



## Short communication

# Determination of mercury and selenium in herbal medicines and hair by using a nanometer TiO<sub>2</sub>-coated quartz tube atomizer and hydride generation atomic absorption spectrometry

Shun-Xing Li<sup>a,b,\*</sup>, Feng-Ying Zheng<sup>a,b</sup>, Shu-Jie Cai<sup>a</sup>, Tian-Shou Cai<sup>a</sup>

<sup>a</sup> Department of Chemistry & Environmental Science, Zhangzhou Normal University, Zhangzhou 363000, China

<sup>b</sup> Fujian Province University Key Laboratory of Analytical Science (Zhangzhou Normal University), Zhangzhou 363000, China

## ARTICLE INFO

## Article history:

Received 1 December 2010

Received in revised form 7 February 2011

Accepted 8 February 2011

Available online 15 February 2011

## Keywords:

Nanometer TiO<sub>2</sub>

Hydride generation atomic absorption spectrometry

Mercury

Selenium

Nanometer TiO<sub>2</sub>-coated quartz tube atomizer

## ABSTRACT

The nanometer TiO<sub>2</sub> particle was coated onto the inner wall of a T-shaped quartz tube atomizer (QTA) and then was used as a new atomizer (NT-QTA) for the determination of Hg and Se by hydride generation atomic absorption spectrometry (HGAAS). After coating 67.4 mg TiO<sub>2</sub> on a quartz tube, the analytical performance of NT-QTA-HGAAS was compared to conventional QTA-HGAAS and it was improved as follows: (a) the linear range of the calibration curves was expanded from 10.0–80.0 ng mL<sup>-1</sup> to 5.0–150.0 ng mL<sup>-1</sup> for Hg, and from 10.0–70.0 ng mL<sup>-1</sup> to 5.0–100.0 ng mL<sup>-1</sup> for Se; (b) the characteristic concentration of was decreased from 2.8 ng mL<sup>-1</sup>/1% to 1.1 ng mL<sup>-1</sup>/1% for Hg and from 1.2 ng mL<sup>-1</sup>/1% to 0.8 ng mL<sup>-1</sup>/1% for Se; and (c) the interference from the coexistence of As on the determination of Hg and Se could be eliminated. The achieved technique was applied for the determination of Hg and Se in herbal medicines and hair.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

It is important to monitor the toxic elements in hair and herbal medicines. Herbal medicines are widely consumed as home remedies and food additives. It is reported that herbal medicines are currently used by about 70–80% of the world's population [1]. Hair is a preferred biomarker of metal exposure because: (a) the concentrations of trace elements in hair were up to ten-fold higher than the levels found in blood or urine samples [2]; (b) the sampling of hair is so simple that it could be a practical biomonitoring tool for large populations [3]; and (c) it is less invasive than blood collection [4].

Mercury is well known for its extremely high toxicity and a very low concentration of mercury may cause health hazard [5]. Health problems can arise from excess as well as deficiency of selenium and a narrow range of selenium concentration differentiates it from an essential nutrient to a toxic material [6].

Mercury and selenium are currently determined by hydride generation atomic absorption spectrometry (HGAAS) [7,8]. An

important advantage is related to the analyte separation from the matrix components, offering considerable suppression of matrix effects [3]. Because quartz has a sufficiently high melting point and a low thermal expansion coefficient, the conventional quartz tube atomizer (QTA) is widely used for the atomization in HGAAS recently [9,10]. The system is called “quartz tube atom trap-hydride generation atomic absorption spectrometry (QTA-HGAAS)”, as illustrated in Fig. 1. The sensitivity improvement is attributed to the increased residence time of the analyte atoms in the light path [10]. Furthermore, the more stable chemical environment due to homogenous temperature in quartz tube enhances the numbers of neutral atoms, thereby increasing the sensitivity. Despite the advantages of this kind of atomizer, curved calibration graphs and low tolerance to the arsenic interferences during the atomization step have been reported [9,11]. The concentrations of Hg and Se in hair and herbal medicines are at the level of ng g<sup>-1</sup> and their content ranges are wide [12]. The sensitivity and linear range of QTA-HGAAS are so limited that it could not be used for the determination of Hg and Se in hair and herbal medicines.

