

# SIMULTANEOUS DETERMINATION OF TRACES OF LEAD AND CADMIUM IN VARIOUS SAMPLES BY DIFFERENTIAL PULSE POLAROGRAPHY AFTER ADSORBING THEIR 1-(2-PYRIDYLAZO)-2-NAPHTHOL ONTO MICROCRYSTALLINE NAPHTHALENE

*Taher, Mohammad Ali\**

Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, I.R. Iran

P.O.Box 76175-133

*Puri, Bal Krishan*

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi-110016, India

**ABSTRACT:** *A highly selective, rapid and economical differential pulse polarographic method has been developed for the determination of trace amounts of cadmium and lead present together in various standard alloys and biological samples after adsorption of their 1-(2-pyridylazo)-2-naphthol complexes on microcrystalline naphthalene. Cadmium and lead complexes are equantitatively adsorbed on microcrystalline naphthalene in the pH range of 8.2-11.0 for cadmium and 8.4-11.5 for lead. After filtration, the solid mass is shaken in 10 mL of 1 M hydrochloric acid and these metals are determined simultaneously by differential pulse polarography (DPP). Detection limits are: 0.07 µg/mL for Cd and 0.1 µg/mL for Pb (signal to noise ratio=2). While linearity is maintained in the concentration range 0.1-150 µg/mL for Cd and 0.1-300 µg/mL for Pb with a correlation coefficient of 0.9996 and relative standard deviations of 0.98 and 1.1%, respectively. 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 and lead have been studied in detail to optimize the conditions for their simultaneous (based upon the difference in their  $E_p$  values) determination in complex materials.*

**KEY WORDS:** *Differential-pulse polarography, Cadmium and lead simultaneous determination, 1-(2-Pyridylazo)-2-naphthol, Microcrystalline naphthalene, Standard alloys and biological samples.*

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\* To whom correspondence should be addressed.

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## INTRODUCTION

The possibility of using 1-(2-pyridylazo)-2-naphthol (PAN) for the analytical purposes was investigated by Cheng and Bray [1]. This reagent reacts with many metal ions to form water-insoluble, colored chelate complexes and has been applied widely in the liquid-liquid extraction-spectrophotometric determination of metals in materials [2]. The most common techniques available for the preconcentration of metals present in aqueous samples are solvent extraction, and column methods, using various adsorbents such as thiol cotton [3], activated carbon [4], green tea leaves [5], chelating resins [6], cellulose [7], and polythioether [8]. Although some of these adsorbents are fairly effective their methods of preparation are lengthy usually involving strict conditions. The desorption of the metal complex is carried out by a slow elution process, thus making the method more time consuming [9]. Solvent extraction is one of the most widely used techniques owing to its simplicity and applicability to both trace and macroscopic quantities of metal ions. However, it is limited because of the mutual solubility of the two phases and frequent formation of emulsion during the shaking process solid-liquid separation after adsorption of metal chelates on naphthalene is more rapid and convenient and can be applied to many types of metal complexes [10-12].

In the literature, attention has been paid to the direct polarographic determination of metals after extraction of their metal complexes into organic solvents [13-17]. Unfortunately, the direct determination of reducible substances by electro chemical methods require that the solvent used should have a fairly high dielectric constant in order to obtain well defined polarograms. Therefore, after extraction the organic phases has to be mixed with a suitable solvent of high dielectric constant to obtain well defined polarograms [18-19]. The main disadvantages of this method are that sensitivity is lost and the preconcentration factor is considerably lowered. Hence, the aim of preconcentration and direct determination of a metal is lost. For direct determination of metal ions after extraction of their metal complexes into molten naphthalene and dissolution of the products in an organic solvent such as dimethylformamide [20], an

inert gas normally  $N_2$  or  $H_2$  has to passed for at least 10-15 min to remove dissolved oxygen, again making the method more time consuming and less reproducible owing to the partial evaporation of the organic solvent.

