) which could be due to its high ionization potential (10.08 eV) (29). Recently, it was confirmed that the addition of small amounts of carbon-containing compounds (e.g., methanol, glycerol) to the plasma could improve the signal intensities of As and Se up to 2–4 times (30–32). These experimental results indicate that the signal enhancement of elements with high ionization potentials (9–11 eV) is mainly attributed to the increased degree of ionization in the plasma.

The aim of this study was to establish a rapid and sensitive

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IC-ICP-MS method for the determination of IO_3^- and I^- in groundwater samples. A short anion-exchange chromatographic column was used instead of the usual long column to achieve the required high sample throughput, and the separation performance was carefully evaluated. In addition, a CH_4 -Ar mixed gas plasma was employed instead of conventional pure Ar-ICP to improve the sensitivity of I. Optimization of the proposed method, the influence of coexistent substances, the analytical feasibility of the technique, and its application to the determination of inorganic iodine species in seven groundwater samples are described.

EXPERIMENTAL

Instrumentation

The Dionex™ ICS900 IC separation system consists of an IC pump, an injection valve, column heater, and an AS-19 anion-exchange column (Thermo Fisher Scientific, USA). The samples were loaded into a 20- μL sample loop with a syringe. The PerkinElmer NexION® 300D ICP-MS instrument was used (PerkinElmer, Inc., Shelton, CT, USA). The eluents were introduced into the ICP-MS with a pneumatic nebulizer and cyclonic spray chamber. The peak areas and peak heights were measured with Chromera® software (PerkinElmer, Inc.). The experimental setup is schematically

represented in Figure 1. CH_4 gas (99.999%) was added into an additional port in the PC3 Peltier cyclonic spray chamber (Elemental Scientific, USA) via a calibrated mass-flow controller (Cole-Parmer, USA), capable of regulating minute flows (measuring range 0-1.0 L min^{-1} , precision 0.01 L min^{-1}) of the gas. The IC-ICP-MS operating parameters are summarized in Table I.

Reagents, Standards, and Samples

High purity water ($\geq 18.2 \text{ M}\Omega\text{-cm}^{-1}$) used for preparation of the

blank, standards, and eluents was obtained from a Millipore® water purification system (Millipore Corporation, France). KI (99.9999%), KIO_3 (99.9999%), and KOH (99.9999%) were purchased from Alfa Aesar Ltd. (Tianjing, P.R. China). Three standard reference materials (SRM) were used to assess method reliability. Groundwater SRM BCR-611 was purchased from the Institute for Reference Materials and Measurements (IRMM, European Commission). Two natural waters GBW 08621 and GBW (E) 080235 were purchased from the

TABLE I
IC-ICP-MS Operation Conditions

IC System	Dionex™ ICS900
Column	AS-19 column (50 mm ×4 mm, 11 μm)
Injection Volume	10 μL
Flow Rate	1 mL min^{-1}
Column Temperature	25 °C
Isocratic Elution	30 mM KOH
Run Time	1 min
ICP-MS System	PerkinElmer NexION® 300D ICP-MS
Nebulizer	PFA MicroFlow Nebulizer
Spray Chamber	Cyclonic (PC3 Peltier Chiller)
Analytes	$^{127}\text{I}^+$
Plasma Gas Flow	16 mL min^{-1}
Auxiliary Gas Flow	1.0 mL min^{-1}
Nebulizer Gas Flow	0.85 mL min^{-1} (CH_4 -Ar mixed plasma) 0.92 mL min^{-1} (Ar plasma)
Optional Gas (CH_4)	3 mL min^{-1}
RF Power	1500 W
Dwell Time	100 ms

