Spectrophotometric Determination of Metal Complexes of 1-(2 Pyridylazo)-2-naphthol in Micellar Medium

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Summary: Spectrophotometeric determination of cadmium(II), mercury(II) and manganese(II) is carried out with 1-(2 pyridylazo)-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 80. The molar absorptivity, Sandell's sensitivity, critical micelle concentration, 1-(2 pyridylazo)-2-naphthol and metal ion concentration are studied. The method has been applied to the determination of these metal ions in municipal sewerage water and pharmaceutical samples.

Introduction

The determination of cadmium and mercury in biological material is important because these metals are toxic. Mercury has no metabolic function to perform in human body and therefore may be considered potentially harmful. Manganese is essential to all organisms as it activates numerous enzymes in various biological systems [1]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions [2,3] due to both rapidity, simplicity and wide applications. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [4,5]. 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 [6-16]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. The use of polyoxyethylene sorbitan mono-oleate (C-18:1) (Tween 80) is reported for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent [17]. The determination of Zn as Zn(II)dithizone complex in micellar media has been reported earlier [18]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants.
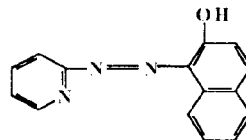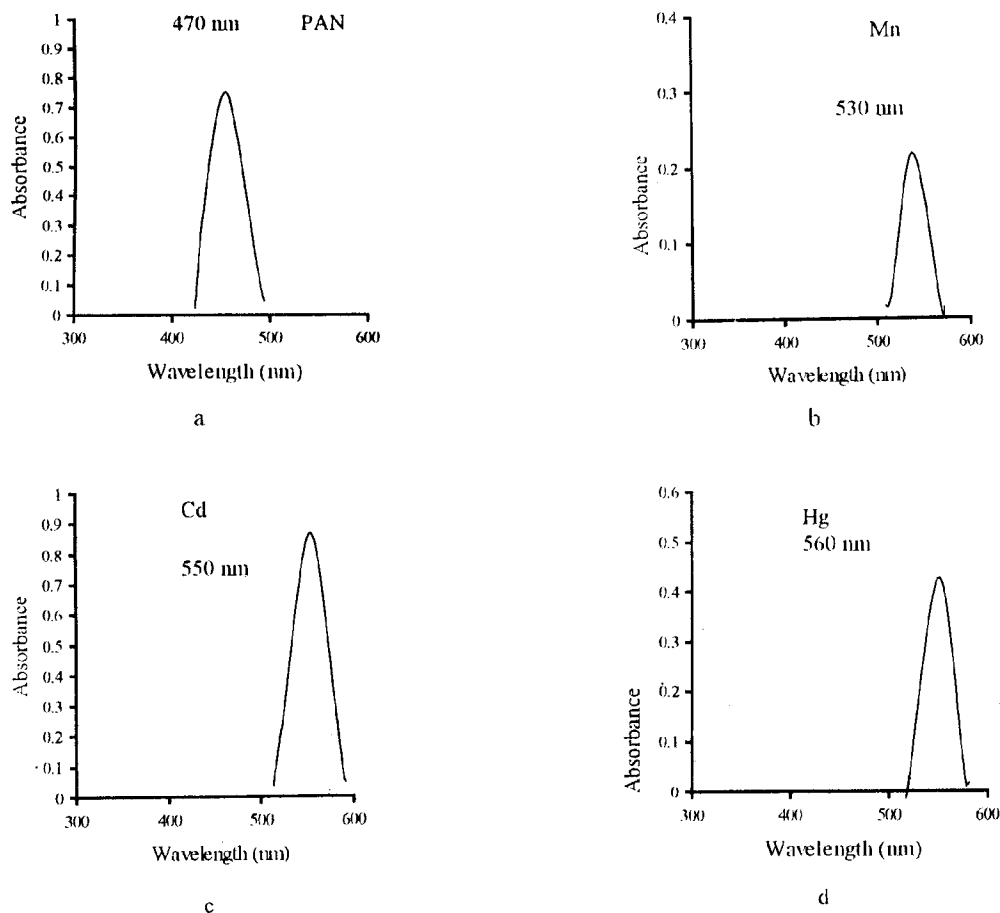

