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Extractive Spectrophotometric determination of Cobalt(II) with Benzildithiosemicarbazone

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An extractive spectrophotometric method for the determination of cobalt(II) using benzildithiosemicarbazone is reported. The cobalt(II)-benzildithiosemicarbazone complex with a molar absorptivity of 7.329×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity of 0.008044 $\mu g/cm^2$ obeys Beer's law in the range 1.0–8.0 ppm of cobalt(II). The instability constant of the complex is determined. The effect of various diverse ions in the determination of cobalt(II) is studied. The method is successfully applied for the determination of cobalt(II) in medicinal and beer samples and the results are compared with atomic absorption spectrophotometer.

INTRODUCTION

Thiosemicarbazones are important sulphur containing organic reagents. The metal chelates of these reagents find wide range of applications in medicine[1, 2] and agriculture.[3, 4] The use of thiosemicarbones in inorganic analysis has been reviewed in detail by Singh *et al.*[5] Because of the ability of thiosemicarbazones in forming intense coloured complexes with various metal ions, they are widely employed in spectrophotometric and extractive spectrophotometric analysis of various cations and anions. But the survey of literature reveals that only a few thiosemicarbazones are employed for the spectrophotometric and extractive spectrophotometric determination of cobalt(II). The authors introduced a new reagent, benzildithiosemicarbazone (BDT) for the selective and extractive spectrophotometric determination of cobalt(II) in medicinal and beer samples. The conditions for effective extraction of cobalt(II) are established by studying the effects of pH, solvent, reagent concentration and salting out agent.

EXPERIMENTAL

Analytical reagent grade chemicals were used in studies. The pH measurements were made on a digital pH meter, model LI-120 (ELICO), and absorbance measurements were made using Shimadzu UV-240 Recording Spectophotometer supplied by Shimadzu Corporation, Japan. Hitachi, Model 170-30 Atomic absorption/flame spectrophotometer manufactured by Hitachi Ltd., Tokyo, Japan is used for the comparison of the results.

Reagents

Cobalt(II) solution: About 4.037 g of cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) is dissolved in distilled water and made up to one litre and is standardised by 2-nitroso-1-naphthol.[6] Lower concentrations of cobalt(II) solutions are prepared by suitably diluting the stock solution with double distilled water.

Benzildithiosemicarbazone(BDT): The reagent was prepared by refluxing methanolic benzil and aqueous thiosemicarbazide in acid medium using the procedure reported by Hussain Reddy *et al.*[7] (m.p. = 234–236°C). A 0.8475×10^{-2} M reagent solution prepared in 40% dimethylformamide was used in the studies.

Buffer solutions: The buffers used in this study were hydrochloric acid-postassium chloride buffer (pH 1.0–2.6, sodium formate-formic acid buffer (pH 2.6–3.4), sodium acetate-acetic acid buffer (pH, 3.4–6.5) and ammonium chloride-ammonium hydroxide buffer (pH, 7.0–11.0).

Preparation of sample solutions

Medicinal samples: Neurobion and neurolen (vitamin $B_1 + B_4 + B_{12}$) medicines are analysed for the determination of cobalt. A known weight of a medicinal sample is treated with a few mL of 0.25 N sulphuric acid in a small beaker. The contents are heated on a hot plate first at low temperature for several minutes and later at higher temperature until the fumes of sulphuric acid cease to evolve. The contents are diluted with a little distilled water and then filtered through acid washed Whatman No. 41 filter paper into a 100 mL standard flask and is made up to the mark with distilled water. This solution is diluted to the required concentration for further studies.

Beer sample: The beer sample manufactured by Golden Eagle Lager Beer Pvt. Ltd. India is used for studies. It is transferred into a distillation flask and distilled completely until the residue is obtained. It is treated with a little amount of distilled water and again evaporated to dryness. The residue is redissolved in 5.0 mL of 1 : 1 hydrochloric acid and filtered through Whatman No. 41 filter paper. The filter paper is washed with distilled water twice and both filtrate and washings are collected in a 25 mL standard flask and finally made up to the mark with distilled water. This solution is diluted to the required concentration for further studies.