In the present paper, we have developed a simple, rapid and economical method for the direct differential-pulse polarographic determination of cadmium and lead simultaneously after adsorption of their PAN complexes onto microcrystalline naphthalene and subsequent desorption by 10 mL of 1 M hydrochloric acid. The extraction-spectrophotometric method can not be applied for the simultaneous determination of these metals using PAN as its complexing reagent because they are extracted in the same *pH* range and absorb at the same wavelengths and moreover the reagent itself absorbs at a wavelength closer to the metal complexes and thus results a large blank correction and making the method tedious [2]. In differential pulse polarography (DPP), these metals are reduced at different potentials, therefore, their simultaneous determination is possible. After desorption of the metal complex with HCl, there is no need to remove naphthalene and HCl itself acts as a supporting electrolyte. The dissolved  $O_2$  may be removed by  $NaBH_4$  solution which provide additional NaCl in the reaction of  $NaBH_4$  with HCl which can also act as a supporting electrolyte and controls the *pH* of the medium at the same time. The reagent PAN selected is inexpensive, easily available and does not interfere in polarographic estimation of these metal ions. Most of the problems with above mentioned polarographic methods are solved by this method. The method is found to be highly selective, rapid, economical and fairly sensitive. The developed procedure has been used for the simultaneous determination of trace amounts of cadmium and lead in various standard alloys and biological samples.

## EXPERIMENTAL

### *Apparatus and reagents*

Polarograms were recorded with an Elico model C1-90 (New Delhi, India) three electrodes' polarography. It was outfitted with a model LR-108 X-Y recorder. An Elico *pH* meter was employed for *pH*

measurements. Cadmium chloride and lead nitrate solutions were prepared by dissolving analytical grade samples in doubly distilled water and standardized by established methods [21]. A 0.1% solution of PAN was prepared in methanol. A 20% solution of naphthalene was prepared in acetone. 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  $pH \approx 9$  was prepared by mixing of 0.5 M ammonia and 0.5 M ammonium acetate solutions in an appropriate ratio. A 4% solution of  $NaBH_4$  was prepared in 0.2 M NaOH solution.

### General procedure

An aliquot of cadmium or lead solution (containing 10-500  $\mu g$  of the metal) was placed in a 100 mL of an Erlenmeyer flask with tightly fitted stopper. To this solution, 1 mL of 0.1% solution of the reagent (PAN) was added and the mixture was diluted to 30-40 mL with water. The  $pH$  was adjusted to  $\approx 9$  with 2 mL of the buffer solution. After 2 min at room temperature, 2 mL of a 20% solution of naphthalene in acetone was added with continuous shaking. The solid mass consisting of naphthalene and the metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was shaken vigorously with 9 mL of 1 M hydrochloric acid and 1 mL of 1 M KCl and the solution transferred to the polarographic cell. After passing  $N_2$  gas for 5 min, the differential-pulse polarogram was recorded. Alternatively the dissolved  $O_2$  from the solution may be removed by adding 3-5 mL of 4% solution of  $NaBH_4$ . When the dissolved  $O_2$  is removed with  $NaBH_4$ , there is no need of adding KCl to the solution.

## RESULTS AND DISCUSSION

Preliminary observations indicated that  $NaBH_4$  is quite effective in the removal of dissolved oxygen from the solution in a few seconds. Another advantage of using  $NaBH_4$  is that it provides  $OH^-$  ions and brings the  $pH$  into the desired range. Thus, it is helpful in adjusting the  $pH$  of the solution. There was no need to add extra NaCl as a supporting electrolyte because a sufficient quantity of NaCl was formed in the reaction.

### 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  $pH$  increased. However a plot of  $E_p$  versus  $pH$  was not linear, indicating that a protonation reaction is not taking part in the over-all electrode process. The peak height decreased considerably above  $pH$  8.0, owing to hydroxide formation. Therefore, all studies were carried out in about 1 M hydrochloric acid.

