



Designation: E 367 – 02

Standard Methods for Chemical Analysis of Ferroniobium¹

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1. Scope

1.1 These methods cover the chemical analysis of ferro-columbium 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
Niobium	40.00 to 75.00
Lead	0.01 max
Manganese	3.00 max
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 methods appear in the following order:

Niobium, Tantalum, and Titanium by the Ion-Exchange Method

Sections

9-30

1.3 *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 5.

2. Referenced Documents

2.1 *ASTM Standards:*

A 550 Specification for Ferrocolumbium²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

¹ These 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 *Annual Book of ASTM Standards*, Vol 01.02.

³ *Annual Book of ASTM Standards*, Vol 14.02.

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition⁴

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁴

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁴

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁵

3. Significance and Use

3.1 These methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications. It is assumed that all who use these 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.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50. Photometers shall conform to the requirements prescribed in Practice E 60.

4.2 Photometric practice prescribed in these methods shall conform to Practice E 60.

5. Safety Precautions

5.1 For precautions to be observed in the use of certain reagents in these methods, refer to Practices E 50.

6. Sampling

6.1 For procedures for sampling the material, and for particle size of the sample for chemical analysis, refer to Practices E 32.

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ Withdrawn from publication, see 1997 *Annual Book of ASTM Standards*, Vol 03.05.

7. Rounding Off Calculated Values

7.1 Calculated values shall be rounded off to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

8. Interlaboratory Studies

8.1 These methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision and bias section.

COLUMBIUM, TANTALUM, AND TITANIUM BY THE ION-EXCHANGE METHOD

9. Scope

9.1 These methods cover the determination of columbium, tantalum, and titanium in ferrocolumbium in concentrations from 40 to 75 %, 0.25 to 7 %, and 0.05 to 5.0 %, respectively.

10. Summary of Test Method

10.1 The sample is dissolved in a hydrochloric-hydrofluoric acid mixture and transferred to an anion-exchange column. Titanium, iron, and other elements are eluted with an ammonium chloride-hydrochloric-hydrofluoric acid mixture. This eluate is treated with boric acid and cupferron, and the precipitate, containing the titanium, is ignited, fused with potassium hydrogen sulfate, and leached in dilute sulfuric acid. The titanium is oxidized to the yellow pertitanate with hydrogen peroxide. Photometric measurement is made at approximately 410 nm. Columbium 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 boric acid to complex the fluorides, and each of the elements, columbium and tantalum, is precipitated with cupferron, ignited, and weighed as the pentoxide. For tantalum in concentrations 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.

11. Interferences

11.1 Any bismuth present will appear in the tantalum fraction, but this element is seldom present in concentrations 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 method for titanium.

12. Apparatus

12.1 *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,⁶ and control the flow rate by a hosecock on the polyvinyl tubing.

12.1.1 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.⁷ 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 hydrofluoric acid.

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

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

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

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

13. Reagents

13.1 *Ammonium Chloride Solution* (240 g/L)—Dissolve 480 g of ammonium chloride (NH₄Cl) 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 13.2-13.4.

13.2 *Ammonium Chloride-Ammonium Fluoride Neutral Mixture*—Transfer 600 mL of the NH₄Cl solution and 40 mL of HF to a plastic beaker. Adjust the pH to 5 to 6 with NH₄OH (approximately 80 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.

13.3 *Ammonium Chloride-Hydrochloric-Hydrofluoric Acid Mixture*—Transfer 240 mL of the NH₄Cl solution, 200 mL of HF and 150 mL of HCl to a plastic bottle. Dilute to 1 L with water, and mix.

13.4 *Ammonium Chloride-Hydrofluoric Acid Mixture*—Transfer 600 mL of the NH₄Cl solution and 40 mL of HF to a plastic bottle. Dilute to 1 L with water, and mix.

13.5 *Ammonium Nitrate Wash Solution* (20 g/L)—Dissolve 20 g of ammonium nitrate (NH₄NO₃) in water, and dilute to 1 L.

13.6 *Boric Acid* (H₃BO₃).

13.7 *Cupferron Solution* (60 g/L)—Reagent No. 115. This solution should be prepared fresh as needed and cooled to 5°C before use.

13.8 *Cupferron Wash Solution*—Add 25 mL of cupferron solution (13.7) to 975 mL of cold HCl (1 + 9), and mix. Prepare as needed.

13.9 *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.

⁶ Tygon-R tubing has been found satisfactory for this purpose.

⁷ Columns available from Ledoux and Co., Inc., Teaneck, NJ, have been found satisfactory for this purpose.

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

13.11 *Ion-Exchange Resin*—Strongly basic anion-exchange resin, 200 to 400 mesh, 8 to 10 % divinyl-benzene cross linkage.⁸ 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 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.

13.12 *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 ($(\text{NH}_4)_2\text{HC}_8\text{H}_5\text{O}_7$) in 1 L of $\text{H}_2\text{SO}_4(1 + 39)$.

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

13.14 *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.

13.15 *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.

13.16 *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 $\text{H}_2\text{SO}_4(1 + 9)$. Cool, transfer to a 500-mL volumetric flask, dilute to volume with $\text{H}_2\text{SO}_4(1 + 9)$, and mix.

13.17 *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.

14. Preparation of Ion-Exchange Column

14.1 Place a 6 to 10-mm layer of acid-resistant poly(vinyl chloride) plastic fiber in the bottom of the column.⁹ Add the resin suspension in small portions to obtain a settled bed of the resin 150 to 180-mm high. Wash the column with approximately 100 mL of $\text{HNO}_3(1 + 9)$, 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.

15. Preparation of Test Solutions

15.1 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 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 columbium on the exchange column. Approximately 6 to 8 drops will be required.

15.2 Transfer 50 mL of HCl-HF acid mixture to the column in 5 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 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 to 15 mL of the HCl-HF acid mixture followed by several washings with the NH_4Cl -HCl-HF acid mixture.

15.3 Pass a total of 300 mL of the NH_4Cl -HCl-HF acid mixture through the column at a flow rate of approximately 100 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.

15.4 Wash the sides of the column with four or five portions (a total of about 25 mL) of the NH_4Cl -HF acid mixture, allowing the solution to drain to the top of the resin each time. Pass a total of 300 mL of the NH_4Cl -HF acid mixture through the column at the flow rate specified in 15.3 (Note 5). Remove the beaker containing the second fraction and reserve this solution for the determination of columbium. Replace the beaker with another 600-mL plastic beaker.

NOTE 5—This point in the preparation of the test solutions provides a convenient and satisfactory place to stop, for example overnight, if the elutions otherwise cannot be carried through as a continuous operation.

15.5 Wash the sides of the column with five or six 5-mL portions of the NH_4Cl - NH_4F neutral mixture. Pass a total of 350 mL of the NH_4Cl - NH_4F neutral mixture through the column, at the flow rate specified in 15.3. Remove the beaker containing the third fraction and reserve this solution for the determination of tantalum as directed in Section 23 or Section 28. Prepare the column for the next sample by adding 50 mL of HCl (1 + 3) in 10-mL increments and discarding the effluents.

TITANIUM BY THE PHOTOMETRIC METHOD

16. Concentration Range

16.1 The recommended concentration range is 0.100 to 2.50 mg of titanium for each 100 mL of solution, using a 2-cm cell.

⁸ Dowex I anion-exchange resin has been found satisfactory. Comparable results may not be obtained with other resins.

⁹ Plastic wool available from the Union Carbide Corp., Chemicals Division, Textile Fibers Dept., 900 First Ave., Needham Heights, MA, has been found satisfactory for this purpose.