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Validation of various vapor generation systems coupled with atomic fluorescence spectrometry for the determination of cadmium-A comparative evaluation of chemical variables, performance characteristics and interferences

Zhongxi Li*[1], Liping Zhou[2]

[1]The Research Center of Analytical Technique & Instrument, Northwest Geological Research Institute,
No. 25, Xiying Road, Xi'an, 710054, (CHINA)
[2]Analytical & Testing Center, Northwest Geological Research Institute, No. 25, Xiying Road, Xi'an, 710054, (CHINA)
Tel. : 86-029-88138203
E-mail: lizhongxi8@163.com

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ABSTRACT

Various vapor generation systems for the determination of Cd by VG-AS have been evaluated in this paper, including KBH_4-HCl, KBH_4-HCl-Co^{2+}-thiourea, KBH_4-HCl-Co^{2+}-8-hydroxyquinoline, KBH_4-$K_3Fe(CN)_6$-HCl-$NH_2OH{\cdot}HCl$ and KBH_4-HCl-$NaIO_3$ systems. It was found that the optimized chemical parameters for various vapor generation systems were keep at the same levels. The effects of recommendatory enhancers such as Co^{2+}-thiourea, Co^{2+}-8-hydroxyquinoline, $K_3Fe(CN)_6$ and $NaIO_3$ were studied and the results revealed that the enhancers did not improve the vapor generation efficiency of Cd besides thiourea-Co^{2+}. The sensitivities, precisions and detection limits of various vapor generation systems were tested and the use of KBH_4-HCl-Co^{2+}-thiourea system could obtain higher sensitivity, better precision and detection limits. In addition, the use of thiourea-Co^{2+}, viz, KBH_4-HCl-Co^{2+}-thiourea system, could reduce the interferences from some coexisting ions.

KEYWORDS

Vapor generation;
Cadmium;
Atomic fluorescence
spectrometry.

INTRODUCTION

Chemical vapor generation(CVG), as a method of sample introduction in atomic spectrometry, is considered as an effective technique and has been in widespread use for nearly 30 years[1,2]. Chemical pre-separation of the analyte from matrix, more efficient sample introduction than conventional pneumatic nebulization of solution, good detection power and high sensitivity are the main advantages of the technique. In recent years, this technique has rapidly developed and other elements have been appended to this group[3-10]. Pohl[11,12] reported the novel developments in the chemical VG of volatile species of the transition and noble metals through the reaction of $NaBH_4$ and the advances in the hydride generation atomic emission spectrometry.

The development of the sensitive method for the determination of trace cadmium become one of the interested research areas for its toxicity and low concentration in real samples; and the hyphenated vapor gen-

