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Spectrophotometric Determination of Co(II) by Using Ethyl Cyano(2-Methyl Carboxylate Phenyl Azo Acetate) (ECA)

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Abstract

A new simple and sensitive spectrophotometric method for the determination of trace amount of Co(II) in the ethanol absolute solution have been developed. The method is based on the reaction of Co(II) with ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ECA) in acid medium of hydrochloric acid (0.1 M) givining maximum absorbance at ((λ_{max} = 656 nm). Beer's law is obeyed over the concentration range (5-60) (µg / ml) with molar absorptivity of (1.5263×10^3 L mol^{-1} cm^{-1}) and correlation coefficient (0.9995). The precision (RSD% < 1%). The stoichiometry of complex was confirmed by Job's method which indicated the ratio of metal to reagent is (2:1). The studied effect of interference elements Zn(II), Cu(II), Na(I), K(I), Ca(II) and Mg(II) on the complexation of Co(II) and have been studied and applied to determine Co(II) in synthetic water samples.

Keywords: Spectrophotometric, determination, cobalt, complex.

INTRODUCTION

Cobalt metal white diagonal bluer and possesses qualities veromagnatise, with many cases of oxidants are (+2, +3, +4, +5). It has atomic number 27 and atomic mass 58.933 gm. Mol^{-1}.[1]. Cobalt used in stained-glass industry and enters in the composition of vitamin B_{12}[2]. It is an important element, not only for industry but

also for biological systems. Many sensitive techniques, such as spectrofluorimetry, x-ray fluorescence, atomic absorption spectrometry have been widely applied to the determination of cobalt[3-5]. Organic reagents were used widely in the spectral estimation of many metal ions, including the cobalt[6].

Several spectrophotometric for the determination of the cobalt in trace amount, for example using 4-(6-nitro-2-benzothiazolylazo) resorcinol[7], bis(5-bromosalicylaldehyde)[8], by dithizone[9], sodium isoamylxanthalate[10], 5-[o-carboxyphenylazo]-2,4-dihydroxybenzoic acid[11], hydroxytriazene as selective chelating agents[12] and quantitative determination of the cobalt containing pthalocyanine fragments mantitumor drugs[13]. Azo compounds are very important class of chemical compounds receiving attention in scientific research, they are highly colored and have been used as dyes and pigments for along times[14]. Synthesis of the ligand ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ECA) and the structure of (ECA) in Figure (1) [15].

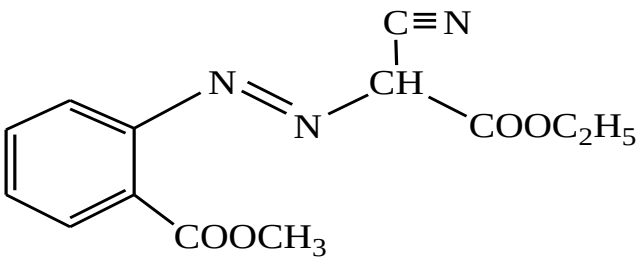

Figure 1: Structure of (ECA)

The objective of this work is therefore to come up with a spectrophotometric method which is selective, sensitive, rapid, involving simple procedures and providing high quality results for cobalt determination in trace amounts of several simples of synthesis water.

EXPERIMENTAL

Apparatus

- UV-Vis spectrophotometer

  A Shimadzu double beam UV-Vis spectrophotometer model UV-1601 (Kyoto, Japan) working at wavelength of 190-1100 nm.

- Digital balance

  Digital analytical-Sartorius (Bp 3015-Germany).

- Phillips Pw, 526 conductmeter
- Dig melt MPA 161 (MSRS) electronic.
- 8400s Shimadzu FT infrared spectrophotometer.

Reagents

Cobalt chloride hexhydrate Fluka AG Buchs SG.

Sodium hydroxide Fluka AG Buchs SG.

Hydrochloride acid Riedel-Dehaen AG.

Ethyl cyano(2-methyl carboxylate phenyl azo acetate) (ligand) (1000 µg / ml)

The ligand was prepared as same in paper[15]. A stock solution of (1000 µg / ml) of ligand was prepared by dissolving (0.1 gm) in ethanol absolute and then made up to (100 ml) in a volumetric flask and was kept ambient bottle a way from sun light.

