



Designation: E367 – 09

Standard Test Methods for Chemical Analysis of Ferroniobium¹

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1. Scope

1.1 These test methods cover the chemical analysis of ferroniobium having chemical compositions within the following limits:

Element	Concentration, %
Aluminum	2.00 max
Carbon	0.30 max
Chromium	2.00 max
Cobalt	0.25 max
Lead	0.01 max
Manganese	3.00 max
Niobium	40.00 to 75.00
Phosphorus	0.05 max
Silicon	4.00 max
Sulfur	0.03 max
Tantalum	7.00 max
Tin	0.15 max
Titanium	5.00 max
Tungsten	0.50 max

1.2 The test methods appear in the following order:

	Sections
Separation of Niobium, Tantalum, and Titanium	10-16
by the Ion-Exchange Test Method	
Titanium by the Photometric Test	17-21
Method [0.05 % to 5.0 %]	
Niobium by the Gravimetric Test	22-23
Method [40 % to 75 %]	
Tantalum by the Gravimetric Test	24-25
Method [1 % to 7 %]	
Tantalum by the Photometric Test	26-30
Method [0.25 % to 1 %]	

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6, and specific warning statements in 11.1.

2. Referenced Documents

2.1 ASTM Standards:²

- A550 Specification for Ferrocolumbium
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)³
- E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definition of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications such as Specification A550. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Photometric Practice

5.1 Apparatus, standard solutions, and other reagents required for each determination are listed in separate sections

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

preceding the procedure. Photometers shall conform to the requirements prescribed in Practice E60.

5.2 Photometric practice prescribed in these test methods shall conform to Practice E60.

6. Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

6.2 Specific warning statements are given in 11.1.

7. Sampling

7.1 For procedures for sampling the material, and for particle size of the sample for chemical analysis, refer to Practices E32.

8. Rounding Off Calculated Values

8.1 Calculated values shall be rounded off to the desired number of places as directed in Practice E29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practice E173, unless otherwise noted in the precision and bias section.

NIOBIUM, TANTALUM, AND TITANIUM BY THE ION-EXCHANGE TEST METHOD

10. Scope

10.1 These test methods cover the determination of niobium, tantalum, and titanium in ferroniobium from 40 % to 75 %, 0.25 % to 7 %, and 0.05 % to 5.0 %, respectively.

11. Summary of Test Method

11.1 The sample is dissolved in a HCl-HF acid mixture and transferred to an anion-exchange column. Titanium, iron, and other elements are eluted with an NH_4Cl -HCl-HF acid mixture. This eluate is treated with boric acid (H_3BO_3) and cupferron, and the precipitate, containing the titanium, is ignited, fused with potassium hydrogen sulfate, and leached in dilute H_2SO_4 . The titanium is oxidized to the yellow pertitanate with hydrogen peroxide. Photometric measurement is made at approximately 410 nm. Niobium is removed by eluting with an ammonium chloride-hydrofluoric acid mixture. Tantalum is removed by eluting with an ammonium chloride-ammonium fluoride solution adjusted to a pH of 5 to 6. The eluates are treated with the H_3BO_3 to complex the fluorides, and each of the elements, niobium and tantalum, is precipitated with cupferron, ignited, and weighed as the pentoxide. For tantalum below 1 %, zirconium is added as a gatherer in the cupferron separation and the tantalum is converted to the pyrogallol complex. Photometric measurement is made at approximately 420 nm. (**Warning**—HF produces very serious burns which may or may not be painful on first contact. Such burns often damage bone and other tissue within the body. Standard procedure is to use gloves and protective clothing when handling this reagent. After the material is added, the closed container, gloves, and all surfaces that may later be touched are rinsed with large quantities of water. Even one drop of HF on

the skin or fingernail must receive immediate first-aid and medical attention should be promptly sought.)

12. Interferences

12.1 Any bismuth present will appear in the tantalum fraction, but this element is seldom present greater than 0.005 % in this ferroalloy. Trivalent antimony, if present, is eluted with the titanium and precipitated with cupferron, but it does not interfere in the photometric test method for titanium.

