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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 886

CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

PHOTOMETRIC DETERMINATION OF MANGANESE

(Manganese content between 0.005 and 1.5 %)

1st EDITION
December 1968

For each individual country the only valid standard is the national standard of that country.

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BRIEF HISTORY

The ISO Recommendation R 886, *Chemical analysis of aluminium and aluminium alloys — Photometric determination of manganese (Manganese content between 0.005 and 1.5 %)*, 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 1961 and led, in 1966, to the adoption of a Draft ISO Recommendation.

In April 1967, this Draft ISO Recommendation (No. 1192) 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	Hungary	Spain
Austria	Ireland	Sweden
Belgium	Israel	Switzerland
Canada	Italy	Thailand
Chile	Japan	Turkey
Czechoslovakia	Netherlands	U.S.A.
France	Norway	U.S.S.R.
Germany	Poland	Yugoslavia
Greece	South Africa, Rep. of	

One Member Body opposed the approval of the Draft :

United Kingdom

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

ISO Recommendation R 886 December 1968

CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

PHOTOMETRIC DETERMINATION OF MANGANESE

(Manganese content between 0.005 and 1.5 %)

1. SCOPE

This ISO Recommendation describes a photometric method for the determination of manganese in aluminium and aluminium alloys.

The method is applicable to the determination of manganese contents between 0.005 and 1.5 %.

However, this method does not apply completely to the following special cases:

(*a*) alloys with a silicon content higher than 10 % and a manganese content less than 0.1 % (see Annex);

(*b*) aluminium alloys containing tin, antimony, bismuth, zirconium, etc.
(In this ISO Recommendation these special cases are not treated.)

2. PRINCIPLE

2.1 Attack of the sample with sodium hydroxide.

2.2 Acidification by sulphuric and nitric acids.

2.3 Oxidation of manganese (II) to manganese (VII) by means of potassium periodate (acidity of solution over 3.5 N approximately), in the presence of phosphoric acid.

2.4 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 Solutions of approximate strength

3.1.1 *Water free from reducing agents*
Bring to the boil water acidified with 10 ml of sulphuric acid (3.1.4) per litre; add a few crystals of potassium periodate (KIO_4) and maintain at boiling point for approximately 10 minutes (see Note 8.1).

3.1.2 *Sodium hydroxide solution,* 200 g/l.
In a nickel dish dissolve 200 g of sodium hydroxide (NaOH) in water and, after cooling, make up the volume to 1000 ml. Keep in a plastic container.

3.1.3 *Sulphurous acid solution*
Pass a current of sulphur dioxide gas (SO_2) through water until saturation point is reached.

3.1.4 *Sulphuric acid,* $d = 1.48$ (approximately 17.5 N).
Carefully add 500 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to water, cool and make up the volume to 1000 ml.

3.1.5 *Sulphuric acid*, $d = 1.84$ (approximately 35.6 N).

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

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

3.1.8 *Fluoroboric acid solution*

In a plastic flask mix 800 ml of saturated boric acid solution at 20 °C with 200 ml of hydrofluoric acid (3.1.7).

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

3.1.10 *Potassium periodate solution*, 50 g/l.

Dissolve 50 g of potassium periodate (KIO_4) in water, add 200 ml of nitric acid (3.1.6) and make up the volume to 1000 ml with water.

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

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

3.2 Standard solutions

3.2.1 *Standard manganese solution*, 1 g/l (1 ml contains 1 mg of manganese).

Either :

(*a*) In a tall-form beaker of suitable capacity (e.g. 600 ml) dissolve 2.877 g of very pure potassium permanganate ($KMnO_4$) in about 200 ml of water. Add 20 ml of sulphuric acid (3.1.4) and reduce the solution by means of some crystals of sodium sulphite (Na_2SO_3) or by a few millilitres of hydrogen peroxide (100 to 110 volumes).

Boil the solution until the excess sulphur dioxide or hydrogen peroxide is eliminated, cool, transfer to a 1000 ml volumetric flask and make up to volume with water.

Or :

(*b*) In a tall-form beaker of suitable capacity (e.g. 600 ml) dissolve 1 g of electrolytic manganese (purity ⩾ 99.9 %) in 20 ml of sulphuric acid (3.1.4) and approximately 100 ml of water. Boil the solution for a few minutes. Cool, transfer to a 1000 ml volumetric flask and make up to volume with water (see Note 8.2).

3.2.2 *Standard manganese solution*, 0.1 g/l (1 ml contains 0.1 mg of manganese).
Take 100 ml of standard solution (3.2.1), 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 *Hotplate* fitted with a mechanical or magnetic stirrer.

4.3 *Electrophotometer* or *spectrophotometer* (wavelength of about 525 nm).

5. SAMPLING

See the appropriate national standard on sampling.

6. PROCEDURE

6.1 Calibration graph

6.1.1 *Preparation of the compensating solution (Term 0).* In a platinum dish place 7 ml of sulphuric acid (3.1.4) and 8 ml of nitric acid (3.1.6) and evaporate to dryness (do not calcine). Take up the residue in a little warm water, add 8 ml of sulphuric acid (3.1.4), 2 ml of nitric acid (3.1.6) and 5 ml of phosphoric acid (3.1.9). Transfer the solution to a vessel of suitable capacity (e.g. 250 ml). Dilute to approximately 70 ml with water and continue according to the procedure described under clause 6.1.3.

