[Jour. Indian Chem. Soc., Vol. 37, No. 3, 1960]

3-OXIMINOMETHYLSALICYLIC ACID AS AN ANALYTICAL REAGENT. PART I. GRAVIMETRIC ESTIMATION OF COPPER AND NICKEL

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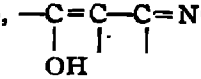
The reactions of 3-oximinomethylsalicylic acid with metallic ions have been fully investigated. It has been found that this reagent behaves very much like salicylaldoxime with respect to colour, solubility, etc. of its metallic derivatives ; but the pH values of incipient precipitation of the metallic ions are somewhat different from those found with salicylaldoxime. Like salicylaldoxime this reagent has also been found to produce an orange-yellow precipitate with titanium in acid solution, though Flagg and Furman (*Ind. Eng. Chem., Anal.* Ed., 1940, 12, 529, 653) did not notice this characteristic reaction of salicylaldoxime.

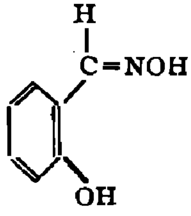
Fe^{III} and U^{VI} yield soluble coloured complexes in acid and alkaline medium respectively. The use of 3-oximinomethylsalicylic acid as a reagent for the gravimetric estimation of copper and nickel, which furnish precipitates of composition $M(C_8H_6O_4N)_2$ ($M=Cu^{II}$ or Ni^{II}), after drying at 110°, has been described. Copper can be effectively separated from Hg^{II}, Pb^{II} Al^{III}, Cd^{II}, Zn^{II}, Mn^{II} and Co^{II} by precipitating it with an excess of 3-oximinomethylsalicylic acid at pH 1.5 to 3.0 ; while for its separation from Fe^{III}, Sb^{III} and Bi^{III}, the precipitation had to be carried out in the presence of sufficient tartaric acid at pH 2.5 to 3.0. Determination of copper has also been made from solutions containing arsenite, arsenate, vanadate and phosphate at pH 2.5 to 3.0. Nickel has been estimated gravimetrically with this reagent at a controlled pH (5.6-6.0)

The reactions of 3-oximinomethylsalicylic acid with various metallic ions have been fully investigated in an effort to find out the possibility of using this substance as an analytical reagent. 3-Oximinomethylsalicylic acid, like salicylhydroxamic acid, salicylaldoxime, salicylamidoxime and *ortho*-hydroxyacetophenone oxime, contains the copper specific group,

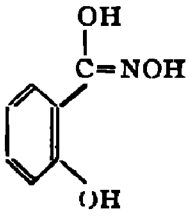


$$\underset{\displaystyle |}{-C} = \underset{\displaystyle |}{C} - \underset{\displaystyle |}{C} = NOH \qquad \text{with OH on the first C}$$

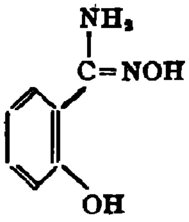
as is evident from their structures shown below:



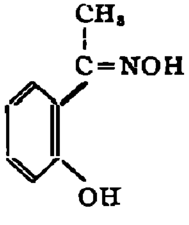
Salicylaldoxime



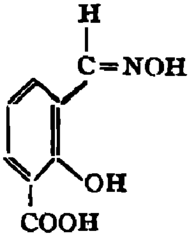
Salicylhydroxamic acid.



Salicylamidoxime.



o-Hydroxyacetophenone oxime.



3 Oximinomethylsalicylic acid.

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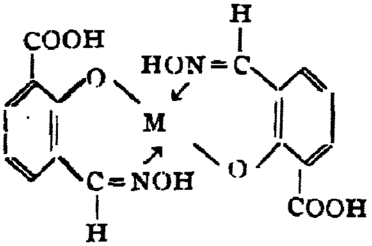
Salicylaldoxime was first employed by Ephraim (*Ber.*, 1930, **63**, 1928; 1931, **64**, 1210) for the detection and gravimetric determination of copper. Later on Flagg and Furman (*loc. cit.*) studied the reactions of this reagent, as also of its 5-chloro, 3:5 dibromo and 5-nitro derivatives, with various metallic ions. Since then several reports have appeared on the use of salicylaldoxime for the separation and determination of metals.

