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Determination of Cadmium in Environmental Sample by Electrochemical Hydride Generation Electrothermal Atomic Absorption with in Situ Trapping in Graphite Tube Atomizer

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ABSTRACT

A homemade batch electrolytic cell with a Sn-Pb alloy cathode used to generate cadmium hydride. Several parameters influencing the electrochemical hydride generation and trapping on the coated graphite tubes, and atomization process have been investigated. Ir-, W-, and Zr- coated graphite tubes were used for trapping cadmium hydride. It was found that Ir-coated graphite provided the best sensitivity of the determination. Thus, this coating was used to trap cadmium hydride prior to atomization. Potential interferences from several ions were studied. Under the optimum conditions the calibration plot calibration curve was linear over the range of 0.5-5 ng L^{-1} with a detection limit of 0.05 ng L^{-1} which was determined by dividing 3σ by the slope of the calibration curve and RSD 5.5 % (n = 5) for 2ng L^{-1} Cd (II) . In order to evaluate the accuracy and recovery of the presented method, the procedure was applied to the analysis of reference materials and river and tap water sample.

Keyword: cadmium in environmental sample, Electrochemical Hydride Generation, Electrothermal Atomic Absorption

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INTRODUCTION

Electrochemical hydride generation (EcHG) has been proposed as a valid alternative to chemical generation as a sample-introduction technique in atomic spectrometry. EcHG has many advantages to chemical hydride generation technique. Some of the most significant advantages of EcHG technique are the elimination of the use of sodium tetrahydroborate reagent which is expensive and a potential source of contamination [1-5]. Sodium tetrahydroborate aqueous solution is unstable and it has to be freshly prepared [1,3-5]. For the electrochemical hydride generation the influence of the oxidation states of the analyte on the hydride yield can be reduced, depending on the cathode material used [6]. In the recent years, many papers have been published related to electrochemical generation of volatile hydrides for sample introduction in atomic spectrometry. Volatile hydrides of Sb[1,2,7-12], Bi [12], Cd[3], As [2,6,8,11-14]Se [2,7,11], Ge[11] , Sn[8,11] have been generated successfully and the elements determined by a variety of spectrometric techniques.

Cadmium is a toxic and persistent pollutant. So that, it is important to be able to accurately monitor the amount of cadmium in both aquatic and terrestrial environments. Cadmium has been determined by atomic absorption spectrometers by chemical hydride generation and has been mentioned in many papers using a quartz tube atomizer [15]and electrothermal devices [16-18]as the atomizing systems. Cadmium has been determined by EcHG using quartz tube atomizer[3], too. Nevertheless, to the best of our knowledge it has not been determined by EcHG-ETAAS and this is the work had done in this paper.

EXPERIMENTAL

Reagents

All the reagents were of analytical reagent grade (Merck) unless otherwise stated. Glassware were soaked in 10% (v/v) nitric acid and rinsed with distilled water. Cadmium (II) stock solution (1gL^{-1}) was prepared by dissolving Cd $(NO_3)_2.4H_2O$ in distilled water. Standard working solutions were prepared by appropriate dilution of the stock solution by 0.01(mol L^{-1}) HCl. 0.5(molL^{-1}) Na_2CO_3 solution was prepared every working day. Tungsten, palladium and platinum permanent chemical modifiers were prepared by dissolving $Na_2WO_4.2H_2O$ (1g L^{-1}) (Aldrich) in distilled water, $PdCl_2$ (1g L^{-1}) in HCl and $H_2PtCl_6.6H_2O$ in distilled water and iridium (1g L^1) by dissolving $IrCl_3.H_2O$ in 1mol L^{-1} HCl.

Instrumentation

A Hitachi Z-2000 atomic spectrometer (Hitachi, Japan) equipped with a graphite furnace atomizer (a pyro tube) was used for atomic absorption measurements. Zeeman Effect was employed during all experiments. A cadmium hollow cathode lamp (Hitachi, Japan) operated at 7.5 mA was used as radiation source at 228.8 nm.

