TECHNICAL SPECIFICATION

ISO/TS 13899-1

First edition
2004-04-01

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

Part 1: Determination of Mo 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 1: Dosage du Mo

Reference number
ISO/TS 13899-1:2004(E)

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Published in Switzerland

Contents

Page

Foreword

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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.

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:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

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order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn.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again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.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 13899-1 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: Determination of Mo content*

— *Part 2: Determination of Nb content*

— *Part 3: Determination of W content*

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

Part 1: Determination of Mo content

1 Scope

This Technical Specification specifies an inductively coupled plasma atomic emission spectrometric method for the determination of molybdenum content in steel.

The method is applicable to molybdenum contents between 0,03 % (mass fraction) and 8,5 % (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 1042:1998, *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

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 necessary, 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 molybdenum, or with emitted light from the internal reference element, simultaneously.

NOTE 1 The method uses a calibration graph based on a very close matrix matching of the calibration solutions to the sample and close bracketing of the contents around the approximate concentration of molybdenum in the sample to be analysed. The concentrations of all elements in the sample must, therefore, be approximately known. If the concentrations are not known, the sample must be analysed by some semi-quantitative method.

NOTE 2 The advantage with this procedure is that all possible interferences from the matrix are automatically compensated, which results in high accuracy. This is most important for spectral interferences, which can be severe in very highly alloyed steels. However, all possible interferences must be kept on a minimum level. Therefore it is essential that the spectrometer used meets the performance criteria specified in the method for the selected analytical lines.

Examples of the analytical lines are given in Table 1.

Table 1 — Examples of analytical lines together with interfering elements

Element	Analytical line nm	Interferences
Molybdenum	202,03	Ta
	281,61	Al, Hf

NOTE 3 These lines have been carefully investigated (see Annex A). The strongest possible interferences are given in Table 1. If other lines are used, they have to be carefully checked so that interferences are not higher than the values given in Annex A. It is recommended to use scandium 363.07 nm. This line is interference-free for the elements and concentrations given in Annex A.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized 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, or 50 % (mass fraction), ρ approximately 1,17 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 Internal standard solution, 1 000 mg/l

Choose a suitable element to be added as internal reference and prepare a 1 000 mg/l solution.

4.7 Molybdenum stock standard solution, 1 000 mg/l

Weigh, to the nearest 0,000 5 g, 0,5 g of high purity molybdenum [minimum 99,95 % (mass fraction)] and dissolve in a mixture of 25 ml hydrochloric acid (4.2) and 25 ml nitric acid (4.3). Keep the temperature of a one-mark volumetric flask the same as that at which the volumetric flask was calibrated. Cool and transfer the solution quantitatively to a calibrated 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

4.8 Molybdenum standard solution, 100 mg/l

Keep the temperature of a one-mark volumetric flask the same as that at which the volumetric flask was calibrated. Using a calibrated pipette, transfer 100 ml of the molybdenum stock standard solution (4.7) into a

calibrated 1 000 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.2). Dilute to the mark with water and mix.

4.9 Molybdenum standard solution, 10 mg/l

Keep the temperature of a one-mark volumetric flask the same as that at which the volumetric flask was calibrated. Using a calibrated pipette, transfer 100 ml of the molybdenum standard solution (4.8) into a calibrated 1 000 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.2). Dilute to the mark with water and mix.

4.10 Standard solutions of interfering elements

Prepare standard solutions for each element of which more than 1 % by mass is contained in the test sample. Use pure metal or chemical substances with molybdenum contents less than 0,001 % (mass fraction).

5 Apparatus

All volumetric glassware shall be class A and 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-AES) and a nebulization system resistant to hydrofluoric acid.

NOTE When a Teflon nebulizer and/or spray chamber are used, surface active agent is recommended to be added in order to avoid liquefaction of spray due to poor wetting of fluid in nebulizer.

The ICP-AES used will be satisfactory if, after optimizing in accordance with 7.4 a) to e), it meets the performance criteria given in 5.1.1 to 5.1.4.

The spectrometer can be either the simultaneous or the sequential type. 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 internal standard can be applied.

5.1.1 Practical resolution of the spectrometer

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

5.1.2 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 a calibration solution for molybdenum. The relative standard deviation shall not exceed 0,4 %.

5.1.3 Background equivalent concentration and detection limit

Calculate the background equivalent concentration (BEC) and detection limit (DL) for the analytical line in a solution containing only the analyte element. The values of BEC and DL shall be below 0,5 mg/l and 0,015 mg/l respectively.