Cobalt(II) (1000 µg / ml)

A stock solution of (1000 µg / ml) of Co(II) was prepared by dissolving (4.039 gm) of cobalt chloride hexhydrate ($CoCl_2.6H_2O$) in ethanol absolute and diluted to (100 ml) in a volumetric flask by the same solvent.

Sodium hydroxide ≃ (0.1 M)

This solution was prepared by dissolving (0.4 gm) of sodium hydroxide in ethanol absolute and diluted to (100 ml) in a volumetric flask by the same solvent.

Hydrochloric acid ≃ (0.1 M)

This solution was prepared by diluting of (1.54 ml) of concentrated hydrochloric acid (37%) and diluted to (250 ml) in a volumetric flask by ethanol absolute.

Procedure

Absorption spectra of complex

The complex is produced from the reaction between (0.2 ml) of ligand (1000 µg / ml) with (0.1 ml) of Co(II) (1000 µg / ml) in a volumetric flask (5 ml) and diluted to ethanol absolute giving maximum absorbance at λ_{max} = 656 nm.

Optimum conditions

Effect of ligand volume

When a various volumes of ligand solution (0.05, 0.1, 0.15, ….. 0.5) ml for (1000 µg / ml) were added to (0.1 ml) of (1000 µg / ml) Co(II) in a volumetric flask (5 ml) and diluted to ethanol absolute.

Effect of hydrochloric acid volume

When a various volumes of HCl solution (0.1, 0.2, 0.3, ….. 1) ml for (0.1 M) were added to (0.2 ml) of (1000 µg / ml) ligand and (0.1 ml) of (1000 µg / ml) Co(II) in a volumetric flask (5 ml) and diluted to ethanol absolute. The absorption spectra were recorded against blank in (λ_{max} = 656 nm) and temperature (25 ˚C).

Effect of sodium hydroxide volume

When a various volumes of NaOH solution (0.1, 0.2, 0.3, ….. 1) ml for (0.1 M) were added to (0.2 ml) of (1000 µg / ml) ligand and (0.1 ml) of (1000 µg / ml) Co(II) in a volumetric flask (5 ml) and diluted to ethanol absolute. The absorption spectra were recorded against blank in (λ_{max} = 656 nm) and temperature (25 ˚C).

Preparation of calibration graph

The content of series of (5 ml) calibration flasks containing (0.2 ml) of ligand (1000 µg / ml) and (0.1 ml) of (0.1 M) HCl with different concentrations (5-60) (µg / ml) of Co(II) (1000 µg / ml) were diluted with ethanol absolute. The absorption spectra were recorded against blank in (λ_{max} = 656 nm) and temperature (25 ˚C).

Effect of interference elements

A stock solution of each element (10000 µg / ml) was prepared by dissolving (2.0845 gm) $ZnCl_2$, (2.682 gm) $CuCl_2.2H_2O$, (2.5421 gm) NaCl, (1.9067 gm) KCl, (2.7691 gm) $CaCl_2$ and (3.9173 gm) $MgCl_2$ in ethanol absolute and then made up to (100 ml) in volumetric flask with the same solvent working solution of (1000, 200, 20) µg / ml of each element was prepared by simple dilution for primary stock solution (10000 µg / ml) in a volumetric flask (5 ml) which contains (0.2 ml) ligand (1000 µg / ml), (0.1 ml) HCl (0.1 M) and (0.1 ml) Co(II) (1000 µg / ml) diluted up to the mark with ethanol absolute. Taken absorbance of each solution in (λ_{max} = 656 nm) against blank.

Application

The sample Co(II) in synthetic a river water, tap water, well water, sewerage water and rain water (1000 µg / ml) was prepared by taking (4.0399 gm) of $COCl_2.6H_2O$ dissolving in all types water and transferred in a volumetric flask (100 ml) diluted up to the mark with same solvent. Transferred (0.1 ml) of synthetic water simple (1000 µg / ml) of Co(II) to a volumetric flask (5 ml) contains (0.2 ml) ligand (1000 µg / ml) and (0.1 ml) HCl (0.1 M) diluted up to the mark with ethanol absolute. Taken absorbance of solution in (λ_{max} = 656 nm) against blank.