The analytical reactions and applications of salicylhydroxamic acid (Bhaduri and Rây, *Science & Culture*, 1952, **18**, 97; *Z. anal. Chem.*, 1957, **154**, 103), salicylamidoxime (Bandyopadhayay and Rây, this *Journal*, 1956, **33**, 65), resacetophenone oxime (Neelakantan, *Curr. Sci.*, 1945, **14**, 320) and of *o*-hydroxyacetophenone oxime (Poddar, *Z. anal. Chem.*, 1957, **284**, 327) for the estimation of copper and nickel have only been recently studied. It might therefore be of interest to investigate the reactions of 3-oximiniomethylsalicylic acid as well, as it is closely related to them. It may be regarded as derived from salicylaldoxime by the replacement of a H atom of its benzene nucleus, in the *ortho* position to hydroxyl, by a carboxyl group. The result of this investigation will naturally show the influence of such a substitution in the benzene ring of the salicylaldoxime molecule. It was further expected that the presence of three functional groups in the molecule of 3-oximinomethylsalicylic acid in positions favourable for chelation might also offer some practical advantage over the other reagents of the group.

An account of the general reactions of 3-oximinomethylsalicylic acid with various metallic ions is recorded in the following section. When compared with the reactions of salicylaldoxime (cf. Flagg and Furman, *loc. cit.*), it will be found that the 3-oximinomethylsalicylic acid resembles salicylaldoxime, in its general behaviour, with respect to colour, solubility, etc. of its metallic derivatives, but the *p*H values of incipient precipitation of metals with this reagent are somewhat lower. Although Flagg and Furman (*loc. cit.*) do not report any reaction of titanium (IV) with salicylaldoxime, it has been found, however, that salicylaldoxime (Banerjea, *Z. anal. Chem.*, 1957, **159**, 123), salicylamidoxime (Bandyopadhayay and Rây, *loc. cit.*), *o*-hydroxyacetophenone oxime (Poddar, *loc. cit.*), salicylhydroxamic acid (Xavier, Chakraburtty and Rây, *Science & Culture*, 1951, **20**, 146) and 3-oximinomethylsalicylic acid, all form yellow coloured precipitates with Ti^{IV} in acid solution. These are insoluble in chloroform and amyl alcohol.

3-Oximinomethylsalicylic acid is considerably more stable than salicylaldoxime and consequently, precipitations of metallic ions by this reagent can be carried out in hot solutions, and the precipitates safely washed with hot water. It is also highly soluble in caustic alkalies due to salt formation. The aqueous solution of the reagent as well as that of its alkali salts keeps quite well, at least for several weeks at room temperature.

Cu^{II} and Ni^{II} compounds of 3-oximinomethylsalicylic acid were prepared as usual by precipitation and dried at 110°; their composition corresponds to $(C_8H_6O_4N)_2M$ (where $M = Cu^{II}$ or Ni^{II}). From the known constitution of the metal salicylaldoxime compounds (Feigl and Bondi, *Ber.*, 1931, **64**, 2814; Cox *et al*, *J. Chem. Soc*, 1935, **459**, 1475) and from the similarity in properties of the metal complexes of these two reagents, the 3-oximinomethylsalicylic acid metal complexes may be represented by the following structure:



The copper and nickel complexes are readily soluble in caustic alkali and ammoniacal solutions. The solubility of these compounds may be due to salt formation either by the free carboxyl group and/or by the =NOH group as in the case of salicylaldoxime complexes (cf. Feigl and Suter, *J. Chem. Soc.*, 1948, 378; Thilo and Friedrich, *Ber.*, 1929, **62**, 2998).

