

Cetyltrimethylammonium-coated magnetic nanoparticles for the extraction of bromate, followed by its spectrophotometric determination

Mohammad Saraji · Nasrin Khaje · Milad Ghani

Received: 20 October 2013 / Accepted: 27 January 2014 / Published online: 13 February 2014
© Springer-Verlag Wien 2014

Abstract We report on a combination of magnetic solid-phase extraction and spectrophotometric determination of bromate. Cetyltrimethylammonium ion was adsorbed on the surface of phenyl-functionalized silica-coated Fe_3O_4 nanoparticles ($\text{Ph-SiO}_2@\text{Fe}_3\text{O}_4$), and these materials served as the sorbent. The effects of surfactant and amount of sorbent, the composition of the desorption solution, the extraction time and temperature were optimized. Under optimized conditions, an enrichment factor of 12 was achieved, and the relative standard deviation is 2.9 % (for $n=5$). The calibration plot covers the 1–50 ng mL^{-1} range with reasonable linearity ($r^2>0.998$); and the limit of detection is 0.5 ng mL^{-1} . The method is not interfered by ionic compounds commonly found in environmental water samples. It was successfully applied to the determination of bromate in spiked water samples.

Keywords Magnetic nanoparticles · Hemimicelles · Cetyltrimethylammonium bromide · Spectrophotometric detection · Bromate · Water samples

Introduction

Bromate does not occur in natural waters, but it can be formed by the oxidation of bromide anions during ozonation of drinking water and possibly, by other oxidants in water [1]. Bromate has been classified as a group 2B potential carcinogen by the International Agency of Research on Cancer. A potential 10^{-4} risk of cancer has been assessed after a lifetime exposure in drinking water containing 5.0 ng mL^{-1} of bromate and a potential 10^{-5} risk at 0.5 ng mL^{-1} [2]. Since

bromate ion is considered as a hazardous substance, the maximum contaminant level of bromate in drinking water, as recommended by the US Environmental Protection Agency (EPA), the European Council (EC) and the World Health Organization (WHO) is 10 ng mL^{-1} [2, 3]. During ozonation of drinking water containing bromide, bromate ion is formed at levels ranging from 3 to 50 ng mL^{-1} [4]. Therefore, controlling and monitoring of bromate is mandatory, and a reliable and sensitive method should be used for the determination of bromate in water samples. Many reports have been devoted to methods used for the determination of bromate in water [2–14]. Among them, ion chromatography (IC) with conductivity detection has been traditionally used and chosen as an official model by the USEPA and International Standards Organization (ISO) [5, 6]. The major problem in this approach is due to the influence of chloride content on the quantification of bromate. To solve the problem and achieve a lower detection limit, various approaches have been employed including the reduction of chloride concentration in the sample using a silver ion cartridge before IC [7]; postcolumn reaction with chlorpromazine [8], *o*-dianisidine [9] and potassium iodide–ammonium heptamolybdate [9] have been applied too. Moreover, very high capacity columns [10], mass spectrometry-based techniques [2, 3, 11, 12], multi-dimensional matrix-elimination ion chromatography [13] and electrochemical techniques [14] can be used to overcome the chloride problem. Meanwhile, some fast and relatively simple methods, which are based on flow-injection (FI) techniques with colorimetric and chemiluminescence detection, have also been reported [6, 15–17].

Mass spectrometry-based techniques have detection limits below 1.0 ng mL^{-1} . Nevertheless, they require costly instrumentation, which limit their applications for routine on-site screening of bromate. The methods based on post-column derivatization and UV–vis detection are capable of measuring BrO_3^- concentration below ng mL^{-1} with less interference.

M. Saraji (✉) · N. Khaje · M. Ghani
Department of Chemistry, Isfahan University of Technology,
Isfahan 84154-83111, Iran
e-mail: saraji@cc.iut.ac.ir

However, some of these methods use carcinogen reagent [9], and other systems are complicated which require an unusual flow cell [8, 9] or additional cost for anion suppressors for delivery of reagents [9, 18].

Since the introduction of magnetic carrier technology in 1973 by Robinson et al. [19], the synthesis and application of magnetic nanosized sorbents have been widely developed. The magnetic nanoparticles have been applied for preconcentration of many organic and inorganic compounds in different matrixes [20–24]. A distinct advantage of this technology is that magnetic nanoparticles can be readily isolated from sample solutions by applying an external magnetic field. Magnetic nanoparticles offer several advantages over the traditional microsized sorbents. They possess not only a high surface area, which can exhibit higher adsorption capacity for analytes, but also strong super paramagnetic properties, which can meet the need of rapid extraction and ease of separation for large volume samples by employing a strong external magnetic field.

