

## Spectrophotometric Determination of Nickel in Steel with Di-2-pyridylmethanone 2-Thiophenecarboxylic Hydrazone

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**Abstract** : Di-2-pyridylmethanone 2-thiophenecarboxylic hydrazone(DPMTCH) was synthesized and used as a chromogenic reagent in the spectrophotometric determination of nickel in steel. The proton disc spectrophotometrically, were  $pK_{a1} = 2.66$  and  $pK_{a2} = 10.98$   $\mu = 0.5(\text{NaCl})$ . Nickel(II) reacts with DPMTCH to form a 1:2 metal-2-ligand ratio complex, the xylene solution of which has an absorption maximum at 417 nm. Beer's law is obeyed over the range 0-1.17 mg  $\text{ml}^{-1}$  of nickel(II). The molar absorptivity of the nickel(II) complex is  $4.17 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The precision of the method was estimated for 4.7 mg of nickel(II), the coefficient of variation for 15 replicate determinations being 0.34 %.

**Keywords** : Nickel determination, Steel, Spectrophotometry, Di-2-pyridylmethanone 2-Thiophenecarboxylic Hydrazone, Solvent extraction.

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### 1. Introduction

In previous papers we have proposed the use of substituted hydrazone ligands, containing the functionality  $-\text{N}=\text{C}\cdot\text{C}=\text{NNH}\cdot\text{C}(=\text{O})-$ , as relatively selective spectrophotometric reagents for certain

metal ions including palladium(II)[1], iron(II)[2], and cobalt(II)[3]. In the present article are described the deprotonation constants of a newly synthesized hydrazone ligand, di-2-

di-2-pyridylmethanone 2-thiophenecarboxylic hydrazone(DPMTCH), in aqueous 40%(v/v) ethanol solution and the extractive spectrophotometric determination of the determination of nickel in some steel samples.

## 2. Experimental

### 2.1 Reagents

DPMTCH. The ligand was synthesized by refluxing a mixture of di-2-pyridyl ketone (0.03 mol) and 2-thiophenecarboxylic hydrazine(0.03 mol) in ethanol with a few drops of glacial acetic acid for about 4h. The crude compound which separated on cooling was recrystallized from ethanol to give lemon-yellow crystals, m. p. 150-151°C. The ligand was identified by infrared spectroscopy, Elemental analysis gave the results: found, C 62.29%, H 3.69%, N 18.23%, O 4.97%, S 10.68%; calculated for C 62.32%, H 3.92%, N 18.17%, O 5.19%, S 10.40%. A  $2 \times 10^{-3}$  M DPMTCH solution was prepared in ethanol. This solution was stable for at least a month, if kept in the dark.

Nickel( II ) solution. Nickel( II ) standards were obtained by dilution of 0.01 M nickel(II) nitrate stock solution prepared from pure(99.999%) metallic nickel. All other reagents were of analytical-reagent grade and were used as received.

### 2.2 Apparatus

Hitachi Model U-3410 double-beam spectrophotometer was used for absorbency measurements with matched 1.00-cm quartz cells. A Toa Dempa HM-5B digital pH meter was used for pH adjustments.

### 2.3 General procedure

Into a 50 ml separating funnel, transfer a suitable aliquot of sample solution containing up to 11.7 µg of nickel(II) , add 4 ml of  $2 \times 10^{-3}$  M DPMTCH in ethanol and 3 ml of 1 M acetate buffer solution adjusted to pH 6.0, and dilute to 25 ml with distilled water. Extract with 10 ml of xylene for 5 min and measure the absorbance of the xylene extract at 417 nm against a reagent blank.

## 3. Results and Discussion

### 3.1 Proton dissociation of DPMTCH

The ligand, DPMTCH, is almost insoluble in water but soluble in common organic solvents. Fig.1 shows the absorption spectra of DPMTCH in aqueous 40%(v/v) ethanol at different pH values. The proton dissociation constants were estimated at  $\mu=0.5$ (NaCl) from the equation

$$\epsilon = \frac{\epsilon_{H_2L} [H^+]^2 + \epsilon_{HL} K_{a1} [H^+] + \epsilon_L K_{a1} K_{a2}}{[H^+]^2 + K_{a1} [H^+] + K_{a1} K_{a2}}$$

by means of a personal computer(NEC 9801vm) by applying the least squares treatment, where  $\epsilon_{H_2L}$ ,  $\epsilon_{HL}$  and  $\epsilon_L$  are the molar absorptivities of the species represented by subscripts, respectively ;  $\epsilon$  is the apparent molar absorptivity of the solution at a selected wavelength.

The values obtained were  $pK_{a1}=2.66$ (one of the two pyridine nitrogens) and  $pK_{a2}=10.98$ (imino group existing in equilibrium with the tautomeric enol form).

