ART. XXXVI.—*The Volumetric Estimation of Copper as the Oxalate, with Separation from Cadmium, Arsenic, Tin, and Zinc;* by CHARLES A. PETERS.

[Contributions from the Kent Chemical Laboratory of Yale University—XCVIII.]

IT is a well known fact that copper oxalate is insoluble in water and scarcely attacked by moderate amounts of dilute nitric acid.* Upon this fact Bournemann† has recently based a method for the separation of copper from cadmium by precipitating copper as the oxalate in the presence of nitric acid, filtering hot, and estimating the copper after ignition, by any of the well known gravimetric methods. Six to ten grams of copper, as the oxide, were used for a single determination, and the errors were large. Bournemann does not recommend this process as an accurate analytical method. Classen‡ describes a method for the separation of metals as oxalates by adding to the solution of the salt of the metals a dilute solution of the potassium oxalate (1 : 6) and concentrated acetic acid to 80 per cent of the total volume. Regarding copper salts in particular, Classen states that precipitation takes place only in dilute solution and then not completely.

It has been the experience of the writer, that the precipitation of copper oxalate from solutions containing at least 0·0128 gm. of the oxide and saturated with the oxalic acid is practically complete. The filtrate in such cases gives no blue color with ammonia, looking down on a column of liquid in a test tube, and only a faint brown color is developed when the filtrate is neutralized, made acid with acetic acid, and tested with potassium ferrocyanide. It is the object of this paper to show that moderate amounts of copper may be determined quantitatively as the oxalate by precipitation with oxalic acid and titration of the precipitate by potassium permanganate, and also to show that moderate amounts of copper may be separated from other metals in the presence of nitric acid, by the addition of considerable amounts of oxalic acid.

Before attempting the quantitative separation of copper from solution by the addition of oxalic acid a few qualitative experiments upon the precipitation of varying amounts of copper sulphate by varying amounts of oxalic acid were tried at different dilutions. In all the experiments the mixtures stood 16–20 hours, and were filtered from 2 to 4 times through four filters folded together, and the filtrates were tested

* Storer, Dictionary of Chemical Solubilities, p. 463.
† Chem. Ztg., xxiii, 565.
‡ Ber., x, b, 1316.

both with ammonia and with potassium ferrocyanide. In cases where the filtrate gave no blue color with ammonia and only a slight precipitate with ferrocyanide the precipitation was considered practically complete and the conditions were regarded suitable for the trial of the method quantitatively. In the following table is recorded the work upon the precipitation of copper sulphate by 0·5 gm., 1·0 gm., and 2·0 gms. of oxalic acid in 50$^{cm^3}$ of solution.

TABLE I.

Dilution 50$^{cm^3}$.

		Oxalic acid added in solution.		Oxalic acid added in crystalline form.	
	CuO taken as $CuSO_4$ gms.	Filtrate treated with NH_4OH	Filtrate treated with $K_4FeC_6N_6$	Filtrated with NH_4OH	Filtrate treated with $K_4FeC_6N_6$
2·0 gms. oxalic acid present.	0·018	blue color	abundant ppt.	blue color	abundant ppt.
	0·031	trace "	" "	trace "	evident "
	0·051	--------	evident "	--------	" "
	0·064	--------	trace "	--------	trace "
1·0 gm. oxalic acid present.	0·018	blue color	abundant ppt.	blue color	abundant ppt.
	0·031	"	" "	trace "	evident "
	0·051	trace "	" "	--------	" "
	0·064	--------	evident "	--------	" "
	0·094	--------	trace "	--------	trace "
0·5 gm. oxalic acid. present.	0·018	blue color	abundant ppt.	blue color	abundant ppt.
	0·031	"	" "	trace "	" "
	0·051	trace "	" "	--------	evident "
	0·064	--------	evident "	--------	trace "
	0·094	--------	trace "	--------	" "

It will be seen readily by comparison of the right and left hand sides of the table above that somewhat smaller amounts of copper may be precipitated completely by the addition of crystallized oxalic acid than by the same amount of oxalic acid already in solution. Thus, when dissolved oxalic acid is added to the solution of 50$^{cm^3}$ amounts of copper sulphate less than 0·040–0·050 gm. are not precipitated completely, while under conditions otherwise the same excepting that the oxalic acid is added in crystalline form, the precipitation of amounts as small as 0·030 gm. is practically complete. The amount of oxalic acid in solution necessary for the complete precipitation (after 16 to 20 hours) of this minimum amount of copper, 0·031 gm. of copper oxide taken as the sulphate, appears, as shown in Table II, A, which follows, to be about 3·5 gms. in 50·0$^{cm^3}$. If the amount of oxalic acid is increased to 5 gms., making the solution saturated for that substance, using the

same volume of liquid, the minimum amount completely precipitable is reduced to 0·0128 gms. but not to one-half that amount.