Recently mixed hemimicelles have been used as novel materials in solid-phase extraction of metal ions [22–24] and organic compounds [25–29]. Hemimicelles are formed by adsorbing of monolayers of surfactants with their head group down on an oppositely charged mineral oxide surface while the hydrocarbon tail-groups protrude into the solution. After the coating of the mineral oxide surface with a monolayer of surfactants, additional surfactant molecules could form a second layer because of the hydrophobic attraction between their organic tails. Admicelles, which have a bilayer structure, are formed after saturation by the adsorbed surfactant. Consequently, the hemimicelle and admicelle are able to interact with analytes through hydrophobic and ionic interaction, respectively. The amount of surfactant adsorbed on the surface of sorbent is greatly dependent on the surfactant concentration and solution pH [25]. Since the surface of the sorbent has a metal oxide coating (such as alumina, silica, titanium dioxide and ferric hydroxide) [23–29], sample pH affects the charge density of the surface and hence, the amount of the adsorbed surfactant. In fact, the type of sorbent (hemimicelle, mixed hemimicelles/admicelle and admicelle) and its capacity are greatly pH dependent. Moreover, conversion of analytes to a suitable form for extraction by the sorbent is also affected by the sample pH [23–29]. Therefore, the study of sample pH on the SPE cannot be carried out in a simple way (e.g. keeping constant all variables except the pH) [25]. In this study, modified phenyl-functionalized silica-coated Fe_3O_4 magnetic nanoparticles ($\text{Ph-SiO}_2@\text{Fe}_3\text{O}_4$ MNPs) were synthesized. The surface of MNPs was coated with cetyltrimethylammonium bromide (CTAB). Due to the hydrophobic surface of $\text{Ph-SiO}_2@\text{Fe}_3\text{O}_4$ MNPs, a monolayer of the surfactants could be adsorbed with their hydrocarbon tail-groups down on phenyl groups of $\text{Ph-SiO}_2@\text{Fe}_3\text{O}_4$ MNPs while head groups protruded into the solution. The outer surface of these

aggregates is ionic, not letting it absorb the other surfactants. The type of sorbent is independent of solution pH because only a monolayer can be formed on the surface of nanoparticles [25]. Also, in comparison to previously used hemimicelles and admicelles for SPE [23–29], in the present method, solution pH does not have any significant effect on the surfactant adsorption and capacity of the sorbent. The new sorbent (CTAB-coated $\text{Ph-SiO}_2@\text{Fe}_3\text{O}_4$ MNPs) was employed for preconcentration of bromate from aqueous samples. After extraction, bromate was converted to bromine by sodium metabisulfite, and then the bromine was reacted with reduced fuchsin to form bromurated red coloured product. The product has a maximum absorbance at 530 nm [30]. To the best of our knowledge, MNPs have not been used previously for the extraction of inorganic anions.

Experimental

Instrumentation

A column-less HPLC system was used for quantification of bromate in extracted sample. The detection system consisted of a UV–Vis spectrophotometric detector (Shimadzu SPD-6AV, www.shimadzu.com), a Rheodyne 7125 injection valve with a 20- μL loop and a Shimadzu LC-6A pump. A piece of capillary PEEK tube (20 cm length, 0.25 mm i.d.) was used to connect injection port to the detector. The carrier phase (pure water) was used at a flow rate of 1.0 mL min^{-1} . The detection was performed at 530 nm.

Infrared (IR) spectra were taken in KBr pressed pellets on a Jasco-FT/IR-350 Infrared Fourier Transform Spectrometer (Tokyo, Japan).

Chemicals and reagents

Tetraethoxysilane (TEOS), polyethylene glycol (PEG), cetyltrimethylammonium bromide (CTAB), sodium metabisulfite, citric acid, HCl, NaOH, potassium bromate (KBrO_3), sodium and potassium salts of different anions, and cations were purchased from Merck (Darmstadt, Germany, www.merck-chemicals.com). Triethoxyphenylsilane (TEOPS) was obtained from Fluka (Buchs, Switzerland, www.sigmaaldrich.com) and basic fuchsin ($\text{C}_{19}\text{H}_{18}\text{N}_3\text{Cl}$) was purchased from Sigma–Aldrich (Mississauga, Canada, www.sigmaaldrich.com).

Fuchsin color developing reagent was prepared using the method reported by Achilli and Romele [30]. Stock solution of fuchsin was obtained by dissolving 100 mg of basic fuchsin in 100 mL of pure water. Then, 0.5 mL of HCl (6 M) was added to 10 mL of stock fuchsin solution, followed by 200 mg of sodium metabisulfite. The solution was diluted to 100 mL with pure water and left to stand overnight for complete

discoloration. The solution, kept in a dark glass bottle, was stable for 1 month at room temperature.

For preparation of the citrate buffer solution, first, 44.8 g of citric acid and 11.3 g of NaOH pellets were dissolved in 500 mL of pure water and then, 45.4 mL of this solution was mixed with 54.6 mL of 1 M HCl to obtain the buffer solution (pH 3.4).

A stock standard solution of bromate was prepared by dissolving the appropriate amount of solid KBrO_3 in pure water. Working standard solutions of bromate were prepared by appropriate dilution of the stock solution with water.

Pure water was prepared by OES (Overseas Equipment & Services) water purification system (OK, USA).

