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Nickel alloys — Determination of tantalum — Inductively coupled plasma optical emission spectrometric method

Alliages de nickel — Détermination du tantale — Méthode par spectrométrie d'émission optique avec source à plasma induit par haute fréquence

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Foreword

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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).

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

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 tantalum — Inductively coupled plasma optical emission spectrometric method

1 Scope

This document specifies an inductively coupled plasma optical emission spectrometric method for the determination of tantalum contents between 0,1 % and 5 % in nickel alloys.

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 in a mixture of hydrofluoric, hydrochloric, nitric and phosphoric acid and fuming after addition of perchloric acid. Addition of hydrofluoric acid and, if desired, of an internal reference element and dilution of the solution to known volume. Nebulization of the solution into an inductively coupled plasma optical emission spectrometer and measurement of the intensity of the emitted light from tantalum, and, where appropriate, from the internal reference element, simultaneously.

An example of the wavelength for tantalum is given in Table 1.

The method uses a calibration based on a very close matrix-matching of the calibration solutions to the sample and bracketing between 0,75 and 1,25 of the approximate content of tantalum in the sample to be analysed. The content of all elements in the sample has, therefore, to be approximately known. If the contents are not known, the sample has to be analysed by some semi-quantitative method. The advantage of this procedure is that all possible interferences from the matrix will be compensated, which will result in high accuracy. This is most important for spectral interferences, which can be severe in very highly alloyed matrixes. All possible interferences shall be kept at a minimum level. Therefore, it is essential that the spectrometer used meets the performance criteria specified in the method for the selected wavelengths.

The line corresponding to 240,06 nm has been investigated. If other lines are used, they shall be carefully checked. The wavelength for the internal reference element should be selected carefully. The use of scandium at 363,07 nm is recommended. This wavelength is interference-free for the elements and contents generally found in nickel alloys.

Table 1 — Example of wavelength for tantalum

Element	Wavelength	Interferences
Tantalum	240,06	Co - Fe - Hf

NOTE The use of an internal reference element is not essential since no relevant differences between laboratories operating with or without internal reference elements were found when the precision test was carried out (see 9.2.2).

5 Reagents

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

5.1 Hydrofluoric acid, HF, ρ = 1,14 g/ml, or ρ = 1,17 g/ml.

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, apply a topical gel containing 2,5 % (mass fraction) calcium gluconate, and seek immediate medical treatment.

5.2 Hydrochloric acid, HCl, ρ = 1,19 g/ml.

5.3 Nitric acid, HNO_3, ρ = 1,40 g/ml.

5.4 Phosphoric acid, H_3PO_4, ρ = 1,70 g/ml.

5.5 Perchloric acid, $HClO_4$, ρ = 1,54 g/ml, or ρ = 1,67 g/ml.

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic material in general. The use of fume hoods (water scrubbed) when using perchloric acid is highly recommended.

5.6 Internal reference element solution, 100 mg/l.

Choose a suitable element to be added as internal reference and prepare a 100 mg/l solution.

5.7 Tantalum standard solution, 10 g/l.

Weigh, to the nearest 0,001 g, 1 g of tantalum [minimum 99,9 % (mass fraction)], place it in a beaker (6.1), cover with an appropriate lid and dissolve it in a mixture of 10 ml of hydrofluoric acid (5.1) and 10 ml of nitric acid (5.3).

Cool and transfer quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 10 mg of tantalum.

5.8 Tantalum standard solution, 1 g/l.

Weigh, to the nearest 0,000 5 g, 0,1 g of tantalum [minimum 99,9 % (mass fraction)], place it in a beaker (6.1), cover with an appropriate lid and dissolve it in a mixture of 10 ml of hydrofluoric acid (5.1) and 10 ml of nitric acid (5.3).

Cool and transfer quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 1 mg of tantalum.

5.9 **Tantalum standard solution**, 100 mg/l.

Transfer 10 ml of the tantalum standard solution (5.8) into a 100 ml one-mark volumetric flask. Add 10 ml of hydrofluoric acid (5.1) and 10 ml of nitric acid (5.3). Dilute to the mark with water and mix.

1 ml of this solution contains 0,1 mg of tantalum.

5.10 **Standard solutions of matrix elements**.

Prepare standard solutions for each element for which the content is higher than 1 % in the test sample. Use pure metals or chemical substances with contents of tantalum less than 10 µg/g.

6 Apparatus

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

Ordinary laboratory apparatus and the following.

6.1 **Polytetrafluoroethylene (PTFE) beakers** or **perfluoroalkyoxy-polymer (PFA) beakers**, preferably with a graphite base.

