

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 60

FERROVANADIUM

(LOW CARBON)

	V	C	Fe	Mn	P	S	Si	Al	Cu	Ni	Cr	Mo	As	U	Ti
ANALYSTS*	VANADIUM	CARBON	IRON	MANGANESE	PHOSPHORUS Gravimetric	SULPHUR Gravimetric	SILICON	ALUMINUM	COPPER	NICKEL	CHROMIUM	MOLYBDENUM	ARSENIC	URANIUM	TITANIUM
1.-----	{ 33.52 ^a 33.51 ^b 33.60 ^c }	0.25	{ 46.98 ^d	3.38	0.057	0.104	1.25	12.55	0.93	0.049	0.016 ^e	0.89	0.004	0.01	0.016 ^e
2.-----	{ 33.50 ^a 33.53 ^f }	.24	{ 47.00 ^d	3.33	.055	.110	1.27	12.46	.95	.043	.025 ^g	.89	.005	-----	.025
3.-----	33.60 ^b	.23	47.06 ^h	3.27	.067	.105	1.31	12.42	.93	.062	.015	.92	.006	less than .01	.018
4.-----	33.67 ⁱ	.21	-----	3.44	.061	.122	1.29	-----	.88	.030	-----	.87	-----	-----	-----
5.-----	33.57 ^j	.23	-----	3.40	.049	.095	1.25	-----	-----	-----	-----	-----	-----	-----	-----
6.-----	33.59 ^k	.23	-----	3.36	.056	.102	1.22	12.50	-----	-----	-----	-----	-----	-----	-----
7.-----	33.58 ^l	.24	-----	3.30	.053	.109	1.36	12.30	-----	-----	-----	-----	-----	-----	-----
8.-----	33.42 ^b	.20	-----	3.42	.056	.110	1.30	12.40	-----	-----	-----	-----	-----	-----	-----
9.-----	33.54 ^k	.24	-----	3.45	.050	.100	1.27	12.58	-----	-----	-----	-----	-----	-----	-----
10.-----	33.48 ^b	.22	-----	3.44	.052	.104	1.29	-----	-----	-----	-----	-----	-----	-----	-----
AVERAGES-	33.55 ^l	.23	47.01	3.38	.056	.106	1.28	12.46	.92	.046	.019	.89	.005	.01	.02
Recommended values -----	33.55	.24	47.0	3.35	.06	.106	1.28	12.5	.94	.046	.02	.89	.005	.01	.02

^a Electrolysis with mercury cathode, reduction with SO₂ and titration with KMnO₄; cf. J. R. Cain, J. Ind. Eng. Chem., 3, 476, 1911.
^b U. S. Steel Corp. Method, FeSO₄-(NH₄)₂S₂O₈-KMnO₄.
^c H₂O₂ reduction in concentrated sulphuric acid.
^d Iron separated by NaOH treatment, then by (NH₄)₂S and tartaric acid, reduced in Jones reductor and titrated with KMnO₄.
^e Colorimetric.
^f HNO₃ oxidation, electrometric titration; cf. J. Ind. Eng. Chem., 13, 939, 1921.

^g Electrometric titration.
^h NaOH-H₂O₂ separation of Fe, SnCl₂ reduction, and KMnO₄ titration.
ⁱ Johnson's method.
^j Davis' modification of Johnson's method.
^k Campagne's method.
^l The atomic weight 51.0 was used for vanadium in all determinations.

* INDEX TO ANALYSTS

- James I. Hoffman, Bureau of Standards.
- Ferrous Laboratory, Bureau of Standards, H. A. Bright in charge.
- T. R. Cunningham and C. E. Plummer, Electro Metallurgical Co., New York, N. Y.
- S. C. King, Vanadium Corp. of America, Bridgeville, Pa.

- Oscar R. Smith, The Atlas Steel Corp., Dunkirk, N. Y.
- United Alloy Steel Corp., Canton, Ohio.
- N. W. Stewart, Standard Steel Works, Burnham, Pa.
- Bethlehem Steel Co., Cambria Works, Johnstown, Pa.
- W. D. Brown, Carnegie Steel Co., Duquesne, Pa.
- John L. Harvey, Carnegie Steel Co., Munhall, Pa.

George K. Burgess

Director

Washington, D. C.,

Nov. 23, 1924.

