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R 550

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF TITANIUM CONTENT

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BRIEF HISTORY

The ISO Recommendation R 550, *Methods of Chemical Analysis of Manganese Ores — Determination of Titanium Content*, was drawn up by Technical Committee ISO/TC 65, *Manganese Ores*, the Secretariat of which is held by the Komitet Standartov, Mer i Izmeritel'nyh Priborov pri Sovete Ministrov SSSR (GOST).

Work on this question by the Technical Committee began in 1957 and led, in 1959, to the adoption of a Draft ISO Recommendation.

In November 1962, this Draft ISO Recommendation (No. 539) 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
Austria
Burma
Chile
Czechoslovakia
France
Germany
Hungary
India
Iran
Ireland
Italy
Japan
Poland
Romania
Spain
U.A.R.
United Kingdom
U.S.S.R.
Yugoslavia

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 December 1966, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 550 December 1966

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF TITANIUM CONTENT

(Atomic mass Ti: 47.90; molecular mass TiO_2: 79.90)

1. GENERAL INSTRUCTIONS

1.1 In the following analysis, use a sample for chemical analysis of air-dried manganese ore, which has been crushed to a size not exceeding 0.10 mm and checked on a sieve of appropriate size.

Simultaneously with the collection of samples for the determination of titanium, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of titanium in ore which is absolutely dry by multiplying the numerical results of the determination of titanium by the conversion factor K, as found from the following formula:

$$K = \frac{100}{100 - A}$$

where A = hygroscopic moisture content, per cent.

1.2 The determination of titanium in manganese ore is carried out by simultaneously analysing three samples of ore with two blank determinations to enable a corresponding correction in the result of the determination to be made.

Simultaneously and under the same conditions, carry out a check analysis of a standard sample of manganese ore, for titanium content.

The arithmetical mean of the three results is accepted as the final result.

The following conditions should be observed:

The maximum difference between the highest and the lowest results should not exceed double the absolute value of the permissible tolerance on the result of the analysis (for the corresponding interval of titanium content), shown in the table under clause 5.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for titanium content should not differ from the result shown in the certificate by more than the ± value of the permissible tolerance (for the corresponding interval of titanium content), shown in the table under clause 5.2, " Accuracy of method ".

For the analysis take a standard sample of the type of ore to which the sample being analysed belongs.

1.3 The test samples should be weighed to an accuracy of ± 0.0002 g.

1.4 Distilled water should be used in the determination and for the preparation of solutions.

1.5 Meanings of the following expressions:

hot water (or solution)	implies a temperature of the liquid of 60 to 70 °C;
warm water (or solution)	implies a temperature of the liquid of 40 to 50 °C;

diluted (1 : 1), (1 : 2), (1 : 5), etc. means that:

the first figure gives the number of parts by volume of concentrated acid or some other solution, and

the second figure gives the number of parts by volume of water.

1.6 Indications as to the concentration of solutions show the quantity of solute (in grammes) in the corresponding volume of the solvent.

1.7 The following symbols and abbreviations are used:

CP	chemically pure
d	relative density
g	gramme
g/l	grammes per litre
l	litre
ml	millilitre
nm	nanometer

2. PRINCIPLE OF METHOD

The test sample of ore is dissolved in the hydrochloric acid. After the separation of the silicic acid, titanium is precipitated with cupferron. Vanadium is separated by fusing the residue with sodium carbonate and extracting it in water. By fusing titanium dioxide with potassium pyrosulphate, titanium is transformed into solution, its content being determined by the photometric method with hydrogen peroxide.

3. REAGENTS REQUIRED

3.1 *Sodium carbonate*, anhydrous, CP.

3.2 *Potassium pyrosulphate* ($K_2S_2O_7$), CP.

3.3 *Ammonium sulphate* ($(NH_4)_2SO_4$), CP, solution (50 g/l).

3.4 *Hydrochloric acid*, CP (*d* 1.19).

3.5 *Sulphuric acid*, CP (*d* 1.84).

3.6 *Sulphuric acid*, CP, diluted (1 : 1).

3.7 *Sulphuric acid*, CP, diluted (1 : 10).

3.8 *Sulphuric acid*, CP, diluted (1 : 20).

3.9 *Sulphuric acid*, CP, diluted (1 : 50).

3.10 *Phosphoric acid*, CP (*d* 1.70).

3.11 *Hydrofluoric acid*, CP, 40%.

3.12 *Ammonia*, CP (*d* 0.91).

3.13 *Cupferron*, CP, solution (30 g/l), freshly prepared.

3.14 *Cupferron*, CP, washing solution (20 ml of cupferron solution (30 g/l) and 40 ml of sulphuric acid (*d* 1.84) per 1 litre of water).

3.15 *Sodium carbonate*, CP, solution (10 g/l).

3.16 *Hydrogen peroxide*, CP, solution 3%.

3.17 *Standard solution of titanium sulphate :* 0.1 g of titanium dioxide, CP, is placed into a platinum crucible and fused with 2 g of potassium pyrosulphate at a temperature of 500 to 600 °C for 35 to 40 min; after cooling the fusion is extracted in 60 to 80 ml of sulphuric acid solution, diluted (1 : 10), containing ammonium sulphate (50 g/l); the solution obtained is placed in a measuring flask of 1 litre capacity, diluted with water up to the mark and then stirred; 1 ml of the solution contains 0.000 06 g of titanium.

