SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II), NICKEL(II) AND COPPER (II) WITH 1-(2 PYRIDYLAZO)-2-NAPHTHOL IN MICELLAR MEDIUM

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Spectrophotometeric determination of cobalt(II), nickel(II) and copper(II) is carried out with **1**-(2 pyridylazo)-2-naphthol as a complexing reagent in aqueous phase using non-ionic surfactant Tween 80. Beer's law is obeyed for Co(II), Ni(II) and Cu(II) over the range 0.5 - 4.0, 0.5 - 4.0 and 0.5 - 3.0 ngmL^{-1} with detection limit (2σ) of 6.7, 3.2 and 3.9 ngmL^{-1}. The λ_{max} molar absorption, molar absorptivity, Sandell's sensitivity of Co(II), Ni(II) and Cu(II) are 580 nm, 570 nm and 555 nm; $\varepsilon_{max} \times (10^4 \text{ mol}^{-1} \text{ cm}^{-1})$ is 0.87, 1.8 and 1.6 and 6.8, 3.3 and 3.9 ng cm^{-2} respectively. The pH at which complex is formed for Co(II), Ni(II) and Cu(II) is 5, 5.5 and 6.5 respectively. The critical micelle concentration (CMC) of Tween 80 is 5%. The present method is compared with that of atomic absorption spectroscopy and no significant difference is noted between the two methods at 95% confidence level. The method has been applied to the determination of Co(II), Ni(II) and Cu(II) in industrial waste water and pharmaceutical samples.

Keywords: Non-ionic -Tween 80, micelle, 1-(2 pyridylazo) -2-naphthol**,** Spectrometry

1. Introduction

Copper is a nutritionally essential metal and is widely distributed in nature [1]. Deficiency of nickel may lead to health problems such as dermatitis, deformities of bones, while excess intake may cause lungs cancer and myocardial infarction [2]. Cobalt is an important essential micronutrient for all living systems [3]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions [4,5] due to its 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 [6, 7]. Because of 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 [8-16]. 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 (Tween 80) is reported for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent [17]. The determination of Cu as Cu(II)1-nitroso-2-naphthol complex in micellar media has been reported earlier [18]. Tween series surfactants are very

soluble in aqueous systems than other non-ionic surfactants.

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 surface active reagent increase in the solubility of PAN has been reported earlier [21, 22]. In the present work, results for the determination of Cu(II), Ni(II) and Co(II) as PAN complexes, in a non-ionic surfactant -Tween 80 using spectrophotometric methods are reported.

2. Experimental

2.1. Reagents

All the chemicals such as 1-(2 pyridylazo)-2-naphthol (Merck and Fluka AG) were of analytical or equivalent grade. Standard stock solutions of (100 μg mL^{-1}) of copper(II), nickel(II) and cobalt(II) were prepared using their nitrates. Other metal ion solutions were prepared from their nitrates or chlorides. Five percent (w/v) Tween 80 solution was made in double distilled water. Buffer solutions of pH 5, pH 5.5 and pH 6.5 were prepared using appropriate mixtures of CH$_3$COOH+ CH$_3$COONa, KH$_2$PO$_4$ and NaOH respectively according to Perrin and Dempsey [23].

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2.2. 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.

3 Procedure

3.1. Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions, 1-(2 pyridylazo)-2-naphthol, and surfactant Tween 80 were added and made upto 25mL volume with distilled water having metal ions concentration of .06 - 10 μg mL^{-1}, PAN 2×10^{-4} M and 5 % Tween 80. The pH and wavelengths used are listed in Table 1.

Table 1. Analytical characteristics of metal (II)-1-(2 pyridylazo) -2-naphtholcomplexes in the presence of surfactant.

Characteristics	Co(II)	Ni(II)	Cu(II)
Beer's law range followed (μg mL^{-1})	0.5-4.0	0.5-4.0	0.5-3.0
Absorption maxima (λ_{max}, nm): (a) micellar	580	570	555
(b) CCl$_4$	590	575	560
Molar absorptivity $\varepsilon_{max} \times$ (10^4 M^{-1} cm^{-1})	0.87	1.8	1.6
Sandell's scale sensitivity (ng cm^{-2})	6.8	3.3	3.9
Detection limit (ng mL^{-1})	6.7	3.2	3.9
pH	5	5.5	6.5
RSD ±	0.04	0.05	0.03

3.2. Spectrophotometric metal ion determination after extraction with CCl$_4$.

The volumes of stock metal and PAN aqueous 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 thrice, the first time with 10 ml, the second time with 10 ml and the third time with 5 ml of CCl$_4$. For 25 ml total volume of the organic layer,

absorbance was measured at the appropriate wavelength for metal ions.

