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

*Alliages de nickel — Détermination de la teneur en titane —
Méthode par spectrophotométrie d'absorption moléculaire au
diantipyrylméthane*

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

This second edition cancels and replaces the first edition (ISO 11433:1993), which has been technically revised in order to incorporate the Amendment ISO 11433:1993/Amd 1:2013.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document specifies a molecular absorption spectrophotometric method for the determination of titanium content in nickel alloys.

The method is applicable to titanium contents between 0,3 % (mass fraction) and 5,0 % (mass fraction).

Molybdenum, if present in the alloy, can cause a high bias in the reported titanium value to the extent of 0,001 % Ti for every 1,0 % Mo.

NOTE 1 Evidence exists that extension of this method is possible for titanium contents down to 0,05 % (mass fraction).

NOTE 2 Modifications in the general method allow the determination of titanium in alloys containing tungsten and/or tantalum.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Principle

Dissolution of a test portion with hydrochloric and nitric acids.

Elimination of hydrochloric and nitric acids by evaporation to fumes in the presence of sulphuric acid.

Formation of a yellow complex with diantipyrylmethane.

Spectrophotometric measurement of the absorption of the coloured complex at a wavelength of about 390 nm.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and grade 2 water as specified in ISO 3696.

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

5.2 Hydrochloric acid solution, 1 + 1.

Add 500 ml of hydrochloric acid (5.1) to 500 ml of water and mix.

5.3 Sulphuric acid solution, 1 + 1.

Slowly, and with constant stirring and cooling, add 100 ml of sulphuric acid, $\rho_{20} = 1,84$ g/ml, to 100 ml of water, allow to cool and mix.

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

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

5.6 Potassium hydrogen sulfate (KHSO₄).

5.7 Ascorbic acid, 100 g/l.

Dissolve 20 g of ascorbic acid (C₆H₈O₆) in water, dilute to 200 ml and mix.

Prepare this solution immediately before use.

5.8 Oxalic acid, 50 g/l.

Dissolve 10 g of oxalic acid dihydrate [(COOH)₂ · 2H₂O] in water, dilute to 200 ml and mix.

5.9 Diantipyrylmethane, 20 g/l.

Dissolve 5 g of diantipyrylmethane monohydrate (C₂₃H₂₄N₄O₂ · H₂O) in water containing 25 ml of hydrochloric acid (5.2), dilute to 200 ml and mix.

5.10 Sodium chloride, 234 g/l.

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

5.11 Titanium standard solution prepared with titanium, 500 mg/l.

Weigh 0,1 g \pm 0,001 g of pure titanium (99,99 % purity) and transfer into a 250 ml beaker.

Add 50 ml of sulfuric acid, $\rho_{20} = 1,84$ g/ml, diluted 1 + 3, cover with a watch glass and heat gently to assist dissolution.

Oxidize the titanium by adding nitric acid (5.4) dropwise until the blue colour is just cleared. Avoid an excess of nitric acid, which will cause the titanium to precipitate.

Cool to room temperature, transfer into a 200 ml volumetric flask, dilute to volume with sulfuric acid, $\rho_{20} = 1,84$ g/ml, diluted 1 + 9, and mix.

1 ml of this standard solution contains 0,5 mg of titanium.

5.12 Titanium standard solution prepared with potassium titanyl oxalate, 200 mg/l.

Dissolve 0,739 g of potassium titanyl oxalate $[K_2TiO(C_2O_4)_2 \cdot 2H_2O]$ in water. Add 50 ml of sulphuric acid (5.3) and heat until sulphuric heavy acid fumes appear. Allow to cool and dilute with water. Transfer into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 0,2 mg of titanium.

5.13 Titanium standard solution, 25 mg/l.

Transfer 10 ml of titanium standard solution (5.11) or 25 ml of titanium standard solution (5.12) into a 200 ml one-mark volumetric flask. Add 25 ml of sulphuric acid (5.3). Allow to cool, dilute with water and mix.

1 ml of this solution contains 25 μ g of titanium.

6 Apparatus

All volumetric glassware shall be class A and calibrated in accordance with ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory equipment and the following.

6.1 Spectrophotometer, suitable for measuring absorbances at a wavelength of 390 nm with 10 mm optical path length cells.

7 Sampling

Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by appropriate national standards.

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

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

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

8 Procedure

8.1 Test portion

According to the presumed titanium content, weigh, to the nearest 0,1 mg, the following mass (m) of the test portion:

- a) for titanium contents between 0,3 % (mass fraction) and 3,0 % (mass fraction): m from 0,19 g to 0,21 g;
- b) for titanium contents between 3,0 % (mass fraction) and 5,0 % (mass fraction): m from 0,10 g to 0,11 g;

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination.

8.3 Determination

8.3.1 Dissolution of the test portion

Place the test portion (8.1) in a 125 ml conical beaker.

Add 10 ml of hydrochloric acid (5.1) and 3 ml of nitric acid (5.4). Heat sufficiently to initiate and maintain the reaction until dissolution is completed.

If the alloy resist dissolution, some adjustments of the acid mixture may be required. Add hydrochloric acid (5.1) in 1 ml increments and continue heating to dissolve the test portion.

8.3.2 Preparation of the final test solution

8.3.2.1 General

Add 7 ml of sulphuric acid solution (5.3) and evaporate until heavy white fumes appear. Allow to cool and proceed as described in 8.3.2.2 or 8.3.2.3, depending on tantalum is present or not.

