ART. XXV.—*The Estimation of Calcium, Strontium, and Barium, as the Oxalates;* by CHARLES A. PETERS.

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

A FORMER article from this laboratory* describes the conditions under which oxalic acid may be titrated by potassium permanganate in the presence of hydrochloric acid, and states that the extra consumption of permanganate which ordinarily takes place when oxalic acid is titrated by permanganate in the presence of hydrochloric acid, may be prevented by the addition of a manganous salt. This fact led to the idea of effecting the solution of the alkaline earth oxalates in hydrochloric acid and titrating the free oxalic acid with permanganate in the presence of a manganous salt, and so to the study of the conditions under which precipitates of strontium and barium oxalates could be obtained sufficiently insoluble for quantitative purposes, the conditions under which calcium oxalate is insoluble being already known.

The permanganate solution was standardized against freshly recrystallized ammonium oxalate, and on oxalic acid, the standards agreeing.

Calcium Oxalate.

It is well known that calcium may be estimated by treating the precipitated oxalate with sulphuric acid and titrating by permanganate the oxalic acid set free.† In the work described in the present article, the precipitate of calcium oxalate has been dissolved in hydrochloric acid and the oxalic acid titrated by permanganate in the presence of a manganous salt. The process was as follows: The boiling hot solution of calcium chloride was precipitated with ammonium oxalate, allowed to stand 12 hours, and the supernatant liquid decanted on asbestos. The precipitate was washed two or three times by decantation with 50–100$^{cm^3}$ of cold water and brought on the felt. The crucible containing the precipitate was returned to the beaker, 100–200$^{cm^3}$ of water were added, together with 5–10$^{cm^3}$ of strong hydrochloric acid and 0·5–1·0 gm. of manganous chloride, and the oxalic acid was titrated at a temperature of 35°–45°. The results given in Table I are obviously excellent, and show that calcium, taken as the oxalate, may be estimated by potassium permanganate in the presence of hydrochloric acid and a manganous salt.

Extended washing with hot water, however, is to be avoided after the precipitant, ammonium oxalate, has been removed.

* Gooch and Peters, this Journal, vii, 466.

† Mohr, Titrirmethode, 6te Aufl., s. 227.

TABLE I.

CaO, taken as $CaCl_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	CaO found. grm.	Error. grm.
0·0656	0·3	100	0·0657	+0·0001
"	"	100	0·0656	0·0000
"	"	150	0·0658	+0·0002
"	"	100	0·0655	−0·0001
0·0985	0·5	175	0·0981	−0·0004
0·1313	0·6	150	0·1315	+0·0002
"	"	200	0·1315	+0·0002

In one experiment, for example, in which the precipitate, on the felt, was washed fourteen times with portions of about 50^{cm^3} each of hot water, each portion bleached from 2–6 drops of approximately one-tenth normal permanganate, making a total loss of 0·0034 grm. of calcium oxide.

Strontium Oxalate.

Souchay and Lenssen* state that strontium oxalate is soluble in 12,000 parts of water. This fact seemed sufficient to warrant the study of the quantitative separation of strontium as the oxalate. In the work which follows strontium oxalate has been precipitated both in alcoholic solution and in water solution, and for convenience these two conditions of precipitation will be discussed separately. All the strontium salts, of established purity, were standardized by precipitation with sulphuric acid in a solution containing at least one-half its volume of alcohol, and with some solutions confirmatory standards were also obtained by evaporization with sulphuric acid.

Precipitation in Alcoholic Solution.—To determine the completeness of the precipitation in alcoholic solution strontium nitrate was precipitated by ammonium oxalate in a solution containing one-third of its volume of alcohol, the mixture was allowed to stand over night, the liquid was filtered off on asbestos, and the precipitate was treated in the capped filtering crucible with sulphuric acid, ignited, and weighed as the sulphate.

The results are given in Table II.