Electrochemical hydride generation system

The experimental set up is illustrated in Fig1.The batch electrolytic cell had four parts that were attached together by four screws. The four–part cell body was made of polymethylmethacrylate. The cathode and the anode chambers, both with the internal volume of 18.4 ml, were separated by an ion exchange membrane (Nafion, Du Pont,USA). The platinum wire having surface area of 1.29 Cm^2 was used as anode. As cathode material, lead-tin alloy wire (ARISON, Singapore, diameter of 0.8 mm, Pb:Sn 37:63) was used. The cathode area was 4.60 Cm^2 for each measurement. It was held parallel to membrane and anode by a polyethylene holder. Nitrogen (96%) was used as the carrier gas being introduced in the cathode chamber and transported into the two glassy vials as the gas-liquid separators and then into the graphite furnace by a capillary Pyrex glass (1 mm inner diameter, 5.5 Cm length). All the connections were polyethylene tubes. A power supply (Matrix Technology Inc., China) of maximum voltage of 30 V was used. A digital multimeter (Escort Instruments Corporation, Taiwan) was applied to control the current to be constant.

Procedure

Graphite tube treatment

For treatment of graphite tube atomizer, two separate 10 µl injection parts of 1g L^{-1} tungsten solution were applied. After each injection, the tube was dried slowly by heating the atomizer at 150° C with ramp mode and hold time of 20 s (10 mL min^{-1}). The second drying step was performed at 200° C with ramp mode and hold time of 20 s (10mL min^{-1} of Ar flow). The third drying step applied at 400°C with the hold time of 25 s (10mL min^{-1} of Ar flow). Two pyrolysis steps with ramp mode and the hold time of 5 s at 1000 and 1300°C were performed (200mL min^{-1} of Ar flow). All the ramp times for the previous steps were 5 s. The atomize stage was performed at 1700°C and the hold time of 2 s (30mL min^{-1} of Ar flow) and the clean stage at 2000°C with the hold time of 4 s(200mL min^{-1} of Ar flow). The cool stage was performed as the end step with the hold time of 10 s and the gas flow (Ar, 99.999 %) of 200 ml min^{-1}.

Analytical Procedure

In each determination process, the following procedures were carried out. 10 ml of the catholyte solution containing known concentrations of the cadmium (that was acidified by diluting stock solution by 0.01mol L^{-1} HCl) was injected to the cathode chamber and carrier gas flow rate was set 10 ml of the anolyte solution (sodium carbonate 0.5 mol l^{-1}) was injected to the anode chamber, too. During applying constant electrolytic current, catholyte medium was varied to alkaline [3] and the generated gaseous products were introduced into the graphite tube atomizer and were trapped till atomization temperature applied. In each run, a new one replaced the lead- tin alloy electrode, the old catholyte was discharged, and the cathode chamber was rinsed by distilled water.

Statistical treatment of data

The use of atomic absorption set software permitted the virtualization of transient signals for each determination step and evaluation of peak height. For Experimental design and statistical treatment of data, Minitab version 14 software (Minitab Inc.) was used.

RESULT AND DISCUSSION

Effect of Chemical Modifiers

Effect of two permanent chemical modifiers was evaluated. Two-separated 10 µL of 1g L^{-1} tungsten solution was injected into the graphite tube atomizer and the furnace temperature program was run after each injection. 6 pg mL^{-1} cadmium solutions were electrolyzed to generate cadmium (II) hydride and furnace temperature program for trapping and atomization was run. The same procedure was applied for palladium 1 g L^{-1} solution. According to the better response obtained, tungsten was used as the permanent chemical modifier.

Effect of Electrode Material and Electrolyte

Effect of electrode material on the obtained absorbance was evaluated by applying some different electrodes such as tin, lead, lead-tin alloy wires and glassy carbon. According to the better signal obtained from lead-tin alloy electrode for a single cadmium concentration, it was used as cathode to generate cadmium hydrides (Fig.2). Three electrolytes - dilute solutions of nitric acid, hydrochloric acid and sulfuric acid – were applied as catholyte solutions. According to the better absorbance signal (peak height), hydrochloric acid dilute solution was used as catholyte.

Effect of Atomization Temperature

To optimize the atomization temperature for cadmium (II) hydrides generated by electrolysis of cadmium (II) solution, the following procedure applied: Graphite furnace was treated as mentioned before in the text by tungsten and or palladium solutions. Then, 6pg ml^{-1} cadmium standard solution was injected into the cathode chamber and the generated hydrides directed into the furnace and temperature program was run from Table 1 in different atomization temperatures. The best signal obtained at 1300.

