ART. XVII.—*The Separation of Iron, Manganese and Calcium by the Acetate and Bromine Methods;* by R. B. RIGGS.

HAVING in hand the analysis of a series of samples containing iron, manganese and calcium in large amounts, it seemed advisable to test the two analytical methods involved, namely, the separation of iron from manganese by precipitating it as a basic acetate, and the separation of manganese from calcium by means of bromine. The object was not so much to test the accuracy of the acetate process as to determine the conditions favorable or otherwise to its successful use. In the case of the manganese-calcium separation on the contrary, the value of the method was in question, for where either or both constituents are present in quantities its accuracy has been doubted.

For convenience and accuracy standardized solutions of the three substances were used. Piano wire was the basis of the ferric chloride solution. This was dissolved in hydrochloric and oxidized by means of nitric acid. The nitric acid was in turn expelled by repeated evaporations with hydrochloric acid. Last traces of ferrous iron were oxidized by bromine. The value of this solution was found by means of a standard* permangate solution.

	Weight of $FeCl_3$ solution taken. grm.	Weight of Fe found. grm.	Weight of Fe in 100 grams of solution. grm.	Mean.
(1.)	20·32	0·14957	0·7378	0·7382
(2.)	20·335	0·15017	0·7385	
(3.)	20·30	0·14957	0·7383	

For the manganese chloride solution, manganese dioxide was the starting point. This was digested with nitric acid, dissolved in hydrochloric and nitric acid—twice evaporated to dryness and filtered—treated three times by the basic acetate process (each time allowing a considerable precipitation of manganese), and recovered from solution each time by a bromine precipitation. The last precipitate was dissolved in hydrochloric acid and the excess of acid expelled by evaporation. This solution was standardized by determining the manganese as pyrophosphate.

	Weight of $MnCl_2$ solution taken grm.	Weight of $Mn_2P_2O_7$ found. grm.	Weight of MnO in 100 grams of solution. grm.	Mean.
(4.)	9·98	0·1346	0·6743	0·6739
(5.)	10·095	0·1360	0·6735	

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* The permanganate solution was standardized with the same wire so that the results are relatively correct.

The solution of calcium chloride was prepared from calcium carbonate purified by repeated precipitations, as carbonate, by means of ammonium carbonate. It was free from iron, alumina and alkalies.

	Weight of $CaCl_2$ solution taken. grm.	Weight of CaO found. grm.	Weight of CaO in 100 grams of solution. grm.	Mean.
(6.)	20·094	0·1133	0·5638	0·5633
(7.)	20·18	0·1136	0·5632	
(8.)	20·19	0·1135	0·5630	

My experiments began with analyses of solutions containing known quantities of the three substances. From this they grew and though the order may be the reverse of a logical one it had best be followed in giving the results.

In the first and second series the quantities of iron and calcium were constant, the manganese was variable. In a third series, containing only manganese and calcium, the proportions of each were varied.

The general mode of operating was the following:

The solutions, containing, in the first and second series, the equivalents of about 0·2 grams of iron and 0·17 grams of calcium oxide and quantities of manganese oxide varying from 0·03 to 0·2 grams, were diluted to 350–400$^{c.c.}$ To secure the usual conditions of analysis, and because ammonium salts tend to hold manganese in solution, 10$^{c.c.}$ of hydrochloric acid were added. The cold solution was neutralized with ammonia containing ammonium carbonate. The precipitate that might be formed was dissolved with as little as possible hydrochloric acid and 5· grams of ammonium acetate[*] added. For the precipitation of the iron and the conversion of the salts of the other elements into acetates, this is an unnecessary excess and because of its possible reducing action on the iron, such an excess should in general be avoided. But, preliminary experiments having been made, it was believed that with proper care the reduction of the iron might be avoided. To further test this opinion and because of the influence of[†] ammonium acetate in holding manganese salts in solution, this excess was added.

Two acetate precipitations were made. The iron was thrown down a third time with ammonia. In but two cases (Nos. 14 and 17) did the third filtrate contain manganese. In making this separation care was taken not to digest the iron precipi-

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[*] The ammonium acetate was prepared by neutralizing ammonia with acetic acid and an amount taken which would be equal to about 5 gr. of the salt.

[†] Experiments seemed to show that the influence of ammonium acetate in holding manganese salts in solution, though the solution be ammoniacal, is somewhat greater than that of the chloride of ammonium.

tate too vigorously nor too long and as a result there was in no case any appreciable reduction.