General procedure

Different aliquots of 10.0 mL solutions each containing constant volumes of 3.0 mL of buffer (pH 6.5), 1.5 mL of 1.695×10^{-2} M reagent, 1.0 mL of 0.1 M lithium nitrate as salting out agent and varying volumes of cobalt(II) solution containing 10 to 100 μg are prepared. Each solution is shaken twice with two 5.0 mL portions of chloroform for 30 sec. The organic phases are mixed and dried with anhydrous sodium sulphate and absorbances are taken at 387 nm against reagent blank. A linear plot passing through the origin is obtained when absorbance is plotted against the amount of the metal ion.

RESULTS AND DISCUSSION

Optimum conditions

The absorption spectra of the BDT and its metal complex are recorded in the wavelength region 300 to 500 nm separately against buffer and reagent blank respectively. Cobalt(II) complex showed maximum absorbance at 387 nm, where the reagent showed negligible absorbance (Fig. 1). The metal forms complex with reagent in 1 : 2 ratio (M : L) under the experimental conditions. The absorbance of the complex remains constant in the pH range 6.0–7.0. Hence further studies were carried out at pH 6.5 using sodium acetate-acetic acid buffer. A 15- fold molar excess of the reagent was necessary to obtain maximum colour intensity. It was observed that the presence of 1.0 mL of 0.1 M lithium nitrate ensured complete extraction. The molar absorptivity and Sandell's sensitivity[8] of the cobalt(II) complex were found to be 7.329×10^3 L mol^{-1} cm^{-1} and 0.0080 $\mu g/cm^2$ respectively and the method obeyed Beer's law in the range of 1.0–8.0 ppm.

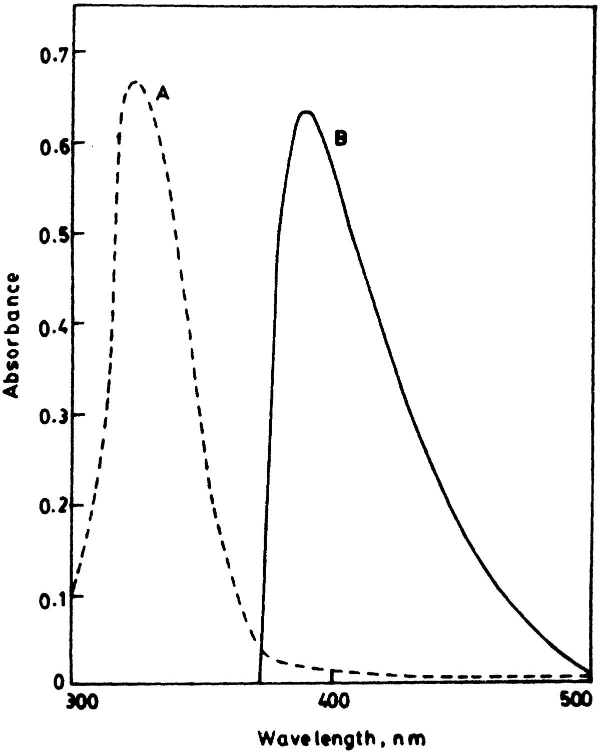

Fig. 1. A Absorption spectra of BDT vs buffer
B Absorption spectra of BDT vs Co(II)

The instability constant calculated from Edmonds and Birnbaum's method[9] was 3.349×10^{-8} and from Asmus' method[10] was 3.3214×10^{-8} at room temperature. The Ringbom plot[11] has a sigmoid shape with a linear segment at intermediate absorptance values 0.34–0.67 and concentration values 1.5–4.0 ppm.

The method has a good reproducibility for a set of ten measurements with 3.0 ppm of cobalt(II). The standard deviation was 0.002521 ppm and the relative standard deviation was 0.67%. Regarding the accuracy the standard error was 0.00084.

Effect of interfering ions

The effect of various cations and anions in the determination of 5.0 ppm of cobalt(II) was studied. Many cations like Al(III), Mn(II), Mg(II), Ti(IV), U(VI), V(V), W(VI), Zr(IV) and Ce(IV) did not interfere. The interference of Cu(II) can be eliminated by using 1.0 mL of 2% thiosulphate solution as masking agent. Ni(II), Pd(II) and Zn(II) can be masked by employing 1.0 mL of 4% citrate solution. The tolerance limits of other anions and cations are presented in Table-1.

