International Standard ISO 5196/2

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Magnesium alloys — Determination of thorium — Part 2 : Titrimetric method

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Foreword

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It has been approved by the member bodies of the following countries :

Australia	Hungary	Romania
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Magnesium alloys — Determination of thorium — Part 2 : Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of thorium in magnesium alloys which do not contain silver.

The method is applicable to products having thorium contents between 0,2 and 5,0 % (m/m).

2 Principle

Dissolution of a test portion in hydrochloric acid. Formation of complexes of iron and cerium by the addition of hydroxylammonium chloride. Formation of a zirconium complex by addition, at approximately 90 °C, of EDTA solution, using xylenol orange as indicator.

Titration of the thorium, at approximately 90 °C in buffered medium, against EDTA solution using xylenol orange as indicator.

3 Reagents

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

3.1 Hydrochloric acid (ϱ approximately 1,1 g/ml), 20 % (m/m) or approximately 6 mol/l solution.

Dilute 500 ml of hydrochloric acid (ϱ approximately 1,19 g/ml), approximately 12 mol/l solution, with water, make up the volume to 1 000 ml and mix.

3.2 Hydrochloric acid (ϱ approximately 1,0 g/ml), approximately 0,005 mol/l solution.

Dilute 5 ml of hydrochloric acid (ϱ approximately 1,19 g/ml), approximately 12 mol/l solution, with water, make up the volume to 1 000 ml and mix.

3.3 Hydroxylammonium chloride, 100 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH.HCl$) in water, make up the volume to 100 ml and mix.

3.4 Ammonium hydroxide solution (ϱ approximately 0,91 g/ml).

3.5 Ammonium hydroxide solution (ϱ approximately 0,98 g/ml).

Dilute 200 ml of the ammonium hydroxide solution (3.4) with water, make up the volume to 1 000 ml and mix.

3.6 Buffer solution

Add 80 ml of approximately 0,25 mol/l [2 % (V/V)] hydrochloric acid solution to 500 ml of 15 g/l potassium chloride solution.

3.7 Zirconium, 0,5 g/l standard solution.

3.7.1 Preparation of the solution

Prepare the solution using one of the following methods.

3.7.1.1 Weigh, to the nearest 0,001 g, 0,500 g of pure zirconium [content ⩾ 99,9 % (m/m)] and place it in a dry beaker. Add 30 ml of methanol and, while cooling, 5 ml of bromine. When the reaction has stopped, heat moderately to complete the attack. Add 40 ml of the hydrochloric acid solution (3.1), bring to the boil and boil until a colourless solution is obtained, maintaining the volume of the solution at approximately 50 ml by adding water.

Cool, transfer, with washing, into a 1 000 ml one-mark volumetric flask and make up to the mark.

3.7.1.2 Dissolve 1,77 g of zirconium oxychloride ($ZrOCl_2.8H_2O$)[1] in water, add 20 ml of the hydrochloric acid solution (3.1), filter and make up the volume to 1 000 ml.

1) The zirconium oxychloride to be used shall not be damp. However, there can be no provision for drying the product in a drying stove, because part of it could change into a form which, while being soluble and able to be determined gravimetrically (see 3.7.2), reacts very slowly with the EDTA.

3.7.2 Calibration of the solution

Calibrate the solution using one of the following methods.

3.7.2.1 Gravimetric method using mandelic acid

Transfer 100 ml of the standard zirconium solution (3.7.1) to a 250 ml beaker. Add approximately 40 ml of water and 60 ml of the hydrochloric acid solution (3.1). Bring to the boil and add 50 ml of 150 g/l mandelic acid solution.

Maintain at approximately 80 °C for 20 min. Allow to cool, then filter through a medium textured filter paper. Wash with a solution containing 40 ml per litre of the hydrochloric acid solution (3.1) and 50 g of mandelic acid per litre. Place the filter in a pre-weighed platinum crucible. Dry, calcine with care at a temperature between 950 and 1 000 °C to constant mass and weigh the zirconium oxide (ZrO_2).

The zirconium content (Zr) of the standard solution, expressed in milligrams per millilitre, is given by the formula :

$$\frac{m \times 0{,}740\ 3}{V}$$

where

m is the mass, in milligrams, of zirconium oxide obtained;

V is the volume, in millilitres, of the standard zirconium solution used for the determination;

0,740 3 is the conversion factor from ZrO_2 to Zr.

3.7.2.2 Gravimetric determination using *p*-bromomandelic acid

Transfer 100 ml of the standard zirconium solution (3.7.1) to a 250 ml beaker and add approximately 70 ml of water. Heat to approximately 80 °C and add slowly, while stirring, 50 ml of 0,1 mol/l *p*-bromomandelic acid solution which has been heated beforehand to approximately 80 °C.

Maintain at approximately 80 °C for 20 min. Check whether the precipitation is complete by adding 2 or 3 ml of 0,1 mol/l bromomandelic acid solution. Cool to ambient temperature, stirring constantly. Filter through medium textured filter paper. Wash carefully with water. Put the filter paper into a pre-weighed platinum crucible. Dry, calcine with care at a temperature between 950 and 1 000 °C to constant mass and weigh the zirconium oxide (ZrO_2).

