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Chemical analysis of aluminium and its alloys — Complexometric determination of magnesium

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FOREWORD

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Chemical analysis of aluminium and its alloys – Complexometric determination of magnesium

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a complexometric method for the determination of magnesium in aluminium alloys.

The method is applicable to the determination of magnesium contents between 0,1 and 12 %.

2 PRINCIPLE

2.1 Acid attack of the test portion, filtration of the insoluble residue and recovery of magnesium in the residue.

2.2 Separation of the major part of the aluminium, zinc, copper, nickel and chromium, by treatment with sodium hydroxide solution in the presence of hydrogen peroxide, potassium cyanide and a small quantity of iron to entrain the magnesium precipitate.

2.3 Dissolution in hydrochloric acid of the residue containing all the magnesium; precipitation of the iron, manganese, aluminium and titanium, by treatment with zinc oxide and potassium permanganate, and filtration.

2.4 Addition to the filtrate of suitable masking agents to prevent any possible interference by heavy metals, and titration of the magnesium with CDTA solution.

3 REAGENTS

3.1 Zinc oxide (ZnO)

Pure analytical reagent.

3.2 Hydrochloric acid (ρ = 1,09 g/ml approximately), solution approximately 6 N.

Dilute 515 ml of hydrochloric acid (ρ = 1,18 g/ml approximately), solution approximately 12 N, with water, and make up the volume to 1 000 ml.

3.3 Hydrochloric acid (ρ = 1,03 g/ml approximately), solution approximately 2 N.

Dilute 170 ml of hydrochloric acid (ρ = 1,18 g/ml approximately), solution approximately 12 N, with water, and make up the volume to 1 000 ml.

3.4 Hydrochloric acid solution approximately 0,05 N.

Dilute 25 ml of hydrochloric acid (3.3) with water, and make up the volume to 1 000 ml.

3.5 Nitric acid (ρ = 1,19 g/ml approximately), solution approximately 6 N.

Dilute 400 ml of nitric acid (ρ = 1,40 g/ml approximately), solution approximately 15 N, with water, and make up the volume to 1 000 ml.

3.6 Sulphuric acid (ρ = 1,26 g/ml approximately), solution approximately 9 N.

Add carefully, while mixing and cooling, 255 ml of sulphuric acid (ρ = 1,84 g/ml approximately), solution approximately 35,6 N, to 600 ml of water. After cooling, make up the volume to 1 000 ml and mix.

3.7 Hydrofluoric acid (ρ = 1,05 g/ml approximately), solution approximately 40 % (*m/m*).

3.8 Sodium hydroxide, solution 240 g/l, approximately 6 N.

In a nickel crucible, dissolve 240 g of sodium hydroxide in water. After cooling, make up the volume to 1 000 ml and mix. Immediately transfer the solution to a plastics container.

3.9 Sodium hydroxide, solution 20 g/l, approximately 0,5 N.

In a nickel crucible, dissolve 20 g of sodium hydroxide in water. After cooling, make up the volume to 1 000 ml and mix. Immediately transfer the solution to a plastics container.

3.10 Ammonia solution (ρ = 0,90 g/ml approximately), solution 28 % (*m/m*) or approximately 14 N.

3.11 Ammonia solution (ρ = 0,955 g/ml approximately), solution approximately 6 N.

Dilute 425 ml of ammonia solution (3.10) with water and make up the volume to 1 000 ml.

3.12 Ammonia solution (ρ = 0,99 g/ml approximately), solution approximately 1 N.

Dilute 70 ml of ammonia solution (3.10) with water and make up the volume to 1 000 ml.

3.13 Iron(III) chloride solution, 1 g of iron per litre.

Dissolve 0,48 g of hydrated iron(III) chloride ($FeCl_3 \cdot 6H_2O$), or 0,3 g of anhydrous ferric chloride ($FeCl_3$), in 16 ml of hydrochloric acid (3.3) and make up the volume to 100 ml.

3.14 Hydrogen peroxide ($\rho = 1{,}11$ g/ml approximately), solution approximately 30 % (*m/m*).

3.15 Potassium cyanide, solution 250 g/l.

Dissolve 25 g of potassium cyanide (KCN) in water and make up the volume to 100 ml. Proceed with caution, because of the toxicity of the cyanide.

Prepare this solution immediately before use.