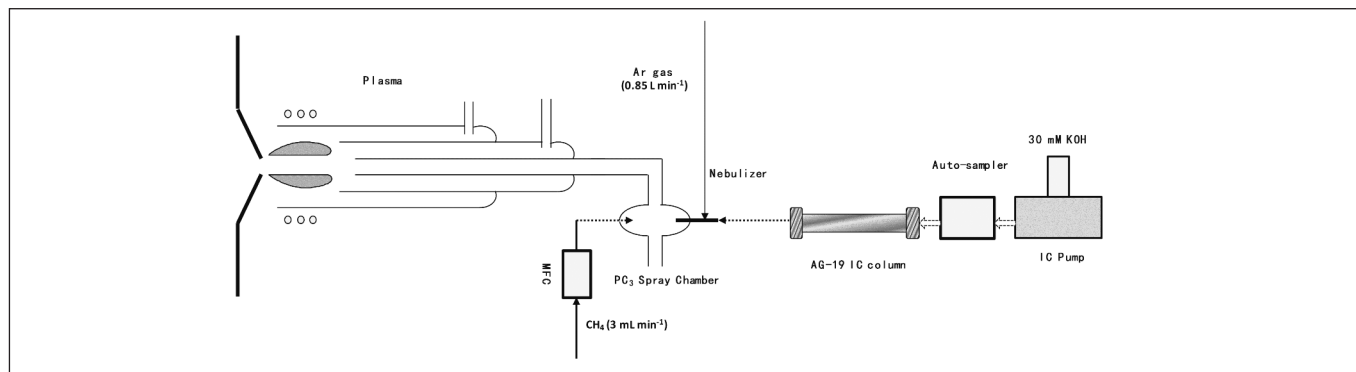


Fig. 1. Diagram of the experimental setup.

National Research Center for Certified Reference Materials, P.R. China. Seven groundwater samples were collected from the Datong basin, Northwest China. All of the eluents and samples were filtered through a 0.45- μm membrane filter (Macherey-Nagel, Germany) and subsequently degassed in an ultrasonic bath before analysis.

RESULTS AND DISCUSSION

Reduction of Separation Times Using a Short Anion Exchange Column

It is well known that IC has shown the most promise as a tool for separating different ions and the effluent can be directly introduced into a highly sensitive and selective ICP-MS via a conventional pneumatic nebulizer and spray chamber. A typical chromatogram of a solution containing $1\ \mu\text{g L}^{-1}$ mixed standards of IO_3^- and I^- by IC-ICP-MS with a conventional IC column (Dionex AS-19, 250 mm \times 4 mm, 7.5 μm) is shown in Figure 2 (dashed line). Under optimal conditions (mobile phase: 30 mM KOH, flow rate: $1\ \text{mL min}^{-1}$), the retention times of IO_3^- and I^- were 3.1 and 14.5 minutes, respectively. To

reduce the total run time of one injection, a short IC column (Dionex AG-19, 50 mm \times 4 mm, 11 μm) was used instead of a long column. As shown in Figure 2 (solid line), the retention times of IO_3^- and I^- were reduced to 0.36 and 0.64 minutes, respectively, with narrower and taller peak profiles. The total run time for one injection was, therefore, less than one minute, allowing a theoretical sample throughput of up to 60 samples per hour.

Signal Improvement by Addition of CH_4 to the Plasma

In comparison with another mono-isotopic elements such as Rh, the sensitivity of I is only one-tenth that of Rh because of the low ionization efficiency of I in the plasma. Some studies have reported that addition of 3–5% carbon-containing compounds could increase the signal intensity of high ionization energy elements in ICP-MS analysis (e.g., As, Se, and Hg) (29, 31–33). To improve the poor sensitivity of I, a carbon source (CH_4 gas) was directly introduced into the plasma by an additional port in the cyclonic spray chamber. A lower nebulizer gas flow rate ($0.85\ \text{mL min}^{-1}$

