

# Simultaneous determination of trace mercury and cadmium in tobacco samples by cold vapor generation-atomic fluorescence spectrometry

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A highly sensitive and simple method was developed for the simultaneous determination of trace cadmium and mercury in tobacco samples by cold vapor generation-atomic fluorescence spectrometry equipped with an intermittent flow reactor. The reaction was accomplished with potassium tetrahydroborate(III) in aqueous solutions. A newly modified atomizer was presented on the basis of the present atomic fluorescence system, which effectively improved the stability of the signals. Special accent was put on the study of the conditions for the generation of volatile cadmium and mercury species were investigated in detail. Some transition metal ions that could be used as sensitivity enhancers, including iron(III), cobalt(II), nickel(II), zinc(II) and molybdenum(VI) in the presence of thiourea. The tolerance to the interference of coexisting ions was carefully examined in this system. Under optimal conditions, the detection limits ( $3\sigma$ ) were evaluated to be  $2.8 \text{ ng l}^{-1}$  for cadmium and  $4.3 \text{ ng l}^{-1}$  for mercury, respectively. The relative standard deviations for 10 replicate determinations of  $0.8 \text{ } \mu\text{g l}^{-1}$  mercury and  $1 \text{ } \mu\text{g l}^{-1}$  cadmium were 3.2% and 2.9%, respectively. The proposed method was successfully applied to the simultaneous determination of mercury and cadmium in tobacco leaf samples.

## Introduction

The toxicological effects of cadmium and mercury on human bodies have received wide concern and extensive study in recent years, and these two elements can accumulate in human issues that may induce biological diseases. Biological samples such as tobacco plants can enrich the toxic elements from the environment-polluted soil, air and water. When a cigarette is smoked, these two toxic elements are inhaled with cigarette smoke into the bronchial system and may cause cancer.<sup>1</sup> Therefore, the development of a sensitive and simple method for the determination of trace cadmium and mercury in tobacco or other biological samples is significant.

In the past few years, a number of techniques have been applied to the determination of Cd and Hg, including flame absorption spectrometry (FAAS),<sup>2</sup> electrothermal atomic absorption spectrometry (ETAAS),<sup>3,4</sup> inductively coupled plasma mass spectrometry (ICP-MS),<sup>5,6</sup> inductively coupled plasma-atomic emission spectrometry (ICP-OES),<sup>7</sup> atomic fluorescence spectrometry (AFS),<sup>8,9</sup> cold vapor atomic absorption spectrometry (CVAAS),<sup>10,11</sup> etc.

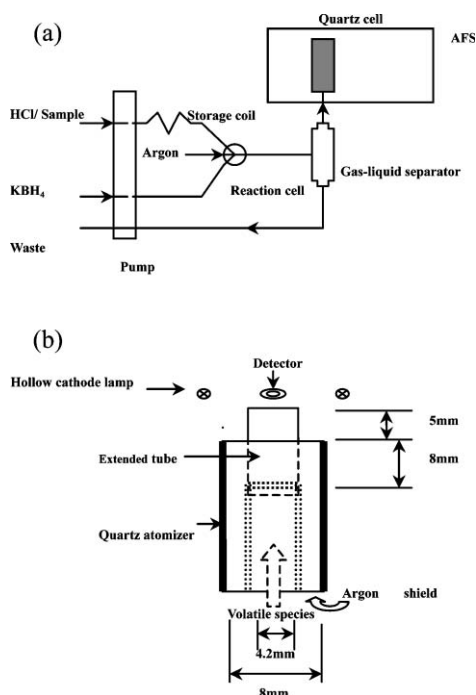
The relatively low boiling point and high volatility of Hg brings forth the possibility of measuring mercury without additional thermal energy supplied by a flame or electrothermal heating. As a consequence, the cold vapor atomic spectrometry technique has become the preferred technique for trace mercury analysis. Matusiewicz *et al.*<sup>10</sup> successfully detected mercury in beer by cold vapor generation using sodium tetrahydroborate(III) as reductant followed by trapping on the gold-coated interior of a graphite furnace AAS atomizer with a detection limit of  $90 \text{ ng l}^{-1}$ . Capelo *et al.*<sup>12</sup> reported a FI-CVAAS system to evaluate the mercury concentration in seafood. Wurl and coworkers<sup>13</sup> used CVAAS coupled with a flow manifold for the direct determination of mercury in seawater. Rahman *et al.*<sup>8</sup> determined mercury in human hair by CVAAS as part of a multi-element analysis study. Although the CVAAS technique for mercury analysis has been studied extensively, the applications of CVAAS technique to mercury

analysis are relatively few compared with CVAAS and mostly concentrated on mercury determination in simple environment samples.<sup>14</sup>

