

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 67 MANGANESE METAL

ANALYSTS*	Mn	C	P	S	Si	Fe	Cu	Ni	Cr	V	Mo	Ti	Co	As	Al	Zr
	MANGANESE	CARBON	PHOSPHORUS	SULPHUR	SILICON	IRON	COPPER	NICKEL	CHROMIUM	VANADIUM	MOLYBDENUM	TITANIUM	COBALT	ARSENIC	ALUMINUM	ZIRCONIUM
1.....	97.26 ^a	0.058	0.241	Not detected ^b	0.407	1.50	0.159	0.045	0.184	0.188	0.017	<0.001	0.02	0.011	Not detected	Not detected
2.....	97.22 ^a	.065	.230	-----	.410	1.51	-----	-----	.187	.188	-----	-----	-----	-----	-----	-----
3.....	97.25 ^a	.060	.234	-----	.405	1.50	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
4.....	97.24	.058	-----	0.003	.39	1.57	.174	.062	.14	.17	-----	-----	-----	-----	-----	-----
-----	97.46 ^a	.062	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	97.21 ^a	.064	-----	-----	.415	1.57	.160	-----	-----	-----	-----	-----	-----	-----	-----	-----
7.....	96.90 ^d	.062	.225	-----	.420	1.70	.16	.05	.15	-----	-----	-----	.01	-----	-----	-----
8.....	97.32 ^a	.060	.227	-----	.401	1.53	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9.....	97.32 ^a	.069	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
10.....	97.13 ^a	-----	.22	-----	.41	1.58	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
11.....	{ 97.37 ^e 97.22 ^a }	.058	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
12.....	97.4 ^a	.060	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
General average	97.25 ^f	.061	.23	-----	.407	1.59	.163	.052	.165	.182	-----	-----	.015	-----	-----	-----
Recommended value	97.25	.06	.235	<.001	.407	1.50	.16	.045	.18	.19	.015	<.001	.02	.011	-----	-----

^a Bismuthate method of Cunningham and Coltman, J. Ind. Eng. Chem., 16, 58; 1924.
^b Test sensitive to 0.001 per cent.
^c Gravimetric, phosphate.

^d Volhard's method, KMnO₄ standardized on Bureau of Standards Standard Sodium Oxalate No. 40b.
^e Julian's method.
^f The atomic weight 54.93 was used for manganese in all determinations.

*INDEX TO ANALYSTS

- | | |
|--|--|
| 1. H. A. Bright, W. C. Fedde, C. P. Larrabee, Ferrous Laboratory, Bureau of Standards. | 7. J. L. Harvey, Carnegie Steel Co., Munhall, Pa. |
| 2. James I. Hoffman, Bureau of Standards. | 8. G. E. Gardner, Electric Furnace Products Co., Sauda, Norway. |
| 3. T. R. Cunningham and R. J. Price, Electro Metallurgical Co., New York, N. Y. | 9. O. R. Smith, W. B. Coleman & Co., Philadelphia, Pa. |
| 4. Crowell & Murray, Cleveland, Ohio. | 10. L. W. Spring, Crane Co., Chicago, Ill. |
| 5. E. A. Loos, The Carpenter Steel Co., Reading, Pa. | 11. G. H. Corey and W. C. Bowden, jr., Ledoux & Co., New York, N. Y. |
| 6. C. E. Nesbit, Carnegie Steel Co., Braddock, Pa. | 12. H. Hutchinson United Alloys Co., Canton, Ohio. |

Washington, D. C.
 October, 16, 1925

GEORGE K. BURGESS,
 Director.

OUTLINE OF THE METHODS USED AT THE BUREAU OF STANDARDS IN THE ANALYSIS
OF STANDARD MANGANESE METAL No. 67 AND FERROMANGANESE No. 68

Manganese.—Manganese was determined by Cunningham and Coltman's modification of the bismuthate method (*Jour. Ind. Eng. Chem.*, **16**, 58; 1924). A 0.3 g sample was used for the ferromanganese and 0.25 for the manganese metal. The residue, of the ferromanganese, insoluble in nitric acid, contained less than 0.005 per cent of manganese.

Carbon.—Carbon was determined by direct combustion of a sample mixed with 2 g of ingot iron and 1 g of copper oxide. The evolved CO_2 was absorbed in ascarite and a blank determined and subtracted.

Phosphorus.—Phosphorus was weighed, by analyst 2, as $\text{Mg}_2\text{P}_2\text{O}_7$, after initial precipitation with molybdate. The alloys were dissolved in concentrated nitric acid, evaporated to dryness, heated at 120°C ., dissolved in dilute hydrochloric acid, and filtered to remove silica. Any phosphorus in the residue was recovered and added to the filtrate. Approximately 0.07 g of iron was added to the filtrate of the manganese metal and a slight excess of ammonium hydroxide added. The precipitate was filtered, dissolved in nitric acid, and nearly neutralized with ammonium hydroxide, and the phosphorus precipitated with molybdate reagent. The solution of the manganese metal was first reduced with ferrous sulphate and sulphurous acid before addition of the molybdate reagent. Phosphorus was determined, by analyst 1, by the alkali-molybdate method. After removal of silica as described, the hydrochloric acid in the filtrate was removed by several evaporations with nitric acid, the solution adjusted to the proper acidity, and the phosphorus precipitated with molybdate reagent. The solution of the manganese metal was likewise first reduced as stated above.

