INTERNATIONAL STANDARD 1178

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

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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, International Standard ISO 1178 replaces ISO Recommendation R 1178-1970 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

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

The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

France

Printed in Switzerland

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

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an alizarin sulphonate photometric method for the determination of soluble zirconium in magnesium alloys containing zirconium as an alloying element. Rare earths, thorium and silver do not interfere.

The method is applicable to the determination of zirconium content between 0,1 and 1,0 %.

The method does not apply completely to the special case of alloys containing lead and/or bismuth, for which it should be modified as described in the Annex.

2 PRINCIPLE

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

Removal, by filtration, of the insoluble residue 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 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 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.

3.3 Magnesium chloride, 420 g/l solution.

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

3.4 Zirconium, 5 g/l standard solution.

Prepare this solution according to one of the following procedures :

3.4.1 Weigh, to the nearest 0,001 g, 0,500 g of pure zirconium (≥ 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 and transfer quantitatively to a 100 ml volumetric flask, make up to volume and mix.

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

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 3.4.2. Use one of the following procedures :

a) GRAVIMETRIC DETERMINATION WITH MANDELIC ACID.

Transfer 10,0 ml of zirconium standard solution (3.4.2) 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 mandelic acid solution 150 g/l.

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 (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 weighed zirconium oxide;

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

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

b) GRAVIMETRIC DETERMINATION WITH *p*-BROMOMANDELIC ACID

Take 10,0 ml of the zirconium standard solution (3.4.2) and place in a beaker of suitable capacity (for example 250 ml). Dilute to approximately 70 ml. Heat to approximately 80 °C and slowly add, while shaking, 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, shaking constantly, then filter through a medium texture filter paper. Carefully wash with water. Place the filter in 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 weighed zirconium oxide;

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

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

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

According to the concentration of the standard zirconium solution prepared as specified in 3.4, 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 just before use.

4 APPARATUS

4.1 Ordinary laboratory equipment.

4.2 Spectrophotometer or

4.3 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 zirconium contents between 0,1 and 0,3 % or 4 g for zirconium contents between 0,3 and 1,0 %.

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 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 (3.3), containing 0,1 g of magnesium, and then the volumes of the zirconium standard solution (3.5) indicated in the following table :

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

Volume of zirconium standard solution (3.5)	Corresponding mass of zirconium
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 a sufficient quantity of water 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 (3.2). 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 any 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*

Carry out the photometric measurements within 1 h, using the spectrophotometer (4.2) at the maximum of the absorption curve (wavelength approximately 525 nm), or with the photoelectric absorptiometer (4.3) 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 *Preparation of the test solution*

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, 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, collecting the filtrate and the washings in a 500 ml volumetric flask. Cool, make up to volume and mix.

NOTE – In order to avoid hydrolysis of weak acid solutions of zirconium, it is necessary to carry out the determination immediately after the preparation of the test solution.

The residue may be used for the determination of the insoluble zirconium (International Standard ISO 2354-1972).

6.4.2 *Development of the colour*

Transfer 10,0 ml of the test solution (6.4.1) to a thoroughly dry conical flask of suitable capacity (for example 100 ml). Add 2,5 ml of the hydrochloric acid (3.1) and 10,0 ml of the sodium alizarin sulphonate solution (3.2). 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 any 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.

6.4.3 *Photometric measurements*

Carry out the photometric measurement within 1 h according to 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.

Calculate the zirconium content, as a percentage by mass, by the formula

$$\text{Zr } \%\ (m/m) = \frac{m_1 \times 5}{m_0}$$

where

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

m_1 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.

ANNEX

SPECIAL CASE OF MAGNESIUM ALLOYS CONTAINING LEAD AND/OR BISMUTH

A.1 PRINCIPLE

Taking into solution the lead and/or bismuth by hydrogen peroxide oxidation during the attack. Determination according to the general method.

A.2 MODIFICATIONS TO THE GENERAL METHOD

A.2.1 Reagents

In addition to the reagents listed in clause 3,

Hydrogen peroxide, ρ approximately 1,12 g/ml, approximately 36 % (*m/m*) solution.

A.2.2 Determination

Replace 6.4.1 with the following :

Preparation of the test solution

Introduce the test portion 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, add 1 ml of the hydrogen peroxide (A.2.1) and allow to stand for 10 min. Heat to boiling and continue boiling for exactly 5 min.

ALLOYS FREE FROM SILVER

Filter the solution on a medium texture filter paper and wash thoroughly with hot water, collecting the filtrate and the washings in a 500 ml volumetric flask. Cool, make up to volume and mix.

ALLOYS CONTAINING SILVER

Add 50 ml of water and boil again for a few minutes to coagulate the silver chloride. Allow to cool to room temperature and filter the solution on a fine texture filter containing some paper pulp. Wash thoroughly with cold water, collecting the filtrate and the washings in a 500 ml volumetric flask. Make up to volume and mix.

NOTE — In order to avoid hydrolysis of weak acid solutions of zirconium, it is necessary to carry out the determination immediately after the preparation of the test solution.

The residue may be used for the determination of the insoluble zirconium (International Standard ISO 2354-1972).