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Determination of trace amounts of Se(IV) by hydride generation atomic fluorescence spectrometry after solid-phase extraction using magnetic multi-walled carbon nanotubes

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ABSTRACT

A sensitive and simple method using magnetic multi-walled carbon nanotubes, as an adsorbent, has been successfully developed for extraction and preconcentration trace amounts of Se(IV) with detection by hydride generation atomic fluorescence spectrometry. The prepared nanoparticles were confirmed by Fourier transform infrared spectra, X-ray diffraction spectrometry, vibrating sample magnetometry, and transmission electron microscopy. These magnetic nanocomposites can be easily dispersed in aqueous samples and retrieved by the application of external magnetic field via a piece of permanent magnet. The main factors affecting the signal intensity such as sample pH value, adsorbent amount, eluent concentration and volume, sample volume, and coexisting ions have been investigated and established. The absorbent could be repeatedly used at least 100 times. The enhancement factor of the proposed method for Se(IV) was 100. The method had a linear calibration plot in the range from 0.05 to 10.0 μg L^{-1} with a standard deviation of 2.3% at 0.5 μg L^{-1} ($n=11$). The limit of detection was as low as 0.013 μg L^{-1}. Accuracy of the method was evaluated by the analysis of water samples and certified reference materials.

1. Introduction

Selenium is an essential micronutrient for humans, which cannot be synthesized in the body, but ingested from food. Although the content of selenium in the human body is very little, it plays an extremely important role in the function of the human body, especially in the prevention of cardiovascular disease, antitumor, cancer, as well as anti-aging [1,2]. But, an upper limit for safe intake was set at 400 μg/day. Excess selenium is harmful to human health [3]. Due to the consumption of food and water with high selenium content, there may be different levels of selenium poisoning symptoms. Therefore, it is important to develop analytical methods for the determination selenium concentrations.

Hydride generation atomic fluorescence spectrometry (HG-AFS) appears as one of the most popular analytical techniques for Se(IV) determination [4–6]. However, the direct determination of trace amounts of Se(IV) in complicated materials is usually difficult owing to matrix interferences and/or insufficient detection power. In order to overcome these problems, a separation and preconcentration step is often required prior to the instrumental measurement, particularly when they exist at trace levels of concentration [7,8]. A number of separation/preconcentration procedures have been widely carried out for this purpose, which include precipitation/co-precipitation, liquid–liquid extraction, and solid-phase extraction (SPE). Among these techniques, SPE procedures are superior to other procedures for their simplicity, flexibility, high preconcentration factor, low cost, and consumption of small volumes of organic solvent [9,10].

Multi-walled carbon nanotubes (MWCNTs) have attracted considerable interest due to their strong adsorption ability, exceptional mechanical properties, high chemical stability, and a large specific surface area. MWCNTs have been used as a new type of adsorbent and offered numerous applications [11–14]. However, disadvantages such as small size and poor dispersion in aquatic phase, limit the application of MWCNTs. At present, nanometer materials, especially Fe_3O_4 magnetic nanoparticles, have become more and more important as adsorbents for solid-phase extraction [15–17], because they can be easily isolated using an external magnetic field placed outside of the extraction container. Therefore, the combination of magnetic properties into MWCNTs system has the advantages of high adsorption capacity of MWCNTs and the separation convenience of magnetic materials. These characteristics allow applications of magnetic MWCNTs for removing many kinds of organic compounds such as cationic dyes [18], aniline [19], polycyclic aromatic hydrocarbons [20], *p*-hydroxybenzoates [21], phthalate acid esters [22], NADH [23], bilirubin [24], and azo dye [25] from different media. However, a few studies on the adsorption of inorganic substances with magnetic MWCNTs were explored [26,27].

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In this work, magnetic MWCNTs composite nanoparticles were synthesized and characterized, which exhibit high dispersibility and excellent magnetic responsibility. The material was applied for separation and enrichment of trace amounts of Se(IV) followed by hydride generation atomic fluorescence spectrometry. The results demonstrated that the established method can be used for Se(IV) determination in environmental water samples and certified reference materials with satisfactory results.

