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II. CHEMISTRY

Analytical Chemistry

SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM(II) AND MERCURY(II) WITH WATER SOLUBLE PYRIDINOL AZO DYES

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1-(2′,3′-dihydroxy pyridyl-4′-azo)benzene-4-sulphonic acid (DHP-4S) and 1-(5′-chloro-2′,3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid (CPD-4S) two water soluble pyridinol azo dyes, have been used in the spectrophotometric determination of Cd(II) and Hg(II). The Sandell's sensitivities of the colour reactions for Cd(II) are 0.0032 μg/cm², 0.0028 μg/cm² and for Hg(II) are 0.0030 μg/cm², 0.0031 μg/cm² with DHP-4S and CPD-4S respectively. Other physico-chemical characteristics of the colour reactions viz., effect of *p*H, Beer's law validity, optimum concentration range, composition etc. have been reported. The effect of interference of foreign ions has also been studied and masking of ions has also been done wherever found necessary in the determination of Cd(II) and Hg(II). The sensitivities of other well-known heterocyclic azo dyes used for the determination of these two ions have also been compared.

Keywords: Spectrophotometry; Mercury (II); Cadmium (II); 1-2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid (DHP-4S); 1-(5′-chloro-2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid (CPD-4S).

INTRODUCTION

HETEROCYCLIC azo dyes, well known for their outstanding photometric sensitivities, constitute an important class amongst the various organic reagents used in the determination of metal ions (Anderson & Nickless, 1967; Shibata, 1972; Marczenko, 1976; and Sandell & Onishi, 1978). PAN and PAR have been used in the determination of more than fifty elements. PAR, a water soluble azo dye, which forms water soluble complexes is considered superior to PAN (Shibata, 1972). 1-(2′, 3′-Dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid (DHP-4S) (I) and 1-(5′-chloro-2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid (CPD-4S) (II) are two water soluble heterocyclic azo dyes which have been used as reagents in the spectrophotometric determination of Cd(II) and Hg(II). The present methods are sensitive enough in comparison to other heterocyclic azo dyes used in the determination of these two metal ions. The metals have also been determined in presence of foreign ions and some of the base metals have been masked by using suitable masking agents if necessary.

EXPERIMENTAL

Reagents

DHP-4S and CPD-4S Solutions : DHP-4S and CPD-4S have been synthesised

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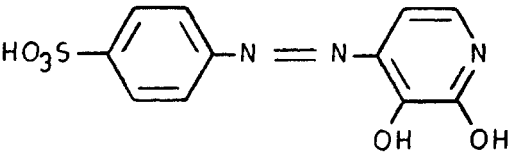
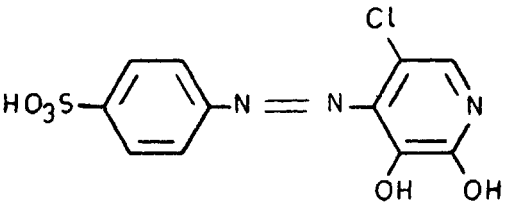


(I)



(II)

(Gupta *et al.*, 1977) by condensing 2, 3-dihydroxypyridine and 5-chloro-2, 3-dihydroxy pyridine with diazotised p-sulphanilic acid respectively. The purity of the reagent was checked by elemental analysis and thin layer chromatography. A stock solution of 1×10^{-3}M of DHP-4S and CPD-4S was prepared by dissolving 0.289 g/l and 0.3245 g/l of the dyes in doubly distilled water respectively.

Metal ion solutions: Stock solutions of cadmium (II) and mercury (II) were prepared by dissolving analytical grade cadmium acetate dihydrate and mercuric perchlorate (prepared by dissolving metallic mercury in perchloric acid) respectively, in doubly distilled water and were standardised by conventional methods.

The *p*H of the solutions were adjusted using perchloric acid and sodium hydroxide solutions.

All other reagents used were of analytical grade.

Apparatus

Spectrophotometer — A Unicam SP-600 spectrophotometer, with 10 mm matched glass cells, was used for absorbance purpose.

*p*H meter — A Beckman *p*H meter model Expandomatic SS-2 was used for *p*H measurements.

Recommended Procedure

To a suitable aliquot containing 4.0 to 31.6 μg of cadmium (II) or 3.0 to 23.0 μg of mercury (II), sufficient excess of DHP-4S solution (Table I) was added followed by 0.8–3.0 ml of 0.02 N sodium hydroxide solution; or to a suitable aliquot containing 4.0 to 20.0 μg of cadmium (II) or 2.5 to 31.0 μg of mercury (II), excess of CPD-4S solution (Table I) was added followed by 0.4–2.0 ml of 0.02N sodium hydroxide solution. The contents were diluted to 10 ml with water and the absorbance was measured against a reagent blank at their respective λ_{max}. The amount of unknown cadmium (II) or mercury (II) in the given sample could be determined from the calibration curve drawn under similar conditions.

