INTERNATIONAL
STANDARD

ISO
11433

First edition
1993-09-15

Nickel alloys — Determination of titanium content — Diantipyrylmethane molecular absorption spectrometric method

Alliages de nickel — Dosage du titane — Méthode par spectrométrie d'absorption moléculaire au diantipyrylméthane

Reference number
ISO 11433:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11433 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 4, *Analysis of nickel alloys*.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Nickel alloys — Determination of titanium content — Diantipyrylmethane molecular absorption spectrometric method

1 Scope

This International Standard specifies a molecular absorption spectrometric method for the determination of titanium in the range of 0,3 % *(m/m)* to 5,0 % *(m/m)* in nickel alloys. Evidence exists that extension of this method is possible for titanium contents down to 0,05 % *(m/m)*.

Modifications in the general method allow the determination of titanium in alloys containing tungsten and/or tantalum.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in hydrochloric and nitric acids. Removal of hydrochloric acid and nitric acid by evaporation to fumes in the presence of sulfuric acid.

Formation of the titanium diantipyrylmethane complex and measurement of the absorbance of the test solution at a wavelength of 390 nm.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Hydrochloric acid, $\rho_{20} = 1,19$ g/ml.

4.2 Hydrochloric acid, $\rho_{20} = 1,19$ g/ml, diluted 1 + 1.

4.3 Sulfuric acid, $\rho_{20} = 1,84$ g/ml, diluted 1 + 1.

Slowly, and with constant stirring, add 100 ml of sulfuric acid to 100 ml of water.

4.4 Nitric acid, $\rho_{20} = 1,41$ g/ml.

4.5 Ammonium hydroxide, solution $\rho_{20} = 0,88$ g/ml.

4.6 Potassium hydrogen sulfate ($KHSO_4$).

4.7 Ascorbic acid, solution.

Dissolve 20 g of ascorbic acid ($C_6H_8O_6$) in water, dilute to 200 ml and mix.

4.8 Oxalic acid, solution.

Dissolve 10 g of oxalic acid dihydrate [$(COOH)_2.2H_2O$] in water, dilute to 200 ml and mix.

4.9 Diantipyrylmethane, solution

Dissolve 4 g of diantipyrylmethane monohydrate ($C_{23}H_{24}N_4O_2.H_2O$) in water containing 25 ml of the hydrochloric acid (4.2), dilute to 200 ml and mix.

4.10 Sodium chloride, solution.

Dissolve 117 g of sodium chloride (NaCl) in water, dilute to 500 ml and mix.

4.11 Titanium, standard reference solution (0,200 g/l).

Dissolve 0,739 g of potassium titanyl oxalate dihydrate [$K_2TiO(C_2O_4)_2.2H_2O$] in water. Add 50 ml of the dilute sulfuric acid (4.3) and evaporate to heavy fumes. Cool and dilute with water. Transfer the cold solution to a 500 ml one-mark volumetric flask, make up to the mark with water and mix.

4.12 Titanium, standard solution (25 mg/l).

Transfer 25,0 ml of the titanium standard reference solution (4.11) to a 200 ml one-mark volumetric flask. Add 20 ml of the dilute sulfuric acid (4.3). Cool the solution, make up to the mark with water and mix.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Unetched conical beakers, of capacity 125 ml.

5.2 Volumetric flasks, of capacities 50 ml, 100 ml, 200 ml, 250 ml and 500 ml, in accordance with ISO 1042, Class A.

5.3 Pipette, of capacity 5 ml, in accordance with ISO 648, Class A.

5.4 Microburette, of capacity 10 ml, graduated in divisions of 0,02 ml, in accordance with ISO 385-1, Class A.

5.5 Molecular absorption spectrometer, capable of measuring absorbance at a wavelength of 390 nm.

6 Sampling and sample preparation

6.1 Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in the case of dispute, according to the relevant International Standard.

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

6.3 If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned by washing with high-purity acetone and dried in air.

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

7 Procedure

7.1 Preparation of test solution

7.1.1 Test portion

Weigh, to the nearest 0,1 mg, a test portion of the sample according to table 1.

Table 1 — Mass of sample to be taken

Expected titanium content % (*m/m*)	**Mass of sample** g
0,3 to 3,0	0,19 to 0,21
3,0 to 5,0	0,099 to 0,11

7.1.2 Dissolution of a test portion in acid

Transfer the test portion to the 125 ml conical beaker (5.1). Add 10 ml of the hydrochloric acid (4.1) and 3 ml of the nitric acid (4.4). Apply sufficient heat to initiate and maintain the reaction until dissolution is complete. If the alloy resists dissolution, some adjustment of the acid mixture may be required. Add hydrochloric acid (4.1) in 1 ml increments and continue heating to dissolve the test portion.

7.1.3 Preparation of the final test solution

Add 7 ml of the dilute sulfuric acid (4.3) and evaporate the solution until heavy white fumes appear. Cool the contents and proceed as directed in 7.1.3.1 or 7.1.3.2, depending on whether tantalum is present or not.

7.1.3.1 In the absence of tantalum add 20 ml of the oxalic acid solution (4.8) and heat to dissolve the salts. Cool the solution and, in tungsten-free alloys, proceed as directed in 7.1.4.

7.1.3.1.1 If the alloy contains tungsten, add sufficient ammonium hydroxide solution (4.5) 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 the hydrochloric acid (4.1). Cool the solution and proceed as directed in 7.1.4.

7.1.3.2 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 the potassium hydrogen sulfate (4.6), 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 (4.8). 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 7.1.4.

