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Steel — Determination of Mo, Nb and W contents in alloyed steel — Inductively coupled plasma atomic emission spectrometric method —

Part 2:
Determination of Nb content

Aciers — Dosage du Mo, du Nb et du W dans les aciers alliés — Méthode par spectrométrie d'émission atomique avec plasma induit par haute fréquence —

Partie 2: Dosage du Nb

Reference number
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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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 13899-2 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

ISO 13899 consists of the following parts, under the general title *Steel — Determination of Mo, Nb and W contents in alloyed steel — Inductively coupled plasma atomic emission spectrometric method*:

- *Part 1: Detemination of Mo content*
- *Part 2: Detemination of Nb content*
- *Part 3: Detemination of W content*

Steel — Determination of Mo, Nb and W contents in alloyed steel — Inductively coupled plasma atomic emission spectrometric method —

Part 2:
Determination of Nb content

1 Scope

This International Standard specifies a method for the determination of the niobium content in steel by means of inductively coupled plasma emission spectrometry.

This method is applicable to niobium contents between 0,005 and 5 % (mass fraction).

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 1042:1983, *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*

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

3 Principle

The sample is dissolved in a hydrochloric, nitric and hydrofluoric acid mixture and fumed with a phosphoric and perchloric acid mixture. Hydrofluoric acid and an internal standard element (if used) are added and the solution is diluted to known volume. The solution is filtered and nebulized into an ICP and the intensity of the emitted light from each element is measured simultaneously with the light emitted from the internal standard element.

The method uses a calibration based on close matrix matching of the calibration solutions to the sample and close bracketing of the niobium content around the approximate concentration of niobium in the sample to be analysed. This compensates for matrix interferences and provides high accuracy, even in highly alloyed steels where spectral interferences can be severe. Nonetheless, all interferences shall be kept to a minimum and it is therefore essential that the spectrometer used meets the performance criteria specified in the method for the selected analytical lines.

In order to accurately matrix match, it is necessary to know the concentration of all elements in the sample (to the nearest percent). To this end, it may be necessary to carry out a preliminary analysis of the sample by some semi-quantitative method.

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.

4.1 Hydrofluoric acid, HF, 40 % (m/m), ρ approximately 1,14 g/ml.

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

4.3 Nitric acid, HNO_3, ρ approximately 40 g/ml.

4.4 Phosphoric acid, H_3PO_4, ρ approximately 1,70 g/ml, diluted 1 + 1.

4.5 Perchloric acid, $HClO_4$, ρ approximately 1,54 g/ml, diluted 1 + 1.

4.6 Fuming acid mixture, mix 100 ml of the phosphoric acid (4.4) and 300 ml of the perchloric acid (4.5).

4.7 Internal standard solution, 1 000 mg/l.

Choose a suitable element to be added as internal standard and prepare a 1 000 mg/l solution. The internal standard chosen shall

- be pure,
- not be present in the sample, and
- not interfere with analytical wavelengths, nor should the internal standard element wavelength be interfered with by elements in the test solution.

The internal standard shall be soluble in the acids used and it shall not cause precipitation. Moreover, the excitation conditions of the analytical line and the internal standard element line should match.

4.8 Niobium stock standard solution, 1 000 mg/l.

Weigh, to the nearest 0,000 1 g, 0,5 g of high purity niobium [min 99,95 % (mass fraction)] and dissolve in a mixture of 30 ml hydrofluoric acid (4.1) and 3 ml nitric acid (4.3). Cool and transfer the solution quantitatively to a calibrated 500 ml one-mark plastic volumetric flask. Dilute to the mark with water and mix. 1 ml of this solution contains 1 mg of Nb.

NOTE It is not permitted to use pre-prepared niobium standard solutions supplied by second parties.

4.9 Niobium standard solution, 100 mg/l.

Transfer, with a calibrated pipette, 25 ml of the niobium stock standard solution (4.8) into a calibrated 250 ml one-mark plastic volumetric flask. Add 2,5 ml of hydrofluoric acid (4.1). Dilute to the mark with water and mix. 1 ml of this solution contains 0,1 mg of Nb.

4.10 Niobium standard solution, 10 mg/l.

Transfer, with a calibrated pipette, 2,5 ml of the niobium stock standard solution (4.8) into a calibrated 250 ml one-mark plastic volumetric flask. Add 2,5 ml of hydrofluoric acid (4.1). Dilute to the mark with water and mix. 1 ml of this solution contains 0,01 mg of Nb.