### Reaction conditions

The reaction conditions were investigated with 25  $\mu g$  cadmium and 25  $\mu g$  of lead. Adsorptions were carried out at different  $pH$ , keeping other variables constant. It was found (by differential-pulse polarography-DPP) that the cadmium and lead-PAN complexes were quantitatively adsorbed on naphthalene in the  $pH$  range 8.2-11.0 and 8.4-11.5 respectively, (Fig. 1). Addition of 0.5-10 mL of buffer, did not have any effect on the adsorption. Therefore, 2.0 mL of the ammonia-ammonium acetate buffer was used in all the subsequent experiments. The reagent concentration was also varied. It was found that adsorptions were quantitative for 0.5-3.0 mL of 0.1% reagent in both the case. Consequently, 1.0 mL of reagent solution was used in subsequent studies.

Various amounts of naphthalene were added to

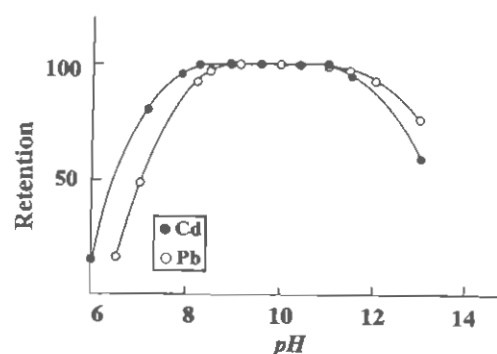


Fig. 1: Effect of the  $pH$  on the adsorption of lead and cadmium-PAN complexes. Lead, 25  $\mu g$  and cadmium, 25  $\mu g$  in 10 mL final solution, reference, reagent blank; mode, normal. Instrument settings: Scan rate, 12  $mV s^{-1}$ ; modulation amplitude, 50 mV; and drop time, 0.5 s.

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 the adsorption indicated that the peak height remained constant over the range 1.0-10 min. Therefore, 2 min of shaking time was used throughout this work.

The volume of the aqueous phase was varied in the range 10-500 mL in steps under the optimum conditions. It was observed that the peak height was almost constant for up to 300 mL of the aqueous phase (preconcentration factor of approximately 30) in case of cadmium, and upto 200 mL of the aqueous phase (preconcentration factor of approximately 20) in the case of lead and then decreased gradually in both the cases. However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase.

Preliminary observations indicated that cadmium or lead complexes were desorbed completely with 10 mL of 0.1-5.0 M hydrochloric acid but, to be on the safe side, 10 mL of 1 M hydrochloric acid was used. Various amounts of  $\text{NaBH}_4$  were added to the sample solutions and it was observed that the peak height remained constant with addition of 3-5 mL of 4%  $\text{NaBH}_4$  solution.

### Calibration

A typical pulse polarogram of cadmium and lead is given in Fig. 2. A calibration graph for the determination of cadmium and lead was prepared according to the general procedure under the optimum conditions developed above for cadmium and lead. The detection limits were  $0.07 \mu\text{g/mL}$  for cadmium and  $0.1 \mu\text{g/mL}$  for lead (signal to noise ratio=2) and the linearity were maintained in the concentration range 0.1-150  $\mu\text{g/mL}$  for cadmium and 0.1-300  $\mu\text{g/mL}$  for lead with a correlation coefficient of 0.9996 and a relative standard deviations of 0.98 and 1.1%, respectively.

### Effect of foreign ions

Various salts and metal ions were added individually to a solution containing 25  $\mu\text{g}$  of cadmium or 25  $\mu\text{g}$  of lead and the general procedure was applied.

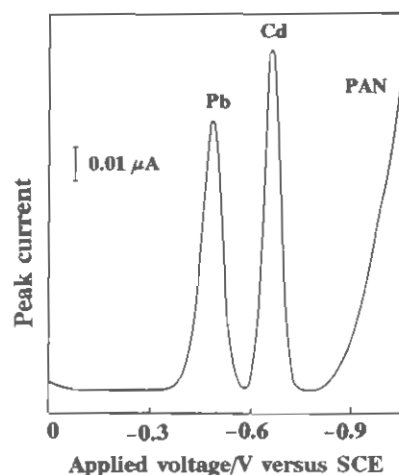


Fig. 2: Typical differential-pulse polarograms of lead and cadmium. Conditions same as Fig. 1.

