



## Extractive spectrophotometric determination of Co(II) using 5-Chlorosalicylaldehyde thiosemicarbazone

Priyanka Rodrigues<sup>1</sup>, Sunetra Chaudhary<sup>1</sup>

<sup>1</sup>(Department of chemistry, Kishinchand Chellaram College, Mumbai, India)

**Abstract:** The complex of 5-Chlorosalicylaldehyde thiosemicarbazone (CSTSC) and Co(II) has been quantitatively extracted in butyl acetate in the pH range of 4.6–5.2 after equilibrating for 60 sec. Up to 6.0  $\mu\text{g mL}^{-1}$  concentration of Co(II), the complex of 5-Chlorosalicylaldehyde thiosemicarbazone with Co(II) in butyl acetate follows Beer's law, with its maximum absorbance occurring at 425 nm. By employing the Jobs continuous variation method, the composition 1:2 has been determined for the Co(II)-CSTSC complex. The extracted complex remained stable for more than 24 hours.  $6.637 \times 10^{-3} \mu\text{g cm}^{-2}$  was determined to be Sandell's sensitivity, whereas  $0.887 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  was the molar absorptivity. Synthetic samples have been effectively analysed using this method.

**Keywords** - Butyl acetate, extraction, Cobalt, CSTSC, Spectrophotometry.

### I. INTRODUCTION

Cobalt is a crucial element for biological systems as well as industry. It is a component of vitamin B<sub>12</sub>, which helps to prevent pernicious anaemia and produce red blood cells [1]. It is extensively used in high-speed steel tools, magnets, and high-temperature alloys because of its strength and excellent resistance to corrosion [2]. Moreover, cobalt acts as a catalyst in industrial operations [3].

Various analytical techniques, like atomic absorption spectrometry [4,5], spectrophotometry [6], voltammetry [7], ICP-OES [8,9], ICP-MS [10,11] have been used for the determination of cobalt. In chemistry, solvent extraction is one of the most promising techniques for separating metal ions at the trace level. The extractive spectrophotometric study of cobalt has been reported with several reagents [12,13]. Thiosemicarbazones are a class of molecules that possess well-established pharmacological and medicinal qualities, such as antiparasitic, antiviral, antimicrobial, antifungal and antitumor activities [14-21]. Thiosemicarbazone compounds have been extensively used in extraction because of their strong reactivity towards metal ions and extremely stable-coloured complexes. While there exist, multiple methods utilising various organic reagents for the extractive determination of Co (II), the situation is still unsatisfactory concerning speed, sensitivity, and selectivity. The current study focuses on spectrophotometric analysis of cobalt (II) with 5-chlorosalicylaldehyde thiosemicarbazone as a reagent. For the study of cobalt, this method offers an extremely reliable, selective and sensitive approach compared to previously reported methods

### II. METHODOLOGY

#### 2.1 Instruments and Chemicals

A quartz cell of 1.0 cm has been used for absorbance studies on the Jasco V-730 UV-VIS spectrophotometer. pH was adjusted with Equiptronics pH meter. Weighing was done using an electronic Contech balance (CA 64). All chemicals were of AR grade, obtained from commercial suppliers. All of the trials used freshly made, doubly distilled water. Hydrochloric acid and water that was double-distilled were utilised to dissolve Cobalt (II) chloride and create a 1000 ppm cobalt solution. Gravimetry using mercurithiocyanate was used to standardise the solution [22]. To get a functional solution, portions were diluted every day.

#### 2.2 Solutions of foreign ions

Anions were dissolved in distilled water whereas metal salts were dissolved in appropriate acids, then water was added to a known volume to create stock solutions of various metal ions and anions.

### 2.3 Synthesis of 5-Chlorosalicylaldehyde thiosemicarbazone

Equimolar amounts of each 5-Chlorosalicylaldehyde (1.567 g) in 25 mL of ethanol were condensed with an aqueous ethanolic solution of thiosemicarbazide (0.911 g) by refluxing the reaction mixture in a water bath for five hours. Precipitate was produced by pouring the mixture into crushed ice. After being filtered out and repeatedly cleaned with water, it was recrystallized from ethanol and then dried. 0.1% reagent solution was prepared by using a recrystallized product.

