Preconcentration and speciation of ultra-trace Se (IV) and Se (VI) in environmental water samples with nano-sized TiO₂ colloid and determination by HG-AFS

Jiaqi Fu, Xu Zhang, Shahua Qian *, Lin Zhang

School of Resource and Environmental Science, Hubei Biomass-Resource Chemistry and Environmental Biotechnology Key Laboratory, Wuhan University, Wuhan 430079, China

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ABSTRACT

A united method for speciation analysis of Se (IV) and Se (VI) in environmental water samples was developed using nano-sized TiO₂ colloid as adsorbent and hydride generation atomic fluorescence spectrometry (HG-AFS) as determination means. When the pH values of bulk solution were between 6.0 and 7.0, successful adsorption onto 1 mL nano-sized TiO₂ colloid (0.2%) was achieved for more than 97.0% of Se (IV) while Se (VI) barely got adsorbed. Therefore, the method made it possible to preconcentrate and determine Se (IV) and Se (VI) separately. The precipitated TiO₂ with concentrated selenium was directly converted to colloid without desorption. Selenium in the resulting colloid was then determined by HG-AFS. The detection limits (3σ) and relative standard deviations (R.S.D) of this method were 24 ng/L and 42 ng/L, 7.8% ($n = 6$) and 7.0% ($n = 6$) for Se (IV) and Se (VI), respectively. This simple, sensitive, and united method was successfully applied to the separation and speciation of ultra-trace Se (IV) and Se (VI) in environmental water samples.

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1. Introduction

Selenium is a metalloid element that naturally occurs in the environment. It can assume four valence states ($-$II, 0, IV, and VI), each with varying reactivity, toxicity, and bioavailability [1]. Selenites and selenates are usually water soluble, and the most frequent species in the water samples are inorganic Se (IV) and Se (VI) [2–4]. Acid and reducing conditions reduce inorganic selenite to elemental selenium, whereas alkaline and oxidizing conditions favour the formation of selenate [5,6]. Selenium is essential yet toxic, and it exhibits a narrow window between essential and toxic concentrations [7]. The toxicity of the different species for selenium differs, in which the toxicity of Se (IV) is stronger than that of Se (VI) [8–10]. Therefore, it is more meaningful to analyze selenium speciation than to determine the total concentration of inorganic selenium in water samples. Sensitive methods for selenium analysis include graphite furnace atomic absorption spectrometry (GFAAS) [3,11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [12] and HG-AFS. Among these methods, only HG-AFS can selectively determine Se (IV) from Se (IV)–Se (VI) mixture, and the concentration of Se (VI) can be calculated by the difference between total inorganic Se and Se (IV) [13,14]. The background values of selenium in some groundwater and surface water, and

selenium in tapwater samples from public water supplies around the world, are usually present at trace levels [1]. Concentrations of selenium in natural water systems range from tens to hundreds of ng/L with inorganic Se (IV) and Se (VI) species dominating [8,15,16]. Such trace analyte levels lead to difficulties in quantifying individual species by HG-AFS. Therefore, methods using preconcentration coupled with a highly sensitive detector are usually applied to the speciation of Se (IV) and Se (VI). Adsorption is one of the methods used to preconcentrate and separate selenium species, which has been proven efficient. Several adsorbents have been successfully applied to preconcentrating selenium species, including activated carbon [16–18], alkyl silica [19], resin [20,21], cross-linked chitosan [22,23], and nano-sized TiO₂ powder [24,25]. However, a desorption procedure is indispensable when using all the adsorbents above, which makes the operation complex and redundant.

Our research group has been working on the analysis of ultra-trace metal ions by using nano-sized TiO₂ colloid as adsorbent coupled with HG-AFS and GFAAS [26,27]. Nano-sized TiO₂ colloid has a smaller particle radius and a larger specific surface area than its powder. Also, the colloid is more stable and dispersive in water without agglomeration. The advantage of using nano-sized TiO₂ colloid coupled with HG-AFS is that it can dispense with desorption. Although slurry sampling does not require desorption procedure either, stabilizers like agar and surfactant are usually needed and success of the slurry sampling technique depends on many parameters such as the sample particle size, stabilizer ratio etc. [28,29]. The method proposed here is much simpler than the conventional

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methods with slurry sampling. The precipitated TiO_2 with concentrated analytes can be directly converted to colloid by adding some HCl aqueous solution. The resulting colloid samples can be determined by HG-AFS directly.

