



A new anionic exchange stir bar sorptive extraction coating based on monolithic material for the extraction of inorganic anion

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ABSTRACT

A novel anionic exchange stir bar sorptive extraction (SBSE) coating based on poly(2-(methacryloyloxy)ethyltrimethylammonium chloride-co-divinylbenzene) monolithic material for the extraction of inorganic anion was prepared. The effect of preparation conditions such as ratio of functional monomer to cross-linker, content of porogenic solvent on the extraction efficiencies were investigated in detailed. The monolithic material was characterized by elemental analysis, scanning electron microscopy and infrared spectroscopy. In order to investigate the extraction capacity of the new coating for inorganic anion, the new SBSE was combined with ionic chromatography with conductivity detection, Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} were selected as detected solutes. Several extractive parameters, including pH value and ionic strength in sample matrix, desorption solvent, extraction and desorption time were optimized. The results showed that strongly ionic strength did not favor the extraction of anlyates. Under the optimum experimental conditions, low detection limits ($S/N=3$) and quantification limits ($S/N=10$) of the proposed method for the target anions were achieved within the range of 0.92–2.62 and 3.03–9.25 $\mu\text{g/L}$, respectively. The method also showed good linearity, simplicity, practicality and low cost for the extraction inorganic anions. Finally, the proposed method was successfully used to detect the two different trademarks of commercial purified water with satisfactory recovery in the range of 70.0–92.6%. To the best of our knowledge, this is the first to use SBSE to enrich inorganic anions.

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1. Introduction

Stir bar sorptive extraction (SBSE) is an “environmental friendly” sample preparation technique which integrates sampling, extraction, purification and enrichment into a signal step. It was introduced by Sandra and co-workers in 1999 [1]. Similar to solid-phase micro-extraction (SPME), SBSE is an equilibrium technique, but the coated amount on the stir bar is 50–250 times higher than that on SPME fiber, which results in a significant increase in recovery and extraction capacity [2]. In the past few years, SBSE has been developed rapidly and successfully applied to the trace analysis of various target analytes in environmental and biological samples with extremely low detection limits by combining with other separation instruments such as HPLC, GC and CE [3–7].

The coating of SBSE plays a key role in the extraction performance. It is regretful that there is only one kind of stir bar coated with polydimethylsiloxane (PDMS) is commercially available at present. Because of the apolar character of PDMS, SBSE has

been mainly applied to extract non-polar and weakly polar compounds, and failed in the extraction of strong polar compounds unless they have been previously derivatized [8,9]. However, sample derivatization of polar analytes to produce more hydrophobic species is not always possible. At the same time, the poisonous derivatization solvent will do harm to human and pollute environment [8]. The above shortcomings limit the development of SBSE. In order to solve the bottleneck of the development and extend the application field of SBSE, a few of lab-made SBSE coatings were prepared. A new dual-phase stir bar was consisted of a short PDMS tube packed with different carbons [10]. The new stir bar showed enhanced extraction yield for polar compounds compared with those by using conventional PDMS stir bar. Guan and co-workers [11] used sol-gel technique to prepare stir bar that provides direct chemical binding of the coating to the substrate, and applied to the extraction of polycyclic aromatic hydrocarbons and organophosphorus pesticides [12]. In order to improve the polarity of the coating on stir bars, a PDMS/ β -cyclodextrin extraction phase has been prepared by sol-gel technique and showed better selectivity to medium polar compounds estrogen and bisphenol A compared to the PDMS stir bar [13]. However, the coatings prepared by sol-gel technology reported previously suffered from cracking of polymer layer. Polyurethane foam [14], poly(phthalazine ether sul-

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Table 1
Extraction efficiency of different SBSE-AE for Br⁻ and SO₄²⁻.

