

## 2-Hydroxy-3-methoxy Benzaldehyde Thiosemicarbazone를 사용하여 마이크로 그램 코발트(II)의 직접 및 유도 분광광도법에 의한 정량

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## Direct and Derivative Spectrophotometric Determination of Cobalt (II) in Microgram Quantities with 2-Hydroxy-3-methoxy Benzaldehyde Thiosemicarbazone

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**요 약.** 분석 시약으로 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC)를 사용하여 코발트(II) 정량을 위하여 빠르고 간단하고 민감한 분광광도법을 개발하였다. 액상에서 금속이온이 pH 6.0에서 HMBATSC와 갈색의 착물을 형성하였다. 이 착물은 375 nm와 390 nm에서 두 개의 최대 흡수 피크를 보였다. 375 nm에서 많은 흡수를 보였고, 반면 390 nm에서는 분명한 흡수를 보이지 않았다. Beer's 법칙에서 Co(II)는 0.059-2.357  $\mu\text{g ml}^{-1}$  범위를 보였다. 이 방법의 몰 흡수와 Sandall's 민감도는 각각  $2.74 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ 와  $0.0024 \mu\text{g cm}^{-2}$  였다. 여러 가지 다른 이온들에 간섭에 대해서도 연구하였다. 화학양론적으로 착체는 1:2 [Co(II)- HMBATSC] 이 었다. 이차 유도 분광광도법에 의한 Co(II)의 정량방법에 대해서도 제안하였다. 제안된 방법을 alloy steels, 비타민 B<sub>12</sub>와 생물학 시료에 있는 Co(II)의 정량에 적용하였다.

**주제어:** 분광광도법, 코발트 정량, HMBATSC

**ABSTRACT.** A rapid, simple and sensitive spectrophotometric method was developed for the determination of cobalt(II) using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a analytical reagent. The metal ion in aqueous medium forms a brown coloured complex with HMBATSC at pH 6.0. The complex has two absorption maxima at 375 nm and 390 nm. At 375 nm, the reagent shows considerable absorbance, while at 390 nm the reagent does not shows appreciable absorbance. Hence, analytical studies were carried out at 390 nm. Beer's law is obeyed in the range of 0.059-2.357  $\mu\text{g ml}^{-1}$  of Co(II). The molar absorptivity and Sandall's sensitivity of the method are  $2.74 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.0024 \mu\text{g cm}^{-2}$  respectively. The interference of various diverse ions has been studied. The complex has 1:2 [Co(II)-HMBATSC] stoichiometry. A method for the determination of cobalt(II) by second order derivative spectrophotometry has also been proposed. The proposed methods were applied for the determination of cobalt(II) in alloy steels, vitamin B<sub>12</sub> and in some biological samples.

**Keywords:** Spectrophotometry, Determination of cobalt, HMBATSC

### INTRODUCTION

Cobalt alloys are used in some industrial products because of their sufficient hardness and resis-

tivity against oxidation at high temperatures, for example, in the manufacturing of turbine blades and cutting tools. Cobalt-60 is used as an efficient radioactive tracer and an anti-cancer treatment

agent in medicine. Some cobalt compounds, such as vitamin B<sub>12</sub> (cyanocobalamin), are imported for biological activities.<sup>1</sup> Therefore, the determination of cobalt is valuable for the quality control of artificial and biological samples in a simple selective and sensitive manner.

A wide variety of techniques are available for spectrophotometric determination of cobalt(II). Solvent extraction spectrophotometry,<sup>2,3</sup> spectrophotometric measurement after pre-concentration with solid polymeric sorbents, such as amberlite XADs<sup>4,5</sup> and polyurethane foams,<sup>6</sup> spectrophotometric procedures using low melting point extractant,<sup>7</sup> simple spectrophotometry in aqueous solution,<sup>8</sup> derivative spectrophotometry,<sup>9</sup> flow injection based techniques<sup>8</sup> and H-point standard addition method in miscellizing solution have also been proposed.<sup>10</sup> Some of these methods have disadvantages such as low sensitivity,<sup>11-15</sup> long time consuming,<sup>16</sup> limitation of pH,<sup>17,18</sup> interference from some ions<sup>11,15,17-19</sup> and difficult condition for complex formation (about 80 °C).<sup>20</sup> In the present paper, a simple, rapid, non-extractable, selective and sensitive method was reported for the spectrophotometric determination of trace amounts of cobalt(II) by complexing with 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC). The reagent forms a brown coloured complex with cobalt(II) in acid medium in the pH range 5.0-7.0 and was stable for more than 72 hours. Hence, a systematic study has been made to develop a spectrophotometric method for the determination of cobalt in alloy steels, vitamin B<sub>12</sub> and in some biological samples.

