UDC 669.721 : 546.711.06

Ref. No. : ISO/R 809-1968 (E)

Transformed

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 809

CHEMICAL ANALYSIS OF MAGNESIUM AND MAGNESIUM ALLOYS

PHOTOMETRIC DETERMINATION OF MANGANESE

PERIODATE METHOD

(Manganese content between 0.01 and 0.8 %)

1st EDITION
August 1968

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 809, *Chemical analysis of magnesium and magnesium alloys – Photometric determination of manganese – Periodate method (Manganese content between 0.01 and 0.8 %)*, 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 by the Technical Committee began in 1957 and led, in 1965, to the adoption of a Draft ISO Recommendation.

In December 1966, this Draft ISO Recommendation (No. 1130) 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 :

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 opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in August 1968, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 809 August 1968

CHEMICAL ANALYSIS OF MAGNESIUM AND MAGNESIUM ALLOYS

PHOTOMETRIC DETERMINATION OF MANGANESE

PERIODATE METHOD

(Manganese content between 0.01 and 0.8 %)

1. SCOPE

This ISO Recommendation describes a photometric method for the determination of manganese in magnesium and magnesium alloys which do not contain zirconium, rare earths, or thorium.

The method is applicable to the determination of manganese content between 0.01 and 0.8 %.

2. PRINCIPLE

2.1 Attack of the sample with sulphuric acid, followed by oxidation with nitric acid.

2.2 Oxidation of manganese (II) to manganese (VII) by means of potassium periodate (acidity approximately 5N), in the presence of phosphoric acid.

2.3 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 *Sulphuric acid*, $d = 1.26$ (approximately 9 N).

Carefully add 25 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to water, cool and make up the volume to 100 ml.

3.3 *Nitric acid*, $d = 1.40$ (approximately 15 N).

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

3.4 *Phosphoric acid*, $d = 1.71$ (approximately 45 N).

3.5 *Hydrofluoric acid*, 40 % (d = approximately 1.15).

3.6 *Water free from reducing agents*

Bring to the boil water acidified with 10 ml per litre of sulphuric acid (3.2); add a few crystals of potassium periodate (3.1) and maintain at boiling point for approximately 10 minutes. (The term "water" without qualification indicates doubly distilled water.)

3.7 *Sodium nitrite solution,* 20 g per litre.

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

3.8 *Standard manganese solution,* 1 g per litre (1 ml contains 1 mg of manganese).

Either :

3.8.1 In a tall-form beaker of suitable capacity (e.g. 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 by adding hydrogen peroxide (100 to 110 volumes). Boil the solution to eliminate excess of sulphur dioxide or hydrogen peroxide, cool, transfer to a 1000 ml volumetric flask and make up to volume with water.

Or :

3.8.2 In a tall-form beaker of suitable capacity (e.g. 600 ml), dissolve 1 ± 0.001 g of electrolytic manganese (purity ⩾ 99.9 %) with 40 ml of sulphuric acid (3.2) and approximately 80 ml of water. Boil the solution for several minutes. Cool, transfer to a 1000 ml volumetric flask and make up to volume.

NOTE. – Free the electrolytic manganese of any surface oxidation present by placing several grammes of the metal in a glass beaker of approximately 250 to 300 ml capacity, containing 60 to 80 ml of sulphuric acid (3.2) and approximately 100 ml of water. Stir and after a few minutes decant the acid solution and introduce some doubly distilled water into the beaker. Decant and wash with doubly distilled water several times; finally, place the manganese in acetone and shake. Decant the acetone, dry the metal in a hot air oven at 100 °C for approximately 2 minutes, then allow to cool in a desiccator.

3.9 *Standard manganese solution,* 0.1 g per litre (1 ml contains 0.1 mg of manganese).

Take 100.0 ml of standard manganese solution (3.8), place in a 1000 ml volumetric flask and make up to volume with water.