TABLE II.

CuO taken as $CuSO_4$ gms.	Oxalic acid added in solution. gms.	Volume at precipitation. cm^3.	Filtrate treated with NH_4OH.	Filtrate treated with $K_4FeC_6N_6$.
		A		
0·031	0·5	50	blue color	abundant ppt.
"	1·0	"	"	" "
"	2·0	"	trace "	" "
"	3·0	"	slight " "	" "
"	3·5	"	--------	evident "
0·0128	5·0	"	no blue	trace "
0·0064	5·0	"	blue color	abundant "
		B		
0·0064	0·5	20	faint blue	abundant ppt.
"	"	15	"	" "
"	"	10	"	faint "
"	"	5	--------	trace "
0·0003	0·5	5*	--------	--------
"	0·1	1†	--------	--------

It appears from the experiments of Table II, B, that the volume of liquid in which precipitation takes place influences the complete precipitation of the copper oxalate. Thus the precipitation of 0·0064 gm. of copper oxide taken as the sulphate by 0·5 gm. of oxalic acid is complete in 5^{cm^3} of liquid. The precipitate which falls from 0·0003 gm. of the oxide taken as the sulphate dissolves in 5^{cm^3} of liquid, but remains visible in 1^{cm^3}.

As a result of the preliminary experiments, it may be said that the presence of a certain minimum amount of copper, varying with the conditions, is essential to complete precipitation. Thus, at a dilution of 50^{cm^3} a saturated solution of oxalic acid will precipitate with practical completeness copper taken as the sulphate in amounts exceeding the equivalent of 0·0128 gm. of copper oxide; that 2·0 gms. of oxalic acid will precipitate almost completely for the same volume of solution the equivalent of 0·03 gm. of copper oxide; and that 1·0 gm. or 0·5 gm. of oxalic acid will precipitate the equivalent of 0·064 gm. of the oxide.

In the quantitative separation of copper as the oxalate the method of treatment was in general as follows. Copper sul-

* Precipitate redissolved.
† Precipitate remained.

phate in 50$^{cm^3}$ of water was thrown down by the addition of dry oxalic acid to the hot solution, and, after standing over night, the precipitate was filtered on asbestos, washed two or three times with small amounts of cold water. The precipitate, still in the crucible, was returned to the beaker in which precipitation took place, 5 or 10$^{cm^3}$ of dilute sulphuric acid (1 : 1) were then added together with a convenient amount of water, and, after heating the liquid to boiling, the oxalic acid was titrated with permanganate, the oxalate of copper dissolving readily as fast as the excess of oxalic acid is removed by the permanganate. The precipitate may also be dissolved in 10$^{cm^3}$ of strong hydrochloric acid,* 0·5 gm. manganous chloride added and titrated at 30°–50°. Experiments 4 and 5 were conducted after this manner. In Table III, A, which follows, are recorded results of the quantitative tests of the method.

TABLE III.

	CuO taken as $CuSO_4$. gms.	Oxalic acid. gms.	Volume at precipitation. cm^3.	CuO found. gms.	Error. gms.
			A		
1	0·0372	0·15	100	0·0286	−0·0086
2	0·1860	0·50	125	0·1831	−0·0029
3	0·0398	"	50	0·0376	−0·0022
4	0·1860	1·0	150	0·1834	−0·0026
5	"	0·5	50	0·1864	+0·0004
6	"	"	"	0·1866	+0·0006
7	"	"	"	0·1866	+0·0006
8	"	1·0	"	0·1866	+0·0006
9	0·0398	"	"	0·0391	−0·0007

In experiments 1–4, deficiencies are found in the amounts of oxalate precipitated at different degrees of dilution and by different amounts of the precipitant which are in agreement with the results obtained in the preliminary work; the results of experiments 5–9, in which 0·5 grm. and 1·0 grm. of oxalic acid act in a total volume of 50$^{cm^3}$, show the precipitation to be essentially complete under these conditions.