TABLE 1 : Literature on the chemical vapor generation systems of cadmium

VG system	Spectr. conditions	Generator	VG conditions	Analytical performance	Interferences	Comments	Ref.
$NaBEt_4$-acid	VG-NDAFS Ar-H_2 mini-flame VG-AAS QTA (flame-heated)	Batch Type A	In aqueous solution Acidity: pH=2.15 (1ml sample) 1.0ml of 1% $NaBEt_4$ Reaction temperature: 40^0C Carrier gas: Ar 1.2 l min^{-1}	LOD 0.2 ng ml^{-1}(AFS) 1ng ml^{-1}(AAS); RSD: 4% (n=5.5ng l^{-1} Cd); linear range: 0~40 ng ml^{-1}	Serious interferences from by Ni^{2+}, Co^{2+}, Cu^{2+} and Au^{3+} at 1μg/ml^{-1} level	At 40^0C, improves sensitivity 3-fold vs. 25^0C, then decrease above 50^0C; Using type A vessel improves sensitivity 6-fold vs. type B	**[13]**
$NaBH_4$-HCl-DDTC In organic medium	VG-AAS QTA (flame-heated)	Batch	In organic medium (DMF); 2ml of sample solution in DMF; 2ml of 1.8mol l^{-1} HCl in DMF; 3ml of 7% $NaBH_4$ in DMF; in presence of DDTC; reaction temperature: 55°C; Carrier gas: N_2 2.2 l min^{-1}	LOD 9.1 ng m_0 2.6 ng RSD: 2.9% linear range: 0~120ng		Blow 40^0C the reaction is slow, between 70 and 40^0C there is a linear increase in background with increasing temperature; the generation of the hydride is faster in the presence rather than the absence of DDTC	**[14]**
$NaBH_4$-HCl-DDAB	VG-ICP-AES	Continuous flow	In surfactant organized media Acidity: 0.4mol l^{-1} (flow rate 0.75ml min^{-1}); 4% m/v $NaBH_4$ in 0.1% m/v NaOH(flow rate 0.75ml min^{-1}); DDAB 10^{-2} mol l^{-1}	LOD 1ng ml^{-1} RSD: 2% (50 ng ml^{-1})	Interferences from Ni^{2+} and Zn^{2+} at 50 μg ml^{-1} level	Operating at lower temperatures for HG can provide a further decrease in detection limit for cadmium; the 'vesicular HG' technique proposed offers five times better detection limits for cadmium than conventional nebulization	**[34]**
KBH_4-HCl-Co^{2+}+thiourea	VG-NDAFS	Intermittent flow reactor	In aqueous solution; acidity: 0.24M HCl (flow rate 5.2ml min^{-1}); 5%m/v KBH_4 in 0.5%m/v KOH solution (flow rate 2.6ml / min^{-1}); 1% thiourea and 1mg L^{-1} Co^{2+}; Carrier gas 800ml min^{-1}	LOD 8 pg ml^{-1} RSD 1.2% (n=115ng ml^{-1}Cd)	Interferences from Cu^{2+}, Ni^{2+}, Pb^{2+}, Bi^{3+} and Au^{3+}.	In the presence of thiourea and cobalt ions, the sensitivity of the determination is greatly increased; the generation efficiency of the volatile cadmium species greatly depends on the type of the generator	**[35]**
$NaBH_4$-HCl	CV-AAS	Flow injection	In aqueous solution Acidity: 1M HCl(1.5 ml min^{-1}); 4% m/v $NaBH_4$ in 1% NaOH(1.5 ml min^{-1})	LOD 0.05 μg l^{-1} RSD 3~4% (5ng ml^{-1} Cd) Liner range: 0.5~6 μg l^{-1}		A comparison between an organic reaction medium and an aqueous medium has shown a similar Cd response; The HCl concentration is an important parameter; a higher HCl concentration is needed.	**[36]**
KBH_4-$K_3Fe(CN)_6$-HCl-NH_2OH•HCl	CV-AAS	Batch	In aqueous solution; acidity: 0.2~ 0.4 M HCl; 4% m/v KBH_4 in 0.4% m/v KOH; 3ml of sample and 2 ml of KBH_4; 3% m/v $K_3Fe(CN)_6$; 1% m/v NH_2OH·HCl; carrier gas N_2 0.8~1.0 l min^{-1}	LOD 11pg ml^{-1} RSD 5.12% (1ng ml^{-1} Cd n=7) Liner range : 0.011~2ng ml^{-1}	Interferences from Fe^{3+}, Zn^{2+}, Cu^{2+}	The liquid-gas separator is modified with dimethyldichlorosilicaane The modified liquid-gas separator can improve the precision	**[32]**

eration atomic spectrometric techniques have attracted great attention for Cd determination since the early papers by D'Ulivo[13] and Cacho[14]. After the early papers, about 40 more studies on VG for Cd have been reported[15-33] and the early literatures have been reviewed by Lampugnani et al[15]. However, the chemical vapor forming characteristic of Cd is different from of the classical hydride-forming elements such as As, Sb, Bi, Ge, Se, Te, Pb, etc. In the previously reported literatures, several attempts have been made to improve

