

Determination of cadmium(II) with 5-Br-PADAP in the presence of CPC and HDPBA

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2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), a trihydroxy phenyl dye and *N*-hydroxy-*N,N'*-diphenylbenzamidine (HDPBA), a reported extractant, in presence of a cationic surfactant (CPC) have been used for the spectrophotometric determination of cadmium(II). The Cd(II)-CPC-(5-Br-PADAP) red coloured complex formed in aqueous medium has been extracted with *N*-hydroxy-*N,N'*-diphenylbenzamidine in dichloromethane in the pH range 8.6-10.6. This extracted complex shows maximum absorbance at $\lambda_{\text{max}} = 560$ nm against reagent blank with molar absorptivity of $9.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The detection limit of the method is $0.01 \mu\text{g ml}^{-1}$. The relative standard deviation (RSD, $n=10$) for solutions containing $0.40 \mu\text{g ml}^{-1}$ Cd(II) is 1.6%. The system obeys Beer's law in the range 0.05 - $1.0 \mu\text{g ml}^{-1}$. The effect of foreign ions and other experimental variables have been studied. Cd(II) has been successfully determined in standard, environmental and biological samples using the present method.

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Cadmium is a ubiquitous element and its concentration in the earth's crust is estimated as $0.2 \mu\text{g g}^{-1}$. It is usually associated with metals like zinc, lead, copper, etc. Cadmium finds its way into water through industrial discharge and deterioration of galvanized pipes². Pollution due to cadmium(II) is one of the most serious environmental problems because of its high toxicity, stability in contaminated sites and complexity of mechanism in biological toxicity³⁻⁶.

Various techniques, e.g., atomic absorption spectrophotometer (AAS)⁷, graphite furnace atomic absorption spectrophotometer (GF-AAS)^{8,9}, flame atomic absorption spectrophotometer (F-AAS)^{10,11}, electrothermal atomic absorption spectrophotometer (ET-AAS)¹², inductively coupled plasma atomic emission spectrometry (ICP-AES)¹³, voltammetry¹⁴, are reported for the determination of cadmium(II). Although, there have been several sophisticated techniques used for the determination of cadmium(II) at trace levels in a variety of complex materials, the

requirement of high maintenance cost, initial equipment cost, skilled personnel are the major demerits of these techniques.

Many spectrophotometric methods are reported for the determination of cadmium(II) in a variety of complex materials. Dithizone¹⁵ reagent is widely used for the spectrophotometric determination of cadmium(II). The method is sensitive but tedious and suffers from metal ions interferences. 4(2-Pyridylazo)-resorcinol¹⁶, has been proposed as the most sensitive reagent for the determination of cadmium(II); however it is not selective. Compounds such as 5,7-dibromo-8-hydroxyquinoline², and pyruvylidene-2-hydrazinobenzothiozole¹⁷ have poor sensitivity and have the problem of matrix interferences. Other reagents, viz., diphenylcarbazone¹⁸, benzil- α -monoxime-isonicotinoylhydrazide¹⁹, rhodamine 6G²⁰, 1,5-bis(di-2-pyridylmethylene)thiocarbonylhydrazide²¹, have also been reported for the trace level spectrophotometric determination of cadmium(II). However, most of these methods face the difficulty of interferences from metal ions like Fe^{3+} , Co^{2+} , Ni^{2+} , Pd^{2+} , Pt^{4+} , Hg^{2+} , Bi^{3+} , etc.

The present note deals with a sensitive and selective method for the spectrophotometric determination of cadmium(II) at trace levels in standard, environmental and biological samples, after digestion with microwave radiation, using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, cetylpyridinium chloride and *N*-hydroxy-*N,N'*-diphenylbenzamidine.

Experimental

A Systronics vis-spectrophotometer (model 106) was used for absorbance measurement. A Systronics digital pH meter (model 335) was employed for the measurement of pH. A Samsung, India, microwave radiation equipment (model CE2877L) was employed for digesting the samples.