Trying to minimize the deficiencies observed for QTA-HGAAS, W-coil [13,14], platinum-coated W-coil [15], gold-coated W-coil [16], and miniature quartz [17] are used for online atom trap and the principle involves generation of volatile species, usually hydrides, trapping these species on the surface of an atom trap held at an optimized temperature, and, finally, revolatilizing the

\* Corresponding author at: Department of Chemistry & Environmental Science, Zhangzhou Normal University, Zhangzhou 363000, China. Tel.: +86 596 2523251; fax: +86 596 2520035.

E-mail address: [lishunxing@fjzs.edu.cn](mailto:lishunxing@fjzs.edu.cn) (S.-X. Li).

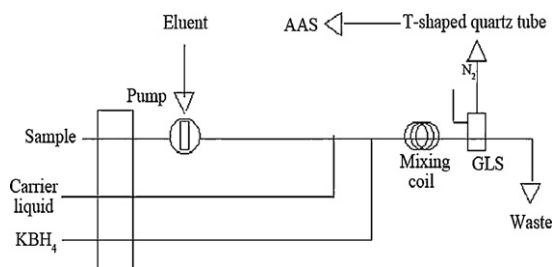


Fig. 1. Schematic diagram of QTA-HGAAS.

analyte species by rapid heating of the trap and transporting them in a carrier gas to a heated quartz tube, as commonly used with HGAAS [10]. Such atom trap technology is complicated, and time-consuming, so its automation is not easy. The alternative method is the developing of a new atomizer to replacing the conventional QTA. A multiple microflame quartz tube atomizer, including two externally heated horizontal concentric quartz tubes [9], has been reported for minimizing the interferences and improving the extent of the calibration range.

Because of the large specific surface area, high adsorption capacity, and strong coordination ability of titanium, nanometer  $\text{TiO}_2$  has been used as solid-phase extractant for the preconcentration of trace elements from sample solution [18–20], but its application on the metal atom trap for HGAAS has not been reported until now. Most of the atoms of nanometer  $\text{TiO}_2$  were on the surface. The unsaturated surface atoms might easily bind with the analyte atoms and then the residence time of the analyte atoms in the light path could be increased. For this purpose, a new atomizer, nanometer  $\text{TiO}_2$ -coated quartz tube, was used for the first time for HGAAS.

## 2. Experimental

### 2.1. Apparatus and reagents

A GBC 932AA model atomic absorption spectrometer (GBC Co., Australia) equipped with a WHG-102A<sub>2</sub> model flow injection hydride generation system (Beijing hanshi Works Co., China) was used for the determinations of Hg, Se, As, Pb, and Sb. Hollow cathode lamps (Photron Pty Ltd, Australia) of Hg, Se, As, Pb, and Sb were used as specific radiation sources. All signals were processed in the peak height mode. A T-shaped quartz tube had a specification of 150 mm tube length, 2 mm wall thickness, 10 mm outer diameter (Beijing kinglass quartz Co., China). An Agilent 7500cx series inductively coupled plasma mass spectrometer (Agilent Technologies Co., USA) was used for the determinations of Cu, Fe, Cd, Zn, Cr, and Co in hair. The pH was controlled with a 320-S model pH meter (Mettler-Toledo Instruments Shanghai Co., China) supplied with a combined electrode. Milli-Q purified water was obtained from a Milli-Q-purified water apparatus (Millipore Co., USA). Other equipment were used, including a KQ-250B model ultrasonic cleaner (Kunshan ultrasonic instrument Co., China), a KSW-40-11 model resistance furnace temperature controller (Shanghai botian medical instrument Co., China), a DHG-9036A model electrothermal thermostatic drying oven (Shanghai jinghong laboratory instrument Co., China), a HJ-6A model magnetic stirrer (Jintan science analysis instrument Co., China), a BS110S model electronic analytical balance (Beijing sartorius balance Co., China), and an MK-III model microwave digestion system (Shanghai Sineo Microwave Chemistry Technology Co., China).

