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Aluminium and its alloys — Determination of chromium — Spectrophotometric method using diphenylcarbazide

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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 2298 was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

It was approved in September 1971 by the Member Bodies of the following countries :

Austria	Ireland	Sweden
Belgium	Italy	Switzerland
Canada	Japan	Thailand
Egypt, Arab Rep. of	Korea, Rep. of	Turkey
Finland	Netherlands	United Kingdom
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The Member Body of the following country expressed disapproval of the document on technical grounds :

France

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Aluminium and its alloys — Determination of chromium — Spectrophotometric method using diphenylcarbazide

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a spectrophotometric method using diphenylcarbazide for the determination of chromium in aluminium and aluminium alloys. This method is applicable to the determination of chromium contents between 0.001 and 0.60 %.

The method is not applicable when the ratio vanadium/chromium is greater than 2.5.

2 PRINCIPLE

2.1 Dissolution of a test portion by a mixture of hydrochloric, nitric and sulphuric acids, evaporation to white H_2SO_4 fumes, taking up with water and possible filtration of the dehydrated silica and recovery of the chromium of the residue after removal of silica.

2.2 Precipitation of the copper by hydrogen sulphide and, after filtration, elimination of the excess of hydrogen sulphide by boiling.

2.3 On a suitable aliquot, oxidation of the chromium by ammonium persulphate in the presence of silver nitrate. Destruction of the excess of ammonium persulphate by boiling and of the permanganate ions formed by sodium nitrite.

2.4 Formation of a coloured complex between the Cr (VI) and the diphenylcarbazide, in the presence of phosphoric acid, and spectrophotometric determination of the complex at a wavelength of about 545 nm.

3 REAGENTS

During the analysis use only double-distilled water or water of equivalent purity.

3.1 Anhydrous potassium pyrosulphate ($K_2S_2O_7$).

3.2 Iron (II) sulphide, for the preparation of hydrogen sulphide.

3.3 High purity aluminium, containing no chromium.

The product shall be in the form of chips obtained by milling or drilling.

NOTE — Immediately before use, pickle the chips in a little nitric acid ($d = 1.40$), (solution approximately 60 % m/m). Wash the pickled chips with water and dry by washing with acetone.

3.4 Acid mixture

Add cautiously to 485 ml of water, while stirring and cooling, 115 ml of sulphuric acid ($d = 1.84$), 35.6 N approximately, 200 ml of hydrochloric acid ($d = 1.18$), solution 12 N approximately and 200 ml of nitric acid ($d = 1.40$), solution 15 N approximately.

3.5 Hydrofluoric acid ($d = 1.05$), approximately 40 % (m/m) solution.

3.6 Acid wash solution

Add 1 ml of sulphuric acid ($d = 1.84$), 35.6 N approximately, to 1 000 ml of water and saturate cold with hydrogen sulphide.

Prepare this solution immediately before use.

3.7 Phosphoric acid, free from reducing substances.

Add 500 ml of phosphoric acid ($d = 1.71$), 45 N approximately, to 500 ml of water. While the solution is still hot, add 0.1 N potassium permanganate solution (3.10), drop by drop, until the pink colouration persists for at least 10 min. Then boil the solution until the pink colour disappears.

3.8 Sulphuric acid ($d = 1.123$), approximately 4.1 N solution.

Add carefully 115 ml of sulphuric acid ($d = 1.84$), 35.6 N approximately, to 800 ml of water, while stirring and cooling. After cooling, make up the volume to 1 000 ml and mix.

3.9 Sulphuric acid, ($d = 1.482$), approximately 17.8 N solution.

Add 500 ml of sulphuric acid ($d = 1.84$), 35.6 N approximately, to 400 ml of water. After cooling, make up the volume to 1 000 ml and mix.

3.10 Potassium permanganate, approximately 0.1 N solution.

3.11 Potassium permanganate, approximately 0.02 N solution.

3.12 Silver nitrate, solution 0.17 g/l.

Dissolve 0.17 g of silver nitrate in water and make up the volume to 1 000 ml.

This solution shall be kept in a dark glass bottle.

3.13 Ammonium persulphate, solution 160 g/l.

Dissolve 16 g of ammonium persulphate $[(NH_4)_2S_2O_8]$ in water and make up the volume to 100 ml.

Prepare this solution immediately before use.

3.14 Sodium nitrite, solution 3.50 g/l.

Dissolve 0.35 g of sodium nitrite ($NaNO_2$) in water and make up the volume to 100 ml.

Prepare this solution immediately before use.

3.15 Diphenylcarbazide, solution in acetone, 5 g/l.

Dissolve 0.5 g of diphenylcarbazide having a melting point over 170 °C and a coefficient of molar absorbance[1] of the order of 4.24×10^4 (about 545 nm) in acetone and make up the volume to 100 ml.

The solution will not keep more than 3 to 4 h.

