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INTERNATIONAL STANDARD



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## Aluminium alloys — Determination of zinc — EDTA titrimetric method

*Alliages d'aluminium — Dosage du zinc — Méthode titrimétrique à l'EDTA*

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## FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 79 has reviewed ISO Recommendation R 1784 and found it technically suitable for transformation. International Standard ISO 1784 therefore replaces ISO Recommendation R 1784-1970 to which it is technically identical.

ISO Recommendation R 1784 was approved by the Member Bodies of the following countries :

Australia	Israel	South Africa, Rep of
Belgium	Italy	Spain
Czechoslovakia	Japan	Sweden
Egypt, Arab Rep. of	Korea, Rep. of	Switzerland
Germany	Netherlands	Thailand
Greece	New Zealand	Turkey
Hungary	Norway	United Kingdom
India	Peru	U.S.A.
Iran	Poland	

The Member Bodies of the following countries expressed disapproval of the Recommendation on technical grounds :

Canada  
France

No Member Body disapproved the transformation of ISO/R 1784 into an International Standard.

1784-76

4851903 0006735 2

# Aluminium alloys – Determination of zinc – EDTA titrimetric method

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an EDTA titrimetric method for the determination of zinc in aluminium alloys not containing cadmium.

This method is applicable to products having a zinc content between 0,10 and 12 % (*m/m*).

## 2 PRINCIPLE

Hydrochloric acid attack and elimination of the excess of acid by evaporation. Taking up of the residue in 2 N hydrochloric acid solution and passage of the solution through a strongly basic anion exchange resin.

Elution of the zinc absorbed on the resin with 0,005 N hydrochloric acid solution.

Titration of the zinc by standard volumetric disodium EDTA solution using dithizone as indicator.

## 3 REAGENTS

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

**3.1 Strongly basic anion exchange resin**, either heteroporous or isoporous, of the polystyrene type with quaternary ammonium groups (for example Dowex 1 × 2, De-Acidite FF SRA 62 or equivalent) in the chloride form, containing from 2 to 3 % cross linking (expressed as a percentage by mass of DVB (divinylbenzene) and preferably with a particle size between 150 and 295 μm (-52 + 100 mesh).

**3.2 Acetone**,  $\rho$  approximately 0,79 g/ml.

**3.3 Hydrochloric acid**,  $\rho$  approximately 1,10 g/ml, solution approximately 6 N.

Dilute 515 ml of hydrochloric acid,  $\rho$  approximately 1,18 g/ml, approximately 12 N, with water and make up the volume to 1 000 ml.

**3.4 Hydrochloric acid**,  $\rho$  approximately 1,03 g/ml, solution approximately 2 N.

Dilute 170 ml of hydrochloric acid,  $\rho$  approximately 1,18 g/ml, approximately 12 N, with water and make up the volume to 1 000 ml.

**3.5 Hydrochloric acid**,  $\rho$  approximately 1,01 g/ml, solution approximately 1 N.

Dilute 85 ml of hydrochloric acid,  $\rho$  approximately 1,18 g/ml, approximately 12 N, with water and make up the volume to 1 000 ml.

**3.6 Hydrochloric acid**, solution approximately 0,005 N.

Dilute 5 ml of hydrochloric acid (3.5) with water and make up the volume to 1 000 ml.

**3.7 Nitric acid**,  $\rho$  approximately 1,4 g/ml, solution approximately 67 % (*m/m*) or 15 N.

**3.8 Hydrogen peroxide**,  $\rho$  approximately 1,135 g/ml, solution approximately 36 % (*m/m*).

**3.9 Ammonium hydroxide solution**,  $\rho$  approximately 0,90 g/ml, solution approximately 28 % (*m/m*) or 14 N.

**3.10 Acetic acid**,  $\rho$  approximately 1,007 g/ml, solution approximately 1 N.

Dilute 58 ml of glacial acetic acid,  $\rho$  approximately 1,05 g/ml, solution approximately 17,4 N, with water and make up the volume to 1 000 ml.

**3.11 Ammonium acetate solution**, 500 g/l.

Dissolve 50 g of ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) in water and make up the volume to 100 ml.

**3.12 Zinc**, standard solution containing 2 g of zinc per litre.

Weigh, to the nearest 0,001 g, 2,00 g of extra pure zinc and dissolve in 50 ml of hydrochloric acid solution (3.3) diluted with approximately 50 ml of water. Dilute and transfer the solution quantitatively to a 1 000 ml volumetric flask. Make up to volume and mix.

