COPPER SALICYLALDOXIME AND ITS USE IN THE HETEROMETRIC MICRODETERMINATION OF COPPER IN THE PRESENCE OF FOREIGN METALS

by

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INTRODUCTION

The chemical behaviour of some metals towards salicylaldoxime has already been studied. The gravimetric separation and determination of copper, zinc or lead has been the subject of many investigations¹. Our aim was to study the *heterometric* determination of metals with salicylaldoxime. It appears to us that the heterometric behaviour of salicylaldoximates at different pil's may contribute to our knowledge of the chemical structure and composition of many compounds of which little is yet known. This is the first report on salicylaldoxime and it deals with the determination of copper.

Although the heterometric determination of copper with oxine is more sensitive and more accurate, nevertheless, as the following material shows, *one* mg of copper in ro ml solution may be determined with an error of 0-3%. The analysed solution may contain $\sim 99\%$ bivalent or $\sim 90\%$ trivalent foreign metals. The titration takes ro-20 minutes.

ENPERIMENTAL

The same apparatus and method were used as in previous reports². In addition the heterometer was provided with a thermostat which maintained the temperature of the titrated solution at 20 °C (\pm 0.1°). (However, we found that the same accuracy was obtained without the use of the thermostat.) In all titrations with copper a blue filter was used. Generally no other filters were used even in the presence of coloured solutions. It was assumed that the coloured foreign salts do not participate in the reaction. Only in the presence of iron (exps. 24-27) a deep red filter was used and in the presence of chromium (exps. 20-23) a green filter was used.

The solution was stirred vigorously during the titration and the readings on the galvanometer were taken only when they became constant. The chemicals used were either analytical reagents or chemically pure. The salicylaldoxime was a Kodak reagent which was dissolved in a few ml alcohol and then diluted with distilled water.

RESULTS

Heterometric *pH*-study

pH-titrations were made in order to study the pH-conditions necessary for carrying out heterometric titrations. Two different buffer mixtures were used (exps. r and 4) References p. 453/454

and the results obtained can be taken from the curves. A blue filter (Fisher) was used in all the heterometric titrations. Analogous results were obtained using a green filter (Fisher). Whichever filter was used, some light was absorbed after the dissolution was completed.

Since the pH's necessary for the dissolution of the precipitates may be different from the pH's needed for precipitation, both cases were studied (Fig. 1 curves 1 and 2) separately. The pH's for the blank heterometric titrations are shown in curves 3 and 5. Analysing curve 1, it is seen that the precipitate once obtained at low pH's is completely insoluble below pH \sim 10.2. At higher pH's the precipitation redissolves.



Fig. 1.

- 1. $3 \text{ ml} 0.005 M \text{ CuSO}_4 + 3 \text{ ml} 0.2 N \text{ CH}_3 \text{ COOH} + 3 \text{ ml} 0.2 N \text{ H}_3 \text{ BO}_3 + 5 \text{ ml} 0.01 M \text{ salicylaldoxime} + 6 \text{ ml H}_2 \text{ O} + x \text{ ml} 0.4 N \text{ NaOH}$
- 2. $3 \text{ ml } 0.005 M \text{ CuSO}_4 + 3 \text{ ml } 0.2N \text{ CH}_3 \text{COOH} + 3 \text{ ml } 0.2N \text{ H}_3 \text{BO}_3 + 5 \text{ ml } 0.01 M \text{ salicylaldoxime} + 8 \text{ ml } 0.2N \text{ NaOH} + 1 \text{ ml } \text{H}_2\text{O} + x \text{ ml } 0.4N \text{ HNO}_3.$
- 3. put-titration curve of exps. 1 and 2.
- 4. 3 ml 0.005*M* CuSO₄ + r ml *N* HNO₃ + r ml *N* CH₃COOH + 2 ml *M* NH₄NO₃ + 4 ml 0.01*M* salicylaldoxime + 9 ml H₂O + x ml *N* NaOH.
 5. pn-titration curve of exp. 4. Blue filter.

