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## **Aluminium and aluminium alloys — Determination of titanium — Spectrophotometric chromotropic acid method**

*Aluminium et alliages d'aluminium — Dosage du titane — Méthode spectrophotométrique à l'acide chromotropique*

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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 1118 was developed by Technical Committee ISO/TC 79, *Light metals and their alloys*.

It was submitted directly to the ISO Council, in accordance with clause 6.13.1 of the Directives for the technical work of ISO. It cancels and replaces ISO Recommendation R 1118-1969, which had been approved by the member bodies of the following countries :

Belgium	Iran	South Africa, Rep. of
Canada	Israel	Spain
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Czechoslovakia	Japan	Switzerland
Egypt, Arab Rep. of	Korea, Rep. of	Thailand
France	Netherlands	Turkey
Germany, F.R.	New Zealand	United Kingdom
Hungary	Norway	U.S.A.
India	Poland	U.S.S.R.

No member body had expressed disapproval of the document.

# Aluminium and aluminium alloys – Determination of titanium – Spectrophotometric chromotropic acid method

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a general method for the spectrophotometric determination of titanium in aluminium and aluminium alloys.

The method is applicable to products having titanium contents between 0,005 and 0,3 % (*m/m*).

However, the method is not applicable completely to alloys having silicon contents greater than 1 % (*m/m*), for which it must be modified as indicated in the annex.

## 2 PRINCIPLE

Attack of a test portion with sodium hydroxide, and acidification of the alkaline solution with nitric acid and sulphuric acid.

Reduction of the iron(III) with ascorbic acid, and formation of the titanium-chromotropic acid complex at a chosen pH value between 2 and 2,50, controlled to within  $\pm 0,05$  pH unit.

Spectrophotometric measurement of the coloured complex at a wavelength of about 470 nm.

## 3 REAGENTS

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

**3.1 Sodium hydroxide**, 200 g/l or approximately 5 N solution.

In a nickel dish, dissolve 200 g of sodium hydroxide in water. After cooling, make up the volume to 1 000 ml and mix. Immediately transfer the solution to a plastic container.

**3.2 Sodium hydroxide**, 80 g/l or approximately 2 N solution.

In a nickel dish, dissolve 80 g of sodium hydroxide in water. After cooling, make up the volume to 1 000 ml and mix.

**3.3 Nitric acid**,  $\rho$  1,40 g/ml, approximately 15 N solution.

**3.4 Sulphuric acid**,  $\rho$  1,48 g/ml, approximately 18 N solution.

Carefully add 500 ml of sulphuric acid,  $\rho$  1,84 g/ml, approximately 36 N solution, to approximately 400 ml of water. After cooling, make up the volume to 1 000 ml and mix.

**3.5 Sulphuric acid**,  $\rho$  1,21 g/ml, approximately 7 N solution.

Carefully add 200 ml of sulphuric acid,  $\rho$  1,84 g/ml, approximately 36 N solution, to approximately 700 ml of water. After cooling, make up the volume to 1 000 ml and mix.

**3.6 Sulphuric acid**,  $\rho$  1,06 g/ml, approximately 2 N solution.

Carefully add 60 ml of sulphuric acid,  $\rho$  1,84 g/ml, approximately 36 N solution, to approximately 500 ml of water. After cooling, make up the volume to 1 000 ml and mix.

**3.7 Sulphurous acid** ( $H_2SO_3$ ), solution saturated at room temperature.

**3.8 Sodium sulphite**, 20 g/l solution.

Dissolve 2 g of sodium sulphite ( $Na_2SO_3$ ) in water and make up the volume to 100 ml.

Prepare immediately before use.

**3.9 Potassium permanganate, 1 g/l solution.**

Dissolve 0,1 g of potassium permanganate in water and make up the volume to 100 ml.

**3.10 Buffer solution, pH approximately 2,9.**

Dissolve 189 g of monochloroacetic acid ( $\text{CH}_2\text{ClCOOH}$ ) in approximately 150 ml of water and add 40 g of sodium hydroxide previously dissolved in approximately 100 ml of water. Carefully mix and cool to room temperature. Filter, if necessary, through a medium texture filter paper and collect the filtrate in a 500 ml volumetric flask. Wash with water, make up to volume and mix.

