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Magnesium and its alloys – Determination of manganese in magnesium alloys containing zirconium, rare earths, thorium and silver – Periodate photometric method

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FOREWORD

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Magnesium and its alloys — Determination of manganese in magnesium alloys containing zirconium, rare earths, thorium and silver — Periodate photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method for the determination of manganese in magnesium alloys containing zirconium, and/or rare earths, and/or thorium, and/or silver.

The method is applicable to the determination of manganese contents between 0.002 and 0.2 %.

2 PRINCIPLE

2.1 Dissolution of a sample by sulphuric acid, followed by oxidation with nitric acid, in the presence of fluoboric acid.

2.2 Oxidation of manganese (II) to manganese (VII) by means of potassium periodate in a medium of acidity approximately 5 N.

2.3 Photometric measurement at a wavelength of about 545 nm.

3 REAGENTS

During the analysis use only distilled water or water of equivalent purity.

3.1 Potassium periodate (KIO_4)

3.2 Sulphuric acid ($\rho = 1.26$ g/ml), approximately 9 N solution.

Carefully add 25 ml of sulphuric acid ($\rho = 1.84$ g/ml), 35.6 N approximately, to 60 ml of water. After cooling, make up the volume to 100 ml and mix.

3.3 Nitric acid ($\rho = 1.40$ g/ml), approximately 15 N solution.

The acid shall be free from nitric fumes. To eliminate these fumes boil for a short while or pass through a current of carbon dioxide.

3.4 Fluoboric acid, 0.4 % (m/m) solution.

Dilute 10 ml of fluoboric acid 40 % (m/m) to 1 000 ml with water.

3.5 Water free from reducing agents

Heat to boiling, water acidified with 10 ml per litre of sulphuric acid (3.2); add a few crystals of 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 sulphuric acid (3.2). 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 sulphuric acid (3.2) 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 sulphuric acid (3.2) and about 100 ml of water. Shake and, after a few minutes, decant the acid solution and introduce into the beaker double distilled water. Repeat the decantation and washing with double 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, 0.1 g/l (1 ml contains 0.1 mg of Mn).

Transfer 100.0 ml of the manganese standard solution (3.7) to a 1 000 ml volumetric flask, make up to volume and mix.

3.9 Manganese standard solution, 0.01 g/l (1 ml contains 0.01 mg of Mn).

Transfer 10.0 ml of the manganese standard solution (3.7) to a 1 000 ml volumetric flask, make up to volume and mix.

4 APPARATUS

4.1 Ordinary laboratory apparatus

All volumetric vessels shall be checked in accordance with the official standards.

4.2 Spectrophotometer, or

4.3 Electrophotometer.

5 SAMPLING

5.1 Laboratory sample[1]

5.2 Test sample

Chips of thickness less than or equal to 1 mm 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) for manganese contents between 0.002 and 0.01 %, 1 g for manganese contents between 0.01 and 0.05 % or 0.5 g for manganese contents between 0.05 and 0.2 %.

6.2 Plotting of the calibration curve

6.2.1 *Preparation of the compensating solution* (Term 0).

Transfer 20 ml of nitric acid (3.3) to a platinum vessel and evaporate to dryness. Take up the residue in a little warm water and transfer the solution to a vessel of suitable capacity (for example, 250 ml). Dilute to about 40 ml with water and add 15 ml of sulphuric acid (3.2), 5 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Continue according to the procedure described in 6.2.3.

6.2.2 *Preparation of the reference solution*

6.2.2.1 Manganese contents between 0.002 and 0.01 %

To a series of six vessels of suitable capacity (for example 250 ml) transfer 4.0 – 6.0 – 8.0 – 10.0 – 15.0 and 20.0 ml respectively of manganese standard solution (3.9), containing 0.04 – 0.06 – 0.08 – 0.10 – 0.15 and 0.20 mg of manganese respectively. Make up the volume to about 40 ml with water. Then add 15 ml of sulphuric acid (3.2), 25 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Continue according to the procedure described in 6.2.3.

6.2.2.2 Manganese contents between 0.01 and 0.2 %

To a series of six vessels of suitable capacity (for example 250 ml) transfer 1.0 – 2.0 – 5.0 – 10.0 – 15.0 and 20.0 ml respectively of manganese standard solution (3.8), containing 0.1 – 0.2 – 0.5 – 1.0 – 1.5 and 2.0 mg of manganese. Make up the volume to about 40 ml with water. Then add 15 ml of sulphuric acid (3.2), 25 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Continue according to the procedure described in 6.2.3.

