

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 64

FERROCHROMIUM

(HIGH CARBON)

	Cr	C	Fe	Mn	P	S	Si	Cu	Ni	V	Mo	Zr	Ti	Al
ANALYSTS*	CHROMIUM	CARBON	IRON	MANGANESE	PHOSPHORUS	SULPHUR	SILICON	COPPER	NICKEL	VANADIUM	MOLYBDENUM	ZIRCONIUM	TITANIUM	ALUMINUM
1.....	67.97 ^a	5.11 ^b	24.02	0.226	0.016	0.066	2.07	0.024	0.323	0.09	0.008	None found	0.032	0.02
2.....	67.95 ^c	5.08	24.02	.230	.015	.071	2.06	.029	.31	.12	.004	None found	.036	.015
3.....	67.82 ^d	5.16	24.15	.205	.017	.072	2.02	.023	.36	.11	-----	-----	.025	.022
-----	68.00 ^d	5.02	-----	.200	.016	-----	-----	-----	.33	-----	-----	-----	-----	-----
5.....	67.77 ^d	5.02	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
6.....	67.75 ^e	4.97	-----	-----	-----	-----	-----	-----	-----	.09	-----	-----	-----	-----
7.....	67.86 ^d	5.10	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
8.....	67.82 ^d	5.16	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
9.....	67.88 ^d	5.16	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
10.....	68.02 ^d	4.99	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
AVERAGES..	67.89 ^e	5.08	24.07	.215	.016	.070	2.05	.025	.331	.10	.006	None found	.031	.019
Recommend- ed Values....	67.9	5.10	24.05	.225	.016	.070	2.05	.025	.33	.11	.006	None found	.034	.02

^a Chromium oxidized with persulphate in presence of silver nitrate, titration with FeSO₄ and KMnO₄.
^b Includes carbon from reburning of ground residue, averaging approximately 0.015 to 0.020 per cent C per run.

^c Electrometric Titration, J. Ind. Eng. Chem., 13, 1053; 1921.
^d Direct fusion with sodium peroxide and titration with FeSO₄ and KMnO₄.
^e The atomic weight 52.0 was used for chromium in all determinations.

*LIST OF ANALYSTS

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- T. R. Cunningham and R. J. Price, Electro Metallurgical Co., New York, N. Y.
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Washington, D. C.
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George K. Burgess
 Director.

OUTLINE OF THE METHODS USED AT THE BUREAU OF STANDARDS IN THE ANALYSIS OF
FERROCHROMIUM STANDARD SAMPLE No. 64

Chromium.—Chromium was determined by oxidation with persulphate and titration with ferrous sulphate and permanganate and also by electrometric titration, cf. Kelley, Jour. Ind. Eng. Chem., **13**, 1053; 1921. A 0.3500 g sample was decomposed with dilute sulphuric acid, the residue was fused with sodium peroxide in a porcelain crucible, dissolved, and added to the main solution. The solution was diluted to a volume of 250 cc, adjusted so that approximately 8 per cent by volume of sulphuric acid was present and then oxidized with persulphate in the presence of silver nitrate. The excess of persulphate was removed by boiling the solution for eight minutes and the oxidized manganese was then reduced by adding 7 cc of hydrochloric acid (1 to 3) and boiling the solution about eight minutes. The solution was cooled and titrated in one case by adding a weighed excess of ferrous sulphate and titrating the excess with permanganate and in the second method by titrating electrometrically with ferrous sulphate.

Carbon.—Carbon was determined by direct combustion of a 0.5000 g sample mixed with 2 g of ingot iron and 1 g of copper oxide, the proper blank corrections being made. A furnace temperature of at least 1,140° C. is necessary for complete combustion of carbon for this grade of alloy.

Manganese.—One g of the alloy was fused with sodium peroxide in a porcelain crucible, filtered on asbestos, the residue dissolved in nitric acid, and the manganese determined by the regular bismuthate method. A few drops of alcohol were added to the water extract of the fusion and the solution boiled for a few minutes before filtration in order to reduce any manganate formed during the fusion.

Phosphorus.—Two g of the alloy was fused with 15 g of sodium peroxide in a nickel crucible lined with sodium carbonate. The fusion was dissolved in dilute nitric acid, a slight excess of ammonia added, the precipitate filtered, washed a few times with water and dissolved in nitric acid. Phosphorus was then precipitated with molybdate and determined by the alkalimetric method. Blank runs were made on the reagents used.

Sulphur.—Two and one-half g of the alloy was fused with 15 g of sodium peroxide in a platinum crucible lined with sodium carbonate. The melt was extracted with water, filtered, and sulphur was precipitated in the acidified extract as BaSO₄ by the use of a large excess of barium chloride. The precipitate was caught on paper, ignited, fused with sodium carbonate, and reprecipitated in the acidified water extract under standard conditions.

Silicon.—Two g of the alloy was decomposed with dilute sulphuric acid and the residue fused with a small amount of sodium peroxide in a platinum crucible lined with sodium carbonate. The solution was dehydrated with sulphuric acid and silicon determined in the usual manner.