To study the insolubility of the copper oxalate in nitric acid the experiments in Section B of the table were made.

In experiments 10–13 amounts of oxalic acid varying from 0·5 gm. to 3·0 gms. appear to precipitate the copper completely in the presence of 5$^{cm^3}$ of strong nitric acid. In experiment 14 the amount of oxalic acid used was not sufficient to throw down all the copper in the presence of 10$^{cm^3}$ of nitric acid, but

* Gooch and Peters, this Journal, vii, 461, 1899.

TABLE III (continued).

	CuO taken as $CuSO_4$. gms.	Oxalic acid. gms.	HNO_3 sp. gr. 1·40. cm^3.	Volume at precipitation. cm^3.	CuO found. gms.	Error. gms.
			B			
10	0·1860	0·5	5·0	55	0·1859	−0·0001
11	"	"	"	"	0·1860	±0·0000
12	0·1990	2·0	"	"	0·1989	−0·0001
13	"	3·0	"	"	0·1990	±0·0000
14	"	2·0	10·0	60	0·1971	−0·0019
15	"	3·0	"	"	0·1987	−0·0003
16	"	"	"	"	0·1985	−0·0005
17	"	5·0	12·0	130	0·1977	−0·0013
18	"	"	"	"	0·1975	−0·0015
19	"	"	25·0	"	0·1837	−0·0153
20	"	"	"	"	0·1831	−0·0159
21	"	"	5·0	"	0·1983	−0·0007
22	"	"	"	"	0·1988	−0·0002
			C			
23	"	2·5	5·0*	65	0·1971	−0·0029
24	"	2·0	"	"	0·1981	−0·0019

the copper does come down completely in the presence of the large amount of the nitric acid upon the addition of more oxalic acid, as seen in experiments 15 and 16. In experiments 17 and 18 with a larger volume of water and a larger absolute amount, though approximately the same percentage, of nitric acid present as in experiments 10–13, there is a slight loss of copper; but in experiments 21 and 22 when the amount of nitric acid is reduced to 5^{cm^3} in the larger total volume the results are normal. Experiments 19 and 20 show the increased loss when still larger amounts of nitric are present. These facts would make it seem best to limit the absolute amount of nitric in solution to about 5^{cm^3}.

One observation may well be noted here; namely, that while one-half gram oxalic acid is all that is needed for the complete precipitation of the copper in the presence of 5^{cm^3} strong nitric acid, still the oxalic acid may be added up to the point of saturation of the solution. More than this causes difficulty owing to the fact that a large amount of water is necessary to wash the precipitated oxalate. About 2·0 gms. of oxalic acid to 50^{cm^3} of water is a convenient proportion.

In experiments 23 and 24, 5^{cm^3} of nitric acid were neutralized with ammonium hydroxide before adding the 5^{cm^3} strong

* About 9 gms. of ammonium nitrate present in addition to the 5^{cm^3} of nitric acid.

nitric acid in excess. The results show the solubility of copper oxalate in ammonium nitrate and exclude the possibility of such a procedure in this work.

Some experiments were made to show the time necessary for the complete precipitation, both in the presence and absence of nitric acid. Following is the record of such work.

TABLE III (continued).

	CuO taken as $CuSO_4$. gms.	Oxalic acid. gms.	HNO_3 sp. gr. 1·40. cm^3.	Volume at precipitation. cm^3.	CuO found. gms.	Error. gms.	Details of filtration.
				D			
23	0·1990	2·0	----	50	0·1984	−0·0006	Filtered hot immediately
24	0·2030	"	----	"	0·2025	−0·0005	Filtered hot immediately
25	0·1990	1·0	----	"	0·1990	±0·0000	Filtered after cooling; stood 15 minutes
26	"	"	----	"	0·1987	−0·0003	Filtered after cooling; stood 15 minutes
				E			
27	"	2·0	5·0	55	0·1943	−0·0047	Filtered after cooling; stood 15 minutes
28	"	"	"	"	0·1969	−0·0021	Stood $2\frac{1}{2}$ hours
29	"	"	"	"	0·1973	−0·0017	Stood 6 hours
30	"	"	"	"	0·1989	−0·0001	Stood 16 hours