U^{VI} produces yellow to orange-red colour with excess of this reagent in alkaline solutions. Fe^{III} develops a violet coloration in acid and a yellow coloration in alkaline medium. These colour reactions have been utilised for their spectrophotometric estimation.

EXPERIMENTAL

3-Oximinomethylsalicylic acid (Furth, *Ber.*, 1883, **16**, 2182) was prepared from 3-aldehydosalicylic acid. The latter was prepared from salicylic acid and hexamethylenetetramine, as described by Duff and Bills (*J. Chem. Soc.*, 1932, 1987).

Preparation of 3-Aldehydosalicylic Acid.—Salicylic acid (40 g.), hexamethylenetetramine (27 g.) and water (300 c.c.) were boiled under reflux for 16 hours; the cooled solution was acidified with 4*N*-HCl (300 c.c.) and the yellow precipitate dried in air. This was extracted with four lots of benzene (100 c.c.) at 70°. The insoluble portion, when recrystallised from boiling water and decolorised with charcoal, yielded the 5-aldehydosalicylic acid. The benzene solution was evaporated and the residue just dissolved in 3*N* ammonia (200 c.c.). The solution was then treated with barium chloride (100 c.c., 10% solution) and 2*N*-NaOH (50 c.c.) at 50°. After 2 hours, the yellow precipitate of barium 3-aldehydosalicylate was collected and decomposed in the cold with HCl (dil., 1 : 4). The 3-aldehydosalicylic acid, thus liberated, was washed with cold water and then recrystallised from boiling water in the presence of iron-free charcoal, m.p. 179° (lit. 179°). The identity of 3-aldehydosalicylic acid was confirmed by the aldehyde reactions and by its melting point, as well as by that of its phenylhydrazone, m.p. 188° (lit. 188°).

Preparation of 3-Oximinomethylsalicylic Acid.—A mixture of 3-aldehydosalicylic acid (1 *M*), hydroxylamine hydrochloride (1 *M*) and NaOH (1.5 *M*) in water (100 c.c.) was slightly warmed at 40° for 24 hours. The clear solution was then cooled and acidified with cold dilute sulphuric acid (1 : 4 by vol.), when 3-oximinomethylsalicylic acid separated in the form of colorless crystals. This was washed with cold water and recrystallised from warm water containing some iron-free charcoal. The product was dried in air; m.p. 193° (lit. 193°).

The acid is soluble in alcohol, ether, benzene, chloroform, etc. It is also fairly soluble in cold and highly soluble in hot water. In aqueous solution it remains unchanged even on boiling.

Determination of the p*H limits for the Precipitation of Metals.*—The *p*H values for the incipient and complete precipitation of metals by this reagent were determined by gradually adding a standard solution of alkali ($\sim$1 *N*-NaOH) with stirring to 200 c.c. of a 0.001*N* solution of the metal, acidified strongly with a mineral acid and containing an excess (25%) of 3-oximinomethylsalicylic acid till a turbidity just appeared. The *p*H of the solution at this point, as determined by a Cambridge Bench Type *p*H meter, indicated the *p*H value for the incipient precipitation of the metal under the prescribed conditions. The dropwise addition of alkali was continued and the *p*H of the solution measured after each addition till the filtrate of an aliquot of the solution under titration, removed at intervals, gave no test for the metal ion with suitable sensitive reagent. Copper was tested for by rubeanic acid, nickel and palladium by dimethylglyoxime, uranium by potassium ferrocyanide, etc. The lowest *p*H value for the filtrate, giving no test for the metal concerned, represented the lowermost *p*H-limit of complete precipitation for the metal under the conditions stated. Table I records these *p*H limits as well as the general reactions of 3-oximinomethylsalicylic acid with various metallic ions.