### 3.2 Reactivity of DPMTCH

The reactivities of DPMTCH with various metal ions at pH 3,6 and 9 are summarized in

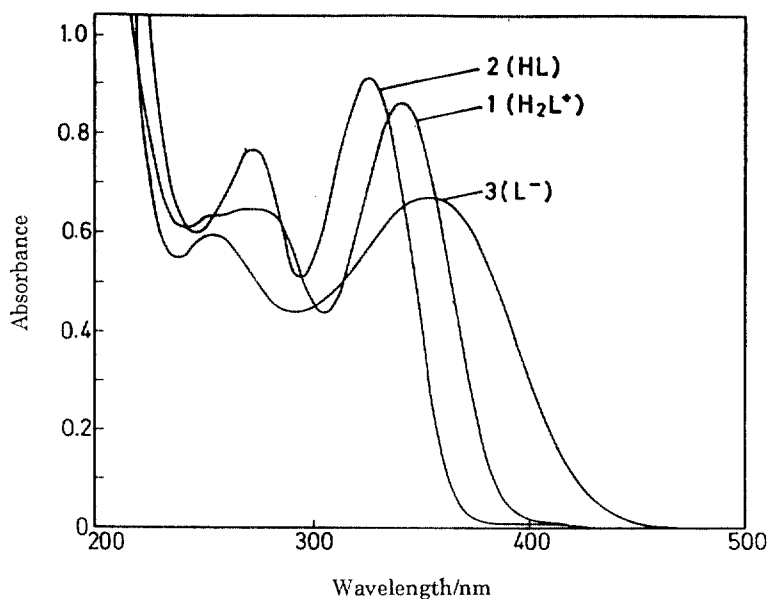


Fig. 1 Absorption spectra of DPMTCH in aqueous 40 % (v/v) ethanol solution at  $\mu = 0.5(\text{NaCl})$ . Concentration of DPMTCH is  $4 \times 10^{-5} \text{ M}$ . (1) pH 1.88; (2) pH 7.11; (3) pH 12.59.

Table 1 Reactivity DPMTCH with different metal ions

Metal ion	pH 3		pH 6		pH 9	
	$\lambda \text{ max/nm}$	$\epsilon / \text{l mol}^{-1} \text{ cm}^{-1}$	$\lambda \text{ max/nm}$	$\epsilon / \text{l mol}^{-1} \text{ cm}^{-1}$	$\lambda \text{ max/nm}$	$\epsilon / \text{l mol}^{-1} \text{ cm}^{-1}$
Fe(II)	-	-	681	14,800	681	14,800
	-	-	384	22,100	383	22,500
Fe(III)	392	350	393	1,100	394	6,000
Co(II)	382	780	403	22,500	405	29,800
Ni(II)	417	28,700	417	47,100	417	47,100
Cu(II)	415	11,600	411	45,600	411	51,900
Zn(II)	-	-	408	49,200	408	54,800
Pd(II)	458	5,400	458	9,100	459	1,300
Cd(II)	-	-	-	-	407	31,400
Mn(II)	-	-	-	-	407	19,300
Hg(II)	-	-	411	2,600	408	34,500
Pb(II)	-	-	-	-	417	950
V(V)	432	10,000	431	950	-	-

*Table 1.* DPMTCH is found to react with nickel(II), copper(II) and zinc(II) in neutral and weakly basic media to give colored uncharged complexes with significantly high molar absorptivities.

### 3.3 Characteristics of the nickel(II) complex

Nickel(II) ion forms a water-insoluble complex with DPMTCH, the complex formation being occurred over the pH range 4.5-12.0. The complex formed is readily extracted into organic solvents, such as carbon tetrachloride ( $\lambda_{\max}$ : 419 nm;  $\epsilon_{419\text{nm}}$ :  $4.88 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), xylene ( $\lambda_{\max}$ : 417 nm;  $\epsilon_{417\text{nm}}$ :  $4.71 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), toluene ( $\lambda_{\max}$ : 417 nm;  $\epsilon_{417\text{nm}}$ :  $4.65 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), chloroform ( $\lambda_{\max}$ : 410 nm;  $\epsilon_{410\text{nm}}$ :  $4.62 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), chlorobenzene, benzene, 1,2-dichloroethane, methyl isobutyl ketone, 4-methyl-2-pentanone, n-butyl acetate

and nitrobenzene. Although the highest absorbance of the nickel(II) complex was obtained in carbon tetrachloride, xylene was chosen as the extractant because of the high toxicity of the former. The species of interest has a wavelength of maximum absorption at 417 nm in this solvent (Fig. 2).

