ANALYSIS OF A FINE MONAZITE SAND FROM BELLEWOOD, NORTH CARO-
LINA.

Silica	1.45
Titanic acid	1.40
Cerium metals as CeO	59.09
Phosphorus pentoxide	26.05
Thoria	1.19
Zirconia, glucina, yttria	2.68
Tantalic acid	6.39
Iron and manganese oxides	0.65
Alumina	0.15
	99.05

The color of this sand was honey-yellow.

LABORATORY OF LEHMANN & GLASER,
BALTIMORE.

[CONTRIBUTIONS FROM METALLURGICAL LABORATORY OF THE OHIO
STATE UNIVERSITY, COLUMBUS, OHIO.]

THE EFFECT OF AN EXCESS OF REAGENT IN THE PRE-
CIPITATION OF BARIUM SULPHATE.

BY C. W. FOULK.
Received July 6, 1896.

"EXCESS of reagent" is a term often used by writers in quantitative chemistry, and the necessity in any given case for adding more of a precipitating reagent than is just sufficient for complete reaction is well known to analysts; but what constitutes such excess, whether it differs for different salts, whether its effect is counteracted by the presence in the solution of other bodies not taking part in the reaction, or whether the effect of such bodies may be counteracted by the addition of a greater amount of precipitant, etc., etc., are questions, the answers to which are difficult to find in chemical literature.

With a view to answer, in part at least, these questions, the following work on the precipitation of barium sulphate was undertaken.

A preliminary experiment, which perhaps is worth noting, was first tried :

A solution of 140 cc. water and five cc. concentrated hydrochloric acid was heated nearly to boiling and 0.1984 gram pure recently ignited barium sulphate was added. This was then stirred up and set aside for one hour, when it was filtered and

the barium sulphate washed well with hot water. The filter and the contents were then ignited and weighed, when it was found that ten milligrams of the sulphate had been dissolved. The filtrate was now divided, and to one-half some sulphuric acid was added, and to the other some barium chloride solution. *A precipitate of barium sulphate was produced in both cases.*

Standard solutions of sulphuric acid and barium chloride were now prepared. These were standardized by precipitation from pure water solutions.

The sulphuric acid used in this work was the chemically pure acid of the laboratory, tested for the ordinary impurities.

The barium chloride was recrystallized from the chemically pure salt.

The hydrochloric acid was the chemically pure acid of the laboratory tested for sulphuric acid.

The graduated ware was calibrated and found to be good.

All the precipitates of barium sulphate were ignited by folding up the moist filter, putting into a platinum crucible, "precipitate end" up and so adjusting the flame that the paper would be charred away without letting the crucible become red hot. Finally the heat was raised and the ignition finished. No lid was used on the crucible. By following this plan no reduction to sulphide need be feared.

A number of the precipitates were moistened with sulphuric acid and ignited. No change was noticed.

In the course of the work the following solutions were made:

<div align="center">

SULPHURIC ACID SOLUTION.

Solution A.

</div>

	cc.		Barium sulphate.
1.	20		0.1978
2.	20		0.1975
3.	20		0.1970
4.	20		0.1978
		Average	0.1970

<div align="center">

Solution B.

</div>

	cc.		Barium sulphate.
1.	50		0.3277
2.	50		0.3271
3.	50		0.3279
		Average	0.3275

Solution C.

cc.		Barium sulphate.
1.	5	0.1944
2.	5	0.1940
	Average	0.1942

Solution D.

cc.		Barium sulphate.
1.	25	0.1544
2.	25	0.1534
3.	25	0.1543
4.	25	0.1538
5.	25	0.1535
6.	25	0.1546
7.	25	0.1539
	Average	0.1542

Rejecting Nos. 2 and 5.

BARIUM CHLORIDE SOLUTIONS.

Solution A.

cc.		Barium sulphate.
1.	20	0.1181
2.	20	0.1812
3.	20	0.1811
4.	20	0.1792
5.	20	0.1802
	Average	0.1805

Rejecting No. 4.

Solution B.

cc.		Barium sulphate.
1.	50	0.1985
2.	50	0.1980
3.	50	0.1086
4.	50	0.1985
	Average	0.1984

Solution C.

cc.		Barium sulphate.
1.	10	0.4004
2.	10	0.4002
3.	10	0.4006
	Average	0.4004

Solution D.

cc.		Barium sulphate.
1.	10	0.3998
2.	10	0.3994
3.	10	0.3996
	Average	0.3996

Note.—The apparent discrepancies in some of the above averages are to be explained by the fact that before beginning the work the burette used had been very carefully calibrated, and the averages were calculated to correct number of cubic centimeters from the readings as given on the burette. In the course of the work this refinement was found to be wholly unnecessary and was therefore disregarded.

