65

INTERNATIONAL STANDARD 553

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

Manganese ores — Determination of vanadium content — Volumetric method and phosphotungstovanadate photometric method

Minerais de manganèse — Dosage du vanadium — Méthode volumétrique et méthode photométrique à l'état de phospho-vanado-tungstate

First edition — 1975-01-15

UDC 669.74 : 543.24 : 546.881

Ref. No. ISO 553-1975 (E)

Descriptors : manganese ores, chemical analysis, determination of content, vanadium, volumetric analysis, photometric analysis.

Price based on 5 pages

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, Technical Committee ISO/TC 65 has reviewed ISO Recommendation R 553 and found it technically suitable for transformation. International Standard ISO 553 therefore replaces ISO Recommendation R 553-1966 to which it is technically identical.

ISO Recommendation R 553 was approved by the Member Bodies of the following countries :

Australia
Austria
Chile
Czechoslovakia
Egypt, Arab Rep. of
France
Germany
Hungary
India
Iran
Ireland
Italy
Japan
Poland
Romania
Spain
United Kingdom
U.S.S.R.
Yugoslavia

No Member Body expressed disapproval of the Recommendation.

The Member Body of the following country disapproved the transformation of ISO/R 553 into an International Standard :

Hungary

Printed in Switzerland

INTERNATIONAL STANDARD ISO 553-1975 (E)

Manganese ores — Determination of vanadium content — Volumetric method and phosphotungstovanadate photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies two methods for the determination of the vanadium content of manganese ores, namely

Method I : a volumetric method, applicable to manganese ores the vanadium content of which exceeds 0,05 % (*m*/*m*);

Method II : a phosphotungstovanadate photometric method, applicable to manganese ores the vanadium content of which is less than 0,05 % (*m*/*m*).

2 REFERENCES

ISO 310, *Manganese ores — Determination of hygroscopic moisture content in analytical samples — Gravimetric method.*

ISO . . ., *Manganese ores and concentrates — Sampling and sample preparation for chemical analysis and determination of moisture content.* [1]

METHOD I — VOLUMETRIC METHOD

3 PRINCIPLE

Oxidation of tetravalent vanadium in sulphate solution by potassium permanganate to the pentavalent form. Titration of pentavalent vanadium with standard volumetric ammonium iron(II) sulphate solution in the presence of phenylantranilic acid as indicator.

4 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

4.1 Urea.

4.2 Sodium carbonate, anhydrous.

4.3 Hydrochloric acid, ρ 1,19 g/ml.

4.4 Sulphuric acid, ρ 1,84 g/ml.

4.5 Sulphuric acid, diluted 1 : 1.

4.6 Sulphuric acid, diluted 1 : 20.

4.7 Phosphoric acid, ρ 1,70 g/ml.

4.8 Hydrofluoric acid, 40 % (*m*/*m*).

4.9 Potassium permanganate, 10 g/l solution.

4.10 Sodium nitrite, 50 g/l solution.

4.11 Sodium diphenylamine sulphonate, 0,8 g/l solution.

4.12 Ammonium iron(II) sulphate, 0,01 N standard volumetric solution.

4.12.1 *Preparation of the solution*

Dissolve 4 g of ammonium iron(II) sulphate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ in sulphuric acid (4.6) and dilute to 1 l with the same acid.

4.12.2 *Standardization of the solution*

Take three test portions from a standard sample of manganese ore having a known vanadium content approximately the same as that of the sample to be analysed and pass them through all the stages of the analysis (7.5).

The titre of the ammonium iron(II) sulphate solution is given by the formula

$$T = \frac{B \times m}{V \times 100}$$

where

T is the titre of the ammonium iron(II) sulphate solution, expressed as grams of vanadium corresponding to 1 ml of the solution;

---

[1] This document, at present at the stage of draft proposal, is intended to complete and replace ISO/R 309, *Methods of sampling manganese ores — Part I — Ore loaded in freight wagons.*

B is the vanadium content, as a percentage by mass, of the standard sample of manganese ore;

m is the mass, in grams, of the test portion from the standard sample;

V is the volume, in millilitres, of ammonium iron(II) sulphate solution used.

Take as the titre the average of the three results.

4.13 Phenylantranilic acid, 2 g/l solution.

Dissolve 0,2 g of the acid while boiling in 100 ml of water containing 0,2 g of sodium carbonate.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum crucible.

6 SAMPLE

Use a test sample which has been crushed to a size not exceeding 0,10 mm (checked on a sieve of appropriate size) and air-dried under laboratory conditions (see ISO . . .).

7 PROCEDURE

7.1 Number of analyses

Carry out the determination simultaneously on three test portions taken from the same test sample.

7.2 Blank test

In parallel with the determination and under the same conditions carry out a blank test in duplicate.

7.3 Check test

In parallel with the determination and under the same conditions, carry out a check analysis of a standard sample of manganese ore of known vanadium content and of the type of ore to which the sample being analysed belongs.

