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Second edition
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Steel and iron — Determination of molybdenum content — Thiocyanate spectrophotometric method

Aciers et fontes — Dosage du molybdène — Méthode spectrophotométrique au thiocyanate

Reference number
ISO 4941:1994(E)

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.

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.

International Standard ISO 4941 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4941:1978), which has been technically revised. The method is now applicable to molybdenum contents between 0,005 % (*m/m*) and 0,125 % (*m/m*). The reason for the upper limit being reduced (from 9 % (*m/m*) in the first edition) is that an international cooperative test showed that the method does not fully comply with the precision criteria suggested for the assessment of a method in an International Standard. A graphical representation of the data obtained in the precision test is given in annex B.

Annexes A and B of this International Standard are for information only.

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Steel and iron — Determination of molybdenum content — Thiocyanate spectrophotometric method

1 Scope

This International Standard specifies a thiocyanate spectrophotometric method for the determination of the molybdenum content in steel and iron.

The method is applicable to molybdenum contents between 0,005 % *(m/m)* and 0,125 % *(m/m)*.

Vanadium and tungsten interfere with the measurement if, because of their contents, the V/Mo ratio is greater than 16 or the W/Mo ratio is greater than 8 (see note 1).

NOTE 1 Greater V/Mo or W/Mo ratios (up to 300) may, however, be permitted, but in such cases it is necessary to carry out the measurement very quickly after the extraction.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

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 4800:1977, *Laboratory glassware — Separating funnels and dropping funnels.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Dissolution of a test portion in an appropriate mixture of acids and decomposition of the carbides by oxidation.

Quantitative formation of a coloured compound of molybdenum, in the presence of thiocyanate, iron(II) and/or copper(II) ions and extraction of this compound using butyl acetate.

Spectrophotometric measurement of the coloured compound at a wavelength of about 470 nm.

4 Reagents

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

4.1 Pure iron, in flake or powder form, with a molybdenum content less than 0,000 5 % *(m/m)* and free from tungsten and vanadium.

4.2 Butyl acetate.

4.3 Nitric acid, ρ about 1,40 g/ml.

4.4 Hydrochloric acid, ρ about 1,19 g/ml.

4.5 Hydrochloric acid, ρ about 1,19 g/ml, diluted (3 + 1).

4.6 Hydrochloric acid, ρ about 1,19 g/ml, diluted (1 + 1).

4.7 Acid mixture I

Add 2 volumes of hydrochloric acid (4.4) to 1 volume of nitric acid (4.3) and mix well.

Prepare the solution immediately before use.

4.8 Acid mixture II

Add 150 ml of orthophosphoric acid (ρ about 1,70 g/ml) to 300 ml of water, and add 360 ml of perchloric acid (ρ about 1,67 g/ml) to this diluted acid (see note 2). Transfer the solution to a 1 000 ml, one-mark volumetric flask, dilute to the mark with water and mix.

NOTE 2 In the preparation of this acid mixture, 360 ml of perchloric acid (ρ about 1,67 g/ml) may be replaced by 150 ml of sulfuric acid (ρ about 1,84 g/ml).

4.9 L(+)Ascorbic acid, 100 g/l solution.

Prepare this solution at the time of use.

4.10 Ammonium thiocyanate, 320 g/l solution.

Store this solution away from light.

4.11 Copper(II), solution corresponding to 70 mg of Cu(II) per litre in a hydrochloric acid medium.

Dissolve 0,188 g of copper(II) chloride dihydrate ($CuCl_2.2H_2O$) or 0,275 g of copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$) in 125 ml of hydrochloric acid (4.4). Transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.12 Tin(II) copper(II) chloride, solution in a hydrochloric acid medium.

Dissolve 80 g of tin(II) chloride dihydrate ($SnCl_2.2H_2O$) in 155 ml of hydrochloric acid (4.4). Add 100 ml of copper(II) solution (4.11). Transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this solution immediately before use.

4.13 Iron, acidic solution corresponding to 10 g of Fe per litre.

Weigh, to the nearest 0,01 g, 10,0 g of the pure iron (4.1). Place the portion in a 1 000 ml beaker, and dissolve by careful addition of 500 ml of the acid mixture II (4.8). After cooling, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.14 Molybdenum, standard solutions.