A typical structure of PAN

Fig. 1:   Absorption spectras of metal(II) complexes with PAN (a) PAN 6 x 10^{-5}M, (b) Mn(II)-complex 4 μgml^{-1}, (c) Cd(II)-complex 4 μgml^{-1} (d) Hg(II)-complex 4 μgml^{-1}

1-(2 Pyridylazo)-2-naphthol (PAN) forms coloured water-insoluble complexes with a large number of metal ions [19,20] and these are suitable for extractive spectrophotometric analysis. The use of surfactant to increase the solubility of PAN by surface active reagent has been reported earlier [21, 22]. The use of Tween 80 is reported in the determination of various metal ions using PAN as a complexing agent. In the present work, results of our study on the determination of Cd(II), Hg(II) and Mn(II) as PAN complexes, in a non-ionic surfactant - Tween 80 using spectrophotometric methods are reported.

Results and Discussion

Fig. 1 shows absorption spectra of (a) a 1-(2 pyridylazo)-2-naphthol,   (b)   for   Mn(II)   1-(2

pyridylazo)-2-naphthol complex, (c) Cd(II) complex (d) and Hg(II) complex. The micelle of non-ionic surfactant with polyoxyethylene group comprises two parts. One is the hydrocarbon tail directed to the interior core of micelle and the other is the hydrated polyoxyethylene group located at outer sphere. Organic compounds and metal chelates having large affinity towards polyoxyethylene group may be incorporated PAN could be dissolved by this phenomenon, because this species has a hydroxyl group, which interacts with the ether oxygen of polyoxyethylene group, by hydrogen bonding. It seems that micelle in solution was formed because 5% Tween 80 solution was above (0.0013 %, w/v) concentration [24]. Fig. 2 shows absorption maximum at (λ_{max} of 470 nm) of the solution containing varying amounts of PAN in presence of constant M(II) concentration increased with increase
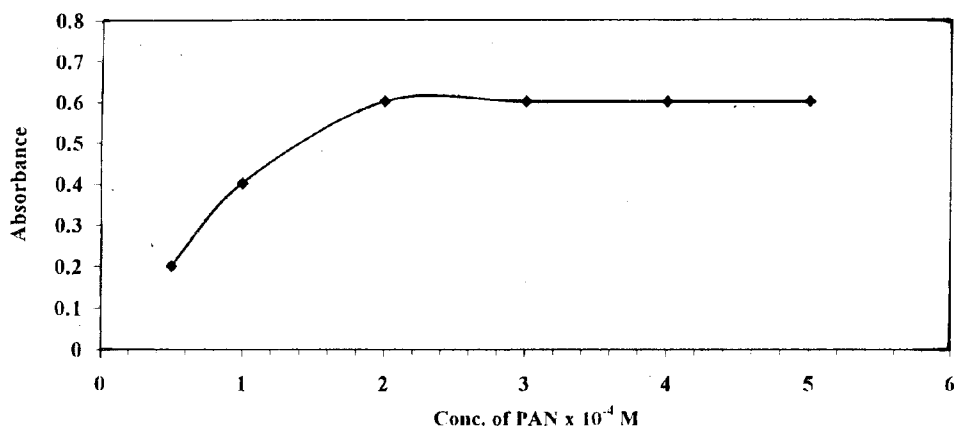
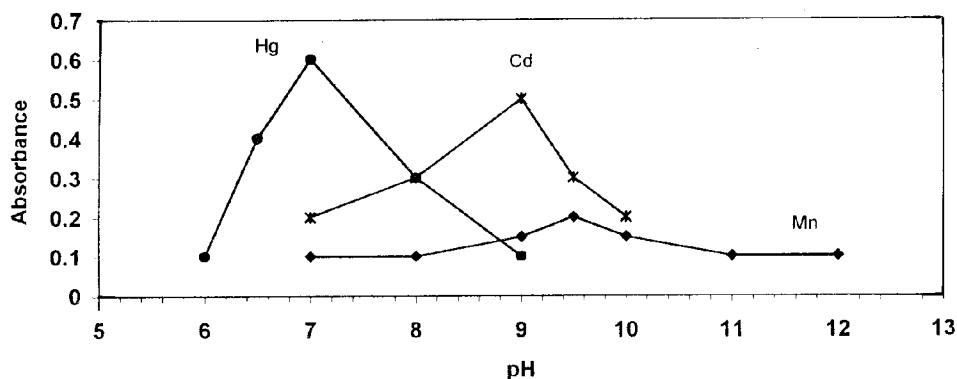Fig. 2: Effect of PAN conc. on the absorbance of M(II) PAN complexes.

