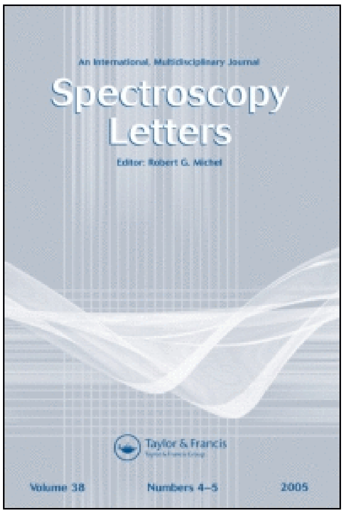

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Improved Performance of On-line Atom Trapping in Flame Furnace Atomic Absorption Spectrometry by Chemical Vapor Generation: Determination of Cadmium in High-Salinity Water Samples

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ABSTRACT On-line atom trapping inside a nickel flame furnace using chemical vapor generation for sample introduction was proposed for the determination of trace cadmium by flame atomic absorption spectrometry (AAS). Cadmium volatile species was generated upon reaction with potassium borohydride and then flushed into a flame furnace for on-line trapping by a flow of nitrogen carrier gas. The middle part of the flame furnace, where the carrier gas impacts, is cooled by the gas flow, and this provides a fine strategy for on-line atom trapping for the purpose of preconcentration. A stainless steel plate is put on the top of the flame burner in the middle to form a flame-free zone, which also greatly lowers the temperature of the flame furnace and facilitates the atom-trapping process. Due to the introduction of chemical vapor generation, matrix effect was greatly alleviated compared with direct pneumatic nebulization for on-line atom trapping in flame furnace AAS. With trapping time of 35 s, the current approach achieved an excellent limit of detection of $20\,\mathrm{ng\,L^{-1}}$. The proposed method was successfully applied for the quantification of cadmium in high-salinity samples.

KEYWORDS atom trapping, cadmium, chemical vapor generation, flame furnace AAS, high salinity sample

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INTRODUCTION

Gas-phase trapping of volatile hydrides/atoms has intrigued great research interest in recent years, due to its efficient enrichment and simple operation.[1–8] The alleviation/elimination of gas-phase interference in hydride atomization is its additional merit. Matusiewicz et al. have well summarized the trapping of atoms and hydrides and its applications in analytical atomic spectrometry.[9,10] Nowadays, the trapping device has been greatly diversified, including tungsten tube,[11] silica trap,[12] integrated atom trap,[2,4,13] and the like.

In our previous work, the marriage of on-line atom trapping with flame furnace AAS was successfully engaged by employing pneumatic nebulization sampling into the flame furnace.[14] Flame furnace AAS is a new flame AAS technique developed by Berndt et al. with significantly improved performance over conventional flame AAS.[15,16] By integrating on-line atom trapping with flame furnace AAS, the sensitivity was further improved (for cadmium, 730-fold over conventional flame AAS). However, the on-line atom trapping method suffered undesirable interference from samples of complicated matrix.

Chemical vapor generation (CVG) enjoys the popularity of sample introduction into atomization cells.[17] In CVG, the analyte is derived into its vapor species and thus the interference caused by the problematic matrix can be alleviated/eliminated. In this work, the advantage of CVG sampling was explored to eliminate the matrix problems for the determination of trace cadmium in high-salinity water samples. It should be pointed out that the matrix effect on Cd chemical vapor generation in solution can also be complicated and serious. For instance, copper and lead ions cause serious interference, and masking agent such as potassium cyanide is needed in the analysis of complicated samples containing these interference ions.[22] It must be mentioned that Arruda et al. also investigated the CVG sample introduction into flame furnace AAS in detail,[18,19] but no on-line atom-trapping process was involved.