Multivariate Optimization

Several variables such as concentration of anolyte, trapping temperature, electrolysis and trapping time, flow rate of carrier gas, electrolytic current, cathode surface area and catholyte concentration were expected to affect the hydride generation efficiency. To find the main factors affecting the electrochemical hydride generation of cadmium, a two level Plackett-Burman design with 12 nonrandomized runs were carried out using the Minitab software. Table 1 lists the upper and lower values given to each factor. Different variables affecting the electrochemical hydride generation of cadmium were studied aqueous standard solution of 2pg ml^{-1} cadmium in HCl. Table 2 shows experimental design matrix and its response (peak height) corresponding to each run. The combined standardized (α = 0.1) main effect Pareto chart for Plackett-Burman design used is shown in Fig. 3.

For electrochemical hydride generation, cathode surface area and electrolytic current were statistically significant. Catholyte and anolyte concentrations were affected as negative sign; while cathode surface area, electrolytic current, carrier gas flow rate, electrolysis and trapping time and the trapping temperature were affected as positive sign. According to the sign of estimated effects associated with non-significant factors, higher value of carrier gas flow rate (50 ml min^{-1}) and lower value of anolyte concentration (0.5 mol l^{-1}) were chosen. Other factors (catholyte concentration, cathode surface area, electrolytic current, electrolysis and trapping time and trapping temperature), often having significant effects on the electrochemical and detection processes, were optimized by univariate method.

Univariate Optimization

Concentration: The optimized concentration of hydrochloric acid (as catholyte) was evaluated by running the determination process for single cadmium (II) solution; maximum absorbance was resulted for 0.01 mol L^{-1} of Catholyte .

Cathode surface area: Cathode surface area was chosen as much as possible (according to the mechanistic limitations) to increase contact of electrode with the solution. Therefore, 4.60 Cm^2 was applied to generate hydrides.

Electrolytic Current: Effect of electrolytic current was evaluated in this work and the constant current was chosen that obtained the best signal – the highest absorbance peak, 80mA was applied as the optimum current.

Electrolysis and Trapping Time: It was expected that the time of electrolysis and the trapping time, affect the signals obtained. However, according to the fact that part of the time of electrolysis was synchronous with the trapping of generated hydrides, we studied both factors at one variable to be optimized and the best signal obtained at 250 seconds.

Trapping Temperature: Effect of trapping temperature on tungsten treated graphite furnace studied in this work. Data obtained from a single cadmium concentration were plotted and absorbance increased by increasing trapping temperature up to 350^{0}C and then decreased. Trapping temperature was chosen 350^{0}C. Optimized and operating conditions for the determination of cadmium by electrochemical hydride generation-electrothermal atomic absorption spectrometry is illustrated in Table 3. The furnace temperature program for trapping and atomization of cadmium hydride is illustrated in Table 4.

Interferences

The effect of some concomitant ions was evaluated by analysis of spiked cadmium (II) solution (2ng L^{-1} in 0.01 mol l^{-1} HCl). The selected ions, as interfering ions, were Cu(II), Co(II) and Ni(II) as transition metals, As(III) and Sb(III) as convenient hydride forming ions, K and Na as alkali metal ions, Ca(II) and Mg(II) as convenient existed ions in water samples and Pb(II) from group (IV) and anions (Table 5).

Analytical Figures of Merit

A calibration curve y = 0.1198 x + 0.033 with a correlation coefficient of 0.9805 was obtained. Where x is the concentration of Cd(II) (ng L^{-1}) and y is the absorbance(peak height). The linear range was 0.5-5 (ng L^{-1}) cadmium with a detection limit of 0.05 ng L^{-1} (based on three times of standard deviation of three measurements of the blank divided by the slope of the calibration graph) and the precision of 5.5 % (R.S.D.) for three replicate determination of 2ng L^{-1} Cd(II).