Fig. 3: Effect of pH on the absorbance of metal(II) PAN complexes.

in PAN concentration up to 2×10^{-4} M. Fig. 3 shows the optimum pH of different metal complexes, which has been taken as the pH of maximum complex formation throughout this work. Following are the optimum pH values for each metal ion used in the present study: Cd(II) pH 9.0, Hg(II) pH 7 and Mn(II) pH 9.5. Optimum pH for each metal complex formation are given in Table 5. Metal to ligand ratio in the complex is 1:2 (M:L), and the complex remained stable for at least 2 h. Fig. 4 shows the calibration curve for Cd, Hg and Mn-PAN complexes showing concentration versus the absorbance. Calibration ranges for these metal complexes are given in Table 1.

Six values were obtained for each parameter, the average of which and the relative standard deviation of the each metal complex for (n=6) are given in Table-1. The sensitivity of the spectrophotometric method in presence of 5 % Tween 40 micelles (expressed as molar absorptivity and Sandell's sensitivity for each metal ions) is given, where the molar absorptivity, the sensitivity of the method is of the order highest for Hg(II) $3 \times (10^4 \text{ mol}^{-1} \text{ cm}^{-1})$, Cd(II) $1.75 \times (10^4 \text{ mol}^{-1} \text{ cm}^{-1})$ and Mn(II) $0.39 \times (10^4 \text{ mol}^{-1} \text{ cm}^{-1})$. The Sandell's sensitivity values are in the order of Mn(II) (14.1), Hg(II) (6.5) and Cd(II) (6.5).

Composition

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. Plot of absorbance versus mole fraction of the metal ion shows at
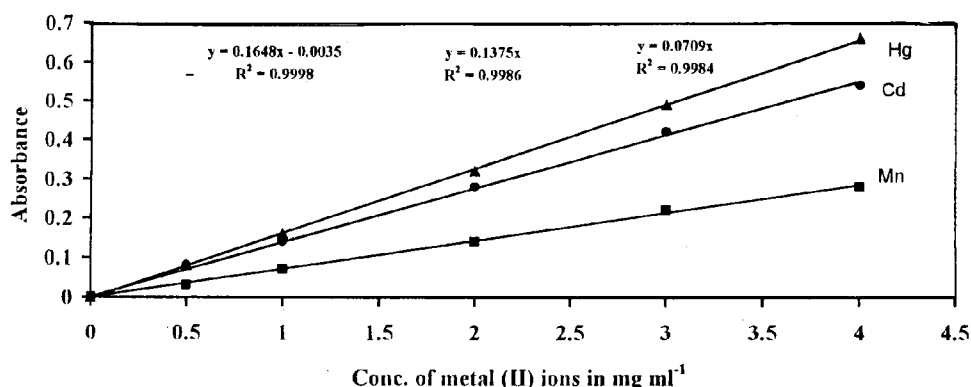
Fig. 4:   Calibration curves for metal(II) PAN complexes.

