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Journal:	*Analytical Methods*
Manuscript ID:	AY-ART-05-2014-001186.R1
Article Type:	Paper
Date Submitted by the Author:	05-Aug-2014
Complete List of Authors:	Nie, Zhe; Peking University, College of Chemistry and Molecular Engineering Zheng, Lingna; Chinese Academy of Sciences, Institute of High Energy Physics Feng, Wei-Yue; Institute of High Energy Physics, CAS, Liu, Chunli; Peking University, College of Chemistry and Molecular Engineering

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Development of Anion-Exchange High-Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry Methods for the Speciation Analysis of Inorganic Selenium and Iodine in Groundwater

Zhe Nie[a], Lingna Zheng[b], Weiyue Feng[b*], Chunli Liu[a*]

This work represents the first report of a method for the simultaneous speciation of inorganic selenium and iodine using high-performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Baseline separation of selenite, selenate, iodide and iodate within a single chromatographic run of 10 min was achieved with the optimized mobile phase of 3 mM ammonium citrate, 25 mM ammonium perchlorate and 2% (v/v) methanol at pH 8.5. The mass spectrometric operating conditions were optimized to detect selenium and iodine simultaneously. Potential matrix effects were addressed and corrected using the standard addition method, and the recoveries (95.7-103%) were satisfactory. The repeatability and intermediate precision were satisfactory (the coefficients of variation were all less than 5% and 8%, respectively). The obtained detection limits were 22 ng L^{-1} and 23 ng L^{-1} for selenite and selenate, respectively, and 4.3 ng L^{-1} and 5.4 ng L^{-1} for iodide and iodate, respectively, which allows for the speciation of selenium and iodine in groundwater at the ultra-trace level. Groundwater samples collected from a candidate site for the Chinese high-level radioactive waste repository were analyzed. Within the three different groundwater samples, selenate was observed to be the dominant Se species; in addition, the iodide concentration increased and the iodate concentration decreased with increasing sampling depth. With its satisfactory sensitivity and accuracy, this method provides a promising tool for studying the environmental behaviors of selenium and iodine, thereby supporting safety assessments of high-level radioactive waste repositories.

Introduction

Selenium-79 and iodine-129 are both fission products of uranium-235. Because of their high solubilities, weak sorptivities and long half-lives (2.95×10^5 y for ^{79}Se and 1.57×10^7 y for ^{129}I), the potential migration of these radionuclides from a waste containment site into the geosphere, with a subsequent impact on environmental systems, is a key issue in the performance assessment of a high-level radioactive waste repository. In the report of ANDRA (the French national radioactive waste management agency), ^{79}Se and ^{129}I are two of the four radionuclides that exhibit a non-negligible flow at the top of repositories by diffusion after 1 million years [1]. The predominant pathway for radionuclide migration is solute transport in groundwater [2]. During the migration process, the chemical form of the radionuclides is one of the important factors that govern their behavior, such as their sorption, diffusion and precipitation. Therefore, insight into the speciation of selenium and iodine in groundwater will help elucidate their biogeochemical behavior in the environment and will provide reliable data for assessment of the geological disposal of high-level radioactive wastes.

Selenium and iodine are both essential micronutrients for humans and animals. As a constituent of Se-dependent enzymes, such as glutathione peroxidase and thioredoxin reductase [3], selenium is important in the cellular defense mechanism against oxidative damage by inhibiting the toxic effects of other heavy metals. However, the range of Se concentration between deficiency and toxicity is very narrow, and the toxicity of Se depends on its chemical form [4]. Iodine participates in the biosynthesis of thyroid hormones, such as thyroxin, T4, and triiodothyronine, T3 [5], which play important roles in the growth and development of living organisms and in the immune defense system [6, 7]. The bioavailability and toxicity of iodine differ among its different chemical forms [8, 9]. Because groundwater is a potential source of domestic water and agricultural water, investigations of the species of selenium and iodine present in groundwater are important for monitoring and controlling their toxicities.