instead of the normal value of $0.92\ \text{mL min}^{-1}$) was used to compensate the plasma cooling effect of carbon addition. Signal intensities of I^+ as a function of the CH_4 gas flow rate, after blank corrections, are illustrated in Figure 3a. The results show that the maximum sensitivity for I^+ with $3\ \text{mL min}^{-1}\ \text{CH}_4$ was five times greater than without addition of CH_4 . Figure 3b compares the results for the iodine species with (solid line) or without (dashed line) addition of CH_4 for the IC-ICP-MS method. As shown in Figure 3b, peak heights and peak areas were improved five-fold in the CH_4 -Ar mixed plasma method over that of the pure Ar plasma method, consistent with both retention times and peak profiles. Compared to the addition of a carbon source (i.e., methanol) to the IC mobile phase, the proposed method (CH_4 -Ar mixed plasma) can avoid affecting the separation procedure. The phenomenon of signal enhancement can be explained by a charge transfer reaction occurring between the positively charged carbon species and the high ionization potential (10.08 eV) in the central channel of the plasma (33, 34).

Analysis Performance of the Method

Coexistent substances (i.e., chloride and sulfate) would compete with target ions for sites on the column, thereby causing the peak to elute faster and peak broadening (35). Figure 4 shows the effect of matrices containing $500\ \text{mg L}^{-1}$ chloride (Cl^-) and $300\ \text{mg L}^{-1}$ sulfate (SO_4^{2-}) on the peak profiles of IO_3^- and I^- , respectively. Although the retention times shifted by less than 4%, the peak height and peak area of the matrix-containing standards were consistent with that of the matrix-free standards. These results indicate that trace level I species can be determined in matrices of anions where concentrations of other ions

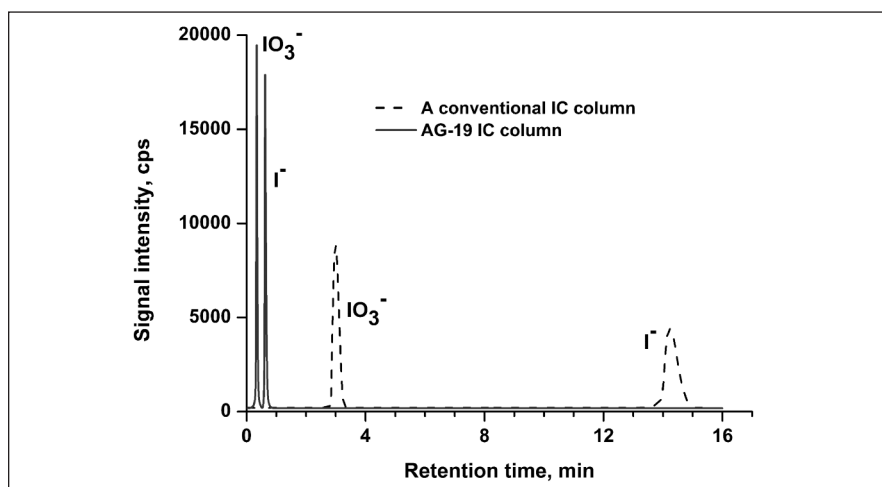


Fig. 2. Typical chromatograms for solution containing $1\ \mu\text{g L}^{-1}\ \text{IO}_3^-$ and $1\ \mu\text{g L}^{-1}\ \text{I}^-$ acquired with IC-ICP-MS (at $m/z\ 79$) using a conventional Dionex AS-19 IC column (dashed line) and a short Dionex AS-19 IC column (solid line). Mobile phase: 30 mM KOH, flow rate: $1\ \text{mL min}^{-1}$.

