



SPECTROPHOTOMETRIC DETERMINATION OF METAL COMPLEXES OF 1-NITROSO-2-NAPHTHOL IN MICELLAR MEDIUM

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Spectrophotometric determination of iron(III), nickel(II) and cobalt(II) is carried out with 1-nitroso-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 40. This replaces a tedious and time consuming solvent extraction method, because these solvents are costly and also toxic. Beer's law was obeyed, for Fe(III), Ni(II) and Co(II) over the range 0.5 - 4.0, 0.5 - 4.0 and 0.12 - 3.0 $\mu\text{g ml}^{-1}$ with detection limit (2σ) of 3.3, 5.8 and 3.1 ng ml^{-1} respectively. The λ_{max} molar absorption, molar absorptivity and Sandell's sensitivity of Fe(III), Ni(II) and Co(II) were (λ_{max} 446 nm), (λ_{max} 483.5 nm) and (λ_{max} 444.5 nm); $\epsilon_{\text{max}} \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ is 1.69, 1.0 and 1.86, 3.3, 5.8 and 3.1 ng cm^{-2} , respectively. The pH at which the complex is formed for Fe(III), Ni(II) and Co(II) is 1, 8 and 5 respectively. The critical micelle concentration (cmc) of 1-nitroso-2-naphthol is 5% solution. 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 iron(III), nickel(II) and cobalt(II) in pharmaceutical and industrial wastewater samples.

Keywords: Nonionic-Tween 40, Micelle, 1-Nitroso-2-naphthol, Spectrometry.

1. Introduction

In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions due to rapidity, simplicity and wide applications [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 [5-12]. Micellar media is mainly used to replace the toxic organic solvents during extraction and to enhance the absorption sensitivities, thus simplifying the procedure [10,13-18]. The spectrophotometric determination of Zn as Zn(II)dithizone complex in micellar media has been reported by us [19].

Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. The use of polyoxyethylene sorbitan mono-oleate (Tween 80) for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent

is reported [11].

Therefore, in the present work polyoxyethylene sorbitan monopalmitate (Tween 40), which is more stable and cheaper among Tween series, has been utilized as a micellar media for the determination of metal ions using 1-nitroso-2-naphthol and was found to give comparable results with that of the reported method [20]. The method has been applied for the analysis of iron(III), nickel(II) and cobalt(II) in pharmaceutical and industrial effluents samples.

2. Experimental

2.1 Reagents

All the chemicals such as 1-Nitroso-2-naphthol (Merck and Fluka Co.) were of analytical- or equivalent-grade. Standard iron(III), nickel(II) and cobalt(II) stock solutions ($100 \mu\text{g ml}^{-1}$) were prepared using their nitrate salts. Other metal ion solutions were prepared from their nitrate or chloride salts. A five percent (w/v) aqueous solution of Tween 40 was made in a 100 ml volumetric flask, and diluted with double distilled water.

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Table 1. Analytical characteristics of metal - 1-nitroso-2-naphthol complexes in the presence of surfactants.

Characteristics	Co(II)	Ni(II)	Fe(III)
Beer's law range followed ($\mu\text{g ml}^{-1}$)	0.12 – 3.0	0.5 – 4.0	0.5 – 4.0
Absorption maxima λ_{max} , (nm): (a) micellar	444.5	452	446
(b) CCl_4	447.8	452	446
Molar absorptivity $\epsilon_{\text{max}} \times 10^4 \text{ mol}^{-1}\text{cm}^{-1}$ by solvent ^a extraction	1.22	1.21	2.82
Molar absorptivity $\epsilon_{\text{max}} \times 10^4 \text{ mol}^{-1}\text{cm}^{-1}$ by micellar	1.86	1.0	1.69
Sandell's scale sensitivity (ng cm^{-2})	3.6	5.8	7.9
Detection limit (ng cm^{-2}) (2σ)	3.1	5.8	3.3
pH	5	8	1
[surfactant] %	5%	5%	5%
[reagent] ($\mu\text{g ml}^{-1}$)	185	185	185
RSD* \pm	12.9	9.06	11.2

a These values were obtained assuming metal complexation were completely extracted. At 95% confidence limit, * n= 6

Buffer solutions of pH 1, 5, and 8 using appropriate mixtures of HCl + KCl, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$, KH_2PO_4 and NaOH respectively were prepared accordingly [21].