The herbal medicines (*Herba Anoectochili* and *Carthamus tinctorius*) were purchased from Zhongmin Supermarket in Zhangzhou, Fujian, China, and they were identified by Professor Chen Yu-lin.

Standard reference material certified human hair (GBW 07601, National Analysis Center for Iron and Steel, Beijing, China) was used to check the accuracy of the analysis procedures in this work. Concentrated nitric acid, 69–70% (Merck KGaA, Germany), and hydrogen peroxide, 30% (Merck KGaA, Germany), were used for digestion of the samples. All other chemicals were of analytical reagent grade from Shanghai Experiment Reagent Co., China. Ultrapure water of  $18 \text{ M}\Omega \text{ cm}^{-1}$  specific resistivity was used to prepare all the solutions and to rinse the previously cleaned laboratory material.

The working standard solutions of Hg, Se, and As were prepared daily by diluting the stock solution ( $1000 \text{ mg L}^{-1}$ , GBC Co., Australia) with  $0.7 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ,  $2.0 \text{ mol L}^{-1} \text{ HCl}$ , and  $1.0 \text{ mol L}^{-1} \text{ HCl}$  solution, respectively. The carrier solution of hydride generation system was  $0.1 \text{ mol L}^{-1} \text{ HCl}$  solution. Potassium borohydride solutions ( $\text{KBH}_4$ , 0.5% for Hg; 1.5% for Se and As, m/v) were prepared daily by dissolving appropriate amount of  $\text{KBH}_4$  in 0.3% (m/v) NaOH solution. All stock solutions were stored in dark at  $4^\circ\text{C}$ .

### 2.2. Coating nanometer $\text{TiO}_2$ on the inner wall of T-shaped quartz tube

Before the coating of nanometer  $\text{TiO}_2$ , the quartz tube was activated as follows: (a) it was ultrasonic vibrated in  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  solution for 20 min; (b) after being washed with ultrapure water, it was ultrasonic vibrated again in  $1 \text{ mol L}^{-1} \text{ HCl}$  solution for 20 min and then was washed ultrasonically with ultrapure water for 10 min; and (c) it was weighted after drying on  $105^\circ\text{C}$  for 24 h.

According to the literatures [21], the procedures of coating the T-shaped quartz tube with nanometer  $\text{TiO}_2$  were:

- Preparation of nanometer  $\text{TiO}_2$  sol: titanium tetraisopropoxide (TTIP) was added to a reaction beaker in the presence of ethanol (EtOH). Acetylacetone (AcAc) was added into ethanol and water in a separate beaker. Then, the two resulting solutions were mixed and stirred at room temperature for 2 h. The optimal molar ratio of TTIP:AcAc: $\text{H}_2\text{O}$ :EtOH was 1:1:3:20 for preparation of  $\text{TiO}_2$  sol.
- Coating the quartz tube: the active tube was immersed immediately into boiling nanometer  $\text{TiO}_2$  sol for 20 min, air-dried at room temperature for 24 h, placed in a furnace at  $105^\circ\text{C}$  for 8 h to remove completely the residual water, heated up to  $400^\circ\text{C}$  at a rate of  $2 \text{ min}^{-1}$  for 2 h, and then weighted after its temperature was decreased naturally to room temperature. The weight of the coating of nanometer  $\text{TiO}_2$  on the inner wall of quartz tube could be calculated by the weight differences. This coating procedure was repeated two times.

### 2.3. Pretreatment and microwave digestion of the herbal medicines and hair

The herbal medicines were rinsed rapidly with Milli-Q purified water for 3 times, heated at  $80 \pm 5^\circ\text{C}$  to constant weigh, and then powdered carefully in an agate mortar.