5.1.4 Graph linearity

The graph is checked by calculating the correlation coefficient. This coefficient shall be more than 0,999.

5.2 Polytetrafluoroethylene (PTFE) beakers

5.3 100 ml polypropylene measuring flask, calibrated in accordance with ISO 1042.

6 Sampling and samples

Carry out sampling in accordance with ISO 14284.

7 Determination procedure

7.1 Test portion

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

7.2 Preparation of test solution, T_n

7.2.1 Place the test portion in a 200 ml Pyrex Erlenmeyer flask.

NOTE A PTFE or PFA beaker with a graphite base can also be used. In this case the solution has not been transferred to an other PTFE beaker after fuming (see 7.2.3).

7.2.2 Add 10 ml HCl (4.2), 2 ml HNO_3 (4.3) and 5 ml H_3PO_4 (4.4). Heat to complete dissolution. Add 15 ml of $HClO_4$ (4.5) and heat until the perchloric acid starts to fume. Continue to fume for 2 min to 3 min (the white smoke shall form on the top of the Erlenmeyer flask).

7.2.3 Cool the solution and add 10 ml of water to dissolve the salts. Some residues can remain undissolved. Transfer the solution and possible undissolved residues quantitatively to a 100 ml PTFE beaker (5.2). Add 2 ml of HF (4.1). Heat slowly till 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 (5.3). If internal standard is used, add, by pipette, 1 ml of the internal standard solution (4.6).

7.2.5 Dilute to the mark with water and mix.

7.3 Optimization of spectrometer

7.3.1 Start the ICP and allow it to warm up in accordance with manufacturer's instructions before taking any measurements.

7.3.2 Optimize the instrument in accordance with 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 5.1.1 to 5.1.4.

7.4 Pre-determination of the test solution

Prepare a calibration solution, K_{10}, corresponding to a molybdenum concentration of 10 % in mass and matrix matched to the test solution as follows.

a) Using a pipette, add 25 ml of the molybdenum stock standard solution (4.7) to one 100 ml volumetric polypropylene flask (5.3) marked K_{10}.

b) Add to the calibration sample, the same amount of the standard solutions of matrix (interfering) elements (4.10), to the nearest 1 %, whose concentrations are above 1 %.

c) Add 5 ml H_3PO_4 (4.4) and 15 ml $HClO_4$ (4.5), and dilute with water and mix.

d) Prepare a blank calibration solution, K_0, prepared in the same way as the calibration solution but leaving out molybdenum.

e) Measure the absolute intensities for the solutions K_0 and K_{10} and plot a calibration graph.

f) Measure the absolute intensities for the test solution, T_n.

g) Calculate the approximate mass of molybdenum, m_s in mg, in the test solution by means of the calibration graph.

NOTE The concentration in the blank test solution can be negative due to the differences between the solutions with and without the matrix elements.

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

For each test solution, n, prepare two matrix matched calibration solutions, K_{Ln} and K_{Hn}, with molybdenum concentrations in K_{Ln} slightly below and, in K_{Hn}, slightly above the concentration in the unknown test solution as follows.

a) Using calibrated pipettes, add molybdenum standard solution (4.7), (4.8) or (4.9) to one 200 ml Pyrex Erlenmeyer flask marked K_{Ln} so that the molybdenum content, m_{Ln} in mg, is approximately $0{,}95 \times m_s$.

NOTE m_{Ln} can be less than above figure at the first trial.

b) Using calibrated pipettes, add molybdenum standard solution (4.7), (4.8) or (4.9) to one 200 ml Pyrex Erlenmeyer flask marked K_{Hn} so that the molybdenum content, m_{Hn} in mg, is approximately $1{,}05 \times m_s$.

NOTE m_{Hn} can be larger than above figure at the first trial.

c) Add to the calibration samples, K_{Ln} and K_{Hn}, the same amount of the standard solutions (4.10) of matrix elements, to the nearest 1 %, whose concentrations are above 1 %.

d) Proceed as specified in 7.2.2 to 7.2.5

7.6 Determination of test solutions

7.6.1 Maintain the temperature of all solutions, K_{Ln}, K_{Hn} and T_n, to within 1 °C. Measure the absolute or ratioed intensity of the analytical line of the lowest calibration solution, K_{Ln}, first, then test sample solution, T_n, and finally the highest calibration solution K_{Hn}. Repeat this sequence three times and calculate the mean intensities I_{Ln} and I_{Hn} for the low- and high-calibration solution and I_T for the test solution respectively.

7.6.2 Determine the mass of molybdenum present in the test solution by interpolation of I_T, from I_{Ln}, I_{Hn}, m_{Ln} and m_{Hn}.

