

Differential Pulse Polarographic Determination of Cadmium After Solid Liquid Extraction and Preconcentration Using PAN

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A highly selective, sensitive, rapid and economical differential pulse polarographic method has been developed for the determination of trace amounts of cadmium in various samples after the adsorption of its 1-(2-pyridylazo)-2-naphthol (PAN) complex on microcrystalline naphthalene in the pH range of 8.2-11.0. After filtration, the solid mass is shaken with 9.0 mL of 1 M hydrochloric acid and cadmium is determined by differential pulse polarography. Cadmium can alternatively be quantitatively adsorbed on [1-(2-pyridylazo)-2-naphthol]-naphthalene adsorbent packed in a column and determined similarly. The detection limit is 0.07 $\mu\text{g/mL}$ (signal-to noise ratio = 2) and the linearity is maintained in the concentration range 0.1-150 $\mu\text{g/mL}$ with a correlation coefficient of 0.9995 and relative standard deviation of $\pm 0.98\%$. Characterization of the electroactive process included an examination of the degree of reversibility. Various parameters such as the effect of pH, volume of aqueous phase and interference of a number of metal ions on the determination of cadmium have been studied in detail to optimize the conditions for determination in various samples.

Key Words: Trace cadmium determination, differential pulse polarography, 1-(2-pyridylazo)-2-naphthol

Introduction

As a powerful ligand, 1-(2-pyridylazo)-2-naphthol (PAN) can react with majority of metal ions in the periodic table to form water-insoluble, colored chelate and has been applied widely to liquid-liquid extraction separation and extraction photometric analysis in analytical chemistry¹⁻³. The most common techniques available for the preconcentration of metals from aqueous samples are solvent extraction and column methods using various adsorbents such as thiol cotton⁴, activated carbon⁵, green tea leaves⁶, chelating resins⁷, cellulose⁸ and polythioether⁹. While some of these adsorbents are fairly effective, their methods of preparation are lengthy and involve rigid conditions. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it cannot be applied directly to metal ions that form stable complexes with the chelating agents only at elevated temperatures. This difficulty can be overcome by using naphthalene as the extractant¹⁰ for thermally stable metal chelates¹¹. Solid-liquid separation after the adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of

metal chelates¹²⁻¹⁴. The preconcentration of metal ions is also possible by passing its aqueous solution over PAN-naphthalene adsorbent taken in a column. The microcrystalline naphthalene method is rapid, but the column method gives a better preconcentration factor¹⁵⁻¹⁷.

Much attention has been given to the direct polarographic estimation of metals after the extraction of their metal complexes into organic solvents¹⁸⁻²². Unfortunately, electrochemical methods for the direct determination of reducible substances require that the solvent should have a fairly high dielectric constant so that a well defined polarogram can be obtained. In this regard, various researchers have mixed the organic phase after extraction with a solvent of high dielectric constant to obtain well defined polarograms²²⁻²⁴. The main disadvantages of these methods are that the sensitivity and preconcentration factor are considerably lower. Thus, the aim of the preconcentration and direct determination of a metal is not achieved. For the direct determination of metal ions after the extraction of their metal complexes into molten naphthalene and dissolution of the product in an organic solvent such as dimethylformamide²⁵, an inert gas (normally N₂ or H₂) has to be passed for at least 10-15 min to remove dissolved oxygen. This procedure makes the method more time consuming and less reproducible owing to the partial evaporation of the organic solvent.

In the present communication, we have developed a simple, sensitive and economical method for the direct differential pulse polarographic determination of cadmium after the adsorption of its 1-(2-pyridylazo)-2-naphthol (PAN) complex on microcrystalline naphthalene and subsequent desorption by 9.0 mL of 1 M hydrochloric acid. After desorption of the metal complex with HCl onto microcrystalline naphthalene there is no need to remove the naphthalene. The dissolved O₂ may be removed by NaBH₄ solutions that provide additional NaCl in the reaction of NaBH₄ with HCl which can also act as a supporting electrolyte and controls the pH of the medium at the same time. The selected reagent, PAN, is very cheap, easily accessible and does not interfere in the polarography estimation of these metal ions. Most problems associated with the abovementioned polarographic methods are solved by this method. The various parameters have been evaluated. The method is found to be highly selective, rapid, economical and fairly sensitive. The developed procedure has been used for the determination of trace amounts of cadmium in various samples.

Experimental

Apparatus

Polarograms were recorded with a three electrode Elico Model CL-90 polarographic analyzer outfitted with an X-Y recorder (model LR-108). A funnel tipped glass tube (60 × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibers 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.

