

SALICYLAMIDOXIME AS AN ANALYTICAL REAGENT. PART II. GRAVIMETRIC ESTIMATION OF COPPER AND NICKEL, AND THEIR SEPARATION FROM OTHER METALS

BY DEBABRATA BANDYOPADHYAY AND PRIYADARANJAN RĀY

The use of salicylamidoxime as a reagent for the gravimetric estimation of copper and nickel by weighing the precipitates of composition $M(C_7H_7O_2N_2)_2$, where $M=Cu$ or Ni , after drying at 110° , is described. Copper can be effectively separated from mercury^{II}, lead, cadmium, zinc, manganese^{II} and cobalt^{II} by precipitating the copper with an excess of the amidoxime at a p_H of 4.0-4.5; while for the separation from iron^{III}, antimony^{III} and bismuth^{III}, the precipitation should be carried out in presence of sufficient tartaric acid at a p_H of 4.0-4.5. Nickel can similarly be separated from zinc quantitatively by precipitation with the reagent at a controlled p_H (7.0-7.5) in the presence of some ammonium chloride to prevent the precipitation of the latter element. Determinations of copper and nickel in mixed solutions have been carried out by precipitating copper in an acetate-buffer of p_H near about 4; in the filtrates nickel was precipitated by adding more of the reagent and then ammonia to adjust the p_H of the solution to 7.5-7.5.

The precipitation reactions of salicylamidoxime with metallic ions have been described in a previous communication (cf. Part I, this issue, 21). It has been stated there that copper and nickel are quantitatively precipitated from 0.001M solutions of the metals at p_H 3.9-6.5 and at 6.5-8.0 respectively for the two elements. These precipitates after drying at 110° have the composition given by $M(C_7H_7O_2N_2)_2$, where $M=Cu$ or Ni . Furthermore, the p_H values of incipient precipitation of some metals in equivalent solutions by salicylamidoxime differ widely. From a consideration of all these facts salicylamidoxime might be expected to furnish suitable methods for the gravimetric determinations of copper and nickel as also for their separation from one another and from other metals. In this respect the amidoxime has several advantages over the aldoxime, which behaves analogously (cf. Welcher, "Organic Analytical Reagents", Vol. III, pp. 259-271, D. Van Nostrand Co., Inc., 1947). In fact, in contrast to salicylaldoxime, salicylamidoxime is rather stable, and consequently precipitations of metallic ions by this reagent can be carried out in hot solutions, and the precipitates can safely be washed with hot water, in which the reagent is fairly soluble. These are some of the factors that minimise entrainment of the precipitates with impurities. Moreover, the reagent is readily soluble in dilute acids and alkalies, and the acid solutions keep quite well, at least for several weeks at room temperature, in which it has been ordinarily used, although a solution in hot water is a good substitute. The reagent can be easily prepared in a pure state, as described in the previous communication (*loc. cit.*). Actual determinations with varying amounts of copper (6 to 100 mg.) and of nickel (6 to 77 mg.) by precipitation with an excess of salicylamidoxime at a p_H of 4.0-4.5 for copper and 7.0-7.5 for nickel have yielded excellent results (cf. Tables I and VII respectively).

As the p_H limits for the precipitation of copper and nickel differ rather widely, a simple precipitation at a controlled p_H might be expected to effect their

separation. But actual experimental results showed that even at a p_H as low as 4 the copper precipitate, obtained in a mixture of copper and nickel, was sufficiently entrained with the latter. Precipitation in the presence of sufficient ammonium chloride also, proved of little use in preventing the adsorption of nickel. This co-precipitation of an unusual type is possibly due to a similarity in the crystal structures of the compounds of the two metals in question.

Copper and nickel can, however, be effectively separated by precipitating the copper compound in an acetate-buffer medium of p_H about 4 (cf. Table VIII). This seems to indicate some specific influence of the acetate in preventing the co-precipitation of the nickel in this case. In the combined filtrate and washings nickel was determined by adding more reagent and adjusting the p_H with ammonia, as in the case of the individual nickel determination.