2. Experimental

2.1. Apparatus

A continuous flow AFS-3100 atomic fluorescence spectrometer (Beijing, China) was employed for the analytical determinations. The instrumental parameters were adjusted according to the manufacturer recommendations, which were shown in Table 1. A permanent magnet was used to enable the isolation of the analytes from the complicated matrix. A Tensor 27 spectrometer (Bruker Co., Germany) was used to obtain Fourier transform infrared (FTIR) spectra. Transmission electron micrographs (TEM) were obtained with a Philips Tecnai-12 microscope (Holland) at an acceleration voltage of 120 kV. The magnetic property was analyzed by using a vibrating sample magnetometer (VSM, LDJ9600).

2.2. Reagents and materials

A Se(IV) stock standard solution at a concentration of 1000 mg L^{-1} was purchased from the BHH Biotechnology Co., Ltd. Working standard solutions were obtained by step-wise dilution with de-ionized water. A 2.5% (m/v) $NaBH_4$ solution was prepared by dissolving $NaBH_4$ in 0.4% (m/v) NaOH solution. The MWCNTs were purchased from Nanotech Port Co. Ltd. (Shenzhen, China) with an average size of 20 nm, which were purified by stirring the MWCNTs in concentrated nitric acid at 60 °C for 12 h, and then dried at 110 °C for 4 h. All the chemicals used were at least analytical reagent grade and obtained from Sinopharm Chemical Reagent Co., Ltd unless otherwise stated. Double de-ionized water (18.2 MΩ cm) was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA) and used throughout the experiments. Reference materials stream sediment (GBW07303a) and soil (GBW07405) were purchased from the BHH Biotechnology Co., Ltd.

Table 1
Operating parameters of the HG-AFS instrument.

Parameters	Settings
Negative high voltage of the PTM (V)	300
Atomizer height (mm)	8
Lamp current (mA)	60
Flow rate of carrier gas (mL min^{-1})	400
Flow rate of shield gas (mL min^{-1})	900
Concentration of $NaBH_4$ (m/v)	2.5%
Flow rate of $NaBH_4$ (mL min^{-1})	8.0
Concentration of HCl (mol L^{-1})	1.0
Flow rate of HCl (mL min^{-1})	8.0
Flow rate of sample solution (mL min^{-1})	3.0
Read time (s)	12
Delay time (s)	3
Injection volume (mL)	1
Read mode	Peak area

2.3. Preparation of iron oxide and magnetic MWCNTs

The magnetic particles were synthesized by a solvothermal method [28]: $FeCl_3{\cdot}6H_2O$ (5.4 g) and $FeCl_2{\cdot}4H_2O$ (2.0 g) were dissolved in a 6 mol L^{-1} hydrochloric acid solution (25 mL), which was then sufficiently degassed with a nitrogen stream. After that, a 25% (v/v) ammonium hydroxide solution (30 mL) was added to the solution with vigorous stirring at 60 °C for 30 min under nitrogen atmosphere. After cooling to ambient temperature, the resultant magnetic particles were attracted to the bottom by a magnet. The black products were washed several times sequentially with sufficient volume of water and ethanol and then dried at 60 °C for 6 h. The fabrication process of magnetic MWCNTs was prepared by previous method after a minor modification [29]. MWCNTs (100 mg) and magnetic particles (100 mg) were dispersed in *N*,*N*-dimethylformamide (5 mL), respectively. After combining the two solutions, the MWCNTs and magnetic particles were dispersed homogeneously by ultrasonic agitation (5 min). During the mixing, the MWCNTs and magnetic particles can assemble spontaneously to form magnetic MWCNTs. The resulting magnetic MWCNTs were washed with sufficient water, and dried at 85 °C for 4 h.

2.4. Samples and sample pretreatment

The water samples were collected locally. The samples were filtered immediately after sampling, and stored at 4 °C. Before experiment, 5 mL 4 mol L^{-1} HCl was added to the samples and the solutions were heated for 15 min in order to reduce Se (VI) to Se (IV). Certified reference materials soil (GBW07405): 0.5000 g of soil is mixed with 10 mL HNO_3 and 5 mL $HClO_4$. After soaking for one night at room temperature, 1 mL H_2O_2 and 1 mL HCl were added and heated at 180 °C to dissolve the soil until the residues become lacte. After cooling, 3 mL 4 mol L^{-1} HCl was added to reduce Se (VI) to Se (IV). Finally, the content was diluted to 50 mL with water and adjusted to pH 4 before use. Certified reference materials stream sediment (GBW07303a): 0.5000 g of stream sediment is mixed with 10 mL HCl and heated at 150 °C for 1 h. After preliminary decomposition, 5 mL HNO_3 and 3 mL $HClO_4$ were added and the mixtures were heated at 250 °C until the solution was nearly dried. After cooling, 3 mL 4 mol L^{-1} HCl was added to reduce Se (VI) to Se (IV). Finally, the residue was diluted to 50 mL with water and adjusted to pH 4 before use.