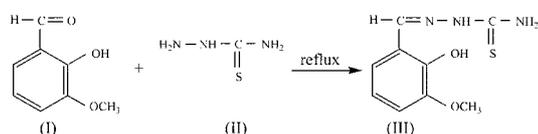
## EXPERIMENTAL

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1 cm Quartz cells and Phillips digital pH meter (model L1 613) respectively.

## REAGENTS

### Preparation of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC)

The reagent (HMBATSC) is prepared by the Sah and Daniels<sup>21</sup> procedure. 11.25 g of 2-hydroxy-3-methoxy benzaldehyde (I) and 4.55 g of thiosemicarbazide (II) are dissolved in sufficient volume of methanol and the mixture is refluxed for 60 minutes. The contents are allowed to cool and the product separated by filtration. A crude sample (yield 80%) is obtained (C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>SN<sub>3</sub>). The resultant product is recrystallised twice from hot methanol. Pure light yellowish green crystals of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) (III) (m.p. 220-222 °C.) are obtained.



A 0.01 M solution of HMBATSC in dimethyl formamide (DMF) was employed in the present studies.

Stock solution of Co(II) ( $1 \times 10^{-2}$  M) is prepared by dissolving appropriate amount of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O in doubly distilled water containing a few drops of conc. HNO<sub>3</sub> in a 100 ml volumetric flask and standardized gravimetrically.<sup>22</sup>

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

### Buffer solutions

The buffer solutions were prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate (pH 1.0-3.0) and 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0). The pH of these solutions was checked with a pH meter.

## PREPARATION OF SAMPLE SOLUTIONS

### Alloy steels

A 0.1-0.5 g of steel sample was dissolved completely in minimum amount of aquaregia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling 5-10 ml of 1:1 H<sub>2</sub>O:H<sub>2</sub>SO<sub>4</sub> mixture was added and evaporated to

dryness. Sulphuric acid treatment was reported three times to remove all the nitric acid. The residue was dissolved in 20 ml of distilled water and filtered and the filtrate was made up to 100 ml in a calibrated volumetric flask with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range.

#### Vitamin B<sub>12</sub>

A sample solution of vitamin B<sub>12</sub> tablet was prepared by grinding 50 tablets of Basiton forte and transfer into a beaker. The powder was dissolved in minimum volume of alcohol, then added 3 ml of 0.01 M nitric acid and evaporated to dryness. The dried mass was again dissolved in alcohol. This was filtered through whatman filter paper and the filtrate was diluted to 100 ml with distilled water. The lower concentrations were prepared by the appropriate dilution of the stock solution.

#### Biological samples (Tea leaf and vehicle exhaust)

The tea leaf samples were supplied by Andhra Pradesh Agricultural research institute (APARI), Hyderabad (A.P.) India. The vehicle exhaust sample was collected from Environment protection training and research institute (EPTRI), Hyderabad (A.P.) India. A 0.1 g of tea leaf sample was taken in a beaker and dissolved in conc. nitric acid ( $\approx 5$  ml) with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 100 ml with water in a calibrated flask. Vehicle exhaust particles (1 g) were dissolved in a mixture of 18 ml of conc. nitric acid, 18 ml of conc. perchloric acid and 2 ml of conc. hydrofluoric acid in a 100 ml teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100 ml with distilled water.

#### Procedure

##### Direct spectrophotometry

In each of set of different 10ml volumetric flasks, 5 ml of buffer solution (pH 6.0), 1 ml of HMBATSC ( $8 \times 10^{-3}$  M) and various volumes of  $1 \times 10^{-4}$  M cobalt(II) solution were taken and made up to the mark with double distilled water. The absorbance was mea-

sured at 390 nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of cobalt(II).

##### Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly  $2400 \text{ nm min}^{-1}$ ); slit width of 1 nm with nine degrees of freedom, in the wavelength range 390-510 nm. The derivative amplitudes measured at wavelengths 414 nm and 452 nm and plotted against amount of cobalt(II) to obtain the calibration.

The calibration graph follows the straight line equation  $Y = a + b$ ; where  $c$  is the concentration of the solution,  $Y$  is measured absorbance or peak or valley height and  $a$  and  $b$  are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as  $A_{390} = 0.2383c + 0.0259$  for zero order method,  $A_{414} = 0.4034c + 0.00282$  and  $A_{452} = 0.3638c + 0.0187$  for second derivative method.

## RESULTS AND DISCUSSION

2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) produced a brown coloured complex with HMBATSC in acidic buffer at pH 6.0.

##### Direct method

The absorption spectra of the solution containing Cobalt(II) complex against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 350 to 500 nm. Typical spectra are presented in Fig. 1. The spectra show that cobalt(II) complex has two absorption maxima at 375 nm and 390 nm. At 375 nm, the reagent shows considerable absorbance while at 390 nm the reagent does not show appreciable absorbance. Hence, 390 nm was chosen for further studies.

The study of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was obtained in the pH range 5.0-7.0. Analytical studies were therefore, carried out at pH 6.0.

A 20 fold molar excess of HMBATSC was necessary for complex and constant colour development. Excess of the reagent has no effect on the

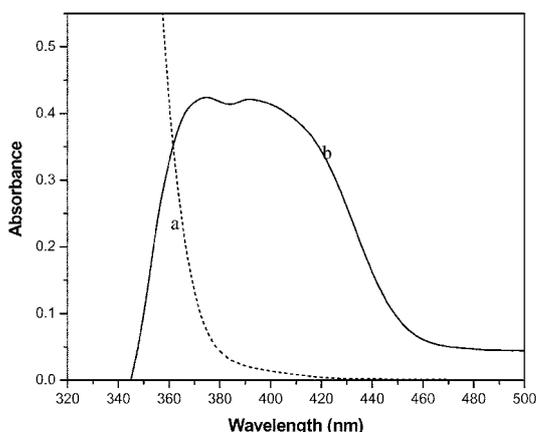


Fig. 1. Absorption spectra of (a) HMBATSC Vs Buffer blank, (b) [Co(II)-HMBATSC] Vs reagent blank [Co(II)] =  $2 \times 10^{-5}$  M; [HMBATSC] =  $4 \times 10^{-4}$  M; pH = 6.0.

absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reactants.

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour complex was observed that the colour development is instantaneous and remains constant for more than 72 hours.

For the possible determination of Cobalt(II) at micro levels, the absorbance of the solution containing different amounts of the metal ion was measured. The linear plot between the absorbance and the amount of cobalt(II) is drawn and the straight line obeyed the equation  $A=0.3868C+0.0085$ . Further, Beer's law was obeyed in the range of 0.059 to  $2.357 \mu\text{g ml}^{-1}$ . The molar absorptivity and Sandell's sensitivity were  $2.47 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and  $0.0024 \mu\text{g cm}^{-2}$  respectively. The standard deviation of the method for ten determinations of  $1.18 \mu\text{g ml}^{-1}$  is  $\pm 0.0052$ .

#### Effect of foreign ions

The effect of various foreign ions that are generally associated with cobalt(II) on its determination under optimum conditions developed was studied and the results are presented in Table 1.