2.2 Apparatus

A UV visible 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. Pye Model 292 pH meter was used for monitoring pH of solutions.

2.3 Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions, 1-nitroso-2-naphthol, and selected surfactant 5 % Tween 40 were added and made upto 25 ml volume with distilled water having metal ions concentration of $0.06 - 10 \mu\text{g ml}^{-1}$, 1-nitroso-2-naphthol ($185 \mu\text{g ml}^{-1}$). The pH values and analytical wavelengths used are listed in Table 1.

2.4 Spectrophotometric metal ion determination after extraction with CCl_4

Appropriate volumes of stock metal and 1-nitroso-2-naphthol 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 twice with 10 ml and then once with 5 ml of CCl_4 . For the 25-ml total volume of the organic layer, absorbance was measured at the appropriate wavelength for metal ions.

2.5 Determination of Fe(III), Co (II) and Ni (II) in industrial effluents and pharmaceutical samples

2.5.1. The industrial waste

Industrial waste-water sample, (1L) 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 5 % Tween 40 and 1-nitroso-2-naphthol was added to a 25 ml flask to obtain $185 \mu\text{g ml}^{-1}$ 1-nitroso-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).

2.5.2. 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 to boiling. The white powder obtained was dissolved in 25 ml water. Working solutions were adjusted to 10 ml for analysis of iron, but for cobalt 10 ml solution was spiked with 20 μg cobalt (II), then determined by proposed method and by AAS (Table 4)

3. Results and Discussion

The reagent 1-nitroso-2-naphthol form stable complexes with several metal ions. A typical reaction is shown below :

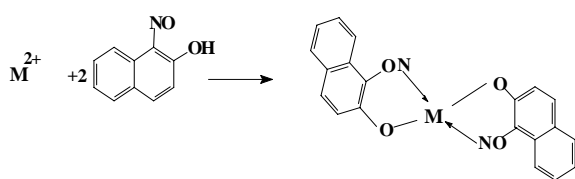


Table 2. Tolerance limits ($\mu\text{g ml}^{-1}$) for interferences of metal ions and salts with 1-nitroso-2-naphthol in 5 % Tween 40

Ion / salt	Co(II)	Ni(II)	Fe(III)
KSCN	1000	1000	1000
NaF	600	600	200
$\text{Na}_2\text{C}_2\text{O}_4$	200	200	50
KClO_3	1000	1000	1000
$\text{Na}_2\text{tartarate}$	1000	1000	1000
$\text{Na}_2\text{citrate}$	500	1000	100
Mg(II)	800	800	800
Al(III)	10	100	100
Cd(II)	2	2	2
Co (II)	-	80	100
Cr (III)	50	30	50
Cr (IV)	8	8	8
Fe (III)	5	10	-
Mn(II)	200	500	500
Ni(II)	5	-	50
Pb (II)	3	3	3
Zn (II)	50	100	50
Cu (II)	5	100	100

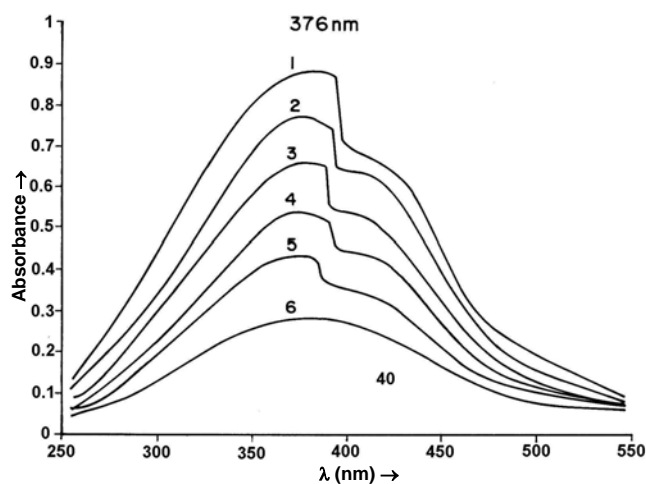


Figure 1. Absorption spectra of saturated 1-nitroso-2-naphthol in various solutions of Tween 40 (1) 10%, (2) 8%, (3) 6%, (4) 5%, (5) 4% and (6) 2%.