MATERIALS AND METHODS

Instrumentation

The instrumental arrangement is shown in Figure 1, and the arrangement of flame furnace system was similar to the previous work.[14] A model SP3520AAPC flame atomic absorption spectrometer equipped with a D_2 lamp for background correction (Shanghai Spectrum Instruments Co., Shanghai, China) was used throughout this work. Working parameters (analytical line, 228.8 nm; hollow cathode lamp current, 4 mA; and spectral bandpass, 0.7 nm) were recommended by the manufacturer. A nickel tube of 10/12 mm id/od and 10 cm in length (J. & J. Ethen, Aachen, Germany) was employed as the flame furnace, with six holes of 2.5 mm in diameter at the bottom to allow flame gases to enter the tube. A piece of stainless steel plate is put on the burner head just below the sampling hole of the flame furnace to generate a flame-free zone, which helps to lower the temperature of the flame furnace in order to facilitate the atom-trapping process. The on-line chemical vapor generation for cadmium was carried out with a commercial flow injection system (model FIA-3110, Vital Instruments Co. Ltd., Beijing, China) in continuous flow mode. The generated cadmium vapor was flushed to the flame furnace with a flow of nitrogen carrier gas through a ceramic tube. In order to facilitate sample introduction, the initial sample introduction hole of the nickel tube was enlarged to 4 mm id, and the ceramic sampling tube was fixed onto a moveable holder. An Infrared Thermometer (Raynger 3i^{TM}1MSCL2U; Raytek, Santa Cruz, CA, USA) was used for the measurement of the temperature within the flame furnace.

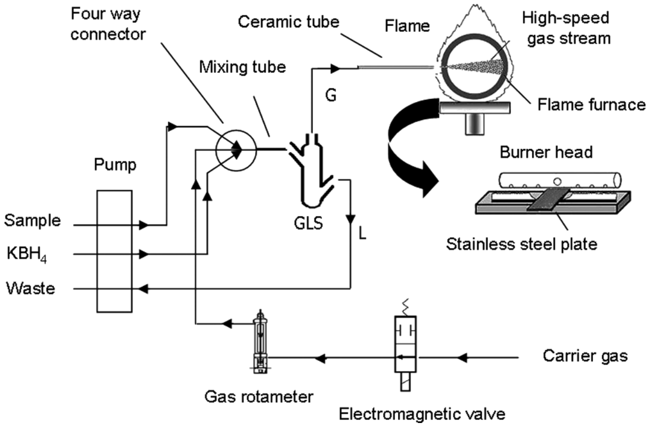

FIGURE 1 **Instrumental arrangement of the CVG on-line atom-trapping flame furnace AAS (not to scale). A stainless steel plate is put on the top of the burner to partially cover the flame and generate a flame-free zone, which lowers the temperature of the flame furnace and facilitates the atom-trapping process.**

Reagents

All reagents used were of the highest purity available but at least of analytical grade. Sub-boiled doubly distilled water (DDW) was used to prepare solutions throughout this work. Standard stock solutions of Cd, Se, Mn, Cr, Ni, Sn, Fe, Pb, Hg, Zn, and Ag (1000 $\mu g\,g^{-1}$) were purchased from the National Research Center for Standard Materials

(NRCSM, Beijing, China). Working solutions in the μg L^{-1} and sub-μg L^{-1} range were obtained by stepwise dilution from the stock solutions. Inorganic acids, salts [KNO_3, NaCl, KCl, $CaCl_2$, $NaHCO_3$, KBr, $Ca(NO_3)_2$, $MgSO_4$, Na_2SO_4, and $Al(NO_3)_3$], and other reagents (thiourea and cobalt chloride) were purchased from Chengdu Kelong Chemical Reagents Co. (Chengdu, China). KBH_4 solutions were prepared daily by dissolving the reagent in 0.5% KOH solution.

Samples

To validate the accuracy of the developed method, a certified reference material, GBW 08608 (Trace Elements in Water), was purchased from NRCSM with proper dilution. Several artificial seawater and artificial brine water samples were synthesized according to ref. 20 to check the accuracy of the proposed method.

Operating Procedure

As shown in the arrangement of the instrumental setup (Fig. 1), a standard (or sample) solution prepared in 4% v/v HCl, 1 μg mL^{-1} $CoCl_2$, and 1 mg mL^{-1} thiourea was continuously pumped at 2.9 mL min^{-1} and mixed on-line with 4% m/v $NaBH_4$ solution also running at 2.9 mL min^{-1} (Fig. 1). After separated from the liquid phase in the gas–liquid separator, the generated cadmium volatile species was swept into the nickel flame furnace for atomization and on-line atom trapping for 35 s. The high-speed gas stream caused strong cooling to the inner surface of the flame furnace, which resulted in the temperature decrease from 850°C to 600°C. Cadmium volatile species was first atomized and then trapped onto the cooled surface immediately. During the sampling stage, a stainless steel plate (4 × 2 mm) was put on the top of the flame burner just below the ceramic sampling tube to generate a flame-free zone (Fig. 1), which helped to lower the temperature of the flame furnace in order to facilitate the atom-trapping process. When the sampling completed, the cooling gas was stopped via an electromagnetic valve and the atomic absorption signal was recorded. A typical temporal profile of 0.1 μg L^{-1} cadmium of three measurements is shown in Figure 2.

