

Highly sensitive method for speciation of inorganic selenium in environmental water by using mercapto-silica-Fe<sub>3</sub>O<sub>4</sub> nanoparticles and ICP-MSChaozhang Huang,<sup>a</sup> Wei Xie,<sup>a</sup> Xiucui Liu,<sup>a</sup> Jianping Zhang,<sup>a</sup> Hanchun Xu,<sup>a</sup> Xiong Li<sup>b</sup> and Zechun Liu<sup>\*a</sup>

Received 14th May 2012, Accepted 26th August 2012

DOI: 10.1039/c2ay25734c

A new method for speciation of inorganic selenium (Se) in environmental water has been developed by using mercapto-silica-Fe<sub>3</sub>O<sub>4</sub> nanoparticles and ICP-MS. Compared with the traditional methods, the current method had higher preconcentration factor and selectivity for speciation of inorganic Se. The parameters affecting the separation, such as pH, eluent type and sample volume, were investigated systematically. Within the pH range of 1–10, Se(IV) could be quantitatively adsorbed on the magnetic nanoparticles (MNPs), while the Se(VI) was not retained in the studied pH range and remained in solution. Without filtration or centrifugation, these Se(IV)-loaded MNPs could be separated easily from the aqueous solution by simply applying an external magnetic field. The Se(IV) adsorbed on the MNPs could be recovered quantitatively using a solution containing 2 mol L<sup>-1</sup> HCl and 0.02 mol L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Total inorganic Se was extracted after reducing of Se(VI) to Se(IV) with L-cysteine, and the assay of Se(VI) was calculated as the difference between the total Se content and Se(IV) content. Under the optimized conditions, the method detection limit obtained for Se(IV) was 0.094 ng L<sup>-1</sup>, while the precision was 8.1% ( $C = 10$  ng L<sup>-1</sup>,  $n = 7$ ). The proposed method based on the MNPs was successfully applied to the speciation of inorganic Se species in environmental water from a tobacco growing area yielding a 282-fold preconcentration factor.

## 1. Introduction

Selenium (Se) is an essential element, which is nevertheless toxic at a high concentration.<sup>1,2</sup> The toxicity, bioavailability and essential nature of Se highly depend on its chemical forms. The organoselenium compounds are less toxic and more bioavailable than the inorganic forms of Se. Se is primarily present as inorganic species, *i.e.*, selenite and selenate ions, in water and soil, because these oxidation states are the most environmentally mobile and geochemically important forms of this element.<sup>3</sup> Studies suggest that many crops, such as tobacco, can enrich the Se from natural water and soil, finally causing the Se to come into the human body and affect human health by means of the food chain.<sup>4</sup> In view of the above facts, the speciation of inorganic Se in environmental water is of great interest because natural water represents one of the main sources of local fauna and flora exposure.

As we know, the level of inorganic Se is fairly low in natural water with complex matrices. Most of the detectors are not sensitive enough to determine these ultra-trace analytes directly. Hence, the separation, purification and preconcentration of

analytes are required. Techniques such as gas chromatography (GC),<sup>5</sup> high performance liquid chromatography (HPLC)<sup>6</sup> and capillary electrophoresis (CE)<sup>7</sup> are the most effective separation techniques for the speciation of Se due to their merits such as high sample throughput, speciation in one analytical run, and the possibility of determining organo-forms. However, these separation techniques are complex and their instrumental and operation costs may be high. Therefore, some non-chromatographic techniques, such as co-precipitation,<sup>8</sup> cloud point extraction,<sup>9</sup> solid phase extraction (SPE)<sup>10</sup> and liquid-phase extraction,<sup>11</sup> have been fully applied in Se speciation and some of the drawbacks inherent in chromatographic separations have been overcome.<sup>12</sup>

Among these non-chromatographic techniques, SPE is widely used due to its important advantages: faster operation, easier manipulation, avoidance or reduction of the use of organic solvents, less stringent requirements for separation, higher preconcentration factor and easier compatibility with analytical instruments such as inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). Speciation of inorganic Se in natural water samples was performed by Pyrzynska *et al.*<sup>13</sup> The procedure included SPE of Se species on an alumina microcolumn and their determination by graphite furnace AAS. A speciation procedure for Se species has been reported by Sahin *et al.*<sup>14</sup> The Se species were determined by AAS after sorption on mercapto-silica. Saygi *et al.*<sup>15</sup> have

