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The Determination of Metals by Means of 8-Hydroxyquinoline

Part I. The Effect of $p_{\rm H}$ on the Precipitation of Magnesium, Zinc, Cobalt, Nickel, Copper and Molybdenum from Acetate Solutions

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THE recent extensive studies on the determination of metals by means of 8-hydroxyquinoline ("oxine") show that the reagent possesses very many desirable analytical qualities. Precipitation is usually effected from acetate or tartrate solutions, but inaccurate results are sometimes obtained, and may arise from insufficient precision in the published account of the conditions. In acetate solutions, the effect of $p_{\rm H}$ on the extent of precipitation is presumably the cause, for, although general statements are given on the amount of acid or alkali to be added, yet exact studies of the range of $p_{\rm H}$ over which the metals are precipitated have not been made. In tartrate solutions additional factors, such as the formation and stability of complex metallic tartrates, probably are of significance. We propose to deal first with the simpler case of acetate solutions; results on the effect of $p_{\rm H}$ on the precipitation of six metal-oxine complexes are given in this communication.

In every instance the total volumes of solutions were 145 c.c. or 160 c.c., according to whether 10 c.c. or 25 c.c. of the standard solution containing the metal

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were used. In each experiment 5 grms. of ammonium acetate and 10 c.c. of a 2 per cent. solution of oxine in N acetic acid were included in the total volume.

MAGNESIUM (Berg, Z. anal. Chem., 1927, 71, 23; Hahn and Vieweg, *ibid.*, p. 122; see also "Organic Reagents for Metals," Hopkin and Williams, Ltd., 1933, p. 41, bibliography):—A solution was used containing 13.9393 grms. of pure magnesium sulphate (MgSO₄.7H₂O) per litre, which corresponds with 13.75 mgrms. of magnesium, with 197.0 mgrms. of Mg(C₉H₆ON)₂.2H₂O, and with 45.22 c.c. N/10 potassium bromate solution per 10 c.c. of solution. Ten c.c. of the solution were found to contain 13.75 mgrms. of magnesium, determined as pyrophosphate. The weight of oxine precipitate, dried at 100° C., and the volumetric determination by means of potassium bromate, agreed with the composition Mg(C₉H₆ON)₂.2H₂O.

The following examples serve to illustrate the method used:-

(1) To 10 c.c. of the magnesium solution 25 c.c. of ammonium acetate (200 grms. per litre), 80 c.c. of water, 20 c.c. of N sodium hydroxide solution and 10 c.c. of oxine (2 per cent.) in N acetic acid were added. The solution was boiled for 3 to 5 minutes, and filtered at once through a sintered-glass crucible (1G3) into a dry flask. The undiluted filtrate was reserved for determination of The precipitate was well washed with boiling water, $p_{\rm H}$ at room temperature. dried to constant weight at 100° C., and weighed [obtained 175 mgrms. of $Mg(C_{9}H_{6}ON)_{2}.2H_{2}O]$. It was then dissolved in 2 N hydrochloric acid, and, after the addition of a small excess of N/10 potassium bromate and bromide, it was titrated with N/10 sodium thiosulphate in the usual way: 40.2 c.c. N/10 potassium bromate solution were required. The $p_{\rm H}$ was measured potentiometrically by means of hydrogen and calomel electrodes and a capillary electrometer: observed E.M.F., 0.762 volt; temp., 19° C.; whence $p_{\rm H}$ equals 8.91.

(2) To 10 c.c. of the magnesium solution, 25 c.c. of ammonium acetate (20 per cent.), 65 c.c. of water, 35 c.c. of N sodium hydroxide solution, and 10 c.c. of oxine (2 per cent.) in N acetic acid were added. Found: 197.0 mgrms. of complex: 45.2 c.c. of N/10 potassium bromate: E.M.F., 0.795 volt; temp., 18° C.; whence $p_{\rm H}$ equals 9.51.