In this work, a method for speciation of Se (IV) and Se (VI) in environmental water samples was developed using nano-sized TiO_2 colloid as adsorbent and HG-AFS as determination means. Under optimum conditions, the adsorption efficiency for Se (IV) reached higher than 97.0% in a short time, while the adsorbent barely adsorbed Se (VI). Therefore, unlike using HG-AFS alone, Se (IV) and Se (VI) could be determined respectively by this method due to the apparent difference of the adsorption affinity. The developed method was simple, fast, sensitive, with no filtration or desorption steps, and it possessed low detection limits for Se (IV) and Se (VI). It was applied to selenium speciation analysis in environmental water samples with satisfactory results.

2. Experimental

2.1. Equipments

A PF6-2 non-dispersive atomic fluorescence spectrometer (Beijing Purkinje General Instruments Co., Ltd., Beijing, China), equipped with an HAF-2 selenium hollow cathode lamp, was used for selenium determination. The instrumental conditions of HG-AFS were listed in Table 1. pH values were measured with the Mettler-Toledo 320-S pH meter (Mettler-Toledo, Greifensee, Switzerland). An LD5-2A centrifuge (Beijing Medical Centrifuge Factory, Beijing, China) was applied to separating the suspensions. Particle size was determined by transmission electron microscope (JEM-100CXII, JEOL). The zeta potential of TiO_2 colloids was determined using a ZetaSizer 3600 (Malvern Instrument, UK).

2.2. Reagents, materials, and solutions

Ultrapure water was used to prepare all solutions. 2.0% (w/w) nano-sized TiO_2 colloid was supplied by Infrared Academy of Wuhan University (Wuhan, China), and was diluted 10 times to 0.2% (w/w) for use. The carrier liquid for AFS was prepared by 1.5% (w/w) KBH_4 and 2.0% (v/v) HCl. Ar (99.99%) was used as carrier gas. HNO_3 and NaOH aqueous solutions were used to adjust the pH. Selenium powder (99.98%) was used to prepare Se (IV) standard stock solution (0.1 g/L). Se (VI) standard stock solution (1.0 g/L) was prepared by using $Na_2SeO_4 \cdot 10H_2O$ as metal ions precursor. A series of standard working solutions were prepared by diluting standard stock solution. The environmental reference material (GSBZ 50031-94) was purchased from Institution for Environmental Reference Materials of Ministry of Environmental Protection (Beijing, China). Environmental water samples were from Donghu Lake (Wuhan, China) and Yangtze River. All salts used to prepare solutions were AR grade or higher.

2.3. Principle of HG-AFS

The carrier liquid for AFS consists of HCl and KBH_4, which can react to generate hydrogen. Se (IV) in the solution reacts with hydrogen to form H_2Se. H_2Se is separated from mother liquor and carried into the atomizer by argon. H_2Se is atomized into hydrogen and selenium atom at the temperature of 170 °C. With the selenium hollow cathode lamp as excitation source, selenium atom can emit fluorescence and the concentration of selenium can be determined from the fluorescence intensity. Considering that HG-AFS cannot detect Se (VI) directly, Se (VI) has to be reduced to Se (IV) first.

2.4. Reduction process of Se (VI) to Se (IV)

A certain volume of concentrated HCl was added into solution containing Se (VI), to obtain a HCl concentration of 3–4 mol/L. The processed solution was kept boiling for 30 min.