It is plain from the results recorded in this table that the precipitation of even small amounts of the strontium salt from a solution containing one-third of its volume of alcohol is practically complete.

To determine the minimum amount of alcohol necessary for the complete precipitation of the strontium oxalate, experi-

* Ann. der Chem. (Liebig), cii. 35.

TABLE II.

SrO, taken as $Sr(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Volume of alcohol.	SrO, found as $SrSO_4$. grm.	Difference. grm.
0·2434	0·8	180	$\frac{1}{3}$	0·2440	+0·0006
0·2434	0·8	"	"	0·2437	+0·0003
0·0022	0·2	100	"	0·0022	0·0000
0·0013	0·2	"	"	0·0014	+0·0001
0·0004	0·04	"	"	0·0004	0·0000

ments were made using varying proportions of 85 per cent alcohol with different amounts of ammonium oxalate, and the filtrates from such experiments were tested for strontium by the addition of more alcohol.

The results are given in Table III.

TABLE III.

SrO, present as $Sr(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume of liquid. cm^3.	Proportion of 85% alcohol.	SrO found in filtrate, weighed as $SrSO_4$. grm.
0·1	0·4	100	$\frac{1}{5}$	0·0000
"	"	"	$\frac{1}{10}$	0·0000
"	"	"	$\frac{1}{20}$	0·0004
0·1	0·2	"	$\frac{1}{5}$	0·0000
"	"	"	$\frac{1}{10}$	0·0009
"	"	"	$\frac{1}{20}$	0·0020
0·1	0·1	"	$\frac{1}{3}$	0·0002

The results in Table III show that when a moderate excess of ammonium oxalate is present, a volume of 85 per cent alcohol, amounting to one-fifth of the whole, is sufficient to complete the precipitation of the strontium as the oxalate.

The conditions under which strontium oxalate is insoluble having been determined, the process for the volumetric estimation of strontium was carried out as follows: The hot solution of a strontium salt was precipitated with ammonium oxalate, 85 per cent alcohol, amounting to from one-fifth to one-third the total volume, was added, the mixture was allowed to stand over night, and the clear liquid was decanted on an asbestos filter. The precipitate was washed with a mixture of equal parts of 85 per cent alcohol and water, transferred to the filter, dried in the filtering crucible over a flame to free it from alcohol, returned to the beaker previously dried, treated with sulphuric acid, or with 5–10$^{cm^3}$ of hydrochloric acid (in the latter case 0·5–1·0 gm. of a manganous salt being added) and the liberated oxalic acid was titrated by permanganate. The results obtained by this method are accurate and are given in Table IV.

TABLE IV.

Volume during titration 150–250$^{cm^3}$.

SrO, taken as $Sr(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Proportion of 85% alcohol.	Acid present during titration.	SrO found. grm.	Error. grm.
0·0974	0·4	100	$\frac{1}{5}$	HCl	0·0973	−0·0001
"	"	"	"	"	0·0983	+0·0009
"	"	"	"	"	0·0975	+0·0001
"	0·8	"	"	"	0·0981	+0·0007
0·1948	0·4	200	"	"	0·1943	−0·0005
"	0·8	"	"	"	0·1942	−0·0006
0·0974	0·4	100	$\frac{1}{3}$	H_2SO_4	0·0970	−0·0004
"	"	"	$\frac{1}{5}$	"	0·0977	+0·0003
"	"	"	"	"	0·0976	+0·0002
0·1948	0·6	150	"	"	0·1938	−0·0010

In the last experiment in which a comparatively large amount of strontium salt was present and the dilution low, there is a slight tendency towards a minus error due probably to the occlusion of some oxalic acid by the strontium sulphate formed. This phenomenon would favor titration at greater dilution when sulphuric acid is used to liberate the oxalic acid from large amounts of strontium oxalate.