2.5. Sample extraction and preconcentration procedure

Briefly, a portion of 10 mL of sample solution containing analyte ions was transferred to a vial; the pH value was adjusted to 4. Then, 10 mg of magnetic MWCNTs were added, and the solution was agitated for 20 min to facilitate adsorption of the Se (IV) onto the nanoparticles. Then, the magnetic adsorbent was separated easily and quickly using a magnet and the supernatant was decanted directly. The magnet was removed and 1 mL 2.5 mol L^{-1} NaOH solution was added as eluent and stirred for 20 min. Finally, the magnet was used again to settle the magnetic nanoparticles, and the eluent was transferred into a test tube for subsequent HG-AFS analysis.

3. Results and discussion

3.1. Characterization of the adsorbent

Fig. 1 shows the FTIR spectra of Fe_3O_4, pre-treated MWCNTs and magnetic MWCNTs. The absorption peaks of the Fe–O bonds (607 cm^{-1}) and the stretching vibration absorption peak of

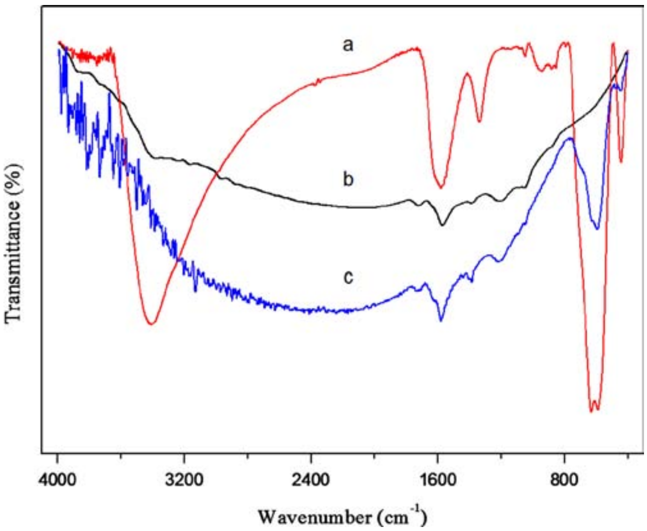

Fig. 1. IR spectra of Fe_3O_4 (a), MWCNTs (b), and magnetic MWCNTs (c).

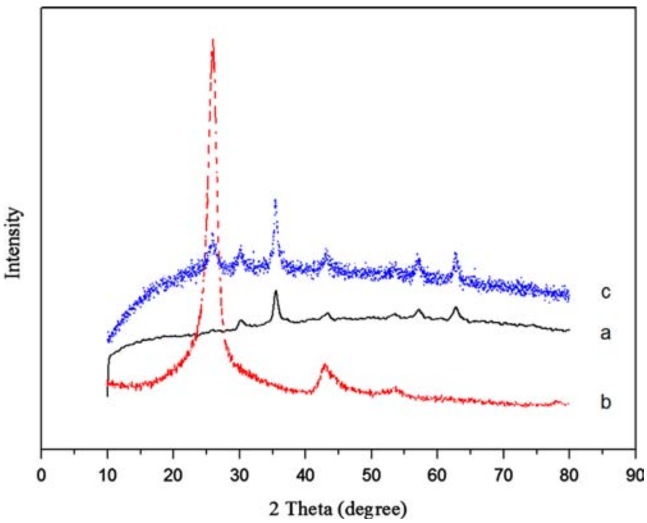

Fig. 2. XRD patterns of Fe_3O_4 (a), MWCNTs (b), and magnetic MWCNTs (c).

hydroxyl group (3410 cm^{-1}) are the characteristics absorption spectrum of the Fe_3O_4 magnetic nanoparticles. The peaks appeared at 1790 cm^{-1} and 1219 cm^{-1} are attributed to carboxylic acid group of MWCNTs, and the peak at 1577 cm^{-1} could be related to the C=C stretching. In spectrum of magnetic MWCNTs, a similar spectrum indicated the presence of C=O and C=C, and the new peak at 599 cm^{-1} is attributed to stretching vibration of the Fe–O bonds, indicating the successful synthesis of magnetic MWCNTs.