Several analytical techniques are available for speciation analysis, including electrochemical methods [10], X-ray adsorption spectrometry [11], catalytic spectrophotometry [12] and chromatographic methods, such as gas chromatography [13], HPLC [14] and capillary electrophoresis [15]. The chromatographic method usually involves coupling of a chromatograph with a selective detector, such as ICP-MS. HPLC is a powerful technique that allows the separation of complex mixtures into individual components, and ICP-MS is a sensitive multi-element detector. Adequate sensitivity and the simple interface between HPLC and ICP-MS make their combination one of the most important techniques for speciation studies. The use of HPLC-ICP-MS for iodine speciation analysis has been limited primarily to marine samples, such as seawater and seaweed [14, 16-18], whereas that for selenium species has been limited mainly to food [19-21] and biological samples [22-24]. Only a few selenium or iodine speciation studies have been reported with regard to groundwater [25, 26], and the literature contains no reports of the application of HPLC-ICP-MS to the simultaneous speciation analysis of inorganic selenium and iodine species.

Therefore, in this work, we developed a method for the quantitative and simultaneous determination of inorganic selenium and iodine species, including selenite, selenate, iodide and iodate, in groundwater. The effects of the mobile phase composition, pH and organic modifier content on the separation, as well as the matrix effects on the measurement, were investigated. The developed method was then applied for the analysis of selenium and iodine species in groundwater samples collected near a candidate site for the Chinese high-level radioactive waste (HLW) repository.

Experimental

Apparatus

The separation of Se and I species was conducted using a PRP-X100 (250 mm × 4.6 mm, 5 μm) anion-exchange column (Hamilton, Reno, NV, USA) and a Waters Acquity UPLC system (Waters, Milford, MA, USA). The UPLC system was equipped with a binary pump and an auto-sampler (with a sample loop of 10 μL). The detection of elements was performed with a Perkin-Elmer NexIon 300D ICP-MS (Perkin Elmer, Branford, CT, USA) equipped with a concentric nebulizer and a cyclonic spray chamber. The dynamic reaction cell (DRC) mode of ICP-MS with O_2 (99.999%) as the reaction gas was used to reduce polyatomic interference. The monitored masses were $^{80}Se^{16}O^+$ (*m/z* 96) for selenium and $^{127}I^+$ for iodine. The ICP-MS performance was checked daily with a NexIon setup solution (Perkin Elmer, Branford, CT, USA) containing 1 μg L^{-1} of Li, Be, Fe, In, Ce, Pb and U.

The chromatograph was coupled to the mass spectrometer via direct connection of the column to the concentric nebulizer with a PEEK tube. Indium (^{115}In) was used as an internal standard by continuously mixing the chromatographic eluate via a T-junction located after the column and before the nebulizer. The operating conditions are summarized in Table 1.

Table 1. ICP-MS operating conditions and HPLC-ICP-MS settings for the speciation of selenium and iodine.

ICP-MS	RF power (W)	1600
	Nebulizer type	Concentric nebulizer with baffled cyclonic spray chamber
Gas flow (L min^{-1})	Plasma	18
	Auxiliary	0.9
	Nebulizer	0.84
Torch alignment (mm)	Horizontal	-0.37
	Vertical	-0.01
	Sampling depth	0.00
	DRC conditions	
DRC (mL min^{-1})	O_2	1.2
	RPq	0.7
Data acquisition	Sweeps per reading	3
	Replicates	1
	Dwell time	125 ms for Se and 175 ms for I
	Monitored isotopes	^{96}SeO$^+$, ^{127}I$^+$
	Internal standards	^{115}In$^+$ (post-column added at 3 rpm)
HPLC	Column	PRP X100 (4.6 × 250 mm, 5 μm)
	Injected volume	10 μL
	Flow rate	1.0 mL min^{-1}
	Elution	Isocratic
	Mobile phase	3 mM ammonium citrate, 30 mM ammonium perchlorate and 2% (v/v) methanol, pH 8.5

Reagents

Ultrapure water with a resistivity of 18.2 MΩ cm^{-1}, which was obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA), was used throughout this work. Solid standards of inorganic selenium and iodine, including NaI, $NaIO_3$, Na_2SeO_3 and Na_2SeO_4, were all of analytical grade and were purchased from the Sinopharm Chemical Reagents Co., Ltd. (Beijing, China). Stock solutions of iodine and selenium containing approximately 5000 mg L^{-1} selenite, selenate, iodide and iodate were prepared weekly in ultrapure water and maintained at 4 °C. Appropriate dilutions of the stock solutions were prepared daily by weight; ultrapure water was added to obtain the required concentrations.

