

DEPARTMENT OF COMMERCE

Bureau of Standards  
Certificate of Analyses

OF  
STANDARD SAMPLE No. 75  
FERROTUNGSTEN

ANALYST*	TUNGSTEN	CARBON	MANGANESE	PHOSPHORUS	SULPHUR (GRAVIMETRIC)	SILICON	COPPER	TIN	ARSENIC	MOLYBDENUM	ANTIMONY	BISMUTH
1-----	75. 21	0. 537	1. 18	0. 013	{ 0. 038 . 033 <sup>a</sup> }	0. 67	0. 042	0. 19	0. 038	0. 239	<0. 002	Not detected.
2-----	75. 26											
3-----	75. 20	. 55	1. 14	. 018	. 040	. 67	. 039	. 178	. 035	. 21	. 01	
4-----	{ 75. 18 <sup>b</sup> 75. 18 <sup>c</sup> }	. 526	1. 16	. 015	. 041	. 67	. 039	. 196	. 039	. 222	Not detected.	Not detected.
5-----	75. 19	. 55	1. 14	. 017	. 036	. 66	. 041	. 156	. 03		Trace.	None.
	75. 20	. 55	1. 15	. 018	. 042	. 70	. 045	. 164	. 033			
7-----	75. 17	. 55	1. 19	. 014	. 040	. 59 <sup>d</sup> . 72 <sup>e</sup>	. 040	. 179	. 033	. 21	Trace. <sup>f</sup>	Trace. <sup>f</sup>
8-----	75. 17	. 536	1. 17	. 017	. 042	. 68	. 036	. 184	. 040	. 22	Not detected.	Not detected.
9-----	75. 20	. 566	1. 14	. 010	. 033	. 69	. 030	{ . 186 <sup>g</sup> . 195 <sup>h</sup> }	. 038			
10-----	75. 30	. 553	1. 16	. 016	. 041	. 646	. 043	. 161	. 031	. 216	Trace.	Trace.
Averages-----	75. 21	. 546	1. 16	. 015	. 039	. 67	. 039	. 179	. 035	. 219		
Recommended values	75. 2	. 54	1. 16	. 015	. 039	. 67	. 039	. 18	. 035	. 23		

<sup>a</sup> Sulphur evolved by Johnson's hot-tube method.  
<sup>b</sup> Dissolved in HNO<sub>3</sub>-HF; ignited WO<sub>3</sub> corrected for Mo and matter insoluble in Na<sub>2</sub>CO<sub>3</sub>.  
<sup>c</sup> Dissolved in HNO<sub>3</sub>-HF and boric acid added to expel HF.  
<sup>d</sup> Silica dehydrated in presence of all of the tungsten.  
<sup>e</sup> Phosphoric acid added to hold up tungsten during dehydration of the silica.

<sup>f</sup> Reported less than 0.01 per cent; tested on 10 g samples.  
<sup>g</sup> Fused with Na<sub>2</sub>O<sub>2</sub>, acidified with HCl, boiled under reflux condenser, tungsten filtered off and tin determined in filtrate.  
<sup>h</sup> Fused with Na<sub>2</sub>O<sub>2</sub>, sulphides precipitated and tin subsequently determined by reduction with iron.

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Washington, D. C.,  
October 1, 1923

*George K. Burgess*  
Director.

OUTLINE OF THE METHODS USED AT THE BUREAU OF STANDARDS FOR THE ANALYSIS  
OF FERROTUNGSTEN STANDARD SAMPLE No. 75

**Tungsten.**—Tungstic acid was precipitated twice and corrected for silica, iron oxide, and molybdenum as described in the suggested method for tungsten.

**Carbon.**—Carbon was determined by direct combustion in oxygen of a 1 g sample mixed with 2 g of ingot iron in a silica boat and heated at a temperature of 1,000 to 1,050° C. The evolved CO<sub>2</sub> was absorbed in ascarite and a blank determined and subtracted.

**Manganese.**—One g of the alloy was dissolved in HNO<sub>3</sub>-HF, 5 ml of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) was added and the solution evaporated to dense fumes. After dilution, the solution was filtered, the residue treated with a 10 per cent solution of NaOH, and the insoluble material filtered, dissolved, and added to the main filtrate. The combined filtrates were heated to fumes of H<sub>2</sub>SO<sub>4</sub>, diluted, and manganese determined by the bismuthate method.