Where M^{2+} stands for Ni(II), while Co(II) and Fe(III) form tris (1-nitroso-2-naphthol)-metal complexes (molar 3:1).

Fig. 1 shows the absorption spectra of saturated 1-nitroso-2-naphthol in varying concentration of Tween 40 (2.0 -10.0 %) at wavelength 250-550 nm (λ_{max} 376 nm). The micelle of non-ionic surfactant with polyoxyethylene group comprises of 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. 1-nitroso-2-naphthol could be dissolved by this phenomenon, because this specie has a hydroxyl group, which interacts with the oxygen of ether polyoxyethylene of group, by hydrogen bonding. It seems that micelle in solution was formed because 5% Tween 40 solution is above (0.0013 %, w/v) concentration [21]. Therefore, 5% Tween 40 solution was used as an optimized concentration throughout this study. Fig. 2 shows absorption spectra of (A) 1-nitroso-2-naphthol (λ_{max} 376 nm), (B) Co(II) complex (λ_{max} 444.5 nm), (C) Ni(II) complex (λ_{max} 452 nm) and (D) Fe(III) complex (λ_{max} 446 nm). Fig 3 indicates the effect of mole ratio of 1-nitroso-2-naphthol concentration for Co(II), Ni(II) and Fe(III) in the complex formation and it is observed that different metals have different mole ratios. For cobalt 20 to 50 m.mole, for nickel it is 40 to 70 m. moles and for iron it is 50 to 70 m moles of the reagent. Therefore, 50 m.mole of the reagent require 1m mole of the metal ion. Fig 4 depicts the effect of pH on the absorbance of the

