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Nickel alloys — Determination of niobium and tantalum — Ion exchange method

Alliages de nickel — Dosage du niobium et du tantale — Méthode par échange d'ions

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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 main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 11434, which is a Technical Report of type 1, was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Sub-Committee SC 4, *Analysis of nickel alloys*.

Originally, this ion exchange method for the determination of niobium and tantalum contents was part of a composite ion exchange procedure which also included determinations of molybdenum, titanium and tungsten contents. Because of the very complexity of the lengthy composite procedure, it was decided to rewrite the method in the present form covering niobium and tantalum only. The interlaboratory precision test-

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ing of the method provided sets of results from only three participating laboratories, which was considered insufficient for statistical evaluation and sub-committee support. Since the results were good and represented a considerable amount of work, it was resolved to publish the method in the form of a Technical Report of type 1.

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Nickel alloys — Determination of niobium and tantalum — Ion exchange method

1 Scope

This Technical Report describes an ion exchange separation method for the determination of niobium in the range of 0,3 % (*m*/*m*) to 5 % (*m*/*m*) and of tantalum in the range of 0,01 % (*m*/*m*) to 5 % (*m*/*m*) in nickel alloys. The elements normally found in nickel alloys do not interfere.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Technical Report 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.*

3 Principle

Pass a solution of the sample in a hydrochloric-hydrofluoric acid mixture through an ion exchange column packed with a strongly basic ion-exchange resin. Remove all elements other than niobium and tantalum by washing.

Separate niobium and tantalum from the resin bed by first selectively eluting niobium and then follow with the elution of tantalum.

Determine the eluted niobium and tantalum gravimetrically as the pentoxides, if present at high levels.

For small contents of tantalum, use coprecipitation with zirconium as cupferrates, ignite to oxides and fuse with potassium pyrosulfate. Dissolve the melt and measure the tantalum spectrophotometrically with pyrogallol at a wavelength of 400 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 Hydrofluoric acid, $\rho_{20} = 1,13$ g/ml, 40 % (*m*/*m*) HF.

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water and seek medical advice.

4.2 Hydrochloric acid, $\rho_{20} = 1,18$ g/ml, diluted 1 + 4.

4.3 Nitric acid, $\rho_{20} = 1,41$ g/ml, diluted 1 + 4.

4.4 Sulfuric acid, $\rho_{20} = 1,84$ g/ml, diluted 1 + 19.

4.5 Anion exchange resin, strongly basic 100 to 200 mesh (8 % cross-linked polystyrene-divinyl benzene matrix).

4.6 Hydrofluoric acid (5,4 mol/l)-**hydrochloric acid** (3,0 mol/l), solution.

Add 1 200 ml of hydrofluoric acid (4.1) to 1 250 ml of hydrochloric acid ($\rho_{20} = 1,18$ g/ml), dilute to 5 litres with water and mix. Prepare and store in a plastics bottle.

4.7 **Ammonium chloride** (4,7 mol/l), stock solution.

Dissolve 750 g of ammonium chloride in 2 litres of water, filter through a fast filter paper, dilute to 3 litres and mix. This reagent is used to prepare other reagents.

4.8 **Ammonium chloride** (1,4 mol/l)-**hydrochloric acid** (1,4 mol/l)-**hydrofluoric acid** (5,4 mol/l), solution.

Add 600 ml of the hydrofluoric acid (4.1) to 720 ml of the ammonium chloride stock solution (4.7). Add 310 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml). Dilute to 2,5 litres with water and mix. Prepare and store in a plastics bottle.

4.9 **Ammonium chloride** (2,6 mol/l)-**hydrofluoric acid** (1,1 mol/l), solution.

Add 120 ml of the hydrofluoric acid (4.1) to 1 390 ml of the ammonium chloride stock solution (4.7), dilute to 2,5 litres with water and mix. Prepare and store in a plastics bottle.

4.10 **Ammonium chloride** (2,6 mol/l)-**ammonium fluoride** (1,1 mol/l), solution.

Add 120 ml of the hydrofluoric acid (4.1) to 1 390 ml of the ammonium chloride stock solution (4.7). Using a pH paper, adjust the acidity to pH 5 to 6 using ammonia solution ($\rho_{20} = 0{,}88$ g/ml) (about 175 ml is required). Cool, dilute to 2,5 litres with water and mix. Prepare and store in a plastics bottle.

4.11 **Cupferron**, solution.

Dissolve 15 g of cupferron [ammonium *N*-nitrosophenylhydroxylamine, $C_6H_5N(NO).ONH_4$] in water, dilute to 250 ml and mix. Filter through a pulp pad before use.

