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ISO RECOMMENDATION
R 320

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF SULPHUR

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July 1963

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BRIEF HISTORY

The ISO Recommendation R 320, *Methods of Chemical Analysis of Manganese Ores—Determination of Sulphur*, 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. 253) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

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

One Member Body opposed the approval of the Draft: Finland.

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 320 July 1963

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF SULPHUR

(Atomic mass S : 32.066)

This ISO Recommendation contains four 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 sulphur, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of sulphur in ore, which is absolutely dry, by multiplying the numerical results of the determination of sulphur 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 sulphur 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 sulphur 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 sulphur content), shown in the tables under clauses 5.2, 9.2 and 15.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for sulphur 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 sulphur content), shown in the tables under clauses 5.2, 9.2 and 15.2, " 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
d	relative density
g	gramme
g/l	grammes per litre
ml	millilitre
mm	millimetre
PFA	pure for analysis

II. GRAVIMETRIC METHOD (First Variant)

FOR SULPHUR CONTENT EXCEEDING 0.01 PER CENT

2. PRINCIPLE OF METHOD

When the ore is fused with sodium carbonate and an oxidizing agent at a temperature of 800 to 900 °C, all sulphur contained in the ore (generally in the form of pyrites and barytes) decomposes into sulphates of sodium. By means of extraction of the fusion with water and filtration, the sulphate ions are separated from other inherent elements, among which are those that hinder the determination. The sulphate ions contained in the water extraction are precipitated with barium chloride, and sulphur is determined in the form of barium sulphate.

3. REAGENTS REQUIRED

3.1 *Barium chloride*, PFA, solution (100 g/l).

3.2 *Magnesium oxide*, PFA.

3.3 *Methyl red indicator*, alcoholic solution, PFA (1 g/l).

3.4 *Sodium carbonate, anhydrous*, PFA.

3.5 *Sodium carbonate*, solution, PFA (10 g/l).

3.6 *Sodium peroxide*, PFA.

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

3.8 *Washing solution.* 10 ml barium chloride solution (100 g/l) and 10 ml hydrochloric acid, diluted 1 : 1, are diluted with water up to 1 litre.

3.9 *Silver nitrate*, PFA, solution (1 g/l).

3.10 *Fusion mixture :* 30 g of powdered anhydrous sodium carbonate, PFA, are mixed with 25 g of magnesium oxide, PFA, and 2 g of potassium chlorate ($KClO_3$), PFA. First, potassium chlorate is finely ground with a small quantity of sodium carbonate in a porcelain mortar. Then the remaining quantity of sodium carbonate and magnesium oxide are added and well mixed together.

3.11 *Ethyl alcohol*, PFA.

4. PROCEDURE

Determination of sulphur may be carried out in accordance with either

procedure A . . . . see clause 4.1, or
procedure B . . . . see clause 4.2.

4.1 Procedure A

4.1.1 Carefully mix 3 to 5 g of manganese ore and 4 to 7 g of fusion mixture in a platinum crucible.

Place the crucible in a muffle furnace and heat at 800 to 900 °C for 20 to 30 min. After cooling, place the crucible in a 300 ml beaker and extract in 75 to 100 ml of hot water. Heat until the extraction is complete, after which take the crucible out and rinse with water.

4.1.2 If the solution is tinted to a green colour by a manganate, the latter is reduced by adding a few drops of ethyl alcohol and heated until complete decolorization is achieved.

4.1.3 Filter the hot solution through an ashless filter into a 500 ml beaker, leaving the greater part of the residue in the beaker, where the extraction has been effected.

4.1.4 Pour 50 ml of hot solution of sodium carbonate (10 g/l) into the beaker with the residue, boil for 5 to 10 min, and filter the solution through the same filter. Repeat this operation 2 to 3 times. Wash off the residue from the beaker onto the filter, and wash 4 times with a hot solution of sodium carbonate. Carefully neutralize the filtrate, the volume of which should be about 250 to 300 ml, with hydrochloric acid, diluted 1 : 1, in the presence of methyl red, subsequently adding to the solution an excess of 1 to 1.5 ml of the same acid.