8 Expression of results

8.1 Method of calculation

The content of molybdenum, w_{Mo}, expressed as a percentage of mass fraction, is given by the formula

$$w_{Mo} = \frac{0,1 \times m_{Mo,T}}{m}$$

where

$m_{Mo,T}$ is the mass, in miligrammes, of the element 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 14 laboratories, using 8 levels of molybdenum contents, each laboratory making three determinations of molybdenum content at each level (see Notes 1 and 2).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5752-1; 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 details of the test samples used and the mean results obtained are given in Tables B.1 and B.2.

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

The data obtained showed a logarithmic relationship between the molybdenum content and the repeatability limit, r, and reproducibility limits, R_W and R, of the test results (see Note 3), as summarized in Table 2. The graphical representation of the data is shown in Figure C.1.

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 specified in ISO 5725-3.

Table 2 — Results for repeatability limit and reproducibility limits

Molybdenum content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_W	R
0,03	0,001 1	0,001 2	0,005 5
0,05	0,001 6	0,001 8	0,007 9
0,1	0,002 7	0,003 2	0,013
0,2	0,004 7	0,005 7	0,021
0,5	0,009 5	0,012	0,041
1	0,016	0,022	0,067
2	0,028	0,040	0,11
5	0,057	0,087	0,21
10	0,098	0,16	0,34

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 Technical Specification;

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 Technical Specification, or any optional operation which may have influenced the results.

Annex A
(informative)

Suggested analytical lines together with possible spectral interferences in determination of molybdenum in steel by ICP-AES

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

Table A.1 — Possible spectral interferences in determination of molybdenum

Interfering elements	Maximum concentration	Apparent concentrations of molybdenum % (mass fraction) Analytical lines	
	% (mass fraction)	202,03 nm	281,61 nm
Ti	5	0,001	0,002
W	5	0,002	0,006
Co	20	0,008	< 0,004
Mn	2	< 0,001	0,002
Mo	30	—	—
Cr	20	0,01	0,004
Ni	100	0,06	< 0,005
Fe	50	0,02	< 0,002
V	1	< 0,001	< 0,001
Hf	5	0,006	0,04
Zr	1	< 0,001	< 0,001
Al	5	0,006	0,04
Nb	5	0,004	< 0,001
Cu	30	< 0,006	< 0,006
Ta	5	0,01	0,001
Re	1	0,003	< 0,001
Y	1	< 0,001	< 0,001

Annex B
(informative)

Additional information on international cooperative tests

Table 2 was derived from the results of international analytical trials carried out in 1996 on 8 test samples in 7 countries involving 14 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1138, August 1996, and are shown in Table B.2. The graphical representation of the precision data is given in Annex C.

The test samples used and participating laboratories are listed in Table B.1 and B.3 respectively.

Table B.1 — Test samples used in the interlaboratory tests

Sample	Chemical composition % (mass fraction)										
	Mo	C	Si	Mn	Ni	Cr	W	V	Co	Al	Nb
JSS 655-10	0,033	0,05	0,07	1	9,8	18	—	—	0,07	0,003	0,5
JSS 601-8	0,108	1,1	—	0,7	0,1	0,8	1,1	0,06	—	—	—
JSS 607-8	0,54	0,8	4,6	0,4	0,05	4	17	0,8	4,6	—	—
JSS 153-9	1,25	0,2	—	0,8	1,0	1,0	—	0,2	—	—	—
JK 37	3,55	0,01	0,06	1,7	31	27	0,02	0,08	0,06	0,008	0,002
Sandvik 254SMO	6,11	0,02	0,04	0,5	18	20	—	—	0,04	0,1	0,02
NBS 153A	8,85	0,9	8,5	0,2	0,17	3,7	1,8	2,1	8,5	—	—