Hair sample were obtained from Zhangzhou, Fujian, China, using the following standard cutting and washing procedures [22]: the hair was first cut into approximately 0.3 cm pieces and mixed to allow a representative sub-sampling of the hair specimen. After cutting, hair was washed four times with a 1:200 (v/v) dilution of Triton X-100. The hair was then rinsed with acetone and allowed to drain. This was followed by three rinses with ultrapure water and two rinses with acetone. The hair was dried in an oven at  $80 \pm 5^\circ\text{C}$  to constant weigh and then powdered carefully in an agate mortar.

On to each *Herba Anoectochili*, *Carthamus tinctorius*, hair of 0.25 g, 0.25 g, and 0.50 g, respectively, 2.0 mL of concentrated  $\text{HNO}_3$  and 1.0 mL of  $\text{H}_2\text{O}_2$  solution were added; the contents were heated

**Table 1**  
Operating conditions of the determination of Hg, Se, and As by NT-QTA-HGAAS.

Element	Lamp current (mA)	Wavelength (nm)	Read time (s)	Slit width (mm)	Carrier gas (mL min <sup>-1</sup> )	Ventilation switch (on/off)	Electrothermal (yes/no)
Hg	3	253.7	25	0.5	100	Off	No
Se	10	196.0	25	0.5	150	On	Yes
As	8	193.7	25	0.5	100	On	Yes

for the decomposition in microwaves digestion system under the pressure of 15 atm, temperature of 250 °C for 10 min; this procedure was repeated three times. After being cooled naturally to room temperature, the decomposed solution of *Herba Anoectochili* and *Carthamus tinctorius*, were diluted to 10 mL and 50 mL for the determination of the concentration of Hg and Se, respectively; the decomposed solution of the hair was diluted to 10 mL for the determination of the concentration of Hg, Se, As, Pb, Sb, Cu, Fe, Cd, Zn, Cr, and Co.

#### 2.4. Operating conditions of the determination of Hg, Se, and As by NT-QTA-HGAAS

The optimal conditions of NT-QTA-HGAAS for the determination of Hg, Se, and As were studied, and shown in Table 1.

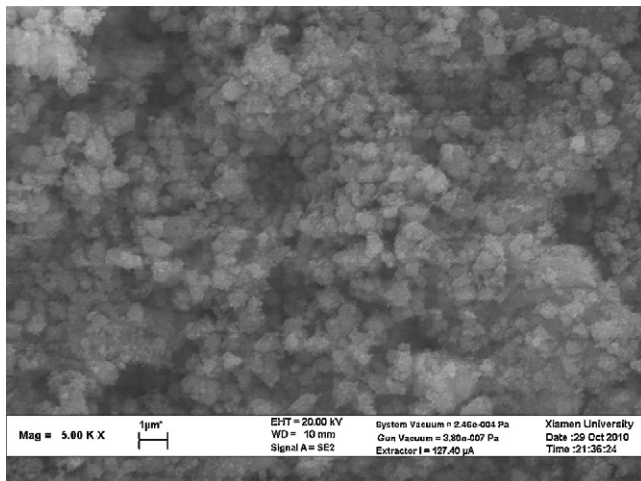
### 3. Results and discussion

In Fig. 2, the scanning electron microscope image was showed that nanoporous TiO<sub>2</sub> films could be coated on the inner wall of T-shaped quartz tube with three-dimensional network and the size of TiO<sub>2</sub> was 30–40 nm. Using a sol–gel dip-coating procedure on quartz tube, the coating weight of nanometer TiO<sub>2</sub> was constant when the coating times was more two times and the coating weights were 56.2 mg for the first time and 67.4 mg for the second time.

#### 3.1. Analytical performance

The linear range of a calibration curve is determined by a lower limit and an upper limit. For the requirement of practical application, the calibration curves were obtained by practical analyses. Using different coating weight of nanometer TiO<sub>2</sub>, the obtained calibration graphs were tested and given in Fig. 3, including the calibration curve and the equations of the calibration curves for Hg, Se, and As.