4.1.5 Heat the solution to boiling point and then add, drop by drop, 10 to 15 ml of a hot solution of barium chloride, stirring all the time. Keep the solution gently boiling until the volume is reduced to 150 to 200 ml. Then allow the precipitate of barium sulphate to settle for 12 hours.

4.1.6 Filter and collect the precipitate on to a fine filter, containing a small quantity of paper pulp, and use a jet of cold washing solution for washing off the residue from the beaker.

Wash the precipitate on the filter 3 or 4 times with the washing solution, and then with warm water until the chlorine ions are completely absent from the washings (test reaction with silver nitrate).

4.1.7 Place the filter with the precipitate in a weighed platinum or porcelain crucible and dry. Carefully ignite and heat at 600 to 700 °C for 30 min. Cool the crucible with the residue in a desiccator and then weigh.

4.2 Procedure B

4.2.1 Carefully mix a test sample of 3 to 5 g of manganese ore, 3 to 5 g of sodium carbonate and 3 to 5 g of sodium peroxide in a nickel crucible.

Place the crucible in a muffle furnace and ignite for 20 to 30 min, at 550 to 600 °C. After cooling, place the crucible in a 500 ml beaker, containing 100 to 150 ml of water, and heat the fused mass until completely disintegrated. Remove the crucible and carefully rinse with hot water over the beaker.

4.2.2 The additional operations (from the reaction of reduction of manganate with alcohol) should be carried out in accordance with Procedure A.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of sulphur is calculated from the following formula:

$$S = \frac{A \times 0.1374 \times 100}{G} \text{ per cent}$$

where A = mass of barium sulphate, in grammes;
0.1374 = conversion factor for barium sulphate to sulphur;
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:

Sulphur content from	Sulphur content to	Permissible tolerance (in absolute value)
0.010 per cent	0.030 per cent	± 0.001 per cent
(over) 0.030 per cent	0.050 per cent	± 0.002 per cent
„ 0.050 per cent	0.100 per cent	± 0.003 per cent
„ 0.100 per cent	0.200 per cent	± 0.006 per cent

III. GRAVIMETRIC METHOD (Second Variant)
FOR SULPHUR CONTENT EXCEEDING 0.01 PER CENT

6. PRINCIPLE OF METHOD

The sample of ore is dissolved in hydrochloric acid in the presence of potassium chlorate. The sulphate ions are precipitated in the form of barium sulphate.

7. REAGENTS REQUIRED

7.1 *Barium chloride*, PFA, solution (100 g/l).

7.2 *Barium nitrate*, PFA, solution (10 g/l).

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

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

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

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

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

7.8 *Methyl red indicator*, alcoholic solution (1 g/l).

7.9 *Sodium carbonate, anhydrous*, PFA.

7.10 *Sodium carbonate*, PFA, solution (10 g/l).

7.11 *Washing solution*. 10 ml of barium chloride solution (100 g/l) and 10 ml of hydrochloric acid (*d* 1.19) diluted with water to 1 litre.

7.12 *Silver nitrate*, PFA, solution (1 g/l).

8. PROCEDURE

8.1 Weigh 2 to 5 g of manganese ore into a 300 ml beaker; add 1 to 2 g of potassium chlorate and dissolve the mixture in 20 to 30 ml of hydrochloric acid (*d* 1.19), moderately heating.

8.2 The sample having dissolved, add 3 to 5 ml of barium chloride solution (100 g/l), and evaporate the liquid until dry.

8.3 Moisten the dry residue with 4 to 5 ml of hydrochloric acid, diluted 1 : 1, moderately heat it on a hot plate (or in a water bath) for 5 to 10 min, and add 150 to 200 ml of hot water. After the salts have dissolved, filter off the residue on a slow filter.

Wash the residue with the washing solution. Place the filter with the residue in a platinum crucible, moisten with 5 to 10 drops of a solution of barium nitrate (10 g/l) and carefully ignite at 500 to 600 °C. Moisten the ignited and cooled residue with 10 to 12 drops of nitric acid, add 10 to 15 ml of hydrofluoric acid, evaporate until dry, and heat to 500 to 600 °C.