VG system	Spectr. conditions	Generator	VG conditions	Analytical performance	Interferences	Comments	Ref.
KBH_4-HCl-Co^{2+}-8-hydroxyquinoline	VG-AFS	Intermittent flow reactor	In aqueous solution; Acidity: 0.36–0.38 M HCl; 2% m/v KBH_4 in 0.5% m/v KOH; 3mg l^{-1} 8-hydroxyquinoline and 1.0 mg l^{-1} Co^{2+}; Carrier gas Ar 300 ml min^{-1}	LOD 10 pg ml^{-1} RSD 1.7% (2ng ml^{-1} Cd n=11) Liner range 0.2~20ng ml^{-1}	The following ions at milligrams per liter level do not result in interference: Fe^{3+}(50); Zn^{2+}(20); Cr^{3+}(5); Sn^{2+}, As^{3+}; Ni^{2+}(2); Te^{6+}; Hg^{2+}(1); Se^{6+}, Cu^{2+}(0.5); Bi^{3+}, Pb^{2+}(0.2) and Ag^{+}(0.1)	The enhancement reagents are crucial to the chemical vapor generation of Cd; the presence of transition metal ions in the form of metal borides catalyzes the hydrogenation reaction; rapid reaction and phase separation are also very important for the vapor generation.	**[19]**
$NaIO_3$–KBH_4–HCl-(Co^{2+})	VG-AFS	Intermittent flow reactor	In aqueous solution; acidity: 0.4 M HCl(flow rate 5.0ml min^{-1}); 3.5 m/v KBH_4 in 0.56% m/v KOH(0.1M, flow rate 3.2 ml min^{-1}); 2.5% m/v $NaIO_3$ in sample solution; carrier gas Ar 400 ml min^{-1}.	Ref 20 LOD 10 pg ml^{-1} Liner range 0.01~4 ng ml^{-1} Ref 33 LOD 35pg ml^{-1} RSD 4.84% (31. 72 ng/g Cd, n=12) Liner range 0~4 ng ml^{-1}	Interferences from Fe^{3+} at 1μg ml^{-1} level, Cu^{2+} at 0.3μg ml^{-1} level, As^{3+} at 0.2μg ml^{-1} level, Se^{4+} and Au^{3+} at 0.25μg ml^{-1} level and Pt^{2+} at 0.3μg ml^{-1} level.	X* or X^{-} reacts with Cd^{2+}or CdH_2(from hydride generation process) to form CdX_2(or Cd_mX_n) and thus producing volatile cadmium -containing species and enhancing the intensity of atomic fluorescence of cadmium; the signal is not significant under cold vapor mode; the maximal enhancement is more than 10-fold; the order of the sensitivity enhancement effect is as follows: $NaIO_3$ > $NaBrO_3$>$NaClO_3$.	**[20, 33]**

Cd vapor generation efficiency and develop a series of Cd chemical vapor generation systems(TABLE 1); and some of these literature data were much inconsistency or even contradictory.

The aim of this study was to evaluate the chemical variables, performance characteristics and interferences of various vapor generation systems for the produce of volatile cadmium species with same vapor generator and under same working conditions; and in an effort to reveal the advantages and disadvantages of each chemical vapor generation system.

EXPERIMENTAL

Reagents and chemicals

All the chemicals used were of the highest purity available and of at least analytical grade. All the glassware and plasticware were acid-washed with 20%(v/v) HNO_3 and rinsed with ultra-pure water. Ultra-pure water, obtained using a Milli-Q system(Millipore), was used throughout.

A1000mg l^{-1} stock standard solution of Cd(II) as nitrate in 2%(v/v) HNO_3(National standard material center of R.P. China); 1000mg l^{-1} stock standard solutions of As^{3+}, Sb^{3+}, Bi^{3+}, Hg^{2+}, Se^{4+}, Te^{4+}, Sn^{2+}, Ge^{4+}, Au^{3+}, Ag^{+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, V^{5+}, Cr^{6+}, Ga^{3+}, Fe^{3+}, Mo^{6+}, Mn^{2+} were purchased from National standard material center of china for study on the interference effects of foreign ions; and the concentrations of Cd were detected by ICP-MS and ensured cadmium-free in those solutions; KBH_4 solutions were prepared daily by dissolving the reagent(Tianjin Institute of Chemical Reagents, China) in the solution of 0.2 %(m/v) potassium hydroxide(Xi'an Chemical Reagents Co, China); thiourea (Xi'an Chemical Reagents Co., China); 8-hydroxyquinoline(Beijing Chemical Reagents Co., China); All mineral acids used were obtained from Xi'an Chemical Reagents Co.

Working standard solutions were prepared daily by three-stage dilution of the 1000mg l^{-1} stock solution

TABLE 2 : Analytical performances for the determination of Cd with various CVG systems