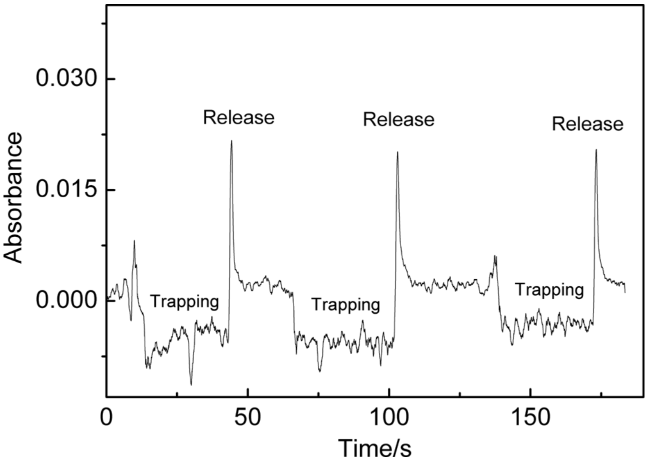

FIGURE 2 Temporal atomic absorbance profiles of 0.1 μg L^{-1} Cd.

RESULTS AND DISCUSSION

Investigation of CVG Conditions for Cadmium

Cadmium can be derived into volatile species by using KBH_4, and thiourea together with cobalt ion is usually used to enhance the generation efficiency.[21–23] Therefore, in this work, the concentrations of HCl, KBH_4, thiourea, and Co^{2+} were first optimized for the determination of cadmium. Finally, optimal concentrations of 4% HCl, 4% KBH_4 (in 0.5 KOH meida), 1.0 mg mL^{-1} thiourea, and 1 μg mL^{-1} Co^{2+} were selected for use. Further experimental results showed that 2.9 mL min^{-1} was the optimal flow rate for introduction of cadmium and KBH_4 solutions.

Atom-Trapping Conditions

Plate Width

In order to facilitate the atom-trapping process, a stainless steel plate was placed on the top of the burner head to generate a flame-free zone, as shown in Figure 1. When the plate width increased from 0 cm (without plate) to 2 cm, the absorbance of Cd increased sharply. The maximal signal was obtained in the range of 2 to 4 cm, and 2-cm plate width was chosen for use.

Carrier Gas Flow Rate

The effect of carrier gas (N_2) flow rate on the absorbance of cadmium was studied in the range 0.3–1.2 L min^{-1}, and the results are shown in

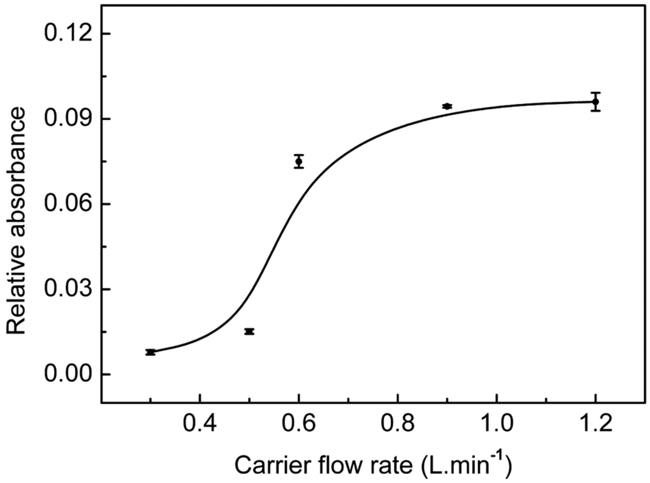

FIGURE 3 The influence of carrier gas flow rate on the cadmium atomic absorbance. The error bars stand for 1 standard deviation of three trials.