The ammonium citrate and ammonium perchlorate used as the mobile phases were prepared from 99.5% citric acid (Sigma-Aldrich, St. Louis, MO, USA), 99.99% perchloric acid (Sigma-Aldrich, St. Louis, MO, USA) and 28%-30% ammonium hydroxide (Sigma-Aldrich, St. Louis, MO, USA). HPLC gradient-grade methanol was obtained from Fisher Scientific (Waltham, MA, USA). The pH of the mobile phases was adjusted using ammonium hydroxide. The solution was filtered through a 0.22 μm membrane before each use.

Samples

The three groundwater samples, which were provided by the Beijing Research Institute of Uranium Geology, were obtained using a double-packer hydraulic test system at different depths from the Beishan No. 3 well located at N 40 ° 45' 29.16" and E 97° 28' 5.7". Beishan is located in northwest China’s Gansu Province and has been considered as a candidate site for a potential Chinese HLW repository [27]. The samples were collected, transported and stored under anoxic conditions. The details of the samples are summarized in Table 6.

These highly mineralized water samples were filtered and diluted 1:1 by volume with ultrapure water before standard addition solutions for the method validation and water samples for the speciation analysis were prepared.

Method development

The chromatographic conditions, including the composition of the mobile phase, the pH and the methanol content as an organic modifier, were optimized to separate the four species (iodide, iodate, selenite and selenate) in a single chromatographic run with minimum analysis time.

The mass spectrometry detection conditions, including the dwell time and sweeps per reading, were optimized to obtain a stable baseline and to maintain 12 data points per peak. The DRC method with O_2 as the reaction gas was applied to reduce the polyatomic interferences of $^{40}Ar_2^+$ at $^{80}Se^+$ by forming $^{80}Se^{16}O^+$ (*m/z* 96). The DRC conditions, including the reaction cell gas flow rate and rejection parameter q (RPq), were optimized to enhance the sensitivity for the simultaneous detection iodine and selenium.

Method validation

The potential matrix effects were assessed by comparing the slopes of the calibration curves obtained using the external standard method and the standard addition method. For the external standard method, we prepared the standard solutions by diluting the stock solutions to the concentration range of 0.2 to 100 μg L^{-1} for iodate and from 0.2 to 50 μg L^{-1} for iodide, selenite and selenate. In the case of the standard addition method, samples from diluted groundwater sample BS0313 were spiked with stock solutions to prepare standard addition solutions with concentrations ranging from 10 to 100 μg L^{-1} for iodate and from 2 to 45 μg L^{-1} for iodide, selenite and selenate. Then, the linearity was tested by calculating the correlation coefficients and standard deviations from the slopes of the linear calibration curves obtained with least-squares regression analysis. The slopes were compared using the *F*-test and *T*-test.

To evaluate the accuracy and precision of the method, the standard addition method was applied because suitable reference materials for iodide and selenium speciation were not available [28]. Therefore, the diluted groundwater sample BS0313 was spiked at two concentration levels: a low level, with 1 μg L^{-1} of each species, and a high level, with 60 μg L^{-1} of iodate and 25 μg L^{-1} of the other three species. The precision was determined under repeatability and intermediate precision conditions. The repeatability of the method was evaluated using the coefficient of variation (CV) calculated from the measurements of nine replicates of water samples at two spiked levels. The intermediate precision was assessed by measuring the samples in triplicate for three consecutive days. The accuracy was estimated by determination of the recoveries of six replicates of the samples.

Calculations of the detection and quantification limits were based on the 3σ/10σ criterion (σ is the standard deviation of 11 measurements of the blank solution). Therefore, the LODs and LOQs were calculated by dividing the 3σ and 10σ by the slopes of the calibration curves for each species and taking into account the dilution ratio.

The standard addition solutions and external standard solutions were prepared daily by weight and filtered through a 0.22 μm membrane.