SBSE-AE	Monomer mixture ^a		Polymerization mixture		Peak area (nS × min)	
	META (% w/w)	DB (% w/w)	Monomer mixture (% w/w)	Porogen solvent (% w/w)	Br ⁻	SO ₄ ²⁻
1	10	90	30	70	19.3	14.5
2	15	85	30	70	33.1	77.0
3	20	80	30	70	13.9	32.6
4	25	75	30	70	22.5	252
5	30	70	30	70	31.2	182
6	35	65	30	70	17.4	75.0
7	30	70	20	80	68.2	232
8	30	70	25	75	61.9	106
9	30	70	35	65	42.4	177
10	30	70	40	60	18.7	162
11	30	70	45	55	149	587
12	30	70	50	50	143	848
13	30	70	55	45	105	1113
14	30	70	60	40	109	480

^a Weight fraction in monomer mixture.

fone ketone) [15] and PDMS/ β -cyclodextrin/divinylbenzene [16] were also selected as SBSE coating. In our previous research, monolithic materials were introduced to act as the coating. A series of coating including hydrophobic, hydrophilic and mix-mode extractive phases based on monoliths for SBSE (SBSEMs) were prepared [17–26]. Polycyclic aromatic hydrocarbons [17], phenols [18,21,22,26], aromatic amines [21,23], steroid sex hormones [19,20], sulfonamides [24] and quinolones antibiotics [25] were successfully extracted by these SBSEMs. It is worth being mentioned that we used vinylpyrrolidone as monomer to prepare a new coating for SBSE which showed a certain degree of absorption for metal ions [21]. To our knowledge, this is the first research that uses SBSE to enrich inorganic metal ions. Up to now, SBSE has been widely and successfully used to extract organic compounds. However, little work has been carried out on the SBSE extraction of ionic species. Using SBSE to extract inorganic ions is worth being studied in order to expand the application field of SBSE.

In the present study, we tried to explore the possibility to use SBSE to extract inorganic anions. Solid-phase extraction (SPE) which uses columns packed with ion exchange resins [27–30] and membrane extraction (ME) that utilizes membranes possess exchangeable functional groups [31] are the most common methods in the extraction and pre-concentration of inorganic ions. Sometimes it is inconvenient for SPE because more steps are involved in the extraction and pre-concentration. Single use and low extractive capacity limit the application of ME. Recently, Hadded and co-workers used quaternary ammonium functionalized latex nanoparticle as SPME coating for the extraction of inorganic anions [32]. The results showed that the new coating could effectively extract anions. However, functionalized latex nanoparticle is non-commercial and difficult to obtain. Therefore, development of a new extraction and pre-concentration mode with simple procedure, relatively high capacity and repeated use will be interesting. To achieve this, a new anionic exchange monolith was prepared and used as SBSE coating (SBSE-AE). The monolith was prepared by *in situ* copolymerization of 2-(methacryloyloxy)ethyltrimethylammonium chloride and divinylbenzene in the presence of a porogen solvent containing cyclohexanol, 1-dodecanol, and water with azobisisobutyronitrile as initiator. The effect of extractive conditions on the extraction performance of SBSE-AE to inorganic anions was conducted in detail. Then, a new methodology combining stir bar sorptive extraction and liquid desorption, followed by ion chromatography with conductivity detector (SBSE-AE/LD-IC/CD) for the analysis of trace of anions in commercial purified water was developed. The results showed that the newly anionic exchange SBSE-AE can effectively extract and concentrate inorganic anions.

2. Experimental

2.1. Chemicals

2-(Methacryloyloxy)ethyltrimethylammonium chloride (META) (72% aqueous solution), divinylbenzene (DB) (80%) and 3-(trimethoxysilyl) propyl methacrylate (γ -MAPS) (95%) were supplied by Alfa Aesar (Tianjin, China); azobisisobutyronitrile (AIBN) (97%, recrystallized before use); cyclohexanol (96%) and 1-dodecanol (97%) were purchased from Shanghai Chemical Co. (China); Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). Potassium bromide (AR) and potassium nitrate (AR) were supplied by Xilong Chemical factory in Guangdong (China); ammonium sulfate (AR) and monopotassium phosphate were purchased from Shanghai Chemical Co. (China). The other compounds used in the present study are analytical reagents.

A standard solution of 10 μ g/mL of each inorganic anion was prepared in Milli-Q water and renewed monthly. The standard mixtures of four anions were prepared by dissolving 1.00 mg of each compound in Milli-Q water in 100 mL volumetric flask. The stock solution was stored at 4 °C and diluted with Milli-Q water to give the required concentration.

