

CCA-1227

YU ISSN 0011-1643

UDC 546.72:546.56

Original Scientific Paper

Gravimetric Separation and Estimation of Cobalt and Copper Using *N-p*-Chlorophenylcinnamohydroxamic Acid

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Received January 21, 1980

N-p-chlorophenylcinnamohydroxamic acid has been used for the gravimetric determination and separation of cobalt and copper in the pH range of 5.4 to 6 and 3.4 to 3.8 respectively. The reagent forms a directly weighable complex having definite composition $(C_{15}H_{11}NO_2Cl)_2Co$ or Cu . The method is sensitive, selective and can be carried out in the presence of several foreign ions.

N-Phenylbenzohydroxamic acid (PBHA) and its derivatives are widely employed as gravimetric reagents for many metal ions¹⁻⁵. PBHA has also been reported as a reagent for the gravimetric estimation of copper and cobalt⁶. However it has been found that the introduction of electrophilic substituents like chlorine on the *N*-phenyl ring of the hydroxamic acid renders the reagent more selective due to the reduced stability of the metal complexes⁷. Hence *N-p*-chlorophenylcinnamohydroxamic acid (*p*-CPCCHA)⁸ was examined for gravimetric separation of cobalt and copper.

The reagent was found to be well suited for gravimetric estimation as well as separation of the above two metals. The precipitate obtained is granular, nonsticky and easily filtrable having low conversion factors (for Co—0.09773 and for Cu—0.1042). The estimations and separation can be carried out in the presence of several foreign ions.

EXPERIMENTAL

Apparatus

The pH measurements were made by the Systronics portable pH meter type 323. Corning brand sintered glass crucible of porosity G₃ was used for filtration. A semimicro balance, VEB Analytik Type SAHM 68 was used for weighing.

Reagents

p-CPCCHA was prepared by the method reported previously⁸. A 2% solution (w/v) of reagent in ethanol was used.

Solution of Co^{++} and Cu^{++} were prepared from A. R. grade cobalt sulphate and copper sulphate, respectively, in glass distilled water. Each ml of the solution contained 10 mg of metal. The cobalt and copper content of the solution was determined by the EDTA method.

Solutions of diverse ions were prepared by the method of West⁹ using A. R. grade chemicals.

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General Procedure

A suitable portion of standard cobalt or copper solution was taken in a 400 ml beaker and diluted to 250 ml with distilled water. The solution was heated to about 80 °C on a water bath (while estimating cobalt 10 ml of 2% hydroxylamine hydrochloride was added to prevent the oxidation of cobalt II to cobalt III). A 2% solution of reagent was slowly added with stirring and the pH of the solution was adjusted between 5.4 and 6 for the precipitation of cobalt and between 3.4 and 3.8 for copper using a 10% sodium acetate solution and 1N H₂SO₄ solution. The solution was heated on a water bath and stirred occasionally. The digested precipitate was filtered in a sintered glass crucible of porosity G₃, washed thoroughly with hot water and finally with 20% aqueous ethanol. The light pink cobalt complex and green copper complex obtained, were dried at 120 °C to a constant weight and weighed directly as (C₁₅H₁₁NO₂Cl)₂Co or Cu.

Gravimetric Separation of Cobalt from Copper Using p-CPCA:

A solution containing known amounts of copper and cobalt was diluted to 250 ml with distilled water. 10% sodium acetate and 1N sulphuric acid were added to adjust the pH between 3.4 and 3.8. The solution was heated to about 80 °C and copper was precipitated, filtered and washed as described above. The filtrate and washings were evaporated to about 200 ml and then sodium acetate was added to adjust the pH between 5.4 and 6 (10 ml of 2% hydroxylamine hydrochloride was added before the subsequent determination of cobalt). 2% ethanolic solution of reagent was added and cobalt determined as reported previously in the general method. If cobalt is precipitated without prior addition of hydroxylamine hydrochloride the results obtained are slightly high probably due to the formation of small amounts of cobaltic complex in the precipitate.

