

# A Rapid Differential Method for Simultaneous Spectrophotometric Determination of Nickel(II) and Cobalt(II) by a Novel Organic Reagent N-(2-thienylmethylene)phenyl hydrazine

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**Summary:** A novel organic reagent N-(2-thienylmethylene) phenyl hydrazine is synthesised and used as a useful chromogenic reagent for rapid simultaneous determination of nickel(II) and cobalt(II) by differential spectrophotometry. This method allows the determination of 0.2-1.23 ppm of nickel(II) and 0.25-1.5 ppm of cobalt(II) in mixtures with good precision and accuracy. It has advantages of simplicity, less time consumption and no prior separations etc.

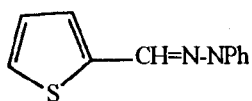
## Introduction

Among many diamine ligands the hydrazines and substituted hydrazines are generally known [1-3] to be good metallochromic reagents. Many heteroazo compounds are also, utilised in environmental analysis [4,5], organic analysis [6], pharmaceutical analysis [7,8] and for the determination of inorganic ions [9-12]. Another class of such a compound, Schiff-bases continue to occupy a prominent position [13-15] as potential ligand in metallorganic chemistry but their

significant metallochromic properties have not been well explored. As a part of our ongoing research program concerning the synthesis and studies of ligational properties of such Schiff-base ligands, we have already studied [16-18] and used Schiff-base ligands as metallochromic reagent and continuing the same, now wish to report herein the utility of such a class of reagent (1) for simultaneous determination of Ni(II) and Co(II).

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(I)

### Results and Discussion

The organic reagent (I) is a stable compound and could be indefinitely stored at room temperature both as a solid as well as a solution. It contains suitably placed donor atoms, which are used for the complex formation reaction.

#### Absorption spectra

In the normal UV-visible spectra the analytical features due to nickel(II) complex (max. absorb at 490 nm) and cobalt(II) complex (max. absorb at 510 nm) showed appreciable overlap. Due to this overlapping character spectrophotometric determination of one in the presence of another metal becomes difficult. Therefore, differential spectrophotometric technique was adopted and successfully used for their determination in the presence of each other. Representative spectra of the complexes are shown in Figure 1. It was found that at room temperature and pH 8.0, the complexes of Ni(II) and Co(II) with organic reagent (I) required a distinct setting period. For reagent (I) complex of Ni(II) the absorbance at 490 nm attained a steady value after 5 minutes and remained at least for 1 h. Similarly, for a Co(II) complex the absorbance at

510 nm attained a steady value after 30 minutes. In order to determine both metals in a mixture, it is therefore, suggested that the metal complexes be set for 30 minutes at room temperature or kept for 10 minutes at 50°C before measurement.

#### Method of determination

For simultaneous determination, fixed concentration of organic reagent and varied Co(II) and Ni(II) concentrations was used. The absorption spectra (Fig. 1) showed the distance ( $\Delta_1$ ) between the maximum at 490 nm and the minimum at 485 nm corresponding to the concentration of Ni(II). Similarly, ( $\Delta_2$ ) and ( $\Delta_3$ ) corresponded to the concentrations of Ni(II) and Co(II) respectively, in pure solutions. The distance ( $\Delta_4$ ) [ $\Delta_4 = \Delta_3 - \Delta_2$ ] between the maximum/minimum and the base line at 515 nm corresponded to the concentration of Co(II) in mixture. Calibration graphs were obtained by plotting  $\Delta_1$  and  $\Delta_2$  values vs Ni(II) concentration and  $\Delta_3$  [ $\Delta_3 = \Delta_2 + \Delta_4$ ] vs Co(II) concentration (Figure 2).

