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International Standard



4193

G-01-01

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## Aluminium and aluminium alloys — Determination of chromium content — Flame atomic absorption spectrometric method

*Aluminium et alliages d'aluminium — Dosage du chrome — Méthode par spectrométrie d'absorption atomique dans la flamme*

First edition — 1981-12-01

UDC 669.71 : 543.422 : 546.76

Ref. No. ISO 4193-1981 (E)

Descriptors : aluminium, aluminium alloys, chemical analysis, determination of content, chromium, atomic absorption spectroscopic method.

## Foreword

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International Standard ISO 4193 was developed by Technical Committee ISO/TC 79, *Light metals and their alloys*, and was circulated to the member bodies in December 1980.

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

Australia	Germany, F. R.	Romania
Austria	Hungary	South Africa, Rep. of
Brazil	India	Spain
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China	Japan	Switzerland
Czechoslovakia	Korea, Rep. of	United Kingdom
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The member body of the following country expressed disapproval of the document on technical grounds :

Netherlands

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# Aluminium and aluminium alloys — Determination of chromium content — Flame atomic absorption spectrometric method

## 1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the chromium content of aluminium and its alloys.

The method is applicable to products having chromium (Cr) contents between 0,003 and 0,6 % (*m/m*).<sup>1)</sup>

## 2 Principle

Dissolution of a test portion in hydrochloric acid and hydrogen peroxide. Aspiration of the solution into an air-acetylene or, preferably, dinitrogen oxide acetylene flame, and comparison of the absorbance of resonance energy of chromium by the test solution (wavelength of 357,9 nm normally) with that of standard solutions.

## 3 Reagents

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

**3.1 Aluminium**, extra pure (purity 99,99 %), free from chromium.

**3.2 Hydrochloric acid**,  $\rho$  approximately 1,1 g/ml, about 20 % (*m/m*) or approximately 6 mol/l solution.

Dilute 500 ml of hydrochloric acid,  $\rho$  approximately 1,19 g/ml, about 38 % (*m/m*) or approximately 12 mol/l solution, with 500 ml of water.

**3.3 Hydrogen peroxide**, about 30 % (*m/m*) solution.

**3.4 Sulphuric acid**,  $\rho$  approximately 1,48 g/ml, about 58 % (*m/m*) or approximately 9 mol/l solution.

While stirring and cooling, add 50 ml of sulphuric acid,  $\rho$  approximately 1,84 g/ml, about 96 % (*m/m*) or approximately 18 mol/l solution, to 40 ml of water. Again cool, dilute to the mark in a 100 ml volumetric flask, and mix.

**3.5 Hydrofluoric acid**,  $\rho$  approximately 1,13 g/ml, about 40 % (*m/m*) solution.

**3.6 Nitric acid**,  $\rho$  approximately 1,4 g/ml, about 68 % (*m/m*) or approximately 15 mol/l solution.

**3.7 Aluminium**, 20 g/l solution.

Weigh, to the nearest 0,01 g, 20 g of previously pickled, extra pure aluminium (3.1), place it in a 1 000 ml beaker and cover with a watch glass. Add, in small portions, 600 ml of the hydrochloric acid solution (3.2) and, if necessary, a drop of metallic mercury to assist the attack. If necessary, warm gently to aid the dissolution, and then add a few drops of the hydrogen peroxide solution (3.3). After cooling, quantitatively transfer the solution thus obtained to a 1 000 ml volumetric flask, dilute to the mark and mix.

**3.8 Chromium**, standard solution corresponding to 0,5 g of Cr per litre.

Weigh, to the nearest 0,001 g, 1,414 g of extra pure potassium dichromate (>99,9 %  $K_2Cr_2O_7$ ), previously dried at 140 °C, and transfer it to a 400 ml tall-form beaker. Dissolve in 20 ml of water and 10 ml of the hydrochloric acid solution (3.2). Add, drop by drop, 10 ml of the hydrogen peroxide solution (3.3) and allow the solution to stand at room temperature until the yellow colour has completely disappeared (up to a half or a whole day, for instance) indicating that the chromium has been totally reduced to the trivalent state. Heat gently, without boiling, in order to decompose the remaining hydrogen peroxide. Transfer the solution to a 1 000 ml volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 0,5 mg of chromium.

**3.9 Chromium**, standard solution corresponding to 0,025 g of Cr per litre.

Transfer 25,0 ml of the standard chromium solution (3.8) to a 500 ml volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 0,025 mg of chromium.

1) The method may also be used for higher chromium contents [up to 1,5 % (*m/m*) for instance].

**3.10 Lanthanum chloride solution.<sup>1)</sup>**

Dissolve 100 g of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) in 200 ml of hydrochloric acid,  $\rho$  approximately 1,19 g/ml, about 38 % (m/m) solution. Quantitatively transfer the solution to a 1 000 ml volumetric flask, dilute to the mark and mix.

**4 Apparatus**

Normal laboratory apparatus and :

**4.1 Burette**, graduated in 0,05 ml.

**4.2 Atomic absorption spectrometer**, fitted with a compressed air-acetylene or dinitrogen oxide acetylene burner.

**4.3 Compressed air** (laboratory installation or gas cylinders).

**4.4 Dinitrogen oxide.**

**4.5 Acetylene.**

**4.6 Chromium hollow-cathode lamp.**

**5 Sampling****5.1 Laboratory sample<sup>2)</sup>****5.2 Test sample**

Use chips, not more than 1 mm thick, obtained by milling or drilling.

**6 Procedure****6.1 Test portion**

Weigh, to the nearest 0,001 g, 1 g of the test sample (5.2).

