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# INTERNATIONAL STANDARD



# 809

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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## Magnesium and magnesium alloys – Determination of manganese – Periodate photometric method (Manganese content between 0,01 and 0,8 %)

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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 809 replaces ISO Recommendation R 809-1968 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys*.

The Member Bodies of the following countries approved the Recommendation :

Argentina	India	South Africa, Rep. of
Austria	Ireland	Spain
Belgium	Israel	Sweden
Bulgaria	Italy	Switzerland
Canada	Japan	Turkey
Chile	Korea, Rep. of	United Kingdom
Czechoslovakia	Netherlands	U.S.A.
France	New Zealand	U.S.S.R.
Germany	Norway	Yugoslavia
Hungary	Poland	

No Member Body expressed disapproval of the Recommendation.

# Magnesium and magnesium alloys – Determination of manganese – Periodate photometric method (Manganese content between 0,01 and 0,8 %)

## 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.<sup>1)</sup>

The method is applicable to the determination of manganese content between 0,01 and 0,8 %.<sup>2)</sup>

## 2 PRINCIPLE

Attack with sulphuric acid, followed by oxidation with nitric acid.

Oxidation of manganese(II) to manganese(VII) by means of potassium periodate (acidity approximately 5 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 double distilled water.

### 3.1 Potassium periodate ( $\text{KIO}_4$ )

**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), approximately 35,6 N, 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 Phosphoric acid**,  $\rho$  1,71 g/ml, approximately 45 N solution.

**3.5 Hydrofluoric acid**, 40 % ( $m/m$ ) solution ( $\rho$  approximately 1,14 g/ml).

### 3.6 Water free from reducing agents

Heat to boiling, water acidified with 10 ml per litre of the sulphuric acid (3.2); add a few crystals of the potassium periodate (3.1) and continue boiling for about 10 min.

**3.7 Sodium nitrite**, 20 g/l solution.

Dissolve 2 g of sodium nitrite ( $\text{NaNO}_2$ ) in a little water and make up the volume to 100 ml.

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

prepared by one of the following methods.

**3.8.1** In a tall-form beaker of suitable capacity (for example 400 ml) dissolve 2,877 g of very pure potassium permanganate ( $\text{KMnO}_4$ ) in about 200 ml of water and add 40 ml of the 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  $\text{SO}_2$  or  $\text{H}_2\text{O}_2$ , cool, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume and mix.

**3.8.2** In a tall-form beaker of suitable capacity (for example 600 ml) dissolve  $1 \pm 0,001$  g of electrolytic manganese (purity above 99,9 %) with 40 ml of the 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 the 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 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.

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 less than 0,01 % see ISO 810, *Magnesium and magnesium alloys – Determination of manganese – Periodate photometric method (Manganese content less than 0,01 %)*.

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

Transfer 100,0 ml of the manganese standard solution (3.8) to a 1 000 ml volumetric flask, make up to volume and mix.

#### 4 APPARATUS

##### 4.1 Ordinary laboratory apparatus

##### 4.2 Spectrophotometer, or

##### 4.3 Photoelectric absorptiometer.

#### 5 SAMPLING

##### 5.1 Laboratory sample<sup>1)</sup>

##### 5.2 Test sample

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

#### 6 PROCEDURE

##### 6.1 Test portion

- For a manganese content between 0,01 and 0,05 % weigh 1,0 g of the test sample (5.2) with an accuracy of  $\pm 0,001$  g.
- For a manganese content between 0,05 and 0,8 % weigh 0,5 g of the test sample (5.2) with an accuracy of  $\pm 0,001$  g.

##### 6.2 Preparation of the calibration curve

###### 6.2.1 Preparation of the compensating solution (Term 0)

Place 20 ml of the nitric 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 vessel of suitable capacity (for example 250 ml). Dilute to approximately 40 ml with water and add 15 ml of the sulphuric acid (3.2), 5 ml of the nitric acid (3.3) and 5 ml of the phosphoric acid (3.4). Continue as described in 6.1.3.

###### 6.2.2 Preparation of the standard matching solutions

Introduce into a series of six vessels of suitable capacity (for example 250 ml) respectively 1,0 – 2,0 – 5,0 – 10,0 – 15,0 and 20,0 ml of the manganese standard solution (3.9) corresponding respectively to 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 the sulphuric acid (3.2), 25 ml of the nitric acid (3.3) and 5 ml of the phosphoric acid (3.4).

##### 6.2.3 Development of the colour

Bring the solutions to the boil and add 0,5 g of the potassium periodate (3.1). Boil for 3 min, then allow the solutions to stand in the warm (approximately 98 °C) for 15 min.

Allow to cool, transfer to 100 ml volumetric flasks and make up to volume with the treated water (3.6).