### 2.4 Procedure

Co(II) solution containing  $5.0 - 60.0 \mu\text{g mL}^{-1}$  concentration, 1.0 mL of 0.1% ( $4.35 \times 10^{-3} \text{ mole/dm}^3$ ) reagent in methanol, and pH 4.8 buffer 4.0 mL were combined in a 10 mL volumetric flask. After adding distilled water to make the final volume 10 mL, the mixture was transferred into a separating funnel. The equilibration of the mixture was carried out with 10 ml of butyl acetate. Both the organic and aqueous layers were separated when equilibrium was achieved. Sodium sulphate in anhydrous form was used to dry the organic phase. Next, using a 1.0 cm-matched cell at a wavelength of 425 nm, the absorbance of the solution was determined in comparison to a reagent blank.

## III. RESULTS AND DISCUSSION

### 3.1 Absorption spectra

The brown complex forms after mixing cobalt (II) with 5-Chlorosalicylaldehyde thiosemicarbazone. This complex can be quantitatively extracted into butyl acetate. The complex Co(II)-CSTSC absorption spectra, when measured in butyl acetate between 300 nm-500 nm and exhibit absorption maxima at 425 nm (Fig.1 Curve A) where the reagent has no impact on the cobalt (II) determination process (Fig.1 Curve B). Hence complex's absorbance was measured at 425 nm.

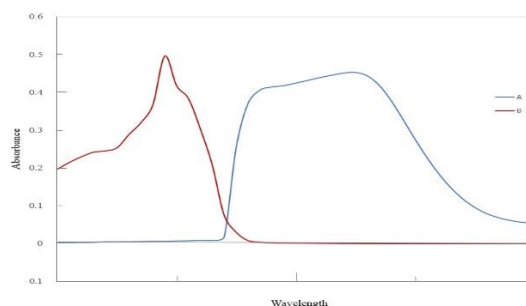


Fig.1: A – Co(II)-CSTSC Complex absorption spectra vs. CSTSC blank  
B – CSTSC absorption spectra vs. butyl acetate blank

### 3.2 pH Study

In the presence of pH 1–10 the extraction of the Co(II)-CSTSC complex in butyl acetate were carried out as per the above procedure. It was observed that maximum extraction of Co(II) ions takes place between pH 4.6–5.2 as the organic phase shows maximum absorbance. Therefore, an optimum pH range of 4.8 was maintained for extraction.

### 3.3 Effect of Solvent

**Different organic solvents like** butyl acetate, ethyl acetate, n-butanol, isoamyl alcohol, cyclohexanone, xylene, benzene, toluene, chloroform, carbon tetrachloride, hexane **were used to study the influence of solvents on the Co(II)-CSTSC complex extraction and absorbance.** Since percentage of cobalt (II) ion extraction as Co(II)-CSTSC complex is 99.9% in butyl acetate, all extractions were carried out in butyl acetate.

### 3.4 Effect of reagent concentration

The reagent concentration required for maximum colour development and quantitative extraction is determined by adding 0.1 mL to 2.0 mL of 0.1% reagent concentration in 30  $\mu\text{g}$  of cobalt (II) solution. The absorbance of the solution was remained constant from 0.5 mL to 2.0 mL. Hence, 1.0 mL of reagent concentration was added to all further studies (Fig.2).

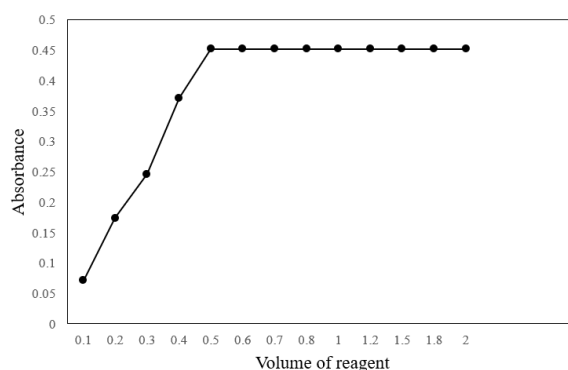


Fig.2: The impact of concentration of reagent on Co(II)-CSTSC complex absorbance

### 3.5 Equilibration time and Stability of colour

The Co(II)-CSTSC complex can be extracted completely by equilibrating for 60 sec. The extracted complex remained stable for more than 24 hours.

