Designation: E1938 – 13

Standard Test Method for Determination of Titanium in Nickel Alloys by Diantipyrylmethane Spectrophotometry[1]

This standard is issued under the fixed designation E1938; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of titanium in nickel alloys in the range 0.3 % to 5.0 %. With appropriate reference materials, the test method may be extended down to 0.05 %.

1.2 Molybdenum, if present, may cause a high bias to the extent of 0.001 % titanium for every 1 % molybdenum.

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 the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards associated with the use of this test method, see Practices E50.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

2.2 *ISO Standards:*[3]

ISO 5725:1986 Precision of Test Methods—Determination of Repeatability and Reproducibility for a Standard Test Method by Inter-Laboratory Tests

ISO 11433:1993(E) Nickel Alloys—Determination of Titanium Content—Diantipyrylmethane Molecular Absorption Spectrometric Method

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 This test sample is dissolved in a mixture of HCl and HNO_3. The solution is evaporated to fumes of H_2SO_4 to remove the HCl and HNO_3. Color is developed with diantipyrylmethane, and the absorbance is measured at 390 nm.

5. Significance and Use

5.1 This test method is used for the determination of titanium in nickel alloy samples by molecular absorption spectrometry to check compliance with compositional specifications. It is assumed that all who use the procedure will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed such as those described in Guide E882.

6. Apparatus

6.1 *Spectrophotometer,* capable of measuring absorbance at a wavelength of 390 nm.

6.2 *Cells,* to fit spectrophotometer, having an optical path of 1 cm.

NOTE 1—Cells having other dimensions can be used, provided suitable adjustments can be made in the amount of sample and reagents used.

7. Reagents

7.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents and water shall conform to Practices E50. The reagents should be free of or contain only minimal amounts (< 0.1 µg/g) of titanium.

[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.08 on Ni and Co and High Temperature Alloys.

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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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

7.2 *Potassium Hydrogen Sulfate* ($KHSO_4$).

7.3 *Ascorbic Acid Solution*—Dissolve 20 g of ascorbic acid ($C_6H_8O_6$) in water, dilute to 200 mL, and mix.

7.4 *Oxalic Acid Solution*—Dissolve 10 g of oxalic acid dihydrate [$(COOH)_2 2H_2O$] in water, dilute to 200 mL, and mix.

7.5 *Diantipyrylmethane Solution*—Dissolve 4 g of diantipyrylmethane monohydrate ($C_{23}H_{24}N_4O_2H_2O$) in water containing 25 mL HCl (1 + 1). Dilute to 200 mL and mix.

7.6 *Sodium Chloride Solution*—Dissolve 117 g of sodium chloride (NaCl) in water, dilute to 500 mL, and mix.

7.7 *Titanium Stock Calibration Solution (200 µg/mL Ti)*—Dissolve 0.739 g of potassium titanyl oxalate dihydrate [$K_2TiO(C_2O_4)_2 2H_2O$] in water. Add 50 mL of H_2SO_4 (1 + 1) and evaporate to dense fumes. Cool, dilute, and transfer the room temperature solution to a 500-mL volumetric flask. Dilute to the mark and mix.

7.7.1 *Alternative Preparation:* Transfer 0.1000 g of titanium metal (purity: 99.9 % minimum) weighed to within ± 0.2 mg to a 500-mL glass volumetric flask. Add 50 mL of H_2SO_4 (1 + 3) and dissolve over low heat. Oxidize the titanium by adding HNO_3 dropwise until the blue color is just discharged (avoid excess HNO_3 which will cause the titanium to precipitate). Cool to room temperature and dilute to volume with H_2SO_4 (1 + 9).

7.8 *Titanium Calibration Solution (25 µg/mL Ti)*—Transfer 25.0 mL of the titanium stock calibration solution to a 200-mL volumetric flask. Add 20 mL of H_2SO_4 (1 + 1). Cool the solution to room temperature, dilute to the mark, and mix.

8. Sampling and Sample Preparation

8.1 Sampling shall be done by normal procedures agreed upon between the parties, or in the event of a dispute, according to the relevant standard, if one is available.

8.2 The laboratory sample is normally in the form of millings or drillings and no further preparation of the sample is necessary.

8.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling operation, it shall be cleaned by washing it with high purity acetone, or other appropriate solvent, and drying in air.

8.4 If the sample contains particles or pieces of widely varying sizes, the test sample should be obtained by riffling.

9. Procedure

9.1 *Preparation of Test Solution:*

9.1.1 *Test Portion*—Weigh the test portion of the sample in accordance with Table 1.

TABLE 1 Weight of Sample to be Taken

Expected Ti Content, %	Weight of Test Portion, g
0.3 to 3.0	0.19 to 0.21
3.0 to 5.0	0.09 to 0.11

9.1.2 *Dissolution of Test Portion*—Transfer the test portion to a 125-mL Erlenmeyer flask and add 10 mL of HC1 and 3 mL of HNO_3. Apply sufficient heat to initiate and maintain the reaction until dissolution is complete. If the alloy resists dissolution, some adjustment in the acid mixture may be required. Add HC1 in 1-mL increments and continue heating to dissolve the test portion.

9.1.3 *Preparation of Final Test Solution:*

9.1.3.1 Add 7 mL of H_2SO_4 (1 + 1) and evaporate the solution until dense white fumes appear. Cool the contents and proceed as directed in 9.1.3.2 or 9.1.3.3, depending on whether tantalum is present in the sample or not.

9.1.3.2 In the *absence of tantalum*, add 20 mL of oxalic acid solution and heat to dissolve the salts. Cool the solution and, in tungsten free alloys, proceed as directed in 9.1.4. If the alloy contains tungsten, add sufficient ammonium hydroxide to make the solution alkaline. Boil the solution until the tungstic acid is dissolved. Cool the solution and re-acidify by adding 20 mL of HC1. Cool the solution and proceed as directed in 9.1.4.

