

The Estimation of Small Metal Traces of Cd (II) From the Alloy and Water Effluents using Fast and Accurate Extractive Spectrophotometric Method with Newly Developed DBA Reagent

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Abstract

Experimental research was reported on the extraction and the spectrophotometric determination of minute quantities of Cd(II), using a fresh novelligand 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) from given sample of alloy. In this work, the fresh ligand was developed and its characterization was conducted using mass spectrophotometer and IR, NMR. A developed analytical ligand (DBA) when reacts with cadmium produces colored compound, this red colored complex, maintained at constant pH 8.9 and again extracted using n-butanol as a selected solvent. Beers law is also validated in the selected concentration range. The optimum parameters like absorption maxima, molar extinction coefficient and sandell's sensitivity to the red compound were also reported to be 450 nm, 1960 L mol⁻¹ cm⁻² and 0.01879 μg cm⁻², respectively. A prepared analytical ligand DBA is found to be effective and efficiently employed for determination of small quantities of Cd (II) metal ions.



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Cd (II);
DBA Reagent;
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Introduction

The accurate identification of cadmium in the samples of industrial liquid effluents, medical, pharmaceutical samples are important because of its toxicity and contribution towards the number of diseases and deaths (Fergusson *et.al* 1989 and Venugopal *et.al*.1979). All these above findings


indicates that even a small traces of cadmium metal has an adverse effects on human health, Therefore, an accurate and simple identification of this cadmium metal at trace level is challenging task.

Various methods were reported for determination of cadmium (II), these are: ratio derivative

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polarography (Ni, 1998), differential pulse polarography (Hussain *et al.* 2002), adsorptive stripping voltammetry (Abbasi *et al.*, 2011), flame AAS (Xiang *et al.*, 2012), EAAS (Li *et al.*, 2009), GF-AAS

(Jahromi *et al.*, 2007), ICP-OES (Salahinejad, 2011), ICP-MS (Jia *et al.*, 2010). The above methods require sophisticated instrumentation, which are costlier and consume more time and money.

Table 1: Comparison between Cd (II) determination methods

Analytical Ligand	λ_{max} (nm)	pH	Beer's law concentration range, ppm	molar extinction coefficient, $L \text{ mol}^{-1} \text{ cm}^{-1}$	M:R	Observations	Reference
Thiazolyazo Reagent	616	9.0	0.003-4.0	2.14×10^5	1:2	Use of nonionic surfactant	Amin, 2001
p-Acetylbenzene diazoaminoozobenzene	475	12.5	0-20	-	1:3	Standing time 10 min and use of high pH	Gao <i>et al.</i> , 2001
Ammonium pyrrolidine dithiocarbamate	323	7.0	0.3-10.0	-	1:2	Use of Tween 80 surfactant	Lee and Choi, 2001
4-(2-Pyridylazo)-resorcinol	510	5.5	0.4-4.9	2.5×10^5	1:1	Excessive use of HClO ₄	Hashem, 2002
p,p'-Dinitrosym-diphenyl carbazid	630-640	0.02N NaOH	0.5-60	2.05×10^4	1:2	Extraction Carried out in strong basic media	Bulgariu <i>et al.</i> , 2005
2,6-Dimethylphenyl diazoamine	523	0.2 M NH ₃	0-0.48	2.27×10^5	1:3 105	Reagent solution -in dimethyl-formamide	Li, 2006
nobenzene Benzilidithiosem	360	10.5	-	0.196×10^4	1:1	Use of strong basic buffer	Reddy <i>et al.</i> , 2008
icarbazone 2-Hydroxy-	440	10.0	5.62-	4.035×10^4	1:2	Color stability one h	Parikh <i>et al.</i> , 2009

4-n- butoxy -5- bromo propioph enone thiosemi carbazono	16.86	103							
Cinnamal dehyde -4- hydroxy benzoyl hydrazono	9.0	5.6 x 104	1:1	Reagent is very sensitive	Gopalakris hna <i>et al.</i> , 2010				
3,5-Bis(4- phenylazo phenyl amin odiazo) 1-(2- Bezoithia zolylaz o)-2- hydroxy-3- naphthoic acid	10.5	2.8 x 105	-	Use of nonionic surfacta nt	Meng <i>et al.</i> , 2011				
2, 4 dimethyl -3H-1,5 benz odiazepine (DBA)	8.5	7.05 x 106	1:1	Oxalate interfere seriously	Amin and Gouda, 2012				
	0.056-	1960	1:1	Sensitive and effective	Present Work				