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proposed a speciation procedure for Se(IV) and Se(VI) based on the SPE of Se(IV) on a resin modified with ammonium pyrrolidine dithiocarbamate (APDC), reduction of Se(VI) to Se(IV) and determination by HG-AAS. Ferri and Sangiorgio<sup>16</sup> have reported a SPE procedure on Chelex-100 resin for Se speciation in polluted waters. The separation and preconcentration of Se(IV)–Se(VI) species by selective adsorption onto nanometer-sized titanium dioxide and determination by graphite furnace AAS have been performed with successful results by Li and Deng.<sup>17</sup>

Recently, the magnetic separation technique (MST) has shown a wide range of applications including shape-selectivity,<sup>18</sup> catalytic chromatographic separations,<sup>19</sup> sorption of metal ions,<sup>20</sup> enzyme encapsulation,<sup>21</sup> DNA transfection<sup>22</sup> and drug delivery.<sup>23</sup> MST is based on a magnetic material, which is attracted to a magnetic field but retains no residual magnetism after the field is removed. This means that suspended magnetic material adhered to the target of interest can be quickly removed from a matrix using a magnetic field, but it does not agglomerate after removal of the field. Although magnetic material has a wide application in drug separation, agricultural chemistry, environmental protection and clinical medicine, no application of magnetic material for speciation of Se has been reported yet.

The aim of this study was to develop a rapid and highly sensitive method using a kind of magnetic nanoparticles as a SPE adsorbent for speciation of inorganic Se species in environmental waters prior to their determination by ICP-MS.

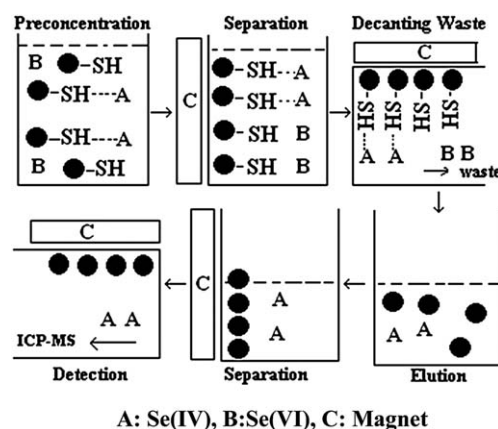
## 2. Experimental

### 2.1 Instrumentation

For the determination of Se, the experiment was performed by a PerkinElmer ELAN DRC-e inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, America) system. The operation conditions used in this work were given in Table 1. Nicolet 6700 Fourier transform infrared spectroscopy (FT-IR) (Thermo, America) and a JEOL EM2010 transmission electron microscope (TEM) (Tokyo, Japan) were used for characterization. The pH values were controlled with an AT-500N automatic titrator (Kem, Japan) supplied with a combined electrode. A T660/H model Ultrasonic oscillator (Elma, Germany) was used to disperse the nanoparticles in solution. A magnet (Nd-Fe-B, 10.0 mm × 8.0 mm × 1.5 mm) was used for magnetic separation.

**Table 1** ICP-MS operational conditions

ICP-MS	
Rf power	1420 W
External gas flow	Ar 15 L min <sup>-1</sup>
Auxiliary gas flow	Ar 0.9 L min <sup>-1</sup>
Carrier gas flow	Ar 1.29 L min <sup>-1</sup>
Sample depth	6.6 mm
Nebulizer	Quartz concentric
Sampler cone	Nickel
Skimmer cone	Nickel
Scanning mode	Peak-hopping
Dwell time	0.1 s
Integration mode	Peak-area
Isotope	<sup>82</sup> Se



