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HIGHLY SELECTIVE SECOND ORDER DERIVATIVE SPECTROPHOTOMETRY FOR SIMULTANEOUS DETERMINATION OF NICKEL (II) AND COBALT (II) USING 2-KETOBUTYRIC ACID THIOSEMICARBAZONE

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ABSTRACT

A simple and highly selective second order derivative spectrophotometric method is proposed for the simultaneous determination of Ni(II) and Co(II) using 2-ketobutyric acid thiosemicarbazone (KBAT) as a sensitive complexing reagent. KBAT forms green and pink color complexes with nickel and cobalt at pH range of 8-11 and 5-10 respectively. Molar absorptivities of Ni-KBAT (1.55×10^4 L cm^{-1} mol^{-1}) and Co-KBAT (1.03×10^4 L cm^{-1} mol^{-1}) were obtained at 330 nm, under optimum pH of 9.5. Calibration graphs for the individual determination by second order derivative spectrophotometry were obtained. Beer's law was obeyed at 369.8 nm for Ni(II) and 410 nm for Co (II) in the concentration ranges 0.30-2.34 μg mL^{-1} Ni and 0.33-2.65 μg mL^{-1}. The zero crossing point at 369.8 nm for nickel and the amplitude measurement at 410 nm for cobalt were employed in the simultaneous determinations. A large number of foreign ions do not interfere in the present method. The present simultaneous method is used for the determination of micro amounts of nickel and cobalt in various steel alloys and biological sample.

KEY WORDS: Derivative spectrophotometry, zero crossing, KBAT, cobalt, nickel

INTRODUCTION

Metal ions in general and transition metals in particular are found to play an important role in industry, agriculture, plant nutrition, biological activities of living beings and medicine. Evidence abound that direct spectrophotometric determination of metals in multicomponent systems is often complicated by interferences from formulation matrix and overlapping spectra. Various approaches aimed at solving this problem such as solving two simultaneous equations (Heilmayer,1943), using absorbance ratios at certain wavelengths (Glenn, 1960; Penarowski et al., 1961; Cho and Pernarowski, 1970), pH- induced differential spectrophotometry (Wahbi and Farghaly,1970), chemometric based techniques such as partial least squares (Wahbi, et al., 1982), orthogonal function methods (Glenn, 1963,; Wahbi and Barary,1981; Wahbi et al., 1982) have been widely used. However, these methods suffer from some limitations in simplicity, analytical time and economics. Spectrophotometric methods often suffer from limitations in sensitivity and selectivity, but are widely used due to the resulting experimental rapidity and simplicity. The selectivity and sensitivity of the spectrophotometric determination methods depend on the type of reaction and chromogenic reagent used (Sandell, 1959).

Derivative spectrophotometry is a useful means of resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixture using the zero crossing technique (Wahbi, *et al.* 1977; Fell, 1978; Bedair, *et al*., 1986, Eskandari, *et. al* 2006) Derivative spectrophotometric analysis of two component mixtures is also carried out without the need to solve simultaneous equations Thiosemicarbazones have found wide applications as analytical reagents. They form the most sensitive class of ligands commonly used as spectrophotometric reagents for the analysis of metal ions (Singh, *et al.,* 1978; Garg and Jain, 1988; Ramanjaneyulu, *et al*., 2002; Reddy, *et al*., 2003; Ramanjanelu, *et al*., 2003; Reddy,*et al*., 2004; Attah, 2004a,b; Kumar,*et.al*. 2007).

This paper reports on a simple, sensitive and highly selective second order derivative method for the simultaneous determination of nickel and cobalt using the zero crossing technique. The method is based on the formation of complexes of Co (II) and Ni (II) ions with 2- ketobutyric acid thiosemicarbazone.

MATERIALS AND METHODS

Reagents

All chemicals used were of analytical reagent grade, and the solutions were prepared with high purity water from a Millipore Milli-Q water purification system device.

