

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE NO. 80

SODA-LIME GLASS

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

ANALYST*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	ZrO ₂	CaO	MgO	MnO	Na ₂ O	K ₂ O	SO ₃	As ₂ O ₅	As ₂ O ₃	Cl	Loss on ignition
1.....	74.09	0.32	0.064	0.02	0.003	4.65	3.23	0.003	16.63	0.04	0.41	0.068	0.031	0.047	0.30
2.....	74.05	.34	.06	.02	.003	4.62	3.22	.003	16.65	.05	.42	-----	-----	-----	.33
3.....	74.17	.38	.068	-----	-----	4.66	3.22	-----	16.81	.05	.36	-----	-----	-----	.33
4.....	74.18	.31	.07	.02	-----	4.61	3.31	.005	16.54	.03	.40	-----	-----	-----	.32
5.....	73.92	.24	¹ .10	.02	.016	4.71	3.39	Trace.	16.94	.06	.39	.073	.062	-----	.29
6.....	74.00	.26	.057	.02	-----	4.71	3.07	-----	17.02	.03	.49	.08	-----	-----	.24
-----	73.76	.40	.07	-----	-----	4.52	3.32	-----	17.63	-----	-----	-----	-----	-----	.30
-----	74.08	.354	.066	-----	-----	4.67	3.26	.003	16.78	.04	.40	-----	-----	-----	.31
-----	74.09	.31	.068	.02	-----	4.75	3.26	Trace.	16.84	.41	.081	.019	Present.	-----	.22
10.....	73.97	.44	.064	-----	-----	4.92	¹ 3.48	-----	17.13	-----	-----	-----	-----	-----	-----
11.....	73.79	.29	.062	-----	-----	4.83	3.35	Trace.	17.01	Trace.	-----	.12	-----	-----	.30
12.....	73.68	.35	.06	-----	-----	4.49	3.36	-----	17.10	.05	.40	-----	.05	-----	.36
13.....	73.94	.41	.07	-----	-----	¹ 5.09	3.04	-----	17.00	¹ .60	-----	-----	-----	-----	.30
Averages..	73.98	.34	.065	.02	.007	4.68	3.25	.004	16.85	.04	.41	.075	.041	.047	.30
Recommended percentages..	74.1	.33	.065	.02	.003	4.65	3.23	.003	16.65	.04	.41	.07	.03	.047	.30

¹Omitted from Average.

All calculations are based on the International Table of Atomic Weights of the Chemical Elements for 1925.

Determinations were not made of selenium, phosphorus pentoxide, or the relationship between the loss on ignition and the gas content of the sample.

* LIST OF ANALYSTS

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Washington, D. C.
June 17, 1927

George K. Bangess
Director

METHODS OF ANALYSIS

The results for silica and the oxides of iron, aluminum, titanium, zirconium, manganese, calcium, magnesium, and potassium were obtained in general by the methods as described by W. F. Hillebrand in "The Analysis of Silicate and Carbonate Rocks," United States Geological Survey Bulletin No. 700.

Sulphur trioxide was determined by treating 5 g of the dried sample in a platinum dish with 25 ml of water, then with 50 ml of concentrated hydrofluoric acid and finally with 10 to 15 ml of perchloric acid (60 per cent). The solution was evaporated first on the steam bath and finally over a hot plate until fumes of perchloric acid just appeared. If the glass was not thoroughly decomposed a further addition of hydrofluoric acid was made and the evaporation repeated. Finally the solution was evaporated to dryness at as low a temperature as possible. The walls of the vessel were then rinsed with water and the solution again evaporated to dryness. After cooling, the residue was washed with 2 ml of concentrated hydrochloric acid, dissolved in 100 ml of water and the solution filtered. After dilution to 200 ml the solution was heated to boiling and 10 ml of a hot 10 per cent solution of barium chloride added. After cooling and standing overnight the solution was filtered and the precipitate washed with hot water until soluble salts were removed, but avoiding excessive washing. The paper and precipitate were transferred to a weighed platinum crucible, heated to destroy carbon and finally ignited at approximately 950° C. to constant weight.

Chlorine was determined by treating 5 g of the dried sample in a platinum dish successively with 0.1 g of silver sulphate, 25 ml of water, 50 ml of hydrofluoric acid (concentrated and free from chlorine) and finally 10 to 15 ml of perchloric acid (60 per cent). The solution was evaporated to incipient fumes of perchloric acid, cooled and diluted with 400 ml of dilute nitric acid (1:99). The precipitate was allowed to settle overnight and the solution then filtered through a tight paper. The precipitate was washed with ten 10 ml portions of cold dilute nitric acid (1:99) and then dissolved by warm dilute ammonia water (5:95), the solution being collected in a 150 ml beaker. After dilution

to 100 ml the solution was rendered faintly acid with nitric acid and treated with a slight excess of dilute silver nitrate solution. It was then heated to boiling and set aside in a dark place to cool. The precipitate was caught on a tared Gooch crucible, washed with cold dilute nitric acid (1:99) until soluble salts were removed and finally a few times with warm water. Finally the crucible and contents were heated for one hour at 120 to 130° C., cooled and weighed as AgCl.