The determination of cadmium by hydride generation atomic spectrometry was first reported by Cacho *et al.*<sup>15</sup> on the basis of the generation of volatile cadmium from an acidic solution of cadmium diethyldithiocarbamate (Cd-DDTC) in dimethylformamide (DMF) using sodium tetrahydroborate(III) as the reducing agent. Several years later, Sanz-Medel<sup>16</sup> and coworkers found that volatile species of cadmium could be detected by AAS at room temperature in the presence of vesicles of didodecyltrimethylammonium bromide (DDAB). Garrido and coworkers<sup>11,17</sup> determined trace cadmium by CVAAS in water and sewage sludge. Guo and coworkers<sup>18</sup> determined cadmium at ultra trace level by CVAAS in the presence of thiourea and cobalt(II). Vargas-Razo *et al.*<sup>19</sup> determined cadmium from aqueous samples by means of FI-CVAAS. Furthermore, some workers<sup>20,21</sup> successfully employed several different trapping procedures for the determination of cadmium by CVAAS, such as iridium- tungsten- or zirconium-coated graphite surface and palladium-coated graphite surface.

Considering that both mercury and cadmium can generate volatile species by means of cold vapor generation, a CVAAS method may be feasible and effective for the simultaneous determination of trace mercury and cadmium. However, there have been no publications, to the best of our knowledge, concerning the simultaneous determination of mercury and cadmium in biological samples by CVAAS.

The main purpose of this paper was to develop a sensitive and simple CVAAS method for the simultaneous determination of trace level of mercury and cadmium. The experimental parameters were studied in detail. A modified atomizer was developed to obtain better signal stability. In addition, sensitivity enhancers, including thiourea and cobalt, nickel, iron, zinc, molybdenum, etc., were evaluated separately. The interference of the co-existing ions was also examined carefully. The proposed method has been successfully applied to the



**Fig. 1** (a) Schematic diagram of the intermittent reactor: storage coil length 50 cm, id 0.7 mm PTFE tubing; gas-liquid separator made of glass with a cylindrical-shaped cavity (height 60 mm, id 15 mm); transfer tubing (from the separator to the atomizer) length 30 cm, id 0.7 mm. (b) Schematic diagram of the modified atomizer: outer quartz tube length 70 mm, id 9 mm; original inner quartz tube length 62 mm, id 4.2 mm; extended tube (PTFE tube) length 13 mm, id 4 mm.

simultaneous determination of trace cadmium and mercury in tobacco leaf samples.

## Experimental

### Apparatus

A model AFS-230 double-channel non-dispersive atomic fluorescence spectrometry equipped with an intermittent flow reactor (Beijing Haiguang Instrument Co., Beijing, China) was used throughout this work. Details about the instrument construction can be obtained elsewhere.<sup>9</sup> Cadmium and mercury high performance hollow cathode lamps (HPHCLs) were used as the excitation sources for the determination of cadmium and mercury; the HPHCLs were especially designed for AFS measurement, which have advantages over electrodeless discharge lamps in both the stability and lifetime. A schematic diagram of the intermittent reactor is shown in Fig. 1a. The working program of the intermittent reactor is described in Table 1. Polytetrafluoroethylene (PTFE) tubing of 0.7 mm id was employed to construct the manifold. The gas-liquid separator used in this work was made of glass. After gas-liquid separation, the cadmium and mercury volatile species were introduced by an argon carrier gas to the AFS detector and measured at room temperature (cold vapor). A modified

**Table 2** Operating parameters of the AFS instrument

Parameter	Cd	Hg
High voltage of PMT/V	300	300
Peak current of lamp/mA	60	30
Atomizer height/mm	8.0	8.0
Flow rate of carrier gas (Ar)/ml min <sup>-1</sup>	500	500
Flow rate of shield gas (Ar)/ml min <sup>-1</sup>	1000	1000
Read time/s	10	10
Delay time/s	1	1
Sample volume/ml	0.2	0.2
Measurement mode	Standard curve	Standard curve
Read mode	Peak area	Peak area

atomizer was used (shown in Fig. 1b) to improve the stability of signals. This instrument was operated with a PC computer.