Use only a freshly prepared solution (one week maximum).

**3.11 Ascorbic acid, 40 g/l solution.**

Dissolve 1 g of ascorbic acid in 25 ml of water.

Prepare immediately before use.

**3.12 Chromotropic acid, 20 g/l solution.**

Dissolve 2 g of chromotropic acid (disodium salt of 1,8-dihydroxynaphthalene-3,6-disulphonic acid) in approximately 70 ml of water containing 0,75 ml of glacial acetic acid,  $\rho$  1,05 g/ml, approximately 18 N solution.

Add 0,2 g of sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) and shake until completely dissolved. Filter, if necessary, through a close texture filter paper and collect the filtrate in a 100 ml volumetric flask. Wash with water, make up to volume and mix.

This solution *should have a very slight pale yellow colour and should be kept in a dark coloured container.* It is stable for about three weeks.

Do not use a dark coloured solution.

**3.13 Mixed reagent, pH approximately 0,50.**

Place approximately 300 ml of water in a 1 000 ml volumetric flask, add 250,0 ml of the sodium hydroxide solution (3.1), 100,0 ml of the sulphuric acid solution (3.4) and 18,0 ml of the nitric acid solution (3.3) and mix. Cool, make up to volume and mix.

**3.14 Titanium, standard solution corresponding to 0,5 g of Ti per litre.**

Prepare the solution according to one of the following methods :

**3.14.1** Weigh, to the nearest 0,001 g, 0,500 g of pure titanium (purity greater than 99,5 %) and place in a beaker of suitable capacity (for example, 600 ml). Dissolve in 125 ml of the sulphuric acid solution (3.5) and oxidize with a few drops of the nitric acid solution (3.3). Boil the solution gently until all nitric acid fumes have been given off.

Cool, dilute suitably, transfer, with washing, to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,5 mg of Ti.

**3.14.2** Weigh, to the nearest 0,000 1 g, 1,848 5 g of potassium titanyl oxalate dihydrate [ $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ] and place in a Kjeldahl flask of approximately 100 ml capacity. Add 1,8 g of ammonium sulphate and 15 ml of sulphuric acid,  $\rho$  1,84 g/ml approximately 36 N solution. Heat carefully until the reaction subsides and boil gently for 10 min. Cool and transfer the solution, with washing, to a beaker of suitable capacity (for example, 250 ml), containing 100 ml of water.

Add a few drops of the potassium permanganate solution (3.9) until a persistent pink colour is obtained. Transfer the solution, with washing, to a 500 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,5 mg of Ti.

**3.15 Titanium, standard solution corresponding to 0,025 g of Ti per litre.**

Take 50,0 ml of the standard titanium solution (3.14), place in a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,025 mg of Ti.

Prepare this solution immediately before use.

**3.16 Titanium, standard solution corresponding to 0,015 g of Ti per litre.**

Take 30,0 ml of the standard titanium solution (3.14) and place in a 1 000 ml volumetric flask. Add 2,0 ml of the sulphuric acid solution (3.5), make up to volume and mix.

1 ml of this standard solution contains 0,015 mg of Ti.

Prepare this solution immediately before use.

**3.17 Titanium, standard solution corresponding to 0,002 5 g of Ti per litre.**

Take 50,0 ml of the standard titanium solution (3.15) and place in a 500 ml volumetric flask. Add 2,50 ml of the sulphuric acid solution (3.5), make up to volume and mix.

1 ml of this standard solution contains 0,002 5 mg of Ti.

Prepare this solution immediately before use.

**4 APPARATUS**

Normal laboratory apparatus, and

**4.1 pH meter**, having an accuracy to within at least 0,02 pH unit and provided with a glass electrode.

**4.2 Spectrophotometer.**

## 5 SAMPLING

### 5.1 Laboratory sample<sup>1)</sup>

### 5.2 Test sample

Chips of thickness not more than 1 mm shall be obtained by milling or drilling.