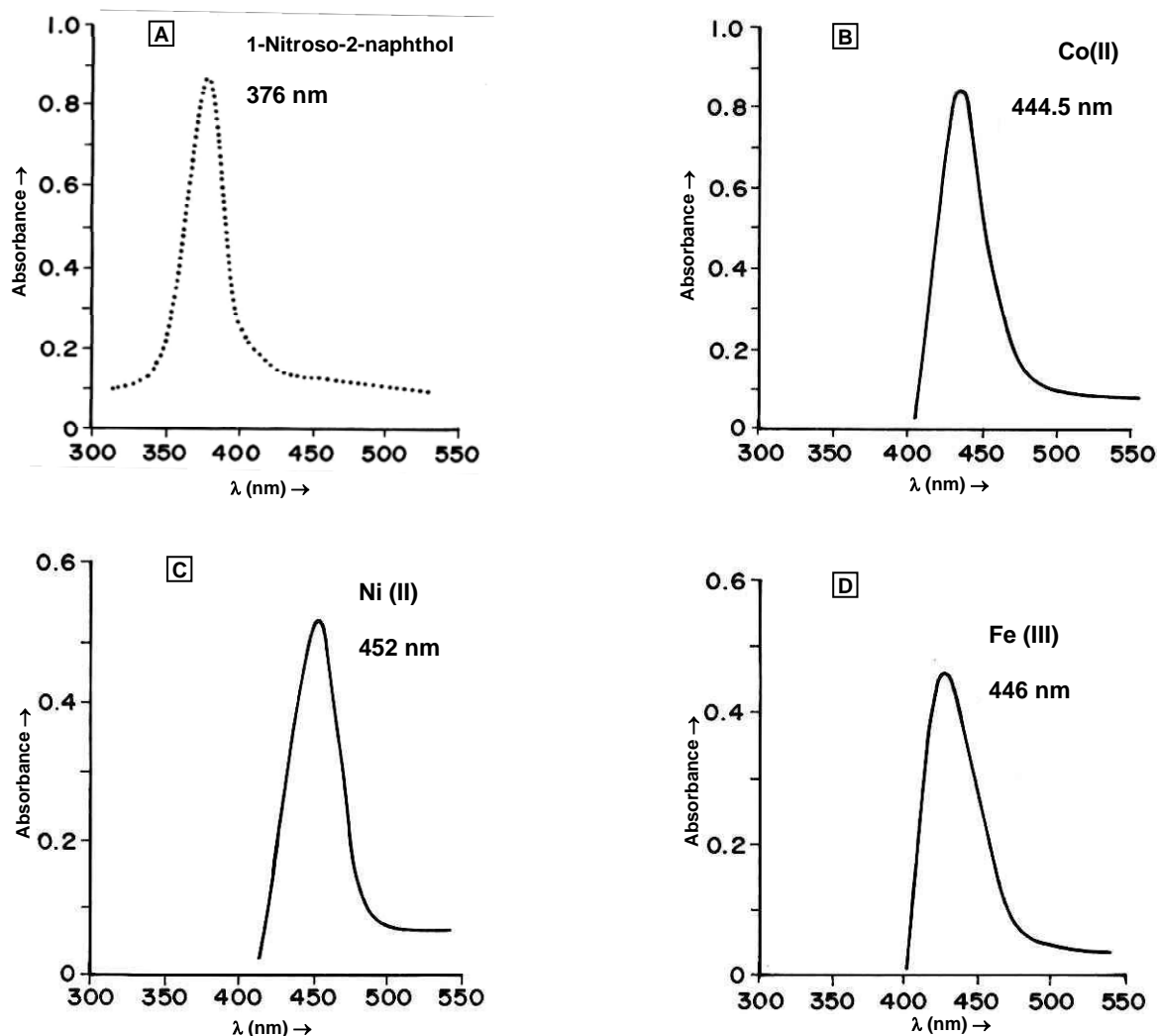


Figure 2. Absorption spectra of metal ions with 1-nitroso-2-naphthol in 5% Tween 40. (A) 1-nitroso-2-naphthol $185 \mu\text{g ml}^{-1}$, (B) $[\text{Co(II)}] 3 \mu\text{g ml}^{-1}$, (C) $[\text{Ni(II)}] 3 \mu\text{g ml}^{-1}$, (D) $[\text{Fe(III)}] 4 \mu\text{g ml}^{-1}$.

complexes, it is found that the maximum absorption varies with the metal. The optimum pH values for each metal ion used in the present study are: 1 for Fe(III), 8 for Ni(II) pH and 5 for Co(II) pH. Fig. 5 depicts the calibration curves constructed at their respective absorption maxima and are linear over the range of 0.12-3.0, 0.5-4.0 and 0.5-4.0 $\mu\text{g ml}^{-1}$ for Co(II), Ni(II) and Fe(III) respectively. This shows an improvement over the results reported for similar study elsewhere [11].

The sensitivity of the present spectrophotometric method expressed as molar absorptivity and Sandell's sensitivity for each metal ion, are given in Table 1. The molar absorptivity $\epsilon_{\text{max}} \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ is of the order $\text{Co(II)} > \text{Fe(III)} > \text{Ni(II)}$. This shows an increase in value from that obtained with solvent extraction of these metal complexes except for Ni (II) where the molar absorptivity slightly

decreased (Table 1). The Sandell's sensitivity values are in the order of Co(II) (3.6 ng cm^{-2}), Ni(II) (5.8 ng cm^{-2}) and Fe(III) (7.9 ng cm^{-2}). As shown in the same Table the detection limits obtained for Co(II), Ni(II) and Fe(III) have significantly improved than the results reported using Tween 80 by Jinsook et al. [11]. It is cleared from Table 1 that these metals can be determined at a fairly low detection limits than those of the atomic absorption spectrometry under usual conditions.

3.1 Composition of the complex

Composition of the complex formed under experimental conditions is investigated by job's method of continuous variations. From Fig. 6 it can be inferred that metal: ligand ratio in case of Ni(II) is 1:2, whereas in case of Co(II) and Fe(III) it is 1:3.