Results and Discussion

Optimization of chromatographic separation

First, the composition of the mobile phase was examined. Although anion-exchange columns permit the use of largely aqueous mobile phases, salts composed of organic anions and cations, such as acetate, formate or citrate salts, are preferable as the chromatographic mobile phase to prevent salt accumulation on the sampler and skimmer cones. Ammonium citrate was tested as a mobile phase because citric acid is a strong tricarboxylic acid, which leads to a relatively high eluent strength at a low concentration. Additionally, perchlorate, a hydrophobic anion, was added to the mobile phase to improve the elution of iodide, which exhibited a strong hydrophobic interaction with the stationary phase of the column. Subsequently, the concentrations of ammonium citrate and ammonium perchlorate were tested to separate the four species in a relatively short time. As indicated by the results in Fig. 1, the retention behavior of iodide was largely dependent on the concentration of perchlorate. The retention time of iodide decreased from 20 min to less than 10 min when the concentration of perchlorate was increased from 5 mM to 25 mM, whereas the other three species were still baseline separated. When the concentration of perchlorate was increased to 30 mM, iodate and selenite began to co-elute. With respect to the influence of citrate, the retention times of the four species decreased at similar rates when the citrate concentration was increased, and co-elution of iodate and selenite was observed when the citrate concentration was greater than 4 mM. Therefore, the optimal mobile phase composition was determined to be 3 mM citrate and 25 mM perchlorate.

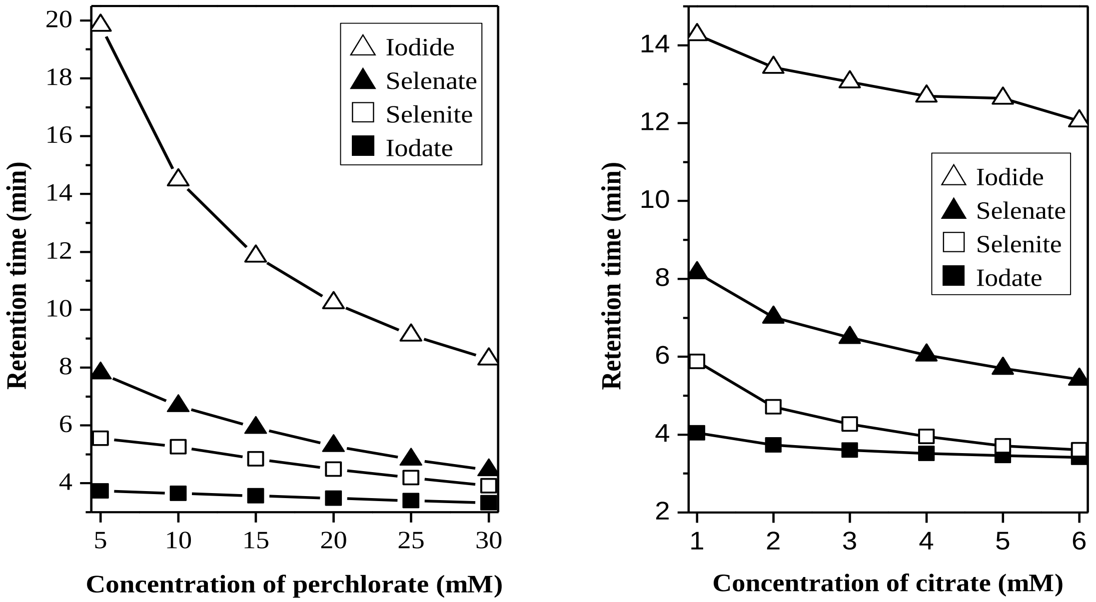

Fig. 1 Dependence of separation on the concentrations of perchlorate and citrate in the mobile phase.