The cobalt and copper contents of the precipitate were calculated using the factor 0.09773 for cobalt and 0.1042 for copper.

RESULTS AND DISCUSSION

The experimental results of the quantitative determination of cobalt and copper are given in Table I. The results of the gravimetric separation of cobalt and copper and the effect of diverse ions in the determination of copper, cobalt are shown in Table II and Table III.

TABLE I
Gravimetric Determination of Cobalt and Copper with p-CPCA

Name of the metal ion	Sample No.	Mass of metal ion taken	Mass of complex	Mass of metal ion found	Error mg
		mg	mg	mg	
Cobalt	(1)	27.99	287.1	28.05	+0.06
	(2)	32.65	334.5	32.69	-0.04
	(3)	37.32	382.4	37.38	+0.06
	(4)	41.98	429.9	42.01	+0.03
	(5)	46.65	476.9	46.61	-0.04
Copper	(1)	20.1	192.5	20.05	-0.05
	(2)	25.12	241.4	25.15	+0.03
	(3)	30.15	288.7	30.08	-0.07
	(4)	35.17	337.7	35.18	+0.01
	(5)	40.20	386.0	40.22	+0.02

TABLE II
Separation of Cobalt from Copper

Metal ion taken/mg		Metal ion found/mg	
Co	Cu	Co	Cu
27.99	30.15	28.03	30.19
32.65	35.17	32.62	35.10
37.65	40.20	37.69	40.24
41.98	25.12	41.99	25.16
46.65	20.1	46.72	20.08

TABLE III
Effect of Foreign Ions in the Gravimetric Estimation of Cobalt and Copper with p-CPCHA

Ion	Added mg	Co taken mg	Co found mg	Cu taken mg	Cu found mg
Pb ⁺²	100	27.99	28.01	20.1	20.09
Zn ⁺²	100	27.99	28.07	20.1	20.04
Be ⁺²	100	27.99	28.00	20.1	20.04
Bi ⁺³	100	27.99	27.97	20.1	20.15
Mg ⁺²	100	27.99	27.98	20.1	20.09
Mn ⁺²	100	27.99	28.02	20.1	20.12
Cd ⁺²	100	27.99	28.00	20.1	20.16
U ⁺⁶	100	27.99	28.07	20.1	20.19
Ca ⁺²	100	27.99	28.07	20.1	20.17
Ni ⁺²	100	27.99	28.05	20.1	20.16
Sn ⁺²	100	27.99	28.04	20.1	20.03
Hg ⁺²	100	27.99	28.08	20.1	20.09
La ⁺³	100	27.99	27.95	20.1	20.17
MoO ₄ ⁻²	100	27.99	27.94	20.1	20.15
PO ₄ ⁻³	100	27.99	28.07	20.1	20.05

Mean of three repetitive analysis.

The effect of several ions were studied in the estimation of cobalt and copper. Pb⁺², Hg⁺², Cd⁺², Zn⁺², Mn⁺², U⁺⁶, La⁺³, MoO₄⁻², Ca⁺², As⁺³, Mg⁺², Bi⁺³, Be⁺², Sn⁺², PO₄⁻³ do not interfere.

Ni⁺² interferes in the determination of cobalt but does not interfere in the determination of copper.

The m. p. of the cobalt complex is 180 °C and 215 °C of the copper complex.

The optimum range of pH for complete precipitation of cobalt and copper was found to be 5.4 to 6 and 3.4 to 3.8 respectively.

