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Magnesium alloys — Determination of insoluble zirconium — Alizarin sulphonate photometric method

Alliages de magnésium — Dosage du zirconium insoluble — Méthode photométrique à l'alizarine sulfonate

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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.

ISO 2354 was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.* This second edition contains the note, added at the end of clause 1, which was circulated in November 1975, in the form of an Addendum, directly to the ISO Council, in accordance with clause 6.12.1 of the Directives for the technical work of ISO.

This second edition cancels and replaces the first edition (i.e. ISO 2354-1972), which had been approved by the Member Bodies of the following countries :

Austria	Ireland	South Africa, Rep. of
Belgium	Israel	Spain
Canada	Italy	Sweden
Egypt, Arab Rep. of	Japan	Switzerland
Finland	Netherlands	Thailand
France	New Zealand	United Kingdom
Germany	Norway	U.S.A.
India	Poland	U.S.S.R.

No Member Body had expressed disapproval of the document .

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Magnesium alloys — Determination of insoluble zirconium — Alizarin sulphonate photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an alizarin sulphonate photometric method for the determination of insoluble zirconium in magnesium alloys containing zirconium as an alloying element.

Rare earths, thorium and silver do not interfere.

The method is applicable to alloys having insoluble zirconium contents between 0,02 and 0,3 % (*m/m*).

NOTE — Hafnium which is normally present in conjunction with zirconium (up to 1 % zirconium) will be determined with zirconium.

2 PRINCIPLE

Hydrochloric acid attack (the normality of the hydrochloric acid and the length of the attack have been conventionally fixed).

Filtration, dissolution of the insoluble residue in perchloric acid in the presence of hydrofluoric acid, and taking of an aliquot.

Formation, when hot, of the zirconium-alizarin sulphonate complex, in 1,5 N hydrochloric medium.

Photometric measurement of the coloured complex at a wavelength of about 525 nm.

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 1,18 g/ml, about 37 % (*m/m*) solution, or approximately 12 N.

3.2 Hydrofluoric acid, approximately 40 % (*m/m*) solution.

3.3 Perchloric acid, ρ approximately 1,54 g/ml, about 60 % (*m/m*) solution.

3.4 Sodium alizarin sulphonate, 1,5 g/l solution.

Dissolve 1,5 g of sodium alizarin sulphonate in about 300 ml of warm water, filter, cool, make up the volume to 1 000 ml and mix.

3.5 Magnesium chloride, 420 g/l solution.

Dissolve 42 g of magnesium chloride hexahydrate ($MgCl_2.6H_2O$) in water, make up the volume to 100 ml and mix.

This solution contains 50 g of magnesium per litre.

3.6 Zirconium, 5 g/l standard solution.

Prepare this solution according to one of the following procedures :

3.6.1 Weigh, to the nearest 0,001 g, 0,500 g of pure zirconium (purity ⩾ 99,9 %) and transfer to a dry beaker. Add 30 ml of methanol and, while cooling, 5 ml of bromine. When the reaction has ceased, heat gently to complete the attack. Add 20 ml of the hydrochloric acid (3.1), heat to boiling and continue boiling until a colourless solution is obtained, maintaining the volume of the solution at approximately 50 ml by adding water.

Cool, transfer quantitatively to a 100 ml volumetric flask, make up to volume and mix.

3.6.2 Disslove 1,77 g of zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) in water, add 10 ml of the hydrochloric acid (3.1), filter, make up the volume to 100 ml and mix.

NOTE — The zirconium oxychloride used shall not be moist. However, it is not possible to dry the product in an oven, as part of it could be transformed into a form which, although soluble and able to be determined by a gravimetric method (see *"Standardization of the solution"*), reacts very slowly with alizarin S.

Standardization of the solution 3.6.2. Use one of the following procedures :

a) GRAVIMETRIC DETERMINATION WITH MANDELIC ACID

Transfer 10,0 ml of the standard zirconium solution (3.6.2) to a beaker of suitable capacity (for example 250 ml). Dilute to about 40 ml and add 30 ml of the hydrochloric acid (3.1). Boil and add 50 ml of 150 g/l mandelic acid solution.

Allow to stand at 80 °C for about 20 min. Allow to cool, then filter through a medium texture filter paper. Wash with a solution containing 20 ml of the

hydrochloric acid solution (3.1) per litre and 50 g of mandelic acid per litre. Transfer the filter to a previously weighed platinum crucible. Dry, carefully ignite to constant mass at a temperature between 950 and 1 000 °C, and weigh the zirconium oxide (ZrO_2).