The operational parameters used for the AFS instrument are given in Table 2.

### Reagents

All reagents were of analytical-reagent grade or higher. Ultrapure water used throughout the experiment was obtained from a Milli-Q water-purification system of Millipore (Bedford, MA, USA).

The mercury and cadmium standard solutions were prepared daily by serial dilution of a 1000 mg l<sup>-1</sup> mercury stock solution (Shanghai Institute of measurement, Shanghai, China) and a cadmium stock solution (Shanghai Institute of measurement, Shanghai, China).

The potassium tetrahydroborate(III) solutions were prepared daily by dissolving the reagent (Shanghai Chemical Reagent Co., Shanghai, China) in 0.5% potassium hydroxide (Shanghai Chemical Reagent Co., Shanghai, China) solution.

A 5% (m/v) thiourea solution was prepared by dissolving thiourea (Shanghai Chemical Reagent Co., Shanghai, China) in ultrapure water.

A solution of 100 mg l<sup>-1</sup> nickel was prepared by dissolving suitable amount of nickel chloride (Shanghai Chemical Reagent Co., Shanghai, China) in ultrapure water. Lower concentrations were obtained by stepwise dilution of the stock solution just before use. Solutions of metal ions employed for the interference and the enhancement study were prepared from the corresponding 1000 mg l<sup>-1</sup> stock standard solution (Shanghai Chemical Reagent Co., Shanghai, China).

A 0.2 mol l<sup>-1</sup> hydrochloric acid carrier solution was prepared from concentrated hydrochloric acid (Tianjin Zhenxing Second Chemical Co. Tianjin, China), which was also applied to acidify the samples.

### Sample pre-treatment

Tobacco leaf samples were dried at 70 °C for 48 h prior to further preparation and then ground and stored in a desiccator. Approximately 0.2 g of samples was accurately weighed and placed in a PTFE vessel, and then 2 ml concentrated HNO<sub>3</sub> and 1 ml 30% H<sub>2</sub>O<sub>2</sub> were added. The vessels were sealed and placed

**Table 1** Working program for the intermittent flow reactor

Step	Flow rate/ml min <sup>-1</sup>	Time/s	Function
1	Sample	5.3	Draw sample solution using sampling tube
	Reductant (2% m/v KBH <sub>4</sub> )	5.3	
2	Sample	0	Chang over of sampling tube into carrier solution
	Reductant (2% m/v KBH <sub>4</sub> )	0	
3	Carrier solution (0.2 mol l <sup>-1</sup> HCl)	7.5	Propel the sample to react with reductant followed by readout
	Reductant (2% m/v KBH <sub>4</sub> )	7.5	
4	Carrier solution (0.2 mol l <sup>-1</sup> HCl)	0	Return to step 1
	Reductant (2% m/v KBH <sub>4</sub> )	0	

in a model Meicheng microwave digestion system (Beijing Meicheng Science and Trade Co., Beijing) for microwave-assistant digestion. The digestion program consisted of three stages with the following power, pressure, and time settings: stage 1 (50% power, 300 kPa, 5 min); stage 2 (80% power, 500 kPa, 3 min); stage 3 (80% power, 800 kPa, 5 min). Because the oxidizing power of  $\text{HNO}_3$  acid inhibited the formation of volatile species, the digestion solution must be heated to near dryness (about 0.5 ml) to eliminate the interference of  $\text{HNO}_3$ . But this operation must be handled gently, and ensure that the digestion can not be heated to dryness. Otherwise, it may result in loss of the mercury and cadmium. After cooling, 5 ml ultrapure water were added, followed by transferring to a 10 ml calibrated flask, concentrated  $\text{HCl}$ , thiourea alongwith  $\text{Ni (II)}$  solutions were added to reach final concentrations of  $0.2 \text{ mol l}^{-1}$   $\text{HCl}$ , 1% (m/v) thiourea and  $0.1 \text{ mg l}^{-1}$  nickel, respectively.