The filtrates from iron, being united, were evaporated to $400–500^{\text{c.c.}}$, $10^{\text{c.c.}}$ of ammonia, followed by $250–350^{\text{c.c.}}$ of bromine water, were added to the hot solution, which was then heated on the water bath until the precipitate gathered leaving a clear colorless supernatant liquid. If digested over a direct flame the separation may be hastened.

The success of this precipitation depends largely on treating the solution hot. If bromine be added to a cold solution the oxidation is slow and often less complete. The addition of bromine to the solution already made ammoniacal seems preferable to a reversal of the order as it insures a more uniform oxidation.

Three bromine separations were made, the manganese precipitate being dissolved in hydrochloric and sulphurous acids. In no case did the third filtrate show calcium. The first and second filtrates from manganese were united. The volume was reduced to $300–400^{\text{c.c.}}$ and the calcium was thrown down as oxalate and weighed as oxide.

The manganese was weighed as pyrophosphate. The iron was determined by the standard solution of permanganate.

The following are the results.

	Weight of Fe taken. grm.	Weight of Fe found. grm.	Weight of CaO taken. grm.	Weight of CaO found. grm.	Weight of MnO taken. grm.	Weight of MnO found. grm.
(9.)	0·2254	0·2251	0·1699	0·1690	0·0341	0·0355
(10.)	0·2248	0·2251	0·1700	0·1687	0·0680	0·0689
(11.)	0·2252	0·2248	0·1700	0·1696	0·1092	0·1094
(12.)	0·2251	0·2251	0·1700	0·1705	0·1500	0·1501
(13.)	0·2254	0·2253	0·1702	0·1697	0·2043	0·2053

Error in weight of	Fe grm.	CaO grm.	MnO grm.
(9.)	0·0003 —	0·0009 —	0·0014 +
(10.)	0·0003 +	0·0013 —	0·0009 +
(11.)	0·0004 —	0·0004 —	0·0002 +
(12.)	0·0000	0·0005 +	0·0001 +
(13.)	0·0001 —	0·0005 —	0·0010 +

Experience tells us, that in dealing with such precipitates as those of iron and manganese, repeated precipitation is necessary. In analyzing this necessity and determining its limitations a series of partial separations was made, and the quantities of manganese and calcium in each of the several respective filtrates was determined. The iron, of which about 0·22 grams was added in each case, was undetermined.

			Weight of MnO found in				
	Weight of Fe taken. grm.	Weight of MnO taken. grm.	1st filtrate from Fe. grm.	2d filtrate. grm.	3d filtrate. grm.	Total. grm.	Error. grm.
(14.)	0·2248	0·3341	0·0342	0·0005	none	0·0347	0·0005+
(15.)	0·2248	0·0678	0·0681	0·0006	trace	0·0687	0·0006+
(16.)	0·2250	0·1088	0·1073	0·0013	none	0·1086	0·0002—
(17.)	0·2252	0·1500	0·1477	0·0024	none	0·1501	0·0001+
(18.)	0·2253	0·2042	0·2003	0·0034	trace	0·2037	0·0005—

		Weight of CaO found in				
		1st Fe filtrate.		2d Fe filtrate.		
	Weight of CaO taken grm.	1st Mn filtrate. grm.	2d Mn filtrate. grm.	grm.	Total. grm.	Error. grm.
(14.)	0·1700	0·1650	0·0025	0·0020	0·1695	0·0005—
(15.)	0·1700	0·1640	0·0044	0·0010	0·1694	0·0006—
(16.)	0·1702	0·1611	0·0074	0·0013	0·1698	0·0004—
(17.)	0·1700	0·1640	0·0038	0·0016	0·1694	0·0006—
(18.)	0·1701	0·1614	0·0059	0·0023	0·1696	0·0005—

In separating calcium from manganese in the first filtrate from iron three precipitations were made. In no case did the third filtrate contain enough calcium to show.

From the above analyses the necessity of two precipitations in separating manganese from iron and calcium from iron and manganese is evident. More than that seem superfluous.

In general the amount of manganese found in the second filtrate from iron is proportional to its total quantity. It frequently happens however that in neutralizing the solution, preparatory to the acetate separation, the manganese is precipitated and partially oxidized, in which case its resolution is impracticable. This oxidation is probably due rather to the action of the air than to any after effect of acetic acid. In separating manganese and calcium the completeness of a single separation seemed to depend, if anything was to be inferred from the above analyses, as well on the nature of the manganese precipitate as on its quantity.