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

$$\frac{m_1 \times 0{,}740\,3}{V}$$

where

m_1 is the mass, in milligrams, of zirconium oxide weighed;

V is the volume, in millilitres, of the standard zirconium solution (3.6.2) taken for the determination;

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

b) GRAVIMETRIC DETERMINATION WITH *p*-BROMOMANDELIC ACID

Transfer 10,0 ml of the standard zirconium solution (3.6.2) to a beaker of suitable size (for example 250 ml). Dilute to approximately 70 ml. Heat to approximately 80 °C and slowly add, while stirring, 50 ml of a 0,1 M *p*-bromomandelic acid solution, previously heated to approximately 80 °C. Allow to stand at approximately 80 °C for 20 min. Check whether precipitation is complete by adding 2 or 3 ml of the 0,1 M *p*-bromomandelic acid solution. Cool to ambient temperature, stirring constantly, then filter through a medium texture filter paper. Carefully wash with water. Transfer the filter paper to a previously weighed platinum crucible. Dry, carefully ignite to constant mass at a temperature between 950 and 1 000 °C and weigh the zirconium oxide (ZrO_2).

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

$$\frac{m_2 \times 0{,}740\,3}{V}$$

where

m_2 is the mass, in milligrams, of zirconium oxide weighed;

V is the volume, in millilitres, of the standard zirconium solution (3.6.2) taken for the determination;

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

3.7 Zirconium, 0,100 g/l standard solution.

According to the concentration of the standard zirconium solution prepared as specified in 3.6, take an appropriate aliquot and dilute in a volumetric flask so as to obtain a solution containing exactly 0,100 g of zirconium per litre.

1 ml of this solution contains 0,1 mg of zirconium.

Prepare this standard solution immediately before use.

4 APPARATUS

Ordinary laboratory apparatus, and

4.1 Spectrophotometer, or

4.2 Photoelectric absorptiometer.

5 SAMPLING

5.1 Laboratory sample[1)]

5.2 Test sample

Chips not more than 1 mm thick, obtained by drilling or milling.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,001 g, 6 g of the test sample (5.2) for soluble zirconium contents between 0,1 and 0,3 % (*m/m*), or 4 g for soluble zirconium contents between 0,3 and 1,0 % (*m/m*).

6.2 Blank test

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

6.3 Preparation of the calibration curve

6.3.1 *Preparation of the standard matching solutions* related to photometric measurements carried out with an optical path of 1 cm.

Introduce into each of nine thoroughly dry conical flasks of suitable capacity (for example 100 ml), 2 ml of the magnesium chloride solution (3.5), containing 0,1 g of

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

magnesium, and then the respective volumes of the standard zirconium solution (3.7) indicated in table 1.

TABLE 1

Volume of standard zirconium solution (3.7)	Corresponding mass of zirconium (Zr)
ml	mg
0*	0
1,0	0,1
2,0	0,2
3,0	0,3
4,0	0,4
5,0	0,5
6,0	0,6
7,0	0,7
8,0	0,8

* Compensation solution.

Then add to each flask the quantity of water necessary to make 10,0 ml, and add 2,5 ml of the hydrochloric acid (3.1) and 10,0 ml of the sodium alizarin sulphonate solution (3.4). Place the conical flasks containing the solutions in a boiling water bath and maintain in the boiling water for 2,5 to 3,5 min, taking care to avoid overheating. Quickly cool to ambient temperature and add to each flask 2,0 ml of the hydrochloric acid (3.1). Transfer quantitatively to 100 ml volumetric flasks, make up to volume and mix.

6.3.2 *Photometric measurements*

Measure the absorbance of each solution (6.3.1) within 1 h, using the spectrophotometer (4.1) at the maximum of the absorption curve (wavelength approximately 525 nm), or with the photoelectric absorptiometer (4.2) fitted with suitable filters, after having adjusted the instrument to zero absorbance against the compensation solution.

6.3.3 *Plotting of the calibration chart*

Plot a graph having, for example, the amounts of zirconium, expressed in milligrams, contained in 100 ml of standard matching solution as abscissae, and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 *Attack of the test portion*

Introduce the test portion (6.1) into a beaker of suitable capacity (for example 600 ml), cover with a watch glass and add the following quantities of reagent according to the mass of the test portion used :

— 4 g test portion : 80 ml of water and 40 ml of the hydrochloric acid (3.1) in small portions;

— 6 g test portion : 120 ml of water and 60 ml of the hydrochloric acid (3.1) in small portions.