Synthesis of complex

A solution of cobalt chloride contains (0.1100 gm) (1 mmole) $CoCl_2.6H_2O$ respectively in ethanol absolute was added to a solution of the ligand (ECA) (0.2500 gm) (2 mmole) in ethanol absolute (5 ml). After stirring for 3 hours colored precipitate was formed at room temperature, the resulting solid was filtered off, recrystallized from ethanol absolute and dried at (50 ˚C).

RESULTS AND DISCUTION

Absorption spectra

The complex is produced from the reaction between (0.2 ml) ligand (1000 µg / ml) with (0.1 ml) Co(II) (1000 µg / ml) giving maximum absorbance at λ_{max} = 656 nm an in Figure (2).

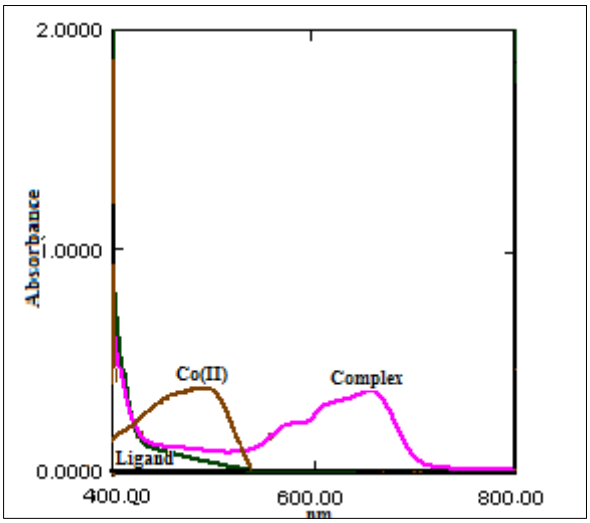

Figure 2: Absorption spectra of (a) 40 (µg / ml) ligand (b) 20 (µg / ml) Co(II) (c) 40 (µg / ml) ligand with 20 (µg / ml) of Co(II) against reagent blank

Optimum conditions for regulation reaction

There are many parameters affecting on the complexation reaction and absorbance of complex which is produced.

Effect of ligand volume

Solution was found that (0.2 ml) of ligand is enough to give a maximum absorption and was considered to be optimum for concentration range of (5-60) (µg / ml) of Co(II)-complex. The results were shown in Table (1).

Table 1: Effect of ligand volume of absorbance value of complex at temperature (26 ˚C)

Vol. of ligand (ml)	Absorbance
0.05	0.349
0.10	0.412
0.15	0.422
0.20	0.432
0.25	0.430
0.30	0.425
0.35	0.421
0.40	0.420
0.45	0.415
0.50	0.409

Effect of hydrochloric acid volume

It was found that the presence of acid in reaction solution effect on increasing the intensity of absorbance for the produced complex, HCl was selected and (0.1 ml) of (0.1 M) was found to be the optimum volume. This acid gives high sensitivity which was selected in subsequent experiments, the results were shown in Table (2).

Table 2: Effect of hydrochloric acid volume on absorbance value of complex at temperature (25 ˚C)

Vol. of hydrochloric acid (0.1M) (ml)	Absorbance
0.0	0.461
0.1	0.511
0.2	0.480
0.3	0.457
0.4	0.450
0.5	0.410
0.6	0.400
0.7	0.391
0.8	0.370
0.9	0.351
1.0	0.330

Effect of sodium hydroxide volume

Existence of sodium hydroxide (0.1-1) ml of (0.1 M) in reaction solution effect on decreasing the intensity of absorbance for the produced complex. The results were shown in Table (3).

Table 3: Effect of sodium hydroxide volume on absorbance value of complex at temperature (25 ˚C)

Vol. of sodium hydroxide (0.1 M) (ml)	Absorbance
0.0	0.461
0.1	0.457
0.2	0.424
0.3	0.352
0.4	0.350
0.5	0.330
0.6	0.321
0.7	0.312
0.8	0.310
0.9	0.300
1.0	0.290

Effect of order of addition

To obtain optimum results, the order of addition of ligand should be the first followed by addition of acid and Co(II). The results were shown in Table (4).

