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Nickel alloys — Determination of niobium — Inductively coupled plasma atomic emmision spectrometric method

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

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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.

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The main task of technical committees is to prepare International Standards. 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.

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.

ISO 22033 was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*, Subcommittee SC 3, *Analysis of nickel, ferronickel and nickel alloys*.

Nickel alloys — Determination of niobium — Inductively coupled plasma atomic emmision spectrometric method

1 Scope

This International Standard specifies an inductively coupled plasma atomic emission spectrometric method for the determination of the mass fraction of niobium between 0,1 % and 10 % in nickel alloys.

2 Normative references

The following referenced documents are indispensable for the application 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 648:1977, *Laboratory glassware — One-mark pipettes*

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

3 Principle

Dissolution of a test portion in a mixture of hydrochloric, nitric and phosphoric acid and fuming with a mixture of phosphoric and perchloric acids. 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 atomic emission spectrometer and measurement of the intensity of the emitted light from niobium, and eventually from the internal reference element, simultaneously.

Examples of the analytical lines for niobium are 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 of the mass fractions between 0,75 and 1,25 of the approximate concentration of niobium in the sample to be analysed. The concentration of all elements in the sample has, therefore, to be approximately known. If the concentrations 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 automatically compensated, which will result in high accuracy. This is most important for spectral interferences, which can be severe in very highly alloyed metals. 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 analytical lines.

Lines corresponding to 309,41 and 316,34 nm have been carefully investigated (see Annex B). The strongest possible interferences are given in Table B.1. If other lines are used, they shall be carefully checked so that interferences are not higher than the values given in Annex B. The analytical line for the internal standard should be selected carefully. The use of Scandium at 363,07 nm is recommended. This line is interference-free for the elements and concentrations generally found in nickel alloys.

Table 1 — Examples of analytical lines for niobium

Element	**Analytical line** nm
Niobium	295,09
	309,41
	316,34
	319,11
	319,50

NOTE The use of an internal standard is not essential since no relevant differences between laboratories operating with or without internal standards were found.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade and only grade 2 water as specified in ISO 3696:1987.

4.1 Hydrofluoric acid, HF, 40 % (mass fraction), ρ = 1,14 g/ml, or 50 % (mass fraction), 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.

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

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

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

4.5 Perchloric acid, $HClO_4$, 60 % (mass fraction), ρ = 1,54 g/ml or 70 %, density about ρ = 1,67 g/ml.

4.6 Internal standard solution, 100 mg/l

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

4.7 Niobium standard solution, 10 g/l

Weigh, to the nearest 0,000 5 g, 1 g of high-purity niobium [min 99,9 % (mass fraction)] and dissolve in a mixture of 10 ml of water, 10 ml of hydrofluoric acid (4.1) and 10 ml of nitric acid (4.3).

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

NOTE 1 ml of this solution contains 10 mg of niobium.

4.8 Niobium standard solution, 1 g/l

Weigh, to the nearest 0,000 5 g, 0,1 g of high-purity niobium [min 99,9 % (mass fraction)] and dissolve in a mixture of 10 ml of water, 10 ml of hydrofluoric acid (4.1) and 10 ml of nitric acid (4.3).

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

NOTE 1 ml of this solution contains 1 mg of niobium.

4.9 Niobium standard solution, 100 mg/l

Using a calibrated pipette (or burette), transfer 1 ml of the niobium standard solution (4.7) into a calibrated 100 ml one-mark volumetric flask. Add 10 ml of hydrofluoric acid (4.1) and 10 ml of nitric acid (4.3). Dilute to the mark with water and mix.

NOTE 1 ml of this solution contains 0,1 mg of niobium.

4.10 Standard solutions of interfering elements

Prepare a standard solution for each element whose mass fraction is higher than 1 % in the test sample. Use pure metal or chemical substances with mass fractions of niobium less than 10 µg/g.