The results in section D would seem to show that a solution containing copper may be precipitated hot as the oxalate and filtered either hot or after cooling with a very slight loss. Tests of the filtrates made with potassium ferro-cyanide confirmed these results. When nitric acid is present, however, the mixture must stand after the addition of the precipitant. In section E the gradual decrease of the minus error is noticed, as the time of standing is extended, the precipitation being practically complete upon standing over night.

Separation from Cadmium.

Bournemann* has used nitric acid for a rough separation of copper from cadmium. This method was tried for a quantitative separation in the presence of 6–10 per cent strong nitric acid. The results are found in section F of the table to follow.

* Loc. cit.

Experiments 33–35 stood six hours before filtering. Experiments 36 and 37 stood over night. Copper is separated from more than twice its weight of cadmium, and the results are accurate.

Separation from Arsenic, in Both Conditions of Oxidation.

For the separation from arsenic, arsenious oxide dissolved in sodium carbonate, and di-hydrogen sodium arseniate were the forms of arsenic used. The results are accurate and are given in sections G and H of the table. In experiments 38–40 and 44 and 45 no nitric acid was added. While the presence of the nitric acid is not necessary for the separation of the copper from the arsenic; still the filtration in the absence of the nitric acid is so slow as to be objectionable. The presence of the nitric acid causes the precipitate to come down in a coarser condition, and in such condition it filters easily and is capable of being washed quickly.

Separation from Tin, in Both Conditions of Oxidation.

For the separation of copper from tin a preparation of stannous chloride (20^{cm^3} giving 0·3746 gm. metallic tin by the battery) containing sufficient hydrochloric acid to prevent deposition of oxy-salts was used. The solution of stannic chloride contained 1·0 gm. metallic tin to every 10^{cm^3}, and was used without hydrochloric acid. The results of the work are found in sections I and K of the table. The experiments go to show that while copper may be separated from small amounts of tin as stannous chloride yet there is a limit to the amount of tin which may be present. One-tenth of a gram of metallic tin is the largest amount that can be present, with 0·15 gm. copper oxide taken as the sulphate, without significant error. Practically the same statement can be made of the separation of copper from tin taken as stannic chloride. Experiment 57 shows a greater loss of copper when the nitric acid is omitted.

Separation of Copper from Iron.

A solution of ferric nitrate was used for the work on the separation of copper from iron. Low results were obtained when a solution of ferrous or ferric sulphate was used as the source of iron. The results of the experiments are recorded in section L of the table, and show that 0·20 gm. copper oxide as the sulphate may be separated from 0·2–0·3 gm. iron oxide taken as the nitrate. In experiment 64 a good result was obtained when no nitric acid was present, save that added in combination with the iron. A comparison of experiments 63 and 65 shows that it is best to avoid the use of large amounts

TABLE III (continued).