### Analytical procedures

According to the working program of the intermittent flow reactor, the sample solution was drawn from sample cups to the storage coil by a peristaltic pump at a flow rate of  $5.3 \text{ ml min}^{-1}$  and then swept by  $0.2 \text{ mol l}^{-1}$   $\text{HCl}$  carrier at a flow rate of  $7.5 \text{ ml min}^{-1}$  to a T-type reactor reacting with a stream of  $7.5 \text{ ml min}^{-1}$  2%  $\text{KBH}_4$ . Consequently, the volatile cadmium and mercury species were introduced to the quartz atomizer by argon carrier for AFS determination.

## Results and discussions

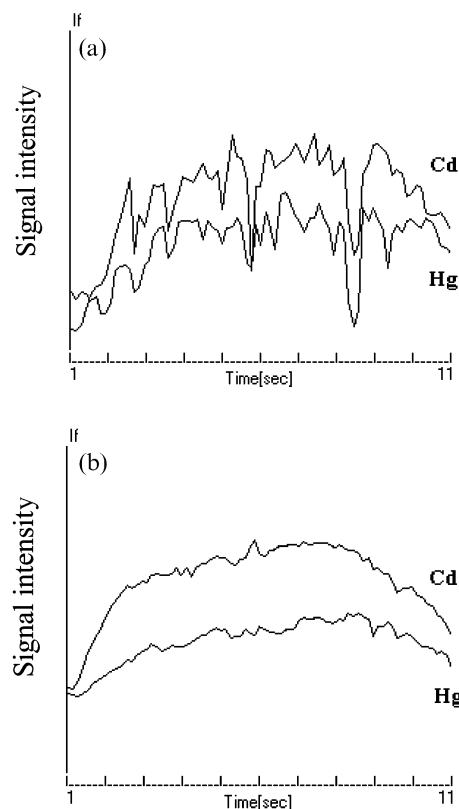
### Modification of quartz atomizer

It was observed that both the fluorescence intensities and stability of Cd and Hg were almost unchanged when the height of atomizer varied from 4 to 14 mm. Therefore, the atomizer height was normally set at 8 mm. In the preliminary stage of this work, it was found that the signals stability (shown in Fig. 2a) was unsatisfactory. Considering that the quartz tube atomizer is a crucial component in the cold vapor method, a modified atomizer was employed to obtain better signal stability. The original atomizer was constructed with two concentric quartz tubes (id 4.2 mm and 9 mm, respectively). As the relative height between the two concentric tubes can not be adjusted, an extended tube was needed to bring a better result. The schematic diagram of the modified atomizer cell is presented in Fig. 1b. As can be seen, a section of PTFE tube with a diameter of 4.0 mm was inserted into the inner quartz tube to increase the length of the inner tube. The length of the extended tubes was evaluated vs. the signal stability and intensity. As shown in Fig. 2b, a better signal stability was observed when the tube length was increased to 13 mm, i.e., 5 mm higher than the outer quartz tube. In addition, the sensitivity using this modified atomizer only slightly decreased (ca. 2%) compared with that of the original atomizer. In the present experiment, a 13 mm (id 4 mm) extended tube was used.

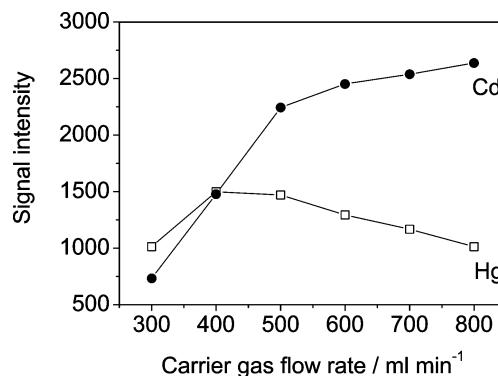
### Evaluation of AFS instrumental parameters

Investigations on the influence of lamp current indicated that the signal intensities of Cd and Hg significantly increased along with increase of the lamp current. This result is similar to that of conventional AFS analysis.<sup>18</sup> Nevertheless, higher lamp current resulted in higher noise which may reduce the lifetime of the lamps. So, as a compromise, a current of 30 mA for the Hg lamp and 60 mA for the Cd lamp was employed in the present work.