4. Application

The determination of Co (II), Ni (II) and Cu (II) in industrial wastewater and pharmaceutical samples.

4.1. The industrial waste

Industrial wastewater sample, 1L obtained from industrial effluent collected from Kotri site area was filtered using Whatman 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 Tween 80 M and 1-(2 pyridylazo)-2-naphthol was added to a 25 ml calibrated flask to obtain final concentration of 5% Tween 80 and 2×10^{-4} M 1-(2 pyridylazo)-2-naphthol. Then 5 mL of the sample was added and the absorbance was measured against the reagent in water as a blank. The same sample, 5 ml was diluted to 25 mL with double distilled water for AAS analysis (Table 4).

4.2. 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 25 mL water. Working solutions were adjusted to 10 ml for analysis of copper, but for cobalt 10 mL solution was spiked with 20 μg cobalt(II), and then determined by proposed method and by AAS (Table 4).

5. Results and Discussion

Figure 1 shows absorption spectra of (a) PAN, (b) for Co(II) with 1-(2 pyridylazo)-2-naphthol complex, (c) Ni(II) complex (d) and Cu(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 other oxygen of polyoxyethylene group, by hydrogen bonding. It seems that micelle in solution was formed because
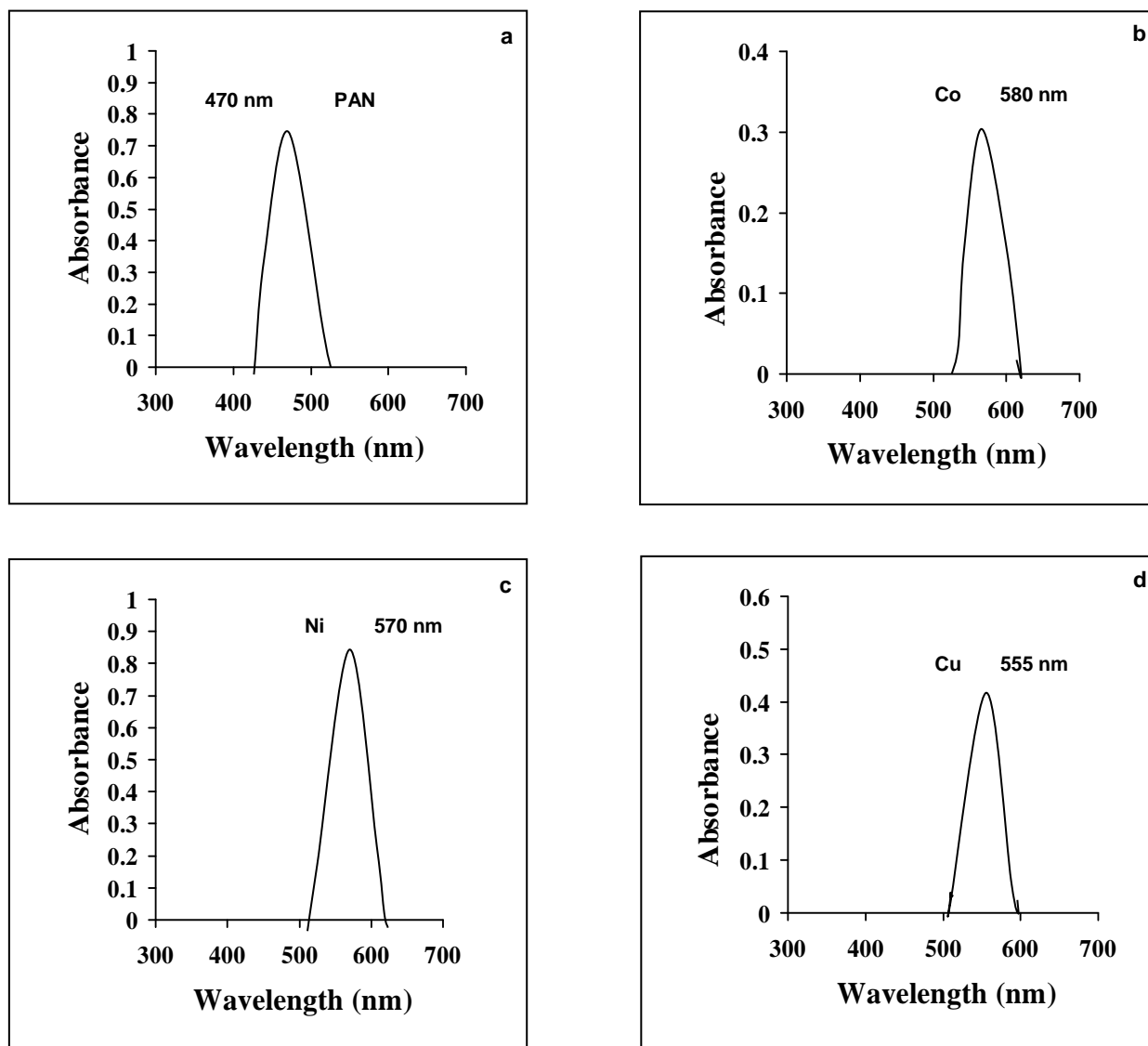
Figure 1.   Absorption spectras of metal(II) complexes with PAN **(**a) PAN 2×10^{-4}M, (b) Co(II)-complex 3 μg mL^{-1}, (c) Ni(II)-complex 3 μg mL^{-1} (d) Cu(II)-complex 3 μg mL^{-1} .

