JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

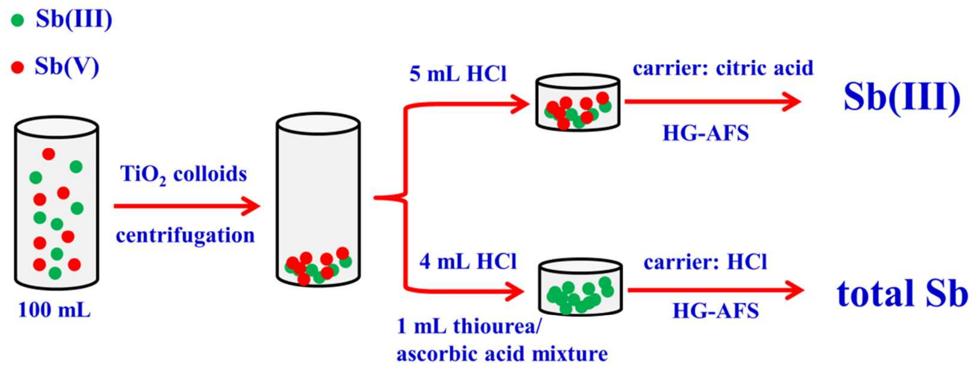
www.rsc.org/jaas

Speciation Analysis of Antimony in Water Samples via Combined Nano-Sized TiO_2 Colloid Preconcentration and AFS Analysis

Xingwen Wang, Xuankun Li, Xu Zhang, Shahua Qian*

Department of Environmental Science, Hubei Biomass-Resource Chemistry and Environmental Biotechnology Key Laboratory, Wuhan University, Wuhan, 430079, P.R. China

A method for the speciation of Sb was developed using nano-sized TiO_2 colloids preconcentration and HG-AFS as a determination means.



Corresponding Author: Tel: 86-27-68778551, Fax: 86-27-68778893, Email: qiansh@whu.edu.cn (Shahua Qian)

Speciation Analysis of Antimony in Water Samples via Combined Nano-Sized TiO_2 Colloid Preconcentration and AFS Analysis

Xingwen Wang, Xuankun Li, Xu Zhang, Shahua Qian*

Department of Environmental Science, Hubei Biomass-Resource Chemistry and Environmental Biotechnology Key Laboratory, Wuhan University, Wuhan, 430079, P.R. China

Abstract: A method for the speciation of Sb(III) and Sb(V) in water samples was developed using nano-sized TiO_2 colloids as an adsorbent and hydride generation atomic fluorescence spectrometry (HG-AFS) as a determination means. The adsorption efficiency for Sb(III) and Sb(V) exceeded 98.0% within a short time when the pH value was 6.0. Two carrier acid solutions, citric acid (1%) for Sb(III) and HCl (2%) for total Sb, were used. After the determinations of Sb(III) and total Sb, Sb(V) could be calculated by subtraction. The effects of such conditions as the Sb(III)/Sb(V) ratio and the presence of coexisting ions were studied. The enrichment factors for Sb(III) and total Sb were both 20. The detection limits of this method were 10 ng/L for Sb(III) and 13 ng/L for total Sb. The relative standard deviations (n=6) were 6.7% for Sb(III) and 4.4% for total Sb, demonstrating good analytical precision. The accuracy of the proposed method was checked with an environmental water sample certified reference material (GSB 07-1376-2001) with a Sb(III) concentration of 1.24±0.26 mg/L. The obtained Sb(III) concentration was 1.22±0.03 mg/L, which was in good agreement with the certified value. The developed method was simple, fast and sensitive with no filtration or desorption steps and provided low detection limits for Sb(III) and Sb(V).

Keywords: Antimony speciation; Nano-sized TiO_2 colloids; HG-AFS

Corresponding Author: Tel: 86-27-68778551, Fax: 86-27-68778893, Email: qiansh@whu.edu.cn (Shahua Qian)

1. Introduction

Water is the source of life. The determination and analysis of the contents of aquatic chemical substrates are important for research on environmental change and the influence of human activities on water quality as well as the prevention of water pollution. Antimony (Sb) exists as Sb^{3+} and Sb^{5+} in the natural aquatic environment, but the toxicity of Sb^{5+} is 10 times higher than that of Sb^{3+}.[1] Therefore, it is more meaningful to analyse antimony speciation than to determine the total concentration of antimony in water samples. The analysis of the speciation of Sb^{3+} and Sb^{5+} is much more difficult than that of total antimony because of the quite low concentrations of antimony in natural water samples. Thus, speciation methods with high sensitivity and selectivity for antimony need to be established.