Curve 2 presents the heterometric curve obtained when the titration was begun at a high pH. The initial precipitation occurs at pH \sim 10.7 and is complete at 10.1. The point at which dissolution begins coincides with the first point of complete precipitation and is equal to pH 10.1-10.3. Between pH's 10-11 the precipitation is incomplete. It is interesting to compare these results with those obtained in exp. 4. using NH₃-NH₄NO₃ as buffer (compare curves 4 and 5) from which it can be seen that the initial precipitation occurs at pH \sim 1.5 and is complete at pH \sim 3.0. From this pH till pH \sim 9.5 the precipitate remains unchanged. At higher pH's the precipitate is redissolved. The difference between the results of curves 1 and 4 may be caused by interference of NH₃ in the high pH-regions. The results with boric acid buffer are more reliable.

Summarising, it may be said that a complete precipitation of CuR_2 occurs in the pil-region of 3-10.

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The effect of acidity on metal complex binders

A heterometric titration was carried out in the presence of sulfuric acid. In 0.1M solution no precipitate occurred. In 0.01M solution (exp. 1a.) a maximum density value was obtained which was similar to the value obtained in 0.1M acetic acid (exp. 1). The point of initial precipitation was obtained in the presence of 0.01M sulfuric acid only after the addition of more than 30% of titrant. In contrast to this, precipitation occurred at once in acetic acid solution. In the sulfuric acid solution therefore the solubility of copper was much higher. In the presence of acetic acid we had the advantage of being able to use masking agents (exps. 5 and 6). In 0.01M sulfuric acid solution copper oxinate is soluble to an extent of $\sim 0.5 \cdot 10^{-4}$ mol per liter. The solubility in 0.1M acetic acid solution was about ten times lower. As experiments 4 and 7 show, buffered citrate or tartrate solutions could be used. Similar results were obtained with citrate or tartrate in acetic acid solution (exps. 5 and 6). In the presence of ethylenediaminetetraacetate copper could not be precipitated whatever the pH.

Determination in the presence of bivalent metals

Experiments 8-15 of Table I and Fig. 2 (the same experimental numbers are used in both cases) show the results of such titrations. Except in the presence of barium, there was no difficulty in the determination of copper and the error was generally 1-2% or 1-2 γ per ml. In the presence of barium the end-point of the titration was shifted and the error was high (exp. 9). The error could probably be eliminated at lower barium concentrations. The titrations lasted 10-20 minutes.



Determination in the presence of bivalent metals

Clear end-points were obtained only in the presence of metal complex-binders. The highest concentration of foreign metal which could be present without interference was in the case of aluminium 0.1M and in the case of chromium or iron 0.05M. In the presence of aluminium