Copper has, however, been separated from zinc, cadmium, manganese^{II}, cobalt^{II}, lead and mercury^{II} by precipitation at a controlled p_H with the amidoxime (cf. Tables II-IV); but in the presence of mercury the addition of a sufficiently large excess of the reagent is essential for the complete precipitation of copper.

Interference by antimony^{III} and bismuth^{III} in copper determination can be prevented altogether by precipitating copper as usual, but in the presence of some tartaric acid as a masking agent. These results are shown in Table V. For the separation of copper from iron^{III}, the presence of tartaric acid is necessary as also of a large excess of the reagent (cf. Table VI).

Estimation of nickel can be carried out even in the presence of zinc by precipitating the nickel complex of the reagent in presence of sufficient ammonium chloride at a p_H of 7.0-7.5 (cf. Table IX); the latter prevents the precipitation of zinc.

EXPERIMENTAL

A pure sample of the reagent was prepared as described in Part I of this communication (*loc. cit.*).

Estimation of Copper

A stock solution of standard copper^{II} chloride was prepared from a known weight of metallic copper (G. R.) by dissolving it in nitric acid and evaporating the solution with hydrochloric acid. Its strength was further determined gravimetrically with salicylaldoxime.

A definite volume of the standard copper solution was just neutralised with pure ammonia and weakly acidified with hydrochloric acid and then diluted to about 100 c.c. with water and warmed on the water-bath. Copper was precipitated by adding an excess of the reagent (3.5-4.0 c.c. of the 1% solution in hot water or dilute hydrochloric acid for every 5 mg. of copper present in the solution) and adjusting the p_H of the solution to 4.0-4.5 (tested by B.D.H. indicator paper) by adding dilute alkali (KOH, NaOH or ammonia). The mixture was digested on the water-bath

for about 5-10 minutes in order to allow the precipitate to settle and then filtered through a sintered glass (Jena) Gooch crucible (No. 4). The precipitate was thoroughly washed with hot water, dried at 110°, for at least one hour, in an air oven, and weighed. The factor for copper is 0.1740. The results are recorded in Table I.

TABLE I

Drying temp. = 110°.

Cu present.	Cu-compound.	Cu found.	Error (mg.).	Cu present.	Cu-compound.	Cu found.	Error (mg.).
0.00610 g.	0.03508 g.	0.00510 g.	±0.0	0.04529 g.	0.026604 g.	0.04629 g.	±0.0
0.01526	0.08775	0.01526	"	0.05189	0.29802	0.05186	-0.03
0.02543	0.14595	0.02538	-0.05	0.06104	0.35100	0.06107	+0.03
0.03612	0.20775	0.03615	+0.03	0.07580	0.43579	0.07583	+0.03
				0.10276	0.59103	0.10283	+0.07

Separation of Copper from Cadmium and Zinc

From mixed solutions containing copper and the other metal, copper was precipitated as in the previous case. In the filtrates the other metals were determined gravimetrically as oximates, after decomposing the excess of the amidoxime by fuming with nitric and sulphuric acids. The results are shown in Table II.

TABLE II

Metals present.	Cu-compound.	Metals found.	Error (mg.).	Metals present.	Cu-compound.	Metals found.	Error (mg.).
Cu, 0.05282 g.	0.30392 g.	0.05288 g.	+0.06	Cu, 0.05282 g.	0.30342 g.	0.05279 g.	-0.03
Cd, 0.05428		0.05418	-0.10	Zn, 0.05102		0.05128	+0.08
Cu, 0.01098	0.06300	0.01096	-0.02	Cu, 0.01046	0.06001	0.01044	-0.02
Cd, 0.03225		Zn, 0.05120
Cu, 0.01203	0.06905	0.01201	-0.02	Cu, 0.01150	0.05594	0.01148	-0.02
Cd, 0.06450		Zn, 0.10291		0.10280	-0.11
Cu, 0.01150	0.05622	0.01152	+0.02	Cu, 0.10450	0.60175	0.10462	+0.02
Cd, 0.09783		0.09777	-0.06	Zn, 0.01024		0.01030	+0.06
Cu, 0.09414	0.54070	0.09408	-0.06	Cu, 0.07845	0.45120	0.07850	+0.05
Cd, 0.01075		0.01077	+0.02	Zn, 0.01024	
Cu, 0.06276	0.36005	0.06266	-0.10	Cu, 0.05492	0.31598	0.05496	+0.06
Cd, 0.01156		Zn, 0.01126	
Cu, 0.03243	0.18614	0.03239	-0.04				
Cd, 0.01236					

