

National Bureau of Standards Certificate of Analysis

Standard Reference Material 57 Refined Silicon

	Si	Fe	Mn	P	S	Cu	Ni	Cr	V	Zr	Ti	Al	Ca	Mg
<i>ANALYSTS*</i>	SILICON	IRON	MANGANESE	PHOSPHORUS	SULPHUR	COPPER	NICKEL	CHROMIUM	VANADIUM	ZIRCONIUM	TITANIUM	ALUMINUM	CALCIUM	MAGNESIUM
1.....	96.75 ^a	0.67	0.035	0.009	0.010	0.021	0.002	0.025	None	0.029	0.087	0.69	0.73	0.01
2.....	96.86 ^b	.65	.033	.007	.003	.015	.005	.025	None	.025	.100	.68	.74	Trace
3.....	96.76 ^c	.64	.034	.007	.004	.021	.002	.025		.020	.103	.66	.70	
4.....	96.90 ^c	.62	.041	.009	.004							.66		
5.....	97.01 ^a	.64		.003							.080		.77	
6.....	97.03 ^c													
7.....	97.00 ^c													
8.....	97.00 ^c													
AVERAGES	96.91 ^d	.65	.036	.007	.005	.019	.002	.024		.025	.093	.67	.74	.01
Recommended values	96.80	.65	.034	.008	.005	.02	.002	.025	None	.025	.10	.67	.73	.01

This certificate has been changed from that issued November 28, 1924, only by deletion of the certified carbon content and the change into the current format. The carbon content determined was found to be temperature dependent. At about 1200° C, a value of 0.087 was obtained; at about 1800° C, a value of 0.12 was obtained.

It is possible that present-day chemical methods of analyses would reveal some differences for the other minor and trace elements certified; however primary use of this standard has been for the determination of silicon and no significant change from the original certified value is expected.

NOTE.—Oxygen and nitrogen were the only other elements found in this alloy. Methods for the determination of these elements in this material are uncertain and it is believed that these, chiefly oxygen, account for the lack of complete summation.

^a Fusion with Na₂CO₃ and KNO₃ in platinum—sulphuric acid dehydrations.
^b Fusion as in (*) and hydrochloric acid dehydrations.

^c Fusion with Na₂O₂ and hydrochloric acid dehydrations.
^d The atomic weight 28.1 was used for silicon in all determinations.

*LIST OF ANALYSTS

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Washington, D. C. 20234 | <ol style="list-style-type: none"> 5. H. E. Campbell, Carnegie Steel Co., Clairton Works, Clairton, Pa. 6. H. E. Slocum, Jones & Laughlin Steel Corp., Pittsburgh, Pa. 7. Central Steel Co., Massillon, Ohio. 8. G. L. Kelley, Edward Budd Manufacturing Co., Philadelphia, Pa. |
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 February 7, 1973
 (Revision of Certificate Nov. 28, 1924)

OUTLINE OF THE METHODS USED AT THE BUREAU OF STANDARDS FOR THE
ANALYSIS OF THE STANDARD SAMPLES OF REFINED SILICON NO. 57 AND
FERROSILICONS NOS. 58 AND 59.

Silicon.—Silicon was determined by double hydrochloric or sulphuric acid dehydrations after fusion with sodium carbonate and potassium nitrate in platinum crucibles. In the case of the refined silicon, a 0.4 g sample was fused with a mixture of 8 g of sodium carbonate and 0.3 g of potassium nitrate; for the ferrosilicons 0.5 g samples were fused in large platinum crucibles with mixtures of 10 g of sodium carbonate and 1.75 g of potassium nitrate. The fusions in all cases were dissolved in large platinum dishes, all evaporations were made in platinum, and silica escaping the double evaporations was recovered by treating the solution with ammonia, (after the addition of a little aluminum with sample No. 57) filtering, dissolving the precipitate in sulphuric acid, and evaporating to fumes of the acid.

Manganese.—A 1 g sample was dissolved in nitrohydrofluoric acid, treated with sulphuric acid, and evaporated to fumes of sulphuric acid. The residue was dissolved in 50 cc of nitric acid (sp. gr. 1.135) and manganese determined by the bismuthate method.

