Toward the use of surface modified activated carbon in speciation: Selective preconcentration of selenite and selenate in environmental waters

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ABSTRACT

This paper describes a novel application of tetrabutylammonium hydroxide-modified activated carbon (AC-TBAH) to the speciation of ultra-trace Se(IV) and Se(VI) using LC-ICP-DRC-MS. The anion exchange functionality was immobilized onto the AC surface enables selective preconcentration of inorganic Se anions in a wide range of working pHs. Simultaneous retention and elution of both analytes, followed by subsequent analysis with LC-ICP-DRC-MS, allows to accomplish speciation analysis in natural samples without complicated redox pre-treatment. The laboratory-made column of immobilized AC (0.4 g of sorbent packed in a 6 mL syringe barrel) has achieved analyte enrichment factors of 76 and 93, respectively, for Se(IV) and Se(VI), thus proving its superior preconcentration efficiency and selectivity over common AC. The considerable enhancement in sensitivity achieved by using the preconcentration column has improved the method's detection limits to 1.9–$2.2\,\mathrm{ng\,L^{-1}}$, which is a 100-fold improvement compared with direct injection. The analyte recoveries from heavily polluted river matrix were between 95.3 and 107.7% with less than 5.0% RSD. The robustness of the preconcentration and speciation method was validated by analysis of natural waters collected from rivers and reservoirs in Hong Kong. The modified AC material is hence presented as a low-cost yet robust substitute for conventional anion exchange resins for routine applications.

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1. Introduction

Because it is both a vital dietary nutrient and a toxic element, selenium has been the focus of many mechanistic studies, analyzing its physiological action and environmental fate. It essentially constitutes the anti-oxidizing enzyme glutathione peroxidase that protects cellular components from peroxidative damage [1]. However, in humans adverse indicated by selenosis are observable with higher levels of intake [2]. In fact, there are narrow concentration boundaries between benefit and toxicity, and these depend heavily on its chemical forms. Studies have revealed that inorganic Se forms, especially Se(IV), are more toxic than other organic derivatives, such as methylated selenium and selenoamino acids [2,3]. Determining the actual species distribution has therefore become the focus in evaluating its presence in environmental systems.

Concentrations of Se in natural water systems range from 0.04 to $0.12\,\mu g\,L^{-1}$ with inorganic Se(IV) and Se(VI) species dominating [2,4]. Such trace analyte levels have been a challenge to the sensitivity of most speciation instrumentation including liquid chromatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS). The strategy for improving the capability of LC-ICP-MS systems to assess real, complex samples begins with developing preconcentration methods. One of the most popular approaches uses solid-phase extraction (SPE) for speciation following preconcentration, most often with anion exchange material by fractional elution [5–7]; this, however, complicates the analysis with more elution procedures and use of chemicals. Other authors have offered relatively low cost SPE methods with modified materials, such as zirconium-loaded activated carbon [8] and lanthanum hydroxide-coated cellulose fibre [9]. However these preconcentration methods are only sensitive to Se(IV) or total Se, for which pre-reduction of Se(VI) is mandatory. In these methods, samples are usually processed by a selected reducing agent, such as sodium borohydride, to transform Se(VI) to Se(IV) for total Se detection. Consequently, Se(VI) is quantified by the difference of Se(IV) and total Se. During the laborious reduction steps, sample loss is possible. Moreover, the selectivity of those extraction materials has restricted the method to differential speciation using separate assays. In contrast, simultaneous preconcentration would be a more reliable approach for consistent species determination.

Compared with commercial anion exchange resins, activated carbon (AC) is a more economical substitute for routine applications and it is being used for many analytical and industrial purposes [10–12]. AC is often characterized by the strong adsorptivity toward organics through hydrophobic interaction and the efficiency is attributed to the microporosity of its steam-activated

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surface. Having pore size of less than 2 nm, these micropores established an extensive surface area for excellent molecule adsorption. In contrast to the overwhelming success of AC in capturing organic molecules [13] and inorganic metal cations [11,14,15], there have been few useful descriptions of its use for anion adsorption. A few authors have attempted to retain inorganic Se on AC; their strategies have involved either pretreating Se(IV) with an organic ligand for complex formation [16] or generation of colloidal Se element from Se(IV) and Se(VI) [17,18] prior to AC adsorption. These methods all require large sample volume (500–1000 mL) to accomplish comparable sensitivity for trace detection. It appears that analyte selectivity is the major limitation in Se preconcentration. We hypothesize that proper modification in the sorption properties of AC could overcome this limitation. In fact, the high porosity and hydrophobicity of AC have served as a platform for customized surface functionalities. Specific retention of certain metal ions of Hg, Pb, Cr, Fe and Cu, has been achieved by immobilizing AC with chemicals such as 1-(2-thiazolylazo)-2-napthol [10], triethylenetetramine [19] and 1-acylthiosemicarbazide [20], in which the high affinity nitrogen- or sulphur-containing moieties interact spontaneously with the heavy metals. This prompted us to tailor a functionalized surface for both Se(IV) and Se(VI) ions retention without laborious sample pretreatment procedures.