### 3.6 Beer's range and sensitivity

Co(II) at 425 nm between the concentration range that varies from 0.5-6.0  $\mu\text{g mL}^{-1}$  obeys Beer's law (Fig.3).  $6.637 \times 10^{-3} \mu\text{g cm}^{-2}$  was determined to be Sandell's sensitivity, and  $0.887 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  was the molar absorptivity.

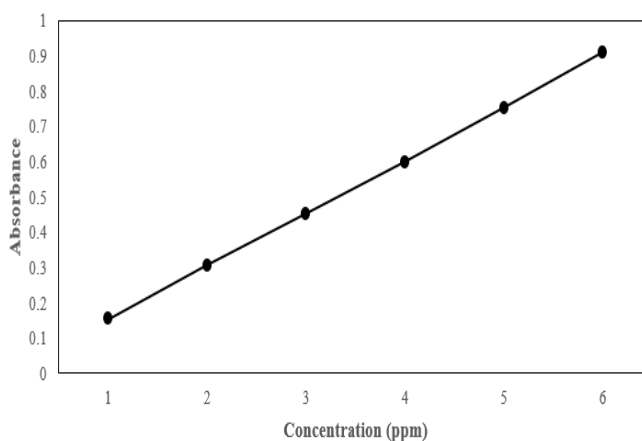


Fig.3: Calibration plot of Co(II)-CSTSC complex

### 3.7 Influence of salting out agents on the absorbance

Ammonium sulphate, calcium chloride, magnesium sulphate, sodium chloride, potassium carbonate, sodium carbonate, sodium nitrate, and sodium sulphate were added as salting out agents to increase the extraction of metal complex in butyl acetate. It was observed that the absorbance of the solution remains the same after adding a salting out agent.

### 3.8 Composition determination of the Co(II)-CSTSC complex

Cobalt (II) and CSTSC solutions were prepared in equimolar concentrations ( $4.35 \times 10^{-4} \text{ M}$ ). The varying proportions of metal and reagents were mixed by keeping the total volume fixed at 2.0 ml. The composition 1:2 of Co (II)-CSTSC complex was determined with Jobs continuous variation method as shown in the (Fig.4). Fig.5 illustrates the mole ratio method.

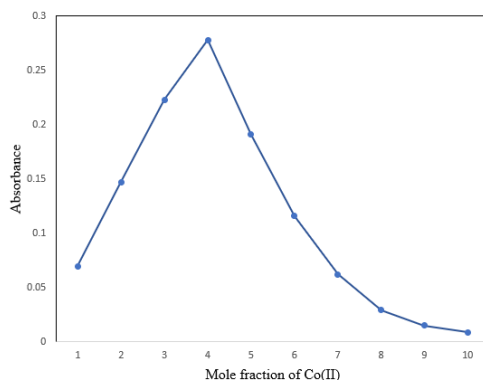


Fig.4: Job's Continuous Variation Method of the Complex of Co(II)-CSTSC

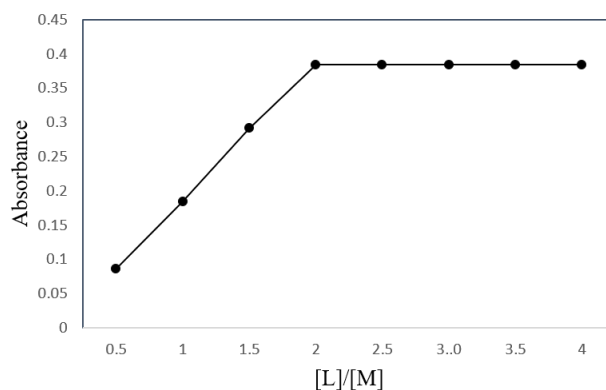


Fig.5: Mole Ratio Method of the Complex of Co(II)-CSTSC

### 3.9 Impact of foreign ions

Co(II)-CSTSC absorbance was investigated with 30.0  $\mu\text{g}$  of cobalt(II) and different concentrations for every foreign ion to determine the impact of interfering ions. The absorbance value's tolerance limit was set at an error of  $\pm 2\%$ .