7.4 Test portion

Weigh, to the nearest 0,000 2 g, 1 to 2 g of the test sample into a 300 ml beaker.

7.5 Determination

7.5.1 Dissolve the test portion (7.5) in the 300 ml beaker in 30 ml of hydrochloric acid (4.3). Add 25 ml of sulphuric acid (4.5), evaporate until sulphuric acid vapours appear, cool, wash the walls of the beaker with water and evaporate again until the sulphuric acid vapours appear. Dissolve the salts in 50 ml of water, filter off the insoluble residue, wash six to eight times with sulphuric acid (4.6), place the filter with the residue into the platinum crucible (5.1) and ignite at a temperature of 500 to 600 °C. Moisten the residue in the crucible with water, add 1 to 2 drops of sulphuric acid (4.4), 5 to 7 ml of hydrofluoric acid (4.8) and evaporate until dry. Ignite the residue at a temperature of 500 to 600 °C, cool, add 2 to 3 g of sodium carbonate (4.2), cover the crucible with a lid and fuse at a temperature of 800 to 900 °C. Extract the fusion in 40 to 50 ml of sulphuric acid (4.6), wash the crucible and the lid with water and remove them; add the solution thus obtained to the main solution.

7.5.2 Add 10 ml of phosphoric acid (4.7) and several drops of potassium permanganate solution (4.9) to the cool, combined solution until pink colouring appears which does not disappear for 1 to 2 min. Reduce the excess of potassium permanganate by adding, drop by drop, sodium nitrite solution (4.10); introduce 2 g of urea (4.1), stir, allow to stand for 1 min and add 80 ml of sulphuric acid (4.5). Cool the solution, add 6 drops of phenylantranilic acid solution (4.13) or 2 ml of sodium diphenylamine sulphonate solution (4.11), stir for 0,5 to 1 min, and titrate with the standard volumetric ammonium iron(II) sulphate solution (4.12) until the crimson colouring of the solution changes to green.

8 EXPRESSION OF RESULTS

8.1 Method of calculation

The vanadium content of the absolutely dry ore is given, as a percentage by mass, by the formula

$$\frac{T\,(V_2 - V_1) \times 100}{m_0} \times \frac{100}{100 - A}$$

where

T is the titre of the ammonium iron(II) sulphate solution (see 4.12.2);

V_1 is the volume, in millilitres, of the ammonium iron(II) sulphate solution used in the blank test;

V_2 is the volume, in millilitres, of the ammonium iron(II) sulphate solution used in the determination;

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

A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 310.

Take as the result the arithmetic mean of the three determinations, provided that the requirement of repeatability (see 8.2) is satisfied.

8.2 Repeatability

The difference between the highest and the lowest results shall not exceed double the absolute value of the permissible tolerance on the result of the analysis (for the corresponding interval of vanadium content) shown in the table below.

Vanadium content, %		Permissible tolerance, % (in absolute value)
from	to	
0,05	0,1	± 0,010
(over) 0,1	0,3	± 0,015
" 0,3	0,5	± 0,020

The average result of the simultaneous check analysis of the standard sample of manganese ore for vanadium content shall not differ from the result shown in the certificate by more than the ± value of the permissible tolerance (for the corresponding interval of vanadium content) shown in the table.

9 TEST REPORT

The test report shall include the following information :

a) indications necessary for the identification of the sample;

b) reference to this International Standard;

c) results of the analysis;

d) the reference number of the results;

e) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the results.

METHOD II – PHOSPHOTUNGSTOVANADATE PHOTOMETRIC METHOD

10 PRINCIPLE

Removal of interfering elements by fusion of a test portion with sodium peroxide and sodium carbonate and extraction of the fused mass with water. Formation, in hydrochloric acid medium, of the yellow phosphotungstovanadate complex. Photometric measurement of the coloured complex at a wavelength of 420 to 430 nm.

11 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

11.1 Sodium carbonate, anhydrous.

11.2 Sodium peroxide.

11.3 Hydrochloric acid, diluted 1 : 1.

11.4 Phosphoric acid, diluted 1 : 2

11.5 Potassium permanganate, 10 g/l solution.

11.6 Sodium nitrite, 10 g/l solution.

11.7 Sodium tungstate ($Na_2WO_4.2H_2O$), 100 g/l solution.

11.8 Hydrogen peroxide, 1 % (perhydrol) solution.

11.9 Standard vanadium solution A.

Dissolve, while heating, 0,229 6 g of ammonium metavanadate in 100 ml of sulphuric acid, diluted 1 : 1. Pour the solution obtained into a 1 l volumetric flask, cool, dilute with water to the mark and stir.

1 ml of the solution contains 0,000 1 g of vanadium. Check the concentration of the solution from time to time.

