

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Simple, Selective and Non-Extractive Spectrophotometric Determination of Co (II) Using Esomeprazole.

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ABSTRACT

Esomeprazole is a new chromogenic reagent used for the determination of cobalt (II) by simple, rapid, sensitive, selective, direct and derivative spectrophotometric method. Esomeprazole forms a greenish yellow coloured Co (II) - esomaoprazole complex shows maximum absorbance at 355 nm at pH 8. Where the reagent blank shows negligible absorbance. Hence, the analytical studies were carried out at 355nm. The method obeyed Beer's law validity in the range 0.8-8.0 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's Sensitivity are calculated and found as $4.56 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.007526 \mu\text{g cm}^{-2}$ respectively. The composition of the complex has 1:2 and stability constant of the complex was calculated as 2.21×10^5 . The effect of various diverse ions also incorporated. The amount of cobalt present in some alloy steel samples was determined by the present method and the results obtained were compared with certified values, the results are quite encouraging compared with certified values.

Keywords: Esomeprazole, Cobalt (II), Spectrophotometry, alloy steel samples

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INTRODUCTION

Cobalt is a ferromagnetic, active chemically, forming many compounds. Cobalt is stable in air and unaffected by water, but is slowly attacked by dilute acids. Cobalt is used in many alloys (super alloys for parts in gas turbine, aircraft engines, corrosion resistant alloys, high-speed steels, cemented carbides), in magnets and magnetic recording media, as catalyst for the petroleum and chemical industries, as drying agent for paints and inks. The radioactive isotope, cobalt-60, is used in medical treatment and also to irradiate food, so as to preserve it.

Although the average level of cobalt in soils is 8ppm, there are soils with as little as 0.1 ppm and others with as high as 70 ppm. In the marine environment cobalt is needed by blue-green algae (cyanobacteria) and other nitrogen-fixing organisms. Cobalt is not found as a free metal and is generally found in the form of ores.

As cobalt is widely dispersed in the environment, humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure.

Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, the uptake by plants and animals is higher and accumulation in plants and animals may occur. Cobalt is beneficial for humans because it is a part of vitamin B₁₂, which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. The total daily intake of cobalt is variable and may be as much as 1 mg, but almost all will pass through the body unabsorbed, except that in vitamin B₁₂.

However, too high concentrations of cobalt may damage human health. When we breathe in too high concentrations of cobalt through air we experience lung effects, such as asthma and pneumonia. This mainly occurs with people that work with cobalt.

When plants grow on contaminated soils they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Soils near mining and melting facilities may contain very high amounts of cobalt, so that the uptake by humans through eating plants can cause health effects like vomiting and nausea, vision problems, heart problems, thyroid damage etc.,

Health effects may also be caused by radiation of radioactive cobalt isotopes. This can cause steril hair loss, vomiting, bleeding, diarrhoea, coma and even death. This radiation is sometimes used with cancer-patients to destroy tumors. These patients also suffer from hair loss, diarrhea and vomiting.

Analytical chemistry of cobalt

A large number of organic compounds were reported as analytical reagents for the determination of cobalt. These include oximes, phenyl hydrazones, azo compounds etc. 1-Nitroso-2-naphthol, proposed by Ilinsky et al [1] was one of the first organic analytical reagents employed for the determination of cobalt. This reagent along with its isomer, 2-Nitroso-1-naphthol was used for the spectrophotometric determination of cobalt in several real samples [2-4]. Many reports are available for the spectrophotometric determination of cobalt. Some of the recent references are listed here.

Syama Sundar and his coworkers [5] employed 1-(benzimidazole-2-yl) ethanone thiosemicarbazone for the extractive spectrophotometric determination of Co(II). A sensitive spectrophotometric method for the determination of Co(II) using 1-methyl,2-acetyl benzimidazole thiosemicarbazone was reported [6]. Chiranjeevi et al [7] developed a facile, rapid and economical flow injection method for the spectrophotometric determination of Co(II) using 3,5-dibromosalicylaldehyde thiosemicarbazone and applied the method for its determination in various environmental samples.

