



Standard Test Method for Determination of Titanium in Nickel Alloys by the Diantipyrylmethane Molecular Absorption Spectrometric Method¹

This standard is issued under the fixed designation E 1938; 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 0.3 through 5.0 % range. 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 % Ti for every 1 % Mo.

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 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 E 50.

2. Referenced Documents

2.1 ASTM Standards:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals²

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory³

E 1452 Practice for Preparation of Calibration Solutions for Spectrophotometric and for Spectroscopic Atomic Analysis³

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method³

2.2 ISO Standards:

ISO 5725:1986 - Precision of Test Methods – Determination of Repeatability and Reproducibility for a Standard Test Method by Inter-Laboratory Tests⁴

ISO 11433:1993(E) - Nickel Alloys - Determination of

Titanium Content - Diantipyrylmethane Molecular Absorption Spectrometric Method⁴

3. Summary of Test Method

3.1 This sample is dissolved in a mixture of hydrochloric and nitric acid. The solution is evaporated to sulfuric acid fumes to remove the hydrochloric and nitric acids. Color is developed with diantipyrylmethane, and the absorbance is measured at 390 nm.

4. Significance and Use

4.1 This practice is used for the analysis of nickel and nickel base 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 E 882.

5. Apparatus

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

5.2 *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.

6. Reagents

6.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents shall conform to Practices E 50. The reagents should be free of or contain only minimal amounts ($< 0.1 \mu\text{g/g}$) of titanium. Calibration solutions shall be prepared in accordance with Practice E 1452.

6.2 *Potassium Hydrogen Sulfate* (KHSO_4).

6.3 *Ascorbic Acid Solution*—Dissolve 20 g ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) in water, dilute to 200 mL and mix.

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

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² *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ Available from American National Standards Institute, 11 West 42nd Street, New York, NY 10036.

6.4 *Oxalic Acid Solution*—Dissolve 10 g of oxalic acid dihydrate [(COOH)₂H₂O] in water and dilute to 200 mL and mix.

6.5 *Diantiprylmethane Solution*—Dissolve 4 g of diantiprylmethane monohydrate (C₂₃H₂₄N₄O₂H₂O) in water containing 25 mL hydrochloric acid (1+1). Dilute with water to 200 mL to mix.

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

6.7 *Titanium Stock Calibration Solution*—Dissolve 0.739 g of potassium titanyle oxalate dihydrate [K₂TiO(C₂O₄)₂H₂O] in water. Add 50 mL of sulfuric acid (1+1) and evaporate to dense fumes. Cool and dilute with water. Cool and transfer the room temperature solution to a 500 mL volumetric flask. Dilute to the mark with water and mix.

Alternative Preparation: Transfer 0.1000 g of titanium metal (purity: 99.9% min.) weighed to within ± 0.2 mg to a 500-mL glass volumetric flask. Add 50 mL of H₂SO₄ (1+3) and dissolve over low heat. Oxidize the titanium by adding HNO₃ dropwise until the blue color is just discharged (avoid excess HNO₃ which will cause the titanium to precipitate). Cool to room temperature and dilute to volume with H₂SO₄ (1+9).

6.8 *Titanium Calibration Solution (25µg/mL)*—Transfer 25.0 mL of the titanium stock calibration solution (see 6.7) to a 200 mL volumetric flask. Add 20 mL of sulfuric acid (1+1). Cool the solution to room temperature, dilute to the mark with water and mix.

7. Sampling and Sample Preparation

7.1 The sampling shall be carried out by normal procedures agreed upon between the parties, or in the event of a dispute, according to the relevant standard, if one is available.

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

7.3 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 and drying in air.

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

8. Interlaboratory Studies (ILS)

8.1 This test method was evaluated by a subcommittee within ISO Technical Committee 155 (ISO/TC 155/SC 4) on analysis of nickel alloys, in accordance with ISO Standard 5725. It was published as ISO Standard 11433. ILS test data were not available for recalculation.