Fig. 2 shows the XRD patterns of Fe_3O_4, MWCNTs and magnetic MWCNTs. The typical peaks of Fe_3O_4 were displayed at 2θ values of about 30.2°, 35.5°, 43.4°, 58.2° and 62.3°. The diffraction peak at $2\theta=26.2°$ is assigned to (002) plane of MWCNTs. In the XRD pattern of magnetic MWCNTs, the five typical peaks of Fe_3O_4 and the two peaks corresponding to the structure of MWCNTs were observed. And after surface modification, the characteristic peak of MWCNTs significantly reduced, while iron oxide peak did not change significantly, indicates that iron oxide nanoparticles have been wrapped on the surface of MWCNTs.

The hysteresis curves measured at $T=293$ K for Fe_3O_4 and magnetic MWCNTs are compared in Fig. 3. The saturation magnetization value was measured to be 46.5 emu g^{-1} for Fe_3O_4 and 38.9 emu g^{-1} for magnetic MWCNTs. Compared with the bare Fe_3O_4, the magnetic strength of magnetic MWCNTs decreased due to the presence of MWCNTs. However, it was sufficient for magnetic separation with a common magnet.

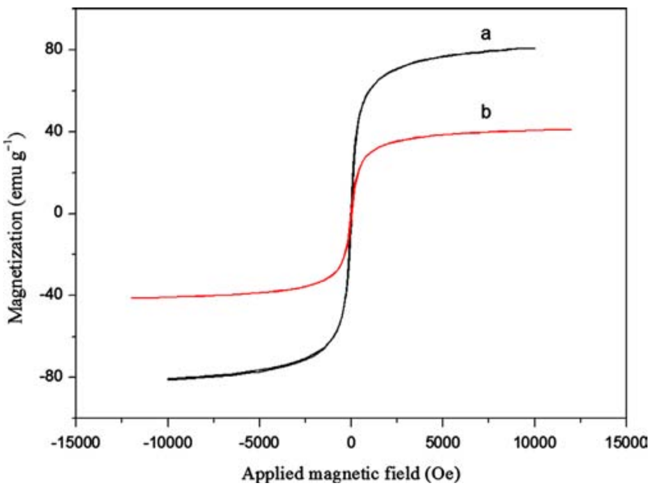

Fig. 3. VSM magnetization curves of Fe_3O_4 (a) and magnetic MWCNTs (b).

The size and morphology of MWCNTs and the magnetic MWCNTs were investigated by TEM. As shown in Fig. 4A, it could be clearly seen that carbon nanotubes were hollow fibrous, which had a mean diameter of about 20 nm. In Fig. 4B, it is observed that the spherical iron oxide particles were coated on the surface of MWCNTs, which made carbon nanotubes composite materials have magnetic properties. Therefore, the MWCNTs could be separated from matrix solution conveniently by an external magnet.

3.2. *Effects of the adsorption conditions*

The pH of the aqueous solution is an important variable that controls the adsorption of the Se(IV) on the MWCNTs–water interfaces. Hence, the effect of pH on the adsorption of Se(IV) onto MWCNTs was investigated in the pH range of 2–8 (Fig. 5a). It can be observed that the adsorption of Se(IV) increases with increasing pH of the solution and reaches a maximum value at pH 4, and then decreases as the pH becomes more basic. It is known that Se(IV) species present in the forms of H_2SeO_3, $HSeO_3^-$, and SeO_3^{2-} depending on the pH values of solution. The pKa values for H_2SeO_3 are 2.8 and 8.5. Therefore, at pH 3–5, the primary species for Se(IV) is $HSeO_3^-$ and the adsorption of $HSeO_3^-$ is mainly accomplished by adsorption reaction. At pH<3, the primary species for Se(IV) is H_2SeO_3, the electrostatic attraction between Se(IV) and MWCNTs is weaker, so the adsorption drops. The species SeO_3^{2-} are predominated gradually with the increase of solution pH. However, the pH$_{zpc}$ (zero point charge) value of MWCNTs is about 5.3, in the pH range higher than the pH$_{zpc}$, the surface charge of MWCNTs is negative and SeO_3^{2-} is hardly adsorbed on the surface of MWCNTs. The subsequent studies were carried out using a sample pH of 4.