Prepare a fresh solution when required.

4.12 **Cupferron-hydrochloric acid**, wash solution.

Add 50 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) to 800 ml of water, mix and cool to less than 10 °C. Add 5 ml of cupferron solution (4.11) and dilute to 1 litre with cold (< 10 °C) water.

4.13 **Mixed oxalic-citric acids**, solution.

With constant stirring, add 25 ml of sulfuric acid ($\rho_{20} = 1{,}84$ g/ml) to 950 ml of water. Add 40 g of ammonium oxalate [$(COONH_4)_2.H_2O$] and 50 g of triammonium citrate [$(NH_4)_3C_6H_5O_7$] and warm to dissolve. Cool, dilute to 1 litre with water, mix and filter through a fast filter paper.

4.14 **Pyrogallol**, solution.

Dissolve 100 g of pyrogallol [1,2,3-trihydroxybenzene, $C_6H_3(OH)_3$] in 400 ml of the mixed oxalic-citric acids solution (4.13). Dilute to 500 ml with the mixed acids solution.

4.15 **Tantalum**, standard reference solution, 0,000 2 g/ml.

Transfer 0,048 8 g of pure tantalum pentoxide (Ta_2O_5) to a silica crucible. Add 1 g of potassium pyrosulfate ($K_2S_2O_7$) and fuse completely. Cool the melt. With constant stirring, dissolve the melt in 75 ml of warm mixed oxalic-citric acids solution (4.13). Cool the solution. Transfer the solution to a 200 ml one-mark volumetric flask, rinsing the beaker with the mixed acids solution (4.13). Dilute to the mark with the mixed acids solution.

4.16 **Zirconium sulfate**, solution.

Dissolve 3,90 g of zirconium sulfate in 75 ml of the dilute sulfuric acid (4.4). Transfer the solution to a 100 ml one-mark volumetric flask using the dilute sulfuric acid. Dilute to the mark with the dilute sulfuric acid and mix.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 **Polytetrafluoroethylene (PTFE) beakers**, of capacity 250 ml.

5.2 **Plastics beakers**, of capacity 600 ml. Polymethylpentene or fluorocarbon polymers have been found to be satisfactory.

5.3 **Polyvinylchloride (PVC) wool**.

5.4 **Volumetric flasks**, of capacities 50 ml, 100 ml and 200 ml, in accordance with ISO 1042, Class A.

5.5 **Pipette**, of capacity 10 ml, in accordance with ISO 648, Class A.

5.6 **Microburette**, of capacity 10 ml, calibrated in divisions of 0,02 ml in accordance with ISO 385-1, Class A.

5.7 **Molecular absorption spectrometer**, suitable for measuring absorbance at 400 nm.

5.8 Ion exchange column

5.8.1 The column is made from polyethylene tubing with an internal diameter of 25 mm and length of 380 mm. The lower (funnel shaped) end of the column is connected to a polyethylene delivery tube, with an internal diameter of 5 mm, fitted with a flow regulating valve (see figure 1).

5.8.2 Transfer approximately 300 g of the resin (4.5) to the 600 ml plastics beaker (5.2).

5.8.3 Add 200 ml of the dilute nitric acid (4.3) to the resin and stir. Allow the resin to settle and decant the nitric acid. Repeat this process four more times. This treatment removes the very fine resin particles.

5.8.4 Repeat the washing described in 5.8.3 using five 200 ml volumes of water.

5.8.5 Repeat the washing described in 5.8.3 using five 200 ml volumes of the dilute hydrochloric acid (4.2).

5.8.6 Repeat the washing described in 5.8.3 using five 200 ml volumes of the hydrofluoric acid-hydrochloric acid solution (4.6).

5.8.7 Insert a pad of the PVC wool (5.3) in the restricted end of the column and pour in sufficient of the resin slurry to produce a settled column which is 260 mm long.

5.8.8 Wash the column five times with 20 ml volumes of the hydrofluoric acid-hydrochloric acid solution (4.6). Adjust the flow rate to 100 ml/h to 125 ml/h.

5.8.9 Whilst the bend in the outlet tube will prevent the resin becoming dry by drainage, the column, when not in use, should be left with the top closed and sufficient solution over the resin bed to prevent drying by evaporation.