5 Apparatus

All volumetric glassware shall be class A and calibrated in accordance with ISO 648:1977 or ISO 1042:1998, as appropriate.

Ordinary laboratory apparatus and:

5.1 Polytetrafluoroethylene (PTFE) beakers

5.2 Polypropylene volumetric flasks, of capacity 100 ml, calibrated according to ISO 1042.

5.3 Atomic emission spectrometer (AES)

The spectrometer shall be equipped with an inductively coupled plasma (ICP) and a nebulization system resistant to hydrofluoric acid. The ICP-AES used will be satisfactory if, after optimising according to 7.3, it meets the performance criteria given in 5.3.

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 standard line, it can be used with the internal reference technique. If the sequential spectrometer is not equipped with this arrangement, an internal reference cannot be used and an alternative technique without an internal standard should be applied.

5.3.1 Practical resolution of the sequential spectrometer

Calculate the bandwidth (full width at half maximum), according to A.2 (see Annex A), for the analytical line used, including the line for internal reference. The bandwidth shall be less than 0,030 nm.

5.3.2 Short-term stability

Calculate the standard deviation of ten measurements of the absolute intensity or intensity ratio of the emitted light of the most concentrated calibration solution for niobium according to A.3 (see Annex A). The relative standard deviation shall not exceed 0,5 %.

5.3.3 Background equivalent concentration

Calculate the background equivalent concentration (BEC) according to A.4 (see Annex A), for the analytical line using a solution containing only the analyte element. The maximum values of BEC obtained should be 0,5 mg/l.

6 Sampling and sample preparation

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

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

6.3 The laboratory sample shall be cleaned by washing with pure acetone and drying in air.

6.4 If brazed alloy tools are used in the preparation of the laboratory sample then the sample shall be further cleaned by pickling in 15 % (mass fraction) nitric acid for a few minutes. It shall then be washed several times with distilled water, followed by washing in acetone and drying in air.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,000 5 g, 0,25 g of the test sample.

7.2 Preparation of test solution T_{Nb}

A PTFE or PFA beaker should be used when using HF (4.1)

7.2.1 Place the test portion in a PTFE or PFA beaker with a graphite base.

7.2.2 Add 5 ml of HF (4.1), 30 ml of HCl (4.2), 3 ml of HNO_3 (4.3) and allow the dissolution of the sample to take place at room temperature. Then add 2,5 ml of H_3PO_4 (4.4). If necessary, heat to complete dissolution. Add 7,5 ml of of $HClO_4$ (4.5) and heat until the perchloric acid starts to fume. Continue to fume for two to three minutes.

7.2.3 Cool the solution and add 10 ml of of water to dissolve the salts. Some residues may remain undissolved. In this case, add 2 ml of HF (4.1) and heat gently for about 20 min until the residues dissolve completely.

NOTE Alternative dissolution procedure: 7.2.2 and 7.2.3

Add 30 ml of HCl (4.2), 3 ml of HNO_3 (4.3) and 5 ml of H_3PO_4 (4.4). Let the dissolution begin at room temperature. If necessary, heat to complete dissolution. Add 2 ml of HF (4.1) and 5 ml of H_2SO_4 (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.

7.2.4 Cool the solution to room temperature and transfer the solution quantitatively to a 100 ml volumetric polypropylene flask. If an internal standard solution (4.6) is used, add, with a calibrated pipette, 10 ml of this internal standard.

7.2.5 Dilute to the mark with water and mix. Proceed as quickly as possible to the analysis.

7.3 Optimisation of spectrometer

7.3.1 Start the ICP-AES and let it run for at least 30 min before taking any measurements.

7.3.2 Optimise the instrument according to the manufacturer's instructions.

7.3.3 Prepare the software to measure the intensity, mean value and relative standard deviation of the analytical lines.

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

7.3.5 Check the instrument performance requirements given in 5.3.1 to 5.3.3.

7.4 Pre-determination of the test solution

Prepare a calibration solution K_{10}, corresponding to a niobium concentration of 10 % (mass fraction) and matrix-matched to the test sample solution as follows.

