RESORCYLALDOXIME AS AN ORGANIC REAGENT

by

AJIT KUMAR MUKHERJEE

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta (India)

INTRODUCTION

Various organic substances have been employed for the gravimetric determination of copper and nickel and their separation from other elements. FEIGL[1] described the use of α-benzoinoxime for the gravimetric determination of copper in different alloys. The aliphatic acidic grouping, $> C(OH)\text{-}C{=}NOH\text{-}$, which is the copper specific group of acyloin oximes[2], is responsible for the insolubility and the colour of their copper compounds. EPHRAIM[3,4] introduced the use of salicylaldoxime for the detection and determination of copper. He also studied the reactions of a number of compounds containing the same reactive grouping as salicylaldoxime. Hydrogen ion concentration is an important factor in the use of salicylaldoxime as an analytical reagent[5]. It has been observed that by controlling the pH of the solution, different elements can be detected and determined in the presence of each other by the use of this reagent[6].

During the systematic investigation of the condensation products formed by the interaction of resorcylaldehyde with different amino-acids and related compounds[7], it was observed that resorcylaldehyde in those compounds could be determined gravimetrically as copper or nickel-resorcylaldoximes. As a result of investigations with resorcylaldehyde and its oxime, it has now been observed that resorcylaldoxime can be used conveniently as an organic reagent for copper and nickel. Resorcylaldoxime has only been used for the detection and determination of iron[8]. A search of the literature did not reveal the use of this compound as a gravimetric reagent for copper or nickel. The reagent was easily prepared, following the method described by ASTIN AND RILEY[9] for salicylaldoxime reagent.

The complex copper and nickel compounds were prepared in the pure state and their properties studied. Copper resorcylaldoxime is precipitated completely, even in fairly acid solution, (pH $>$ 1.40). The precipitation of nickel resorcylaldoxime begins at pH 4.2 and is quantitative between pH 5.54 and 6.55. Resorcylaldoxime does not give any precipitate with cadmium or zinc even in alkaline solution. Cobalt gives no precipitate in acid solution, but in alkaline solution it gives a blood-red coloration. Uranium (VI), manganese and lead also give colorations at different pH values, but the reactions are not very sensitive. Copper and nickel, however, could not be separated by this reagent, as copper was always found to give a low results in the presence of nickel.

The complex salts of copper and nickel are stable, insoluble in water, and dilute acetic acid, and could be weighed in sintered glass gooch crucibles after drying at 95-100° C for one hour.

The copper and nickel complexes have the composition, $Cu(C_7H_6O_3N)_2$ and $Ni(C_7H_6O_3N)_2$, respectively. The conversion factor for copper is 0.1729 and for nickel, 0.1618. A distinct opalescence is observed with solutions containing 1 part of copper per 40,000 part or 1 part of nickel per 200,000 part; 0.25 p.p.m. of nickel gives a distinct coloration. Like salicylaldoxime, resorcylaldoxime has been successfully used for the direct determination of copper in brass. The reagent has some advantages over several known methods. Resorcylaldoxime is quite stable and could be preserved for long periods. From magnetic moment measurements on the complexes formed, it can be concluded that copper and nickel resorcylaldoxime compounds are penetration complexes with planar dsp^2 hybrid bonds.

EXPERIMENTAL

Reagent. Resorcylaldoxime was prepared according to the method of MARCUS[10]. Freshly prepared 1-2% solution of resorcylaldoxime (m.p. 198-99° C) were used in this work The reagent solution (approximately 1%) could also be prepared by following the method employed by ASTIN AND RILEY *(loc. cit.)* for salicylaldoxime 1 25 g of resorcylaldehyde was dissolved in the minimum amount (5 ml) of alcohol and 0.75 g of hydroxylamine hydrochloride (in 5 ml water) added. The resulting mixture was thoroughly shaken, 5 ml absolute alcohol was added to it, and the volume made up to 100 ml with water This solution can be readily prepared during the process of estimation.