**Phosphorus.**—A 5 g sample was dissolved in HNO<sub>3</sub>-HF, 10 ml of H<sub>2</sub>SO<sub>4</sub> was added, and the solution evaporated to dense fumes of H<sub>2</sub>SO<sub>4</sub>. The solution was treated with dilute HCl, boiled, and the tungstic acid removed by filtration. A slight excess of NH<sub>4</sub>OH was added to the filtrate and the solution boiled, filtered, and the precipitate dissolved in HNO<sub>3</sub>. Phosphorus was then determined by the alkali-molybdate method. The phosphorus in the tungstic acid residue was recovered by precipitation with magnesia mixture in the presence of tartrate.

**Sulphur.**—GRAVIMETRIC. A 3 g sample was fused with 16 g of Na<sub>2</sub>CO<sub>3</sub> and 3 g of KNO<sub>3</sub> in a large platinum crucible. The melt was dissolved in an excess of HCl, evaporated, and baked to remove silica and tungsten. The last traces of tungsten in the silica filtrate were removed with cinchonine and the sulphur then precipitated in reduced solution with BaCl<sub>2</sub>. Blanks were carried through all steps.

**Evolution.**—A 3 g sample was heated for two to three hours at 950° C. in a stream of hydrogen saturated with HCl and the evolved H<sub>2</sub>S was absorbed in ammoniacal CdCl<sub>2</sub>.

**Silicon.**—A 2 g sample was fused with 12 g of Na<sub>2</sub>O<sub>2</sub> in an Armco iron crucible. The melt was dissolved in an excess of HCl, the solution evaporated, and the residue baked for one hour at 105° C. The residue was taken up in HCl, diluted, and filtered. The filtrate was made slightly ammoniacal, filtered, the residue dissolved in 60 ml of H<sub>2</sub>SO<sub>4</sub> and the acid solution evaporated to dense fumes, cooled, diluted, filtered, and the silica so recovered added to the main portion. The two papers and residues were slowly heated until the carbon was consumed, and then finally at a temperature of 1,000° C. for 20 minutes. After cooling and weighing, the residue was treated with HF and H<sub>2</sub>SO<sub>4</sub>, carefully evaporated to dryness, heated at 750° C. for about five minutes, cooled, and weighed.

**Copper, Bismuth, Tin, Etc.**—Four 5 g samples were separately fused with 20 g portions of Na<sub>2</sub>O<sub>2</sub>. The melts were dissolved in dilute H<sub>2</sub>SO<sub>4</sub> and sulphides precipitated, filtered, combined, etc., as directed in the method given later for tin. The sulphides were again precipitated and copper and bismuth separated from the sulpho group by treatment with sodium sulphide. Bismuth was tested for by the oxychloride method and copper determined by electrolysis.

The alkaline sulphide solution of the sulpho group was acidified, the sulphides filtered out, and dissolved in HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>. Arsenic was removed by distilling at a temperature not over 108° C. after removing the HNO<sub>3</sub> and reducing the arsenic. A small amount of aluminum was added to the solution remaining after the distillation, and aluminum, tin, and antimony separated from molybdenum by precipitation with ammonia. The solution was filtered and molybdenum determined in the filtrate by precipitating as MoS<sub>3</sub> and igniting the sulphide to MoO<sub>3</sub>. Tin and antimony were separated by Clark's oxalic method. Antimony was reduced with sulphite and titrated with permanganate, and tin was reduced with test lead and titrated with iodine.

RECOMMENDED METHOD FOR DETERMINATION OF TUNGSTEN IN FERROTUNGSTEN

**Special Solutions Required.**—CINCHONINE SOLUTION.—Dissolve 125 g of cinchonine in a mixture of 500 ml of HCl (sp. gr. 1.19) and 500 ml of distilled water.

CINCHONINE WASH SOLUTION.—Dilute 30 ml of the above solution to 1 liter.

AMMONIA WASH SOLUTION.—Dilute 200 ml of NH<sub>4</sub>OH (sp. gr. 0.90) with water, add 10 ml of HCl (sp. gr. 1.19), and dilute to 1 liter.