The equation of solutions of sulphuric acid and of barium chloride is : Twenty cc. barium chloride solution $=$ 21.8 cc. sulphuric acid. That is, when mixed in these proportions they will, theoretically, mutually precipitate each other and give 0.1970 gram barium sulphate.

The effect of bringing these two solutions together in this proportion was first tried. The barium chloride solution plus water to make the whole volume up to 140 cc. was heated to boiling and the sulphuric acid run in from the burette.

		Barium sulphate.	Error.
1.	20 cc. $BaCl_2A$+21.8 cc. H_2SO_4A	0.1966	—0.0004
2.	20 " " " " "	0.1973	+0.0003
3.	20 " " " " "	0.1979	+0.0009

Solutions of $BaCl_2B$ and H_2SO_4, when brought together in their molecular proportions, weighed as follows :

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2B$+ 30.2 cc. H_2SO_4B	0.1979	—0.0005
2.	50 " " " " "	0.1976	—0.0008

These had stood twenty-two hours before filtration, and the results, while not very close, show at least that in water solutions precipitation is practically complete without the presence of an excess of reagent.

A series of precipitations was now made in order to determine the effect of varying quantities of hydrochloric acid upon the precipitation when the two reagents were brought together in their molecular proportions.

The barium chloride solution, water to make the volume up to 140 cc., and the hydrochloric acid were heated to boiling and the sulphuric acid run in cold from the burette.

The same quantities of barium chloride and sulphuric acid were used as above. The time of standing before filtration is

marked over each set.   Three precipitations were made with each portion of the hydrochloric acid.

SERIES I.

	1. Five cc. hydrochloric acid. Twenty-five hours. Barium sulphate.	2. Ten cc. hydrochloric acid. Twenty-nine hours. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Thirty-three hours. Barium sulphate.	4. Twenty cc. hydrochloric acid. Forty-four hours. Barium sulphate.
1........	0.1908	0.1879	0.1827	0.1875
2........	0.1902	0.1870	0.1844	0.1863
3........	0.1904	0.1881	0.1838	0.1873

It was thought that after standing twenty-four hours precipitation would be complete and a longer time would have no effect. The results of series No. 4 seem to show differently, however. Accordingly another series was run in which the time of standing was regulated.   Otherwise the precipitations were made as above.

These stood twenty-three hours before filtration.

SERIES II.

	1. Five cc. hydrochloric acid. Barium sulphate.	2. Ten cc. hydrochloric acid. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Barium sulphate.
1	0.1902	0.1870	0.1852
2	0.1884	0.1854	0.1849
3	0.1904	0.1846	0.1827

	4. Twenty cc. hydrochloric acid. Barium sulphate.	5. Twenty-five cc. hydrochloric acid. Barium sulphate.	6. Thirty cc. hydrochloric acid. Barium sulphate.
1	0.1832	0.1822	0.1766
2	0.1885	0.1793	0.1833
3	0.1850	0.1789	0.1733

The above results show three things :   (1) That less barium sulphate is precipitated in the presence of larger amounts of hydrochloric acid, but this solubility is not proportional to the amount of hydrochloric acid.   (2) That the greatest variation of results takes place in the presence of the larger amounts of acid.   In other words parallel precipitations don't " check." (3) A much longer time is required to reach the maximum of precipitation in the presence of the larger amounts of hydrochloric acid.   See No. 4, Series I.

The effect of a small excess of sulphuric acid was now tried. Three solutions each containing fifty cc. barium chloride B, sixty cc. water and twenty cc. hydrochloric acid were heated to boiling and the amounts of sulphuric acid B, indicated below, were run in from a burette.

These stood twenty-four hours and weighed as follows:

SERIES III.

								Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ B	+ 31.2 cc. H_2SO_4 B	= 1 cc. excess	= 0.1839	—0.0145
2.	50 " "	+ 32.2 " "	= 2 " "	= 0.1881	—0.0103
3.	50 " "	+ 33.2 " "	= 3 " "	= 0.1971	—0.0013

The filtrates from the above gave no further precipitate on standing several days.