2.2. Equipments and materials

Ionic chromatography (IC) analyses were carried out DIONEX ICS-2500 IC instrument equipped with GP50 Gradient Pump, ED40 electrochemical detector operated in the conductivity mode and P/N9750E-029 manual injector. All experiments were performed at room temperature.

The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Chromatographic conditions

The separation was performed on an IonPac AS14A (250 mm \times 4.0 mm i.d.). The mobile phase consisted of a mixture of 25% (v/v) 32 mM Na₂CO₃, 25% (v/v) 4 mM NaHCO₃ and 50% (v/v) water. Eluent suppression was provided by a DZS-4A operated in the recycle mode under the 200 mA current. The flow rate was 1.0 mL/min and injection volume was 50 μ L.

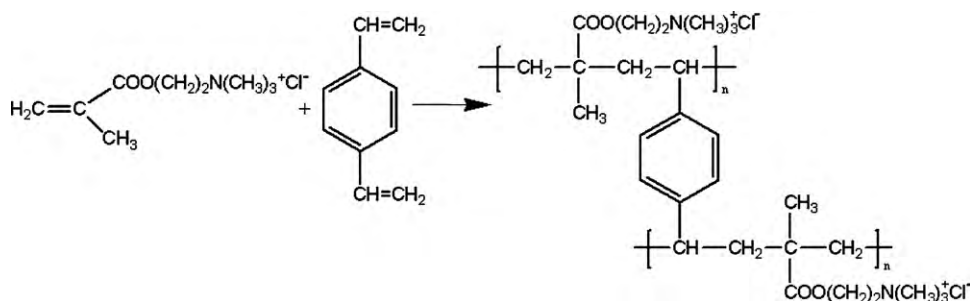


Fig. 1. The reaction sketch of poly (META-co-DB).

2.4. Preparation of SBSE-AE

Before the polymerization, some pretreatment procedure of glass stir bar should be taken in order to facilitate the succedent reaction. The procedure of preparation of glass bar, pretreatment and chemical modifications of the glass bar was described previously [17–19]. AIBN was used as polymerization initiator (1% (w/w) of the total monomer amount) in the all polymerization reaction. Different monomers and porogen concentrations were used for different polymers (Table 1). The monomer mixtures and porogen (80% (w/w) cyclohexanol, 10% (w/w) 1-dodecanol and 10% (w/w) water) were mixed ultrasonically into a homogenous solution then the reactant solution was purged with nitrogen for 3 min. Subsequently, the reactant mixture was poured into a glass tube with definite diameter (3 mm i.d.). The stir bar that has been pretreated was vertically immersed into the reactant mixture. The tube was sealed with septa and kept at 70 °C for 24 h. After the polymerization, the glass tube was carefully cut off with grindstone. Firm and integrated monoliths could be obtained. The monolithic material on the bar was then Soxhlet-extracted with methanol for 24 h or dipped in methanol for 48 h to remove the residue monomer, porogen, uncross-linked polymer and initiator. Finally, the stir bar was dried in air for 1 h to obtain the final SBSE-AE (30 mm length and 1.0 mm monoliths thickness). Before use, the bar was rinsed with 10 mM NaOH and then with a plenty of water for at least 24 h. The SBSE-AE can be regenerated with 100 mM buffer of Na₂CO₃–NaHCO₃ (pH 10). We also recommend the bar should be stored in the same buffer. Generally, the SBSE-AE can be used at least 20 times. The polymerization equation can be found in Fig. 1.

2.5. Extraction and desorption mode

Stirring extraction and stirring liquid desorption modes were used. The samples were stirred with the prepared bars at 400 rpm at room temperature. A 50 mL mix solution of Br[−] and PO₄^{3−} (1.0 μg/mL each) was used for the study of the effect of polymerization parameters on extraction efficiency. In the study of optimized conditions for the extraction of inorganic anions, 50 mL mix solution of 4 anions (100 μg/L each) was used. After the extraction, the SBSE-AE was removed and immersed in 3.0 mL desorption solvent, stirred for a certain time to release the extracted analytes. The stripping solution was used directly for IC-CD analysis.