8.3.2.2 Absence of tantalum

Add 20 ml of oxalic acid (5.8) and heat to dissolve the salts. Allow to cool and, for tungsten-free alloys, proceed as described in 8.3.3.

If the alloy contains tungsten, add sufficient ammonium hydroxide (5.5) to make the solution alkaline. Boil the solution until the tungstic acid is dissolved. Allow to cool and re-acidify by adding 20 ml of hydrochloric acid (5.1). After cooling, proceed as described in 8.3.3.

8.3.2.3 Presence of tantalum

Add 30 ml of water, heat to dissolve the salts and allow to cool. Filter the solution through a tightly packed filter pulp pad. Wash the precipitate with warm water and retain the filtrate.

Place the pad and the precipitate in a platinum crucible, ignite at 800 °C and allow to cool.

Add 1 g of potassium hydrogen sulfate (5.6), cover the crucible with a platinum lid and fuse carefully over an appropriate flame.

Allow to cool and place the crucible in a 150 ml beaker containing 20 ml of oxalic acid (5.8). Heat gently until the melt is dissolved. Wash and remove the crucible. Combine this solution with the original filtrate and proceed as described in 8.3.3.

8.3.3 Dilutions

8.3.3.1 Dilution for titanium contents ≤ 1 %

Transfer the test solution to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

8.3.3.2 Dilution for titanium contents between 1 % and 5 %

Transfer the test solution to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

8.4 Colour development

Transfer 5,0 ml aliquots of the test solution (8.3.3.1 or 8.3.3.2) to each of two 50 ml one-mark volumetric flasks.

Add 5,0 ml of hydrochloric acid solution (5.2), 5,0 ml of ascorbic acid (5.7) and 20,0 ml of sodium chloride (5.10) to both volumetric flasks. Swirl the solutions and allow to stand for a few minutes.

Add 10,0 ml of diantipyrylmethane (5.9) to one of the volumetric flasks.

Dilute the solutions in both flasks to the mark with water, mix and allow to stand for 40 min at room temperature.

8.5 Spectrophotometric measurement

Carry out the spectrophotometric measurement of both solutions (8.4) at a wavelength of 390 nm, in 10 mm optical path length cells, against water as the reference.

Subtract the absorbance of the compensating solution from the absorbance of the test solution containing the titanium-diantipyrylmethane complex.

8.6 Establishment of the calibration curve

Transfer 0 ml, 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml and 5,0 ml of the titanium standard solution (5.13) to a series of 50 ml one-mark volumetric flasks.

Add 5,0 ml of hydrochloric acid solution (5.2), 5,0 ml of ascorbic acid (5.7) and 20,0 ml of sodium chloride (5.10) to each volumetric flask. Swirl the solutions and allow to stand for a few minutes.

Add 10,0 ml of diantipyrylmethane (5.9) to the solutions. Dilute the solutions to the mark with water, mix and allow to stand for 40 min at room temperature.

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.

Measure the absorbance of the calibration solutions as described in 8.5. Subtract the absorbance of the zero member from the absorbance values of each of the other calibration solutions.

Establish the calibration graph by plotting the net absorbance values against the titanium concentrations, expressed in micrograms per millilitre, in the calibration solutions.

8.7 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 grade whose titanium content is known.

9 Expression of results

9.1 Method of calculation

Determine the concentration of titanium in the test solution (see 8.5) and in the blank test (8.2) by means of the calibration graph.

The titanium content, w_{Ti} , expressed as a percentage by mass, is given by [Formula \(1\)](#):

$$w_{Ti} = \frac{(\rho_{Ti} - \rho_{Ti,0}) \times V}{m} \times 10^{-3} \quad (1)$$

where

ρ_{Ti} is the concentration of titanium in the test solution, expressed in micrograms per millilitre;
 $\rho_{\text{Ti},0}$ is the concentration of titanium in the blank test solution, expressed in micrograms per millilitre;
 V is the volume of the test solution (8.3.3.1 or 8.3.3.2), expressed in millilitres;
 m is the mass of the test portion, expressed in grams.

9.2 Precision

9.2.1 Laboratory tests

Eleven laboratories in four countries participated in the testing of this procedure using four samples having the nominal composition given in [Table 1](#). Each sample was analysed in duplicate on different days.

Table 1 — Nominal composition of test samples [% (mass fraction)]

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

9.2.2 Statistical evaluation

Results from the interlaboratory test programme were evaluated in accordance with ISO 5725:1986, using the means of the duplicate results. The data were tested for statistical outliers by the Cochran and Dixon tests described in ISO 5725:1986.

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 the others. Dixon's test is to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

Repeatability and reproducibility were also calculated according to ISO 5725:1986 at the 95 % confidence level. The results of this assessment are given in [Table 2](#).

Table 2 — Results of statistical evaluation [% (mass fraction)]

Sample label	Mean	Repeatability	Reproducibility
RE-1	1,49	0,041	0,084
RE-2	0,37	0,019	0,038
RE-3	3,69	0,050	0,088
RE-4	5,09	0,063	0,139

10 Test report

The test report shall include the following information:

- the method used by reference to this document, i.e. ISO 11433;
- all information necessary for the identification of the sample, the laboratory, and the date of analysis or of the test report;
- results and the units in which they are expressed;
- any unusual characteristics noted during the determination;

- e) any operation not specified in this document or any operation that could have influenced the results;
- f) the signature of the responsible person.

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