**PROCEDURE.**—Transfer 1 g of the alloy, ground to pass a 100 mesh sieve, to a 100 ml flat-bottomed platinum dish provided with a platinum or gold

cover. Treat with 10 ml of HF (48 per cent) and add 10 to 15 ml HNO<sub>3</sub> (sp. gr. 1.84), a few drops at a time, until the metal is decomposed. The reaction is usually *quite vigorous* and the dish should be kept well covered to prevent mechanical loss. After no further action is noted when HNO<sub>3</sub> is added, digest on the steam bath for 10 to 15 minutes. Remove and rinse the lid and wash down the sides of the dish with a fine jet of water. Evaporate the solution to the point where tungsten just begins to separate, add 10 ml of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) and slowly evaporate to dense fumes of the acid.

Cool the dish and contents, add 75 ml of dilute HCl (1:10), digest for 10 minutes, transfer the solution to a 400 or 600 ml beaker, and thoroughly scrub out the dish. To remove the small amounts of tightly adhering tungsten and iron rinse the dish successively with 2 to 3 ml of warm concentrated HCl, water, three to four drops of  $\text{NH}_4\text{OH}$ , water, and 1 to 2 ml of HCl. Dilute the solution to 250 ml and boil for about five minutes. Remove from the source of heat, add 10 ml of cinchonine solution and digest for one hour or longer, with occasional stirring at a temperature of 80 to 90° C. Stir in some paper pulp and allow the precipitate to settle before filtering.

Filter on a tight 11 cm paper containing a little ashless paper pulp and wash several times by decantation with 30 to 40 ml portions of hot cinchonine wash solution. Transfer the remainder of the precipitate to the filter, wash a few times with hot dilute cinchonine and then several times with hot 1 per cent HCl to remove most of the cinchonine. (See note 1 regarding routine tungsten determinations.)

Return the paper and precipitate to the original beaker, add 50 to 75 ml of hot water, stir with a glass rod and digest until the paper is broken up. Add 10 ml of  $\text{NH}_4\text{OH}$  (sp. gr. 0.90) and boil gently for a few minutes. Rinse down the sides of the beaker with a little warm "ammonia wash solution," and filter through a tight 11 cm paper. Collect the filtrate in a 400 or 600 ml beaker and wash 8 to 10 times with hot 0.5 per cent ammonium chloride solution. The residue on the paper (A) is treated as directed later for recovery of tungsten. Boil the filtrate to expel the excess of  $\text{NH}_4\text{OH}$ , add 20 ml of HCl (sp. gr. 1.19), 10 ml of  $\text{HNO}_3$  (sp. gr. 1.42), and slowly boil down to a volume of about 50 ml, whereby most of the tungsten will be precipitated. Dilute to 250 ml, add 10 ml of cinchonine solution and some paper pulp, and digest, with occasional stirring, for several hours at a temperature of 80 to 90° C. To recover the tungsten in residue A, place the funnel and paper over a 250 ml beaker and treat as follows: Wash the paper several times with hot 10 per cent HCl to remove iron, several times with 0.5 per cent ammonium chloride solution, twice with "ammonia wash solution," and then five or six times with hot 0.5 per cent ammonium chloride. Ignite the paper in a clean porcelain crucible at a temperature not exceeding 750° C. If a residue remains digest it with a little 10 per cent solution of NaOH and filter into the beaker containing the acid washings. Evaporate to about 50 ml, add 5 ml of cinchonine, and digest for several hours. If a precipitate appears,

filter through a tight 11 cm paper containing some ashless paper pulp and then filter the main tungsten precipitate on the same filter. Wash well with hot cinchonine wash solution.

Transfer the paper and contents to a large weighed platinum crucible, slowly char the paper, and finally ignite at a temperature below 750° C. until the carbon has burned off completely. Cool, carefully moisten with five to six drops of HF and carefully evaporate to dryness to expel any silica. Ignite to constant weight at a temperature of 700 to 750° C.