The determination of total arsenic was made by treating 5 g of the dried sample in a large platinum dish with 25 ml of water and then with 25 ml of nitric acid (sp. gr. 1.42), 20 ml of sulphuric acid (1:1), and 50 ml of concentrated hydrofluoric acid. The solution was evaporated to fumes of sulphuric acid at as low a temperature as possible, cooled and the sides of the dish rinsed down with water. The solution was again evaporated to fumes of sulphuric acid, cooled, diluted with 25 ml of water and again cooled. The residue was transferred by means of 175 to 200 ml of concentrated hydrochloric acid (sp. gr. 1.19) to a 750 ml flask fitted with a two-hole stopper carrying a thermometer and an upwardly inclined outlet tube. The latter was provided with a hole on the side about 1 cm from the end within the flask to allow free circulation. Ten grams of Cu_2Cl_2 was added to the flask, the stopper quickly inserted and connection made with a vertical water condenser having its lower end dipping into a beaker containing 150 ml of distilled water and immersed in ice water. The flask was heated until at the end of 30 to 40 minutes 75 ml of solution was distilled over and the temperature had reached approximately 107° C. The distillation was continued at this temperature until 25 ml more distillate was collected. The distillate was transferred to a 400 ml beaker, cooled and neutralized with solid sodium hydroxide until alkaline to phenolphthalein. It was then made just acid with dilute sulphuric acid and treated with 2 g of sodium bicarbonate and titrated with *N*/100 iodine solution, starch being added just short of the end point. The iodine solution was standardized against pure arsenious oxide. The volume of the iodine solution required multiplied by the arsenic titre of the solution represents the total

in the sample and this divided by the weight of sample and multiplied by 100 represents the percentage.

The determination of quinquivalent arsenic was carried out in the same way with the exception that no nitric acid was employed and special precautions were taken to free the hydrofluoric acid from reducing substances, such as organic matter which would cause reduction of the quinquivalent arsenic and its subsequent loss as the trifluoride. A determination in which the sulphuric acid becomes dark colored at the fuming point should be viewed with suspicion. The volume of iodine solution multiplied by the arsenic titre represents the arsenic present in the quinquivalent form. This value is computed to arsenic pentoxide and the percentage found by dividing by the weight of the sample and multiplying by 100. The percentage of trivalent arsenic was found by deducting the percentage of arsenic in the quinquivalent condition from the percentage of total arsenic and computing the remainder to arsenic trioxide.

The following notes serve to indicate some of the precautions that must be observed in order to avoid errors.

Silica.—When alkali carbonates have been employed to effect decomposition of the sample and the resulting melt is dissolved in water instead of hydrochloric acid quartz or porcelain dishes, excessive incrustation by silica occurs. In such cases the dishes in which the evaporations are conducted suffer attack and the silica so introduced may amount to more than that which can not be separated from the dishes by careful scrubbing.

Single evaporations do not yield all of the silica, regardless of whether the evaporation is made with hydrochloric, sulphuric, or perchloric acids. The small precipitate of iron, aluminum, titanium, and zirconium hydroxides, obtained by ammonia, is not capable of gathering the silica which escapes a single dehydration.

Results for silica are usually low because of such factors as careless dehydration, incomplete removal of silica from the dish, incomplete recovery or nonrecovery of silica that escapes two dehydrations, and retention of alkali salts. Careless dehydration includes both under and over drying; that is, either stopping short of a bone-dry mass or overheating. Drying for a longer period than one hour at 110° C. or at a higher temperature causes low results for silica through the formation of magnesium silicate which is then partially dissolved by hydrochloric acid; that which dissolves causes a loss of silica while that remaining insoluble causes loss of magnesia unless the nonvolatile residue is afterwards dissolved and added to the fil-

trate from the dehydrated silica. If alkali salts are not removed they suffer more or less decomposition with the formation of alkali silicates during final ignition of the silica. These are broken up during the treatment with sulphuric and hydrofluoric acids and weighed as sulphates, thus causing low results for silica.

A less common error, causing high results, is the final ignition of the silica at a temperature too low to completely expel retained water. A temperature of 1,200° C. is needed.

"R₂O₃."—The nonvolatile residue obtained in the determination of silica must be dissolved and combined with the filtrate from the silica, for it sometimes contains substances other than the "R₂O₃" oxides. Serious error in the determination of alumina may result if this nonvolatile residue is weighed with the ammonia precipitate.

For a correct determination of "R₂O₃" in soda-lime glass, it is essential that the hydrogen sulphide group be first removed and that a double precipitation with ammonia be made. If the former is not done, any quinquivalent arsenic originally present in the glass and escaping the evaporation for silica is carried down, while small amounts of the platinum derived from crucibles and dishes are also held. Double precipitation with ammonia is essential to insure freedom from salts of the alkalis and alkaline earths. Neglect of these precautions may cause positive errors of from 0.1 to 0.3 per cent. This error finally falls on the alumina.