## 6 PROCEDURE

### 6.1 Determination of the optimum pH value for the development of the colour

If the colour reaction is carried out at a pH value determined exactly by experiment, the value of the absorbance for a given quantity of titanium is almost constant. It is therefore necessary to predetermine with the particular instrument being used — by operating in the pH range between 2 and 2,50 and by using a given quantity (for example 8,0 ml) of the standard titanium solution (3.17) — the interval of  $\pm 0,05$  pH unit which ensures almost constant values of the absorbance following the procedure specified in 6.2.1, 6.2.3 and 6.2.4.

Subsequently, use the pH value thus found for the preparation of the calibration curve and for the determination.

### 6.2 Plotting of the calibration curve

#### 6.2.1 Titanium content between 0,005 and 0,03 % (m/m)

##### 6.2.1.1 PRELIMINARY TEST FOR ADJUSTMENT OF pH VALUE

Into a series of six beakers of suitable capacity (for example, 100 ml), place 10,0 ml of the mixed reagent solution (3.13) and add 0 (compensation solution) — 1,0 — 2,0 — 4,0 — 8,0 — 12,0 ml respectively of the standard titanium solution (3.17). Then add, drop by drop, the potassium permanganate solution (3.9) to each beaker until a persistent pale pink colour is obtained.

Eliminate the excess potassium permanganate with a slight excess of the sodium sulphite solution (3.8), add 10,0 ml of the buffer solution (3.10), 1,0 ml of the ascorbic acid solution (3.11), 5,0 ml of the chromotropic acid solution (3.12), dilute to approximately 45 ml and mix.

Using a graduated pipette or a burette, add to each solution, while checking with the pH meter (4.1), the sodium hydroxide solution (3.2) or the sulphuric acid solution (3.6), as applicable, while stirring, in sufficient quantity to give a pH value corresponding to the optimum determined in 6.1.

NOTE — For correction of the pH value, it is not absolutely necessary

to use the alkaline or acid solutions in the concentration specified in the method; i.e. approximately 2 N. More dilute or more concentrated solutions may be used, provided that the quantity of alkaline or acid solution necessary for the correction of the pH value does not exceed approximately 2 ml. This is in order not to increase excessively the volume of solution, bearing in mind the quantities of reagents which have to be added for development of the colour, and the final volume (50,0 ml).

Note the volume of sodium hydroxide or sulphuric acid used for the adjustment of the pH, and discard the solutions.

#### 6.2.1.2 PREPARATION OF THE STANDARD SOLUTIONS, related to spectrophotometric measurements carried out in cells having optical path lengths of 4 or 5 cm

Into a series of six 50 ml volumetric flasks, place 10,0 ml of the mixed reagent solution (3.13) and add the volumes of standard titanium solution (3.17) indicated in table 1.

TABLE 1

Volume of standard titanium solution (3.17)	Corresponding mass of titanium
ml	mg
0*	0
1,0	0,002 5
2,0	0,005
4,0	0,010
8,0	0,020
12,0	0,030

\* Compensation solution.

Then add, to each flask, the quantity of the sodium hydroxide solution (3.2) or the sulphuric acid solution (3.6) used in the preliminary test (see 6.2.1.1) for the adjustment of the pH of the solution of relevant titanium concentration, and mix.

#### 6.2.2 Titanium content between 0,03 and 0,3 % (m/m)

##### 6.2.2.1 PRELIMINARY TEST FOR ADJUSTMENT OF pH VALUE

Into a series of seven beakers of suitable capacity (for example, 100 ml), place 10,0 ml of the mixed reagent solution (3.13) and add 0 (compensation solution) — 1,0 — 2,0 — 4,0 — 6,0 — 8,0 — 12,0 ml respectively of the standard titanium solution (3.16). Then add, drop by drop, the potassium permanganate solution (3.9) to each beaker until a persistent pale pink colour is obtained.

Continue according to the procedure specified in 6.2.1.1, from the second paragraph onwards.

1) Sampling of aluminium and aluminium alloys will be the subject of a future International Standard.