Table 4: Effect of order of addition on absorbance value of complex at temperature (25 ˚C)

	Order of addition	Absorbance
I	Co(II) + ligand + HCl	0.381
II	Co(II) + HCl + ligand	0.505
III	Ligand + HCl + Co(II)	0.592
IV	Ligand + Co(II) + HCl	0.512
V	HCl + Ligand + Co(II)	0.513
VI	HCl + Co(II) + Ligand	0.540

Effect of temperature

The resulting complex of the proposed method was studied at room temperature (25 ˚C), the absorbance values remain constant. The results were shown in Table (5).

Table 5: Effect of temperature on absorbance value of complex

Temp. (˚C)	Absorbance
20	0.530
25	0.593
30	0.521
35	0.480
40	0.420

Effect of time on the complex formation

The results show that the complex produced was stable between (5-25) minutes, absorbance value stable. The results were shown in Table (6).

Table 6: Effect of time on the complex formation at temperature (25 ˚C)

Time (min.)	Absorbance
0	0.550
5	0.593
10	0.592
15	0.593
20	0.593
25	0.593

Calibration graph

Employing the conditions described in the procedure**,** a linear calibration graph for Co(II)-complex is obtained, Figure (3), which shows that Beer's law is obeyed, the concentration range of (5-60) µg / ml.

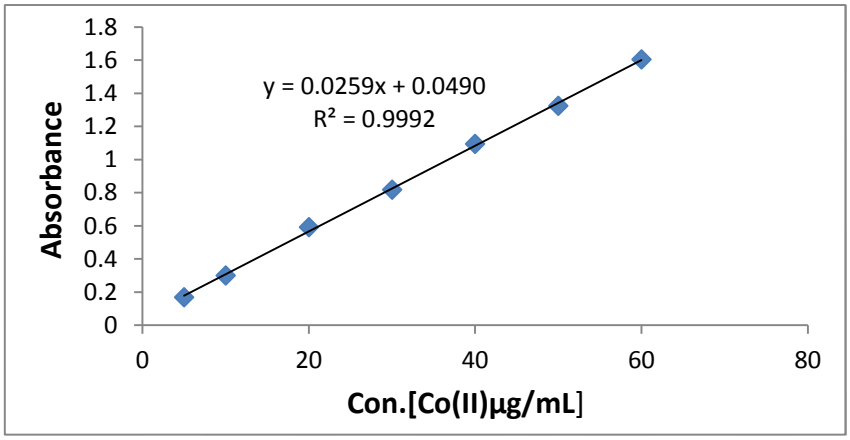

Figure 3: Calibration graph of Co(II)-complex

Precision and accuracy

Under the optimum condition, the precision and accuracy of the method was calculated. The results were shown in Table (7).

Table 7: Precision and accuracy of the method

Element	Taken (µg / ml)	Found (µg / ml)	RE %	RSD % n = 5	Recover %
Co(II)	10	09.691	3.090	0.3149	096.910
	40	40.386	-0.965	0.1257	100.965
	60	60.077	-0.128	0.0000	100.128

Table 8: Method validation of the spectrophotometery determination of Co(II) with ligand in ethanol absolute

Parameter	Value
λ_{max} (nm)	656
slope	0.0259
intercept	0.0490
R^2	0.9992
r	0.9995
ε_{max} (L mol^{-1} cm^{-1})	1.5263×10^3
sandell index (µg cm^{-2})	0.3861×10^2

Structure of the complex

The stoichciometry of the complex between Co(II) and ligand was investigated using Job's method, the results show that 1:2 Co(II) to ligand complex was formed, Figure (4).