Antimony speciation in water samples is usually investigated by on-line instrumental hyphenated techniques or a combination of preconcentration and instrumental analysis.[2-4] Séby determined Sb^{3+} and Sb^{5+} in water using high-pressure liquid chromatography−inductively coupled plasma−mass spectrometry (HPLC-ICP-MS), achieving detection limits of 0.1 μg/L for Sb^{3+} and Sb^{5+}.[5] High pressure liquid chromatography−inductively coupled plasma−atomic emission spectrometry (HPLC-ICP-AES),[6] high pressure liquid chromatography−atomic fluorescence spectrometry (HPLC–AFS),[7, 8] gas chromatography−inductively coupled plasma−mass spectrometry (GC-ICP-MS), GC-AFS, GC-AAS[2] and graphite furnace−atomic absorption spectrometry (GF-AAS)[9] were reported to provide good performance in the analysis of trace Sb^{3+} and Sb^{5+} in water samples. In recent years, several studies have reported antimony speciation utilising the combination of preconcentration and instrumental analysis. A 2 ng/L determination limit was obtained using liquid-phase micro-extraction combined with ETAAS.[10] Solid-phase extraction using carbon nano-tubes combined with ETAAS was also proposed by López-García et al. for antimony speciation, with a determination limit of 50 ng/L.[11] In most cases, the concentrations of Sb^{3+} and total Sb were analysed first due to the different complexation or hydrogenation behaviours of Sb^{3+} and Sb^{5+}, after which the concentration of Sb^{5+} can be calculated by subtraction.

In recent years, our research group has been working on the analysis of ultra-trace metal ions using nano-sized TiO_2 colloids as an adsorbent paired with highly sensitive HG-AFS and GFAAS, yielding some promising results.[12-16] Compared with nano-sized TiO_2 powder, the colloids possess the advantage of easily changing from the solid phase to the colloid phase after adsorption and centrifugation. The dosage of colloids is low because of their high adsorption capacity, and an autosampler can be used because the viscosity of resulting solution is close to that of aqueous solution. Moreover, the concentrated analyte samples in colloidal form can be directly analysed by AAS or AFS without desorption. In this work, nano-sized TiO_2 colloids were used for the preconcentration of Sb^{3+} and Sb^{5+} in environmental water samples because the adsorption could reach 98% in a pH range of 5.0 to 8.0.

HG-AFS is one of the most sensitive methods for the determination of antimony, and it is also the Chinese standard method for the determination of total antimony in mineral water. The measurement conditions were explored to apply this method to the antimony speciation (Sb^{3+}, Sb^{5+}) after pre-concentration. The results showed that Sb^{5+} has only a slight influence on the determination of Sb^{3+} when 1% citric acid buffer solution was used as the carrier liquid, and the Sb^{5+} concentration can be calculated as the difference between the total antimony and Sb^{3+} concentrations.

A combination method using nano-sized TiO_2 colloids as an adsorbent for preconcentration and HG-AFS as a determination means was suggested by this work for the speciation of Sb^{3+} and Sb^{5+}, which was simple and fast (without desorption after preconcentration). The detection limits of our method were 10 ng/L for Sb^{3+} and 13 ng/L for total Sb. The relative standard deviations (n=6) were 6.7% for Sb^{3+} and 4.4% for total Sb. This method was also applied to the speciation of Sb^{3+} and Sb^{5+} in environmental water samples, and the results were satisfactory.

