ART. XXXIX.—*The Separation and Determination of Mercury as Mercurous Oxalate*; by C. A. PETERS.

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

IT is stated in the literature* that oxalic acid, neutral and acid oxalates of the alkalies, precipitate mercurous salts, and that oxalic acid and the double oxalates of potassium produce no precipitate with mercuric chloride solution. Starting with these facts, the attempt was made to estimate mercurous salts: volumetrically, by precipitating with ammonium oxalate and determining the oxalic acid by potassium permanganate; and gravimetrically by direct weighing of the precipitate.

The Volumetric Estimation.

The mercurous nitrate solution used was standardized by the battery, and contained about 12 gms. of metallic mercury to the liter. To obviate the tendency of the mercury salt to break down and form basic salts† upon the addition of a large amount of water if no nitric acid is added, the solution was prepared in the following manner. About 20 gms. of mercurous nitrate were ground in a mortar, transferred to a flask, and 200–300^{cm}³ water added. After shaking well, the solution was filtered and the filtrate diluted to one liter. Five ^{cm}³ of this solution when precipitated with a sodium chloride solution gave a filtrate from which only a very slight darkening in color could be obtained, even upon several hours standing, when treated with hydrogen sulphide, thus showing the absence of a mercuric salt.

A solution made in the above manner had not changed its standard after a period of eight weeks. The potassium permanganate solution (approximately $\frac{n}{10}$) was standardized against lead oxalate.

It was first attempted to estimate the mercurous salts as follows. The mercurous oxalate was precipitated cold by means of ammonium oxalate, stirred well, and allowed to settle, the completion of the precipitation being determined by addition of more ammonium oxalate. The precipitate was collected on asbestos, washed once or twice with cold water, and (still in the crucible) treated in a beaker with 5^{cm}³ of strong hydrochloric acid. To the solution diluted to 100–200^{cm}³ 1 gm. of a manganous salt was added, and the oxalic acid was titrated with permanganate at the ordinary temperature of the room. The end color was not stable and was hard to determine. Three experiments, using 0.1217 of

*Rose und Finkener. *Handbuch der Analytischen Chemie*, i, 319.

†Graham Otto, *Handbuch*, iii, 1102.

mercury in form of mercurous nitrate, gave plus errors of 0.0011 gms., 0.0017 gms. and 0.0028 gms. respectively, or 1.5 per cent. The precipitate when dissolved in sulphuric acid and titrated gave no better results. To obviate this difficulty the ammonium oxalate solution was matched on the permanganate and the oxalic acid in the filtrate determined. The results obtained by this method, given in the following table, are quite accurate.

1	Hg taken as Hg ₂ (NO ₃) ₂ gms.	Hg found. gms.	Excess of ammonium oxalate	HCl Sp. gr. 1.16 cm ³	MnCl ₂ .4H ₂ O gms.	H ₂ SO ₄ 1:1 cm ³	Error as Hg
			app. $\frac{n}{10}$ cm ³				
A							
1	0.1825	0.1823	0.90	5.	.5	----	-0.0002
2	0.1217	0.1218	0.93	5.	.5	----	+0.0001
3	0.1217	0.1206	0.99	5.	.5	----	-0.0011
4	0.1217	0.1210	4.05	5.	.5	----	-0.0007
5	0.3042	0.3034	4.97	5.	.5	----	-0.0008
B							
6	0.1217	0.1220	0.93	----	----	5	+0.0003
7	0.1217	0.1211	0.97	----	----	5	-0.0006
8	0.1825	0.1827	0.89	----	----	5	+0.0002
9	0.3042	0.3040	0.82	----	----	5	-0.0002
10	0.1217	0.1202	4.10	----	----	5	-0.0015

In the experiments recorded in section A of the table the filtrate was titrated in the presence of hydrochloric acid and a manganous salt, at a temperature of 20°-40°.* In the experiments under section B sulphuric acid was added and the solution heated in the usual manner. An excess of ammonium oxalate as shown in expts. 4, 5 and 10, interferes in no way.

The separation of mercurous salt from small quantities of mercuric salts, by the means of dilute nitric acid, sp. gr. 1.15, was next attempted. It is stated† that mercurous oxalate is insoluble in cold dilute nitric acid, while mercuric oxalate is more or less soluble in the same reagent. Before attempting any separation, however, there are three factors with reference to the action of the nitric acid which need to be determined—first, the maximum amount of nitric acid that may be present in titration of an oxalate without interference; second, the maximum amount of nitric acid that may be present in a precipitation of mercurous oxalate without having any perceptible solvent action upon the same; and, third, the amount of mercuric oxalate which will be held in solution by given amounts of nitric acid.

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

† Souchay and Lenssen, Ann. d. Chem., cii, 43.

To determine the amount of nitric acid that may be present in the titration of an oxalate, 10cm^3 of $\frac{n}{10}$ ammonium oxalate were titrated with permanganate at a dilution of 100cm^3 with sulphuric acid at 80°C . The event proved that 10cm^3 of nitric acid, sp. gr. 1.15, may be present without appearance of interfering action. The maximum amount of nitric acid which may be present without action upon the mercurous salt was determined as shown in the following experiments.