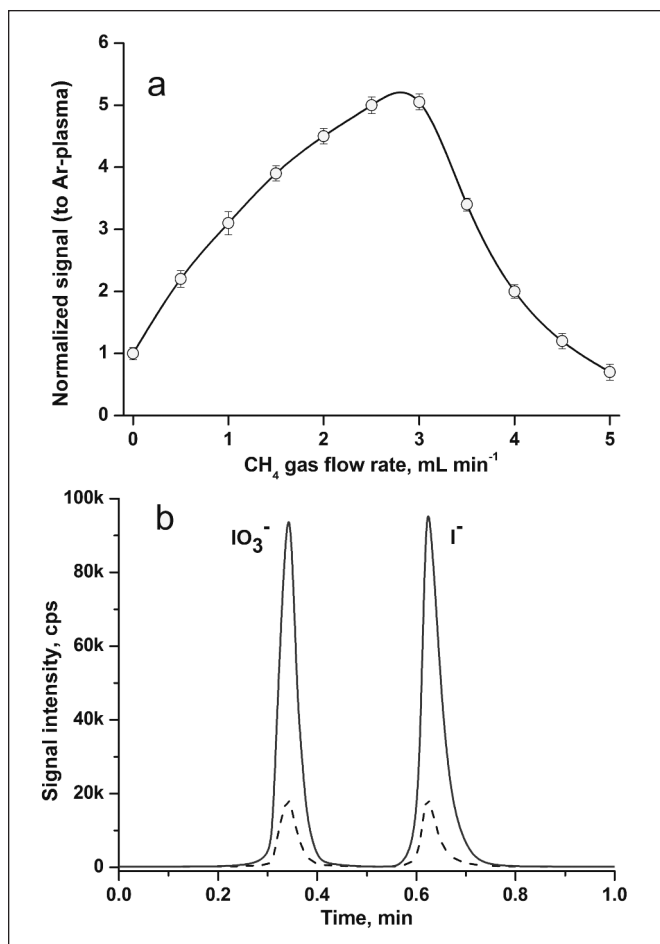


Fig. 3. Effects of CH₄ gas flow rate on the normalized signal (to pure Ar plasma) of total iodine (a) and chromatographic peak profiles of the iodine species (b). The dotted line represents not using CH₄ gas, the straight line indicates with addition of 3 mL CH₄ gas. An amount of 1 μg L⁻¹ I⁻ standard was used in the ICP-MS test, and a mixture of 1 μg L⁻¹ IO₃⁻ and I⁻ standards was used in the IC-ICP-MS analysis.

are 5–6 orders of magnitude higher than that of iodine.

Calibration curves based on peak areas were linear (with correlation coefficients of 0.998) for IO₃⁻ and I⁻ in the range tested (0.1–500 μg L⁻¹). The limit of detection (LOD) is defined as the concentration which gives peak heights of 3 times the amplitude of the baseline noise. As listed in Table II, the LODs were 0.005 and 0.006 μg L⁻¹ for IO₃⁻ and I⁻, respectively. Compared to prior literature (26, 27), the LOD was around 3–8 times lower, with the total run time per sample reduced

from 12–16 minutes to 1 minute (Table II). The accuracy was assessed using three water SRMs. As shown in Table III, the data for IO₃⁻ and I⁻ obtained by the proposed method were in agreement with the certified values. The recoveries of the iodine species were measured using a groundwater sample spiked with 30 μg L⁻¹ IO₃⁻ and I⁻. As shown in Figure 5, satisfactory recoveries were found for IO₃⁻ (98.2 ± 2.6%, n=3) and I⁻ (101.4 ± 3.0%, n=3).