The ignited precipitate must be tested for iron and molybdenum as follows: Add 5 g of  $\text{Na}_2\text{CO}_3$  to the crucible containing the tungsten trioxide and fuse, running the fusion around the side of the crucible to remove all tungsten trioxide. Cool, dissolve the melt in 50 ml of hot water, digest the solution for 30 minutes and remove and wash the platinum crucible. If a residue remains, filter on a tight paper and thoroughly wash with hot water. Ignite, and deduct the difference from the weight of the impure  $\text{WO}_3$ . Correct for any impurities found in a blank run on the sodium carbonate. Add 2 to 3 g of tartaric acid to the alkaline filtrate, saturate with hydrogen sulphide, add  $\text{H}_2\text{SO}_4$  (1:1) until the solution contains 2 ml per 100 ml in excess, and pass  $\text{H}_2\text{S}$  through the solution for a few minutes. Digest for one to two hours at a temperature of 50 to 60° C., filter and wash the sulphides with a 0.5 per cent  $\text{H}_2\text{SO}_4$  solution saturated with  $\text{H}_2\text{S}$ . Char the paper in a tared porcelain crucible, ignite to constant weight at a temperature not above 525° C. and subtract the weight of oxide found from the weight of the impure  $\text{WO}_3$ . If the amount of oxide found exceeds 2.5 mg it is advisable to dissolve the weighted residue and reprecipitate the sulphides in order to completely free them from tungsten. The sodium carbonate should likewise be tested for impurities and suitable correction made.

NOTE.—In routine work thoroughly wash the precipitate of impure tungsten that is first obtained, with hot cinchonine solution and finally several times with warm 1 per cent HCl. Gently ignite the filter and residue of crude  $\text{WO}_3$  in a platinum crucible until the carbon is consumed. Add a few drops of  $\text{HNO}_3$ , dry in a radiator, and ignite to constant weight at a temperature of 700 to 750° C. Cool and weigh. Add 5 g of  $\text{Na}_2\text{CO}_3$  and fuse, running the fusion around the side of the crucible to remove all  $\text{WO}_3$ . Dissolve the melt in hot water and digest. Filter and wash well with hot water. Ignite in the crucible first used, cool and weigh. The difference between the weight of the crucible plus residue and the weight of the crucible plus impure tungsten oxide represents  $\text{WO}_3$ . The  $\text{Na}_2\text{CO}_3$  should be tested for water insoluble material and suitable correction made, if any be found. If the alloy contains molybdenum the sodium carbonate extract should be tested for molybdenum as directed above.

(OVER)

## RECOMMENDED METHOD FOR THE DETERMINATION OF TIN IN FERROTUNGSTEN

**General.**—The alloy is fused with  $\text{Na}_2\text{O}_2$  in an Armco iron crucible, the tin precipitated with  $\text{H}_2\text{S}$ , and separated from molybdenum by precipitating with  $\text{NH}_4\text{OH}$  after adding some aluminum. It is not convenient to start with more than 5 g of sample. To secure the advantages of working with more material, two 5 g samples can be separately fused, precipitated with  $\text{H}_2\text{S}$ , and later combined after the sulphide precipitates are dissolved in  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ . If the tin is quite low (less than 0.03 per cent) three or four 5 g samples should be combined.

**Procedure.**—Mix 5 g of the finely powdered metal (100 mesh or finer) with approximately 20 g of dry  $\text{Na}_2\text{O}_2$  in a 40 ml Armco iron crucible stamped from No. 20 gauge metal. These crucibles can be purchased from the Consolidated Metal Products Co., Dayton, Ohio.

Cover with a porcelain or iron crucible lid and fuse the contents of the crucible by heating, first at a low temperature, and then gradually raising the temperature until complete fluidity of the mass occurs. The temperature should not be raised too rapidly lest spattering occur. When the charge is molten, rotate the crucible to take care of unattached particles of the alloy along the sides of the crucible and also to stir up the fusion. Keep the charge molten for five to six minutes, heat to bright redness for a minute, and then allow to cool. If the fusion is carefully made little or no spattering will occur and complete decomposition will be obtained.

Place the crucible in an 800 ml covered beaker containing about 375 ml of water, warm for a few minutes; remove the crucible, and rinse it well with warm water. Add 15 g of tartaric acid and make the solution slightly acid with  $\text{H}_2\text{SO}_4$  (1:1) and heat just below boiling temperature until a clear solution is obtained. A little iron scale from the crucible may remain insoluble; in which case the solution may be filtered through a rapid paper and washed with hot dilute  $\text{H}_2\text{SO}_4$  (1:50).

Add an excess of 5 ml of  $\text{NH}_4\text{OH}$  (sp. gr. 0.90) to the clear solution, dilute to 500 ml, heat to  $70^\circ\text{C}$ ., and treat with a brisk stream of  $\text{H}_2\text{S}$  for 30 minutes. Add  $\text{H}_2\text{SO}_4$  (1:1) until the solution contains an excess of approximately 2 ml per 100 ml of solution, stir well, and pass  $\text{H}_2\text{S}$  into the solution for about 10 minutes.

