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R 1118

CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

DETERMINATION OF TITANIUM

(SPECTROPHOTOMETRIC METHOD WITH CHROMOTROPIC ACID)

1st EDITION
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BRIEF HISTORY

The ISO Recommendation R 1118, *Chemical analysis of aluminium and aluminium alloys – Determination of titanium (Spectrophotometric method with chromotropic acid)*, was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys*, the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question led to the adoption of a Draft ISO Recommendation.

In July 1968, this Draft ISO Recommendation (No. 1606) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in September 1969, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 1118 September 1969

CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

DETERMINATION OF TITANIUM

(SPECTROPHOTOMETRIC METHOD WITH CHROMOTROPIC ACID)

1. SCOPE

This ISO Recommendation describes a general method for the spectrophotometric determination of titanium in aluminium and aluminium alloys.

The method is applicable to the determination of titanium contents between 0.005 and 0.3 %.

However, the method does not apply completely to the case of alloys with a silicon content greater than 1 %, for which it must be modified as indicated in the Annex.

2. PRINCIPLE

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

2.2 Reduction of the Fe (III) with ascorbic acid and formation of the complex titanium-chromotropic acid at a pH value between 2 and 2.50, controlled within ± 0.05 pH units.

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

3. REAGENTS

3.1 *Sodium hydroxide* solution, 200 g per litre (approximately 5 N).

In a nickel dish, dissolve 200 g of sodium hydroxide in water. After cooling, make up the volume to 1000 ml and mix. Immediately transfer the solution to a plastic container.

3.2 *Sodium hydroxide* solution, 80 g per litre (approximately 2 N).

In a nickel dish, dissolve 80 g of sodium hydroxide in water. After cooling, make up the volume to 1000 ml and mix.

3.3 *Nitric acid,* $d = 1.40$ (approximately 15 N).

3.4 *Sulphuric acid,* $d = 1.48$ (approximately 17.7 N).

Carefully add 500 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to approximately 400 ml of water. After cooling, make up the volume to 1000 ml and mix.

3.5 *Sulphuric acid,* $d = 1.21$ (approximately 7.1 N).

Carefully add 200 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to approximately 700 ml of water. After cooling, make up the volume to 1000 ml and mix.

3.6 *Sulphuric acid,* $d = 1.06$ (approximately 2 N).

Carefully add 60 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to approximately 500 ml of water. After cooling, make up the volume to 1000 ml and mix.

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

3.8 *Sodium sulphite* solution, 20 g per litre.

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* solution, 1 g per litre.

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 ($CH_2ClCOOH$) 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 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* solution, 40 g per litre.

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

Prepare immediately before use.

3.12 *Chromotropic acid* solution, 20 g per litre.

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, $d = 1.05$ (approximately 17.4 N solution). Add 0.2 g of sodium metabisulphite ($Na_2S_2O_5$) and shake until completely dissolved. Filter through a close texture filter 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 can no longer be used after it has been kept for about three weeks.

Dark coloured solutions should not be used.

3.13 *Mixed reagent*, pH approximately 0.50.

Place approximately 300 ml of water in a 1000 ml volumetric flask, then add 250.0 ml of sodium hydroxide solution (3.1), 100.0 ml of sulphuric acid solution (3.4), 18.0 ml of nitric acid solution (3.3) and mix. Cool, make up to volume and mix.

3.14 *Standard titanium solution* containing 0.5 g of titanium per litre.

Prepare the solution according to one of the following methods :

3.14.1 Weigh, to the nearest 1 mg, 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 sulphuric acid solution (3.5) and oxidize with a few drops of nitric acid (3.3). Boil the solution gently until all nitric acid fumes have been given off.

Cool, dilute suitably, transfer, with washing, to a 1000 ml volumetric flask, make up to volume and mix.

3.14.2 Weigh, to the nearest 0.1 mg, 1.8485 g of potassium titanyl oxalate [$K_2TiO(C_2O_4)_2 . 2\ H_2O$] and place in a Kjeldahl flask of approximately 100 ml capacity. Add 1.8 g of ammonium sulphate and 15 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N). Heat carefully until the reaction subsides and boil gently for 10 minutes.