Phosphorus.—A 5 g sample was dissolved in nitrohydrofluoric acid and evaporated several times with nitric acid (sp. gr. 1.42). The residue was taken up in dilute nitric acid and 2 g of boric acid added. Phosphorus was then precipitated with molybdate and determined by the usual sodium hydroxide titration.

Sulphur.—A 2.5 g sample was fused with 30 g of sodium carbonate and 3.5 g of potassium nitrate in a platinum crucible. The fusion was dissolved in hydrochloric acid, silica removed by dehydration, and sulphur determined as BaSO₄ in the filtrate from the silica.

Iron.—Iron was determined by reduction with stannous chloride and titration with potassium permanganate according to the Zimmerman-Reinhardt method. The samples were dissolved in nitrohydrofluoric acid, fumed thoroughly with sulphuric acid, converted to chlorides, and finished as noted, correction being made for vanadium.

Chromium and vanadium.—Chromium and vanadium were determined colorimetrically. Five-gram samples of the alloys were dissolved in nitrohydrofluoric acid, fumed with sulphuric acid, diluted, nearly neutralized with sodium hydroxide and then poured into an excess of sodium hydroxide containing sodium peroxide. The solution was filtered through asbestos, and chromium and vanadium were determined colorimetrically and by electrometric titration in the filtrate.

Titanium and zirconium.—Five-gram samples of the alloys were dissolved in nitrohydrofluoric acid, fumed with sulphuric acid, diluted, nearly neutralized with sodium hydroxide and then poured into an excess of sodium hydroxide. The precipitate was filtered and dissolved in hydrochloric acid. The iron was removed by double precipitation with ammonium sulphide in the presence of tartaric acid. Titanium and zirconium in the filtrate were precipitated with cupferron, weighed, and the zirconium determined as phosphate according to Lundell and Knowles *J. Ind. Eng. Chem.*, **12**, 562; 1920.

Copper and aluminum.—Three-gram samples of the alloys were dissolved in nitrohydrofluoric acid, fumed with sulphuric acid, diluted and the copper precipitated with hydrogen sulphide, ignited, weighed as CuO and tested for platinum. The filtrate was boiled to remove hydrogen sulphide and poured into an excess of sodium hydroxide. The solution was filtered, a slight excess of hydrochloric acid was added, and the aluminum was precipitated as phosphate in the presence of ammonium acetate. cf. Lundell and Knowles, *J. Ind. Eng. Chem.*, **14**, 1136; 1922. An ether separation was made on No. 59 and the aluminum was separated from iron with sodium hydroxide and determined as Al₂O₃ with the proper corrections for SiO₂ and P₂O₅.

Calcium and magnesium.—Five-gram samples of the alloys were dissolved in nitrohydrofluoric acid, fumed with sulphuric acid, and taken up in dilute hydrochloric acid. A slight excess of ammonia was added, the solutions were boiled a few minutes and the precipitates filtered. Calcium was precipitated in 0.5 per cent oxalic acid-ammonium oxalate solution and reprecipitated in slightly ammoniacal solution. Standards Nos. 57 and 58 were run as outlined above, but the ammonia precipitate on No. 59 was dissolved in hydrochloric acid and an ether separation made to remove most of the iron. The acid extract was oxidized, treated with an excess of ammonia, the precipitate filtered, and the filtrate added to the filtrate from the first ammonia separation. Calcium was then determined in the combined filtrates. The calcium filtrates were tested for magnesium with ammonium phosphate in the usual way.

Nickel.—Nickel was determined by the dimethyl glyoxime method after solution of the alloys in nitrohydrofluoric acid and evaporation with sulphuric acid.

SUGGESTED METHOD FOR THE DETERMINATION OF SILICON IN FERROSILICON ALLOYS

Fusion of ferrosilicon alloys in platinum with sodium carbonate and nitre though an excellent method for refined analysis is not as satisfactory for general purposes as is fusion with sodium peroxide in a pure iron crucible. Such a fusion, followed by dehydration with hydrochloric acid, is more convenient and gives accurate results if carefully made.

