8-Hydroxyquinoline as a Complexing Reagent for the Determination of Cd(II) in Micellar Medium

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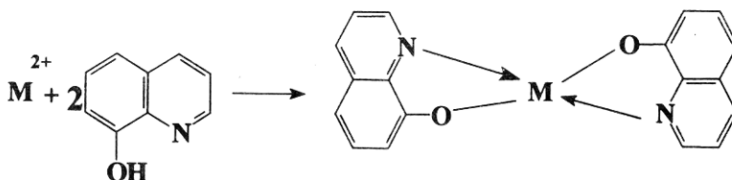*Shah Abdul Latif University Khairpur, Sindh, Pakistan*

Summary: Spectrophotometric determination of cadmium(II) is carried out with 8-hydroxyquinoline as a complexing reagent in aqueous phase using cationic surfactant cetylpyridinium chloride. Beer's law is obeyed over the concentration range 0.5-8.0 µg ml⁻¹. The λ_{max} molar absorption, molar absorptivity and Sandell's sensitivity were 400 nm; ε_{max} = 0.75×10^4 mol⁻¹ dm³.cm⁻¹ is 0.75 and (14.9) ng cm⁻². Validation of this method has been made by comparing the results with those obtained by Atomic Absorption Spectroscopy (AAS). No significant difference was observed in the results obtained by the two methods at 95% confidence level. The method is simple, accurate, economical and can be applied for the determination of cadmium(II) in industrial wastewater samples.

Introduction

The determination of cadmium in biological material is important because this metal is toxic. 8-Hydroxyquinoline is used as a complexing reagent and reacts with almost every metal in the periodic table to form uncharged chelates [1-2]. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [3–4]. Due to the solubility of several compounds in micelles (aggregates of surfactants), many analytical techniques for the determination of metal ions in aqueous system have been developed and modified [5–13]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. The determination of Cu(II), Co(II) and Ni(II) as complexes of ammoniumpyrrolodinedithiocarbamate in cationic micellar media has been reported earlier [14].

8-hydroxyquinoline has a hydrogen atom that is replaceable by a metal, and a hetrocyclic nitrogen atom, which forms with this, metals a five-membered ring [15]. It is a bidentate ligand and forms stable complexes with several metal ions, a typical reaction is followed:

In the present work, cetylpyridinium chloride (CPC) has been utilized as micellar media for the determination of Cd(II) metal ions using 8-hydroxyquinoline. The method was successfully applied for the determination of Cd(II) in industrial waste-water samples.

Results and Discussion

Fig. (1) (A) shows the absorption spectra of 8-hydroxyquinoline, the absorption maxima is at 344 nm, (B) Cd(II)-8-hydroxyquinoline complex with absorption maxima at 400 nm. It seems that micelle in solution was formed at 0.02 mol dm⁻³ CPC. Fig. (2) shows a graph of the absorption maxima (λ_{max} 344 nm) of the solution containing varying amounts of 8-hydroxyquinoline. It can be seen that the absorption increases with an increase in the concentration of 8-hydroxyquinoline up to 5×10^{-5} mol dm⁻³. Fig. (3) shows the absorption maxima at pH 8.0. Fig. (4) shows calibration graph of obtained by plotting absorption maxima against varying concentration of metal ions. Metal to ligand ratio in the complex is 1:2 (M:L). The complex remained stable for 2 h. The molar absorptivity of the method is 0.75×10^4 mol⁻¹.

Suggested reaction of metal(II) with 8-hydroxyquinoline to form
bis[8-hydroxyquinoline]metal(II) complex

dm^3.cm^{-1}. The Sandell's sensitivity value is (14.9) ng cm^{-2}. Detection limit is (14.9) ng ml^{-1}. Improvement was found in the molar absorptivity, determination range, Sandell's sensitivity and detection limit than reported by P. Becher et al., [15].