Synthesis of $\text{Ph-SiO}_2@Fe_3O_4$ MNPs

The magnetic nanoparticles were produced according to the procedure described in our previous work [20]. For the synthesis of Fe_3O_4 , 11.2 g $FeCl_3 \cdot 6H_2O$ and 3.9 g $FeCl_2 \cdot 4H_2O$ were dissolved in 50 mL of 0.4 M HCl. The solution was rapidly poured into 500 mL of ammonia solution (0.7 M) under ultrasonic agitation. After continuous ultrasonication for 2 h, a black precipitate was formed and separated by a strong magnet with 1.4 T magnetic field ($10 \times 2.5 \times 2.5$ cm). The precipitate was washed with pure water. The Fe_3O_4 was then coated with a silica shell containing phenyl groups, using a mixture of TEOPS and TEOS via a sol-gel process. The Fe_3O_4 precipitate was ultrasonically dispersed in 150 mL of pure water. Twenty milliliters of the suspension was added to 200 mL of 2-propanol and sonicated for 20 min. Under continuous ultrasonication, 5.36 g of PEG, 20 mL of water, 10 mL of ammonia solution (25 %), 0.5 mL of TEOS and 0.7 mL of TEOPS were added into the suspension. The mixture was shaken for 24 h. The $\text{Ph-SiO}_2@Fe_3O_4$ MNPs were separated by the magnetic field, washed with water and methanol, and dried at room temperature.

Extraction procedure

5 mL of $\text{Ph-SiO}_2@Fe_3O_4$ MNPs suspension (10 mg mL^{-1}) was added to 5 mL of CTAB solution (10 mg mL^{-1}) and the mixture was sonicated for 1 min to adsorb CTAB on the surface of nanoparticles. 25 mL of standard solution of bromate or water sample was added to the above mixture and sonicated for 1 min for the dispersion of the nanoparticles in the sample solution; then it waited for 20 min for the complete extraction to occur. After that, the magnetic sorbents were collected by the magnetic field (during 1 min) and supernatant water was decanted. In order to desorb the analytes from the sorbent, 1 mL of iodide solution (0.3 M) was added to the sorbent. The mixture was shaken for 5 min and 100 μL of the extract was collected in a vial and mixed with 5 μL of citrate buffer solution (pH 3.4). Then, 5 μL of color developing

reagent was added and the solution was left for 30 min to complete the reaction [30]. Finally, 20 μL of the solution was injected into the detection system.

Results and discussion

Characterization of the magnetic adsorbent

Characterization of the $\text{Ph-SiO}_2@Fe_3O_4$ MNPs was previously studied by scanning electron microscopy and X-ray diffractometry [20]. The IR spectrometry was used to confirm the immobilization of CTAB on $\text{Ph-SiO}_2@Fe_3O_4$ MNPs. The FTIR spectra for the $\text{Ph-SiO}_2@Fe_3O_4$ MNPs, CTAB-coated $\text{Ph-SiO}_2@Fe_3O_4$ MNPs and CTAB are shown in Fig. 1. The broad band in the range $3,100\text{--}3,600 \text{ cm}^{-1}$ is due to O-H stretch, which corresponds to the hydroxyl groups attached to the $\text{Ph-SiO}_2@Fe_3O_4$ surface, and also the water molecules chemically adsorbed to the magnetic particle surface. The strong bands within the $2,800\text{--}3,000 \text{ cm}^{-1}$ region are attributed to two different C-H stretching vibrations of CTAB, and the band at $\sim 1,470 \text{ cm}^{-1}$ is attributed to C-N band. The FTIR spectra show that the surface of $\text{Ph-SiO}_2@Fe_3O_4$ MNPs was successfully modified with CTAB.

Optimization of extraction procedure

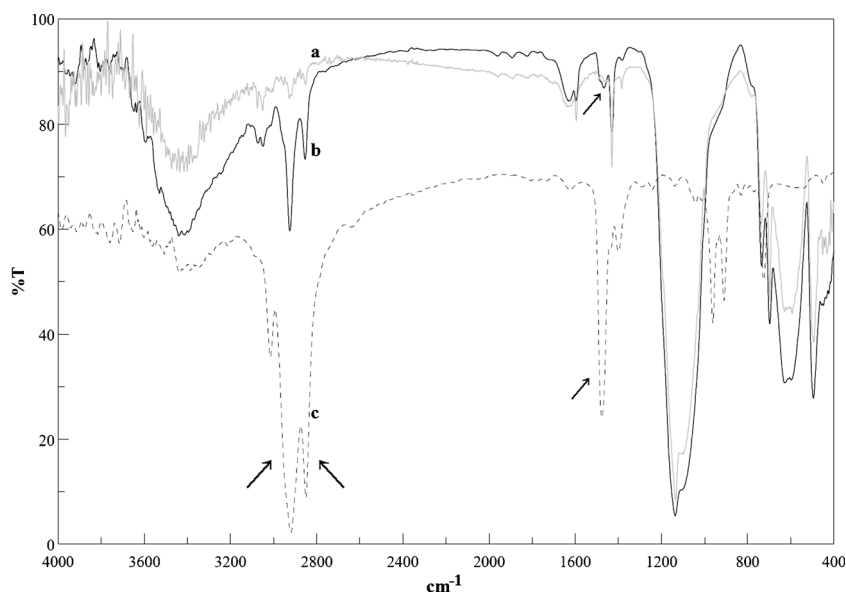
To optimize the extraction efficiency of the method various experimental parameters including surfactant and sorbent amount, desorption media, extraction time and sample temperature were investigated. The peak area of the analyte was used to evaluate the extraction efficiency under different extraction conditions. All of the experiments were performed in triplicate.