2. Materials and Methods

2.1 Reagents

All chemicals and reagents used throughout this study were of analytical grade or higher purity. Nanometre-size TiO_2 colloids (2.0% w/w) were supplied by Infrared Academy of Wuhan University (Wuhan, China). The characterisation of the used TiO_2 colloids was presented in our previous work.[15] Sb(III) standard solutions (1000 mg/L) were prepared using antimony trioxide and diluting to 1000 mL. A total of 100 mg L^{-1} Sb(V) was oxidised from Sb(III) standard solutions (1000 mg/L) by potassium permanganate and sulphuric acid. A series of standard working solutions were prepared by diluting the standard stock solution with 2% (v/v) HCl. Thiourea-ascorbic acid solution (5% w/w) was dissolved with high-purity deionised water. The AFS carrier liquid for total Sb was prepared as 1.5% (w/w) KBH_4 and 2.0% (v/v) HCl. The AFS carrier liquid for Sb(III) was prepared as 1.5% (w/w) KBH_4 and 1% (w/w) citric acid. HCl and NaOH aqueous solutions were used to adjust the pH of the solutions. Ar (99.99%) was applied as a carrier gas. Water samples were drawn from Donghu Lake (Wuhan, Hubei Province, China) and Yangtze River (Wuhan, Hubei Province, China). The environmental reference material (GSB 07-1376-2001) was purchased from the Institution for Environmental Reference Materials of the Ministry of Environmental Protection (Beijing, China). All of the solutions were prepared with ultra-pure water (resistivity >18.0 MΩ/cm).

2.2 Instruments

A PF6-2 non-dispersive atomic fluorescence spectrometer (Beijing Purkinje General Instruments Co, Ltd, Beijing, China) equipped with a HAF-2 antimony hollow cathode lamp was used for antimony determination. The principle for the analysis of ions was described in our previous work.[15] The instrumental conditions for the analysis are listed in **Table 1.** The pH values were measured using a Mettler-Toledo 320-S pH meter (Mettler-Toledo, Greifensee, Switzerland). An LD5-2A centrifuge (Beijing Medical Centrifuge Factory, Beijing, China) was used to separate the suspensions. The zeta potentials of TiO_2 colloids in the presence and absence of Sb(III) or Sb(V) were determined using a Zetasizer 3600 (Malvern Instrument, UK).

Table 1 Instrument conditions for the analysis of Sb

Negative high voltage /V	Flow rate of Ar /mL min^{-1}	Lamp current /mA		Atomization T / ℃
		Main	Auxiliary	
280	400	30	30	170

2.3 Methods

2.3.1 Determination of the adsorption ratio for Sb(III) and Sb(V)

First, 10-mL standard solutions of Sb(III) or Sb(V) (100 μg/L) were placed in a centrifuge tube (100 mL) containing 70 mL of ultra-pure water and then supplemented with 0.5 mL of nano-sized TiO_2 colloids. The pH of the mixture was adjusted to a fixed value. The mixed solution was shaken for 1 min by hand and then centrifuged for 20 min at 4,500 rpm. The supernatant was transferred to a volumetric flask (100 mL), after which 10 mL of thiourea-ascorbic acid solution (5% w/w) and 2 mL of conc. HCl were added. The solution was subsequently diluted to 100 mL. The Sb(III) or Sb(V) concentration of the supernatant was determined by AFS with a 2% HCl carrier solution. The fluorescence obtained was compared to that of Sb(III) or Sb(V) standard solution (10 μg/L) without adsorption to calculate the adsorption ratio of nano-sized TiO_2 colloids.

2.3.2 Preconcentration and determination of Sb(III) in water samples

First, 100-mL water samples were added to a centrifuge tube (120 mL) after air pumping filtration using a 0.45-μm filtration membrane. Next, 0.5 mL of nano-sized TiO_2 colloids was added to the centrifuge tube. The pH of the solution was adjusted to 6.0. The solution was centrifuged for 20 min at 4,500 rpm.

After centrifugation, the TiO_2 precipitates containing Sb were reconverted to colloids with 2% HCl to a total volume of 5 mL. The concentration of Sb(III) in the resulting colloid samples was determined using a citric acid buffer carrier solution (1% w/w, pH=4.38).

2.3.3 Preconcentration and determination of Sb(V) in water samples

After centrifugation, the TiO_2 precipitates containing Sb were reconverted to colloids to a total volume of 5 mL by the addition of 1 mL of thiourea-ascorbic acid solution and 4 mL of 2% HCl. The concentration of total Sb was determined with carrier HCl (2% v/v). The concentration of Sb(V) in the water samples could be calculated as the difference between the total Sb and Sb(III). A 20-fold preconcentration was used in this work because it is convenient for centrifugation, as the capacity of the centrifugation tube was 100 mL.