6.2.3 *Development of the colour*

Heat the solution to boiling and add 0.5 g of potassium periodate (3.1). Continue boiling for 5 min, then allow the solutions to remain hot (at about 98 °C) for 15 min.

Allow to cool, transfer quantitatively to 100 ml volumetric flasks and make up to volume with water free from reducing agents (3.5).

6.2.4 *Photometric measurement*

Choose cells of optical paths appropriate to the instrument used. Measure the optical densities using the spectrophotometer (4.2) at a wavelength of about 545 nm or the electrophotometer (4.3) fitted with appropriate filters, having set the instrument to zero optical density against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of sodium nitrite solution (3.6) and repeat the optical density measurements (Δ_{Ed}). In order to obtain the value for the optical density 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 optical densities corresponding to the solution of term 0, coloured and decolorized.

6.2.5 *Plotting the calibration curve*

Draw a graph, plotting, for example, as abscissae the quantities of manganese, expressed in milligrams, contained in 100 ml of the reference solution, and as ordinates, the corresponding values of the optical density.

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[1] The International Standard relating to the sampling of deliveries will be studied as soon as Technical Committee ISO/TC 69, *Application of statistical methods* has indicated the methods of a general nature to be adopted.

6.3 Determination

6.3.1 *Preparation of the test solution*

6.3.1.1 Manganese contents between 0.002 and 0.01 %

Transfer the test portion (6.1) to a vessel of suitable capacity (for example 250 ml), cover with a watch glass, add 10 ml of water, then, in small portions, 30 ml of sulphuric acid (3.2). When the reaction is complete add 25 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Boil the solution for a few minutes.

6.3.1.2 Manganese contents between 0.01 and 0.05 %

Transfer the test portion (6.1) to a vessel of suitable capacity (for example 250 ml), cover with a watch glass, add 10 ml of water, then, in small portions, 25 ml of sulphuric acid (3.2). When the reaction is complete add 25 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Boil the solution for a few minutes.

6.3.1.3 Manganese contents between 0.05 and 0.2 %

Transfer the test portion (6.1) to a vessel of suitable capacity (for example 250 ml), cover with a watch glass, add 10 ml of water and then, in small portions, 20 ml of sulphuric acid (3.2). When the reaction is complete add 25 ml of nitric acid (3.3) and 5 ml of fluoboric acid solution (3.4). Boil the solution for a few minutes.

6.3.2 *Development of the colour*

To the solution obtained in accordance with 6.3.1.1, 6.3.1.2 or 6.3.1.3, add the quantity of water necessary to make up the volume to about 60 ml. Continue according to the procedure described in 6.2.3.

6.3.3 *Blank test*

Carry out a blank test in parallel with the analysis, in accordance with the following instructions.

6.3.3.1 Manganese contents between 0.002 and 0.01 %

Transfer 25 ml of nitric acid (3.3) and 10 ml of sulphuric acid (3.2) to a platinum vessel, and evaporate to dryness.

Take up the residue in a little warm water and transfer the solution quantitatively to a vessel of suitable capacity (for example 250 ml). Dilute to about 40 ml with water and add 20 ml of sulphuric acid (3.2) and 5 ml of fluoboric acid solution (3.4). Continue according to the procedure described in 6.2.3.

6.3.3.2 Manganese contents between 0.01 and 0.05 %

Transfer 25 ml of nitric acid (3.3) and 5 ml of sulphuric acid (3.2) to a platinum vessel and evaporate to dryness.

Continue according to the procedure described in 6.3.3.1, second paragraph.

6.3.3.3 Manganese contents between 0.05 and 0.2 %

Transfer to a platinum vessel 25 ml of nitric acid (3.3) and evaporate to dryness.

Continue according to the procedure described in 6.3.3.1, second paragraph.

6.3.4 *Photometric measurements*

Carry out the photometric measurements in accordance with the procedure described in 6.2.4, having set the instrument to zero optical density against water (Δ_{Ec}). Then destroy the permanganic acid with 2 drops of sodium nitrite solution (3.6) and repeat the measurement (Δ_{Ed}). The difference between these two values gives the optical density 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 optical density relating 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 optical densities corresponding to the blank test solution, coloured and decolorized.

7 EXPRESSION OF RESULTS

By means of the calibration curve (see 6.2.5), determine the quantity of manganese, expressed in milligrams, corresponding to the value of the photometric measurement of the test solution.

The manganese content (Mn) is given, as a percentage by mass, by the formula :

$$\frac{m_1}{10\, m_0}$$

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 form in which they are expressed;

c) any particular details arising in the course of the test;

d) all operations not covered by the present International Standard, or all optional operations, which may have affected the results.

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