Reaction system		Hot atomization	Cold atomization
KBH_4-HCl-Co^{2+}+thiourea	Calibr. functions[a]	I_f^d=1415.1C_{Cd}^e+21.3	I_f^d = 583.1C_{Cd}^e-11.2
	R.S.D.[b](%)	0.98	0.76
	D.L[c](ng ml^{-1})	0.004	0.003
KBH_4-HCl	Calibr. functions[a]	I_f^d=972.0C_{Cd}^e+17.6	I_f^d = 381.7C_{Cd}^e-8.1
	R.S.D[b](%)	1.2	1.6
	D.L[c](ng ml^{-1})	0.010	0.005
KBH_4-HCl-Co^{2+}-8-hydroxyquinoline	Calibr. functions[a]	I_f^d = 953.4C_{Cd}^e+9.2	I_f^d = 367.5C_{Cd}^e+3.2
	R.S.D[b](%)	1.2	1.8
	D.L[c](ng ml^{-1})	0.012	0.005
$NaIO_3$-KBH_4-HCl	Calibr. functions[a]	I_f^d = 717.3C_{Cd}^e+1.7	
	R.S.D[b](%)	2.3	
	D.L[c](ng ml^{-1})	0.018	

[a]Based on the five experimental points for the calibration curve; [b]Relative standard deviation for 1ng/ml^{-1} Cd(n=7); [c]$3\sigma_{n-1}$ of 11 runs of the blank; [d]Signal intensity; [e]Concentration(ng/l^{-1}).

with acid-matched diluted HCl.

Apparatus

A model AFS2202 double-channel non-dispersive atomic fluorescence spectrometer(NDAFS, Beijing Hanguang Instrument Co., Beijing, China) was operated under conditions summarized in TABLE S1. A cadmium hollow cathode lamp(HCL), which was specially designed for AFS, was used in this work. Using this lamp, experiment showed that the irradiation intensity was increased 3~5-fold and the detection limit was improved 2~3-fold. A programmable intermittent flow hydride generator, as described previously was used throughout the work[37]; and the working program of the intermittent flow reactor used in this work is listed in TABLE S2.

Procedures

At the beginning of first step, the sampling tube was placed in the test solution, and then the pump propelled the solution into the storage coil. Second, the pump was stopped for 3s, thus allowing the sampling tube to be changed over to the carrier solution. At this stage, the sample stayed in the storage coil that was in front of the mixing joint of the manifold and consequently no reaction occurred between the sample solution and the reductant. Third, the carrier solution was propelled, pushing the sample and the reductant into the mixed coil and gas-liquid generator. At this stage, the volatile species were formed and transported to the quartz furnace. In a hydrogen-argon-air entrained micro-flame, the gaseous molecular compounds were atomized and determined by AFS. After the third step, the pump was stopped again and made ready for the next determination.

Sample pretreatment

0.2ml of whole blood reference material was accurately transferred and placed in a 25ml beaker, to which 5ml of concentrated nitric acid was added. Covered with glass and soaked for 6~12h. After that, 1ml of perchloric acid was added and gently heated on a hot plate until white fume appearance. After cooling, washed the wall of beaker and the glass with water and gently heated to dryness. Then, 3ml of 1.2M HCl was added and gently warmed. Finally the suitable enhancers (including Co^{2+}+thiourea, Co^{2+}-8-hydroxyquinoline and $NaIO_3$) were added; and the solution was transferred into a 10ml volumetric flask and diluted to volume with water.

RESULT AND DISCUSSION

The effect of chemical variables

The literature data from TABLE 1 shown that the chemical variables, viz., concentrations of HCl and BH_4^- were largely scattered while the use of various vapor generation systems for the produce of volatile Cd species. Firstly, the chemical variables were optimized in order to evaluate the performance characteristics and the interferences of various VG systems. Optimization studies were performed under the same vapor generator, gas-liquid separator and operating parameters. The potassium hydroxide concentration(0.2%, m/v) was kept constant for different reductant concentrations; and

TABLE 3 : Comparison of the effects of coexisting ions on the generation of the volatile Cd species with different vapor generation systems(n=3)