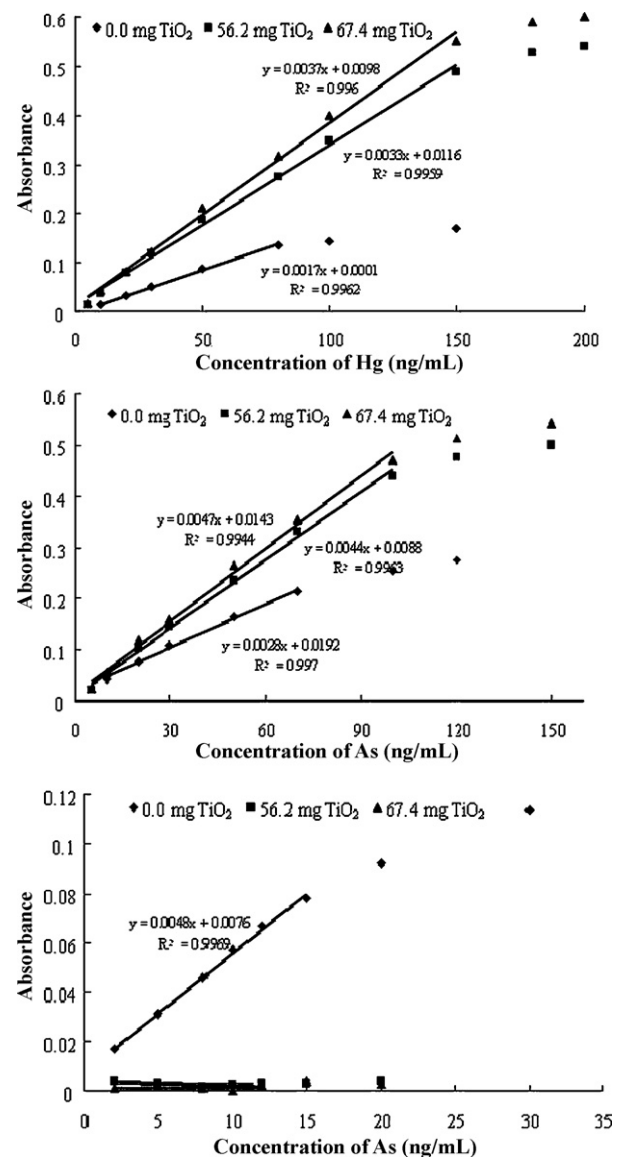
After coating 56.2 mg or 67.4 mg TiO<sub>2</sub> on the quartz tube, the linear range of the calibration curve of both Hg and Se was



**Fig. 2.** Scanning electron microscope image of nanoporous TiO<sub>2</sub> films.

improved. When 67.4 mg TiO<sub>2</sub> was coated on the inner wall of quartz tube, the linear range of the calibration curve was lengthened from 10.0–80.0 ng mL<sup>-1</sup> to 5.0–150.0 ng mL<sup>-1</sup> for Hg and from 10.0–70.0 ng mL<sup>-1</sup> to 5.0–100.0 ng mL<sup>-1</sup> for Se, compared with QTA-HGAAS. The advantage of NT-QTA-HGAAS on the applicable concentration scope was obvious.

The curvature of a calibration curve could be affected by stray light [23]. The effect of stray light on the calibration curve of Hg and Se might be improved by the coating of nanometer TiO<sub>2</sub>, because nanometer TiO<sub>2</sub> particles possess super high absorption surface, special optic absorbing quality and quantum effect, the nanometer TiO<sub>2</sub> particles have high capacity to absorb UV irradiation, including the metal detection wavelength and the stray light. But it could



**Fig. 3.** Effect of nanometer TiO<sub>2</sub> coating on the linear range of calibration curves of Hg, Se, and As.

**Table 2**  
Effect of nanometer size TiO<sub>2</sub> coating on the characteristic concentration and detection limit of Hg and Se.

Coating weight of TiO <sub>2</sub> (mg)	Characteristic concentration (ng mL <sup>-1</sup> /1%) <sup>a</sup>		Detection limit (ng mL <sup>-1</sup> ) <sup>b</sup>	
	Hg	Se	Hg	Se
0.0	2.8	1.2	2.0	1.6
56.2	1.1	0.9	1.1	1.1
67.4	1.1	0.8	0.9	1.0

<sup>a</sup>  $S = 0.0044C/A$ ,  $S$ : characteristic concentration,  $C$ : mass concentration of sample,  $A$ : average absorbance of standard solution.

