Art. XXXIX.—*The Precipitation of Copper Oxalate in Analysis*; by F. A. Gooch and H. L. Ward.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxcix.]

It has been shown by Peters, in a paper from this laboratory on the volumetric estimation of copper as the oxalate,* that copper oxalate may be precipitated by oxalic acid with practical completeness from solutions of copper sulphate, provided the volume of the liquid is not too great and that the amount of copper present in solution exceeds a certain minimum value. It was shown that when the amount of copper present falls below a certain minimum either precipitation does not take place or it is incomplete. It was noted that the minimum was variable with the concentration of the precipitant, oxalic acid, and to some extent dependent upon the condition of the precipitant, the minimum being smaller when the oxalic acid was added in crystalline form rather than in solution to the liquid containing the copper salt. Peters' observations in respect to the effect, concentration and condition of the oxalic acid in solution of 50^{cm^3} are summarized in the following statement:

Minimum amount of copper, taken as the sulphate, which must be present in order that nearly complete precipitation may take place	Amount of oxalic acid used.		Volume of liquid
grm.	Crystalline grm.	In solution grm.	cm³.
0·010	5	5†	50
0·025	2	3·5	50
0·040	1	--	50
0·050	0·5	--	50

† Saturated solution poured upon the copper salt dissolved in the least amount of water.

It was also noted that when a saturated solution of oxalic acid, containing 0·1 grm. of oxalic acid to 1^{cm^3}, was slowly added to a drop of the copper solution containing 0·0003 grm. of copper the precipitated oxalate first formed dissolved completely in a volume of 5^{cm^3} of the precipitant.

In the procedure for the quantitative determination of copper by precipitation as the oxalate, Peters recommends a volume of 50^{cm^3}, with 0·5 grm. to 2 grm. of crystallized oxalic acid as the precipitant for 0·15 grm. of copper. An increase of the oxalic acid beyond this degree up to the point of saturation of the solution is apparently without effect. In subsequent work

---

* This Journal, x, 359, 1900.

involving separations Peters used volumes as high as 85^{cm^3}, of which concentrated nitric acid made up 5^{cm^3}, with 3 grm. of oxalic acid.

With regard to the time required for completing the precipitation, Peters showed that when no added nitric acid is present precipitates formed in the hot solutions at a volume of 50^{cm^3} may be filtered, either at once or after cooling, without loss; but that when the nitric acid is added the mixture must stand before filtration, best over night.

The fact that small amounts of precipitated copper oxalate may be redissolved in a sufficient excess of the precipitant points to an appreciable degree of solubility of the precipitate in the solution of oxalic acid. The observation that very considerable amounts of copper oxalate fail to come down at all until a certain minimum of the copper salt is present, while precipitation is nearly complete when that minimum is reached, indicates supersaturation of the precipitant by copper oxalate; while the capacity of the liquid for supersaturation is apparently limited to some extent by increase in concentration of the oxalic acid. The solubility coefficient of the copper oxalate under the conditions is made up, therefore, of at least two factors, of which one depends upon the normal solubility in the solution of oxalic acid which constitutes the medium of precipitation, while the other depends upon the solubility due to supersaturation. In order that small amounts of copper may be precipitated it is necessary to find means of eliminating or at least limiting the capacity of the medium for supersaturation; and in order that large amounts, as well as small amounts, of copper may be determined with the highest degree of accuracy it is necessary to reduce to the lowest point the normal solubility of the oxalate under the conditions of precipitation. The present paper is an account of the experimental study of conditions under which small as well as large amounts of copper may be determined by the oxalate method.

The Normal Solubility of Copper Oxalate.