**Table 2 – Impact of foreign ions on extraction of Co(II)-CSTSC complex**

Interfering ions	Tolerated amount in $\mu\text{g}$	Interfering ions	Tolerated amount in $\mu\text{g}$	Interfering ions	Tolerated amount in $\mu\text{g}$
Fluoride	40000	Oxalate	10000	V(V)	4000
Chloride	40000	Acetate	10000	Bi(II)	4000
Bromide	40000	pyrophosphates	10000	U(VI)	4000
Iodide	40000	Sulfite	2000	Al(III)	4000
Nitrite	40000	Permanganate	2000	Pb(II)	4000
Nitrate	40000	Na(I)	10000	Zn(II)	4000

thiosulfate	40000	K(I)	10000	Cd(II)	4000
<i>Peroxydisulfate</i>	40000	Ca(II)	5000	Hg(II) <sup>a</sup>	1000
sulphate	40000	Mg(II)	5000	Ag(I) <sup>b</sup>	1000
Urea	40000	W(VI)	5000	Ru(III) <sup>c</sup>	500
Thiourea	40000	Mn(II)	5000	Sn(IV)	500
EDTA	40000	Th(III)	5000	Fe(III)	200
Bromate	40000	Ba(II)	5000	Ni(II)	200
<i>Iodate</i>	40000	Sr(II)	5000	Ce(IV)	200
<i>Chlorate</i>	40000	Cr(III)	4000	Pd(II) <sup>d</sup>	200
Tartrate	10000	La(III)	4000	Cu(II) <sup>e</sup>	200

<sup>a</sup>masked with 40 mg Iodide, <sup>b</sup>masked with 40 mg chloride, <sup>c</sup>masked with 20 mg thiourea, <sup>d</sup>masked with 1.0 mL 0.1% DMG, <sup>e</sup>masked with 1.0 mL 0.1% EDTA

### 3.10 Precision and accuracy

Ten different 3.0 µg mL<sup>-1</sup> cobalt containing solutions absorbance were measured in order to determine accuracy and reproducibility. The standard deviation and these ten readings average was computed. It was discovered that the standard deviation and relative standard deviation was 0.0139 and 0.46 % respectively. The reproducibility of results with a 95% confidence level, based on the standard deviation, was 2.993 ± 0.0086.

### 3.11 Application

#### 3.11.1 Determination of cobalt ion concentration in synthetic mixtures

Using the suggested method, cobalt ions were determined from a number of synthetic mixtures with different cobalt (II) and other metal ion compositions. Table 3 presents the findings.

**Table 3: Cobalt (II) content analysis in a synthetic mixture**

Composition of mixtures in µg	Amount present in µg	Found by present method in µg
Co (40), Cu (200), Pb (200)	40.0	40.05
Co (40), Fe (200), V (200)	40.0	39.93
Co (40), Mn (100), Ce (100)	40.0	39.91
Co (40), Al (50), Ni (50)	40.0	40.02

## IV. CONCLUSION

This method provides high sensitivity and selectivity for spectrophotometric detection of Co(II) in microgram amounts. The brown complex of 5-CSTSC with Co(II) in butyl acetate follows Beer's law up to 6.0 µg mL<sup>-1</sup>, with its maximum absorbance occurring at 425 nm and stable for more than 24 hours. . The Sandell's sensitivity was 6.637 X 10<sup>-3</sup> µg cm<sup>-2</sup> and 0.887 X 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> was the molar absorptivity. The amount of Co(II) can be measured very quickly from synthetic mixtures as the method is simple and rapid.

### Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## REFERENCES

1. J. Montaña, F. Valente, A. Alonso, J. Lomillos, R. Robles, M. Alonso, "Relationship between Vitamin B<sub>12</sub> and Cobalt Metabolism in Domestic Ruminant", *Animals*, 10(10), 2020, pp. 1855.
2. M. Safavi, F. Walsh, Electrodeposited Co-P alloy and composite coatings: A review of progress towards replacement of conventional hard chromium deposits, *Surface and Coatings Technology*, 422, 2021, pp.127564.
3. S. Gupta, R. Fernandes, R. Patel, M. Spreitzer, N. Patel, "A review of cobalt-based catalysts for sustainable energy and environmental applications", *Applied Catalysis A: General*, 661, 2023, pp. 119254  
<https://doi.org/10.1016/j.apcata.2023.119254>
4. E. Yazıcı, M. Firat, D. Chormey, E. Bakirdere, S. Bakirdere, "An accurate determination method for cobalt in sage tea and cobalamin: Slotted quartz tube-flame atomic absorption spectrometry after preconcentration with switchable liquid-liquid microextraction using a Schiff base", *Food Chemistry*, 302, 2020, pp.125336.
5. T. Borahan, B. Zaman, B. Polat, E. Bakirdere, S. Bakirdere, "An accurate and sensitive effervescence-assisted liquid phase microextraction method for the determination of cobalt after a Schiff base complexation by slotted quartz tube-flame atomic absorption spectrophotometry in urine samples", *Anal. Methods*, 13 (5), 2021, pp. 703-711  
<https://doi.org/10.1039/D0AY02264K>
6. A. Zalov, Kerim Kuliev, Sevil Shiralieva, Shafa Mammadova, Konul Aliyeva, Saliga Gahramanova, "Extraction-photometric determination of cobalt (II) with 5-(4-Hydroxybenzylidene)-2,4-tiazolidindion in different objects", *Journal of Pharmacognosy and Phytochemistry*, 8 (1), 2019, pp. 2612-2616.
7. D. Widowati, F. Kurniawan, S. Ramadhan, "Analysis of Cobalt(II) and Nickel(II) in Water Medium using Voltammetry Techniques", *Chemistry and Materials*, 2(2), 2023, pp. 35-40  
<https://doi.org/10.56425/cma.v2i2.52>
8. P. Kargarghomsheh, F. Tooryan, G. Sharifiarab, M. Moazzen, N. Shariatifar, M. Arabameri, "Evaluation of Trace Elements in Coffee and Mixed Coffee Samples Using ICP-OES Method", *Biol. Trace Elem. Res.*, 8, 2023.  
<https://doi.org/10.1007/s12011-023-03795-w>
9. K. Petrova, V. Baranovskaya, N. Korotkova, "Direct inductively coupled plasma optical emission spectrometry for analysis of waste samarium-cobalt magnets", *Arabian Journal of Chemistry*, 15(1), 2022, pp.103501.  
<https://doi.org/10.1016/j.arabjc.2021.103501>
10. E. Tanvir, K. Whitfield, J. Ng, P. Shaw, "Development and Validation of an ICP-MS Method and Its Application to Determine Multiple Trace Elements in Small Volumes of Whole Blood and Plasma", *Journal of Analytical Toxicology*, 44(9), 2020, pp.1036-1046,  
<https://doi.org/10.1093/jat/bkaa033>
11. H. Kim, G. Lee, G. Pyo, E. Kwon, K. Myung, S. Cheong, "Nickel, cobalt, and chromium in nail sticker and tip products in Korea", *Contact Dermatitis*, 88(5), 2023, pp. 389-394,  
<https://doi.org/10.1111/cod.14279>
