DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 78

BURNT REFRACTORY

[All results are based on a sample dried for one hour at 105 to 110° C.]

ANALYSTS	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	MgO	CaO	K_2O	Na_2O	P_2O_5	V_2O_5	Loss on ignition
1	20. 78	{ 69. 81[a] / 69. 90[b] }	0. 73	3. 34	0. 12	0. 52	0. 32	2. 90	0. 54	0. 61	0. 04	0. 27
	20. 56	69. 93	1. 17[c]	3. 18[c]	. 09	. 70[c]	. 51	2. 55[c]	. 77[c]	. 57	. 07	. 19[c]
	22. 00[c]	69. 00[c]	1. 04	3. 68[c]		. 32[c]	. 48	2. 68	. 38[c]			. 34[c]
4	20. 65	69. 98	. 75	3. 30	. 12	. 51	. 34	2. 96	. 50	. 64	. 035	
5	20. 85	70. 20	. 72	3. 39	. 13	. 38	. 20[c]	2. 73	. 58	. 58		. 24
6	20. 60	69. 88	. 75	3. 40		. 53	. 24	2. 83	. 54	. 66		. 27
7	20. 70	70. 41	. 70	3. 45		. 58	. 40	3. 06[c]	. 50			. 26
8	20. 69	69. 67	. 84	3. 34	. 12	. 51	. 40	2. 88	. 50	. 63	. 044	. 28
Averages	20. 69	69. 97	. 79	3. 37	. 12	. 51	. 38	2. 83	. 53	. 62	047	. 26

[a] Alumina obtained by weighing the ignited ammonia precipitate and subtracting the weight of the coprecipitated oxides.

[b] Alumina obtained by subtracting the coprecipitated P_2O_5 and V_2O_5 in the weighed ignited precipitate obtained after separation with sodium hydroxide, acidification of the filtrate, and precipitation with ammonia.

[c] Omitted from the average.

Analyst No. 8 found 0. 005 per cent MnO.

LIST OF ANALYSTS

1. James I. Hoffman, Bureau of Standards.
2. Carl Doering, The U. G. I. Contracting Co., Philadelphia, Pa.
3. W. M. Stedman, Baltimore & Ohio R. R. Co., Baltimore, Md.
4. Mariner & Hoskins, Chicago, Ill.
5. C. E. Nesbitt, Carnegie Steel Co., Braddock, Pa.
6. H. H. Craver, Pittsburgh Testing Laboratory, Pittsburgh, Pa.
7. J. M. Lindgren, technical analyst, Applied Chemistry Testing Work Department, University of Illinois, Urbana, Ill.
8. L. P. Chase, Illinois Steel Co., South Chicago, Ill.

GEORGE K. BURGESS,
Director.

Washington, D. C
March 15, 1927

*See attached sheet for revised values for Na_2O and Li_2O. (3-1-1955)

METHODS OF ANALYSIS USED AT THE BUREAU OF STANDARDS

[Most of the cooperating analysts used essentially the same methods for silica, alumina, and iron as are here given, but varied considerably in detail in the methods used for the other constituents. Analyst No. 8 put the sample into solution by fusion with pyrosulphate.]

Drying.—Dry for one hour at 105 to 110° C.

Solution of the sample.—Thoroughly mix 0.5000 g of the dried sample with 7 to 8 g of sodium carbonate in a platinum crucible and cover the mixture with an additional gram of sodium carbonate. Gradually heat the covered crucible and its contents until the mass is molten, and then apply the full heat of a Meker or Fischer burner for one hour. Cool, and dissolve the melt in a covered platinum dish in 200 cc of 10 per cent (by volume) hydrochloric acid. If there is any indication of undecomposed sample, filter the solution, and wash the residue with water. Ignite the paper and residue in the same crucible as was used for the fusion, and fuse the residue with a small amount of sodium carbonate. Dissolve the cooled melt in dilute hydrochloric acid and add the solution to the original filtrate

