



Electrochemical Complexation Studies of Cadmium (II) for its Ultra Trace Determination

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Abstract

A selective and sensitive method for determination of cadmium by differential pulse polarography is presented. The method is based on complexation of Cd(II) ions with citric acid in potassium nitrate medium, followed by electrochemical reduction of Cd(II)-complex by DPP. Optimal conditions were obtained at citric acid concentration of 0.1 M, reduction potential of -0.56V (vs SCE) and scan rate of 12mV/sec. Under optimized conditions linear calibration curves were established for the concentration of Cd(II) in the range of 0.008-30 µg/ml, with the detection limit of 0.008 ppm. The method was successfully applied to the ultra trace determination of Cd(II) in waste waters from industries. Interferences were also evaluated.

Keywords: Cadmium, DPP, waste waters.

Introduction

The term heavy metal refers to any metallic chemical element with five times or more the specific gravity of water and is toxic or poisonous at low concentrations. Heavy metals are among the most common environmental pollutants and their occurrence in water and biota indicate the presence of natural and anthropogenic sources¹. Recently methods such as AAS and *uv*-spectrophotometry were reported in estimation and assessment of heavy metal contamination in diverse environmental samples from various places²⁻⁵.

Cadmium is one of the most hazardous heavy metal and its toxicological action results from interaction with essential elements such as zinc⁶. Cadmium poisoning is an occupational hazard associated with industrial processes such as metal plating, production of Ni-Cd batteries, etc. inhalation of cadmium containing fumes can result initially in metal fume fever, but may progress to pneumonitis, pulmonary edema and death⁷. Cadmium is also a potential environmental hazard and human exposures to environmental cadmium are primarily the result of burning of fossil fuels and municipal wastes⁸. Cadmium and several cadmium containing compounds are known carcinogens and can induce many types of cancer⁹. The Central Pollution Control Board, India, has set maximum permissible limit of 2 mg/L and 1 mg/L for cadmium in inland surface waters and public sewer, respectively¹⁰.

Owing to the serious health effects of cadmium exposure, it has become imperative to develop rapid and sensitive analytical methods for ultra trace determination of cadmium. Voltammetry is a class of electroanalytical methods used in analytical chemistry and various industrial processes. In voltammetry, information about an analyte is obtained by measuring current as potential is varied^{11,12}. Pulse polarography and stripping

voltammetry are sensitive electroanalytical techniques comparable with AAS, neutron activation analysis and spectrophotometry for the analysis of trace metals¹³. However, formation of intermetallic compounds in stripping voltammetry is detrimental to the analysis¹⁴. Therefore, the suitability of DPP is envisaged in the present studies.

The polarographic complexation studies of Cd(II) with oxalic acid, salicylic acid, polymethacrylic acid, polygalacturonic acid, cephalosporin antibiotics, 2-mercaptobenzothiazole and luminol, have been reported. Rozik and Trnková demonstrated electroreduction of Cd(II) by cyclic voltammetry, linear sweep voltammetry and elimination voltammetry with linear scan¹⁵⁻²⁰. Recently, voltammetric studies for sensitive determination of Cd(II) in diverse matrices have been reported by many scientists²¹⁻²³. DPP determination of arsenic, antimony, selenium and thorium on similar lines were described earlier²⁴⁻²⁷.

Material and Methods

Instrumentation: A microprocessor based pulse polarographic analyzer (Model CL-362) in combination with a drop-timer assembly, all from Elico limited, Hyderabad, India, was used for polarographic measurements. Current voltage curves were recorded by an Epson printer (Epson-LX-300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode (DME) as the working electrode; pulse amplitude, 50 mV; pulse duration, 57ms; clock time of pulse, 0.5s; scan rate, 12mV/sec and charging current compensation, 20%. Potentials were measured against a saturated calomel electrode (SCE). Platinum wire was used as auxiliary electrode while ammonium acetate buffer was the supporting electrolyte.

An atomic absorption spectrophotometer (Model – AA 2380) from Perkin Elmer, USA, was used. The instrument has a

wavelength range from 1900-9000A⁰. A Czerny tuner grating monochromator is used which separates adjacent lines, thus widening the linear range of calibration curve. Slit-Width is selectable in 3 steps of 1.9, 3.8 and 9.5A⁰. Point-Focus burner optics permits a high sensitivity analysis by passing a light beam of very small size through the flame. Lamp current control is adjustable in 20 steps at 2 mA intervals. Sample aspiration flow control is adjustable by variable 3-line flow system.

Sample preparation: Glassware and polyethylene containers were soaked in 2 M nitric acid for atleast one week and washed with double distilled water prior to use. Samples of waste waters were collected from different sites of Marudhar and Basni Industrial Areas of Jodhpur. These samples were filtered to separate particulate matter and these were acidified with HCl to pH ~ 2 for storage purposes²⁸. A 50 mL aliquot was digested with an oxidizing mixture of nitric acid and sulfuric acid to destroy biological materials. The contents were heated till the solution fumed and then were transferred to a volumetric flask with required volume of double distilled water.

