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

Aciers et fontes — Détermination des teneurs en molybdène — Méthode spectrophotométrique au thiocyanate

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 4941:1994), which has been technically revised.

The main changes are as follows:

— the normative references have been revised;

— the precision data has been updated.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document specifies a thiocyanate spectrophotometric method for the determination of molybdenum contents in steel and iron. The method is applicable to molybdenum mass fractions between 0,005 % and 0,125 %.

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.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

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

ISO 4800, *Laboratory glassware — Separating funnels and dropping funnels*

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

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

Quantitative formation of a coloured complex 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 complex at a wavelength of about 470 nm.

5 Reagents

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

5.1 Pure iron, in flake or powder form, with a molybdenum content less than 0,000 5 % (mass fraction) and free from tungsten and vanadium.

5.2 Butyl acetate.

5.3 Nitric acid, ρ approximately 1,40 g/ml.

5.4 Hydrochloric acid, ρ approximately 1,19 g/ml.

5.5 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted (3 + 1).

5.6 Hydrochloric acid, ρ approximately 1,19 g/ml, diluted (1 + 1).

5.7 Acid mixture I.

Add 2 volumes of hydrochloric acid (5.4) to 1 volume of nitric acid (5.3) and mix well. Prepare this mixture immediately before use.

5.8 Acid mixture II.

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

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

5.9 L(+)- ascorbic acid solution, 100 g/l.

Prepare this solution just before use.

5.10 Ammonium thiocyanate solution, 320 g/l.

Store this solution away from light.

5.11 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 di-hydrate ($CuCl_2 \cdot 2H_2O$) or 0,275 g of copper(II) sulfate penta-hydrate ($CuSO_4 \cdot 5H_2O$) into 125 ml of hydrochloric acid (5.4). Transfer the solution into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

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

Dissolve 80 g of tin(II) chloride di-hydrate ($SnCl_2 \cdot 2H_2O$) in 155 ml of hydrochloric acid (5.4). Add 100 ml of copper(II) solution (5.11). Transfer the solution into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

Prepare this solution just before use.

5.13 Iron, 10 g/l solution

Weigh, to the nearest 0,01 g, 10,0 g of the pure iron (5.1). Place the portion into a 1 000 ml beaker, and dissolve by careful addition of 500 ml of the acid mixture II (5.8). After cooling, transfer into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.14 Molybdenum, standard solutions.

5.14.1 Molybdenum standard solution, corresponding to 500 mg/l of Mo.

Weigh, to the nearest 0,1 mg, 0,500 g of molybdenum [minimum purity 99,95 % (mass fraction), see NOTE]. Transfer the portion into a 1 000 ml beaker. Add 500 ml of hydrochloric acid (5.4) and heat; add two drops of nitric acid (5.3) to aid dissolution. Cool the solution.

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

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

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

5.14.2 Molybdenum standard solution, corresponding to 5 mg/l of Mo.

Transfer 10,0 ml of the molybdenum standard solution (5.14.1) into a 1 000 ml, one-mark volumetric flask. Add 500 ml of hydrochloric acid (5.4) 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.

6 Apparatus

During the analysis, unless otherwise stated only ordinary laboratory apparatus and the following should be used.

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

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

6.2 Spectrophotometer, suitable for measuring the absorbance of the solutions at a wavelength of 470 nm with 10 mm or 20 mm optical path length cells.

6.3 Cells, with optical path lengths of 10 mm and 20 mm.

7 Sampling and preparation of the test samples

Sampling and preparation of the samples shall be carried out in accordance with ISO 14284 or appropriate national standards for steel and cast iron.

8 Procedure

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

8.1 Test portion

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

8.2 Determination

8.2.1 Preparation of the test solution

Place the test portion (8.1) in a 250 ml conical flask and carefully add 30 ml of the acid mixture I (5.7).

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

Add 50 ml of the acid mixture II (5.8). Heat until gentle boiling starts and continue heating until dense white fumes are given off.

When acid mixture II (5.8) 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 (5.8) 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 (5.3).