4.11 Standard solutions of interfering and matrix elements.

Prepare standard solutions for each element above 1 % (mass fraction) in the test sample. Use pure elements or oxides with niobium contents less than 10 µg/g (mass fraction). Commercial certified standard solutions can also be used if the niobium content is less than the value specified above.

NOTE If a large amount of an element is to be added (e.g. iron), it might be more advantageous to use the pure metal and weigh the correct amount (see 7.3 and 7.4). In this case, use the dissolution procedure described in 7.1.2.

5 Apparatus

As it, for obvious reasons, is impossible to use volumetric glassware in this application, the laboratory has to make sure that the plastic pipettes and flasks to be used are calibrated in accordance with ISO 648 or ISO 1042 as appropriate.

Ordinary laboratory apparatus and

5.1 Atomic emission spectrometer, equipped with an inductively coupled plasma (ICP) and a nebulization system resistant to hydrofluoric acid.

When a teflon nebulizer is used, it is recommended that a surface active agent should be added to improve wetting in the nebulizer and spray chamber. Modern nebulizers are, however, often manufactured in plastic materials with better wetting-characteristics than Teflon and can therefore (as is the case with sapphire nebulizers) be used without a surface active agent.

The ICP-ES spectrometer used will be satisfactory if, after optimising according to 7.2.1 to 7.2.4, it meets the performance criteria given in 5.1.2 to 5.1.4.

The spectrometer can be either the simultaneous or the sequential type. A sequential type can be used either with or without an internal standard. However, if a sequential spectrometer is to be used with an internal standard, it shall be fitted with an arrangement which allows for the simultaneous measurement of the internal standard line.

5.1.1 Analytical lines

This standard does not specify any particular emission line. It is mandatory that each laboratory carefully investigate the line/lines available on its own equipment to find the most suitable one regarding sensitivity and freedom from interferences.

In Table 1, however, two suggestions are given together with possible interferences. These lines have been carefully investigated (see Annex B).

The line for the internal standard element should be selected according to 4.7. It is, however, recommended to use Sc 363.07 nm. This line is interference free for the elements and concentrations given in Annex B.

Table 1 — Examples of analytical lines together with interfering elements

Element	Wavelength nm	Possible interferences
Nb	309,41	V, Cr, Ni
Nb	316,34	Fe, Cr, V, W, Ti

5.1.2 Minimum practical resolution of the spectrometer

Calculate the bandwidth, according to Clause A.1, for the wavelength used including the line for the internal standard. The bandwidth shall be less than 0,030 nm.

5.1.3 Minimum short-term precision

Calculate the short-term precision according to Clause A.2. The relative standard deviation shall not exceed 0,5 % of the mean absolute or ratioed intensities for concentrations 100 to 1 000 times the LOD (6.1.4) mg/l. For concentrations 10 to 100 times the LOD, the RSD shall not exceed 5 %.

5.1.4 Limit of Detection (LOD) and Limit of Quantification (LOQ)

Calculate the LOD and LOQ, according to Annex A, Clause A.3, for the analytical line used. The values shall be below the values in Table 2.

Table 2 — Limit of Detection (LOD) and Limit of Quantification (LOQ)

Element	**LOD** mg/l	**LOQ** mg/l
Nb	0,05	0,25

5.2 Polytetrafluoroethylene (PTFE) beakers

5.3 100 ml polypropylene volumetric flask

6 Sampling and samples

Sampling and preparation of the laboratory sample shall be carried out in accordance with ISO 14284 or appropriate national standards for steels.

7 Procedure

7.1 Preparation of test solution, T_n

7.1.1 Weigh, to the nearest 0,000 5 g, a test portion of the laboratory sample in accordance with Table 3, and transfer it to a PTFE beaker.

Table 3 — Test portion

Expected content % (mass fraction)	**Test portion** g
0,005 to 0,5	0,5
0,5 to 5	0,25

7.1.2 Add 10 ml of HCl (4.2), 2 ml of HNO_3 (4.3) and 5 ml of HF (4.1). Heat to complete dissolution. Make sure that all deposits that may have formed on the walls of the beaker are washed down using a glass stick with a rubber head. Add 20 ml of fuming acid mixture (4.6) and heat until the perchloric acid starts to fume. Continue to fume for 2 to 3 min (the white smoke must be on the top of the PTFE beaker).