Surfactant and sorbent amount

The influence of surfactant content was studied by adding different volumes of CTAB solution (10 mg mL^{-1}), ranging from 1 to 8 mL, to 5 mL of $\text{Ph-SiO}_2@Fe_3O_4$ MNPs suspension. By adding CTAB solution up to 5 mL, the bromate extraction efficiency was increased remarkably, and then decreased at higher surfactant amounts. After saturation of the MNPs surface with surfactant (maximum adsorption of surfactant probably depends on its initial amount and the hydrophobicity of the $\text{Ph-SiO}_2@Fe_3O_4$ MNPs surface), the excess surfactant in the bulk solution competed with the MNPs to adsorb bromate anion. Consequently, extraction efficiency would decrease rapidly with increasing the amount of the surfactant. Therefore, an amount of 5 mL CTAB was chosen as the optimum value.

To evaluate the effect of quantity of $\text{Ph-SiO}_2@Fe_3O_4$ MNPs on the extraction efficiency, the amount of the sorbent was

Fig. 1 FTIR spectra of (a) Ph-SiO₂@Fe₃O₄ MNPs, (b) CTAB-coated Ph-SiO₂@Fe₃O₄ MNPs and (c) CTAB



studied between 10 and 90 mg (1–9 mL of the sorbent suspension). A constant amount of CTAB (50 mg) was added into the sorbent suspension. The results showed that the peak area of the analyte reached its maximum using 5 mL (50 mg) of the sorbent. Therefore, 5 mL suspension of Ph-SiO₂@Fe₃O₄ MNPs was selected for subsequent extractions.

Desorption conditions

For the desorption of organic compounds from the admicelles, organic solvents such as methanol and acetonitrile have the ability to disrupt the aggregation of surfactant molecules on the surfaces of nanoparticles and elute the analytes [24–28]. In the present work, during the extraction, analyte interact with cetyltrimethylammoniumion (CTA⁺) to form a reversible ion-pair complex. To elute the analyte from the sorbent, the eluent had to contain a suitable anion (A⁻) to exchange with bromate ions according to the reversible equilibrium process given by Eq. (1):



Larger anions have stronger affinity to form ion-pair with the CTA⁺ and hence promote desorption efficiency of the analyte from the sorbent. To investigate the effect of eluent composition on desorption of bromate, different solutions including NaI, NaBr, NaCl and NH₄PF₆ at concentration level of 0.2 M were studied. After extraction, the sorbents were eluted by 1 mL of the eluents under ultrasonication for 5 min. As can be seen in Fig. 2, desorption efficiency was increased with increasing anion size from Cl⁻ to I⁻. Despite large size of PF₆⁻, due to interfering of the anion with color developing

reagent and producing a positive response in blank signal it is not a suitable eluent. According to the results, NaI solution was used as desorption solution in further experiments.

To study the effect of NaI concentration on the desorption efficiency of bromate, different concentrations of NaI solution from 0.1 to 0.5 M were tested. It was seen that signal enhanced continuously up to 0.3 M NaI and then remained constant. Therefore, 0.3 M NaI was considered as optimal value.

Sample temperature and extraction time

The effect of extraction temperature was studied over the range of 25–55 °C. The extraction efficiency was slowly decreased with the temperature being enhanced up to 55 °C. Increasing the temperature of sample solution could enhance mass transfer rates of analytes due to increasing diffusion rate and the reduction of equilibrium time. On the other hand, temperature increased BrO₃⁻-CTA⁺ ion-pair solubility in

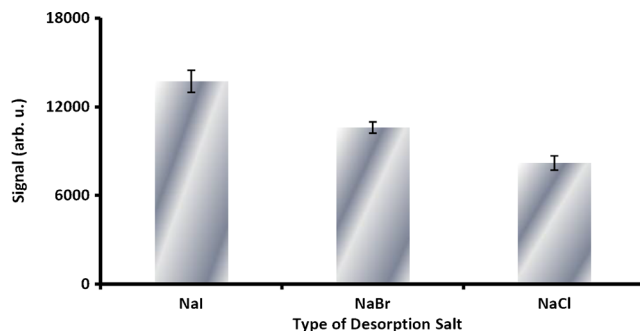


Fig. 2 Effect of type of desorption salt on the extraction efficiency (sample volume, 25 mL; concentration of bromate, 5 ng mL⁻¹; amount of surfactant, 5 mL; Ph-SiO₂@Fe₃O₄ MNPs amount, 5 mL; extraction time, 30 min at room temperature; desorption condition, washing with 1 mL of various salt solutions at 0.1 M concentration level)

water and reduced the extraction efficiency [31]. In micro solid-phase extraction using nanoparticles, due to high specific surface area of the sorbent and the absence of internal diffusion resistance [20], diffusion rate of the analytes is very high. Therefore, the mass transfer rate of the analytes was very fast and relatively independent of sample temperature. Consequently, decreasing the extraction efficiency was most probably due to increasing BrO_3^- -CTA⁺ ion-pair solubility at higher temperatures. In the subsequent experiments, the extraction was performed at room temperature as the optimum temperature.

In order to realize completeness of the extraction, the effect of extraction time on the adsorption of analyte was studied. Results showed that 20 min was sufficient for the adsorption of bromate anions. Regarding relatively fast desorption time (5 min), the overall time needed for sample preparation was about 25 min.

Analytical performance characteristics

Based on the results, the optimized extraction conditions for the determination of bromate by the method were obtained using 50 mg of the sorbent, desorption with 0.3 M NaI (5 min ultrasonication) and 20 min extraction time at room temperature.

