Asian Journal of Chemistry Vol. 16, No. 2 (2004), 983–989

Preconcentration of Cadmium onto Amberlite XAD-4 Resin Loaded with 5-Br-PADAP and Determination by Anodic Stripping Differential Pulse Polarography

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A procedure for separation and preconcentration of trace amounts of cadmium has been proposed. For the retention of cadmium a column of Amberlite XAD-4 loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) was used. Cadmium is quantitatively retained on the column at pH 9.5. The cadmium was removed from the column with 10.0 mL of 1 M nitric acid and determined by anodic stripping differential pulse polarography. A preconcentration factor of 100 was obtained. The detection limit value for the preconcentration of 1000 mL of aqueous solution of cadmium was 0.035 μg/mL. The precision for eight replicate determinations at the 1 μg/mL cadmium levels was 0.36% relative standard deviation (RSD), calculated with the peak height obtained. The calibration graph using the preconcentration system for cadmium was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 150 μg/mL. The method was successfully applied to the determination of cadmium in natural samples.

Key Words: Trace cadmium determination, Anodic stripping differential pulse polarography, 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol, Amberlite XAD-4.

INTRODUCTION

Cadmium is a cumulative toxic metal whose presence in the environment is of increasing concern. The main organs for cadmium accumulation in humans are kidney, liver, lung and pancreas. Cadmium toxicity may be manifested by a variety of syndromes and effects including real dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects[1].

Solid phase extraction (SPE) is one of the most important methods for separation and preconcentration of trace elements in samples[2–6]. In the solid phase extraction, various sorbents have been used. Amberlite XAD-4 resin is a well-known member of amberlite XAD resins and has found widespread application for separation/enrichment of trace metal ion.

Anodic stripping polarography has always been regarded as one of the most sensitive techniques for trace metal analysis[7–12]. The very low detection limits achieved by anodic stripping polarography are due to the preconcentration of analyzate from the sample solution during the deposition step.

In the present work, we have developed a simple, sensitive and economical method for the direct anodic stripping differential pulse polarographic determination of cadmium after adsorption of its 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) on amberlite XAD-4 resin and subsequent desorption by 10.0 mL of 1 M nitric acid. After desorption of the metal, the desorbed solution is transferred to polarographic cell and cadmium determined by anodic stripping differential pulse polarography. The HNO_3 can also act as a supporting electrolyte and controls the pH of the medium at the same time. The various parameters have been evaluated. The method is found to be highly selective, rapid, economical and sensitive. The developed procedure has been used for determination of trace amounts of cadmium in various samples.

EXPERIMENTAL

A polarograph model 757 VA computerized (Metrohm) was used to plot the polarograms. Polarograms were recorded with a three-electrode system. The reference electrode was Ag/AgCl; the working electrode was hanging mercury electrode (HMDE) and the auxiliary electrode was a platinum wire. A funnel tipped glass tube (60 × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibres and then filled with a flat glass rod. All glassware and columns were washed with a mixture of concentrated sulfuric acid and concentrated nitric acid (1 + 1) before use. A Beckman pH meter was used for pH measurements. Cadmium chloride solution was prepared by dissolving analytical grade sample in doubly distilled water and standardized by established methods[13]. A 0.02% solution of 5-Br-PADAP was prepared in ethanol. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations respectively. Buffer solution of pH *ca.* 9.5 was prepared by mixing 0.05 M $NaHCO_3$ and 0.1 M NaOH solutions in appropriate ratio.

Preparation of Amberlite XAD-4 column loaded with 5-Br-PADAP: Amberlite XAD-4 was treated with an ethanol : hydrochloric acid : water (2 : 1 : 1) solution overnight. Then resin was rinsed with deionized water until supernatant water pH got neutral. The packing of the column must be done using ethanol as eluent since water makes resin beads float. The resin was saturated with the reagent by passing 3.0 mL of a 0.02% 5-Br-PADAP solution in ethanol at a flow rate of 1 mL min^{-1}. Afterwards it was washed with water until reagent excess was eliminated from the resin. All experiments were done in a funnel-tipped glass tube (60 × 6 mm) which was used as a column for preconcentration. It was plugged with polypropylene fibre and then filled with XAD-4 to a height of 1.0–1.2 cm (0.3 g). Before sample loading the column must be preconditioned by passing a buffer solution. Then the column could be used repeatedly atleast 10 times.

