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Research Article

**5- (2-HYDROXYBENZYLIDENE) -2,4-TIAZOLIDINDION AS  
ANALYTICAL REAGENT FOR EXTRACTION-  
PHOTOMETRIC DETERMINATION OF COBALT (II)**<sup>1</sup>K. A. Aliyeva<sup>1</sup>Department of Analytical Chemistry, Azerbaijan State Pedagogical University,  
[kerim.kuliev.69@mail.ru](mailto:kerim.kuliev.69@mail.ru)

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**Abstract:**

The possibility of using 5- (2-hydroxybenzylidene) -2,4-thiazolidinedione (L) for photometric determination of cobalt (II) has been studied. The best extractants were dichloroethane, chloroform and carbon tetrachloride. With a single extraction with chloroform, 97.6% of cobalt is recovered as a complex. The cobalt (II) complex is extracted into chloroform in the pH range 4.0-5.3. The maximum analytical signal for the complexation of cobalt with L is observed at 530 nm. The molar absorption coefficient is  $3.28 \times 10^4$ . The ratio of components in the complex is Co: L = 1: 2. The extract of the cobalt complex obeys the basic law of light absorption at a concentration of 0.25-16  $\mu\text{g} / \text{ml}$ . Based on the results of spectrophotometric studies of cobalt(II) with L, methods for determining cobalt in different objects have been developed.

**Keywords:** cobalt, 5- (2-hydroxybenzylidene) -2,4-thiazolidinedione, extraction-photometric method.**Corresponding author:****K. A. Aliyeva,**Department of Analytical Chemistry, Azerbaijan State Pedagogical University,  
[kerim.kuliev.69@mail.ru](mailto:kerim.kuliev.69@mail.ru)

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**INTRODUCTION:**

Cobalt (II) is a biologically active metal. It has been established that excessive "technogenic" intake of cobalt compounds in the body has a toxic effect on metabolism. An excess of cobalt salts causes morphological changes in the cell and thereby has a carcinogenic effect on it. They play an important role in biological processes in the body, and are an indicator of some diseases. For example, the absence of cobalt in the body causes acobaltosis [1].

This requires continuous monitoring of industrial pollutants and the migration of toxic substances in the environment and creates the need for the implementation of operational and reliable control of the content of heavy metals with toxic properties.

For the photometric determination of cobalt, reagents with an o-nitrosophenol group or a similar structure with an oxime group are rather selective [2, 3]. The most widely used methods are those that use organic reagents derived from nitrosonaphtholes, pyridine azo compounds, of which 4- (2-pyridylazo) -resorcinol is widespread [4]. The optimal experimental conditions for the quantitative sorption of Co (II) - 4- (2-pyridylazo) resorcinol were found. The proposed method has been applied to determine cobalt in various water samples [5].

A spectrophotometric method was developed for the determination of Co (II) with N- (O-hydroxybenzylidene) pyridin-2-amine. The proposed method is applied to determine Co (II) in pharmaceutical samples [6].

The complex formation of cobalt with dithiophenols and hydrophobic amines was studied. Extraction photometric methods for the determination of cobalt in various natural and industrial objects have been proposed [7–8].

For the extraction-photometric determination of cobalt in various natural and industrial objects, mixed-ligand complexes (RLC) of cobalt with 4- (2-pyridylazo) resorcinol and 1,4-diphenyl-3-(phenylamino) -1H-1,2,4-triazole [9], with 4- (2-pyridylazo) resorcinol and tetrazolium salts [10].

We have studied the possibility of using 5- (2-hydroxybenzylidene) -2,4-thiazolidinedione (L) for the photometric determination of cobalt (II).

**MATERIALS AND METHODS:****Instruments:**

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer (Japan) and

KFK 2 photocolormeter (USSR). Glass cells with optical path of 10 or 5 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode.

Muffle furnace was used for dissolution of the samples. IR spectra were recorded on a spectrophotometer "Specord M80" (Germany). <sup>1</sup>H-NMR spectra were recorded on "Bruker" Fourier Transform (300,18 MHz) in C<sub>6</sub>D<sub>6</sub>.