Digest the precipitate for one to two hours at a temperature of  $60$  to  $70^\circ\text{C}$ . Filter on an 11 cm paper containing a little paper pulp and wash the precipitated sulphides with hydrogen sulphide water containing 0.5 per cent of  $\text{H}_2\text{SO}_4$  and 0.5 per cent of tartaric acid. For umpire work and more especially if it is desired to determine molybdenum on the same sample, it is desirable to treat the first sulphide filtrate as follows: Gently boil the solution to remove  $\text{H}_2\text{S}$ , add 10 to 15 ml of bromine water, and boil for a few minutes. Cool somewhat and add  $\text{NH}_4\text{OH}$  in 5 ml excess. Warm to  $70^\circ\text{C}$ ., precipitate with  $\text{H}_2\text{S}$ , acidify, filter, and wash as before.

Return the two papers and precipitates to the beaker in which the precipitation was made, add 10 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84), warm for a few minutes, cool, add 25 ml of  $\text{HNO}_3$  (sp. gr. 1.42), and evaporate slowly to fumes of  $\text{H}_2\text{SO}_4$ . Cool, add 20 ml of  $\text{HNO}_3$ , and again evaporate to fumes. The solution should now be clear and of a light color. If not, repeat the treatment with  $\text{HNO}_3$ .

Dilute the cooled solution to 75 ml and warm for a few minutes. Some tungstic acid may separate at this stage, particularly if two sulphide precipitations were made. If this occurs, filter the solution through a tight paper containing a little paper pulp and wash with dilute  $\text{H}_2\text{SO}_4$  (1:100). Even though tungsten is not present at this stage it is advisable to filter the solution to remove the small sulphur ball that is usually present.

To the filtered solution add 10 ml of a 5 per cent solution of  $\text{Al}_2(\text{SO}_4)_3$  and precipitate the aluminum and tin by adding gradually, while thoroughly stirring the solution, an excess of 5 cc of  $\text{NH}_4\text{OH}$ . Heat to boiling, allow to settle, filter, and wash the precipitate with a hot 1 per cent solution of  $\text{NH}_4\text{Cl}$ . For umpire work the precipitate should be dissolved in hot  $\text{HCl}$  (1:1) and the precipitation with  $\text{NH}_4\text{OH}$  repeated. Molybdenum can, if desired, be determined in the combined ammoniacal filtrates.

**NOTE.**—The addition of the aluminum solution can be omitted if it is not desired to later determine antimony. However, if the tin is very low (<0.02 per cent) it is desirable to add a few ml of the 5 per cent aluminum solution.

Place an Erlenmeyer flask (300 to 500 ml) under the funnel containing the precipitate, dissolve the precipitate with 80 ml of hot  $\text{HCl}$  (1:1) and wash the filter thoroughly with a hot 2 per cent solution of  $\text{HCl}$ .

The tin is next reduced from the stannic to the stannous condition with test lead. This operation may be made as follows: Adjust the volume of the solution in the flask to about 250 ml, add 35 ml of  $\text{HCl}$  (sp. gr. 1.19) and insert a 3-hole rubber stopper carrying gas inlet and outlet tubes and having the third hole closed by a small cork stopper. For the outlet tube it is advisable to use an air condenser about 20 cm in length and about 0.25 cm in diameter. Add 1 to 2 g of test lead, start a slow current of carbon dioxide from a Kipp generator or a cylinder, heat gradually to boiling, and boil gently for about 40 minutes. Finally cool in ice water to about  $10^\circ\text{C}$ . after increasing the current of  $\text{CO}_2$  in order to prevent back pressure. This may be detected by placing a bubbling tube at the top of the gas outlet. When the solution has cooled, remove the bubble tube and add 5 ml of starch solution through the gas outlet tube. Take out the small cork stopper and insert the tip of a 15 or 25 ml buret containing a standard 0.03 *N* solution of iodine. Titrate to a permanent blue tint. The titration should be corrected by duplicate blank determinations carried through all steps of the procedure and the titer of the iodine solution should be obtained by reducing weighed amounts of pure tin with test lead as rected above.