As can be seen in Fig. 3, an increase of the argon carrier flow rate resulted in an improvement in the fluorescence signals intensity of Cd. However, with regard to Hg, there was a maximum intensity as the flow rate increased up to  $500 \text{ ml min}^{-1}$  and then the intensity decreased. These results may indicate that the



**Fig. 2** Fluorescence profile of cadmium ( $1 \mu\text{g l}^{-1}$ , upper line) and mercury ( $0.8 \mu\text{g l}^{-1}$ , lower line) (a) without prolonged tube, (b) with prolonged tube.



**Fig. 3** Effect of the carrier gas (Ar) flow rate on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) and Hg ( $0.8 \mu\text{g l}^{-1}$ ) in the presence of 1% (m/v) thiourea, and  $0.1 \text{ mg l}^{-1}$   $\text{Ni(II)}$ .

volatile species of Cd are more unstable than Hg, and a higher argon carrier gas flow rate is needed for Cd detection. In this work,  $500 \text{ ml min}^{-1}$  of carrier gas was chosen to gain better sensitivity.

An argon shield gas was employed in this system to isolate the volatile species from the outside air. When the flow rate was less than  $900 \text{ ml min}^{-1}$ , the fluorescence signal intensity of these two elements decreased. There was a plateau appearing between  $1000$  to  $1200 \text{ ml min}^{-1}$ . Considering the higher cost of argon, a  $1000 \text{ ml min}^{-1}$  argon shield gas was used.

Studies on the effect of the injection volume of analyte showed that 0.2 ml was optimal for these two elements as less volume produced lower fluorescence signal, and higher volumes than 0.2 ml did not improve the sensitivity.

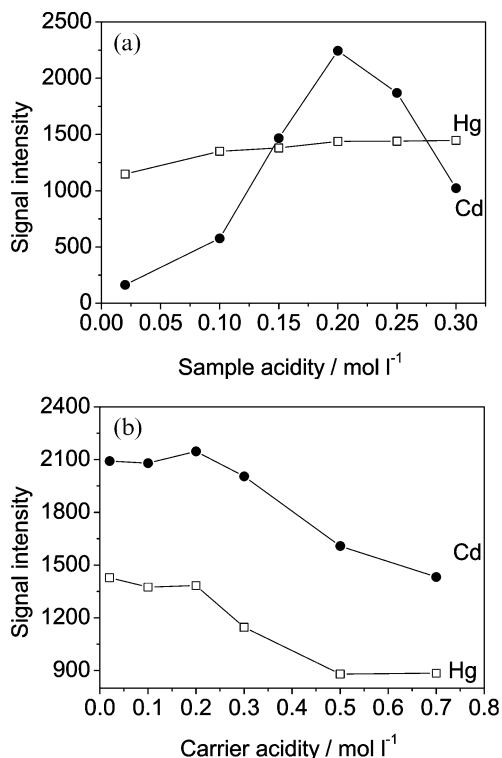
We also tested the effect of flow rates of both sample and reductant on the fluorescence signal intensity. By increasing their flow rates, the intensity of the signal for both elements could be improved. In this work, the appropriate flow rate and time are listed in Table 1.

It is well known that  $\text{Cd}^0$  has no tendency to exist in acidic solutions and volatile species of Cd are more unstable than Hg. The length of the transfer tubing between the GLS and the atomizer played an important role in the CVAFS method. The longer the transfer tubing to the atomizer, the more  $\text{Cd}^0$  deposits on the tubing. However, our experimental results demonstrated that the signals of both Hg and Cd showed no marked decrease as the length of the transfer tubing increased from 30 to 90 cm. While tubing length shorter than 25 cm produced inferior peak shape, a PTFE tubing of *ca.* 30 cm length was employed in the present work to give a good sensitivity and signal-to-noise ratio.