Procedure for the sorption of cadmium on the column: 10–1000 mL of sample solution of cadmium ions in the range of 0.1–1500 μg was transfered into a beaker and 5 mL of buffer solution (pH 9.5) was added to it. This solution must be passed through the column at a flow rate of 3.0 mL min^{-1}. After this solution had been passed, the column was washed with 10 mL of deionized water. The adsorbed cadmium on the column was then eluted with 10.0 mL nitric acid solution at a flow rate of 1.0 mL min^{-1}. The eluent was collected in a 10 mL volumetric flask and cadmium was determined by anodic stripping differential pulse polarography.

RESULTS AND DISCUSSION

Anodic stripping differential pulse polarography: In the present work, the differential pulse polarogram for cadmium was obtained in HNO_3 medium as supporting electrolyte. A sample solution was transferred into polarography cell, after the removal of dissolved oxygen by passing purified nitrogen gas for 5 min. The polarograms were recorded by sweeping the potential from –0.2 to –0.8 V *vs.* reference electrode. Cadmium was deposed on a hanging mercury drop electrode at –0.59 V for 60 s, while stirring the solution. The amalgamate cadmium was stripped by differential pulse polarography by scanning of potential of the electrode between –0.2 and –0.8 V with scan rate of 15 mV s^{-1} and pulse amplitude of 50 mV (Fig. 1).

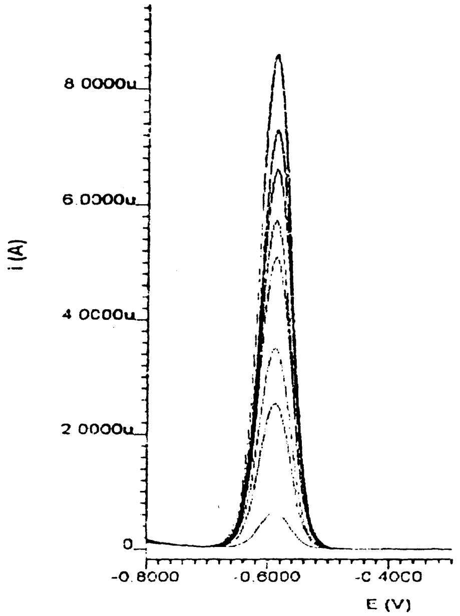

Fig. 1. Typical differential pulse anodic stripping polarograms in a series of cadmium solutions, 1, 3, 4, 6, 7, 8, 9, 10 μg/mL (from down to up); supporting electrolyte (1 M HNO_3) = 10 mL; buffer = 5.0 mL; reference = reagent blank;scan rate = 15 mV s^{-1}; pulse amplitude = 50 mV

Reaction conditions: These were established with the use of 10 μg of cadmium. The effect of pH on the adsorption of cadmium was examined in the pH range 5–11 and the percentage retention of metal on the adsorbent was calculated (Fig. 2). Cadmium was adsorbed quantitatively at the pH 9.5.

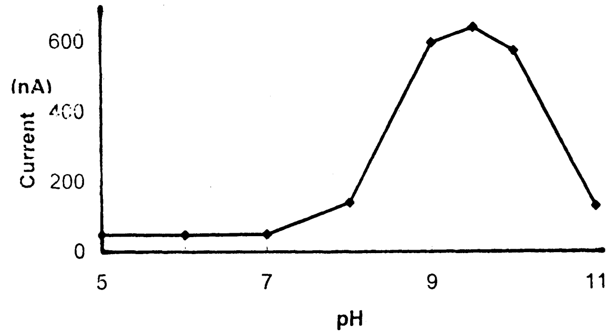

Fig. 2. Effect of pH on adsorption/retention of cadmium. Cadmium = 10.0 μg; conditions same as Fig. 1.

The flow rate was varied from 0.2 to 5 mL min^{-1}. It was found that a flow rate of 0.2–4.0 mL min^{-1} did not affect adsorption. A flow rate of 3 mL min^{-1} was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10–1200 mL under the optimum conditions, keeping the other variables constant. It was observed that the signal height was almost constant up to 1000 mL (preconcentration factor of 100). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase. Preliminary observations indicated that cadmium was desorbed completely with 10.0 mL of 1 M nitric acid. Therefore, 10.0 mL of 1 M nitric acid was used in the present work.

Sorption capacity: The sorption capacity of the amberlite XAD-4 resin loaded with 5-Br-PADAP for cadmium was also evaluated. The resin had a sorption capacity of 4 μmol of cadmium per gram of XAD-4 resin.

