ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 313

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF TOTAL IRON CONTENT

1st EDITION

July 1963

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Printed in Switzerland

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

BRIEF HISTORY

The ISO Recommendation R 313, *Methods of Chemical Analysis of Manganese Ores—Determination of Total Iron 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.

Work on this question by the Technical Committee began in 1954 and led, in 1957, to the adoption of a Draft ISO Recommendation.

In October 1958, this Draft ISO Recommendation (No. 246) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

Austria	Germany	Poland
Bulgaria	Hungary	Portugal
Burma	India	Republic of South Africa
Chile	Ireland	Romania
Czechoslovakia	Italy	Spain
Finland	Japan	United Kingdom
France	Netherlands	U.S.S.R.

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 July 1963, to accept it as an ISO RECOMMENDATION.

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF TOTAL IRON CONTENT

(Atomic mass Fe : 55.85 ; molecular mass FeO : 71.85 ; molecular mass Fe_2O_3 : 159.70)

This ISO Recommendation contains three parts:

I. INTRODUCTION

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 total iron, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of total iron in ore which is absolutely dry by multiplying the numerical results of the determination of iron 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 total iron 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 total iron 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 total iron content), shown in the tables under clauses 5.2 and 9.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for total iron 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 total iron content), shown in the tables under clauses 5.2 and 9.2, " 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 and the residues should be weighed to an accuracy of ± 0.0002 g.

1.4 Distilled water should be used during the procedure 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:

d	relative density
g	gramme
g/l	grammes per litre
ml	millilitre
mm	millimetre
PFA	pure for analysis

II. DICHROMATE METHOD — FIRST VARIANT

2. PRINCIPLE OF METHOD

The sample of ore is dissolved in concentrated hydrochloric acid (d 1.19). Trivalent iron is reduced with stannous chloride. The surplus stannous chloride is oxidized with mercuric chloride.

The reduced iron is titrated with a solution of potassium dichromate in the presence of sodium diphenylamine sulphonate indicator.

3. REAGENTS REQUIRED

3.1 *Hydrochloric acid*, PFA (d 1.19).

3.2 *Stannous chloride solution*, PFA (100 g/l). 10 g of stannous chloride are dissolved while heating in 50 ml of hydrochloric acid (d 1.19) to which are added 50 ml of water.

3.3 *Mercuric chloride solution*, PFA, (50 g/l).

3.4 *Sodium diphenylamine sulphonate indicator solution* (0.8 g/l).

3.5 *Acid mixture :* 250 ml of sulphuric acid (d 1.84) are carefully poured into 750 ml of water; when the mixture is cool, add to it 50 ml of phosphoric acid (d 1.7).

3.6 *Standard solution of potassium dichromate :* 1.7558 g of potassium dichromate, PFA, re-crystallized and dried at a temperature of 180 to 200 °C, are dissolved in a small quantity of distilled water and placed in a measuring flask of 1 litre capacity; add more water until the level of the solution reaches the mark. 1 ml of this solution is required for 0.002 g of iron.

4. PROCEDURE

4.1 Weigh 0.5 to 1 g of manganese ore, depending on iron content, into a 100 ml beaker. Add 10 to 15 ml of hydrochloric acid (d 1.19) and heat until the attack is complete. Add the stannous chloride solution (100 g/l) drop by drop until the solution is decolorized, adding subsequently an excess of not more than 1 to 2 drops. Transfer the reduced solution of iron to a 500 ml flask, washing the sides of the beaker with water. Add 5 ml of mercuric chloride solution (50 g/l), stir and leave to stand for 2 to 3 min. During this time a small quantity of white silky precipitate of mercurous chloride (Hg_2Cl_2) should be formed. If the solution does not yield the precipitate or if, on the contrary, it yields too much precipitate, and especially if the precipitate is tinted by metallic mercury to a dark colour, the determination should be repeated.

4.2 Dilute the solution with cold water to approximately 200 to 250 ml. Add 25 ml of acid mixture and 2 ml of the sodium diphenylamine sulphonate indicator. Stir and titrate with potassium dichromate solution until the mixture changes colour from green to violet-blue.

NOTES

1. Depending on the percentage of iron, the mass of the test sample is determined as follows:

   up to and including 5.0 per cent of iron . . . .   1 g of ore,

   over 5.0 per cent of iron . . . .   0.5 g of ore.

2. In the presence of copper and arsenic, the determination of iron is effected on the lines of the second variant, the copper being first separated with hydrogen sulphide.

3. The presence of lead does not interfere with the determination of iron.

4. If the ore being analysed does not decompose completely in hydrochloric acid, add 0.5 g of sodium fluoride or fuse the insoluble residue with sodium carbonate, or with potassium pyrosulphate.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of total iron is calculated from the following formula:

$$Fe = \frac{VT \times 100}{G} \text{ per cent}$$

where

V = number of millilitres of potassium dichromate solution used in titration;

T = titre of potassium dichromate solution, expressed in grammes of iron;

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:

Total iron content		Permissible tolerance (in absolute value)
from (over)	to	
	1.00 per cent	± 0.02 per cent
1.00 per cent	2.00 per cent	± 0.03 per cent
2.00 per cent	3.00 per cent	± 0.04 per cent
3.00 per cent	5.00 per cent	± 0.06 per cent
5.00 per cent		± 0.10 per cent

III. DICHROMATE METHOD — SECOND VARIANT
FOR ORES CONTAINING COPPER, LEAD AND ARSENIC

6. PRINCIPLE OF METHOD

The sample of ore is dissolved in hydrochloric acid. Silicic acid having been removed, lead, arsenic and copper are separated with hydrogen sulphide. The iron hydroxide is precipitated with ammonia, the residue is dissolved in hydrochloric acid, the trivalent iron is reduced with stannous chloride and titrated with potassium dichromate solution in the presence of sodium diphenyl-amine sulphonate indicator.