Here we present a novel laboratory-made SPE column packed with tetrabutylammonium hydroxide-immobilized AC material (AC-TBAH) for Se(IV) and Se(VI) preconcentration. After simple modification on the porous surface of AC, it was assigned anion exchange functionality for retaining both inorganic Se species. The modified AC thereby represents a low-cost substitution for conventional anion exchange resin. The retention as well as recovery behaviors of Se(IV) and Se(VI) on the material were thoroughly studied, enabling simultaneous analyte preconcentration, consequently, individual species determination without additional redox treatment perturbing the original species distribution. The sorbent worked over a wide range of sampling pHs, matching the range of natural acidity (pH 7–8) of the analyzed natural water samples without adjustment. It was found that the selective adsorption for Se anions was substantially improved by the modified AC and has accomplished outstanding enrichment factors using only small sample volumes for off-line preconcentration. Both analytes were eluted from the AC-TBAH column in a single fraction followed by LC-ICP-MS speciation with dynamic reaction cell (DRC) which essentially removed the well-known argon interference in MS detection. The combined advantages from both instrumentation and sample enrichment have achieved excellent method sensitivity for trace Se speciation in environmental waters.

2. Experimental

2.1. Instrumentation

The liquid chromatographic system comprised a PerkinElmer LC series 200 binary pump (PerkinElmer, Waltham, MA, USA) and an autoinjector fitted with a 200 μL sample loop. A PRP-X100 anion exchange column (150 mm × 4.6 mm, 3 μm; Hamilton, Reno, NV, USA) equipped with a PRP-X100 guard column was used.

ELAN DRC II ICP-MS instrument (PerkinElmer, Waltman, MA, USA) with Meinhard nebulizer and a cyclonic spray chamber was used in the total Se determinations. The sample solution was directly aspirated through a sampling tube (0.55 mm i.d.). In speciation analysis, the LC system was hyphenated to the ICP-DRC-MS *via* teflon tubing that directed column eluent to the nebulizer. Dynamic reaction cell (DRC) was employed to remove polyatomic interference with Ultra High Purity methane gas. The operation parameters for both instruments are summarized in Table 1.

Table 1
Operation parameters of LC-ICP-DRC-MS.

Parameter	Setting
ICP-DRC-MS	PerkinElmer ELAN DRC II
RF Power	1175 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1 L min^{-1}
Nebulizer gas flow	0.90 L min^{-1}
Cones	Pt and Ni
AutoLens	Engaged
Mass monitored	^{78}Se
Dwell time	50 ms
DRC reaction gas	Methane
DRC gas flow	0.2 mL min^{-1}
DRC RPq	0.4
LC	PerkinElmer Series 200 pump
Column	Hamilton PRP-X100 (150 mm × 4.6 mm, 3 μm)
Injection volume	20 μL
Mobile phase	40 mM NH$_4$NO$_3$, pH 7.5
Flowrate	1.5 mL min^{-1}

2.2. Chemicals and reagents

Activated carbon (DARCO G-60, powdered, 100 mesh) was obtained from Sigma–Aldrich (St. Louis, MO, USA). 1.0 M tetrabutylammonium hydroxide (TBAH) solution was purchased from Fluka (St. Louis, MO, USA). Acidic solution was prepared from concentrated nitric acid (ARISTA, BDH, UK) for SPE eluent.

MilliQ water (Millipore, Billerica, MA, USA) of 18.2 MΩ cm was used throughout the entire work in preparation of all aqueous solutions. 1000 μg L^{-1} stock solutions of the inorganic selenium species were prepared by appropriate dissolution of sodium selenate anhydrous (Sigma–Aldrich) and sodium selenite pentahydrate (Fluka). Elemental selenium standard purchased from VHG Labs (Manchester, NH, USA) was used for total elemental determinations.