Analytical performance data (i.e. linear dynamic range, precision, limit of detection and enrichment factor) were investigated under optimized conditions (Table 1). The linear dynamic range was in the range of 1–50 ng mL⁻¹ (six points). The regression equation was $y=522.6x+12317$ with a determination coefficient (r^2) of 0.9980. Limit of detection (LOD), calculated based on $S/N = 3$ and peak-to-peak noise, was 0.5 ng mL⁻¹. The LOD value obtained by the method was about 20 times lower than the regulated value for drinking water (10 ng mL⁻¹ BrO_3^-) [2]. Precision of the method was measured by five replicate analyses of standard solution of bromate spiked at two concentration levels (2 and 20 ng mL⁻¹). The relative standard deviations (RSDs) were 3.6 % and 2.9 %, respectively.

The enrichment factor was calculated as the ratio of the analyte concentration in the desorption solution to its initial concentration in the sample solution. The enrichment factor was obtained by three replicate extractions of water sample

Table 1 Analytical performance characteristics of the method

Linear range (ng mL ⁻¹)	Determination coefficient (r^2)	Precision ^a (%)	LOD (ng mL ⁻¹)	Enrichment factor
1–50	0.9980	3.6 ^b 2.9 ^c	0.5	12

^a Expressed as relative standard deviation ($n=5$)

^b Water sample spiked at 2 ng mL⁻¹

^c Water sample spiked at 20 ng mL⁻¹

spiked with the analyte at 5 ng mL⁻¹. The enrichment factor value was 12.

To make a comparison between the present method and other conventional methods for the determination of bromate, analytical performance data of the methods were summarized in Table 2. As can be seen, the LOD of the method is comparable or lower than those obtained by the other techniques except complex hyphenated systems such as SPE-ICP-MS and LC-MS/MS. In comparison with ICP-MS and LC-MS/MS, the method is simple, inexpensive, and fast. In addition, fewer species at very high concentration may interfere in the quantification of bromate by the method. Compared to ASTM and EPA standard methods [5, 34], the present method has fewer interferences, lower LOD and better precision.

Interference study

Romele and Achilli reported that the detection of bromate ion using fuchsin reagent could not be influenced by common anions present in water (e.g. NO_3^- , Cl^- , SO_4^{2-} , Br^- , F^- , ClO_3^- , NO_2^- , and ClO_2^-) at given concentration levels [30, 32]. However, interferences from some cations (Ca^{2+} , Mg^{2+} , Zn^{2+} and Cu^{2+}) at the concentration found in drinking water samples were observed [30]. Therefore, an additional step had to be performed to remove cations by passing the sample through a strong cation exchange resin [30].

In this study, the effects of some anionic and cationic substances as probable interfering compounds that may exist in the water samples, on the extraction efficiency of bromate were examined. A standard aqueous solution containing 10 ng mL⁻¹ of bromate and a known concentration of interfering compounds was analyzed by the method. The sorbent at two quantities was used (Table 3): 1) 50 mg of the sorbent containing 50 mg of CTAB, and 2) 10 mg of the sorbent containing 12 mg of CTAB. The tolerable concentration of coexisting ions was defined as maximum concentrations, creating an error of $\pm 5\%$ in bromate signal [33].

In the present method, the outer surface of the sorbent was cationic, so substances with positive charge could not be adsorbed and extracted by the nanoparticles. Unlike the previously described method [30], the present technique was free from cationic interferences and no further treatment was needed to clean-up the extracted sample before detection.

As can be seen in Table 3, using lower amount of the sorbent (10 mg), some anions can interfere in the extraction and determination of bromate ions at even low concentration levels.

This could be attributed to the competition of BrO_3^- and other anions for the sorption sites [26]. Using insufficient sorbent amount, due to low capacity, the active sites of the sorbent would be occupied with interfering ions and thus the extraction efficiency of analyte would be reduced. However, using 50 mg of the sorbent, the tolerance limits of different

Table 2 Comparison of the present method with other methods applied for the extraction and determination of bromate