Reagents

Cadmium chloride solution was prepared by dissolving analytical grade solid (Merck) in doubly distilled water and standardized by established methods²⁶. A 0.1% solution of PAN (Merck) was prepared in methanol. A 20% solution of naphthalene (Merck) was prepared in acetone. Solutions of alkali metal salts (Merck) (1%) and various metal salts (Merck) (0.1%) were used for studying the interference of anions and cations respectively. A buffer solution of pH~9 was prepared by mixing 0.5 M ammonia and 0.5 M ammonium

acetate solutions in an appropriate ratio.

Preparation of loaded PAN-naphthalene adsorbent

A mixture consisting of 1 g of PAN, 20 g of naphthalene, 10 mL of water and 100 mL of acetone was stirred on the hot plate arrangement at ~ 40 °C for a few minutes to obtain a clear solution of the reagent and naphthalene. Then it was mixed with 1000-1500 mL of distilled water at room temperature. The coprecipitated mixture was further stirred for 3 h and allowed to stand for 12 h at room temperature. The supernatant solution was drained off with a siphon and the mixture was washed twice with doubly distilled water. The final adsorbent is a slurry of PAN-naphthalene in water and it is stored in a bottle.

General procedure for microcrystalline naphthalene method

An aliquot of cadmium solution (containing 1.0-1500 μg) was placed in a 100 mL Erlenmeyer flask with a tightly fitting stopper. Then 2 mL of 0.1% of the reagent (PAN) was added to it and the mixture was diluted to 30-40 mL with water. The pH was adjusted to ~ 9 with 2 mL of the buffer. The solution was mixed well and allowed to stand for a few seconds. Then 2 mL of a 20% solution of naphthalene in acetone was added to it with continuous shaking. The so formed solid mass consisting of naphthalene and metal complex was separated by filtration on Whatman filter paper. The residue was shaken vigorously with 9.0 mL of 1 M hydrochloric acid and 1 mL of 1 M KCl and the solution was transferred to the polarographic cell. After passing N_2 gas for 5 min, the differential pulse polarogram was recorded. Alternatively dissolved O_2 may be removed from the solution by adding 3-5 mL of a 4% solution of NaBH_4 . When the dissolved O_2 is removed with NaBH_4 , there is no need to add KCl to the solution.

General procedure for the column method

An aliquot of cadmium solution containing 1.0-1500 μg of cadmium was placed in a 25 mL beaker. The pH of this solution was adjusted to ~ 9 with 2 mL of a buffer solution and diluted to ~ 15 mL with distilled water. The column loaded with the adsorbent PAN-naphthalene was conditioned to pH 9 with 2-3 mL of buffer and then the metal solution was passed through the column at a flow rate of 1 mL/min. The packing was washed with a small volume of water. Desorption of the metal was carried out by passing 9.0 mL of 1.0 M HCl at a flow rate of 1 mL/min and the solution was transferred to the polarographic cell. After the addition of 1 mL of 1 M KCl solution, the differential pulse polarogram was recorded.

Results and Discussion

Reversibility of cadmium process

In the present work, the differential pulse polarogram for cadmium in HCl-KCl or HCl-NaCl medium as supporting electrolyte show peak half widths of 60 ± 1 mV in both normal and reverse scan modes, indicating the reversibility of the reduction process involving two electrons^{27,28} (Figure 1). The plot of the applied potential versus the $\log [i/(i_d-i)]$ in DC polarography has a slope of -28.7 mV. For a two electron reduction process at ambient temperature (approximately, 25 °C) the theoretical gradient is -29.5 mV. Consequently, the experimental value of n (number of electrons taking part in the reduction process) is 2.06. The agreement

(within 2.0%) between the observed value and theoretical value can be taken as an indication that the electrode process is effectively reversible²⁹.