Table-1: Analytical characteristics of metal (II)- 1-(2 pyridylazo)-2-naphthol complexes in the presence of surfactants

Characteristics	Cd(II)	Hg(II)	Mn(II)
Beer's law range followed (μgml^{-1})	0.5-4.0	0.5 – 4.0	0.5 – 4.0
Absorption maxima			
(λ_{max}, nm): (a) micellar	550	560	530
(b) CCl$_4$	560	552	-
Molar absorptivity $\times$ (10^4 mol^{-1} cm^{-1})	1.75	3	0.39
Sandell's scale sensitivity (ng /cm^2)	6.5	6.7	14.1
pH	9.0	7	9.5
[Tween 80]	5%	5%	5%
[Reagent] $\times$ (10^{-4} M)	2	2	2
RSD $\pm$	0.002	0.003	0.003

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

Study of interferences by foreign ions

Interferences in the determination of Cd(II), Hg(II) and Mn(II) with 1-(2 pyridylazo)-2-naphthol in presence of 5 % Tween 80 were studied and the results are shown in the Table 2. The criterion for the studies was a $\pm$ 4.0 % change in absorbance for 2.0 μg ml^{-1} of M(II) in final 10 ml solution. The amount of foreign ion tolerated (i.e which changes absorbance by $\leq$ $\pm$ 4.0 %) is given in the Table. 2, cations of Fe, Co, Cd, Hg, Ni, Mn, and Zn interfere. As has been reported, the complexation reaction between M(II) and PAN is completely masked by EDTA and cyanate at low concentration, whereas ascorbic acid, Br', Cl', I', and SCN' do so at relatively higher concentrations. As has been reported, the iron(II) chelate is unstable [25]. Furthermore, no suitable masking reagents were found for iron(II), while iron (III) can be eliminated by the addition of

Table.-2: Tolerance limits (μg ml^{-1}) for interference's Of metal ions and salts with 1-(2 pyridylazo)-2-naphthol in 5 % Tween 80

Ion / salt	Cd(II)	Hg(II)	Mn(II)
Chlorides	200	200	200
Iodide	200	200	200
Ascorbate	400	400	400
Cyanate	100^c	100	100
Bromide	200	200	200
Borate	200	200	200
KSCN	1000	1000	1000
NaF	600	600	200
Na$_2$C$_2$O$_4$	200	200	50
KClO$_3$	1000	1000	1000
Na$_2$tartarate	1500	1500	1500
EDTA	100^c	100	100
Acetate	600	600	600
Na$_2$citrate	500	1000	100
KCN	500^b	500	500
Mg(II)	3000	3000	3000
Al(III)	300	300	300
Cd(II)	-	100^b	100
Co(II)	100^b	100	100
Cr(III)	50	30	50
Cr(IV)	8	8	8
Fe(III)	100^{a,b}	100	100
Mn(II)	100^b	100	-
Ni(II)	100^b	100	100
Pb(II)	500^a	500	500
Zn(II)	100	100	100
Hg(II)	100^b	-	100
Fe(II)	100^b	100	100
Cu(II)	100	100	100

a masked by citrate , b interferences strongly, c masked the complexation between M(II) and PAN. The concentration of metal ions is 2.0 μg ml^{-1}

ammonium oxalate or citrate before colour development. Alkali and alkaline-earth metal ions did not interfere. Though, masking agents such as citrate, phosphate, fluoride and thiocyanate are generally useful to overcome interference due to cations, only citrate is found suitable in the present case, presence

Table 3 Recovery (%) of known samples added to tap water.

Metal ions	Amount added (μg)	Amount found (μg ml⁻¹)	Recovery (%)
Cd(II)	1.0	0.99	99 ± 1
Hg(II)	1.0	0.97	97 ± 3
Mn(II)	1.0	0.98	98 ± 2

Table-4: Determination of Cd(II), Hg(II) and Zn(II) ions in municipal sewerage wate and pharmaceutical samples

Sample Municipal sewerage water	Metal ions determined		AAS	
	Cadmium (μgml⁻¹)	Mercury (μgml⁻¹)	Cadmium (μgml⁻¹)	Mercury (μgml⁻¹)
	0.60 (0.6)	0.50 (0.40)	0.61 (0.5)	0.51 (0.4)
Theragran-M Tablet (Bristol-Myers Squibb Pak.)		Manganese (mg/tab)	Manganese (mg/tab)	
		4.9 (0.4)	5.0 (0.6)	

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

of 1.0 10⁻³M of citrate enhances the tolerance limits of Fe(III), and Pb(II) from 100, and 500 μg to ≥ 500, and 1000 μg, respectively.