Iron.—One g of the alloy was decomposed with dilute sulphuric acid (1 to 6) and the residue fused in a porcelain crucible with a little sodium peroxide. The chromium was oxidized with persulphate in dilute sulphuric acid solution and the solution poured into a slight excess of sodium hydroxide. The precipitate was dissolved in hydrochloric acid and iron determined by reduction with stannous chloride and titration with permanganate.

Vanadium.—A 3 g sample of the alloy was fused with 20 g of sodium peroxide in an iron crucible. The fusion was dissolved in water, the peroxide expelled by boiling and the solution was acidified with nitric acid. A slight excess of ammonia was added and the precipitate filtered, dissolved in dilute sulphuric acid and vanadium determined by the ammonium persulphate method and also by electrometric titration.

Aluminum and Titanium.—A 4 g sample was fused with 25 g of sodium peroxide in an iron crucible. The fusion was dissolved in water and the peroxide removed by boiling. The solution was partially neutralized with dilute sulphuric acid and filtered through a strong paper. Aluminum was determined in the filtrate as AlPO₄. The sodium hydroxide precipitate was dissolved in hydrochloric acid and the most of the iron removed with ether. The remainder of the iron was removed with ammonium sulphide in the presence of ammonium tartrate and titanium precipitated with cupferron and determined as TiO₂; cf. Lundell and Knowles, Jour. Ind. Eng. Chem., **12**, 562; 1920.

Copper and Molybdenum.—A 5 g sample was decomposed with dilute sulphuric acid and the residue fused with sodium peroxide. Copper and molybdenum were precipitated with hydrogen sulphide in the presence of tartaric acid. The sulphides were dissolved, treated with sodium hydroxide and the solution filtered. The precipitate was dissolved in dilute sulphuric acid and copper precipitated with hydrogen sulphide and ignited to CuO. Molybdenum in the sodium hydroxide filtrate was also precipitated as sulphide after acidification and carefully ignited to MoO₃.

Nickel.—One g of the alloy was fused with sodium peroxide, the fusion dissolved in water and filtered and the precipitate was dissolved in dilute hydrochloric acid and the nickel determined by the dimethyl glyoxime method.

SUGGESTED METHOD FOR THE DETERMINATION OF CHROMIUM

The persulphate oxidation method used at the bureau is to be preferred where the best obtainable values are desired. However, direct fusion with sodium peroxide in a porcelain crucible and subsequent titration with ferrous sulphate and permanganate is simpler and can be safely recommended for all commercial purposes.

Solutions Required.—1. *Potassium permanganate 0.1 N.*—Dissolve 3.2 g of potassium permanganate 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 standard 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.) and add 5 cc of dilute H_2SO_4 (1 to 1). 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 fully decolorize 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 $KMnO_4$ is equivalent to 0.001733 g of chromium.

2. *Standard ferrous ammonium sulphate.*—Dissolve 43 g of the salt in 250 cc of cold water, add 40 cc of sulphuric acid (1 to 3), dilute to 1 liter with distilled water, and mix thoroughly. Large amounts of the solution can be conveniently mixed by means of a stream of carbon dioxide from a cylinder. As the ferrous ammonium sulphate solution gradually weakens in reducing power it is necessary to standardize it daily or at the same time the ferrochrome is analyzed. The solution can be standardized against either potassium dichromate or sodium oxalate.

The first method is somewhat simpler and more satisfactory for routine work as the conditions prevailing both the standardization and in the analysis are practically identical. No "blank" corrections are necessary where the amounts of dichromate, ferrous salt, and permanganate are approximately those prevailing in the analysis. The second method is employed chiefly for checking the accuracy of the results obtained with potassium dichromate and in cases where only occasional analyses are made and pure dichromate is not readily available.

To prepare pure potassium dichromate, recrystallize at least twice the purest grade of the salt obtainable, dry the crystals at 150° C., grind to a fine powder, and again dry at 150° C. to constant weight. Keep the prepared salt in a ground-glass stoppered bottle. Transfer 1.0000 g of the pure dichromate, which contains approximately the same amount of chromium as a 0.5000 g sample of 70 per cent ferrochromium, to an 800 cc beaker. Dissolve in cold water, acidify with 40 cc of sulphuric acid (1 to 3) and dilute with cold water to 500 cc. Add a slight excess of the ferrous sulphate solution, approximately 190 cc, and titrate the excess ferrous salt with 0.1 N permanganate to the first faint permanent darkening of the clear green color. The calculations involved are illustrated as follows: In a standardization, 190.0 cc of the ferrous solution was used and 5.04 cc of 0.1 N permanganate was required to titrate the excess.

$$\begin{aligned} 1 \text{ cc of } 0.1 \text{ N } K_2Cr_2O_7 & \text{ contains } 0.004903 \text{ g } K_2Cr_2O_7 \\ 1 \text{ g of } K_2Cr_2O_7 & = 203.96 \text{ cc of } 0.1 \text{ N } K_2Cr_2O_7 \end{aligned}$$

then

$$\begin{aligned} 203.96 + 5.04 & = 209.0 \text{ cc of equivalent } 0.1 \text{ N solution reduced by the ferrous solution} \\ \frac{209.0}{190} & = 1.100, \text{ the } 0.1 \text{ N normality factor.} \end{aligned}$$