3.16 Hydroxylammonium chloride, solution approximately 0,25 M.

Dissolve 1,8 g of hydroxylammonium chloride ($NH_2OH \cdot HCl$) in water and make up the volume to 100 ml.

3.17 Bromine water

Saturated solution at room temperature.

3.18 Potassium permanganate, solution 10 g/l.

Dissolve 1 g of potassium permanganate ($KMnO_4$) in water and make up the volume to 100 ml.

3.19 Ethanol, solution 25 % (*V/V*).

Dilute 250 ml of ethanol analytical grade ($C_2H_5 \cdot OH$) ($\rho = 0{,}79$ g/ml) with water and make up the volume to 1 000 ml.

3.20 Ethylene glycol-bis (3-aminoethyl ether) tetra-acetic acid (EGTA), solution approximately 0,05 M.

Dissolve 1,9 g of EGTA [$(HOCOCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2COOH)_2$] in about 25 ml of sodium hydroxide solution (3.9) and make up the volume to 100 ml with water.

3.21 Magnesium, standard solution containing 1,000 g of magnesium per litre.

Weigh, to the nearest 0,001 g, 1 g of pure magnesium (purity greater than 99,95 %) and dissolve in a mixture of 30 ml of hydrochloric acid (3.2) and about 200 ml of water. Transfer the solution quantitatively to a 1 000 ml volumetric flask, make up the volume and mix.

1 ml of this solution contains 1 mg of magnesium.

3.22 Magnesium, standard solution containing 0,200 g of magnesium per litre.

Transfer 100,0 ml of standard magnesium solution (3.21), to a 500 ml volumetric flask, add 6 ml of hydrochloric acid (3.2), make up to volume and mix.

1 ml of this standard solution contains 0,2 mg of magnesium.

3.23 1,2-diaminocyclohexanetetra-acetic acid (CDTA), standard solution 0,035 M.

3.23.1 *Preparation of the solution*

Place 12,05 g of CDTA ($C_6H_{10}[N(CH_2COOH)_2]_2H_2O$) in about 500 ml of water containing 10 ml of sodium hydroxide solution (3.8), and stir for a few minutes. Add slowly, while stirring, sodium hydroxide solution (3.8) until the solid suspension dissolves. Dilute to about 800 ml with water, filter through a close-texture filter and collect the filtrate in a 1 000 ml volumetric flask. Wash with water, collecting the washings in the same flask, then make up to volume and mix.

Store the solution, preferably, in plastics containers.

3.23.2 *Standardization of the solution*

In a beaker of suitable capacity (600 ml, for example) place 5 g of ammonium chloride (NH_4Cl), 25,0 ml of standard magnesium solution (3.21), containing 25,0 mg of magnesium, and dilute to about 250 ml with water. Add 100 ml of ammonia solution (3.10), cool to room temperature, add 0,05 to 0,1 g of indicator (3.25) and titrate with CDTA solution (3.23.1) until the colour of the indicator changes from blue to pale grey (practically colourless). This colour must not vary on addition of two drops in excess of CDTA solution.

3.23.3 *Calculation*

The strength of the CDTA solution, expressed in milligrams of magnesium per millilitre, is given by the following formula :

$$\frac{b}{a}$$

where

a is the volume, in millilitres, of CDTA solution used for the titration of the aliquot of the standard magnesium solution (3.21);

b is the mass, in milligrams, of magnesium contained in the aliquot of the standard magnesium solution (3.21) used for the titration.

3.24 CDTA, standard solution 0,01 M.

3.24.1 *Preparation of the solution*

Prepare a 0,01 M solution according to the method indicated in 3.23.1, using, however, 3,5 g of CDTA and about 5 ml of sodium hydroxide solution (3.8).

3.24.2 *Standardization of the solution*

Proceed as indicated in 3.23.2, using, however, a 30,0 ml aliquot of standard magnesium solution (3.22), containing 6,0 mg of magnesium, and titrating with CDTA solution (3.24.1).

3.24.3 *Calculation*

Proceed as indicated in 3.23.3.

3.25 Indicator

Mix 0,1 g of methyl-thymol blue (sodium salt of 3,3′ bis (NN′-dicarboxy-methyl)-aminomethyl-thymol-sulphonphthalein) with 10 g of sodium chloride. Use 0,05 to 0,1 g of the mixture for the titration.