5% Tween 80 solution was above (0.0013 %, w/v) concentration [24]. Fig. 2 shows an increase in the absorption of PAN solution concentration from 2×10^{-4} M in presence of constant metal (II) concentration. Fig. 3 shows the optimum pH for each metal i.e. 5.0 for Co(II), 5.5 for Ni(II) and 6.5 for Cu(II). Calibration curve ranges for Co, Ni and Cu-PAN complexes are given in Table 1.

Six values are 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 molar absorptivity and Sandell's sensitivity for Co(II) Ni(II) and Cu(II)

$(10^4$ mol^{-1}cm^{-1}), 0.87, 1.8 and 1.6 and 6.8, 3.3 and 3.9 ng cm^{-2}.

5.1.   Composition

Composition of the complex formed under experimental conditions is investigated by Job's method of continuous variations. Fig. 4 shows a Plot of absorbance versus mole fraction of the metal ion indicating a maximum which corresponds to 1:4 (M: L) ratio in the complex for M(II) ions.
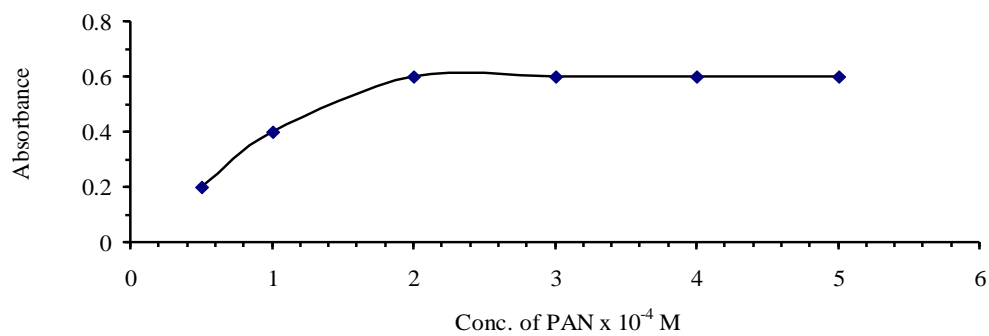
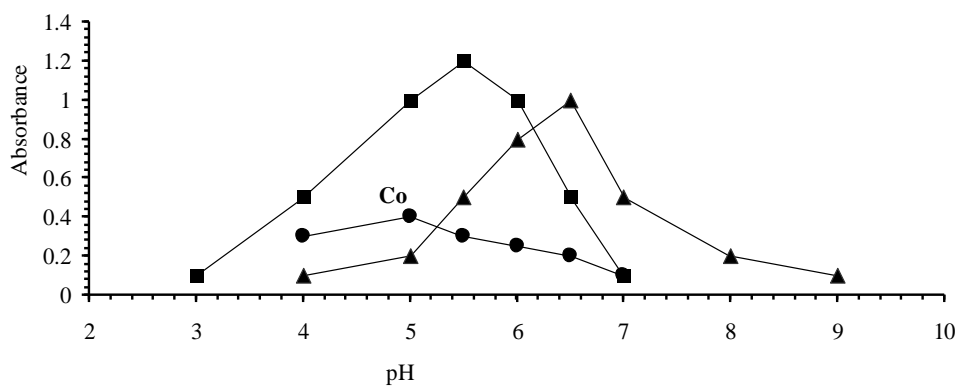Figure 2.   Effect of PAN concentration on the absorbance of metal (II) PAN complexes

