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RESEARCH ARTICLE

Ran SUO, Weijuan AN, Na LI

Determination of ultratrace cadmium in food and environmental samples by ETAAS after vapor generation and *in situ* preconcentration

Abstract A method is described for the determination of ultratrace cadmium by coupling a continuous flow vapor generation system with *in situ* preconcentration technique and electrothermal atomic absorption spectrometry (ETAAS). A graphite tube coated with Ir as permanent chemical modifier was used for trapping cadmium vapor species. The effects of the flow rates of carrier gas and sample injection in vapor generation systems on the trapping measurement for cadmium were respectively investigated. Graphite tubes with different characteristic surfaces were comparatively studied for trapping cadmium vapor. The experimental results showed that the permanent chemical modifier of Ir is an alternative to the thermolabile modifier of Pd for simplifying the trapping measurement. The trapping efficiency of cadmium on the graphite tube coated with Ir was estimated. The trapping temperature and time were also investigated. A detection limit (3σ) of $0.005\ \mu g \cdot L^{-1}$ was obtained for this proposed method. The relative standard deviation (RSD) was 1.4% for $0.5\ \mu g \cdot L^{-1}$ of Cd ($n = 11$). This method can be applied to the determination of ultratrace cadmium in food and environmental samples with good agreement between the certified and found values.

Keywords vapor generation, ETAAS, permanent chemical modifier, *in situ* preconcentration, cadmium

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Ran SUO (✉), Weijuan AN, Na LI
College of Food Science, Agricultural University of Hebei, Baoding 071001, China
E-mail: ransuo@yahoo.com.cn

Ran SUO
School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China
Tianjin Rice Technical Engineering Center, Tianjin 300457, China

1 Introduction

Cadmium is one of the most toxic elements to human health even at low levels. This kind of environmental pollutant can produce accumulated levels in soils and plants, allowing it to enter the food chain and accumulate in humans. For this reason, years of effort have been devoted to the development of more sensitive, fast and accurate approaches to determine cadmium in biological and environmental systems and food samples. Among the most important analytical techniques for monitoring this element is atomic spectrometry, in particular, electrothermal atomic absorption spectrometry (ETAAS) (Andrew et al., 2000; Mark et al., 2001). The ultratrace levels of Cd usually present in such samples and the complexity of the matrices make it necessary to use separation and preconcentration procedures, such as extraction methods and sorption on resin, to improve the sensitivity of determination and eliminate the interference of matrices. However, those procedures have some disadvantages, such as being of a laborious nature.

The gaseous phase enrichment techniques after vapor generation, which separates the analyte from the matrices, offers the unique advantages of higher sensitivity and selectivity, and speediness (Guo et al., 2000). Initially, Drasch et al. (1980) reported the enrichment technique of *in situ* trapping on a graphite furnace after hydride generation for the determination of arsenic in biological samples. So far, the *in situ* trapping of analyte on a graphite furnace after vapor generation has been the most successful application of the gaseous enrichment technique to atomic spectrometry for trace and ultratrace analysis (Matusiewicz et al., 1996; Dimiter, 1999; Dimiter, 2000). Heidi et al. (1997, 1998) reported on the *in situ* preconcentration techniques for the determination of cadmium in water and urine samples with ETAAS following vapor generation from organized media (DDAB). A graphite tube coated with Pd was used for trapping cadmium and the detection limit for Cd could be improved to $0.005\ \mu g \cdot L^{-1}$. An uncoated graphite tube was also used for trapping measurements of cadmium in environmental samples, and the detection limit of $0.010\ \mu g \cdot L^{-1}$ was obtained (Henryk et al., 1997). The application of the *in situ* trapping technique coupled with ETAAS to the determination of cadmium was mainly focused on an environmental sample, water (Leonardo et al., 2003). In this work, a method for the determination of trace cadmium in food and environmental samples by ETAAS following vapor generation and *in situ* trapping on a graphite furnace coated with Ir as permanent chemical modifier is proposed, with merits of higher sensitivity and selectivity, simplicity and convenience.

2 Materials and methods

2.1 Apparatus

A Perkin-Elmer Model 1100B atomic absorption spectrometer equipped with an HGA-700 graphite furnace and a deuterium background corrector was employed in this work. A cadmium hollow cathode lamp (General Research Institute of Nonferrous Metals, Beijing, China) was operated at 10 mA. The 228.8 nm resonance line of Cd was selected as the analysis line, with an instrumental spectral bandwidth of 0.7 nm.