Method	LOD (ng mL ⁻¹)	RSD (%)	Interfering substances		Real sample	Reference
			Anion	Cation		
UV-Vis spectrophotometric detection (BrO ₃ ⁻ was converted to Br ₂ by sodium metabisulfite and then Br ₂ was reacted with reduced fuchsin to form a brominated red coloured product)	1	6	No interference of NO ₃ ⁻ , SO ₄ ²⁻ , Br ⁻ and ClO ₃ ⁻ at normal concentration levels found in drinking water	Ca ²⁺ , Mg ²⁺ , Zn ²⁺ and Cu ²⁺ have interference at normal concentration levels found in drinking water	Drinking water	[30]
HPLC-conductivity detection (separation of inorganic anions on a high capacity PPM [®] ion exchange column)	1000	2.93	–	–	Sea water	[10]
CZE ^b -UV-Vis spectrophotometric detection	0.1 (1 in tap water)	–	–	–	Drinking water	[35]
SPE-ICP-MS ^c	0.057	0.5–11	Cl ⁻ (> 265 µg mL ⁻¹)	No interference	Raw and drinking water	[11]
SPE-LC-MS/MS ^d	0.045	–	SO ₄ ²⁻ and CO ₃ ²⁻	No interference	Bottled, natural and treated water	[12]
MDME-IC-CD ^e	60	–	No interference	–	Sea water	[13]
FIA ^f -UV-Vis (BrO ₃ ⁻ was converted to Br ₂ in the presence of excess Br ⁻ and then Br ₂ was reacted with <i>o</i> -dianisidine to form a brominated <i>o</i> -dianisidine (colored product))	6	6.2	No interference	–	Ozonized water	[6]
FIA ^f -UV-Vis (oxidation of prochlorperazine with bromate to produce a pink colored product)	2.3	1.1	I ⁻ (>10 ⁻⁵ M), ClO ₃ ⁻ and ClO ₂ ⁻ (>5×10 ⁻⁷ M), NO ₂ ⁻ (>10 ⁻⁷ M)	No interference	Drinking and tap water	[15]
FIA-chemiluminescence detector (bromate was reacted with sulphite in acid medium using the steroid hydrocortisone as sensitiser)	10	2	Br ⁻ , Cl ⁻ and NO ₂ ⁻	–	–	[16]
Multisyringe FIA-UV-Vis (oxidation of phenothiazines with bromate to produce colored compounds)	6	1.6	NO ₂ ⁻ , ClO ₂ ⁻ and ClO ⁻	–	Tap water	[17]
USEPA ^g (IC-CD)	20	0.8–10	–	–	Drinking and reagent water	[5]
ASTM ^h (IC-CD)	2.73	16.7 (The upper limit for acceptable precision)	Cl ⁻ (>200 µg mL ⁻¹), CO ₃ ²⁻ (>300 µg mL ⁻¹), F ⁻ and low molecular weight monocarboxylic acids (at µg mL ⁻¹ concentrations)	No interference	Raw, drinking and bottled water	[34]
IC-PCR ^k :						
NaBr-NaNO ₂ (post column reagent)	0.17	7.5	Interference by some matrix ions	–	River water	[9]
<i>o</i> -dianisidine (post column reagent)	0.24	10.7	ClO ₂ ⁻	–		
KI-(NH ₄) ₆ Mo ₇ O ₂₄ (post column reagent)	0.19	8.4	No interference	–		

Table 2 (continued)

Method	LOD (ng mL ⁻¹)	RSD (%)	Interfering substances		Reference
			Anion	Cation	
FIA-UV-Vis (reaction of reduced fuchsin with bromate to produce a red colored product)	0.5	2.9–3.6	See Table 3	No interference	Tap, well and river water This method
^a Porous polymeric monolithic					
^b Capillary zone electrophoresis					
^c SPE-ICP-MS Solid-phase extraction-inductively coupled plasma mass spectrometry					
^d LC-MS/MS Liquid chromatography-tandem triple-quadrupole mass spectrometry					
^e MDME-IC-CD Multi-dimensional matrix-elimination ion chromatography-conductivity detection					
^f FIA Flow-injection analysis					
^g USEPA United states environmental protection agency					
^h ASTM American society for testing and materials					
^k PCR Post-column reaction					

Table 3 Interferences study for the determination of 10 ng mL⁻¹ bromate by the present method

Interfering ion	Limit of interfering (µg mL ⁻¹)	
	50 mg MNPs (containing 50 mg CTAB)	10 mg MNPs (containing 12 mg CTAB)
Ca ²⁺ , K ⁺ , Fe ²⁺ , Na ⁺ , Cd ²⁺ , Zn ²⁺	100000	100000
Cl ⁻ , NO ₃ ⁻	800	10
ClO ₃ ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , IO ₃ ⁻	600	1
ClO ₂ ⁻ , ClO ⁻ , NO ₂ ⁻	10	– ^a

^a Not investigated

anions are at higher concentration levels. ClO₂⁻, ClO⁻ and NO₂⁻ have no effect on the determination of bromate at concentration up to 10 µg mL⁻¹. These ions may be normally found at sub-µg mL⁻¹ level in drinking or ground waters. At concentration higher than 10 µg mL⁻¹, they must be removed, masked, or separated prior to the extraction.

In comparison with EPA and ASTM methods [5, 34], a higher concentration of interfering ions can be tolerated by the method. The concentration of interfering ions in the most environmental water samples is lower than those limits obtained in this work. Therefore, the method is practically applicable for analysis of real water samples.

Analysis of real sample

In order to investigate the applicability of the method in real sample analysis, determination of bromate in tap, well (a local well) and Zayandeh-rood river water samples was performed by standard addition technique. The results showed that the water samples analyzed were either free of bromate or had concentrations below the method detection limit. To

Table 4 Accuracy and recovery of bromate in fortified environmental water samples

Sample	Bromate added (ng mL ⁻¹)	Bromate found (ng mL ⁻¹)	Accuracy (%)	Recovery ^a (%)
Tap water	2.0	2.1	3.0	103
	5.0	4.9	-2.2	98
	10.0	10.5	5.1	105
Zayandeh-rood river water	2.0	1.9	-4.9	95
	5.0	4.6	-7.9	92
	10.0	9.4	-6.3	94
Well water	2.0	1.9	-5.0	96
	5.0	4.8	-3.8	96
	10.0	10.4	4.2	104

^a The RSDs are between 3.6 and 4.3 % (n=3)

investigate accuracy of the method, the water samples were spiked at three concentration levels. The results were accurate with the relative error varying from -7.9 to 5.1 % (Table 4). Linearity of the method in real sample analysis was investigated using three concentration levels (2, 5 and 10 ng mL^{-1} of bromate). The r^2 values were higher than 0.9950. Relative recovery, which is defined as the ratio of the peak area of the spiked real water extracts to the peak area of spiked pure water extracts, were between 92 and 105 %. Clearly, these results demonstrate that the method is suitable for extraction and determination of bromate in environmental water samples.