1 ml of this solution contains 2 mg of zinc.

**3.13 (Ethylenedinitrilo)tetraacetic acid (EDTA), disodium salt**, 0,02 M standard volumetric solution.

### 3.13.1 Preparation

Dissolve approximately 7,5 g of disodium EDTA, dihydrate, in water, filter if necessary, and make up the volume to 1 000 ml. Keep in a plastics bottle.

### 3.13.2 Standardization

Take 25,0 ml of the standard zinc solution (3.12), corresponding to 50,0 mg of zinc, and place in a vessel of suitable capacity (for example 400 ml). Dilute to about 100 ml, introduce a piece of litmus paper (3.14) into the solution and, stirring constantly, add ammonium hydroxide solution (3.9) until the litmus changes colour. Remove the piece of litmus paper and wash with water.

Add 10 ml of the acetic acid solution (3.10) and 10 ml of the ammonium acetate solution (3.11). Check the pH of the solution by means of indicator paper (3.15). This value should be between 5 and 5,5. If necessary, bring it back to the indicated value by adding acetic acid solution (3.10) drop by drop. Then add 50 ml of the acetone (3.2), 2 ml of the dithizone solution (3.16) and titrate with the disodium EDTA solution (3.13) until the indicator changes from red to orange-yellow. This colour should not vary after the addition of 2 drops of the disodium EDTA solution in excess.

### 3.13.3 Calculation

The correction factor,  $f$ , corresponding to the fact that the solution is not exactly 0,02 M, is given by the formula

$$f = \frac{38,24}{V}$$

where

38,24 is the volume in millilitres, of 0,02 M disodium EDTA solution (theoretical value : 1 ml  $\triangleq$  1,307 6 mg of zinc) necessary for the titration of 50,0 mg of zinc (50,0 : 1,307 6 = 38,237 9);

$V$  is the volume, in millilitres, of the disodium EDTA solution (3.13) used for the titration of 25,0 ml of the standard zinc solution (3.12) (2 mg  $\times$  25,0 = 50,0 mg).

### 3.14 Litmus paper.

**3.15 Indicator paper** for pH within the range 5 to 6, with 0,2 unit intervals.

**3.16 Dithizone** [(phenylazo)thioformic acid, 2-phenylhydrazide], ethanolic solution, 0,25 g/l.

Dissolve 0,025 g of dithizone (1,5-diphenyl-3-formazan-thiol) in 95 % (V/V) ethanol and make up the volume to 100 ml with the same ethanol.

It is preferable to prepare the solution just before use.

## 4 APPARATUS

Ordinary laboratory equipment, and

**4.1 Glass column**, 20 mm diameter, approximately 400 mm tall, provided with a stopcock.

## 5 SAMPLING

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

### 5.2 Test sample

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

## 6 PROCEDURE

### 6.1 Preparation of the ion exchange column

First remove any fine particles present in the anion resin (3.1) by means of successive washings with dilute hydrochloric acid (3.6), decanting until a clear solution is obtained. Then allow the resin to stand for several hours (preferably overnight) in hydrochloric acid solution (3.6). Place a little glass wool at the bottom of the column (4.1), above the stopcock, as a support for the resin.

While shaking, transfer the suspension of resin to the prepared column, taking care to avoid the formation of air bubbles or channels, and operate so as to obtain, after decantation, a column of resin approximately 150 mm high. Wash the column with approximately 100 ml of hydrochloric acid solution (3.6) at a rate of 5 to 7 ml/min.

Condition the exchange column by introducing, at the same rate, 200 ml of hydrochloric acid solution (3.4), to which 0,5 ml of the nitric acid solution (3.7) has been added.

While the exchange column is being prepared and during the analysis, the resin should always be covered by the liquid.

### NOTES

- 1 When not in use, the resin in the exchange column should always be covered by hydrochloric acid (3.6).
- 2 The conditioning of the resin should be carried out immediately before use.

### 6.2 Test portion

Weigh, to the nearest 0,001 g, approximately 2 g of the test sample (5.2).

### 6.3 Blank test

Carry out, parallel with the analysis, a blank test using the same procedure and the same quantities of all the reagents.

### 6.4 Preparation of the test solution

Introduce the test portion (6.2) into a beaker of a suitable capacity (for example 400 ml) fitted with a watch glass, then add, in small portions and with care, 50 ml of hydrochloric acid solution (3.3).