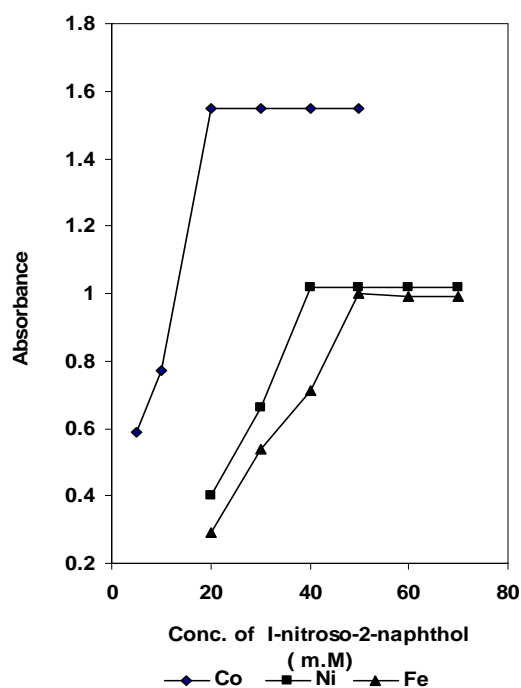


Figure 3. Effect of amounts of 1-Nitroso-2-naphthol on the absorbance of metal ions.

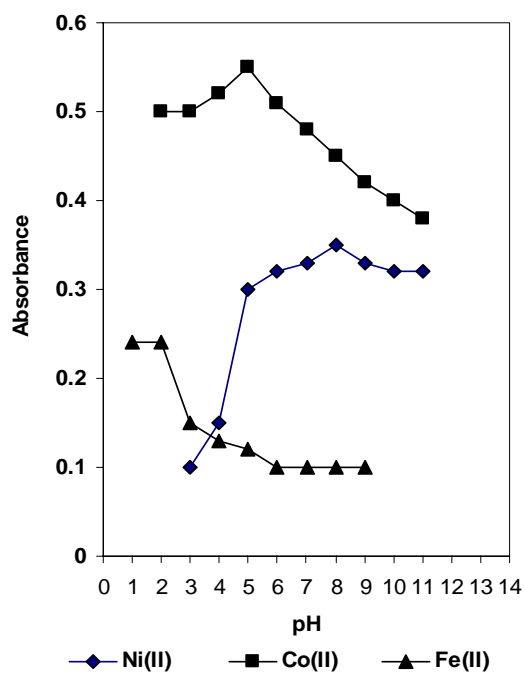


Figure 4. Effect of pH on the absorbance 1-Nitroso-2-naphthol complexes of metal ions ($2.0 \mu\text{g ml}^{-1}$).

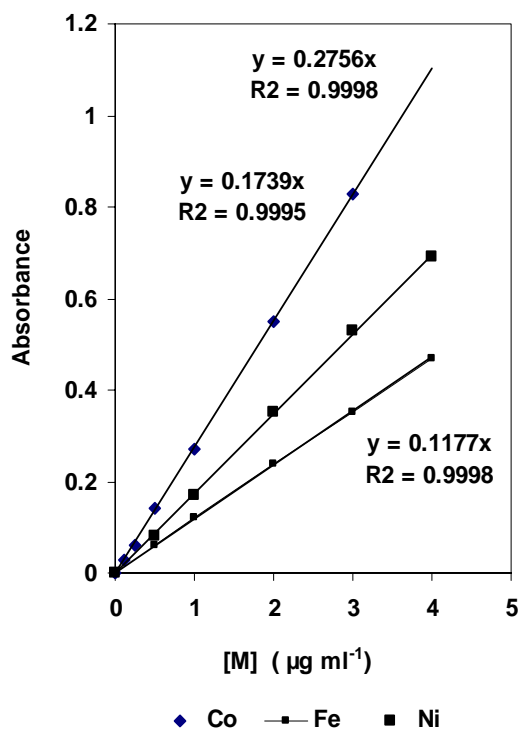


Figure 5. Calibration curves for metal ions with 1-Nitroso-2-naphthol complexes.