Preparation of 2-ketobutyric acid thiosemicarbazone

The reagent (KBAT) was prepared by the reported procedure (Attah, 2004a)
A 5×10^{-3}M solution of KBAT in ethanol was used in the present studies

Cobalt (II) solution

Stock solution of Co(II) (1×10^{-2}M) was prepared by dissolving appropriate amount of cobaltous chloride in distilled water in a 250 mL volumetric flask. The Co(II) solution was standardized titrimetrically (Vogel, 1985)

Nickel (II) solution

Stock solution of Ni (II) (1×10^{-2}M) was prepared by dissolving appropriate amount of nickel chloride hexahydrate in distilled water in a 250 mL volumetric

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flask. The solution was standardized gravimetrically (Vogel, 1985)

Buffer solution

The buffer solution was prepared by mixing 0.4M glycine, 0.4M sodium chloride with 0.8M sodium hydroxide (pH 9.5) and checked using a pH meter.

Procedure for individual second derivative spectrophotometric determination of nickel and cobalt

5 ml of buffer solution of pH 9.5 was taken into 10 mL volumetric flasks and various aliquots of 2.0×10^{-4} M solutions of nickel and cobalt were added separately, 1.5 mL of 5×10^{-3} M KBAT was added to each flask. The contents were made up to the mark with distilled water. The absorbances of the solutions were measured at the wavelength range 325-420 nm against reagent blanks in the second derivative mode

Procedure for simultaneous second order derivative spectrophotometric determination of mixture of nickel and cobalt

Mixed solutions of 2×10^{-4} M Ni (II) and Co (II) were each treated with 5mL of buffer solutions of pH 9.5, 1.5mL of 5×10^{-3} M KBAT was added and the volume of the mixtures were adjusted in a 10 mL volumetric flask with distilled water. The absorbances of the mixtures were measured at the wavelength range 325-420 nm against reagent blank solutions in the second derivative mode.

Procedure for the analysis of alloy steel samples

A 0.5 g of steel sample was dissolved in a minimum amount of aqua- regia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling, 5-10 mL of 1:1 H_2O: H_2SO_4 mixture was added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue was dissolved in 20 mL of distilled water, filtered and the filtrate was made up to 100 mL with distilled water in a volumetric flask. The sample solution was appropriately diluted to obtain the concentration in the required range. 1mL of the sample solution was then mixed with 5 mL of buffer of pH 9.5 in a 10 mL volumetric flask and 1.5mL of 5×10^{-3}M KBAT added and made up to the mark with distilled water. The absorbances were measured at 369.8 nm for nickel and 410 nm for cobalt against a reagent blank in the second derivative mode. The concentrations of nickel and cobalt were obtained from predetermined calibration plots.

Procedure for the analysis of biological sample (tea leaf)

The tea leaf sample was obtained from Andhra Pradesh Agricultural Research Institute (APARI), Hyderabad, India. A 0.1 g of tea leaf sample was taken in a beaker and dissolved in 5 mL concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 100 ml with distilled water in a volumetric flask. An aliquot (1mL) of the sample solution was taken into a 10mL volumetric flask containing 5 mL of buffer solution of pH 9.5 and 1.5 mL of 5×10^{-3}M KBAT was added and the solution made up to the mark with distilled water. The absorbance was measured at 369.8 nm for nickel and 410 nm for cobalt in the second derivative mode. The concentration of nickel and cobalt were obtained from predetermined calibration plots.

Apparatus

The absorbance measurement was recorded using a Shimadzu UV-Visible scanning spectrophotometer (model UV-160A), fitted with 1cm quartz cells. The pH measurements were obtained using a Phillips digital pH meter (model LI 613).The second-order derivative spectra were recorded with a scan speed of 2400 nm min^{-1} using a slit width of 1 nm with nine degrees of freedom, in the required wavelength range (nm). The derivative amplitudes measured at the required wavelengths were plotted against amount of nickel (II) and cobalt (II) to obtain the calibration curves.