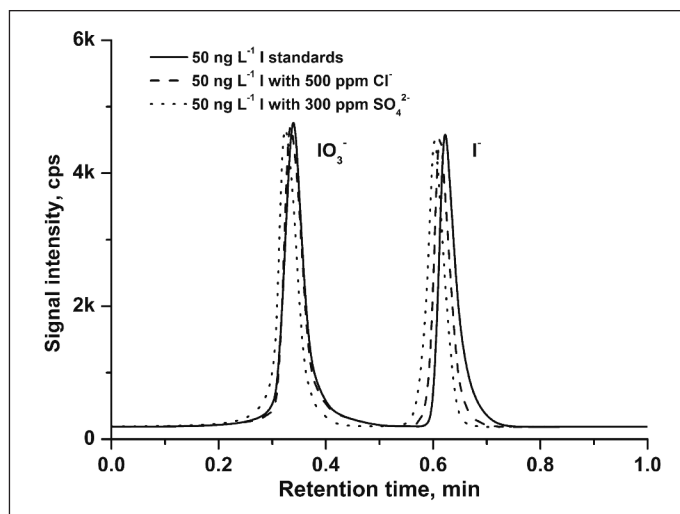


Fig. 4. Effects of matrices containing 500 mg L⁻¹ chloride (dashed line) and 300 mg L⁻¹ sulfate (dotted line) on the peak profiles of IO₃⁻ and I⁻. 1 μg L⁻¹ mixture of IO₃⁻ and I⁻ standards was used to test.

Groundwater Sample Analysis

The proposed method was applied to the determination of I species in seven groundwater samples. Sampling extended from the mountain front plains (Datong basin edge) to the flat alluvial plain regions (central Datong basin). As shown in Table IV, the concentrations of IO₃⁻ and I⁻ were in the range of 17.3–49.0 μg L⁻¹ and 0.28–1010 μg L⁻¹, respectively. Overall, the inorganic I species (IO₃⁻ plus I⁻) in the three samples from the mountain front plains were significantly lower than in the four samples from the flat alluvial plain regions. IO₃⁻ was the main species at the basin edge, while I⁻ was the main species in the central basin (Figure 6). Different distributions of I species at the edge and center of the basin suggested that the mobilization process of iodine was associated with complex redox conditions (36). A comparison of inorganic I species (IO₃⁻ and I⁻) with the total iodine concentrations indicated the presence of some unknown iodine species (i.e., organic I compounds) in these groundwater samples. A more in-

TABLE II
Analytical Figures of Merit for Different HPLC-ICP-MS Methods

Analytical Method	Detection Limit ($\mu\text{g L}^{-1}$)		Retention Time (min)		Total Run Time (min)
	IO_3^-	I^-	IO_3^-	I^-	
IC-ICP-MS ^a	0.050	0.040	4.4	9.5	12
SEC-ICP-MS ^b	0.025	0.025	9.7	15.4	16
This work ^c	0.005	0.006	0.36	0.64	1

^a Separation with Dionex AS16 ion exchange column (26).

^b Separation with TSK G3000PWSEC column (27).

^c Separation with Dionex AG-19 ion exchange column and analysis by the mixed Ar-CH₄ plasma ICP-MS.

TABLE III
Results of IO_3^- and I^- in Three Standard Reference Materials (SRMs) by the Proposed Method ($\mu\text{g L}^{-1}$, n=3)

SRMs	IO_3^-		I^-	
	Detected Values	Certified Values	Detected Values	Certified Values
BCR-611 Groundwater	0.11 ± 0.01	- ^c	9.2 ± 0.2	9.0 ± 1.1
GBW08621 Natural Water ^a	2.13 ± 0.04	2.14	N.D. ^b	- ^c
GBW(E)080235 Natural Water	N.D. ^b	- ^c	202 ± 4	200 ± 10

^a Actual samples diluted 100,000-fold.

^b Not detected.

^c Not available.

depth study by examining the fragmentation pattern with organic mass spectrometry (LC-MS-MS) would be required to identify the organic I species present.

CONCLUSION

The combination of a short anion-exchange column (Dionex AG-19) IC system with CH₄-Ar mixed plasma ICP-MS was used to determine amounts of iodate and iodide in groundwater samples. The total separation time per sample reduced from 12–16 minutes to 1 minute, and the analytical sensitivity of iodine was improved five-fold. The detection limit was 0.005 $\mu\text{g L}^{-1}$ for IO_3^- and 0.006 $\mu\text{g L}^{-1}$ for I^- , while the relative standard deviation for five injections of 0.2 $\mu\text{g L}^{-1}$ I^- or IO_3^- was 1.2–3.3%. The adopted system for separation and detection provides an excellent, rapid, and sensitive technique for iodine speciation.