(left: 3 mM ammonium citrate + x mM ammonium perchlorate, right: 25 mM ammonium perchlorate + x mM ammonium citrate, 10 μg L^{-1} of each species)

Note that the chromatographic separations were strongly affected by the pH of the mobile phase. Although the degree of deprotonation of the eluent and analytes increased with pH, their effects were opposite: a higher degree of deprotonation of citrate (pK2 = 4.77 and pK3 = 6.39) as an eluent led to a stronger eluent strength and a shorter retention time, whereas for the analyte, a greater degree of deprotonation resulted in a stronger interaction with the column and a longer retention time. As shown in Fig. 2, the separation of the four species was only achieved at high pH (pH = 8-9), which was the joint effect of deprotonation of the eluent and analyte. Therefore, the pH of the mobile phase was adjusted to 8.5.

Notably, the addition of a small proportion of methanol to the mobile phase improves the detection sensitivity of ICP-MS for Se 29. However, excess methanol results in the accumulation of carbon on the cones, which affects instrumental stability and sensitivity 30. The effects of different proportions of methanol on the detection of Se were tested. As indicated by the results presented in Fig. 3, the retention times of the Se species were not affected by methanol; however, the sensitivity and peak shape were improved.

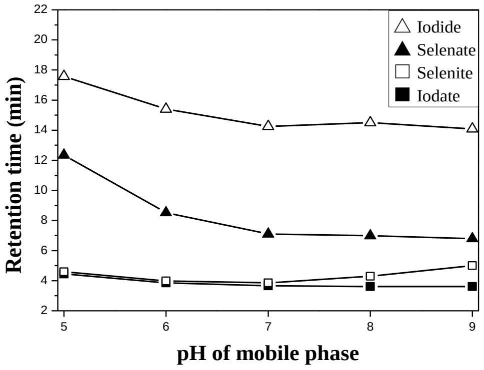

Fig. 2 Dependence of separation on the pH of the mobile phase. (3 mM ammonium citrate + 25 mM ammonium perchlorate, 10 μg L^{-1} of each species).

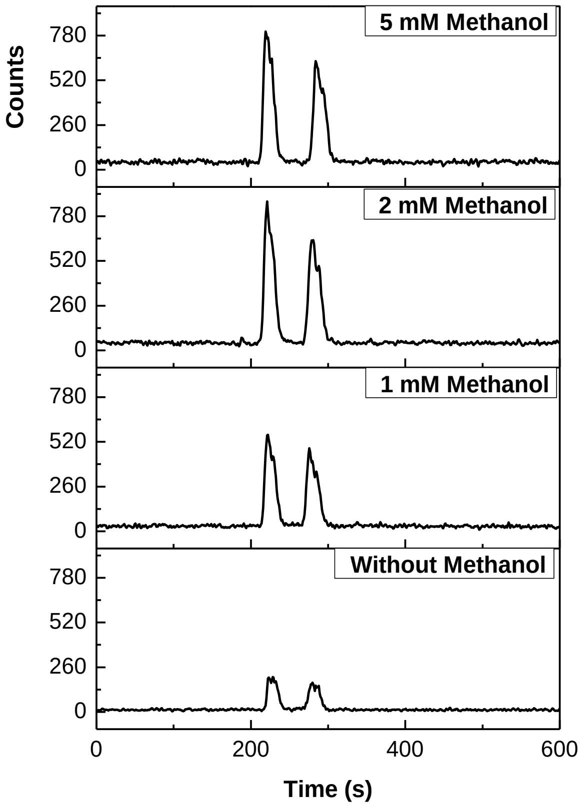

Fig. 3 Effects of methanol on selenium detection (selenite and selenate at 10 μg L^{-1}).

Therefore, the composition of the mobile phase was finally set to 3 mM ammonium citrate, 25 mM ammonium perchlorate and 2% (v/v) methanol at pH 8.5. A typical chromatogram of a mixture containing selenium and iodine is shown in Fig. 4.

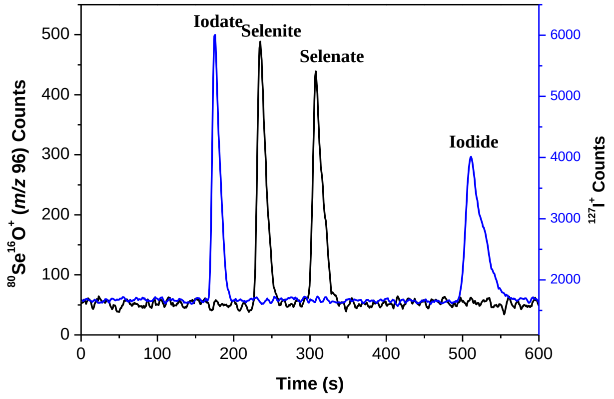

Fig. 4 Chromatograms of a mixture of selenium and iodine standards (each species at 5 μg L^{-1}).