6.1.2 *Preparation of manganese solutions.* Introduce into a series of six vessels of suitable capacity (e.g. 250 ml to 300 ml), respectively : 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ml of the standard manganese solution (3.2.2), corresponding respectively to 0.1, 0.2, 0.5, 1.0, 1.5 and 2 mg of manganese. To each vessel add 15 ml of sulphuric acid (3.1.4), 10 ml of nitric acid (3.1.6) and 5 ml of phosphoric acid (3.1.9) and make up the volume to about 70 ml with water.

6.1.3 *Development of the colour.* Place the vessels specified in clauses 6.1.1 and 6.1.2 on a hot-plate fitted with a stirrer (see Note 8.3) and bring the solutions to the boil. Then add to each solution 10 ml of potassium periodate solution (3.1.10) and continue boiling until the characteristic colour develops.

Boil for another 5 minutes (15 to 30 minutes if the concentration of manganese is less than or equal to 0.2 mg of manganese in 100 ml of solution). Cool to room temperature, transfer the solutions into as many 100 ml volumetric flasks, previously rinsed with treated water (3.1.1), and make up to volume with treated water (3.1.1).

6.1.4 *Photometric measurement.* Measure the optical densities at a wavelength of about 525 nm, having set the instrument to zero optical density against water (Δ_{Ec}). Then destroy the permanganic acid by means of two drops of sodium nitrite solution (3.1.11) and repeat the measurements of the optical density (Δ_{Ed}). To obtain the value of the optical density due to the manganese taken, 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 0, coloured and decolourized.

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

6.2 Test portion

Chips, not more than 1 mm thick, obtained by milling or drilling.
Mass : 1 ± 0.001 g.

6.3 Blank test

Parallel to the analysis and using the same technique, carry out a blank test.

Into a platinum dish, place 8 ml of nitric acid (3.1.6) and 12 ml of sulphuric acid (3.1.4) and evaporate to dryness (do not calcine). Take up the residue with a little warm water, add 2 ml of nitric acid (3.1.6) and 18 ml of sulphuric acid (3.1.4). Transfer the solution to a vessel of suitable capacity (e.g. 250 to 300 ml), add 40 ml of sodium hydroxide solution (3.1.2) and mix. Heat until a clear solution is obtained, cool, add 5 ml of phosphoric acid (3.1.9) and dilute to about 70 ml with water. . . Continue from this point according to the procedure described in clause 6.4.2.

6.4 Determination

6.4.1 *Attack of the test portion and preparation of the main solution.* Place the test portion in a platinum vessel of suitable capacity (e.g. 100 ml) and add, in small amounts, 40 ml of sodium hydroxide solution (3.1.2). Cover the vessel with a platinum lid and heat gently to facilitate the attack. Move the lid slightly and evaporate with care until a syrupy consistency is reached. Cool, wash the lid and the walls of the vessel with the smallest possible quantity of warm water (e.g. 30 ml) and heat gently. Transfer the alkaline solution into a glass beaker of suitable capacity (e.g. 250 to 300 ml) containing 30 ml of sulphuric acid (3.1.4) and 10 ml of nitric acid (3.1.6). Carefully wash the platinum vessel and the lid with warm water and add the washings to the acid solution contained in the glass beaker.

If manganese hydroxide separates out and adheres to the walls of the platinum vessel, transfer into the vessel a little of the acid solution, add several drops of sulphurous acid solution (3.1.3) and mix. Then again transfer the solution into the glass beaker and wash the platinum vessel with warm water.

Concentrate the solution to a volume of approximately 65 ml if the manganese content is less than 0.1 %.

For the determination of manganese contents greater than 0.1 % transfer the solution into a 100 ml or 250 ml volumetric flask, depending on the manganese content. Cool to 20 °C, make up to volume and mix. Depending on the assumed manganese content, the dilution of the main solution, the aliquot to be taken and corresponding quantities of reagents to be added to the aliquot are given in the following Table.

TABLE

Assumed manganese content	Volume of main solution	Volume of aliquot to be taken	Corresponding mass of test portion	Volume of sulphuric acid (3.1.4)	Volume of nitric acid (3.1.6)
%	ml	ml	g	ml	ml
0.005 to 0.1	–	total	1	–	–
0.1 to 0.4	100	50	0.5	5	5
0.4 to 1	250	50	0.2	10	5
1 to 1.5	250	25	0.1	10	5

6.4.2 *Colour reaction.* Into a vessel of suitable capacity (e.g. 250 ml) introduce the aliquot taken and the corresponding quantities of sulphuric acid (3.1.4) and nitric acid (3.1.6). (For manganese contents below 0.1 % develop the colour reaction in the vessel in which the main solution was prepared.) Add 5 ml of phosphoric acid (3.1.9), dilute to about 70 ml with water, then place the vessel on a hotplate fitted with a stirrer (see Note 8.3) and bring the solution to the boil. Then add 10 ml of potassium periodate solution (3.1.10) and continue boiling until the characteristic colour develops.

Boil for another 5 minutes (15 to 30 minutes if the quantity of manganese present is less than or equal to 0.2 mg). Cool to room temperature, transfer the solution to a 100 ml volumetric flask previously rinsed with treated water (3.1.1) and make up to volume with treated water (3.1.1).