

## Spectrophotometric Determination of Hg(II) as Complex with 8-Hydroxyquinoline in Micellar Medium

G. A. SHAR AND G. A. SOOMRO

Department of Chemistry  
Shah Abdul Latif University Khairpur, Sindh, Pakistan.

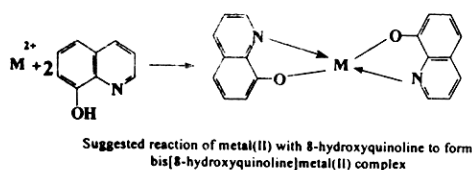
(Received 12<sup>th</sup> August, 2004, revised 21<sup>st</sup> March, 2005)

**Summary:** Spectrophotometric determination of mercury (II) is carried out with 8-hydroxyquinoline as a complexing reagent in aqueous phase using cationic surfactant cetylpyridinium chloride (CPC). Beer's law is obeyed over the concentration range 0.5–4.0  $\mu\text{g ml}^{-1}$ . The  $\lambda_{\text{max}}$  molar absorption, molar absorptivity and Sandell's sensitivity was 395 nm;  $\epsilon_{\text{max}}$  ( $\times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ ) is 0.65 and (30.9)  $\text{ng cm}^{-2}$ . Validation of this method has been made by comparing the results with those obtained by Atomic Absorption Spectroscopy (AAS). No significant difference is 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 mercury (II) in industrial waste-water samples.

### Introduction

The determination of mercury in biological material is important because this metal is toxic. Mercury has no metabolic function to perform in human body and therefore may be considered potentially harmful. 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 ammoniumpyrrolidinedithiocarbamate in cationic micellar media has been reported earlier [14].

8-hydroxyquinoline has a hydrogen atom that is replaceable by a metal, and a heterocyclic 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 Hg(II) metal ions using 8-hydroxyquinoline. The method was successfully applied to the determination of these metal ions 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) Hg(II)-8-hydroxyquinoline complex with absorption maxima at 395 nm. It seems that micelle in solution was formed at 0.02 M CPC. Fig. (2) shows a graph of the absorption maxima ( $\lambda_{\text{max}}$  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  $5 \times 10^{-5}$  M. Fig. (3) shows the absorption maxima at pH 9.0. 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  $0.65 \times (10^4 \text{ mol}^{-1} \text{ cm}^{-1})$ . The Sandell's sensitivity values is (30.9)  $\text{ng cm}^{-2}$ . Detection limit is (30.85)  $\text{ng ml}^{-1}$ . The improvement was found in the 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

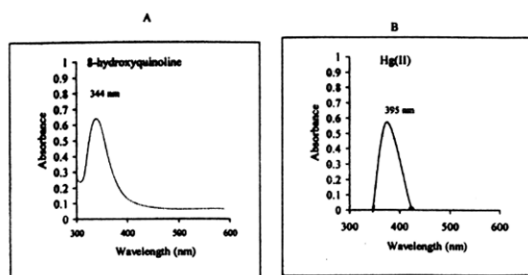


Fig. 1: Absorption spectra of Hg(II) with 8-hydroxyquinoline in SDS 1% (A) 8-Hydroxyquinoline  $6 \times 10^{-5}$  M, (B) Hg(II)-8-hydroxyquinoline complex, Hg  $2 \text{ mg mL}^{-1}$ .

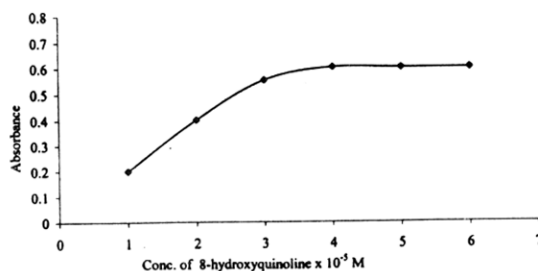


Fig. 2: Effect of 8-hydroxyquinoline conc. on the absorbance of Hg(II) complex in CPC.

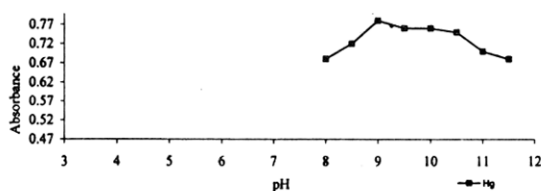


Fig. 3: Effect of pH on the absorbance of Hg(II)-8-hydroxyquinoline complex.

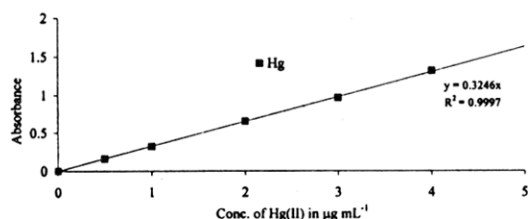


Fig. 4: Calibration graph of Hg(II)-8-hydroxyquinoline complex.