**Reagents and Solutions:**

Standard solution (1 mg/ml) of Co(II) was prepared by dissolving in water an exact sample of CoSO<sub>4</sub> · 7H<sub>2</sub>O in water containing 2 ml of conc. H<sub>2</sub>SO<sub>4</sub>, and diluted with water to 1 l [2]. The working solutions were prepared just before use by dilution of the standard solution with redistilled deionised water. Solutions of L in chloroform (0.01M) were used. The extractant was purified chloroform. Acetate buffers of pH 4, 5 and 6 were prepared by mixing 0.05 M solutions of CH<sub>3</sub>COONa and acetic acid. 4. Phosphate buffers of pH 7 and 8 were prepared by mixing 0.05 M solutions of KH<sub>2</sub>PO<sub>4</sub> and 0.01 M NaOH. The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

**General Procedure:****Procedure for the extraction:**

Aliquots of Co (II) solution, L solution (up to 2.0 mL) and buffer solution (pH ranging from 3.0 to 9) were introduced into 100-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 25 mL. Then 3.0 mL of chloroform was added (the volume of the organic phase was 5 mL). and the funnels were shaken for a defined period of time (up to 5 min). When the equilibrium was reached, the organic layer was separated from the aqueous layer. A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.

**Determination of cobalt in sewage water and bottom sediments**

1/ taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of HNO<sub>3</sub>, was transferred to a 50 ml flask and diluted to the mark with water. Cobalt was determined in aliquots of the solution using the procedure proposed by us [21].

**Determination of cobalt in plant samples**

A portion of the plants (25-50 g ) were crushed and dried in a porcelain dish, first at 60-70 ° C, then at a

temperature of 105 ° C. The dry residue was ashed in a muffle furnace at 500 ° C. The ash was dissolved in diluted (1: 1) HNO<sub>3</sub> and evaporated to wet salts, which were then dissolved in water, filtered into a 100 ml volumetric flask and diluted with distilled water to the mark. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

### RESULTS AND DISCUSSION:

Cobalt (II) with 5-(2-hydroxybenzylidene) -2,4-thiazolidinedione (L) forms a colored complex that dissolves well in non-polar organic solvents. Dichloroethane, chloroform and carbon tetrachloride turned out to be the best extractants. With a single

extraction with chloroform, 97.8% of cobalt is recovered as a complex. The complex is extracted into chloroform in the range of pH = 4.0-5.3. With a decrease in the pH of the aqueous phase, the extraction of Co(II) gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form L and, most likely, in solution it is in undissociated form. At pH 9.5, the complex is practically not extracted, which is apparently due to the hydrolysis of the cobalt ion. The optimal condition for the formation and extraction of the complex is  $8 \times 10^{-4}$  mol / l concentration of L.

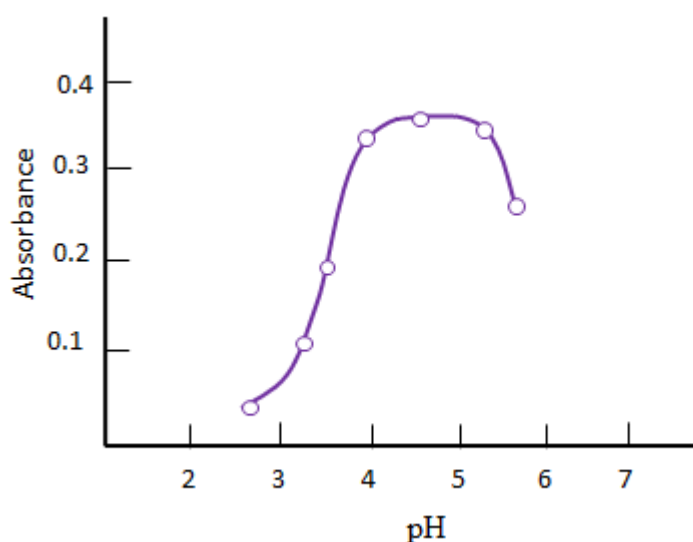


Fig.1. The dependence of the optical density of the complex on the pH of the aqueous phase.