Mobile phase buffers were made up with ammonium nitrate (Sigma–Aldrich, St. Louis, MO, USA), adjusted to pH 7.5 by ammonium hydroxide.

Methane gas (Hong Kong Specialty Gases, Hong Kong) for the DRC application was of 99.999% purity grade. Daily operation of ICP-MS used liquefied argon gas (Hong Kong Oxygen & Acetylene, Hong Kong) of 99.9995% purity.

2.3. Preparation for preconcentration

2.3.1. Modification of activated carbon

10 g AC was weighed into a 250 mL Erlenmeyer flask containing 150 mL MilliQ water followed by the addition of 800 μL 1.0 M TBAH solution. The mixture was magnetically stirred for 3 days as suggested by previous work [21]. After complete adsorption, the suspension was filtered and thoroughly rinsed with MilliQ water. The TBAH-immobilized AC sorbent was dried overnight in an oven at 80 °C.

For comparison, another batch of nitric acid-oxidized sorbent (AC-HNO$_3$) was prepared according to the described procedures [22]. 5 g AC was suspended in 100 mL concentrated HNO$_3$. After 24 h, the mixture was filtered and rinsed until neutralized. The oxidized sorbent was dried similarly as above.

2.3.2. Preparation of SPE column

A preconcentration column was prepared by packing uniformly 0.40 g sorbent in a 6 mL syringe barrel (Terumo, Tokyo, Japan). The sorbent was held in place in the column with two small portions of clean glass wool (Merck, Darmstadt, Germany). The glass wool was previously acid-treated to leach trace metal contamination in 10% nitric acid, followed by thorough rinsing with MilliQ water and finally dried.

2.4. Sample analysis

2.4.1. Sample collection

Fresh water samples were collected from different locations of rivers and reservoirs in Hong Kong, namely Kam Tin River, Yuen Long River, Plover Cove Reservoir and High Island Reservoir, during daytime in February 2010. Sample collection was carried out using clean polypropylene bottles which were wrapped with aluminum foil. Samples were not acidified to avoid species interconversion. Samples were filtered through 0.45 μm membrane and subject to immediate analysis. Any pending samples were stored at 4 °C.

2.4.2. Total elemental analysis

The sample was first screened by ICP-MS for total elemental content, using the TotalQuant method in ELAN DRC II software. More precise total Se determination was carried out against calibration standards.

2.4.3. Preconcentration and speciation procedures

The packed SPE column was briefly conditioned with 5 mL MilliQ water. 200 mL sample was passed through the column at 2 mL min^{-1}. No adjustment was needed if the acidity of the sample fell within pH 6–8. Both retained Se(IV) and Se(VI) species were simultaneously eluted by 5 mL 0.5 M HNO$_3$ at the same flowrate. The enriched eluent was subsequently filtered through 0.2 μm nylon syringe filter (Alltech, Deerfield, IL, USA) for LC injection. The column was used once only.

3. Discussion

3.1. Activated carbon sorbent

Activated carbon is well-known as an excellent sorbent material for organic compounds and metallic cations. Unlike its analogue porous graphitic carbon (PGC), which does not contain ionized surface groups but delocalized layers of polarizable pi electrons [23], the sorption property of AC is governed by the textural characteristics and the wide content of acidic functionalities such as phenolic, carboxylic, hydroxyl and carbonyl groups [24,25]. Therefore, it is feasible to boost the adsorption capacities by modifying the sorbent surface with appropriate treatment. El-Sheikh has successfully produced an oxidized surface of AC with increased number of acidic oxides for retaining metal ions [22]. We have performed preliminary trials on the nitric acid-oxidized AC for Se retention. However, it was found that only about 20% of both Se(IV) and (VI) analytes was recovered. This can be explained by the electrostatic nature of deprotonated surface oxygen species, which are specific to cationic counterparts. In this regard, it is reasonable to establish an anion exchange surface with appropriate reagents.

Being a highly hydrophobic sorbent, AC adsorbs strongly the large hydrophobic group of a selected surfactant/ion pairing agent while the ionic part sticks out in the bulk solution acting as an ion exchanger [26]. In this study, the anion exchange functionality on the AC surface was assigned by the positively charged ammonium ion of surfactant TBAH. Besides, due to the high porosity of AC it has offered great surface area to host high density of TBAH functionality.