Among the various ions studied, all the anions and the cations Pb(II), Cd(II), Te(IV), U(VI), Na(I),

Table 1. Tolerance limit of foreign ions Amount of Co(II) =  $1.18 \mu\text{g ml}^{-1}$

Diverse ion	Tolerance limit ( $\mu\text{g ml}^{-1}$ )	Diverse ion	Tolerance limit ( $\mu\text{g ml}^{-1}$ )
EDTA	1860	Pb (II)	1025
Ascorbic acid	1760	Cd (II)	880
Iodide	1270	Te (IV)	750
Citrate	1215	U (VI)	480
Phosphate	950	Na (I)	460
Tartrate	900	K (I)	390
Oxalate	880	Li (I)	320
Bromide	800	Th (IV)	280
Urea	760	W(VI)	250
Nitrate	720	Ce (IV)	210
Sulphate	680	Ti (IV)	200
Bromate	640	Zn (II)	150
Acetate	600	Cu (II)	12, 130 <sup>a</sup>
Thiosulphate	560	Al (III)	110
Formate	450	Ni (II)	6, 107 <sup>a</sup>
Thio Urea	380	Fe (II)	11, 112 <sup>b</sup>
Chloride	355	V (V)	5.8, 110 <sup>c</sup>
Fluoride	200	Cr (III)	88
		Zr (IV)	80
		Mn (II)	74
		Ru (III)	65
		Pd (II)	60
		Mo (VI)	59
		Pt (IV)	55

In the presence of a) 1860  $\mu\text{g}$  of EDTA; b) 1270  $\mu\text{g}$  of iodide; c) 950  $\mu\text{g}$  of Phosphate.

K(I), Li(I), Th(IV), W(VI), Ce(IV), Ti(IV), Zn(II) and Al(III) do not interfere even when present in more than 100 fold excess. Cr(III), Zr(IV), Mn(II), Ru(III), Pd(II), Mo(VI) and Pt(IV) are tolerable when present between 50-90 fold excess. Cu(II) and Fe(II) interfere when present in more than 10-fold excess, Ni(II) and V(V) interfere when present in more than 5-fold excess. However, in the presence of 1860  $\mu\text{g}$  of EDTA, Cu(II) and Ni(II) do not interfere even in 100-fold excess. Fe(II) is tolerable up to 90-fold excess in presence 1270  $\mu\text{g}$  of iodide. In presence of 950  $\mu\text{g}$  of phosphate, V(V) is tolerable up to 100 fold excess.

#### Composition and stability of the complex

The stoichiometry of the complex was determined by Job's method (Fig. 2) and molar ratio method and found to be 1:1 (metal : reagent). The stability

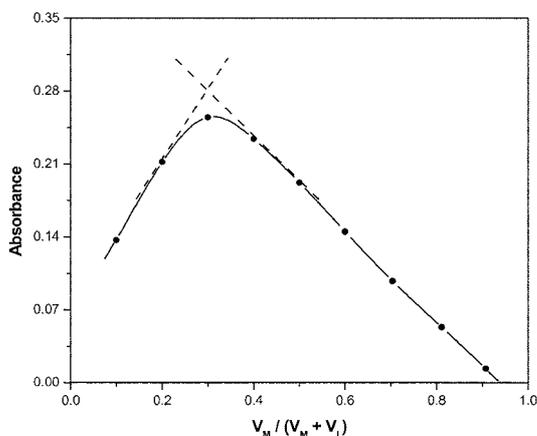


Fig. 2. Job's curve  $[Co(II)] = [HMBATSC] = 1 \times 10^{-3} M$ ; Wavelength = 390 nm; pH = 6.0.

constant was determined by Job's method as  $6.719 \times 10^{11}$ .

**Applications**

The present method was applied for the determination of Co(II) in alloy steels, vitamin B<sub>12</sub> and biological samples.

**Alloy steels**

To known aliquots of the sample solutions were taken in different 10 ml volumetric flasks, 5 ml of buffer solution (pH 6.0), 950 μg of phosphate (to mask vanadium), 1270 μg of iodine (to mask Fe(II)) and 1860 μg of EDTA (to mask Ni(II)) and 1ml of HMBATSC ( $8 \times 10^{-3} M$ ) were added to each flask. The contents were made up to the mark with distilled water and the absorbance was measured at 390 nm. The amount of cobalt was calculated from a predetermined calibration plot and is given in Table 2.