Hg taken as $\text{Hg}_2(\text{NO}_3)_2$ gms.	Excess of ammonium oxalate approximately $\frac{n}{10}$ cm^3	HNO_3 Sp. gr. 1.15 cm^3	Volume at precipitation	Hg found gms.	Error.
0.1122	1.64	10	100	0.1087	-0.0035
"	2.62	6	"	0.1098	-0.0024
"	1.59	6	"	0.1096	-0.0026
"	1.53	5	"	0.1109	-0.0013
"	1.40	5	"	0.1134	+0.0012
"	1.50	5	"	0.1115	-0.0007
"	1.70	4	"	0.1116	-0.0006
"	1.59	8	200	0.1096	-0.0036
"	6.62	8	"	0.1111	-0.0011
"	7.72	8	"	0.1108	-0.0014
"	2.59	5	"	0.1107	-0.0015
{ 0.1010	2.07	5	"	0.1003	-0.0007

Working under the conditions stated in the above table, it is plain that 5cm^3 of nitric acid, sp. gr. 1.15, may be used before its solvent action is sufficient to interfere with the accuracy of the process.

To determine the amount of mercuric salt that would be held up by 5cm^3 of nitric acid, sp. gr. 1.15, the following experiments were made.

Hg taken as $\text{Hg}_2(\text{NO}_3)_2$ gms.	HNO_3 Sp. gr. 1.15 cm^3	Ammonium oxalate $\frac{n}{10}$ cm^3 in excess	Volume cm^3	Time before precipitation.
0.0335	4	0.75	100	5 hours.
0.0095	4	1.00	100	No. ppt. 20 hours
0.0143	5	6.5	100	"
0.0238	5	1.5	100	Slight ppt. 20 hours
0.0238	5	5.5	100	25 minutes.

Five cm^3 of dilute nitric acid (sp. gr. 1.15) will prevent the precipitation of small amounts of mercuric salt, 10-20 mgms. calculated as mercury, depending upon the amount of ammonium oxalate present in excess. This amount of nitric acid has no apparent solvent action on a precipitate of mercurous oxalate under conditions already stated and does not interfere

with the titration of an oxalate by permanganate as already shown.

Carrying out the process of separation of mercurous from mercuric salts, the precipitation was made as described for the estimation of mercurous salts alone, excepting that nitric acid and mercuric salt were added. The experiments in A, B, and C, of the accompanying table show the amounts of mercuric salt from which the mercurous oxalate may be separated with 2^{cm}³ of nitric acid. In experiments in section A the results are quite accurate, but an excess of ammonium oxalate tends to increase the results a little as seen in experiments under B. An increase in the amount of mercuric salt present causes also, as shown in section C, the results to be a trifle high.

	Hg taken as Hg ₂ (NO ₃) ₂ gms.	Hg(NO ₃) ₂ present calculated as Hg. gms.	Ammonium oxalate		HNO ₃ Sp. gr. 1.15 cm ³	Volume at precipitation.	Hg found. gms.	Error.
			app. $\frac{n}{10}$ in excess. cm ³					
A	0.1217	0.0067	0.86	2	100	0.1232	—0.0015	
	“	“	0.92	“	“	0.1220	+0.0003	
	“	“	0.97	“	“	0.1218	+0.0001	
	“	“	0.90	“	“	0.1224	+0.0007	
	“	“	0.91	“	“	0.1213	—0.0004	
B	0.1221	“	3.92	“	“	0.1237	+0.0016	
	0.1217	“	3.93	“	“	0.1235	+0.0018	
	0.1242	“	8.75	“	“	0.1263	+0.0021	
C	0.1217	0.0134	0.87	“	“	0.1230	+0.0013	
	“	“	0.86	“	“	0.1232	+0.0015	
D	“	“	3.93	4	“	0.1218	+0.0001	
	“	“	3.90	“	“	0.1211	—0.0006	
E	0.2244	0.0067	1.88	“	115	0.2244	±0.0000	
	“	“	1.91	“	130	0.2240	—0.0004	
EE	“	0.0141	2.98	“	100	0.2230	—0.0014	
	“	“	2.94	“	“	0.2241	—0.0003	
F	“	0.0067	8.88	“	“	0.2289	+0.0045	
	“	“	8.90	“	“	0.2285	+0.0041	
G	0.2424	“	1.75	“	200	0.2432	+0.0008	
	“	“	2.00	“	“	0.2414	—0.0010	
	“	“	2.96	“	“	0.2421	—0.0003	
H	0.2245	0.0134	1.74	“	“	0.2271	+0.0026	
	“	“	1.81	“	“	0.2256	+0.0012	
I	0.1122	0.0144	6.62	5	“	0.1121	—0.0001	
K	“	0.0240	6.54	5	“	0.1136	+0.0014	
	“	“	6.57	5	“	0.1130	+0.0008	

In experiments D, using 4^{cm}³ of nitric acid even in the presence of an excess of ammonium oxalate, the results are accurate. In experiments E the amount of mercurous salt

was doubled and the results are accurate. In EE the amount of mercuric salt was also doubled and the results are still fairly accurate; but when a large excess of ammonium oxalate is present as in experiments F, even with the smaller amount of mercuric salt, the results are high. At a dilution of 200^{cm}³ the results are normal as seen in experiments G; but the introduction of more mercuric salt, as in experiments H, causes a plus error.