3.2. Effect of loading pH

The pH of the sample solution affects the retention behavior of Se(IV) and (VI) by determining their degrees of ionization as well as the concentration of competing hydroxyl anion derived from a basic medium. In order to investigate the retention profile, the recovery of a series of 50 μg L^{-1} standards was measured after SPE sampling at different pHs. Fig. 1 shows that an acidic condition has a greater
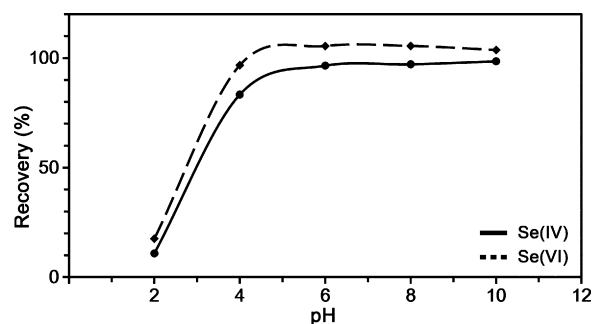
Fig. 1. Effect of sample pH on the preconcentration efficiency of 10 μg Se(IV) and (VI). Refer to text for optimized experimental conditions.

impact on the recoveries as a result of analyte protonation and in view of their pK_a values (Se(IV): 2.50, 8.54; Se(VI): −2.1, 1.8) [27]. The result suggested that the influence of competing hydroxyl was negligible even at basic pH. The working pH of AC-TBAH for both analytes lies between 6 and 8, compatible to the typical values of 7–8 found in natural water samples. Therefore, no pH adjustment was required for routine sample analysis.

3.3. Effect of sample flowrate

Sample flowrate is an important factor to allow sufficient ion-pairing interaction between the flowing analytes and the stationary functional groups. As shown in Fig. 2, the recovery of both analytes was preserved before the retention was affected at higher flowrate. Since the flowrate also determines the efficiency of the sampling procedure, a flowrate of 2 mL min^{-1} was adopted without sacrifice of analyte recovery.

3.4. Effect of eluent volume and concentration

Based on the pK_a values, acidic medium protonates and releases Se(IV) and Se(VI) anions which are electrostatically adsorbed on the sorbent. Nitric acid solution was used because of its compatibility to the LC mobile phase. The concentration of HNO$_3$ was first optimized to quantitatively recover the analyte without diluting the enriched fraction. From Figs. 3 and 4, 5 mL of 0.5 M HNO$_3$ is effective to complete the elution.

The optimum conditions for Se(IV) and (VI) preconcentration was determined as 200 mL sample loading with pH 6–8 at 2.0 mL min^{-1}, and eluting with 5 mL 0.5 M HNO$_3$. In fact, a relatively small sample size of 200 mL was sufficient to achieve a significant enrichment factor in this work compared with other reports of off-line preconcentrations that used 500–1000 mL sample [5,28,29]. Chromatograms of a 0.5 μg L^{-1} standard before and after AC-TBAH enrichment are illustrated in Fig. 5.
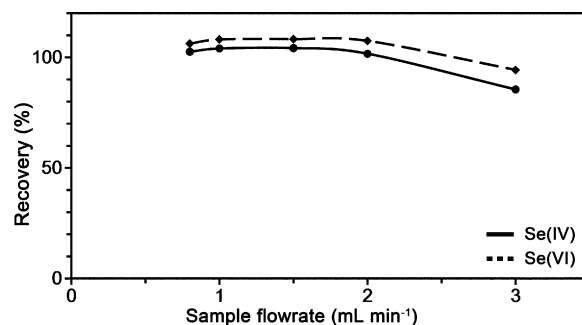
Fig. 2. Effect of sampling flowrate on the preconcentration efficiency of 10 μg Se(IV) and Se(VI). Refer to text for optimized experimental conditions.
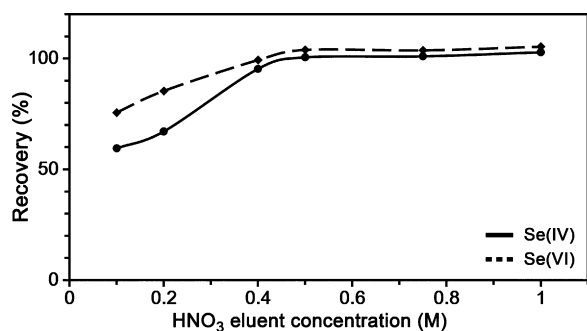
Fig. 3. Effect of the HNO$_3$ concentration on the recovery efficiency of 10 μg Se(IV) and Se(VI). Refer to text for optimized experimental conditions.
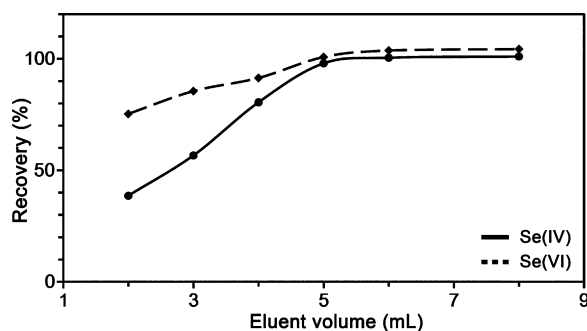