Composition

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. Fig. (5) Plot of absorbance versus mole fraction of the metal ion
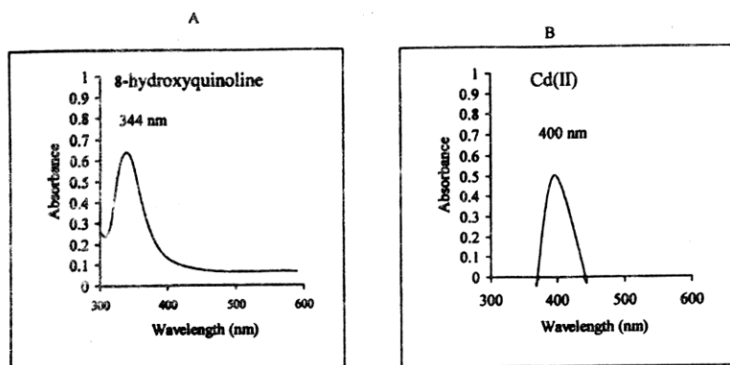
Fig. 1: Absorption spectra of Hg(II) with 8-hydroxy-quinoline in SDS 1%. **(A)** 8-Hydroxyquinoline 6×10^5 M, **(B)** Hg(II)-8-hydroxyquinoline complex, Hg = 2 µgml^{-1}
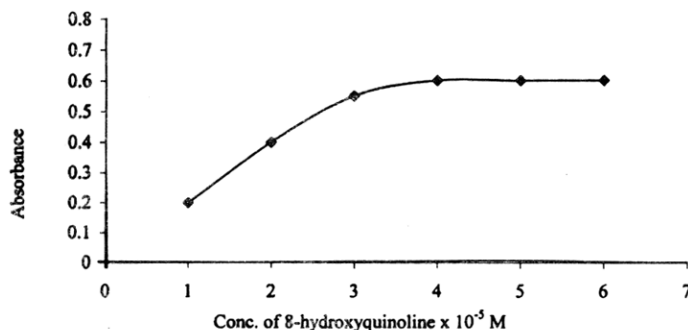
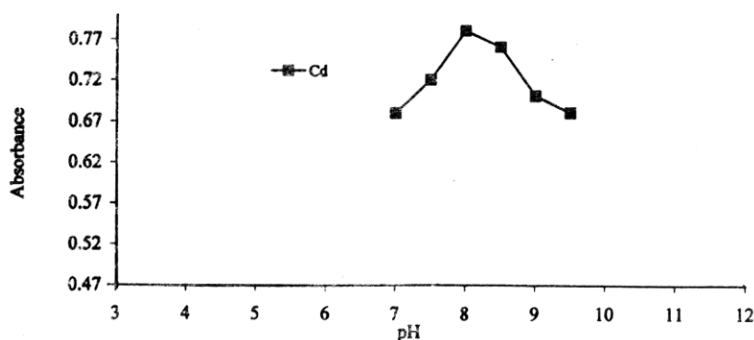Fig. 2: Effect of 8-hydroxyquinoline conc. On the absorbance of Cd(II)-complex in CPC.

Fig. 3: Effect of pH on the absorbance of Cd(II)-8-hydroxyquinoline complex.
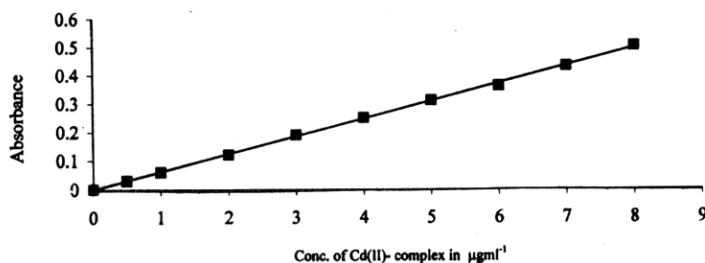
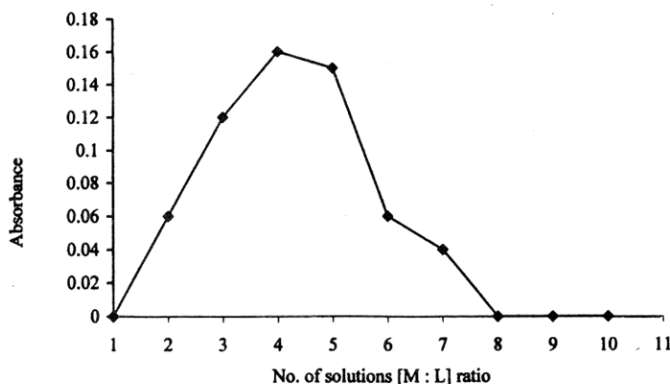Fig. 4: Calibration graph of Cd(II)-8-hydroxyquinoline complex in CPC.