4. PROCEDURE

4.1 Dissolve, while heating, a test sample of 1 to 2 g of manganese ore in 30 ml of hydrochloric acid (*d* 1.19). After the ore has been dissolved, add 25 ml of sulphuric acid solution, diluted (1 : 1), evaporate the solution until the vapours of sulphuric acid appear, cool, dilute it with 40 to 50 ml of water and filter the insoluble residue off.

4.2 Wash the filter and the residue six to eight times with sulphuric acid solution, diluted (1 : 20), place into a platinum crucible, dry, ignite and calcinate at a temperature of 500 to 600 °C. Moisten the residue in the crucible with water, add two or three drops of sulphuric acid (*d* 1.84), 5 to 7 ml of hydrofluoric acid (40 %) and evaporate on a sand bath until dry. Ignite the residue at a temperature of 500 to 600 °C, cool it, add 2 to 3 g of potassium pyrosulphate and fuse at a temperature of 500 to 600 °C. Extract the fusion in 40 to 50 ml of sulphuric acid, diluted (1 : 10), wash the crucible with sulphuric acid, diluted (1 : 50), over the beaker, take it out of the beaker and add the obtained solution to the main one.

4.3 Neutralize the combined solutions with ammonia (*d* 0.91) until the precipitate of hydroxides begins to separate; then dissolve the precipitate once again in sulphuric acid, diluted (1 : 1), adding in excess 20 ml of sulphuric acid per each 100 ml of the solution. The solution being cooled to a temperature of 10 to 15 °C, add to it a small quantity of ashless paper pulp and, continuously stirring it, add by fine jet 20 to 25 ml of a freshly prepared cupferron solution (30 g/l) (3.13). The solution over the residue is allowed to stand for 30 to 40 min; then filter it through a filter of an average density, and wash eight to ten times with sulphuric acid, diluted (1 : 20), containing a small quantity of cupferron (3.14).

4.4 It is better to carry out the filtration and rinsing of titanium cupferronate under a slight suction, a platinum cone being placed under the filter.

4.5 Place the filter with the residue into a platinum crucible, carefully dry it, ignite and calcinate. The ignition and calcination of the residue of titanium cupferronate should be carried out very carefully as the residue can easily be fused and volatilized.

4.6 Mix the ignited residue with 3 to 5 g of sodium carbonate (anhydrous) and fuse it at a temperature of 900 to 1000 °C for 30 to 35 min.

4.7 After cooling, extract the fusion in 50 to 60 ml of hot water, heat to boiling, boil for 5 to 10 min, filter the insoluble residue through a filter of an average density and wash eight to ten times with hot sodium carbonate solution (10 g/l). Discard the filtrate. Place the filter and the residue into the platinum crucible in which fusing with sodium carbonate was carried out, dry, ignite and calcinate carefully, and after cooling, fuse with 5 g of potassium pyrosulphate at a temperature of 500 to 600 °C for 25 to 35 min.

4.8 After cooling, extract the fusion in 40 to 50 ml of sulphuric acid, diluted (1 : 10), to which add 10 ml solution of ammonium sulphate (50 g/l). Filter the solution thus obtained through a filter of an average density into a 100 ml measuring flask; wash the filter three to four times with sulphuric acid, diluted (1 : 10). To check the insoluble residue, ignite in the platinum crucible and fuse for the second time with a small quantity of potassium pyrosulphate, then extract it in sulphuric acid, diluted (1 : 10). If hydrogen peroxide gives the solution a yellow colour, add the solution obtained to the main one. Add to the solution 2 ml of phosphoric acid (*d* 1.70), 2 ml of 3 % hydrogen peroxide solution, dilute up to the mark with the sulphuric acid, diluted (1 : 10), thoroughly stir and carry out the photometry using a blue light filter (wavelength = 420 to 430 nm).

4.9 The percentage content of titanium is found

(*a*) by the calibration curve method, or

(*b*) by the comparison method from the value of the optical density of the solution being tested.

(*a*) *Calibration curve method*

To construct the calibration curve, corresponding volumes of standard solution of titanium are used covering both the extreme (maximum and minimum) and the intermediate titanium content for the given type of ore; they are taken through all the stages of the analysis. The percentage content of titanium is found from the calibration curve on the basis of the optical density of the solution.

(*b*) *Comparison method*

Take a specified volume of the standard solution of titanium having a titanium content close to that of the analysed sample of ore and pass it through all the stages of the analysis.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of titanium is calculated

(*a*) by the calibration curve method, graphically;

(*b*) by the comparison method, from the following formula:

$$\mathrm{Ti} = \frac{D_{\mathrm{x}}\ C_{\mathrm{st}} \times 100}{D_{\mathrm{st}}\ G} \text{ per cent}$$

where D_{x} = optical density of solution being analysed, as compared with the blank test;

C_{st} = concentration of the standard solution, expressed in grammes of titanium;

D_{st} = optical density of the standard solution of titanium;

G = mass of sample of ore, in grammes.

5.2 Accuracy of method

The permissible tolerances, per cent (absolute value), are given in the table below:

Titanium content		Permissible tolerance (in absolute value)
from (over)	to	
	0.05 %	± 0.003 %
0.05 %	0.1 %	± 0.010 %
0.1 %	0.5 %	± 0.020 %
0.5 %	1.00 %	± 0.030 %

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