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

When the reaction appears to be complete, add hydrogen peroxide (3.8) drop by drop, until the copper is completely dissolved. Complete the attack of the test portion by heating gently. Then evaporate just to crystallization. After cooling, take up with approximately 100 ml of dilute hydrochloric acid (3.4) and heat to facilitate dissolution.

Filter through a close texture filter, previously washed with hot hydrochloric acid (3.3) and then with hot water. Wash the residue and the filter with hot dilute hydrochloric acid (3.4) (about 30 to 50 ml) and, depending on the zinc content, use one of the two procedures described below :

#### 6.4.1 Zinc content between 0,10 and 1,5 % (m/m)

Collect the filtrate and the washings in a beaker and cool to room temperature. Adjust the volume to about 150 ml with hydrochloric acid (3.4) and add 0,5 ml of the nitric acid solution (3.7).

#### 6.4.2 Zinc content greater than 1,5 % (m/m)

Collect the filtrate and the washings in a 200 ml volumetric flask, cool to room temperature, make up to the mark with hydrochloric acid (3.4) and mix. Take an aliquot as indicated in the following table.

Zinc content	Volume of aliquot to be taken	Corresponding mass of test portion
% (m/m)	ml	g
1,5 to 3	100,0	1
3 to 6	50,0	0,50
6 to 12	25,0	0,25

Introduce the aliquot into a beaker of suitable capacity, dilute to about 150 ml with hydrochloric acid solution (3.4) and add 0,5 ml of nitric acid solution (3.7).

#### 6.5 Ion exchange

Pass the test solution or the aliquot (see 6.4.1 and 6.4.2) through the exchange column (6.1) at a rate of 5 to 7 ml/min. Wash the beaker and the exchange column with four successive 25 ml portions of hydrochloric acid solution (3.4) and then wash the resin with 100 ml of hydrochloric acid solution (3.5), still at the rate of 5 to 7 ml/min.

NOTE — In the case of alloys containing lead, the quantity of hydrochloric acid (3.5) must be increased from 100 to 200 ml.

Elute the zinc retained by the resin by passing 250 ml of hydrochloric acid solution (3.6) through the exchange column at the same rate (see note below). Collect the eluate in a vessel of suitable capacity (for example 400 ml). Concentrate the eluate to a volume of about 100 ml.

NOTE — If bismuth is present in the alloy, it will be retained on the column and will be seen as a light-coloured band at the top of the column. It should be removed by washing the column with 200 ml of 7,5 N nitric acid solution followed by 200 ml of water. The column should then be conditioned as in 6.1.

#### 6.6 Titration

Place litmus paper (3.14) in the eluate and add, while shaking, ammonium hydroxide solution (3.9) until the paper changes colour.

Remove the litmus paper and wash with water. Add 20 ml of the acetic acid solution (3.10) and 10 ml of the ammonium acetate solution (3.11). Check the pH of the solution using indicator paper (3.15). This value should be between 5 and 5,5. If necessary, bring it back to the indicated value by adding acetic acid solution (3.10) drop by drop. Then add 50 ml of the acetone (3.2) and cool to about 5 °C. Finally add 2 ml of the dithizone solution (3.16) and titrate immediately with the standard volumetric disodium EDTA solution (3.13) until the indicator changes colour from red to orange-yellow. The colour should not vary after the addition of 2 drops of the disodium EDTA solution in excess.

#### 7 EXPRESSION OF RESULTS

The zinc (Zn) content, as a percentage by mass, is given by the formula

$$\frac{(V_0 - V_1) \times f \times 1,3076 \times D}{10 m}$$

where

$V_0$  is the volume, in millilitres, of the standard volumetric disodium EDTA solution (3.13) used for the titration of the zinc present in the test solution or aliquot taken;

$V_1$  is the volume, in millilitres, of the standard volumetric disodium EDTA solution (3.13) used for the titration of the zinc present in the same aliquot of the blank test;

$f$  is the correction factor (3.13.3) of the standard volumetric disodium EDTA solution (3.13);

$D$  is the ratio between the volume of the test solution and the volume of the aliquot taken;

$m$  is the mass, in grams, of the test portion;

1,3076 is the mass, in milligrams, of zinc corresponding to 1 ml of exactly 0,02 M disodium EDTA solution.

#### 8 TEST REPORT

The test report shall include the following information :

- reference to the method used;
- results and the method of expression used;
- any characteristics noted during the determination;
- any operations not specified in this International Standard, or regarded as optional, which may have affected the results.