3. Results and Discussion

3.1 Effects of HCl, citric acid and KBH_4 on the speciation analysis

Under the acidic environment provided by the carrier solutions, KBH_4 can reduce Sb(III) to produce corresponding the hydride (H_3Sb). H_3Sb is atomised into hydrogen and antimony atoms in the atomiser cell and then analysed by hydride generation atomic fluorescence spectrometry (HG-AFS). The acid type and concentration as well as the concentration of KBH_4 could affect the speciation analysis of Sb. In total antimony mineral water national standard methods, the acidity of the sample solution system is 1% HCl, and the carrier liquid is 2% HCl. As shown in **Fig. 1**, under these conditions, Sb(V) can be partially reduced to Sb(III), even in the absence of ascorbic acid. Therefore, Sb(III) and Sb(V) cannot be distinguished.

However, when acetic acid (HAc) or citric acid (CA) buffer solution were used as the carrier liquids, the fluorescence signals of Sb(V) and Sb(III) were absent and strong, respectively, and the fluorescence of the former had little effect on that of latter. Although increasing the citric acid and HCl concentrations could improve the sensitivity toward both Sb(III) and Sb(V), the effect of Sb(V) on the signal of Sb(III) could be no longer be ignored. Moreover, the TiO_2 colloids become unstable with increasing citric acid concentration.

KBH_4 concentrations in the range of 1% to 4% have little effect on the speciation analysis of Sb. Therefore, the concentrations of KBH_4, citric acid and HCl were selected as 1.5% (w/w), 1% (w/w) and 2.0% (v/v), respectively, in this work.

3.2 Influence of Sb(V) on Sb(III) fluorescence intensity

Different proportions of Sb(III) (10 μg/L) and Sb(V) (0 to 90 μg/L) were prepared. The mixtures were determined according to 2.3.2 to investigate the effect of the ratio of Sb(V) to Sb(III) on the determination. The relative fluorescence signals of the mixtures were presented in **Fig. 2**.

As shown in **Fig. 2**, in this method, within the range of Sb(III)/Sb(V) from 10/0 to 10/90, the presence of Sb(V) had little effect on the determination of Sb(III). The concentration of Sb(III) could be determined alone when 1% CA was used as the carrier liquid.

3.3 Effect of pH on the adsorption of Sb(III) and Sb(V) over TiO_2 colloids

When pH is lower than 4.0, the nano-sized TiO_2 colloids disperse well and cannot be separated from the bulk solution effectively. Therefore, the pH value should be set higher than 4.0 to separate the colloidal particles from the solution. A series of pH values were chosen to determine the adsorption efficiencies for Sb(III) and Sb(V) according to method 2.3.1. The effect of pH on the adsorption of antimony species is illustrated in **Fig. 3**.

As shown in **Fig. 3**, the adsorption of Sb(III) and Sb(V) is slightly dependent on pH. The adsorption efficiency for Sb(III) and Sb(V) could exceed 98.0% when the pH was between 4.0 and 7.0. The high adsorption ratio indicated that both Sb(III) and Sb(V) showed high adsorption affinity onto TiO_2 colloids.

To verify the electrostatic attraction between TiO_2 colloid surface and Sb species, the zeta potential of the TiO_2 samples with adsorbed Sb(III) and Sb(V) was measured, and the results are shown in **Fig. 4**. The results showed noticeable changes in the surface potential of TiO_2 colloids in the presence of either 50 μg/L Sb(III) or 50 μg/L Sb(V). The clear change in the point of zero charge (pH_{pzc}) indicated that both Sb(III) and Sb(V) formed inner-sphere complexes with TiO_2 colloids. The same zeta potential patterns were also observed in the adsorption of Ge(IV) over TiO_2 colloids[16] and the adsorption of As(III)/As(V) onto TiO_2 nano-powder,[17] whereas a different pattern was observed for the adsorption of Se(IV)/Se(VI) onto TiO_2 colloids.[15]

3.4 Effect of nano-sized TiO_2 colloid concentration on the adsorption efficiency

Different volumes of nano-sized TiO_2 colloids (0.05 mL to 0.6 mL) were, respectively added to 100 mL 10 μg/L Sb(III) and Sb(V) solutions. The sorption efficiency of Sb(III) was relatively low when the TiO_2 colloid amount was less than 0.4 mL. Quantitative sorption (>98.0%) of Sb(III) occurred with the increase of TiO_2 colloid amount (higher than 0.4 mL in this work). 0.5 mL TiO_2 colloids was chosen for the latter study, which resulted in complete adsorption of Sb(III) and Sb(V) and facilitated the experiments operation.