It will be noticed that the manganese errors, with but one exception (16) are positive and the calcium errors, with one exception (12), are negative. This is to be anticipated. The positive error in the case of manganese comes from the use of a non-volatile precipitant. The negative error of calcium is probably owing to the fact that the oxalate is not absolutely insoluble.

The indications being that two precipitations are necessary, where the calcium and manganese are either or both present in quantities, a series of separations was made varying both constituents. That the conditions of the previous analyses might be approximately kept, 5 grams of ammonium chloride and 10 grams of ammonium acetate were added in each case. Only the calcium of the first manganese filtrate was determined.

	Weight of MnO taken. grm.	Weight of CaO taken. grm.	Weight of CaO found in 1st filtrate. grm.	Loss. grm.
(19.)	0·2042	0·1702	0·1639	0·0063
(20.)	0·1020	0·1705	0·1638	0·0077
(21.)	0·0508	0·1702	0·1662	0·0042
(22.)	0·0207	0·1702	0·1682	0·0018
(23.)	0·2039	0·0848	0·0779	0·0069
(24.)	0·1020	0·0849	0·0831	0·0018
(25.)	0·0516	0·0855	lost	----
(26.)	0·0204	0·0846	0·0833	0·0013
(27.)	0·2037	0·0423	0·0399	0·0024
(28.)	0·1023	0·0427	0·0421	0·0006
(29.)	0·0512	0·0424	0·0415	0·0009
(30.)	0·0203	0·0428	0·0421	0·0007
(31.)	0·2037	0·0171	0·0141	0·0030
(32.)	0·1023	0·0173	0·0158	0·0015
(33.)	0·0509	0·0170	0·0167	0·0003
(34.)	0·0207	0·0171	0·0162	0·0009

These results indicate that the amount of calcium, carried down with the manganese, depends largely on the relative quantities of manganese and calcium. However this may be it is evident that where the amounts of each are not less than 0·02 grams a double precipitation of manganese should be made.

Having introduced such large quantities of ammonium salts into the solutions the question of effect on the oxalate precipitate was raised. Attention has been called to the negative calcium error. Is this due simply to the solubility of the oxalate or is it the sum of large positive* and larger negative errors?

In answer to this suggestion a number of calcium determinations were made, in which the previous conditions, as to quantity of ammonium salts and volume of solution, were observed.

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* The source of positive error would be the reagents and glass ware. The operations, excepting the precipitation of manganese by bromine, were carried on in platinum. The ammonium hydrate and sulphurous acid were freshly prepared. The other reagents were carefully tested.

	Weight of CaO taken. grm.	Weight of CaO found. grm.	Error. grm.
(35.)	0·1136	0·1131	0·0005 —
(36.)	0·1138	0·1135	0·0003 —
(37.)	0·1136	0·1136	0·0000
(38.)	0·1139	0·1137	0·0002 —
(39.)	0·1136	0·1132	0·0004 —
(40.)	0·1138	0·1133	0·0005 —

The solutions 300$^{c.c.}$ contained approximately 5 grams of the chloride, 5 grams of the acetate and 10 grams of the bromide of ammonium. The inference is that their influence in restraining the oxalate precipitation is slight.

Summary: In precipitating iron as basic acetate it is probably better to avoid a great excess of the acetate. A considerable excess need not however interfere with the separation. While an acetate solution favors the reduction of iron, with care this reduction may be avoided. The precipitate should not be digested too vigorously nor too long.

In neutralizing the solution, preparatory to the acetate separation, a slight precipitate of manganese, due to oxidation, is almost always formed. This influences more or less markedly the completeness of a single separation. It cannot be wholly avoided, though the effect of the presence of ammonium salts, in holding manganese salts in solution, is probably beneficial. While the manganese remains in solution oxidation cannot take place.

In precipitating manganese from an ammoniacal solution by means of bromine the presence of acetates is desirable. The oxidation is more rapid, hence more complete than in a solution free from acetates. Bromine water should be added to the hot ammoniacal solution. If the solution be cold the oxidation is slow and in the end often incomplete. The addition of bromine to the solution already made ammoniacal seems preferable to a reversal of this order as it insures a more uniform oxidation.

Where either the calcium or the manganese is in excess of 0·02 grams two precipitations are necessary.

In conclusion it may be said that, in the hands of a careful analyst, both methods are, according to present standards accurate.

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