Another series was run, using five cc. hydrochloric acid instead of twenty cc., but conducted otherwise in the same manner except that they stood from Friday to the following Monday and undoubtedly the maximum of precipitation was reached.

SERIES IV.

					Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ B + 31.2 cc. H_2SO_4 B	= 1 cc. excess	= 0.1951	0.0033
2.	50 " " " + 32.2 " " "	= 2 " "	= 0.1963	0.0021
3.	50 " " " + 33.2 " " "	= 3 " "	= 0.1964	0.0020

It was now decided to use larger amouuts of sulphuric acid in excess, but in order to hurry matters along, cut down the time of standing before filtration.

In the following series, accordingly, the barium sulphate was filtered off after standing three hours. The whole volume of solution in each case was 150 cc.

SERIES V.

	Barium chloride B. cc.	Hydrochloric acid. cc.	Sulphuric acid B.	No. of cc. in excess of the theoretical am't for precipitation.	Barium sulphate weighed.	Error.
1	50	15	35.2	5	0.1458	0.0526
2	50	15	40.2	10	0.1590	0.0394
3	50	15	45.2	15	0.1688	0.0296
4	50	15	50.2	20	0.1762	0.0222

A steady increase following the larger amounts of sulphuric acid is seen, but it is to be noted that 30.2 cc. sulphuric acid in

three hours did not bring down so large a precipitation as 31.2 cc. sulphuric acid did in twenty-four hours though in the presence of a larger portion of hydrochloric acid. See Series III.

In order to get comparative results the various conditions of the precipitation had to be more carefully regulated. The above results show this very plainly.

Accordingly, the following problem was set : How great an excess of sulphuric acid is required to precipitate completely as sulphate, the barium from fifty cc. of barium chloride B, in the presence of five cc. hydrochloric acid in one hour, the whole volume of solution, after adding the sulphuric acid, to be 150 cc. ?

Instead of adding a certain number of cc. in excess the sulphuric acid was now measured in equivalents, 30.2 cc. the exact amount to precipitate fifty cc. barium chloride was called one equivalent and different multiples of it were taken.

The barium chloride, water, and hydrochloric acid were heated on the water-bath and the sulphuric acid run in cold from the burette.

SERIES VI.

	Barium chloride B. cc.	Hydro- chloric acid. cc.	Sul- phuric acid B.	Eqivalents sul- phuric acid.	Barium sulphate.	Error.
1	50	5	37.8	1.25	0.1564	0.0420
2	50	5	45.3	1.50	0.1624	0.0360
3	50	5	52.8	1.75	0.1784	0.0200
4	50	5	60.4	2.00	0.1857	0.0127
5	50	5	68.9	2.25	0.1842	0.0142

The fact that No. 5 was lower than No. 4 was referred to the lowering of temperature produced by the addition of the sixty-eight cc. cold sulphuric acid.

The following plan was now adopted :

The sulphuric acid was measured out into beakers and also heated on the water-bath. It was then added to the barium chloride solution, the beakers being washed out three times with hot water, using about four or five cc. each time and the washings also added.

SERIES VII. (Continued from above.)

	Barium chloride B. cc.	Hydro-chloric acid. cc.	Sul-phuric acid B.	Equivalents sulphuric acid.	Barium sulphate.	Error.
6	50	5	67.9	2.25	0.1931	—0.0053
7	50	5	75.5	2.50	0.1935	—0.0049
8	50	5	83.0	2.75	0.1956	—0.0028
9	50	5	90.5	3.00	0.1963	—0.0021
10	50	5	39.4	4.00	0.1961	—0.0023
11	50	5	49.2	5.00	0.1962	—0.0022

Note.—The last two results were obtained with a stronger sulphuric acid solution, which was run in cold.

A rapid increase is seen with the first additions of sulphuric acid, the difference becoming less as the sulphuric acid increases.

Another peculiarity was also seen in each one of these series. Although the solutions had been well stirred on bringing the reagents together, had settled clear in a few minutes, and the supernatant liquid had remained clear, yet in running through the filter the filtrates soon became cloudy and a copious precipitate of barium sulphate settled out.

This could be due only to the agitation produced by running through the filter. Later an experiment was tried on this point. Fifty cc. of barium chloride solution, 0.0992 barium sulphate + five cc. hydrochloric acid and water to make the total volume up to 150 cc., was heated in a flask and two equivalents of sulphuric acid added. This was then shaken for ten minutes, allowed to settle for fifty minutes, and then the precipitate was filtered off and weighed.