Precipitation in Water Solution.—In order to determine the degree of precipitation of strontium salts in water solution, 0·0974 grm. of strontium oxide, taken as the nitrate, was precipitated by ammonium oxalate, the mixture was allowed to stand over night, filtered on asbestos, the precipitate was washed with water containing one-half of its volume of 85 per cent alcohol, treated in the capped crucible with a few drops of sulphuric acid, ignited, and weighed as the sulphate. The result gave 0·0973 grm. of strontium oxide. The precipitation, therefore, of strontium oxalate, in water solution with a sufficient excess of ammonium oxalate present, is practically complete.

To determine the amount of ammonium oxalate necessary for the precipitation of strontium salts in water solution, experiments were made in which strontium oxalate was precipitated in the presence of varying amounts of ammonium oxalate, allowed to stand over night, the clear liquid was decanted on asbestos, and the precipitate was washed two or three times with 10–20$^{cm^3}$ of cold water. The results obtained by the estimation of the oxalic acid by permanganate show that an amount of ammonium oxalate several times larger than that required for the theoretical formation of strontium oxalate is necessary for the separation of the strontium oxalate. The experiments are recorded in Table V.

TABLE V.

SrO, taken as $Sr(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Acid present during titration.	SrO found. grm.	Error. grm.
0·0487	0·064	100	H_2SO_4	0·0441	−0·0046
"	0·0768	"	"	0·0465	−0·0022
"	0·16	"	"	0·0488	−0·0001
0·0974	0·128	"	"	0·0939	−0·0025
"	0·16	"	"	0·0959	−0·0015
"	0·32	"	"	0·0975	+0·0001

The solvent action of a large amount of water on a precipitate of strontium oxalate was tested by washing a precipitate equivalent to 0·0974 grm. of the oxide with 150$^{cm^3}$ of cold water. The precipitate, when weighed as the sulphate, showed a loss of 0·0033 grm. as the oxide, which amount was subsequently recovered from the filtrate by the addition of ammonium oxalate and alcohol. Plainly excessive washing with water is to be avoided. In the estimation, therefore, of strontium when precipitated as the oxalate in water solution the amount of water used in washing was limited. It was found that 30–40$^{cm^3}$ of water judiciously applied was sufficient to wash out the ammonium salt without producing appreciable solvent effect upon the strontium oxalate.

The process of treatment was similar to that used in the precipitations from alcoholic solution, excepting that no alcohol was added to the solution, that the washing was effected with a limited amount of water, and that, there being no alcohol present to affect the titration, the precipitate was not dried before treatment with permanganate. The results are given in Table VI.

TABLE VI.

SrO, taken as $Sr(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Acid present during titration.	SrO found. grm.	Error. grm.
		A			
0·0974	0·5	100	H_2SO_4	0·0966	−0·0008
"	"	"	"	0·0985	+0·0011
"	"	"	"	0·0977	+0·0003
"	"	"	"	0·0963	−0·0011
"	0·8	"	"	0·0981	+0·0007
"	"	"	"	0·0966	−0·0008
"	1·0	"	"	0·0965	−0·0009
"	2·0	"	"	0·0963	−0·0011
"	"	"	"	0·0970	−0·0004
0·0778	0·5	"	"	0·0792	+0·0014
"	"	"	"	0·0767	−0·0011
"	"	"	"	0·0776	−0·0002
"	"	"	"	0·0776	−0·0002
0·0974	0·8	250	"	0·0973	+0·0001
"	2·0	"	"	0·0975	−0·0001