It is to be noted in the first place that the character of precipitated copper oxalate depends upon the conditions of precipitation. When oxalic acid is added to a cold concentrated solution of a salt of copper the copper oxalate precipitated is of extreme fineness and tends to pass through the closest filters. The precipitate formed in hot solution is, on the other hand, crystalline and easily separated by filtration of this liquid. The solubility of the precipitate, as well as the ease with which it may be separated from the liquid, turns upon the conditions of precipitation and treatment. In the experiments to be described, attention is first called to the degree of insolubility to be expected in the case of a precipitate formed by oxalic acid in hot aqueous solutions of neutral copper sulphate or copper nitrate and in amounts in excess of the precipitable minimum. In the experiments of which details are given in Table I, definite portions of a solution of the copper salt were diluted with water to the volume stated, heated to boiling, and treated with crystallized oxalic acid. After standing over night in contact with the solution, the precipitate was collected upon asbestos in a perforated crucible and washed carefully with small amounts of water. The crucible with its contents was placed in a beaker and covered with about 200^{cm^3} of hot water containing 25^{cm^3} of dilute sulphuric acid (1:4), and approximately N/10 potassium permanganate of known standard was added to coloration. Pure copper sulphate was used for the experiments of A; and in those of B, copper nitrate, made by dissolving pure electrolytic copper in nitrate acid, evaporating off the excess of acid and dissolving in water, was used. The solutions of these salts were standardized electrolytically by the method of the rotating cathode.* The permanganate used in these and in all succeeding experiments was standardized against N/10 arsenious acid by acting with a measured volume of it upon a known amount of the standard arsenious acid, adding potassium iodide and titrating the excess of the arsenious acid in presence of acid potassium carbonate, by iodine also standardized against the arsenious acid, the difference between the arsenious acid taken and the arsenious acid determined by the iodine being the measure of the value of the permanganate.

Throughout the series of experiments, the error of the determination increases with the dilution. That the errors found in titration actually represent approximately losses in copper, at least for the smaller volumes, is shown by the difference, in two cases, between the result of titration and the electrolytic determination of copper in the filtrates from the precipitated oxalate. For a volume of 10^{cm^3}, the average error in the titration of the oxalate precipitated, either from the solution of the sulphate or from a solution of the nitrate, is 0·0002 grm.; for 50^{cm^3} it is 0·0011 grm.; for 100^{cm^3}, 0·0053 grm.; for 200^{cm^3}, 0·0203 grm. For similar concentrations of the copper salt and of the oxalic acid the deficiency in the copper indicated by titration of the precipitated oxalate increases more rapidly than the dilution, a fact which suggests some specific action of water, perhaps hydration affecting the solubility or hydrolysis affecting the composition of the copper oxalate. That time and temperature are not essential factors

---

* This Journal, xv, 320, 1903.

TABLE I.

Effects of Concentration in Water Solution.

Copper taken grm.	Volume at precipitation cm^3.	Oxalic acid used grm.	Copper found grm.	Error grm.	Average error grm.
			A		
		Experiments with copper sulphate.			
0·0100	10	0·5	0·0097	−0·0003	0·0002
0·0100	10	0·5	0·0098	−0·0002	
0·0502	10	0·5	0·0500	−0·0002	
0·0502	50	2·0	0·0491	−0·0011	0·0012
0·0502	50	2·0	0·0491	−0·0011	
0·0504	50	2·0	0·0491	−0·0013*	
0·0504	100	4·0	0·0468	−0·0036†	0·0052
0·0502	100	4·0	0·0448	−0·0054	
0·0502	100	5·0	0·0449	−0·0053	
0·0502	100	5·0	0·0437	−0·0065	
0·0506	200	10·0	0·0303	−0·0203	0·0203
			B		
		Experiments with copper nitrate.			
0·0455	10	0·5	0·0457	+0·0002	0·0002
0·0570	50	2·0	0·056	−0·0009	0·0009
0·0455	100	5·0	0·0402	−0·0053	0·0056
0·0455	100	5·0	0·0395	−0·0060	

* Copper determined electrolytically in filtrate = 0·0013 grm.
† Copper determined electrolytically in filtrate = 0·0039 grm.

in the precipitation of the oxalate, at moderate dilution from solutions of the neutral salt, was shown when Peters filtered, without appreciable loss, precipitates from 50$^{cm^3}$ of hot solution either at once and hot or as soon as the liquid had cooled. The experiments of Table II show in addition that the precipitates, whether thrown down in hot solution or in cold solution, possess after long standing the same degree of insolubility.