Sulphur.—Sulphur was determined by direct solution in nitric acid (sp. gr. 1.42) and precipitation as BaSO_4 , after repeated evaporation with hydrochloric acid.

Silicon.—Silicon was determined by sulphuric acid dehydration. The residue of ferromanganese No. 68 insoluble in sulphuric acid was filtered, fused with sodium carbonate, and added to the main solution before dehydration with sulphuric acid.

Iron.—Two g of No. 67 and 1 g of No. 68 were dissolved in nitric-hydrochloric acid, fumed with sulphuric acid, diluted, and treated with a slight excess of ammonium hydroxide. The precipitate was filtered, dissolved in hydrochloric acid, and the iron precipitated by pouring the solution into a solution of sodium hydroxide. The precipitate was dissolved and reprecipitated with sodium hydroxide. The second precipitate was dissolved in hydrochloric acid and the iron determined by reduction with stannous chloride and titration with permanganate.

Chromium and Vanadium.—Five g of the alloy was dissolved in dilute sulphuric acid, and the residue fused with sodium carbonate and added to the main solution. Practically all of the manganese was removed by a double separation with ammonium hydroxide. (Approximately 0.02 g of iron was added to No. 67 to obtain a tenfold excess of iron over the vanadium present.) The precipitate was dissolved in dilute sulphuric acid and chromium oxidized by the persulphate-silver nitrate method and titrated with ferrous sulphate-permanganate and vanadium determined in the same solution by the ammonium persulphate method. Chromium and vanadium were also titrated electrometrically.

Titanium, Aluminum, Copper, Cobalt, and Nickel.—A 10 g sample was dissolved in hydrochloric acid, oxidized with a little nitric acid and evaporated to dryness, taken up in dilute hydrochloric acid, and filtered. The residue was ignited, heated with sulphuric and hydrofluoric acids to remove silica, fused with potassium acid sulphate, and later added to the acid extract from the ether separation. The hydrochloric acid solution was treated with ether to remove most of the iron. The acid extract from the ether separation was fumed with sulphuric acid, diluted, and copper removed with hydrogen sulphide, ignited, and weighed as CuO , which was examined for other members of the hydrogen sulphide group. The filtrate was boiled, the iron oxidized with nitric acid, and a double ammonium hydroxide precipitation made. The ammonia precipitate was dissolved, and the solution nearly neutralized, and poured into an excess of sodium hydroxide. The solution was filtered and the filtrate examined for aluminum by the addition of ammonium phosphate. Titanium was determined in the precipitate by the cupferron method. (*Cf. Lundell and Knowles, Jour. Ind. Eng. Chem.*, **12**, 562; 1920.) The ammonia filtrate was adjusted to 10 per cent acidity with hydrochloric acid and the cobalt precipitated with an excess of nitroso B naphthol. This precipitate was filtered, ignited in porcelain, and fused with potassium acid sulphate. The melt was dissolved in 10 per cent sulphuric acid, oxidized with potassium persulphate, and the cobalt and traces of manganese precipitated with sodium hydroxide. The precipitate was dissolved, and the cobalt again precipitated with nitroso B naphthol, ignited, and weighed as Co_3O_4 . Nickel was determined in the nitroso B naphthol filtrates by double precipitation with dimethyl glyoxime after the addition of sufficient tartaric acid to render the ammonia solution clear before addition of the glyoxime reagent.

MODIFIED BISMUTHATE METHOD FOR THE DETERMINATION OF MANGANESE IN MANGANESE METAL AND FERROMANGANESE

Reagents required.—(1) **DILUTE NITRIC ACID** (sp. gr. 1.135).—Mix 300 cc of nitric acid (sp. gr. 1.42) and 700 cc of distilled water. Test for proper gravity.

(2) **DILUTE NITRIC ACID** (3 : 97).—Mix 30 cc of recently boiled nitric acid (sp. gr. 1.42) and 970 cc of distilled water. Add a little sodium bismuthate and shake well.

(3) **SODIUM BISMUTHATE (80 PER CENT GRADE)**.—The oxidizing power of the reagent can be tested as follows: Shake one-half gram of the reagent with 4 g of potassium iodide and a little water in a stoppered flask. Add 15 cc of hydrochloric acid and allow to stand in the dark, with occasional shaking until the bismuthate has entirely decomposed. Dilute to 300 cc and titrate with 0.1 *N* sodium thiosulphate, using starch as an indicator at the end. One cc of 0.1 *N* Na₂S₂O₃ equals 0.0140 g NaBiO₃. About 26 g of 80 per cent bismuthate are required to oxidize 1 g of manganese.