In the precipitation by ammonia, a very slight excess is permissible and this is best judged by the use of an indicator, such as methyl red. The use of this indicator precludes the presence of such oxidizing agents as nitric acid or bromine, which destroy it. If the yellow color changes to orange during the short boiling period it should be restored by the addition of more ammonia. The precipitate must be washed with an electrolyte, preferably neutral ammonium chloride, to prevent loss through the formation of a colloidal solution. When the precipitate is dissolved preliminary to reprecipitation care must be exercised to avoid loss of undissolved hydroxides retained in the pores of the filter. The final precipitate must be heated at approximately 1,200° C. to insure removal of all water, and the hygroscopic oxide must then be carefully protected to prevent reabsorption of water. For this purpose the crucible must be cooled in a desiccator containing a powerful desiccant, such as fresh sulphuric acid, and weighed quickly while covered with a well fitting cover.

For an accurate determination of the small amount of the " R_2O_3 " group in sample No. 80, it is preferable to start with a 5.0 g sample.

Total Iron as Ferric Oxide.—In general, the amount of iron present in glass is so small as to render its determination on a 1 g sample quite difficult. In accurate analyses determination should be made on 5 to 10 g samples. Of the volumetric methods, those based on electrometric titration are simple, accurate, and preferable when many analyses are to be made. In any reduction-oxidation method the effect of the reducing agent on constituents other than iron must be considered. Thus, titanium as well as iron is reduced by zinc and sulphuric acid, and failure to correct for its effect would lead to high results for iron. Platinum introduced from utensils during the course of an analysis interferes with reductions made with stannous chloride or sulphuric acid. Reduction with hydrogen sulphide and titration with permanganate give results somewhat higher than the true value.

Titanium and Zirconium.—The determination of titanium may be conveniently made on the solution of the mixed oxides from a 1 g sample. Zirconium, however, is present in such small amounts that at least a 5.0 g sample should be used.

Calcium Oxide.—For correct results it is necessary that double precipitations be made. With respect to the separation of magnesium and the alkalis from the lime there is no advantage in igniting the first oxalate precipitate before reprecipitation unless compounds are present that are precipitable by ammonia. These should be absent if prior separations have been properly performed.

Calcium oxalate is preferably washed with a cool, dilute solution of ammonium oxalate and excessive washing must be avoided. When titration is to follow no more water should be used than is necessary to remove the oxalate wash water.

Calcium oxide is markedly hygroscopic and should not be cooled over calcium chloride.

Magnesia.—As with lime, a correct determination of magnesia requires double precipitation. The initial precipitate never has the true stoichiometric composition of magnesium ammonium phosphate, regardless of the method of precipitation.

The ignition of the precipitate should not be unduly hastened until all carbonaceous material has been burned out. A final ignition temperature of from 1,000 to 1,100° C. is sufficient. The magnesium pyrophosphate thus obtained contains any lime that escaped

precipitation as oxalate, and almost all of the manganese originally present.

The calcium oxide in the residue can be recovered by dissolving the ignited pyrophosphate in a little dilute sulphuric acid (1:4) and then adding sufficient ethyl alcohol to make about 90 to 95 per cent of the final volume. The small precipitate that appears after several hours is filtered off, washed with alcohol until free from phosphoric acid, dried, dissolved in warm dilute hydrochloric acid and the calcium precipitated with ammonia and ammonium oxalate. The amount of calcium oxide thus found is added to that previously obtained and is deducted as tricalcium phosphate from the weight of the ignited magnesium pyrophosphate. The recovery approximates about 0.1 mg for each 100 ml of solution used in the precipitation and washing of the calcium oxalate.

Manganese.—This element is best determined on a 5 to 10 g sample of the glass after solution in hydrofluoric-sulphuric acids, evaporation to fumes of the latter and direct oxidation with bismuthate in a solution containing 20 to 25 per cent by volume of nitric acid and about 5 ml of sulphuric acid per 100 ml. Perchloric acid may be substituted for sulphuric acid in the attack, the solution evaporated to dryness and the residue taken up in dilute nitric acid.

Sodium and Potassium Oxides.—The principal difficulties in the determination of the alkalis by the J. Lawrence Smith method consist in removing all the lime, magnesia, and the excess of barium introduced to remove sulphates. The first can be removed by careful treatment with ammonium carbonate at the start and proper digestion with a moderate excess of ammonium oxalate in a solution free from ammonium salts before filtration and evaporation of the mixed chlorides at the end of the analysis. For the complete removal of magnesia it is essential that a saturated solution of calcium hydroxide be maintained at all times during extraction of the sintered mass, and that the insoluble matter should never be washed with hot water. The removal of barium by ammonium carbonate must be complete to prevent its presence with the final mixed chlorides.

Corrections for Impurities in the Reagents.—All results should be corrected by careful blank determinations carried out at the time of the analysis. This precaution is of the utmost importance in the determination of compounds such as ferric oxide, that are present in very small amount.