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

Table 1: Effect of foreign salts and metal ions

Salt or Ion	Tolerance limit
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , NaCl, $\text{KNO}_3$	1 g
$\text{NH}_4\text{Cl}$ , $(\text{NH}_4)_2\text{SO}_4$ , $\text{NH}_4\text{Br}$ , NaF	500 mg
Thiourea	600 mg
KI	400 mg
$\text{K}_2\text{CO}_3$ , KSCN	100 mg
Potassium sodium tartrate	100 mg
Tri sodium citrate	50 mg
$\text{Na}_2\text{EDTA}$	100 $\mu\text{g}$
Mn(II), Zn(II), Mo(VI)	50 mg
Cr(III), Se(VI), Ti(VI), Ga(III), Al(III)	20 mg
U(VI), V(V), Te(IV), Bi(III)	5 mg
Fe(III), Rh(III), Ru(III), Pd(II), Os(VIII)	2 mg
Co(II), Ni(II), Sn(II), Cr(VI), Sb(III), Cu(II)	1 mg

Solution containing 25  $\mu\text{g}$  of cadmium and 25  $\mu\text{g}$  lead and general procedure was applied.

Table 2 : Analysis of samples for cadmium and lead

Sample	Composition %	Concentration of cadmium & lead %	
		Certified Value	Found <sup>a</sup>
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; Si, 0.078%	Cd 0.0155 Pb 0.0135	Cd 0.0159±0.0009 Pb 0.0135±0.0005
NIST SRM 94c Zn-Base Die Casting Alloy	Sn, 0.006; Ni, 0.006; Mn, 0.014; Fe, 0.018; 0.042; Cu, 1.01; Al, 4.13%	Cd 0.002 Pb 0.006	Cd 0.0021±0.0002 Pb 0.0062±0.0003
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; Al, 3.88%	Cd 0.005 Pb 0.0083	Cd 0.0051±0.0002 Pb 0.0080±0.0006
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; Al, 5.15%	Cd 0.015 Pb 0.0135	Cd 0.014±0.001 Pb 0.0133±0.0003
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; As, 2.3±0.3; P, (1100); Cr(1.3); Cs(1.2); Tl(0.13); and Hg, (0.056) µg g <sup>-1</sup>	Cd 6.7±0.5 <sup>b</sup> Pb 5.5±0.8 <sup>b</sup>	Cd 6.5±0.9 <sup>b</sup> Pb 5.4±0.7 <sup>b</sup>
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; Cu, 3.5±0.3; Sc, (0.013) µg g <sup>-1</sup>	Cd 0.026 <sup>b</sup> Pb 0.60 <sup>b</sup>	Cd 0.024±0.005 <sup>b</sup> Pb 0.58±0.01 <sup>b</sup>
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). Hg, (0.05) µg g <sup>-1</sup>	Cd 0.82±0.03 <sup>b</sup> Pb 0.91±0.04 <sup>b</sup>	Cd 0.80±0.08 <sup>b</sup> Pb 0.90±0.06 <sup>b</sup>
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; As, 12 µg g <sup>-1</sup>	Cd 0.82 <sup>b</sup> Pb 105 <sup>b</sup>	Cd 0.80±0.06 <sup>b</sup> Pb 105±0.9 <sup>b</sup>

a) Mean value of four determinations.

b) µg g<sup>-1</sup>, ±s. d.

### Determination of cadmium and lead in standard alloys

The proposed method were 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, NIS SRM 627 Zn-Base Alloy CE, NIST SRM 629 Zn-Base Alloy E.

An appropriate amount of the sample of the standard alloy was completely dissolved in ≈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  $\approx 50$  mL of this solution was taken, cadmium and lead were determined by the general procedure (Table 2).

#### **Determination of cadmium and lead in pepperbush, chlorella, mussel and pond sediment**

The accuracy and applicability of the proposed method has been applied to the determination of cadmium and lead 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 ( $\approx 50$  mL) of the pretreated sample solution was taken [22] and analyzed by the general procedure. The results are given in Table 2 which are in good agreement with the certified values.

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