##### 6.2.4 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 ( $\Delta_{Ec}$ ). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.7) and repeat the measurement ( $\Delta_{Ed}$ ). 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  $\Delta_{Tc}$  and  $\Delta_{Td}$  are the values of absorbance corresponding to the term 0 solution, coloured and decolourized.

##### 6.2.5 Plotting of the calibration chart

Plot a graph having for example, the amount of manganese, expressed in milligrams, contained in 100 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

###### 6.3.1.1 MANGANESE CONTENT BETWEEN 0,01 AND 0,05 %

Place the test portion in a vessel of suitable capacity (for example 250 ml) and cover with a watch-glass. Add 10 ml of water, then, in small portions, 25 ml of the sulphuric acid (3.2). Once the reaction is complete, add 25 ml of the nitric acid (3.3) and 2 or 3 drops of the hydrofluoric acid (3.5). Boil the solution for a few minutes.

###### 6.3.1.2 MANGANESE CONTENT BETWEEN 0,05 AND 0,4 %

Place the test portion in a vessel of suitable capacity (for example 250 ml) and cover with a watch-glass. Add 10 ml of water, then, in small portions, 20 ml of the sulphuric acid (3.2). Once the reaction is complete, add 25 ml of the nitric acid (3.3) and 2 or 3 drops of the hydrofluoric acid (3.5). Boil the solution for a few minutes.

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

**6.3.1.3 MANGANESE CONTENT BETWEEN 0,4 AND 0,8 %**

Place the test portion in a vessel of suitable capacity (for example 250 ml) and cover with a watch-glass. Add 10 ml of water, then, in small portions, 10 ml of the sulphuric acid (3.2). Once the reaction is complete, add 5 ml of the nitric acid (3.3) and 2 or 3 drops of the hydrofluoric acid (3.5).

Boil for a few minutes. Transfer the solution to a 100 ml volumetric flask, allow to cool and make up to volume with water. Take 20 ml of this solution (corresponding to 0,1 g of the test portion) and place them in a vessel of suitable capacity (for example 250 ml). Add 15 ml of the sulphuric acid (3.2) and 25 ml of the nitric acid (3.3).

**6.3.2 Development of the colour**

To the solution obtained according to 6.3.1.1, 6.3.1.2 or 6.3.1.3 add the quantity of water necessary to obtain a volume of about 60 ml, then 5 ml of the phosphoric acid (3.4). Continue as 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 CONTENT BETWEEN 0,01 AND 0,05 %**

Place 25 ml of the nitric acid (3.3) and 5 ml of the sulphuric acid (3.2) in a platinum dish 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 approximately 40 ml with water and add 20 ml of the sulphuric acid (3.2), 5 ml of the phosphoric acid (3.4) and 2 or 3 drops of the hydrofluoric acid (3.5). Continue as described in 6.2.3.

**6.3.3.2 MANGANESE CONTENT BETWEEN 0,05 AND 0,4 %**

Place 25 ml of the nitric acid (3.3) in a platinum dish and evaporate to dryness. Take up the residue . . . (continue as described in 6.3.3.1).

**6.3.3.3 MANGANESE CONTENT BETWEEN 0,4 AND 0,8 %**

Place 25 ml of the nitric 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 vessel of suitable capacity (for example 250 ml). Dilute to approximately 40 ml with water and add 16 ml of the sulphuric acid (3.2), 3 ml of the nitric acid (3.3), 5 ml of the phosphoric acid (3.4) and 2 or 3 drops of the hydrofluoric acid (3.5). Continue as described in 6.2.3.

**6.3.4 Photometric measurements**

Carry out the photometric measurements according to the procedure described in 6.2.4 after having adjusted the instrument to zero absorbance against water ( $\Delta_{E_c}$ ). Then destroy the permanganic acid with 2 drops of the sodium nitrite solution (3.7) and repeat the measurement ( $\Delta_{E_d}$ ). 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 aliquot of the test solution, or of the test solution itself, is given by the difference

$$[(\Delta_{E_c} - \Delta_{E_d}) - (\Delta_{B_c} - \Delta_{B_d})]$$

where  $\Delta_{B_c}$  and  $\Delta_{B_d}$  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 aliquot of the test solution, or of the test solution itself.

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

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

where

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

$m_1$  is the mass, in milligrams, of manganese found in the aliquot of the test solution, or in the test solution itself;

$R$  is the ratio of the volume of the test solution to the volume of the aliquot taken.

**8 TEST REPORT**

The test report shall include the following particulars :

- the reference of the method used;
- the results and the method of expression used;
- any unusual features noted during the determination;
- any operation not included in this International Standard, or regarded as optional.

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