3.16 Base solution, of 4.000 g of aluminium per litre.

Weigh, to the nearest 0.001 g, 4.000 g of high purity aluminium (3.3), previously pickled, and place in a beaker of suitable capacity (1 000 ml for example) and add, in small portions, 180 ml of acid mixture (3.4). When the reaction is completed, add 20 ml of dilute sulphuric acid (3.9) and heat the solution until white H_2SO_4 fumes are liberated. After cooling, take up with water, heat to complete the dissolution of the salts, filter if necessary and transfer the solution quantitatively to a 1 000 ml volumetric flask. Make up to volume and mix.

1 ml of this solution contains 4 mg of aluminium.

3.17 Base solution of 2.000 g of aluminium per litre.

Weigh, to the nearest 0.001 g, 2.000 g of high purity aluminium (3.3), previously pickled, and place in a beaker of suitable capacity (600 ml for example) and add, in small portions, 134 ml of acid mixture (3.4). When the reaction is completed, add 10 ml of dilute sulphuric acid (3.9) and heat the solution until white H_2SO_4 fumes are liberated. After cooling, take up with water, heat to complete the dissolution of the salts, filter if necessary, and transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume and mix.

1 ml of this solution contains 2 mg of aluminium.

3.18 Chromium standard solution, 0.200 g of chromium per litre.

Weigh, to the nearest 0.1 mg, 0.565 7 g of potassium dichromate ($K_2Cr_2O_7$), of high purity, previously dried at 140° and cooled in a desiccator. Dissolve with a little water, transfer to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0.2 mg of chromium.

3.19 Chromium standard solution, 0.010 g of chromium per litre

Transfer 50.0 ml of standard chromium solution (3.18) to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0.010 mg of chromium.

3.20 Chromium standard solution, 0.001 g of chromium per litre.

Transfer 25.0 ml of standard chromium solution (3.19) to a 250 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 1 μg of chromium.

Prepare this solution immediately before use.

4 APPARATUS

4.1 Ordinary laboratory apparatus.

NOTE — If the glassware has been washed with the sulpho-chromic mixture, care must be taken to rinse it well before use in order to ensure that every trace of chromium is removed.

4.2 Spectrophotometer.

5 SAMPLING

5.1 Laboratory sample [2]

5.2 Test sample

Chips of thickness less than or equal to 1 mm, obtained by drilling or milling.

1) The coefficient of molar absorbance is given by the ratio of optical density at about 545 nm (optical path = 1 cm) to the concentration of chromium, expressed in gram atoms per litre of solution.

2) The International Standard relating to sampling from supplies will be studied as soon as Technical Committee ISO/TC 69, *Application of statistical methods,* has specified the general principles to be followed.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0.001 g, 1 g of the test sample (5.2).

6.2 Blank test

In parallel with the analysis, carry out a blank test, using 1 g of high purity aluminium (3.3), weighed to the nearest 0.001 g, and the same quantities of all the reagents used for the analysis, following the same procedure.

NOTE – As the interference of aluminium on the colour of the chromium diphenylcarbazide complex for low chromium contents is almost negligible, the blank test can be carried out in the absence of aluminium. In this case, transfer 25 ml of acid mixture (3.4) to a beaker of suitable capacity (250 ml for example), bring to dryness cautiously and heat until the sulphuric acid is completely eliminated. After cooling, take up with a little hot water and add 20 ml of acid mixture (3.4) and 5 ml of sulphuric acid (3.9). Cover the beaker with a watch glass and continue heating until white H_2SO_4 fumes are liberated. Allow to cool and then proceed according to the method described for the test solution (starting at the 7th line of 6.3.1).

6.3 Determination

6.3.1 *Preparation of the test solution*

Place the test portion (6.1) in a beaker of suitable capacity (250 ml for example) and cover it with a watch glass.

Add 45 ml of acid mixture (3.4) in small portions to the beaker; when the reaction subsides, warm gently to aid the attack. When the attack is complete, add 5 ml of sulphuric acid (3.9), cover the beaker and continue heating until white H_2SO_4 fumes are liberated. Allow to cool, take up with about 150 ml of hot water and heat the solution to complete the dissolution of the salts.

If there is separation of silica, filter through a close-textured filter and wash the silica with hot water, collecting the filtrate and washings in a beaker of suitable capacity (250 ml for example). Place the filter and its contents in a platinum crucible, dry and ignite the filter cautiously, then heat at about 1 000 °C for 20 min. After cooling, add to the crucible 1 ml of sulphuric acid solution (3.9), about 4 ml of hydrofluoric acid solution (3.5) and then nitric acid, drop by drop, until the solution becomes clear. Heat cautiously until white H_2SO_4 fumes are released. Then ignite the crucible to dryness. If a considerable residue is left in the crucible, fuse it with 1 to 2 g of potassium pyrosulphate (3.1), take up the mass with a little hot water and add this solution to the test solution.

Heat the test solution to boiling and concentrate it to a volume of approximately 100 ml, then pass a rapid stream of hydrogen sulphide [obtained from iron sulphide (3.2)] through the hot solution for about 20 min. Turn off the flow of hydrogen sulphide and boil for 1 min in order to aid coagulation of the precipitate. Then filter the solution through a close-textured filter and wash the precipitate with the acid wash solution (3.6), collecting the filtrate and washings in a beaker of suitable capacity (250 ml for example). Discard the filter and the precipitate. Boil the solution to remove hydrogen sulphide, then transfer it to a 500 ml volumetric flask. Make up to volume and mix.