Determination of Silica.—Evaporate the solution of the melt to dryness and dehydrate in an oven at a temperature of 105 to 120° C. for one-half hour. Take up the dry mass in 150 cc of dilute hydrochloric acid (5 per cent by volume), heat until the salts are in solution and immediately filter through a No. 40 Whatman or similar paper. Wash very thoroughly with dilute hydrochloric acid (5 per cent by volume) and finally with hot water. It is very important that the silica be washed free from sodium salts. Repeat the dehydration and filtration. Reserve the filtrate for the determination of alumina. Dry the two papers in a platinum crucible, heat so that the papers char without inflaming, burn the carbon at a low temperature, and finally heat at 1,200° C. in a covered crucible. Cool in a desiccator containing a good desiccant, such as fresh sulphuric acid, not calcium chloride, and quickly weigh the covered crucible. Repeat the heating until constant weight is obtained.

After constant weight has been attained, carefully moisten the silica in the crucible and add a few drops of sulphuric acid (1:1) and 10 to 20 cc of hydrofluoric acid. Evaporate, carefully expel the sulphuric acid, and again ignite to constant weight. The difference between the two weights is SiO_2. To this must be added the silica recovered from the iron, alumina, etc. (Described below.)

Determination of Alumina.—Fuse the nonvolatile residue from the silica with a small quantity of alkali pyrosulphate, cool, take up the melt in water and add it to the filtrate from the silica determination. Dilute this solution to 350 cc, add a few drops of methyl red indicator, heat to boiling and add ammonium hydroxide until the red color just changes to a light yellow. Boil for 1 to 3 minutes, and if the red color of the indicator reappears, discharge it by adding more ammonium hydroxide. Immediately filter through a No. Whatman or similar paper and wash five times with hot 5 per cent ammonium chloride solution. Return the precipitate to the beaker in which the precipitation was made by cautiously washing it off the paper with a strong jet of water, place the beaker under the funnel, and then pour 50 cc of hot dilute hydrochloric acid (1:1) through the paper. After the acid treatment the paper must be thoroughly washed with hot water, and owing to the fact that a small amount of aluminum may still remain in the paper, this paper should be reserved and ignited with the alumina.

Repeat the precipitation, filtration, and washing as before. If the precipitate is too large to handle in the crucible, dry the paper and contents on a watch glass and then transfer it carefully to a platinum crucible, which has been weighed with the cover. Heat carefully so that the paper chars without inflaming, burn the carbon at as low a temperature as possible, and finally cover and heat at 1,200° C. Cool in a desiccator containing a good desiccant, such as fresh sulphuric acid, never calcium chloride. Weigh quickly while covered. Repeat the heating until constant weight is obtained. The precipitate contains th Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, and V_2O_5 which w present in the sample besides the SiO_2 which escap

the double dehydration. These substances must be determined and subtracted to arrive at the true weight of alumina.

Recovery of Silica.—Fuse the mixed oxides with alkali pyrosulphate, cool and dissolve the melt in 100 cc of 10 per cent (by volume) sulphuric acid. Evaporate to incipient fumes of sulphuric acid, cool, add 150 to 200 cc of warm water, heat until the salts are in solution, and immediately filter off the small amount of silica. Ignite, weigh, treat with hydrofluoric and sulphuric acids as previously described, and again weigh. Add this silica to that previously obtained. Fuse the small nonvolatile residue with a pinch of pyrosulphate, dissolve the cooled melt in a little dilute sulphuric acid and add the solution to the main one.

Determination of Phosphorus (P_2O_5) and Vanadium (V_2O_5).—Nearly neutralize the filtrate obtained in the silica recovery with sodium hydroxide and pour this solution slowly and with constant stirring into 150 cc of a 10 per cent solution of sodium hydroxide containing 1.0 g of sodium peroxide. Digest on the steam bath for one hour, cool and filter through a ter which has previously been treated with sodium ydroxide of the same strength. Wash moderately with hot water. Reserve the precipitate for the determination of iron, titanium, and zirconium.

The filtrate contains the vanadium and phosphorus and will also contain chromium as chromate when this element is present. If present, determine chromium colorimetrically in the alkaline filtrate. Then acidify with nitric acid and determine vanadium colorimetrically by development of the color with peroxide.