All chemicals used were of AR grade (Merck). A standard stock solution ($1000 \mu\text{g ml}^{-1}$ Cd(II)) was prepared by dissolving 0.2282g of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) in 100 ml of doubly distilled water. Working standard solutions were prepared by appropriate dilution of the stock solution. A 2.86×10^{-4}

mol dm⁻³ [0.01% (w/v)] solution of 5-Br-PADAP was prepared in methanol. A 2.80×10⁻³ mol dm⁻³ [0.1% (w/v)] of CPC was prepared in doubly distilled water. A NaOH-H₃BO₃ buffer (pH 9.5) was used for adjusting the pH. *N*-Hydroxy-*N,N'*-diphenylbenzamidine (HDPBA) was synthesized²² by equimolar addition reaction of *N*-phenylbenzimidoyl chloride [C₆H₅-CCl=N-C₆H₅] with *N*-phenylhydroxylamine [C₆H₅NHOH] in absolute dry ether medium at low temperature, resulting in high yield of hydroxyamidine hydrochloride, which was treated with dilute ammonium hydroxide solution to give free base of HDPBA. The product was crystallized at least three times either from 60 % aqueous ethanol or petroleum ether (b. pt. 60-80°): benzene (1:2) mixture and vacuum dried. A triply crystallized free base has the purity greater than 99%. The yield of the free base generally varied between 40-70 %. Solutions of HDPBA in dichloromethane (3.47×10⁻³ mol dm⁻³, 0.1% (w/v)) was employed for extraction.

Procedure

Determination of cadmium(II)

An aliquot of the standard solution containing up to 10 µg Cd(II) was taken in a 125 ml separatory funnel. The pH of the solution was adjusted to 9.5 by addition of 4 ml borate buffer solution. To the above solution, 0.5 ml of 0.1% cetylpyridinium chloride (CPC) and 1 ml of 0.01% 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) solution was added and made up to 10 ml with distilled water. This solution was shaken vigorously for 2 min with 5 ml of *N*-hydroxy-*N,N'*-diphenylbenzamidine (HDPBA) in dichloromethane. The organic layer was separated and drained into a 25 ml beaker. The aqueous layer was washed twice with 1 ml fresh dichloromethane. The combined extract was dried over anhydrous sodium sulphate (≈ 2g). The total organic phase was made up to the mark with dichloromethane in a 10 ml volumetric flask. The absorbance of the complex was measured against a reagent blank at λ_{max} 560 nm.

Preparation of standard natural phosphate sample

Standard natural phosphate sample BCR-32 (0.5g) was weighed accurately in a teflon high-pressure micro wave acid-digestion bomb and to this 3 ml of 12:4:1, HF : H₂SO₄ : HNO₃ acid mixture was added. The bomb was sealed tightly and then positioned in the carousel of the microwave radiation unit set at 850 W. The system was operated at full power for 10-15 min. The digest was evaporated to near dryness. The

dried residue was again digested in the oven using only 2 ml conc. HNO₃ acid. The digested contents were mixed with 5 ml of 1 mol dm⁻³ boric acid solution and the volume was made up to 25 ml. An aliquot (1 ml) of the final solution was pipetted using a Glaxo variable volume micropipette into a 125 ml separatory funnel and analysed by the present as well as earlier reported methods (Table 1).

Preparation of fly ash and coal ash samples

A weighed amount of the solid sample (1.0g) was taken in a teflon high-pressure microwave acid-digestion bomb and to this 3 ml conc. HNO₃ was added and digested as above for 7-10 min. The excess of acid was removed by heating with dil. HCl over a hot plate at 80 °C. The digest was evaporated to near dryness. This sample was dissolved in dil. HCl (0.1 mol dm⁻³), filtered and diluted to a known volume. An aliquot (1 ml) of the final solution was pipetted into a 125 ml separatory funnel and contents were analysed by the present and the reported methods (Table 1).

Preparation of biological samples

Whole blood sample (1.0 ml) or urine sample (2.0 ml), perchloric acid (0.2 ml) and conc. HNO₃ (0.5 ml) were placed in a high pressure micro wave acid-digestion bomb. The bomb were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated for 5 min, at 500W. The digest was evaporated to near dryness and the dried residue was then dissolved in 5.0 ml of distilled water and filtered. An aliquot (1.0 ml) was pipetted into a 125 ml separatory funnel and contents were analysed by the present and the reported methods (Table 1).

Results and discussion

The absorption spectra obtained for the system Cd(II)-CPC-(5-Br-PADAP)-HDPBA complex showed absorption maximum at 560 nm against a reagent blank. The reagent blank exhibits appreciable absorption in this region and therefore it was used as reference for all absorbance measurements.