NOTE – If the Cu content of the sample is less than 0.01 % and the sample contains no bismuth, tin, cadmium, etc., the treatment with hydrogen sulphide need not be carried out.

6.3.2 *Taking of the aliquot*

According to the presumed chromium content, take the aliquot indicated in the table below.

Place the aliquot in a beaker of suitable capacity (250 ml for example) and add the quantity of sulphuric acid (3.8) indicated in the table.

6.3.3 *Development of the colour*

Add to the beaker 1 ml of phosphoric acid solution (3.7), 1 ml of silver nitrate solution (3.12), 5 ml of ammonium persulphate solution (3.13) and, if necessary, bring the volume of the solution to about 100 ml with water. Cover the beaker with a watch glass and heat the solution to boiling. If, after 1 min of boiling, the colouration of permanganic acid does not appear, add 5 drops of potassium permanganate solution (3.11); the solution should then become pale pink. Boil the solution for 30 min, allowing it to become concentrated to a volume of about 35 ml (do not allow it to fall below 35 ml). Remove the beaker from the source of heat and rinse the walls of the beaker and the watch glass with hot water. By means of a fine pointed pipette, immediately add sodium nitrite solution (3.14), cautiously, drop by drop, until the pink colouration of permanganic acid disappears.

Presumed chromium content	Volume of aliquot to take	Mass corresponding to test sample	Volume of sulphuric acid (3.8) to add
%	ml	g	ml
from 0.001 to 0.02	100.0	0.2	0
from 0.02 to 0.10	25.0	0.05	1
from 0.10 to 0.60	5.0	0.01	2

When the pink colouration becomes weak, wait 1 min between the addition of successive drops. Do not add a single drop of sodium nitrite solution in excess. (In order to ensure that no excess sodium nitrite remains, 0.50 to 1 g of urea may be added.)

Allow to cool, add 4 ml of phosphoric acid solution (3.7), transfer the solution quantitatively to a 100 ml volumetric flask and make up the volume to about 90 ml. Add 5 ml of diphenylcarbazide solution (3.15), make up to volume and mix.

NOTE – It is advisable to carry out all the operations from oxidation of the chromium to the development of colour consecutively, without interruption.

6.3.4 *Spectrophotometric measurements*

In the 30 min following the addition of the diphenylcarbazide solution, carry out the spectrophotometric measurement of the test solution and the blank test solution at a wavelength of about 545 nm, after having adjusted the spectrophotometer (5.2) to zero optical density against water. Choose the optical path appropriate to the instrument used.

6.4 Establishment of the calibration curve

6.4.1 *Preparation of the standard solutions*

6.4.1.1 Chromium contents between 0.001 and 0.02 %

Transfer to a series of eight beakers of suitable capacity (250 ml for example), each already containing 50.0 ml of the base solution (3.16) – corresponding to 0.2 g of aluminium – the quantities of standard chromium solution (3.20) indicated in the following table :

Standard chromium solution (3.20)	Corresponding mass of chromium
ml	µg
0[1)]	0
2.0	2
6.0	6
10.0	10
20.0	20
30.0	30
40.0	40
50.0	50

1) Compensating solution

6.4.1.2 Chromium contents between 0.02 and 0.60 %

Transfer to a series of eight beakers of suitable capacity (250 ml for example), each already containing 25.0 ml of the base solution (3.17) – corresponding to 0.05 g of aluminium – the quantities of standard chromium solution (3.20) indicated in the following table :

Standard chromium solution (3.20)	Corresponding mass of chromium
ml	µg
0[1)]	0
5.0	5
10.0	10
20.0	20
30.0	30
40.0	40
50.0	50
70.0	70

1) Compensating solution

Then proceed with the colour development, following, for each solution, the methods described in 6.3.3.

6.4.2 *Spectrophotometric measurements*

In the 30 min following the addition of the diphenylcarbazide solution, carry out the spectrophotometric measurements on the standard solutions 6.4.1.1 and 6.4.1.2 at a wavelength of about 545 nm, after having adjusted the spectrophotometer (5.2) to zero optical density against water. Choose the optical path appropriate to the instrument used.

Deduct the value for the chromium-free solution (compensating solution) from the readings for the solutions to which chromium has been added.

6.4.3 *Plotting of the calibration curves*

Prepare two graphs – one in the presence of 0.20 g of aluminium (6.4.1.1) and the other in the presence of 0.05 g of aluminium (6.4.1.2) – placing, for example, on the abscissa the values, expressed in micrograms, of the quantities of chromium contained in 100 ml of standard solution, and on the ordinate the corresponding values of the optical density.

7 EXPRESSION OF RESULTS

By means of the appropriate calibration curve (see 6.4.3), determine the quantity of chromium corresponding to the values of the optical densities measured.

The chromium content (Cr) is given, as a percentage by mass, by the formula :

$$\frac{(m_1 - m_2) \times D}{m_0} \times 100$$