Table B.2 — Detailed results obtained in interlaboratory tests

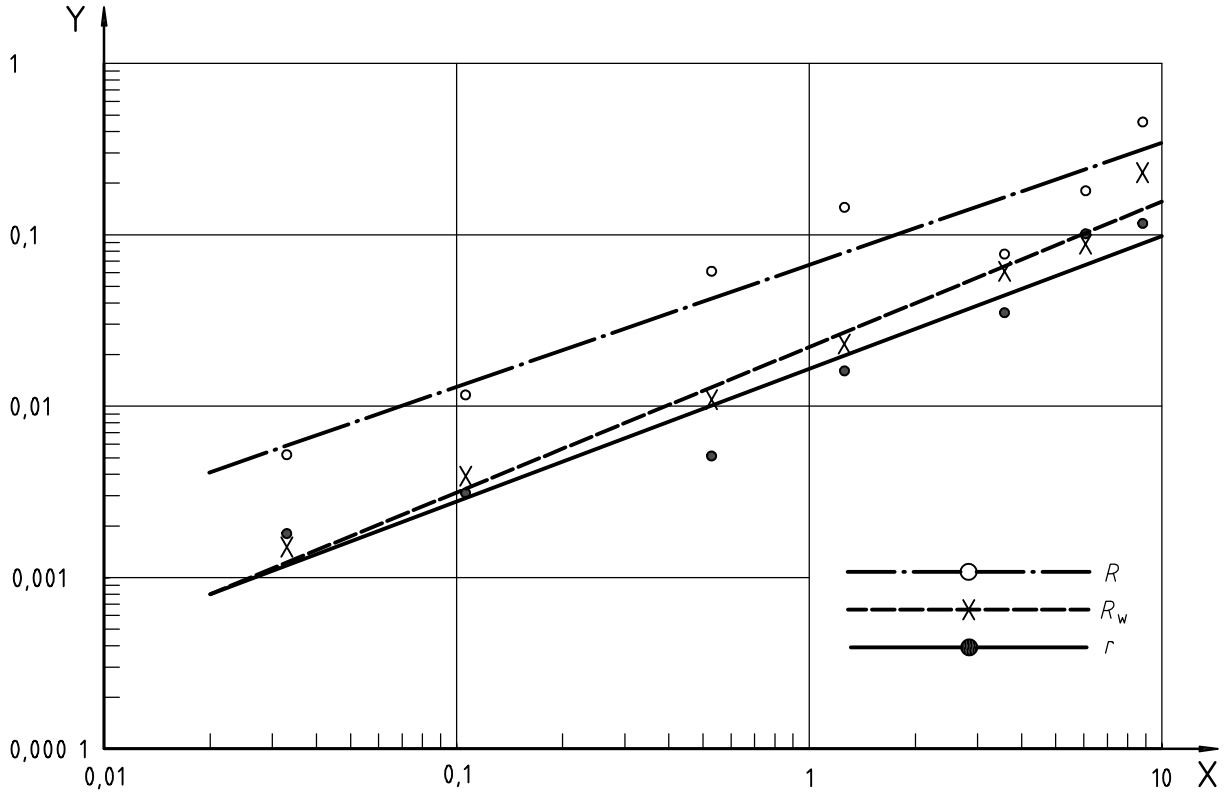
Sample	Molybdenum content % (mass fraction)		Precision data		
	Certified	Found	Repeatability limit	Reproducibility limits	
		$\overline{w}_{Mo}$	r	R_W	R
JSS 655-10	0,033	0,033	0,001 8	0,001 5	0,005 2
JSS 601-8	0,108	0,106	0,003 1	0,003 9	0,011 6
JSS 607-8	0,54	0,529	0,005 1	0,010 9	0,061 1
JSS 153-9	1,25	1,260	0,016	0,023	0,144
JK 37	3,55	3,580	0,035	0,061	0,077
Sandvik 254SMO	6,11	6,083	0,101	0,088	0,180
NBS 153A	8,85	8,832	0,116	0,230	0,454

Table B.3 — List of participating laboratories

Country	Laboratories
Canada	Sherrit International Corp.
China	Inst. of Daye Special Steel Co. Ltd.
Czech Republic	Nova Hut
France	Ugine Aubert & Duval CTIF
Italy	CSM ENEA AST Terni
Japan	Nippon Yakin Kogyo Co. Ltd. Aichi Steel Works, Ltd. Daido Steel Co. Ltd.
Sweden	Sandvik Steel
US	Allegheny Ludlum Steel LECO Corp.

Annex C
(informative)

Graphical representation of precision data



Key

X molybdenum content, % (mass fraction)

Y precision, %

lg r = 0,777 6 lg $\overline{w}_{Mo}$ – 1,788 1

lg R_W = 0,844 5 lg $\overline{w}_{Mo}$ – 1,652 2

lg R = 0,712 4 lg $\overline{w}_{Mo}$ – 1,176 1

where $\overline{w}_{Mo}$ is the average molybdenum content, expressed as a percentage by mass, obtained from three determinations in each laboratory.

Figure C.1 — Logarithmic relationships between molybdenum content, $\overline{w}_{Mo}$, and the repeatability limit, r, and reproducibility limits, R_W and R

ICS 77.080.20

Price based on 11 pages