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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 319

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF TOTAL MANGANESE CONTENT

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BRIEF HISTORY

The ISO Recommendation R 319, *Methods of Chemical Analysis of Manganese Ores — Determination of Total Manganese 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. 252) 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
Burma	Ireland	South Africa
Chile	Italy	Romania
Czechoslovakia	Japan	Spain
France	Netherlands	United Kingdom
Germany	Poland	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 MANGANESE CONTENT

(Atomic mass Mn : 54.94; molecular mass MnO₂ : 86.94)

This ISO Recommendation contains three parts:

- I. Introduction section 1,
- II. Bismuthate method sections 2 to 6,
- III. Volumetric permanganate method sections 7 to 11.

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

Calculate the content of total manganese in ore which is absolutely dry, by multiplying the numerical results of the determination of total manganese 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 manganese 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 manganese 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 manganese content), shown in the tables under clauses 6.2 and 11.2, "Accuracy of method".

The average result of the simultaneous check analysis of the standard sample of manganese ore for total manganese 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 total manganese content), shown in the tables under clauses 6.2 and 11.2, "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:

cm	centimetre
<i>d</i>	relative density
g	gramme
g/l	grammes per litre
ml	millilitre
mm	millimetre
PFA	pure for analysis

II. BISMUTHATE METHOD

2. PRINCIPLE OF METHOD

The determination of total manganese in manganese ore by the bismuthate method is based on the oxidization of divalent manganese with sodium bismuthate in a nitric acid solution to septivalency, with a subsequent reduction of manganese acid (HMnO_4) by a standard solution of ferrous ammonium sulphate, and titration of the excess with a standard solution of potassium permanganate.

It is essential that the oxidization should be carried out in nitric acid diluted 1 : 3, devoid of free oxides of nitrogen. The concentration of manganese should not exceed 0.10 g per 250 ml of the solution.

3. REAGENTS REQUIRED

- 3.1 *Nitric acid*, PFA, diluted 1 : 3.
- 3.2 *Nitric acid*, PFA, diluted 3 : 97, free from oxides of nitrogen (the removal of the oxides of nitrogen is effected by passing a current of oxygen or air through the nitric acid (*d* 1.40) until there is a complete decolorization of the latter).
- 3.3 *Sulphuric acid*, PFA (*d* 1.84).
- 3.4 *Sulphuric acid*, PFA, diluted 1 : 9.
- 3.5 *Hydrofluoric acid*, PFA (40 per cent).
- 3.6 *Sodium carbonate, anhydrous*, PFA.
- 3.7 *Sodium oxalate, anhydrous*, precipitated in the presence of alcohol, PFA.
- 3.8 *Sodium nitrite* (NaNO_2), PFA, solution (50 g/l).
- 3.9 *Sodium bismuthate*. The reagent should contain not less than 70 to 78 per cent of active oxygen, as calculated for NaBiO_3 , or more than 0.002 per cent of chlorine ions, or more than 0.001 per cent of manganese.
- 3.10 *Ferrous ammonium sulphate* ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$). 90 g of ferrous ammonium sulphate, PFA, are dissolved in 1 litre of sulphuric acid, diluted 5 : 95.
- 3.11 *Hydrogen peroxide*, PFA, 30 per cent (perhydrol).
- 3.12 *Standard solution of potassium permanganate*, 0.25 N. 7.9 g of potassium permanganate, PFA, are dissolved in 1 litre of distilled water. The solution thus obtained is allowed to stand for 6 days and then it is siphoned off or filtered through a layer of glass wool and ignited asbestos into a dark glass flask without disturbing any precipitate of manganese dioxide. The solution contained in the flask should be protected from dust and gases, and kept in a cool place. The solution should not be standardized earlier than the day following filtration.

4. STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION (THEORETICAL TITRE)

4.1 Against sodium oxalate

4.1.1 Weigh 0.25 to 0.5 g of sodium oxalate, dried to constant weight at a temperature of 110 to 120 °C, into a flask of 500 ml capacity. Add to it 250 ml of sulphuric acid, diluted 1 : 9, heat the solution to a temperature of 70 to 80 °C and then titrate with the potassium permanganate solution until a permanent pink colour is reached.