Conclusion

A method based on surfactant-coated $\text{Ph-SiO}_2@Fe_3O_4$ magnetic nanoparticles and spectrophotometric detection was developed for the trace determination of bromate ion in environmental water samples. In this work, the advantages of nanoparticles as the sorbent including high adsorption capacity and facile extraction were combined with the advantages of spectrophotometric detection, including simplicity, speed, and inexpensiveness. There was no need to further clean-up the extracted sample because the method was free of common interferences found in water samples (metal ions, Cl^- , NO_3^- , SO_4^{2-}). Although the sorbent was not highly selective and other large anions can be adsorbed on the sorbent. However, it was not a serious problem because concentration of such anions found in natural and drinking water samples are usually below the interfering limit of the method (Table 3). Compared to other methods (especially complex hyphenated systems) the method had low detection limit and good precision. Moreover, the method was simple and fast.

Acknowledgments The authors wish to thank research council of Isfahan University of Technology (IUT) and Center of Excellence in Sensor and Green Chemistry for financial support of this project.

References

1. Gunten UV, Oliveras Y (1998) Advanced oxidation of bromide-containing waters: bromate formation mechanisms. *Environ Sci Technol* 32:63–70. doi:10.1021/es970477j
2. Eickhorst T, Seubert A (2004) Germanium dioxide as internal standard for simplified trace determination of bromate, bromide, iodate and iodide by on-line coupling ion chromatography-inductively coupled plasma mass spectrometry. *J Chromatogr A* 1050:103–109. doi:10.1016/j.chroma.2004.04.084
3. Reddy-Noone K, Jain A, Verma KK (2007) Liquid-phase microextraction–gas chromatography–mass spectrometry for the determination of bromate, iodate, bromide and iodide in high-chloride matrix. *J Chromatogr A* 1148:145–151. doi:10.1016/j.chroma.2007.03.027
4. Xu C, Shi J, Zhou W, Gao B, Yue Q, Wang X (2012) Bromate removal from aqueous solutions by nano crystalline akaganeite ($\beta\text{-FeOOH}$)-coated quartz sand (CACQS). *Chem Eng J* 187:63–68. doi:10.1016/j.cej.2012.01.087
5. US EPA method 300.1 (1997) The determination of inorganic anions in water by ion chromatography
6. Alonso-Mateos A, Almendral-Parra MJ, Fuentes-Prieto MS (2008) Sequential and simultaneous determination of bromate and chlorite (DBPs) by flow techniques: kinetic differentiation. *Talanta* 76:892–898. doi:10.1016/j.talanta.2008.04.059
7. Joyce RJ, Dhillon HS (1994) Trace level determination of bromate in ozonated drinking water using ion chromatography. *J Chromatogr A* 671:165–171. doi:10.1016/0021-9673(94)80235-1
8. Walters BD, Gordon G (1997) An ion chromatographic method for measuring $<5 \mu\text{g/L}$ bromate ion in drinking water. *Anal Chem* 69:4275–4277. doi:10.1021/ac9703008
9. Echigo S, Minear RA, Yamada H, Jackson PE (2001) Comparison of three post-column reaction methods for the analysis of bromate and nitrite in drinking water. *J Chromatogr A* 920:205–211. doi:10.1016/S0021-9673(01)00533-7
10. Evenhuis CJ, Buchberger W, Hilder EF, Flook KJ, Pohl CA, Nesterenko PN, Haddad PR (2008) Separation of inorganic anions on a high capacity porous polymeric monolithic column and application to direct determination of anions in seawater. *J Sep Sci* 31:2598–2604. doi:10.1002/jssc.200800205
11. Cai Q, Guo ZX, Yu C, Zhang W, Yang Z (2003) Bromate assay in water by inductively coupled plasma mass spectrometry combined with solid-phase extraction cartridges. *Anal Bioanal Chem* 377:740–748. doi:10.1007/s00216-003-2151-3
12. Snyder SA, Vanderford BJ, Rexing DJ (2005) Trace analysis of bromate, chlorate, iodate, and perchlorate in natural and bottled waters. *Environ Sci Technol* 39:4586–4593. doi:10.1021/es047935q
13. Zakaria P, Bloomfield C, Shellie RA, Haddad PR, Dicoski GW (2011) Determination of bromate in sea water using multi-dimensional matrix-elimination ion chromatography. *J Chromatogr A* 1218:9080–9085. doi:10.1016/j.chroma.2011.10.029
14. Wang B, Cheng L, Dong S (2001) Construction of a heteropolyanion-modified electrode by a two-step sol–gel method and its electrocatalytic applications. *J Electroanal Chem* 516:17–22. doi:10.1016/S0022-0728(01)00677-5
15. Uraisin K, Takayanagi T, Nacapricha D, Motomizu S (2006) Novel oxidation reaction of prochlorperazine with bromate in the presence of synergistic activators and its application to trace determination by flow injection/spectrophotometric method. *Anal Chim Acta* 580:68–74. doi:10.1016/j.aca.2006.07.045
16. Esteves da Silva JCG, Dias JRM, Magalães JMCS (2001) Factorial analysis of a chemiluminescence system for bromate detection in water. *Anal Chim Acta* 450:175–184. doi:10.1016/S0003-2670(01)01376-9
17. Oliveira SM, Segundo MA, Rangel AOSS, Lima JLFC, Cerda V (2011) Spectrophotometric determination of bromate in water using multisyringe flow injection analysis. *Anal Lett* 44:284–297. doi:10.1080/00032719.2010.500771
18. Weinberg HS, Yamada H, Joyce RJ (1998) New, sensitive and selective method for determining sub-microgram/l levels of bromate in drinking water. *J Chromatogr A* 804:137–142. doi:10.1016/S0021-9673(98)00152-6
19. Robinson PJ, Dunnill P, Lilly MD (1973) The properties of magnetic supports in relation to immobilized enzyme reactors. *Biotechnol Bioeng* 15:603–606. doi:10.1002/bit.260150318
20. Saraji M, Khaje N (2013) Phenyl-functionalized silica-coated magnetic nanoparticles for the extraction of chlorobenzenes, and their determination by GC-electron capture detection. *J Sep Sci* 36:1090–1096. doi:10.1002/jssc.201200863
21. Takafuji M, Ide S, Ihara H, Xu Z (2004) Preparation of poly(1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions. *Chem Mater* 16:1977–1983. doi:10.1021/cm030334y