TABLE II.

Effects of Temperature at Precipitation and Titration after Standing Over Night.

Copper taken grm.	Volume cm^3	Oxalic acid grm.	Copper found grm.	Error grm.	Precipitation	Filtration
0·0502	50	2·0	0·0491	0·0011	hot	cold
0·0502	50	2·0	0·0492	0·0010	hot	hot
0·0502	50	2·0	0·0490	0·0012	cold	hot
0·0502	50	2·0	0·0491	0·0011	cold	cold

If any part of the apparent loss of copper oxalate precipitated from solutions of oxalic acid is due to hydrolysis of the normal oxalate, and formation of a basic oxalate as the product of hydrolytic action, it should be possible to obviate such apparent loss by increasing the active acidity of the solution and thus inhibiting hydrolysis, providing that the solubility of the normal oxalate is not made greater thereby. The experiment shows that beyond a reasonable degree of concentration the results are not affected by the use of oxalic acid up to the point of saturation of the solution. It is worth while therefore to look somewhat more carefully into the effect of stronger acids present at the time of precipitation. In Table III are shown the details of experiments in which the active acidity was increased by the addition of either free sulphuric acid or free nitric acid to the solution of the copper salt before precipitation was brought about by oxalic acid. These experiments were made under conditions otherwise similar to those of Table I. The copper sulphate was used in standard solutions. The copper nitrate was prepared in solution for each experiment by dissolving weighed electrolytic copper in nitric acid, evaporating the solution to dryness, moistening the residue with a few drops of nitric acid and dissolving in water.

A comparison of the results of Table III with the results of corresponding experiments in Table I brings out the facts that the apparent error is actually diminished by the presence of even very small amounts of sulphuric acid or nitric acid in the liquid, while, within reasonable limits, the addition of more acid produces no further effect. At the higher dilution, the effect of the active acid is marked. At a volume of 100^{cm^3} the average error of deficiency shown in Table I is cut in two by the addition of $0·1^{cm^3}$ to 5^{cm^3} of nitric acid and of $0·5^{cm^3}$ to 2^{cm^3} of sulphuric acid. At smaller volume of 50^{cm^3} the effect is not so marked, but it is still obvious. These results favor strongly the hypothesis that copper oxalate is increasingly subject to hydrolysis as dilution increases, and that the tendency to form a basic salt may be checked by the presence of the stronger acids in suitable amounts. Even very large amounts of nitric acid produce a surprisingly small increase in the apparent solubility of the oxalate.

Losses due to solubility of copper oxalate may evidently be kept at low limits by restricting the volume of the solution of oxalic acid in which precipitation takes place; but too much concentration is likely to introduce error due to mechanical inclusion of oxalic acid in the precipitates. The natural alternative to a close restriction of the volume of the aqueous solution is the limitation of the solvent power of a larger volume of liquid by partially substituting for water some other

TABLE III.

The Effect of Active Acids.

Copper taken grm.	Volume of the liquid cm³.	Oxalic acid used grm.	Volume of sulphuric acid or of nitric acid cm³.	Copper found grm.	Error grm.	Average error grm.
			A			
		Volume at precipitation approximates 100 cm³.				
			H_2SO_4			
0·0502	100	4·0	0·1	0·0454	−0·0048	−0·0024
0·0502	100	4·0	0·5	0·0481	−0·0021	
0·0502	100	4·0	1·0	0·0484	−0·0018	
0·0502	100	4·0	2·0	0·0474	−0·0028	
0·0502	100	4·0	2·0	0·0481	−0·0021	
			HNO_3			
0·0515	100	4·0	0·1	0·0499	−0·0016	−0·0031
0·0530	100	4·0	0·1	0·0505	−0·0025	
0·0502	100	4·0	0·1	0·0471	−0·0031	
0·0502	100	4·0	0·1	0·0472	−0·0030	
0·0502	100	5·0	5·0	0·0471	−0·0031	
0·0502	100	5·0	5·0	0·0468	−0·0034	
0·1500	100	2·0	0·1	0·1476	−0·0024	
0·2377	100	4·0	0·1	0·2356	−0·0021	
0·2530	100	4·0	0·1	0·2497	−0·0033	
0·2897	100	4·0	0·1	0·2880	−0·0067	
			B			
		Volume at precipitation 50 cm³.				
0·1333	50	4·0	0·1	0·1327	−0·0006	
0·1366	50	2·0	0·1	0·1360	−0·0006	
0·1443	50	2·0	0·1	0·1434	−0·0009	
0·2388	50	2·0	0·1	0·2384	−0·0004	
0·0502	50	2·0	4·0	0·0494	−0·0008	
0·0504	50	4·0	25·0	0·0491	−0·0013	
0·0504	50	4·0	40·0	0·0487	−0·0017	