9.1.3.3 In the *presence of tantalum*, add 30 mL of water, heat to dissolve the salts and cool again. Filter the solution through a tightly packed filter pulp pad. Wash the precipitate with warm water. Retain the filtrate. Transfer the pad and precipitate to a platinum crucible, ignite at 800 °C, and cool. Add 1 g of potassium pyrosulfate, cover the crucible with a platinum lid and fuse carefully over a flame. Cool and transfer the crucible to a 150-mL beaker containing 20 mL of the oxalic acid solution. Heat carefully until the melt is dissolved. Wash and remove the platinum crucible. Combine the oxalate solution with the original filtrate and proceed as directed in 9.1.4.

9.1.4 *Dilutions:*

9.1.4.1 *Dilution for Less Than 1 % Titanium*—Transfer the test solution (see 9.1.3.2 or 9.1.3.3) to a 100-mL volumetric flask, dilute to the mark, and mix.

9.1.4.2 *Dilution for 1 % to 5 % Titanium*—Transfer the test solution (see 9.1.3.2 or 9.1.3.3) to a 250-mL volumetric flask, dilute to the mark, and mix.

9.2 *Color Development:*

9.2.1 With a pipet, transfer 5.0-mL aliquots of the test solution to each of two 50-mL volumetric flasks.

9.2.2 Add 5.0 mL of HC1 (1 + 1), 5.0 mL of ascorbic acid solution and 20.0 mL of NaCl solution to both volumetric flasks. Mix the solutions and allow to stand for a few minutes.

9.2.3 Add 10.0 mL of diantipyrylmethane solution to one of the volumetric flasks.

9.2.4 Dilute both flasks to the mark, mix, and allow to stand for 40 min.

9.3 *Spectrophotometric Measurement:*

9.3.1 Using a 1-cm cell, measure the absorbance of both solutions against water as the reference at a wavelength of 390 nm with the spectrophotometer.

9.3.2 Subtract the background absorbance of the test solution from the absorbance of the test solution containing the diantipyrylmethane complex.

9.4 *Blank Test*—Perform a blank test in parallel with the determination following the same procedure and using the same quantities of reagents.

TABLE 2 Nominal Composition of Test Samples (in %)

Test Material	Al	Co	Cr	Fe	Hf	Mo	Nb	Ta	Ti	W	Ni
RE-2	0.5	0.5	20	18		3	5		1.0		Balance
RE-1	5.5	10	9		1.6			2.6	1.5	10	Balance
RE-3	1.9	19	22				1	1.4	3.7	2	Balance
RE-4	3.0	10	14			4			5.0	4	Balance

TABLE 3 Results of Statistical Analysis—Titanium

Test Material[A]	Mean %	Repeatability Index, r (Practice E1601)	Reproducibility Index, R (Practice E1601)
RE-2	0.37	0.019	0.038
RE-1	1.49	0.041	0.084
RE-3	3.69	0.050	0.088
RE-4	5.09	0.063	0.139

[A] Material compositions are summarized in Table 2.

9.5 *Calibration:*

9.5.1 Using a microburette, transfer (0, 1.0, 2.0, 3.0, 4.0 and 5.0) mL of the titanium calibration solution to a series of 50-mL volumetric flasks.

9.5.2 Add HC1 (1 + 1), ascorbic acid and NaCl solution to each of the volumetric flasks. Mix the solutions and allow to stand for a few minutes.

9.5.3 Add 10.0 mL of diantipyrylemethane solution to each of the solutions, dilute to the marks, and mix. Allow to stand for 40 min. This series corresponds to (0, 0.5, 1.0, 1.5, 2, and 2.5) µg titanium per millilitre.

9.5.4 Measure the absorbance of the calibration solutions as described in 9.3. Subtract the measured absorbance of the 0 µg/mL calibration solution from the absorbance values of the remaining calibration solutions.

9.5.5 Plot the corrected absorbance values against the respective concentrations of titanium, in micrograms per millilitre, in the calibration solutions.

9.6 *Number of Determinations*—Perform the determinations at least in duplicate.

9.7 *Check Test,* The performance of the test method may be checked by analyzing, in parallel with the determinations and following the same procedure, one or more samples of the same type alloy whose titanium content is known.

10. Calculation

10.1 Determine the concentration of the titanium in the test solutions and the blank by means of the calibration graph.

10.2 Calculate the titanium content C_{Ti}, expressed as a percentage by weight of the test portion using the formula:

$$C_{Ti} = (A - B)C(10^{-4})/5D \quad (1)$$

where:

A = the titanium concentration in µg/mL of the test solution,
B = the titanium concentration in µg/mL of the blank test solution,
C = the final dilution volume in mL of the test solution, and
D = the sample weight in g.

11. Precision and Bias[4]

11.1 *Precision*—Eleven laboratories in four countries participated in testing this method under the auspices of ISO/TC155/SC4 in the late 1980s and published as ISO 11433:1993(E). Four samples of nominal composition given in Table 2 were tested to obtain the statistical information, as evaluated by ISO 5725:1986 and equivalent to Practice E1601, summarized in Table 3. Precision may be judged by examination of these data.

11.2 *Bias*—No information on the accuracy of this test method is known because accepted reference standards were not used in the interlaboratory study. The user of this test method is encouraged to use accepted reference materials, if available, to determine the accuracy of this test method as it applies in a specific laboratory.

12. Keywords

12.1 molecular absorption spectrometry; nickel alloy; spectrophotometric; titanium content

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1025.