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 Test portion and preparation of test solution

7.1.1 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 niobium and tantalum contents % (*m*/*m*)	Mass of sample g
0,3 to 3,0 (Nb) 0,01 to 3,0 (Ta)	1,99 to 2,01
3,0 to 5,0 (Nb,Ta)	0,99 to 1,01

7.1.2 Transfer the test portion to the 250 ml PTFE beaker (5.1). Dissolve the sample in a mixture of 10 ml of the hydrofluoric acid (4.1), 50 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and 10 ml of nitric acid ($\rho_{20} = 1{,}41$ g/ml). Apply sufficient heat to initiate and maintain the reaction until dissolution is complete. Evaporate the solution just to dryness. **Do not bake the salts.** Cool the residue, add 25 ml of the hydrofluoric acid and again evaporate just to dryness. Cool the residue, add 100 ml of the hydrofluoric acid-hydrochloric acid solution (4.6) and heat the mixture gently to dissolve the solids. Cool the solution to room temperature.

7.2 Separation of niobium and tantalum

7.2.1 Transfer the test solution to the resin bed and pass it through the bed. Collect the eluate in a 1 000 ml plastics beaker. Allow the solution to drain to just above the resin bed. Wash the PTFE beaker with 15 ml to 20 ml of the hydrofluoric acid-hydrochloric acid solution (4.6). Repeat when the previous washings drain to just above the resin bed. Wash the inside walls of the column with a fine jet of the hydrofluoric acid-hydrochloric acid solution.

7.2.2 Wash the resin bed with 300 ml of the hydrofluoric acid-hydrochloric acid solution (4.6) added in 50 ml increments. Discard the eluate.

7.2.3 Wash the resin bed with 300 ml of the ammonium chloride-hydrochloric acid-hydrofluoric acid solution (4.8) added in 50 ml increments. Discard the eluate.

7.3 Elution of niobium

Elute the niobium from the resin bed with 350 ml of the ammonium chloride-hydrofluoric acid solution (4.9) and collect the eluate in a 600 ml plastics beaker. Determine the niobium content in this solution as directed in 7.7.

7.4 Elution of tantalum

After elution of niobium, elute the tantalum from the resin bed with 350 ml of the ammonium chloride-ammonium fluoride solution (4.10) and collect the eluate in a 600 ml plastics beaker. Determine the tantalum content in this solution as directed in 7.6 or 7.7.

NOTE 1 If only tantalum is to be determined, niobium, if present, must always be eluted from the column before proceeding with the elution of tantalum.

7.5 Regeneration of the resin bed

Prepare the resin bed for subsequent separations by passing 100 ml of the hydrofluoric acid-hydrochloric acid solution (4.6) through the bed. Discard the eluate.

7.6 Determination of tantalum contents of 0,01 % (*m*/*m*) to 0,3 % (*m*/*m*)

7.6.1 Colour development

7.6.1.1 Add 15 g of boric acid (H_3BO_3) to the eluate obtained in 7.4, and stir the solution until the acid dissolves. Acidify with 60 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and add 1,0 ml of the zirconium sulfate solution (4.16). Mix and cool the solution to 10 °C.

7.6.1.2 Add slowly while stirring constantly, 30 ml of the cupferron solution (4.11). Then add a little paper pulp, mix, and allow to stand for 15 min.

7.6.1.3 Filter the solution through an ashless pulp pad. Transfer all the particles from the beaker to the pad with the cold cupferron wash solution (4.12). Wash the pad and precipitate five times with 20 ml volumes of the cupferron wash solution. Remove excess liquid from the pad by suction and transfer the pad and precipitate to a silica crucible.

7.6.1.4 Char the pad without flaming and ignite at 600 °C for 60 min. Cool, add 1 g of potassium pyrosulfate ($K_2S_2O_7$) and fuse the mixed oxides. Cool the melt.

7.6.1.5 While stirring constantly, dissolve the melt in 40 ml of the warm oxalic-citric acids solution (4.13). Cool the solution. Transfer the solution to a 50 ml one-mark volumetric flask (5.4) using the oxalic-citric solution. Dilute to 50 ml with the oxalic-citric acids solution and mix.

7.6.1.6 Using a pipette (5.5), transfer 10,0 ml of the solution to a 50 ml volumetric flask (5.4) containing 25 ml of the pyrogallol solution (4.14). Dilute to 50 ml with the oxalic-citric acids solution (4.13). Mix and allow to stand for 10 min. (This is the test solution.)

7.6.1.7 Dilute 25 ml of the pyrogallol solution (4.14) to 50 ml with the oxalic-citric acids solution (4.13) in a 50 ml volumetric flask (5.4). Mix and allow to stand for 10 min. (This is the compensating solution.)