miscible liquid less capable of dissolving the precipitated oxalate. The experiments of Table IV were made to test the effect of alcohol as suggested by Gibbs.* The results given in A show the effects of alcohol without nitric acid; those of B show the effect of alcohol with nitric acid.

It is plain that the presence of alcohol improves the results of the process as compared with the results obtained at similar dilutions of the oxalic acid solution, either with or without nitric acid; and, if the effect of nitric acid in the aqueous

---

* This Journal, xliv, 214, 1867.

Table IV.

The Effect of Alcohol.

Copper taken grm.	Volume of liquid cm.	Per cent of alcohol in liquid	Oxalic acid used grm.	Nitric acid present cm^3.	Copper found grm.	Error
			A			
		Precipitation in absence of nitric acid.				
0·0502	100	20	1·0	----	0·0492	−0·0010
0·0502	100	20	2·0	----	0·0491	−0·0011
0·0502	100	40	2·0	----	0·0491	−0·0011
0·0502	50	50	2·0	----	0·0499	−0·0003
0·0202	50	50	2·0	----	0·0499	−0·0003
			B			
		Nitric acid present in the liquid.				
0·0502	100	20	1·0	5	0·0493	−0·0009
0·0502	100	20	2·0	5	0·0491	−0·0011
0·0502	100	40	4·0	5	0·0497	−0·0005
0·0502	50	40	2·0	2	0·0497	−0·0005

solution is to prevent the formation of a basic salt, it would seem that the alcohol not only makes the precipitate more insoluble but checks hydrolytic action as well. In a volume of 100$^{\text{cm}^3}$ containing 20 per cent of alcohol the error approximates −0·0010 grm.; and for a volume of 50$^{\text{cm}^3}$ containing 50 per cent alcohol the error is still negative though reduced to −0·0003. The effect of nitric acid accompanying the alcohol is not marked.

In further experiments it was found that the addition of acetic acid, as proposed by Classen,* is even more effective than the use of alcohol, or of alcohol with nitric acid. In Table V are given the details of experiments in which the precipitation of copper oxalate was made in presence of considerable amounts of acetic acid. When considerable amounts of copper are present the precipitates formed in solutions containing acetic acid are apt to be very finely divided and consequently difficult to filter. A better condition of the precipitate is obtained, however, if, with the acetic acid, there is also present a moderate amount of nitric acid. The results of experiments in which both acetic acid and nitric acid were used are given in the table. The results of experiments in which sulphuric acid was present with acetic acid are also appended.

From these results it is apparent that acetic acid when present to the amount of 25 per cent of the liquid produces in volumes

---

* Ber. Dtsch. Chem. Gesellsch., x, b, 1316.

TABLE V.

The Effect of Acetic Acid.