$C_{Co(II)} = 3.38 \times 10^{-5}$  M;  $C_R = 8.0 \times 10^{-4}$  M; KФК-2,  $\lambda = 490$  nm  $l = 1$  cm

The complex of cobalt with L is stable in aqueous and organic solvent and does not decompose for two days, and after extraction it lasts more than a month. Maximum optical density is achieved within 5 minutes. The complex is stable when heated to 80 °

C. The results of studying the ratio  $V_{ag} / V_o$  to extract Co (II) in the form of Co-L showed that the optimum  $V_{ag} / V_o$  is 5 / 5-90 / 5.

The maximum analytical signal in the complexation of cobalt with L is observed at 530 nm. L max absorbs at 254 nm. Bathochromic shift is 276 nm. The molar absorption coefficient is  $3.28 \times 10^4$ .

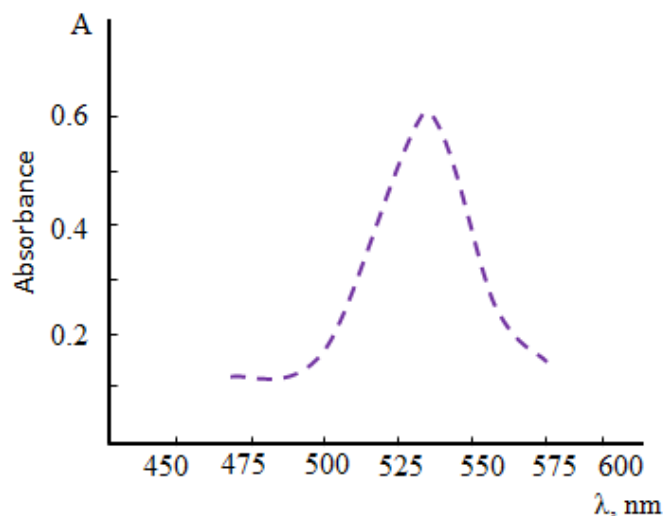


Fig.2. Absorption spectra

$C_{Co(II)}=3.38 \times 10^{-5} M$ ;  $C = 8.0 \times 10^{-4} M$ ;  $C\Phi-26$ ,  $l = 1$  cm

The stoichiometry of the studied complexes was established by the methods of equilibrium shift, the

relative output of Starik Barbanel and the straight line [11]. All methods showed that the ratio of components in the complex is Co: L = 1: 2.

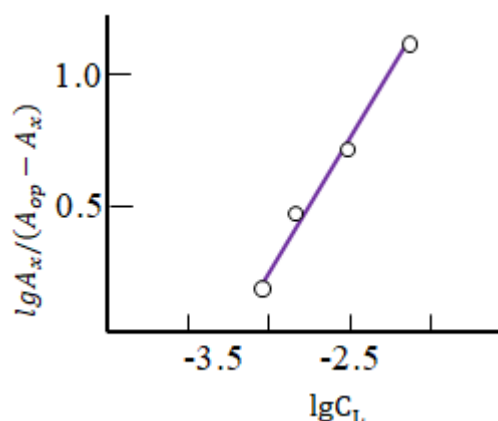


Fig. 3. Determination of the ratio of components by equilibrium shift method

$C_{Co(II)}=3.38 \times 10^{-5} M$ ;  $C\Phi-26$ ,  $l=1$  cm.

The Co(II) complex with L was synthesized and investigated by chemical analysis and IR spectroscopy. The IR spectrum of the complex is compared with the spectrum of the reagent. The observed band in the region of 1593-1448  $cm^{-1}$  corresponds to the aromatic ring ( $C = C$ ). In the IR spectra of the complex in the region of 3040-3020  $cm^{-1}$  there are strong absorption bands associated with  $\nu_{CH}$  in the aromatic core.

The absorption bands at 820–710  $cm^{-1}$  can be attributed to C – H deformation vibrations, the absorption bands at 1610–1450  $cm^{-1}$  to the stretching vibrations of phenyl rings, and the absorption bands at 1380  $cm^{-1}$  to  $\nu_{CN}$ .  $\nu_{CS}$  is observed at 685  $cm^{-1}$ , and  $\nu_{CO}$  is observed at 1291  $cm^{-1}$ . The absorption bands at 440  $cm^{-1}$  and 573  $cm^{-1}$  correspond to  $\nu$  (Co – O) and  $\nu$  (Co – N), respectively [12,13].