Using 5^{cm}³ of nitric acid, the larger amount of mercuric salt, together with a large excess of ammonium oxalate, as recorded in experiments K, the error is raised a trifle; but with a smaller amount of mercurous salt as in experiment I the result is normal.

In precipitating mercurous salts by ammonium oxalate $\left(\frac{n}{10}\right)$ it is an easy matter to keep the excess of the precipitant within the limits of 1 or 2^{cm}³, because the mercurous oxalate, when properly stirred, settled very rapidly.

The Gravimetric Estimation.

All the conditions described above in the volumetric estimation of mercurous oxalate, for the separation of mercurous from mercuric salts, may be applied to the gravimetric estimation of mercurous oxalate. The precipitate is collected on a weighed asbestos filter, washed two or three times with cold water and dried over sulphuric acid to a constant weight. Amounts of mercurous oxalate equivalent to 0.1217 and 0.2244 gms. of metallic mercury dried to a constant weight over sulphuric acid in about 15 hours; a larger amount equivalent to 0.3 gm. of metallic mercury, required about 2 days to dry to a constant weight. Souchay and Lenssen* state that mercurous oxalate breaks up at 100°; consequently this temperature cannot be used for drying. For example, a precipitate containing 0.1122 gms. mercury as the oxalate which when brought to a constant weight at the ordinary temperature over sulphuric acid weighed 0.1371 gms., and was heated and weighed as follows:

After 7 hours at 110°, weight =	0.1338 gms.
“ 2 “ “ “	0.1328 “
“ 7 “ “ “	0.1302 “

The result shows a loss of 0.0069 gms. for 16 hours heating, and agrees with the statement of Souchay and Lenssen.

The following experiments give the results of the gravimetric work, in which the drying was effected, by exposure for 15 hours or less, at ordinary temperatures, over sulphuric acid. The larger amounts of nitric acid present in the separations cause the precipitate to be more granular and aid in the filtering process.

* Ann., ciii, 308.

	Hg taken as $\text{Hg}_2(\text{NO}_3)_2$ gms.	Hg present as $\text{Hg}(\text{NO}_3)_2$ gms.	Excess ammonium oxalate present app. $\frac{n}{10}$ cm^3	HNO_3 Sp. gr. 1.15 cm^3 .	Volume at precipi- tation cm^3 .	Hg found. gms.	Error. gms.
K	0.1217	----	2.4	----	100	0.1217	± 0.0000
	"	----	"	----	"	0.1217	± 0.0000
	0.1122	----	"	----	"	0.1124	$+ 0.0002$
L	"	0.0067	0.93	2	"	0.1130	$+ 0.0008$
	"	"	0.93	"	"	0.1112	$- 0.0010$
M	"	"	4.40	"	"	0.1124	$+ 0.0002$
N	"	0.0135	0.72	4	"	0.1125	$+ 0.0003$
O	0.2244	0.0071	1.68	"	"	0.2253	$+ 0.0009$
	"	"	2.46	"	"	0.2241	$- 0.0003$
P	"	0.0048	0.54	"	200	0.2248	$+ 0.0004$
	"	"	2.44	"	"	0.2245	$+ 0.0001$

In section K are experiments showing the accuracy of the process where a mercurous salt is precipitated in the absence of a mercuric salt. A small amount of mercuric salt was introduced in experiments L, and an excess of ammonium oxalate in experiment M, a still larger amount of mercuric salt was present in experiment N, and a larger amount of mercurous salt in experiments under O. In experiments in section P a dilution of 200cm^3 was employed both with and without an excess of ammonium oxalate. All the results are within reasonable limits of error.

The work may be summed up briefly as follows: Mercurous nitrate may be estimated volumetrically by precipitating as the oxalate and determining the excess of the precipitant with permanganate.

The precipitated mercurous oxalate may also be estimated gravimetrically by drying it over sulphuric acid and weighing directly.

In solutions containing 2–5 per cent dilute nitric acid, sp. gr. 1.15, mercurous salts may be separated quantitatively as the oxalate from small quantities of mercuric salts.

If about 0.12 gm. of mercury is present as the nitrate in 100cm^3 of water, about 12 per cent of that amount of mercury as the mercuric salt may be present without interfering with the accuracy of the estimation, and even 20 per cent may be present before an appreciable rise in the result is apparent. If the amount of mercurous salt present is doubled, the amount of mercuric salt which may be present is cut down about one-half.

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