Coexisting ions	Concentration μg ml^{-1}	Signal change(%)			
		KBH_4-HCl	KBH_4-HCl-Co^{2+}+thiourea	KBH_4-HCl-Co^{2+}-8-hydroxyquinoline	$NaIO_3$–KBH_4–HCl
Ag^+	0.025	-39	-33	-37±2	-20
As^{5+}	1	±3	±2	±3	±4
Au^{3+}	0.05	+15	-13	+12	+13
	0.10	+6	-25	+6	+5
Co^{2+}	0.25	+25	±3	±3	+11
	1	±3	±2	-7	+21
Cr^{6+}	1	-32	±2	±2	±3
Cu^{2+}	0.10	-24	-5	-11	-6
	0.2	-46	-14	-21	-13
	0.5	-85	--39	-46	-32
Fe^{3+}	0.25	-14	±2	±2	±2
	2	-62	±3	-6	-23
	10	-78	±3	-47	-56
	50	ND	-7	ND	ND
Ga^{3+}	1.0	+30	-8	+23	+11
Ge^{4+}	1.0	-12	-8	-10	-10
Hg^{2+}	1.0	±2	±3	±2	±2
Mo^{6+}	1.0	-13	-7	-12	-13
Mn^{2+}	2	±3	±2	±2	±1
Ni^{2+}	0.25	-15	±2	-4	-5
	0.5	-32	+10	-7	-8
	1.0	-58	-6	-13	-17
Pb^{2+}	0.025	-37	-25	-26	-28
	0.050	-51	-37	-43	-46
Sb^{5+}	0.1	-6	±2	-6	±2
	1.0	-63	±2	-37	-13
Se^{6+}	1.0	-13	±2	-9	-14
Sn^{2+}	0.2	-8	-5	-6	-6
	1.0	-42	-21	-35	-34
Te^{6+}	0.2	-80	-58	-75	-70
V^{5+}	1.0	+40	+4	+10	+28
Zn^{2+}	5.0	-49	±2	±2	±2

the ratio of sample flow rate to reductant flow rate was 2:1 in this study. The effects of two parameters on peak-area signal for Cd are illustrated in figure 1(a,b,c and d).

From figure 1, it can be clearly seen that the optimized chemical parameters for various vapor generation systems are keep at the same levels. Using 3%(m/v) KBH_4 as reductant, the optimum acidity is 0.25~0.3 mol l^{-1} HCl; and using the higher concentration of KBH_4, the optimum range of acidity can be shifted to a higher value and obtained a wider range. Using 5%(m/v) KBH_4 as reductant, the optimum acidity is 0.30~0.45mol l^{-1} HCl. The molar ratio of reductant-to-acid input rates, $[BH_4^-]:[H^+]$, is 1.1 to 1.5-fold, which is similar to the reported date by Lampugnani[15]. At higher KBH_4 concentrations(>4%), the fluorescence intensity gently drops due to dilution, a consequence of the increased hydrogen production and shorter residence time of volatile cadmium species in the atomizer; In this work, 4% KBH_4 was used as reductant and 0.3mol l^{-1} HCl was chosen as the optimal acidity for all chemical vapor generation systems.

These results as well as the literature data from TABLE 1 may appear inconsistent. Garrido[36] reported that the more "vigorous" conditions, such as at higher acid concentration(1mol l^{-1} HCl) and higher $NaBH_4$ concentration, were needed to produce volatile Cd species in an aqueous medium. However, experimental results show that the "milder" conditions can also produce volatile Cd species.

Concentration of Cd 2ng/ml^{-1}; (a): KBH_4-HCl

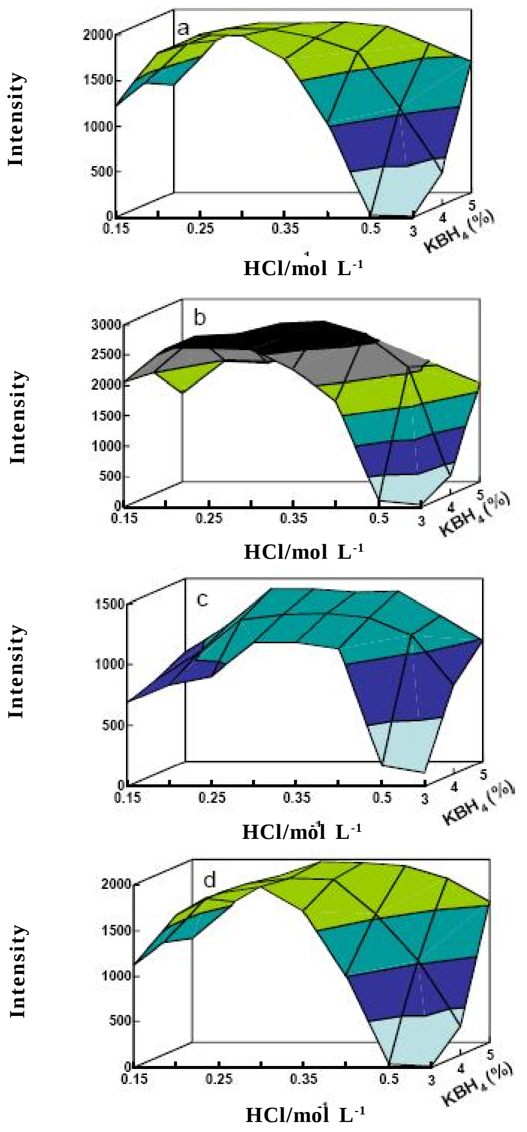

Figure 1: Effect of HCl concentration and KBH_4 concentration (m/v) on the cadmium atomic fluorescence signal