Tejam and Thakkar [8] employed 1-phenyl 1,2-butane dione dioxime as a new reagent for the extractive spectrophotometric determination of Co(II) at trace levels. Reddy [9] proposed cyanex 923 for the extractive spectrophotometric determination of Co(II) in synthetic and pharmaceutical samples.

A selective method for the FIA spectrophotometric determination of Co(II) based on the use of pyridoxal 4-phenylthiosemicarbazone as reagent was developed by Enrique Cristofol de Alcaraz et al [10]. Gonez Ariza [11] and his coworkers used picolinaldehyde 4-phenyl-3-thiosemicarbazone for the spectrophotometric determination of small amounts of cobalt in the presence of iron.

The sensitive spectrophotometric method for the determination of cobalt using 2-(2-Quinolinyloxy)-5-diethyl amino benzoic acid has developed by Liang Wang [12]. Z. Li and co-workers [13] reported a method for the spectrophotometric determination of cobalt using 2-(2-quinolinyloxy)-5-dimethyl-aminobenzoic acid as a new chromogenic reagent. Eskandari and karkaragh [14] have developed a method for facile spectrophotometric determination of cobalt using alpha-benzilmonoxime.

A. Safavi et al [15] has developed a method for indirect kinetic spectrophotometric determination of cobalt based on the redox reaction with Fe(III) in the presence of 1,10-phenanthroline. Oliver R. Hunt et al [16] developed a method for spectrophotometric determination of cobalt with sulfosalicylic acid. Demetrius G. Themelis et al [17] developed a selective method for the spectrophotometric determination of Co(II) using 2,2-dipyridyl-2-pyridylhydrazone and flow injection method. R.S. Lokhande, N.G. Jain, and N. Sari et al [18] developed a selective spectrophotometric determination of Co (II) using 5-Nitrosalicylaldehyde Thiosemicarbazone. M. Magalali Raju and K. Ramakrishna et al [19] developed spectrophotometric determination of Co(II) using 3,4-dihydroxy benzaldehyde-1-(3-chloro-2-quinoxalinyloxy) hydrazone .

The authors have developed a sensitive, selective and rapid method for the spectrophotometric determination of cobalt using 5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl) methyl] sulfinyl]-1H-benzimidazole (Esomeprazole)

EXPERIMENTAL

Instrumentation

The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively.

Reagents and Chemicals

All chemicals and solvents used were of analytical reagent grade, and doubly distilled water was used for preparation of all solutions and experiments. The working solutions were prepared by diluting the stock solution to an appropriate volume.

Esomeprazole Solution

Esomeprazole is 5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl) methyl] sulfinyl]-1H-benzimidazole, is a white crystalline powder freely soluble in water and its molecular formula is $C_{17}H_{19}N_3O_3S$. (M.Wt:345.11). The structure of esomeprazole is given in Fig. 1.

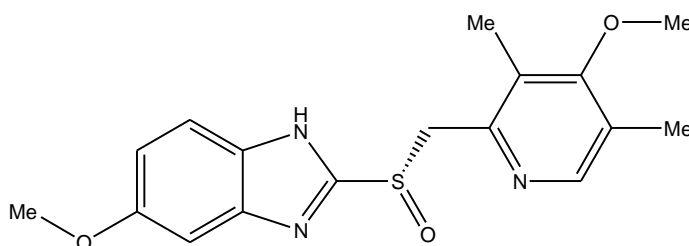


Fig. 1 (S)-5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl)-methyl]sulfinyl]-1H benzimidazole (ESOMEPRAZOLE)

Characterization

Esomeprazole was characterized by IR, $^1\text{H-NMR}$ and Mass spectral data.

IR (KBr) ν_{max} : 3346, 3168, 2961, 2928, 2683, 1657, 1597, 1449, 1255, 1218, 1092, 876, 710 cm^{-1} are present resembles various groups/chemical species present in the reagent.