Statistical analysis

The data on the amounts of Ni (II) and Co (II) obtained were reported as the mean ± SD (standard deviation) for five determinations (Tables 1, 3, 4)

RESULTS AND DISCUSSION

Derivative spectra

Cobalt and nickel form pink and green color complexes with KBAT at pH 9.5 respectively (Attah, 2004a). The second derivative spectra of Ni(II)-KBAT and Co(II)-KBAT complexes at their optimum pH of 9.5 were recorded in the wavelength region 325-450 nm as shown in Figures 1-2. From the derivative spectrum (Fig.1), the Ni (II) complex shows a zero crossing point at 348.6 nm with maximum amplitude at 365 nm, although at higher concentration (2.344 μg mL^{-1}), a slight shift of about 4 nm with the zero crossing point is observed. For the Co (II) complex (Fig.2), two zero crossing points at 340.2 and 369.8 nm are observed with maximum derivative amplitude at 385 nm and sufficient amplitude for up to 420 nm. However, negative derivative amplitude also occurs between the two zero crossing points.

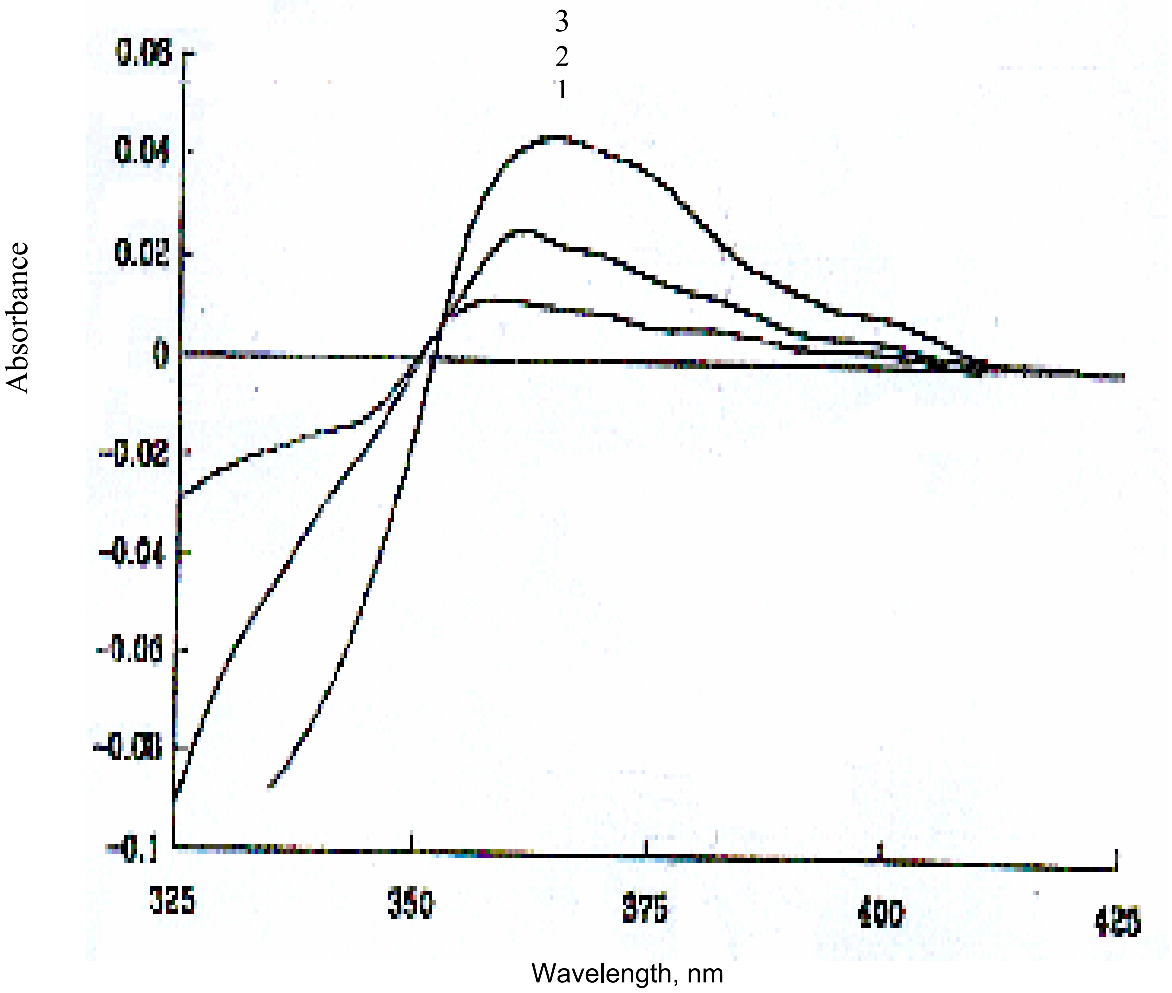

Fig. 1: Second order derivative spectra of Nickel (II)-KBAT against blank
Conditions: Ni (II) µg mL^{-1} : 1 = 1.172, 2 = 1.758, 3 = 2.344, pH = 9.5

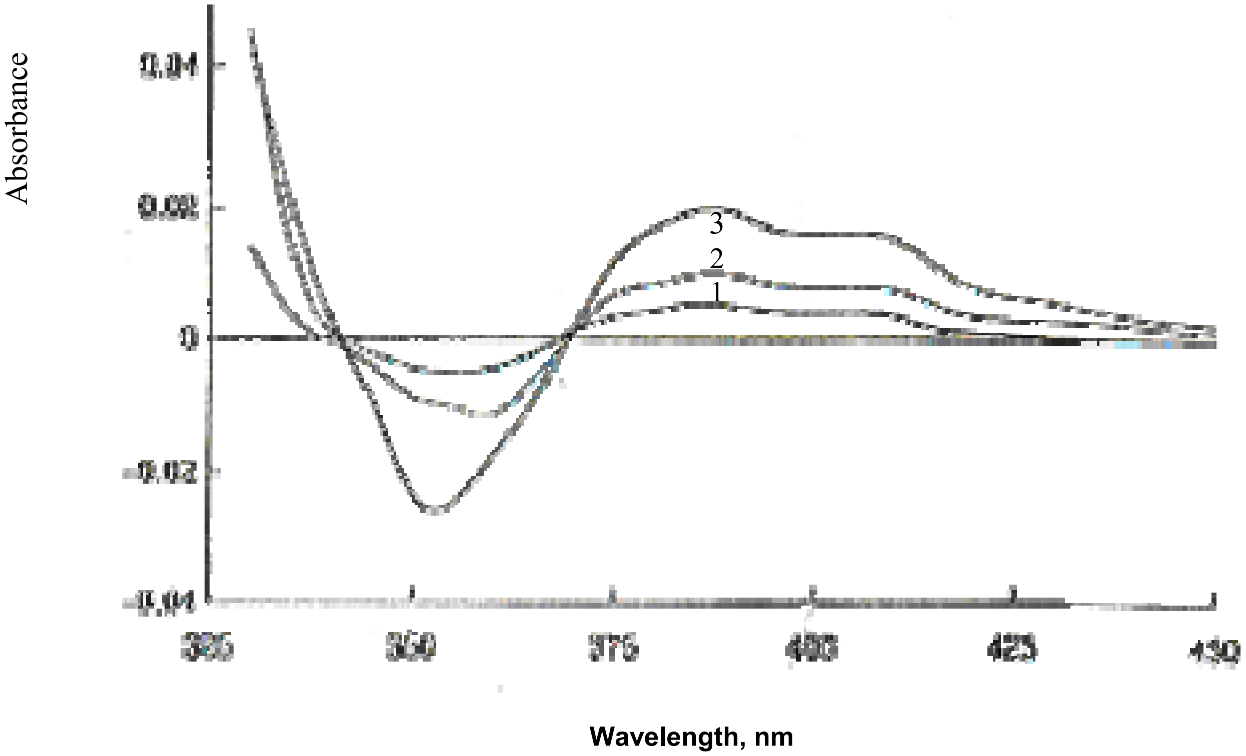

Fig. 2: Second order derivative spectra of Cobalt (II)-KBAT against blank
Conditions: Co (II) µg mL^{-1} : 1 = 1.172, 2 = 1.779, 3 = 2.360, pH = 9.5

Verification of Beer's law validity

Calibration curve for the individual determination of Ni (II) using the second derivative amplitude at 369.8 nm is presented in Fig.3.