chemical vapor generation system; (b): KBH_4-HCl-Co^{2+}+ thiourea chemical vapor generation system, the presence of 1μg ml^{-1} Co^{2+} and 1%(m/v) thiourea in the final test solution; (c): $NaIO_3$–KBH_4–HCl chemical vapor generation system, the presence of 2.5%(m/v) $NaIO_3$ in the final test solution; d: KBH_4-HCl-Co^{2+}-8-hydroxyquinoline chemical vapor generation system, the presence of 1μg/ml^{-1} Co^{2+} and 2μg/ml^{-1} 8-hydroxyquinoline in the final test solution.

The influence of enhancement reagents on the generation of volatile cadmium species

Since Cacho et.al.[14] found that diethyldithio carbamate(DDTC) showed a positive effect on the generation of volatile cadmium species in the organic medium, the followers of Guo[35], Peng[32], Sun[19] and Li[20,23] have respectively found that thiourea-Co^{2+}, $K_3Fe(CN)_6$, Co^{2+}-8-hydroxyquinoline and $NaIO_3$ greatly improved the vapor generation efficiency of Cd. In this study, the recommendatory enhancers were tested in aqueous solution; and the influences of their concentrations on the atomic fluorescence intensities are shown

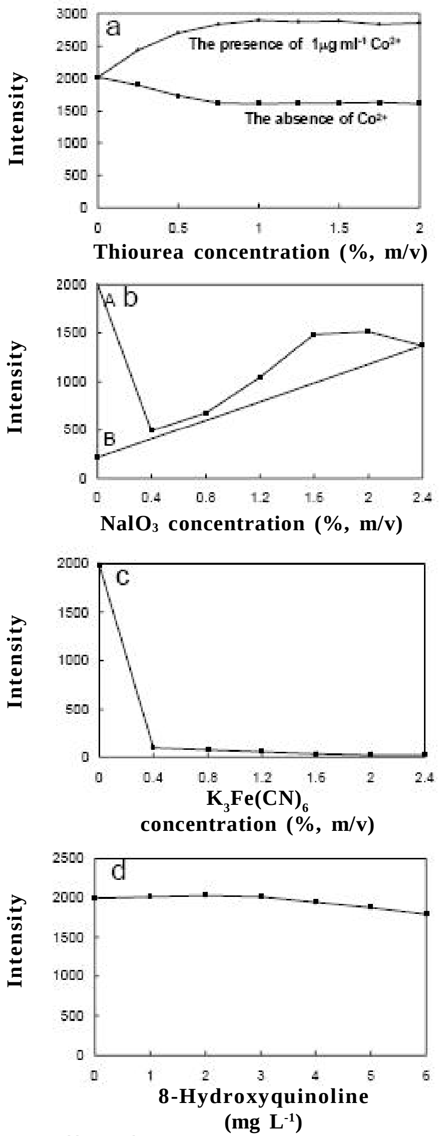

Figure 2 : Effect of enhancement reagents on the cadmium atomic fluorescence signal. Concentration of Cd 2ng ml^{-1}; 0.3mol l^{-1} HCl; 4%(m/v) KBH_4 in 0.2%(m/v) KOH; (a): KBH_4-HCl- Co^{2+}+ thiourea chemical vapor generation system; (b): $NaIO_3$–KBH_4–HCl chemical vapor generation system; (c): KBH_4-K_3 $Fe(CN)_6$-HCl-NH_2OH•HCl chemical vapor generation system; (d): KBH_4-HCl-Co^{2+}-8-hydroxyquinoline chemical vapor generation system, the presence of 1μg/ml^{-1} Co^{2+} in the final test solution