2.5. Determination of adsorption efficiency for Se (IV)

10 mL working solution (0.2 mg/L) of Se (IV) and about 70 mL ultrapure water were well mixed in a centrifuge tube (120 mL). The mixture was added with a certain dosage of nano-sized TiO_2 colloid and was adjusted to a certain pH value with HNO_3 and NaOH aqueous solutions. The resulting solution was subjected to centrifugation under 4500 rpm for 20 min. After centrifugation, the supernatant was transferred to a volumetric flask (100 mL) and 5 mL conc. HCl was added. The solution was then diluted to 100 mL. The Se (IV) concentration of the supernatant was determined by HG-AFS. The fluorescence obtained was compared with that of Se (IV) working solution (20 μg/L) without adsorption to calculate the adsorption efficiency of nano-sized TiO_2 colloid for Se (IV).

2.6. Determination of adsorption efficiency for Se (VI)

2 mL working solution (1 mg/L) of Se (VI) was added into a centrifuge tube containing about 40 mL ultrapure water. The same treating steps with Se (IV) were taken, namely the addition of nano-sized TiO_2 colloid, adjustment of pH, and centrifugation. Since only Se (IV) will generate the hydride, Se (VI) needs to be reduced to Se (IV) in order to obtain an analytical signal for HG-AFS. After centrifugation, supernatant was transferred to a beaker (250 mL). Se (VI) in the supernatant was converted to Se (IV) by the reduction process. The resulting solution was then diluted to 100 mL. The fluorescence of the above solution was compared with that of Se (IV) working solution (20 μg/L) to calculate the adsorption efficiency for Se (VI).

2.7. Preconcentration and determination of Se (IV), Se (VI) and total inorganic Se in water samples

All the vessels were washed with HCl (1:1) before use. Water samples were collected in an Erlenmeyer flask after air pumping filtration (0.45 μm nitrocellulose). 100 mL water sample was collected in a centrifuge tube and 1 mL nano-sized TiO_2 colloid (0.2%) was added. The pH of the solution was adjusted within a range from 6.0 to 7.0. The solution was then centrifuged for 20 min with 4500 rpm. After centrifugation, 50 mL of the supernatant was transferred into a beaker (250 mL) for the analysis of Se (VI). The residual supernatant was discarded. A small amount of 2.0% (v/v) HCl was added to the precipitated TiO_2 to make it into colloid again. The colloid was transferred to a colorimetric tube and diluted to 5 mL by 2.0% (v/v) HCl. Se (IV) in the resulting colloid was then determined by HG-AFS.

20 mL conc. HCl was added into the above mentioned beaker filled with 50 mL supernatant. The mixed solution was kept boiling for 30 min to convert Se (VI) to Se (IV). When the solution got cool, 1 mL nano-sized TiO_2 colloid (2.0%) was added and pH value was adjusted to 6.0–7.0. The following treating steps were the same with that of Se (IV). The fluorescence of the obtained colloid sample was determined by HG-AFS and the concentration of Se (VI) was gained.

Another 50 mL water sample was prepared for the determination of total inorganic Se. The water sample was determined by following the same treating steps of Se (VI). The concentrations of Se (IV), Se (VI) and total inorganic Se were all calculated by standard calibration curve method. The standard curve was

Table 1
Instrumental conditions of HG-AFS for the determination of Se (IV).

Negative high voltage (V)	Flow rate of Ar (mL/min)	Lamp current (mA)		Atomization T (°C)	Atomizer H (mm)
		Main	Auxiliary		
280	500	45	45	170	8
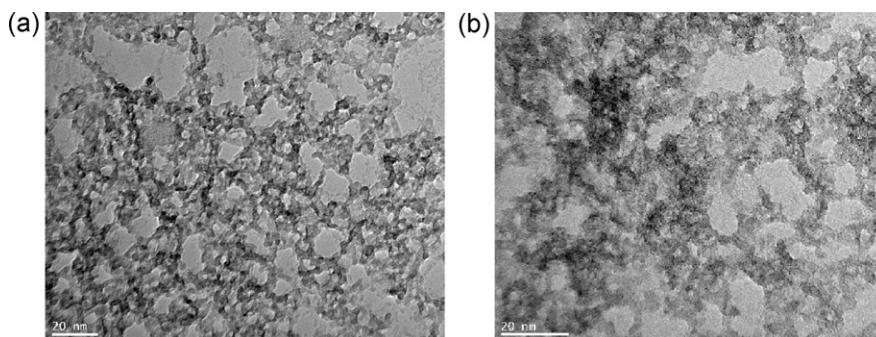
Fig. 1. TEM images of nano-sized TiO$_2$ colloid: (a) original group; (b) control group.

obtained with the samples determined in colloid state, with an R^2 of 0.999.