**Fig. 1** The procedure of the presented method.

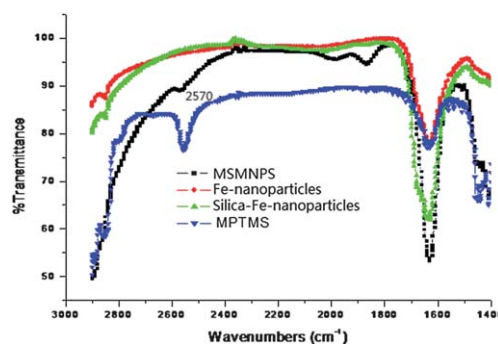
### 2.2 Standard solutions and reagents

All reagents used were of spec-pure or at least of analytical reagent grade. High purity deionized water (18.2 MΩ cm) obtained from a Labconco system (Kansas City, MO, USA) was used throughout this work. The Se(IV) and Se(VI) stock solutions (1 mg mL<sup>-1</sup> as Se) were prepared from analytical reagent grade SeO<sub>2</sub> (ACROS, Geel, Belgium) and Na<sub>2</sub>SeO<sub>4</sub> (Alfa Aesar, MA, USA), by dissolving the appropriate amounts in high purity deionized water. The standard stock solutions (1 g L<sup>-1</sup>) of other elements were prepared from their salts by a conventional method. Tetraethoxysilane (TEOS) and mercaptopropyltrimethoxysilane (MPTMS) were purchased from Wuhan University Chemical Factory (Wuhan, China). NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>4</sub>NO<sub>3</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, ethanol and acetic acid were purchased from the First Reagent Factory (Shanghai, China). Buffer solutions were prepared by mixing different ratios of NH<sub>3</sub>·H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub> with high purity deionized water. All containers were treated with 10% HNO<sub>3</sub> for at least 24 h, rinsed with high purity deionized water, and dried at room temperature before usage.

A series of standard solutions with different Se(IV) concentrations were prepared in a mixed solution of 0.02 mol L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 2.0 mol L<sup>-1</sup> HCl prior to their determination by ICP-MS and a calibration curve was obtained.

### 2.3 Preparation of nanostructured silica-Fe<sub>3</sub>O<sub>4</sub>

The magnetite nanoparticles (MNPs) were prepared by the conventional co-precipitation method with some modifications.<sup>24</sup>



**Fig. 2** FT-IR spectra of MSMNPs.

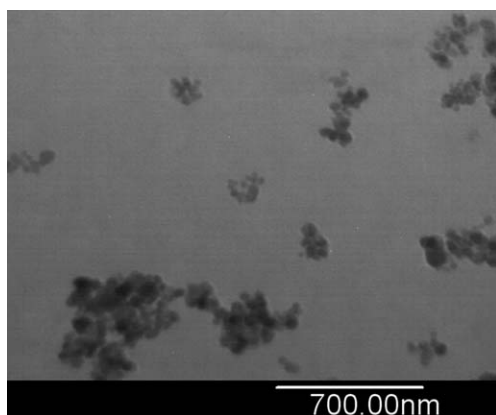


Fig. 3 TEM of MSMNPs.

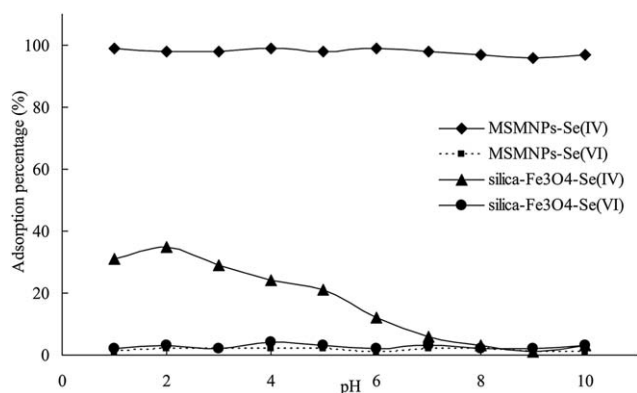


Fig. 4 The dependence of adsorption percentage of Se(IV) and Se(VI) on pH.

