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Steels and cast irons — Determination of molybdenum content — Photometric method

Aciers et fontes — Dosage du molybdène — Méthode photométrique

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FOREWORD

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4941 was developed by Technical Committee ISO/TC 17, *Steel*, and was circulated to the member bodies in August 1976.

It has been approved by the member bodies of the following countries :

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The member bodies of the following countries expressed disapproval of the document on technical grounds :

Australia
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Steels and cast irons — Determination of molybdenum content — Photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method for the determination of the molybdenum content of steels and cast irons.

The method is applicable to steels and cast irons having molybdenum contents between 0,003 and 9 % (*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.

NOTE — 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 REFERENCE

ISO/R 377, *Selection and preparation of samples and test pieces for wrought steel.*

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 *n*-butyl acetate.

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

NOTE — When the conditions of the procedure are respected, the coefficient of molecular absorption is 18 930 ± 60.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Iron, in flake or powder form, with a molybdenum content less than 0,005 % and free from tungsten and vanadium.

4.2 *n*-Butyl acetate.

4.3 Nitric acid, ρ about 1,40 g/ml, about 14 M solution.

4.4 Hydrochloric acid, ρ about 1,19 g/ml, about 12 M solution.

4.5 Hydrochloric acid, about 9 M solution (3 + 1).

4.6 Hydrochloric acid, about 6 M solution (1 + 1).

4.7 Acid mixture I.

To 1 volume of the nitric acid (4.3) add 2 volumes of the hydrochloric acid (4.4) and mix well.

Prepare the solution immediately before use.

4.8 Acid mixture II.

Add 150 ml of phosphoric acid, ρ about 1,70 g/ml, to 300 ml of water, and add this diluted acid to 360 ml of perchloric acid, ρ about 1,67 g/ml. Dilute to 1 000 ml with water and mix.

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

4.9 Ascorbic acid, 100 g/l solution.

Prepare this solution at the moment 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 medium about 1,5 M.

Dissolve 0,188 g of copper(II) chloride dihydrate ($CuCl_2.2H_2O$) or 0,275 g of copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$) in 125 ml of the hydrochloric acid (4.4). Make up the volume to 1 000 ml with water and mix.

4.12 Tin(II) copper(II) chloride, solution in a hydrochloric medium about 2 M.

Dissolve 80 g of tin(II) chloride in 155 ml of the hydrochloric acid (4.4). Add 100 ml of the copper(II) solution (4.11). Make up the volume to 1 000 ml with water and mix.

Prepare the solution immediately before use.

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

Dissolve 10 g of the iron (4.1) in 500 ml of the acid mixture II (4.8) used for the determination; after cooling, make up the volume to 1 000 ml with water and mix.

4.14 Molybdenum, standard solution corresponding to 500 mg of Mo per litre.

Weigh, to the nearest 0,001 g, 1,261 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) or 0,920 g of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] and dissolve in 500 ml of the hydrochloric acid (4.4). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

4.15 Molybdenum, standard solution corresponding to 5 mg of Mo per litre.

Transfer 10,0 ml of the standard molybdenum solution (4.14) 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.

1 ml of this solution contains 5 µg of Mo.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Gilson separating funnel (spherical separating funnel), capacity 125 ml.

5.2 Spectrophotometer

or

5.3 Photometer, fitted with suitable filters, with a maximum transmission at 470 nm.

5.4 Cells, having an optical path length of 0,5, 1,0 and 2,0 cm.

6 SAMPLING

Sampling shall be carried out in accordance with ISO/R 377 or appropriate national standards for other types of steel and for cast iron.

7 PROCEDURE

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

NOTE — Measure all the reagents, without exception, using a pipette, preferably with one mark, in particular the *n*-butyl acetate (4.2) the volume of which is used for the calculation of the concentration of molybdenum.

7.1 Test portion

According to the presumed molybdenum content, weigh, to the nearest 0,001 g, the following masses (m) of sample, remaining within the tolerance of ± 10 % of the specified mass :

a) Mo contents less than 0,125 % : m about 1 g;

b) Mo contents from 0,125 to 2,5 % : m about 0,25 g, with the addition of 0,75 g of the iron (4.1);

c) Mo contents greater than 2,5 % : m about 0,3 g, with the addition of 1,7 g of the iron (4.1).

7.2 Determination

7.2.1 *Preparation of test solution*

Place the test portion (7.1) in a 250 ml conical flask and 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) in cases 7.1 a) and 7.1 b) or 100 ml of acid mixture II (4.8) in case 7.1 c).

Heat to gentle boiling and continue heating until dense white fumes are given off.

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

When acid mixture II is made up of sulphuric and phosphoric acids, heating shall be continued and the complete decomposition of the carbides achieved by the addition of nitric acid.

NOTE — The precipitated tungsten dissolves because of the presence of phosphoric acid.

Cool and transfer the solution quantitatively to a 100 ml one-mark volumetric flask in cases 7.1 a) and 7.1 b) or a 200 ml one-mark volumetric flask in case 7.1 c).

Dilute to the mark with water and mix. Solution A of volume V_2 is thus obtained.