Compared to ordinary sorbents (microsized adsorbents), magnetic MWCNTs offer a significantly higher surface area-to-volume ratio and a short diffusion route, which results in high extraction capacity and high extraction efficiencies. Also, magnetic MWCNTs can be rapidly collected from sample solution by applying magnetically assisted separation, thus shorter extraction times can be achieved. Therefore, satisfactory results can be obtained with fewer amounts of these adsorbents. As shown in Fig. 5b, by increasing amounts of the magnetic MWCNTs due to increase in the surface area and accessible sites to the adsorption of the analytes, the signal intensity increased gradually. With higher

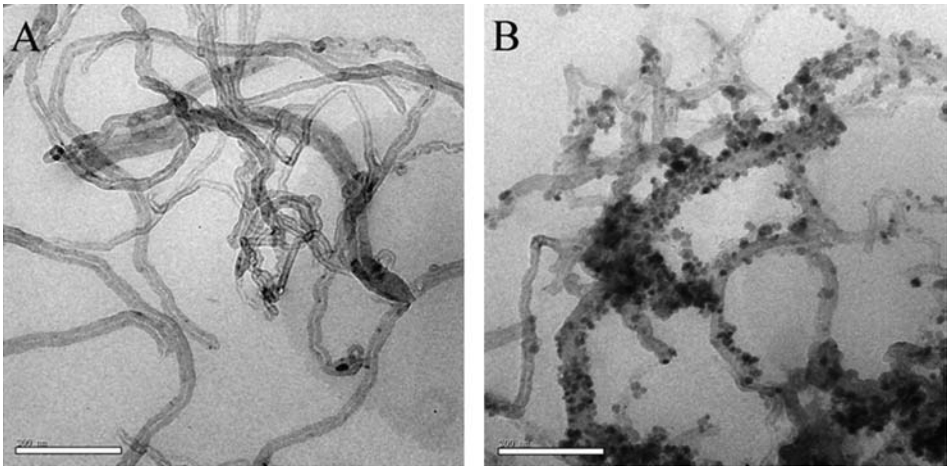

Fig. 4. TEM of MWCNTs (a) and magnetic MWCNTs (b).