3.5 Adsorption isotherms of Sb(III) and Sb(V) on TiO_2

To study the adsorption isotherms, a series of Sb(III) or Sb(V) working solutions were prepared with concentrations of 0.1, 0.5, 0.6, 0.8, 1.0, 1.5 and 2.0 mg/L, respectively. The relationship between q_e and c_e was simulated using the Langmuir isotherm model (Eq. (1)):

$$q_e = \frac{K q_{max} c_e}{1+K c_e} \quad (1)$$

where q_e is the amount of solute adsorbed per gram of TiO_2 colloids (μg/g). c_e is the equilibrium concentration (μg/L). K and q_{max} (μg/g) represent the equilibrium constant and maximum adsorption capacity of the solute on the TiO_2 surface, respectively.

As shown in **Fig. 5**, the amount of both Sb(III) and Sb(V) adsorbed onto the TiO_2

colloids increased sharply and then plateaued as the corresponding equilibrium concentration increased. The experimental data could be well simulated by the Langmuir isotherm model, which indicated both Sb(III) and Sb(V) could form a single adsorption layer over the TiO_2 colloids. The calculated maximum adsorption amount was 46.4 mg/g and 70.8 mg/g for Sb(III) and Sb(V), respectively.

3.6 Influence of coexisting ions on the adsorption and preconcentration of Sb(III)

The effect of coexisting ions in real water on the adsorption and preconcentration of Sb(III) was studied. Various amounts of ions were added to a 100-mL solution containing 0.25 μg/L Sb(III). The resulting solution contained K^+ (1.8 mg), Na^+ (4 mg), Ca^{2+} (2 mg), Mg^{2+} (2.4 mg), Cl^- (74.55 mg), SO_4^{2-} (9.9 mg), NO_3^- (3.1 mg) and F^- (0.005 mg). Although there are many other ions co-existing in the environmental samples, the concentration of the ions used above were 200 (F^-)-3×10^6 (Cl^-) times that of Sb(III), and the extraordinarily high concentration of the chosen ions could compensate for the effects of other coexisting ions. The enrichment procedure was then followed according to 2.3.2. The recovery of Sb(III) was 99.5%, which showed that coexistent ions had little effect on the proposed method.

3.7 Detection limit and relative standard deviation

The detection limit (D.L.) of the analysis method was obtained by Eq. (2).

$$\text{D.L.} = 3\sigma \times \frac{c}{\overline{X}} = 3c \times \frac{\sigma}{\overline{X}} = 3c \times RSD \qquad (2)$$

where $\overline{X}$ is the mean signal of the independent analysis of a sample with a known concentration (c) close to the LOD. σ is the standard deviation, and *RSD* is the relative standard deviation.

3.7.1 Detection limit (D.L.) of Sb(III)

A 50 ng/L Sb(III) solution was enriched 20 times according to 2.3.2 and subjected to AFS. The detection limit and the relative standard deviation (*RSD*, *n*=6) of Sb(III) were 10 ng/L and 6.7%, respectively.

3.7.2 Detection limit of total Sb

A 100 ng/L Sb solution (containing Sb(III) 50 ng/L, Sb(V) 50 ng/L) was enriched 20 times according to section 2.3.3 and subjected to AFS. The detection limit and the *RSD* (*n*=6) of total Sb were 13 ng/L and 4.4%, respectively.