The results of chemical analysis are given in table.1.

**Table 1.** Elemental analysis results of L and Co-L

Compound	%	C	H	N	Fe
L	Found	54.48	3.25	6.47	-
	Calculated	54.29	3.19	6.33	-
Co- L	Found	46.83	2.62	5.67	10.95
	Calculated	46.69	2.53	5.45	10.89

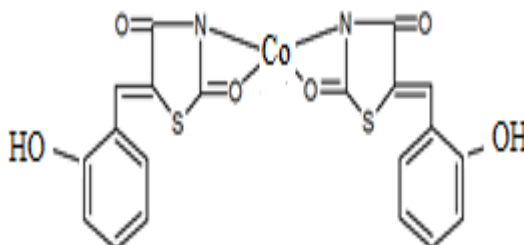
A thermogravimetric study of the Co-L complex showed that its thermal decomposition occurs in two stages. The dehydration temperature (90 ° C - 110 ° C) on the DTA curve by the endothermic effect (weight loss 5.09%) indicates the dehydration of the complex. In the temperature range of 385-450 °C, the maximum rate of mass loss is observed, which is associated with the removal of L (weight loss 39.88%). The end product of thermolysis of the complex is CoO.

The Nazarenko method has been established that the complexing form of iron is  $\text{Co}^{2+}$  [14, 15]. At the

same time, the number of hydrogen atoms, which it displaces from one L molecule, turned out to be equal to 1.

The calculations performed showed that the mixed-ligand complex in the organic phase does not polymerize and is in monomeric form ( $\gamma = 1.05$ ) [16].

Based on the ratio of components in the resulting complexes, the number of protons being displaced, and the ionic form of cobalt, one can imagine the probable structure of the complexes on Co - L.



It was established that with L the colored complexes also form ions of Fe (III), V (IV), Cu (II), Ni (II), Mo (VI), Pt (II), Mn (II), Cd (II), Zn (II), Pd (II) and  $\text{UO}_2^{2+}$ . The selectivity of the determination increases significantly in the presence of masking agents or when the pH of the medium changes. When using a 0.01 M solution of EDTA, Ti (IV), V (IV),

Nb (V), Ta (V), Mo (VI), Fe (III) and Ni (II) do not interfere with the determination. Large amounts of fluoride, oxalate, thiosulfate, bromide, chloride, tartrate, sulfate, acetate and citrate ions do not interfere with the determination. Thiocyanate, thiourea and phosphate ion interfere, even when present in small quantities.

Table 2. The influence of foreign ions on the determination of cobalt (II) with L (30 µg of Co (II) taken, n = 3, P = 0.95)

Ion	Molar excess of the ion	Masking agent	Found, Co µg	S <sub>r</sub>
Ni(II)	50	ЕДТА	29.5	0.04
Fe(II)	50		29.8	0.04
Cd(II)	200		30.5	0.03
Al(III)	180		29.8	0.03
Fe(III)	50	Ackorbic acid	30.2	0.05
Zr(IV)	50		29.8	0.05
Cu(II)	25	Thiourea	29.8	0.04
Hg(II)	40		30.5	0.05
Ti(IV)	30	Ackorbic acid	29.6	0.03
V(IV)	20		30.5	0.05
Mo(VI)	10	ЕДТА	29.8	0.05
W(VI)			29.8	0.03
Cr(III)	120		30.2	0.03
Nb(V)	50	$C_2O_4^{2-}$	29.7	0.05
Ta(V)	50	Ackorbic acid	30.2	0.03
$UO_2^{2+}$	50		29.8	0.05
Salicylic acid	25		29.8	0.05
Sulfosalicylic acid	30		30.5	0.04
Ackorbic acid	120		29.6	0.03
Wine acid	120		30.2	0.03
Oxalate	48		29.8	0.05
Fluoride	45		29.8	0.04
H <sub>3</sub> PO <sub>4</sub>	30		30.4	0.04
Thiourea	20		29.6	0.03

The calculations performed showed that the complex in the organic phase does not polymerize and is in monomeric form. The extract of the complex obeys the basic law of absorption at a concentration of 0.25-16 µg / ml. The data obtained for the construction of the calibration curve were processed by the method of least squares [17]. Based on the equation of the

calibration graphs, the limit of photometric detection and the limit of quantitative determination of cobalt were calculated.