Thus it is evident that the reagent (p-CPCHA) is a useful reagent for gravimetric determination and separation of cobalt and copper. It is comparable to other recommended reagents for gravimetric estimation of co-

balt¹⁰⁻¹⁴ and copper¹⁵⁻¹⁹. In most of the mentioned methods for the determination and separation of cobalt Cu^{+2} , Cd^{+2} , Zn^{+2} , Pb^{+2} , Ni^{+2} interfere while the proposed method is free from all the interferences except Ni^{+2} . The present reagent is more favourable for cobalt than α -nitroso- β -naphthol¹⁰ because the precipitate has a definite composition and does not need to be ignited for oxidation. Similarly in the mentioned methods for the determination and separation of copper Zn^{+2} , Ni^{+2} , Co^{+2} , Mn^{+2} , Cd^{+2} etc. interfere while with the proposed method no interferences occur. The high molecular weight of the complex, the low conversion factor for cobalt and copper and higher selectivity are also suitable for gravimetric estimation.

Composition of the Complex

The cobalt complex is pink, granular and nonsticky with the composition $(\text{C}_{15}\text{H}_{11}\text{NO}_2\text{Cl})_2\text{Co}$. It is soluble in alcohol, acetone, chloroform and benzene and the complex is of definite composition. The elemental analysis was as follows:

Calc'd.: Co 9.762; C 59.568; H 3.64 ; Cl 11.748; N 4.633%
Found: Co 9.951; C 59.935; H 4.068; Cl 12.502; N 4.99 %

The cobalt complex is pink, granular and nonsticky with the composition $(\text{C}_{15}\text{H}_{11}\text{NO}_2\text{Cl})_2\text{Cu}$. It is soluble in alcohol, acetone, chloroform and benzene, and the complex has a definite composition.

The elemental analysis was as follows:

Calc'd.: Cu 10.428; C 59.123; H 3.613; Cl 11.6603; N 4.598%
Found: Cu 10.564; C 59.357; H 3.941; Cl 11.785 ; N 4.89 %

The infrared spectra of the *N-p*-CPCHA in nujol showed peaks at 3060, 1640 and 930 cm^{-1} due to stretching vibrations of O—H, C=O and N—O respectively. After complex formation the peak due to O—H vibration disappears. The absorption peaks (determined in KBr pellets) due to carbonyl stretching vibration in the spectra of Co and Cu-*N-p*-CPCHA complexes are shifted to lower frequency and are located at 1580 and 1590 cm^{-1} , respectively, due to bonding of carbonyl oxygen atom to the metal ($-\text{C}=\text{O}-\text{M}$). The intensity of the peak due to N=O stretching vibrations in Co and Cu complexes increases and the peaks are located at 965 and 960 cm^{-1} , respectively. These shifts in frequencies of the C=O and N—O bonds are in agreement with the reported literature²⁰⁻²¹.

CONCLUSION

The reagent is suitable for gravimetric estimation due to the high mol. wt. of the complex with a low conversion factor. Several common elements normally associated with cobalt and copper do not interfere. The procedure is simple and the reagent can be prepared earlier.

Acknowledgment. — The authors are thankful to Prof. S. G. Tandon, Head Department of Chemistry, Ravishankar University, Raipur for providing facilities and obliged to C.D.R.I., Lucknow for infrared spectra and the microanalysis of the complexes. One of the authors (Miss K. R. Paul) is thankful to the Ravishankar University, Raipur for the award of fellowship.

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SAŽETAK

**Gravimetrijsko odjeljivanje i određivanje kobalta i bakra sa
N-p-klorfenilcinamohidroksamnom kiselinom**

K. R. Paul i V. K. Gupta

N-p-klorfenilcinamohidroksamna kiselina upotrijebljena je za gravimetrijsko odjeljivanje i određivanje kobalta u području $5,4 < \text{pH} < 6,0$ i bakra u području $3,4 < \text{pH} < 3,8$. Reagens stvara s kobaltom i bakrom komplekse točno određena sastava ($\text{C}_{15}\text{H}_{11}\text{NO}_2\text{M}$, (M = Co ili Cu), koji se mogu kvantitativno odrediti direktnom odvagom. Metoda je osjetljiva i selektivna, a može se koristiti i u nazočnosti većeg broja stranih iona.

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Prispjelo 21. siječnja 1980.