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ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 312

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF ACTIVE OXYGEN

CONVENTIONALLY EXPRESSED AS MANGANESE DIOXIDE

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BRIEF HISTORY

The ISO Recommendation R 312, *Methods of Chemical Analysis of Manganese Ores — Determination of Active Oxygen conventionally expressed as Manganese Dioxide*, 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. 245) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

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

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.

ISO Recommendation R 312 July 1963

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF ACTIVE OXYGEN

CONVENTIONALLY EXPRESSED AS MANGANESE DIOXIDE

(Atomic mass Mn: 54.94; molecular mass MnO_2: 86.94)

This ISO Recommendation contains two parts:

I. Introduction . . . . . section 1,

II. Volumetric method, by reducing with ferrous ammonium sulphate . . . sections 2 to 6.

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 active oxygen (conventionally expressed as manganese dioxide), take three more test samples for the determination of hygroscopic moisture.

Calculate the content of active oxygen (conventionally expressed as manganese dioxide) in ore which is absolutely dry by multiplying the numerical results of the determination of active oxygen 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 active oxygen (conventionally expressed as manganese dioxide) 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 active oxygen (conventionally expressed as manganese dioxide) 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 manganese dioxide content) shown in the table under clause 6.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for active oxygen (conventionally expressed as manganese dioxide) content should not differ from the result shown in the certificate by more than the $\pm$ value of the permissible tolerance (for the corresponding interval of manganese dioxide content), shown in the table under clause 6.2, " 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 $\pm$ 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. VOLUMETRIC METHOD, BY REDUCING WITH FERROUS AMMONIUM SULPHATE

2. PRINCIPLE OF METHOD

The method is based on dissolving a sample of ore in an excess of standard solution of ferrous ammonium sulphate in a sulphuric acid solution. During the reaction, an equivalent quantity of ferrous ammonium sulphate is oxidized by the manganese dioxide contained in the test sample of ore. The surplus of ferrous ammonium sulphate is titrated with potassium dichromate solution in the presence of sodium diphenylamine sulphonate as indicator.

3. REAGENTS REQUIRED

3.1 *Ferrous ammonium sulphate* $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, PFA, solution (60 g/l).
60 g of ferrous ammonium sulphate are dissolved in 1 litre of sulphuric acid diluted (1 : 7).

3.2 *Sulphuric acid*, PFA, diluted (1 : 7).

3.3 *Phosphoric acid*, PFA (*d* 1.7).

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

3.5 *Standard solution of potassium dichromate*, PFA. Dissolve 8.780 g. of potassium dichromate, re-crystallized and dried at 180 to 290 °C, in 100 ml of water; pour the solution into a measuring flask of 1 litre capacity, dilute up to the mark with water and mix well.

4. STANDARDIZATION OF POTASSIUM DICHROMATE SOLUTION

4.1 Against standard sample of ore

4.1.1 To determine the titre of the potassium dichromate solution, take three samples of the standard sample of manganese ore, having approximately the same content of manganese dioxide as that of the sample being analysed, and pass them through all the stages of the analysis.

4.1.2 The titre of the potassium dichromate solution is found from the following formula:

$$T = \frac{AG}{V \times 100}$$

where

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

A = content of manganese dioxide in the standard sample of ore, per cent;

G = mass of sample of the standard sample of ore, in grammes;

V = number of millilitres of potassium dichromate solution equivalent to the percentage of manganese dioxide in the sample of the standard sample of ore.

5. PROCEDURE

5.1 Weigh 0.25 g of manganese ore into a conical flask of 300 ml capacity. Add 50 ml of the ferrous ammonium sulphate solution (60 g/l).

5.2 Close the flask with a stopper with two outflow pipes; allow a current of carbon dioxide to pass through it; thoroughly mix and, without stopping the current of CO_2, heat the contents of the flask moderately until the ore is dissolved (until the dark-coloured particles have disappeared).

5.3 Cool the contents of the flask (without stopping the current of carbon dioxide). Open the flask: add 10 ml of phosphoric acid (*d* 1.7) and 2 ml of sodium diphenylamine sulphonate indicator solution. Dilute with cold water (from which the air has been removed by boiling) to 150 ml and titrate off the surplus of ferrous ammonium sulphate with the potassium dichromate solution until the solution becomes permanently violet-blue. The correlation between the solutions of ferrous ammonium sulphate and potassium dichromate is established under test conditions. For this purpose pour into a conical flask from a burette the same number of millilitres of ferrous ammonium sulphate as was used to dissolve the sample of ore. Add 10 ml of phosphoric acid (*d* 1.7), 2 ml of the indicator solution, and dilute with cold water to 150 ml. Titrate with potassium dichromate solution.

6. EXPRESSION OF RESULTS

6.1 Method of calculation

The percentage content of manganese dioxide is calculated from the following formula:

$$MnO_2 = \frac{T\,(V_1 - V_2)\,100}{G} \text{ per cent}$$

where

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

V_1 = number of millilitres of potassium dichromate solution used in the titration of the ferrous ammonium sulphate solution, while establishing the correlation;

V_2 = number of millilitres of standard potassium dichromate solution used in the titration of the excess of ferrous ammonium sulphate in the procedure of the analysis of ore;

G = mass of sample of ore, in grammes.

6.2 Accuracy of method

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

Active oxygen content •		Permissible tolerance (in absolute value)
from (over)	to	
	50.00 per cent	± 0.15 per cent
50.00 per cent	70.00 per cent	± 0.20 per cent
70.00 per cent	90.00 per cent	± 0.25 per cent

• Conventionally expressed as manganese dioxide.