3.7.3 Accuracy of the method

An environmental reference material (GSB 07-1376-2001) with a Sb(III) concentration of 1.24±0.26 mg/L was analysed. The environmental reference material was diluted by a certain factor gradually because it was too thick to be determined. The reference material solution after diluting was determined by 2.3.2. The obtained Sb(III) concentration was 1.22±0.03 mg/L, which was in good agreement with the certified value. The *t* value was 1.63 (α=0.05, *n*=6), which was lower than the critical value (2.571). The *t*-test results indicated that the analysed value was not statistically significantly different from the certified value. The RSD for the analysis of the reference material was 2.5%, which was much lower than the RSD obtained in section 3.8.1 (6.7%). The analysis of samples with lower concentrations will most likely result in higher RSD values, while the analysis of samples with higher concentrations will most likely yield lower RSD values.

3.8 Analysis of natural water samples

The above-mentioned method was used for the analysis of Sb(III) and Sb_{total} in water samples from Donghu Lake and the Yangtze River. The results were listed in Table 2. The concentrations of Sb(V) were found to be 0.07 and 0.06 μg/L for Donghu Lake and the Yangtze River, respectively.

Table 2 Determination of Sb(III) and total antimony (Sb_{total}) species in water samples (sample volume: l00 mL, final volume: 5 mL, *n*=3).

Sample	Added (μg/L)		Found (μg/L)		Recovery (%)	
	Sb (III)	Sb_{total}	Sb (III)	Sb_{total}	Sb (III)	Sb_{total}
Donghu	———	———	0.13±0.02	0.20±0.04	———	———

Lake	0.20	0.40	0.32±0.02	0.57±0.02	95.0±6.0	92.5±3.2
Yangtze River	———	———	0.00	0.06±0.01	———	———
	0.10	0.20	0.10±0.01	0.26±0.02	100.0±10.0	100.0±7.7

4. Conclusions

The innovation of this method lies in the application of nano-sized TiO_2 colloids as an adsorbent for the speciation of Sb(III) and Sb(V) to increase the detection limit. Sb(III) and Sb(V) could be selectively analysed by the use of appropriate carrier solutions. The results suggested that this method had many advantages, such as a simple preconcentration process (without desorption), good selectivity and anti-interference ability, low detection limit and good precision. The detection limit (D.L.) and the relative standard deviation (RSD, *n*=6) of this method were 10 ng/L and 6.7% for Sb(III), respectively, and 13 ng/L and 4.4% for total Sb, respectively. The proposed method can be applied to determine ultra-trace Sb(III) and Sb(V) in environmental water samples with highly satisfactory results.

Acknowledgment

This research was financially supported by the National Natural Science Foundation of China (Grant No. 20877059) and National Major Science and Technology Projects: Water Pollution Control and Management (2013ZX07503-001).

References

1. E.Russeva and I.Havezov, *Anal. Lab.*, 1998, 115-127.
2. R. Miravet, E. Hernández-Nataren, A. Sahuquillo, R. Rubio and J. F. López-Sánchez, *TrAC Trends in Analytical Chemistry*, 2010, 29, 28-39.
3. Z. Ge and C. Wei, *Journal of Chromatographic Science*, 2013, 51, 391-399.
4. S. L. C. Ferreira, W. N. L. dos Santos, I. F. dos Santos, M. M. S. Junior, L. O. B. Silva, U. A. Barbosa, F. A. de Santana and A. F. de S. Queiroz, *Microchem J.*, 2014, 114, 22-31.
5. F. Séby, C. Gleyzes, O. Grosso, B. Plau and O. F. X. Donard, *Analytical and*