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1					2	Resinning	Max.	•	Approx.		Frent	
number		Supple	men!s		ີ	of precip. at ml	opue. density value	found 1	time in min	òç	Y	Y/m!
1	m CH_COOH $M + 4$ m	H.O	y desensa ya a sa a sa angan ya ya na angan ya ya na angan ya na angan ya na sa angan ya na sa angan na sa ang		8	0 1	1:0	30	15	00		0 0
ia i	H,SO. + 4	H,O				1.1	0.70	¢	10 4			
12 13	Na ₂ -tartrate $M + 3$:,			100	1 0	0.88	τ 0	11	0.0	0.0	0.0
ω 13	", Na ₃ -citrate $M + 3$ ".	:			100	I 0	0.87	ω 0	12	00	00	0.0
+ 12	,, , , + 1 ml	HNO3 0.5.N	$+ 2 \text{ ml H}_{0}$		100	0.3	0.71	307	17	2.2 3	1) 1)	ia ia
یں در	", Na ₂ -tartrate $M + 1$ ",	CH ³ COOH 71	+ 12		100	0.1	0.88	2.97	12	-1.0	9-5	1.0
6 2	". Na ₃ -citrate $M + 1$ ".	\$	+- 13 = z		100	t.0	0 65	2.98	33	-0.7	6.6	0.7
7:2	Nag-tartrate $M + 1$	HNO30.2N	+ 3 :: .:		C01	0.1	0 76	2.96	13	-1.3	12.3	1.2
	$MgSO_4$. $+$ 1 ,	CH3COOH W	+- 13 7 7		2.0	0.1	0.75	3.00	17	20	61	1.9
9:2	$H_{\text{BaCl}_{2}}M + I$:	· +- 1) : :		0.36	0.3	0 73	33 33				
10, 2,	$\frac{1}{2}$ $\frac{1}$:	-+- 1 :		0.76	02	0.75	2.96	20	-I.3	12.3	1.2
11 2,	$\frac{1}{2} MnCl_{2} M + 1$:	+ 2 ,, ,,		160	03	0.72	2.97	15	-1.0	0.5	1.0
12 2	$NiCl_2M + 1$;	+- 17 : :		0 85	0.2	0 63	2.95	21	—I.7	16	1.6
13 2,	$C_{C}(NO_{3})_{2}N + 1$		+ -> :		0.S4	0.3	0.7S	3.00	12	0.0	0.0	00
14 2 .	$\frac{1}{1}$ CdSO ₁ M + 1	"	+ 12 = =		<u>5</u> +.0	0.3	0.75	3.06	15	2.0	6I	1.9
З 2	$\frac{1}{2} Pb(NO_3)_2 M + 1 \dots$:			t: 0	0.5	0.64	3.0 <u>5</u>	21	1.7	16	1.6
16 1,	$HCl_3 M + I$	"	+ 2 ml \a ₃ -tartrate .W +		3.6	0.j	0.51	303	зо	1.0	. 9. .:	1,0
Ϊ7 Ι,	27 77 77 77 77 77 77 77 77 77 77 77 77 7		+ + + +			0.6	0.62	بہ 50	23 23	1.7	16	1.6
IS I,	" " 0.5 <i>W</i> + I "	=	+2 ", Nag-citrate M +	1 ,, ,,	6.9	1.1	0.46	3.0.2	17	0.7	6.6	0.7
19 I,	·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ··	:	+ 22 = +	1 ,, ,,		1.1	0.46	3.02	17	0.7	6,6	0.7
20 I,	,, Cr(NO ₃) ₃ ,,		+ 1.2 :	14 2 3 *	37	10	0.35	3.07	16	:3 :3	1212	1) 1)
21 I,			+ 2 Na ₂ -tartrate .N +	: : : :		1.7	0.57	3 IO	†1	μ ů	28	2.8
22 I,	· · · · · · · · · · · · · · · · · · ·	:		••• •• ••		0.6	0.62	3 00	20	0.0	0.0	0.0
23 I,	* * * + * *	:	+ 2 " Na ₃ -citrate M +	I ., ., *		1.8	0.36	3 00	6 1	0.0	0.0	0.0
24 I,	, FeCl ₃ ,		+ 2 " Nag-tartrate M +	1u = = =	دب ن	0.3 2	0.74	8	19			
25 I,	•		+ 2 ,. Na ₃ -citrate M +	1) 2 2 #		+.0	0.56	3.07	13	2.3	22	12 12
26 1,		:	+2 Na ₂ -tartrate M +	I ,, ,, **		0 2	0.54	8	21			
1 40	· · · · · · · · · · · · · · · · · · ·	Ŧ	+2 , Na _n -citrate M +	I ., ., **		0.6	0.45	3.04	13	د.	12	1.2

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TABLE I

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(exps. 16-19) or chromium (exps. 20-23) either neutral or acid citrate or tartrate solutions could be added. Citrate probably reduces the maximum density values. The titration time was increased in the presence of acetic acid aluminum tartrate. In the presence of iron, better results were obtained if a red filter was used (exps. 24-27). The tartrate solutions gave no end-points and therefore only citrate solutions could be used. The titration time was generally 15-20 minutes and the error was 0.3%. The concentration of copper amounted in all cases to less than 10%. A factor which must be taken into consideration is the point at which initial precipitation occurs. The more titrant added before precipitation occurs, the more soluble is the analysed compound apparently, and the more restricted becomes the determination. From our results we learned that in the presence of aluminium or chromium, the use of tartrate is generally to be preferred. On the other hand, the point of initial precipitation was close to the beginning in the presence of iron citrate (exps. 25 and 27). In the above experiments which were carried out either in neutral or acidic solutions, the composition of the insoluble compound obtained was CuR₂.