6.2 **Polypropylene volumetric flasks**, of capacity 100 ml, calibrated in accordance with ISO 1042.

6.3 **Optical emission spectrometer**, equipped with inductively coupled plasma.

This shall be equipped with a nebulization system resistant to hydrofluoric acid. The instrument used will be satisfactory if, after optimising in accordance with 8.3, it meets the performance criteria given in this subclause.

The spectrometer can be either a simultaneous or a sequential one. If a sequential spectrometer can be equipped with an extra arrangement for simultaneous measurement of the internal reference element wavelength, it can be used with the internal reference method. If the sequential spectrometer is not equipped with this arrangement, an internal reference cannot be used and an alternative method without an internal reference element should be applied.

Calculate the bandwidth (full width at half maximum), in accordance with A.2, for the line used and for the line of the internal reference element. The bandwidth shall be less than 0,030 nm.

Calculate the standard deviation of 10 measurements of the absolute intensity or of the intensity ratio between tantalum and the internal reference element, by using the most concentrated calibration solution for tantalum in accordance with A.3. The relative standard deviation shall not exceed 0,4 %.

Calculate the background equivalent concentration (BEC) in accordance with A.4, for the analytical line using a solution containing only the analyte element. The maximum values of BEC obtained should be 0,8 mg/l.

7 Sampling and sample preparation

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. No further preparation 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 brazed alloy tools are used in the preparation of the laboratory sample, the sample shall be further cleaned by pickling in 15 % (mass fraction) nitric acid for a few minutes. It shall then be rinsed several times with distilled water, followed by washing in acetone and drying in air.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,001 g, 0,25 g of the test sample.

8.2 Preparation of test solution, T_{TA}

A PTFE or PFA beaker (6.1) shall be used when using HF (5.1).

8.2.1 Place the test portion in a PTFE or PFA beaker, preferably with a graphite base.

8.2.2 Add 5 ml of hydrofluoric acid (5.1), 30 ml of hydrochloric acid (5.2), 3 ml of nitric acid (5.3), cover with an appropriate lid and allow the dissolution of the sample to take place overnight at room temperature. Then, add 2,5 ml of phosphoric acid (5.4). If necessary, heat to complete dissolution. Add 7,5 ml of perchloric acid (5.5) and heat until the perchloric acid starts to fume. Continue to fume for 2 min to 3 min.

NOTE 5 ml of phosphoric acid (5.4) and 5 ml of perchloric acid (5.5) can also be used, instead of 2,5 ml of phosphoric acid (5.4) and 7,5 ml of perchloric acid (5.5).

8.2.3 Cool the solution and add 10 ml of water to dissolve the salts. Some residues may remain undissolved. In this case, add 2 ml of hydrofluoric acid (5.1) and heat gently for about 20 min until the residues dissolve completely.

8.2.4 The following is an alternative dissolution procedure for 8.2.2 and 8.2.3.

Add 30 ml of hydrochloric acid (5.2), 3 ml of nitric acid (5.3) and 5 ml of phosphoric acid (5.4), or 20 ml of hydrochloric acid (5.2), 10 ml of nitric acid (5.3) and 5 ml of phosphoric acid (5.4). Cover with an appropriate lid and let the dissolution begin at room temperature. If necessary, heat to complete dissolution. Add 2 ml of hydrofluoric acid (5.1) and 5 ml of sulphuric acid (ρ = 1,84 g/ml) and heat until sulfuric acid starts to fume. Cool the solution and add 10 ml of water to dissolve the salts. Heat gently until the residues dissolve completely.

8.2.5 Cool the solution to room temperature and transfer the solution quantitatively to a 100 ml volumetric polypropylene flask. If an internal reference element solution (5.6) is used, add 10 ml of this solution.

8.2.6 Dilute to the mark with water and mix. Proceed as quickly as possible to the measurement.

8.3 Optimization of the spectrometer

8.3.1 Start the inductively coupled plasma optical emission spectrometer and let it stabilize in accordance with the manufacturer's instructions before taking any measurements.

8.3.2 Optimize the instrument in accordance with the manufacturer's instructions.

8.3.3 Prepare the software for measurements of the intensity, and for the calculation of the mean value and relative standard deviation corresponding to the appropriate wavelengths.

8.3.4 If an internal reference element is used, prepare the software to calculate the ratio between the intensity of the analyte and that of the internal reference element. The intensity of the internal reference element shall be measured simultaneously with that of the analyte.