7.4.1 Using a calibrated pipette (or burette), add 2,5 ml of the niobium standard solution (4.7) to a 100 ml volumetric polypropylene flask (5.2) marked K_{10}.

7.4.2 In this volumetric flask K_{10}, add volumes of standard solutions (4.10) necessary to match the sample matrix to be tested, for each element whose concentration is above 1 %.

The matrix should be matched to the nearest percent.

7.4.3 Add 2,5 ml of H_3PO_4 (4.4), 7,5 ml of $HClO_4$ (4.5) and 10 ml of the internal standard solution (4.6). Dilute with water and mix.

7.4.4 Also prepare a zero member solution, K_0, prepared in the same way as the calibration solution K_{10} omitting niobium.

7.4.5 Measure the absolute intensities (I_0 and I_{10}) for the solutions K_0 and K_{10}.

7.4.6 Measure the absolute intensity I_{TNb} for the test solution T_{Nb}.

7.4.7 Calculate the approximate concentration of niobium, K_{TNb}, in % (mass fraction), in the test solution by means of the following formula:

$$K_{\mathrm{TNb}} = \frac{I_{\mathrm{TNb}}\left(K_{10} - K_0\right)}{I_{10} - I_0}$$

7.5 Preparation of calibration solutions for bracketing, $K_{\mathrm{l,Nb}}$ and $K_{\mathrm{h,Nb}}$

For each test solution T_{Nb}, prepare two matrix-matched calibration solutions, $K_{\mathrm{l,Nb}}$ and $K_{\mathrm{h,Nb}}$ with niobium concentrations in $K_{\mathrm{l,Nb}}$ slightly below and in $K_{\mathrm{h,Nb}}$ slightly above the concentration in the unknown test solution as follows:

7.5.1 Using calibrated pipettes (or burettes), add niobium standard solution (4.8) or (4.9) to one PTEF or PFA beaker marked $K_{\mathrm{l,Nb}}$ so that the mass fraction of niobium $K_{\mathrm{l,Nb}}$, in %, is approximately $K_{\mathrm{TNb}} \times 0{,}75 < K_{\mathrm{l,Nb}} < K_{\mathrm{TNb}} \times 0{,}95$. Select $K_{\mathrm{l,Nb}}$ in such a way as to take a volume easily with a calibrated pipette.

7.5.2 Using calibrated pipettes (or burette), add niobium standard solution (4.8) or (4.9) to one PTEF or PFA beaker marked $K_{\mathrm{h,Nb}}$ so that the mass fraction of niobium $K_{\mathrm{h,Nb}}$, in %, is approximately $K_{\mathrm{TNb}} \times 1{,}05 < K_{\mathrm{h,Nb}} < K_{\mathrm{TNb}} \times 1{,}25$. Select $K_{\mathrm{h,Nb}}$ in such a way to take an easy volume with a calibrated pipette.

7.5.3 Add to the calibration solutions $K_{l,Nb}$ and $K_{h,Nb}$ all matrix elements whose mass fractions are above 1 % in the test sample solution, using the appropriate amount of standard solutions (4.10) to match the equivalent matrix concentration to the nearest 1 %.

7.5.4 Proceed as directed in 7.2.2 to 7.2.5.

7.6 Measurement of test solutions

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

8 Expression of results

8.1 Method of calculation

Calculate the concentration of niobium, K_{Nb} in %, in the test solution T_{Nb}, by means of the formula:

$$K_{Nb}\ \% = \frac{I_{TNb}\left(K_{h,Nb} - K_{l,Nb}\right)}{I_{h,Nb} - I_{l,Nb}}$$

8.2 Precision

8.2.1 Laboratory tests

Eleven laboratories issued from six countries participated in an inter-laboratory test programme under the auspices of ISO/TC 155/SC 3/WG 8, involving three determinations of niobium at ten levels. Each laboratory did two determinations under repeatability conditions as defined in ISO 5725-1, 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.