4.14.1 Stock solution, corresponding to 500 mg of Mo per litre.

Weigh, to the nearest 0,1 mg, 0,500 g of molybdenum [minimum purity 99,95 % (*m/m*), see note 3]. Transfer the portion to a 1 000 ml beaker. Add 500 ml of hydrochloric acid (4.4) and heat; add two drops of nitric acid (4.3) to aid dissolution. Cool the solution.

Transfer the solution to a 1 000 ml, one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this stock solution contains 500 µg of Mo.

NOTE 3 Pure metals, especially those in powder form, are subject to changes in their stoichiometry as a result of oxidation. It is therefore advisable to check the oxygen content prior to use.

4.14.2 Standard solution, corresponding to 5 mg of Mo per litre.

Transfer 10,0 ml of the molybdenum stock solution (4.14.1) to a 1 000 ml, one-mark volumetric flask. Add 500 ml of the hydrochloric acid (4.4), dilute to the mark with water and mix.

Prepare this solution immediately before use.

1 ml of this standard solution contains 5 µg of Mo.

5 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory apparatus, and

5.1 Gilson separating funnel (spherical funnel), of nominal capacity 100 ml and type 3 in accordance with ISO 4800.

5.2 Spectrophotometer.

5.3 Cells, with optical path lengths of 1,0 cm and 2,0 cm.

6 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel and iron.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

7.1 Test portion

Weigh, to the nearest 0,1 mg, about 1,00 g of the test sample.

7.2 Determination

7.2.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml conical flask and carefully add 30 ml of acid mixture I (4.7).

Heat gently until effervescence ceases. The tungsten present partially precipitates.

Add 50 ml of acid mixture II (4.8). Heat until gentle boiling starts and continue heating until dense white fumes are given off.

When acid mixture II (4.8) is made up of perchloric and orthophosphoric acids, heating shall be continued until the carbides have completely decomposed: the chromium, if present, is then oxidized.

When acid mixture II (4.8) is made up of sulfuric and orthophosphoric acids, heating shall be continued and the complete decomposition of the carbides shall be achieved by the addition of nitric acid (4.3), (see note 4).

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

If there is a residue or precipitate in the solution, filter part of it through a dry filter, collecting the filtrate in a dry beaker after having discarded the first fraction.

Transfer 20,0 ml of the solution to a 50 ml one-mark volumetric flask, add 10 ml of hydrochloric acid (4.4), dilute to the mark with water and mix. This is test solution A.

NOTE 4 The precipitated tungsten dissolves because of the presence of orthophosphoric acid.

7.2.2 Preparation of the compensating solution

Weigh, to the nearest 0,1 mg, 1,00 g of the pure iron (4.1). Place it in a 250 ml conical flask and carefully add 30 ml of acid mixture I (4.7). Proceed as specified in 7.2.1, beginning at the second paragraph. This is compensating solution B (see note 5).

NOTE 5 The compensating solution thus prepared permits the subtraction, during the measurement, of the absorption of the molybdenum caused by the pure iron (4.1) and all the reagents.

7.2.3 Formation and extraction of the coloured compound

7.2.3.1 Test solution

Take 25,0 ml of the test solution A (7.2.1) and transfer it to a separating funnel (5.1).

Using a pipette, add, shaking after each addition, the reagents in the following order:

- 5 ml of copper (II) solution (4.11);
- 10 ml of hydrochloric acid (4.5);
- 5 ml of L(+) ascorbic acid solution (4.9).

Shake and wait for 3 min until the colour of the solution decreases in intensity. Add 25,0 ml of butyl acetate (4.2), see note 6, and mix by inversion.

NOTE 6 It is essential that all solutions without exception are measured using one-mark pipettes, particularly the butyl acetate (4.2) into which the molybdenum complex is extracted.

Using a pipette, immediately add 5 ml of ammonium thiocyanate solution (4.10) and shake gently for 1 min to extract the molybdenum compound into the organic layer. Allow to separate.