Method validation

LINEARITY AND MATRIX EFFECTS

Seven different concentration levels of groundwater samples were prepared using the external standard and standard addition methods. The analysis was conducted in triplicate, and the results are shown in Table 2. As shown, the correlation coefficients were greater than 0.999 for all species and the linearity range spans two or three orders of magnitude; these results were satisfactory because they covered the natural range of these species in groundwater.

The slopes of the calibration curves were compared using the *F*-test and *T*-test. An *F*-test was first applied to compare the standard deviations (SDs) of the two slopes. For iodate and iodide, the F_{cal} values were greater than the F_{tab} of 5.05 (95% confidence interval and five degrees of freedom); therefore, the Satterthwaite approximation was used to calculate the corrected t_{exp} values and degrees of freedom (DF). For selenite and selenate, the F_{cal} values were less than the F_{tab} of 5.05; thus, the combined variance and the t_{exp} values were calculated (see Table 3). We subsequently examined the matrix effects by comparing the t_{exp} values with the t_{tab} values. For iodate and iodide, the obtained t_{exp} values were lower than the t_{tab} values; i.e., the matrix effect did not significantly influence the detection of iodate and iodide. However, in the cases of selenate and selenite, the t_{exp} values were greater than the t_{tab} values, which indicates that the matrix effects were significant; in fact, the matrix effects enhanced the ionization of Se species according to the increased slopes. Therefore, analysis of the groundwater sample had to be performed using the standard addition method.

Table 2. Calibration curves for the external standard and standard addition methods.

	External standard				Standard addition			
	Range (μg L^{-1})	R^2	Slope	Slope standard deviation[a]	Range (μg L^{-1})	R^2	Slope	Slope standard deviation
Selenite	0.2-50	0.9997	269.8	2.157	0-45	0.9993	305.2	3.576
Selenate	0.2-50	0.9995	251.2	2.540	0-45	0.9995	284.9	2.947
Iodide	0.2-50	0.9999	3965	7.039	0-45	0.9999	4013	16.30
Iodate	0.2-100	0.9999	3078	4.592	0-100	0.9995	3157	32.35

[a] Standard deviation of slope (n = 7), calculated as follows: $S_b = \frac{S_{y/x}}{\sqrt{\Sigma(x-\bar{x})^2}}$ $S_{y/x} = \sqrt{\frac{\Sigma(y-\hat{y})^2}{n-2}}$

Table 3. Statistical comparison of the slopes of the calibration curves.

	Slope	DF[a]	Slope SD	F_{exp}[b]	t_{exp}[c]	Corrected DF[c]	t_{tab}[d]
ES[e]-Selenite	269.8	5	2.157	2.748	22.38		4.587
SA[f]-Selenite	305.2	5	3.576				
ES-Selenate	251.2	5	2.540	1.346	22.92		4.587
SA-Selenate	284.9	5	2.947				
ES-Iodide	3965	5	7.039	5.364	1.102	6.802	5.408
SA-Iodide	4013	5	16.30				
ES-Iodate	3078	5	4.592	49.63	1.407	5.201	6.869
SA-Iodate	3157	5	32.35				

[a] Degrees of freedom calculated as $v = n - 2$

[b] F values calculated as follows: $F_{exp} = \frac{S_1^2}{S_2^2}$, $F_{tab} = 5.050$ (P = 0.05, $v_1 = 5$, $v_2 = 5$)