Application to water analysis

In order to evaluate the accuracy and recovery of the proposed method, standard reference materials SRM 2670 (freeze-dried urine) from NIST (USA), JB-1, as powder obtained from the geological survey of Japan (GSJ) were analysed for their cadmium contents. The powder was dissolved in 15 mL of a mixture of 500 mL HF, 165 mL H2SO4 and 40 mL HNO3 at 150 °C in a Teflon beaker overnight and were analysed for their cadmium (II) contents. To show the applicability of the method tap water and river water sample were collected from city of Mashhad (North East of Iran). The samples were diluted 1:10000 with 0.01mol L^{-1} HCl and spiked with standard cadmium solutions. The results obtained are presented in Table6

CONCLUSIONS

In this method very low detection limits and high sensitivity can be achieved but linear range is limited .In situ trapping of cadmium hydride (in the graphite furnace atomizer) lead to such a mentioned result . Due to the high sensitivity and low detection limit of the method, major dilution of real sample is needed. The effect of interferences in electrochemical hydride generation of cadmium with in situ trapping may be different by the type of interfering species. It is well known that the interfering ions can modify some of the reactions that lead to the generation of the hydride on the cathode surface. The metal ions reduced and deposited on the cathode surface modify the hydrogen over potential of the material and reduce the efficiency of the hydride-generation process. If reduction of the analyte and subsequent hydride generation occurs on defined active sites on the surface, it is probable that reduction of the interference not only affects the nature of the surface but also affects reduction of the analyte on the cathode [19]. It is known that volatile hydride forming elements- such as As (III) and Sb (III) – cause mutual interferences[20]. These elements produce trapping interference, although liquid phase interferences cannot be neglected. For real samples with high interfering ion concentrations, suitable separation of interfering ions is required.

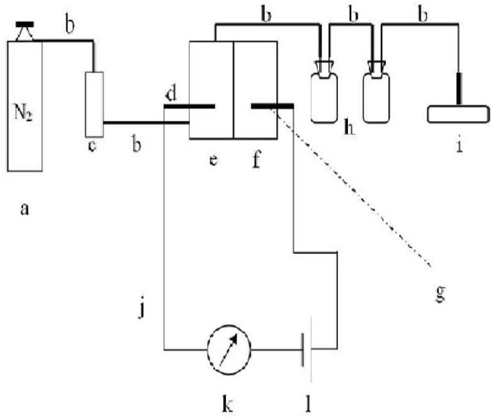

Figure1: The schematic diagram of the analytical system; a, Carrier gas source; b, Polyethylene tubes(inner diameter of 3mm); c, flow meter; d, Cathode; e, Cathode chamber; f, Anode chamber; g, Anode; h, Gas-liquid separators(inner volume of 25ml); i, Graphite tube atomizer; j, Cu wire connections; k, multimeter; l, DC power supply.