4 APPARATUS

Ordinary laboratory apparatus.

NOTE – All volumetric vessels shall be checked according to the official standards.

4.1 pH meter

5 SAMPLING

5.1 Laboratory sample[1]

5.2 Test sample

Chips of thickness less than or equal to 1 mm obtained by drilling or milling.

6 PROCEDURE

6.1 Test portion

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

6.2 Blank test

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

6.3 Determination

6.3.1 *Preparation of the test solution*

Place the test portion in a beaker of suitable capacity (for example, 400 ml), and cover with a watch glass. Add about 50 ml of water and, in small amounts, cooling if necessary, 50 ml of hydrochloric acid (3.2). When the reaction subsides, heat gently to assist the attack and add 10 ml of nitric acid solution (3.5). Heat, without boiling, until the release of hydrogen ceases, then boil gently for about 10 min. Rinse the walls of the beaker and watch glass with hot water, collecting the washings in the same beaker; dilute to about 150 to 200 ml with hot water and filter (see Note 8.1) on a close-texture filter containing a little moistened filter paper. Wash carefully eight to ten times both the filter and the residue with hot hydrochloric acid (3.4), collecting the filtrate and washings in a beaker of suitable capacity (400 ml, for example). If there is considerable residue, place the filter and residue in a platinum crucible, dry in an oven having a natural draught (temperature about 120 °C), then ignite carefully until combustion of the filter is complete (the temperature must not exceed 550 °C), taking care that the filter paper does not catch alight (to avoid loss of magnesium). After cooling, place in the crucible 5 ml of hydrofluoric acid (3.7), 2 ml of sulphuric acid (3.6) and finally, drop by drop, nitric acid (3.5) until a perfectly clear solution is obtained. Evaporate this solution until complete elimination of the white sulphuric acid fumes and then heat for 10 min (the temperature must not exceed 700 °C). Allow to cool, take up with a few millilitres of hot water and 1 to 2 ml of hydrochloric acid (3.2). Heat gently, filter if necessary and add the solution obtained to the test solution. If the presumed magnesium content is equal to or less than 1,5 %, carry out the determination on the whole of the test solution, concentrating this to about 100 ml.

If the presumed magnesium content is greater than 1,5 %, transfer the test solution quantitatively to a 200 ml volumetric flask, make up to volume and mix. Take an aliquot of the test solution, in accordance with the following table, and place in a beaker of suitable capacity (for example, 250 ml).

Presumed magnesium content	Volume of the test solution	Volume of aliquot to be taken	Corresponding mass of test portion	Presumed corresponding mass of magnesium
%	ml	ml	g	mg
0,1 to 1,5	about 100	total	2	2 to 30
1,5 to 3,5	200,0	100,0	1	15 to 35
3,5 to 7	200,0	50,0	0,5	17,5 to 35
7 to 12	200,0	25,0	0,25	17,5 to 30

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[1] The International Standard relating to sampling from supplies will be studied as soon as Technical Committee ISO/TC 69, *Applications of statistical methods*, has specified the general principles to be followed.

6.3.2 *Separation of magnesium and other hydroxides*

Adjust the volume of the test solution to about 100 ml (for magnesium contents 0,1 to 1,5 %), or the volume of the aliquot taken (for magnesium contents greater than 1,5 %), add 5,0 ml of iron(III) chloride solution (3.13) and mix. Transfer the solution quantitatively and slowly, while stirring, to a beaker of about 400 ml capacity containing 70 ml (or 100 ml if the whole of the test solution is used) of sodium hydroxide solution (3.8). Use the smallest possible quantity of lukewarm water for washing. Mix carefully, add 2 ml (3 ml if the whole of the test solution is used) of hydrogen peroxide solution (3.14) then boil for 5 to 10 min. Remove the source of heat, add 5 ml (7,5 ml if the whole of the test solution is used) of potassium cyanide solution (3.15) then boil gently for 5 min. Dilute, if necessary, to about 200 ml (about 270 ml if the whole of the test solution is used) with hot water, cover the beaker with a watch glass and keep it hot, without allowing it to boil, for 20 min. Add a little moistened filter paper and mix. Then filter through a close-texture filter paper and wash the residue and filter carefully five times with hot sodium hydroxide solution (3.9). Retain the beaker.