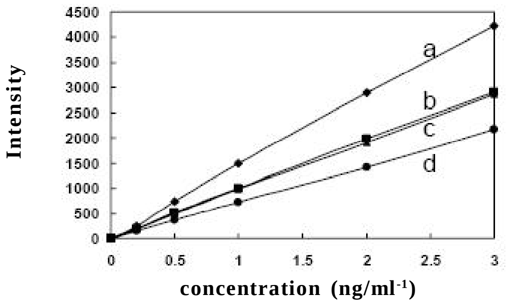

Figure 3 : Comparative study of the calibration graphs obtained for Cd with various vapor generation. 0.3mol l^{-1} HCl; 4%(m/v) KBH_4 in 0.2%(m/v) KOH; (a): KBH_4-HCl-Co^{2+}+ thiourea chemical vapor generation system, the presence of 1μg/ml^{-1} Co^{2+} and 1%(m/v) thiourea in the final test solution; (b):KBH_4-HCl chemical vapor generation system; (c) : KBH_4-HCl-Co^{2+}-8-hydroxyquinoline chemical vapor generation system, the presence of 1μg/ml^{-1} Co^{2+} and 2μg/ml^{-1} 8-hydroxyquinoline in the final test solution. d: $NaIO_3$-KBH_4-HCl chemical vapor generation system, the presence of 2.5%(m/v) $NaIO_3$ In the final test solution

in figure 2. The experimental results reveal that the enhancement reagents do not improve the vapor generation efficiency of Cd besides thiourea-Co^{2+}; and in the presence of thiourea and cobalt ions, the sensitivity of Cd is only increased 50%(Figure2 a). The experimental results are contrary to the reports by the predecessors[19,20,32,33,35].

The addition of $NaIO_3$ in test solution(Figure 2b), the signal of Cd is attenuated 3 to1.3-folds and the depressed extent is dissimilar duo to the concentration of $NaIO_3$. Experimental results also reveal that the same vapor generation device which is used for the generation of volatile Cd species with KBH_4-HCl-$NaIO_3$ just now, is employed for the generation of volatile Cd species with the absence of $NaIO_3$(C=0) system again, viz. KBH_4-HCl system. Comparing with the initial intensity(Figure 2b, A), the repeated determination attenuated intensity by 5-fold(Figure2b B). The signal of Cd is slowly increased when the absence of $NaIO_3$ solution is determined again and again; and the signal can come back to the initial intensity after about repetition 50-times. There are no well-established theories to explain the experimental phenomenon; and two possible speculations are helpful in explaining the experimental phenomenon: (1) the inner-surface property of GLS is changed by iodide, which leads to stay the generation of volatile Cd species or adsorb the volatile Cd species;(2) the rudimental I^- or I_2 that is absorbed on the surface of transport PTFE tubing, which destroys the volatile Cd species or depresses the transport efficiency of volatile Cd species.

In the presence of potassium ferricyanide(Figure 2 c), the signal of Cd is depressed remarkably and almost no atomic fluorescence signal is detected. The reasonable reason is that Fe^{3+} added causes the most interference.

In addition, we find that the hungered and contaminative surface is inferior to the formation of volatile Cd species; and in the absence of enhancement reagents, this phenomena appears extraordinary prominence. The above inconsistent results may be due to the reason that the inner-surface properties of the mixing tubing and GLS are not suited for the formation or release of volatile Cd species in the beginning, which brings on lower sensitivity. For example, in ref 19, the initial intensity(in the absence of 8-8-hydroxyquinoline) of Cd at 2ng/ml^{-1} level was less than 100 [Figure 2 Cd(a)]; and in ref.[20], the initial intensity(in the absence of $NaIO_3$) of Cd at 1ng/ml^{-1} level was less than 100(Figure 3).

In study we also find that the following operation can enhance the sensitivity of Cd by HG-AFS: at first experiment, the mixing tubing and GLS is drastically cleaned with 2~3mol l^{-1} HCl; and then a higher concentration Cd standard solution(10~20ng/ml^{-1}) and the reductant are propelled into the mixing tubing and GLS to saturate the inner-surface of mixing tubing and GLS. It may be duo to the reason that the saturated inner-surfaces of mixing tubing and GLS are preferential for the release of volatile Cd species.

Analytical performance

Under optimized operating conditions, the sensitivities, precisions and detection limits of various vapor generation systems for the determination of Cd by VG-AFS were evaluated. Calibration graphs obtained in various vapor generation systems are plotted in figure 3 for comparative purposes. As can be seen, the use of KBH_4-HCl- Co^{2+}+ thiourea vapor generation system gives the maximal slope; the use of $NaIO_3$-KBH_4-HCl chemical vapor generation system obtains the minimum slope; and the slopes are same for KBH_4-HCl- Co^{2+}-8-hydroxyquinoline and KBH_4-HCl chemical vapor generation systems.