The formation of the red coloured complex was maximum between pH 8.6-10.6. Above and below this range, the extraction of the complex decreases. Therefore, pH 9.5 was kept constant throughout the experiment by using NaOH-H₃BO₃ buffer solution. The effect of various organic solvents on the formation and extraction of Cd(II)-CPC-(5-Br-PADAP)-HDPBA complex was studied. The

Table 1—Determination of cadmium(II) in standard, environmental and biological samples by the present and reported methods

Sample	Amt of Cd(II) added	Cd(II) found		F-test ^c	t-test ^f
		Present method (n=6) ^d ±	Dithizone method ¹⁵ (n=5)		
<i>Standard natural phosphate sample</i>					
BCR-32 20 µg g ⁻¹ Cd, 250 µg/g Zn, and known amount of P ₂ O ₅ , SiO ₂ , TiO ₂ , K ₂ O, Na ₂ O, MnO, MgO, Fe ₂ O ₃ , CaO, F	-	19.6±0.08 ^a	19.4±0.13 ^a	0.41	0.02
<i>Environmental samples</i>					
Fly ash (NTPC, Korba) 4.7 µg g ⁻¹ Cd (Certified amt)	-	4.51±0.09 ^a	4.45±0.11 ^a	0.16	0.53
Coal ash (Century Cement, Baikunth, District-Raipur) 3.4 µg g ⁻¹ Cd (Certified amt)	-	3.20±0.16 ^a	3.30±0.20 ^a	0.66	0.48
<i>Biological samples^e</i>					
Blood	1.0 ^b	1.0±0.23 ^b	0.97±0.20 ^b	0.87	0.53
Urine	1.0 ^b	0.96±0.06 ^b	0.95±0.15 ^b	0.07	0.94

^aCadmium content in µg g⁻¹^bCadmium content in µg ml⁻¹^cSample obtained from Pathology Department, Medical College Hospital, Raipur, C.G.^dValues are means ± standard deviations^eTabulated F-value at 95% confidence level is 6.26 for N₁=6, N₂=5 (i.e., for n₁=N₁-1, 5 degrees of freedom, n₂=N₂-1, 4 degrees of freedom)^fTabulated t-value at 95% confidence level is 2.262 for N₁+N₂=11 (or n = N₁+N₂-2, 9 degrees of freedom)

quantitative extraction of the complex (> 95%) was observed in dichloromethane, chloroform, benzene, toluene and ethyl acetate. The molar absorptivity (dm³ mol⁻¹ cm⁻¹) and wavelength of maximum absorption values (nm) of the above Cd(II) complex in these solvents are as follows: dichloromethane (9.50×10⁴; 560), chloroform (9.50×10⁴; 560), benzene (6.07×10⁴; 560), toluene (2.75×10⁴; 550) and ethyl acetate (4.38×10⁴; 560). Thus, dichloromethane and chloroform both showed similar spectral properties. However, dichloromethane was selected as the best solvent due to the highest colour sensitivity and selectivity of the complex and less toxic behaviour than chloroform.

The ambient room temperature, i.e., 25±2 °C was sufficient for maximum colour development of the complex in dichloromethane. However, no change in absorbance was observed up to 35 °C. Above 40 °C the solution became turbid. All experimental work was thus carried out at room temperature. The absorbance of the complex in dichloromethane was found to be stable for at least 12 h.

The constant and maximum colour of the complex was achieved when the concentration of 5-Br-PADAP in the final aqueous solution was varied between (1.71-4.0) × 10⁻⁵ mol dm⁻³. Hence, the present investigation was carried out at 2.86×10⁻⁵ mol dm⁻³ of 5-Br-PADAP.

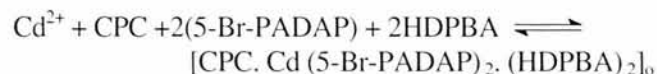
The results obtained indicate that at least (0.86-2.25) × 10⁻³ mol dm⁻³ HDPBA in dichloromethane was adequate for the complete extraction of the Cd(II) complex. Therefore, 1.74 × 10⁻³ mol dm⁻³ HDPBA was used throughout the experiment.