OUTLINE OF THE METHODS USED AT THE BUREAU OF STANDARDS FOR THE ANALYSIS
OF FERROVANADIUM STANDARD SAMPLES Nos. 60 AND 61

Vanadium.—Vanadium was first separated from chromium, iron, molybdenum, etc., by electrolysis with a mercury cathode as follows: Four-tenths (0.4000) of a gram of the sample was treated with 30 cc of sulphuric acid (1-3) and 5 cc of nitric acid (1.42) in a 200 cc platinum dish. When the reaction had ceased, the cover glass was rinsed, 2 cc of hydrofluoric acid was added, and the solution was carefully evaporated to fumes of sulphuric acid. The fumed solution was cooled and the salts dissolved by heating after the addition of 50 cc of water. The cooled solution was nearly neutralized with ammonium hydroxide, transferred to the mercury cell (used by J. R. Cain, *J. Ind. Eng. Chem.*, **3**, 476; 1911), and electrolyzed with a current of 5 to 6 amperes until every trace of iron was removed—about 2 hours. When electrolysis was complete, the electrolyte was removed and the mercury washed several times with water while the current was continued. The solution containing the vanadium was treated with 3 cc of sulphuric acid (1-1), heated to boiling, and sufficient strong permanganate solution added to give a good pink color. The vanadium was then reduced to the quadrivalent state by passing a stream of sulphur dioxide through the boiling solution for a few minutes. The excess of sulphur dioxide was removed by continuing the boiling and passing a rapid stream of carbon dioxide through the solution until the escaping steam gave no test for sulphur dioxide. The solution was cooled to 70 to 80° C. and titrated with standard, approximately 0.1*N* permanganate. The titration was corrected by a blank determination on a solution of like volume and acidity.

Carbon.—Carbon was determined by direct combustion of a 2 g sample mixed with 2 g of ingot iron, and absorption of CO₂ in ascarite.

Manganese.—Manganese was determined by the bismuthate method after removal of the vanadium by double separation with sodium hydroxide and sodium peroxide.

Phosphorus.—Phosphorus was determined as Mg₂P₂O₇. The precipitation with molybdate reagent was made at 20° C. after reduction of the vanadium with ferrous sulphate and sulphurous acid according to the procedure of Cain and Tucker, *J. Ind. Eng. Chem.*, **5** (1913), 647; and Lundell and Hoffman, *Ibid.*, **15**, 1923, 171.

Sulphur.—Sulphur was determined gravimetrically, the sample being dissolved in nitric acid (1.42). The ignited BaSO₄ was fused with sodium carbonate and examined for vanadium.

Silicon.—Silicon on standard No. 60 was determined by solution of 1 g of the sample in nitrosulphuric acid and evaporation to fumes of sulphuric acid. For standard No. 61, high silicon over 4 per cent, a factor weight 0.9352 g of the alloy was fused with 8 g of sodium peroxide in a 40 cc crucible of pure iron. The fusion was dissolved in water, acidified with sulphuric acid and evaporated to fumes, etc.

Aluminum.—Aluminum was determined as AlPO₄, after separation from vanadium by a modification of Johnson's method. One gram for No. 60 (and 5 g for No. 61) was dissolved in a platinum dish with nitrosulphuric acid containing a little hydrofluoric acid. The solution was evaporated to fumes of sulphuric acid, cooled, diluted to 150 cc, nearly neutralized with 10 per cent sodium hydroxide and then poured *slowly and with* constant stirring into 160 cc of 10 per cent sodium hydroxide. The solution and precipitate were transferred to a 500 cc graduated flask. An aliquot of 250 cc was filtered, diluted to 350 cc, heated to boiling and the aluminum precipitated by the careful addition of hydrochloric acid and the use of methyl red as an indicator. The acid was added until the yellow solution *just turned pink* and then several drops of dilute ammonia (1-20) were added to discharge the pink color. The second precipitate was dissolved in hydrochloric acid and the aluminum precipitated in the presence of ammonium acetate as AlPO₄; cf. Lundell and Knowles, *J. Ind. Eng. Chem.*, **12**, 1136; 1922.

Chromium.—Chromium was determined colorimetrically after fusion of the alloy with sodium peroxide. In addition for standard No. 61, a 3 g sample was dissolved in nitrohydrochloric acid, diluted to 250 cc, near

tralized with sodium hydroxide, and poured into a slight excess of sodium carbonate. The precipitate of iron, chromium, and small amounts of vanadium was filtered, dissolved in dilute sulphuric acid and the paper ignited, fused, and added to the main solution. Chromium was titrated electrometrically with the proper vanadium correction according to the method of Kelley, *J. Ind. Eng. Chem.*, **13**, 939; 1921.

Nickel.—Nickel was determined by the dimethyl gloxime method. The most of the vanadium and aluminum were removed by a sodium hydroxide-peroxide separation, the precipitate dissolved, and the nickel precipitated by dimethyl gloxime in the presence of tartrate.

Iron.—Iron was determined by titration with permanganate after reduction in the Jones reductor. The iron was first separated from the most of the vanadium by a sodium hydroxide and sodium peroxide separation and then completely freed from vanadium, titanium, and chromium by a double precipitation with ammonium sulphide in the presence of tartrate.