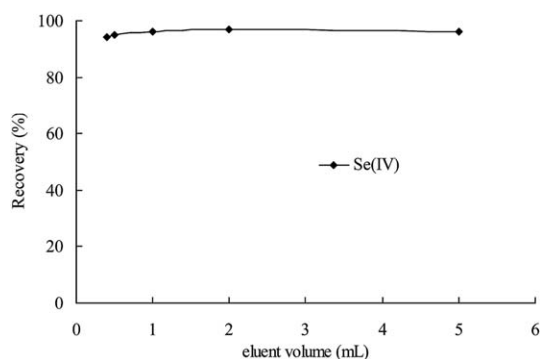


Fig. 5 The effect of eluent volume on the recovery of Se(IV).

11.68 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 4.30 g  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring at 85 °C. 20 mL 30%  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was then added to the solution. The color of the bulk solution changed from orange to black immediately. The magnetite precipitates were washed twice with deionized water and once with 0.02 mol  $\text{L}^{-1}$  sodium chloride by magnetic decantation. The washed magnetite was stored in high purity deionized water at a concentration of 40 mg  $\text{mL}^{-1}$ . Then, the magnetite suspension prepared above (20 mL) was placed in a 250 mL round-bottomed flask and allowed to settle. The supernatant was removed, and an aqueous solution of

Table 2 Effect of coexisting ions on the adsorption of Se(IV)<sup>a</sup>

Co-existing ions	Tolerance limit of ions (mg $\text{L}^{-1}$ )
$\text{Na}^+$	15 000
$\text{K}^+$	5000
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	2500
$\text{Al}^{3+}$ , $\text{Fe}^{3+}$	100
$\text{Ni}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$	10
$\text{Cl}^-$	25 000
$\text{NO}_3^-$	10 000
$\text{SO}_4^{2-}$	1000

<sup>a</sup> Note: the concentration of Se(IV) for study is 1  $\mu\text{g L}^{-1}$ .

Table 3 Comparison of detection limits found in the literature for determination of Se(IV) following different analytical techniques ( $\mu\text{g L}^{-1}$ )

Analytical technique	Se(IV)
MSPE-ICP-MS	0.00009
HPLC-MW-HG-ICP-MS <sup>a</sup> (ref. 29)	4.5
CE-HG-AFS <sup>30</sup>	25
HPLC-HG-AAS <sup>31</sup>	2.4
HPLC-ICP-MS <sup>32</sup>	>5
HPLC-ICP-MS <sup>33</sup>	0.05
HF-LPME-ETV-ICP-MS <sup>b</sup> (ref. 11)	0.0005
SPE-FI-ETAAS <sup>34</sup>	0.01

<sup>a</sup> HPLC-MW-HG-ICP-MS = high-performance liquid chromatography-focused microwave digestion-hydride generation-inductively coupled plasma mass spectrometry. <sup>b</sup> HF-LPME-ETV-ICP-MS = hollow fiber-liquid phase microextraction-electrothermal vaporization-inductively coupled plasma mass spectrometry.

tetraethoxysilane (TEOS; 10% (v/v), 80 mL) was added, followed by glycerol (60 mL). The pH of the suspension was lowered to 4.6 using glacial acetic acid, and the mixture was then stirred and heated at 90 °C for 2 h, under a nitrogen atmosphere. After cooling to room temperature, the suspension was washed sequentially with deionized water (3 × 500 mL), methanol (3 × 500 mL) and deionized water (5 × 500 mL). The silica magnetite composite was stored in deionized water at a concentration of 100 mg  $\text{mL}^{-1}$ .

## 2.4 Preparation of mercapto-silica- $\text{Fe}_3\text{O}_4$ magnetic nanoparticles (MSMNPs)

100 mL silica-coated magnetite prepared above was washed with ethanol (2 × 100 mL) and then diluted to 180 mL with 1% MPTMS in 95% ethanol and 16 mmol  $\text{L}^{-1}$  acetic acid (pH 4.5). The solution was transferred to a 500 mL 3-necked round bottom flask and then stirred and heated at 60 °C for 2 h, under a nitrogen atmosphere. After that, the resulting nanospheres were washed with deionized water three times and with methanol twice, and then dried into powders at room temperature under vacuum. Finally, ~10 g MSMNPs was stored in a sample kit and kept in a dark place.