3. Results and discussion

3.1. Preparation and characterization of SBSE-AE

According to our previous research, the contents of monomer and porogen play a key role in the extraction performance for SBSE based on monolithic materials [17,18,23,24]. In present study, when the effect of monomer and porogen concentrations on extraction efficiency was investigated, ternary porogen (80% (w/w)

cyclohexanol, 10% (w/w) 1-dodecanol and 10% (w/w) water) was used and kept constant. Br[−] and SO₄^{2−} were selected as test analytes. Considering the extraction performance and useful longevity, the optimized conditions for the preparation of poly (META-co-DB) were the proportion of META kept 30% in the monomer mixture, while the ratio of monomer mixture to porogen was 55–45% (w/w) (Table 1, Bar 13). Expected extraction performance and longevity can be obtained under the optimized preparation conditions (can be reused at least 20 times). The SBSE-AE showed good bar to bar reproducibility. The RSD (*n* = 3) of enrichment factors for Br[−] and SO₄^{2−} were 4.96% and 8.39%, respectively.

The news monolith prepared under the optimal conditions (Bar 13) was characterized by EA, IR and SEM. Elemental analysis on the monolith demonstrated that its carbon content was 71.6% (w/w) and nitrogen content was 4.21% (w/w) indicating that META and DB were successfully incorporated into the monolith during the polymerization process. FT-IR measurement (Appendix B Fig. S1a) of the final monolithic structure further confirmed the polymerization of META and DB. The spectrum showed a strong peak around 2928.62 cm^{−1}, which could be attributed to the CH₃ and CH₂ groups. Strong adsorption in the 990.85 cm^{−1} was the particular adsorption band for quaternary ammonium. The adsorption observed at 1629.21, 1598.70 and 1485.19 cm^{−1} indicated the existence of phenyl groups. Appendix B Fig. S1b showed the SEM image of the poly (META-co-DB) monolith at 50,000 magnifications. It could be seen that the pore size and microglobules of the monolithic material are very even. The existence of even pore size distribution ensured the new monolith possessed good permeability and favorable mass transfer in extraction applications.

3.2. Optimization of SBSE-AE for inorganic anions

Since the coating of SBSE-AE possesses some quaternary ammonium groups on the poly (META-co-DB) monolith structure, it exhibits strong anionic exchange interaction with analytes. In order to investigate the extractive ability of SBSE-AE for inorganic anions, the SBSE-AE was applied to extract trace concentration of four anions in water samples. Several main parameters include pH value, desorption solvent, ionic strength, extraction and desorption time were studied in detail for optimizing the extraction conditions.

3.2.1. The effect of pH value

Fig. 2 shows the effect of sample pH on the extraction efficiency. The results showed that when the other conditions were constant, the pH value strongly affected the extraction efficiency of SBSE-AE for inorganic anions. The extraction efficiencies improved with the increase of pH values and reached the maximum then decreased when the pH values increased continuously. This change trend could be explained as follows: More and more quaternary ammonium groups were activated with the increase of sample pH value, therefore the interaction between coating and analytes became stronger and led the improvement of extractive efficiencies.

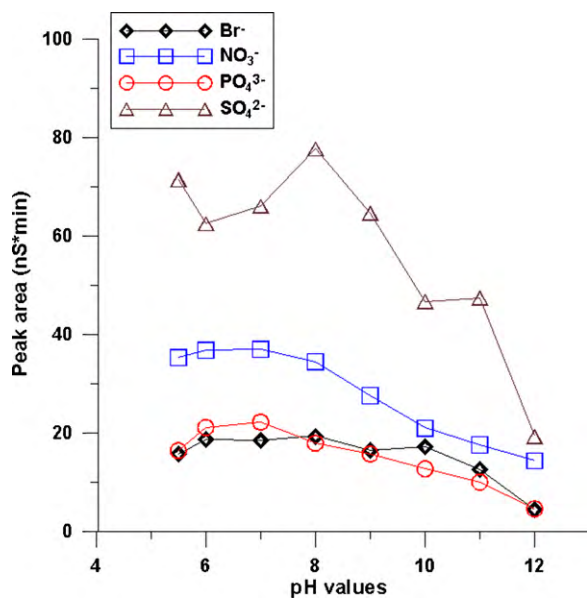


Fig. 2. The effect of pH of the sample matrix on extraction efficiency. Conditions: extraction and desorption time were 2.0 and 2.0 h, respectively; 10 mmol/L NaOH was selected as desorption solvent; no salt was added. The sample pH values were adjusted by 0.1 mol/L citric acid and 1.0 mol/L NaOH.