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

$$T = \frac{G \times 0.16396}{V}$$

where

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

G = mass of sodium oxalate, in grammes;

0.16396 = conversion factor for the titre of potassium permanganate solution, expressed as sodium oxalate, to the titre of manganese;

V = number of millilitres of potassium permanganate solution used for titrating the test sample of sodium oxalate.

4.1.3 The titre of the potassium permanganate solution is established with not less than three test samples of sodium oxalate, the mean of three closely coinciding results being taken as the final result.

4.1.4 It is advisable to check periodically the titre of the potassium permanganate solution by means of test samples of potassium permanganate, PFA (0.25 to 0.3 g), passing them through all the stages of the analysis.

5. PROCEDURE

5.1 Weigh 0.2 g of manganese ore into a 100 ml beaker, cover it with a watch-glass, and dissolve by heating in 50 ml of nitric acid, diluted 1 : 3, carefully adding, drop by drop, 30 per cent hydrogen peroxide, until the attack is complete.

Filter the solution obtained through a medium filter into a 750 ml conical flask; wash the filter several times with nitric acid, diluted 1 : 3, place it in a platinum crucible, and ignite. Cool, add a few drops of water, 2 to 3 drops of sulphuric acid (d 1.84) and 2 to 3 ml of hydrofluoric acid, and evaporate to dryness. Heat the dry residue, and fuse it with 2 to 3 g of sodium carbonate. Extract the fusion in nitric acid, diluted 1 : 3, and add the solution to the original filtrate.

- 5.2 To maintain the required degree of acidity in the resultant combined solution, add nitric acid, diluted 1 : 3, up to a volume of 250 ml.
- 5.3 In order to destroy organic matter and to oxidize other reducers, carefully add to the solution, which has been heated to boiling, 1 g of sodium bismuthate, in small portions. If, during boiling, the pink colour of manganic acid disappears or the residue of manganese dioxide dissolves, it is necessary to add a further quantity of sodium bismuthate.
- 5.4 The formation of a permanent precipitate of manganese dioxide indicates complete oxidation of the organic and other matter. Whilst still boiling, add, drop by drop, from a pipette, a solution of sodium nitrite (50 g/l) until complete solution of the precipitate of manganese dioxide. Then boil the clear solution for 15 to 25 min until the nitric oxides are driven off.
- 5.5 Should the nitric oxides not be driven off, the subsequent oxidation of the divalent manganese with sodium bismuthate will not follow quantitatively.

If, as a result of boiling, the volume of the solution is decreased, make up to 250 ml with distilled water.

- 5.6 Cool the solution to a temperature of 15 to 20 °C, add 6 to 8 g of sodium bismuthate, and stir vigorously for 2 min. Add 200 ml of cold water, and immediately filter the solution through a funnel packed with ignited asbestos and glass wool. The filtrate should be quite clear. Thoroughly wash the flask and the filter with nitric acid, diluted 3 : 97, until the drops of the washings are absolutely colourless.

Add to the solution, from a burette, 50 ml of a standard ferrous ammonium sulphate solution (90 g/l), and, after having thoroughly stirred the solution, titrate the surplus salt with 0.25 N standard potassium permanganate solution. Simultaneously, determine the relation between the standard solution of the ferrous salt and that of potassium permanganate, using for this purpose a volume of standard ferrous ammonium sulphate solution equal to that added to the solution of ore for reducing the manganic acid. Repeat the determination not less than three times, and find the mean value. On the basis of the relation thus obtained, find the number of millilitres of the standard solution of potassium permanganate (KMnO_4) equivalent to the manganese content of the ore.