The investigations were made with Spectrophotometry, for determination of Cd(II); since it is simple, fast and require cheap analytical reagents. This method has got great demand and highly accepted in the field of industrial and environment applications. The merits of spectrophotometric method over an earlier methods were reported by Sandell (1965) and Morrison and Freiser (1996). Several researchers

have devised and reported various analytical reagents for Cd (II) estimations (Ling *et al*, 1996; Zhang, 1998; Amin, 2001; Gao *et al*, 2001; Lee and Choi, 2001; Hashem, 2002; Bulgariu *et al*, 2005; Li, 2006; Reddy *et al*, 2008; Parikh *et al*, 2009; Gopalakrishna *et al*, 2010; Meng *et al*, 2011; Wen *et al*, 2011; Amin and Gouda, 2012).

The structure determination of novel ligand has been reported using NMR, IR spectrum studies and detail observations are elaborated in the Appendix I.

Table 1 presents the comparison between the current and earlier spectrophotometric extraction methods.

The aim of this research is to extract traces of Cd (II) with newly developed DBA ligand. Efforts have been also done to determine Cd (II) in the small quantities from synthetic and alloy samples. Besides, the effects of pH, wavelength, and choice of optimum

molar ratio on the extraction of Cd (II) have been also conducted.

Experimental Techniques

Instruments used

In this work, a calibrated Ultra violet visible spectrophotometer (Model: Shimadzu 2450, 10 mm quartz cell) was used in the measurement of absorbance and pH measurement were done with a calibrated digital pH meter (Make: Elico LI-120). The important experimental parameters have been reported and are presented in Table 2

Table 2: Important Experimental variables

Parameter maintained	Remark
Maximum Absorbance	450 nm
Solvent used	n- butanol as best among studied
pH required	8.9
Equilibration time observed	60 seconds
Stability of Cadmium- reagent	48 hrs
Optimum Beer's concentration limit	1 to 10 mg/ml
Molar extinction coefficient	1960 L mol ⁻¹ cm ⁻²
Sandell's sensitivity	0.01879 mg/ cm ²
Mole ratio of Cd (II) : DBA	1:1

Formulation of DBA Ligand

A reaction between one mole of o-phenylenediamine and one moles of Acetyl acetone in presence of Ethanol (solvent) were carried out for formulation of novel ligand (Fig.1). The product achieved is then heated in water bath at constant temperature of 100°C in a round bottom glass flask, maintain under total reflux for 2 hrs. The acquired solution is then transferred in ice bath to produce crystals. A resultant solid product is then further recrystallized by using solvent as ethanol. After the reagent (M.P. 274°C)

is synthesized, it is then characterized by NMR and IR spectrum and easily employed in the determination small Cd (II) traces using spectrophotometry extraction. A stock solution of devised ligand in the 0.05% concentration in a methanol is ready for further investigations. The newly devised reagent DBA and Cadmium have strong complex formation tendency due to presence of electron donor nitrogen atom present in the reagent.

Reaction Scheme

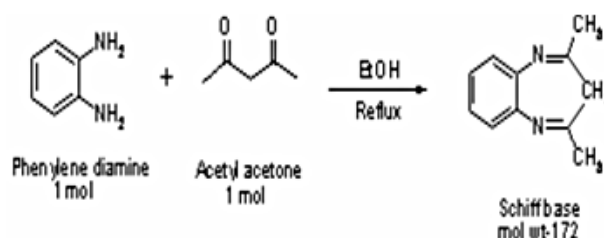


Fig.1: Preparation Of Analytical Reagent 2, 4-Dimethyl -3H- 1,5 Benzodiazepine (Dba)

Stock Solution

The stock solution of 100 ppm concentration of Cd⁺² was ready by adding 0.2282mg of cadmium sulfate (3 CdSO₄ · 8 H₂O) (Merck) crystals in a 100 ml distilled water. Moreover, additional sets of dilute solutions were made by adopting standard operating procedure.

pH selection for Extraction

In this study, various Buffer solutions with varying pH was used for Cd (II) extraction, and molar ratio

between organic and aqueous phase was constantly monitored at 1:1. The impact of pH on the variation of absorbance as indicated in the figure 2. A same figure depicts that the values of absorbance are increasing with rise in pH and attains a highest magnitude at pH 8.9 and further increase in pH beyond the 8.9, the absorbance decline sharply. Hence, the buffer of pH 8.9 was selected in future research work.