However, more and more OH^- groups would compete with the absorptive sites on the monolith with analytes when higher sample pH values were used, thus, the extraction ability of SBSE-AE decreased when pH values continuously increased. From the result we also could see that the extraction maximum for NO_3^- and PO_4^{3-} was at pH 7.0, while for Br^- and SO_4^{2-} the optimum pH value was 8.0. The difference of extraction performance for NO_3^- and PO_4^{3-} between pH 7.0 and 8.0 was not significant. Therefore, setting the pH value of matrix at 8.0 was used in the following research.

3.2.2. The effect of ionic strength

At the beginning of this experiment, the ionic strength in the sample matrix was adjusted by inorganic salts such as NaCl and Na_2CO_3 . However, the signal of the four analytes was strongly suppressed by the addition of these inorganic salts (the chromatogram can be seen in Fig. S2). Therefore, sodium citrate was selected to change the ionic strength. In previous research [12,20], the increase of ionic strength favored the extraction of organic compounds. However, in present study, we found that the extraction performance of inorganic anions sharply decline with the increase of ionic strength. For example, the Br^- and PO_4^{3-} could not be extracted when only 5% (w/w) salt was added. The reason may be that the exchange sites in the coating first combined with higher concentration of anionic ions in the salt. Thus, there are not enough exchangeable sites for analytes. According to the results, no addition of salt was recommended in the extraction of inorganic anions by SBSE-AE.

3.2.3. The effect of desorption solvent

Because anion-exchange contributes to the extraction of anions on SBSE-AE, NaOH aqueous solvent was selected as desorption solvent. Different concentration of NaOH solvent was used to desorb the analytes from monolith and the results were showed in Fig. 3. The results indicated that the extractive performance reached maximum for all ions when the concentration of NaOH was 10 mM. Therefore, 10 mM NaOH was selected as desorption solvent in the following experiments.

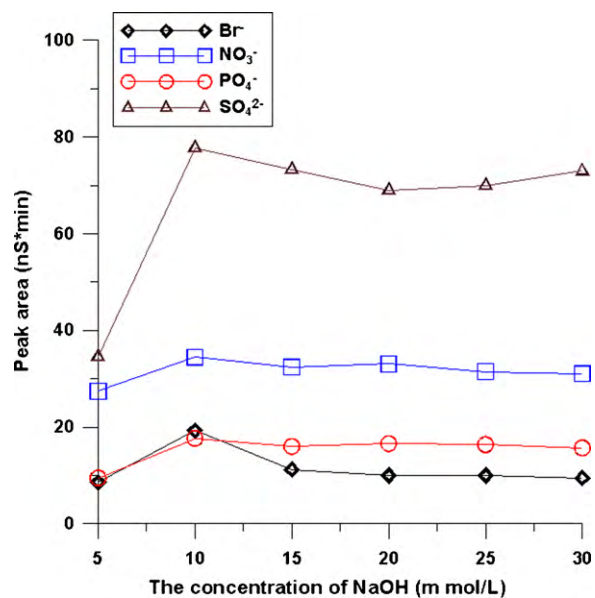


Fig. 3. The effect of desorption solvent on extraction efficiency. Conditions: extraction and desorption time were 2.0 and 2.0 h, respectively; pH value was 8.0; no salt was added.

3.2.4. The effect of extraction and desorption time

Fig. 4 shows the effect of extraction time on the extraction performances for anions. The extraction time varied from 0.5 h min to 3 h. Results indicated that the extraction performance quickly increased when the extraction time increased from 0.5 to 2.5 h and kept constant afterwards. For PO_4^{3-} ion, it did not be extracted until the extraction time prolonged to 1.5 h. The effect of liquid desorption time was also studied varying the time from 0.5 to 3.5 h. It was found that 3.0 h was needed for desorption of target ions from SBSE-AE when the extraction time was 2.5 h. Consequently, 2.5 and 3.0 h were adopted for extraction and desorption procedure, respectively, in the following research.