### 3.4 Effect of pH

The effect of the pH of the aqueous phase on the absorbance of the organic phase was studied with solutions containing 4.7 mg of nickel (Fig. 3). A maximum and constant absorbance is obtained over the pH range 4.5-12.0. Further absorbance measurements were made at pH 6.0.

### 3.5 Effect of amount of DPMTCH

Varying amounts of  $2 \times 10^{-3} \text{ M}$  DPMTCH solution in ethanol were added to a solution containing 4.7  $\mu\text{g}$  of nickel(II) and the complex was extracted according to the general procedure.

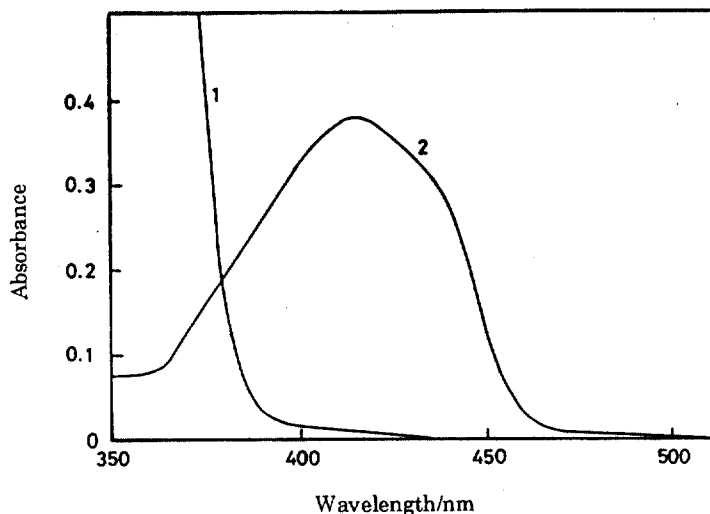


Fig. 2. Absorption spectra of DPMTCH and its Ni(II) complex extracted into xylene. (1) reagent blank vs. xylene; (2) Ni(II) complex vs. reagent blank; Ni(II) taken. 4.70  $\mu\text{g}$ ; pH, 6.0; DPMTCH,  $2 \times 10^{-3} \text{ M}$  4ml.

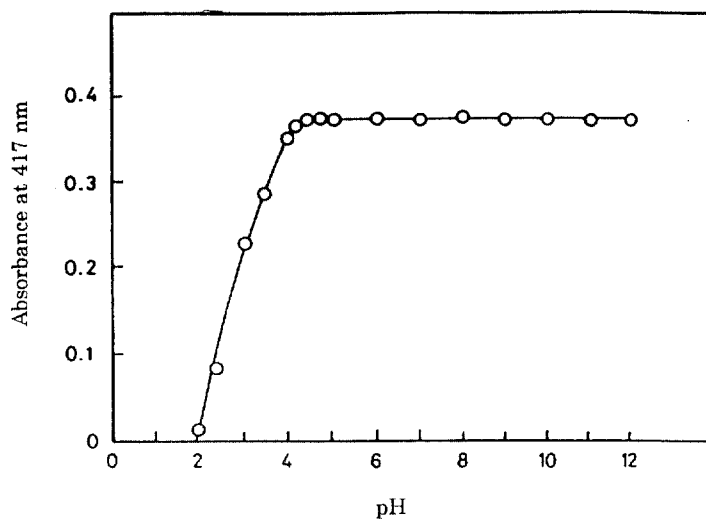


Fig. 3 Effect of pH  
Ni(II), 4.70  $\mu\text{g}$ ; DPMTCH,  $2 \times 10^{-3}$  M 4 ml.

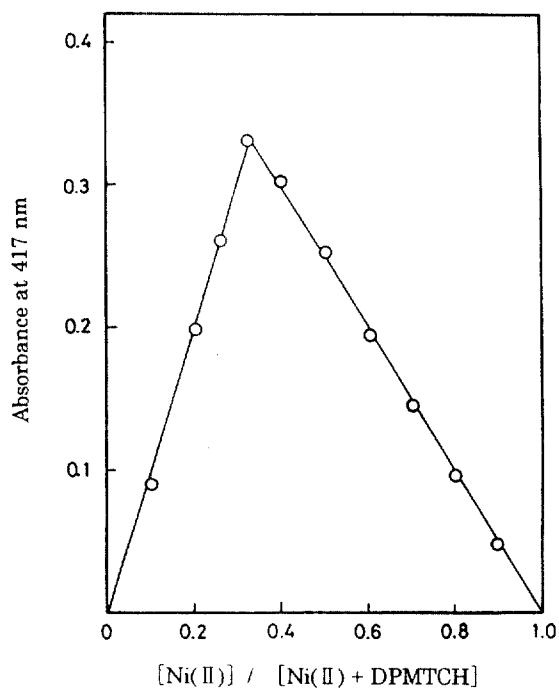


Fig. 4. Continuous variation plot for Ni(II)-DPMTCH system.  
[Ni(II)] + [DPMTCH],  $2 \times 10^{-5}$  M; pH, 6.0.