22. Mashhadizadeh MH, Karami Z (2011) Solid phase extraction of trace amounts of Ag, Cd, Cu, and Zn in environmental samples using magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole and their determination by ICP-OES. *J Hazard Mater* 190:1023–1029. doi:10.1016/j.jhazmat.2011.04.051
23. Karatapanis AE, Fiamegos Y, Stalikas CD (2011) Silica-modified magnetic nanoparticles functionalized with cetylpyridinium bromide for the preconcentration of metals after complexation with 8-hydroxyquinoline. *Talanta* 84:834–839. doi:10.1016/j.talanta.2011.02.013
24. Faraji M, Yamini Y, Rezaee M (2010) Extraction of trace amounts of mercury with sodium dodecyl sulphate-coated magnetite nanoparticles and its determination by flow injection inductively coupled plasma-optical emission spectrometry. *Talanta* 81:831–836. doi:10.1016/j.talanta.2010.01.023
25. Merino F, Rubio S, Perez-Bendito D (2004) Evaluation and optimization of an on-line admicelle-based extraction-liquid chromatography approach for the analysis of ionic organic compounds. *Anal Chem* 76:3878–3886. doi:10.1021/ac049736v
26. Shariati S, Faraji M, Yamini Y, Rajabi AA (2011) Fe₃O₄ magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions. *Desalination* 270:160–165. doi:10.1016/j.desal.2010.11.040
27. Bagheri H, Zandi O, Aghakhani A (2011) Extraction of fluoxetine from aquatic and urine samples using sodium dodecyl sulfate-coated iron oxide magnetic nanoparticles followed by spectrofluorimetric determination. *Anal Chim Acta* 692:80–84. doi:10.1016/j.aca.2011.02.060
28. Zhao X, Cai Y, Wu F, Pan Y, Liao H, Xu B (2011) Determination of perfluorinated compounds in environmental water samples by high-performance liquid chromatography-electrospray tandem mass spectrometry using surfactant-coated Fe₃O₄ magnetic nanoparticles as adsorbents. *Microchem J* 98:207–214. doi:10.1016/j.microc.2011.01.011
29. Zhao X, Shi Y, Wang T, Cai Y, Jiang G (2008) Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples. *J Chromatogr A* 1188:140–147. doi:10.1016/j.chroma.2008.02.069
30. Romele L, Achilli M (1998) Spectrophotometric determination of low levels of bromate in drinking water after reaction with fuchsin. *Analyst* 123:291–294. doi:10.1039/A706130G
31. Saraji M, Hajialiakbari Bidgoli AA, Farajmand B (2011) Hollow fiber-based liquid–liquid–liquid microextraction followed by flow injection analysis using column-less HPLC for the determination of phenazopyridine in plasma and urine. *J Sep Sci* 34:1708–1715. doi:10.1002/jssc.201000929
32. Achilli M, Romele L (1999) Ion chromatographic determination of bromate in drinking water by post-column reaction with fuchsin. *J Chromatogr A* 847:271–277. doi:10.1016/S0021-9673(99)00190-9
33. Neves AIP, Albert-Garcia JR, Calatayud JM (2007) Chemiluminometric determination of the pesticide 3-indolyl acetic acid by a flow injection analysis assembly. *Talanta* 71:318–323. doi:10.1016/j.talanta.2006.04.003
34. ASTM standard D6581: Standard test method for bromate, bromide, chlorate, and chlorite in drinking water by chemically suppressed ion chromatography. doi:10.1520/D6581
35. Takayanagi T, Ishida M, Mbuna J, Driouch R, Motomizu S (2006) Determination of bromate ion in drinking water by capillary zone electrophoresis with direct photometric detection. *J Chromatogr A* 1128:298–302. doi:10.1016/j.chroma.2006.06.056