The schematic diagram of the system of continuous flow vapor generation and *in situ* trapping in a graphite tube is shown in Fig. 1.

A Qwave 3000 microwave digestion system (Questron Corporation, USA) equipped with PTFE vessels was used to digest the samples.

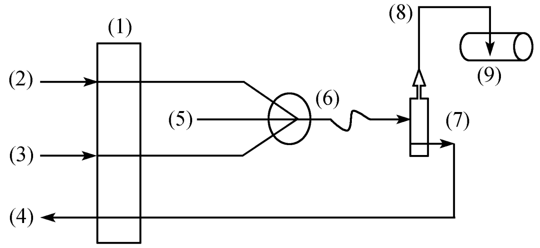

Fig. 1 Schematic diagram of the vapor generation and trapping system

Note: Numbers of (1)–(9) represent peristaltic pump, KBH_4, sample, waste, carrier gas, mixing tube, gas/liquid separator (GLS), transfer line and graphite tube, respectively.

2.2 Reagents

A standard stock solution of $1.00\ mg \cdot L^{-1}$ cadmium GBW (E)080402 stabilized in 1% HNO_3 was provided by National Research Center for GeoAnalysis (China). The working standard solution of Cd was prepared by stepwise dilution of appropriate aliquots of the stock solutions as required just before use. Orthophenanthroline solution ($0.5\ mg \cdot L^{-1}$) was prepared by dissolving in diluted hydrochloric acid solution. One $g \cdot L^{-1}$ Co^{2+} was prepared from $CoCl_2 \cdot 6H_2O$. The solution of $20\ g \cdot L^{-1}$ potassium tetrahydroborate was freshly prepared by dissolving KBH_4 powder in $5\ g \cdot L^{-1}$ potassium hydroxide solution and stored in polyethylene bottles.

The iridium modifier solution of $2.50\ g \cdot L^{-1}$ was prepared by dissolving 0.5973 g $(NH_4)_3IrCl_6$ in diluted HCl and diluting to 100 mL with water. The zirconium modifier solution of $2.50\ g \cdot L^{-1}$ was prepared by dissolving 0.8831 g $ZrOCl_2 \cdot 8H_2O$ in 10 mL diluted HCl and diluting to 100 mL with water. The palladium modifier solution of $2.50\ g \cdot L^{-1}$ was prepared by dissolving 0.8336 g $PdCl_2$ in 10 mL of $0.1\ mol \cdot L^{-1}$ HNO_3 and diluting to 500 mL with water.

Certified reference materials (CRMs) were Peach leaf (GBW 08501), Tea (GBW 08505), Rice flour (GBW 08502) and Wheat flour (GBW 08503), supplied by the National Research Center for Certified Reference Material (China).

All reagents used in this work were of analytical grade or higher purity. Doubly de-ionized water was used throughout the test.

2.3 Coating graphite tubes

Ir and Zr coating was conducted by injecting four 50 μL aliquots of iridium and zirconium modifier solutions ($2.50\ g \cdot L^{-1}$) respectively into the graphite tubes. Each injection was followed by the temperature program shown in Table 1. Sufficient Ir and Zr coating could last the lifetime of the tube provided that the clean-out temperature was not over 2300°C (James et al., 1999).

For Pd coating, 50 μg of Pd was injected into the graphite tube before each atomization cycle, following the procedure described previously (Lian et al., 1998).

Table 1 Temperature program for graphite tube coating

step	temperature/°C	ramp time/s	hold time/s	internal gas flow/ ($mL \cdot min^{-1}$)
1	110	10	50	300
2	130	30	50	300
3	1200	30	20	300
4	2000 (for Ir) 2600 (for Zr)	1	3	300

2.4 Sample pretreatment

Approximately 0.5 g of each sample was accurately weighed and transferred to the PTFE liners of the microwave-assisted digestion system, to which 10 mL of concentrated HNO_3 and 2.5 mL of 30% H_2O_2 were added.

