TECHNICAL SPECIFICATION

ISO/TS 13899-3

First edition
2005-02-15

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

Part 3:
Determination of W 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 3: Dosage du W

Reference number
ISO/TS 13899-3:2005(E)

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Published in Switzerland

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Foreword

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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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

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An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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/TS 13899-3 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

ISO/TS 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 3:
Determination of W content

1 Scope

This Technical Specification specifies a method for the determination of tungsten content in steel by means of inductively coupled plasma atomic emission spectrometry.

This method is applicable to tungsten contents between 0,1 % and 20 % (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 1042:1998, *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*

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 inductively coupled plasma (ICP) spectrometer and the intensity of the emitted light from the 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 tungsten content around the approximate concentration of tungsten 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 content of all elements in the sample (to the nearest %). To this end, it may be necessary to carry out a preliminary analysis of the sample by a 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 % (mass fraction), 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 1,40 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,
- shall not be present in the sample, and
- shall 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 Tungsten stock standard solution, 1 000 mg/l

Weigh, to the nearest 0,001 g, 0,5 g of high purity tungsten [minimum 99,95 % (mass fraction)] and dissolve in a mixture of 10 ml hydrofluoric acid (4.1) and 20 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 W.

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

4.9 Tungsten standard solution, 100 mg/l

Transfer, with a calibrated micropipette, 25 ml of the tungsten stock standard solution (4.8) into a calibrated 250 ml one-mark plastic volumetric flask. Add 5 ml of hydrofluoric acid (4.1) and 10 ml of nitric acid (4.3). Dilute to the mark with water and mix. 1 ml of this solution contains 0,1 mg of W.

NOTE If calibrated micropipettes of suitable volume are not available it would be more advantageous to use more concentrated standard solutions. These solutions must, however, be prepared for each series of analysis, in order to avoid possible precipitation.

4.10 Standard solutions of interfering and matrix elements

Prepare standard solutions for each element of which more than 1 % (mass fraction) is contained in the test sample. Use pure elements or oxides with tungsten contents less than 10 µg/g. Commercial certified standard solutions can also be used if the tungsten 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

The plastic pipettes and flasks to be used shall be 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 polytetrafluoroethylene (PTFE) 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 of plastic materials with better wetting-characteristics than PTFE 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 investigates the line/lines available on its own equipment to find the most suitable one regarding sensitivity and freedom from interferences.

In Table 1, however, a suggestion is given together with possible interferences.

The line for the internal standard element should be selected according to 4.7.

Table 1 — Example of analytical line and lines for internal standard element

Element	Wavelength nm	Possible interferences
W	207,91	Cr, V, Mo
Sr (as internal standard)	407,77	
Sc (as internal standard)	363,07	
Cd (as internal standard)	214,44	

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 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 (5.1.4) 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 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
W	1	5

5.2 Polytetrafluoroethylene (PTFE) beakers

5.3 100 ml polypropylene volumetric flasks

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 steel.

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
0,1 to 5	0,5
5 to 20	0,1

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 polypropylene volumetric 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 ml 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 Optimise 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_2 or K_{20}, corresponding to a tungsten content of 2 % or 20 % (mass fraction) and matrix-matched to the test solution. Prepare also a blank calibration solution, K_0, prepared in the same way as the calibration solution, but leaving out tungsten.

7.3.1 Add, using a pipette;

- 10 ml of the tungsten stock standard solution (4.8) to a 100 ml volumetric flask (5.3) marked K_2 (corresponds to a W content of 2 %) or
- 20 ml of the tungsten stock standard solution (4.8) to a 100 ml volumetric flask (5.3) marked K_{20} (corresponds to a W content of 20 %).

7.3.2 For all matrix elements, with concentrations above 1 % in the unknown sample, add, using the standard solutions (4.10), the same amount of the matrix elements (to the nearest %) to the calibration samples K_2 or K_{20}. Remember to calculate on the actual sample weight used (0,5 or 0,1 g). Add also internal standard solution (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 polypropylene volumetric flask (5.3) marked K_0. Also internal standard solution (4.7) if this is to be used.

7.3.4 Add 20 ml of the 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_2 or K_{20}.

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_2 or K_{20}.