2.8. Particle size determination of nano-sized TiO$_2$ colloid

The original group of nano-sized TiO$_2$ colloid was prepared by directly diluting 0.5 mL nano-sized TiO$_2$ colloid (2.0%) to 10 mL with ultrapure water. As for control group, about 80 mL ultrapure water and 0.5 mL nano-sized TiO$_2$ colloid (2.0%) was added into a centrifuge tube. The pH value of the mixture was adjusted to 6.0–7.0. After centrifugation at 4500 rpm for 20 min, the precipitated TiO$_2$ was converted to colloid with 2.0% HCl. The obtained colloid was diluted with ultrapure water to 10 mL for testing. The particle size of nano-sized TiO$_2$ colloid in each group was determined by means of TEM.

3. Results and discussion

3.1. Particle size of nano-sized TiO$_2$ colloid

Two groups of nano-sized TiO$_2$ colloid were prepared for TEM test and their results are shown in Fig. 1a and b. Seen from the results of original group (Fig. 1a), the particles of nano-sized TiO$_2$ colloid were coralloid and dispersed well. The size of particle was less than 5 nm and its specific surface area was large which made nano-sized TiO$_2$ colloid possess a strong adsorption ability. By comparing the results of the two groups, similar patterns of the colloid particles and same particle sizes were observed. It showed that HCl could well convert the precipitated nano-sized TiO$_2$ to colloid without affecting the structure of colloid particles. And the viscosity of the obtained colloid solution was close to that of aqueous solution owing to the little use of adsorbent and its small particle size. Therefore this method was suitable for autosampler to obtain precise results.

3.2. Selective adsorption and separation of Se (IV) and Se (VI)

When pH is lower than 4.0, the particles of nano-sized TiO$_2$ colloid disperse well and cannot be effectively separated from the bulk solution. Therefore, the pH value should be set higher than 4.0 theoretically in order to separate nano-sized TiO$_2$ colloid from the solution. A series of pH values were adjusted to determine the adsorption efficiencies for Se (IV) and Se (VI).

The amount of nano-sized TiO$_2$ colloid (0.2%) used for adsorption was 1 mL. The effect of pH on adsorption for selenium species was shown in Fig. 2. The adsorption efficiency for Se (IV) could reach 97.0% or higher when pH was between 6.0 and 8.0, while the adsorbent barely adsorbed Se (VI) with pH being 6.0–7.0. Thus, Se (IV) and Se (VI) showed apparently different adsorption properties on nano-sized TiO$_2$ colloid surface when the pH value of solution was between 6.0 and 7.0.

TiO$_2$ surface was positively, null and negatively charged when the pH value is lower than the isoelectric point, at isoelectric point and higher than isoelectric point, respectively [30]. Selenite or selenate species in a solution may be H$_2$SeO$_3$, HSeO$_3^-$, and SeO$_3^{2-}$, or H$_2$SeO$_4$, HSeO$_4^-$, and SeO$_4^{2-}$, depending on the pH values of solution. The pK_a values for selenic acid (H$_2$SeO$_4$) are <1 and 1.7, and those for selenious acid (H$_2$SeO$_3$) are 2.75 and 8.5 [31]. Therefore, at pH 6.0–7.0, the primary species for Se (IV) and Se (VI) are SeO$_4^{2-}$ and HSeO$_3^-$ respectively [32]. It allows the efficient adsorption of TiO$_2$ for Se (IV). The electrostatic attraction between Se (VI) and TiO$_2$ is too weak to get Se (VI) well adsorbed by TiO$_2$.