Table 2. Determination of cobalt in alloy steel samples

Sample	Composition (%)	Amount of Cobalt (%)		Relative error (%)
		Certified value	Present method*	
JSS 607/6 High speed steel	16.96 w; 4.14 Cr; 0.86 V <sup>a</sup> ; 0.32 Si; 0.30 Mo; 0.30 Mn; 0.75 C; 0.012 P; 0.006 S; rest Fe <sup>b</sup>	4.72	4.69	-0.64
High speed steel	6-18.5 W, 5.5 Mo; 4.15 Cr; 0.4 Mn; 0.35 Si; 0.05 S; Rest Fe <sup>b</sup>	9.25	9.28	+0.32
Eligiloy M-1712	20 Cr; 15 Ni <sup>c</sup> ; 15 Fe <sup>b</sup> ; 7 Mo; 2 Mn; 0.15 C; 0.05 Be	40.0	40.14	+0.35
Udimet-700	15 Cr; 4.3 Al; 5.21 Mo; 0.08 C; 0.003 B	18.00	18.10	+0.55

\*= Average of five determinations; a = masked with 950 μg of phosphate; b = masked with 1270 μg of iodide; c = masked with 1860 μg of EDTA.

Table 3. Determination of cobalt in vitamin B<sub>12</sub> tablet

Sample and composition (mg/tablet)	Amount of cobalt (μgm <sup>-1</sup> )		Relative error (%)	
	AAS method	Present method*		
	BASITON FORTE			
Thiamino mononitrate(B <sub>1</sub> )	: 10			
Riboflavine (B <sub>2</sub> )	: 10			
Pyridoxime hydrochloride	: 3			
Niacinamide	: 100	7.42	7.45	+0.40
Cyanocobalamine	: 15			
Folic acid	: 1.5			
Calcium pentathenate	: 50			
Sodium ascarbate	: 150			

\*Average of five determinations

**Vitamin B<sub>12</sub>**

To known aliquots of the sample solutions were taken in different 10ml volumetric flasks, 5 ml of buffer solution (pH 6.0) and 1ml of HMBATSC ( $8 \times 10^{-3} M$ ) were added to each flask. The contents were made up to the mark with distilled water and the absorbance was measured at 390 nm. The amount of cobalt was calculated from a predetermined calibration plot and is given in Table 3.

**Biological samples (Tea leaf and vehicle exhaust)**

An aliquot (10-50 ml) of the sample solution (procedure as described above) was taken individually and cobalt was determined from predetermined calibration plot. The results are presented in Table 4.

Table 4. Analysis of cobalt in biological samples

Sample	Amount of cobalt (mg/g)	
	Certified value	Present method*
Tea leaves	0.12 ± 0.008	0.110 ± 0.08
Vehicle exhaust	3.3 ± 0.3	3.15 ± 0.3

\*Average of five determinations

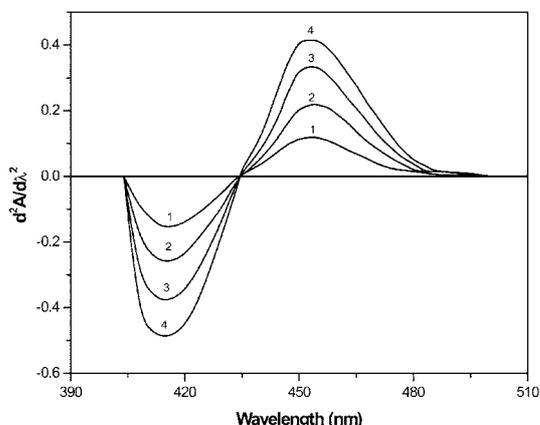


Fig. 3. Second derivative spectra of Co(II) – HMBATSC Vs reagent blank Co(II) ( $\mu\text{g ml}^{-1}$ ) = (1) 0.2357; (2) 0.4714; (3) 0.7071; (4) 0.9428.

### Second order derivative method

The second order derivative curves recorded (Fig. 3) for experimental solutions showed the derivative amplitudes were measured at 414 nm (valley) and 452 nm (peak) for different concentrations of Co(II) and plots were made between the amount of Co(II) and the derivative amplitude. The plots were linear and obeyed Beer's law in the range 0.030-3.535  $\mu\text{g ml}^{-1}$  and 0.059-3.535  $\mu\text{gml}^{-1}$  at 414 nm, 452 nm respectively.