TABLE I

Physico-chemical characteristics of the complexes

Characteristics	Cd-(DHP-4S) complex	Cd(CPD-4S) complex	Hg (DHP-4S) complex	Hg (CPD-4S) complex
λ_{max}, nm	540	545	540	550
Vol. of 0.02N NaOH per 10 ml	0.8–5.2	0.4–3.0	0.3–3.0	0.2–2.5
Moles of reagent required per mole of metal ion for full complexation	5	6	5	7
Beer's law validity, ppm	0.0–3.2	0.0–2.2	0.0–2.6	0.0–3.6
Optimum concentration range, ppm	0.4–3.16	0.4–2.0	0.3–2.3	0.25–3.1
Composition (M : L)	1 : 2	1 : 2	1 : 2	1 : 2
Sandell's sensitivity $\mu g/cm^2$	0.0032	0.0028	0.0030	0.0031
Molar extinction coefficient (ε) 1 $mole^{-1}$ cm^{-1}	3.5×10^4	3.95×10^4	6.6×10^4	6.4×10^4

RESULTS AND DISCUSSION

Cd(II) and Hg(II) form magenta coloured, water soluble complexes with both (DHP-4S) and (CPD-4S) respectively. The complexes are highly stable (minimum 6 hrs). The effect of *p*H has revealed that maximum complexation occurs in alkaline medium (Table I). The formation of stable complexes of Cd(II) and Hg(II) with DHP-4S and CPD-4S have been made the basis of their determination spectrophotometrically. The coloured complexes are also formed by Fe(II), Co(II), Ni(II) and Cu(II) (Chauhan *et al.*, 1979) and thus interfere in the determination of these metal ions, but some of these cations are masked by suitable masking agents wherever necessary. Fe(II) does not form complex above *p*H 8.0 and thus has no interference in the determination of Cd(II) and Hg(II) at high *p*H. The physico-chemical characteristics of the complexes are summarised in table I. The sensitivities of other heterocyclic azo dyes used in the determination of these ions have also been compared in tables II and III.

Effect of Diverse Ions

The ions F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SCN^-, SO_4^{2-}, SO_3^{2-}, Ti(IV), V(V), Cr (III), Mn(II) Al(III), In(III), Sb(III), alkaline earths — UO_2 (II), Mo(VI), W(VI), lanthanides and Th(IV) do not interfere in the determination of these metal ions. The precipitates formed at higher *p*H of some polyvalent cations, viz., Ti(IV), Zr(IV), Th(IV), lanthanides etc., are removed by centrifugation wherever necessary. The tolerance limits of other ions, which do not cause a deviation of more than $\pm$ 2 per cent in the absorbance are given below parenthesis.

Cd(II)-(DHP-4S) and Cd(II) (CPD-4S) systems : $S_2O_3^{2-}$, I^- (800 fold); thiourea, oxalate (140 fold); citrate, tartarate (100 fold); phosphate (60 fold); borate (20 fold); Fe(II) (10 fold above *p*H 10); Hg(II) (10 fold masked by $S_2O_3^{2-}$); Ag(I),

TABLE II

Comparison of sensitivities of heterocyclic azo dyes for the determination of mercury (II)

S. No.	Heterocyclic azo dye	λ_{max} (nm)	Sensitivity ($\mu g/cm^2$)	References
1	4-(2-pyridylazo) resorcinol	500	0.0029	Ueda, J.(1971)
2	5-hydroxy-4 (8-hydroxy-7-quinolylazo) naphthalene-2, 7-disulphonic acid	540	0.0055	Cherkesov *et al.* (1970)
3	3-(8-hydroxy-7-quinolylazo) naphthalene-1, 5-disulphonic acid	540	0.0045	—do—
4	1-(4-methyl-2-thiazolylazo)-2-naphthol	580	0.0400	Kolsova, I. V. (1970)
5	(2-pyridylazo)-1-naphthol	560	0.011	—do—
6	1-(2-thiazolylazo)-2-naphthol	580	0.0345	—do—
7	1-(2-quinolylazo)-2-acenaphthylen-2-ol	540	0.0033	Singh, I. *et al.* (1976)
8	Ammonium (2′-amino-3′-hydroxy pyridyl-4′-azo) benzene-4-arsonate	535	0.0055	Varma *et al.* (in press)
9	2-(4-antipyrylazo)-5-dimethylaminophenol	600	0.0100	Kolsova, I. V. (1969)
10	Ammonium (2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-arsonate	535	0.0032	Varma *et al.* (in press)
11	1-(2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid	540	0.0030	Present method
12	1-(5′-chloro-2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid	550	0.0031	Present method

TABLE III

Comparison of sensitivities of heterocyclic azo dyes for the determination of Cd(II)

S. No.	Heterocyclic azo dye	λ_{max} (nm)	Sensitivity ($\mu g/cm^2$)	References
1	(2-pyridylazo)-1-naphthol	555	0.0025	Shibata, S. (1972)
2	1-(5-chloro-5-pyridylazo)-2-naphthol	566	0.0018	Shibata *et al.* (1972)
3	4-(2-pyridylazo) resorcinol	495	0.0014	Kitano & Ueda (1970)
4	Arsenazo III, Iodide/allyl alcohol	600	0.0029	Mikhailova & Yurukowa (1974)
5	6-(Benzothiazol-2-ylazo)-2, 4-dichlorophenol	550	0.0028	Armeanu & Dragusin (1973)
6	1-(2-quinolylazo)-2-acenaphthylen-2-ol	550	0.0024	Singh, *et al.* (1976)
7	2-(2-pyridyl azo)-p-cresol	575	0.0036	Shibata, S. (1972)
8	1-(2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid	540	0.0032	Present method
9	1-(5′-chloro-2′, 3′-dihydroxy pyridyl-4′-azo) benzene-4-sulphonic acid	545	0.0028	—do—

Au(III) [15 fold Ag(I) masked by I^-]; Zn(II), Ni(II), Co(II), Cu(II) interfered seriously, so did EDTA and CN^-.

Hg(II) (DHP-4S) and Hg(II) (CPD-4S) Systems: Citrate, tartarate (500 fold); I^- (60 fold); oxalate (50 fold); borate, phosphate (20 fold); Fe(II) (10 fold above *p*H 10); Ag(I) and Au(III) (10 fold); Zn(II), Cu(II), Ni(II), Co(II), Cd(II) interfere seriously, so did EDTA, CN^-, $S_2O_3^{2-}$, S^{2-}, thiourea also.

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