In order to verify the electrostatic attraction between TiO$_2$ colloid surface and selenium species, zeta potential of TiO$_2$ samples with adsorbed Se (IV) and/or Se (VI) was measured. Results were shown in Fig. 3. The results showed no significant changes in the
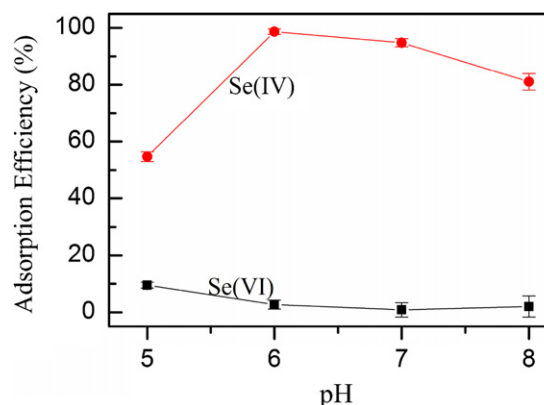
Fig. 2. Effect of pH on the adsorption for selenium species: (■) 20 μg/L Se (VI); (●) 20 μg/L Se (IV). The volume of nano-sized TiO$_2$ colloid (0.2%) used for adsorption was 1 mL.

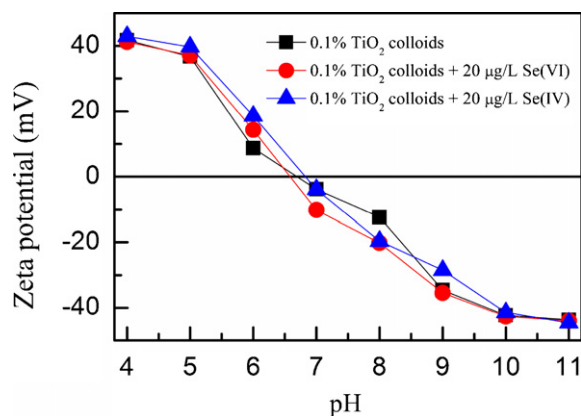**Fig. 3.** Zeta potential of 0.1% TiO$_2$ colloids as a function of pH, 20 μg/L Se (IV) and 20 μg/L Se (VI).
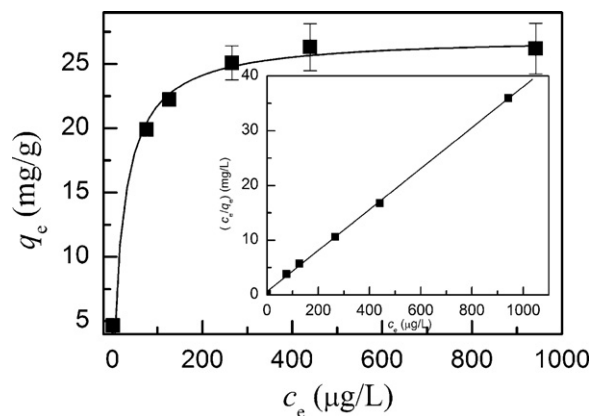

Fig. 4. Dependence of the adsorption amount with the equilibrium concentration of Se (IV). The solid line corresponds to the fits of the data to Eq. (2). Inset: Linear fit of Langmuir adsorption isotherm of Se (IV) on nano-sized TiO$_2$ colloid.

surface potential of TiO$_2$ colloids in the presence of either 20 μg/L Se (IV) or 20 μg/L Se (VI). The same zeta potential patterns was also observed in the adsorption of 50 μmol/L Se (VI) (even up to 500 μmol/L) onto anatase TiO$_2$ nano-powder [33]. The unobvious change of the point of zero charge (pH$_{pzc}$) indicated that both Se (IV) and Se (VI) formed out-sphere complexes with TiO$_2$ colloids. Therefore, Se (IV) showed stronger adsorption affinity than Se (VI) because of its relative higher electrostatic attraction with TiO$_2$ colloids.