<sup>b</sup>  $D = (3 \times S_b)/K$ ,  $D$ : detection limit,  $S_b$ : standard deviation of blank values,  $K$ : slope of the standard curve.

**Table 3**  
Analytical results for metals in herbal medicines and hair ( $\mu\text{g g}^{-1}$ ,  $n = 3$ ).

Samples	Added		Found		Recovery, %	
	Hg	Se	Hg	Se	Hg	Se
<i>Herba Anoectochili</i>	0.00	0.00	0.47 ± 0.05	5.18 ± 0.63	–	–
	0.50	5.00	0.95 ± 0.10	10.22 ± 1.14	96.0	100.8
<i>Carthamus tinctorius</i>	0.00	0.00	0.74 ± 0.07	18.35 ± 2.00	–	–
	0.40	10.00	–	–	97.5	100.8
Human hair	0.00	0.00	0.18 ± 0.04	0.39 ± 0.05	–	–
	0.20	0.50	–	–	95.0	102.0
Hair (GBW 07601)	0.00	0.00	0.37 ± 0.05	0.90 ± 0.14	–	–
	0.40	0.60	–	–	100.0	101.7
			0.33 ± 0.05	0.58 ± 0.10		
			0.73 ± 0.13	1.19 ± 0.15		

not improve the sensitivity of As. The nanometer TiO<sub>2</sub> had great adsorption capacity for arsenic atom or its hydrides, so the ground state arsenic atoms could not be released. The interference from the arsenic coexistence on the determination of Hg and Se could be eliminated.

As shown in Fig. 3, the slope of the standard curve of both Hg and Se (i.e., the sensitivity of the analytical method) was increased with the increase of the coating weight of TiO<sub>2</sub> on the quartz tube. The effect of the TiO<sub>2</sub> coating on characteristic concentration and detection limit of Hg and Se was shown in Table 2. When the analytical method of QTA-HGAAS was replaced by NT-QTA-HGAAS, the detection limits were improved from 2.0 ng mL<sup>-1</sup> to 0.9 ng mL<sup>-1</sup> for Hg and from 1.6 ng mL<sup>-1</sup> to 1.0 ng mL<sup>-1</sup> for Se; the characteristic concentration of was decreased from 2.8 ng mL<sup>-1</sup>/1% to 1.1 ng mL<sup>-1</sup>/1% for Hg and from 1.2 ng mL<sup>-1</sup>/1% to 0.8 ng mL<sup>-1</sup>/1% for Se. Furthermore, the analytical performance of NT-QTA-HGAAS (i.e., the efficiency of nanometer TiO<sub>2</sub>-coated quartz tube atomizer) was stable for at least 100 determination cycles.

### 3.2. Application

The achieved methodology was applied to herbal medicines and hair. Hg and Se concentrations in herbal medicines and hair were summarized in Table 3. The results showed that: (a) there is a good agreement for Hg and Se in hair (GBW 07601) between the experimental values (0.33  $\mu\text{g g}^{-1}$  for Hg and 0.58  $\mu\text{g g}^{-1}$  for Se) and certified values (0.36 ± 0.05  $\mu\text{g g}^{-1}$  for Hg and 0.60 ± 0.03  $\mu\text{g g}^{-1}$  for Se); (b) the interference of 9 metal species in hair (GBW 07601) on the determination of Hg and Se could be eliminated, containing As (0.28 ± 0.04  $\mu\text{g g}^{-1}$ ), Pb (8.80 ± 0.90  $\mu\text{g g}^{-1}$ ), Sb (0.09 ± 0.01  $\mu\text{g g}^{-1}$ ), Cu (8.80 ± 0.90  $\mu\text{g g}^{-1}$ ), Fe (54.00 ± 6.00  $\mu\text{g g}^{-1}$ ), Cd (0.11 ± 0.02  $\mu\text{g g}^{-1}$ ), Zn (190.00 ± 5.00  $\mu\text{g g}^{-1}$ ), Cr (0.37 ± 0.05  $\mu\text{g g}^{-1}$ ), and Co (0.07 ± 0.01  $\mu\text{g g}^{-1}$ ); and (c) the recoveries of herbal medicines and hair were reasonable for trace analysis, in a range of 95.0–102.0%. No systematic error could be seen in the added-found method for Hg and Se determination in herbal medicines and hair. So, the precision and accuracy of the method were good.