Copper-3-oximinomethylsalicylic Acid.—A warm solution of copper chloride (G.R.), acidified with HCl (G.R.), was treated with a little over twice the molar proportion of the pure 3-oximinomethylsalicylic acid, dissolved in water containing a few c.c. of absolute alcohol, and to this mixture dilute alkali was gradually added to adjust the *p*H value of the solution to about 2.5 to 3.0 (tested with B.D.H. indicator paper). The mixture was set aside on the water-bath for about 10 minutes, after which a light yellowish green precipitate of the copper compound was filtered. The precipitate was then thoroughly washed with hot water, first by decantation, then on the filter-bed till free of the reagent (tested with ferric chloride for violet coloration) and finally dried to a constant weight at 110°. [Found: N, 6.63; Cu, 15.07. Calc. for $Cu(C_8H_6O_4N)_2$: N, 6.61; Cu, 15.01%].

The copper compound is insoluble in water, but soluble in strong acids, caustic alkalies and in ammonia. It is insoluble in organic solvents. The substance is somewhat soluble in hot concentrated solution of sodium acetate and of ammonium chloride.

Nickel (II)-*3-oximinomethylsalicylic Acid.*—A warm acidified solution of nickel chloride (G.R.) was treated with a little more than twice its molar proportion of the pure 3-oximinomethylsalicylic acid, dissolved in aqueous alcohol, and to this mixture dilute ammonia was added dropwise to adjust the *p*H of the solution near about 6.0 (tested by B.D.H. indicator paper). The mixture was kept on the water-bath for about 10 to 15 minutes and then the precipitated nickel compound was filtered, washed thoroughly with hot water containing a little alcohol, and finally dried for one hour to a constant weight at 110°. [Found: N, 5.38; Ni, 14.02. Calc. for $Ni(C_8H_6O_4N)_2$: N, 5.31; Ni, 14.03%].

TABLE I

Reactions of 3-oximinomethylsalicylic acid with metallic ions.

Metal ion.	Nature of reaction.	pH of incipient pptn. in 0.001M soln. of the metallic ion.	Remarks.
Ag^+	Pale yellow precipitation in neutral solution.	6.5	Soluble in ammonia and acetic acid ; decomposed by alkali on warming.
Pb^{2+}	Pale yellow ppt	6.0	Soluble in ammonia and alkali, insoluble in hot water.
Hg^{2+}	White ppt.	6.2	Soluble in ammonia, but slowly decomposed on warming
Cu^{2+}	Light yellowish green ppt.	1.8	Soluble in strong alkali and ammonia, but unaffected by boiling water. Precipitation complete between pH 2.1 and 6.0 even in presence of alkali acetates, tartrates and ammonium chloride with an excess of the regent.
Ni^{2+}	Light green ppt.	5.7	Soluble in NaOH and ammonia solns. ; also slightly soluble in strong soln. of ammonium chloride. Precipitation complete between pH 5.7 and 6.5.
Pd^{2+}	Light yellow ppt.	...	Soluble in NaOH soln. Precipitation is quantitative in faintly acid soln.
Fe^{3+}	Violet colour below pH 2.9 ; orange-red at pH 2.96 to 6.72 ; yellow at pH 7 to 10.12.	...	Discharged by F^-, PO_4^{3-} and $C_2O_4^{2-}$.
Cd^{2+}	Yellowish white ppt.	7.3	Soluble in ammonia.
Zn^{2+}	White ppt.	6.8	Soluble in ammonia or NaOH solution.
Co^{2+}	Deep brown coloured ppt. in conc. soln.	6.9	Soluble in caustic alkalies and ammonia.
Mn^{2+}	Brown ppt	8.5	Soluble in alkali or ammonia solutions.
UO_2^{2+}	Orange red soln. at pH 6.7 ; deep orange-yellow soln. at pH 7.5 to 11.	...	Not extractable with chloroform and amyl alcohol.
Bi^{3+}	Pale yellow ppt.	7.5	Soluble in ammonia or alkali.
Ti^{4+}	Faint yellow colour in strong sulphuric acid ; deep yellow ppt. at pH 2.0.	2.0	Insoluble in amyl alcohol but decomposed by alkalies.
VO_3^-	Dirty green ppt. in conc. vanadate soln. at pH 1 to 2	1.0	Insoluble in amyl alcohol.
MoO_4^{2-}	Faint yellow colour in acid soln.	...	Discharged by alkali and by an excess of acid.
Th^{4+}	Pale yellow ppt.	2.5	Precipitation complete at pH 4 to 5.
Zr^{4+}	White ppt.	2.5	Precipitation complete at pH 4 to 5.

