



Aluminium and aluminium alloys — Determination of chromium — Spectrophotometric method using diphenylcarbazide, after extraction

Aluminium et alliages d'aluminium — Dosage du chrome — Méthode spectrophotométrique à la diphénylcarbazide, après extraction

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FOREWORD

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International Standard ISO 3978 was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys*, and was circulated to the Member Bodies in November 1975.

It has been approved by the Member Bodies of the following countries :

Australia	India	Spain
Belgium	Italy	Turkey
Czechoslovakia	Japan	U.S.A.
Egypt, Arab Rep. of	Mexico	U.S.S.R.
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The Member Bodies of the following countries expressed disapproval of the document on technical grounds :

Switzerland
United Kingdom

Aluminium and aluminium alloys – Determination of chromium – Spectrophotometric method using diphenylcarbazide, after extraction

1 SCOPE

This International Standard specifies a spectrophotometric method using diphenylcarbazide, after extraction, for the determination of chromium in aluminium and aluminium alloys.

2 FIELD OF APPLICATION

This method is applicable to chromium contents between 0,002 and 0,60 % (m/m) of chromium (Cr).¹⁾

3 PRINCIPLE

Dissolution of a test portion by a mixture of hydrochloric, nitric and sulphuric acids and evaporation to white SO_3 fumes. Taking up with water, filtration, if necessary, of the dehydrated silica and recovery of the chromium from the residue, after removal of the silica.

Oxidization of the Cr(III) to Cr(VI) by ammonium hexanitrocerate and extraction of the Cr with isobutylmethylketone. Passage of the Cr into an aqueous solution and formation of a coloured complex between the Cr(VI) and the diphenylcarbazide.

Spectrophotometric measurement of the coloured complex at a wavelength of about 545 nm.

4 REAGENTS

Throughout the analysis use only reagents of analytical grade and only distilled water or water of equivalent purity.

4.1 Nitric acid, ρ about 1,40 g/ml, solution about 15 N.

4.2 Sulphuric acid, ρ about 1,83 g/ml, solution about 36 N.

4.3 Sulphuric acid, ρ about 1,23 g/ml, solution about 8 N.

4.4 Hydrofluoric acid, ρ about 1,13 g/ml, 40 % (m/m) solution or about 23 N.

4.5 Hydrochloric acid, ρ about 1,1 g/ml, 20 % (m/m) solution or about 6 N.

NOTE — During the analysis use this solution at a temperature of 5 or 10 °C. Store the solution in a refrigerator and, during the analysis, in an ice bath.

4.6 Hydrochloric acid, ρ about 1,01 g/ml, 1,81 % (m/m) solution or about 0,5 N.

Dilute 84 ml of the hydrochloric acid solution (4.5) to 1 000 ml.

NOTE — Use this reagent cold, like the preceding reagent (4.5).

4.7 Acide mixture

Mix, in a convenient sized receptacle, 200 ml of hydrochloric acid, ρ about 1,19 g/ml, solution about 12 N, 200 ml of the nitric acid solution (4.1) and 400 ml of water. Add cautiously, while shaking and cooling, 120 ml of the sulphuric acid solution (4.2). After cooling, make up the volume to 1 000 ml.

Store the mixture in a receptacle made of dark glass.

4.8 Ammonium hexanitrocerate, solution 0,04 N in Ce and 2 N in H_2SO_4 .

Dissolve 2,19 g of ammonium hexanitrocerate $((\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6])$ in a little water and add 25 ml of the sulphuric acid solution (4.3). Transfer the solution quantitatively to a 100 ml volumetric flask, make up to volume and mix.

4.9 Isobutylmethylketone, purified.

To a separating funnel of convenient size (for example 1 000 ml), transfer 250 ml of isobutylmethylketone $[\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2]$ previously cooled to 5 to 10 °C, and add 250 ml of the hydrochloric acid solution (4.6) cooled to the same temperature. Shake vigorously for 1 min; then allow the two phases to separate. Run off the acid phase and discard it. Collect the isobutylmethylketone in a suitable receptacle.

NOTE — The reagent should be used cold.

1) This method may be extended to chromium contents of up to 1,5 % (m/m).

4.10 Diphenylcarbazide, 10 g/l solution in acetone.

Dissolve 0,25 g of diphenylcarbazide, having a melting point over 170 °C, in a little acetone, transfer quantitatively to a 25 ml volumetric flask, cool to 5 to 10 °C and make up to volume with the same acetone.

Prepare this solution immediately before use.

4.11 Nickel chloride, 200 g/l solution in hydrochloric acid.

Dissolve 20 g of nickel chloride hexahydrate in a little water, add 60 ml of hydrochloric acid, ρ about 1,19 g/ml, solution about 12 N, and make up the volume to 100 ml with water.