The microwave power was set at 800 W. The samples were heated to 170°C in 10 minutes, remaining at 170°C for 20 minutes. After digestion, the solutions were gently heated on a hot plate to near dryness. The residues were diluted to the desired volume with $0.37\,\mathrm{mol\cdot L^{-1}}$ HCl. The final sample solutions were prepared containing $0.37\,\mathrm{mol\cdot L^{-1}}$ hydrochloric acid, $0.5\,\mathrm{mg\cdot L^{-1}}$ orthophenanthroline and $1.0\,\mathrm{mg\cdot L^{-1}}$ cobalt ion for the subsequent vapor generation. In all cases, a suite of reagent blanks were processed through the digestion procedure.

2.5 Procedure

The enhancement reagents, orthophenanthroline and cobalt, were used to improve the vapor generation efficiency of cadmium, which was described in the previous paper (Sun and Suo, 2004). The sample and the reducing agent solution of $20\,\mathrm{g\cdot L^{-1}}$ KBH_4 were separately pumped through a peristaltic pump in a continuous mode at a flow rate of $4\,\mathrm{mL\cdot min^{-1}}$. The vapor was generated in the mixing tube and transported by the carrier gas of argon into the graphite furnace where it was sequestered. The furnace temperature program for cadmium vapor trapping and determination is shown in Table 2. In step 2, the quartz tip of the transfer line was inserted into the furnace while the temperature reached 300°C. After trapping for 40 s, the quartz tip was lifted up and the atomizer was purged of protective gas with argon in order to remove the residual vapor (step 3). The collected analyte was atomized and determined in step 4.

Table 2 Temperature program for trapping and measurement

step	temperature/°C	ramp time/s	hold time/s	internal gas flow/ $(\mathrm{mL\cdot min^{-1}})$	read
1	120	1	10	300	–
2	300	10	40	0	–
3	300	1	10	300	–
4	1600	0	4	0	yes
5	2300	4	10	300	–

3 Results and discussion

3.1 Effect of the trapping surface character

The hydride collection on the interior surface of the graphite tube was a process of thermal or catalytic decomposition and deposition (Lee, 1982; Sturgeon et al., 1989). The trapping surface characteristic was expected to affect the vapor trapping efficiency. The tube pretreated with noble or carbide-forming metal, which could significantly improve the efficiency of both preconcentration and atomization, was attractive in the in-atomizer trapping techniques. In the determination of Cd with vapor generation and *in situ* preconcentration ETAAS, the modifier Pd was generally used for trapping cadmium vapor due to its efficient adsorption (Heidi et al., 1997). However, the thermal instability of Pd-coating resulted in recoating before each trapping. Considering the simplicity of manipulation, permanent modification was focused on (Dimiter et al., 2000). The permanent chemical modifiers, such as Ir, W and Zr, were favored because these coatings needed to be applied only once during the lifetime of the tube. In this work, the performance of the uncoated tube and Ir-, Zr- and Pd-coated tubes were comparatively investigated for trapping cadmium vapor by fixing the atomization temperature at 1600°C and varying the trapping temperatures (Fig. 2). It was obvious that the Pd-coating was the most favorable surface while the uncoated tube seemed to be less efficient for trapping. In the cases of Pd- and Ir-coating, the lower trapping temperatures gave the maximum signals while the Zr-coated tube needed higher temperatures for the maximum signal, indicating that they may work in different ways. Although the Ir-coating was slightly less efficient than the Pd-coating for trapping cadmium vapor at the lower trapping temperatures below 300°C, the Ir-coating served as an alternative to the Pd-coating because the recoating before each trapping cycle was unnecessary.

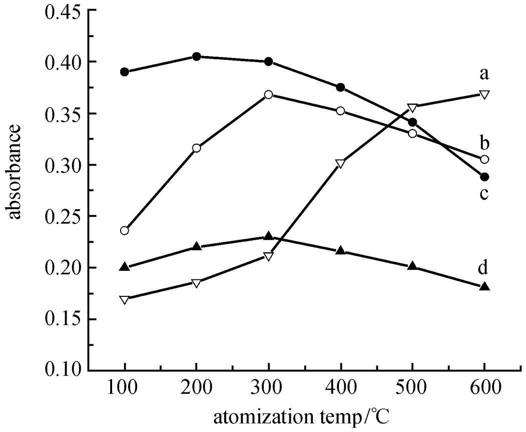

Fig. 2 Effects of trapping temperature on the signal
Note: (a) Zr-coated, (b) Ir-coated, (c) Pd-coated and (d) uncoated.