From the above experimental result, the optimized parameters for the extraction of inorganic anions from water matrix with the SBSE-AE were the following: the pH value of matrix was 8.0;

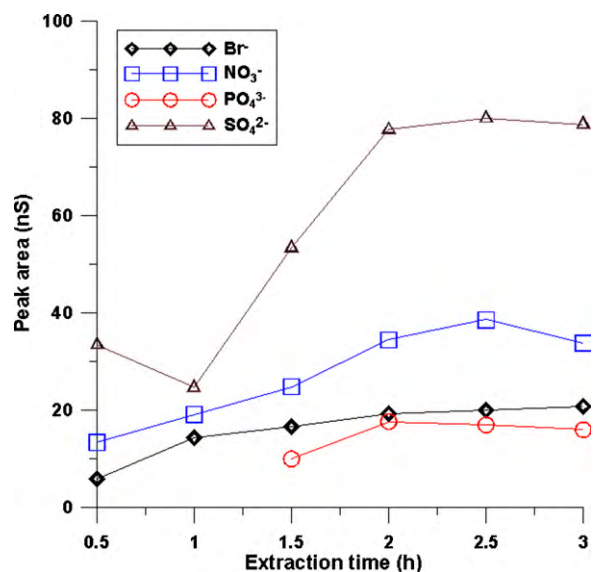


Fig. 4. The effect of extraction time on extraction efficiency. Conditions: desorption time was 2.0 h; pH value was 8.0; 10 mmol/L NaOH was selected as desorption solvent; no salt was added.

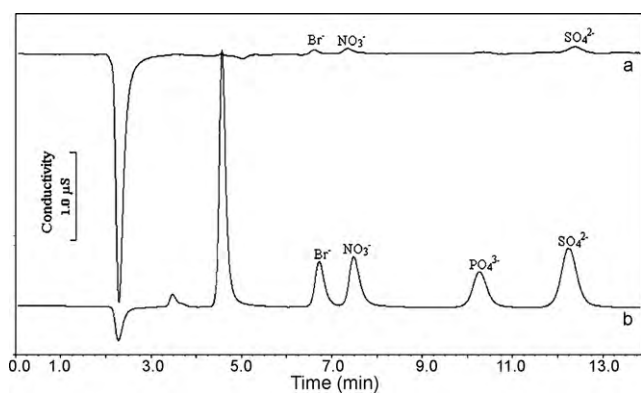


Fig. 5. IC chromatograms of four inorganic anions. Direct injection of spiked water sample with each anion at 100 ng/mL. Spiked water sample with each anions at 100 ng/mL and treated with SBSE-AE.

using 10 mM NaOH as desorption solvent; no salt was added in the matrix; extraction and desorption time were 2.5 and 3.0 h, respectively.

3.3. Validation of the SBSE-AE/LD-IC/CD method

Blank water samples spiked with four target anions were taken for analysis to evaluate the developed method under the above-optimized conditions. The typical chromatogram is showed in Fig. 5. Table 2 shows the data of linear dynamic range, correlation coefficients, the limit of detection (LOD), limit of quantitative detection (LOQ) and reproducibility for the inorganic anions. It can be seen from Fig. 5 that the peak heights for the four ions obviously increase after enrichment. For example, it was difficult to find the peak of PO_4^{3-} when 100 $\mu\text{g/L}$ sample was directly injected without enrichment, however, the peak height reached 286 nS after enrichment under the same conditions. As listed in Table 2, the linear dynamic range of a 50 mL sample was 5.0–150 $\mu\text{g/L}$ for NO_3^- and SO_4^{2-} , and 10–150 $\mu\text{g/L}$ for Br^- and PO_4^{3-} with good linearity ($R^2 > 0.98$). The LOD and LOQ were determined at a concentration at which signal-to-noise ratios were equal to 3 and 10, respec-

Table 2
Linear characteristics and inter-assay precisions achieved for the inorganic anions by SBSE-AE.

Inorganic anions	Linear range ^a	Regression line			LOD ^b ($\mu\text{g/L}$)	LOQ ^c ($\mu\text{g/L}$)	Inter-assay ^d variability (RSD%, $n = 4$)
		Slope	Intercept	R^2			
Br^-	10.0–150.0	0.2071	0.1105	0.9907	2.62	8.67	7.30
NO_3^-	5.0–150.0	0.4024	2.2011	0.9898	1.45	4.78	8.96
PO_4^{3-}	10.0–150.0	0.1898	0.9494	0.9945	2.80	9.25	5.86
SO_4^{2-}	5.0–150.0	0.8239	1.1334	0.9976	0.92	3.03	6.60

^a Spiked level includes 5.0, 10, 20, 50, 100 and 150 $\mu\text{g/L}$, respectively.