No. of solution	1	2	3	4	5	6	7	8	9	10	11
M ions (ml)	0	1	2	3	4	5	6	7	8	9	10
Reagent (ml)	10	9	8	7	6	5	4	3	2	1	0

Fig. 5: Job's plot of metal:ligand ratio.

shows at maximum which corresponds to 1:2 (M:L) ratio in the complex for M(II) ions.

Study of interference's by foreign ions

In the determination of Cd(II) ions with 8-hydroxyquinoline in presence of 0.02 mol dm^{-3} % CPC, interference by foreign ions were studied and all the results are shown in the Table-1. For these metal ions KSCN, KClO$_3$, and sodium tartarate did not interfere until their amount reached 1000 µg ml^{-1}. Interference of Co(II), Ni(II) and Pb(II) is serious than other species. Interference was eliminated by adjusting pH of the complex.

Validation of method

Proposed method was verified by standard addition method, and the results were compared with AAS, which are in good agreement as given in Table-2.

Table-1:Tolerance limits (µg ml^{-1}) for interference's of metal ions and salts with 8-hydroxyquinoline in 0.02 mol dm^{-3} CPC

Ion / salt	Cd(II)
KSCN	1000
NaF	600
Na$_2$C$_2$O$_4$	200
KClO$_3$	1000
Na$_2$tartarate	1000
Na$_2$citrate	500
Mg (II)	150
Al(III)	200
Cd(II)	-
Co (II)	4
Cr (III)	50
Cr(VI)	8
Fe(III)	15
Mn(II)	80
Ni(II)	5
Pb(II)	3
Zn(II)	50
Cu(II)	100

The conc. of metal ions is 2µg ml^{-1}

Table-2:Percent recovery (%) of known samples added to tap water

Metal ions	Amount added ($\mu g\ ml^{-1}$)	Amount Found ($\mu g\ ml^{-1}$)	Recovery (%)
Cd(II)	1.0	0.99	99 ± 1

At 95%, n= 6

Table-3:Determination of Cd(II) ions in industrial waste-water samples

Sample	Metal ions determined	
Industrial waste water from Kotri SITE	Present method Cadmium ($\mu g\ ml^{-1}$)	AAS method Cadmium ($\mu g\ ml^{-1}$)
	0.40	0.41
	(0.6)	(0.5)

Application

The proposed spectrophotometric method was applied for the determination of Cd(II) in industrial waste-water samples. Results are summarized in Table-3.

Experimental

A UV/Vis Spectrophotometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic absorption spectrophotometer, model Spectra AA. 20 Varian was used for metal ion determination. The Pye Model 292 pH meter was used.

Reagents

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard Cd(II) stock solutions of (100 μg ml^{-1}) were prepared dissolving their nitrate salt. Other metal ions solutions were prepared from their nitrate or chloride salts. Surfactant (CPC) 0.02 mol dm^{-3} solution was prepared by dissolving that in a 100 ml volumetric flask, and was diluting to the mark with double distilled water. Buffer solution of pH 8 was prepared by taking 0.025 mol dm^{-3} sodium borate (50 ml) and 0.1M HCl (20.5 ml) mixtures and adjusting the volume to 100 ml according to Perrin and Dempsey [16].

Procedure

Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions, 8-hydroxyquinoline, and surfactant CPC

0.02 mol dm^{-3} were added and made up to 25 ml volume with distilled water having metal ions concentration 0.06-10 $\mu g\ ml^{-1}$, concentration of 8-hydroxyquinoline 5 × 10^{-5} mol dm^{-3} and 0.02 mol dm^{-3} surfactant. The pH values and analytical wavelength used are listed in Table-4.

Table–4: Analytical characteristics of Cd (II)-8-hydroxyquinoline complex in the presence of surfactant (CPC).