Cool and transfer the solution, with washing, to a beaker of suitable capacity (for example, 250 ml) already containing 100 ml of water.

Add a few drops of 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 *Standard titanium solution* containing 0.025 g of titanium per litre.

Take 50.0 ml of standard titanium solution (3.14.1 or 3.14.2), place in a 1000 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 *Standard titanium solution* containing 0.0025 g of titanium per litre.

Take 50.0 ml of standard titanium solution (3.15) and place in a 500 ml volumetric flask. Add 2.50 ml of sulphuric acid solution (3.5), make up to volume and mix.

1 ml of this standard solution contains 0.0025 mg of Ti.

Prepare this solution immediately before use.

3.17 *Standard titanium solution* containing 0.015 g of titanium per litre.

Take 30.0 ml of standard titanium solution (3.14) and place in a 1000 ml volumetric flask. Add 2.0 ml of 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.

4. APPARATUS

4.1 *Usual laboratory apparatus.*

4.2 *pH meter*, having a precision of at least 0.02 pH units and provided with a glass electrode.

4.3 *Spectrophotometer.*

5. SAMPLING

5.1 Laboratory sample*

5.2 Test sample

Chips of thickness not more than 1 mm, 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 optical density of 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 (e.g. 8 ml) of standard titanium solution (3.16) – the interval of ± 0.05 pH units which ensures almost constant values of the optical density following the procedure given in clauses 6.2.1, 6.2.3 and 6.2.4.

6.2 Plotting of the calibration curve

6.2.1 *Titanium content between 0.005 and 0.03 %*

6.2.1.1 PRELIMINARY TEST FOR ADJUSTMENT OF pH VALUE. In each 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 and 12.0 ml respectively of standard titanium solution (3.16). Then add the potassium permanganate solution (3.9) to each beaker, drop by drop, until a persistent pale pink colour is obtained.

Eliminate the excess potassium permanganate with a slight excess of sodium sulphite (3.8), then add 10.0 ml of buffer solution (3.10), 1.0 ml of ascorbic acid solution (3.11), 5.0 ml of chromotropic acid solution (3.12), dilute to approximately 45 ml and mix.

Using a graduated pipette or burette, add to each solution, while checking with the pH meter (4.2), sodium hydroxide solution (3.2) or sulphuric acid (3.6) as applicable, while stirring, in sufficient quantity to give a pH value corresponding to the optimum determined in clause 6.1 (see clause 8.1).

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

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* The ISO Recommendation relating to the sampling from delivery batches will be studied as soon as Technical Committee ISO/TC 69, *Statistical treatment of series of observations*, has fixed the general principles to be adopted.

6.2.1.2 PREPARATION OF THE STANDARD SOLUTIONS, related to spectrophotometric measurements carried out with an optical path of 5 or 4 cm.

In each of six 50 ml volumetric flasks, place 10.0 ml of mixed reagent solution (3.13) and add the volumes of standard titanium solution (3.16) indicated in Table 1 below.

TABLE 1

Volume of standard titanium solution (3.16)	**Corresponding mass of titanium**
ml	mg
0 *	0
1.0	0.0025
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 sodium hydroxide (3.2) or sulphuric acid (3.6) used in the preliminary test (see clause 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 %*

6.2.2.1 PRELIMINARY TEST FOR ADJUSTMENT OF pH VALUE. In seven beakers of suitable capacity (for example, 100 ml), place 10.0 ml of mixed reagent solution (3.13) and add 0 (compensation solution), 1.0, 2.0, 4.0, 6.0, 8.0 and 12.0 ml respectively of standard titanium solution (3.17). Then add potassium permanganate solution (3.9), drop by drop, to each beaker until a persistent pale pink colour is obtained.

Continue according to the procedure described in the second paragraph of clause 6.2.1.1.

6.2.2.2 PREPARATION OF THE STANDARD SOLUTIONS, related to spectrophotometric measurements carried out with an optical path of 1 cm.