		TABL	е I.		
₽н	Complex Mgrms.	$N/10 \text{ KBrO}_3$ c.c.	$\mathcal{P}_{\mathbf{H}}$	Complex Mgrms.	N/10 KBrO ₈ c.c.
5.32		—	9.28	194.5	44.65
5.42			9.51	197.0	45.2
5.56		_	9.73	197.0	45.2
5.64			10.36	197.0	45.2
6·10		_	11.00	197.0	$45 \cdot 2$
6.73		_	11.50	197.0	45.2
7.00	_		$12 \cdot 15$	197.0	-5.2
7.26		_	12.41	197.0	45.2
7.71	7.0	1.6	12.67	197.0	45.2
7.90	22.0	5.05	12.84	132.0	30.3
8.08	86.4	19.85	13.00	51.0	11.7
8·24	114.7	26.35	13.23		
8.50	147.6	33.9	13.57		
8.63	158.0	36.25	13.76		
8.72	164.0	37.6	14.00		
8·91	175.0	40.2	14.24		
9.11	184·0	42.3	14.32		

The complete results, using throughout 10 c.c. of magnesium solution, 5 grms. of ammonium acetate, 10 c.c. of oxine (2 per cent.) in N acetic acid, with varying quantities of N sodium hydroxide solution or N acetic acid in a total volume of 145 c.c., are given in Table I and Fig. 1 (p. 391). Between $p_{\rm H}$ 7 and 8, some coprecipitation of oxine took place; the precipitates obtained over this range were, therefore, dissolved in 2 N hydrochloric acid, and the pure magnesium-oxine complex was precipitated from alkaline tartrate solution.

Complete precipitation under the conditions specified takes place between $p_{\rm H}$ 9.44 and 12.66, the horizontal portion of the curve extending over the range 35-62 c.c. of N sodium hydroxide solution.

ZINC (Hahn and Vieweg, *loc. cit.*).—A solution of zinc (1·284 grm. per litre), dissolved in dilute acetic acid, was used. The oxine complex, dried at 120° – 130° C., agrees excellently with the composition $Zn(C_9H_6ON)_2$, and, dried at 100° C., is the dihydrate, $Zn(C_9H_6ON)_2.2H_2O$. Twenty-five c.c. of the stock solution (32·1 mgrms. of zinc, equivalent to $173\cdot4$ mgrms. of $Zn(C_9H_6ON)_2$ and to $39\cdot27$ c.c. of N/10 potassium bromate) in a total volume of 160 c.c. were used for each determination, exactly as in the case of magnesium. The complex compounds precipitated from acid solution are well crystallised, and, to complete precipitation from the more strongly acidic solutions, these must be boiled for at least 5 minutes; the precipitates obtained from the solutions of highest $p_{\rm H}$ are apparently amorphous. The results are given in Table II, and are shown graphically in Fig. 2 (p. 393).

Complete precipitation, therefore, extends from $p_{\rm H} 4.58$ to 13.4, which corresponds with solutions of total volume of 160 c.c. containing 5 grms. of ammonium acetate and from 80 c.c. of N acetic acid to 70 c.c. of N sodium hydroxide solution and 10 c.c. of oxine (2 per cent.) dissolved in N acetic acid.

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⊅ н	Complex	$N/10 \text{ KBrO}_3$	⊅ н	Complex	$N/10 \text{ KBrO}_3$
	Mgrms.	c.c.		Mgrms.	c.c.
3.53			8.08	173.4	39.25
3.68			8.85	173.4	39.25
3.94		_	9.50	173.4	39.25
4.20	26.0	5.95	10.36	173.4	39.25
4.33	91 ·0	20.6	10.96	173.4	39.25
4.43	147.0	33.5	11.78	173.4	39.25
4.50	168.0	38.05	12.91	$173 \cdot 4$	39.25
4.70	$173 \cdot 4$	39.25	13.33	173.4	39.25
4·91	$173 \cdot 4$	39.25	13.52	157.0	35.55
5.43	$173 \cdot 4$	39.25	13.76	77.5	17.6
6.02	$173 \cdot 4$	39.25	13.85	11.5	$2 \cdot 6$
6.61	$173 \cdot 4$	39.25	14.00		
7.34	173.4	39.25	14.20	_	

