zinc; the mean of the only rapid analyses of solution A where the precipitation was complete (Nos. 1, 3 and 5, Table 4) is 0.1983 g. In the case of the other solutions (B and C) the mean of all the determinations where complete precipitation was assured (except Nos. 5 and 8, Table 5), was assumed to be the correct value and the error calculated on this basis.

The deposit was generally of a fine steel-gray color and metallic luster. It was noticed that the character of the precipitate is very dependent on the surface of the cathode; on one cathode which had been treated for a long time with acids and thus had its surface roughened, the precipitate was always of a dark color and had a tendency to oxidize, as shown by experiments 5 and 8 (Table 5), where this cathode was used.

Summary.

1. With electromagnetic rotation of the electrolyte 0.1 g. zinc can be completely precipitated by 4.5 amperes in 30 minutes on a nickel gauze cathode. About 8 g. of sodium hydroxide should be used, and the electrolysis should be conducted at as low a temperatue as possible.

2. For quantities of zinc up to 0.2 g. the current-strength should be 4.5 amperes for 15 minutes and then about 1.5 amperes for 20 minutes. (Other conditions are the same as in 1).

3. The testing of the liquid remaining after electrolysis is essential.

4. It is highly improbable that complete precipitation of 0.2 g. zinc can be obtained with 5 amperes in 15-20 minutes, as stated by Exner and Ingham. From the results obtained it would also seem improbable that the concordant results obtained by Miss Languess with 10-13 amperes in 3 minutes represent complete precipitation.

The work on which this and the preceding articles are based was done during the spring and summer of 1907 in the electro-chemical laboratory of the Royal Technical High School at Berlin. I take this occasion to thank Professors von Knorre and Peters, and Dr. Arndt, of that laboratory, for their interest in this work and the many kindnesses shown me during its course.

UNIVERSITY OF MINNESOTA,
Minneapolis, Minn.,
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CLAY ANALYSIS—AN EXAMINATION OF THE RESIDUE LEFT AFTER VOLATILIZATION OF THE SEPARATED SILICA WITH HYDRO-FLUORIC AND SULPHURIC ACIDS.

First Paper.

BY W. R. BLOOR.

It has been generally assumed that the residue left after volatilization of the separated silica with hydrofluoric and sulphuric acids in the ordinary process of clay analysis is composed of iron and aluminium oxides and as such is to be added in with them.

With the view of testing the correctness of this assumption, an examination was made of a number of these residues, obtained in the course of a series of analyses of clays of the State of Washington. The method used in separating the silica was that outlined in Bulletins 176 and 305, U. S. Geol. Survey, special precautions being taken to ensure complete fusion. From 6·8 g. of sodium carbonate per gram of clay were used and the fusion was continued with frequent rotation of the crucible for fifteen minutes after the melt was quiescent. The silica was obtained by double evaporation (to approximate dryness except in Nos. 1, 5, 7 and 10, which were allowed to dry for three hours at 125°), with intervening filtration, and washed until the washings gave no cloudiness with silver nitrate solution. After blasting to constant weight, it was moistened with water and sulphuric acid and volatilized with hydrofluoric acid. The weighed residue was fused with potassium bisulphate and taken up with water and a little sulphuric acid. Any residue was filtered off and weighed as insoluble matter. Fe_2O_3 and Al_2O_3, etc., were determined in the usual manner. CaO was obtained by double precipitation. The first precipitation was generally slow and was allowed a day or so to complete. The precipitate was filtered off, dissolved in dilute hydrochloric acid and reprecipitated, the second precipitation taking place immediately. MgO was obtained as usual. TiO_2 was found in all cases where it was present in the clay, but was not determined. Blanks were run for all reagents.

All the samples mentioned in the following table were ordinary clays with the exception of Nos. 10 and 11, which were argillaceous limestones.

The average composition of the residue as drawn from the accompanying table is: Fe_2O_3, Al_2O_3, etc., (precipitable by ammonia in presence of ammonium salt) 57.36%; CaO, 21.48%; MgO, 14.05%. The residue averages 1.01% of the separated silica.

In Nos. 1, 5, 7 and 10 the mass was allowed to dry for three hours on a hot plate at 125° with the result that while there was an increase in the total residue of about 40% the amount of Fe_2O_3 and Al_2O_3 was increased only about 7%. Later experiments also go to show that drying at this temperature does not materially increase the amount of Fe_2O_3 and Al_2O_3 in the residue.

When the residue compared with the silica is large (Nos. 1, 2, 3, 5, 7, 10 and 11) the percentage of Fe_2O_3 and Al_2O_3 present, is larger, but not markedly so (increase of 4½%).

When the per cent. of CaO is high in the original sample (Nos. 3, 4, 8, 9, 10, 11, 13, 14, 16, 17, 20, 21 and 22—averaging 2.01%) the percentage of Fe_2O_3 and Al_2O_3 in the residue is lower (decrease of 4%), while the percentage of CaO is somewhat higher (7% increase), than the average.