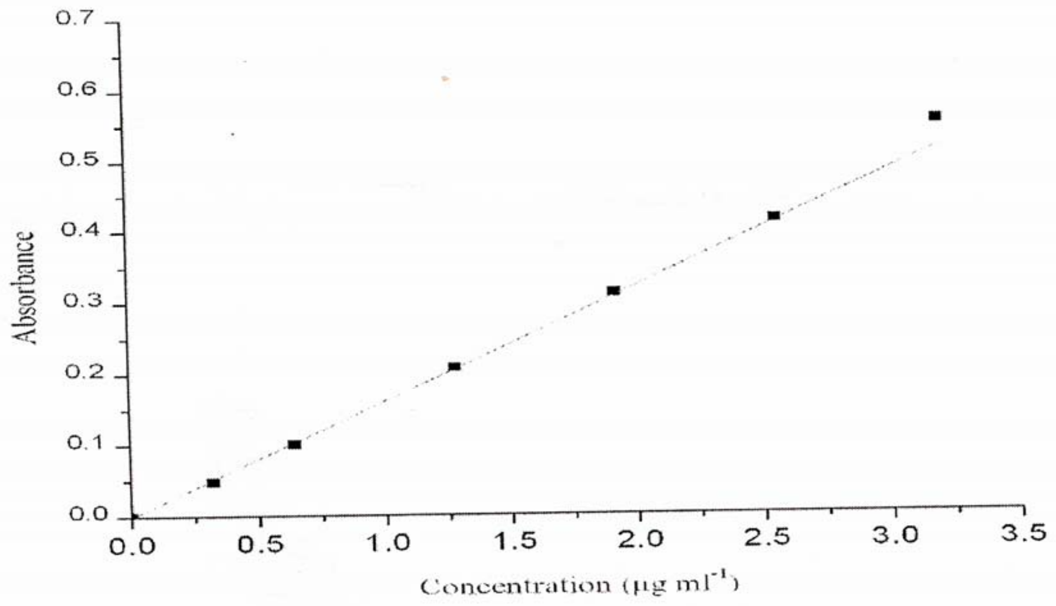

Fig. 3: Calibration graph for Ni (II) - KBAT complex by second derivative spectrum
$\lambda = 369.8$ nm, pH = 9.5

Simultaneous determination of Ni (II) and Co (II)

The results of mixtures of 0.585-2.340 μg mL^{-1} Ni (II) and 0.590-2.360 μg mL^{-1} Co (II) obtained from the second derivative spectra are presented in Table1.Table 2 shows the results of the effect of foreign ions on the determination of Ni (II) and Co (II). The results of the analysis of steel alloys are presented in Table 3, while that of the biological sample, tea leaf is presented in Table 4.

For this system, the derivative amplitudes vary with the concentrations of the metals. This will allow for the simultaneous determination of Ni(II) and Co(II) by measuring the derivative amplitudes of Ni (II) at 369.8 nm (Co zero cross) while Co (II) can be estimated at 410 nm where Ni (II) has no absorption without the use of simultaneous equation. Since it is reported that the use of zero crossing points in derivative spectrophotometry accounts for improved selectivity, it is necessary that the zero crossing wavelengths do not change with varying concentrations of the related species. To evaluate this condition, changes in the pre-mentioned zero crossing wavelengths for nickel and cobalt were tested in the presence of different concentrations of the individual ions. According to the results as shown in Figs.1 and 2, no shift in the zero crossing points were observed at lower concentrations for both complexes, but at a higher concentration of 2.344 μg mL^{-1}, although a slight shift of ≈4 nm was observed in the zero crossing point for the nickel complex, the calibration graph was linear within the range of determination.