The above results provided the basis for the separation of Se (IV) and Se (VI). Considering that the environmental water samples contained both Se (IV) and Se (VI), effect of Se (VI) on the adsorption for Se (IV) was studied. Se (IV)–Se (VI) mixed solution was prepared with each concentration being 20 μg/L, followed by determination of adsorption efficiency for Se (IV). The adsorption efficiency reached higher than 97.0%, showing that 20 μg/L Se (VI) would not interfere the full adsorption for Se (IV). Therefore, when analysing environmental water samples, the trace Se (VI) in it would not affect the adsorption for Se (IV) either.

3.3. Relations between ion strength and nano-sized TiO$_2$ colloid amount

100 mL 20 μg/L Se (IV) solution was prepared with an adjusted pH value between 6.0 and 7.0. Several different volumes of nano-sized TiO$_2$ colloid (0.2%) were adopted. The adsorption efficiency increased from 46% to 97% when raising the volume of nano-sized TiO$_2$ colloid (0.2%) from 0.3 mL to 0.5 mL. In consideration of convenience, 1 mL was adopted to be the volume of nano-sized TiO$_2$ colloid for adsorption efficiency determination.

As for Se (VI) determination in environmental water samples, prereduction procedure was required. According to the reduction process introduced above, 20 mL conc. HCl was added as the reductant. Therefore, a large amount of NaOH aqueous solution was needed to adjust the pH of solution to be 6.0–7.0. The solution was of high ion strength (approx. 3.4 mol/L) after neutralization, and the adsorption efficiency for Se (IV) was 57.4%. It was not unexpected that adsorption efficiency for Se (IV) on nano-sized TiO$_2$ colloid decreased with the increase of ionic strength since out-sphere complex was formed [32]. In order to possess higher adsorption efficiency, dosage of nano-sized TiO$_2$ was optimized. It turned out that 1 mL nano-sized TiO$_2$ colloid (2.0%) could fully adsorb Se (IV) in high ion strength samples. Therefore, 1 mL nano-sized TiO$_2$ colloid (2.0%) was adopted as the adsorbent dosage after reducing Se (VI) in environmental water samples to Se (IV).

3.4. Adsorption isotherm of Se (IV) on TiO$_2$

To study the adsorption isotherms, a series of Se (IV) working solution were prepared with the concentration being 0.1, 0.5, 0.6, 0.8, 1.0 and 1.5 mg/L, respectively. The experiments were carried out under the optimized conditions. As shown in the inset of Fig. 4, a good linear fit (the correlation coefficient R is 0.9996) of the experimental data to Eq. (1) indicates the adsorption of Se (IV) onto TiO$_2$ colloids follows the Langmuir isotherm model.

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{Kq_{max}} \tag{1}$$

$$q_e = \frac{Kq_{max}c_e}{1 + Kc_e} \tag{2}$$

where q_e is the amount of solute adsorbed by gram of TiO$_2$ colloid (mg/g). c_e is the equilibrium concentration (μg/L). K (L/μg) and q_{max} (mg/g) represent Langmuir equilibrium constant and the adsorption maximum capacity of the solute on the TiO$_2$ surface, respectively. However, when using Eq. (1), a high weight is given to the data with largest errors. For this reason, K and q_{max} values were recovered from the nonlinear fit of the experimental data to Eq. (2). The adsorption constants and adsorption capacity are $4.05(\pm1.96) \times 10^{-2}$ and 27.10 ± 1.65 for Se (IV) adsorption onto TiO$_2$ colloids, respectively (Fig. 4). The adsorption maximum capacities of selenium on the nano-sized TiO$_2$ colloid are comparable with those obtained by CTAB-modified alkyl silica [Se (VI), 5.0 mg/g] [19], Diaion HP-2MG [Se (IV), 5.20 mg/g] [21] and nano-sized TiO$_2$ powder [Se (IV), 14.6 mg/g] [24]. The results gained above showed that the interaction between TiO$_2$ and Se (IV) is mainly a physical interaction.

