ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 629

CHEMICAL ANALYSIS OF STEELS
DETERMINATION OF MANGANESE
(SPECTROPHOTOMETRIC METHOD)

1st EDITION
November 1967

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 629, *Chemical Analysis of Steels — Determination of Manganese — (Spectrophotometric Method)*, was drawn up by Technical Committee ISO/TC 17, *Steel*, the Secretariat of which is held by the British Standards Institution (BSI).

Work on this question by the Technical Committee began in 1955 and led, in 1965, to the adoption of a Draft ISO Recommendation.

In February 1966, this Draft ISO Recommendation (No. 914) 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
Australia
Austria
Belgium
Brazil
Canada
Chile
Czechoslovakia
Denmark
France
Germany
Hungary
India
Israel
Italy
Japan
Korea, Rep. of
Netherlands
New Zealand
Norway
Poland
Republic of South Africa
Romania
Spain
Sweden
Switzerland
Turkey
U.A.R.
United Kingdom
U.S.A.
U.S.S.R.
Yugoslavia

One Member Body opposed the approval of the Draft:

Portugal

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in November 1967, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 629 November 1967

CHEMICAL ANALYSIS OF STEELS

DETERMINATION OF MANGANESE

(SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This ISO Recommendation describes a spectrophotometric method for the determination of manganese in steels.

1.2 The method is applicable to manganese contents between 0.01 and 4%.

2. PRINCIPLE OF THE METHOD

After solution of the steel, the manganese is oxidized to the permanganate ion by sodium periodate and determined spectrophotometrically.

3. REAGENTS *

3.1 **Water free from organic matter.** Bring to the boil demineralized water acidified with 10 ml per litre of sulphuric acid (3.4), add several crystals of sodium periodate (3.2) and keep boiling for 10 minutes.

3.2 **Sodium periodate,** pure for analysis.

3.3 **Potassium permanganate,** pure for analysis (purity over 99.5%).

3.4 **Sulphuric acid** (d=1.83 approximately).

3.5 **Nitric acid** (d=1.40 approximately).

3.6 **Perchloric acid** (d=1.67 approximately).

NOTE. — 60% perchloric acid (d=1.54 approximately) may also be used (1000 ml of perchloric acid d=1.67 are equivalent to 1270 ml of perchloric acid d=1.54).

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* Verify by blank tests that the relevant reagents are free from manganese. Wherever necessary, the results should be corrected accordingly.

3.7 **Hydrochloric acid** ($d=1.19$ approximately).

3.8 **Sulphuric-phosphoric acid mixture.** To 600 ml of water add in the following order, carefully and stirring at the same time, 100 ml of sulphuric acid (3.4) and 150 ml of phosphoric acid ($d=1.71$); cool and dilute to 1000 ml with water.

3.9 **Hydrogen peroxide,** 100 volumes (30%).

3.10 **Sulphur dioxide.**

3.11 **Sodium periodate solution,** 50 g per litre. Dissolve 50 g of sodium periodate (3.2) in 500 ml of water and dilute to 1000 ml with water.

3.12 Standard manganese solution

3.12.1 *Stock solution.* Dissolve 2.877 g of potassium permanganate (3.3) in 500 ml of water, and add 10 ml of sulphuric acid (3.4). Decolourize the solution with hydrogen peroxide (3.9) or with a stream of sulphur dioxide (3.10). In the latter case, eliminate the excess of reagent by boiling. Adjust the solution when cold to 1000 ml in a volumetric flask.

1 ml of the stock solution contains 1.00 mg of manganese.

3.12.2 *Standard solution A.* Take 100 ml of the stock solution and dilute to 1000 ml in a volumetric flask.

1 ml of standard solution A contains 0.1 mg of manganese.

3.12.3 *Standard solution B.* Take 250 ml of the standard solution A and dilute to 1000 ml in a volumetric flask.

1 ml of standard solution B contains 0.025 mg of manganese.

4. APPARATUS

Ordinary laboratory equipment.
Spectrophotometer.

5. SAMPLING

In accordance with ISO Recommendation R 377, *Selection and Preparation of Samples and Test Pieces for Wrought Steel.*

6. PROCEDURE

6.1 For manganese contents between 0.05 and 4%

6.1.1 *Test portion*

1 ± 0.001 g for assumed manganese contents between 0.05 and 2%.
0.5 ± 0.001 g for assumed manganese contents equal to or greater than 2%.

6.1.2 *Plotting of calibration curve.* Into a 250 ml conical flask introduce 1 g of pure iron free from manganese, add 50 ml of sulphuric-phosphoric acid mixture (3.8) and heat gently until effervescence ceases. When the attack is complete, oxidize with a few drops of nitric acid (3.5) and add 20 ml of perchloric acid (3.6). * Evaporate until white perchloric acid fumes are given off and keep at this temperature for 10 minutes.

After cooling, take up with water, dilute to 70 to 80 ml and boil. If necessary, filter, washing with hot water acidified with 2 ml of perchloric acid (3.6) per litre.