8.3.5 Check the instrument performance criteria given in 6.3.

8.4 Pre-determination of the test solution

8.4.1 Prepare a calibration solution, K*x*, matrix matched to the test sample solution as follows.

8.4.2 In a 100 ml volumetric polypropylene flask (6.2) marked K*x*, prepare a calibration solution K*x*, corresponding to the approximate content of tantalum in the sample, in per cent, as indicated in Table 2.

Table 2 — Pre-determination of the test solution

Estimated content %	K*x* equivalent content %	K*x* identification	Tantalum standard solution	Standard solution volume ml
0,10 to 1,0	1,0	K1	5.9	2,5
1,0 to 5,0	5,0	K5	5.9	12,5

8.4.3 In this volumetric flask K*x*, add volumes of standard solutions (5.10) necessary to match the sample matrix to be tested, for each element for which the content is above 1 %.

The matrix should be matched to the nearest per cent.

8.4.4 Add 2,5 ml of phosphoric acid (5.4) and 7,5 ml of perchloric acid (5.5) and 10 ml of the internal reference element solution (5.6). Dilute to the mark with water and mix.

8.4.5 Also prepare a zero member solution, K_0, prepared in the same way as the calibration solution K*x* omitting tantalum.

8.4.6 Measure the absolute intensities (I_0 and I_x) for the solutions K_0 and K*x*.

8.4.7 Measure the absolute intensity I_{TTa} for the test solution T_{Ta}.

8.4.8 Calculate the approximate content of tantalum, w_{TTa}, in percent, in the test solution, by means of Formula (1):

$$w_{TTa} = \frac{I_{TTa}\left(w_x - w_0\right)}{I_x - I_0} \tag{1}$$

8.5 Preparation of calibration solutions for bracketing, $K_{l,Ta}$ and $K_{h,Ta}$

8.5.1 For each test solution TTa prepare two matrix matched calibration solutions, $K_{l,Ta}$ and $K_{h,Ta}$, with the tantalum concentrations in $K_{l,Ta}$ slightly below, and in $K_{h,Ta}$ slightly above, the concentration in the unknown test solution as described in 8.5.2 to 8.5.5.

8.5.2 Add tantalum standard solution (5.8) or (5.9) to one PTFE or PFA beaker marked $K_{l,Ta}$ so that the content of tantalum $w_{l,Ta}$, in per cent, is approximately $K_{TTa} \times 0,75 < K_{1,Ta} < K_{TTa} \times 0,95$. Select $K_{1,Ta}$ in such a way to take an easy volume with a pipette.

8.5.3 Add tantalum standard solution (5.8) or (5.9) to one PTFE or PFA beaker marked $K_{h,Ta}$ so that the content of tantalum w_h,Ta, in per cent, is approximately $K_{TTa} \times 1,05 < K_{h,Ta} < K_{TTa} \times 1,25$. Select $K_{h,Ta}$ in such a way as to take an easy volume with a pipette.

8.5.4 Add, to the calibration solutions $K_{1,Ta}$ and $K_{h,Ta}$, all matrix elements where the contents are above 1 % in the test solution, using the appropriate volume of standard solutions (5.10) to match the matrix composition to the nearest per cent.

8.5.5 Proceed as specified in 8.2.2 to 8.2.6.

8.6 Measurement of test solutions

Measure the absolute or ratioed intensity of the analytical line of the lowest calibration solution $K_{1,Ta}$ first, then measure the test sample solution, T_{Ta} and finally measure the highest calibration solution $K_{h,Ta}$. Repeat this sequence three times and calculate the mean intensities $I_{l,Ta}$ and $I_{h,Ta}$ for the low and high calibration solution and I_{TTa} for the test solution, respectively.

9 Expression of results

9.1 Method of calculation

Calculate the mass fraction of tantalum, w_{Ta}, in percent, in the test solution T_{Ta}, by means of Formula (2):

$$w_{Ta} = w_{l,Ta} + \frac{\left(I_{Ta} - I_{l,Ta}\right)\left(w_{h,Ta} - w_{l,Ta}\right)}{I_{h,Ta} - I_{l,Ta}} \qquad (2)$$

9.2 Precision

9.2.1 Laboratory tests

Ten laboratories from seven countries participated in an interlaboratory test programme under the auspices of ISO/TC 155/SC 3/WG 8, involving three determinations of tantalum at eight levels. Each laboratory did two determinations under the repeatability conditions defined in ISO 5725-1:1994, i.e. one operator, same apparatus, identical operating conditions, same calibration and a minimum period of time. The third determination was done on a different day using the same apparatus with a different calibration.