## 2.5 General procedure

The operation procedure of the magnetic SPE is presented in Fig. 1 and the details are described as follows: a portion of sample solution containing the studied ions was transferred to a

**Table 4** Analytical results for inorganic Se speciation in certified reference material of GSBZ50031-94[203708] environmental water (mean  $\pm$  S.D.,  $n = 3$ )

Sample	Element	Certified (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )
GSBZ50031-94[203708]	Se(IV)	—	0.81 $\pm$ 0.07
	Se(VI)	—	7.28 $\pm$ 0.72
	Total	8.15 $\pm$ 1.09	8.09 $\pm$ 0.71

250 mL beaker, the pH values was adjusted to the desired value with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O, and the final volume was diluted to the desired volume. Then, 50 mg of MSMNPs was added, and the solution was ultrasonicated for 10 min to facilitate adsorption of the Se(IV) onto the silica nanoparticles. Then the magnetic adsorbent was separated easily and quickly by using a strong flat permanent magnet and the supernatants were decanted directly. 5 mL deionized water was added for washing and then decanted directly. A mixture containing 2.0 mol L<sup>-1</sup> HCl and 0.02 mol L<sup>-1</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was added as eluent and ultrasonicated for 2 min. Finally, the eluted ions were detected by ICP-MS.

For determination of total Se, 0.5% (w/v) L-cysteine was added into the sample solutions, and the mixtures were heated for 30 min in boiling water. The resultant solutions were adjusted to pH 7 with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O and immediately analyzed according to the general procedure.

The concentration of Se(VI) in the samples was obtained by subtracting the Se(IV) from the total Se.

High purity deionized water was chosen as the blank solution and subjected to the sample operation as described above and the blank values were determined. The determined values and total Se were obtained after subtracting the blank value.

## 2.6 Sample preparation

Pool water samples were collected from Longyan tobacco growing area and Wuyishan tobacco growing area, respectively. The samples were filtered through a 0.45  $\mu$ m membrane (Agilent, Takatura, Japan) and stored in a refrigerator (4 °C). The samples were adjusted to pH 7 with 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O before analysis.

## 3. Results and discussion

### 3.1 Characterization of MSMNPs

To ascertain the presence of MPTMS on silica-Fe<sub>3</sub>O<sub>4</sub>-nanoparticles, FT-IR spectra were obtained from Fe<sub>3</sub>O<sub>4</sub>-

nanoparticles, silica-Fe<sub>3</sub>O<sub>4</sub>-nanoparticles, MPTMS and MSMNPs. From the spectra (Fig. 2), it can be seen that a characteristic feature of MSMNPs when compared with Fe<sub>3</sub>O<sub>4</sub>-nanoparticles and silica-Fe<sub>3</sub>O<sub>4</sub>-nanoparticles is an S–H bond around 2570 cm<sup>-1</sup>, which is visible in the MPTMS spectra. It showed that –SH was grafted on the surface of the silica-coated magnetic nanoparticles after modification.

The prepared MSMNPs were also characterized by TEM. From Fig. 3, it could be seen that the average diameter of the MSMNPs, measured by TEM, was 70–90 nm.

### 3.2 Selectivity of MSMNPs to analytes

The effect of pH on the static adsorption of Se(IV) and Se(VI) was tested separately by equilibrating 50 mg of MSMNPs with 50 mL of sample solutions containing 1  $\mu$ g L<sup>-1</sup> of the target analyte under different pH conditions. The mixtures were dispersed by ultrasonication for 10 min at room temperature, and then magnetically separated. The supernatants were measured for unextracted analyte by ICP-MS. Fig. 4 shows the effect of pH on the adsorption (*R*%) of inorganic Se species on MSMNPs and silica-Fe<sub>3</sub>O<sub>4</sub>. It could be seen that Se(IV) was adsorbed quantitatively on the MSMNPs within a wide pH range of 1–10, however, it could not be retained quantitatively on silica-Fe<sub>3</sub>O<sub>4</sub>. And the adsorption behavior of Se(VI) on the two adsorbents is similar, it was not retained and remained as free species in solution. The results indicated that the adsorbability of the MSMNPs to the Se(IV) is related to the –SH on the adsorbent. This result is similar to that reported in ref. 14. For further experiments, pH 7 which is close to the original pH of natural water was chosen for preconcentration of Se(IV).