7.1.3 Cool the solution and add 10 ml of water to dissolve the salts. Some residues can remain undissolved. Add 2 ml of HF (4.1). Heat slowly for 20 min when the residues will dissolve completely.

7.1.4 Cool the solution to room temperature and transfer the solution quantitatively to a 100 ml volumetric polypropylene flask (5.3). If an internal standard is to be used, add 1 ml of the internal standard solution (4.7). It is strongly recommended that some kind of automatic system be used when adding the internal standard, since it is most important that the volume added is exactly the same for each flask.

7.1.5 Dilute to the mark with water and mix.

7.1.6 Filter all solutions through a medium paper filter. Discharge the first 2 to 3 ml.

7.2 Preparation for spectrometric measurements

7.2.1 Start the ICP and allow it to warm up according to the manufacturer's instructions before any measurement.

7.2.2 Optimize the instrument according to the manufacturer's instructions.

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

7.2.4 If an internal standard is to be 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.

7.2.5 Check the instrument performance requirements given in 5.1.2 to 5.1.4.

7.3 Pre-analysis of the test solution

Prepare a calibration solution, $K_{0,5}$ or K_5, corresponding to a niobium content of 0,5 or 5 % (mass fraction) depending on the expected content, and matrix-matched to the test solution. Prepare also a blank calibration solution, K_0, in the same way as the calibration solution but leaving out niobium.

7.3.1 Add, using a pipette,

- 2,5 ml of the niobium stock standard solution (4.8) to a 100 ml volumetric polypropylene flask (5.3) marked $K_{0,5}$ (corresponds to a Nb content of 0,5 %), or
- 12,5 ml of the niobium stock standard solution (4.8) to a 100 ml volumetric flask (5.3) marked K_5 (corresponds to a Nb content of 5 %).

7.3.2 For all matrix elements with concentrations above 1 % in the unknown sample, add (using the standard solutions, 4.11) the same amount of the matrix elements (to the nearest percent) to the calibration samples $K_{0,5}$ or K_5. Remember to calculate on the actual sample weight used (0,5 or 0,25 g). Also add internal standard (4.7) if this is to be used.

7.3.3 Add all matrix elements as in 7.3.2 to a second 100 ml volumetric polypropylene flask (5.3) marked K_0. Also add internal standard (4.7) if this is to be used.

7.3.4 Add 20 ml of fuming acid mixture (4.6) to the two flasks, dilute with water and mix.

7.3.5 Measure the absolute or ratioed intensities for the solutions K_0 and $K_{0,5}$ or K_5.

7.3.6 Measure the absolute or ratioed intensities for the test solution, T_n.

7.3.7 Calculate the approximate concentration in the test solution by interpolation between the absolute or ratioed intensities of the solutions K_0 and $K_{0,5}$ or K_5.

7.4 Preparation of calibration solutions for bracketing, K_{Ln} and K_{Hn}

For each sample, n, prepare two matrix matched calibration samples, K_{Ln} and K_{Hn}, with niobium concentrations in K_{Ln} slightly below and in K_{Hn} slightly above the concentration in the unknown sample as described in 7.4.1 and 7.4.2.

7.4.1 Use the result obtained in 7.3.7 and calculate the approximate amount of Nb, m_{S} (in mg), in the dissolved portion of the unknown sample. Add, using a calibrated pipette, $m_{\mathrm{Ln}} = (m_{\mathrm{S}} - 0{,}05 \times m_{\mathrm{S}})$ of the appropriate niobium standard solution (4.8, 4.9 or 4.10) to one PTFE beaker marked K_{Ln} and $m_{\mathrm{Hn}} = (m_{\mathrm{S}} + 0{,}05 \times m_{\mathrm{S}})$ to a second one marked K_{Hn}.

7.4.2 For all matrix elements, with concentrations above 1 % in the unknown sample, add, using the standard solutions (4.11), the same amount of the matrix elements (to the nearest percent) to the calibration samples K_{Ln} and K_{Hn}.

7.4.3 Proceed as specified in 7.1.2 to 7.1.6.

7.5 Analysis of test solutions

7.5.1 Measure the absolute or ratioed intensity of the analytical line, beginning with the lowest calibration solution, K_{Ln}. Continue with test solution, T_{n}, and then the highest calibration solution K_{Hn}. Repeat this sequence three times and calculate the mean intensities I_{Ln}, I_{Hn} for the low and high calibration solution and I_{T} for the test solution, respectively.