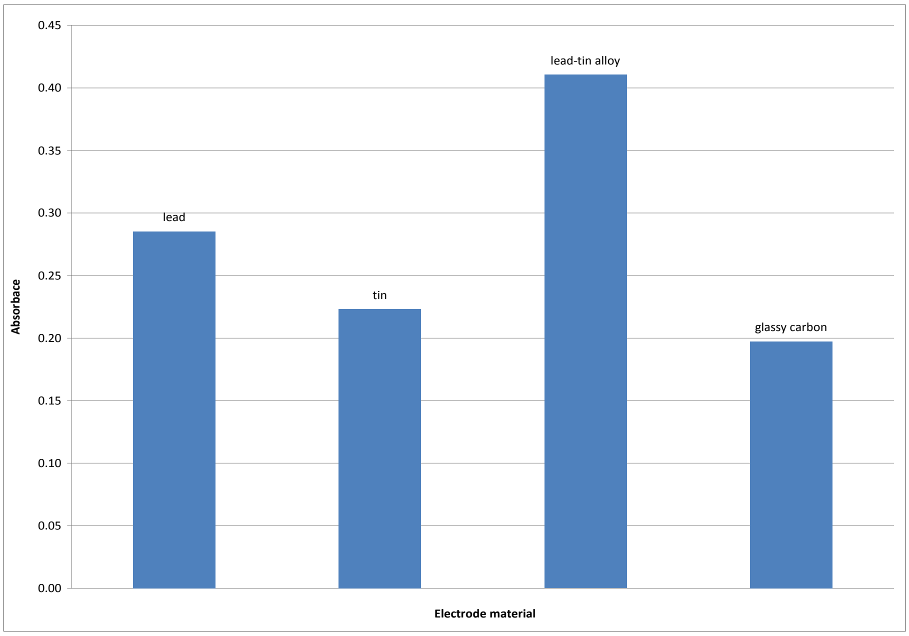

Figure 2: Effect of cathode material on the analytical signal of 2ng L^{-1} Cd; 0.05 mol L^{-1} HCl; Carrier gas flow rate, 30 mL min^{-1}; Cathode area, 4.60 Cm^2; Electrolytic current, 100 mA; Electrolysis and trapping time, 200 sec; Trapping temperature, 300^0C

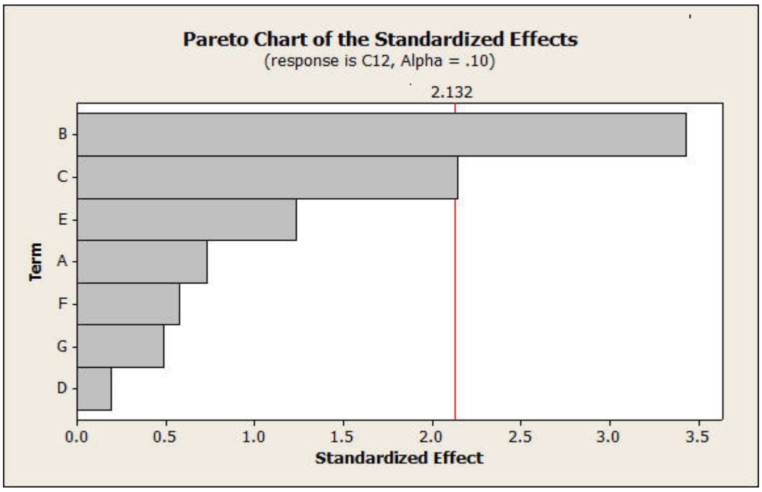

Figure 3: Standardized main effect Pareto chart for Plackett-Burman design for electrochemical hydride generation of Cd.

Table 1. Experimental definition for Plackett-Burman design.

Variable	Symbol(Key)	Low(-)	High(+)
Catholyte concentration(mol L^{1-})	A	0.005	0.100
Cathode area (Cm^2)	B	3.50	4.60
Electrolytic current(mA)	C	60.0	120
Carrier gas flow rate(mLmin^{-1})	D	10.0	30.0
Electrolysis and trapping time(sec)	E	120	300
Trapping temperature(^{0}C)	F	100	400
Anolyte concentration(mol L^{-1})	G	0.500	0.800

Table 2. Plackett-Burman design for determination of significant variables

Run	A	B	C	D	E	F	G	Absorbance
1	+	-	+	-	-	-	+	0.2130
2	+	+	-	+	-	-	-	0.3046
3	-	+	+	-	+	-	-	0.4731
4	+	-	+	+	-	+	-	0.3601
5	+	+	-	+	+	-	+	0.4206
6	+	+	+	-	+	+	-	0.5242
7	-	+	+	+	-	+	+	0.4581
8	-	-	+	+	+	-	+	0.3802
9	-	-	-	+	+	+	-	0.2551
10	+	-	-	-	+	+	+	0.2482
11	-	+	-	-	-	+	+	0.3789
12	-	-	-	-	-	-	-	0.2970

Table 3.Operating conditions for hydride generation and detection in this work.

Current (mA)	80
Time of Electrolysis and Trapping (s)	250
Carrier Gas Flow Rate (mL min^{-1})	30
Sample Volume (mL)	10
Wave Length (nm)	228.8
Lamp Current (mA)	7.5
Slit Width (nm)	1.3
Background Correction	Zeeman Effect
Tube Type	Pyrolitic graphite tube
Signal Measurement	Peak Height
Cathode Area (Cm^2)	4.60
Catholyte Concentration (mol L^{-1})	0.01
Anolyte Concentration (mol L^{-1})	0.5
Trapping Temperature (^0C)	350

Table 4 Furnace temperature program for trapping and atomization of cadmium hydride

Stage No.	Start Temp. (°C)	End Temp. (°C)	Ramp Time (s)	Hold Time (s)	Ar Flow (mLmin-1)	Comments
1	150	300	65	400a	10	Trapping
6	1300	1300	0	2	30	Atomization
7	1800	1800	0	4	200	cleaning
8	0	0	0	10	200	Cooling

Table 5. Tolerance limit coexisting ion on the determination of 2 (ng L^{-1}) Cd(II).

