

SIMULTANEOUS DETERMINATION OF NI (II) AND CO (II) USING CINNAMALDEHYDE THIOSEMICARBAZONE BY FIRST ORDER DERIVATIVE SPECTROPHOTOMETRIC TECHNIQUE

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ABSTRACT

Cinnamaldehyde thiosemicarbazone (CMTSC) was used as chromogenic reagent for Simultaneous spectrophotometric determination of Ni (II) and Co (II) ions. The reagent (CMTSC) gives intense yellow colour water soluble complexes with Ni (II) and Co (II) in presence of micellar medium (Triton-X-100 (5%) at pH 9.0. The maximum absorbance was observed at λ_{max} 440 and 400 nm for Ni (II) and Co (II) respectively. The molar absorptivity and sandell's sensitivity for Ni (II) and Co (II) complexes are found to be 4.77×10^4 , 4.70×10^4 L.mol⁻¹.cm⁻¹ and 0.0012, 0.0012 $\mu\text{g}/\text{cm}^2$ respectively. The reagent (CMTSC) forms 1:1 [M:L] complexes with Ni (II) and Co (II) with stability constants 8.17×10^5 and 10.10×10^6 respectively. The

First order derivative spectrophotometric technique has been developed for the simultaneous determination of Ni (II) and Co (II) at λ_{max} 460 and 420 nm. The present simultaneous method was used for the determination of micro amounts of Co (II) & Ni (II) in some alloy steels and soil samples.

KEY WORDS: Co (II), Ni (II), CMTSC, Simultaneous Derivative spectrophotometry.

INTRODUCTION

Hydrazones are important organic analytical reagents for the spectrophotometric determination of metal ions in microgram quantities. They react with metal ions forming

colour complexes and act as chelating agents. The potential applications of hydrazone derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh et.al^[1].

The great interest towards derivative spectrophotometry was due to the increased resolution of spectral bands, that means it is resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using zero-crossing technique.²⁻³ In the absence of zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture^[4-5] Hydrazone reagents are widely used in our laboratories for the derivative spectrophotometric determination of metal ions^[5-8]. Derivative spectrophotometric analysis of two-component mixtures was also carried out without need to solve simultaneous equations^[6-7] In the light of good analytical characteristics of hydrazones, here in we report the simultaneous first order derivative spectrophotometric determination of Ni (II) and Co (II) using CMTSC. The proposed simultaneous method involves the use of peak-to-base line measurement technique.

EXPERIMENTAL PART-MATERIALS & METHODS

Apparatus: Shimadzu 16A microcomputer based U.V-Visible spectrophotometer equipped with 1.0 cm quartz cells used for all absorbance studies and amplitude measurements in derivative spectrophotometry. An ELICO LI-120 digital pH meter was used in pH adjustments.

Recommended procedure for Simultaneous determination of Ni (II) and Co (II)

For simultaneous determination of Ni (II) and Co (II), a solution containing both Ni (II) and Co (II) in the optimum concentration range 0.176-0.727 $\mu\text{g/mL}$ of Ni (II) and 0.142-0.637 $\mu\text{g/mL}$ of Co (II) are used. The absorption spectra indicates that Ni (II) and Co (II) complexes shows maximum amplitude in derivative spectrophotometric technique at λ_{max} 460 and 420 nm respectively. Calibration curves are prepared between amplitude and amount of metal ion at their respective wavelength. The amount of metal ion [Ni (II) or Co (II)] was calculated from calibration graphs.

At λ_{max} 420 nm Co (II) complex has a zero crossing point, which is independent of the metal ion concentration and at this wavelength Ni (II) has appreciable amplitude shown in Figure.2. Hence, simultaneous first order derivative spectrophotometric determination of Ni (II) and Co (II) has been carried out by measuring peak-base line technique at 460 nm and

420 nm respectively without employing the simultaneous equations. Calibration plots were constructed at 460 nm and 420 nm by plotting the derivative amplitudes against the corresponding amounts of Ni (II) and Co (II) respectively. The plots thus obtained are linear obeying the relationship.

