

DEPARTMENT OF COMMERCE

Bureau of Standards
Certificate of Analyses
 OF
STANDARD SAMPLE No. 61
FERROVANADIUM
 (HIGH 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.....	{31.11 ^a 31.09 ^b }	1.15	{52.76 ^c 52.82 ^d }	3.60	0.243	0.002	7.75	0.03	0.28	1.34	0.57 ^e	0.72	0.004	0.01	0.26 ^f
2.....	{31.15 ^a 31.10 ^f }	1.17	52.75 ^c	3.58	.247	.004	7.72	.024	.30	1.33	.52 ^g	.71	.003	-----	.24
3.....	31.27 ^{a,h}	1.15	52.84 ^d	3.45	.241	.003	7.81	.01	.30	1.30	.48	.72	.006	-----	.19
4.....	31.14 ⁱ	1.09	-----	3.45	.230	.003	7.70	.03	-----	1.32	-----	.63	-----	-----	-----
5.....	31.16 ^j	1.17	-----	3.50	.237	.005	7.87	-----	-----	1.34	-----	.67	-----	-----	-----
-----	31.25 ^k	1.12	-----	3.66	.236	.005	7.75	.03	-----	-----	-----	-----	-----	-----	-----
7.....	31.69 ⁱ	1.13	-----	3.60	.23	.004	7.61	-----	-----	-----	.50	-----	-----	-----	-----
8.....	31.30 ^b	1.13	-----	3.55	.246	-----	7.90	-----	.35	-----	-----	-----	-----	-----	-----
9.....	31.21 ^k	1.14	-----	3.58	.200	-----	7.78	.03	-----	-----	-----	-----	-----	-----	-----
10.....	31.21 ^b	1.13	-----	3.65	.204	-----	8.02	-----	-----	-----	-----	-----	-----	-----	-----
11.....	31.11 ^f	1.13	-----	3.54	-----	-----	7.81	-----	-----	-----	.51	-----	-----	-----	-----
12.....	30.97 ^k	1.15	-----	3.65	.245	.006	7.86	.02	-----	-----	-----	-----	-----	-----	-----
AVERAGES.....	31.12 ^l	1.14	52.79	3.57	.233	.004	7.80	.025	.31	1.33	.52	.70	.004	.01	.23
Recommended values.....	31.15	1.15	52.8	3.57	.243	.003	7.78	.02	.29	1.33	.52	.72	.004	.01	.23

^a Electrolysis with mercury cathode, reduction with SO₂ and titration with KMnO₄; cf. J. R. Cain, J. Ind. Eng. Chem., 3, 478; 1911.
^b U. S. Steel Corp. method, FeSO₄-(NH₄)₂SO₄-KMnO₄.
^c Iron separated by NaOH treatment, then by (NH₄)₂S and tartaric acid, reduced in Jones reductor and titrated with KMnO₄.
^d NaOH-H₂O₂ separation of Fe, SnCl₄ reduction and KMnO₄ titration.
^e Colorimetric.

^f HNO₃ oxidation and electrometric titration; cf. J. Ind. Eng. Chem., 13, 939; 1921.
^g Electrometric titration.
^h Same value obtained with method^b.
ⁱ Johnson's method.
^j Davis' modification of Johnson's method.
^k Campaigne's method.
^l The atomic weight 51.0 was used for vanadium in all determinations.

***INDEX TO ANALYSTS**

- | | |
|---|--|
| 1. James I. Hoffman, Bureau of Standards. | 7. N. W. Stewart, Standard Steel Works, Burnham, Pa. |
| 2. Ferrous Laboratory, Bureau of Standards, H. A. Bright in charge. | 8. Bethlehem Steel Co., Cambria Works, Johnstown, Pa. |
| 3. T. R. Cunningham and C. E. Plummer, Electro Metallurgical Co., New York, N. Y. | 9. W. D. Brown, Carnegie Steel Co., Duquesne, Pa. |
| 4. S. C. King, Vanadium Corp. of America, Bridgeville, Pa. | 10. John L. Harvey, Carnegie Steel Co., Munhall, Pa. |
| 5. Oscar R. Smith, The Atlas Steel Corp., Dunkirk, N. Y. | 11. G. L. Kelley, Edward Budd Manufacturing Co., Philadelphia, Pa. |
| 6. United Alloy Steel Corp., Canton, Ohio. | 12. W. F. Lantz, Bethlehem Steel Co., Bethlehem, Pa. |

George K. Burgess

Director

Washington, D. C.,
 Nov. 28, 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

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.