	CuO taken as $CuSO_4$. gms.	Element from which copper was separated. gms.	Oxalic acid. gms.	HNO_3 sp. gr. 1·40. cm^3.	Volume at precipitation. cm^3.	CuO found. gms.	Error. gms.
		CdO taken as $CdSO_4$.		F			
33	0·1990	0·10	2·0	5·0	60	0·1983	−0·0007
34	"	0·20	"	"	65	0·1987	−0·0003
35	"	0·30	"	"	70	0·1987	−0·0003
36	"	0·40	"	"	75	0·1994	+0·0004
37	"	0·50	"	"	80	0·1996	+0·0006
		As_2O_3 taken as Na_3AsO_3.		G			
38	"	0·10	"	----	55	0·1991	+0·0001
39	"	0·20	"	----	60	0·1987	−0·0003
40	"	0·50	"	----	75	0·1986	−0·0004
41	"	0·10	"	5·0	60	0·1994	+0·0004
42	"	0·20	"	"	75	0·1992	+0·0002
43	"	0·60	"	"	85	0·1995	+0·0005
		As_2O_5 taken as H_2KAsO_4.		H			
44	"	0·10	"	----	60	0·1985	−0·0005
45	"	0·20	"	----	70	0·1990	±0·0000
46	"	0·10	"	5·0	65	0·1990	±0·0000
47	"	0·20	"	"	75	0·1992	+0·0002
48	"	0·30	"	"	85	0·1985	−0·0005
49	0·2030	0·30	3·0	"	85	0·2026	−0·0004
	Cu taken as $CuSO_4$.	Sn taken as $SnCl_2$ + HCl.		I		Cu found.	
50	0·1590	0·0468	2·0	5·0	55	0·1581	−0·0909
51	"	0·0936	"	"	60	0·1603	+0·0013
51*a*	"	"	"	"	"	0·1591	+0·0001
52	"	"	"	"	"	0·1594	+0·0004
53	"	0·1873	"	"	65	0·1603	+0·0013
54	"	0·2809	"	"	70	0·1914	+0·0324
55	"	"	3·0	"	75	0·1988	+0·0398
		Sn taken as $SnCl_4$.		K			
56	"	0·10	2·0	"	55	0·1581	−0·0009
57	"	0·10	"	----	"	0·1565	−0·0025
58	"	0·20	"	5·0	"	0·1577	−0·0013
59	"	0·50	"	"	60	0·1562	−0·0028
	CuO taken as $CuSO_4$.	Fe_2O_3 taken as $Fe(NO_3)_3$.		L		CuO found.	
60	0·1990	0·136	2·0	5·0	60	0·1987	−0·0003
61	"	0·272	"	"	"	0·1983	−0·0007
62	"	0·364	"	"	"	0·1988	−0·0002
63	"	0·544	"	"	65	0·1971	−0·0019
64	"	0·272	"	----	60	0·1995	+0·0005
65	"	0·544	"	2·0	"	0·1998	+0·0008
66	"	0·218	"	"	65	0·1999	+0·0009
		ZnO taken as $ZnSO_4$.		M			
67	"	0·028	"	5·0	60	0·2007	+0·0017
68	"	0·057	"	"	65	0·2008	+0·0018
69	"	"	"	"	"	0·2008	+0·0018
70	"	0·085	"	"	70	0·2035	+0·0045

of nitric acid when the larger amounts of ferric nitrate are present.

For a practical application of the above separation of copper from iron a convenient amount of finely ground chalcopyrite (0·5 gm.) was roasted 2–3 hours in a porcelain crucible until all sulphur was driven off, washed into a beaker, strong nitric acid about 5^{cm^3} was added and, with the beaker covered, allowed to evaporate slowly on a hot plate, nearly to dryness. A little dilute nitric acid was added, the solution was filtered, the residue was washed with water containing dilute nitric acid, the filtrate, about 50^{cm^3} in volume, was precipitated with 2·0 gms. oxalic acid, and the precipitate was estimated after standing 12–16 hours, as previously described. The washing with water acidified with nitric acid is important because the finely ground ferric oxide remaining undissolved passes through the filter when washed with water alone, but gives no trouble if the water be acidic. The results of two estimations are here given.

Chalcopyrite. gms.	Copper found by battery.	Copper found by oxalate method.	Difference.
0·5000	31·00%	30·92%	−0·08%
1·0000	"	31·25	+0·25

Separation of Copper from Zinc.

The separation of copper from zinc was not altogether successful owing to the tendency of the zinc oxalate to come down with the copper oxalate. Some experiments are given in section M of the table.

The separations of copper from bismuth and antimony were unsuccessful.

The work may be briefly summarized as follows: Copper exceeding in amount the equivalent of 0·0128 gm. of the oxide to 50^{cm^3} of solution as the sulphate may be separated completely, even in the presence of a moderate amount of strong nitric, by the addition of sufficient amount of oxalic acid.

Copper may be separated from cadmium, arsenic, iron, and small amounts of tin, when precipitated by oxalic acid in a volume of $50·0^{cm^3}$ containing 5^{cm^3} strong nitric acid. Inasmuch as the completeness of precipitation of the copper depends upon the presence of a certain minimum amount of the copper salt this method is not applicable when the amount of copper falls below 0·0128 gm. of the oxide to 50^{cm^3} of solution.

The author wishes to thank Professor F. A. Gooch for much kind help given in the preparation of this paper.