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ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

**ISO RECOMMENDATION
R 1178**

CHEMICAL ANALYSIS OF MAGNESIUM AND ITS ALLOYS

**DETERMINATION OF SOLUBLE ZIRCONIUM
(ALIZARIN SULPHONATE PHOTOMETRIC METHOD)**

1st EDITION

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BRIEF HISTORY

The ISO Recommendation R 1178, *Chemical analysis of magnesium and its alloys – Determination of soluble zirconium (Alizarin sulphonate photometric 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 a Draft ISO Recommendation.

In December 1968, this Draft ISO Recommendation (No. 1750) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

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

One Member Body opposed the approval of the Draft :

France

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in January 1970, to accept it as an ISO RECOMMENDATION.

CHEMICAL ANALYSIS OF MAGNESIUM AND ITS ALLOYS

DETERMINATION OF SOLUBLE ZIRCONIUM

(ALIZARIN SULPHONATE PHOTOMETRIC METHOD)

1. SCOPE

This ISO Recommendation describes 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 contents between 0.1 and 1.0 %.

However, the method does not apply completely to the case of alloys containing lead and/or bismuth, for which it must be modified as indicated in the Annex.

2. PRINCIPLE

- 2.1 Hydrochloric acid attack (the normality of the hydrochloric acid solution and the length of the attack have been conventionally fixed).
- 2.2 Removal, by filtration, of the insoluble residue and taking of an aliquot.
- 2.3 Formation, when hot, of the zirconium-alizarin sulphonate complex, in 1.5 N hydrochloric medium.
- 2.4 Photometric measurement of the coloured complex at a wavelength of about 525 nm.

3. REAGENTS

3.1 *Hydrochloric acid* ($d =$ approximately 1.18), 37 % (m/m), or approximately 12 N.

3.2 *Sodium alizarin sulphonate solution*, 1.5 g/l.

Dissolve 1.5 g of sodium alizarin sulphonate in about 300 ml of warm water, filter, cool and make up the volume to 1000 ml.

3.3 *Magnesium chloride solution*, 420 g/l.

Dissolve 42 g of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in water and make up the volume to 100 ml.

3.4 *Zirconium, standard solution*, 5 g/l.

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 ($\geq 99.9\%$) 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 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 and make up to volume.

3.4.2 Dissolve 1.77 g of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$)* in water, add 10 ml of hydrochloric acid (3.1), filter and make up the volume to 100 ml.

Standardization of the solution 3.4.2. Use one of the following procedures :

- (a) GRAVIMETRIC DETERMINATION WITH MANDELIC ACID. Transfer 10.0 ml of standard zirconium solution (3.4.2) to a beaker of suitable capacity (for example 250 ml). Dilute to about 40 ml and add 30 ml of 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 minutes. Allow to cool, then filter through a medium texture filter paper. Wash with a solution containing 20 ml of 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 1000 °C, and weigh the zirconium oxide (ZrO_2). The zirconium (Zr) content of the standard solution, expressed in milligrammes per millilitre, is given by the following formula :

$$\frac{A \times 0.7403}{V}$$

where

A is the mass, in milligrammes, of weighed zirconium oxide;

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

0.7403 is the conversion factor of ZrO_2 to Zr.

- (b) GRAVIMETRIC DETERMINATION WITH *p*-BROMOMANDELIC ACID. Take 10.0 ml of standard zirconium 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 minutes. 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 1000 °C and weigh the zirconium oxide (ZrO_2).

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

$$\frac{A \times 0.7403}{V}$$

where

A is the mass, in milligrammes, of weighed zirconium oxide;

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

0.7403 is the conversion factor of ZrO_2 to Zr.

- 3.5 *Zirconium, standard solution*, 0.100 g/l. According to the concentration of the standard zirconium solution prepared as specified in clause 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 electrophotometer.*

* The zirconium oxychloride used should 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.

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 Test portion

Weigh, to the nearest 0.001 g, 6 g of 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 Plotting of the calibration curve

6.3.1 Preparation of standard 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 magnesium chloride solution (3.3), containing 0.1 g of magnesium, and then the volumes of standard zirconium solution (3.5) indicated in the following table :

Volume of standard zirconium 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

* Compensating solution

Then add to each flask a sufficient quantity of water to make 10.0 ml, and add 2.5 ml of hydrochloric acid (3.1) and 10.0 ml of 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 1/2 to 3 1/2 minutes, taking care to avoid any overheating. Quickly cool to ambient temperature and add to each flask 2.0 ml of hydrochloric acid (3.1). Transfer quantitatively to 100 ml volumetric flasks, make up to volume and mix.

6.3.2 Photometric measurements. Measure the optical density of each solution within 1 hour, using the spectrophotometer at the maximum of the absorption curve (wavelength of about 525 nm) or the electrophotometer fitted with a suitable filter, having set the instrument to zero optical density against the compensating solution.

6.3.3 Plotting of the curve. Draw a graph plotting, for example, on the abscissae the amounts, expressed in milligrammes, of zirconium (Zr) contained in 100 ml of the standard solution, and on the ordinates, the corresponding values of the optical density.

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

When the reaction has ceased, heat to boiling and continue boiling for exactly 5 minutes, 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 (ISO Recommendation under study).

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 hydrochloric acid (3.1) and 10.0 ml of sodium alizarin sulphonate solution (3.2). Place the conical flask in a boiling water bath and maintain in the boiling water for 2 1/2 to 3 1/2 minutes, taking care to avoid any overheating. Quickly cool to ambient temperature and then add to the flask 2.0 ml of 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 hour according to the procedure described in clause 6.3.2, having set the instrument to zero optical density against the blank test solution.

7. EXPRESSION OF RESULTS

By means of the calibration curve (see clause 6.3.3) determine the quantity of zirconium corresponding to the value of the photometric measurement. The zirconium (Zr) content expressed as a percentage by mass is given by the following formula :

$$\text{Zr \% (m/m)} = \frac{A \times 5}{E}$$

where

- A* is the mass, in milligrammes, of zirconium found in the aliquot of the test solution;
- E* is the mass, in grammes, of the test portion.

8. TEST REPORT

Report the following information :

- (a) the reference of the method used;
- (b) the results and the method of expression used;
- (c) any characteristics noted during the determination;
- (d) any operations not specified in this ISO Recommendation, or regarded as optional, which may have affected the results.