$$\text{Ni (II) } A_{460 \text{ nm}} = 0.66846X + 2.66667 \times 10^{-4}$$

$$\text{Co (II) } A_{420 \text{ nm}} = 0.68153X + 0.00125$$

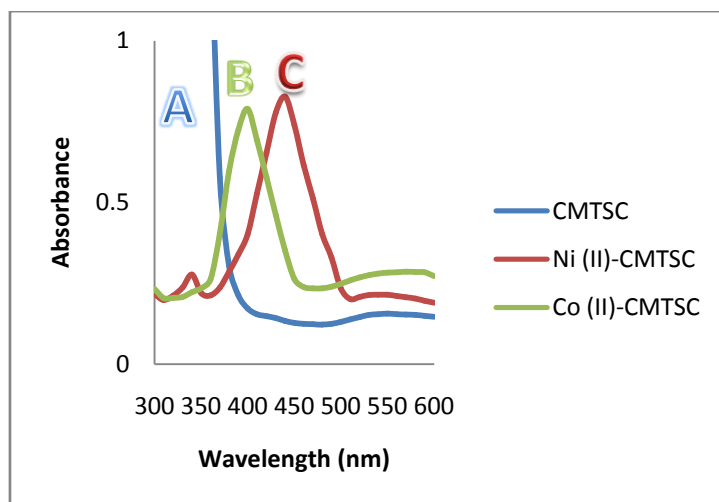


Figure.1: Zero order Absorption Spectra

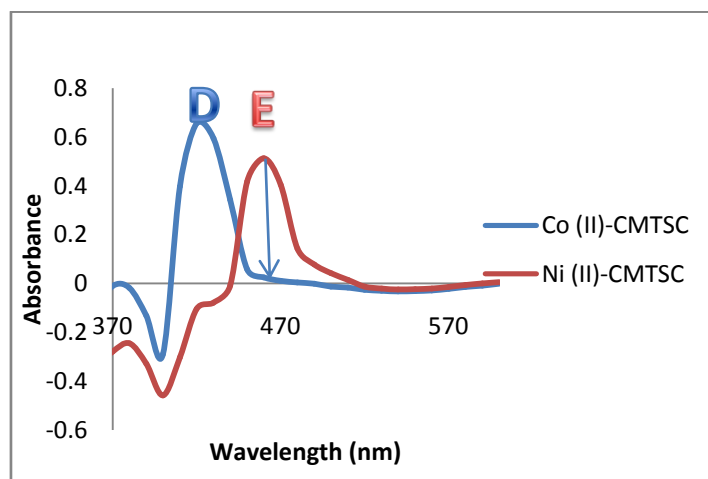


Fig.2: Simultaneous first order Derivative Spectra

- (a) Reagent CMTSC Vs water blank, (D) Co (II)-CMTSC
 (b) Co (II)-CMTSC Complex Vs Reagent blank, (E) Ni (II)-CMTSC
 (c) Ni (II)-CMTSC Complex Vs Reagent blank.

$$[\text{Ni (II) \& Co (II)}] = 1.5 \times 10^{-5}, \quad [\text{CMTSC}] = 3 \times 10^{-3} \text{ M,}$$

$$\text{pH} = 9.0 \quad \text{Triton X-100 (5\%)} = 0.5 \text{ mL}$$

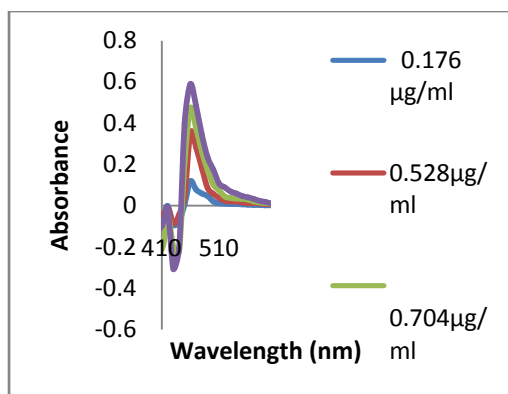


Figure.3: Typical first order derivative spectra Ni (II)-CMTSC

[Ni (II)] = 1.5×10^{-6}
 [CMTSC] = 3×10^{-3}
 pH = 9.0
 Triton-X-100 (5%) = 0.5 mL
 λ_{max} = 460 nm

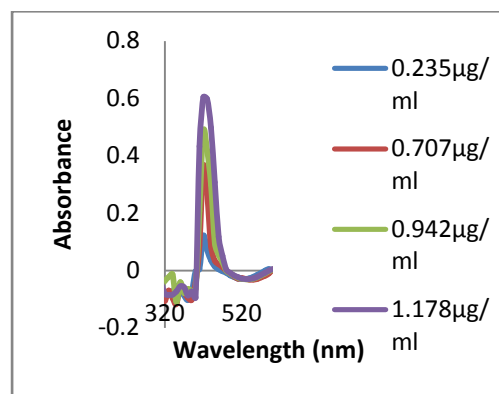
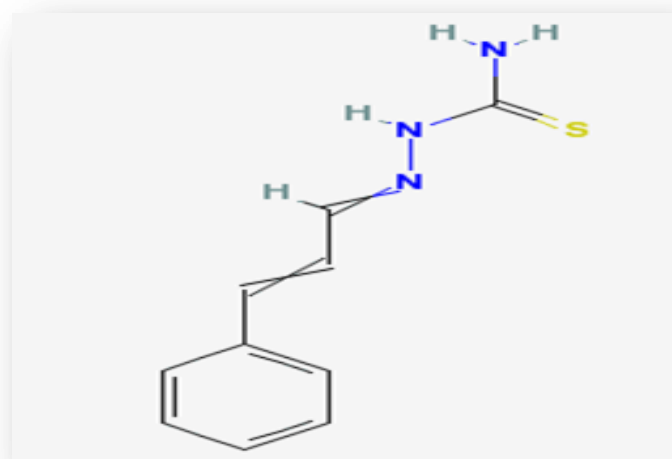


