INTERNATIONAL STANDARD ISO 810

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Magnesium and magnesium alloys – Determination of manganese – Periodate photometric method (Manganese content less than 0,01 %)

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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 810 replaces ISO Recommendation R 810-1968 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

Argentina
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South Africa, Rep. of
Spain
Switzerland
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Turkey
United Kingdom
U.S.A.
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Yugoslavia

No Member Body expressed disapproval of the Recommendation.

Printed in Switzerland

Magnesium and magnesium alloys — Determination of manganese — Periodate photometric method (Manganese content less than 0,01 %)

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method for the determination of manganese in magnesium and magnesium alloys which do not contain zirconium, rare earths, or thorium[1].

The method is applicable to the determination of manganese content less than 0,01 %.[2]

2 PRINCIPLE

Attack of the sample with sulphuric acid, followed by oxidation with ammonium persulphate.

Oxidation of manganese(II) to manganese(VII) by means of potassium periodate (acidity approximately 2 N), in the presence of phosphoric acid.

Photometric measurement at a wavelength of about 525 nm.

3 REAGENTS

For the preparation of solutions and during the analysis, use doubly distilled water.

3.1 Potassium periodate (KIO_4).

3.2 Ammonium persulphate [$(NH_4)_2S_2O_8$].

3.3 Sulphuric acid, ρ 1,26 g/ml, approximately 9 N solution.

Carefully add 25 ml of sulphuric acid (ρ 1,84 g/ml), approximately 35,6 N, to 60 ml of water. After cooling make up the volume to 100 ml and mix.

3.4 Phosphoric acid, ρ 1,71 g/ml, approximately 45 N solution.

3.5 Water free from reducing agents

Heat to boiling, water acidified with 10 ml per litre of the sulphuric acid (3.3); add a few crystals of the potassium periodate (3.1) and continue boiling for about 10 min.

3.6 Sodium nitrite, 20 g/l solution.

Dissolve 2 g of sodium nitrite ($NaNO_2$) in a little water and make up the volume to 100 ml.

3.7 Manganese standard solution, 1 g/l (1 ml contains 1 mg of Mn),

prepared by one of the following methods.

3.7.1 In a tall-form beaker of suitable capacity (for example 400 ml) dissolve 2,877 g of very pure potassium permanganate ($KMnO_4$) in about 200 ml of water and add 40 ml of the sulphuric acid (3.3). Reduce the permanganate solution by adding a few crystals of sodium sulphite or hydrogen peroxide (36 % (*m*/*m*)). Boil the solution to remove excess SO_2 or H_2O_2, cool, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

3.7.2 In a tall-form beaker of suitable capacity (for example 600 ml) dissolve 1 ± 0,001 g of electrolytic manganese (purity above 99,9 %) with 40 ml of the sulphuric acid (3.3) and about 80 ml of water. Boil the solution for a few minutes. Cool, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

NOTE — Free the electrolytic manganese from any surface oxide by placing a few grams of the metal in a glass beaker, of about 250 to 300 ml capacity, containing 60 to 80 ml of the sulphuric acid (3.3) and about 100 ml of water. Shake and, after a few minutes, decant the acid solution and introduce into the beaker doubly distilled water. Repeat the decantation and washing with doubly distilled water several times; then place the metallic manganese in acetone and shake. Decant the acetone, dry the metal in a hot air oven at 100 °C for about 2 min and allow it to cool in a desiccator.

3.8 Manganese standard solution, 0,02 g/l (1 ml contains 0,02 mg of Mn).

Transfer 20,0 ml of the manganese standard solution (3.7) to a 1 000 ml volumetric flask, make up to volume and mix.

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[1] These special cases are treated in ISO 2353, *Magnesium and its alloys — Determination of manganese in magnesium alloys containing zirconium, rare earths, thorium and silver — Periodate photometric method.*

[2] For manganese contents greater than 0,01 %, see ISO 809, *Magnesium and magnesium alloys — Determination of manganese — Periodate photometric method (Manganese content between 0,01 and 0,8 %).*

4 APPARATUS

4.1 Ordinary laboratory apparatus

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, 2 g of the test sample (5.2).