Copper and Nickel complexes (a) Copper-resorcylaldoxime was obtained by the interaction of copper acetate (1 mol) and resorcylaldoxime (2 mol) in aqueous alcoholic medium (between pH 2.15 and 3.5). The greenish-grey precipitate was then filtered, washed with cold water and a small quantity of alcohol, and finally dried over concentrated sulphuric acid. The compound is insoluble in cold and hot water, as well as in dilute acetic acid, chloroform, benzene and toluene but soluble in acetone, dioxane, pyridine and absolute alcohol. The compound loses one molecule of water at 90-95° C.

[Found: Cu, 16.51, N, 7 10, C, 43.62; H, 3 05 and H_2O, 4.63%; $Cu(HO.C_6H_3O.CH = NOH)_2.H_2O$ requires Cu, 16.49, N, 7.25; C, 43.56; H, 3.60 and H_2O, 4.66%.]

(b) Nickel-resorcylaldoxime: Nickel acetate (1 mol) and resorcylaldoxime (2 mol) reacted in aqueous alcoholic medium to give a light green precipitate. The precipitate washed first with water and then with a small amount of alcohol, was finally dried *in vacuo* over concentrated sulphuric acid.

The compound is insoluble in hot as well as in cold water, and also in benzene, chloroform and toluene, but is fairly soluble in dioxane, acetone and pyridine. [Found: Ni, 15 39 and N, 7.33%. $Ni(OH.C_6H_3O.CH = NOH)_2\ H_2O$ requires Ni, 15 42 and N, 7.34%.]

Magnetic measurements The magnetic susceptibilities of the copper and nickel compounds were measured, using a Gouy balance in a magnetic field of strength 9 02·10³ gauss, and taking all the necessary precautions[11]. The results of the measurements at 30° C are tabulated below:

	$\chi_g \cdot 10^{-6}$	$\chi_m \cdot 10^{-6}$	$\chi_m \cdot 10^{-6}$ (corr)	μB (effective)
Copper-resorcylaldoxime	3 358	1295	1360	1.73
Nickel-resorcylaldoxime	—0.1046	. ..	...	Diamagnetic

Solutions and apparatus Standard copper and nickel solutions were prepared by dissolving E. Merck's reagent quality copper chloride or copper sulphate and nickel chloride respectively in distilled water. The copper concentration in the solutions was determined iodometrically. The strength of nickel solution was determined by precipitation with dimethylglyoxime. Solutions of other metal ions were obtained by dissolving their salts (C.P.) in distilled water.

All pH measurements were made using a Cambridge pH meter (Bench type). Sintered glass gooch crucibles (Jena No. 4) were used for filtration, drying, and weighing of the copper and nickel precipitates.

Reactions with different metal ions

CHIEN AND SHIH (*loc. cit.*) reported that resorcylaldoxime gave a purple colour with slightly acid solutions of ferric iron. The reagent, however, gave no coloration with ferrous iron. In the present investigation it was observed that resorcylaldoxime gave precipitates or colours with the following ions at controlled pH:

TABLE I

Ion	*Colour or ppt.*	*pH approx*
Cu^{+2}	ppt.	<1.05
Ni^{+2}	ppt.	4.2
Mn^{+2}	ppt.	8.6
Hg^{+2}	ppt.	6.5
Co^{+2}	red-colour.	>7.5
UO_2^{+2}	orange-colour.	>8

The reagent had no action on Al^{+3}, Sn^{+2}, Zn^{+2}, Cd^{+2}, Cr^{+3}, Ag^{+}, VO_3^{-} or Ce^{+4} ions.

Determination of copper

(i) *Procedure.* The copper solution in a 250 ml Jena beaker was made up to 125 ml and to this 20-25 ml of reagent solution (1%) was added, and then the necessary amount of alkali or sodium acetate solution to maintain the proper pH of 1.8 to 2.85. The mixture was warmed slightly on the water bath, kept for 1/2-1 hour, filtered through a weighed gooch crucible, and washed several times with cold water. The precipitate was dried at 100-105° C for one hour, cooled and weighed. Some representative results are recorded in Table II: (Factor for copper is 0.1729).