4.12 Aluminium base solution, 20 g/l.

Weigh, to the nearest 0,001 g, 20 g of high purity aluminium (titre not less than 99,99 %, free from chromium) and transfer to a beaker of suitable capacity (for example 1 000 ml). Add 1 ml of the nickel chloride solution (4.11) and, in small portions, 200 ml of hydrochloric acid, ρ about 1,19 g/ml, solution about 12 N, diluting if necessary with water. When the reaction is complete, add 200 ml of the nitric acid solution (4.1), cool, then add 120 ml of the sulphuric acid solution (4.2). Heat the solution cautiously until white SO_3 fumes are liberated and continue heating for 10 min. Allow to cool, take up with water and heat until a clear solution is obtained. Transfer the solution quantitatively to a 1 000 ml volumetric flask and, after cooling, make up to volume and mix.

NOTE — If necessary, filter the solution through a medium textured filter, before transferring it to the volumetric flask. In this case, collect the washings quantitatively in the volumetric flask.

4.13 Chromium, standard solution corresponding to 0,020 g of Cr per litre.

Weigh, to the nearest 0,000 1 g, 0,565 7 g of high purity potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), previously dried at 140 °C and cooled in a desiccator. Place in a beaker of convenient size (for example 400 ml) and dissolve in about 100 ml of water. Add 10 ml of hydrochloric acid, ρ 1,19 g/ml, solution about 12 N, and 25 ml of 95 % (V/V) ethanol. Heat to boiling and concentrate the solution to 10 to 20 ml. Then add 10 ml of the sulphuric acid solution (4.2) and 5 ml of the nitric acid solution (4.1). Heat the solution until white SO_3 fumes are given off and continue heating for 10 min. Cool, take up with water and heat until a clear solution is obtained. Transfer the solution quantitatively to a 1 000 ml volumetric flask and, after cooling, make up to volume and mix.

Transfer 50,0 ml of the solution thus obtained to a 500 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,020 mg of Cr.

4.14 Chromium, standard solution corresponding to 0,002 g of Cr per litre.

Transfer 50,0 ml of the standard chromium solution (4.13) to a 500 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 2 μg of Cr.

Prepare this solution immediately before use.

5 APPARATUS

Usual laboratory equipment and

5.1 Spectrophotometer.

NOTES

- 1 The use of separating funnels fitted with PTFE taps is essential.
- 2 If the glass apparatus has been washed with sulpho-chromic mixture, care should be taken to rinse it well before use, in order to ensure that every trace of chromium is removed.

6 SAMPLING

6.1 Laboratory sample¹⁾

6.2 Test sample

Chips 1 mm thick or less shall be obtained by milling or drilling.

7 PROCEDURE

7.1 Test portion

Weigh, to the nearest 0,001 g, 1 g of the test sample (6.2).

7.2 Blank test

In parallel with the analysis, carry out a blank test using a 10,0 ml aliquot of the aluminium solution (4.12). Place this aliquot in a 30 ml graduated tube. Dilute to about 20 ml with water, add 2,0 ml of the ammonium hexanitrocerate solution (4.8) and then proceed according to the method described in the second paragraph of 7.3.2 and in 7.3.3 to 7.3.6, using the same amounts of all the reagents as used for the analysis.

1) The sampling of aluminium and aluminium alloys will form the subject of a future International Standard.

7.3 Determination

7.3.1 Preparation of the test solution

Transfer the test portion (7.1) to a beaker of suitable capacity (for example 250 ml) and cover it with a watch glass. Add to the beaker, in small portions, 50 ml of the acid mixture (4.7).

NOTE — If the determination is to be carried out on alloys prepared from extra pure aluminium, add a few drops of the nickel chloride solution (4.11) before adding the acid mixture.

Once the reaction is complete, wash the walls of the beaker and the watch glass with a little water, collecting the washings in the beaker. Heat the beaker until white SO_3 fumes are liberated and continue heating for about 10 min.

Allow to cool, take up with 40 to 60 ml of water and heat the solution to complete the dissolution of the salts. If silica has separated, filter through a close textured filter, washing the silica with warm water and collecting the filtrate and the washings in a volumetric flask of convenient size, according to the quantity of Cr to be determined (see table 1). Place the filter and its contents in a platinum crucible, cautiously dry and ignite the filter, then heat at about 1 000 °C for 20 min.

After cooling, add to the crucible 2 drops of the sulphuric acid solution (4.2), 1 ml of the nitric acid solution (4.1), and a few millilitres of the hydrofluoric acid solution (4.4) and heat cautiously until white SO_3 fumes are liberated. Then heat the crucible just to dryness, allow to cool, take up the residue with a little water, heat, if necessary, to complete the dissolution and add this solution to the volumetric flask.

The final volume of the test solution, the aliquot to be taken for the determination as well as the volume of the aluminium solution to be added, are given in table 1.