Molybdenum and Copper.—Molybdenum was separated from vanadium by precipitation with hydrogen sulphide in a 2 per cent sulphuric acid solution containing tartaric acid. The filtrate was oxidized and tested for complete precipitation of molybdenum. After complete recovery of molybdenum, the sulphides were dissolved and molybdenum separated from copper and iron by treatment with sodium hydroxide. Molybdenum was then precipitated by lead acetate and weighed as lead molybdate. The precipitate of copper and iron obtained with sodium hydroxide was dissolved, the iron removed with ammonium hydroxide, and the copper precipitated as CuS and ignited to CuO.

Titanium.—Titanium was determined as TiO₂ after precipitation with cupferron; cf. Lundell and Knowles, *J. Ind. Eng. Chem.*, **12**, 562; 1920. A 5 g sample was dissolved in nitrohydrochloric acid and evaporated to dryness. The dehydrated residue was treated with dilute hydrochloric acid, and filtered. The residue was ignited, treated with hydrofluoric and sulphuric acids to remove silica, then fused with sodium carbonate and the recovery later added to the acid extract from the ether separation. The bulk of the iron in the main filtrate was removed with ether. The acid extract from the ether separation was fumed with sulphuric acid, diluted, treated with potassium persulphate to oxidize vanadium and chromium and then with sodium hydroxide to precipitate iron and titanium. The solution was filtered, and the precipitate dissolved in hydrochloric acid and the iron removed by ammonium sulphide in the presence of tartaric acid. Titanium was precipitated in the filtrate by cupferron, and the ignited TiO₂ tested and corrected for any vanadium present.

Arsenic.—Arsenic was distilled as the trichloride from a 10 g sample, and precipitated as the sulphide. The arsenic sulphide was dissolved in ammonia, the arsenic oxidized with nitric acid, precipitated as silver arsenate in acetic acid-sodium acetate solution and titrated as in Volhard's method.

SUGGESTED METHOD FOR THE DETERMINATION OF VANADIUM

The electrolysis method employed at the Bureau of Standards is the most suitable method for very accurate determinations. The ammonium persulphate method described below is very satisfactory for all general purposes and is simpler and shorter than the electrolysis method.

Solutions Required.—*Ammonium persulphate (15 per cent).*—Make up as needed by dissolving 15 g of the salt in 100 cc of distilled water. This salt should be 95 per cent pure and its purity tested by adding 30 cc of a standard ferrous solution to 0.3 g of the persulphate, adding 200 cc of hot water and titrating the excess of ferrous salt with potassium permanganate. One cc of 0.1 *N* ferrous solution equals 0.01141 g of (NH₄)₂S₂O₈.

Potassium ferricyanide indicator.—Dissolve 0.1 g of the salt in 100 cc of water. This solution should be made up fresh daily.

Standard ferrous ammonium sulphate, approximately 0.1 N.—Dissolve 42 g of the c.p. salt in 200 cc of cold water, add 20 cc of sulphuric acid 1-1, dilute to a liter and mix thoroughly.

Potassium permanganate, 0.1 N.—Dissolve 3.2 g of KMnO_4 in 1,000 cc of distilled water, allow to age 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 0.25 to 0.30 g of sodium oxalate in 250 cc of hot water (80 to 90° C.) and add 10 cc of dilute H_2SO_4 (1-1). 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 0.0051 g of vanadium in the following method.

Method.—Treat 0.5000 g of the alloy, dried at 105 to 110° C., in a 250 cc covered beaker with a mixture of 60 cc of sulphuric acid (1-3) and 25 cc of nitric acid (1-1). If the alloy fails to decompose readily because the silicon content is high, it may be necessary to add a small amount of hydrofluoric acid. In this event a 200 cc platinum dish should be substituted for the beaker. When the reaction has abated, rinse the cover glass and evaporate the solution until copious fumes of sulphuric acid are evolved. Cool, add 100 cc of water and heat until the salts are dissolved. Transfer the solution to an 800 cc beaker, dilute to 400 cc and to the cooled solution add an approximately 0.1 *N* solution of potassium permanganate until a strong pink color has developed which remains permanent for thirty seconds. Next reduce the vanadium by the use of an approximately 0.1 *N* solution of ferrous ammonium sulphate added until a drop of the solution withdrawn from the beaker and placed on a drop of potassium ferricyanide indicator shows ferrous iron present—about 35 cc of solution. Add 5 cc of the ferrous ammonium sulphate in excess, stir the solution at least one minute, oxidize the excess of ferrous sulphate with 8 cc of 15 per cent ammonium persulphate and stir the solution vigorously for *one minute*. Titrate the solution with an 0.1 *N* potassium permanganate solution, added with constant stirring until a faint pink color appears which remains permanent for thirty seconds. Determine “blank” by dissolving 0.4 g of “ingot iron” in 60 cc of H_2SO_4 (1-3) and 5 cc of nitric acid (1.42) and putting the solution through all of the operations of the analysis. If the alloy contains an appreciable amount of chromium, a weight of pure $\text{K}_2\text{Cr}_2\text{O}_7$ equivalent to the amount of chromium in the sample is dissolved in the acids together with the ingot iron.