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

Allow to cool and transfer the solution quantitatively into 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 a 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 test solution into a 50 ml one-mark volumetric flask, add 10 ml of hydrochloric acid (5.4), dilute to the mark with water and mix. This is test solution A.

8.2.2 Preparation of the compensating solution

Weigh, to the nearest 0,1 mg, 1,00 g of the pure iron (5.1). Place it in a 250 ml conical flask and carefully add 30 ml of the acid mixture I (5.7). Proceed as specified in 8.2.1, beginning at the second paragraph. This is compensating solution B.

NOTE The compensating solution thus prepared permits the subtraction, during the measurement, of the absorption of the molybdenum caused by the pure iron (5.1) and all the reagents.

8.2.3 Formation and extraction of the coloured complex

8.2.3.1 Test solution

8.2.3.1.1 Take 25,0 ml of the test solution A (8.2.1) and transfer it into a separating funnel (6.1).

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

— 5 ml of copper (II) solution (5.11);

— 10 ml of hydrochloric acid (5.5);

— 5 ml of L(+)- ascorbic acid solution (5.9).

8.2.3.1.3 Shake and wait for 3 min until the colour of the solution decreases in intensity. Add 25,0 ml of butyl acetate (5.2), and mix by inversion.

8.2.3.1.4 It is essential that all solutions without exception are measured using one-mark pipettes, particularly the butyl acetate (5.2) into which the molybdenum complex is extracted.

8.2.3.1.5 Using a pipette, immediately add 5 ml of ammonium thiocyanate solution (5.10) and shake gently for 1 min to extract the molybdenum complex into the organic layer. Allow to separate.

8.2.3.1.6 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 (5.12) to the separating funnel (6.1). 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.

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

8.2.3.1.8 Care shall 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.

8.2.3.2 Compensating solution

Take 25,0 ml of the compensating solution B (see 8.2.2), transfer it to a separating funnel (6.1) and proceed in accordance with 8.2.3.1, beginning at 8.2.3.1.2.

8.2.4 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the test solution (see 8.2.3.1) using the spectrophotometer (6.2) at a wavelength of about 470 nm, in a cell (6.3), after adjusting the spectrometer to zero absorbance against the compensating solution (see 8.2.3.2). The following optical path lengths are used:

— for Mo contents < 0,025 % (mass fraction): 20 mm;

— for Mo contents > 0,025 % (mass fraction): 10 mm.

Care should be taken when selecting the 20 mm cells to ensure that the optical path length is exactly twice that of the 10 mm 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.

8.3 Establishment of the calibration curve

8.3.1 Preparation of the calibration solutions, related to spectrophotometric measurements performed using cells with an optical path length of 10 mm

Transfer successively into a series of six separating funnels (6.1), 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 (5.2) to each funnel and mix by inversion.

Continue in accordance with 8.2.3.1, beginning at 8.2.3.1.5.

8.3.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the calibration solutions (see 8.3.1) in accordance with the indications given in 8.2.4, after adjusting the spectrometer (6.2) to zero absorbance against the zero member (see Table 1).

Use an appropriate spectrometer software or an off-line computer for regression calculations or prepare a graphical representation.

8.3.3 Plotting the calibration curve

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

Table 1 — Composition of the calibration solutions

Reagent	Volumes, for calibration solution number ml					
	0 [a]	1	2	3	4	5
Iron solution (5.13)	10	10	10	10	10	10
Copper(II) solution (5.11)	5	5	5	5	5	5
Molybdenum standard solution (5.14.2)	0	5,0	10,0	15,0	20,0	25,0
Hydrochloric acid (5.6)	25	20	15	10	5	0
L(+)- ascorbic acid solution (5.9)	5	5	5	5	5	5
[a] Zero member.						

9 Expression of results

9.1 Method of calculation

Convert the absorbance measured in 8.2.4 to the corresponding concentration, expressed in micrograms per millilitre, of molybdenum in the coloured test solution by using the calibration curve 8.3.3.