Validity of the method was tested by investigating mixture of samples containing both Co(II) and Ni(II) ions in variable proportions [10-60  $\mu\text{g}$  of Ni(II) and 12-50  $\mu\text{g}$  of Co(II)]. The results of determination showed that the nickel and cobalt were simultaneously determined for samples containing 0.5 ppm nickel(II) and 0.5 ppm cobalt(II) complexes. The standard deviations are 0.01 ppm for nickel(II) and 0.012 ppm for cobalt(II) whereas the

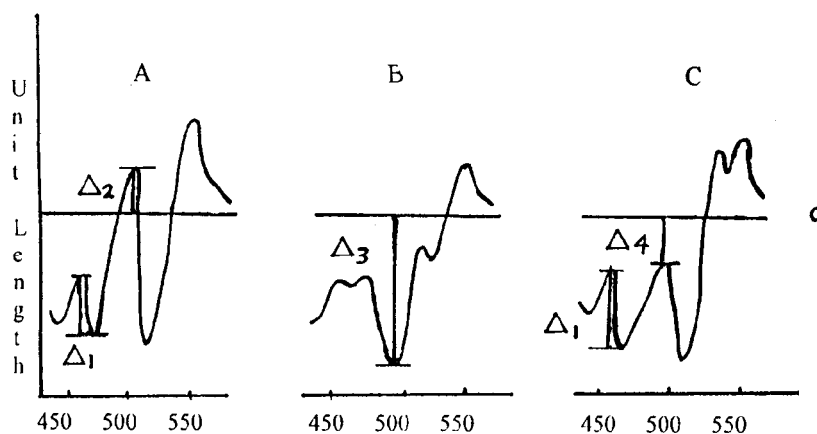


Fig. 1: Absorption spectra of Metal(II) complexes (A) Ni(II) complex (B) Co(II) complex (C) Mixture of Ni(II) and Co(II) complex.

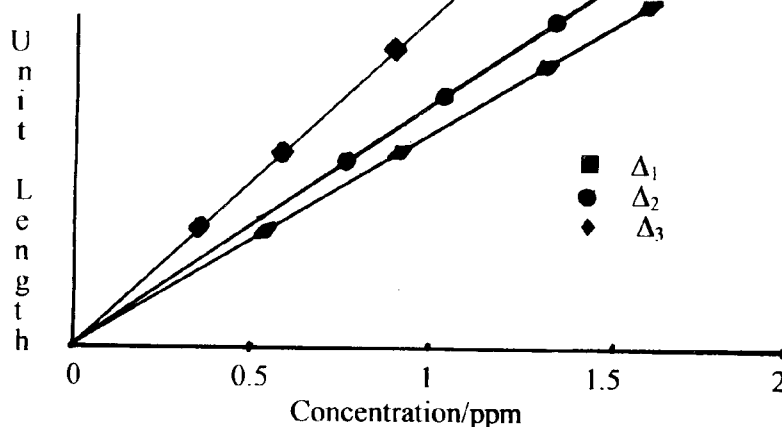


Fig. 2: Calibration graphs for Ni(II) and Co(II).

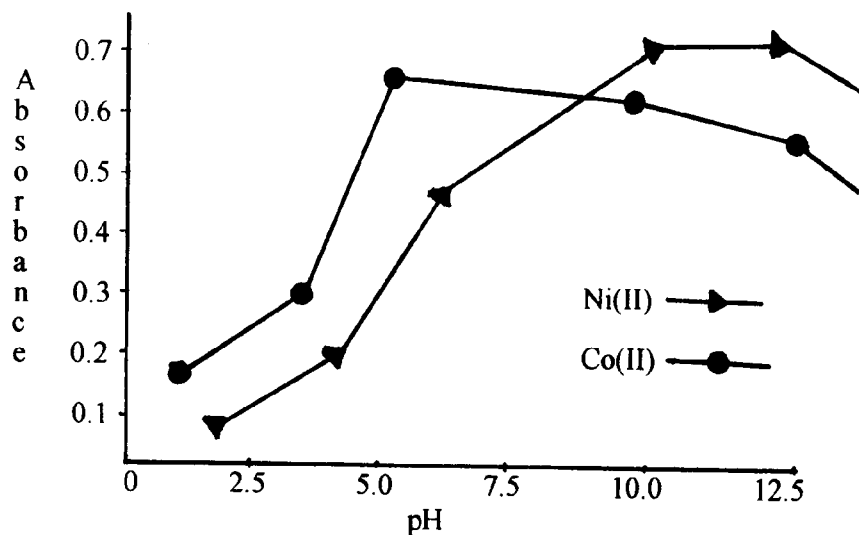


Fig. 3: Absorbance of metal(II) complexes at varied pH values.

relative standard deviations are 2% for nickel(II) and 2.3% for cobalt(II).