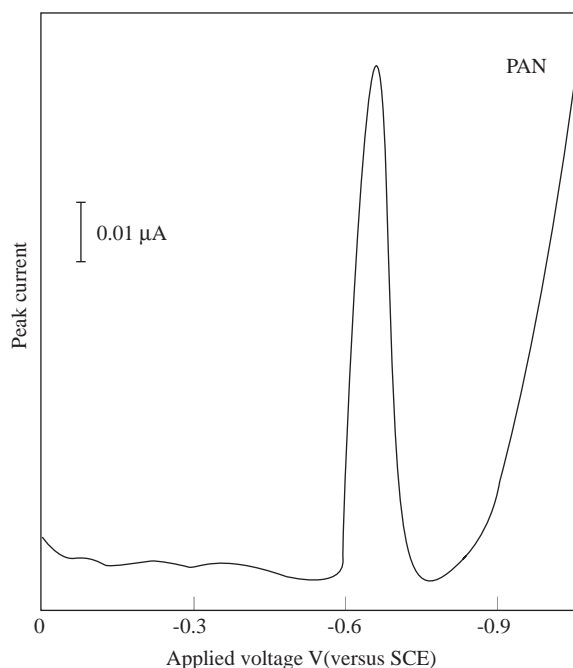


Figure 1. A typical differential pulse polarogram of cadmium. Cadmium = 25 μg , buffer = 2.0 mL (0.1%), medium = KCl-HCl (9 mL HCl + 1 mL KCl), reference = reagent blank. Instrumental setting: scan rate = 12 mV/sec, X = Y = 10.0 mV/cm, drop time = 0.5 s.

Effect of pH on differential pulse polarogram

The effect of pH on the polarograms was studied. The shape of the differential pulse polarograms and peak heights were found to be almost constant when the pH is <7.0 . However, the peak potential (E_p) shifted towards the more negative potential as the pH is increased. A plot of E_p versus pH was not linear, indicating that a protonation reaction is not taking part in the overall electrode process. The peak height was considerably decreased above pH 8.0, owing to hydroxide formation. Therefore, all electrochemical studies were carried out in 1 M hydrochloric acid.

Retention capacity of chelating agent supported on naphthalene

The retention capacity of the adsorbent was determined by the batch method. This experiment was carried out by taking 300 μg of cadmium, 2 mL of buffer and a suitable amount of the adsorbent material in a 100 mL separatory funnel. It was diluted to 30 mL, shaken with a mechanical shaker for 30 min and filtered through filter paper. The amount of cadmium in the filtrate was determined. The naphthalene-chelating agent material on the filter paper was dried and weighed on a balance. The retention capacity of cadmium is found to be proportional to the amount of PAN on naphthalene. The maximum capacity was found to be 5.3 mg of Cd/g of PAN.

Reaction conditions

The reaction conditions were investigated with 25 μg of cadmium. Adsorption was carried out at different pH, keeping other variables constant. It was found that the cadmium-PAN complex was quantitatively adsorbed on naphthalene in the pH range 8.2-11.0 (Figure 2). The addition of 0.5-10 mL buffer did not have any effect on adsorption. Therefore, 2.0 mL of the ammonia-ammonium acetate buffer was used in all subsequent experiments. The PAN concentration was also varied. It was found that adsorptions were quantitative for 0.5-3.0 mL of 0.1% PAN in both cases. Consequently, 1.0 mL of PAN solution was used in subsequent studies.

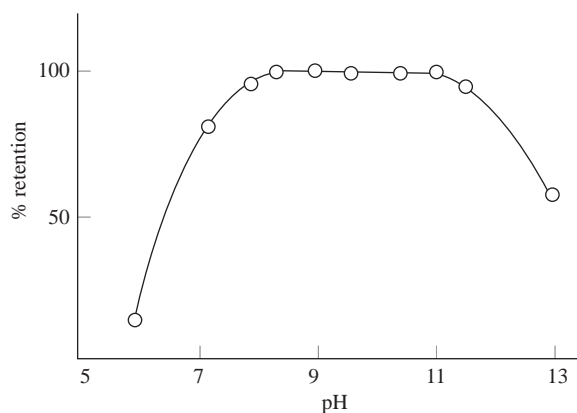


Figure 2. Effect of pH on adsorption of cadmium complex. Conditions and instrumental setting same as Figure 1.

Various amounts of naphthalene were added to the sample solutions, keeping other variables constant; it was observed that the peak height remained constant with the addition of 1.0-4.0 mL of 20% naphthalene solution. Therefore, 2 mL of 20% naphthalene solution was used in subsequent studies. The effect of shaking time on adsorption indicated that peak height remained constant over the range 1.0-10 min. Therefore, 2 min of shaking time was recommended in the present work.

In the column method a flow rate of 0.2 to 8 mL/min was applied. It was found that a flow rate of 0.2-5.0 mL/min did not affect adsorption. A flow rate of 1 mL/min was recommended in all experiments.

The volume of the aqueous phase was varied in the range 10-500 mL in steps under optimum conditions. It was observed that peak height was almost constant for up to 300 mL of the aqueous phase (preconcentration factor of approximately 30). However, for convenience, all experiments were carried out with 40 mL of the aqueous phase.