$^1\text{H NMR}$ (DMSO- d_6 , 500 MHz) δ 2.20 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.60 (d, 1H), 4.77(d, 1H), 6.97, 6.99 (m, 2H, Ar-H), 7.65 (m, 1H, Ar-H), 8.25 (s, 1H, Pyridine ring), 9.57 (s, 1H, NH) ppm.

MS m/z: found 345.11 [M^+]; calcd. 345. Anal $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$.

0.01M stock solution of Co (II) was prepared by dissolving requisite amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and standardized gravimetrically [20]. The working solutions were prepared by diluting the stock solutions with distilled water.

Buffer solutions

The buffer solutions were prepared by mixing 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0) and 2.0M ammonia + 2.0M ammonium chloride (pH 8.0-12.0). The pH of these solutions was checked with the above mentioned pH meter.

Procedure:

Aliquots of solutions containing 5 ml of buffer solution (pH 8.0), 0.5 ml of ESMPZL ($2.873 \times 10^{-4}\text{M}$) in DMF, 1.5 ml of DMF taken in each of a set of 10 ml volumetric flasks, varying amounts of Co(II) were added and diluted to 10 ml in a volumetric flask with distilled water. The absorbance of these solutions was measured at 355 nm against reagent blank and plotted against the amount of cobalt. A straight line is obtained which corresponds to the equation $A_{355} = 0.13301 C - 0.0305$. (C is the amount of cobalt in $\mu\text{g/ml}$).

Determination of cobalt in alloy steel sample

In order to demonstrate the usefulness of proposed method, it was applied to the determination of cobalt in standard alloy steel samples for which the cobalt content was known. The results obtained were found to be in good agreement with certified values.

Preparation of alloy steel samples solution

A 0.1-0.5 g of the sample is dissolved in a mixture of 2 ml HCl and 10 ml HNO_3 . The resulting solution is evaporated to a small volume. To this 5 ml of 1:1 $\text{H}_2\text{O}:\text{H}_2\text{SO}_4$ mixture is added and evaporated to dryness. The residue is dissolved in 15 ml of distilled water and filtered through what man filter paper No.41, The filtrate is collected in a 100 ml volumetric flask and made up to the mark with distilled water.

Procedure

A known aliquot of the sample solution is taken in a 25 ml volumetric flask containing 10ml of buffer solution of pH 8, 0.5ml of 0.5M citrate solution (to mask iron) and 1 ml of $2.873 \times 10^{-4}\text{M}$ reagent solution. The contents were made up to the mark with distilled water and the absorbance was measured at 355 nm. The amount of cobalt was calculated from a predetermined calibration plot.

RESULTS AND DISCUSSION

Absorption spectra

The reaction of esamoprazole with Co (II) at room temperature gives a greenish yellow colored water soluble complex. The Co (II) - esamoprazole complex shows maximum absorbance at 355nm where the reagent blank does not absorb appreciably. So the absorbance was carried out at λ_{\max} 355nm.

Effect of pH on the absorbance of the experimental solution

The plot between absorbance and of pH reveals that the metal complex shows (Fig.1) maximum and constant absorbance in the pH range 7.5-10.0. Therefore, pH 8.0 was selected for further studies (Table.1)