### Effect of foreign ions

The effect of various cations and anions on the derivative amplitude was studied and it was noticed that all the ions that did not interfere in the zero order determinations of Co(II) also did not interfere in second order derivative method. The metal ions Cu(II) and Fe(II) were interfered in 10-fold excess, Ni(II) and V(V) were interfered in 5-fold excess in zero order method, but in second order derivative method. Cu(II) and Fe(II) were tolerable up to 25 fold excess. Further, V(V) and Ni(II) were interfere 5-fold excess in second order derivative method.

### APPLICATIONS

#### Analysis of alloys and steels

A known aliquot of the sample solution was taken in a 10 ml volumetric flask containing 5 ml of buffer solution (pH 6.0) and 950  $\mu\text{g ml}^{-1}$  of phosphate (to mask V(V)) and 1ml of HMBATSC ( $8 \times 10^{-3}$  M) solution. The contents of the flask were made up to the mark with distilled water. The second derivative spectrum of the solution was recorded. The derivative amplitude at 452 nm was measured and the amount of cobalt(II) was computed from the predetermined calibration plot and presented in Table 5.

Table 5. Determination of Cobalt(II) in alloy steel samples

Sample	Amount of cobalt (%)		Relative error (%)
	Certified value	Present method*	
High speed steel <sup>a</sup>	9.25	9.30	0.54
BCS-483 <sup>b</sup>	1.94	1.91	-1.54
JSS-607-6 <sup>c</sup> (High speed steel)	4.72	4.76	0.85

\*Average of five determinations. a: 9.25% Co; 0.40% Mn; 0.35% Si; 0.05% S; 0.05% P; 5.50% Mo; 6-18.5% W; 4.15% Cr; Rest Fe. b: 10.8% W; 3.21% Cr; 0.54% V<sup>x</sup>; 0.29% Mn; 0.17% Mo; 1.94% Co; Rest Fe. c: 16.96%W; 4.14% Cr; 0.86% V<sup>x</sup>; 0.32% Si; 0.30% Mo; 0.30% Mn; 0.75% C, 0.012% P; 0.006% S; 4.72% Co; Rest Fe. x = masked with 950 mg of phosphate.

Table 6. Comparison of results of Co(II)

Parameter	Zero order	second derivative	
Analytical wave length (nm)	390	414	452
Beer's law range ( $\mu\text{gml}^{-1}$ )	0.059-2.357	0.030-3.535	0.059-3.535
Angular coefficient (m)	0.3933	0.4034	0.3638
Y-intercept (b)	0.0013	0.0282	0.0187
Correlation coefficient (r)	0.9998	0.9997	0.9995
Standard deviation (s)	$\pm 0.0052$	0.0118	0.0157

Table 7. Comparison with other methods

Reagent	$\lambda_{\max}$ (nm)	$\epsilon^*$	Ref.
3-hydroxy piconaldehyde thiosemicarbazone	450	0.78	23
Phthaldehyde thiosemicarbazone	385	0.56	24
Piconaldehyde thiosemicarbazone	410	0.74	25
Salicylaldehyde thiosemicarbazone	400	1.1	26
Acenaphthaquinone thiosemicarbazone	410	0.48	27
Biacetyl monoxime thiosemicarbazone	325	0.49	28
1,2-Cyclohexanedione bithiosemicarbazone	450	0.64	29
2,2'-Dihydroxy benzophenone thiosemicarbazone	380	0.12	30
Furoin thiosemicarbazone	365	0.81	31
2-Hydroxy acetophenone thiosemicarbazone	360	1.0	32
5-bromo salicylaldehyde thiosemicarbazone	410	1.28	33
2-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone	390	2.47	Present method

$\epsilon^*=10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$

### Comparison of results

The analytical characteristics of the zero and second order derivative methods in the present investigations for Co(II) were compared and presented in Table 6. The results in this table reveal that second order derivative method is more sensitive and selective than the zero order method.

The sensitivity of the zero order method in the present investigations was compared with those of some reported methods and presented in Table 7. The proposed method is found to be more sensitive than the reported methods.

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