Characteristics	Cd(II)
Beer's law range ($\mu g ml^{-1}$)	0.5 – 8.0
Absorption maxima (λ_{max} (nm): (a) micellar	400
(b) CCl_4	395
Molar absorptivity ($\times 10^4\ mol^{-1}.dm^3.cm^{-1}$) by micellar	0.75
Molar absorptivity ($\times 10^4\ mol^{-1}.dm^3.cm^{-1}$) by extraction	0.60
Sandell's sensitivity (ng cm^{-2})	14.9
Detection limit (ng ml^{-1})	14.9
pH	8
[CPC] mol dm^{-3}	0.02
[Reagent] (10^{-5} mol $dm^{-3)}$	5
RSD ±	0.03

At 95%, n= 6

Spectrophotometric metal ion determination after extraction with CCl_4.

Appropriate volumes of stock metal, 8-hydroxyquinoline and aqueous buffer solutions were placed in a separating funnel and 10 ml of CCl_4 was added. The organic layer was transferred to a 25 ml volumetric flask. In order to obtain complete extraction, the process was repeated twice, with 10 ml and then once with 5.0 ml of CCl_4. For the 25.0 ml total volume of the organic layer, absorbance was measured at the 395 nm wavelengths for metal ions.

Determination of Cd(II) in industrial waste-water

Industrial wastewater sample, 11 obtained from industrial effluent collected from Kotri SITE area was filtered using Whatman No. 2 filter paper. Concentrated nitric acid 4 ml and 30 % hydrogen peroxide 2 ml were added to the filtrate. The resulting solution was preconcentrated in an oven at 110 °C to a final volume of 25 ml. Appropriate amounts of surfactant and 8-hydroxyquinoline was added to a 25 ml calibrated flask to obtain final concentration of 0.02 mol dm^{-3} and 5 × 10^{-5} mol dm^{-3} 8-hydroxyquinoline. Then 5 ml of the sample was added and the absorbance was measured against blank reagent. The same sample, 5-ml was diluted to

25 ml with double distilled water for AAS analysis (Table-4).

Conclusions

Determination of trace amounts of Cd(II) can be carried out directly using 8-hydroxyquinolinel in cationic micellar media of 0.02 mol dm^{-3} CPC in aqueous solution. The method is simple and rapid with greater sensitivity, better selectivity, and improved precision and replaces extraction with toxic organic solvents. Cd(II) contents in waste-water samples determined by the present method are in the agreement with the values obtained by atomic absorption spectrometry.

Acknowledgment

References

1. J. Jago, P. E. Wilson and B. M. Lee, *Analyst.*, **96**, 349 (1971).

2. W. J. Simmons, *Anal. Chem.*, **45**, 1947 (1973).

3. M. P. San Andres, M. L. Marina, and S. Vera, *Talanta*, **41**, 179 (1994).

4. M. A Sanz. M. F. Fernandez. *Anal. Chem.*, **58**, 2161 (1986).

5. H. C. Gin, L. Hong and P. J. Mai, *Talanta,* **41**, 1357 (1994).

6. A. L. Garcia, E. B. Gonzalez, J. L. Garcia Alonso, A. S. Medel, *Anal. Chim. Acta.,* **264**, 241 (1992).

7. T. Okada, *Anal. Chem.*, **64**, 2138 (1992).

8. E. Paramauro, A. B. Prevot, E. Pelizzetti, *Anal. Chim. Acta.,* **264**, 303 (1992).

9. L. J. Cline Love, J. G. Habarta, J. G. Dorsey, *Anal. Chem.,* **56**, 1132 (1984).

10. X. Jin, M. Zhu, E. D. Conte, *Anal. Chem.,* **71**, 514 (1999).

11. G. A. Shar, G. A. Soomro and M. I. Bhanger *J.Chem. Soc. Pak.,* **26** (2), 143 (2004).

12. A. K. Malik, K. N. Kaul, B.S. Lark, W. Faubel and A.L.J. Rao, *Turk. J. Chem.,* **25**, 99 (2001).

13. J. Yun, H. Choi *Talanta,* **52**, 893 (2000).

14. G. A. Shar and M. I. Bhanger, *The Nucleus,* **40** (1), (2003).

15. P. Becher, in M. J. Schiek (Ed.) *Surfactant Science Series*, vol. **1**, Marcel Dekker, NewYork, p, 481 (1966)

16. D.D. Perrin and B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapmann and Hall, London, 1974.