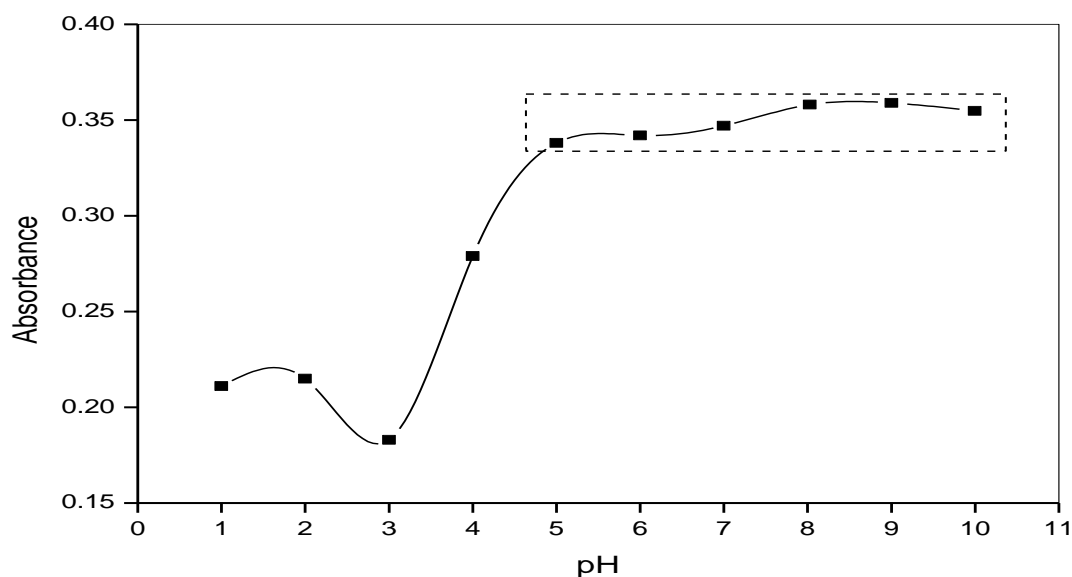


Figure 1: Effect of pH on absorbance of Co(ESMPZL) system

$$[\text{Co(II)}] = 4 \times 10^{-5} \text{M}; [\text{ESMPZL}] = 2.873 \times 10^{-4}$$

Effect of reagent concentration on absorbance of the complex solution

The minimum amount of reagent to acquire maximum color intensity with a given amount of Co (II) was evaluated from the absorbance measurements of experimental solution with different amounts of reagents (Table.2) . The results prove that a 15-fold molar excess of the reagent was required for the development of maximum color intensity with a given amount of cobalt (II).

Table 1: Effect of pH on the absorbance of Co (II)-ESMPZLcomplex

$$[\text{Co(II)}] = 4 \times 10^{-5} \text{M}; [\text{ESMPZL}] = 2.873 \times 10^{-4} \text{M}$$

S.No.	pH	Colour of the Complex	λ_{\max}	Absorbance
1	2.0	No colour reaction	-	-
2	3.0	No colour reaction	-	-
3	4.0	No colour reaction	-	-
4	5.0	Light yellow	357	0.678
5	6.0	Light yellow	362	0.723
6	7.0	Yellow	355	0.890
7	8.0	Yellow	355	0.960
8	9.0	Yellow	352	0.840
9	10.0	Light yellow	360	0.602

Table 2: Effect of reagent concentration on the absorbance of the complex

[Co(II)] = 4.0×10^{-5} M; λ_{\max} = 355 nm; pH = 8.0; [ESMPZL] = 2.873×10^{-4} M

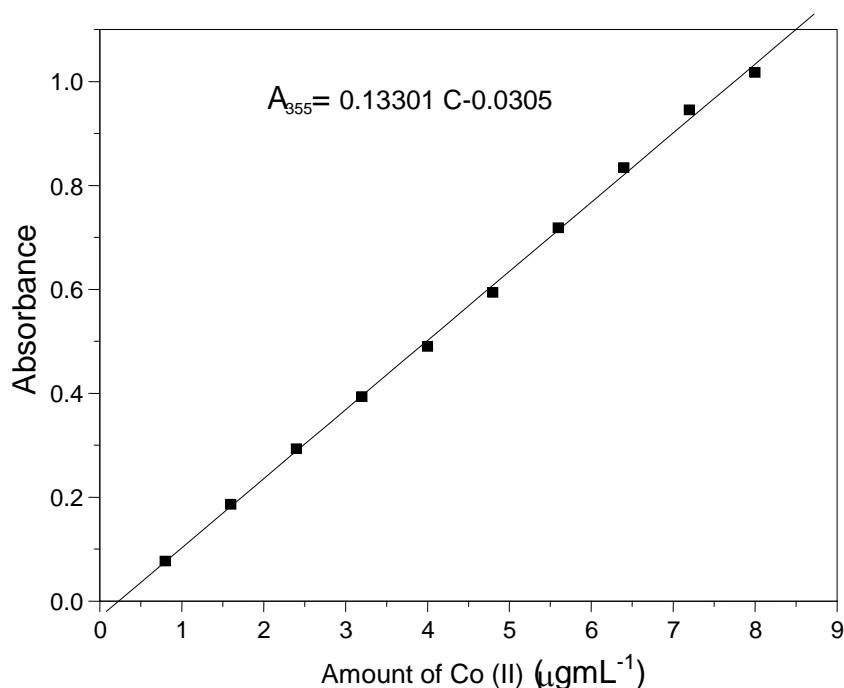
S.No.	Concentration of ESMPZL $\times 10^4$ M	[M] : [L]	Absorbance
1	0.1	1 : 1	0.331
2	0.2	1 : 2	0.490
3	0.3	1 : 3	0.650
4	0.4	1 : 4	0.810
5	0.5	1 : 5	0.965
6	0.6	1 : 6	0.942
7	0.7	1 : 7	0.931