Separation of Copper from Cobalt, Manganese and Lead

In the case of separation from lead, mixed solutions containing copper nitrate and lead acetate were used as the absence of chloride and sulphate was essential.

The mixed solution containing copper and the other metal was neutralised with sodium carbonate, acidified with acetic acid and diluted to 150 c.c. with water. This was warmed on the water-bath for some time to expel the carbon dioxide, and the copper was precipitated as usual with the amidoxime at a p_H of 4.0-4.5. The precipitate was filtered, washed, dried and weighed as usual, while in the combined filtrate and washings the other metal was determined gravimetrically as the sulphate as usual after decomposing the organic matter by fuming with sulphuric and nitric acids. The results of some determinations are shown in Table III.

TABLE III

Metals present.	Cu-compound.	Metals found.	Error (mg.).	Metals present.	Cu-compound.	Metals found.	Error (mg.).
Cu, 0.05492 g. Co, 0.05788	0.31590 g.	0.05495 g. ...	+0.03 ...	Cu, 0.05230 g. Mn, 0.00931	0.30032 g.	0.05225 g. 0.00935	-0.05 +0.04
Cu, 0.05544 Co, 0.01158	0.31868	0.05546 0.01160	+0.02 +0.02	Cu, 0.01307 Mn, 0.05819	0.07527	0.01309 ...	+0.02 ...
Cu, 0.01150 Co, 0.06367	0.06619	0.01152 ...	+0.02 ...	Cu, 0.05561 Pb, 0.05228	0.31960	0.05560 ...	+0.01 ...
Cu, 0.05230 Mn, 0.04888	0.30022	0.05223 ...	-0.07 ...	Cu, 0.01145 Pb, 0.05228	0.06574	0.01144 ...	-0.01 ...
				Cu, 0.05496 Pb, 0.02098	0.31583	0.05494 0.02095	-0.02 -0.03

Separation of Copper from Mercury

This can be effected by precipitating the copper from mixed solutions containing copper^{II} chloride and mercury^{II} chloride at a p_H of 4.0-4.5, but a relatively large excess of the amidoxime, determined by the amount of mercury present, is required to effect complete precipitation of copper (cf. Table IV).

The mixed solution containing copper^{II} and mercury^{II} chlorides was neutralised with caustic soda, acidified with HCl, diluted to 200 c.c. with water, warmed and treated with an excess of the reagent solution, p_H adjusted to 4.0-4.5, and the copper precipitate was worked up as usual. In the filtrate mercury was determined gravimetrically as the sulphide. The results are shown in Table IV.

TABLE IV

Metals present.	Volume of 1% reagent soln.	Cu-compound.	Metals found.	Error.
Cu, 0.05256 g.	60 c.c.	0.30180 g.	0.05250 g.	-0.06 mg.
Hg, 0.04830	
Cu, 0.06302	50	0.36237	0.06305	+0.03
Hg, 0.01449			0.01451	+0.02
Cu, 0.01046	10	0.05420	0.00943	-1.03
Hg, 0.04830		
Cu, 0.01046	30	0.06020	0.01047	+0.01
Hg, 0.04830		

Separation of Copper from Antimony and Bismuth

To the mixed solution containing copper^{II} chloride and antimony^{III} chloride or copper^{II} nitrate and bismuth^{III} nitrate, as the case may be, sufficient free mineral acid was added to afford a clear solution. This was treated with about 2.5 g. of Rochelle salt and then with sodium carbonate solution till a light blue colour just appeared. The solution was then acidified carefully by adding the requisite mineral acid to bring its p_H between 4 and 5. This was then diluted to about 200 c.c. with water, warmed on the water-bath, and copper precipitated by adding an excess of 1% aqueous solution of the amidoxime and then adjusting the p_H , if required, to 4.0-4.5 by adding a dilute solution of caustic potash. The copper precipitate was filtered, washed, dried and weighed as usual. In the filtrate antimony was determined volumetrically by the bromate method, and bismuth determined gravimetrically as the oxide (Bi_2O_3), after precipitation with ammonium carbonate; all organic matter was previously decomposed by fuming with sulphuric and nitric acids. The results of a number of determinations are recorded in Table V. That tartaric acid did not interfere with the determination of copper is shown by the first two results in the table.