4. APPARATUS

4.1 *Ordinary laboratory apparatus*

All volumetric apparatus should comply with national standards.

4.2 *Electrophotometer* or *spectrophotometer* (wavelength about 525 nm).

5. SAMPLING

5.1 **Laboratory sample**

See the appropriate national standard on sampling.

5.2 **Test sample**

Chips not more than 1 mm thick should be obtained from the laboratory sample by milling or drilling.

6. PROCEDURE

6.1 Calibration graph

6.1.1 *Preparation of the compensating solution (Term 0).* Place 20 ml of 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 (e.g. 250 ml). Dilute to approximately 40 ml with water and add 15 ml of sulphuric acid (3.2), 5 ml of nitric acid (3.3) and 5 ml of phosphoric acid (3.4). Continue as described under clause 6.1.3.

6.1.2 *Preparation of the manganese solutions.* Introduce into a series of six vessels of suitable capacity (e.g. 250 ml) respectively 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ml of standard manganese 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 sulphuric acid (3.2), 25 ml of nitric acid (3.3) and 5 ml of phosphoric acid (3.4).

6.1.3 *Development of the colour.* Bring the solutions to the boil and add 0.5 g of potassium periodate (3.1). Boil for 3 minutes, then allow the solutions to stand in the warm (approximately 98 °C) for 15 minutes.

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

6.1.4 *Photometric measurement.* Measure the optical densities at the maximum of the absorption curve (wavelength about 525 nm), having set the instrument to zero optical density with water (Δ_{Ec}). Then destroy the permanganic acid by the addition of 2 drops of sodium nitrite solution (3.7) and repeat the optical density measurement (Δ_{Ed}). In order to obtain the value for the optical density due to the manganese added, 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 term zero solution coloured and decolourized.

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

6.2 Test portion

(*a*) For a manganese content between 0.01 and 0.05 % weigh 1.0 g of the test sample (5.2) with an accuracy of ± 0.001 g.

(*b*) For a manganese content between 0.05 and 0.8 % weigh 0.5 g of the test sample (5.2) with an accuracy of ± 0.001 g.

6.3 Determination

6.3.1 *Attack of the test portion*

6.3.1.1 MANGANESE CONTENT BETWEEN 0.01 AND 0.05 %

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

6.3.1.3 MANGANESE CONTENT BETWEEN 0.4 AND 0.8 %

Place the test portion in a tall-form beaker of suitable capacity (e.g. 250 ml) and cover with a watch-glass. Add 10 ml of water, then, in small portions, 10 ml of sulphuric acid (3.2). Once the reaction is complete, add 5 ml of nitric acid (3.3) and 2 or 3 drops of 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 (e.g. 250 ml). Add 15 ml of sulphuric acid (3.2) and 25 ml of nitric acid (3.3).

6.3.2 *Colour reaction.* To the solution obtained according to clause 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 phosphoric acid (3.4). Continue as described in clause 6.1.3.

6.3.3 *Blank test.* Carry out the following blank test in parallel with the analysis.

6.3.3.1 MANGANESE CONTENT BETWEEN 0.01 AND 0.05 %

Place 25 ml of nitric acid (3.3) and 5 ml of 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 (e.g. 250 ml). Dilute to approximately 40 ml with water and add 20 ml of sulphuric acid (3.2), 5 ml of phosphoric acid (3.4) and 2 or 3 drops of hydrofluoric acid (3.5). Continue as described in clause 6.1.3.

6.3.3.2 MANGANESE CONTENT BETWEEN 0.05 AND 0.4 %

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

6.3.3.3 MANGANESE CONTENT BETWEEN 0.4 AND 0.8 %

Place 25 ml of 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 (e.g. 250 ml). Dilute to approximately 40 ml with water and add 16 ml of sulphuric acid (3.2), 3 ml of nitric acid (3.3), 5 ml of phosphoric acid (3.4) and 2 or 3 drops of hydrofluoric acid (3.5). Continue as described in clause 6.1.3.