The effect of surfactants on the Cd(II)-(5-Br-PADAP)-HDPBA complex was studied. In the presence of anionic and non ionic surfactants the Cd(II)-(5-Br-PADAP)-HDPBA complex gave a low absorption, whereas in the presence of cationic surfactant, the absorption of the chromogenic system increased markedly. A study on the effect of concentration of CPC indicates that a concentration range of (0.84-2.0) × 10⁻⁴ mol dm⁻³ CPC solution was sufficient for maximum colour development of Cd(II)-CPC-(5-Br-PADAP)-HDPBA complex. Therefore, 1.40 × 10⁻⁴ mol dm⁻³ CPC solution was used constant throughout the experiment.

The system obeyed Beer's law in the range 0.05-1.0 µg ml⁻¹ of Cd(II) with excellent linearity in terms of correlation coefficient value (*r* = 0.99). The sensitivity of the Cd(II)-CPC-(5-Br-PADAP)-HDPBA complex, calculated in terms of molar absorptivity, is 9.5 × 10⁴ dm³ mol⁻¹ cm⁻¹ at λ_{max} 560 nm. The precision of the method in terms of relative standard deviation (n=10) for the determination of 0.4 µg ml⁻¹ Cd(II) is 1.6%. The detection limit of the method is 0.01 µg ml⁻¹ Cd(II).

The composition of the cadmium complex was determined by the curve fitting method. The molar ratio of metal: 5-Br-PADAP, CPC and HDPBA was determined by plotting logarithmic value of distribution ratio of metal $[\log \{A_{eq}/(A_{max}-A_{eq})\}]$ (where A_{max} = maximum absorbance of the complex at a level of $0.4 \mu\text{g Cd(II) ml}^{-1}$ organic phase and A_{eq} = absorbance of Cd(II) complex at equilibration with different known concentrations of reagents, viz., CPC / 5-Br-PADAP / HDPBA versus logarithmic values of varied known concentrations of CPC / 5-Br-PADAP / HDPBA in dichloromethane.

The slope of the curves for 5-Br-PADAP, CPC and HDPBA were found to be very close to 1 in the case of CPC, 2 for 5-Br-PADAP and 2 for HDPBA. Thus, a 1:1:2:2 molar ratio complex of Cd(II): CPC: 5-Br-PADAP: HDPBA in dichloromethane was predicted. The overall reaction can be expressed as follows:



Effect of diverse ions

The effect of addition of diverse ions was investigated. Only Pb^{2+} and Zn^{2+} were found to interfere in the determination of cadmium. A greater tolerance limit for these ions can be achieved by using several masking method. A 100-fold excess of Pb^{2+} could be masked with 1ml of 0.1% sodium fluoride. A 500-fold excess of Zn^{2+} ions could be masked with 1ml of 1% glycerol (Table 2).

The F-test²³ was performed at 95% probability to compare the result of the present method with that of the dithizone method¹⁵. Since in all the cases the values of F ($\text{sd}_1^2/\text{sd}_2^2$, variance ratio of standard dithizone and present method) were less than the tabulated F values at the 95% confidence level, it may be concluded that there is no significant difference in the precision of the present and dithizone method. The t-test²³ was performed at 95% confidence level. Again, in all cases, the calculated t-values were less than the tabulated values of t, indicating no statistical difference between the results obtained by the present method and the dithizone method. Thus, both the F-test and t-test show a high degree of agreement between the values obtained by present method and by the dithizone method. The calculated F-test and t-test values are shown (Table 1).

The present method for determination of cadmium is sensitive ($\epsilon = 9.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and selective and is applicable to standard samples, environmental

Table 2—Tolerance limit of diverse ions in the determination of $0.4 \mu\text{g ml}^{-1}$ Cd(II)

Ion added	Tolerance limit, ^a $\mu\text{g ml}^{-1}$
Ni^{2+}	5
Cr^{6+} , Cu^{2+}	10
V^{5+}	15
Fe^{3+}	20
Se^{4+} , Hg^{2+} , Pd^{2+}	25
^b Pb^{2+}	40
Ru^{3+} , Ag^+ , Co^{2+}	50
Ca^{2+} , As^{3+}	150
Bi^{3+} , Sn^{4+} , Zn^{2+}	200
SCN^- , PO_4^{3-}	500
Cl^-	1100
K^+	1500
F, oxalate	2000
Tartaric acid	2500
SO_4^{2-} , thiosulfate, glycerol	3000