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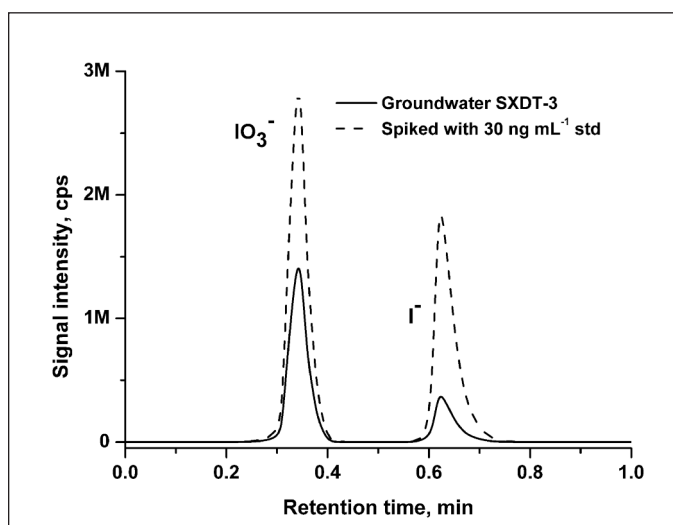


Fig. 5. Groundwater chromatograms for the recovery test using a groundwater sample (SXDT-3) collected from mountain front plains of the Datong basin.

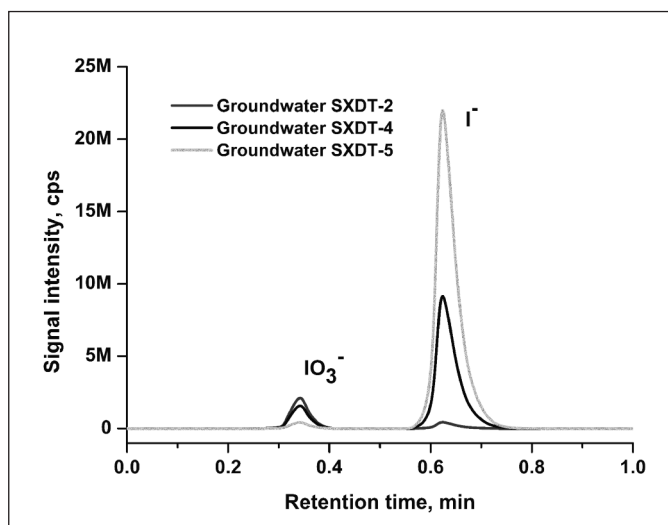


Fig. 6. Typical groundwater chromatograms for samples collected at different regions of the Datong basin.

TABLE IV
Results of IO₃⁻ and I⁻ in 7 Groundwater Samples by the Proposed Method (μg L⁻¹, n=3)

Sample	Area	Inorganic Iodine			Total I ^a
		IO ₃ ⁻	I ⁻	Sum (IO ₃ ⁻ + I ⁻)	
SXDT-1	Mountain front plains	17.3 ± 0.4	0.280 ± 0.022	17.6	18.2 ± 0.3
SXDT-2	Mountain front plains	45.2 ± 0.6	9.26 ± 0.18	54.5	59.0 ± 1.0
SXDT-3	Mountain front plains	30.2 ± 0.5	7.73 ± 0.25	37.9	43.0 ± 1.1
SXDT-4	Flat alluvial plain regions	33.6 ± 0.5	192 ± 5	226	296 ± 4
SXDT-5	Flat alluvial plain regions	9.20 ± 0.5	462 ± 11	471	471 ± 10
SXDT-6	Flat alluvial plain regions	4.54 ± 0.4	888 ± 26	893	1041 ± 17
SXDT-7	Flat alluvial plain regions	49.0 ± 1.2	1,010 ± 32	1059	1079 ± 21

^a Direct analysis by ICP-MS without IC separation.

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