(4) **ASBESTOS**.—Asbestos for this work should be thoroughly digested in nitric acid (sp. gr. 1.42) and then washed free from acid with distilled water.

(5) **STANDARD POTASSIUM PERMANGANATE SOLUTION**.—Dissolve 3.2 g of KMnO₄ in 1,000 cc of distilled water, allow to age for at least 10 days, and filter through purified asbestos. Standardize the permanganate solution against Bureau of Standards sodium oxalate as follows:

In a 400 cc beaker dissolve 0.28 to 0.30 g of sodium oxalate in 200 cc of hot water (80 to 90° C.), add 10 cc of dilute H₂SO₄ (1 : 1), and titrate at once with the permanganate solution, stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10 to 15 cc per minute, and the last 0.5 to 1 cc must be added dropwise, with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause an end point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The temperature of the solution should not be below 60°C. by the time the end point is reached. One cc of 0.1 *N* KMnO₄ equals 0.001099 g of manganese.

METHOD.—(A) **SOLUTION OF THE SAMPLE**.—All samples should be crushed to approximately 100 mesh and dried at 105 to 110° C.

FERROMANGANESE.—The weight of sample is governed by the manganese content; for 80 per cent ferromanganese from 0.2500 to 0.3000 g should be used. As there is no difficulty in obtaining a uniform sample, it is preferable to weigh out individual portions of the 100-mesh sample. The following procedure as regards the quantity of acid and final volume presupposes the presence of approximately 0.20 g of manganese. Dissolve the sample in 60 cc of nitric acid (1.42) and boil in a covered flask or beaker until nitrous fumes cease to be evolved. (If the sample contains over 1 per cent of chromium, dilute the solution with an equal volume of water, filter, ignite the residue, fuse it with a little sodium carbonate, dissolve the fusion in a little nitric acid and add it to the main solution.) Oxidize the carbon by adding, in small portions, 2 to 2.5 g of ammonium persulphate. Boil the solution about 10 minutes and add small amounts of bismuthate to the boiling liquid until a precipitate of manganese dioxide has formed. Dissolve the precipitate by dropwise addition of sulphurous acid, adding an excess of 1 cc after the precipitate has dissolved. Boil the solution about five minutes to completely expel oxides of nitrogen, dilute to 200 cc, cool with ice, and treat as described later.

MANGANESE METAL.—Dissolve 0.2500 g of sample in 250 cc of nitric acid (1.135) in a 750 cc Erlenmeyer flask provided with a cut-off funnel to prevent loss by spraying, make a preliminary oxidation with bismuthate, and then reduce with sulphurous acid. Dilute the solution to a volume of 250 cc by adding nitric acid (1.135), cool with ice, and finish the determination as described later.

(B) **OXIDATION OF MANGANESE**.—If the preceding directions have been followed, the manganese will be present in a concentration of approximately 0.001 g per cc of nitric acid (sp. gr. 1.135). This concentration of manganese and nitric acid, together with a temperature of 10 to 15° C., are the conditions which insure maximum stability of the permanganic acid, formed as further described. Add approximately 7.0 g of sodium bismuthate (80 per cent) to the flask, agitate briskly for one minute, dilute with 250 cc of cold water, and filter immediately on a layer of prepared asbestos supported on a 2-inch alundum or perforated porcelain

plate resting in a large glass funnel. The filter can be washed free from manganese more readily if not allowed to run dry during the filtering and washing. To insure complete oxidation of the manganese to permanganic acid, it is essential that the sodium bismuthate (80 per cent NaBiO_3) be used in the ratio of at least 26 g every gram of manganese in solution. Wash the filter and residue with cold 3 per cent nitric acid until the washings are entirely colorless and immediately treat the filtrate and washings as described in the next paragraph.

Weigh accurately 9.000 g of ferrous ammonium sulphate, taken from a bottle of the well-mixed salt, and add to the filtered solution of permanganic acid. Stir briskly and as soon as the reduction is complete and the salt has dissolved, titrate the excess ferrous salt with 0.1 *N* potassium permanganate. The manganese value of the ferrous salt is obtained in the following manner:

Two hundred and fifty cc of nitric acid (sp. gr. 1.135) contained in a 750 cc Erlenmeyer flask are treated with approximately 2 g of sodium bismuthate and the solution is vigorously agitated for one minute, diluted with 250 cc of cold water, and immediately filtered on a layer of acid washed asbestos as previously described. Five (5.000) g of the ferrous ammonium sulphate are added to the filtrate and the resulting solution is immediately titrated with 0.1 *N* KMnO_4 until a faint pink color appears. The excess of permanganate used to cause an end point color must be determined in both titrations.

NOTE.—Chromium in amounts less than 2 per cent does not cause any interference if the reactions are rapidly done in cold solutions. Larger amounts interfere to some extent and should be separated prior to the final oxidation with bismuthate.