When the reaction has ceased[1], heat to boiling and continue boiling for exactly 5 min. Filter the solution on a medium texture filter paper and wash thoroughly with hot water.

NOTE — For this determination, the residue from the filtration described in 6.4.1 of ISO 1178, *Magnesium alloys — Determination of soluble zirconium — Alizarin sulphonate photometric method*, may be used.

6.4.2 *Preparation of the test solution*

Transfer the filter paper, containing the residue, to a platinum vessel of suitable capacity (for example 40 ml). Dry carefully, then ignite at a temperature between 600 and 800 °C to remove the carbon completely. Allow to cool, add 5 ml of water, 1 ml of the hydrochloric acid (3.2) and 2 ml of the perchloric acid (3.3). Carefully evaporate the contents of the vessel almost to dryness and allow to cool. Wash the walls of the vessel with a little water and add a further 2 ml of the perchloric acid (3.3). Carefully evaporate almost to dryness.

NOTE — If, by mischance, the contents of the crucible have been brought to complete dryness, add 2 ml of water and 1 ml of the hydrochloric acid (3.1) and heat for a few minutes before continuing the operations.

6.4.2.1 ALLOYS NOT CONTAINING SILVER

Transfer the contents of the crucible quantitatively to a 100 ml volumetric flask, carefully washing with water. Make up to volume and mix.

6.4.2.2 ALLOYS CONTAINING SILVER

Transfer the contents of the crucible quantitatively to a beaker of suitable capacity (for example 250 ml), washing carefully with water. Add 15 ml of the hydrochloric acid (3.1) and boil for a few minutes. Add 50 ml of water and boil again to assist the coagulation of the silver chloride. Allow to cool to room temperature and filter through a fine texture filter paper containing a little cellulose pulp. Wash the precipitate and the filter with water, collecting the filtrate and the washings in a 100 ml volumetric flask. Make up to volume and mix.

1) When lead and/or bismuth are present in the alloy it is advisable to take these into solution by oxidation with hydrogen peroxide. To do this, add, when the reaction has ceased, 1 ml of hydrogen peroxide, ρ approximately 1,12 g/ml, about 36 % (m/m) solution, and allow to stand for 10 min. Continue as in the general cases, heating to boiling and continuing to boil for exactly 5 min.

6.4.3 *Development of the colour*

In accordance with the expected content of insoluble zirconium and the type of alloy under examination, take the aliquot of the test solution, obtained according to 6.4.2.1 or 6.4.2.2, indicated in table 2. Transfer to a thoroughly dried conical flask of suitable capacity (for example 100 ml), and add the quantity of water necessary to bring the volume to 10,0 ml. Then add the quantity of hydrochloric acid indicated in table 2.

TABLE 2

Expected content of insoluble zirconium	Volume of the aliquot of the test solution	Volume of hydrochloric acid (3.1)	
		Test solution 6.4.2.1	Test solution 6.4.2.2
% (*m*/*m*)	ml	ml	ml
from 0,02 to 0,15	10,0	2,5	1,0
from 0,1 to 0,3	5,0	2,5	1,75

Add 10,0 ml of the sodium alizarin sulphonate solution (3.4). Place the conical flask in a boiling water bath and maintain in the boiling water for 2,5 to 3,5 min, taking care to avoid overheating. Quickly cool to ambient temperature and then add to the flask 2,0 ml of the hydrochloric acid (3.1). Transfer quantitatively to a 100 ml volumetric flask, make up to volume and mix.

6.4.4 *Photometric measurements*

Measure the absorbance of the test solution within 1 h in accordance with the procedure described in 6.3.2, after having adjusted the instrument to zero absorbance against the blank test solution.

7 EXPRESSION OF RESULTS

By means of the calibration curve (see 6.3.3), determine the quantity of zirconium corresponding to the value of the photometric measurement.

The zirconium (Zr) content is given, as a percentage by mass, by the following formulae :

with 10,0 ml of the test solution (6.4.2)

$$\frac{m_3}{m_0}$$

with 5,0 ml of the test solution (6.4.2)

$$\frac{m_3 \times 2}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_3 is the mass, in milligrams, of zirconium found in the aliquot of the test solution.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

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

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