In tab. 3 shows the main spectrophotometric characteristics of the method for determining Co(II) with L.

Table 3. Formation conditions and some chemical and analytical properties of Co(II) with L

Parameter	Value
Color	red
pH <sub>op</sub>	4.0-5.3
λ <sub>max</sub> (nm)	530
Bathochromic shift	254
Molar absorptivity (L · mol <sup>-1</sup> · cm <sup>-1</sup> )	3.28 · 10 <sup>4</sup>
Sandell's sensitivity (ng · cm <sup>-2</sup> )	1.85
R, %	97.8
The equation of calibration curves	0.028+0.29x
Correlation coefficient	0.9954
lg K <sub>e</sub>	6.25
Stability constant (β)	9.62
Beer's law range (µg · mL <sup>-1</sup> )	0.25-16
Limit of detection (LOD): ng · mL <sup>-1</sup>	13
Limit of quantification (LOQ): ng · mL <sup>-1</sup>	42

In tab. 4 shows the data allowing to compare the analytical characteristics of the photometric cobalt (II) methods developed by us with some already known [3, 9, 16] methods. As can be seen from the

table, the methods proposed by us are quite selective, sensitive, they are expressive and allow to determine even small amounts of these metals and to obtain reproducible results.

**Table 4.** Comparative characteristics of cobalt determination methods

Reagent	pH	Solvent	$\lambda$ , nm	$\varepsilon \times 10^{-4}$	Beer's law range ( $\mu\text{g} \cdot \text{ml}^{-1}$ )
1-nitrosophthol-2 [3]	pH $\geq$ 3	Chloroform	415	2.9	
Nitroso R-salt [3]	слабокислая		500	1.5	
Bromopirogall red [18]	2.0		575	1.08	0.25-110
PAR + chloride 2- (4-iodophenyl) -3- (4-nitrophenyl) -5-phenyl-2H-tetrazolium [9]	4.7		515	1.4	
L	4.2–5.5	Chloroform	528	3.22	0.25-16

Based on the results of spectrophotometric studies of cobalt(II) with L, methods for the determination of cobalt in plants have been developed. in sewage and bottom sediments (tabl. 5 and 6).

**Table 5.** The results of the determination of cobalt (II) in plants (n = 6, P = 0.95)

Analysis object	Reagent	Found, mg/kg	S	$S_r$	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
<i>beans</i>	1-nitrosophthol-2	0.20	0.0050	0.024	0.20 $\pm$ 0.0053
	8-mercaptoquinoline	0.19	0.0044	0.023	0.19 $\pm$ 0.0050
	L	0,18	0.0034	0.019	0.18 $\pm$ 0.0039
<i>peas</i>	1-nitrosophthol-2	0.11	0.0038	0.035	0.11 $\pm$ 0.0040
	8-mercaptoquinoline	0.13	0.0055	0.049	0.13 $\pm$ 0.0058
	L	0.12	0.0046	0.038	0.12 $\pm$ 0.0048
Wheat	1-nitrosophthol-2	0.12	0.0046	0.038	0.12 $\pm$ 0.0048
	8-mercaptoquinoline	0.12	0.0031	0.026	0.12 $\pm$ 0.0033
	L	0.14	0.0034	0.019	0.14 $\pm$ 0.004

**Table 6.** Results of determination of cobalt (II) in wastewater and bottom sediments (n = 6, P = 0.95).

Analysis object		Added, mg/kg	Found mg / kg (with addition)	$\bar{X}$	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$	$S_r$
Sewage water	Sample 1	2.0	2.48	0.48	0.48 $\pm$ 0.07	0.073
	Sample 2	5.0	6.15	1.15	1.15 $\pm$ 0.12	0.082
Bottom sediments	Sample 1	5.0	6.26	1.26	1.26 $\pm$ 0.05	0.064
	Sample 2	5.0	6.95	1.95	1.95 $\pm$ 0.07	0.069

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