COBALT (Berg, Z. anal. Chem., 1929, 76, 196).—The solution used contained 14·104 grms. per litre of cobalt sulphate, $CoSO_4.7H_2O$, which corresponds with 29·56 mgrms. of cobalt, with 40·11 c.c. of N/10 potassium bromate, and with 173·9 mgrms. of $Co(C_9H_6ON)_2$ per 10 c.c. of solution. Determination by evaporation and ignition to $CoSO_4$, showed 10 c.c. of the solution to contain 29·53 mgrms. of cobalt. The gravimetric oxine method was not used, as the composition of the precipitate, dried at 120° C., was indefinite, corresponding approximately with $3Co(C_9H_6ON)_2.2H_2O$. The volumetric procedure gave excellent results, and the

		IABLE	111		
Þн	Complex Mgrms.	N/10 KBrO ₃ c.c.	¢н	Complex Mgrms.	N/10 KBrO ₃ c.c.
3.68			7.80	173.9	40·1
3.86			8.50	$173 \cdot 9$	40 ·1
4 ∙03		_	9.32	$173 \cdot 9$	40·1
4.10	27.1	6.25	10.15	173-9	40·1
4·17	81.7	$21 \cdot 15$	11.15	$173 \cdot 9$	40·1
4·23	158.9	36.65	11.80	$173 \cdot 9$	40·1
4 ·27	173-9	40.1	12.68	17 3 ·9	40·1
4.55	173.9	40.1	13.80	173-9	40·1
5.42	173-9	40·1	14.15	$173 \cdot 9$	40·1
6.16	173.9	40.1	14.53	173-9	40.1
7.00	173.9	40·1	14.80	$128 \cdot 8$	29.7



titration figures are calculated also in terms of mgrms. of $Co(C_9H_6ON)_2$, for comparison with the other elements studied. The method used was as for magnesium, but for solutions containing more than 20 c.c. of N sodium hydroxide solution it was necessary to add the oxine before the alkali, otherwise precipitation of cobalt hydroxide took place.

The results given in Table III and Fig. 1 (supra) show the range for complete precipitation to be from $p_{\rm H}$ 4.33 corresponding with the presence of 11.5 c.c. of

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glacial acetic acid to $p_{\rm H}$ 14.5 corresponding with 100 c.c. of 5 N sodium hydroxide solution per 145 c.c., the total volume of the solution.

NICKEL (Berg, Z. anal. Chem., 1929, 76, 191).—For these determinations, the solution contained 6.554 grms. per litre of nickel sulphate, NiSO₄.6H₂O, the calculated amount of nickel per 25 c.c. of solution being, therefore, 36.60 mgrms. Determination by means of dimethylglyoxime showed 25 c.c. of the solution to contain 36.38 mgrms. of nickel, which are equivalent to 49.60 c.c. of N/10 potassium bromate and to 214.9 mgrms. of Ni(C₉H₆ON)₂.

The procedure was exactly as for cobalt, and in this case, also, the gravimetric method was not used, as the precipitate dried at 120° C. corresponded in composition with Ni(C₉H₆ON)₂.0.23H₂O.

The results are summarised in Table IV and Fig. 2 (p. 393). The range of complete precipitation is from $p_{\rm H}$ 4.33 (that is, 11.5 c.c. of glacial acetic acid) to 14.58 (that is, 115 c.c. of 5 N sodium hydroxide solution) in 160 c.c., the total volume of the solution.

TABLE IV

$\phi_{\mathbf{H}}$	Complex	N/10 KBrO.	<i>Ф</i> п	Complex	N/10 KBrO.
	Mgrms.	c.c.	гн	Mgrms.	c.c.
3.25		_	8.75	215.8	49·8
3.66	<u> </u>		9.60	$215 \cdot 8$	49.8
4·10			10.45	215.8	49.8
4.33	120.2	27.95	11.33	$215 \cdot 8$	49.8
4·41	200.0	46.15	12.16	$215 \cdot 8$	49 ·8
4.48	$215 \cdot 8$	49 ·8	12.93	$215 \cdot 8$	49.8
4·80	$215 \cdot 8$	49 ·8	13.50	$215 \cdot 8$	49.8
5.35	$215 \cdot 8$	49·8	13.70	215.8	49·8
5.85	$215 \cdot 8$	49 ·8	13.89	215.8	49·8
6.25	215.8	49 ·8	14.12	215.8	49.8
7.15	215.8	49.8	14.53	$215 \cdot 8$	49.8
7.85	215.8	49 ·8	14.80	152.0	35.05

COPPER (Berg, J. pr. Chem., 1927, 115, 178; Z. anal. Chem., 1927, 71, 185).— A solution containing 3.443 grms. per litre of copper sulphate, $CuSO_4.5H_2O$, was used, corresponding with 21.93 mgrms. of copper per 25 c.c. of solution. Determination by means of potassium iodide and sodium thiosulphate showed 25 c.c. to contain 21.94 mgrms. of copper, which is equivalent to 121.3 mgrms. of $Cu(C_9H_6ON)_2$.