SrO, taken as $SrCl_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Acid present during titration.	SrO found. grm.	Error. grm.
		B			
0·0974	0·8	100	HCl	0·0971	−0·0003
"	"	"	"	0·0980	+0·0006
"	"	"	"	0'0975	+0·0001
"	"	"	"	0·0980	+0·0006
"	"	"	"	0·0973	−0·0001
"	"	"	"	0·0978	+0·0004
		C			
0·2425	0·384	125	H_2SO_4	0·2376	−0·0049
0·2436	"	"	"	0·2402	−0·0034
"	0·64	"	"	0·2411	−0·0025
"	0·8	"	"	0·2367	−0·0069
"	2·0	"	"	0·2376	−0·0060
"	"	"	"	0·2402	−0·0034
		D			
0·2436	0·8	250	H_2SO_4	0·2443	+0·0007
"	"	"	"	0·2446	+0·0010
"	2·0	"	"	0·2440	+0·0004
"	"	"	"	0·2431	−0·0005
		E			
0·2436	0·8	500	H_2SO_4	0·2396	−0·0040
"	2·0	"	"	0·2403	−0·0033
"	2·0	"	"	0·2413	−0·0023
"	4·0	"	"	0·2410	−0·0026
"	8·0	"	"	0·2407	−0·0029
0·4872	2·0	"	"	0·4837	−0·0035
"	4·0	"	"	0·4855	−0·0017
0·5430	5·0	"	"	0·5422	−0·0008
0·4579	10·0	"	"	0·4554	−0·0025
0·7307	5·0	"	HCl	0·7262	−0·0045

In the experiments recorded in section A of Table VI, the strontium oxalate was treated with sulphuric acid and titrated at 80°, the volume being 200–300$^{cm^3}$; while in the experiments given in section B, the precipitate was treated with hydrochloric acid and titrated at 35°–45°, at a volume of 100–200$^{cm^3}$, after the addition of 0·5–1·0 grm. of manganous chloride. The results show that 0·1 grm. of strontium salt, calculated as the oxide, may be estimated as the oxalate with a fair degree of accuracy when precipitated in 100–250$^{cm^3}$ of water by a sufficient excess of ammonium oxalate. In the experiments recorded in section C, in which the amount of strontium salt in 125$^{cm^3}$ of water is increased, a negative error is introduced,

which is not diminished by the presence of a large amount of ammonium oxalate, but when the dilution is increased to 250$^{cm^3}$, as is the case in the experiments given in section D, so that the conditions correspond more nearly to those recorded in sections A and B, the errors fall to a minimum. In the experiments recorded in section E, in which the dilution is increased to 500$^{cm^3}$, an error is introduced which is not prevented by the presence of a large excess of ammonium oxalate and which is independent of the amount of strontium salt used. Eight of the water filtrates and wash waters obtained in the experiments recorded in Table VI were tested for traces of strontium by the addition of alcohol, and in all cases a small amount of strontium was found, amounting in the average to 0·0010 grm. in 100$^{cm^3}$ of water.

Barium Oxalate.

Barium oxalate according to Souchay and Lenssen* is soluble in 2,590 parts of cold water, and according to Bergman† is scarcely at all soluble in alcohol. The attempt was made to estimate barium by precipitation with ammonium oxalate in a mixture containing alcohol. It was found that in filtrates from oxalate precipitations in which 0·1–0·2 grm. of barium oxide, taken as the nitrate, had been precipitated in volumes of 100$^{cm^3}$ containing 30$^{cm^3}$ of absolute alcohol, and allowed to stand over night, treatment with sulphuric acid gave barium sulphate amounting in the average to no more than 0·0001 grm. of barium oxide. The insolubility of barium oxalate under these conditions, therefore, is practically complete.

The process for the estimation of barium was as follows: Ammonium oxalate was added to a solution of a barium salt, containing 30 per cent of its volume of alcohol, the mixture was allowed to stand over night, filtered on asbestos, the precipitate was washed by decantation with 100–200$^{cm^3}$ of water containing 30 per cent of its volume of alcohol, and dried over a flame to insure the removal of alcohol. The crucible containing the precipitate was returned to the beaker also previously dried over a flame, 100–200$^{cm^3}$ of water, 5–10$^{cm^3}$ of strong hydrochloric acid, and 0·5–1·0 grm. of manganous chloride were added, and the solution was titrated at 35°–40° with permanganate. The results of the experiments, given in Table VII, A, show that barium, either as the nitrate or chloride, may be estimated in the manner described with a fair degree of accuracy.