When the layers are well separated, remove the aqueous layer and discard it. Using a pipette, add 10 ml of tin(II) copper(II) chloride solution (4.12) to the separating funnel (5.1). Shake for about 1 min, allow to separate, remove the aqueous layer and discard it. Collect the organic layer in a flask fitted with a ground stopper (see note 7).

Ensure that only the organic layer is transferred to the flask.

NOTE 7 Care must be taken to prevent contamination of the organic layer. However, some water droplets in suspension in the organic layer are unavoidable. These will interfere with the spectrophotometric measurement, unless sufficient time is allowed for them to settle at the bottom of the flask.

7.2.3.2 Compensating solution

Take 25,0 ml of the compensating solution B (see 7.2.2), transfer it to a separating funnel (5.1) and proceed in accordance with 7.2.3.1, beginning at the second paragraph.

7.2.4 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the test solution (see 7.2.3.1) using the spectrophotometer (5.2) at a wavelength of about 470 nm, in a cell (5.3), after adjusting the spectrometer to zero absorbance against the compensating solution (see 7.2.3.2). The following optical path lengths are used:

— for Mo contents $< 0{,}025$ % (*m/m*): 2 cm,

— for Mo contents $> 0{,}025$ % (*m/m*): 1 cm.

Care should be taken when selecting the 2 cm cells to ensure that the optical path length is exactly twice that of the 1 cm cells used to establish the calibration graph.

When the V/Mo ratio is greater than 16 and/or the W/Mo ratio is greater than 8, carry out the measurements during a period not exceeding 30 min after the extraction.

7.3 Establishing the calibration graph

7.3.1 Preparation of the calibration solutions, related to spectrophotometric measurements performed using cells with an optical path length of 1 cm

Transfer successively to a series of six separating funnels (5.1), marked from 0 to 5, the volumes of reagents indicated in table 1.

Shake each funnel and wait for 3 min until the colour of the solutions decreases in intensity.

Add 25,0 ml of butyl acetate (4.2) to each funnel and mix by inversion.

Continue in accordance with 7.2.3.1, beginning at the third last paragraph, just after note 6.

7.3.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the calibration solutions (see 7.3.1) in accordance with the indications given in 7.2.4, after adjusting the spectrometer (5.2) to zero absorbance against the zero member (see table 1).

7.3.3 Plotting the calibration graph

Prepare the calibration graph by plotting the absorbance values against the molybdenum concentrations, expressed in micrograms per millilitre, in the measured solutions.

Table 1

Reagent	Volumes, in millilitres, for calibration solution number					
	0 [1]	1	2	3	4	5
Iron solution (4.13)	10	10	10	10	10	10
Copper(II) solution (4.11)	5	5	5	5	5	5
Molybdenum standard solution (4.14.2)	0	5,0	10,0	15,0	20,0	25,0
Hydrochloric acid (4.6)	25	20	15	10	5	0
L(+) ascorbic acid solution (4.9)	5	5	5	5	5	5

1) Zero member.

8 Expression of results

8.1 Method of calculation

Convert the absorbance measured in 7.2.4 into the corresponding concentration, expressed in micrograms per millilitre, of molybdenum in the coloured test solution by using the calibration graph plotted in 7.3.3.

The molybdenum content, w_{Mo}, expressed as a percentage by mass, is given by the equation:

$$w_{Mo} = \rho_{Mo} \times V_1 \times \frac{50}{V_0} \times \frac{V_2}{20} \times \frac{1}{m} \times \frac{1}{10^4} \times \frac{1}{b}$$

$$= \rho_{Mo} \times 25 \times \frac{50}{25} \times \frac{100}{20} \times \frac{1}{m} \times \frac{1}{10^4} \times \frac{1}{b}$$

$$= \rho_{Mo} \times \frac{1}{40m} \times \frac{1}{b}$$

$$= \frac{\rho_{Mo}}{40mb}$$

where

V_0 is the volume, in millilitres, of the test solution used for the determination (see 7.2.3.1);

V_1 is the volume, in millilitres, of butyl acetate (4.2) used for the determination (see 7.2.3.1);

V_2 is the volume, in millilitres, of the test solution (see 7.2.1);

ρ_{Mo} is the concentration, expressed in micrograms per millilitre, of molybdenum in the coloured test solution;

m is the mass, in grams, of the test portion (7.1);

b is the optical path length, in centimetres, of the cell used for the measurements.

