DPP Determination of Cadmium after Adsorption of its Piperazine Dithiocarbamate Complex onto Microcrystalline Naphthalene

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Cadmium piperazine dithiocarbamate complex is quantitatively adsorbed onto micrystalline naphthalene in the pH range of 3.4 - 11.0. Cadmium-piperazine dithiocarbamate-naphthalane complex is filtered, shaken with 10 ml of 1 M HCl and cadmium determined polarographically. The condition for its estimation in complex materials is optimised. Linearity exists in the concentration range of 0.07-10 ppm with a correlation factor of 0.9997. Ten replicate determinations of a sample solution containing 112 µg of cadmium gave a relative standard deviation of ± 0.78%. The detection limit is 0.07 ppm (signal to noise ratio = 2).

Solvent extraction is one of the most widely used technique for preconcentration of metal ions, but it is often tideous. Further, the concentration factor obtained can be limited by the mutual solubility of two phases. Recently, certain materials such as thiol cotton [1] siland glass beads [2], amberlite XAD-2 resin [3], amberlite XAD-4 resin [4], cellulose [5] and various metal oxides and hydroxides [6] have been used as adsorbent for metal complexes. Column methods are fairly effective for the preconcentration of metal ions but they are time consuming because both flow rate and elution are low. Further, the preparation of these adsorbent is also a time consuming process.

Metal complexes can be extracted into organic solvents [7-9]. But electrochemical methods need solvents of a fairly high dielectric constant. Mixed solvent could be used [10]. But by such dilution, preconcentration factor is considerably lowered. Metal ions could be extracted into molten naphthelene and then dissolved in DMF [11,12]. This medium needs prolonged dearation and this results in partial solvent loss.

The present paper reports extraction of Cd piperazine dithiocarbamate into microcrystaline napthalene, followed by desorption in HCl. Dearation is achieved by addition of $NaBH_4$. This has the added advantage of providing base electrolyte (NaCl) of suitable pH.

EXPERIMENTAL

Polarograms were recorded using a three electrode cell and an Elico Model CL-90 Polarographic Analyzer fitted with a X-Y recorder model LR-108. All atomic absorption measurements were made using an atomic absorption spectrometer model Varian AA 475. An Elico Model L1-120 pH meter was used for pH measurements.

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Cadmium chloride solution was prepared by dissolving A.R. sample in double distilled water and standardised by known methods [12]. Sodium piperazine dithiocarbamate was prepared by the method of Marcotrigiano [13]. Hydrochloric acid and naphthalene were of L.R. grade and tested polarographically before use. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations respectively. Sodium acetate/acetic acid (0.2 M) and aqueous ammonia/ammonium acetate buffers were used for pH adjustment. Twice distilled water was used wherever required.

General Procedure

An aliquot of cadmium solution (2-13 µg) was taken in a 100 ml Erlenmeyer flask with a tightly fitting stopper. To this solution, 2 ml of 0.2% dithiocarbama e solution in water was added and diluted to 30-40 ml. Two ml of aqueous ammon ia/ ammonium acetate buffer of pH 8.0 was added. The solution was mixed well and allowed to stand for a few seconds. Then 2 ml of 20% solution of naphthalene in acetone was added to the solution with continuous shaking. The solid mass consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No-1041). The residue was shaken vigorously with 10 ml of 1 M hydrochloric acid and then transferred to the polarographic cell. After addition of 3-4 ml of $NaBH_4$ solution, the differential pulse polarogram was recorded.

RESULTS AND DISCUSSIONS

Polarographic operating parameters are given in Table 1. The plots of the d.c. waves against square root of the height of mercury column are linear. Plots of E vs log $[i/(i_l-i)]$ were linear with slopes of -28.7 mV. The experimental value of n (no. of electrons taking part in reduction process) is 2.02 ± 0.03.

Differential pulse polarograms of Cd in HCl - NaCl medium (by both normal and reverse modes) show half-peak widths of 62 ± 1 mV (Fig 1) indicating the reversibility of the reduction process involving 2 electrons.