Figure 3. It was found that the signal increased sharply when the carrier gas flow increased from 0.3 to 0.9 L min^{-1}, and then leveled off. In this work, the flow rate of 1.2 L min^{-1} was employed. It seems that higher flow rates may be beneficial to the trapping process as the cooling effect may be more efficient. However, at higher flow rates, the dilution of the cadmium volatile species and short residence time of the analyte in the atomizer would be dominant, leading to the decreased atom densities.

Trapping Time

Trapping time (corresponding with sampling time) is a key factor on the cadmium absorption signal, as shown in Figure 4. With short trapping time, the sampling amount was small and the temperature of flame furnace was not cooled down enough for efficient trapping. As the trapping process went on, the volatile cadmium species was atomized and trapped, and the temperature of the tube was also decreased. Obviously, the trapping process would eventually reach an equilibrium, as the further decreased temperature can influence the atomization and trapping process. The trend shown in Figure 4 revealed such a phenomenon. A trapping time of 35 s was selected for the subsequent work.

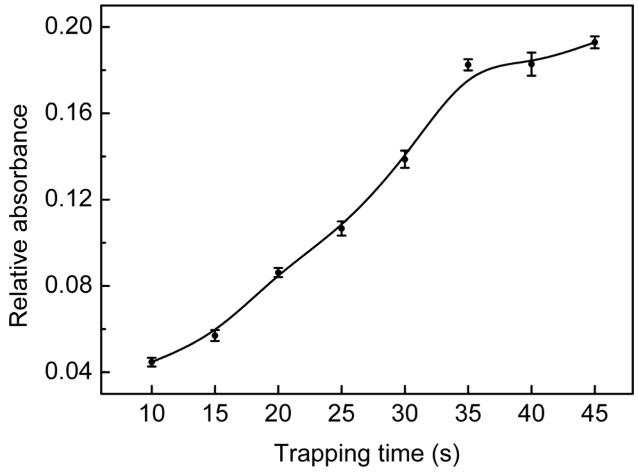

FIGURE 4 Effect of trapping time (sampling time) on the cadmium absorbance. The error bars stand for 1 standard deviation of three trials.

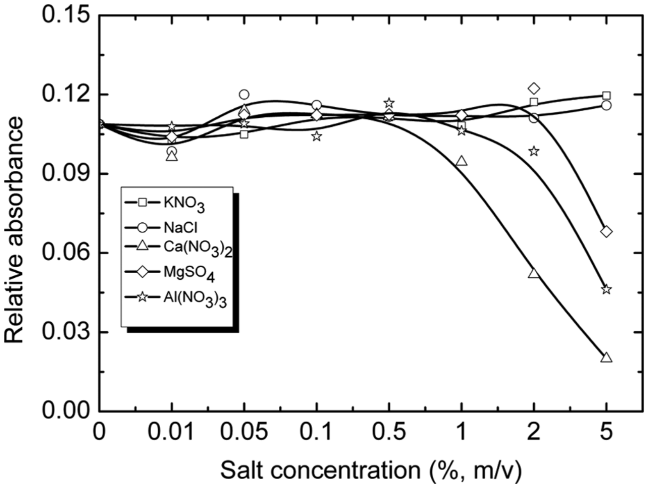

FIGURE 5 The influence of the concentrations of common salts on the absorbance of cadmium (1.0 μg L^{-1}).

Interferences

The interference may arise from two stages: chemical vapor generation and trapping process. The interferences from those frequently studied elements in previous works on cadmium CVG were evaluated. When the Cd concentration was 1 ng mL^{-1}, no significant interference was observed from 0.05 mg L^{-1} Cu(II) and Ag(I), 0.1 mg L^{-1} As(III), Se(IV), Bi(III), Sn(II), Ni(II), and Pb(II), 0.5 mg L^{-1}

TABLE 1 Analytical Characteristic of the Proposed Method for Cd Determination

Trapping time, s	35
Sample volume, mL	1.7
Calibration equation (C), μg L^{-1}	$A = 0.0898C + 0.0128$
Upper linear range, μg L^{-1}	4
Correlation coefficient (R^2)	0.9978
Limit of detection (3σ), ng L^{-1}	20
Precision @ 1 μg L^{-1} (RSD, $n = 9$)	1.9%

C: Concentration of cadmium
A: Absorbance of cadmium

TABLE 2 **Comparison of the Limit of Detection for Cadmium by the Proposed Method with Those by Various Analytical Atomic Spectrometric Methods**