Validity of Beer's law

The calibration plot between absorbance and concentration of Co (II) shows (Fig.2) that Beer's law is obeyed by the system in the concentration range 0.7 - 9.02 $\mu\text{g mL}^{-1}$ of Co (II). The straight line obeys the equation $A_{355} = 0.13301 C - 0.0305$. The molar absorptivity and sandell's sensitivity of the method were found as $4.56 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.007526 \mu\text{g cm}^{-2}$ respectively.

Composition and stability of the complex

The composition of the complex was determined using Job's continuous variation method (Fig.3) . The results indicate a 1: 2 stoichiometry between the metal ion and the reagent, which was confirmed by molar ratio method. The stability constant of the complex was determined using job's method as 2.21×10^5


Figure 2: Calibration plot between Co (II) concentrations on absorbance

[ESMPZL] = 2.873×10^{-4} M; λ_{\max} = 355 nm ;

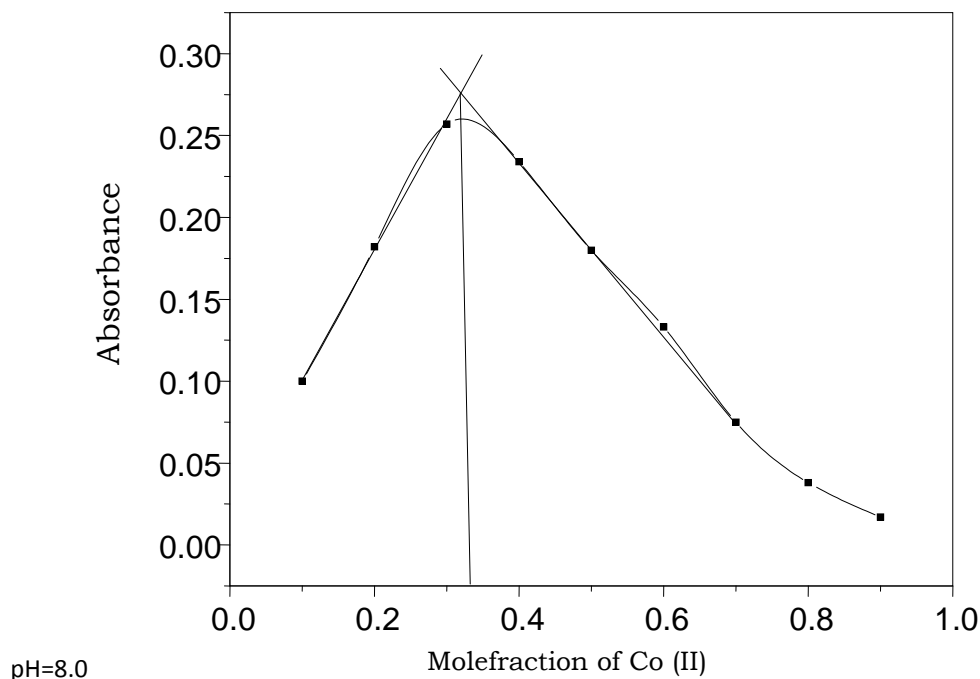


Figure 3: Job's method of continuous variation of Co(II)-ESMPZL complex

$$[\text{Co(II)}] = [\text{ESMPZL}] = 4 \times 10^{-5} \text{M}; \text{pH} = 8.0; \lambda_{\text{max}} = 355 \text{ nm}$$