Copper taken grm.	Volume of liquid cm^3.	Per cent of acetic acid	Stronger acid used cm^3.	Oxalic acid used cm^3.	Copper found grm.	Error grm.
A						
Precipitation in presence of acetic acid.						
0·0511	100	25	....	2·0	0·0502	—0·0009
0·0511	100	33	....	2·0	0·0504	—0·0007
0·0511	100	50	....	4·0	0·0510	—0·0001
0·1533	100	50	....	4·0	0·1530	—0·0003
B						
Precipitation in presence of acetic acid and nitric acid.						
0·0511	105	50	5	4·0	0·0510	—0·0001
0·0511	110	50	10	4·0	0·0506	—0·0005
0·0511	100	50	10	4·0	0·0510	—0·0001
0·1530	100	50	10	4·0	0·1529	—0·0001
0·1530	100	50	10	4·0	0·1530	—0·0000
C						
Precipitation in presence of acetic acid and sulphuric acid.						
0·0511	100	50	5	2·0	0·0508	—0·0003
0·0511	100	50	10	2·0	0·0413	—0·0098
0·0511	100	50	10	4·0	0·0512	+0·0001
0·0511	100	50	10	4·0	0·0513	+0·0002

of 100$^{cm^3}$ about the same effect as alcohol, and when present to the amount of 50 per cent it diminished still further the solvent power of the medium for the oxalate. The presence of nitric acid to 10 per cent of the entire volume does not materially affect the solubility. Sulphuric acid to 10 per cent of the volume of the liquid is without apparent effect upon the solubility of copper oxalate, provided the oxalic acid is also present in the proportion of 4 grm. to 100$^{cm^3}$ of the liquid. Treatment by oxalic acid in a medium consisting of acetic acid of half-strength, with or without nitric to the extent of 10 per cent by volume, is plainly the best of the procedures studied for the complete precipitation of copper oxalate in ideal condition; provided, however, that the copper is present in amount sufficient to break up the condition of supersaturation, let us say to the amount of 0·0500 grm.

The Prevention of Supersaturation.

Various means have been tried in the effort to break up supersaturation of the precipitating medium with small amounts of copper oxalate. Of these details an account is given below, in Table VI.

The supersaturated solution (A) was frozen and the mass melted, following procedure which has been found to be successful in hastening the deposition of small amounts of ammonium magnesium arsenate:* the supersaturated solution (B) was evaporated to dryness, and the residue extracted with water: alcohol was added (C) to the solution of the copper salt before attempting precipitation by oxalic acid: acetic acid of 50 per cent strength (D) was used as the medium in which precipitation was attempted by oxalic acid.

TABLE VI.

The Precipitation of Small Amounts of Copper.

Copper taken grm.	Volume of liquid cm^5.	Oxalic acid grm.	Alcohol at precipitation cm^3.	Acetic acid at precipitation cm^3.	Nitric acid at precipitation cm^3.	Copper found grm.	Error grm.
A The effect of freezing, melting and boiling.							
0·0010	50	1·0	----	----	----	none	----
0·0020	50	1·0	----	----	----	0·0005	—0·0015
0·0030	50	1·0	----	----	----	0·0024	—0·0006
0·0040	50	1·0	----	----	----	0·0030	—0·0010
0·0050	50	1·0	----	----	----	0·0039	—0·0011
0·0100	50	1·0	----	----	----	0·0088	—0·0012
0·0200	50	1·0	----	----	----	0·0188	—0·0012
0·0502	50	1·0	----	----	----	0·0490	—0·0012
B The effect of evaporation to dryness and extraction of the residue with 50$^{cm^3}$. of water.							
0·0010	50	1·0	----	----	----	0·0004	—0·0006
0·0020	50	1·0	----	----	----	0·0018	—0·0002
0·0030	50	1·0	----	----	----	0·0027	—0·0003
0·0040	50	1·0	----	----	----	0·0036	—0·0004
0·0100	50	1·0	----	----	----	0·0095	—0·0005
0·0200	50	1·0	----	----	----	0·0196	—0·0004
0·0502	50	1·0	----	----	----	0·0499	—0·0005
C The effect of precipitation in 50 per cent alcohol.							
0·0010	50	2·0	25	----	----	none	----
0·0020	50	2·0	25	----	----	none	----
0·0030	50	2·0	25	----	----	0·0015	—0·0015
0·0040	50	2·0	25	----	----	0·0020	—0·0020
0·0050	50	2·0	25	----	----	0·0016	—0·0034
0·0100	50	2·0	25	----	----	0·0085	—0·0015
0·0200	50	2·0	25	----	----	0·0198	—0·0002
0·0502	50	2·0	25	----	----	0·0499	—0·0003

---

* Gooch and Phelps, this Journal, xxii, 488, 1906.