**6.2.2.2 PREPARATION OF THE STANDARD SOLUTIONS**, related to spectrophotometric measurements carried out in cells having optical path lengths of 1 cm

Into a series of seven 50 ml volumetric flasks, place 10,0 ml of the mixed reagent solution (3.13) and add the volumes of standard titanium solution (3.16) indicated in table 2.

TABLE 2

Volume of standard titanium solution (3.16)	Corresponding mass of titanium
ml	mg
0*	0
1,0	0,015
2,0	0,030
4,0	0,060
6,0	0,090
8,0	0,120
12,0	0,180

\* Compensation solution.

Then add, to each flask, the quantity of the sodium hydroxide solution (3.2) or the sulphuric acid solution (3.6) used in the preliminary test (see 6.2.2.1) for the adjustment of the pH of the solution of relevant titanium concentration, and mix.

### 6.2.3 Development of the colour

Add, drop by drop, the potassium permanganate solution (3.9) to each flask until a persistent pale pink colour, is obtained.

Eliminate the excess potassium permanganate with a very slight excess of the sodium sulphite solution (3.8), and add 10,0 ml of the buffer solution (3.10), 1,0 ml of the ascorbic acid solution (3.11) and 5,0 ml of the chromotropic acid solution (3.12). Shake after the addition of each reagent; make up to volume and mix.

### 6.2.4 Spectrophotometric measurements

Make the spectrophotometric measurements not less than 15 min and not more than 40 min after addition of the chromotropic acid solution (3.12) using the spectrophotometer (4.2) at the maximum of the absorption curve (wavelength of about 470 nm) after having set the instrument to zero absorbance against the compensation solution.

### 6.2.5 Plotting of the curve

Plot the two graphs, giving, for example, the values, expressed in milligrams, of the quantities of titanium contained in 50 ml of standard solution, as abscissae, and the corresponding values of the absorbance as ordinates.

## 6.3 Determination

### 6.3.1 Test portion

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

### 6.3.2 Blank test

Simultaneously with the analysis and following the same procedure, carry out a blank test using the same quantities of all the reagents used for the analysis, but reducing to 10,0 ml the quantity of the sulphuric acid solution (3.4) used to acidify the alkaline attack solution (see 6.3.3).

### 6.3.3 Attack of the test portion

Place the test portion (6.3.1) in a container of suitable capacity (for example, a 250 ml beaker) and add 25,0 ml of the sodium hydroxide solution (3.1). Cover with a watch glass and if necessary heat gently to start the reaction. As soon as the attack is complete, rinse the watch glass and the walls of the beaker with a little warm water. Then boil for a few minutes. Allow to cool, dilute to approximately 60 ml and add 1,80 ml of the nitric acid solution (3.3) and 16,50 ml of the sulphuric acid solution (3.4).

Mix and boil until the salts are dissolved. If any manganese dioxide separates out, add a few drops of the sulphurous acid solution (3.7) and boil for a few minutes.

### 6.3.4 Preparation of the test solution

Cool to room temperature and transfer the solution (6.3.3) to a 100 ml volumetric flask. Wash with water, make up to volume and mix.

NOTE — It is advisable not to interrupt the determination at this point, in order to avoid hydrolysis of the titanium in solution.

If necessary, filter the solution (or a part of the solution) through a dry close-textured filter paper and collect the filtrate in a dry container.

### 6.3.5 Preliminary test for the adjustment of pH value

Into a beaker of suitable capacity (for example, 100 ml), place a 10,0 ml aliquot of the test solution (6.3.4) if the titanium content is assumed to be less than 0,15 % (m/m), or a 5,0 ml aliquot plus 5,0 ml of the blank test solution (6.3.2) if the titanium content is assumed to be more than 0,15 % (m/m).

Add, drop by drop, the potassium permanganate solution (3.9) until a persistent pale pink colour is obtained. Continue according to the procedure specified in 6.2.1.1, from the second paragraph onwards.