The substance is insoluble in water, but soluble in acids, alkalies and ammonia.

From an examination of the various reactions of 3-oximinomethylsalicylic acid with different metal ions, it was observed that copper and nickel could be quantitatively precipitated at *p*H 2.5 to 3.0 and 5.6 to 6.0 respectively. The *p*H values of incipient precipitation of some of the metals by this reagent are also widely different. It was therefore expected that this reagent would prove useful for the gravimetric estimations of copper and nickel, and for the separation of copper from nickel and many other metals.

Copper was separated from Hg^{II}, Pb^{II}, Cd^{II}, Zn^{II}, Ni^{II}, Mn^{II}, Co^{II} and Al^{III} by a simple *p*H control, using this reagent. Separation of copper from Sb^{III}, Bi^{III} and Fe^{III} was effected in the presence of sufficient tartaric acid as a masking agent. Determination of copper from solutions containing arsenite, arsenate, vanadate, molybdate and phosphate was also carried out at *p*H 2.5 to 6.0 Nickel was precipitated at *p*H 5.6 to 6.0.

Estimation of Copper

A stock solution of copper chloride was prepared by dissolving a definite weight of metallic copper (G.R.) in HNO_3 (G.R.) and evaporating the solution repeatedly with HCl to remove nitrous fumes. The solution was then diluted to a definite volume with distilled water and its strength was further determined gravimetrically with salicylaldoxime.

A definite volume of the standard copper solution was just neutralised with pure ammonia, acidified to remove the turbidity and then diluted approximately to 150 c.c. The solution was then warmed on the water-bath and afterwards treated with an excess of the reagent (10 c.c. of 1% solution in warm water for every 5 mg. copper present). Copper was then precipitated and washed as described for the preparation of the copper compound. It was filtered through an asbestos Gooch and dried at 110°.

The factor for copper is 0.1501. The results are recorded in Table II.

TABLE II

Total volume of solution = 200 c.c. Drying temp. = 110°. Factor · 0.1501.

Copper present.	Cu-precipitate.	Cu found.	Error.
0.01301 g	0.08650 g.	0.01298 g.	− 0.03 mg.
0.01561	0.10440	0.01567	+ 0.06
0.02615	0.17425	0.02614	− 0.01
0.03916	0.26071	0.03913	− 0.03
0.05211	0.34760	0.05218	+ 0.01
0.06518	0.43222	0.06518	± 0.00
0.07819	0.52040	0.07812	− 0.07
0.09120	0.60751	0.09126	+ 0.06
0.10421	0.69460	0.10420	− 0.01

Separation of Copper (II) *from various Cations and Anions.*—Solutions of copper salt and those of other cations or anions of known strength were mixed together in different proportions, and each of the mixtures was treated exactly in the same manner as in the case of estimating copper, as described above. In the separation of copper from lead, standard solutions of the nitrate of the metals were used and their *p*H values were adjusted with nitric acid or caustic soda solution. In presence of Fe^{III}, Sb^{III} and Bi^{III}, 3-4 g. of tartaric acid was added as a masking agent. Some typical results out of many are shown in Table III.