TABLE V

Metals present.	Cu-compound.	Metals found.	Error.
Cu, 0.01308 g.	0.07542 g.	0.01312 g.	+0.04 mg.
Cu, 0.10450	0.60180	0.10470	+0.10
Cu, 0.04184	0.23998	0.04176	-0.08
Sb, 0.02394	
Cu, 0.05282	0.30382	0.05284	+0.02
Sb, 0.00599	
Cu, 0.01046	0.05995	0.01043	-0.03
Sb, 0.02993		0.02981	-0.12
Cu, 0.04253	0.24492	0.04261	+0.08
Bi, 0.04889		0.04898	+0.09
Cu, 0.06543	0.37620	0.06545	+0.02
Bi, 0.01528	
Cu, 0.01309	0.07544	0.01313	+0.04
Bi, 0.07334	

Separation of Copper from Iron

Copper has been separated from iron^{III} by precipitating the former in presence of tartaric acid at a p_H of 4.0-4.5 by using a large excess of the reagent. About 3.5-4.0 c.c. of 1% solution of the reagent for each 5 mg. of copper and in addition 8-9 c.c. of the same for each 5 mg. of iron present have been found necessary for complete separation.

The mixed solution containing copper^{II} and iron^{III} chlorides and sufficient HCl was treated with 3 g. of Rochelle salt; this was diluted to 150 c.c. and warmed on the water-bath. The hot solution was treated with the requisite quantity of the reagent solution, prepared in 0.1N hydrochloric acid, and the p_H adjusted thereafter to 4.0-4.5 by adding dilute caustic potash solution. The copper precipitate was worked up as usual, and in the filtrate iron was determined gravimetrically as Fe_2O_3 , after decomposing the organic matter. The results of some of the determinations are shown in Table VI.

TABLE VI

Metals present.	Volume of 1% reagent soln.	Cu-compound.	Metals found.	Error.
Cu, 0.05230 g. Fe, 0.01082	40 c.c.	0.29741 g.	0.05168 g. ...	-0.062 mg. ...
Cu, 0.01046 Fe, 0.00541	10	0.05875	0.01022 ...	-0.24 ...
Cu, 0.05282 Fe, 0.00054	40	0.30385	0.05286 ...	+0.04 ...
Cu, 0.06276 Fe, 0.06042	150	0.36101	0.06281 ...	+0.05 ...
Cu, 0.03136 Fe, 0.03021	80	0.18040	0.03138 0.03020	± 0.0 -0.01
Cu, 0.01046 Fe, 0.03021	60	0.06017	0.01046 0.03013	± 0.0 -0.08

Estimation of Nickel

A stock solution of nickel chloride was prepared and its strength was determined gravimetrically as nickel-dimethylglyoxime. A known volume of the nickel solution was diluted to about 100 c.c. by adding water, warmed on the water-bath, added an excess of the reagent solution (about 4 c.c. of the 1% solution, in 0.1N-HCl or hot water, for every 5 mg. of the nickel present) and dilute ammonia was then gradually added till the p_H of the solution came within the range of 7.0-7.5 (tested by B.D.H. indicator paper). This was then digested on the water-bath till the precipitate settled down (about 10-15 minutes required). The precipitate was then filtered off on a No. 4 sintered glass (Jena) Gooch crucible, washed thoroughly with hot water of p_H near about 7 (adjusted by adding a few drops of dilute ammonia) and then dried at 110° for at least one hour and weighed. The factor for nickel is 0.1628. Results are recorded in Table VII.