## 4. Conclusions

It has been demonstrated that the optimized technique can be used for the determination of ultra trace concentrations of Hg and Se in biological samples. A simple AA flame spectrometer, a flow injection hydride generation system, and the conventional QTA coated with nanometer TiO<sub>2</sub> are all that are needed. The achieved method has some advantages such as online, low cost, and easy manufacturing. Although the achieved improvement of the sensitivity is modest, the modified online method has much importance in comparison with the other offline enrichment techniques such as adsorption or extraction because of its simplicity, direct application, and less volume of sample required.

Secondly, the linear range of calibration curves is expanded as 5.0–150.0 ng mL<sup>-1</sup> for Hg and 5.0–100.0 ng mL<sup>-1</sup> for Se, the concentration scope of NT-QTAT-HGAAS is wider than QTA-HGAAS.

Thirdly, the coexistence of arsenic cause serious interference on the determination of the Hg and Se by QTA-HGAAS. But it could be eliminated by NT-QTAT-HGAAS.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20775067 and 20977074), Outstanding Youth Science Foundation of Fujian Province, China (No. 2010J06005), the Science & Technology Committee of Fujian Province, China (No. 2008F5063), and the Program for New Century Excellent Talents in Fujian Province University (No. 200720).

## References

- [1] K. Chan, Some aspects of toxic contaminants in herbal medicines, *Chemosphere* 52 (2003) 1361–1371.
- [2] M.J.L. Alonso, A.B. Barrera, J.A.C. Juan, J.M.F. Bermúdez, P.B. Barrera, Selenium levels in related biological samples: Human placenta, maternal and umbilical cord blood, hair and nails, *J. Trace Elem. Med. Biol.* 19 (2005) 49–54.
- [3] M.A. Dowell, C.F. Dillon, J. Osterloh, P.M. Bolger, E. Pellizzari, R. Fernando, O.R. Montes, S.E. Schober, T. Sinks, R.L. Jones, K.R. Mahaffey, Hair mercury levels in US children and women of childbearing age: reference range data from NHANES 1999–2000, *Environ. Health Perspect.* 112 (2004) 1165–1171.