A reasonably constant absorbance was obtained for 0.4-10.1 ml of the reagent solution. Four milliliters the reagent solution was therefore used throughout the experiment.

### 3.6 Conformance to Beer's law

A calibration curve for the determination of nickel(II) was prepared under the optimum conditions established. A good linear relationship was obtained between the absorbance of the organic phase and the concentration of nickel(II) up to about  $2 \times 10^{-7}$

M ( $1.17 \mu\text{g ml}^{-1}$ ). The molar absorptivity of the extracted species was calculated to be  $4.71 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 417 nm. The Sandell sensitivity for an absorbance of 0.001 is  $1.2 \text{ ng cm}^{-2}$  at this wavelength. The precision of the method was estimated for  $4.7 \mu\text{g}$  of nickel(II), the coefficient of variation for 15 replicate determinations being 0.34%.

Job's method of composition of the complex continuous variations was used to evaluate the stoichiometric ratio of metal to ligand in the

Table 2 Effect of foreign ions on determination of 11.7 mg nickel(II)

Tolerance limit ( [Ion] / [Ni(II)] )	
$\leq 10,000$	F <sup>-</sup> , I <sup>-</sup> , Br <sup>-</sup> , SCN <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , tartrate, urea, thiourea, L-ascorbic acid
$\leq 5,000$	P <sub>2</sub> O <sub>7</sub> <sup>4+</sup>
$\leq 1,000$	citrate
$\leq 500$	PO <sub>4</sub> <sup>3-</sup>
$\leq 100$	Li <sup>+</sup> , Ag <sup>+</sup> , Cs <sup>+</sup> , Tl <sup>+</sup> , Be <sup>2+</sup> , Mg <sup>2+a)</sup> (50), Ca <sup>2+</sup> , Mn <sup>2+b)</sup> (25), Sr <sup>2+</sup> , Pd <sup>2+a,b)</sup> (0) Cd <sup>2+b)</sup> (0), Ba <sup>2+</sup> , Hg <sup>2+a,d,e)</sup> (0), Pb <sup>2+a,b)</sup> (1), Al <sup>3+a)</sup> (25), Cr <sup>3+a)</sup> (50), Y <sup>3+</sup> , Rh <sup>3+</sup> , La <sup>3+</sup> , Ti <sup>4+</sup> , Zr <sup>4+</sup> , Pt <sup>4+</sup> , Cr <sup>6+</sup> , Mo <sup>6+</sup> , W <sup>6+</sup>
$\leq 90$	Ga <sup>3+</sup>
$\leq 50$	Fe <sup>3+f)</sup> (0), Ce <sup>3+</sup> , Au <sup>3+c)</sup> (0), V <sup>5+</sup> , U <sup>6+</sup>
$\leq 10$	Sn <sup>4+</sup>
$\leq 5$	Sb <sup>3+</sup> , Bi <sup>3+</sup> , Os <sup>8+</sup>
$\leq 0\sim 1$	Fe <sup>2+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ir <sup>3+</sup> , CN <sup>-</sup> , EDTA

Numerical values in parentheses denote tolerance limit in the absence of masking agent.

- 0.4 ml of 0.2 M citric acid was added.
- 4 ml of 0.2 M tartaric acid was added.
- 4 ml of 0.2 M potassium thiocyanate was added.
- 4 ml of 0.2 M sodium thiosulfate was added.
- 4 ml of 0.2 M potassium iodide was added.
- 4 ml of 0.2 M potassium fluoride was added.

steel samples. The sample was dissolved as follows : To a 0.1 g amount of sample in a Erlenmeyer flask was added 30 ml of aqua regia. The mixture was heated on a hot plate until the decomposition was complete. After addition of concentrated perchloric acid(15 ml) the mixture was heated again and evaporated almost to dryness. The residue was then dissolved in 50 ml of water. The iron(III) in the solution was removed by extracting it from 7-8 M hydrochloric acid solution with MIBK [4]. The aqueous phase was evaporated almost to dryness, and the residue was dissolved in water, which was followed by the dilution to 250 ml with water. A suitable aliquot of this solution was taken and analyzed for nickel according to the general procedure. The results given in Table 3 are in reasonable agreement with the certified values.

#### 4. Conclusion

The acid-base characteristic of a newly synthesised hydroxy ligand, DPMTCH, was investigated spectrophotometrically. The optimum conditions for the extractive spectrophotometric determination of nickel(II)

with this reagent were established, which allowed the determination of up to 1.17 ppm of nickel(II). The proposed method was satisfactorily applied to the determination of nickel in standard reference steel samples.

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