5.7 If V_1 millilitres of the potassium permanganate solution have been used in establishing this relationship, and V_2 millilitres in titrating the surplus ferrous ammonium sulphate, then the difference ($V_1 - V_2 = V$) is equal to the number of millilitres of the solution of potassium permanganate equivalent to the volume of the ferrous salt solution used in reducing manganic acid, formed as a result of the oxidization of the manganese contained in the sample of ore.

NOTES

- 1. Should the result of the check analysis of the standard sample not corroborate the content of manganese shown on the certificate, it will be necessary to repeat the determination of manganese in the ore being analysed and in the standard sample by the same method and, simultaneously, to check the titre of the standard potassium permanganate solution.
- 2. The asbestos used in titration should not contain organic admixture or other matter that may be titrated by the solution of potassium permanganate.
- 3. To clean the asbestos, split it up into fibres, treat while heating with concentrated hydrochloric acid, and wash thoroughly with distilled water. Then treat it while heating with nitric acid, diluted 1 : 3, and wash with water to remove chlorine ions. Dry the washed asbestos, and heat to a temperature of 500 to 600 °C.

6. EXPRESSION OF RESULTS

6.1 Method of calculation

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

$$Mn = \frac{TV \times 100}{G} \text{ per cent}$$

where T = titre of potassium permanganate solution, expressed in grammes of manganese;

V = number of millilitres of standard potassium permanganate solution equivalent to the number of millilitres of standard ferrous ammonium sulphate solution used in reducing manganic acid;

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:

Manganese content		Permissible tolerance (in absolute value)
from (over)	to	
	20.00 per cent	± 0.10 per cent
20.00 per cent	40.00 per cent	± 0.15 per cent
40.00 per cent		± 0.20 per cent

III. VOLUMETRIC PERMANGANATE METHOD

7. PRINCIPLE OF METHOD

The method is based on the oxidization of the ions of divalent manganese into tetravalency with potassium permanganate in a hot (not less than 80 °C) solution neutralized with zinc oxide and containing a surplus of the latter. The reaction does not proceed stoichiometrically, because of the formation of a certain quantity of manganites of divalent manganese, producing a precipitate.

8. REAGENTS REQUIRED

- 8.1 *Hydrochloric acid*, PFA (*d* 1.19).
- 8.2 *Hydrochloric acid*, PFA, diluted 1 : 50.
- 8.3 *Sulphuric acid*, PFA, diluted 1 : 1.
- 8.4 *Hydrofluoric acid*, PFA (40 per cent).
- 8.5 *Ferric chloride* ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), PFA, free from salts of divalent iron and manganese. Add 10 ml of hydrochloric acid (*d* 1.19) to 50 g of ferric chloride, dissolve in 75 to 100 ml of water and dilute with water up to 1 litre.
- 8.6 *Potassium permanganate*, PFA
- 8.7 *Zinc oxide*, PFA, free from admixtures that may be titrated with a solution of potassium permanganate under the conditions of the analysis. The reagent is heated to a temperature of 800 °C and finely ground in a porcelain mortar.
- 8.8 *Standard solution of potassium permanganate*. 12 g of potassium permanganate, PFA, are dissolved in 1 litre of distilled water. The solution thus obtained is allowed to stand for 6 days, and then it is siphoned off or filtered through a layer of glass wool and ignited asbestos into a dark glass flask without disturbing the precipitate of manganese dioxide. The solution contained in the flask should be protected from dust and gases. The solution of potassium permanganate should not be standardized earlier than the day following its filtration.

The potassium permanganate solution is standardized

against potassium permanganate see clause 9.1, or

against standard sample of ore see clause 9.2,

by analysing three test samples and finding the mean value of three closely coinciding results.

9. STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION

9.1 Against potassium permanganate

- 9.1.1 To standardize potassium permanganate solution, dissolve corresponding test samples of potassium permanganate, PFA, in 20 to 30 ml of water, add 10 ml of hydrochloric acid (*d* 1.19), and evaporate until dry. Dissolve the dry residue in 5 ml of hydrochloric acid (*d* 1.19), and pass through all the stages of the analysis under the same conditions as the ore being analysed.