It gave barium sulphate 0.1979, a minus error of 0.0013 as against an error of —0.0127 in Series VI, with two equivalents.

It seems that in the presence of hydrochloric acid unless there is a sufficient amount of sulphuric acid present to effect complete precipitation, a delicate balance is formed which is affected by a difference in time of standing, in temperature, and amount of agitation on stirring. To avoid adding so large a volume of sulphuric acid solution " C " was prepared.

Series VIII was now run. Both solutions were heated on the water-bath and brought together as described above. Solution

in each case was stirred one and one-half minutes and allowed to settle one hour.

SERIES VIII.

	Barium chloride B. cc.	Hydro-chloric acid. cc.	Sul-phuric acid C. cc.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	20.4	4	0.1971	—0.0013
2	50	5	25.5	5	0.1978	—0.0006
3	50	5	30.6	6	0.1981	—0.0003
4	50	5	35.7	7	0.1980	—0.0004
5	50	5	40.8	8	0.1984	0.0000
6	50	5	45.9	9	0.1985	+0.0001
7	50	5	51.0	10	0.1984	0.0000
8	50	5	56.1	11	0,1985	+0.0001

At last the proper excess to effect complete precipitation under the conditions described above had been found. Seven or eight times the theoretical amount seems necessary. It is to be noted that the change is extremely slow when near the critical point.

A short series was precipitated and weighed, using other solutions, the equation of which was as follows :

Fifty cc. $BaCl_2$, $x = 1$ cc $\pm$ H_2SO_4 $D = 0.1992$ $BaSO_4$.
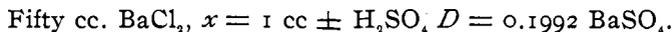
SERIES IX.

	Barium chloride x. cc.	Hydro-chloric acid. cc.	Sul-phuric acid D. cc.	Equiva-lents sul-phuric acid.	Barium sulphate.	Error.
1	50	5	3	3	0.1957	—0.0035
2	50	5	4	4	0.1992	0.0000
3	50	5	5	5	0.1983	—0.0009
3	50	5	5	5	0.1992	0.0000

In this series the sulphuric acid was run in cold.

The maximum amount of precipitate seems to be reached here with less sulphuric acid than when a more dilute solution was used. The same is true of the precipitations made in the presence of ten cc. hydrochloric acid.

Series X was now run, the precipitations being made in exactly the same manner as those of Series VIII, except that ten cc. of hydrochloric acid was put into the solutions instead of five cc.

SERIES X.

	Barium chloride B. cc.	Hydro-chloric acid. cc.	Sul-phuric acid C.	Equiva-lents sul-phuric acid.	Barium sulphate.	Error.
I	50	10	30.6	6	0.1964	—0.0020
2	50	10	35.7	7	0.1974	—0.0010
3	50	10	40.8	8	0.1981	—0.0003
4	50	10	45.9	9	0.1982	—0.0002
3	50	10	40.8	8	0.1970	—0.0014
4	50	10	45.9	9	0.1982	—0.0002

In the presence of ten cc. hydrochloric acid then, a somewhat greater excess of sulphuric acid is required than with five cc. hydrochloric acid.

A short series with the stronger solution gave

SERIES XI.

	Barium chloride B. cc.	Hydro-chloric acid. cc.	Sul-phuric acid D.	Equiva-lents sul-phuric acid.	Barium sulphate.	Error.
I	50	10	5	5	0.1975	—0.0017
2	50	10	6	6	0.1982	—0.0010
3	50	10	7	7	0.1992	0.0000
3	50	10	7	7	0.1991	—0.0001

Series XII. was conducted exactly as Nos. VIII. and X., excepting that fifteen cc. hydrochloric acid was used.

SERIES XII.

	Barium chloride B. cc.	Hydro-chloric acid. cc.	Sul-phuric acid C.	Equiva-lents sul-phuric acid.	Barium sulphate.	Error.
I	50	15	30.6	6	0.1957	—0.0027
2	50	15	35.7	7	0.1955	—0.0029
3	50	15	40.8	8	0.1965	—0.0019
4	50	15	45.9	9	0.1973	—0.0011
5	50	15	51.0	10	0.1972	—0.0012
6	50	15	56.1	11	0.1984	0.0000
7	50	15	61.2	12	0.1983	—0.0001

The point to be noted in this series is that more sulphuric acid is required in the presence of the larger amount of hydrochloric acid.