13. Apparatus

13.1 *Ion-Exchange Columns*—The columns must be constructed of polystyrene tubing approximately 300-mm long and 25 mm in inside diameter. A suitable column can be prepared as follows: Insert a waxed, No. 5 rubber stopper containing a 5-mm hole into the bottom of the polystyrene tube. Insert into the hole and flush with the upper surface of the stopper a 150-mm length of polystyrene tubing, having a 5-mm outside diameter and a 2-mm bore. Attach another 150-mm length of this tubing to the smaller tube with an approximately 50-mm length of polyvinyl tubing,⁴ and control the flow rate by a hosecock on the polyvinyl tubing.

13.1.1 If a number of determinations are to be made, it is convenient to arrange the columns so that they can be operated with a minimum of attention. Plastic columns equipped with fittings of polystyrene have been developed for such an assembly.⁵ Inlet and outlet tubes are polyethylene; flexible connections, where necessary, are of polyvinyl tubing. The flow rate is controlled by hosecocks on these flexible connections. The system must be carefully assembled and checked to avoid possible leakage of the solutions containing HF.

13.2 *Plastic Ware*—Polyethylene, polypropylene, or TFE-fluorocarbon.

13.2.1 *Bottles*, 250-mL and 1-L capacity.

13.2.2 *Graduated Cylinders*, 50-mL and 250-mL capacity.

13.2.3 *Griffin-Form Beakers and Covers*, 250-mL, 600-mL, and 1-L capacity.

14. Reagents

14.1 *Ammonium Chloride Solution* (240 g/L)—dissolve 480 g of ammonium chloride (NH_4Cl) in 1600 mL of water by warming, cool, dilute to 2 L, and mix. Filter, if necessary. Use this stock solution to prepare the solutions described in 14.2-14.4.

14.2 *Ammonium Chloride-Ammonium Fluoride Neutral Mixture*—Transfer 600 mL of the NH_4Cl solution and 40 mL of HF to a plastic beaker. Adjust the pH from 5 to 6 with NH_4OH (approximately 80 mL to 85 mL will be required), dilute to 1 L with water, and mix.

NOTE 1—This solution must be prepared with care. If the pH is too low, the volume specified will not completely elute the tantalum; if the pH is too high, tantalum will precipitate in the column, thus leading to error in the determinations being run as well as the one which follows.

⁴ Tygon-R tubing has been found satisfactory for this purpose.

⁵ Columns available from Ledoux and Co., Inc., Teaneck, NJ, have been found satisfactory for this purpose.

14.3 *Ammonium Chloride-Hydrochloric-Hydrofluoric Acid Mixture*—Transfer 240 mL of the NH_4Cl solution, 200 mL of HF and 150 mL of HCl to a plastic bottle. Dilute to 1 L with water, and mix.

14.4 *Ammonium Chloride-Hydrofluoric Acid Mixture*—Transfer 600 mL of the NH_4Cl solution and 40 mL of HF to a plastic bottle. Dilute to 1 L with water, and mix.

14.5 *Ammonium Nitrate Wash Solution* (20 g/L)—Dissolve 20 g of ammonium nitrate (NH_4NO_3) in water, and dilute to 1 L.

14.6 *Boric Acid* (H_3BO_3).

14.7 *Cupferron Solution* (60 g/L)—Dissolve 6 g of cupferron in 80 mL of cold water, dilute to 100 mL, and filter. This solution should be prepared fresh as needed and cooled to 5 °C before use.

14.8 *Cupferron Wash Solution*—Add 25 mL of cupferron solution (14.7) to 975 mL of cold HCl (1 + 9), and mix. Prepare as needed.

14.9 *Hydrochloric-Hydrofluoric Acid Mixture*—Add 250 mL of HCl to 300 mL of water, add 200 mL of HF, dilute to 1 L with water, and mix.

14.10 *Hydrogen Peroxide* (H_2O_2), 30 %.

14.11 *Ion-Exchange Resin*—Strongly basic anion-exchange resin, 200 mesh to 400 mesh, 8 % to 10 % divinyl-benzene cross linkage.⁶ Since the mesh size of the resin may vary considerably from lot to lot, air-dry the resin and pass it through a No. 270 (53- μm) sieve (Note 2). Most of the fines are removed from the fraction passing the No. 270 sieve as follows: Prepare a suspension of the resin in HCl (1 + 9). Allow the coarser fraction to settle 10 min to 15 min and remove the fines by decantation. Repeat the process several times until most of the very fine material has been removed from the suspension.

NOTE 2—Material retained on the No. 270 sieve may be used for other purposes.