9.2.2 Wavelength for measurement

Concerning the wavelength taken for obtaining the results that have been statistically evaluated, all the laboratories operated at 240,06 nm. No relevant difference between laboratories operating with or without an internal reference element was found.

9.2.3 Statistical evaluation

A statistical evaluation was carried out in accordance with ISO 5725-1:1994, ISO 5725-2:1994 and ISO 5725-3:1994. Results from one laboratory were rejected as a consistent outlier.

This evaluation showed that the performances of the method were not satisfactory enough for tantalum levels lower than 0,1 % on one hand and higher than 5 % on the other hand.

Results of the evaluation were used to calculate the smoothed values of the repeatability, r, the within-laboratory reproducibility, Rw, and the between-laboratory reproducibility, R, for the contents of tantalum between 0,1 % and 5 %, which are given in Table 3.

Table 3 — Repeatability and reproducibility limits

Content of tantalum %	**Repeatability limit** r	**Within laboratory reproducibility limit** Rw	**Between laboratory reproducibility limit** R
0,1	0,001 4	0,004 6	0,011 3
0,2	0,002 8	0,008 2	0,020 3
0,5	0,007 0	0,017 5	0,044 1
1,0	0,013 9	0,031 3	0,079 4
2,0	0,027 6	0,055 7	0,142 8
5,0	0,068 4	0,119 7	0,310 3

9.3 Trueness

The determined mean contents in the test samples (see Annex B) are given in Table 4 together with the accepted values. Two of the values are certified. Comparing both sets of values allow the conclusion that trueness is satisfactory.

Table 4 — Evaluation of trueness

Sample No.	**Name**	**Accepted value**	**Value found**
		% (mass fraction)	
8-1 - Ta[a]	ETI 569[b]	0,020	0,009 0
8-2 - Ta	ETI 673[b]	0,141	0,138 8
8-3 - Ta	MBH 211X 11224	0,316	0,320 9
8-4 - Ta	ETI 596[b]	1,19	1,231 2
8-5 - Ta	ETI 597[b]	2,30	2,368 6
8-6 - Ta	MBH 919X 1867	3,41	3,460 1
8-7 - Ta[a]	ETI 2042[b]	7,92	7,986 2
8-8 - Ta[a]	ETI 1868[b]	8,89	8,921 8

[a] Samples for which the precision data were unsatisfactory.

[b] Not certified.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) the method used by reference to this document, i.e. ISO 23166;

c) the results and the unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which may have influenced the results;

f) signature of the responsible person.

Annex A
(normative)

Checking the performance of an inductively coupled plasma optical emission spectrometer

A.1 General

A joint working group (ISO/TC 47/SC 1) involving representatives from ISO/TC 47, ISO/TC 17 and ISO/TC 155 was formed in 1995 to establish guidelines for inductively coupled plasma spectrometry. The project reached the stage of a committee draft (ISO/CD 12235, *Guidelines for use of inductively coupled plasma atomic emission spectrometry (ICP-AES)*) but the work was not completed. This annex is abstracted from this committee draft and was used in the tests in this document.

A.2 Resolution of a spectrometer

The resolution of a spectrometer can be defined as the wavelength difference, Δλ, between two lines which can still just be observed separately. In practice, the parameter full width at half maximum (FWHM, or F) is used as a resolution assessment.

Ideally, the resolution should be of the same order as the physical line width in plasma emission spectra, i.e. 2 pm to 5 pm (1 pm = 10^{-12} m). In practice, however, the observed width of the emission lines and, consequently, the resolution will often be determined by the bandwidth of the spectrometer being used. As long as broadening resulting from aberrations can be neglected, this bandwidth is given by Formula (A.1):

$$F = \left({}^{d_\lambda}\!\big/_{d_\mathrm{x}} \right) \left(b_\mathrm{i} + b_\mathrm{o} \right) / 2 \tag{A.1}$$

where

b_i and b_o are the widths of the entrance slit and exit slit respectively;

d_λ / d_x is the reciprocal linear dispersion which is given by:

$$d_\lambda / d_x = \mathrm{d}(\cos \beta) / nL$$

in which

L is the focal length of the spectrometer;

n is the order number;

d is the reciprocal of the grove density in the grating;

β is the diffraction angle.

Normally, commercial spectrometers present resolutions in the range of 4 pm to 30 pm. A good resolution is of great importance to cope with the frequent spectral interferences which occur in inductively coupled plasma optical emission spectrometry. Since a line with a wavelength in the second order will have the same diffraction angle β as a line with a wavelength 2λ in the first order, a spectrometer shall either have an order-sorting possibility or an optical filter to avoid an order overlap.