Application

The proposed spectrophtometric method was applied to the determination of Cd(II), Hg(II) and Mn(II) in municipal sewerage water and pharmaceutical samples. Results are shown in Table 4.

Experimental

Reagents

All the chemicals such as 1-(2 pyridylazo)-2-naphthol (Merck and Fluka Co.) were of analytical-grade or guaranteed-grade. Standard cadmium(II), mercury(II) and manganese(II) stock solution (100 μg ml⁻¹) were prepared using their nitrate salts. Other metal ion solutions were prepared from their nitrate or chloride salts. Five- percent (w/v) Tween 80 solution was made that Tween 80 weighing 5.0 g was dissolved in a 100 ml volumetric flask, and was diluted to the mark with double distilled water.

Buffer solutions of pH 7, pH 9 and pH 9.5 were prepared using appropriate mixtures of KH₂PO₄ + NaOH, Na₂B₄O₇ 10H₂O and NaOH respectively according to Perrin and Dempsey [23]

Apparatus

An UV/VIS Spectrometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic absorption spectrometer, model Spectra AA. 20 Varian was used for comparative metal ion

determination. The Pye Model 292 pH meter was used for monitoring pH of solutions.

Procedure

Spectrophotometric metal ion determination in micellar solution.

Appropriate volumes of stock solutions of metal ions, 1-(2 pyridylazo)-2-naphthol, and selected surfactant 5 % Tween 80 were added and made up to 25ml volume with distilled water having metal ions concentration of .06 - 10 μg ml, 1-(2 pyridylazo)-2-naphthol 2 × 10⁻⁴ M and 5 % Tween 80. The pH values and analytical wavelength used are listed in Table 1.

Spectrophotometric metal ion determination after extraction with CCl₄.

Appropriate volumes of stock metal and 1-(2 pyridylazo)-2-naphthol aqueous solutions were placed in a separating funnel and 10 ml of CCl₄ was added. The organic layer was transferred to a 25-ml volumetric flask. In order to obtain complete extraction, the process was repeated twice, the first time with 10 ml and the second time with 5 ml of CCl₄. For the 25-ml total volume of the organic layer, absorbance was measured at the appropriate wavelength for metal ions.

Determination of Cd(II), Hg(II) and Mn(II) in (a) municipal sewerage (b) pharmaceutical sample

Municipal sewerage water sample, 1L obtained from municipal sewerage falling in Fuleli canal (Hderabad) was filtered using Whatman filter No. 2 paper. Ascorbic acid (10 mg), 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 5 % Tween 80 and 1-(2 pyridylazo)-2-naphthol was added to a 25 ml calibrated flask to obtain final concentration of 5 % Tween 80, appropriate buffer and 2 × 10⁻⁴ M 1-(2 pyridylazo)-2-naphthol. Then 5 ml of the sample was added and the absorbance was measured against water. The same sample, 5-ml was diluted to 25 ml with double distilled water for AAS analysis (Table 4).

Pharmaceutical sample:

A tablet of Theragran-M (Bristol-Myers Squibb, Pak) was transferred to a crucible to which was added 0.5 g potassium bisulphate dissolved in 2

ml water, 6 ml hydrochloric acid (37%) and 3 ml nitric acid (65%). The mixture was heated on flame. The white powder obtained was dissolved in 25ml water. Working solutions were adjusted to 10 ml for analysis of manganese(II), then determined by proposed method and by AAS (Table 4)

Conclusions

Determination of trace amount of Cd(II), Hg(II) and Mn(II) can be carried out directly using 1-(2 pyridylazo)-2-naphthol, in non-ionic micellar media of 5 % Tween 80 in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, and improved precision and replaces extraction with toxic organic solvents. Cd(II), Hg(II) and Mn(II) content in various in municipal sewerage water and pharmaceutical samples determined by the present method are in agreement with the values obtained by atomic absorption spectroscopy.

Acknowledgment

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