The other side of the question was now taken up, namely, the precipitation of sulphuric acid with an excess of barium chloride in the presence of hydrochloric acid.

A new difficulty at once presented itself. The old trouble in filtering barium sulphate was experienced. When a small amount of hydrochloric acid was present it was found utterly impossible to do it under the conditions which had previously been followed.

Various experiments were made to avoid this trouble and at last the following scheme was adopted :

The volume was kept at 150 cc. as in the other work. The sulphuric acid, water, and hydrochloric acid were heated on the water-bath and the barium chloride solution, also hot, was added drop by drop with constant stirring. The beakers were then set back on the bath and the solutions stirred at intervals for thirty minutes. They were then set off and stirred at intervals again until cold.

Just before pouring upon the filter the precipitate was stirred up and the filter filled several times. At first a small portion ran through, but this was poured back, and, generally, the rest could be filtered without trouble.

A series was run according to this description, except that the volume was 250 cc.

The exact time of standing before filtering was not noted in this case. It was probably about four or five hours.

SERIES XIII.

	Sul- phuric acid B.	Hydro- chloric acid.	Barium chloride C.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1967	—0.0017
2	30.2	10	19.8	4	0.1959	—0.0025
3	30.2	10	14.9	5	0.1965	—0.0019

There was nothing satisfactory to be derived from this series, so Series XIV was run. The volume here was kept down to 150 cc.

SERIES XIV.

	Sul- phuric acid B.	Hydro- chloric acid.	Barium chloride C.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1975	—0.0009
2	30.2	10	19.8	4	0.1994	+0.0010
3	30.2	10	24.9	5	0.1983	—0.0001
4	30.2	10	29.8	6	0.2005	+0.0021

Two of these precipitates weigh heavier than theory demands. This could come only from contamination with barium chloride. To test this No's 3 and 4 were transferred to beakers, boiled up with about seventy-five cc. of water and again filtered, ignited, and weighed.

They then gave

    3. 0.1980 barium sulphate = —0.0004 error.
    4. 0.1987   ‘‘   ‘‘   = +0.0003   ‘‘

Another series was run in exactly the same manner, except that more care was taken in washing. Each precipitate was washed with boiling water until the filtrate no longer reacted with silver nitrate.

SERIES XV.

	Sulphuric acid B.	Hydrochloric acid.	Barium chloride C.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.				
1	30.2	10	9.9	2	0.1965	—0.0019
2	30.2	10	14.9	3	0.1982	—0.0001
3	30.2	10	19.8	4	0.1975	—0.0008
4	30.2	10	24.9	5	0.1988	+0.0004
5	30.2	10	29.8	6	0.1994	+0.0010

No's 4 and 5, on being boiled up with water and reweighed, gave

    3. 0.1981 = —0.0003 error.
    4. 0.1975 = —0.0009   ‘‘

At its best, however, this method of working was unsatisfactory. The precipitate seemed always on the point of running through the filter and indeed traces generally did go through. The following scheme was accordingly tried in Series XVI.

The volume was kept as before at 150 cc., but thirty cc. of hydrochloric acid instead of ten was put into each solution. The precipitates were not stirred up after being thrown down. In presence of this large excess of acid the precipitates soon became coarse and crystalline and settled rapidly. *No trouble whatever was experienced in filtering them.*

SERIES XVI. (These had stood about four hours.)

	Sulphuric acid E.	Hydrochloric acid.	Barium chloride C.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.				
1	20	30	4.6	1.5	0.0947	—0.0289
2	20	30	6.2	2.0	0.0997	—0.0239
3	20	30	9.3	3.0	0.1114	—0.0122
4	20	30	12.4	4.0	0.1169	—0.0067
5	20	30	15.5	5.0	0.1207	—0.0029
6	20	30	18.6	6.0	0.1192	—0.0044

These filtrates, on standing over night, all showed further precipitates of barium sulphate. The series was accordingly continued, this time the solutions standing about seven hours before being filtered.

The precipitates were crystalline and filtered easily and rapidly and the filtrates, on further standing, showed no traces of barium sulphate.

In spite, however, of the greatest care in washing, it was impossible to get rid of the occluded barium chloride before ignition.

SERIES VII.