Procedure.—1. Transfer 0.5000 g (use 0.4000 g for 90 per cent silicon) of the finely powdered sample (150 mesh) to a 50 cc pure iron crucible made from No. 20 gauge (0.032-inch thickness) ingot iron, add approximately 13 g of sodium peroxide, mix thoroughly with a platinum or iron rod and carefully clean the rod of adhering particles by scraping with another rod. Cover the mixture with a layer of about 2 g additional peroxide. Heat the crucible and contents on a hot plate for 5 to 10 minutes to expel any water in the peroxide which would cause splattering in the subsequent fusion. Carefully fuse over a low flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly. When the fusion is molten, rotate the crucible carefully to stir up any unattacked particles on the bottom or sides, the crucible and contents being maintained at a low red heat. Just before completion of the fusion, which requires only three or four minutes, increase the temperature to bright redness for a minute. If the reaction has proceeded too violently, due to too rapid heating, use of insufficient sodium peroxide, or to lack of thorough mixing, appreciable loss will occur and the work should be repeated.

2. Cover the crucible and allow it to cool until the fusion has solidified, and tap the bottom of the crucible, while still warm, several times on an iron plate, which will loosen the fused mass in a solid cake. When the crucible and cake have completely cooled, transfer the cake to a large (275 cc) gold or preferably platinum dish. Cover the dish with a clock glass and cautiously add 50 cc of cold water. When the reaction ceases wash the small amount of adhering matter in the crucible into the dish with a little water. Cool the solution and carefully add an excess of hydrochloric acid. Evaporate to dryness, preferably on a steam bath, but do not bake at a temperature above 110° C. If platinum or gold dishes are not available for solution of the fused cake, the latter can be disintegrated with water in a pure nickel dish and the contents then transferred to a porcelain dish containing sufficient hydrochloric acid to provide an excess of acid. It is not desirable to dissolve the fusions directly in porcelain because of the action of the alkaline solution on the porcelain.

3. When the residue is dry, allow the dish to cool, add 10 cc of hydrochloric acid (sp. gr. 1.13), cover the dish, and heat gently for a few minutes. Dilute with 100 cc of hot water, digest for a few minutes, and filter through an 11 cm paper. Wash about eight times with hot 5 per cent hydrochloric acid, twice with warm 5 per cent sulphuric acid and then a few times with hot water. Reserve paper and residue.

4. Evaporate the filtrate to dryness and bake the covered casserole or dish at 110° C. for one hour. Heating at a higher temperature is unnecessary and also disadvantageous. Cool, add 10 cc of hydrochloric acid (1-1), digest on the steam bath for 10 minutes, add 100 cc of warm water, filter immediately, and wash about eight times with cold 1 per cent hydrochloric acid, once with cold 5 per cent sulphuric acid and then a few times with cold water.

5. Place the paper and silica from the *second* dehydration in a large partially covered platinum crucible and char the paper without inflaming. Add the paper containing the silica from the first dehydration, char as before, and then ignite carefully until the carbon has been burned off. Great care should be exercised in igniting the papers, as the current of air produced by a burning filter is sufficient to carry finely divided silica out of the crucible. When the carbon of the filter paper has been completely burned, gradually heat the tightly covered crucible to the full heat of a blast lamp and continue the heating at 1,050 to 1,110° C. for 25 minutes. Cool in a desiccator, weigh, and check for constant weight by additional heating for 10 minutes at the above temperature. Add sufficient sulphuric acid (1-1) to moisten the silica and then 15 to 20 cc of pure hydrofluoric acid (48 per cent). Evaporate to dryness, ignite, and weigh. The loss represents silica which contains 46.76 per cent silicon. A blank, not omitting the same amount of hydrofluoric acid, should be carried through all stages of the operation.

The silica remaining in the filtrate after the second dehydration is practically negligible, averaging about 0.0006 to 0.0010 g after dehydrations with hydrochloric acid and 0.0010 to 0.0015 g after dehydrations with sulphuric acid.