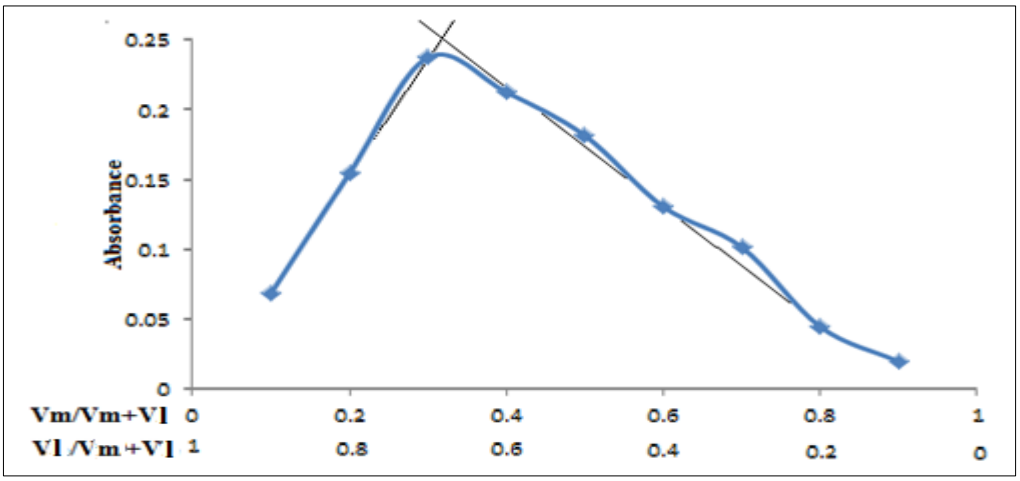

Figure 4: Job plots [ECA] = [Co(II)] = 3×10^{-4} M

Infrared spectrum of complex

The infrared spectrum of complex Figure (5), shown the strong absorption band at the (1627) cm^{-1}, (1435) cm^{-1}, (420) cm^{-1} and (526) cm^{-1} due to υ(C=O) ester, υ(N=N), (M-N) and (M-O) respectively.

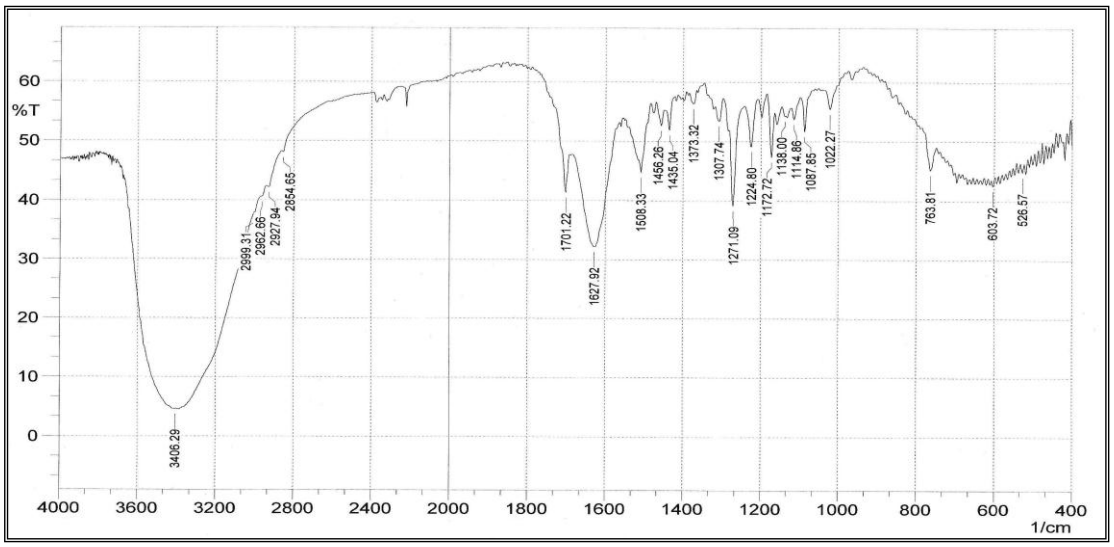

Figure 5: Infrared spectrum of $[Co(ECA)_2]Cl_2$

The formation of the complex produced suggest occurring as follows, Figure (6).