7.6.2 Preparation of calibration solutions

Transfer, using the 10 ml microburette (5.6), 0 ml; 2,0 ml; 4,0 ml; 6,0 ml and 8,0 ml of the tantalum standard reference solution (4.15) to a series of 50 ml volumetric flasks (5.4) containing 25 ml of the pyrogallol solution (4.14). Dilute to 50 ml with the oxalic-citric acids solution (4.13). Mix and allow to stand for 10 min. These calibration solutions are equivalent to 0 % (*m*/*m*); 0,10 % (*m*/*m*); 0,20 % (*m*/*m*); 0,30 % (*m*/*m*) and 0,40 % (*m*/*m*) of tantalum in the sample.

7.6.3 Spectrometric measurement

7.6.3.1 Use cells with 2 cm optical path length. Measure the absorbance of the test solution (see 7.6.1.6), against the compensating solution (see 7.6.1.7) as the reference at a wavelength of 400 nm with the molecular absorption spectrometer (5.7).

7.6.3.2 Use cells with 2 cm optical path length. Measure the absorbance of the calibration solutions (7.6.2) against the zero tantalum calibration solution as the reference, at a wavelength of 400 nm with the molecular absorption spectrometer (5.7).

7.6.4 Preparation of the calibration graph

Plot the absorbance readings for the calibration standards (see 7.6.3.2) against the content of tantalum, expressed as a percentage by mass.

7.6.5 Calculation

7.6.5.1 Determine the content of tantalum in the test samples (and the blank test) using the absorbance values found in 7.6.3.1.

7.6.5.2 Calculate the tantalum content w_{Ta} in the sample, expressed as a percentage by mass, as follows:

$$w_{\mathrm{Ta}} = \frac{2}{m} \times (w_{\mathrm{Ta},1} - w_{\mathrm{Ta},2})$$

where

$w_{\mathrm{Ta},1}$ is the tantalum content, expressed as a percentage by mass, found in 7.6.5.1;

$w_{Ta,2}$ is the tantalum content, expressed as a percentage by mass, found for reagent blank test in 7.6.5.1;

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

7.7 Determination of niobium and/or tantalum contents of 0,3 % (m/m) to 5,0 % (m/m)

7.7.1 Add 15 g of boric acid (H_3BO_3) to each of the eluates 7.3 (niobium) and 7.4 (tantalum), and stir the solutions until the acid dissolves. Acidify each silution with 60 ml of hydrochloric acid ($\rho_{20} = 1{,}18$ g/ml) and cool to 10 °C. Add slowly while stirring constantly, 40 ml of the cupferron solution (4.11). Then add a little ashless filter pulp. Allow the solution to stand for 15 min and stir occasionally.

7.7.2 Filter each solution through an ashless filter pulp pad. Transfer all the particles from the beakers to the pads with the cupferron wash solution (4.12). Wash each pad and precipitate five times with 20 ml volumes of cold cupferron wash solution. Remove excess liquid from the pads by suction and transfer each pad and precipitate to a pre-ignited and weighed silica crucible.

7.7.3 Char the pads without flaming and ignite each crucible at 1 000 °C for 60 min. Cool and weigh the niobium pentoxide and the tantalum pentoxide residues, respectively.

7.7.4 Calculate the niobium content w_{Nb} or tantalum content w_{Ta}, expressed as percentage by mass, as follows:

$$w_{Nb} \text{ or } w_{Ta} = \frac{(m_1 - m_2) \times F}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of either Nb_2O_5 or Ta_2O_5;

m_2 is the mass, in grams, of blank residue;

F is the conversion factor: 69,90 for niobium and 81,90 for tantalum.

7.8 Blank test

Carry out a blank test in parallel with the determination throughout the entire procedure.

7.9 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 niobium and tantalum contents are known.

8 Expression of results

8.1 Calculation

Calculate the niobium and tantalum contents, expressed as percentages by mass, of the test sample as directed in 7.6.5 and 7.7.4.

8.2 Precision

8.2.1 Laboratory tests

Only three laboratories in two countries participated in the testing of this procedure using six samples of nominal composition given in table 2. Each sample was analysed in duplicate on different days. Because of the insufficient data available, no further statistical analysis was done. The reported data are summarized in tables 3 and 4.

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

Sample	Al	Co	Cr	Fe	Hf	Mo	Nb	Ta	Ti	W	Ni
RE-1	6	10	9	—	1,6	—	—	3	2	10	Remainder
RE-2	0,5	—	20	18	—	3	5	—	1	—	Remainder
RE-6	4	8	16	—	—	2	1	2	4	2	Remainder
RE-8	6	—	14	—	—	4	2	—	1	—	Remainder
RE-9	3	9	12	—	—	2	—	4	4	4	Remainder