TABLE VI (continued).

The Precipitation of Small Amounts of Copper.

Copper taken grm.	Volume of liquid cm³.	Oxalic acid grm.	Alcohol at precipitation cm³.	Acetic acid at precipitation cm³.	Nitric acid at precipitation cm³.	Copper found grm.	Error grm.
D							
The effect of precipitation in acetic acid.							
Volume 50^{cm^3} : 50 per cent acetic acid.							
0·0010	50	2	----	25	----	0·0010	0·0000
0·0020	50	2	----	25	----	0·0021	+0·0001
0·0031	50	2	----	25	----	0·0027	—0·0004*
0·0041	50	2	----	25	----	0·0041	0·0000*
0·0051	50	2	----	25	----	0·0049	—0·0002*
0·0102	50	2	----	25	----	0·0098	—0·0004*
0·0204	50	2	----	25	----	0·0098	—0·0006*
0·0511	50	2	----	25	----	----	----†
0·0010	50	2	----	25	5	0·0010	0·0000
0·0020	50	2	----	25	5	0·0021	+0·0001
0·0031	50	2	----	25	5	0·0033	+0·0002
0·0041	50	2	----	25	5	0·0042	+0·0001
0·0051	50	2	----	25	5	0·0043	—0·0002
0·0102	50	2	----	25	5	0·0103	+0·0001
0·0204	50	2	----	25	5	0·0204	+0·0000
0·0511	50	2	----	25	5	0·0512	+0·0001
Volume 100^{cm^3} : 50 per cent acetic acid.							
0·0010	100	4	----	50	3	0·0010	0·0000‡
0·0020	100	4	----	50	3	0·0021	+0·0001‡
0·0031	100	4	----	50	5	0·0031	0·0000
0·0041	100	4	----	50	5	0·0041	0·0000
0·0051	100	4	----	50	5	0·0051	+0·0002
0·0102	100	4	----	50	5	0·0103	+0·0001
0·0204	100	4	----	50	5	0·0196	—0·0008§
0·0511	100	4	----	50	5	0·0510	—0·0001
Volume 150^{cm} : two-thirds acetic acid.							
0·0010	150	4	----	100	----	0·0013	+0·0003
0·0010	150	4	----	100	5	0·0012	+0·0002

* Filtration imperfect. † Filtration impossible.
‡ Precipitation formed slowly. § Filtration imperfect.

From these results it appears, first, that by precipitating at a volume of 50^{cm^3}, freezing, melting, and boiling, the condition of supersaturation may be broken up, the oxalate obtained being soluble in the proportion of about 0·0011 grm. to 50^{cm^3} of liquid; secondly, that by precipitation at a volume of 50^{cm^3}, evaporation to dryness, and extraction with the same volume of water, the copper may be recovered to an amount within about 0·0004 grm. of that taken; thirdly, that treatment by oxalic acid in 50 per cent alcohol fails to precipitate about 0·0020 grm. of copper from amounts less than 0·0200 grm., while for amounts exceeding that limit the copper is nearly all recovered; and, fourthly, that in volumes of 50^{cm^3} or 100^{cm^3}, consisting of 50 per cent acetic acid, the copper oxalate is thrown down completely, the presence of nitric acid to the extent of 10 per cent making the filtration more effective without influencing the solubility, while at a volume of 150^{cm^3} the precipitation is complete provided the acetic acid makes up two-thirds of the volume.

The best and most convenient procedure for the precipitation of small amounts as well as large amounts of copper oxalate ideal in composition consists, therefore, in adding 2 grm. or 4 grm. of oxalic acid to 50^{cm^3} or 100^{cm^3}, respectively, of the 50 per cent acetic acid solution of the copper salt containing 5 per cent to 10 per cent of nitric acid. The permanganate titration of the washed oxalate, in presence of sulphuric acid, gives very accurate determinations of the copper.