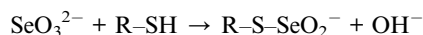
Se(IV) and Se(VI) are present as SeO<sub>3</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup> in aqueous solution, respectively. According to the theory of valency, the covalent bond of SeO<sub>4</sub><sup>2-</sup> is saturated, while the covalent bond of SeO<sub>3</sub><sup>2-</sup> isn't saturated; hence, only SeO<sub>3</sub><sup>2-</sup> can have a chance to react with –SH. And according to the HSAB (Hard–Soft–Acid–Base) theory, Se(IV) is a softer acid, –O– is a harder base, and –S– is a softer base, therefore, Se(IV) tends to combine with

**Table 5** Analytical results for inorganic Se speciation in environmental water (mean  $\pm$  S.D.,  $n = 3$ )

Sample	Species	Added (ng mL <sup>-1</sup> )	Determined (ng mL <sup>-1</sup> )	Recovery (%)
Environmental water (Longyan)	Se(VI)	0	1.23 $\pm$ 0.06	99.1
		1	2.21 $\pm$ 0.18	
	Se(IV)	0	0.81 $\pm$ 0.07	103.3
		1	1.87 $\pm$ 0.16	
Environmental water (Wuyishan)	Se(VI)	0	1.02 $\pm$ 0.07	98.0
		1	1.98 $\pm$ 0.12	
	Se(IV)	0	0.45 $\pm$ 0.04	94.5
		1	1.37 $\pm$ 0.12	



–S–. Many studies<sup>25–27</sup> have been done on the reaction mechanism of Se(IV) with –SH, and these studies showed that the principle of the reaction of  $\text{SeO}_3^{2-}$  with –SH can be expressed by the following reaction equation:



### 3.3 The optimization of elution conditions

From Fig. 4, it was found that the Se(VI) could not be retained on the MSMNPs. Hence, the approach to elute the Se(IV) was to oxidize the Se(IV) adsorbed on the MSMNPs into Se(VI) which couldn't be adsorbed on the MSMNPs. Among the various oxidizing agents, namely  $\text{HNO}_3$  (1–4 mol L<sup>–1</sup>),  $\text{KMnO}_4$  (0.01–0.08 mol L<sup>–1</sup>),  $\text{H}_2\text{O}_2$  (1.0–3.0 mol L<sup>–1</sup>),  $\text{KIO}_3$  (0.01–0.05 mol L<sup>–1</sup>) and  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.01–0.04 mol L<sup>–1</sup>), only  $\text{H}_2\text{O}_2$  was found to elute about 41% of Se(IV) retained on the MSMNPs, while the other oxidizing agents couldn't elute the Se(IV). However, a mixed solution of 0.02 mol L<sup>–1</sup>  $\text{K}_2\text{Cr}_2\text{O}_7$  in 2.0 mol L<sup>–1</sup> HCl can remove retained Se(IV) from the MSMNPs quantitatively because the oxidation of  $\text{K}_2\text{Cr}_2\text{O}_7$  can be improved under acidic conditions. The experimental results (Fig. 5) also indicated that 0.5 mL of the mixed solution was sufficient for quantitative recovery of Se(IV).

It should be pointed out that the MSMNPs couldn't be regenerated due to the oxidation of functional groups (–SH) on the adsorbent by the oxidizing eluent. Fortunately, the preparation of MSMNPs was quite easy and around 10 g of MSMNPs could be prepared for one batch, which is sufficient enough for 200 runs.

### 3.4 Effect of sample volume

In order to obtain a higher enrichment factor, a large volume of sample solution is required. Thus, the effect of sample volume on the magnetic SPE of Se(IV) was studied. In this experiment, the mass of the Se(IV) was fixed at 0.5 ng and the volume of the sample solution ranged from 10–200 mL. Then, the samples with different volume were studied according to the general procedure. It was found that quantitative recovery for Se(IV) could be obtained by using 50 mg of MSMNPs when the sample volume was less than 150 mL. Therefore, a theoretical enrichment factor of 300 could be achieved by this method. Hence, the method is very suitable for preconcentration of ultra-trace Se(IV) from large volumes of sample solution.