8.2.2 Wavelength for measurements

Concerning the wavelength taken for measurements which have been statistically evaluated, four laboratories operated at 309,42 nm, four operated at 316,34 nm, one at 319,11 nm and one at 319,50 nm. No relevant difference between laboratories operating with or without an internal standard was found.

8.2.3 Statistical analysis

Statistical analysis was done in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3. Results from one laboratory were rejected as a consistent outlier.

Results of the evaluation were used to calculate the smoothed values for repeatability r, and within-laboratory reproducibility, R_w, and between-laboratory reproducibility, R, which are given in Table 2.

Table 2 — Repeatability and reproducibility limits

Niobium content (mass fraction) %	**Repeatability limit** r	**Within laboratory reproducibility limit** R_w	**Between laboratory reproducibility limit** R
0,1	0,005 7	0,007 4	0,013 7
0,2	0,007 9	0,010 7	0,020 9
0,5	0,012 2	0,017 2	0,036 5
1.0	0,016 9	0,024 7	0,055 6
2.0	0,023 5	0,035 4	0,084 8
5.0	0,036 2	0,057 0	0,148 0
10,0	0,050 3	0,081 7	0,225 6

8.3 Trueness

The determined mean concentrations in the test samples (See Annex C) are given in Table 3 together with the accepted values. Two of the values are certified. Comparing both sets of values allow to conclude that trueness is satisfactory.

Table 3 — Evaluation of trueness

Sample No.	**Name**	**Accepted value** % (mass fraction)	**Value found** % (mass fraction)
8-10-Nb	ETI 2028 [a]	0,10	0,090 7
8-9-Nb	ETI 599 [a]	0,30	0,316 5
8-8-Nb	ETI 621 [a]	0,50	0,504 0
8-7-Nb	ETI 404 [a]	1,0	0,986 1
8-6-Nb	ETI 427 [a]	1,2	1,195
8-5-Nb	ETI 394 [a]	2,0	2,010
8-4-Nb	ETI 709 [a]	2,8	2,867
8-3-Nb	EMRC 377-1	3,50	3,505
8-2-Nb	BCS 351	5,20	5,231
8-1-Nb	ETI 421 [a]	7,8	7,606

[a] Value not certified.

9 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 International Standard

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 International Standard, or any optional operation which may have influenced the results.

Annex A
(normative)

Checking the performance of an ICP instrument

A.1 Introduction

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) but the work was not completed. This annex is abstracted from this committee draft and was used in the tests of this International Standard.

A.2 Resolution of a spectrometer

The resolution of a spectrometer can be defined as the wavelength difference, $\Delta\lambda$, between two lines which can still just be observed separately. In practice, the parameter FWHM (Full Width at Half Maximum) is used as a resolution measure.

Ideally, the resolution should be of the same order as the physical line width in ICP-OES 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 (r_{bp}) of the spectrometer being used. As long as broadening resulting from aberrations can be neglected, this bandwidth is given by:

$$r_{\mathrm{bp}} = \mathrm{FWHM} = (\mathrm{d}\lambda/\mathrm{d}x)(w_{\mathrm{i}} + w_{\mathrm{o}})/2 \qquad \text{(A.1)}$$

where

w_{i} and w_{o} are the widths of the entrance slit and exit slit respectively;

$\mathrm{d}\lambda/\mathrm{d}x$ is the reciprocal linear dispersion which is given by:

$$\mathrm{d}\lambda/\mathrm{d}x = \mathrm{d}(\cos\beta)/nL \qquad \text{(A.2)}$$

where

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 ICP-OES. 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 must either have an order-sorting possibility or an optical filter to avoid an order overlap.