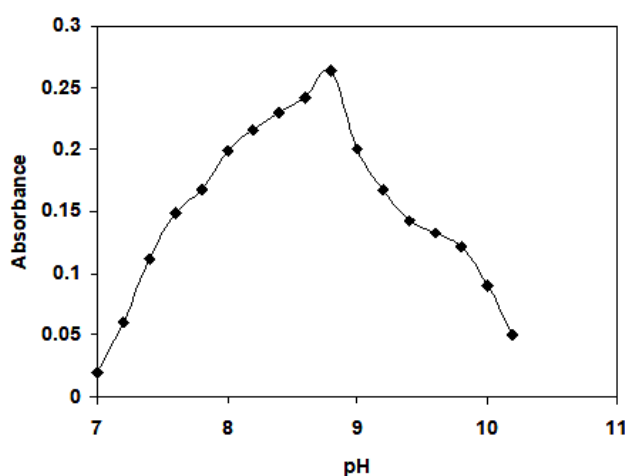


Fig. 2: pH

Solvent Selection for Extraction

In this laboratory experiments various organic solvents were tested to for right selection of extraction solvent and experimental results achieved to the

various solvents are summarized in Figure 3. From presented results, n-butanol was found to be best solvent for extraction of Cd (II).

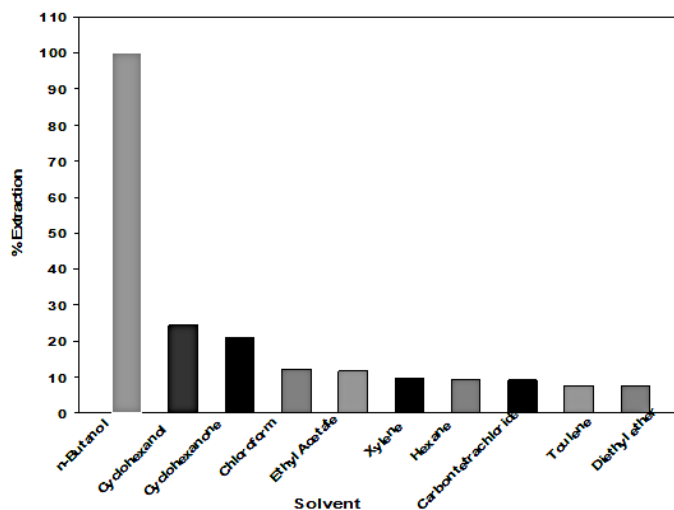


Fig.3: Effect of solvent on Cd (II) extraction

Selection of Wavelength

Fig.4 shows that absorbance increases with increase in wavelength and realizes a highest absorbance at 450 nm wavelength. Further, increase in wavelength, the values of absorbance declines sharply. The magnitude of wavelength corresponds to highest absorbance is suggested for future research work.

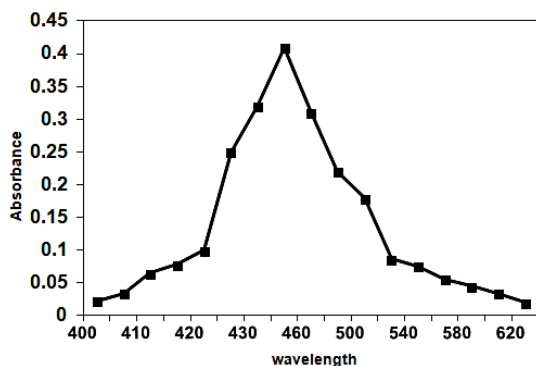


Fig. 4: Selection of wavelength.

Method of Experiment

The mixture of 1 cm³ solution of cadmium sulphate with 0.05% DBA novel ligand in methanol was prepared. The solution pH was constantly monitored at 8.9 with slowly addition of buffer solution (A buffer was prepared by mixing 1 mole L⁻¹ of NH₄OH with 1.8 mole L⁻¹ of NH₄Cl). This solution is then subjected to gravity separation in a separating glass funnel with additional of 10 ml n-butanol. Due to effect of gravity the phases are separated into organic and aqueous phase. Out of these two phases, an organic phase placed under a UV Spectrophotometer at wavelength of 450 nm, to record the absorbance.

Formulation of Calibration Curve

As discussed above, the similar procedure was followed in the development of calibration curve. The Cd (II) samples of various concentrations (1–10 ppm) were prepared, mixed with the DBA reagent, and extracted with n-butanol. Further, its absorbance measured, and Calibration curve was developed (Fig.5).