8.4 Fuse the residue in the crucible with 3 to 4 g of sodium carbonate at 950 to 1000 °C. Place the crucible with the melt in a 150 ml beaker, and extract in 50 ml of hot water, while heating. Filter the solution through a medium filter into a beaker of 300 to 400 ml capacity, then carefully wash the beaker and the filter 8 to 10 times with a hot solution of sodium carbonate (10 g/l).

8.5 Discard the filter with the residue, and carefully neutralize the solution (whose volume is about 300 ml) with hydrochloric acid (*d* 1.19) in the presence of methyl red, adding an excess of 1 ml of the acid, then heat the solution to boiling.

Add, drop by drop, to the boiling solution, whilst stirring continuously, 10 to 15 ml of hot barium chloride solution (100 g/l).

Cover the beaker with a watch-glass, and keep the solution simmering for 10 min. Remove the beaker from the hot plate, and allow to stand for 12 hours.

Filter off the precipitate on a thick filter, wash 5 to 6 times with the washing solution and then with warm water until the chlorine ions are completely removed (test reaction with silver nitrate solution).

8.6 Place the filter containing the barium sulphate precipitate in a platinum or porcelain crucible which has been heated and weighed, carefully ignite and heat at 600 to 700 °C. Cool the crucible with the precipitate in a desiccator and then re-weigh.

9. EXPRESSION OF RESULTS

9.1 Method of calculation

The percentage content of sulphur is calculated from the following formula:

$$S = \frac{A \times 0.1374 \times 100}{G} \text{ per cent}$$

where

A = weight of barium sulphate, in grammes;

0.1374 = conversion factor for barium sulphate to sulphur;

G = mass of sample of ore, in grammes.

9.2 Accuracy of method

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

Sulphur content from	Sulphur content to	Permissible tolerance (in absolute value)
0.010 per cent	0.030 per cent	± 0.001 per cent
(over) 0.030 per cent	0.050 per cent	± 0.002 per cent
„ 0.050 per cent	0.100 per cent	± 0.003 per cent
„ 0.100 per cent	0.200 per cent	± 0.006 per cent

IV. COMBUSTION METHOD

10. PRINCIPLE OF METHOD

The method is based on burning the sample of ore either in a current of oxygen at 1350 to 1400 °C, or in a current of carbon dioxide at 1200 to 1250 °C, the sulphur being evolved as sulphur dioxide SO_2. The sulphur dioxide is carried by the current of oxygen or carbon dioxide into an absorption vessel containing water. The sulphurous acid formed in the reaction is titrated with iodine solution in the presence of starch as indicator.

11. REAGENTS REQUIRED

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

11.2 *Caustic potash* in stick form, PFA.

11.3 *Caustic potash*, PFA, solution (300 g/l).

11.4 *Calcium chloride, anhydrous*, in grain form, PFA.

11.5 *Starch solution*, indicator (5 g/l). 0.5 g of soluble starch ground in a mortar are mixed with 20 ml of water and poured in a thin stream into a vessel containing 80 ml of boiling water.

11.6 *Standard solution of iodine*, 0.005 N. 0.635 g of crystalline iodine, PFA, and 1.3 g of potassium iodide, PFA, are placed in a 100 ml beaker and dissolved in 50 ml of water. When the iodine is dissolved, the solution is diluted with water to 1 litre.

12. STANDARDIZATION OF IODINE SOLUTION

12.1 Against standard sample of ore

12.1.1 To determine the titre of the iodine solution, take three test samples of the standard sample of manganese ore, having approximately the same sulphur content as that of the sample being analysed, and pass them through all the stages of the analysis. Determine the average value of three closely coinciding results.

12.1.2 The titre of iodine solution is found from the following formula:

$$T = \frac{A \quad G}{V \times 100}$$

where T = titre of iodine solution, expressed in grammes of sulphur;
A = sulphur content in the standard sample of ore, per cent;
G = mass of test sample of the standard sample of ore, in grammes;
V = number of millilitres of iodine solution used in the titration.