Table 1

Polarographic Operating Parameters

Parameter	Setting	Parameter	Setting
Scan Rate	12 mV.sec^{-1}	Direction	Negative
Initial Potential	0.0	Range	-1.0 V
Modulation Amplitude	50 mV	Operation Mode	Diff. Pulse
Display Direction	Normal	Sensitivity	0.1 µA/V
Drop time	0.5 sec	Temperature	25 ± 1°C
X-axis range	100 mV/cm	Y-axis range	100 mV/cm

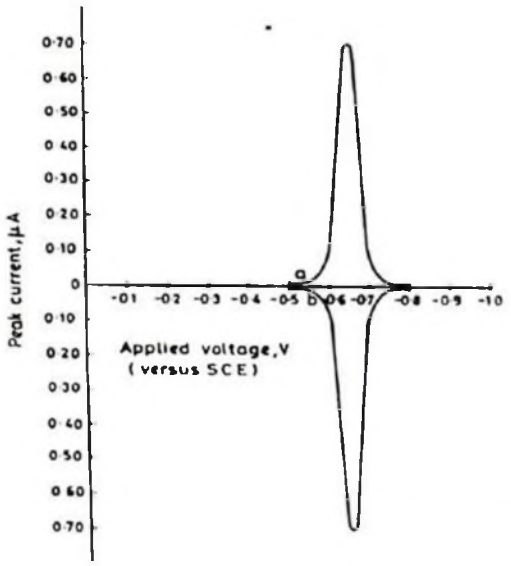


Fig. 1 Differential pulse polarograms of cadmium
Cadmium: 112 μg, reagent: 2.0 mL (0.2%), naphthalene: 2.0 mL (20%), reference: reagent blank, mode: normal (a), reverse (b), Instrumental settings as described in Table 1.

Preliminary observations indicated that cadmium complex is desorbed completely with 10 ml of 0.1 - 5.0 M hydrochloric acid but 1 M of hydrochloric acid is used as optimum. Addition of 3-4 ml of 4% $NaBH_4$ solution effectively removed O_2 quickly and does not interfere with the metal ions. Further $NaBH_4$/HCl medium itself produce enough sodium chloride which acts as a supporting electrolyte; it also adds some OH ions and maintaines proper pH-range to obtain a well defined polarogram.

Optimisation of Conditions

The pH of the solution was varied by adding 4% $NaBH_4$ solution keeping other variables constant. The $E_{1/2}$ shifted to more negative potential with increase pH (Table 2). But the plot of $E_{1/2}$ vs pH was not linear. However, the shape of DPP and peak heights were almost constant over the pH range of 1.0-8.0. The peak height decreased considerably beyond pH 8.0 probably due to cadmium hydroxide formation. All studies were carried out with ammonia / ammonium acetate buffer.

Table 2

Effect of pH on DPP

pH	E_p vs SCE (V)	i_p (μA)
0.61	0.66	0.71
1.00	0.65	0.70
2.50	0.65	0.70
4.00	0.65	0.69
5.11	0.66	0.70
6.20	0.67	0.70
7.50	0.69	0.69
8.11	0.71	0.65
8.79	0.71	0.50

Average of 5 determinations

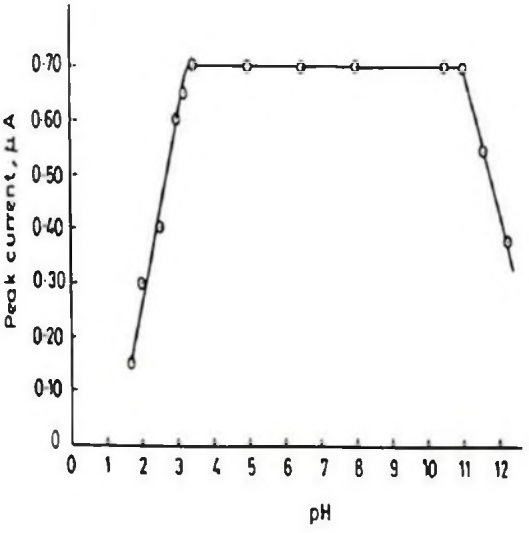


Fig.2 Effect of pH on adsorption of cadmium complex,
conditions same as Fig. 1.

Effect of Parameters on Adsorption

Adsorptions were carried out at different pH, keeping other variables constant. It was found that the cadmium-piperazine dithiocarbamate complex was quantitatively adsorbed on nephthalene in the pH range 3.4-11.0 (Fig.2). Addition of 1-5 ml of buffer did not cause any effect on the adsorption. Therefore 2.0 ml of the aqueous ammonia/ ammonium acetate buffer was employed in the subsequent determinations.