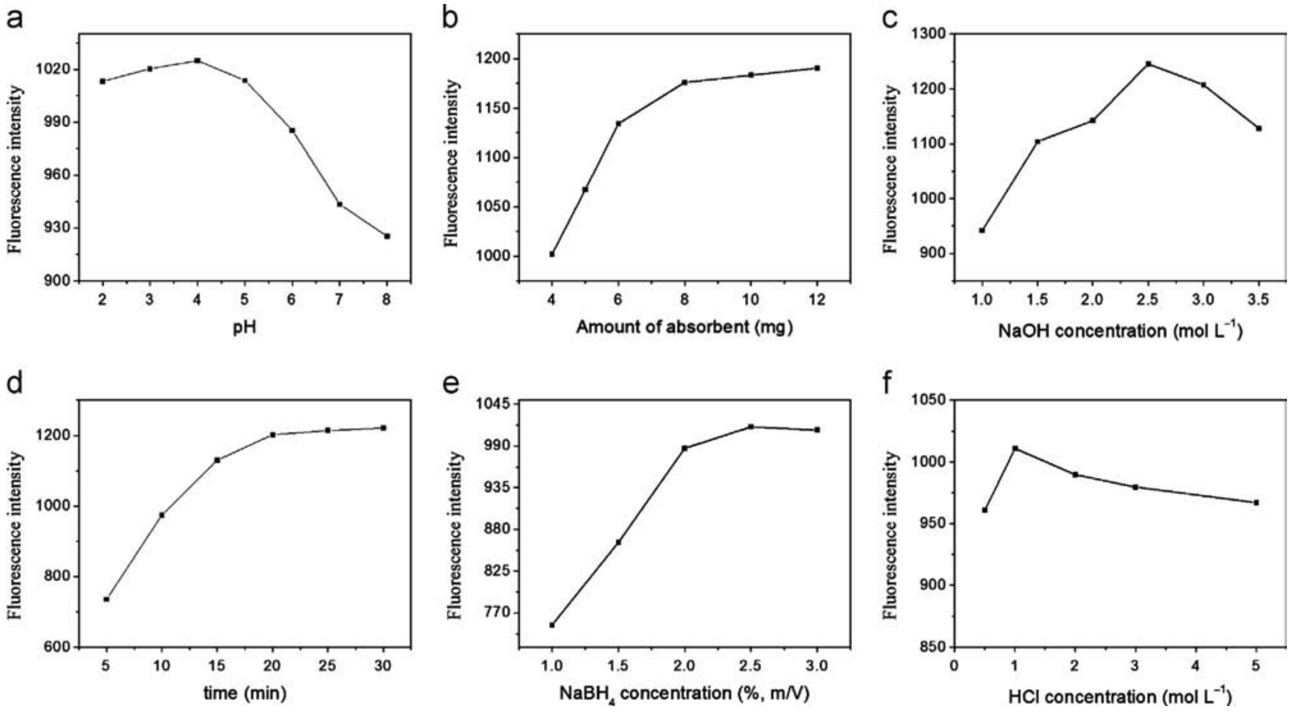

Fig. 5. Effects of (a) sample solution pH, (b) absorbent amount, (c) NaOH concentration, (d) elution time, (e) $NaBH_4$ concentration, and (f) HCl concentration on the fluorescence signal of Se(IV). The HG-AFS conditions as in Table 1.

amounts of the adsorbent, the signal intensity was almost constant, indicating the magnetic MWCNTs showed an excellent capability to retain the Se(IV) ions, and quantitative extraction of the Se(IV) was achieved using only 10 mg of the magnetic MWCNTs under the optimum conditions. Therefore, in the subsequent experiments, 10 mg of magnetic MWCNTs was used for the following experiment.

For studying effect of extraction time on signal intensity of Se(IV), the extraction times were varied in the range of 5–30 min. It was found that after 20 min, the signal intensities of the Se(IV) had no significant variation. Thus, the extraction time of 20 min was selected for further studies.

3.3. *Effects of desorption conditions*

Superparamagnetic magnetic MWCNTs can be easily collected by applying an external magnetic field placed outside of the extraction container. Therefore, no centrifugation or filtration of the sample is needed after the extraction. After collection of the magnetic MWCNTs from the sample solution, desorption conditions were evaluated. Various desorbing reagents were used to find the best desorbing solution for the adsorbed Se(IV). In this work, HCl, H_2SO_4, and NaOH were selected as the eluent. The results indicated that a high and sharp peak of the Se(IV) signal curve was obtained with NaOH as the eluent. In addition, a satisfactory eluent should effectively elute the adsorbed analytes with small volume, which is needed for a high enrichment factor, but should not affect the accurate determination of the analytes. For this reason, 1 mL of various concentrations (1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mol L^{-1}) of NaOH were investigated to elute the adsorbed Se(IV). Fig. 5c shows the experimental results that 2.5 mol L^{-1} NaOH was sufficient for quantitative elution of Se(IV). Hence, 2.5 mol L^{-1} NaOH was selected as eluent for the subsequent experiments. By using 2.5 mol L^{-1} NaOH as eluent, the effect of eluent volume on the desorption of Se(IV) was studied with eluent volume varying from 0.5 to 5 mL. It was found that

1.0 mL of 2.5 mol L^{-1} NaOH was sufficient to recover Se(IV) quantitatively. Therefore, 1.0 mL of eluent was selected for the subsequent experiments.

Desorption times were evaluated in the range of 5–30 min and the results were presented in Fig. 5d. It can be seen that the time of 20 min is sufficient to quantitative desorption of Se(IV) by 1 mL of the 2.5 mol L^{-1} NaOH solution.