7. REAGENTS REQUIRED

7.1 *Ammonium hydroxide*, PFA (*d* 0.91).

7.2 *Ammonium chloride*, PFA.

7.3 *Iron sulphide*, PFA (to obtain hydrogen sulphide).

7.4 *Hydrochloric acid*, PFA (*d* 1.19).

7.5 *Hydrochloric acid*, PFA, diluted 1 : 1.

7.6 *Hydrochloric acid*, PFA, diluted 1 : 2.

7.7 *Hydrochloric acid*, PFA, diluted 1 : 50.

7.8 *Nitric acid*, PFA (*d* 1.40).

7.9 *Sulphuric acid*, PFA (*d* 1.84).

7.10 *Hydrofluoric acid*, PFA (40 per cent).

7.11 *Potassium chlorate* ($KClO_3$), PFA.

7.12 *Potassium pyrosulphate* ($K_2S_2O_7$), PFA.

7.13 *Sodium carbonate*, PFA, anhydrous.

7.14 The other reagents are as in the first variant.

8. PROCEDURE

8.1 Weigh 1 g of manganese ore into a 100 to 150 ml beaker, dissolve in 20 to 30 ml of hydro-chloric acid (*d* 1.19) whilst lightly heating, add 1 g of potassium chlorate and continue heating.

After the ore has been completely dissolved, evaporate the solution to dryness. Dissolve the dry residue in 20 ml hydrochloric acid (*d* 1.19), add 50 ml of water, filter off the residue of silicic acid and wash with hydrochloric acid, diluted 1 : 50. Place the filter with the residue in a platinum crucible and ignite carefully. Add 2 drops of water, 2 drops of sulphuric acid (*d* 1.84) and 3 to 4 ml of 40 per cent hydrochloric acid, and evaporate until completely dry. Heat the dry residue to a temperature of 450 to 500 °C. When the residue has cooled, fuse it with 2 to 3 g of anhydrous sodium carbonate or with potassium pyrosulphate. Extract the fusion with 15 to 20 ml of hydrochloric acid, diluted 1 : 2, and add the solution obtained to the principal filtrate.

8.2 To the combined solutions add, drop by drop, ammonium hydroxide until permanent turbidity is reached. Dissolve the turbidity by adding, drop by drop, hydrochloric acid (d 1.19) and add an excess of the latter of 5 ml per 100 ml of solution. Allow hydrogen sulphide to pass through the solution, heated to boiling point, for 20 to 25 min.

8.3 Keep the solution with the residue of lead, copper and arsenic sulphides on a warm plate for 30 to 40 min, and filter off the residue on a medium filter.

Wash the residue on the filter 8 to 10 times with hydrochloric acid, diluted 1 : 50, saturated with hydrogen sulphide, and discard.

8.4 Evaporate the filtrate to half its initial volume, add 10 ml of nitric acid (d 1.40) to the hot solution, heat it to boiling and allow to boil for 2 to 3 min, until the nitric oxides are dispelled.

Add 10 g of ammonium chloride, and immediately precipitate the iron hydroxide with ammonia, adding until the solution begins to give off a strong smell. Heat the solution to boiling, and boil for 3 to 5 min. Filter off the residue of hydroxides on a fast filtering filter. After filtering has been completed, wash the sides of the beaker with water 4 to 5 times. Wash the residue 8 to 10 times with a hot solution of ammonium chloride (10 g/1), and then dissolve it on the filter in 20 to 30 ml of hydrochloric acid, diluted 1 : 1, collecting the solution in the beaker in which the precipitation was effected.

8.5 To ensure complete extraction of iron, wash the filter with hydrochloric acid, diluted 1 : 50, and then with hot water.

Evaporate the solution down to 10 to 15 ml, and continue as in the procedure described for the first variant.

NOTE. In the presence of a large percentage of vanadium, fuse the sample of manganese ore with sodium carbonate (anhydrous), extract the fusion with water, filter off the precipitate and dissolve it in hydrochloric acid. Further procedure is carried out as given above.

9. EXPRESSION OF RESULTS

9.1 Method of calculation

See first variant.

9.2 Accuracy of method

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

Total iron content		Permissible tolerance (in absolute value)
from (over)	to	
	1.00 per cent	± 0.02 per cent
1.00 per cent	2.00 per cent	± 0.03 per cent
2.00 per cent	3.00 per cent	± 0.04 per cent
3.00 per cent	5.00 per cent	± 0.06 per cent
5.00 per cent		± 0.10 per cent