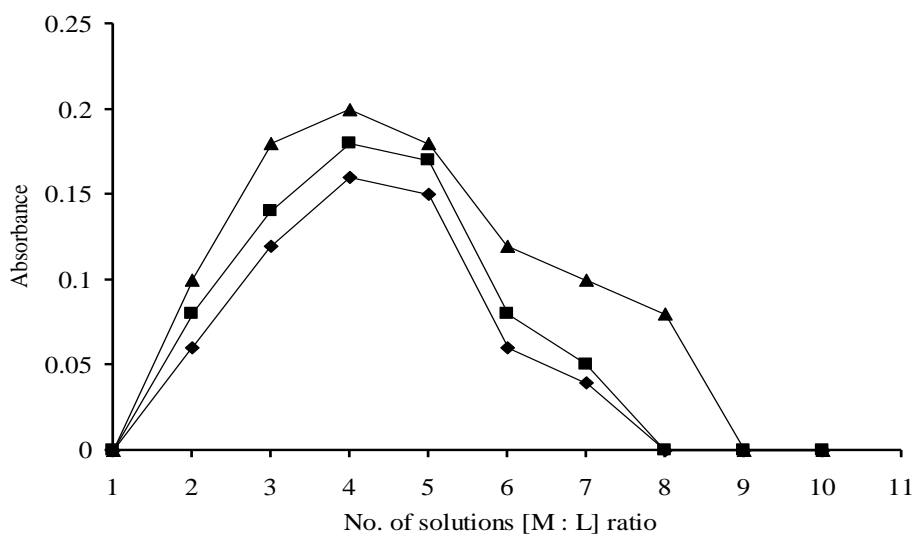Figure.3.   Effect of pH on the absorbance of metal (II)-PAN complexes

Figure 4.   Job's plot of metal : ligand ratio

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Table. 2. Tolerance limits ($\mu g\ mL^{-1}$) for interference's of metal ions and salts with 1-(2 pyridylazo)-2-naphthol in 5 % Tween 80

Ion*/salt	Co(II)		Ni (II)		Cu (II)	
Chloride	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	
$Na_2C_2O_4$	200		200		50	
$KClO_3$	1000		1000		1000	
Na_2tartarate	1500		1500		1500	
EDTA	100	c	100		100	
Acetate	600		600		600	
Na_2citrate	500		1000		100	
KCN	500	b	500		500	
Mg(II)	3000		3000		3000	
Al(III)	300		300		300	
Cd(II)	100		100	b	100	
Co(II)	–		100		100	
Cr(III)	50	b	30	b	50	b
Cr(VI)	8	b	8	b	8	b
Fe(III)	100	a, b	100		100	
Mn(II)	100	b	100		100	
Ni(II)	100	b	–		100	
Pb(II)	500	a	500		500	
Zn(II)	100	b	100		100	
Hg(II)	100	b	–		100	
Fe(II)	100	b	100		100	
Cu(II)	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 $\mu g\ mL^{-1}$.

5.2.   Study of interferences by foreign ions

Interferences in the determination of Co(II), Ni(II) and Cu(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 ± 4.0 % change in absorbance for 2.0 $\mu g\ mL^{-1}$ of metal (II) in final 10 mL^{-1} solution. The amount of foreign ion tolerated (i.e. which changes absorbance by $\geq$ ± 4.0 %) is given in the Table. 2; Fe, Cd (II), Hg (II), Mn (II) and Zn (II) interfere. Cu (II) and Ni (II) cause interference in the determination of other metal ions. As has been reported, the complexation between metal (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 are found for iron(II), while iron (III) can be eliminated by the addition of 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 of 10^{-3}M of citrate enhances the tolerance limits of Fe(III), and Pb(II) from 100, and 500 μg to $\geq$ 500 and 1000 $\mu g\ mL^{-1}$ respectively.