Coexisting ion	Maximum tolerance ratio
Cu(II), Co(II), Ni(II)	10
Sn (II), Ag (I), Zn(I), Pb (II)	50
As(III), Sb(III), Bi (III), Se (IV)	3
K(I), Na(I), Li (I), Mg (II), Ba(II), Fe(II), Fe(III),Ca (II), Al (III),Cr(III)	500
NO_3^- ,SO_4^{2-},PO_4^{2-} Cl^- ,Br^- ,SCN^-	1000

Table 6 Results (mean± standard deviation based on three replicate analyses) of determination of cadmium in reference materials, water samples.

Sample	Cd (II) added (ng L^{-1})	Cd(II) found (ng L^{-1})	%Recovery
Tap water	_	0.80±0.002	
	0.30	1.09±0.002	99
	0.80	1.57±0.003	98
River water	0.00	2.70±0.002	
	0.40	3.00±0.002	97
	0.90	3.65±0.003	101
Reference material	Certified value (µg g^{-1})	Measured value (µg g^{-1})	Recovery %
SRM 2670	0.088	0.081±0.0003	92
JB-1	0.11	0.10±0.005	91

REFERENCES

[1] Menemenlioğlu İ , Korkmaz D, and Ataman OY. Spectrochim Acta Part B 2007; 62:40-47.
[2] Šíma J, Rychlovský P ,and Dědina J. Spectrochim Acta Part B 2004; 59:125-133.
[3] Arbab-Zavar M H, Chamsaz M, Youssefi A, and Aliakbari M. Anal Chim Acta 2005; 546:126-132.
[4] Hashemi M, Arbab-Zavar M H ,and Sarafraz-Yazdi A. Talanta 2004; 64:644-649.
[5] Arbab-Zavar M H and Hashemi M. Talanta 2000; 52:1007-1014.
[6] Li X, Jia J, and Wang Z. Anal Chim Acta 2006; 560:153-158.
[7] Ding WW, and Sturgeon RE. J Anal At Spectrom 1996; 11: 421-425.
[8] Denkhaus E, Beck F ,Bueschler P, Gerhard R and Golloch A, Freseniu. J Anal Chem 2001; 370:735-743.
[9] Kratzer J,Dědina J. Spectrochim Acta Part B 2005; 60:859-864.
[10] Bolea E, Arroyo D, Laborda F.and Castillo J R. Chim Acta 2006; 569:227-233.
[11] Bolea E , Laborda F, Castillo J R. and Sturgeon R E. Spectrochim Acta Part B 2004; 59:505-513.
[12] Bings N H, Stefanka Z and Mallada S R. Anal Chim Acta 2003; 479: 203-214.
[13] Ding W W, and Sturgeon R E. Spectrochim Acta Part B 1996; 54: 1325-1334.
[14] Pyell U, Dworschak A, Nitschke E, and Neidhart B, Fresenius. J Anal Chem 1999; 363:495-498.
[15] Ritschdorff E T , Fitzgerald N , Mclaughlin R L J and Brindle I D. Spectrochim Acta Part B 2005; 60:139-143.
[16] Matusiewicz H, Kopras M ,and Sturgeon R E. Analys 1997; 122:331-336.
[17] Luna A S , Pereira H B , Takase I, Gonçalves R A, Sturgeon R E and Campos R C. Spectrochim Acta Part B 2002; 57:2047-2056.
[18] Bermejo-Barrera P, Moreda-Piñeiro J, Moreda Piñeiro A, Bermejo-Barrera A. At Spectrosc 1996;11:1081-1086.
[19] Laborda F, Bolea E, Castillo JR. Anal Bioanal Chem 2007; 388, 743-751.
[20] Bolea E, Laborda F, Belarra M A Castillo J R. Spectrochimica Acta Part B 2001; 56,2347-2360.