The temperature was maintained at $25 \pm 1^{\circ}\text{C}$ for all the experiments. The test solutions were deaerated by bubbling purified nitrogen for 20 mins prior to observations. Nitrogen was purified by passing it through a vanadous chloride scrubbing solution²⁹. Double distilled water was used for preparation of stock solution for all experimental work. Chemicals used were of Analytical Grade. Stock solution of Cd(II) was prepared from cadmium nitrate (Hi Media Laboratories Pvt. Ltd., Mumbai, India).

Results and Discussion

Electrochemical characteristics: The electrochemical behavior of cadmium was investigated in different non- complexing and complexing supporting electrolytes, out of which a complexing medium of citric acid in 0.1 M KNO₃ was found most adequate where Cd(II) gave a well-defined DC polarographic wave at -0.56V for the reduction of Cd(II) to Cd(0) as shown in figure-1.

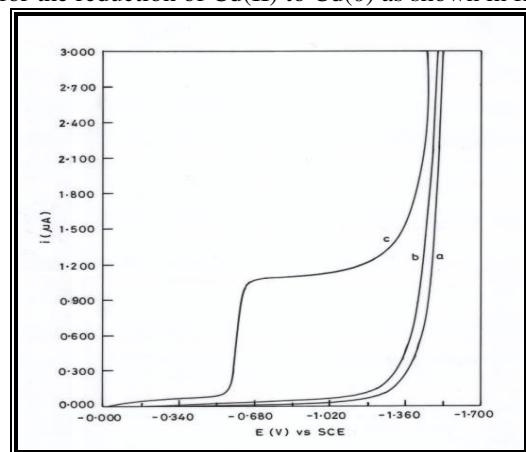


Figure-1

DC polarogram of cadmium(II) (a) Blank solution of 0.1M KNO₃, (b) Blank solution of 0.1M citric acid in 0.1M KNO₃, (c) 3.0×10^{-4} M cadmium(II) in 0.1M citric acid/0.1M KNO₃

The nature of polarographic wave of Cd(II) in 0.1 M citric acid in 0.1 M KNO₃ was studied by plotting log-plot analysis, where a slope value of 0.0284 was obtained. This revealed that the electrode process involving two-electron reduction, corresponding to Cd(II) \rightarrow Cd(0) was reversible.

Optimum DPP conditions: Cd(II) also showed a sharp DP peak in presence of 0.1 M citric acid in 0.1 M KNO₃ at -0.56 V. it was noted that the peak current increased linearly with the concentration of cadmium up to 30 ppm. DP polarograms at different concentration of cadmium are recorded in figure-2. The calibration curve is drawn in figure-3, and its characteristics are given in table-1.

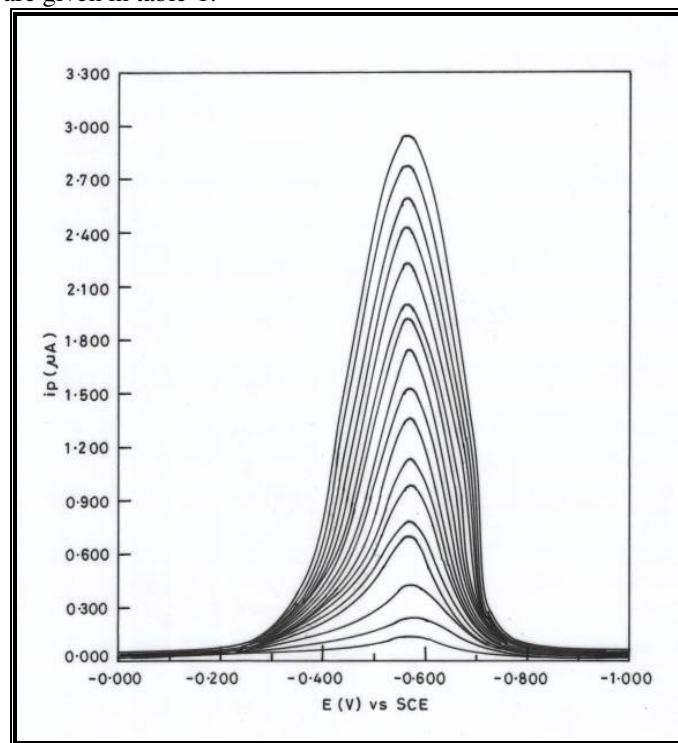


Figure-2
DP polarograms of cadmium(II) at different concentrations in 0.1M citric acid/0.1M KNO₃