TABLE III

Cu estimated								
13–91 mg.	Wt. ratio Cu/Zn	8.09	4.61	2.3	1.15	0.85	0.23	0.15
	%Error	+0.01	−0.02	−0.04	−0.08	+0.11	−0.31	−0.04
39–91	Wt. ratio Cu/Cd	5.40		4.64		3.85		1.03
	%Error	+0.09		−0.09		−0.14	−0.02 to −0.10	
13–65	Wt. ratio Cu/Co	1.18		0.95		0.24		
	%Error	+0.03		+0.62		−0.23		
13–65	Wt ratio Cu/Mn	6.48		1.04		0.26		
	%Error	+0.05		+0.06		+0.23		
26–65	Wt. ratio Cu/Pb	6.15		2.29		0.57		
	%Error	−0.07		+0.045		−0.08		
13–78	Wt. ratio Cu/Hg	6.23		1.50		0.25		
	%Error	+0.06		+0.025		−0.15 to −0.30		
13–52	Wt. ratio Cu/Sb	2.88		0.87		0.77		
	%Error	+0.61		−0.07		+0.02		
13–65	Wt. ratio Cu/Bi	6.00		1.20		0.24		
	%Error	+0.06		−0.04		−0.15		
26–52	Wt. ratio Cu/Al	1.39		0.37		0.31		
	%Error	−0.15		−0.08		+0.08		
26–64	Wt. ratio Cu/Fe	5.35	2.68	1.32		1.07		0.54
	%Error	−0.15	−0.025	+0.03		−0.08		−0.075
18–74	Wt. ratio Cu/Ni	4.33	3.23	1.08		0.65		0.215
	%Error	+0.05	±0.0	+0.28		−0.13		+0.27
13	Wt. ratio Cu/As^{III}	1.35	0.68			Wt. ratio Cu/As(V)		0.17
	%Error	−0.23	−0.23			%Error		−0.15
52	Wt. ratio Cu/Mo	0.96	0.48					
	%Error	0.0	−0.20					
13–26	Wt. ratio Cu/V	5.0	1.86					
	%Error	+0.08	−0.18					
13–26	Wt. ratio Cu/H_3PO_4	0.56	0.28					
	%Error	+0.08	−0.23					

Estimation of Nickel

A definite volume of a standard solution of nickel was just neutralised with sodium carbonate solution and the turbidity removed with HCl (dil.). The solution was then diluted to about 150 c.c., warmed on the water-bath, and treated with an excess of the reagent solution. The *p*H of the solution was adjusted to 5.6 to 6.0 (tested with B.D.H. indicator paper) by adding dilute hydrochloric acid or alkali solution as necessary. The precipitate was filtered, dried and weighed as in the case of copper. The results are recorded in Table IV.

TABLE IV

Total volume of solution = 200 c.c. Drying temp. = 110°. Factor = 0.1403.

Ni present.	Ni precipitate.	Ni found.	Error.
0.01716	0 12205 g.	0.01712 g.	−0.04
0 05720	0.40780	0.05718	−0.02
0.08580	0.61201	0.08578	−0.02
0.10296	0.73385	0.10291	−0.05
0.13728	0.97860	0.13720	−0.08

DISCUSSION

The reactions of 3-oximinomethylsalicylic acid are comparable to those of salicylaldoxime, but the *p*H values for the incipient precipitation of the metals by the former are somewhat lower. This suggests (cf. Irving and Williams, *Nature*, 1948, **162**, 746 ; Martell and Calvin, "Chemistry of the Metal Chelate Compounds", p. 170, Prentice Hall Inc., 1952) that the 3-oximinomethyl complexes are somewhat more stable than the corresponding aldoxime or amidoxime complexes. The results of this investigation naturally show the influence of a carboxyl substituent in the benzene ring of the salicylaldoxime molecule.

The *p*H's of incipient precipitation, in equimolecular solutions, of copper and nickel are widely different. Furthermore, zinc and cadmium do not form any definite compound with the 3 oximinomethylsalicylic acid, and their precipitation is prevented altogether in the presence of ammonium chloride. These facts are indicative of a greater selectivity of 3-oximinomethylsalicylic acid than that of salicylaldoxime.

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Received September 7, 1959.