14.12 *Oxalate-Citrate-Sulfuric Acid Solution*—Dissolve 35 g of ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and 35 g of diammonium hydrogen citrate ($(\text{NH}_4)_2\text{HC}_3\text{H}_5\text{O}_7$) in 1 L of H_2SO_4 (1 + 39).

14.13 *Pyrogallol* ($\text{C}_6\text{H}_3\text{-1,2,3-(OH)}_3$).

14.14 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 20 g of sodium hydroxide (NaOH) in 150 mL of water, cool, dilute to 200 mL, and mix. Store in a plastic bottle.

14.15 *Tantalum, Standard Solution* (1 mL = 0.500 mg Ta)—Transfer 0.1221 g of tantalum pentoxide (Ta_2O_5) to a platinum crucible. Add 2.5 g of potassium hydrogen sulfate (KHSO_4) and heat to fuse the oxide. Dissolve the cooled melt in warm oxalate-citrate-sulfuric acid solution. Transfer to a 200-mL volumetric flask, cool, dilute to volume with oxalate-citrate-sulfuric acid solution and mix.

14.16 *Titanium, Standard Solution* (1 mL = 0.100 mg Ti)—Transfer 0.0834 g of titanium dioxide (TiO_2) to a platinum crucible. Add 1 g of KHSO_4 , and heat to fuse the oxide. Cool, and dissolve the melt in 50 mL of warm H_2SO_4 (1 + 9). Cool, transfer to a 500-mL volumetric flask, dilute to volume with H_2SO_4 (1 + 9), and mix.

14.17 *Zirconium Solution* (1 mL = 1 mg Zr)—Dissolve 0.5 g of zirconium metal in 10 mL of HF in a plastic bottle, and dilute to 500 mL. An equivalent amount of zirconyl chloride may be substituted for the zirconium metal.

15. Preparation of Ion-Exchange Column

15.1 Place a 6-mm to 10-mm layer of acid-resistant poly(vinyl chloride) plastic fiber in the bottom of the column. Add the resin suspension in small portions to obtain a settled bed of the resin 150-mm to 180-mm high. Wash the column with approximately 100 mL of HNO_3 (1 + 9), and then perform three elution cycles with alternate additions of 100 mL of HCl (1 + 9) and 100 mL of HCl (3 + 1) to remove the remainder of the fines. Finally, wash the column with 200 mL of HCl (1 + 3) to a level about 20 mm above the resin.

NOTE 3—Resin columns prepared in this way have been used for several years; the only maintenance may be to empty and refill the column with the resin charge if the flow rate becomes excessively slow due to packing.

16. Preparation of Test Solutions

16.1 Transfer a 0.5-g sample, weighed to the nearest 0.1 mg, to a 250-mL plastic beaker. Add 40 mL of the HCl-HF acid mixture. Place a plastic cover on the beaker, and heat gently. After the reaction ceases, add HNO_3 dropwise until the solution clears (Note 4). Digest on the steam bath for 20 min to 30 min to remove nitrous oxide fumes. Rinse the plastic cover and wall of the beaker with the HCl-HF acid mixture, and dilute the solution to 70 mL with the same acid mixture.

NOTE 4—The addition of HNO_3 should be kept to a minimum because of its strong replacing power for niobium on the exchange column. Approximately 6 drops to 8 drops will be required.

16.2 Transfer 50 mL of HCl-HF acid mixture to the column in 5-mL to 10-mL increments. Drain the acid to a level 100 mm above the resin bed, collecting the eluate in a 600-mL plastic beaker. Transfer the sample solution in 5-mL to 10-mL increments to the column. As the sample solution moves down the column, continue to add the small increments until all of the solution has been transferred. Wash the beaker four or five times with 4-mL portions of the HCl-HF acid mixture, transferring the washings to the column. Wash the sides of the column with 10 mL to 15 mL of the HCl-HF acid mixture followed by several washings with the NH_4Cl -HCl-HF acid mixture.

16.3 Pass a total of 300 mL of the NH_4Cl -HCl-HF acid mixture through the column at a flow rate of approximately 100 mL/h to 125 mL/h. Allow the solution to drain to the top of the resin. Remove the beaker containing the first fraction and reserve this solution for the determination of titanium. Replace the beaker with another 600-mL plastic beaker.

⁶ Dowex I anion-exchange resin has been found satisfactory. Comparable results may not be obtained with other resins.