Choice of Mole Ratio of Cd (II) to Novel ligand

The perfect selection of molar ratio of Cd (II) to DBA ligand, using different methods has been predicted and presented in Figure 6. The Job's continuous variation is one of the commonly used methods in most of the cases to fix up the

composition ratio between metal ions and analytical reagent. The result achieved from Job's continuous variation method was further verified using other recommended methods namely slope ratio and mole ratio. In this work, appropriate mole ratio of Cd (II) to DBA ligand was fixed to be 1:1.

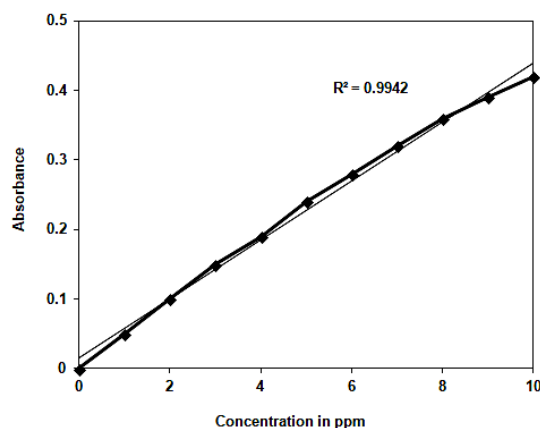


Fig. 5: Calibration curve of Cd (II)

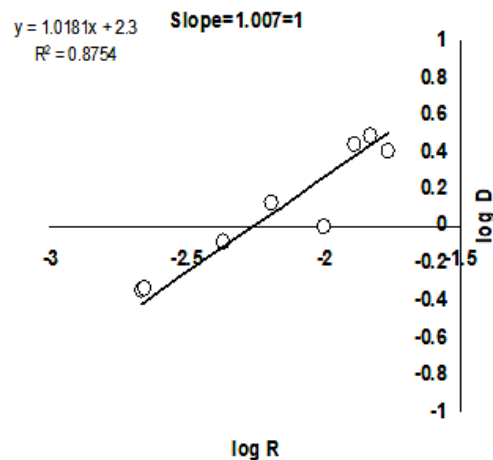


Fig. 6: Choice of molar ratio of Cd (II) to novel reagent

Influence of Diverse Ions

To validate the potential varied applications of the developed analytical techniques, the impact of various diverse ions are experimentally examined by carrying out determination of 100 µg/mL Cd (II) ions with a small quantity of diverse ion solutions, using the developed experimental methodology. The limits of tolerance between higher value of actual absorbance of given ions and value expected for plain Cd (II) ion was set to be within ±2%

discrepancy. The results clearly depicts that utmost of the metal ions can be accepted in considerable set limit of tolerance (Table 3). The interference effects

of these ions are suppressed with several agents in the actual determinations of Cd (II), as indicated in the Table 4.

Table 3: Interference of different ions in Cd (II) determination

S. No.	Name of ions	Amount Tolerated in mg
1	Chloride, Nitrite, Sulphate, Sulphide	19
2	Perchlorate	17
3	Iodate	15
4	Ti (IV), Cr(II), Mn(II), Sn(II), Pb(II)	14
5	Mo(VI), Cr(VI)	11
6	Ammonium, K (I)	17

Table 4: Suppressing reagents

Interfering Ion	Suppressing reagent
Zn (II)	Cyanide
Cr (II)	Ammonia
Al (II)	Triethanolamine
Mn (II)	Aluminium fluoride
Co (II)	Ascorbic acid
Ni (II)	Conc. HNO ₃

Different Analytical Reagents for Cd (II) Determination and their Drawbacks

Table 5 shows the assessment between various analytical reagents used by the previous workers and DBA ligand for the estimation of Cd(II). A present experimental work confirms that the developed DBA reagent seems to be better than that of some reported reagents.

Table 5: Different analytical reagents for Cd (II) determination and their drawbacks

Analytical Reagents	Disadvantages	Reference
4-(2-thiazolylazo)-resorcinol (TAR)	Interference of Some common metals like Fe(III), Ni(II), Co(II), Cu(II)	32
1,10-phenanthroline	Basic pH in the varying range of 8.2 to 9.6 was used.	33
Thiazolylazochromogenic reagent	solvent is toxic	34
N-hydroxy-N,Ni-diphenyl bezamidine	Less pH range is required	35
1-(2-Bezothiazolylazo)-2-hydroxy-3-naphthoic acid	Oxalate	36
interfere seriously		

Testing of Precision and Accuracy

The precision of the present method was determined by testing different concentrations of cadmium (each sample was analyzed minimum at least three

times). The relative standard was in the limit of 0 – 2% confirms that this method is highly precise and reproducible, the average percentage extraction in tested samples were indicated in Table 5.