* Ann. der Chem. (Liebig), xc, 102. † Bergman's Essays, i, 320.

TABLE VII.

BaO, taken as $Ba(NO_3)_2$. grm.	Ammonium oxalate. grm.	Volume at precipitation. cm^3.	Acid present during titration.	BaO found. grm.	Error. grm.
		A			
0·1165	0·2	100	HCl	0·1177	+0·0012
"	"	"	"	0·1170	+0·0005
"	"	"	"	0·1164	−0·0001
"	"	"	"	0·1151	−0·0014
"	"	"	"	0·1165	0·0000
"	"	"	"	0·1176	+0·0011
"	"	"	"	0·1164	−0·0001
0·2330	0·4	"	"	0·2319	−0·0011
"	"	"	"	0·2335	+0·0005
"	"	"	"	0·2342	+0·0012
BaO, taken as $BaCl_2$.					
0·0942	"	"	"	0·0952	+0·0010
"	"	"	"	0·0939	−0·0003
"	"	"	"	0·0941	−0·0001
0·1884	0·4	"	"	0·1893	+0·0009
"	"	"	"	0·1892	+0·0008
		B			
0·0942	0·2	200	H_2SO_4	0·0858	−0·0086
0·1884	0·4	"	"	0·1732	−0·0152
0·0942	0·2	500	"	0·0857	−0·0085

In the experiments given in section B of Table VII, the precipitate of barium oxalate was treated with sulphuric acid after the addition of the stated amount of water. The results show a large loss of oxalic acid probably due to the occlusion of some of the oxalic acid by the barium sulphate. This fact must prevent the use of sulphuric acid in an analytical process which depends upon the liberation of oxalic acid from barium oxalate.

Gravimetric Estimation of the Oxalates of Strontium and Barium.

It is well known that calcium may be weighed as the carbonate after a careful ignition of the oxalate, and it would seem probable that strontium might also be weighed as the carbonate. Precipitates of strontium oxalate, on asbestos, were ignited in a capped crucible from 2–8 minutes in the flame of a Bunsen burner and weighed as the carbonate, and in a single case the carbonate thus produced was converted by treatment with sulphuric acid to the sulphate and weighed as such. The results are given in Table VIII, and, while they show slight losses, the results are fairly accurate.

TABLE VIII.

	SrO, taken as $Sr(NO_3)_2$. grm.	SrO, calculated from $SrCO_3$ found. grm.	SrO, calculated $SrSO_4$ found. grm.
1	0·1120	0·1113	----
2	0·1120	0·1116	----
3	0·2435	0·2425	0·2437

Precipitates of barium oxalate were also ignited from 5–10 minutes and weighed as the carbonate. The results are given in Table IX, and are fairly accurate.

TABLE IX.

BaO, taken as $Ba(NO_3)_2$. grm.	BaO, found as $BaCO_3$. grm.	Difference. grm.
0·2912	0·2909	−0·0003
"	0·2901	−0·0011
"	0·2901	−0·0011

The results of this work may be summarized as follows: In the estimation of calcium by titration of the oxalate with permanganate, accurate results may be obtained when hydrochloric acid (with a manganous salt) is used as the solvent. Strontium salts may be precipitated by ammonium oxalate with practical completeness in a solution containing one-fifth its volume of 85 per cent alcohol, and with approximate completeness from water solutions at a dilution not exceeding 250^{cm^3}. Furthermore, strontium oxalate may be titrated by permanganate with accuracy when either sulphuric acid or hydrochloric acid (with a manganous salt) is used to liberate the oxalic acid. Barium salts may be precipitated with practical completeness by ammonium oxalate in a solution containing one-third its volume of alcohol (85 per cent) and the barium oxalate thus obtained may be dissolved in hydrochloric acid and titrated by permanganate after the addition of a manganous salt. Strontium and barium oxalates may be converted to the carbonates by ignition and weighed as such.