SUMMARY

1. The initial precipitation of copper-salicylaldoxime occurs at $p_{\rm H} \propto 1.5$. Between $p_{\rm H} 1.5$ and 3.0, the precipitation is incomplete. A complete precipitation occurs in the p_H-region of 3-10. Between $p_{\rm H} 10.7$ and 10.7 the precipitate redissolves At higher $p_{\rm H}$'s a clear solution is obtained.

2. The solubility of copper salicylaldoximate is about ten times greater in 0.01M sulfuric acid ($0.5 \cdot 10^{-4}$ mol) than in 0.1M acetic acid.

3. In 10 ml of 0.1M acetic acid solution in the presence of $\sim 99\%$ foreign bivalent metals, one mg copper could be determined heterometrically with an error of 1-2%.

4. In the presence of $\sim 95\%$ alumin um or chromium, either citrate or tartrate (0 2M) were used as masking agents. In the presence of iron ($\sim 95\%$), clear end-points were obtained only with citrate. One mg of copper could be determined with an error of 0.3%.

5. Whichever pit is used, copper is not precipitated in the presence of ethylenediaminetetraacetate.

RÉSUMÉ

1. La précipitation du cuivre-salicylaldoxime commence au pH \sim 1 5 Entre les pH 1 5 et 3.0, la précipitation est incomplète; elle est quantitative du pH 3 au pH 10. Entre les pH 10.1 et 10.7 le précipité se redissout. Aux pH plus élevés on obtient une solution limpide.

2. Lusplubilité du cuivre-salicylaldoxime est environ dix fois plus grande dans l'acide sulfurique 0.01M ($\bigcirc 0.5 \cdot 10^{-4}M$) que dans l'acide acétique 0.1M.

3. Dans 10 ml de solution d'acide acétique 0.1M, on peut doser 1 mg de cuivre par hétérométrie avec une erreur de 1-2% (en présence d'environ 99% de métaux bivalents étrangers.

4. En présence de $\sim 95\%$ d'aluminium ou de chrome, soit le citrate, soit le tartrate peut être utilisé comme agent de masquage. En présence de fer ($\sim 95\%$) on n'obtient des points d'équivalence nets qu'avec le citrate. I mg de cuivre peut être dosé avec une erreur de 0-3%.

5. Le cuivre ne précipite pas en présence d'éthylènediaminotétraacétate, quel que soit le pil.

ZUSAMMENFASSUNG

1. Der Beginn der Fällung von Kupfer-Salicylaldoxim geschieht bei p $H \frown i$ 5. Die Fällung ist im pH-Gebiet 1.5-3.0 unvollständig. Sie ist vollständig im pH-Gebiet 3-10. Zwischen pH10.1-10.7 findet Auflösung statt und in höherem pH-Gebiet wird eine klare Lösung erhalten.

2. Die Löslichkeit von Kupfer-Salicylaldoxim ist 10 mal höher in 0.01M Schwefelsäure als in 0.1M Essigsäure.

3. 1 mg Kupfer kann in Gegenwart von $\sim 99\%$ an Fremdmetallen in einer 0.1M essigsauren Lösung mit einem Fehler von 1-2% bestimmt werden.

4. In Gegenwart von $\sim 95\%$ Aluminium oder Chrom wird Citrat oder Tartrat zur Maskierung verwendet. In Gegenwart von Eisen ($\sim 95\%$) wird ein klarer Endpunkt nur in Gegenwart von Citrat erreicht. Im Kupfer kann mit 0-3% Fehler bestimmt werden.

5. Die Fällung von Kupfer wird in Gegenwart von Äthylendiamintetraacetat verhindert unabhängig vom ph.

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