[c] t_{exp} calculated as follows: if $F_{exp} < F_{tab}$, then $t_{exp} = \frac{|Slope_{es} - Slope_{sa}|}{\sqrt{S_c^2\left(\frac{1}{n_1}+\frac{1}{n_2}\right)}}$, $S_c^2 = \frac{v_1 S_1^2 + v_2 S_2^2}{v_1 + v_2}$, where S_c^2 is the combined variance, S is the standard deviation of the slope and v is its degrees of freedom; if $F_{exp} \geq F_{tab}$,, then $t_{exp} = \frac{|Slope_{es} - Slope_{sa}|}{\sqrt{\frac{S_1^2}{n_1}+\frac{S_2^2}{n_2}}}$ and $v = \frac{\left(S_1^2/n_1 + S_2^2/n_2\right)^2}{\frac{\left(S_1^2/n_1\right)^2}{n_1-2}+\frac{\left(S_2^2/n_2\right)^2}{n_2-2}}$ and t_{exp} and v are corrected using the Satterthwaite approximation.

[d] P = 0.001, v = 10, $t_{tab} = 4.587$; v = 7, $t_{tab} = 5.408$; v = 6, $t_{tab} = 6.869$

[e] ES: the external standard method.

[f] SA: the standard addition method.

PRECISION AND ACCURACY

The results obtained for repeatability and intermediate precision are shown in Table 4. Repeatability was evaluated from the coefficients of variation (CVs) of the peak areas. The CVs at the high concentration level were slightly lower than the CVs at the low level; however, both were satisfactory, ranging from 1% to 4%. In terms of intermediate precision, the results were very good (1.68-4.01%) at the low concentration level and acceptable (2.12-7.93%) at the high concentration level.

Table 4. Accuracy and precision of the method obtained in spiked water samples.

Species	Repeatability[a]		Intermediate precision[b]		Recovery and CV[c]	
	Low level[d]	High level[e]	Low level	High level	Low level	High level
Selenite	4.08	2.51	1.68	2.12	95.7 (2.0)	99.6 (2.5)
Selenate	3.21	2.56	4.01	2.80	90.2 (3.0)	102 (2.6)
Iodide	3.18	1.34	2.27	7.93	102 (1.9)	97.0 (0.90)
Iodate	2.75	2.42	1.80	5.79	103 (0.62)	98.4 (0.98)

[a] n = 9

[b] n = 3

[c] n = 6

[d] Selenite, selenate, iodide and iodate 1 µg L^{-1}.

[e] Selenite, selenate, iodide 25 µg L^{-1}; iodate 60 µg L^{-1}.

The results obtained from the accuracy experiments are presented in Table 4. Satisfactory recoveries (in the range of 90.2% to 103%) and CV values less than 3% were obtained with the spiked matrix, thereby confirming the good accuracy of the method.

LIMITS OF DETECTION AND QUANTIFICATION

The limits of detection and quantification were calculated as 3σ/s and 10σ/s, where σ is the standard deviation of 11 measurements of a blank and *s* is the slope of the calibration curve obtained using the standard addition method, with the dilution ratio taken into account. The results are presented in Table 5. The detection limits for selenite and selenate were 22 and 23 ng L^{-1}, respectively, and those for iodide and iodate were 4.3 and 5.4 ng L^{-1}, respectively. The quantification limits for selenite and selenate were 73 and 78 ng L^{-1}, respectively, and those for iodide and iodate were 14 and 18 ng L^{-1}, respectively. The low instrumental noise and stable baseline resulted from the proper data acquisition conditions (dwell time = 125 ms for Se and 175 ms for I and sweep number = 3), and the use of DRC to reduce the interference of polyatomic ions resulted in low detection limits. Given the levels of these species in the environment, the proposed method allows satisfactory quantitative detection of these species.

Table 5. Limits of detection and quantification of the method.

Species	LOD[a] (ng L^{-1})	LOQ[a] (ng L^{-1})
Selenite	22	73
Selenate	23	78
Iodide	4.3	14
Iodate	5.4	18

[a] n = 11

Although many selenium and iodine speciation methods based on HPLC-ICP-MS have been reported, none of the reported technique achieved the simultaneous separation and detection of selenium and iodine. Among the speciation studies of selenium or iodine in saline or mineralized water reported by other authors, the LODs for selenite and selenate ranged from 0.2 μg L^{-1} to 0.35 μg L^{-1} and from 0.35 μg L^{-1} to 0.8 μg L^{-1}, respectively [25, 28, 31, 32], and the LODs for iodide and iodate ranged from 0.025 μg L^{-1} to 0.052 μg L^{-1} and from 0.25 μg L^{-1} to 0.061 μg L^{-1}, respectively [16, 22, 33]. We concluded that the proposed method improved the detection limits by one order of magnitude for selenium and iodine species and allowed for the simultaneous determination of selenium and iodine.