Destroy the peroxide by boiling, dilute to 200 cc with water, precipitate the aluminum with a slight excess of ammonium hydroxide and filter. The aluminum hydroxide will carry down the P_2O_5 and V_2O_5. Dissolve the precipitate in nitric acid and precipitate the phosphorus by molybdate with no regard to vanadium which in these refractories is too small in amount to influence the precipitation. Finish the determination by dissolving the yellow precipitate in ammonium hydroxide, reprecipitating with magnesia mixture and weighing as $Mg_2P_2O_7$. The alkalimetric method is also satisfactory.

Determination of the Oxides of Iron, Titanium and Zirconium.—Dissolve the precipitate reserved for e determination of iron, titanium and zirconium in 25 cc of hot dilute hydrochloric acid (1:2), dilute with water to a volume of 200 cc, heat nearly to boiling and saturate with hydrogen sulphide. Allow to cool, filter and wash any platinum sulphide which may have separated with a 1 per cent solution of sulphuric acid saturated with hydrogen sulphide. To the filtrate and washings add 5 to 8 g of tartaric acid and render the solution slightly ammoniacal. Now gas with a rapid stream of hydrogen sulphide for five minutes, allow to settle at the side of the steam bath, filter and wash the precipitate with a dilute solution of ammonium sulphide containing 5 g of ammonium chloride per liter. Do not let the paper run dry, and cover the funnel between additions of the solution. Reserve the filtrate for the determination of titanium and zirconium.

Dissolve the iron sulphide in hot dilute hydrochloric acid (1:1) to which has been added a little potassium chlorate, evaporate the solution to dryness, take up the residue in 25 cc of 5 per cent (by volume) hydrochloric acid, and determine iron by the Zimmermann-Reinhardt method.

The filtrate from the ammonium sulphide precipitation contains the titanium and zirconium. Precipitate these with cupferron, in a cold sulphuric acid solution (10 per cent by volume), wash with cold hydrochloric acid (10 per cent by volume) and *very cautiously* dry in a weighed platinum crucible. Char the paper, burn the carbon and finally ignite at 1,200° C. Weigh as TiO_2+ZrO_2. It is not necessary to destroy tartaric acid preliminary to the cupferron precipitation. (See Lundell and Knowles, J. Am. Chem. Soc., **42**, 1439–1448; 1920.) Fuse the titania and zirconia with pyrosulphate, dissolve in 100 cc of dilute sulphuric acid (10 per cent by volume), add hydrogen peroxide, and 0.5 g of diammonium phosphate. Allow to stand beside the steam bath over night, and if any precipitate forms filter, wash with a 5 per cent solution of ammonium nitrate, ignite and weigh as ZrP_2O_7. (See Lundell and Knowles, J. Am. Chem. Soc., **41**, 1801–1808; 1919.)

Lime and Magnesia.—In these determinations a 1.000 to 3.000 g sample should be used. The sample may be put into solution by fusion with sodium carbonate directly and subsequent elimination of silica or by preliminary treatment with nitric, sulphuric, and hydrofluoric acids. The treatment with nitric, sulphuric, and hydrofluoric acids will not entirely dissolve this sample, and it is necessary to evaporate to fumes of sulphuric acid, cool, dilute with water, filter, ignite and fuse the insoluble residue with sodium carbonate

or pyrosulphate. The fused mass is then dissolved and added to the original filtrate.

After the sample has been put in solution by either of the above methods and the silica eliminated, nearly neutralize the solution with sodium hydroxide, pour it into an excess of sodium hydroxide containing sodium carbonate, filter, and wash a few times with a 1 per cent solution of sodium carbonate. The precipitate contains the calcium, magnesium, iron, etc. Dissolve the precipitate in hydrochloric acid, precipitate twice with ammonium hydroxide and in the combined filtrates determine calcium by precipitation as the oxalate and ignition to the oxide. In the filtrate from the calcium determine magnesium by precipitation as magnesium ammonium phosphate and ignition to $Mg_2P_2O_7$.

Alkalies.—Determine alkalies by the J. Lawrence Smith method.

In the foregoing determinations corrections based on a blank carried through all the steps of the methods is very important, and it is very desirable that a known amount of alumina be added to the blank so that conditions are more nearly like those in the actual analysis.

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