In the column method, peak height was almost constant up to an aqueous phase volume of 500 mL. Therefore, a preconcentration factor of 50 can be achieved by the column.

Preliminary observations indicated that cadmium was desorbed completely with 9.0 mL of 0.1-5.0 M hydrochloric acid but to be on the safe side 9.0 mL of 1 M hydrochloric acid was used.

Calibration

The detection limit was 0.07 $\mu\text{g}/\text{mL}$ (signal-to-noise ratio = 2) and the linearity was maintained in the concentration range 0.1-150 $\mu\text{g}/\text{mL}$ with a correlation coefficient of 0.9995 and a relative standard deviation of $\pm 0.98\%$ (Figure 3).

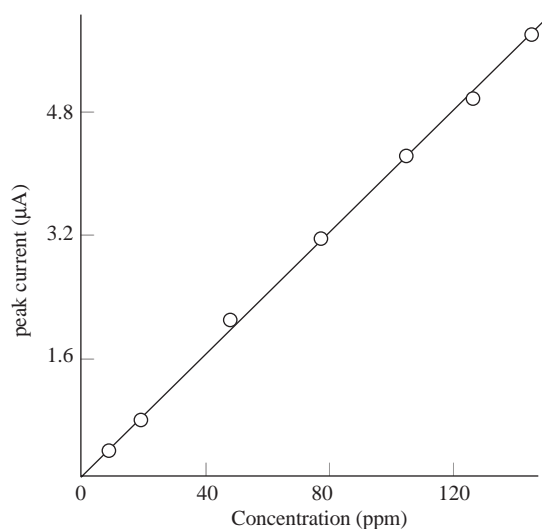


Figure 3. Calibration curve for cadmium. Conditions and instrumental setting same as Figure 1.

Interferences

Various salts and metal ions were added individually to a solution containing 25 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. Interferences.

Salt or Ion	Tolerance limit
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, NaCl, KNO_3	1 g
NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, NH_4Br , NaF	650 mg
Thiourea	600 mg
KI	450 mg
K_2CO_3 , KSCN	120 mg
Potassium sodium tartrate	110 mg
Tri sodium citrate	60 mg
Na_2EDTA	100 μg
Mn(II), Zn(II), Mo(VI)	55 mg
Cr(III), Se(VI), Ti(VI), Ga(III), Al(III)	30 mg
U(VI), V(V), Te(IV), Bi(III)	8.0 mg
Fe(III), Rh(III), Ru(III), Pd(II), Os(VIII)	4.0 mg
Co(II), Ni(II), Sn(II), Cr(VI), Sb(III), Cu(II)	2.0 mg

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, and NIST SRM 629 Zn-Base Alloy E. An aliquot (50-100

mL) of the pretreated sample solution was taken³⁰ and analyzed by the general procedure. The results are given in Table 2, which is in good agreement with the certified values.

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 ± 0.0008 ^c
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 ± 0.0002 ^c
NIST SRM 627 Zn-Base Alloy CE	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	0.0046 ± 0.0004 ^d
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	0.016 ± 0.001 ^c
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); and Hg, (0.056) μg g ⁻¹	6.7 ± 0.5 ^b	6.5 ± 0.4 ^{b,c}
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 ± 1.0; Sr, 40 ± 3; Co, 0.87 ± 0.05; Pb, 0.60; Cu, 3.5 ± 0.3; Sc, (0.013) μg g ⁻¹	0.026 ^b	0.025 ± 0.003 ^{b,d}
Contd. 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) μg g ⁻¹	0.82 ± 0.03 ^b	0.80 ± 0.03 ^{b,c}
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 μg g ⁻¹	0.82 ^b	0.84 ± 0.04 ^{b,d}

^a Mean of four determinations. ^b μg g⁻¹ ±, s.d.

^c Column method was applied.

^d Microcrystalline naphthalene method was applied.

Determination of cadmium in pepperbush, chlorella, mussels 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. An aliquot (50-100 mL) of the pretreated sample solution was taken³⁰ and analyzed by the general procedure. The results are given in Table 2 they are in good agreement with the certified values.

Conclusions

It is difficult to obtain a well defined polarogram in the traditional analysis for metals after the extraction of their complexes into an organic solvent owing to the low dielectric constant of the organic phase. Sensitivity is lost if it is mixed with another solvent of a high dielectric constant. Another major disadvantage is the removal of dissolved oxygen, which is a tedious and time consuming process. Moreover, the reproducibility of the method is affected by the partial evaporation of organic solvent. The reported method has solved most of these problems and has been successfully tested for the determination of cadmium in various environmental samples and standard alloys.

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