TABLE II

'Cu' taken in g	*Wt of 'Cu' ppt. in g*	*'Cu' found in g*
0.00518	0.0302	0.00521
0.01358	0.0784	0.01356
0.02589	0.1493	0.02581
0.03366	0.1946	0.03364
0.03625	0.2095	0.03622

(ii) *Effect of the concentration of the reagent.* The precipitation of copper resorcylaldoxime depends on the amount of reagent present in solution. It was found that precipitation of copper was complete only in the presence of large excess of reagent, (at least 6-7 times by weight). It was noted that best results were obtained using 15-25 ml of a 1% reagent solution for the determination of 4 mg of copper. This is evident from Table III.

TABLE III

Cu^{+2} taken: 0.003827 g and pH of the solution: 1.8-2.2

Reagent taken in g	Reagent required theoretically in g	Wt of 'Cu' ppt. in g	'Cu' found in g
0.05	0.01865	0.0209	0.003612
0.09	0.01865	0.0215	0.003716
0.12	0.01865	0.0221	0.003818
0.20	0.01865	0.0221	0.003818
0.40	0.01865	0.0222	0.003822

(iii) *Determination of copper in presence of other ions.* It is clear from the results in Table IV that copper could be determined in presence of Cd^{+2}, Zn^{+2}, Pb^{+2} and Co^{+2} between pH 1.8 and 2.4 with resorcylaldoxime.

TABLE IV

'Cu' taken in g	*Metal ions added in g*	*Wt of 'Cu' ppt. in g*	*'Cu' found in g*
0.019135	(Cd^{+2}) .00792	0.1103	0.01907
0.019135	.01056	0.1104	0.01907
0.019135	.03960	0.1096	0.01894
0.01248	(Zn^{+2}) .00350	0.0721	0.01247
0.01248	.01750	0.0718	0.01241
0.01248	.07020	0.0715	0.01236
0.015308	(Ni^{+2}) .00299	0.0881	0.01524
0.015308	.00598	0.0876	0.01515
0.015308	.02990	0.0860	0.01487
0.015308	(Pb^{+2}) .00445	0.0886	0.01531
0.015308	.02172	0.0885	0.01530
0.015308	.08720	0.0882	0.01523
0.019135	(Co^{+2}) .01282	0.1106	0.01912
0.019135	.02564	0.1102	0.01905
0.019135	.12820	0.1094	0.01891

(iv) *Analysis of copper in brass.* Copper in brass has been estimated by this method, with as satisfactory results as with salicylaldoxime. Two different varieties of the alloy

the alloy in the

12.65: (Table V).

id made up to 100

nl with water.

'Cu' found in g
0.00287
0.01138
0.0316
0.0945

ution, in a 250 ml
as then added and
re was kept on the
lass gooch crucible,
for nickel is 0.1618.

		'Ni' found in g
0.00149	0.0092	0.00148
0.00598	0.0366	0.00592
0.01495	0.0922	0.01491
0.01943	0.1203	0.01945
0.02980	0.1849	0.02990

References p. 339.

ERRATA

Anal. Chim. Acta, 12 (1955) 337, line 5 from bottom, for $4r_2^2df_2$ read $4\pi r_2^2df_2$; line 1 from bottom, for $4r_1^2df_1$ read $4\pi r_1^2df_1$.

p. 340, line 7, for $\dfrac{4r_1^2df_1}{4r_2^2df_2}$ read $\dfrac{4\pi r_1^2df_1}{4\pi r_2^2df_2}$

(ii) *Effect of the reagent concentration.* As in the case of copper it was found that at least 6-7 times the theoretical quantity of reagent was required for complete precipitation of nickel. Results are shown in Table VII.