TABLE 1

Expected Cr content	Final volume of the test solution (7.3.1)	Aliquot to be taken for the determination	Volume of aluminium solution (4.12) to be added
% (m/m)	ml	ml	ml
from 0,002 to 0,05	100,0	20,0	0
from 0,03 to 0,3	250,0	10,0	8,0
from 0,2 to 1,5	1 000,0	10,0	9,5

7.3.2 Oxidation of Cr(III) to Cr(VI)

Introduce the aliquot and the appropriate quantity of the aluminium solution (4.12) into a 30 ml graduated tube. Add 2,0 ml of the ammonium hexanitrocerate solution (4.8) and mix the liquids with a glass rod ending in a ring (perpendicular to the rod, diameter of the ring slightly less than the diameter of the tube).

Remove and rinse the rod, as well as the walls of the tube, with a small jet of water, collecting the washings in the tube until a volume of 30 ml is obtained.

Introduce the tube into a boiling water bath for 25 min. Remove the tube, cool it first under a jet of cold water and then in a bath of ice until a temperature of 5 to 10 °C is attained.

NOTE — Use the same bath of ice to store the hydrochloric acids (4.5) and (4.6), isobutylmethylketone (4.9) and diphenylcarbazine solution (4.10).

7.3.3 Extraction of Cr(VI)

Transfer the solution quantitatively to a 100 ml separating funnel having a reference mark at 45 ml. Wash the tube with a little water and collect the washings in the same funnel until a volume of 45 ml is obtained. Introduce into the funnel 4,5 ml of the cooled hydrochloric acid solution (4.5), mix, add 25 ml of the cold isobutylmethylketone (4.9) and shake for 1 min. Allow the two phases to separate, then run off the acid phase and place it in another 100 ml separating funnel. Add to this funnel 25 ml of cold isobutylmethylketone and shake for 1 min. Allow the two phases to separate, run off the acid phase and discard it. Transfer the organic phase from the second funnel quantitatively into the first, allow the last drops of the acid phase to separate, run them off and discard them. Add to the organic phase 25 ml of the cold hydrochloric acid solution (4.6), shake for 5 s, allow the two phases to separate, run off the acid phase and discard it.

7.3.4 Passing of Cr(VI) into aqueous solution

Extract the Cr(VI) present in the organic phase three consecutive times, each time using 25 ml of water and shaking for 30 s. Each time run off the aqueous phase, collecting it in a 100 ml volumetric flask.

7.3.5 Development of the colour

Add to the flask 2,5 ml of the sulphuric acid solution (4.3), mix and add 2,0 ml of the cold diphenylcarbazine solution (4.10). Make up to volume and mix.

7.3.6 Spectrophotometric measurements

After 10 min and, in any case, before 60 min have elapsed, carry out the spectrophotometric measurements of the test solution and the blank test solution, at a wavelength of about 545 nm, after adjusting the spectrophotometer (5.1) to zero absorbance against water.

Use appropriate optical path lengths according to the characteristics of the apparatus used for the measurements.

7.4 Establishment of the calibration curve

7.4.1 Preparation of the reference solutions

To a series of eight 30 ml graduated tubes, in which has already been placed 10,0 ml of the aluminium solution

(4.12), add the quantities of the standard chromium solution (4.14) or (4.13) indicated in table 2.

TABLE 2

Volume of standard Cr solution (4.14)	Corresponding mass of Cr
ml	µg
0*	0
2,0	4
5,0	10
10,0	20
Volume of standard Cr solution (4.13)	
ml	
2,0	40
4,0	80
6,0	120
8,0	160

* Blank test of the reagents used for the calibration curve.

For each reference solution, carry out the oxidation of the chromium and the other successive operations at intervals of about 20 min, so that the spectrophotometric measurements may be carried out between 10 and 60 min after the addition of the diphenylcarbazide solution (4.10).

At the specified rate, add to each tube 2,0 ml of the ammonium hexanitrocerate solution (4.8), then proceed according to the method described in the second and following paragraphs of 7.3.2 and in 7.3.3 to 7.3.6.

7.4.2 Plotting of the calibration curve

Deduct the measurement of the solution free from chromium (zero term) from the readings of the solutions to which chromium has been added.

Plot a graph with, for example, on the abscissa the values expressed in micrograms of the quantities of chromium

contained in 100 ml of the reference solution and on the ordinate the corresponding absorbance values.

NOTE — When renewing the diphenylcarbazide, even if it comes from the same producer, it is advisable to establish the molar index of absorbance, by checking one or more points on the calibration curve.

8 EXPRESSION OF RESULTS

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

$$\frac{(A_1 - A_2) \times f \times 100 \times 100 \times D}{1\,000\,000\,m}$$

where

A_1 is the unitary absorbance of the aliquot of the test solution;

A_2 is the unitary absorbance of the corresponding aliquot of the blank test solution;

f is a factor evaluated from the calibration curve (relationship between the concentration of Cr and the corresponding absorbance);

D is the ratio of the volume of the test solution to the volume of the aliquot taken for the colour reaction;

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

9 TEST REPORT

The test report shall include the following information :

- the reference of the method used;
- the results, as well as the form in which they are expressed;
- any particular details noted during the test;
- any operation not specified in this International Standard or any optional operations.