12. L. Subramanyam Sarma, J. Rajesh Kumar, C. Jaya Kumar, A. Varada Reddy, "A Sensitive Extractive Spectrophotometric Determination of Cobalt (II) in Real Samples Using Pyridoxal-4-phenyl-3-thiosemicarbazone", *Analytical Letters*, 36(3), 2003, pp. 605-618,  
<https://doi.org/10.1081/AL-120018251>
13. S. Aliyev, E. Suleymanova, L. Magarramova, S. Ibrahimova, A. Zalov, "Liquid-Liquid Extraction and Spectrophotometric Characterization of A New Ternary Ion-Association Complex of Cobalt(II)", *International Journal of Innovative Science, Engineering & Technology*, 5(8), 2018,52-62.
14. S. Khan, A. Asiri, K. Al-Amry, M. Malik, "Synthesis, Characterization, Electrochemical Studies, and In Vitro Antibacterial Activity of Novel Thiosemicarbazone and Its Cu(II), Ni(II), and Co(II) Complexes", *The Scientific World Journal*, 2014, 2014, 592375.  
<https://doi.org/10.1155/2014/592375>
15. E. Çakmakçı, E. Subaşı, E. Öztürk, A. Şahiner, B. Yüksel, "Cobalt(II), nickel(II), palladium(II) and zinc(II) metallothiosemicarbazones: Synthesis, characterization, X-ray structures and biological activity", *Inorganica Chimica Acta*, 551, 2023,121462.  
<https://doi.org/10.1016/j.ica.2023.121462>
16. D. Martins, R. Souza, Marjorie Caroline L. Freire, N. Mesquita, I. Santos, D. Oliveira, N. Junior, R. Paiva, M. Harris, C. Oliveira, G. Oliva, A. Jardim, "Insights into the role of the cobalt (III)-thiosemicarbazone complex as a potential inhibitor of the Chikungunya virus nsP4", *J Biol. Inorg. Chem.*, 28, 2023, pp. 101-115.  
<https://doi.org/10.1007/s00775-022-01974-z>
17. L. Fernandes, J. Silva, D. Martins, M. Santiago, C. Martins, A. Jardim, G. Oliveira, M. Pivatto, R. Souza, E. Franca, V. Defflon, A. Machado, C. Oliveira, "Fragmentation Study, Dual Anti-Bactericidal and Anti-Viral Effects and Molecular Docking of Cobalt(III) Complexes", *Int. J. Mol. Sci.*, 21(21), 2020, 8355, pp.01-17  
<https://doi.org/10.3390/ijms21218355>
18. K. Melha, "In-vitro antibacterial, antifungal activity of some transition metal complexes of thiosemicarbazone Schiff base (HL) derived from N<sup>4</sup>-(7'-chloroquinolin-4'-ylamino) thiosemicarbazide", *Journal of Enzyme Inhibition and Medicinal Chemistry*, 23(4), 2008, pp. 493-503,  
[10.1080/14756360701631850](https://doi.org/10.1080/14756360701631850)
19. R. Alcaraz, P. Muñoz, M. Cavia, Ó. Palacios, K. Samper, R. García, A. Pérez, J. Tojal, C. Girón, "Thiosemicarbazone-metal complexes exhibiting cytotoxicity in colon cancer cell lines through oxidative stress", *Journal of Inorganic Biochemistry*, 206, 2020, pp. 110993,  
<https://doi.org/10.1016/j.jinorgbio.2020.110993>
20. A. Paden King, Hendryck A. Gellineau, Jung-Eun Ahn, Samantha N. MacMillan, Justin J. Wilson, "Bis(thiosemicarbazone) Complexes of Cobalt (III). "Synthesis, Characterization, and Anticancer Potential", *Inorg. Chem.*, 56(11), 2017, pp. 6609-6623  
<https://doi.org/10.1021/acs.inorgchem.7b00710>
21. M. Sobiesiak, M. Cieślak, K. Królewska, J. Kaźmierczak-Barańska, B. Pasternak, E. Budzisz, *New J. Chem.*, 40(11), 2016, 9761-9767
22. G. Jeffery, J. Bassett, J. Mendham, R. Denney, Vogel's textbook of quantitative chemical analysis, Longman, Green, 463, 1961.