#### Effect of pH

Absorbance of metal complexes is affected by pH. Figure 3 shows that a constant zone is observed in moderately basic media and the use of ammonia-ammonium chloride buffer (pH 8.0) is considered to be the most convenient and suitable in this procedure.

Figure 4 shows absorbance of nickel(II) and cobalt(II) complexes measured at varied molar ratio. At room temperature, pH 8.0, fixed concentration of reagent (I) solution and varied concentration of metal (II) complexes, the absorbance of nickel(II) complex was measured at 490 nm and that of cobalt(II) complex solution at 510 nm. Figure 3 showed that both the stoichiometric ratios of nickel(II) and cobalt(II) complexes were found to be one to two. These results inturn indicated that the

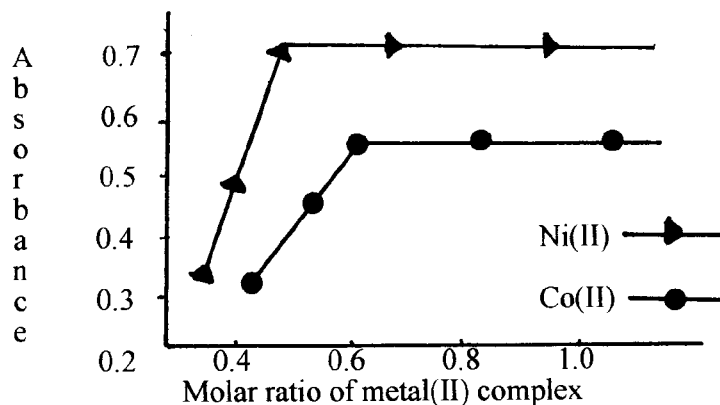


Fig. 4: Absorbance of metal(II) complexes at varied molar ratio

concentration of reagent (I) is twice to that of the total concentration of metal (II) in the test solution.

#### Effect of foreign ions

In order to assess the possible application of the reaction, the effect of foreign ions on simultaneous spectrophotometric determination of 0.5 ppm of nickel and 0.5 ppm of cobalt(II) was studied by first applying the recommended procedure to solutions containing 500-fold concentration ratio of interfering ion to nickel(II). If interference occurred, the ratio was diminished until interference was ceased. The criterion of interference was deviation greater than  $\pm 5\%$  from the concentration of nickel(II) and cobalt(II) taken. For this purpose almost eighteen foreign ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^+$ ,  $\text{Mg}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were tested and of those  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  interfered significantly ( $>5\%$ ) in simultaneous determination of both nickel(II) and cobalt(II) ions whereas chromium only interfered ( $>5\%$ ) in the determination of cobalt(II).

#### Experimental

Chromagenic reagent (I) was prepared, characterized as reported [19] earlier by us. Absorption spectra were recorded on a U-2000 spectrophotometer with 1 cm cells. Philips PW 9409 digital pH meter was used for the measurement of pH. All chemical used were analytical reagent grade.

#### Standard solutions

A standard solution of Ni(II) and Co(II) was prepared as their chloride respectively in distilled water and were standardised [20] with EDTA.

Organic reagent solution (0.03%) was prepared in ethanol

For the preparation of buffer solution (pH 8.0) ammonium chloride (6.0 g) and aqueous ammonia (15 M, 1.0 mL) were mixed together and then diluting to 100 mL with distilled water.

#### Recommended procedure

To a calibrated flask (50 mL) was added sample solutions (upto 30 mL) containing nickel (10-60  $\mu\text{g}$ ) and cobalt (12-45  $\mu\text{g}$ ), organic reagent (I) solution (0.03%, 5 mL) and buffer solution (pH 8.0, 5 mL). The volume was made up to the mark with distilled water, warmed for 10 minutes at  $50^\circ\text{C}$  and measured at 490 and 510 nm respectively.

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