Fig. 4. Effect of eluent volume on the recovery efficiency of 10 μg Se(IV) and Se(VI). Refer to text for optimized experimental conditions.
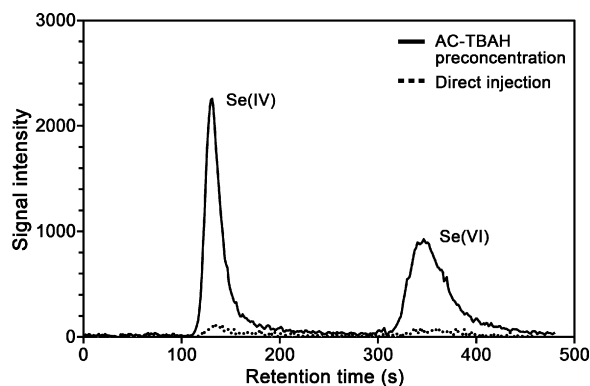

Fig. 5. Overlay chromatograms of 0.5 μg L^{-1} Se(IV) and (VI) standard with and without AC-TBAH preconcentration following the optimized procedures. The LC-ICP-DRC-MS instrument conditions for speciation are summarized in Table 1.

Table 3
Results of speciation and total elemental analysis for Se in water samples (ng L^{-1}).

	Se(IV)[a]	Se(VI)[a]	Total Se[b]
Kam Tin River	3210 ± 32	663 ± 15	3940 ± 196
Yuen Long River	401 ± 19	5.96 ± 0.33	415 ± 25
Plover Cove Reservoir			
Location 1	394 ± 19	6.05 ± 0.34	409 ± 83
Location 2	377 ± 18	5.24 ± 0.25	354 ± 56
Location 3	366 ± 18	6.76 ± 0.38	397 ± 42
High Island Reservoir			
Location 1	283 ± 10	5.62 ± 0.24	287 ± 58
Location 2	249 ± 8.0	7.44 ± 0.37	272 ± 23

The values are mean ± SD ($n = 3$).
[a] Determined by the proposed preconcentration and speciation method using LC-ICP-DRC-MS.
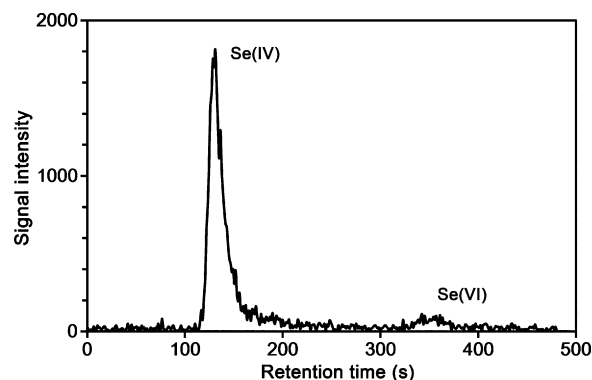[b] Determined by ICP-MS.

Fig. 6. Typical chromatogram of a river sample after optimized AC-TBAH preconcentration. 401 ng L^{-1} Se(IV) and 5.96 ng L^{-1} Se(VI) were found in this water sample collected from Yuen Long River. The LC-ICP-DRC-MS instrument conditions for speciation are summarized in Table 1.

3.5. Analytical performance

Dynamic reaction cell (DRC) has been applied in the speciation of enriched Se(VI) and (VI) using LC-ICP-MS. The use of an appropriate reaction gas offers a substantial improvement in detection sensitivity for ^{78}Se, which has been well-known to suffer from severe isobaric interferences (e.g. ^{40}Ar^{38}Ar$^+$). Our previous work has comprehensively described the optimized DRC conditions for ^{78}Se detection at sub-ppb levels [30]. The AC-TBAH preconcentration procedure described in the present work further extends this method's sensitivity.