- [4] M. Legrand, C.J. Sousa Passos, D. Mergler, H.M. Chan, Biomonitoring of mercury exposure with single human hair strand, *Environ. Sci. Technol.* 39 (2005) 4594–4598.
- [5] S.X. Li, F.Y. Zheng, Y. Huang, J.C. Ni, Thorough removal of inorganic and organic mercury from aqueous solutions by adsorption on Lemna minor powder, *J. Hazard. Mater.* 186 (2011) 423–429.
- [6] A. Mehdi, A. Aliakbar, Determination of Se(IV) in natural waters by adsorptive stripping voltammetry of 5-nitropiazselenol, *J. Hazard. Mater.* 174 (2010) 788–794.
- [7] M. Tuzen, I. Karaman, D. Citak, M. Soylak, Mercury(II) and methyl mercury determinations in water and fish samples by using solid phase extraction and cold vapour atomic absorption spectrometry combination, *Food Chem. Toxicol.* 47 (2009) 1648–1652.
- [8] I. Lavill, J.M. Gonzalez-Costas, C. Bendicho, Improved microwave-assisted wet digestion procedures for accurate Se determination in fish and shellfish by flow injection-hydride generation-atomic absorption spectrometry, *Anal. Chim. Acta* 591 (2007) 225–230.
- [9] É.M.M. Flores, A.M. Nunes, V.L. Dressler, J. Dédina, Multiple microflame quartz tube atomizer: study and minimization of interferences in quartz tube atomizers in hydride generation atomic absorption spectrometry, *Spectrochim. Acta B* 64 (2009) 173–178.
- [10] O.Y. Ataman, Vapor generation and atom traps: atomic absorption spectrometry at the ng/L level, *Spectrochim. Acta B* 63 (2008) 825–834.
- [11] J. Dédina, Atomization of volatile compounds for atomic absorption and atomic fluorescence spectrometry: on the way towards the ideal atomizer, *Spectrochim. Acta B* 62 (2007) 846–872.
- [12] R.P. Choudhury, A.N. Garg, Variation in essential, trace and toxic elemental contents in *Murraya koenigii*-A spice and medicinal herb from different Indian states, *Food Chem.* 104 (2007) 1454–1463.
- [13] S. Titretir, E. Kendüzler, Y. Arslan, İ. Kula, S. Bakırdere, O.Y. Ataman, Determination of antimony by using tungsten trap atomic absorption spectrometry, *Spectrochim. Acta B* 63 (2008) 875–879.
- [14] İ. Kula, Y. Arslan, S. Bakırdere, S. Titretir, E. Kendüzler, O.Y. Ataman, Determination and interference studies of bismuth by tungsten trap hydride generation atomic absorption spectrometry, *Talanta* 80 (2009) 127–132.
- [15] M. Xi, R. Liu, P. Wu, K. Xu, X. Hou, Y. Lu, Atomic absorption spectrometric determination of trace tellurium after hydride trapping on platinum-coated tungsten coil, *Microchem. J.* 95 (2010) 320–325.
- [16] İ. Kula, Y. Arslan, S. Bakırdere, O.Y. Ataman, A novel analytical system involving hydride generation and gold-coated W-coil trapping atomic absorption spectrometry for selenium determination at ng l<sup>-1</sup> level, *Spectrochim. Acta B* 63 (2008) 856–860.
- [17] İ. Menemenlioğlu, D. Korkmaz, O.Y. Ataman, Determination of antimony by using a quartz atom trap and electrochemical hydride generation atomic absorption spectrometry, *Spectrochim. Acta B* 62 (2007) 40–47.
- [18] S.X. Li, N.S. Deng, Separation and preconcentration of Se(IV)/Se(VI) species by selective adsorption onto nanometer-size titanium dioxide and determination by graphite furnace atomic absorption spectrometry, *Anal. Bioanal. Chem.* 374 (2002) 1341–1345.
- [19] S.X. Li, N.S. Deng, F.Y. Zheng, Spectrophotometric determination of tungsten (VI) enriched by nanometer-size titanium dioxide in water and sediment, *Talanta* 60 (2003) 1097–1104.
- [20] F.Y. Zheng, S.H. Qian, S.X. Li, X.Q. Huang, Speciation analysis of antimony by preconcentration of Sb(III) and Sb(V) in waters onto nanometer-size titanium dioxide and selective determination by flow injection-hydride generation-atomic absorption spectrometry, *Anal. Sci.* 22 (2006) 1319–1322.
- [21] A. Sadeghzadeh, M.S. Ghamsari, F. Hajiesmaeilbaigi, Sol-gel template synthesis and characterization of aligned anatase-TiO<sub>2</sub> nanorod arrays with different diameter, *Mater. Chem. Phys.* 113 (2009) 856–860.
- [22] D.A. Bass, D. Hickok, D. Quig, K. Urek, Trace element analysis in hair: factors determining accuracy, precision, and reliability, *Alt. Med. Rev.* 6 (2001) 472–481.
- [23] E.G. Su, A.I. Yuzefovsky, R.G. Michel, J.T. McCaffrey, W. Slavin, Linearization of calibration curves of manganese, copper, silver, thallium and chromium in Zeeman graphite furnace atomic absorption spectrometry, *Spectrochim. Acta B* 49 (1994) 367–385.