Calibration and sensitivity: Since it is possible to retain 0.035 μg of cadmium from 1000 mL of solution passing through the column, the desorption with 10.0 mL nitric acid gives a detection limit of 0.035 μg/mL for cadmium at the minimum instrumental settings. The linearity was maintained in the concentration range of 0.10 μg/mL to 150 μg/mL cadmium in first aqueous solution or 0.01 to 150 μg/mL cadmium in final nitric acid solution with a correlation factor of 0.9995 and relative standard deviations of ±0.36% (Fig. 3).

Effect of foreign ions: Various salts and metal ions were added individually to a solution containing 10 μg of cadmium and the general procedure was applied. The tolerance limit (error < 3%) is given in Table-1. Among the salts examined, most did not interfere at the g-mg level. Among the metal ions studied, many did not interfere even at the milligram level. Thus the method is highly selective without the use of masking agents. The proposed procedure has therefore been applied to the determination of cadmium in alloys and biological samples without any prior separations.

TABLE 1
EFFECT OF DIVERSE SALTS AND METAL IONS

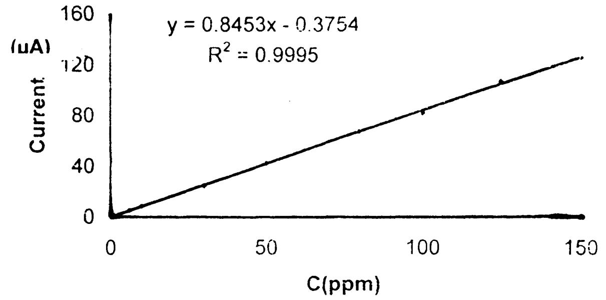

Fig. 3: The calibration curve for cadmium. Conditions same as in Fig. 1.

Salts or ions	Tolerence limit (mg)
$CH_3COONa{\cdot}3H_2O$, NaCl, KNO_3	1000
Thiourea	600
NH_4Cl, $(NH_4)_2SO_4$	500
NaF, NH_4Br	500
KI	400
K_2CO_3, KSCN, Potassium sodium tartrate	100
Trisodium citrate	50
Mn^{2+}, Mo^{6+}, Zn^{2+}	50
Ga^{3+}, Al^{3+}, Cr^{3+}, Se^{6+}, Ti^{6+}	20
Co^{2+}, Ni^{2+}, Cr^{6+}, Sb^{3+}	11
U^{6+}, V^{5+}, Te^{4+}, Bi^{3+}	5
Ru^{3+}, Fe^{3+}, Rh^{3+}, Pd^{2+}, Os^{8+}	2
Sn^{2+}, Cu^{2+}	1

Determination of cadmium in standard alloys: The proposed method has been applied to the determination of cadmium in National Institute of Standards and Technology. Standard reference materials: NIST SRM 629 Zinc Alloy, NIST SRM 94c Zn-Base Die Casting Alloy, NIST SRM 627 Zn-Base Alloy CE, NIST SRM 629 Zn-Base Alloy E.

An appropriate amount sample of the standard alloy was completely dissolved in *ca.* 20 mL of hydrochloric acid (1 + 1) by heating on a water-bath and then 2 mL of 30% hydrogen peroxide was added to the solution. The excess of peroxide was decomposed by heating the solution on a water-bath. The solution was cooled and filtered if needed and the filtrate was diluted to 100 mL with double distilled water in a calibrated flask and 50–100 mL of this solution was taken. Cadmium was determined by the general procedure (Table-2).