Table 1: Simultaneous Determination of binary mixtures of Ni (II) and Co (II) with KBAT by Second Derivative Spectrophotometry

AMOUNT TAKEN (µg mL^{-1})		AMOUNT FOUND (µg mL^{-1})* (n = 5)	
Ni	Co	Ni	Co
1.172	0.590	1.170 ± 0.006	0.582 ± 0.008
1.758	1.185	1.752 ± 0.008	1.176 ± 0.005
2.344	1.185	2.336 ± 0.011	1.174 ± 0.005
0.580	1.185	0.578 ± 0.008	1.174 ± 0.005
1.172	1.185	1.164 ± 0.005	1.176 ± 0.005
1.172	1.779	1.165 ± 0.005	1.766 ± 0.005
1.172	2.360	1.164 ± 0.005	2.354 ± 0.005

*Values are mean ± SD

Table 2: Tolerance limit of diverse ions (µg mL^{-1})

Diverse ions	In 2.34 µg mL^{-1} Ni(II)	In 2.65 µg mL^{-1} Co(II)
Na$^+$, K$^+$, Li$^+$, Mg$^+$, Ca$^+$, Ba$^+$, Sr$^+$	2000	2000
Thiocyanate, F$^-$, Cl$^-$, I$^-$, Tartrate, thiourea	1000	1000
Oxalate, citrate, ascorbate, phosphate, thiosulphide	500	500
Al(III),Pd(II),Pb(II),SN(II),Hg(II),Ti(IV), Ce(II), V(V), Cr(III), Fe(II), Mn(II), Cu(II)	200	200
EDTA	50	50

Table 3: Determination of Ni (II) and Co (II) in alloy steel samples

Sample	Certified value (%)		*Amount found (%) n=5	
	Ni	Co	Ni	Co
Alloy steel A	11.22	23.72	11.007 ± 0.125	23.688 ± 0.027
Alloy steel B	8.67	0.22	8.644 ± 0.045	0.228 ± 0.008
BCS 406/1	0.14	0.16	0.139 ± 0.007	0.1498 ± 0.005
Permute	21.0	30.0	21.035 ± 0.258	29.815 ± 0.169
Fenicoloy	29.0	17.0	28.808 ± 0.173	16.898 ± 0.097

***Values are mean ± SD**

Table 4: Determination of nickel and cobalt in biological sample

Sample	Certified value µg mL^{-1}		*Present method µg mL^{-1} (n = 5)	
	Ni	Co	Ni	Co
Tea leaves NIES no.7	6.50	0.12	6.52 ± 0.022	0.11± 0.013

Calibration, accuracy and precision

Calibration curves for the individual determination of Ni (II) and Co (II) using the second derivative amplitudes at 369.8 and 410nm respectively were linear in the concentration ranges 0.25-2.340 μg mL^{-1} for Ni (II) (Fig.3) and 0.30-2.360 μg mL^{-1} for Co (II). The results of mixtures for five different concentrations of 0.585-2.340 μg mL^{-1} Ni (II) and 0.590-2.360 μg mL^{-1} Co(II) (Table1), reveal satisfactory reproducibilities and accuracies. The precision (SD, n =5) in a mixture containing 2.340 μg ml^{-1} Ni (II) and 1.18 μg ml^{-1} Co (II) are ±0.2 and ± 0.1μg mL^{-1} respectively.

Effect of diverse ions

The effects of foreign ions on the determination of Ni (II) and Co (II) were studied to determine the tolerance levels of these ions in the present method. Solutions containing 2.94 μg mL^{-1} Ni (II) and 2.95 μg mL^{-1} Co (II) and the various amounts of other ions were prepared and the proposed second derivative procedure for their determination was followed.. Based on these results (Table 2), the selectivity of nickel and cobalt determinations was observed. A large number of foreign ions do not interfere in the studies. At concentrations of 2000 μg mL^{-1}, alkali and alkali earth metals do not interfere with the analyte but below 50 μg mL^{-1} EDTA interferes seriously.

Applications

From the results of known amounts of nickel and cobalt determined in order to assess the proposed method, the applicability of the method for the simultaneous determination of nickel and cobalt in binary mixtures was demonstrated (Table 1)

The present method was used for the determination of nickel and cobalt in various alloy steels and biological sample.

CONCLUSION

The suggested method shows that KBAT can be adopted as a sensitive complexing reagent for the simultaneous determination of nickel and cobalt using the zero crossing technique. The method is highly selective and is suitable for the determination of nickel and cobalt in real samples without solving any simultaneous equation.

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