### 3.5 Effect of ultrasonication time

Ultrasonication times for adsorption and elution were also optimized so as to minimize the time required for sample processing. The experimental results indicate that the quantitative recovery for Se(IV) was achieved when the ultrasonication time of the sample was greater than 9 min for adsorption and greater than 1.5 min for elution, respectively. Finally, an ultrasonication time of 10 min for adsorption and 2 min for elution was used in the subsequent experiments.

### 3.6 Effect of co-existing ions

In order to assess the possible analytical applications of the recommended speciation/preconcentration procedure, the effect

of some foreign ions which interfere with the determination of Se(IV) ions and/or often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The results are summarized in Table 2. It can be seen that all the values of the tolerance limit of ions for potential interferences are greater than those typically found in real environmental water samples.<sup>28</sup> This demonstrates the method has a good tolerance to interference and is suitable for speciation of inorganic Se in environmental water.

### 3.7 Analytical performance

A series of standard solutions with different Se(IV) concentrations were prepared and subjected to the sample operation prior to their determination by ICP-MS and a calibration curve after preconcentration was obtained. Highly purified deionized water was chosen as the blank solution and subjected to MSPE. According to the IUPAC definition, the detection limits of the method are 0.094 ng L<sup>–1</sup> for Se(IV), with an enrichment factor of 282. The relative standard deviation (R.S.D.) was 8.1% ( $C_{\text{Se(IV)}} = 10 \text{ ng L}^{-1}$ ,  $n = 7$ ). The enrichment factor was calculated as follows:

enrichment factor =

$$\frac{\text{the slope of the calibration after preconcentration}}{\text{the slope of the calibration before preconcentration}}$$

A comparison of LODs obtained by this method with several other approaches reported in the literature for speciation of Se is shown in Table 3. As can be seen, the LODs of this method are much lower than those obtained by HPLC-MW-HG-ICP-MS,<sup>29</sup> CE-HG-AFS,<sup>30</sup> HPLC-HG-AAS,<sup>31</sup> HPLC-ICP-MS,<sup>32</sup> HPLC-ICP-MS,<sup>33</sup> FI-SPE-ETAAS<sup>34</sup> and HF-LPME-ETV-ICP-MS.<sup>11</sup>

Adsorption capacity is an important factor to evaluate the property of the adsorption material, because it determines how many MSMNPs are required to quantitatively concentrate the Se(IV) from a given solution. The method used for capacity study was adapted based on the method recommended by Maquieira *et al.*,<sup>35</sup> and the maximal adsorption capacity for Se(IV) was found to be 12.3 mg g<sup>–1</sup>.

### 3.8 Sample analysis

In order to establish the validity of the proposed procedure, the method has been applied to the determination of the content of Se(IV, VI) in a standard water sample (GSBZ50031-94[203708]), and the analytical results are listed in Table 4. As can be seen, a good agreement between the determined value and the certified value could be obtained.

The method was applied to the speciation of dissolved inorganic Se in environmental water samples, and the analytical results along with the recoveries for the spiked waters are given in Table 5. The Se speciation results indicated that the Se species in Se(VI) form is more abundant than that of Se(IV) in environmental waters of the tobacco growing area. And the recoveries for the environmental water samples were found to be in the range of 94.5–103.3%.

## 4. Conclusions

A new kind of MSMNPs was synthesized and employed as a SPE adsorbent for speciation of inorganic Se in environmental water. These noble magnetic nanoparticles could be easily produced in large quantity. With larger surface area and highly active surface sites, these nanoparticles could quantitatively absorb the Se(IV) from a large sample solution in a very short time within a pH range of 1–10. And the separation of Se(IV)-loaded magnetic adsorbent from the solution could be easily achieved via an external magnetic field. Compared with the established methods, the proposed method has high enrichment factor and very low LODs for quantitative determination of Se(IV) and Se(VI) in environmental water.

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