^b $S/N = 3$.

^c $S/N = 10$.

^d Assays at 100 $\mu\text{g/L}$ level.

Table 3
Results of determination and recoveries of two commercial purified water samples spiked with four inorganic anions.

Commercial purified water samples	Spiked ($\mu\text{g/mL}$)	Detected ($\mu\text{g/mL}$)				Recovery (%)			
		Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Sample 1	0.00	ND	42.3	ND	14.4				
	50.00	42.8	83.8	40.4	60.7	85.6	82.1	80.8	92.6
	150.00	118.3	167.1	122.4	146.7	78.9	83.2	81.6	88.2
Sample 2	0.00	ND	36.3	ND	16.2				
	50.00	44.6	79.6	35.1	61.3	89.2	86.7	70.2	90.3
	150.00	121.5	160.2	105.0	140.1	81.0	82.6	70.0	82.6

ND: not detected.

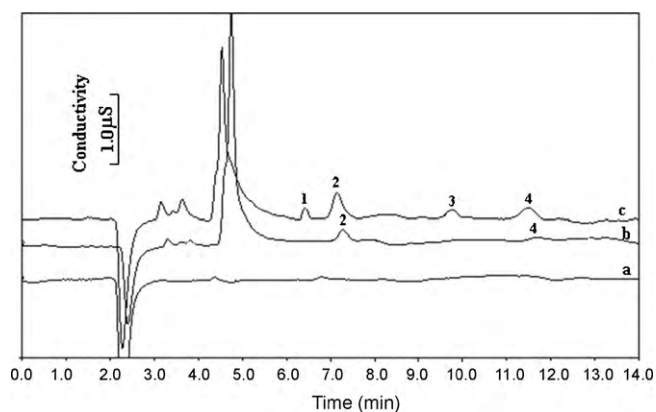


Fig. 6. IC chromatograms of commercial purified water samples. (a) directly injected without treatment with SBSE-AE; (b) treated with SBSE-AE; (c) spiked with each inorganic anions at 50 ng/mL and treated with SBSE-AE: peaks: 1, Br^- ; 2, NO_3^- ; 3, PO_4^{3-} ; 4, SO_4^{2-} .

tively, and those were in the range of 0.92–2.62 and 3.03–9.25 $\mu\text{g/L}$, respectively. The precision of the proposed method was evaluated using inter-assay repeatability calculated as RSD on four replicates, and were found the RSDs between 5.86% and 8.96%, respectively. Fig. 5 and data in Table 2 indicate that the SBSE-AE possesses expected high extraction capacity for the inorganic anions. Due to the high extraction capacity of the SBSE-AE, great enhancement of the signal can be obtained, which indicates a lower detection limit.

3.4. Analysis of commercial purified water

Two different trademarks of commercial purified water were analyzed by the present methodology. Some anionic ions were detected (Fig. 6 and Table 3). 50 mL of real water samples spiked with 50 and 150 $\mu\text{g/L}$ of each analytes were extracted by the overall SBSE-AE procedure mentioned above. Acceptable recoveries were obtained, the recoveries varied from 70.0% to 92.6% for the target analytes in the all water samples (Table 3), demonstrating good method feasibility.

4. Conclusions

A novel enrichment method for inorganic anions has been developed using SBSE with poly(2-(methacryloyloxy)-ethyltrimethylammonium chloride-co-divinylbenzene) monolith as coating. The new SBSE can effectively enrich trace concentration of inorganic anions in samples with low ionic strength by anionic exchange interaction between coating and analytes. The combination of SBSE-AE/LD-IC/CD was successfully applied to the determination of inorganic anions in commercial purified water. In comparison with the existing extraction methods for anions determination, the proposed method was simple, sensitive, inexpensive and stable. Therefore, we hope that the present work can become a practical and useful method in inorganic anions analysis, and at the same time, expand the application field of SBSE.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.05.063.

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