Adsorptions were carried out by varying amounts of reagent at a constant pH. It was found that adsorptions were quantitative for 0.6-5.0 ml of 0.2% reagent. 2.0 ml of reagent were used in subsequent studies.

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 0.2-4.0 ml of 20% naphthalene solution. Therefore, 2 ml of 20% naphthalene was used in subsequent studies.

The effect shaking time on the adsorption was studied. It was observed that peak height remained constant over the range of 1-50 minutes of shaking. One minute of shaking time was maintained in the present work.

Volume of the aqueous phase was varied in the range of 10-600 ml under the optimum condition. It was observed that the peak height was almost constant upto 300 ml of the aqueous phase (preconcentration factor of 30) and then decreased gradually. In all the experiments, 40 ml of the aqueous phase was maintained due to convenience.

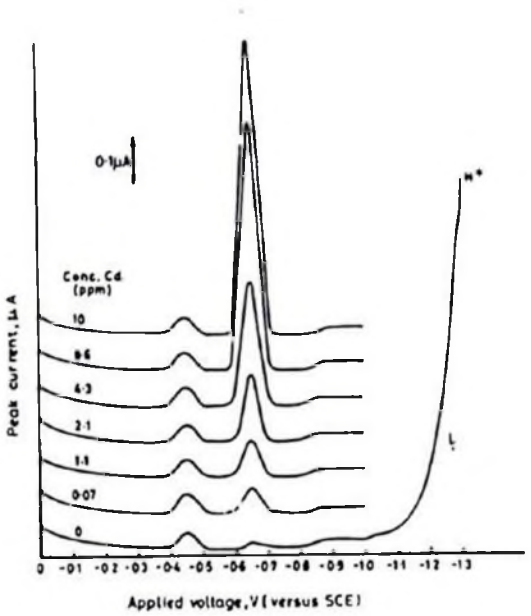


Fig.3 Typical differential pulse polarogram for a series of cadmium concentrations; conditions same as Fig.1.

Calibration

A calibration curve for the determination of cadmium was prepared according to the general procedure under optimum conditions developed above. The detection limit was 0.07 ppm (signal to noise ratio=2) and the linearity was maintained in the concentration range of 0.07-10 ppm with a correlation factor of 0.9997. Ten replicate determinations of a sample solution containing 112 μg of cadmium gave a relative standard deviation of ± 0.78%.

Effect of Foreign Ions

The effect of various salts on the adsorption and subsequctly on differential pulse polarographic determination of 112 μg of cadmium was studied. Anions in the following salts did not interfere - sodium tartrate, sodium oxalate, sodium citrate,

sodium hydrogen phosphate, sodium carbonate, sodium sulphate, sodium acetate, potassium nitrate, potassium bromide, potassium iodide (100 mg each). Among the cations studied - U(VI), Se(VI), Mo(VI), Ti(IV), Cr(III), Mn(II), Zn(II) and Pb(II) (50 mg each); V(V), Te(IV), Bi(III), Al(III), Ni(II), Sn(II), Co(II) and Cu(II) (25 mg each); Os(VIII), Sb(III), Rh(III) Ru(III) and Pd(II), Tl(I) (5 mg each), Fe(III) and Ir(III) interfered; however, 5 mg of Fe(III) and 10 mg of Ir(III) could be tolerated after masking Fe(III) with triethanolamine, and carrying adsorption of Ir(III) at pH 9.4. EDTA interfered seriously probably due to the higher formation constant of the cadmium-EDTA complex than cadmium piperazine dathiocarbamate. Adsorption was almost nil in the presence of 1 mg EDTA.

Analytical Applications For Determination of Cadmiun

In Standard Alloys

A 1.0 g sample of the standard alloy was dissolved in 50-60 ml of hydrochloric acid (1+1) by heating on a hot plate, then 3-5 ml of 30% hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the solution. The solution was cooled, filtered if needed and diluted to 100 ml with water in a standard flask. An aliquot of this solution was taken and analyzed by the general procedure after masking iron with triethanolamine solution. The results are given in Table 3.