Table 2
Comparison of analytical performances of AC-TBAH preconcentration and direct injection for inorganic Se speciation.

	AC-TBAH preconcentration		Direct injection	
	Se(IV)	Se(VI)	Se(IV)	Se(VI)
Limit of detection (ng L^{-1})	2.2	1.9	305	321
Limit of quantitation (ng L^{-1})	5.1	4.3	711	748
Sensitivity (L ng^{-1})	21348	27393	280	292
Linearity	0.9985	0.9991	0.9940	0.9970
Recovery in spiked sample (%)				
0.05 μg L^{-1}	95.3–105.3	100.2–107.7	–	–
1.0 μg L^{-1}	100.8–106.5	98.3–103.2	–	–
10 μg L^{-1}	99.3–104.0	100.7–106.2	–	–
RSD (%)				
0.05 μg L^{-1}	5.0	4.3	–	–
1.0 μg L^{-1}	2.5	1.8	–	–
10 μg L^{-1}	2.1	1.4	–	–

The AC-TBAH preconcentration has achieved enrichment factors (EF) of 76 and 93 for Se(IV) and (VI), respectively. The EF was calculated as the ratio of the two slopes of the calibration curves obtained by preconcentration and direct injection [31]. The calibration curves were prepared by the preconcentration of standards ranging from 0.01 to 20 μg L^{-1}. Another set of calibration curves was produced similarly using plain AC sorbent. Comparing with plain AC, AC-TBAH is obviously superior in terms of preconcentration efficiency and specificity.

As a result of analyte enrichment, the limits of detection (LOD) were significantly improved to 2.2 and 1.9 ng L^{-1} and the limits of quantitation (LOQ) were 5.1 and 4.3 ng L^{-1} for Se(IV) and (VI), respectively. These values were calculated according to the FDA guidelines as three and seven times the standard deviation of five blank extractions divided by the slope of the calibration curve [32]. The method sensitivity was improved by the order of hundred in contrast to direct sample injection without preconcentration [33,34]. The obtained LODs were also comparable to other speciation studies with offline preconcentration techniques [5,28].

In order to demonstrate the applicability of the preconcentration method, recovery tests were performed on spiked water samples. Water samples collected from polluted Kam Tin River in Hong Kong were found, by ICP-MS, to contain high levels (0.1–500 mg L^{-1}) of Na, Mg, Al, K, Ca, Mn, Fe, Sn, Ba, N, Cl, etc. Besides, much of the organic matter naturally existing in river samples [35] is potential interference in AC adsorption. Therefore, the river sample was used to evaluate the method robustness in real sample matrix. From the river samples spiked at three concentration levels of Se, namely, 0.05, 1.0 and 10 μg L^{-1}, 95.3–106.5% of Se(IV) and 98.3–107.7% of Se(VI) were recovered. By evaluating the peak area of seven preconcentration replicates, precision was expressed in relative standard deviation (RSD) values between 1.4 and 5.0%. The recovery and reproducibility data has proven high selectivity of the laboratory-made AC-TBAH sorbent for retention and preconcentration of Se(IV) and Se(VI) with negligible matrix effect even in the presence of interfering species. The analytical characteristics of the speciation method with AC-TBAH enrichment are summarized in Table 2.

The preconcentration method using AC-TBAH sorbent was successfully applied to Se speciation in water samples collected from two local livestock farm-based and down-river from a town, and two reservoirs. Since matrix-matched reference material for inorganic Se speciation was not available, the method was validated using water samples by comparing speciation results with total Se determination. As illustrated in Table 3, the content of individual Se(IV) and Se(VI) species are in good agreement with total Se concentration. Se(IV) was found to be the predominant species in all locations. Due to the AC-TBAH preconcentration, trace Se(VI) was also quantified even in clean reservoir water, which is typically below the detection limit of direct injection method. A typical speciation chromatogram of a river sample using the developed AC-TBAH preconcentration method is presented in Fig. 6.

4. Conclusion

The novel application of TBAH-modified AC in the Se(IV) and (VI) preconcentration was described and developed for LC-ICP-DRC-MS speciation. The modification procedure conveniently produced low-cost sorbent based on AC material. More importantly, it was proven that TBAH functionalization has crucially improved the sorption selectivity toward anionic Se species, hence also improving its preconcentration efficiency. The instrumentation and sample enrichment have achieved excellent method sensitivity for trace Se speciation in environmental waters.

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