In standardizing against sodium oxalate it is necessary to add the ferrous ammonium sulphate solution by means of an accurately calibrated pipette or burette instead of an automatic pipette. Transfer 100 cc of the approximately 0.1 N ferrous solution to a 600 cc beaker, dilute to 300 cc with cold 5 per cent sulphuric acid, add 2 cc of phosphoric acid and titrate immediately with 0.1 N $KMnO_4$ to a faint permanent pink color. Determine the "blank" on the same volume of water and acids and deduct. The permanganate is standardized against Bureau of Standards sodium oxalate as previously described. When standardizing against sodium oxalate, it is necessary in the actual analysis to determine a "blank" to counteract the influence of the green color of the chromium sulphate upon the permanganate end point. This "blank" can be determined on the solution used in the analysis and is obtained as described later.

Method.—1. Transfer 0.5000 g of the sample of ferrochromium (dried at 105 to 110° C.) to a 3 heavy walled porcelain crucible. Samples of low-carbon ferrochromium should be crushed to pass through a 40-mesh screen, while high carbon ferrochromium and chromium metal should be reduced to 100 mesh. Add approximately 8 g of sodium peroxide and thoroughly mix the contents of the crucible with a small rod, being careful to clean the rod, which can be done conveniently by scraping with another rod. Cover the mixture with 1 to 2 g of sodium peroxide. Carefully fuse the contents of the covered crucible, preferably in an electric muffle heated to 600 to 700° C. Five minutes fusion at a low red heat after the mass has melted will insure complete decomposition. When the charge has melted, the crucible should be given a slight rotary motion to stir up any unattached particles.

2. Place the cooled crucible and cover in a 600 cc beaker and dissolve the contents of the crucible in 200 cc of water. When the melt has dissolved, remove the crucible and cover, add 1 g of sodium peroxide and boil the solution 10 minutes to completely decompose the excess of peroxide.

3. Allow the precipitate to settle and filter through a pad of ignited asbestos, preferably in a Büchner funnel. An asbestos rather than a paper filter should be used as the alkaline solution extracts organic matter from the paper. The precipitate is thoroughly washed with hot water, and at no time should the precipitate be allowed to run dry during the filtering and washing. If desired, the precipitate can be subsequently dissolved in dilute sulphuric acid and tested for chromium by adding a slight excess of sodium peroxide; the amount of chromium retained is negligible if the precipitate is not allowed to run dry during the filtration.

4. Cool the filtrate, acidify with 50 cc of sulphuric acid (1 to 1), again cool to room temperature, transfer to an 800 cc beaker, dilute with cold water to 500 cc and add a measured excess of ferrous ammonium sulphate. The point at which reduction is complete can be told by the deep, green color developed. The ferrous salt can be added either as an approximately 0.12 *N* solution or in weighed portions from a bottle of the well-mixed salt. If the solution of ferrous salt is used, approximately 180 cc will be required for a 70 per cent alloy; if the salt is added, 8 g will usually be sufficient. Titrate the excess of ferrous salt with standard 0.10 *N* potassium permanganate. The first faint permanent darkening of the clear, green color is taken as the end point, which is quite sharp and well defined to the practiced eye. If the ferrous salt has been standardized against dichromate, subtract the required number of cc of 0.1 *N* permanganate from the number of cc of 0.1 *N* ferrous solution. The difference represents the number of cc of 0.1 *N* ferrous solution which multiplied by 0.001733 g gives the grams of chromium present.

Where the ferrous solution has been standardized against sodium oxalate, it is necessary, as stated before, to subtract a "blank" from the permanganate titration. This "blank" is obtained as follows: When the end point is reached and the readings have been noted, add about 5 cc excess of the ferrous solution and oxidize the excess of ferrous iron by adding 8 cc of a 15 per cent solution of ammonium persulphate. *Stir the liquid vigorously for one minute.* Carefully add 0.1 *N* permanganate to the solution with constant stirring until the same end point is obtained as before. The volume of permanganate required, usually 0.2 to 0.4 cc, constitutes the "blank" to be deducted from the volume of the permanganate titration. For example in the determination of chromium in a 0.5000 g sample 190.0 cc of a 0.11 *N* ferrous solution and 11.00 cc of a 0.1 *N* permanganate (11.40 - 0.4 cc blank) were employed. The calculations are as follows:

$$\begin{aligned} 190.0 \times 1.100 &= 209.0 \text{ cc } 0.1 \text{ } N \text{ ferrous solution} \\ 209.0 - 11.00 &= 198.00 \text{ cc} \\ 198.0 \times 0.001733 \times 2 \times 100 &= 68.62 \text{ per cent Cr} \end{aligned}$$

The above calculations are given for exactly 0.1 *N* permanganate; if the permanganate is not 0.1 *N* the volume used must be converted to the equivalent volume of 0.1 *N* by multiplying by the proper factor.