In each of seven 50 ml volumetric flasks, place 10.0 ml of mixed reagent solution (3.13) and add the volumes of standard titanium solution (3.17) indicated in Table 2 below.

TABLE 2

Volume of standard titanium solution (3.17)	**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 sodium hydroxide (3.2) or sulphuric acid (3.5) used in the preliminary test (see clause 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 to each flask potassium permanganate solution (3.9), drop by drop, in sufficient quantity to obtain a persistent pale pink colour.

Eliminate the excess potassium permanganate with a very slight excess of sodium sulphite solution (3.8), and add 10.0 ml of buffer solution (3.10), 1.0 ml of ascorbic acid (3.11) and 5.0 ml of chromotropic acid (3.12). Mix after addition of each reagent. Make up to volume and mix.

6.2.4 *Spectrophotometric measurements.* Make the spectrophotometric measurements not less than 15 minutes and not more than 40 minutes after addition of the chromotropic acid (3.12) using a spectrophotometer (4.3) at the maximum of the absorption curve (wavelength of about 470 nm) after having set the instrument to zero optical density against the compensation solution.

6.2.5 *Plotting of the calibration curve.* Plot the two graphs giving, for example, the values, expressed in milligrammes, of the quantities of titanium contained in 50 ml of standard solution, as abscissae, and the corresponding values of optical density as ordinates.

6.3 Determination

6.3.1 *Test portion.* Weigh, to the nearest 1 mg, approximately 1 g of test sample (5.2).

6.3.2 *Blank test.* Simultaneously 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 sulphuric acid (3.4) used to acidify the alkaline attack solution (see clause 6.3.3).

6.3.3 *Attack of the test portion.* Place the test portion (6.3.1) in a container of suitable capacity (e.g. a 250 ml beaker) and add 25.0 ml of 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 nitric acid (3.3) and 16.50 ml of sulphuric acid (3.4).

Mix and boil until the salts are dissolved. If any manganese dioxide separates out add a few drops of sulphurous acid (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 (see clause 8.2). If necessary, filter the solution (or only part of the solution) through a dry close-textured filter and collect the filtrate in a dry container.

6.3.5 *Preliminary test for the adjustment of pH value.* In 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 %, 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 %.

Add the potassium permanganate (3.9), drop by drop, until a persistent pale pink colour is obtained. Continue according to the procedure described in the second paragraph of clause 6.2.1.1.

6.3.6 *Development of the colour.* In 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 clause 6.3.5). Add the quantity of sodium hydroxide (3.2) or sulphuric acid (3.6) used for the pH adjustment (see clauses 6.3.5 and 8.1).

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

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 as described in clause 6.3.6 *but without the addition of chromotropic acid (3.12).*

6.3.8 *Spectrophotometric measurements.* Make the spectrophotometric measurements not less than 15 minutes and not more than 40 minutes after addition of the chromotropic acid (4.12) using the spectrophotometer (4.3) at the maximum of the absorption curve (wavelength of about 470 nm) after having set the instrument to zero optical density against water.

Let

Δ_E represent the optical density measured for the aliquot of the test solution (6.3.4);

Δ_{Ec} represent the optical density of the basic colour of the corresponding aliquot of the test solution;

Δ_B represent the optical density measured for a corresponding aliquot of the blank test solution (6.3.2).

7. EXPRESSION OF RESULTS

Calculate for the test solution the optical density of the titanium-chromotropic acid complex $[\Delta_E - (\Delta_B + \Delta_{Ec})]$.

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

The percentage, by mass, of titanium is given by the following formula :

$$\frac{A \times D}{10 \times E}$$

where

A is the mass, expressed in milligrammes, 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;

E is the mass, expressed in grammes, of the test portion (6.3.1).

8. NOTES

8.1 For the 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 also 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 the development of the colour, and the final volume (50.0 ml).

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

9. TEST REPORT

Report the following information :

(*a*) the reference of the method used;

(*b*) the results and the method of expression used;

(*c*) any special features noted during the determination;

(*d*) any operations not specified in this ISO Recommendation, or regarded as optional, which may have affected the results.