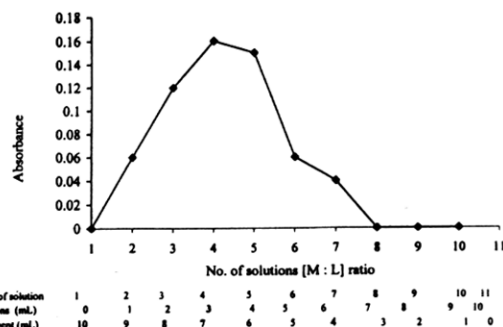


Fig. 5: Job's plot of metal:ligand ratio.

method of continuous variations. Fig. (5) Plot of absorbance versus mole fraction of the metal ion 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 Hg(II) ions with 8-hydroxyquinoline in presence of 0.02 M % CPC, interference by foreign ions were studied and all the results are shown in the Table-2. For these metal ions KSCN, KClO<sub>3</sub>, and sodium tartarate did not interfere until their amount reached  $1000 \mu\text{g mL}^{-1}$ . Interference of Cd (II), 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-3.

Table-1: Analytical characteristics of Hg (II)-8-hydroxyquinoline complex in the presence of surfactant (CPC).

Characteristics	Hg(II)
Beer's law range ( $\mu\text{g mL}^{-1}$ )	0.5 - 4.0
Absorption maxima	395
( $\lambda_{\text{max}}$ (nm): (a) micellar	
(b) CCl <sub>4</sub>	390
Molar absorptivity	0.65
$\times (10^4 \text{ mol}^{-1}\text{cm}^{-1})$ by micellar	
Molar absorptivity	0.66
$(10^4 \text{ mol}^{-1}\text{cm}^{-1})$ by extraction	
Sandell's sensitivity ( $\text{ng cm}^{-2}$ )	30.9
Detection limit ( $\text{ng mL}^{-1}$ )	30.8
pH	9
[CPC] (M)	0.02
[Reagent] ( $10^{-5}\text{M}$ )	5
RSD $\pm$	0.03

At 95%,  $n = 6$

Table-2: Tolerance limits ( $\mu\text{g ml}^{-1}$ ) for interference's of metal ions and salts with 8-hydroxyquinoline in 0.02M CPC

Ion / salt	Hg(II)
KSCN	1000
NaF	600
$\text{Na}_2\text{C}_2\text{O}_4$	200
$\text{KClO}_3$	1000
$\text{Na}_2\text{tartarate}$	1000
$\text{Na}_2\text{citrate}$	500
Mg (II)	150
Al(III)	200
Cd(II)	2
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  $2 \mu\text{g ml}^{-1}$

Table-3: Percent recovery (%) of known samples added to tap water

Metal ions	Amount added ( $\mu\text{g ml}^{-1}$ )	Amount found ( $\mu\text{g mL}^{-1}$ )	Recovery (%)
Hg(II)	1.0	0.99	$99 \pm 1$

At 95%, n= 6

Table-4: Determination of Hg(II) ions in industrial wastewater samples

Sample	Metal ions determined	
	Present method Mercury ( $\mu\text{g ml}^{-1}$ )	AAS method Mercury ( $\mu\text{g ml}^{-1}$ )
Industrial waste	0.50	0.51
water from Kotri	(0.40)	(0.4)
SITE		

At 95%, n= 6, coefficient of variation is given in parenthesis.

#### Application

The proposed spectrophotometric method was applied for the determination of Hg(II) in industrial wastewater samples. Results are shown in Table-4.

#### 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 Hg(II) stock solutions of ( $100 \mu\text{g ml}^{-1}$ ) were prepared dissolving their nitrate salt. Other metal ions solutions were prepared from their nitrate or chloride salts. Surfactant (CPC) 0.02 M 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 9 was prepared by taking 0.025 M sodium borate (50 ml) and 0.1 HCl (4.6 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 M were added and made up to 25 ml volume with distilled water having metal ions concentration  $0.06\text{--}10 \mu\text{g ml}^{-1}$ , concentration of 8-hydroxyquinoline  $5 \times 10^{-5}$  and 0.02 M surfactant. The pH values and analytical wavelength used are listed in Table-1.

#### Spectrophotometric metal ion determination after extraction with $\text{CCl}_4$

Appropriate volumes of stock metal, 8-hydroxyquinoline and aqueous buffer solutions were placed in a separating funnel and 10 ml of  $\text{CCl}_4$  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  $\text{CCl}_4$ . For the 25.0 ml total volume of the organic layer, absorbance was measured at the 390 nm wavelengths for metal ions.

#### Determination of Hg(II) in industrial waste-water

Industrial wastewater sample, 1l 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  $110^\circ\text{C}$  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 M and  $5 \times 10^{-5}\text{M}$  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 Hg(II) can be carried out directly using 8-hydroxyquinoline in cationic micellar media of 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. Hg(II) contents in wastewater samples determined by the present method are in the agreement with the values obtained by AAS.

### Acknowledgment

The author acknowledges the financial support of the Higher Education Commission for this project.

### References

1. I.J. Jago, P. E. Wilson 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 and A. Sanz 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** (1-4), (2003).
15. P. Becher, in M. J. Schiek (Ed.) *Surfactant Science Series*, **1**, Mareel Dekker, New York, p, 481 (1966).
16. D.D. Perrin, B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapman and Hall, London, (1974).