**6.2 Preparation of the calibration curve****6.2.1 Preparation of the standard solutions**

Into a series of nine 100 ml volumetric flasks, introduce the volumes of standard chromium solutions (3.9 and 3.8) shown in the table, using the burette (4.1). Add to each flask, 50 ml of aluminium solution (3.7) and, if an air-acetylene flame is used and if the operator considers this necessary, add 5 ml of the lanthanum chloride solution (3.10). Dilute to the mark and mix.

**6.2.2 Spectrometric measurements**

Switch on the spectrometer (4.2), fitted with the chromium hollow-cathode lamp (4.5), sufficiently in advance to allow it to stabilize. Adjust the wavelength to about 357,9 nm, and the sensitivity and the slot according to the characteristics of the apparatus. Adjust the pressures of the air and acetylene, or of the nitrous oxide and acetylene, according to the characteristics of the aspirator-burner.

Table

Standard chromium solution (3.9)	Corresponding mass of chromium	Corresponding chromium content (%) for test portions of	
		1 g/100 ml	0,1 g/100 ml
ml	mg		
0*	0	0	0
1,0	0,025	0,002 5	
2,0	0,05	0,005	
4,0	0,10	0,010	
8,0	0,20	0,020	0,20
20,0	0,50	0,050	0,50
Standard chromium solution (3.8)			
ml			
2,0	1,0	0,10	1,0
3,0	1,5	0,15	1,5
4,0	2,0	0,20	2,0

\* Blank test of the calibration curve reagents.

1) The use of this solution is optional. Usually, its addition is not indispensable to eliminate the influence of aluminium on chromium, in the presence of an air-acetylene flame.

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

Aspirate the standard solutions (6.2.1) into the flame and measure their absorbances. Take care to ensure that the volume of standard solutions aspirated per unit time into the flame is kept constant throughout the procedure for preparation of the calibration curve.

#### NOTES

- 1 Aspirate water into the burner after each measurement.
- 2 If necessary, appropriately amplify the signal of the spectrometer for the first five readings for example.

### 6.2.3 Plotting the graph

Plot a graph, having, for example, the masses, in milligrams, of chromium contained in 100 ml of the standard solutions as abscissae, and the corresponding values of absorbance, corrected for the blank test of the calibration curve reagents (zero term), as ordinates.

## 6.3 Determination

### 6.3.1 Preparation of the test solution

Transfer the test portion (6.1) to a 250 ml beaker and cover with a watch glass. Add about 30 to 40 ml of water, then, in small portions, 30 ml of the hydrochloric acid solution (3.2), warming gently, if necessary, to complete the dissolution. Add a few drops of the hydrogen peroxide solution (3.3) and heat for about 10 min to remove the excess hydrogen peroxide.

If undissolved matter remains, indicating the presence of silicon, filter the solution, transfer the filter paper and undissolved matter to a platinum crucible and incinerate, taking care that it does not inflame. Calcine at about 550 °C. After cooling, add 2 ml of the sulphuric acid solution (3.4), 5 ml of the hydrofluoric acid solution (3.5) and, drop by drop, the nitric acid solution (3.6) in such a manner as to obtain a clear solution (about 1 ml). Evaporate to dryness and calcine again, at about 700 °C, for a few minutes, to completely volatilize the silicon. After cooling, bring the non-volatile matter into solution with the least possible quantity of the hydrochloric acid solution (3.2), filter, if necessary, and quantitatively add this filtrate to that already obtained.

#### 6.3.1.1 Chromium contents between 0,003 and 0,20 % (m/m)

Quantitatively transfer the solution (6.3.1) to a 100 ml volumetric flask, add, if an air-acetylene flame is used and if the operator considers this necessary, 5 ml of the lanthanum chloride solution (3.10), dilute to the mark and mix.

#### 6.3.1.2 Chromium contents greater than 0,20 % (m/m)

Quantitatively transfer the solution (6.3.1) to a 100 ml volumetric flask, dilute to the mark and mix. Transfer 10,0 ml of this solution to another 100 ml volumetric flask and add 45 ml of the aluminium solution (3.7). Finally, if an air-acetylene flame is used and if the operator considers this necessary, also add 5 ml of the lanthanum chloride solution (3.10), dilute to the mark and mix.

### 6.3.2 Blank test

Carry out a blank test, in parallel with the analysis, using the same procedure and the same quantities of all reagents used in the determination, but replacing the test portion (6.1) by 1 g, weighed to the nearest 0,001 g, of the extra pure aluminium (3.1).

### 6.3.3 Spectrometric measurements

Measure the absorbances of the test solution (6.3.1.1 or 6.3.1.2), the blank test solution (6.3.2), and the standard solutions (6.2.1), proceeding as specified in 6.2.2, and taking care to bracket the measurement of the absorbance of the test solution and of the blank test solution between two standard solutions having chromium contents as close as possible, respectively, to that to be determined.

## 7 Expression of results

By means of the calibration curve, determine the quantity of chromium corresponding to the spectrometric measurements of the test solution and of the blank test solution.

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

$$\frac{(m_1 - m_2) \times R}{10 \times m_0}$$

where

$m_0$  is the mass, in grams, of the test portion (i.e. 1 g);

$m_1$  is the mass, in milligrams, of chromium found in the test solution (total or aliquot);

$m_2$  is the mass, in milligrams, of chromium found in the blank test solution;

$R$  is the ratio between the dilution-volume of the test solution and the volume of the standard solutions for calibration ( $R = 1$  for test solutions prepared in accordance with 6.3.1.1, and  $R = 10$  for test solutions prepared in accordance with 6.3.1.2).

## 8 Test report

The test report shall include the following information :

- a) identification of the test sample;
- b) the reference of the method used;
- c) the results and the method of expression used;
- d) any unusual features noted during the determination;
- e) any operations not included in this International Standard, or regarded as optional.