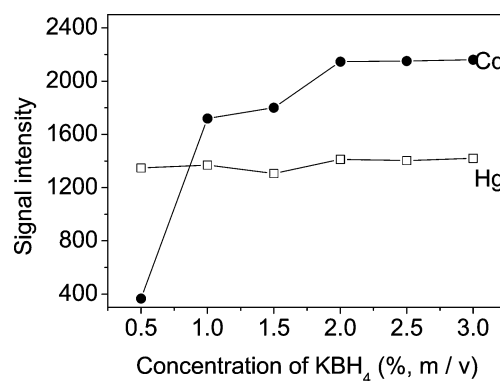
### Optimization of chemical variables

When 2%  $\text{KBH}_4$  was used as the reductant, the relationship between acidity and the signals of Hg and Cd is shown in Fig. 4a. Although the volatile Hg species can be generated over a wide range of acidity, the generation efficiency of Cd is closely dependent on the HCl acidity. Only when the acidity was strictly controlled in the range  $0.18 \sim 0.25 \text{ mol l}^{-1}$  HCl, could satisfactory results be obtained. It should also be noted that the optimal acidity range of the analytes shifted to higher values when the concentration of  $\text{KBH}_4$  in solutions increased. The influence of the HCl concentration in the carrier solution on the determination of Hg and Cd is shown in Fig. 4b. As can be seen, the acidity in the carrier solution reached a maximum value for Cd at *ca.*  $0.2 \text{ mol l}^{-1}$  HCl and further increase of acidity resulted in a lower fluorescence signal. Otherwise, the signal of Hg decreased slowly with the increase of the acidity of carrier solution. Therefore,  $0.2 \text{ mol l}^{-1}$  HCl in both the sample and carrier solution were employed in this work.

The concentration of  $\text{KBH}_4$  has an effect on the generation efficiency of the hydride-forming elements. The results shown in Fig. 5 illustrate that Cd fluorescence signals significantly



**Fig. 4** (a) Effect of HCl concentration in sample on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) and Hg ( $0.8 \mu\text{g l}^{-1}$ ) in the presence of 1% m/v thiourea, and  $0.1 \text{ mg l}^{-1}$  Ni(II). (b) Effect of HCl concentration in carrier on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) and Hg ( $0.8 \mu\text{g l}^{-1}$ ) in the presence of 1% m/v thiourea, and  $0.1 \text{ mg l}^{-1}$  Ni(II).



**Fig. 5** Effect of  $\text{KBH}_4$  concentration on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) and Hg ( $0.8 \mu\text{g l}^{-1}$ ) in the presence of 1% m/v thiourea, and  $0.1 \text{ mg l}^{-1}$  Ni(II).

increased with increase of the concentration of the reductant. A  $\text{KBH}_4$  concentration of 2% was necessary to obtain the maximum fluorescence intensity of Cd. Otherwise, the signals of Hg remained constant when the concentration of the reductant ranged from 0.5–2.5%. As the noise increased when the concentration of  $\text{KBH}_4$  increased, a 2%  $\text{KBH}_4$  in 0.5% KOH solution was employed as the reducing agent.

### Studies on sensitivity enhancement

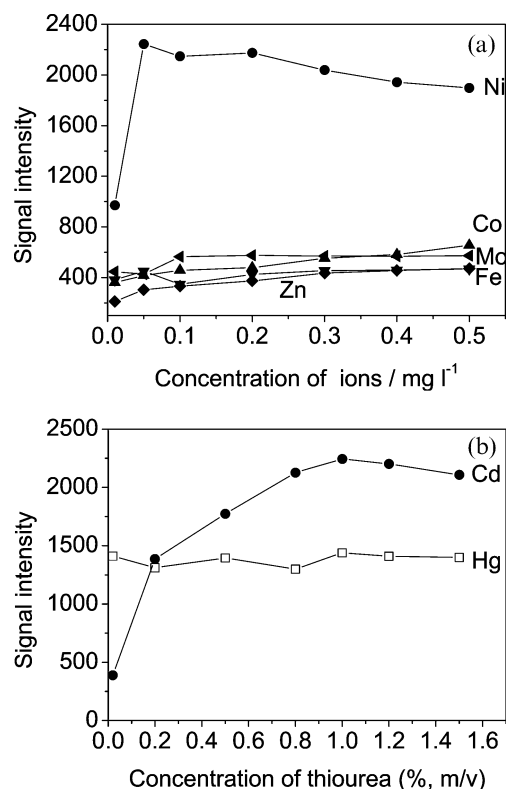
Several years ago, some workers tried to improve the sensitivity of Cd by means of using organic medium such as DDTC<sup>15</sup> and DDAB<sup>16</sup> to generate cadmium hydride compounds. They deemed it difficult to generate a cadmium hydride compound in aqueous solutions. However, other workers found that the generation efficiency of volatile cadmium species can be enhanced greatly in the presence of thiourea and cobalt<sup>2,9</sup> or nickel(II),<sup>19</sup> which might work as catalyzers.