3.4. Effect of sample volume

In order to obtain a higher enrichment factor, a larger volume of sample solution is required. The effect of sample solution volume on the extraction of Se(IV) was studied by using different volumes (50–300 mL) of aqueous solution spiked with a fixed 5 μg of Se(IV) under the optimal conditions. The samples with different volume operated according to the general procedure. It was found that quantitative recovery for Se(IV) could be obtained when sample volume was less than 100 mL. With an elution volume of 1 mL, a theoretical enrichment factor of 100 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. However, for convenience, all the experiments were carried out with 10 mL of the aqueous phase.

3.5. Effects of the detection conditions

The effects of other chemical variables on the Se(IV) atomic fluorescence signal were also investigated. In the present method, $NaBH_4$ is used not only as the reductant, but also as the hydrogen supply to sustain the argon-hydrogen flame. The concentration of $NaBH_4$ had a large impact on the hydride generation process and the argon-hydrogen flame. In the HCl system, at the optimal acidity, when $NaBH_4$ solution concentrations were increased from 1% to 2.5% (m/v), the Se(IV) signal intensity increased sharply (Fig. 5e). However, the peak area signals remained constant when the concentration of $NaBH_4$ was in the range of 2.5–3% (m/v). Meanwhile, higher $NaBH_4$ concentrations than 3% (m/v) would result in a violent reaction in the gas–liquid separator and eventually lead to an unstable signal. Thus 2.5% (m/v) of $NaBH_4$ solution was used as the optimal reductant solution.

HCl is the most common and efficient inorganic acid in the generation of Se(IV) hydride, which has a remarkable influence on the generation efficiency of the volatile Se(IV) species. In this work, the HCl concentrations of the carrier solution were studied. The influence of HCl concentration on the Se(IV) fluorescence intensity was optimized from 0.5 to 5.0 mol L^{-1}. As shown in Fig. 5f, the signal intensity improved with the increase of the HCl concentration from 0.5 to 1.0 mol L^{-1}, and decreased gradually with the HCl concentration further increased. In the ensuing investigation, 1.0 mol L^{-1} HCl was used as the optimal carrier acidity.

3.6. Adsorption capacity

The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of Se(IV) from the solutions. The adsorption capacity was carried out by retaining solution volume of Se(IV) (100 mL) and amount of sorbent constant (10 mg) and gradually increasing solution concentration. The maximum adsorption capacity has been calculated to be 2.5 mg g^{-1}.

3.7. The interferences

In order to demonstrate the selectivity of the developed method for the determination of Se(IV), the effects of interference by coexisting ions on the separation and preconcentration of analytes were examined under the optimum conditions described above. Tolerance limit was defined as the ratios of interference to Se(IV), for a ±5.0% signal change. The results showed that 500-fold concentration of Fe^{3+}, 400-fold concentration of Co^{2+}, 300-fold concentration of Cu^{2+}, Mn^{2+}, 200-fold concentration of Sn^{2+}, Zn^{2+}, and Pb^{2+}, 100-fold concentration of Ni^{2+}, 50-fold concentration of Cd^{2+} have no influence on the signals of Se(IV). The influence of some inorganic ions such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, CO_3^{2-}, PO_4^{3-} could exist at least 10000-fold. Sorption experiment has also carried out. The lower degrees of sorption for Fe^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} were 4.75, 17.50, 11.25, 14.25, 13.75, 17.8, 18.75, and 21.12, respectively. This is attributed to the fact that the surface charge of MWCNTs is positive at the optimized pH of 4, which lead to desorption of some cationic species. These results demonstrate that the method has a good tolerance to interference and is suitable for Se(IV) detection direct without masking reagents or further pretreatments.

3.8. Analytical performance

The analysis of a series solutions containing 0.05, 0.1, 0.5, 1.0, 5.0, and 10.0 μg L^{-1} Se(IV), respectively, gave a calibration function of $F=241.16C+23.55$ (F, the signal intensity and C, the concentration of Se(IV), expressed in μg L^{-1}) with a correlation coefficient of 0.9998. Detection limit for Se(IV) based on 3σ/s definition (where σ is the standard deviation of the blank signals and s is the slope of the linear calibration graph) were found to be 0.013 μg L^{-1}. Relative standard deviation of the proposed procedure determined by 11 replicates of samples containing 0.5 μg L^{-1} Se(IV) was calculated to be 2.3%. The comparison of the detection limits and enrichment factors in the present work with those reported in the literatures [30–35] are given in Table 2. Accordingly, the proposed

Table 2
A comparison of performance by the present procedure versus some of the reported methods.