	Sulphuric acid E.	Hydrochloric acid.	Barium chloride C.	Equivl's Barium chloride.	Barium sulphate.	Error.
1	20	30	18.6	6	0.1258	+0.0022
2	20	30	21.7	7	0.1252	+0.0016
3	20	30	24.8	8	0.1268	+0.0032
4	20	30	27.9	9	0.1260	+0.0024

Nos. 2, 3 and 4 were boiled up with water, rewashed, ignited and weighed.

	Barium sulphate.	Error.						
2	0.1236	0.0000	Filtrate reacted strongly with silver nitrate.					
3	0.1238	+0.0002	"	"	"	"	"	"
4	0.1253	+0.0017	"	"	slightly	"	"	"

No. 4 boiled up the second time 0.1237 $BaSO_4 = + 0.0001$ error. The filtrate in this case reacted strongly with silver nitrate.

To test this boiling up process No. 4 was treated the third time. This time the precipitate weighed 0.1235 and the filtrate did *not* react with silver nitrate.

A last experiment was made to determine the effect of barium

chloride upon the direct solubility of barium sulphate in hydro-chloric acid.

0.1248 gram barium sulphate was put in 120 cc. water and thirty cc. hydrochloric acid and beaker marked "*A*."

0.1228 gram barium sulphate was weighed into another beaker with 105 cc. water, thirty cc. hydrochloric acid and fifteen cc. barium chloride *C*. This beaker was marked "*B*."

Both were heated on the water-bath with frequent stirring and then stood over night.

On being filtered and weighed,

> "*A*" gave —0.1106 barium sulphate = 0.0142 loss.
> "*B*" " —0.1228 " " = 0.000 "

To further test precipitate "*B*" it was boiled up with water as those of Series XVII, and re-weighed. It lost by this oper-ation 0.0002, which is practically nothing.

From the results obtained in this investigation the following conclusions seem justified :

(1) In the precipitation of a barium salt with sulphuric acid in the presence of hydrochloric acid, a very large excess of sul-phuric acid is required.

(2) This excess should be greater the greater the amount of hydrochloric acid present in the solution.

(3) It should be greater the shorter the time of standing before filtration. In fact a very great excess seems to effect immediate precipitation.[1]

(4) The greater the excess of sulphuric acid the less stirring seems necessary to bring down the precipitate in a given time.

(5) While barium sulphate obtained by precipitating a barium salt with sulphuric acid in the presence of hydrochloric acid is coarse, crystalline and easily filtered,[1] that obtained by precipi-tating sulphuric acid with a barium salt in the presence of hydrochloric acid is fine and much disposed to run through the filter unless special precautions are taken.

(6) In general a large excess of barium chloride is required to completely precipitate the sulphuric acid in the presence of hydrochloric acid.

[1] *J. Anal. Appl. Chem.*, 5, 278.

(7) As the hydrochloric acid increases the amount of barium chloride should also be increased.

(8) The greater the amount of hydrochloric acid present the coarser and more crystalline in character is the precipitated barium sulphate. In precipitating in the presence of large amounts of hydrochloric acid the solution should be quite concentrated.

(9) The barium sulphate so obtained, will, however, be contaminated with adhering barium chloride, and no amount of washing before ignition can entirely free it from this occluded chloride. If, after ignition, the precipitate be boiled up with water, again washed, ignited and weighed, and this process be continued until a constant weight is obtained, the sulphate may be entirely freed from the barium salt.

Some subsequent work in this line has shown that heavy precipitates sometimes require three or four treatments before a constant weight is obtained.

(10) Both in the precipitation of barium with sulphuric acid and of sulphuric acid with barium, very concordant results may be obtained if the conditions under which the precipitations are made are similar, but these results may be quite far from correct. A note of this commonplace occurrence in analytical work is made here, because by following the usual method of testing the filtrate for an excess of the precipitating reagent, a strong reaction might be obtained and yet not more than ninety per cent. of the original precipitate be down.

In conclusion I wish to express my thanks to Professor N. W. Lord for helpful suggestions during the course of this work.

DISCUSSION.[1]—T. S. Gladding : I have already shown (see this Journal, **16,** 398 ; **17,** 181, 397, 772 ; **18,** 446) that correct results may be obtained if the barium chloride solution be added drop by drop instead of all at once. This is confirmed by Lane (**18,** 682) and is now virtually admitted by Lunge, who precipitates (**18,** 686) by "quick additions (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do.)"

[1] Buffalo Meeting. Aug., 1896.