Effect of foreign ions

The effect of various anions and cations normally associated with Mn (II) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by +2% were calculated and presented in **Table 1**. Almost all the tested anions possess high tolerance levels (>100 fold). The metal ions Pd (II), Au (III), Ni (II), Mo (VI), Co (II), Fe (II), and V (V) interfere in 30-45 fold excess.

Table 3: Tolerance limit of foreign ions in the determination of 1.698 $\mu\text{g/ml}$ of Co(II)
 $\text{pH} = 8.0; \lambda_{\text{max}} = 355 \text{ nm}$

Foreign ion	Tolerance limit ($\mu\text{g/ml}$)	Foreign ion	Tolerance limit ($\mu\text{g/ml}$)
EDTA	1667	U (VI)	82.80
Iodide	253.8	W (VI), Th (IV), La (III)	63.95
Nitrate	130.53	Cu (II)	45
Chloride	54.62	Mg (II)	32.41
Acetate	43.7	Mo (VI)	19.2
Fluoride	20.54	Sn (II)	14.84
Thiosulphate	15.5	Al (III), Ru (III), Sr (II)	13.49
Oxalate	8.85	Ni (II), Cd (II)	12
		Zr (IV)	10.73
		Ti (IV), Se (IV), Cr (VI)	6.96
		Pd (II), Al (III)	<1

Statistical analysis of the data

Statistical analysis of the data obtained in the experiment on cobalt with ESMPZL system is carried out. The standard deviation and relative standard deviation are calculated and the data is presented in the table .4.

Table 4: Statistical analysis of the data

[Co (II)] = 4×10^{-5} M; [ESMPZL] = 2.873×10^{-4} M pH = 8.0; λ_{\max} = 355 nm

S.No.	Volume of metal ion (1ml)	Volume of reagent (1 ml)	Absorbance (x)	d (X – M)	d ² (X - M) ²
1	1	1	0.960	0	0
2	1	1	0.957	-0.003	0.000009
3	1	1	0.958	-0.002	0.000004
4	1	1	0.963	0.003	0.000009
5	1	1	0.957	-0.003	0.000009
6	1	1	0.955	-0.005	0.000025
7	1	1	0.958	-0.002	0.000004
8	1	1	0.965	0.005	0.000025
9	1	1	0.964	0.004	0.000016
10	1	1	0.963	0.003	0.000009

Standard Deviation (S.D.) = 0.00332 for ten determinations ; R.S.D. = 0.348 %

Applications

The amount of cobalt present in some alloy steel samples was determined by the present method and the results obtained were compared with certified values. The data is given in Tables. 5 and 6.

Table 5: Determination of Co (II) in Elegiloy

Sample	Cobalt (II) (%)		Error %
	Certified	Found	
Elegiloy M-1712 ^a	40.00	39.58	1.05 %

Table 6: Determination of Co(II) in Alloy steel samples

Sample	Amount of Co(II) (%)		Error (%)
	Certified	Found*	
High speed steel (6-18% W, 5.5% Mo, 4.15% Cr, 0.4% Mn, 0.35% Si, 0.05% S, Rest Fe)	9.26	9.29	+0.32
Udimet-700 (15% Cr, 4.3%Al,5.21% Mo, 0.08% C,0.003% B)	18.00	18.10	+0.55

CONCLUSIONS

The proposed methods for the spectrophotometric determination of cobalt (II) in steel alloys samples was rapid, simple, selective and sensitive. In this method, organic, toxic, carcinogenic solvents are avoided for the extraction of color derivatives; it indicates the present method is non-toxic and safer than those methods using other organic solvents.

Statistical analysis of the results indicates that the method yields good values. The results obtained in the spectrophotometric determination of Co (II) in various steel and alloy samples was compared with the certified values and the results were quite encouraging.



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