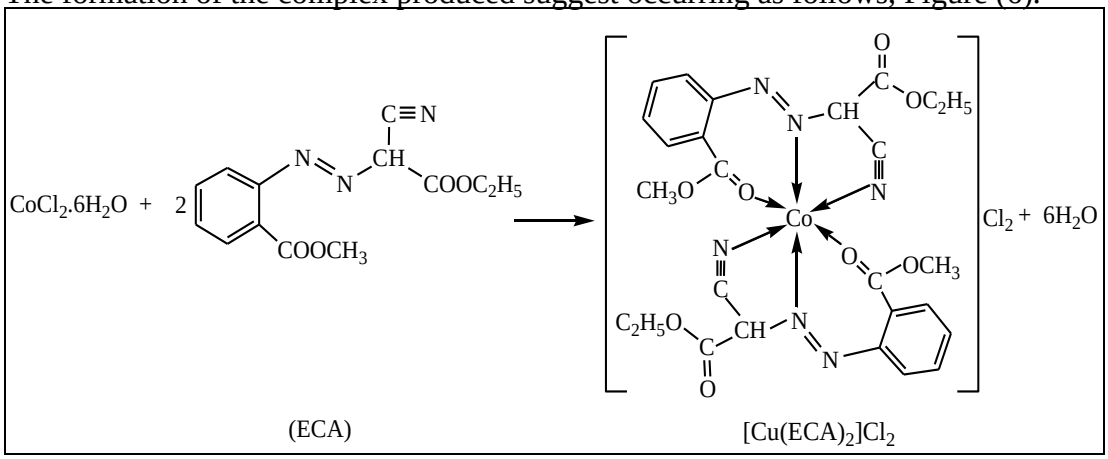

Figure 6: Suggest product formation pathway

Table 9: Physical properties of complex

Formula	Molecular weight (g/mol)	Colour	M. p. ˚C or dec.	Metal% Found (Calc.)	Molar conductivity ($S.cm^2mole^{-1}$) in Ethanol (10^{-3} M)
$[Co(ECA)_2]Cl_2$	679.93	Deep green	95 (dec.)	8.50 (8.66)	80

Effect of interference elements

We have studied the effect of interference elements (Zn(II), Cu(II), Na(I), K(I), Mg(II), Ca(II)), on the complexation of Co(II). The results showed that interference elements are not affected on to determination of Co(II) as ECA complex, Table (10).

Table 10: Effect of interference elements on the determination of Co(II) as (ECA) complex

Element of interference	Conc. element interference (µg / ml)	Found as	Taken of Co(II) (µg / ml)	Found of Co(II) (µg / ml)	RE %	Recover %
Zn(II)	20	$ZnCl_2$	20	20.1	-0.500	100.5
	200		20	20.0	0.000	100.0
	1000		20	19.9	0.500	099.5
Cu(II)	20	$CuCl_2.2H_2O$	20	20.0	0.000	100.0
	200		20	20.0	0.000	100.0
	1000		20	19.9	0.500	099.5
Na(I)	20	NaCl	20	19.9	0.500	099.5
	200		20	20.1	-0.500	100.5
	1000		20	20.0	0.000	100.0
K(I)	20	KCl	20	19.9	0.500	099.5
	200		20	20.0	0.000	100.0
	1000		20	20.0	0.000	100.0
Ca(II)	20	$CaCl_2$	20	20.1	-0.500	100.5
	200		20	20.0	0.000	100.0
	1000		20	19.9	0.500	099.5
Mg(II)	20	$MgCl_2$	20	20.0	0.000	100.0
	200		20	19.9	0.500	099.5
	1000		20	19.9	0.500	099.5

Application

The method was successfully applied for determination of Co(II) in synthetic a river water, tap water, well water, sewerage water and rain water. The results were shown Table (11).

Table 11: Results for analysis of Co(II) in a simple synthetic

Element	Simple	Taken (µg / ml)	Found (µg / ml)	RE %	Recover %
Co(II)	River water	20	20.00	0.000	100.00
	Tap water	20	20.05	-0.250	100.25
	Well water	20	19.91	0.450	099.55
	Sewerage water	20	20.04	-0.200	100.20
	Rain water	20	19.95	0.250	099.75

CONCLUSTION

A new reagent (ECA) for determination of cobalt(II). Selective and sensitive spectrophotometric method for determination of trace amount of Co(II) in the ethanol solution.

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