Technique	Limit of detection, ng L^{-1}	Reference
This work	20	This work
HG *in situ* trapping flame AAS	50	3
PN-FF-AAS	15	14
PN-FF-AAS (fullerene)	100	26
FI-HG-AAS	30	24
TS-FF-AAS (C_{18} column)	30	27
USN-FF-AAS	600	28
GF-AAS	8[a]	29
HG-AFS	10	25

[a]Based on 50-µL sample volume. PN-FF-AAS, pneumatic nebulization flame furnace AAS; HG, hydride generation; GF-AAS, graphite furnace AAS, FI-HG-AAS, flow injection hydride generation AAS; TS-FF-AAS, thermospray flame furnace AAS; USN-FF, ultrasonic nebulization flame furnace AAS; HG-AFS, hydride generation atomic fluorescence spectrometric.

Hg(II), 5 mg L^{-1} Cr(III) and Mn(II), and 10 mg L^{-1} Fe(III) with recoveries for Cd in the range of 94% to 107%. The interference from five macro constituents in common environmental samples (K, Na, Ca, Mg, and Al) were also carefully studied using 1.0 µg L^{-1} Cd, and the results are shown in Figure 5. Both K and Na cause no significant interference given that their concentrations are less than 5%, and the toleration limits for Ca, Mg, and Al were 0.5%, 2%, and 1%, respectively. Compared with our previous work,[14] the toleration limits for K, Na, Ca, and Mg were increased at least by 50, 1000, 250, and 400 folds, respectively. The results again showed the efficient matrix separation of chemical vapor generation, as documented in many references. On the other hand, this also permits the potential application of the proposed method for the analysis of high-salinity samples for trace cadmium.

Analytical Figures of Merit and Its Potential Application

The analytical figures of merit for the proposed method for Cd determination are summarized in Table 1. The limit of detection (LOD, 3σ) was found to be 20 ng L^{-1}, which is comparable with the reference values for Cd by various methods (Table 2).[3,14,24–29]

The proposed method was validated by analyzing a certified reference material and several artificial water samples with high salinity, and the analytical results are given in Table 3. The CRM was analyzed after suitable dilution, while spiked-recovery tests were carried out for the artificial water samples. Good agreement was achieved for the CRM (*t*-test, $t_{exp} < t_{tab}$, p = 0.95, N = 3) and recoveries ranging from 91% to 107% showed the validity of the proposed method.

CONCLUSION

Chemical vapor generation was successfully employed to eliminate the matrix interferences encountered in on-line atom-trapping flame furnace AAS. The proposed method was successfully applied

TABLE 3 **Analytical Results for Cadmium in CRM GBW 08608 and Several Artificial Water Samples**

Sample	Certified, ng g^{-1}	Cadmium added, ng mL^{-1}	Cadmium found, ng mL^{-1} [a]	Recovery, %	*t*-test (t_{tab} = 4.3, p = 0.95, N = 3)
GBW 08608	11.2 ± 0.5	—	10.7 ± 0.3[b]	—	$2.89 < t_{tab}$
Artificial brine[c]	—	0.00	0.50 ± 0.02	—	—
		0.50	1.03 ± 0.01	106	
		1.00	1.57 ± 0.02	107	
Artificial seawater[d]	—	0.00	0.16 ± 0.01	—	—
		1.00	1.07 ± 0.01	91	
		2.00	2.16 ± 0.01	100	

[a]Average ±1 standard deviation of three trials.

[b]ng g^{-1}.

[c]Composition of artificial seawater: NaCl 26.726 g kg^{-1}, $MgCl_2$ 2.260 g kg^{-1}, $MgSO_4$ 3.248 g kg^{-1}, $CaCl_2$ 1.153 g kg^{-1}, $NaHCO_3$ 0.198 g kg^{-1}, KCl 0.721 g kg^{-1}, KBr 0.058 g kg^{-1}, and H_3BO_3 0.058 g kg^{-1}.

[d]Composition of artificial brine: NaCl 17.32%, KCl 0.18%, $MgSO_4$ 1.66%, Na_2SO_4 2.75%, MgO 0.037%, and B_2O_3 0.106%, m/m.

to the analysis of high-salinity water samples for trace cadmium. At the current stage, only cadmium was studied, but the proposed method could be extended to several other elements with low appearance temperature.

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