Collect the filtrate in a 100 ml volumetric flask and make up to volume with water. This gives solution S_1.

Into a series of six 250 ml conical flasks

		1	2	3	4	5	6	
Introduce		0	2.0	5.0	10.0	15.0	20.0	ml of standard solution A
containing		0	0.20	0.50	1.00	1.50	2.00	mg of manganese
and corresponding to								
for a test portion of	**and a test volume of**							
1 g	40 ml	0	0.050	0.125	0.25	0.375	0.50	% of manganese
	10 ml	0	0.20	0.50	1.00	1.50	2.00	
0.5 g	40 ml	0	0.10	0.25	0.50	0.75	1.00	
	10 ml	0	0.40	1.00	2.00	3.00	4.00	

Dilute the above volumes to 25 ml with water; add 10 ml of solution S_1 and 20 ml of the sulphuric-phosphoric acid mixture (3.8). Bring to the boil, add 10 ml of sodium periodate solution (3.11) and continue as indicated in clause 6.1.4, "Determination". Make photometric measurements in cells with a suitable optical path at a wavelength of approximately 545 nm; plot the calibration curve or calculate the angular coefficient if it is a straight line.

Each solution in the range is measured with reference to that containing no added manganese.

6.1.3 *Attack.* Introduce the test portion (1 g or 0.5 g depending on the assumed manganese content) into a 250 ml conical flask together with 50 ml of sulphuric-phosphoric acid mixture (3.8) (see Note below). Heat gently until effervescence ceases. When the attack is complete oxidize with a few drops of nitric acid (3.5) and add 20 ml of perchloric acid (3.6). * Evaporate until white perchloric acid fumes are given off and keep at this temperature for 10 minutes.

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* As perchloric acid fumes attack wood, the use of fume cupboards and benches made of wood or organic material should be avoided when using perchloric acid. All exposed parts should be washed at regular intervals. These fumes may cause explosions in the presence of ammonia or nitric acid fumes.

After cooling, take up with water, dilute to 70 to 80 ml and boil. If necessary, filter, washing with hot water acidified with 2 ml of perchloric acid (3.6) per litre. Collect the filtrate in a 100 ml volumetric flask and make up to volume with water. This gives solution S_2.

NOTE. — For steels that do not dissolve readily in the sulphuric-phosphoric acid mixture (3.8), add also 10 ml of hydrochloric acid (3.7) and 10 ml of nitric acid (3.5) to facilitate the solution.

6.1.4 *Determination.* Introduce into a 250 ml conical flask the following quantities of solution S_2 and reagents, depending on the assumed manganese content:

Assumed Mn content	Original test portion	Test volume of solution S_2	Mass of the equivalent test portion	Water added	Sulphuric-phosphoric acid mixture added
0.05 to 0.50%	1 g	40 ml	0.40 g	10 ml	5 ml
0.10 to 1.00%	0.5 g	40 ml	0.20 g	10 ml	5 ml
0.20 to 2.00%	1 g	10 ml	0.10 g	25 ml	20 ml
0.40 to 4.00%	0.5 g	10 ml	0.05 g	25 ml	20 ml

Bring to the boil, add 10 ml of sodium periodate solution (3.11), boil for 2 minutes and maintain at 90 °C for 10 minutes. Cool to ambient temperature. Transfer to a 100 ml volumetric flask and make up to volume with water (3.1). Mix.

Make photometric measurements in cells with a suitable optical path at a wavelength of approximately 545 nm relative to the corresponding reference test.

6.1.5 *Reference test.* Take the same volume of solution S_2 as for the determination, add 25 ml of water and the necessary quantity of sulphuric-phosphoric acid mixture (3.8), 2 or 3 drops of hydrochloric acid (3.7) and boil for several minutes.

The manganese which has been partially oxidized by perchloric acid is thus reduced. Cool and make up to 100 ml with water not treated with sodium periodate (3.2).

6.2 For manganese contents less than 0.05%

6.2.1 *Test portion* 2 ± 0.001 g.

6.2.2 *Plotting of calibration curve.* Into each of six 250 ml conical flasks introduce 2 g of pure iron, free from manganese, add 50 ml of sulphuric-phosphoric acid mixture (3.8) and heat gently until effervescence ceases. When the attack is complete, oxidize with a few drops of nitric acid (3.5) and add 20 ml of perchloric acid (3.6). * Evaporate until white perchloric acid fumes are given off and maintain at this temperature for 10 minutes.

After cooling, take up with water, dilute to 70 to 80 ml and bring to the boil. If necessary, filter, washing with hot water acidified with 2 ml of perchloric acid (3.6) per litre. Collect the filtrate in a 100 ml volumetric flask and make up to volume with water. Take from each volumetric flask 40 ml of the solution and introduce it into a series of six 250 ml conical flasks.

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* As perchloric acid fumes attack wood, the use of fume cupboards and benches made of wood or organic material should be avoided when using perchloric acid. All exposed parts should be washed at regular intervals. These fumes may cause explosions in the presence of ammonia or nitric acid fumes.