TABLE- 2
ANALYSIS OF SAMPLES FOR CADMIUM

Sample (%)	Composition (%)	Concentration of cadmium (%)	
		Certified value	Found[a]
NIST SRM 629 Zinc alloy	Fe, 0.017; Cu, 1.50; Al, 5.15; Mg, 0.094; Sn. 0.012; Cr, 0.0008; Mn, 0.0017; Ni, 0.0075; Pb, 0.0135; Si, 0.078%	0.0155	0.0152 ± 0.0007
NIST SRM 94c Zn-base die casting alloy	Sn, 0.006; Ni, 0.006; Mn, 0.014; Fe, 0.018; Mg, 0.042; Cu, 1.01; Pb, 0.006; Al, 4.13%	0.002	0.0019 ± 0.0003
NIST SRM 627 Zn-base alloy E	Cu, 0.132; Mg, 0.030; Fe, 0.023; Sn, 0.0042; Cr, 0.0038; Mn, 0.014; Ni, 0.0029; Si, 0.021; Pb, 0.0083; Al, 3.88%	0.005	0.0048 ± 0.0005
NIST SRM 627 Zn-base alloy E	Cu, 0.50; Mg, 0.094; Fe, 0.17; Sn, 0.012; Cr, 0.0008; Mn, 0.017; Ni, 0.0075; Si, 0.078; Pb, 0.0135; Al, 5.15%	0.015	0.014 ± 0.002
NIES, No. 1 pepperbush	K, 1.15 ± 0.06; Mg, 0.408 ± 0.020; Ca, 1.38 ± 0.07; Mn, 0.203 ± 0.17% Fe, 205 ± 17; Zn, 340 ± 20; Ba, 165 ± 10; Na, 106 ± 13; Rb, 75 ± 4; Sr, 36 ± 4; Co, 23 ± 3; Cu, 12 ± 1; Ni, 8.7 ± 0.6; Pb, 5.5 ± 0.8; As, 2.3 ± 0.3; P, (1100); Cr, (1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) $\mu g\ g^{-1}$	6.7 ± 0.5[b]	6.6 ± 0.6[b]
NIES, No. 3 Chlorella	K, 1.24 ± 0.06; Ca, 0.49 ± 0.03; Fe, 0.185 ± 0.010; Mg, 0.33 ± 0.02; P, (1.7)% Mn, 69 ± 5; Zn, 20.5 ± 0.1; Sr, 40 ± 3; Co, 0.87 ± 0.05; Pb, 0.60; Cu, 3.5 ± 0.3; Sc, (0.013) $\mu g\ g^{-1}$	0.026[b]	0.024 ± 0.004[b]
NIES, No. 6 Mussels	Na, 1.00 ± 0.03; K, 0.54 ± 0.02; Ca, 0.13 ± 0.01; Mg, 0.21 ± 0.01; P, (0.77)% Zn, 106 ± 6; Mn, 16.3 ± 1.2; Fe, 158 ± 8; As, 9.2 ± 0.5; Cu, 4.9 ± 0.3; Ni, 0.93 ± 0.06; Cr, 0.63 ± 0.07; Ag, 0.027 ± 0.003; Al, (220); Sr, (17); Se, (1.5); Co, (0.37); Pb, 0.91 ± 0.04; Hg, (0.05) $\mu g\ g^{-1}$	0.82 ± 0.03[b]	0.78 ± 0.06[b]
NIES, No. 2 pond sediment	Fe, 6.53 ± 0.35; Al, 10.6 ± 0.5; Ca, 0.81; K, 0.68; Na, 0.57% Zn, 343; Cu, 210; Cr, 75; Ni, 40; Co, 27; Pb, 105; As, 12 $\mu g\ g^{-1}$	0.82[b]	0.80 ± 0.05[b]

[a] Mean of four determinations. [b] $\mu g\ g^{-1}$, ± s.d.

Determination of Cadmium in Pepperbush, Chlorella, Mussel and Pond Sediment: The accuracy and applicability of the proposed method has been applied to the determination of cadmium in National Institute for Environmental Studies (NIES) No. 1, Pepperbush; NIES, No. 3, Chlorella; NIES, No. 6, mussels and NIES No. 2, pond sediment. A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (-5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. An aliquot (50–100 mL) of the pre-treated sample solution was taken and analyzed by the general procedure. The results are given in Table-2 which is in good agreement with the certified values.

Conclusion

The main advantages of this procedure are: (i) the preparation of the extractor system is simple and fast; (ii) during cadmium desorption the 5-Br-PADAP reagent remains in the resin, which allows using the column several times; (iii) a good enrichment factor (100x) can be achieved. The achieved recovery measured by standard addition technique showed that the proposed procedure had good accuracy. The proposed procedure has been applied for cadmium determination in various samples. 5-Br-PADAP reagent is fairly sensitive and selective for cadmium but, with the preconcentration step and the use of anodic stripping differential pulse polarography, its sensitivity and selectivity have been further improved. It is not possible to develop selective methods for metal ions using this adsorbent in spectrophotometry, since many metal-5-Br-PADAP complexes absorb at close wavelengths. However, with the use of anodic stripping differential pulse polarography this problem can be easily solved. The proposed procedure has been applied for cadmium determination in various samples.

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(*Received*: 21 August 2003; *Accepted*: 20 December 2003) AJC-3303