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.

9.1.2 *Dissolution of Test Portion*—Transfer the test portion to a 125-mL Erlenmeyer flask and add 10 mL of HCl and 3 mL of HNO₃. 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

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 |

required. Add HCl 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 H₂SO₄ (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 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 reacidify by adding 20 mL of HCl. 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 9.1.3.1 or 9.1.3.2) to a 100-mL volumetric flask, dilute to the mark with water and mix.

9.1.4.2 *Dilution for 1 to 5 % Titanium*—Transfer the test solution (see 9.1.3.1 or 9.1.3.2) to a 250-mL volumetric flask, dilute to the mark with water and mix.

9.2 Color Development:

9.2.1 With a pipet, transfer 5.0-mL aliquots of the test solution (see 9.1.4.1 or 9.1.4.2) to each of two 50-mL volumetric flasks.

9.2.2 Add 5.0 mL of HCl (1+1), 5.0 mL of ascorbic acid solution (see 6.3) and 20.0 mL sodium chloride solution (see 6.6) to both volumetric flasks. Mix the solutions and allow to stand for a few minutes.

9.2.3 Add 10.0 mL diantiprylmethane solution (see 6.5) to one of the volumetric flasks.

9.2.4 Dilute both flasks (see 6.2.2 and 6.2.3) to the mark with water, 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 (see 9.2.4) against water as the reference at a wavelength of 390 nm with the spectrophotometer (see 5.1).

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

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

9.5 *Calibration:*

9.5.1 Using a microburette, transfer 0, 1.0, 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 HCl (1+1), ascorbic acid and sodium chloride solution to each of the volumetric flasks as described in 9.2.2.

9.5.3 Add 10.0 mL of diantipyrylemethane solution (see 6.5) to 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*—Carry out 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 (see 9.5.5) using the absorbance readings obtained in 9.3.2 and 9.4.

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 (see 10.1),

B = the titanium concentration in µg/mL of the blank test solution (see 10.1),

C = the final dilution volume in mL of the test solution (see 9.1.4.1 or 9.1.4.2), and

D = the sample weight in g.

11. Precision and Bias⁵

11.1 *Precision*—Eleven laboratories cooperated in the testing of this test method and obtained the statistical information summarized in Table 2 and Table 3.

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

12. Keywords

12.1 colorimetric; molecular absorption; nickel; spectrophotometric; titanium content

⁵ Supporting data are available from ASTM International Headquarters, Request RR:E01-1025.

TABLE 2 Nominal Composition of Test Samples (in %)

| Test Material | Al | Co | Cr | Fe | Hf | Mo | Nb | Ta | Ti | W | Ni |
|---------------|-----|-----|----|----|-----|----|----|-----|-----|----|---------|
| RE-1 | 5.5 | 10 | 9 | | 1.6 | | | 2.6 | 1.5 | 10 | Balance |
| RE-2 | 0.5 | 0.5 | 20 | 18 | | 3 | 5 | | 1.0 | | 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 SD (S_r , ISO 5725) ^B | Reproducibility SD (S_R , ISO 5725) ^C | Reproducibility (R , ISO 5725) ^D | R_{rel} % |
|----------------------------|--------|---|---|--|-------------|
| RE-2 | 0.37 | 0.007 | 0.012 | 0.038 | 10 |
| RE-1 | 1.49 | 0.015 | 0.026 | 0.084 | 5.6 |
| RE-3 | 3.69 | 0.018 | 0.026 | 0.088 | 1.3 |
| RE-4 | 5.09 | 0.022 | 0.044 | 0.139 | 1.2 |

^A Material compositions are summarized in Table 2.

^B Equivalent to minimum standard deviation, S_M , (see Practice E 1601).

^C Equivalent to reproducibility standard deviation, S_R , (See Practice E 1601).

^D Equivalent to reproducibility index, R , (See Practice E 1601).

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