The calculation of relative standard deviation is as.

$$\text{Mean} = \bar{X} = (\sum X_i) / N$$

Where X_i sample value, N total numbers of samples

$$\text{Standard deviation} = S = \sqrt{\sum (X_i - \bar{X})^2 / (N-1)}$$

$$\% \text{ Relative Standard deviation, } (S_r) = S / \bar{X} \times 100$$

The relative standard deviation is found to be in the limit of 0 to 2 %

The % extraction and % relative standard deviation Figure 7 presents the % Extraction and % relative standard deviation with various samples tested. The % extraction was found to be 98.5, 99.7 and 96 % for solder alloy, Nichrome alloy and drinking water samples respectively. Whereas the % standard deviations were observed to be 1.5, 1.03 and 1.3 for solder alloy, Nichrome alloy and drinking water samples respectively.

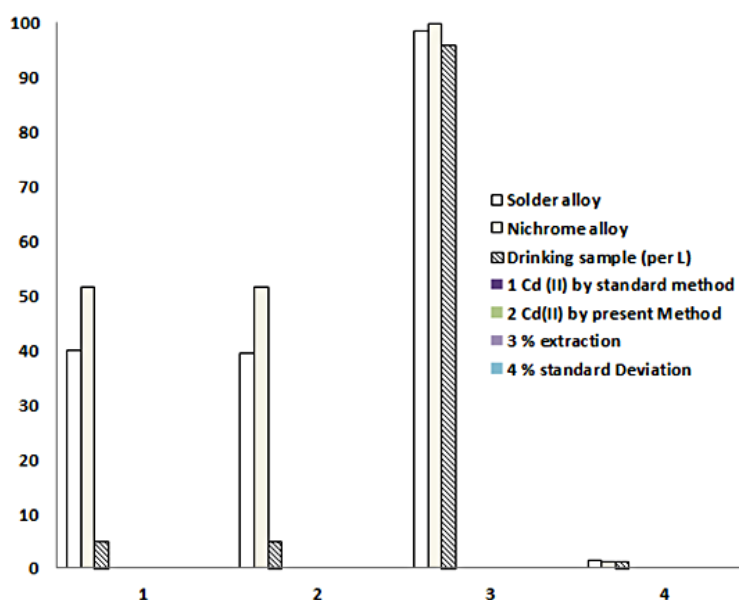


Fig. 7: % Extraction and % relative standard deviation of various tested samples

Table 6: Applications of present study

Sr. No.	Samples	Cd(II) determined by standard method	Cd(II) determined by present method	% extraction	% standard Deviation
1	Solder alloy	40%	39.4%	98.5	1.5
2	Nichrome alloy	51.48%	51.43%	99.70	1.02
3	Drinking sample (per L)	0.005 ppm	0.0048 ppm	96	1.3

Applications of Present Work

The present work demonstrates the development of new fresh analytical ligand for effective and efficient estimation of Cd (II) metal ions from given mixture. This analysis method was employed

for estimation of Cd (II) traces in an area like alloy, water treatment, food industries. The newly developed analytical ligandis appears to be bestover the other reagents.

Conclusion

The present experimental investigations demonstrates that a newly synthesized, fresh analytical reagent was showed to be accurate, cheap, less time consuming for spectrophotometric estimation of Cd(II).

Advantages of the developed method are as follows:-

- Reagent is easily synthesized and purified.
- The process of extraction is one step, fast and accurate.
- It require very low reagent concentration of analytical reagent
- The developed method used DBA reagent by maintaining constant pH 8.6 is seems to be better as compared to earlier method of 1,10-phenanthroline analytical reagent with varying pH 8.2 to 9.8
- In this developed method most of the ions do not interfere in the extraction process.

- This developed method possesses main benefits like simple, single step, fast, accurate and cost effective. Hence, it can be used forestimation of small traces of Cd(II)from the alloy and water effluents.

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Conflict of Interests

Authors hereby state that, in this research work any sort of conflict of interest is not involved.

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