Bioanalytical Chemistry, 2012, 404, 2939-2948.
6. N. Ulrich, *Analytica Chimica Acta*, 1998, 359, 245-253.
7. I. De Gregori, W. Quiroz, H. Pinochet, F. Pannier and M. Potin-Gautier, *Talanta*, 2007, 73, 458-465.
8. I. De Gregori, W. Quiroz, H. Pinochet, F. Pannier and M. Potin-Gautier, *Journal of chromatography. A*, 2005, 1091, 94-101.
9. D. Mendil, H. Bardak, M. Tuzen and M. Soylak, *Talanta*, 2013, 107, 162-166.
10. J. M. Serafimovska, S. Arpadjan and T. Stafilov, *Microchemical Journal*, 2011, 99, 46-50.
11. I. López-García, R. E. Rivas and M. Hernández-Córdoba, *Talanta*, 2011, 86, 52-57.
12. S. H. Qian, H. Lin, X. Q. Li, M. Xiao, H. B. Deng and L. J. Xiang, *Wuhan University Journal of Natural Sciences*, 2007, 2, 349-352.
13. S. Qian, S. Zhang, Z. Huang, M. Xiao and F. Huang, *Microchimica Acta*, 2009, 166, 251-254.
14. S. Qian, Z. Huang, J. Fu, J. Kuang and C. Hu, in *Analytical Methods*, 2010, vol. 2, p. 1140.
15. J. Fu, X. Zhang, S. Qian and L. Zhang, *Talanta*, 2012, 94, 167-171.
16. L. Xiang, X. Zhang, M. Lu, S. Qian and S. Mo, *Journal of Analytical Atomic Spectrometry*, 2012, 27, 359-363.
17. M. Pena, X. Meng, G. P. Korfiatis and C. Jing, *Environmental Science & Technology*, 2006, 40, 1257-1262.

Figure Captions

Fig. 1 Fluorescence of Sb(III) and Sb(V) with HCl, CA and HAc carrier solutions. Sb(III)=10 μg/L, Sb(V)=10 μg/L, mixture: 10 μg/L Sb(III) and 10 μg/L Sb(V)

Fig. 2 Effect of Sb(V) on the fluorescence intensity of Sb(III)

Fig. 3 Effect of pH on the adsorption ratio for Sb(III) and Sb(V)

Fig. 4 Zeta potential of 0.1% TiO_2 colloids as a function of pH for 50 μg/L Sb(III) and 50 μg/L Sb(V)

Fig. 5 Dependence of the adsorption amount on the equilibrium concentration of Sb(III) and Sb(V). Lines represent the fit of the data to the Langmuir adsorption isotherm model