NOTE – Add 3 g of iron(II) sulphate to the filtrate, mix well and discard.

6.3.3 *Dissolution of the residue*

Open the filter over the beaker which has been used for the separation of magnesium and other hydroxides and transfer the greatest possible quantity of the residue into the beaker with the aid of a jet of hot water. Wash the filter with a hot mixture of 50 ml of hydrochloric acid (3.3) and 2 ml of hydroxylammonium chloride solution (3.16) then complete the washing with hot water, taking care to achieve a final volume as small as possible (less than 80 ml). Heat to complete the dissolution of the residue, filter through a medium-texture filter, wash the filter and the beaker first with hot water then with hot hydrochloric acid (3.4), collecting the filtrate and the washings in a beaker of suitable capacity (for example, 400 ml). If necessary, concentrate the solution a little. Add bromine water (3.17) in small portions until there is a persistent bromine colour, then add 3 ml in excess. Boil to remove excess of bromine water, adjust the volume of the solution to about 70 ml and cool to room temperature.

6.3.4 *Precipitation of hydroxides*

The operation described in this clause shall be carried out without interruption.

With the aid of a pH meter, adjust the pH value of the solution to 4,4 ± 0,2 using first ammonia solution (3.11) (up to approximately pH 4), followed by ammonia solution (3.12) (pH value 4,4 ± 0,2). Mix, heat to boiling, remove the source of heat, add 0,3 g of zinc oxide (3.1) and mix carefully (see Note 8.2). Add potassium permanganate solution (3.18) drop by drop until a persistent pink colour is obtained. Heat until boiling commences, remove the source of heat and add 2 ml of ethanol (3.19). Mix carefully, cover the beaker with a watch glass and allow to stand on a boiling water bath. After 5 min, add a further 2 ml of ethanol (3.19), mix and allow to stand on a boiling water bath for 10 min. Add a little moistened filter paper and mix. Filter through a close-texture filter, wash the filter and residue eight times with hot water and collect the filtrate and washings in a beaker of suitable capacity (600 ml, for example). Discard the filter and residue.

6.3.5 *Titration*

Adjust the volume of the solution to about 250 ml, cool to room temperature and make slightly alkaline with ammonia solution (3.11). If the solution is colourless, add 8 ml of potassium cyanide solution (3.15). If, on the other hand, the solution is coloured blue, add potassium cyanide solution (3.15) drop by drop, while stirring, until the solution is decolourized, then add 8 ml of the same cyanide solution (3.15) in excess. Add 1 ml of EGTA solution (3.20) (see Note 8.3), 100 ml of ammonia solution (3.10) and about 0,05 to 0,1 g of indicator (3.25). Stir the solution (preferably with a mechanical stirrer) and titrate with CDTA solution (3.24) if the presumed magnesium content is equal to or less than 0,5 %, or with CDTA solution (3.23) if the presumed magnesium content is greater than 0,5 %. Continue the titration until the colour of the indicator changes from blue to pale grey (practically colourless). This colouration must not vary on addition of two drops in excess of CDTA solution.

7 EXPRESSION OF RESULTS

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

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

where

V is the volume, in millilitres, of CDTA solution (3.23 or 3.24) used for the titration of the magnesium in the test solution or in the aliquot taken for the determination;

V_1 is the volume, in millilitres, of CDTA solution (3.23 or 3.24) used for the titration of magnesium in a similar volume of the blank test solution (6.2);

t is the strength, expressed in milligrams of magnesium per millilitre (3.23.3 or 3.24.3), of CDTA solution (3.23 or 3.24);

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

m is the mass, in grams, of the test portion.

8 NOTES

8.1 If the test solution is perfectly clear, it is not necessary to filter.

8.2 0,3 g of zinc oxide (ZnO) may be mixed with a very small quantity of water and the resultant paste added quantitatively to the test solution.

8.3 EGTA will effectively mask any manganese which may not have been precipitated by means of the zinc oxide. Tests have shown that only fractions of milligrams of manganese can be present in the filtrate; the quantity of EGTA solution used can neutralize the action of 3 to 4 mg of manganese.

9 TEST REPORT

The test report shall include the following information :

a) the reference of the method used;

b) the results, as well as the form in which they are expressed;

c) any particular details noted in the course of the test;

d) any operations not specified in this International Standard, or any optional operations which may have affected the results.

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