In the present work, several transition metal ions were studied in detail, which could increase the sensitivity of the Cd, including Co(II), Ni(II), Fe(III), Zn(II) and Mo(VI) in the presence of thiourea. Fig. 6a showed the effect of these ions on the signals of Cd. The results indicated that some transition metal ions improved the fluorescence intensity of Cd. These ions were assumed to form a particularly structured complex compound with thiourea that accelerated the generation efficiency of the Cd volatile species. It can be clearly seen that  $0.05 \sim 0.1 \text{ mg l}^{-1}$  Ni gave a much higher signal than that of other ions in the presence of 1% (m/v) of thiourea.

We also found that the concentration of thiourea had an effect on the Cd signals. As can be seen in Fig. 6b, the fluorescence intensity of Cd increased to a maximum with the thiourea concentration up to 1.0%, and then slightly decreased. On the other hand, the employment of thiourea and transition metal ions at lower levels has no favorable effect on the signals of Hg. Therefore, a combination of 1% (m/v) of thiourea and  $0.1 \text{ mg l}^{-1}$  Ni(II) was chosen to give the maximal signal intensities.

### Investigation of interference

In the present study, the effects of some concomitant ions and their concentrations on the determination of  $1.0 \mu\text{g l}^{-1}$  Hg and Cd were investigated. The results are listed in Table 3. As can be seen, no significant interferences were observed from  $100 \text{ mg l}^{-1}$  Ba(II), Ca(II), and Mg(II);  $10 \text{ mg l}^{-1}$  Mn(II);  $1 \text{ mg l}^{-1}$  Cr(III);  $0.1 \text{ mg l}^{-1}$  Cu(II), Pb(II) and Sn(II) for the determination of mercury. Also,  $100 \text{ mg l}^{-1}$  Ba(II), Ca(II), Mg(II);  $10 \text{ mg l}^{-1}$  Mn(II);  $1 \text{ mg l}^{-1}$  Cr(III), Sn(II), have no significant influence on the determination of Cd. It can clearly be seen that among the common ions, copper and silver cause the most serious interference for cadmium determination. Guo *et al.*<sup>9</sup> reported



**Fig. 6** (a) Effect of transition ions concentration on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) in the presence of 1% m/v thiourea. (b) Effect of thiourea concentration on the atomic fluorescence signals of Cd ( $1 \mu\text{g l}^{-1}$ ) and Hg ( $0.8 \mu\text{g l}^{-1}$ ) in the presence of  $0.1 \text{ mg l}^{-1}$  Ni (II).

**Table 3** Effect of co-existing ions on determination of  $1 \mu\text{g l}^{-1}$  of Cd and Hg

Species	Concentration ( $\text{mg l}^{-1}$ )	Concentration ratio		Signal change (%)	
		[M]/[Hg]	[M]/[Cd]	Hg	Cd
Ag(I)	0.1	100	100	-22	-38
Ag(I)	0.05	50	50	-4	-3
Ba(II)	100	100000	100000	0	0
Ca(II)	100	100000	100000	0	0
Cr(III)	1	1000	1000	0	0
Cu(II)	0.1	100	100	+5	-56
Cu(II)	0.05	50	50	-1	-19
Cu(II)	0.02	20	20	0	0
Mg(II)	100	100000	100000	0	0
Mn(II)	10	10000	10000	-2	+3
Pb(II)	1	1000	1000	-15	-11
Pb(II)	0.1	100	100	0	-4
Sn(II)	1	1000	1000	-9	+4
Sn(II)	0.1	100	100	0	0

that the interference of Cu could be eliminated using potassium cyanide. However, this course may induce the hazard of possible production of toxic HCN vapor, as the concentration of Cu in tobacco leaves is lower than 20 times the concentration of Cd.<sup>22</sup> The higher tolerance of concomitant ions ensured that

**Table 5** Analytical results of the Cd and Hg in Tea leaf certified reference material (GBW 07605)

Sample	Certified concentration ( $\mu\text{g g}^{-1}$ )		Found concentration ( $\mu\text{g g}^{-1}$ )	
	Cd	Hg	Cd	Hg
Tea leaf (GBW 07605)	$0.057 \pm 0.008$	(0.013)	$0.055 \pm 0.005$	0.012

the proposed method could be applied to the determination of Hg and Cd in tobacco leaf samples, considering the existing concentrations of those concomitant ions in tobacco leaves.