7.1.4 Dilutions

7.1.4.1 Dilution for less than 1 % (*m/m*) titanium

Transfer the test solution (7.1.3.1 or 7.1.3.1.1 or 7.1.3.2) to a 100 ml one-mark volumetric flask (5.2), make up to the mark with water and mix.

7.1.4.2 Dilution for 1 % (*m/m*) to 5 % (*m/m*) titanium

Transfer the test solution (7.1.3.1 or 7.1.3.1.1 or 7.1.3.2) to a 250 ml one-mark volumetric flask (5.2), make up to the mark with water and mix.

7.2 Colour development

7.2.1 Using a pipette (5.3), transfer 5,0 ml aliquots of the test solution (7.1.4.1 or 7.1.4.2) to each of two 50 ml one-mark volumetric flasks (5.2).

7.2.2 Add 5,0 ml of the dilute hydrochloric acid (4.2), 5,0 ml of the ascorbic acid solution (4.7) and 20,0 ml of the sodium chloride solution (4.10) to both volumetric flasks. Mix the solutions and allow to stand for a few minutes.

7.2.3 Add 10,0 ml of the diantipyrylmethane solution (4.9) to one of the volumetric flasks.

7.2.4 Make up the solutions in both flasks (7.2.2 and 7.2.3) to the marks with water, mix and allow to stand for 40 min.

7.3 Spectrometric measurement

7.3.1 Using 1 cm cells, measure the absorbance of both solutions in 7.2.4 against water as the reference, at a wavelength of 390 nm with the molecular absorption spectrometer (5.5).

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

7.4 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents.

7.5 Calibration

7.5.1 Using a microburette (5.4), transfer 0 ml, 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml and 5,0 ml of the titanium standard solution (4.12) to a series of 50 ml one-mark volumetric flasks.

7.5.2 Add the dilute hydrochloric acid, ascorbic acid and sodium chloride solutions as described in 7.2.2.

7.5.3 Add 10,0 ml of the diantipyrylmethane solution (4.9) to the solutions. Dilute the solutions to the marks with water and mix. Allow to stand for 40 min.

This series corresponds to 0 µg, 0,5 µg, 1,0 µg, 1,5 µg, 2,0 µg and 2,5 µg of titanium per millilitre.

7.5.4 Measure the absorbance of the calibration solutions as described in 7.3. Subtract the measured absorbance of the 0 µg/ml calibration solution from the absorbance values of the remaining calibration solutions.

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

7.6 Number of determinations

Carry out the determination at least in duplicate.

7.7 Check test

The performance of the method may be checked by analysing, in parallel with the determination and following the same procedure, one or more samples of the same alloy type whose titanium content is known.

8 Expression of results

8.1 Calculation

8.1.1 Determine the concentration of titanium in the test solution (see 7.3.2), and in the blank test (7.4) by means of the calibration graph (7.5.5).

8.1.2 Calculate the titanium content w_{Ti}, expressed as a percentage by mass, of the test portion using the formula

$$w_{Ti} = \frac{(\rho_{Ti} - \rho_{Ti,0})V}{m} \times 10^{-3}$$

where

ρ_{Ti} is the titanium concentration, in micrograms per millilitre, in the test solution (8.1.1);

$\rho_{Ti,0}$ is the titanium concentration, in micrograms per millilitre, in the blank test solution (8.1.1);

V is the volume, in millilitres, of the test solution (7.1.4.1 or 7.1.4.2);

m is the mass, in grams, of the test portion (7.1.1).

8.2 Precision

8.2.1 Laboratory tests

Eleven laboratories in four countries participated in the testing of this procedure using four samples of nominal composition given in table 2. Each sample was analysed in duplicate on different days.

8.2.2 Statistical analysis

8.2.2.1 Results from the interlaboratory test programme were evaluated according to ISO 5725, using the means of the duplicate results. The data were tested for statistical outliers by the Cochran and Dixon tests given in ISO 5725.

8.2.2.2 The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to others. Dixon's test is to determine if the mean from laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

8.2.2.3 Repeatability and reproducibility were calculated according to ISO 5725 at the 95 % confidence level. Results of the statistical analyses are given in table 3.

8.2.2.4 One laboratory was rejected as a Cochran outlier for sample RE-1.

9 Interferences

Molybdenum, if present, may cause a high bias in the reported titanium value (see 8.1.2) to the extent of 0,001 % *(m/m)* Ti for every 1,0 % *(m/m)* Mo.

10 Test report

The test report shall include the following information:

a) the reference to the method used;

b) the results of the analysis;

c) the number of independent replications;

d) any unusual features noted during the analysis;

e) any operation not included in this International Standard or regarded as optional.

Table 2 — Nominal composition of test samples [% *(m/m)*]

Sample	Al	Co	Cr	Fe	Hf	Mo	Nb	Ta	T	W	Ni
RE-1	6,5	10	9	—	1,6	—	—	2,6	1,5	10	Remainder
RE-2	0,5	0,5	20	18	—	3	5	—	1,0	—	Remainder
RE-3	1,9	19	22	—	—	—	1	1,4	3,7	2	Remainder
RE-4	3,0	10	14	—	—	4	—	—	5,0	4	Remainder

Table 3 — Results of statistical analysis

Sample reference	Mean, [% *(m/m)*]	Within-laboratory standard deviation	Between-laboratory standard deviation	Repeatability	Reproducibility
RE-1	1,49	0,015	0,026	0,041	0,084
RE-2	0,37	0,007	0,012	0,019	0,038
RE-3	3,69	0,018	0,026	0,050	0,088
RE-4	5,09	0,022	0,044	0,063	0,139

UDC 669.245:543.422:546.22

Descriptors: nickel alloys, chemical analysis, determination of content, titanium, molecular absorption spectrometric method.

Price based on 4 pages