Figure.4: Typical first order derivative of Co (II)-CMTSC

[Co (II)] = 1.5×10^{-6}
 [CMTSC] = 3×10^{-3}
 pH = 9.0
 Triton-X-100 (5%) = 0.5 mL
 λ_{max} = 420 nm

RESULTS AND DISCUSSION

Cinnamaldehyde semithiocarbazone (CMTSC) was a novel type of reagent. The above reagent was easily synthesized as any other Schiff base. Aldehyde-4-hydroxybenzoylhydrazone reagents are not exploited much for spectrophotometric determination of metal ions. Moreover, the derivative methods using this class of reagents are scarce.



Structure of CMTSC

Interference

The effect of foreign ions was studied to know the selectivity of the derivative methods. The amount of foreign ions, which brings about change in amplitude by $\pm 2\%$, was taken as the tolerance limit. Interference of various ions which often accompany with Ni (II) and Co (II) has been studied in the determination of $0.440 \mu\text{g/mL}$ of Ni (II) and $0.441 \mu\text{g/mL}$ of Co (II).

The data obtained in derivative method is also incorporated. It is noticed that all the ions that do not interfere in the zero-order determination of metal ions also do not interfere in the first derivative analysis. The tolerance limit values, for many anions and cations are higher in the first order derivative methods than those in the zero-order determination of metal ions. The interference of associated metal ion such as Fe (III) was decreased by adding the masking agent fluoride.

APPLICATIONS

The simultaneous first derivative spectrophotometric determination of Ni (II) & Co (II), some alloy steels and soil samples. The results are presented in Table 1, 2 & 3 respectively.

Table.1: Simultaneous determination of Ni (II) and Co (II) in Alloy steel samples

Alloy sample	Certified (%)		Amount found (%)		Error (%)	
	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
(a) Eligiloy M-1712	15.00	40.00	15.10	39.94	+0.67	-0.15
(b) BCS 406/1	0.14	0.016	0.128	0.017	-1.54	+0.63
(c) Alloy steel	11.22	23.72	11.30	23.68	+0.71	-0.16

*Average of three determinations; (a) 20% Cr, 40% Co, 15% Ni, 0.15% C, 15% Fe, 2% Mn, 7% Mo, 0.05% Be. (b) 0.066% Mn, 1.06% Cr, 0.05% Mo, 0.14% Ni, 0.016% Co, 0.091% Cu, 0.19% V^z. (c) 51.15% Fe, 11.22% Ni, 5.09% Cu, 23.72% Co, 6.9% Al, 0.79% Ti, 0.235% Mn, 0.57% Si.

Table.2: Simultaneous first-order derivative determination of Co (II) and Ni (II) in synthetic binary mixtures

Amount taken ($\mu\text{g/mL}$)		Amount found ($\mu\text{g/mL}$)		Error (%)	
Ni (II)	Co (II)	Ni (II)	Co (II)	Ni (II)	Co (II)
0.2347	0.2357	0.2340	0.2362	-0.29	+0.21
0.4694	0.2357	0.4685	0.2352	-0.23	-0.21
0.7041	0.2357	0.7049	0.2354	+0.11	-0.12
0.9388	0.2357	0.9382	0.2361	-0.06	+0.16
1.1785	0.2357	1.1780	0.2365	-0.04	+0.33
0.2347	0.2357	0.2352	0.2362	+0.21	+0.21

0.2347	0.4714	0.2344	0.4708	-0.12	-0.10
0.2347	0.7071	0.2354	0.7081	+0.29	+0.14
0.2347	0.9428	0.2340	0.9420	-0.29	-0.08
0.2347	1.1735	0.2362	1.1742	+0.63	+0.05

*Average of three determinations.

Table.3: Determination of Ni (II) and Co (II) in Soil samples

Sample and composition (ppm)	Amount in ppm				Relative error (%)	
	Certified (GSI) value (ppm)		Amount found by present method* (ppm)			
	Ni (II)	Co (II)	Ni (II)	Co (II)	Ni	Co (II)
S-18 20.20 Pb (II) 20.30 Zn (II) 88.85 Cu (II)	50.50	40.35	50.84	39.98	+0.67	-0.92

* Average of best three among five determinations.

CONCLUSIONS

The present method, using CMTSC as spectrophotometric reagent for the simultaneous determination of Ni (II) and Co (II) in presence of Triton X-100 is simple, rapid, reasonably sensitive and selective. The present method is not laborious and there is no need of heating the components or pre-extraction. Large amounts bromide, iodide, tartarate and nitrate do not interfere in the present method.

This method was also free from the interference of strontium, arsenic, tungsten, lanthanum and other rare earth metals. Triton X-100 enhances the stability of the metal complexes. Further, the simultaneous determination of Ni (II) and Co (II) carried out without the need of employing the simultaneous equation.

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