TABLE-1
TOLERANCE LIMIT OF DIVERSE IONS IN THE DETERMINATION OF COBALT(II)

[Amount of Co(II) = 5.0 ppm].

Diverse ion	Tolerance Limit (ppm)	Diverse Ion	Tolerance Limit (ppm)
Ag(I)	10	Bromide	250
Al(III)	250	Chloride	200
Cd(II)	50	Citrate	100
Cu(II)	None	EDTA	None
Cr(III)	50	Fluoride	250
Fe(III)	250	Iodide	200
Mn(II)	50	Nitrate	250
Mo(VI)	50	Oxalate	None
Mg(II)	250	Phosphate	None
Ni(II)	25	Sulphate	200
Pd(II)	10	Tartrate	200
Ti(IV)	250	Thiocyanate	50
U(VI)	250	Thiosulphate	250
V(V)	100	Thiourea	200
W(VI)	250		
Zn(IV)	150		
Zr(IV)	200		

Application of the method for medicinal and beer samples

Cobalt present in medicinal and beer samples was determined by the present method. Known aliquots of medicinal and beer sample solutions are transferred into different 25 mL separating funnels containing 3.0 mL of buffer, 1.0 mL of 1.0 M lithium nitrate and 1.5 mL of 1.695×10^{-2} M reagent solutions. Each solution is shaken twice with two 5.0 mL portions of chloroform for 30 seconds. The organic phases are collected, and dried with anhydrous sodium sulphate. The absorbances of the organic phases are measured at 387 nm against reagent bank. The amounts of cobalt(II) present in both the samples are computed from the predetermined calibration plot. These results are compared with AAS method and are shown in Table-2 and Table-3 respectively.

TABLE-2
ANALYSIS OF MEDICINAL SAMPLES FOR THE DETERMINATION OF COBALT(II)

Sample	Amount of cobalt(II) found (ppm)		Difference
	BDT method	AAS method	
(a) Neurobion	14.01	14.30	
	14.40	14.60	
	14.60	14.20	
	14.40	14.80	
Average	14.375	14.475	0.1
(b) Neurolen	14.10	13.90	
	14.20	14.30	
	13.80	14.00	
	13.90	13.70	
Average	14.0	13..975	0.025

TABLE-3
ANALYSIS OF BEER SAMPLE FOR THE DETERMINATION OF COBALT (II)

S. No.	Amount of cobalt(II) found (ppm)		Difference
	BDT method	AAS method	
1.	1.14	1.13	
2.	1.18	1.15	
3.	1.21	1.18	
4.	1.24	1.16	
5.	1.12	1.20	
Average	1.178	1.64	0.014

REFERENCES

1. N.N. Orlova, V.A. Aksevova, D.A. Slidavkin, N.S. Boganova and G.N. Pershin, *Russ. Toxic*, 348 (1968).
2. K. Butler, U.S. Patent, No. 3, 382, 266 (1968).
3. N.P. Bun Hoi, T.B. Loc and N.D. Xyong, *Bull. Soc. Chem. (France)*, 694 (1955).
4. H.C. Patering, H.H. Buskirk and G.E. Underwood, *Cancer Res.*, **64**, 367 (1964).
5. R.B. Singh, B.S. Garg and R.P. Singh, *Talanta*, **25**, 619 (1978).
6. A.I. Vogel, A Text Book of Quantitative Analysis, Longmans, p. 529 (1961).
7. A. Krishna, K. Hussain Reddy and D. Venkata Reddy, *Inorg. Chim. Acta*, **13**, 173 (1990).
8. E.B. Sandell, Colorimetric determination of Trace Metals, 3rd Edn., Interscience, New York, p. 84 (1949).
9. S.M. Edmonds and Birnbaum, *J. Am. Chem. Soc.*, **63**, 1471 (1941).
10. E. Asmus, *Z. Anal. Chem.*, **178**, 104 (1960).
11. A. Ringbom, *Z. Anal. Chem*, **115**, 332 (1939).

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