### 6.3.6 Development of the colour

Into a 50 ml volumetric flask, place an aliquot of the test solution (6.3.4) — together with any necessary additional volume of the blank test solution (6.3.2) — of the same volume as that used for the pH adjustment (see 6.3.5).

Add the quantity of the sodium hydroxide solution (3.2) or the sulphuric acid solution (3.6) used for the pH adjustment (see 6.3.5).

Then add, drop by drop, the potassium permanganate solution (3.9) until a persistent pale pink colour is obtained. Continue according to the procedure specified in 6.2.3, second paragraph.

#### 6.3.7 Assessment of the colour of the test solution (basic colour)

If the alloy being tested contains elements which form coloured ions in a solution (for example chromium), take from the test solution a third aliquot, equal to that used for the analysis. Place this aliquot in a 50 ml volumetric flask and develop the colour according to the procedure specified in 6.3.6 *but without the addition of the chromotropic acid solution* (3.12).

#### 6.3.8 Spectrophotometric measurements

Make the spectrophotometric measurements not less than 15 min and not more than 40 min after addition of the chromotropic acid solution (3.12) using the spectrophotometer (4.2) at the maximum of the absorption curve (wavelength of about 470 nm), after having set the instrument to zero absorbance against water.

Let

$A_0$  — represent the absorbance measured for the aliquot of the test solution (6.3.4);

$A_1$  — represent the absorbance of the basic colour of the corresponding aliquot of the test solution (6.3.4);

$A_2$  — represent the absorbance measured for a corresponding aliquot of the blank test solution (6.3.2).

## 7 EXPRESSION OF RESULTS

Calculate, for the test solution, the absorbance of the titanium-chromotropic acid complex [ $A_0 - (A_1 + A_2)$ ].

The quantity of titanium corresponding to the above difference is calculated by means of the calibration curve (see 6.2.5).

The titanium (Ti) content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times D}{10 m_0}$$

where

$m_0$  is the mass, in grams, of the test portion (6.3.1);

$m_1$  is the mass, in milligrams, of titanium found in the aliquot of the test solution (6.3.4) taken for the determination;

$D$  is the ratio of the volume of the test solution to the volume of the aliquot taken for the determination.

## 8 TEST REPORT

The test report shall contain 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 special features noted during the determination;
- e) any operations not specified in this International Standard, or regarded as optional, which may have affected the results.

## ANNEX

**SPECIAL CASE OF ALUMINIUM ALLOYS IN WHICH THE SILICON CONTENT  
IS GREATER THAN 1 % (m/m)****A.1 PRINCIPLE**

For alloys in which the silicon content is relatively high, it is necessary to evaporate the alkaline solution of the test sample to a syrupy consistency in order to guarantee that the silicon is completely dissolved. The determination is then carried out according to the general method.

**A.2 MODIFICATIONS TO THE GENERAL METHOD****A.2.1** *Replace sub-clause 6.3.2, "Blank test", by the following :*

Simultaneously with the analysis and following the procedure for the special case, carry out a blank test using the same quantities of all the reagents used for the analysis but reducing to 10,0 ml the quantity of the sulphuric acid solution (3.4) used to acidify the alkaline attack solution (see A.2.2).

**A.2.2** *Replace sub-clause 6.3.3, "Attack of the test portion", by the following :*

Place the test portion (6.3.1) in a platinum container of suitable capacity (for example, a crucible or basin of approximately 200 ml) and add 25,0 ml of the sodium hydroxide solution (3.1). Cover with a platinum lid and if necessary heat gently to start the reaction. When the attack is completed, rinse the platinum cover and the walls of the platinum receptacle with warm water, and evaporate the solution to a syrupy consistency, taking care to avoid any spattering. After cooling, dissolve in approximately 40 ml of warm water, heat gently to complete dissolution, then boil for a few minutes. Cool, dilute to approximately 60 ml, and add 1,80 ml of the nitric acid solution (3.3) and 16,50 ml of the sulphuric acid solution (3.4).

Mix and boil until the salts have dissolved. If any manganese dioxide separates out, add a few drops of the sulphurous acid solution (3.7) and boil for a few minutes.