Table 3

Determination of Cd in Standard Alloys
Average of ten determination, ± Stanadrad deviation

Sample & Composition	Cadmiun Found (%)
N.B.S., SRM-94C Zn Alloy of composition Pb=0.0.006; Sn=0.006; Ni=0.006; Mn=0.014 Fe=0.018; Mg=0.042; Cu=1.01; Al=4.13 Cd=0.002	0.0022±0.0003
N.B.S., SRM-627 Zn-base die-casting alloy C of composition Cu=0.132; Mg=0.030; Fe=0.023; Pb=0.0083; Sn=0.0042, Cr=0.0038; Mn=0.014, Ni=0.0029; Si=0.021; Al=3.88; Cd=0.005	0.0051± 0.0004
N.B.S., SRM-627 Zn-bse die-casting alloy E of composition Cu=0.50; Mg=0.094; Fe=0.17; Pb=0.0135; Sn=0.012; Cr=0.0075; Si=0.078; Al=5.15 Cd=0.015	0.016± 0.004
NIES, No.1 Pepperbush of composition K=1.51±0.06; Mg=0.408±0.020; Ca=1.38±0.07; Mn=0.203±0.017; Mg=0.408±0.020 (µg/g); Fe=205±17; Pb=5.5±0.8; Cr=(1.3); Cs=(1.2); Tl=(0.13); Hg=(0.056); P=(1100); As=2.3±0.3; Zn=340±20; Cd=6.7±0.5; Ni=8.7±0.6; Co=23±3; Sr=36±4;Rb=75±4; Na=106±1.3; Ba=165±10;	0.0007±0.0002

In Liquid Environmental Samples

A 100 ml of tap water from the laboratory of the Department of Chemistry, IIT, Delhi, was analyzed directly by the general procedure while water samples from tube well from IIT, Delhi was analyzed with standard addition method [15]. However, oxidative digestion method was adopted for pretreatment of samples obtained from Yamuna river, Wazirpur industrial effluents, New Delhi and Okhala Canal, New Delhi, India [16]. A 100 ml of water sample from these sources was taken, 5 ml of concentrated nitric acid added to it, heated the solution almost to dryness on a hot plate, then dissolved the residue in 5 ml of 1 M hydrochloric acid and finally made the solution to a volume of 100 ml in a standard flask. An aliquot of the solution was taken and analyzed by the general procedure after masking Fe(III) with triethanolamine. The results are given in Table 4.

In Solid Environmental Samples

Solid samples (Sediment from Yamuna river near Wazirpur industrial waste disposal point and soil near Wazipur Industrial area, New Delhi, India) were dried in an oven at 200°C for 2 hours. A 1 g of dried sample was decomposed with 50-60 ml of hydrochloric acid (1+1). Then 3-5 ml of 30% hydrogen peroxide was added. The mixture was heated on a hot plate till the sample dissolved completely and evaporated to

Table 4

Determination of Cadmium in Different Samples

Average of five determinations, ± standard deviation

	Sample from different sources	Amount found(μg/l) by DPP	AAS
in Liquid Environmental Samples in New Delhi, India			
I	Industrial effients from electroplating and ceramic industry, Wazirpur Industiral Area	6021±3	6010±5
II	Okhla Canal, Near Okhla Industrial Area,	210±5	200±4
III	Yamuna River, Near Wazirpur Industrial Area	0.871±0.003	0.870±0.005
IV	Tubwell water from IIT	0.014±0.002#	0.015±0.003
V	Tapwater from the laboratory of IIT	0.725±0.002	0.720±0.005
in Solid Environmental Samples from New Delhi, India			
I	Sediment of Yamuna river near Wazirpur industrial waste disposal point	100±4	100±2
II	Soil near Wazirpur Industrial area,	0.121±0.003	0.120±0.005

by standard Addition Method.

almost dryness. Then the residue was dissolved in 10 ml of 1 M hydrochloric acid, diluted with 10 ml of water, filtered if needed, made the solution upto 100 ml in a standard flask by diluting it with water [17]. An aliquot of the solution was taken and analyzed by the general procedure after masking iron. The results are included in Table 4.

CONCLUSION

The reported method has been tested successfully for the estimation of cadmium in a number of standard alloys and environmental samples. The preconcentration factor of 30 obtained by this method may be further improved by using piperazine dithiocarbamate-cetyltrimethylammoniumbromide (CTMAB)-naphthalene adsorbent filled in a column. However it is time consuming. Instead of piperazine dithiocarbamate, other dithiocarbamates like diethyldithiocarbamates, xanthantes and other complexing agents may also be used. But dithiocarbamates are better for the differential pulse polarogaphic estimation of metals after adsorption of their metal complexes onto micro crystalline naphtahalene since a large range of potential is available. Final estimation of cadmium may also be carried out by cyclic voltammetric technique using gold-amalgamated electrode.

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