11.10 Standard vanadium solution B (freshly prepared).

Transfer 10 ml of the standard vanadium solution (A) to a 100 ml flask, dilute to the mark with sulphuric acid, diluted 1 : 20, and stir.

1 ml of the solution contains 0,000 01 g of vanadium.

11.11 Methyl orange, 1 g/l solution.

12 APPARATUS

Ordinary laboratory apparatus and

12.1 Iron crucible.

12.2 Photoelectric absorptiometer fitted with a blue (wavelength 420 to 430 nm) light-filter.

13 SAMPLE

Use a test sample which has been crushed to a size not exceeding 0,10 mm (checked on a sieve of appropriate size) and air-dried under laboratory conditions (see ISO . . .).

14 PROCEDURE

14.1 Number of analyses

Carry out the determination simultaneously on three test portions taken from the same test sample.

14.2 Blank test

In parallel with the determination and under the same conditions, carry out a blank test in duplicate, to enable a corresponding correction in the result of the determination to be made.

14.3 Check test

In parallel with the determination and under the same conditions, carry out a check analysis of a standard sample of manganese ore of known vanadium content and of the type of ore to which the sample being analysed belongs.

14.4 Test portion

Weigh, to the nearest 0,000 2 g, 1 g of the test sample into the iron crucible (12.4).

14.5 Determination

14.5.1 Mix with the test portion (14.4) in the iron crucible 8 to 10 g of a 1 : 1 mixture of sodium carbonate (11.1) and sodium peroxide (11.2), cover with a lid and fuse at a temperature of 700 to 800 °C. Cool, then extract the fusion by heating in 100 ml of water. If the solution above the residue is of green colour, add several drops of alcohol, heat to boiling and boil until the green colour disappears. After cooling, transfer the solution with the residue into a 200 to 250 ml volumetric flask, dilute to the mark with water, stir and allow to stand until the precipitate has settled. Filter the solution through a dry filter into a dry beaker. By means of a pipette, transfer 25 ml of the filtrate to a 100 ml beaker, add 2 or 3 drops of methyl orange solution (11.11), neutralize with hydrochloric acid (11.3) until the indicator colour changes and add 5 ml of the acid in excess. Evaporate the solution until dry (for the separation of silicic acid), add to the dry residue 3 ml of hydrochloric acid (11.3) and 8 to 10 ml of hot water (60 to 70 °C) and extract while heating. Filter the solution obtained through a filter of average density into a 50 ml flask and wash the filter three or four times with hot water (60 to 70 °C). Cool the solution, add 0,5 ml of hydrogen peroxide solution (11.3) and, while stirring, add, drop by drop, potassium permanganate solution (11.5) until a pink colour stable for 2 to 3 min appears. Then add, drop by drop, sodium nitrite solution (11.6) until complete decoloration of the solution and then add 1 or 2 drops in excess. Add 2 ml of phosphoric acid (11.4) and 1 ml of sodium tungstate solution (11.7). Dilute with water to the mark and stir.

After 10 min carry out the photometric measurement using the blue light-filter. To determine the zero of the apparatus, take an aliquot portion of the solution of the ore contained in the volumetric flask and pass it through all the stages of analysis but without adding sodium tungstate.

14.5.2 Determine the percentage of vanadium in the test sample, from the absorbance of the solution being tested, using either of the following methods :

a) *Calibration curve method*

To construct the calibration curve, take corresponding volumes of standard vanadium solution covering both the extreme (maximum and minimum) and the intermediate contents of vanadium in the given type of ore and pass them through all the stages of the analysis, including the determination of the absorbance, parallel with the sample being analysed.

b) *Comparison method*

Take a definite volume of standard vanadium solution of a concentration approaching that of the weighed quantity of the sample being analysed, and pass it through all the stages of the analysis.

15 EXPRESSION OF RESULTS

15.1 Method of calculation

The vanadium content of the absolutely dry ore is calculated, as a percentage by mass, either

a) as the value read directly from the calibration curve and multiplied by the factor $100/(100 - A)$, or

b) by the comparison method using the formula

$$\frac{D_x \times m_1 \times 100}{D_{st} \times m_0} \times \frac{100}{100 - A}$$

where

D_x is the absorbance of the solution being analysed;

D_{st} is the absorbance of the standard vanadium solution;

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

m_1 is the mass, in grams, of vanadium in the volume of standard vanadium solution used for the determination;

A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 310.

Take as the result the arithmetic mean of the three determinations, provided that the requirement of repeatability (see 15.2) is satisfied.

15.2 Repeatability

The difference between the highest and the lowest results shall not exceed double the absolute value of the permissible tolerance on the result of the analysis (for the corresponding interval of vanadium content) shown in the table below.

Vanadium content, %		**Permissible tolerance, %** (in absolute value)
from (over)	to	
	0,01	± 0,000 5
0,01	0,03	± 0,001 5
0,03	0,05	± 0,002 5