No.	Silica content of 1 gm. of clay	Total residue by weight	Al$_2$O$_3$ etc.	F$_2$O$_3$	Al$_2$O$_3$, Fe$_2$O$_3$ % total residue	CaO	CaO % total residue	MgO	MgO % total residue	Residue insoluble in KHSO$_4$, H$_2$SO$_4$	Total residue by addition	Residue % of original SiO$_2$	No.
1	0.5324	0.0072	0.0023	0.0008	43.66	0.0007	9.72	0.0022	30.55	0.0006	0.0071	1.35	1
2	0.5724	0.0062	0.0006	0.0020	41.94	0.0005	8.06	0.0014	22.58	0.0007	0.0052	1.08	2
3	0.6374	0.0080	0.0018	0.0020	54.30	0.0020	28.57	0.0007	10.00	0.0005	0.0070	1.02	3
4	0.6244	0.0036	0.0000	0.0010	30.00	0.0004	12.12	0.0014	42.12	0.0009	0.0033	0.58	4
5	0.5260	0.0074	0.0028	0.0018	64.00	0.0020	28.17	0.0000	0.00	0.0005	0.0071	1.40	5
6	0.5703	0.0046	0.0006	0.0018	52.17	0.0013	22.73	0.0000	0.00	0.0005	0.0042	0.80	6
7	0.6144	0.0080	0.0025	0.0031	71.80	0.0008	10.25	0.0012	15.38	none	0.0078	1.30	7
8	0.5496	0.0040	0.0020	0.0014	83.00	0.0007	17.07	0.0000	0.00	"	0.0041	0.73	8
9	0.5964	0.0051	0.0029	0.0010	88.63	0.0000	0.00	0.0005	11.36	"	0.0044	0.85	9
10	0.1434	0.0078	0.0025	0.0039	80.00	0.0011	13.75	0.0005	6.25	"	0.0080	5.40	10
11	0.1420	0.0037	0.0005	0.0029	76.44	0.0008	17.77	0.0003	6.60	"	0.0045	2.60	11
12	0.8076	0.0027	0.0014	0.0000	53.85	0.0009	34.60	0.0006	11.54	"	0.0026	0.33	12
13	0.5876	0.0028	˙0.0006	0.0000	20.69	0.0017	58.62	0.0005	20.69	"	0.0029	0.48	13
14	0.5787	0.0013	0.0000	0.0000	0.00	0.0012	70.59	0.0005	29.41	"	0.0017	0.22	14
15												0.54	15
15	0.7455	0.0043	0.0024		60.00	0.0010	25.00	0.0006	15.00	"	0.0040		
16	0.5805	0.0027	0.0010		40.00	0.0008	32.00	0.0004	16.00	0.0007	0.0029	0.46	16
17	0.6249	0.0019	0.0010		43.42	0.0013	56.52	0.0001	0.43	none	0.0023	0.30	17
18	0.5660	0.0036	0.0029		85.30	0.0002	5.88	0.0003	8.82	"	0.0034	0.68	18
19	0.6612	0.0020	0.0020		100.00	0.0000	0.00	0.0000	0.00	"	0.0020	0.30	19
20	0.6324	0.0050	0.0043		93.48	0.0003	6.52	0.0000	0.00	"	0.0046	0.79	20
21	0.6316	0.0026	0.0011		37.93	0.0013	44.83	0.0005	17.24	"	0.0029	0.41	21
22	0.6186	0.0038	0.0015		41.66	0.0005	13.88	0.0016	44.44	"	0.0036	0.61	22

Taking the results as a whole and in spite of the fact that the quantity of material in each case is small, and the liability to error, consequently great, the average results show a suprising constancy and justify the conclusion that in the analysis of clay by the method outlined above, the silica so separated is contaminated to some degree by the main constituents of the clay. The amount of contamination by substances other than Fe_2O_3 and Al_2O_3 is however, except in extreme cases, so small that it may be neglected unless extreme accuracy is required.

W. F. Hillebrand[1] states as follows: "Quite as rarely (as barium) is calcium or magnesium ever a component of the residue, if the decomposition of the rock powder was complete at the outset." Since the results obtained differ almost entirely from this statement, it was thought well to consider some of the possibilities of error in the experiment. The main ones may be summed up as follows: (1) insufficient washing of the separated silica; (2) incomplete decomposition of the clay at the outset; (3) evaporation in porcelain may have induced contamination; (4) different action of clay and rock powder in fusion or subsequent treatment. The first two may be dismissed as following in the main the general usage in silicate analysis. The third possibility was made the subject of a second series of experiments. A sample of ordinary clay was taken and prepared very carefully. After fusion in the regular way duplicate samples were evaporated in porcelain (Royal Berlin) and in platinum dishes, the silica volatilized and the residues analyzed as before. The results as yet are not sufficiently definite to throw any light on the point in question.

PULLMAN, WASH.

THE CONSTANTS AND VARIABLES OF THE PARR CALORIMETER.

BY S. W. PARR.

The calorimeter using sodium peroxide as a medium of combustion was first described in the October number of this Journal[2], 1900.

The chief element in the process as outlined at that time was the establishment of the ratio between the true heat of combustion of the fuel used and the total heat of the reaction developed by the process. For example, if the total indicated heat of a hydrocarbon, burning in a closed chamber by means of sodium peroxide were found to be 10,000 calories, then the true heat of combustion would be 7300 calories, and the other 2700 units would represent the heat of combination of the carbon dioxide and water with the chemical employed. The constant, therefore, representing the part of the reaction which was to be credited to combustion, was 73 per cent. This factor was determined empirically

[1] Bull., **305**, U. S. Geol. Survey, 80.

[2] This Journal, **22**, 646.