The atomization temperatures of cadmium adsorbed onto the two different characteristic trapping surfaces, Ir-coated and uncoated, were also comparatively investigated by fixing the trapping temperature at 300°C. The results (Fig. 3) showed that the optimum cadmium atomization temperature was 1600°C for an Ir-coated tube and 1400°C for an uncoated tube.

3.2 Effect of carrier gas

Argon was used as the carrier gas in the vapor generation system to sweep and transport the cadmium vapor into the

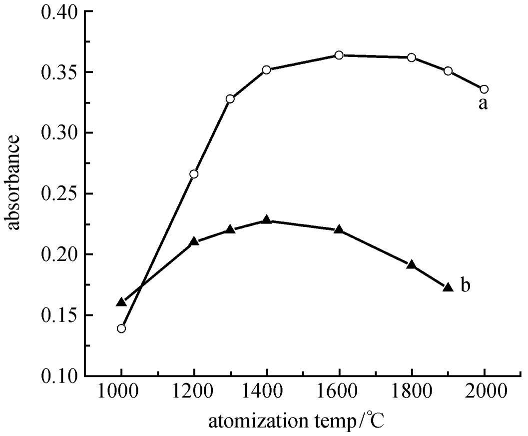

Fig. 3 Effects of atomization temperature on the signal
Note: (a) Ir-coated; (b) uncoated.

graphite furnace. The flow rate of the carrier gas affected the processes of cadmium vapor generation, release and transportation. Firstly, when the carrier gas went through the reaction solutions, the bubbles produced mixed the analyte and reductant well, and facilitated cadmium vapor generation. Secondly, the bubbles in the solutions provided a large surface-to-volume ratio that benefited the separation of the resultant volatile species from the liquid phase as quickly as possible and minimized its residence time in the liquid phase, otherwise, the analyte phase separation efficiency would be impaired because the cadmium vapor would be captured by the liquid phase before its escape. Finally, increasing the flow rate of the carrier gas would shorten the residence of cadmium vapor in the transfer line, thereby lowering the risk of its decomposition and adsorbing on the interior surface of the transfer line. However, a short residence time of cadmium vapor in the graphite tube was unfavorable for the trapping. The trapping efficiency should decrease with increasing carrier gas flow rate. The effect of the carrier gas flow rate was investigated and the results showed that the absorbance signal increased with increasing the carrier gas flow rate and decreased after reaching a flow rate over 400 mL·min^{-1}. In this work, a carrier gas flow rate of 400 mL·min^{-1} was selected.

3.3 Effect of sample flow rate and trapping time

The effect of sample and reagent flow rates was investigated with a flow ratio of sample to reagent 1:1 and a trapping time of 40 s for 0.5 μg·L^{-1} of cadmium. As expected, the signal increased linearly with increasing the sample flow rate until over 8 mL·min^{-1}. The signal reached a peak when the sample flow rate was over 12 mL·min^{-1}. Probably, a bigger volume of the sample flow rate was unfavorable to the well reaction and the escape of cadmium vapor generated from the liquid phase. The sample flow rate selected for subsequent experiments was 4 mL·min^{-1}, which was convenient for application of the continuous flow vapor generation system in this study.

Similarly, the signal increased linearly with increasing the trapping time until over 50 s when the signal started to increase by slow degrees. The measurement sensitivity of the proposed method would be improved with increasing the amount of cadmium trapped. However, the amount of cadmium trapped would reach a steady value with prolongation of the trapping time because of the limited capacity of the graphite tube for trapping cadmium. In this work, a trapping time of 40 s was selected to avoid time-consuming analysis.

3.4 Efficiency of overall trapping process

The efficiency of the overall trapping process (ε) was determined by different particular processes, i.e. the vapor generation reaction (ε_1), the phase separation of vapor species (ε_2), the transportation of vapor to graphite furnace (ε_3) and the vapor trapping on graphite furnace surface (ε_4): $\varepsilon=\varepsilon_1\times\varepsilon_2\times\varepsilon_3\times\varepsilon_4$.