The molybdenum content, w_{Mo}, expressed as a percentage by mass, is given by Formula (1):

$$\begin{aligned} w_{Mo} &= \rho_{Mo} \times V_1 \times \frac{50}{V_0} \times \frac{V_2}{20} \times \frac{1}{m} \times \frac{1}{10^4} \times \frac{1}{b} \\ &= \rho_{Mo} \times 25 \times \frac{50}{25} \times \frac{100}{20} \times \frac{1}{m} \times \frac{1}{10^4} \times \frac{1}{b} \\ &= \rho_{Mo} \times \frac{1}{40\,m} \times \frac{1}{b} \\ &= \frac{\rho_{Mo}}{40\,m} \times \frac{1}{b} \end{aligned} \quad (1)$$

where

V_0 is the volume, expressed in millilitres, of the test solution used for the determination (see 8.2.3.1);

V_1 is the volume, expressed in millilitres, of butyl acetate (5.2) used for the determination (see 8.2.3.1);

V_2 is the volume, expressed in millilitres, of the test solution (see 8.2.1);

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

m is the mass, expressed in grams, of the test portion (8.1);

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

9.2 Precision

A planned trial of this method was carried out by 16 laboratories, using 10 levels of molybdenum content, each laboratory making three determinations of the 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 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 composition of the test samples used is given in Table A.1, Annex A, and the smoothed precision data are given in Table 2.

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

The data obtained showed a logarithmic relationship between the molybdenum contents and the repeatability (r) and reproducibility (R_w and R) limits of the test results. These data are summarized in Table 2. The graphical representation of the data is shown in Figure B.1.

Table 2 — Smoothed precision data

Molybdenum content % (mass fraction)	**Repeatability limit** r % (mass fraction)	**Reproducibility limits**	
		R_w % (mass fraction)	R % (mass fraction)
0,005	0,000 6	0,001 3	0,001 9
0,01	0,000 9	0,001 8	0,002 5
0,02	0,001 3	0,002 5	0,003 2
0,05	0,002 1	0,003 7	0,004 7
0,10	0,002 9	0,005 1	0,006 2
0,125	0,003 3	0,005 7	0,006 7

10 Test report

The test report shall include the following information:

a) all the information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) method used by reference to this document, i.e. ISO 4941:2024;

c) results and unit in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which might have influenced the results.

Annex A
(informative)

Additional information on the international interlaboratory test

An international interlaboratory test was carried out on nine steel samples and one cast iron sample in 8 countries involving 16 laboratories.

The results of the trials were reported in Reference [3].

Table 2 shows the precision data obtained from their re-evaluation carried out in 2021.

The graphical representation of the precision data is given in Annex B.

The composition of test samples used is listed in Table A.1.

The experimental results of the test are reported in Table A.2.

Table A.1 — Composition of test samples used in the international interlaboratory test

Sample	Chemical composition % (mass fraction)							Interference ratio	
	Mo	C	Si	Mn	P	S	Cr	V/Mo	W/Mo
ECRM 096-1 (unalloyed steel)	0,003 0	0,113	0,263	1,35	0,019	0,000 9	0,019	1,2	
ECRM 481-1 (cast iron)	0,011 0	3,91	2,29	0,448	0,019	0,004	0,063		
BCS 405 (low alloy steel)	0,017 4	0,058	1,38	1,28	0,017	0,060	0,210	18,8	
JSS 651-1 (stainless steel)	0,054 2	0,041	0,69	1,33	0,026	0,005 2	18,26		
BCS 455-1 (low alloy steel)	0,140	0,598	0,25	0,40	0,052	0,055	0,21		1,43
JSS 606-8 (high-speed steel)	0,577	0,760	0,28	0,31	0,016	0,000 8	4,00	1,4	29,6
F 112-1 (low alloy steel)	1,214	0,348	1,00	0,191	-	-	4,28	0,5	1,47
ECRM 283-1 (high alloy steel)	3,407	1,219	0,345	0,217	0,290	0,290	4,15	0,96	2,83
ECRM 285-1 (high alloy steel)	5,067	0,003	0,015	0,013	0,002 4	0,002 4	0,034	<0,01	
NBS 153a (tool steel)	8,85	0,902	0,270	0,192	0,007	0,007	3,72	0,2	0,20