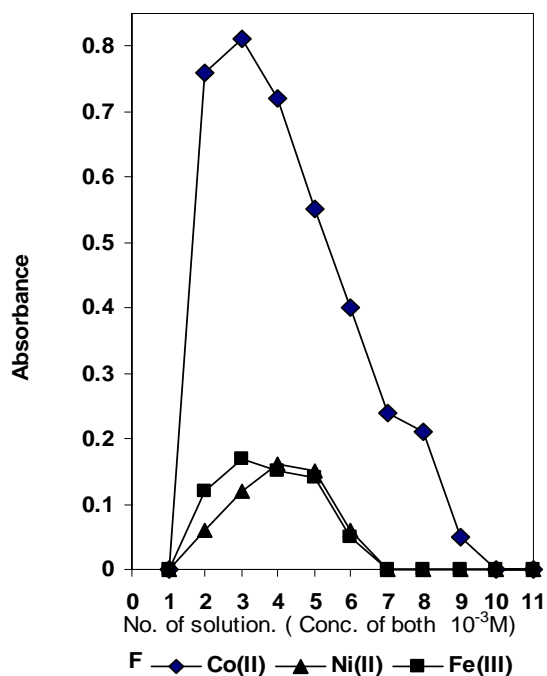


Figure 6. Job's plot of metal : ligand ratio.

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

Metal ions	Amount added ($\mu\text{g ml}^{-1}$)	Amount found ($\mu\text{g ml}^{-1}$)	Recovery (%)
Co(II)	1	0.99	99 \pm 1
Ni(II)	1	0.97	97 \pm 3
Fe(III)	1	0.98	98 \pm 2

At 95%, n = 6

Table 4. Determination of Fe(III), Ni(II) and Co(II) ions in industrial effluents and pharmaceutical samples.

Sample	Metal ions determined			
	Present method		AAS	
Industrial waste water from Kotri Site	Iron ($\mu\text{g ml}^{-1}$)	Nickel ($\mu\text{g ml}^{-1}$)	Iron ($\mu\text{g ml}^{-1}$)	Nickel ($\mu\text{g ml}^{-1}$)
	0.45 (3.9)	0.40 (2.0)	0.47 (0.9)	0.41 (0.8)
Theragran-M tablet (Bristol-Myers Squibb Pak.)	Cobalt ($\mu\text{g/tab}$)	Iron (mg/tab)	Cobalt($\mu\text{g/tab}$)	Iron (mg/tab)
	39.0 (3.6)	26.7 (4.8)	39.1 (1.4)	(26.6) (1.1)

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

3.2 Interferences by foreign ions

Interference in the determination of the Co(II), Ni(II) and Fe(III) with 1-nitroso-2-naphthol in the presence of 5 % Tween 40 is studied. The results are shown in Table 2. The metal salts, KSCN, KClO₃ and Na₂tartrate did not normally interfere until their amount reached 1000 $\mu\text{g ml}^{-1}$. It is found that the interfering effects among analyte ions Fe(III), Co(II), Ni(II), Cd(II), Cr(IV), Pb(II), Al(III) and Cu(II) are serious than by other ions. Fe(III) complex strongly absorbs at pH 1. Fe(III) could be determined by adjusting the pH value only. For a mixed solution of Co(II) and Cu(II), ammonia is used as a masking agent for Cu(II), oxalate is used for Co(II), thus interfering effects or these metal ions were completely eliminated.

3.3 Validation of method

The proposed method was verified by % recovery test using standard addition technique. The results were compared with those obtained

from AAS and were found in good agreement. Table 4 shows the results, which were verified by t-test at 95% confidence level. No significant difference was noted.

4 Application

The proposed spectrophotometric method was applied to the determination of iron(III), nickel(II) and cobalt(II) in pharmaceutical and industrial effluent samples. The results are shown in Table 4.

5 Conclusions

Determination of trace amounts of iron(III), nickel(II) and cobalt(II) in aqueous media can be carried out directly using 1-nitroso-2-naphthol in non-ionic micellar media of 5 % Tween 40. The method is simple and rapid with greater sensitivity, better selectivity, improved precision and replaces extraction with toxic organic solvents. Fe(III), Ni(II) and Co(II) contents in industrial effluents and pharmaceuticals are in agreement with the values obtained by atomic absorption spectrometry.

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