Τ	ABLE	V

₽н	Complex Mgrms.	₽н	Complex Mgrms.	₽н	Complex Mgrms.
2.92		4 ·00	113.0	9.66	$121 \cdot 2$
3.08		4·10	116.0	10.40	121.2
3.22		4.40	119-2	11.50	121.2
3.36		4.95	120.8	12.45	121.2
3.45	23.6	5.36	121.2	13.66	$121 \cdot 2$
3.57	59·0	5.80	121.2	14.00	121.2
3·6 9	80.6	6.48	121.2	14.33	121.2
3 ·83	101.8	7.53	$121 \cdot 2$	14.50	121.2
3.95	108.0	8.50	121.2	14.80	80.0

The method was exactly as for zinc. When working with copper in alkaline solution it is necessary to use a fine-mesh sintered glass crucible. The volumetric procedure is inapplicable in this case. Results are given in Table V and Fig. 1 (p. 391). The range for complete precipitation is from $p_{\rm H} 5.33$, *i.e.* 10 c.c. of N acetic acid to $p_{\rm H} 14.55$, *i.e.* 110 c.c. of 5 N sodium hydroxide solution in 160 c.c., the total volume of the solution.



MOLYBDENUM (Geilmann and Weibke, Z. anorg. Chem., 1931, 199, 347).— A solution of ammonium molybdate (10.435 grms. per litre) was used; 10 c.c. of this were found to contain 56.64 mgrms. of molybdenum (weighed as PbMoO₄) and 56.38 mgrms. of molybdenum by means of a-benzoin oxime (Knowles, *Bur. Stand.* J. Res., 1932, 9, 1). The latter precipitate was bulky and difficult to handle.

The procedure for the oxine precipitation was exactly as for magnesium. The complex was dried at $130^{\circ}-140^{\circ}$ C., and weighed as $MoO_2(C_9H_6ON)_2$; the calculated weight for complete precipitation is $245 \cdot 4$ mgrms. The volumetric process cannot be used, for it is remarkable that the complex after drying is insoluble in both acid and alkali, and is not dissolved even by *aqua regia*.

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The results given in Table VI and Fig. 2 (p. 393) show that the range of complete precipitation is from $p_{\rm H}$ 3.60, corresponding with from 20 c.c. of glacial acetic acid, to $p_{\rm H}$ 7.33, corresponding with 9 c.c. of N sodium hydroxide solution. The total volume was 145 c.c.

TABLE VI

₽н	Complex Mgrms.	₽н	Complex Mgrms,	∕∕∕н	Complex Mgrms.
2.66		4.64	245.6	7.43	193.8
3.08		5.03	245.6	7.50	80.0
3.28	8.0	5.51	245.6	7.70	
3.34	120.0	5.90	245.6	8.08	
3.46	$215 \cdot 4$	6.66	245.6	8.78	
3.70	$245 \cdot 6$	6.90	245.6	9.74	
3.95	$245 \cdot 6$	7.25	$245 \cdot 6$	10.66	
4·20	245.6	7.40	$245 \cdot 6$	12.0	

SEPARATIONS BASED ON THE FOREGOING RESULTS.—It does not necessarily follow that processes of separation can be based on the results given above, for complicating factors, such as the formation of mixed crystals, might cause coprecipitation of more than one complex at a p_{μ} at which only one is precipitated, if alone. Not all the separations which appear to be possible from the curves have been tried, but all those which we have examined (see below) have proved to be entirely satisfactory. The method consisted in precipitating one metal at a p_{μ} value approximating to the middle point of the horizontal portion of the curve, filtering off the complex, washing with some 25 c.c. of hot water, and adjusting the $p_{\rm H}$ of the filtrate and washings to a point definitely on the horizontal zone for the second metal. Both complexes were well washed with hot water and determined as described in the preceding sections.