TABLE VII

Drying temp. = 110°

Ni present.	Ni-compound.	Ni found.	Error.
0.00662 g.	0.04064 g.	0.00662 g.	±0.0 mg.
0.02597	0.15958	0.02599	+0.02
0.05143	0.31557	0.05138	-0.05
0.06212	0.31891	0.06218	+0.06
0.07740	0.47569	0.07744	+0.04

Estimation of Copper and Nickel when present together

The mixed solution containing copper and nickel was neutralised with dilute ammonia till a turbidity just appeared. To this were added 6 c.c. of 6N acetic acid and 10 c.c. of a 10% solution of sodium acetate. The mixture was then diluted to 100 c.c. with water and warmed on the water-bath; copper was then precipitated in hot solution by adding 4.0-4.5 c.c. of an 1% solution of salicylamidoxime in hot water for every 5 mg. of copper present. This was then digested on the water-bath for about 10 minutes and then filtered hot through a No. 4 sintered glass (Jena) Gooch crucible. The precipitate was washed thoroughly with hot water, then dried at 110° for one hour and weighed. In the combined filtrate and washings nickel was precipitated by adding more of the reagent (about 4 c.c. of the 1% solution for every 5 mg. of nickel present) and then adjusting the p_H to 7.0-7.5 with ammonia. The results of some of the determinations are recorded in Table VIII.

TABLE VIII

Metals present.	* p_H .	Wt. of compounds.	Metals found.	Error.
Cu, 0.01569 g.	3.92	0.09001 g.	0.01566 g.	-0.03 mg.
Ni, 0.01527		0.09386	0.01529	+0.02
Cu, 0.04759	3.98	0.27301	0.04750	-0.09
Ni, 0.01578		0.09712	0.01581	+0.03
Cu, 0.09336	3.88	0.53610	0.09328	-0.08
Ni, 0.01604		0.09871	0.01607	+0.03
Cu, 0.01674	4.08	0.09619	0.01673	-0.01
Ni, 0.04837		0.29657	0.04829	-0.08
Cu, 0.01569	3.98	0.09001	0.01566	-0.03
Ni, 0.09267		0.56956	0.09273	+0.06
Cu, 0.05308	3.94	0.30499	0.05307	-0.01
Ni, 0.05423		0.33282	0.05418	-0.05

The p_H values refer to the filtrate only.

Separation of Nickel from Zinc

An excess of ammonium chloride has been found to prevent the precipitation of zinc.

The mixed solution containing nickel and zinc was treated with about 4 g. of ammonium chloride, diluted to 200 c.c. with water and heated on the water-bath. To the warm solution was added an excess of the reagent (about 4.0-4.5 c.c. of the 1% solution of salicylamidoxime, in 0.1N-HCl for every 5 mg. of nickel present) and nickel was precipitated by adding dilute ammonia dropwise till the p_H of the solution rose to 7.0-7.5 (tested by B.D.H. indicator paper). The mixture was digested on the water-bath for a few minutes and then the precipitate was filtered, washed, dried and weighed as usual.

In the combined filtrate and washings, zinc was estimated gravimetrically as the oxinate, after decomposing the organic matter. The results of some of the determinations are shown in Table IX. The first two results in the table indicate that ammonium chloride does not interfere with the determination of nickel.

TABLE IX

Metals present.	Ni-compound.	Metals found.	Error.
Ni, 0.01399 g. Zn, nil	0.08618 g.	0.01403 g.	+0.04 mg.
Ni, 0.12562 Zn, nil	0.77276	0.12581	+0.19
Ni, 0.10184 Zn, 0.01024	0.62580	0.10190 ...	+0.06 ...
Ni, 0.01069 Zn, *0.05120	0.06580	0.01071 ...	+0.02 ...
Ni, 0.01247 Zn, 0.10240	0.07623	0.01242 ...	-0.05 ...
Ni, 0.06219 Zn, 0.01024	0.38231	0.06224 0.01030	+0.05 +0.06
Ni, 0.06281 Zn, 0.05120	0.38594	0.06284 0.05128	+0.05 +0.08