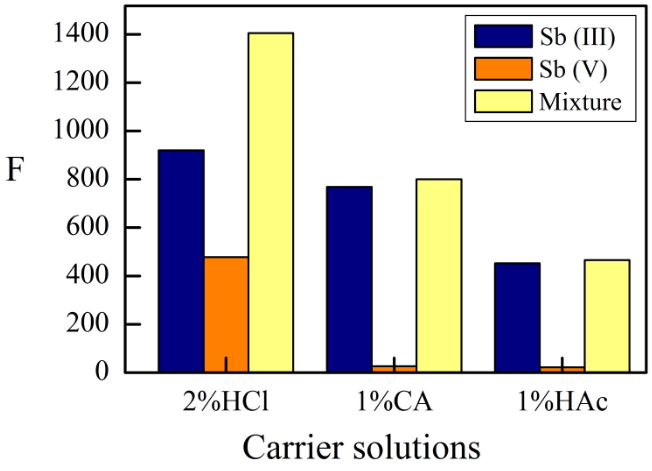


Figure 1

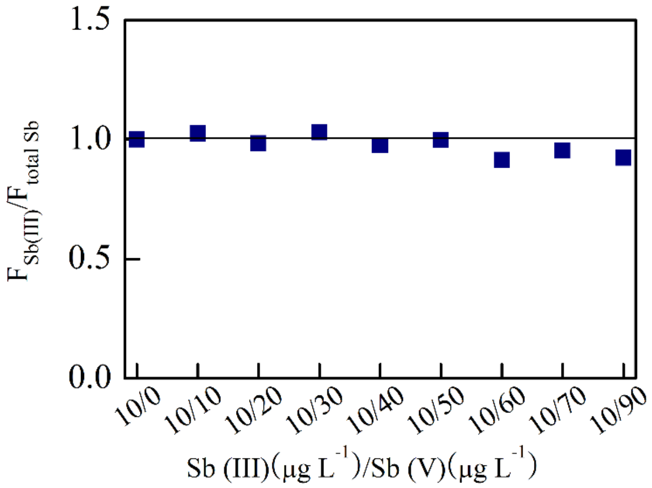


Figure 2

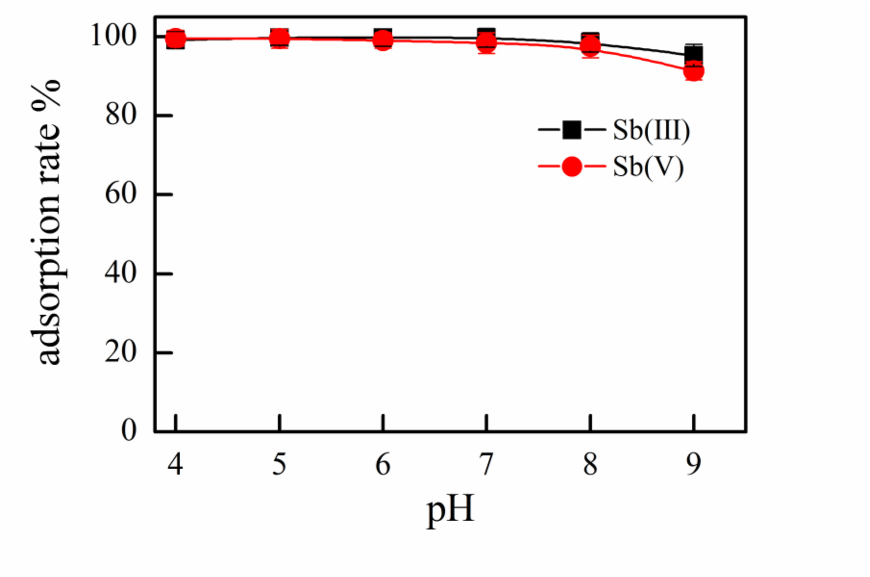


Figure 3

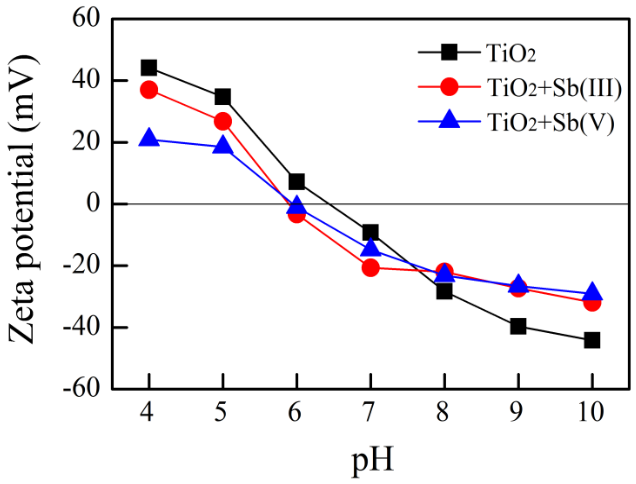


Figure 4

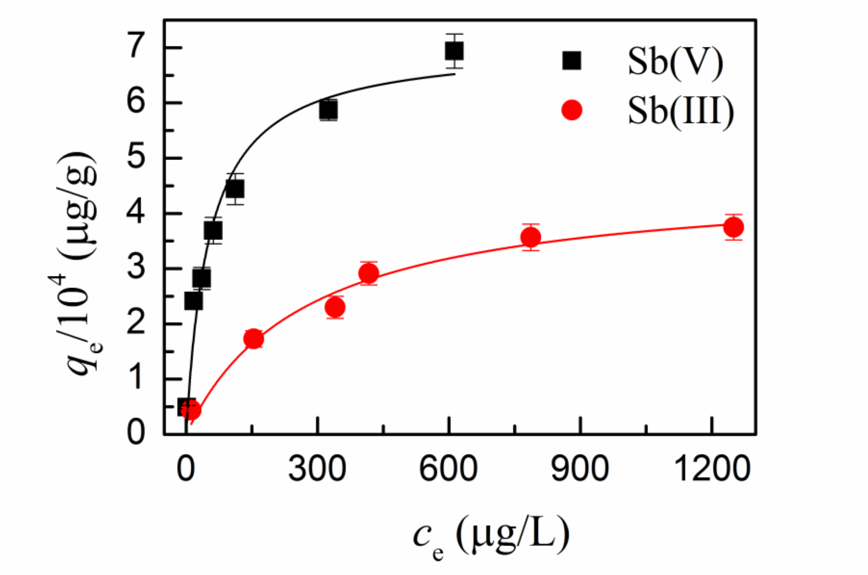


Figure 5