^aIons were considered to interfere when they caused change in complex absorbance by $\pm 2\%$. ^b masked with 1ml of 0.1% sodium fluoride. ^c masked with 1ml of 1% glycerol

and biological samples with high reproducibility and low linear working range between 0.05 to $1.0 \mu\text{g ml}^{-1}$ Cd(II). This method is considerably superior to other reported methods when comparing analytical parameters viz. linear range and molar absorptivity value. The linear range ($\mu\text{g ml}^{-1}$ Cd(II)) and molar absorptivity value ($\epsilon = \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\times 10^4$) of some of the reported methods using different reagents are as under: 5,7-Dibromo-8-hydroxyquinoline², 0.1-30, 0.53; dithizone¹⁵, 1-10, 0.62; *N*-Phenylcinna-mohydraxamic acid + 4(2-pyridylazo)-resorcinol (PAR)¹⁶, 0.25-2.25, 4.8; Pyruvylidene-2-hydrazinobenzothiozole¹⁷, 1.0-10, 0.46; diphenylcarba-zone¹⁸, 0.29-3.65, 7.33; Benzil- α -monoxime-isonicotinoyl-hydrazone¹⁹, 0.45-4.5, 2.5; rhodamine 6G²⁰, 0.0-0.6, 9.0; 1,5-Bis(di-2-pyridylmethylene-thiocarbonohydrazide)²¹, 0.1-1.7, 5.64.

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References

- Abbasi, S A, Abbasi N & Soni R, *Heavy Metals in the Environment*, (Mittal Publications, New Delhi) 1998.

- 2 Ahmad M J & Chawdhury M T I, *Anal Sci*, 20 (2004) 987.
- 3 Liva M, Munoz-Olivas R & Camara C, *Talanta*, 51 (2000) 381.
- 4 Sohrabi M R, Abdolmaleki P, Davallo M, Robbani M & Ebrahimi R, *Indian J Chem*, 43A (2004) 2582.
- 5 Oehme F W, *Toxicity of Heavy Metals in the Environment*, Part 1, (Marcel Dekker, New York) 1979.
- 6 Manahan S E, *Environmental Chemistry*, (Lewis Publishers, New York) 1999.
- 7 Mehara R & Juneja M, *J Indian Chem Soc*, 81 (2004) 349.
- 8 Chan M S & Huang S D, *Talanta*, 51 (2000) 381.
- 9 Silva M M, Goreti M, Vale R & Garanao E B, *Talanta*, 50 (1999) 1035.
- 10 Hammond J L, Lee Y I, Noble C O, Beck J N, Proffitt C E & Sneddon J, *Talanta*, 47 (1998) 261.
- 11 Goswami A & Singh A K, *Talanta*, 58 (2002) 669.
- 12 Bhattacharya S S, Mandal B & Das A K, *J Indian Chem Soc*, 72 (1995) 757.
- 13 Zouragh M, Torres A G & Pavon J M C, *Talanta*, 56 (2002) 753.
- 14 Marino G, Bergamini M F, Teixeira M F S & Cavalheiro E T G, *Talanta*, 59 (2003) 1021.
- 15 Paradkar R P & Williams R R, *Anal Chem*, 66 (1994) 2752.
- 16 Agrawal Y K & Desai T A, *Analyst*, 111 (1986) 305.
- 17 Carmen L S, *Anal Chim Acta*, 117 (1980) 349.
- 18 Das H K & Purkayastha G D, *J Indian Chem Soc*, 78 (2001) 323.
- 19 Chandrasekhar K B & Reddy K H, *J Indian Chem Soc*, 78 (2001) 340.
- 20 Kartikeyan S, Rao T P, Iyer C S P & Damodaran A D, *Talanta*, 40 (1993) 771.
- 21 Rodriguez A M G, Torres A G D, Pavon J M C & Ojedo C B, *Talanta*, 40 (1993) 1861.
- 22 Satyanarayana K & Mishra R K, *Anal Chem*, 47 (1974) 1609.
- 23 Christian G D, *Anal Chem*, (John Wiley, New York) 1986.