TABLE 4 : The results[a] for the determination of cadmium in whole blood reference materials with various CVG systems

		CRMs		
		GBW09132	GBW09133	GBW09134
Found value (ng/ml^{-1})	KBH_4-HCl-Co^{2+}+thiourea	1.13±0.20	4.13±0.23	8.64±0.36
	KBH_4-HCl	N.D	1.83±0.26	4.13±0.42
	KBH_4-HCl-Co^{2+}-8-hydroxyquinoline	0.79±0.36	3.12±0.23	5.73±0.38
	$NaIO_3$-KBH_4-HCl	N.D	2.24±0.36	4.99±0.41
Certified value(ng ml^{-1})		1.05±0.17	4.22±0.33	8.84±0.49

[a]Mean±S.D., n=3

The precisions were obtained for seven measurements of Cd solutions at 1ng/ml^{-1}; the detection limits were simply calculated as three times the standard deviation of eleven standard blank values. The results are summarized in TABLE 2. As can be seen, the use of KBH_4-HCl-Co^{2+}+ thiourea vapor generation system gives better precision and detection limit than the other vapor generation system; and lower detection limits are obtained under cold vapor mode owing to a better signal-to background ratio. However, the use of $NaIO_3$-KBH_4-HCl system, the signal was not significant under cold vapor mode.

Evaluation of interference

The effects of coexisting ions on the generation of the volatile Cd species with various vapor generation systems are shown in TABLE 3. As can be seen, coexisting ions such as Ag^+, Cr^{6+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, Mo^{6+}, Ni^{2+}, Pb^{2+}, Sb^{5+}, Sn^{2+}, Te^{6+}, $V^{5+}$and Zn^{2+} badly effect on the determination of Cd by VG-AFS with KBH_4-HCl vapor generation system. In addition, it appears that the use of thiourea and Co^{2+} can reduce the interferences from some coexisting ions(including depressed and enhanced effects). Similarly, minor signal improvements are obtained in the in the presence of Co^{2+}-8-hydroxyquinoline or $NaIO_3$.

It is important to notice that the presence of Fe^{3+} significantly suppresses the production of volatile Cd species besides the use of KBH_4-HCl-Co^{2+}-thiourea vapor generation system; and it is well know that iron is a major element and widely exists in many samples. Therefore, the vapor generation systems of KBH_4-HCl, KBH_4-HCl-Co^{2+}-8-hydroxyquinoline and KBH_4-HCl-$NaIO_3$ are only fit for the determination of Cd in simple samples. Additionally, Cu^{2+} and Pb^{2+} cause the most serious interference on the determination of Cd by VG-AFS; and elimination of such interferences by adding KCN to the borohydride solution is reported by Garrido[38].

Comparison of the four methods for the determination of cadmium in blood

In order to further evaluate the feasibility of the four vapor generation systems for the determination of Cd in real sample, various vapor generation systems were coupled with atomic fluorescence spectrometry and applied these to the determination of cadmium in the following certified whole blood certified reference materials(GBW 09132, 09133 and 09134); the results are listed in TABLE 4.

The comparison of the results of Cd with different vapor generation systems clearly shows that low values were obtained with the chemical vapor generation systems of KBH_4-HCl, KBH_4-HCl-Co^{2+}-8-hydroxyquinoline and $NaIO_3$-KBH_4-HCl; and the concentrations of Cd in the certified reference materials obtained by the vapor generation system of KBH_4-HCl-Co^{2+}+thiourea were in good agreement with the certified values of these CRMs including those with very low Cd content(e.g. GBW 09132).

CONCLUSIONS

The hyphenated vapor generation atomic spectrometric techniques have become a well-rounded technique for the determination of Cd at ng/ml^{-1} levels. However, this technique is still being a series of doubts such as critical chemical variables, serious interference, amphibolous reaction mechanism and inconsistent literature data. In this paper, various vapor generation systems for the produce of volatile Cd species were systemically evaluated from four points of view, including the effect of chemical variables, the effect of enhancers, analytical performances and Interferences. The experimental results revealed that the use of KBH_4-HCl-Co^{2+}- thiourea was a top-priority system for the determination of Cd by VG-AFS.

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