If there is a residue or precipitate in solution A, 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 solution A to a 50 ml one-mark volumetric flask fitted with a ground stopper, add 10 ml of the hydrochloric acid (4.4), dilute to the mark with water and mix. Solution B is thus obtained.

7.2.2 *Preparation of the compensating solution*

Dissolve, in the appropriate volume of the acid mixtures, the same quantity of iron (4.1) as added to the test portion (0, 0,75 or 1,7 g) and proceed as indicated in 7.2.1 until a solution D is obtained, similar to the test solution B.

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

7.2.3 *Formation and extraction of the coloured compound*

NOTE — Measure all the reagents, without exception, using a pipette, preferably with one mark, in particular the *n*-butyl acetate (4.2) the volume of which is used for the calculation of the concentration of molybdenum.

7.2.3.1 TEST SOLUTION

Take an aliquot portion V_0 of solution B (7.2.1) equal to 25,0 ml if the molybdenum content is less than 1 %, or 10,0 ml if the molybdenum content is greater than or equal to 1 %, and transfer to a separating funnel (5.1).

If 10,0 ml of solution B has been taken, add 15 ml of compensating solution D (7.2.2).

In all cases, add in order :

- 5 ml of the copper solution (4.11),
- 10 ml of the hydrochloric acid (4.5), and
- 5 ml of the ascorbic acid solution (4.9).

Shake and wait for 3 min until the colour of the solution decreases in intensity. Add a volume V_1 of 25,0 ml of the *n*-butyl acetate (4.2) if the molybdenum content is less than or equal to 0,5 % or of 50,0 ml if it is greater, and mix by simple inversion.

Immediately add 5 ml of the 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. Add 10 ml of the 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.

The drops of water in suspension in the organic layer collect at the bottom of the flask and do not interfere with the measurement.

7.2.3.2 COMPENSATING SOLUTION

Take 25,0 ml of compensating solution D (7.2.2) and proceed in accordance with 7.2.3.1, beginning at "In all cases, add in order . . .".

7.2.4 *Photometric measurements*

Carry out the photometric measurements on the test solution (7.2.3.1), using the spectrophotometer (5.2) at a wavelength of about 470 nm or the photometer fitted with suitable filters (5.3), after having adjusted the instrument to zero absorbance against the compensating solution (7.2.3.2).

Generally, the following optical path lengths are used :

- for Mo contents less than 0,025 % : 2 cm;
- for Mo contents between 0,025 and 4 % : 1 cm;
- for Mo contents greater than 4 % : 0,5 cm.

NOTE — When the V/Mo ratio is greater than 16 and/or the W/Mo ratio is greater than 8, the measurements shall be carried out in a period not exceeding 30 min after the extraction.

7.3 Establishment of the calibration curve

7.3.1 *Preparation of the reference solutions*, related to photometric measurements carried out with cells having 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 the following table :

Reagent	Volumes, in millilitres, for reference number :					
	0	1	2	3	4	5
Iron solution (4.13)	10	10	10	10	10	10
Copper solution (4.11)	5	5	5	5	5	5
Standard molybdenum solution (4.15)	0	5,0	10,0	15,0	20,0	25,0
Hydrochloric acid (4.6)	25	20	15	10	5	0
Ascorbic acid solution (4.9)	5	5	5	5	5	5

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

Add to each funnel 25,0 ml of the *n*-butyl acetate (4.2) and mix by simple inversion. Continue in accordance with 7.2.3.1, beginning at "Immediately add 5 ml of the ammonium thiocyanate solution . . .".

Repeat this operation five times.

7.3.2 *Photometric measurements*

Carry out the photometric measurements on the reference solutions (7.3.1) in accordance with the indications given in 7.2.4, after having adjusted the instrument (5.2 or 5.3) to zero absorbance against the reference solution "0".

7.3.3 *Plotting of the calibration curve or calculation of the angular coefficient of the straight line*

From the means of the measured values of the absorbances and the masses, in micrograms, of Mo contained in the reference solutions, the calibration curve may be plotted or its angular coefficient (*a*) calculated.

8 EXPRESSION OF RESULTS

The molybdenum (Mo) content is given, as a percentage by mass, by the formula

$$\frac{D}{a \times d} \times V_1 \times \frac{50}{V_1} \times \frac{V_2}{20} \times \frac{1}{m} \times \frac{1}{10^4}$$

$$= \frac{D \times V_1 \times V_2}{a \times d \times V_0 \times m \times 4\,000}$$

where

D is the ratio of the absorbance of the test solution to that of its compensating solution;

a is the absorbance of an *n*-butyl acetate solution containing 1 µg of molybdenum complexed with thiocyanate per millilitre, measured with an optical path length of 1 cm (7.3.3);

d is the optical path length, in centimetres, used for the measurement (7.2.4);

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

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

V_2 is the volume, in millilitres, of solution A (7.2.1) used for the determination;

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

9 TEST REPORT

The test report shall include the following particulars :

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

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

c) any unusual features noted during the determination;

d) any operation not specified in this International Standard, or any optional operations which may have influenced the result.