#### Analytical figures of merit

The superposition of this two group indicated the reliability of the proposed method for simultaneous determination of Hg and Cd. The linear graphs corresponded to equations:

$$I_f = -30.0 + 1725.0 C_{\text{Hg}} \quad r = 0.9993 \quad (1)$$

$$I_f = 10.1 + 2214.9 C_{\text{Cd}} \quad r = 0.9991 \quad (2)$$

$$I_f = -12.8 + 1703.6 C_{\text{Hg}} \quad r = 0.9996 \quad (3)$$

$$I_f = 29.5 + 2221.5 C_{\text{Cd}} \quad r = 0.9992 \quad (4)$$

where  $C_{\text{Hg}}$  and  $C_{\text{Cd}}$  represented the concentration ( $\mu\text{g l}^{-1}$ ) of Hg and Cd, respectively. Eqn. (1) and (2) described the linear graphs for the simultaneous determination and eqn. (3) and (4) described those for individual determination of Hg and Cd, respectively. The favorable correlations showed evidence for the reliability of the proposed method. The calibration graphs were linear up to a concentration of  $6 \mu\text{g l}^{-1}$  and  $10 \mu\text{g l}^{-1}$  for Cd and Hg, respectively. The repeatability, evaluated by the relative standard deviation, is 2.9% for  $1 \mu\text{g l}^{-1}$  Cd and 3.2% for  $0.8 \mu\text{g l}^{-1}$  Hg, respectively. The limit of detection calculated as the concentration giving a signal of three times the standard deviation of the blank, was  $2.8 \text{ ng l}^{-1}$  and  $4.3 \text{ ng l}^{-1}$  for Cd and Hg, respectively.

#### Sample analysis

The proposed method has been applied to the simultaneous determination of Cd and Hg in some tobacco leaf samples. The accuracy of the developed method was tested with recovery experiments by spiking standard solutions into the digest solution. The analytical results and recoveries are shown in Table 4. The concentrations of Cd and Hg in tobacco leaves were found to range from  $0.358$  to  $0.710 \mu\text{g g}^{-1}$  and from  $0.046$  to  $0.082 \mu\text{g g}^{-1}$ , respectively, which were in good agreement with the results of conventional HG-AFS. To validate the accuracy of the proposed method, a tea leaves certified reference material (GBW 07605) was analyzed. The results are shown in Table 5, and are in good agreement with the certified value.

**Table 4** Analytical results of Cd and Hg in tobacco leaves ( $n = 6$ )

Samples	Determined concentration ( $\mu\text{g g}^{-1}$ )		Added concentration ( $\mu\text{g g}^{-1}$ )		Obtained concentration $\mu\text{g g}^{-1}$		Recovery (%)	
	Cd	Hg	Cd	Hg	Cd	Hg	Cd	Hg
1	$0.453 \pm 0.003$	$0.071 \pm 0.003$	0.500	0.100	$0.978 \pm 0.004$	$0.165 \pm 0.003$	105	94
2	$0.576 \pm 0.002$	$0.064 \pm 0.005$	0.500	0.100	$1.081 \pm 0.003$	$0.160 \pm 0.005$	101	96
3	$0.532 \pm 0.004$	$0.082 \pm 0.002$	0.500	0.100	$1.012 \pm 0.005$	$0.184 \pm 0.003$	96	102
4	$0.358 \pm 0.007$	$0.057 \pm 0.003$	0.500	0.100	$0.843 \pm 0.005$	$0.151 \pm 0.004$	97	94
5	$0.710 \pm 0.002$	$0.046 \pm 0.002$	0.500	0.100	$1.245 \pm 0.003$	$0.150 \pm 0.005$	107	104

## Conclusion

Trace mercury and cadmium were successfully simultaneously determined by CV-AFS in the present system. The modified atomizer was shown to be effective and feasible for improving the stability of the fluorescence signal. Thiourea combined with nickel(II) was found to be effective sensitivity enhancers for cadmium determination compared with other reagents. Finally, the method was successfully used to determine the concentration of mercury and cadmium in tobacco leaves. The proposed method is simple, sensitive and reliable enough to determine trace cadmium and mercury in environmental and biological samples.

## Acknowledgements

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