8.2 Precision

A planned trial of this method was carried out by 16 laboratories in eight countries, at 10 levels of molybdenum, each laboratory making three determinations of molybdenum content at each level (see notes 8 and 9).

The test samples used are listed in table A.1.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained for the five samples in this range showed a logarithmic relationship between molybdenum content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 10) as summarized in table 2. The graphical representation of the figures is shown in figure B.1.

NOTES

8 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

9 The third determination was carried out at a different time (on a different day) by the same operator as in note 8, using the same apparatus with a new calibration.

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

Table 2

Molybdenum content % (*m*/*m*)	**Repeatability** r	**Reproductibility** R	R_w
0,005	0,000 6	0,001 8	0,001 2
0,01	0,000 8	0,002 3	0,001 5
0,02	0,001 2	0,002 8	0,001 9
0,05	0,001 8	0,003 7	0,002 5
0,10	0,002 5	0,004 6	0,003 2
0,125	0,002 8	0,005 0	0,003 5

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 the analysis;

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

c) the results, and the form 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
(informative)

Additional information on the international cooperative tests

The full results of the trials were reported in document ISO/TC 17/SC 1 N 936, April 1992. The graphical representation of the precision data for all samples is given in annex B together with the equations for the five samples with the lowest concentrations.

The test samples used are listed in table A.1.