TABLE VII

(Ni^{+2} taken 0.01495 g; 1% reagent solution)

Amount of reagent in ml	*pH of the solution*	*Wt of 'Ni' ppt. in g*	*'Ni' found in g*
5	5.5	0.0914	0.01478
10	5.5	0.0918	0.01485
15	5.5	0.0922	0.01493
20	5.5	0.0926	0.01498
30	5.5	0.0928	0.01502

(iii) *Determination of nickel in presence of other ions*

TABLE VIII

Wt of Ni taken in g	*Metal ions added in g*	*Wt of Ni ppt. in g*	*Ni found in g*
0.01495	(Cd^{+2}) 0.00792	0.0920	0.01488
0.01495	0.03960	0.0928	0.01501
0.01495	0.07920	0.0932	0.01508
0.01196	(Co^{+2}) 0.01282	0.0738	0.01194
0.01196	0.05128	0.0743	0.01201
0.01196	0.06410	0.0742	0.01200
0.01794	(Zn^{+2}) 0.0035	0.1108	0.01792
0.01794	0.0525	0.1116	0.01808
0.01794	0.0702	0.1114	0.01802
0.01495	(Mn^{+2}) 0.01671	0.0931	0.01506
0.01495	0.06684	0.0932	0.01507
0.01495	0.10030	0.0938	0.01517
0.01196	(Pb^{+2}) 0.00445	0.0744	0.01203
0.01196	0.02670	0.0745	0.01201
0.01196	0.08720	0.0748	0.01210

It is clear from the above results (Table VIII) that nickel can be determined in presence of Cd^{+2}, Co^{+2}, Zn^{+2}, Mn^{+2} and Pb^{+2} with resorcylaldoxime.

SUMMARY

Resorcylaldoxime has been used successfully for the determination of copper and nickel in presence of several metallic ions by controlling the pH. Copper-resorcylaldoxime is quantitatively precipitated from acid solution (pH 1.4). With nickel, precipitation begins at pH 4.2 and is complete between 5.54 and 6.55.

RÉSUMÉ

La résorcylaldoxime est proposée pour le dosage du cuivre et du nickel, en présence de plusieurs ions métalliques, à pH contrôlés. Le composé cuivre-résorcylaldoxime précipite quantitativement en solution acide (pH 1.4). Avec le nickel, la précipitation commence au pH 4.2 et est complète entre les pH 5.54-6.55.

ZUSAMMENFASSUNG

Das Resorcylaldoxim wird für die Bestimmung von Kupfer und Nickel vorgeschlagen, in Gegenwart von verschiedenen Metallionen bei verschiedenen pH-Werten. Die Kupfer-Resorcylaldoxim-Verbindung fällt in saurer Lösung (pH 1.4) quantitativ aus. Mit dem Nickel beginnt die Ausfällung bei pH 4.2 und ist beendet zwischen pH 5.54-6.55.

ACKNOWLEDGEMENT

My sincere thanks are due to Professor P. RAY of the Indian Association for the Cultivation of Science, Calcutta, for his helpful suggestions and guidance during the course of the present work.

REFERENCES

[1] F. FEIGL, *Ber.*, 56 (1923) 2083.
[2] F. FEIGL, P. SICHER AND A. SINGER, *ibid.*, 58 (1925) 2294.
[3] F. EPHRAIM, *ibid.*, 63 (1930) 1928.
[4] F. EPHRAIM, *ibid.*, 64 (1931) 1210.
[5] L. BIEFIELD AND D. HOWE, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 251.
[6] M. GAHIDE, *Bull. Soc. Chim. Belg.*, 45 (1936) 9; *C.A.*, 30 (1936) 6671.
H. HOLZER, *Z. anal. Chem.*, 95 (1932) 932.
M. ISHEBASHI AND H. KISHI, *Bull. Chem. Soc. Japan*, 10 (1935) 362.
T. G. PEARSON, *Z. anal. Chem.*, 112 (1938) 179.
H. L. RILEY, *J. Chem. Soc.*, (1933) 895.
[7] P. RAY AND A. K. MUKHERJEE, *J. Indian Chem. Soc.*, 27 (1950) 707.
[8] S. L. CHIEN AND T. M. SHIH, *J. Chinese Chem. Soc.*, 5 (1937) 154.
[9] S. ASTIN AND H. J. RILEY, *J. Chem. Soc.*, (1933) 314.
[10] E. MARCUS, *Ber.*, 24 (1891) 3651.
[11] P. RAY AND D. N. SEN, *J. Indian Chem. Soc.*, 25 (1949) 483.

Received February 7th, 1955