The overall efficiency, representing an efficiency of vapor formation, release, transportation and trapping, was roughly estimated for 0.5 μg·L^{-1} of cadmium by comparing the integrated absorbance data related to the trapped analyte and the analyte introduced by conventional liquid sampling: $\varepsilon=A_{\mathrm{trapping}}/A_{\mathrm{conventional}}$, where the same atomization efficiency for both sampling techniques were assumed. The trapping measurement was carried out with the proposed procedure. The conventional measurement was carried out by using the same coated graphite furnace and programming temperature as that used in the trapping measurement. The results showed that the efficiency of the overall trapping process was 5.3%. The efficiencies of the vapor formation and release ($\varepsilon_1\varepsilon_2$) were estimated by analyzing the amounts of cadmium remaining in the waste solution and deposited on the reaction tube after vapor generation. The analysis with conventional sampling ETAAS revealed that 41.0% of the initial analyte had reacted and was released. The amounts of cadmium depositing on the interior wall of the gas/liquid separator and transfer line were also analyzed after being thoroughly washed with several aliquots of diluted HNO_3. The obtained result was 35.2% of the initial analyte, which meant that only 5.8% of the initial analyte reached the atomizer and most of the generated cadmium vapor was lost in the processes of release and transportation. From the results, the efficiency of vapor trapping on the Ir-coated graphite tube was estimated to be 91%.

3.5 Evaluation of interference

In this study, the effects from potential interference ions were examined for the determination of 0.5 μg·L^{-1} Cd with the proposed procedure. Variation over ± 10% in the analytical signal that resulted from foreign ions was taken as interference. The following concentrations of foreign ions at $mg \cdot L^{-1}$ level did not result in interference: Fe(III), Mn(II), and Zn(II) (20 $mg \cdot L^{-1}$); Cr(III) (5 $mg \cdot L^{-1}$); Sn(II), As(III) and Sb(III) (2 $mg \cdot L^{-1}$); Te(IV), Hg(II) and Co(II) (1 $mg \cdot L^{-1}$); Se(IV) and Cu(II) (0.5 $mg \cdot L^{-1}$); Bi(III), Pb(II) and Ni(II) (0.2 $mg \cdot L^{-1}$), and Ag(I) (0.1 $mg \cdot L^{-1}$).

The presence of orthophenanthroline in the reaction medium played a role in depressing the interference of some ions.

3.6 Analytical figures of merit

Using the proposed method, analytical figures of merit including calibration curve, detection limit and precision of replicate measurements were evaluated. A calibration curve was established by plotting the integrated absorbance based on the cadmium concentrations in the range of 0.05–1.0 $\mu g \cdot L^{-1}$. Five concentrations were used and triplicate analyses were carried out at each concentration. The obtained regression equation was $Y = 0.837X + 0.0018$ with a linear correlation coefficient of 0.9961, where Y is the integrated absorbance and X is the concentration expressed in $\mu g \cdot L^{-1}$. The detection limit was calculated on the basis of 3σ criterion, with eleven replicated measurements of the blank signal. A detection limit of 0.005 $\mu g \cdot L^{-1}$ was obtained. The precision was evaluated by analyzing eleven replicates of the standard solution containing 0.5 $\mu g \cdot L^{-1}$ Cd. The relative standard deviations (RSD) obtained was 1.4%.

3.7 Sample analysis

The proposed method was applied to the real sample analysis of certified reference materials for validating its accuracy. The results are summarized in Table 3. The accuracy of the proposed method is evident, with which the found values (average ± *SD*, $n = 7$) agreed with the certified values at 95% confidence level. To avoid possible matrix effects, the calibration curve was achieved using the method of standard addition. In comparison with the slope of calibration curves between the standard addition method and the direct standard method, there was no significant interference. Therefore, the direct standard calibration method can also be used for the analysis of food and environmental samples.

Table 3 Analytical results (average ± *SD*, $n = 7$)

CRMs	certified value/($\mu g \cdot g^{-1}$)	found value/($\mu g \cdot g^{-1}$)
wheat flour (GBW 08503)	0.031±0.002	0.028±0.007
rice flour (GBW 08502)	0.020±0.002	0.024±0.009
peach leaf (GBW 08501)	0.018±0.004	0.016±0.004
tea (GBW 08505)	0.023±0.004	0.019±0.006

4 Conclusions

A method for the determination of ultratrace cadmium was established in combination with a continuous flow system for vapor generation with *in situ* preconcentration of the cadmium vapor species in a graphite furnace coated with Ir as permanent chemical modifier. Compared with the thermally unstable modifier, the application of a permanent modifier simplified the measurement manipulation simultaneous with high sensitivity and convenience of the proposed method for the analysis of food and environmental samples that often have complicated matrices. This approach provides a feasible alternative to the conventional sampling method ETAAS.

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