Table A.1

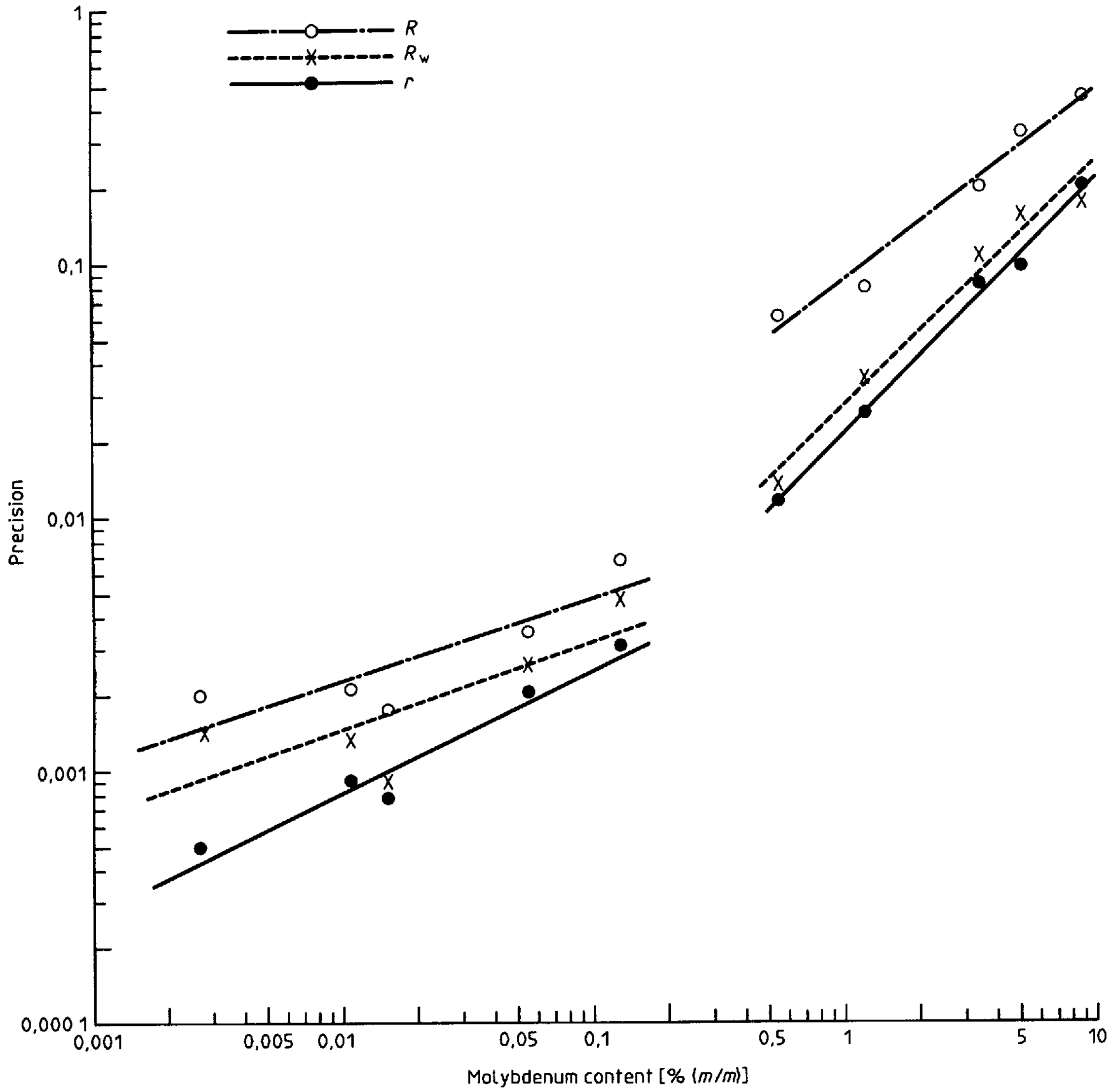
Sample	Molybdenum content % (*m/m*)			Precision data		
	Certified	Found		Repeatability	Reproducibility	
		$\bar{w}_{\text{Mo},1}$	$\bar{w}_{\text{Mo},2}$	r	R	R_w
ECRM 096-1 (unalloyed steel) [V: 0,003 6 % (*m/m*)]	0,003	0,002 7	0,002 8	0,000 5	0,002 0	0,001 5
ECRM 481-1 (cast iron)	0,011	0,010 9	0,010 9	0,000 9	0,002 1	0,001 4
BCS 405 (low-alloy steel) [V: 0,32 % (*m/m*)]	0,017	0,015 6	0,015 8	0,000 8	0,001 8	0,000 9
JSS 651-10 (stainless steel)	0,054	0,054 9	0,054 8	0,002 0	0,003 4	0,002 6
BCS 455-1 (low-alloy steel) [W: 0,20 % (*m/m*)]	0,140	0,132	0,132	0,003 1	0,006 8	0,004 8
JSS 606-8 (high-speed steel) [V: 0,83 % (*m/m*) W: 17,16 % (*m/m*)]	0,58	0,549	0,552	0,011 0	0,065 4	0,013 4
F-112-1 (low-alloy steel) [V: 0,60 % (*m/m*) W: 1,78 % (*m/m*)]	1,21	1,274	1,272	0,025 4	0,075 6	0,037 9
ECRM 283-1 (high-alloy steel) [V: 3,28 % (*m/m*) W: 9,66 % (*m/m*)]	3,41	3,440	3,434	0,085 9	0,190	0,114
ECRM 285-1 (high-alloy steel) [V: 0,02 % (*m/m*)]	5,07	5,061	5,073	0,093 6	0,339	0,169
NIST 153a (tool steel) [V: 2,06 % (*m/m*) W: 1,76 % (*m/m*)]	8,85	8,840	8,833	0,199	0,428	0,177

$\bar{w}_{\text{Mo},1}$: general mean within a day
$\bar{w}_{\text{Mo},2}$: general mean between days

Annex B

(informative)

Graphical representation of precision data



$\lg r = 0{,}485\,2 \lg \overline{w}_{\mathrm{Mo},1} - 2{,}115$

$\lg R_{\mathrm{w}} = 0{,}327\,9 \lg \overline{w}_{\mathrm{Mo},2} - 2{,}172$

$\lg R = 0{,}309\,0 \lg \overline{w}_{\mathrm{Mo},1} - 2{,}025$

where

$\overline{w}_{\mathrm{Mo},1}$ is the average molybdenum content, expressed as a percentage by mass, obtained within a day;
$\overline{w}_{\mathrm{Mo},2}$ is the average molybdenum content, expressed as a percentage by mass, obtained between days.

Figure B.1 — Logarithmic relationship between molybdenum content (w_{Mo}) and the repeatability (r) or reproducibility (R and R_{w})

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Descriptors: steels, iron, chemical analysis, determination of content, molybdenum, spectrometric method.

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