The zirconium (Zr) content of the standard solution, expressed in milligrams per millilitre, is given by the formula :

$$\frac{m \times 0{,}740\ 3}{V}$$

where

m is the mass, in milligrams, of zirconium oxide obtained;

V is the volume, in millilitres, of the standard zirconium solution used for the determination;

0,740 3 is the conversion factor from ZrO_2 to Zr.

3.8 Disodium ethylene diamine tetraacetate (EDTA), 0,01 mol/l standard volumetric solution.

3.8.1 Preparation of the solution

Dissolve approximately 3,75 g of EDTA in water, filter if necessary and make up the volume to 1 000 ml. Keep in a plastics bottle.

3.8.2 Calibration of the solution

Weigh, to the nearest 0,001 g, 1 g of very pure magnesium, and place it in a 400 ml beaker. Add 15 ml of water, cover the beaker with a watch glass, and then add in small amounts, and with care, 30 ml of the hydrochloric acid solution (3.1). When the reaction has stopped, add 10 ml of the standard zirconium solution (3.7). Bring to the boil and boil for exactly 5 min leaving the beaker covered.

Add 30 ml of hydroxylammonium chloride solution (3.3) and make up the volume of the solution to approximately 200 ml by adding hot water. Bring to a slow boil and add 1 ml of the xylenol orange solution (3.9). Boil for 2 to 3 min.

Titrate with the EDTA solution (3.8.1) until the indicator turns from red to yellow, maintaining the temperature at a minimum of 85 °C. Use the stirrer (4.2) and regulate the hotplate to 90 °C in order to better observe the end point of the colour change.

This colour shall not vary after the solution has been brought to the boil again.

3.8.3 Calculation

The correction factor corresponding to the fact that the concentration of the solution is not exactly 0,01 mol/l, is given by the formula

$$\frac{5{,}49}{V}$$

where

V is the volume, in millilitres, of EDTA solution (3.8) used for titration against 10,0 ml of the standard zirconium solution (3.7);

5,49 is the volume, in millilitres, of 0,01 mol/l EDTA solution (theoretical value : 1 ml ≡ 0,91 mg zirconium) necessary for titration against 5,0 mg Zr (5,0 : 0,91 = 5,494 5).

3.9 Xylenol orange, 1 g/l solution.

Dissolve 0,1 g of xylenol orange in water, make up the volume to 100 ml and mix.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 pH meter.

4.2 Mechanical or magnetic stirrer, equipped with a hotplate.

5 Sampling

5.1 Laboratory sample[1)]

5.2 Test sample

Chips having a thickness no greater than 1 mm, obtained by milling or drilling the laboratory sample.

6 Procedure

6.1 Test portion

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

6.2 Blank determination

Simultaneously with the determination, carry out a blank determination following the same procedure and using the same reagents as used for the determination, but reducing the quantity of hydrochloric acid (3.1) used to 15 ml.

6.3 Determination

6.3.1 Preparation of the test solution

Place the test portion (6.1) in a 400 ml beaker. Add 15 ml of water, cover the beaker with a watch glass, and then add in small amounts and with care, 30 ml of the hydrochloric acid solution (3.1). When the reaction has stopped, bring to the boil and boil for exactly 5 min, still keeping the beaker covered. If there is a residue, filter through a medium textured filter paper, wash the beaker and the residue with hot hydrochloric acid solution (3.2), adding the washings to the test solution (discard the residue).

6.3.2 Complexing

Add 30 ml of the hydroxylammonium chloride solution (3.3) and bring the volume of the solution to approximately 200 ml by adding hot water. Bring to a slow boil and add 1 ml of the xylenol orange solution (3.9). Boil for 2 or 3 min.

Maintain the temperature of the solution at a minimum of 85 °C and complex the zirconium by adding the EDTA solution (3.8) very slowly until the indicator turns from red to yellow. Use the stirrer (4.2) and regulate the hotplate to 90 °C in order to better observe the end point of the colour change.

This colour shall not vary after the solution has been brought to the boil again.

6.3.3 Titration of thorium

Cool and add the ammonium hydroxide solution (3.4), stirring mechanically, until the indicator starts to change colour. Using the pH meter (4.1) as the means of control, adjust the pH of the solution to 1,6 by adding the ammonium hydroxide solution (3.5).

Then add 10 ml of the buffer solution (3.6) in order to restore the red colour of the indicator. Bring to the boil and immediately titrate the thorium by adding, very slowly, the standard EDTA solution (3.8) until the indicator turns from red to yellow. During titration the temperature of the solution shall be maintained at a minimum of 85 °C. Use the stirrer (4.2) and regulate the hotplate to 90 °C in order to better observe the end point of the colour change.

This colour shall not alter when two drops of EDTA solution in excess are added.

7 Expression of results

The thorium (Th) content, expressed as a percentage by mass, is given by the formula

$$\frac{(V - V_1) \times f \times 2{,}32}{10 \times m}$$

where

V is the volume, in millilitres, of EDTA solution (3.8) used for the titration of thorium in the test portion;

V_1 is the volume, in millilitres, of EDTA solution (3.8) used for the titration of thorium in the blank determination;

f is the correction factor (see 3.8.3) for the EDTA solution (3.8);

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

2,32 is the mass, in milligrams, of thorium which corresponds to 1 ml of exactly 0,01 mol/l EDTA solution.

8 Test report

The test report shall include the following information :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noticed during the determination;

d) any operations not included in this International Standard, or regarded as optional.

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

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