Table 3.   Percent recovery of known amount added to tap water.

Metal ions	Amount added ($\mu g\ mL^{-1}$)	Amount found ($\mu g\ mL^{-1}$)	Recovery (%)
Co(II)	1.0	0.99	99 ± 1
Ni(II)	1.0	0.97	97 ± 3
Cu(II)	1.0	0.98	98 ± 2

At 95% n = 6

5.3.   Application

The proposed spectrophotometric method is applied for the determination of Co(II), Ni(II) and Cu(II) in industrial waste water and pharmaceutical samples. Results are shown in Table 4.

6.   Conclusions

Determination of trace amount of Co(II), Ni(II) and Cu(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

Table 4. Determination of Co(II), Ni(II) and Cu(II) ions in indusrial waste water and pharmaceutical samples

Sample	Metal ions determined (μg mL^{-1})			
	Present method		AAS	
	Copper	Nickel	Copper	Nickel
Industrial waste water, Kotri SITE area.	58.10	0.40	58.90	0.41
	(0.40)	(2.0)	(0.5)	(0.8)
	Cobalt		Cobalt	
	(μg /tablet)		(μg /tablet)	
Theragran-M tablet	39.0		39.1	
(39.0 μg /tablet)	(0.4)		(1.4)	

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

replaces extraction with toxic organic solvents. Co(II), Ni(II) and Cu(II) content in various industrial waste water and pharmaceutical samples determined by the present method are in agreement with the values obtained by atomic absorption spectroscopy.

Acknowledgement

References

[1] P. Richter, M.I, Toral, A.E. Tapia, and E. Fuenzalida, Talanta, **122**, (1997) 1045.

[2] F.W. Sunderman, J. Am. Clin. Pathol. ,**35**, (1961) 2039.

[3] V.J. Hammond and W.C.Price, J. Opt. Soc. Am., **43** (1972) 924.

[4] W. J. Simmons**,** Anal. Chem., **45** (1973) 1947.

[5] Chem. Eng. News **54**, No. 6 (1976) 6.

[6] Chem. Eng. News **54**, No. 6 (1976) 7.

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

[8] M. A Sanz and M. F. Fernandez., Anal. Chem., **58** (1986) 2161.

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

[10] A.L. Garcia, E.B. Gonzalez, J.L.G. Alonso and A. Sanz Medel. Anal. Chim. Acta, **264**, (1992) 241.

[11] T. Okada, Anal. Chem., **64** (1992) 2138.

[12] E. Paramauro, A.B. Prevot and E. Pelizzetti, Anal. Chim. Acta**., 264** (1992) 303.

[13] L.J.C. Love, J.G. Habarta and J.G. Dorsey, Anal. Chem., **56** (1984) 1133.

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

[15] J. Yun and H. Choi, Talanta, **52**, (2000) 893.

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

[17] J. Yun and H. Choi, Talanta, **52**, (2000) 893.

[18] G.A. Shar and M.I. Bhanger, J. Chem. Soc. Pak**., 24**, No. 3 (2002) 176.

[19] R.G. Anderson and G. Nickless, Analyst, **92**, (1967) 207.

[20] S. Shibata, in Chelates in Analytical Chemistry, Vol. IV, Ed. H. A. Flachka and A. J. Barnard, Jr. Dekker, New York (1972).

[21] H. Watanabe, Talanta, **21** (1974) 295.

[22] S.F. Jiang, Fenxi Huaxue, **8** (1980) 530.

[23] D.D Perrin and B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London (1974).

[24] P. Beeher and M. J. Schiek (Ed.) Surfactant Science Series, Vol. 1, Marcel and Dekker, New York, (1966) p. 481.

[25] S. Shibata in Chelates in Analytical Chemistry, Vol. **IV**, Ed. H. A. Flachka and A. J. Barnard, Jr. Marcel and Dekker, New York (1972).

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