UDC 669.71 : 543.24 : 546.47

Ref. No. : ISO/R 1784-1970 (E)

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 1784

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

DETERMINATION OF ZINC

VOLUMETRIC METHOD

1st EDITION

July 1970

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 1784, *Chemical analysis of aluminium and its alloys – Determination of zinc – Volumetric method*, 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 Draft ISO Recommendation No. 1784 which was circulated to all the ISO Member Bodies for enquiry in January 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

The following Member Bodies opposed the approval of the Draft :

Canada
France

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council which decided to accept it as an ISO RECOMMENDATION.

ISO Recommendation | R 1784 | July 1970

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

DETERMINATION OF ZINC

VOLUMETRIC METHOD

1. SCOPE

This ISO Recommendation describes a volumetric method for the determination of zinc in aluminium alloys not containing cadmium.

This method is applicable to the determination of zinc contents between 0.10 and 12 %.

2. PRINCIPLE

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

2.2 Elution of the zinc absorbed on the resin with hydrochloric acid solution (0.005 N)

2.3 Titration of the zinc by EDTA standard solution using dithizone indicator.

3. REAGENTS

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 D.V.B. (divinylbenzene) and preferably with a particle size between 150 and 295 μm (− 52 + 100 mesh).

3.2 *Acetone* (d = approximately 0.79).

3.3 *Hydrochloric acid* (d = approximately 1.10), solution approximately 6 N.
Dilute 515 ml of hydrochloric acid (d = approximately 1.18) approximately 12 N, with water and make up the volume to 1000 ml.

3.4 *Hydrochloric acid* (d = approximately 1.03), solution approximately 2 N.
Dilute 170 ml of hydrochloric acid (d = approximately 1.18), approximately 12 N, with water and make up the volume to 1000 ml.

3.5 *Hydrochloric acid* (d = approximately 1.01), solution approximately N.
Dilute 85 ml of hydrochloric acid (d = approximately 1.18) approximately 12 N, with water and make up the volume to 1000 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 1000 ml.

3.7 *Nitric acid* (d = approximately 1.4), solution approximately 67 % (m/m) or 15 N.

3.8 *Hydrogen peroxide* (d = approximately 1.135), solution approximately 36 % (m/m).

3.9 *Ammonia* (d = approximately 0.90), solution approximately 28 % (m/m) or 14 N.

3.10 *Acetic acid* (d = approximately 1.007), solution approximately N.
Dilute 58 ml of glacial acetic acid (d = approximately 1.05), solution approximately 17.4 N, with water and make up the volume to 1000 ml.

3.11 *Ammonium acetate solution*, 500 g/l.
Dissolve 50 g of ammonium acetate (CH_3COONH_4) in water and make up the volume to 100 ml.

3.12 *Standard zinc 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 1000 ml volumetric flask. Make up to volume and mix.

1 ml of this solution contains 2 mg of zinc.

3.13 *Disodium ethylenediaminetetracetate* (EDTA), standard volumetric solution 0.02 M.

3.13.1 PREPARATION OF THE SOLUTION. Dissolve approximately 7.5 g of EDTA in water, filter if necessary, and make up the volume to 1000 ml. Keep in a plastics bottle.

3.13.2 STANDARDIZATION OF THE SOLUTION. Take 25.0 ml of 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 ammonia solution (3.9) until the litmus changes colour. Remove the piece of litmus paper and wash with water.

Add 10 ml of acetic acid solution (3.10) and 10 ml of 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 acetone (3.2), 2 ml of dithizone solution (3.16) and titrate with the EDTA solution (3.13) until the indicator changes from red to orange-yellow. This colour should not vary after the addition of two drops of EDTA solution in excess.

3.13.3 CALCULATION. The correction factor, corresponding to the fact that the solution is not exactly 0.02 M, is given by the following formula :

$$\frac{38.24}{V}$$

where

38.24 is the volume in millilitres, of EDTA solution 0.02 M (theroretical value : 1 ml $\widehat{=}$ 1.3076 mg of zinc) necessary for the titration of 50.0 mg of zinc (50.0 : 1.3076 = 38.2379);

V is the volume, in millilitres, of EDTA solution (3.13) used for the titration of 25.0 ml of standard zinc solution (3.12) (2 mg × 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*, ethanolic solution, 0.25 g/l.
Dissolve 0.025 g of dithizone (diphenylthiocarbazone) in ethanol 95 % (V/V) and make up the volume to 100 ml with the same ethanol.

It is preferable to prepare the solution just before use.

4. APPARATUS

4.1 *Ordinary laboratory equipment.*

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

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 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 (4.2), 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 per minute.

Condition the exchange column by introducing, at the same rate, 200 ml of hydrochloric acid solution (3.4), to which 0.5 ml of 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. (See section 8.)

6.2 Test portion

Weigh, to the nearest 0.001 g, approximately 2 g of 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).

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 dissolving.

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 %.* 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 nitric acid (3.7).

* The ISO Recommendation relating to sampling from supplies will be discussed as soon as Technical Committee ISO/TC 69, *Applications of statistical methods*, has fixed the general principles to be followed.

6.4.2 *Zinc content greater than 1.5 %.* 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
%	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 clauses 6.4.1 and 6.4.2) through the exchange column (6.1) at a rate of 5 to 7 ml per minute. 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 (see clause 8.3) of hydrochloric acid solution (3.5), still at the rate of 5 to 7 ml per minute.

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 section 8). Collect the eluate in a vessel of suitable capacity (for example 400 ml). Concentrate the eluate to a volume of about 100 ml.

6.6 Titration

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

Remove the litmus paper and wash with water. Add 20 ml of acetic acid solution (3.10) and 10 ml of ammonium acetate solution (3.11). Check the pH value 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 acetone (3.2) and cool to about 5 °C.

Finally add 2 ml of dithizone solution (3.16) and titrate immediately with EDTA solution (3.13) until the indicator changes colour from red to orange-yellow. The colour should not vary after the addition of two drops of EDTA solution in excess.

7. EXPRESSION OF RESULTS

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

$$\frac{(V - V_1) \times f \times 1.3076 \times D}{10m}$$

where

V is the volume, in millilitres, of EDTA solution (3.13) used for the titration of the zinc present in the test sample solution or aliquot taken;

V_1 is the volume, in millilitres, of 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 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 grammes, of the test portion;

1.3076 is the mass, in milligrammes, of zinc corresponding to 1 ml of EDTA solution exactly 0.02 M.