6.2 Preparation of the calibration curve

6.2.1 *Preparation of the standard matching solutions*

Introduce into a series of six vessels of suitable capacity (for example 250 ml) respectively 0 (compensating solution) – 1,0 – 2,0 – 5,0 – 8,0 and 10,0 ml of the manganese standard solution (3.8) containing respectively 0 – 20 – 40 – 100 – 160 and 200 µg of manganese and corresponding under the test conditions to 0,0 – 0,001 – 0,002 – 0,005 – 0,008 and 0,01 % of manganese.

Make up the volume to about 50 ml with water. Then add 10 ml of the sulphuric acid (3.3) and 0,05 g of the ammonium persulphate (3.2). Boil for 4 to 5 min. Add 1 ml of the phosphoric acid (3.4) and 0,05 g of the potassium periodate (3.1) and bring to the boil. Boil for 5 min.

6.2.2 *Development of the colour*

Add 0,5 g of the potassium periodate (3.1) and place on a sand bath for 30 to 40 min at a temperature of about 98 °C, without bringing to the boil. Remove from the sand bath. Allow to cool and make up to 50 ml in a volumetric flask with the treated water (3.5).

6.2.3 *Photometric measurements*

Carry out the photometric measurements using the spectrophotometer (4.2) at the maximum of the absorption curve (wavelength approximately 525 nm), or the photoelectric absorptiometer (4.3), fitted with suitable filters, after having adjusted the instrument to zero absorbance against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.6) and repeat the measurement (Δ_{Ed}). In order to obtain the value of the absorbance due to the manganese introduced, calculate for each dilution the differences

$$[(\Delta_{Ec} - \Delta_{Ed}) - (\Delta_{Tc} - \Delta_{Td})]$$

where Δ_{Tc} and Δ_{Td} are the values of absorbance corresponding to the term 0 solution coloured and decolourized.

6.2.4 *Plotting of the calibration chart*

Plot a graph having, for example, the amount of manganese, expressed in milligrams, contained in 50 ml of standard matching solution as abscissae, and the corresponding values of absorbance as ordinates.

6.3 Determination

6.3.1 *Preparation of the test solution*

Place the test portion in a vessel of suitable capacity (for example 250 ml) and cover with a watch-glass. Add 20 ml of water, then, in small portions, 30 ml of the sulphuric acid (3.3). Then transfer the solution to a 250 ml conical flask and rinse the beaker with 10 ml of water. Add 0,05 g of the ammonium persulphate (3.2). Boil for 4 to 5 min.

6.3.2 *Development of the colour*

To the solution obtained according to 6.3.1 add 1 ml of the phosphoric acid (3.4) and 0,05 g of the potassium periodate (3.1). Bring to the boil. Keep boiling for 5 min. Add 0,5 g of the potassium periodate (3.1) and place on a sand bath for 30 to 40 min, at a temperature of about 98 °C, without boiling. Remove from the sand bath. Allow to cool and make up to 50 ml in a volumetric flask with the treated water (3.5).

6.3.3 *Blank test*

Carry out the following blank test in parallel with the analysis. Place 20 ml of the sulphuric acid (3.3) in a platinum dish and evaporate to dryness. Take up the residue in a little warm water and transfer the solution to a 250 ml conical flask. Rinse the dish with water and make up the volume to about 50 ml with water. Then add 10 ml of the sulphuric acid (3.3) and 0,05 g of the ammonium persulphate (3.2). Boil for 4 to 5 min. Continue as described in 6.3.2.

6.3.4 *Photometric measurements*

Carry out the photometric measurements according to the procedure described in 6.2.3, after having adjusted the instrument to zero absorbance against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.6) and repeat the measurement (Δ_{Ed}).

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

The difference between these two values gives the absorbance due to permanganic acid. At the same time and under the same conditions carry out the photometric measurements relating to the blank test solution.

The absorbance due to the manganese of the test solution is given by the difference

$$[(\Delta_{Ec} - \Delta_{Ed}) - (\Delta_{Bc} - \Delta_{Bd})]$$

where Δ_{Bc} and Δ_{Bd} are the values of absorbance corresponding to the solution of the blank test coloured and decolourized.

7 EXPRESSION OF RESULTS

By means of the calibration graph, determine the mass of manganese, in milligrams, corresponding to the value of the photometric measurement of the test solution.

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

$$\text{Mn}\ \%\ (m/m) = \frac{m_1}{10\, m_0}$$

where

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

m_1 is the mass, in milligrams, of manganese found in 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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