Note that the proposed method was only optimized and validated for inorganic selenium and iodine species. The analysis of organic species with this method could be problematic, for example, if the organic iodine was not eluted, it will accumulate on the column and influence the determination of the later samples.

Application to real groundwater samples

The method was applied to the determination of the four species (selenate, selenite, iodide and iodate) in three groundwater samples. The mean concentrations observed for three replicates are shown in Table 6. All four species were present in the three groundwater samples. With respect to selenium speciation, the dominant species identified in these groundwater samples was selenate, which is consistent with the results reported by other authors [25, 34] and with the fact that selenite is more prone to precipitation and sorption [35] than selenate [pK_{sp} ($CaSeO_3$, 298.15 K) = 6.40, pK_{sp} ($CaSeO_4$, 298.15 K) = 2.68, pK_{sp} ($MgSeO_3$, 298.15 K) = 5.82, pK_{sp} ($CaSeO_4$, 298.15 K) = 1.13 [36]]. In the case of iodine, no dominant species was identified; however, an interesting phenomenon was observed in that the iodide concentration increased and the iodate concentration decreased with increasing depth. The opposite results were observed for samples of seawater, which was interpreted by biological mediation [37]; however, in the case of groundwater, because of the complex geological and biological environment of the groundwater and the relatively small sample size, a solid conclusion cannot be drawn without further studies.

Table 6. Details and analytical results of the groundwater samples (concentration, μg L^{-1}, shown as the mean ± S.D.[a]).

Sample coding	Collection date	Depth (m)	Analtical results			
			Selenite	Selenate	Iodide	Iodate
BS0305	2005/09/07	208-308	0.57 ± 0.08	20 ± 0.8	0.51 ± 0.06	54 ± 3
BS0313	2013/07/10	390-400	0.52 ± 0.06	9.1 ± 0.7	8.0 ± 0.09	53 ± 0.1
BS0309	2009/08/28	~550	1.1 ± 0.2	8.8 ± 0.6	32 ± 0.6	12 ± 1

[a] n = 3

Conclusions

A method for the simultaneous determination of inorganic selenium and iodine species in groundwater using HPLC-ICP-MS has been presented for the first time, including the optimization and validation of this method. For the analysis of groundwater samples, this method includes the use of filtration as a pretreatment and quantification at the ultra-trace level using the standard addition method. The four species, selenite, selenate, iodide and iodate, can be determined in groundwater samples collected at different depths with satisfactory sensitivity and accuracy, which provides a promising tool for studying the environmental behaviors of selenium and iodine, thereby supporting the assessment of the safety of nuclear waste-disposal repositories.

Acknowledgements

The authors are grateful to the Institute of High Energy Physics (IHEP) for cooperation in conducting this work. Dr. Rui Su from the Beijing Research Institute of Uranium Geology (BRIUG) is acknowledged for providing the groundwater samples. This work was supported by the Special Foundation for High-level Radioactive Waste Disposal (2007-840, 2012-851) and by the National Natural Science Foundation of China (NSFC, Nos. 11075006, 91026010).

Notes and references

[a] Beijing National Laboratory for Molecular Sciences, Fundamental Science Laboratory on Radiochemistry & Radiation Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.
b CAS Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
Address correspondence to: Prof. Chunli Liu, College of Chemistry and Molecular Engineering, Peking University, 5 Yiheyuan Road, Beijing, 100871, China.
E-mail: liucl@pku.edu.cn.
Phone: (+86)010-62765905. Fax: (+86) 010-62765905.
Prof. Weiyue Feng, Institute of High Energy Physics, Chinese Academy of Sciences, 19B Yuquan Road, Shijingshan District, Beijing, 100049, China, E-mail: fengwy@ihep.ac.cn

Phone: (+86)010-88233209 Fax: (+86)010-88233209

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