On the basis of the results obtained the following binary separations should also be possible:--Magnesium from molybdenum, cobalt from magnesium, molybdenum from nickel, copper from magnesium, and copper from molybdenum, but it is obvious that zinc, cobalt, nickel, or copper cannot be separated from one another in acetate solutions.

SEPARATION OF MOLYBDENUM AND COBALT.—The aqueous solution (80 c.c.), containing molybdenum, cobalt, and ammonium acetate (5 grms.), was boiled and 60 c.c. of N sodium hydroxide solution and 10 c.c. of 5 per cent. oxine in 2 N acetic The mixture was boiled for 5 minutes and the cobalt complex acid were added. filtered off. The molybdenum complex was precipitated by the addition of glacial acetic acid (7.55 c.c.) to the boiling filtrate.

Taken		Found		Error, per cent.	
Mo Mgrms.	Co Mgrms.	Mo Mgrms.	Co Mgrms.	Mo	Co
56.68	14.78	56.56	14.81	-0.52	+0.50
56.68	29.56	56.73	29.48	+0.09	-0.27
70.85	$22 \cdot 17$	70.68	22.17	-0.54	0.00
85.02	5·91	84·96	5.89	-0.01	-0.33
11.33	33.99	11.33	33 ·99	0.00	0.00

SEPARATION OF NICKEL AND MAGNESIUM.—The aqueous solution (80 c.c.), containing nickel, magnesium, ammonium acetate (5 grms.), and glacial acetic acid (5 c.c.), was boiled, and 10 c.c. of 5 per cent. solution of oxine in 2 N acetic acid were added. After being boiled for 5 minutes the nickel complex was filtered off. The filtrate was boiled, 30 c.c. of 20 per cent. sodium hydroxide solution were added, and after being boiled for 5 minutes the precipitated magnesium complex was filtered off.

Taken		Found		Error, per cent.	
Mg Mgrms.	Ni Mgrms.	Mg Mgrms.	Ni Mgrms.	Mg	Ni
2.76	21.92	2.77	21.91	+0.36	-0.05
3.43	7.61	3.43	7.63	0.00	+0.26
6.87	36.54	6.86	36.60	-0.12	+0.16
13.74	14.64	13.71	14.64	-0.50	0.00
16.50	25.02	16.53	25.04	+0.12	+0.08

SEPARATION OF MOLYBDENUM AND ZINC.—To the aqueous solution (80 c.c.), containing molybdenum, zinc, and ammonium acetate (5 grms.) were added 40 c.c. of 2 N sodium hydroxide solution. The mixture was boiled, and the zinc complex precipitated by the addition of 10 c.c. of 5 per cent. oxine solution in 2 N acetic acid. To precipitate the molybdenum complex from the filtrate, 8.5 c.c. of glacial acetic acid were added.

Taken		Found		Error, per cent.	
Mo Mgrms.	Zn Mgrms.	Mo Mgrms.	Zn Mgrms.	Mo	Zn
56 .68	33.25	56.68	33.25	0.00	0.00
19.28	16.60	19.29	16.60	+0.02	0.00
29.03	27.30	29.03	27.32	0.00	+0.07
28.34	8.25	28.34	8.26	0.00	+0.12
9.62	15.52	9.61	15.52	-0.10	0.00

SEPARATION OF MAGNESIUM AND ZINC.—The aqueous solution (80 c.c.), containing magnesium, zinc, ammonium acetate (5 grms.) and glacial acetic acid (2.5 c.c.) was boiled, and 10 c.c. of 5 per cent. oxine solution in 2 N acetic acid were added to precipitate the zinc complex. To the boiling filtrate were added 30 c.c. of 17.8 per cent. (w/v) sodium hydroxide solution to precipitate the magnesium complex.

Taken		Found		Error, per cent.	
Zn Mgrms.	Mg Mgrms.	Zn Mgrms.	Mg Mgrms.	Zn	Mg
18.21	2.76	18.20	2.75	0.06	-0.36
10.52	6.18	10.50	6·19	-0.19	+0.16
9·5 8	9.62	9.57	9.62	-0.10	0.00
6.43	12.37	6.44	12.36	+0.12	-0.09
3.32	15.11	3.32	15.13	0.00	+0.13

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