Procedure	Detection technique	Detection limit (μg L^{-1})	Calibration range (μg L^{-1})	Enrichment factor	R.S.D (%)	Ref.
coprecipitation	EDXRF[a]	0.13	5–100	–	3.4	30
coprecipitation	HG-AFS	0.014	0.05–10.0	18	2.5	31
SPE[b]	HG-AFS	0.017	0.05–4.5	11	1.8	32
SPE[c]	HG-AFS	0.11	0.04–4.0	13	3.3	33
UA-HF-LPME[d]	GF-AAS	0.08	0.2–5.0	35	4.5	34
HF-LPME[e]	HPLC-UV	0.02	0.05–10.0	130	3.7	35
Magnetic MWCNTs	HG-AFS	0.013	0.05–10.0	100	2.3	This work

[a] Energy dispersive X-ray fluorescence spectrometry.
[b] Solid phase extraction with a PTFE knotted reactor.
[c] Solid phase extraction with a PTFE tubing packed Mg-$FeCO_3$ LDHs.
[d] Ultrasound assisted-hollow fiber liquid-phase microextraction with 2 mL sample.
[e] Hollow fiber liquid-phase microextraction with 50 mL sample.

Table 3
Analytical results for real water samples.

Sample	Original ($\mu g\ L^{-1}$)	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)	RSD (%)
Tap water	0.063±0.004	0.100	0.157±0.003	96.3	2.1
		0.500	0.576±0.007	102.3	1.9
Lake water	0.103±0.003	0.100	0.201±0.005	99.0	1.4
		0.500	0.601±0.002	99.6	1.2

Table 4
Analysis of standard reference materials ($n=3$).

Sample	Certified ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$)	RSD (%)
Soil (GBW07405)	1.6±0.2	1.70±0.07	2.1
Stream sediment (GBW07303a)	0.57±0.05	0.54±0.02	1.4

method showed a very good sensitivity, high enrichment factor and low detection limits, which can be attributed to the large surface area and high extraction efficiencies of the magnetic nanocomposites in comparison with the other microsized sorbent materials. Moreover, compared with bare MWCNTs and magnetic nanoparticles, the composite material had a larger adsorption capacity and rapid equilibrium time. The signal intensity was observed to enhance significantly about 6.8 and 2.7 times. More importantly, the composite material eliminated the small size and poor dispersion of MWCNTs as well as the gather phenomenon of Fe_3O_4 nanoparticles.

Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that the magnetic multi-walled carbon nanotubes can be repeatedly used up to 100 times without loss of analytical performance, which proved a long lifetime of these magnetic nanocomposites.

3.9. *Applications of the method*

To test the applicability of the optimized method to real samples, it was applied to the determination of Se(IV) in tap and lake water samples. The analytical results are shown in Table 3. The accuracy of the method was verified by the analysis of the samples spiked with known amounts of Se(IV). The recoveries of the Se(IV) from the spiked samples are in acceptable range (96.3–102.3%). The method has been further applied to the determination of the content of Se(IV) in standard reference materials: Soil (GBW07405) and Stream sediment (GBW07303a), and the analytical results are listed in Table 4. It can be seen that the concentrations of Se(IV) in the standard reference materials obtained by the present method were in good agreement with the certified values, indicating that this method is of high accuracy and precision.

4. Conclusion

In this study, we reported a convenient and efficient separation and preconcentration procedure for Se(IV) via magnetic MWCNTs composite nanoparticles. The obtained materials were developed as magnetic SPE sorbents to extract Se(IV) from large volume of samples. After adsorption of analytes from water samples, the sorbents can be collected easily with a magnet for elution due to superparamagnetism of materials, which avoids the time-consuming column passing or filtration operation. In addition, due to the large surface area of nanomaterial and strong adsorption ability of MWCNTs, a lower amount of magnetic nanoparticle sorbents can be used with high adsorption capacity and extraction efficiency to Se(IV), which extended the scope of application of magnetic SPE technology.

Acknowledgments

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