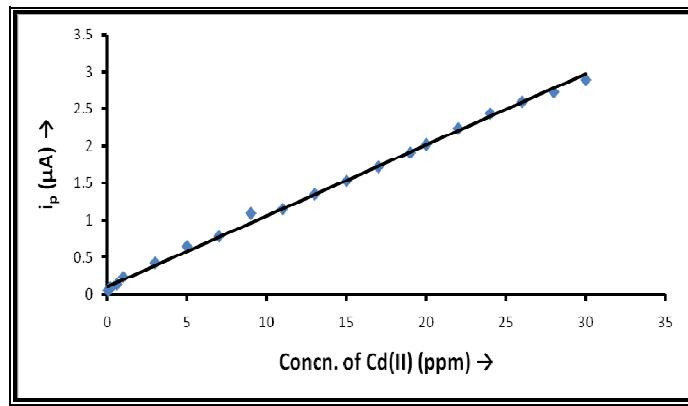


Figure-3
The plot of calibration curve (ppm) vs peak current

Table-1
Characteristics of calibration curve of Cd(II)

Slope	0.0959
Intercept	0.0968
Coefficient of Correlation (r)	0.9989

Accuracy and Precision: The reproducibility of DPP determinations was evaluated by making individual measurements of solution containing 0.5 µg/mL Cd(II), where a relative error of 0.8% indicated that DPP method for cadmium determination was accurate and precise.

Interference: Interference from some common metal ions present in industrial wastes was evaluated, where DP peaks of copper, lead and zinc were found to be at +0.032 V, -0.37 V and -1.0 V, respectively. These were well separated from that of cadmium at -0.56 V (as shown in figure-4) and thus, did not interfere in the ultra trace determination of cadmium.

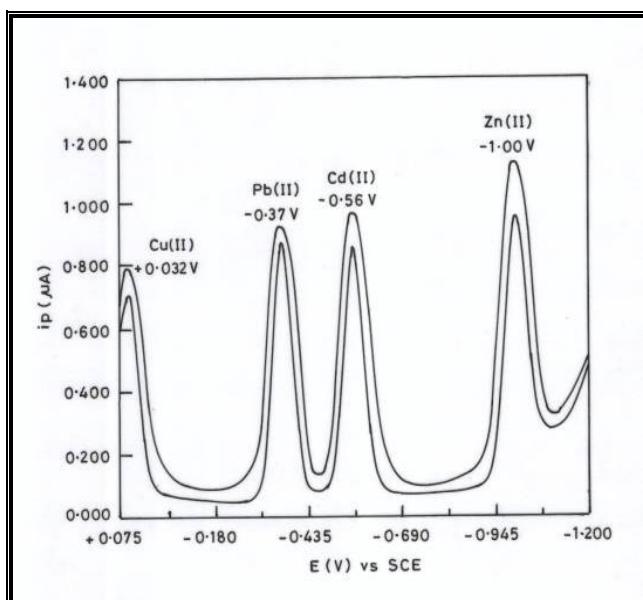


Figure-4
DP polarogram of Cd(II) in presence of Cu(II), Pb(II) and Zn(II) in 0.1M citric acid/0.1M KNO₃, Cu(II) = 7 ppm; Pb(II) = 16 ppm; Cd(II) = 9 ppm and Zn(II) = 5 ppm

Limit of Determination: The minimum amount of Cd(II) which could be determined under these experimental conditions was 0.008 ppm.

Analytical Applications: The digested samples were taken into the polarographic medium of 0.1 M citric acid in 0.1 M KNO₃. DP polarograms were recorded in the potential range of -0.3 V to -0.8 V and peak currents were measured at -0.56 V after making the blank corrections.

Quantitation in all observations was made by standard addition method³⁰. The results of cadmium determination in industrial waste water samples are listed in table-2.

Table-2
Industrial waste water analysis for cadmium contents by DPP

Water sample	Concentration of cadmium in ppm	
	Marudhar*	Basni*
1	2.459	3.910
2	2.523	3.927
3	2.494	3.832
4	2.339	3.791
5	2.360	3.863
Average	2.435	3.864
S.D. (±)	0.081	0.0558
R.S.D. (%)	3.32	1.44

*= Industrial area, n= Number of determinations= 3

The validity of DPP determinations of Cd(II) in 0.1 M citric acid in 0.1 M KNO₃ was demonstrated by comparing the results with AAS method. The comparative data are presented in table-3.

Table-3
Determination of cadmium(II) by DPP and AAS

	Sample	Cd(II) Concen. (ppm)®	
		DPP	AAS
1.	Marudhar ^a	2.435	2.435
2.	Basni ^a	3.864	3.865

a = Industrial area, ® = Average of three determinations.

Conclusion

The detailed study of Cd(II) in complexing medium of 0.1 M citric acid in 0.1 M KNO₃ has enabled its ultra trace determination without interference of possibly associated metal ions, viz. copper, lead and zinc. Further the results obtained by DPP are in good agreement with those obtained by AAS method. A detection limit of 0.008 µg/mL was obtained. However, some non-electrochemical methods such as flame AAS, electrothermal atomization AAS, isotope dilution-inductively coupled plasma-mass spectrometry, and solid phase spectrophotometry, are also described for cadmium determination³¹⁻³⁵.

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