3.5. Effect of coexistent ions

The effect of some ordinary ions in real water was studied. Various amounts of different ions were added into 100 mL solution containing 0.05 μg Se (IV), and resulting solution contained Na$^+$ (92 mg), K$^+$ (3.9 mg), Mg^{2+} (4.8 mg), Ca^{2+} (4 mg), Cl$^-$ (149.1 mg), NO$_3^-$ (6.2 mg), SO$_4^{2-}$ (19.2 mg) and F$^-$ (4.5 μg). The enrichment procedure was then followed. The recovery of Se (IV) analysis was $107.3 \pm 4.9\%$ ($n = 3$), which showed that the coexistent ions had little effect on the proposed method.

3.6. Detection limit and relative standard deviation

6 parallel 100 ng/L Se (IV) solution (100 mL) and 6 parallel 200 ng/L Se (VI) (50 mL) were analyzed according to the procedures

Table 2
Speciation of Se (IV) and Se (VI) in environmental water samples (sample volume: l00 mL; final volume: 5 mL; $n = 3$).

Samples	Se added		Se found		Recovery (%)	
	Se (IV)	Se (VI)	Se (IV)	Se (VI)	Se (IV)	Se (VI)
Donghu water (μg/L)	–	–	0.13 ± 0.01	0.24 ± 0.02	–	–
	0.10	0.20	0.23 ± 0.01	0.44 ± 0.01	100.0 ± 2.0	100.0 ± 1.3
Yangtze River water (μg/L)	–	–	0.10 ± 0.01	0.20 ± 0.01	–	–
	0.10	0.20	0.19 ± 0.00	0.39 ± 0.02	90.0 ± 1.0	95.0 ± 1.3

of analyzing Se (IV) and Se (VI) in water samples. The detection limit (3σ) and the relative standard deviation (R.S.D) of this method for Se (IV) were 24 ng/L and 7.8%, respectively. The detection limit (3σ) and the relative standard deviation (R.S.D) of this method for Se (VI) were 42 ng/L and 7.0%, respectively. The detection limit (3σ) of this method was much lower than some other methods for selenium speciation [4,10,25,34–36].

3.7. Analysis of environmental reference material and real water samples

An environmental reference material (GSBZ 50031-94) with a Se (IV) concentration of 26.2 ± 2.4 μg/L was analyzed. 2 mL environmental reference material was added into about 90 mL pure water. The resulting solution was treated and determined according to the preconcentration and determination of Se (IV) in environmental water samples. The sample was concentrated to 5 mL and its theoretical Se (IV) concentration was 0.4 times as much as that of environmental reference material. Therefore, the obtained concentration was multiplied by 2.5 times in order to make a comparison with the certified value. The result was 26.2 ± 2.7 μg/L ($n = 4$), which was in good agreement with the certified value.

The above-mentioned method was used for the analysis of Se (IV) and Se (VI) in water samples from Donghu Lake and Yangtze River. The results were listed in Table 2. In order to compare and convince these results with the proposed method, the speciation analysis of those two water samples was also carried out by using conventional method (State Standard of the People's Republic of China, No. GB/T 8538-2008) after preconcentration. The concentration of total inorganic selenium for Donghu Lake and Yangtze River were respectively found to be 0.34 ± 0.02 μg/L and 0.30 ± 0.01 μg/L, which were coincidence with the results obtained by using the proposed method (0.37 ± 0.03 μg/L and 0.30 ± 0.02 μg/L). All the results showed that it was a satisfactory method for speciation of ultra-trace Se (IV) and Se (VI) in environmental water samples.

4. Conclusion

The innovation of this method lies in the application of nano-sized TiO_2 colloid as sorbent for speciation of ultra-trace Se (IV) and Se (VI). Se (IV) and Se (VI) have different adsorption properties by using nano-sized TiO_2 colloid as adsorbent under certain pH values, which guarantees their separation. Coupled with HG-AFS, the colloid with adsorbed selenium can be determined directly. By introducing adsorbent, the detection limit is lowered significantly with preconcentration procedure. Compared with the traditional methods which require desorption process, the method introduced in this paper appears to be more advantaged with short-time separation and preconcentration, simple operation and fast analysis. Consequently, this method can be applied to determining ultra-trace Se (IV) and Se (VI) in environmental water samples with great success.

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