7.5.2 Plot the measured intensities I_{Ln} and I_{Hn} versus the amount of Nb, m_{Ln} and m_{Hn}, in the calibration solutions. Determine the amount of Nb, m_{T}, in the test solution by interpolation of the measured intensity I_{T} between I_{Ln} and I_{Hn}.

8 Expression of results

8.1 Method of calculation

The content of niobium, expressed as a percentage by mass, w_{Nb} (%) is given by the formula

$$w_{\mathrm{Nb}} = \frac{m_{\mathrm{Nb}} \times 0{,}1}{m}$$

where

m_{Nb} is the amount, expressed in milligrams, of niobium in the test solution;

m is the mass, in grams, of the test portion.

8.2 Precision

A planned trial of this method was carried out by 13 laboratories, at eleven levels of niobium, each laboratory making three determinations (see Notes 1 and 2) of niobium at each level.

NOTE 1 Two of the three determinations were carried out 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.

NOTE 2 The third determination was carried out at a different time (on a different day) by the same operator as in Note 1, using the same apparatus with a new calibration.

The test samples used are listed in Annex C.

The results obtained were treated statistically in accordance with ISO 5725, Parts 1, 2 and 3.

The data obtained showed a logarithmic relationship between niobium content and repeatability (r) and reproducibility (R and R_W) of the test results (see Note 3) as summarized in Table 4. The graphical representation of the data is shown in Figure D.1.

Table 4 — Results for repeatability and reproducibility limits

Niobium content % (mass fraction)	**Repeatability limit** % (mass fraction) r	**Reproducibility limits** % (mass fraction) R_W	 R
0,005	0,000 32	0,000 54	0,001 0
0,01	0,000 52	0,000 88	0,001 6
0,02	0,000 84	0,001 4	0,002 6
0,05	0,001 6	0,002 7	0,005 0
0,1	0,002 6	0,004 4	0,008 0
0,2	0,004 1	0,007 2	0,013
0,5	0,007 7	0,014	0,025
1,0	0,012	0,022	0,040
2,0	0,020	0,036	0,065
5,0	0,038	0,068	0,122

NOTE 3 From the two values obtained on day 1, the repeatability limit (r) and reproducibility limit (R) were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained on day 2, the within laboratory reproducibility limit (R_W) was calculated using the procedure given in ISO 5725-3.

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;

b) the method used by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) the analytical line used;

e) any unusual features noted during the determination;

f) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A
(normative)

Procedure for the determination of instrumental criteria

A.1 Practical resolution of the spectrometer

Resolution is subject to theoretical definition but its practical assessment normally involves a wavelength scan across the spectral line of interest, plotting the profile, measurement of the peak width at half the peak height and calculation of the resolution in manometers. An example is shown in Figure A.1.

A.2 Minimum short-term precision

An important parameter for assessing the suitability of an instrument for a given determination is the short term stability of the emission signal, namely the closeness of agreement between the values obtained on the same test sample solution by repeating measurements in rapid succession.

It is the standard deviation of the mean results, expressed as a percentage of the concentration (relative standard deviation, RSD).

Make ten consecutive measurements on the same solution and calculate the relative standard deviation.

A.3 Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of detection and limit of quantification represent two of the parameters for an analytical method. Both are derived from the standard deviation of the repeatability.

Prepare two solutions, each containing the analyte element of interest at a concentration level of zero and ten times the detection limit respectively. These solutions should also contain concentrations of acids, fusion agents and matrix elements similar to those in the samples to be analysed.

Spray the zero test solution for approximately 10 s and take 10 readings at the pre-set integration time. Thereafter, do the same for the solution containing 10 times the detection limit.

From the intensity readings, calculate the mean intensities X_{10}, X_0 and the standard deviation of the zero member s_0.

Calculate the net mean intensity (X_{n10}) for the solution at 10 times the detection limit using the following equation:

$$X_{n10} = X_{10} - X_0$$

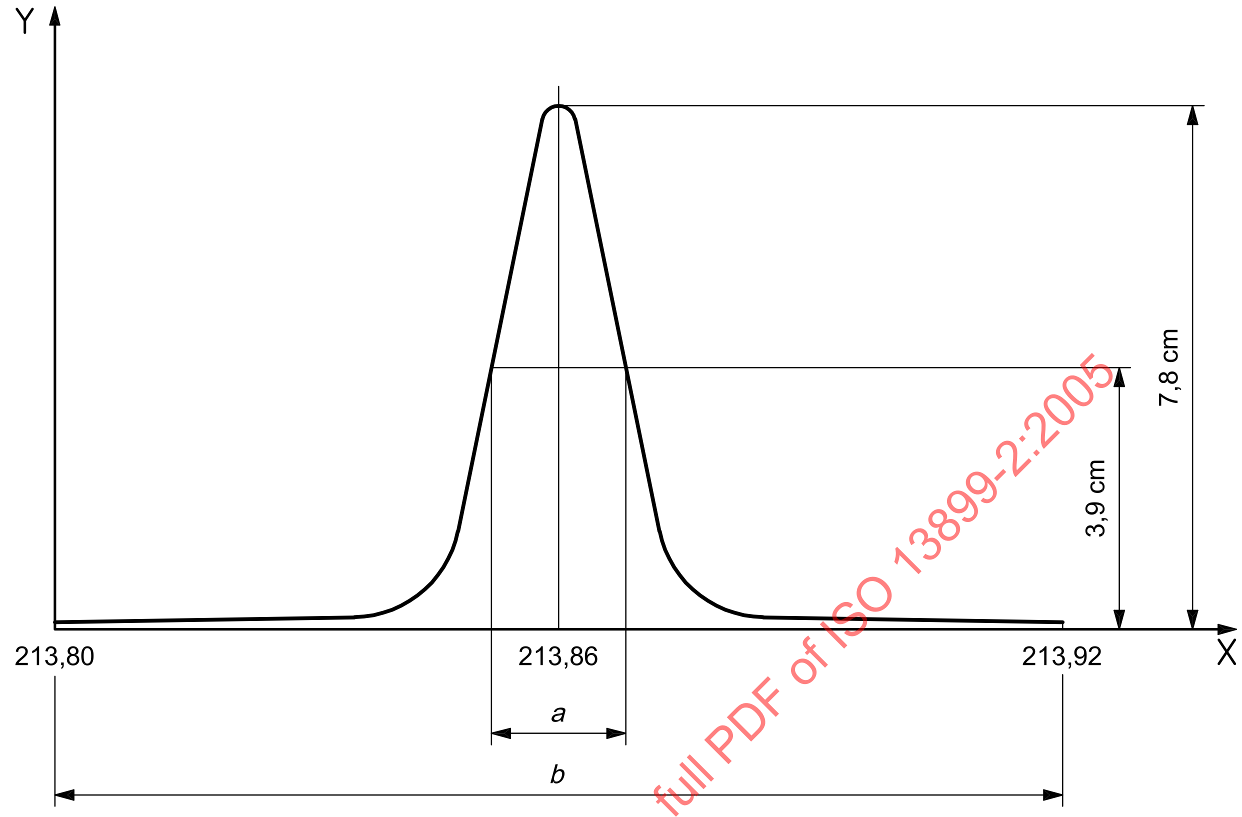
Calculate the detection limit using the following equation:

$$\mathrm{LOD} = 3 \times s_0 \times \frac{\rho_{10}}{X_{n10}}$$

Where ρ_{10} is the concentration, expressed in mg/l, of the solution at 10 times the detection limit.

The limit of quantification is then given as

$$\mathrm{LOQ} = 5 \times \mathrm{LOD}$$



$$\text{Resolution} = (213{,}92 - 213{,}80) \times \frac{2}{15} = 0{,}016 \text{ nm}$$

Key

x wavelength for zinc, nm

y intensity, au (arbitrary unit)

[a] Half peak width = 2 cm.

[b] Peak window = 15 cm.

Figure A.1 — Example of calculation of practical resolution

Annex B
(informative)

Suggested lines together with possible spectral interferences in the determination of Nb in steel by ICP-AES

The following interferences have been detected from elements, normally found in steel. The interferences are expressed as the apparent content when the interfering element is present with a maximum concentration.

Table B.1 — Possible spectral interferences in the determination of Nb

Interfering element	**Content in alloy** % (mass fraction)	**Apparent contents** % (mass fraction)	
		Nb 309,41 nm	Nb 316,34 nm
Ti	5	< 0,001	0,002
W	5	0,005	0,009
Co	20	< 0,001	0,001
Mn	2	< 0,001	<0,001
Mo	30	< 0,001	0,003
Cr	20	0,001	0,001
Ni	30	0,002	< 0,001
Fe	50	0,001	< 0,001
V	1	0,01	0,000 1
Al	5	< 0,001	< 0,001
Cu	30	< 0,001	< 0,001
Si	1	0,000 4	< 0,001