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**INTERNATIONAL STANDARD**



**320**

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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**Manganese ores — Determination of sulphur —  
Barium sulphate gravimetric methods and sulphur dioxide  
titrimetric method after combustion**

*Minerais de manganèse — Dosage du soufre — Méthodes gravimétriques à l'état de sulfate de baryum et méthode  
titrimétrique à l'état de dioxyde de soufre après calcination*

First edition — 1975-02-01

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UDC 669.74 : 543.21 : 546.22

Ref. No. ISO 320-1975 (E)

**Descriptors** : manganese ores, chemical analysis, determination of content, sulphur, gravimetric analysis, combustion analysis.

Price based on 7 pages

# Manganese ores — Determination of sulphur — Barium sulphate gravimetric methods and sulphur dioxide titrimetric method after combustion

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies three methods for the determination of the sulphur content of manganese ores, namely :

**Methods I and II** : barium sulphate gravimetric methods, applicable to manganese ores the sulphur content of which exceeds 0,01 % (*m/m*);

**Method III** : a sulphur dioxide titrimetric method after combustion.

## 2 REFERENCES

ISO 310, *Manganese ores — Determination of hygroscopic moisture content in analytical samples — Gravimetric method.*

ISO . . . , *Manganese ores and concentrates — Sampling and sample preparation for chemical analysis and determination of moisture content.*<sup>1)</sup>

## METHOD I — GRAVIMETRIC METHOD (FIRST VARIANT)

### 3 PRINCIPLE

Conversion of all the sulphur contained in a test portion of the ore (generally in the form of pyrites and barytes) into sulphates of sodium, by fusion of the ore with sodium carbonate and an oxidizing agent at a temperature of 800 to 900 °C. Extraction of the fusion with water, followed by filtration, to separate the sulphate ions from other inherent elements some of which hinder the determination. Precipitation of the sulphate ions contained in the filtrate with barium chloride and determination of the sulphur in the form of barium sulphate.

### 4 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

#### 4.1 Potassium chlorate.

4.2 Sodium carbonate, anhydrous.

4.3 Magnesium oxide.

4.4 Sodium peroxide.

4.5 **Fusion mixture**, consisting of 30 g of anhydrous sodium carbonate, 25 g of magnesium oxide and 2 g of potassium chlorate. Finely grind the potassium chlorate (4.1) with a small quantity of the anhydrous sodium carbonate (4.2) in a porcelain mortar. Then add the remaining quantity of sodium carbonate and the magnesium oxide (4.3) and mix well.

4.6 Ethanol.

4.7 Sodium carbonate, 10 g/l solution.

4.8 Hydrochloric acid, diluted 1 : 1.

4.9 Barium chloride, 100 g/l solution.

4.10 Washing solution.

Add 10 ml of barium chloride solution (4.9) to 10 ml of hydrochloric acid (4.8) and dilute to 1 l with water.

4.11 Silver nitrate, 1 g/l solution.

4.12 Methyl red indicator, 1 g/l alcoholic solution.

### 5 APPARATUS

Ordinary laboratory apparatus and

5.1 Platinum crucible (for procedure A) or

5.2 Nickel crucible (for procedure B).

5.3 Muffle furnace.

1) This document, at present at the stage of draft proposal, is intended to complete and replace ISO/R 309, *Methods of sampling manganese ores — Part I — Ore loaded in freight wagons.*

## 6 SAMPLE

Use a test sample which has been crushed to a size not exceeding 0,10 mm (checked on a sieve of appropriate size) and air-dried under laboratory conditions (see ISO . . . ).

## 7 PROCEDURE

### 7.1 Number of analyses

Carry out the determination simultaneously on three test portions taken from the same test sample.

### 7.2 Blank test

In parallel with the determination and under the same conditions, carry out a blank test in duplicate, to enable a corresponding correction in the result of the determination to be made.

### 7.3 Check test

In parallel with the determination and under the same conditions, carry out a check analysis of a standard sample of manganese ore of known sulphur content and of the type of ore to which the sample being analysed belongs.

### 7.4 Test portion

Weigh, to the nearest 0,00 2 g, 3 to 5 g of the test sample.

### 7.5 Determination

#### 7.5.1 Procedure A

7.5.1.1 Transfer the test portion (7.4) to the platinum crucible (5.1), add 4 to 7 g of fusion mixture (4.5) and carefully mix. Place the crucible in the muffle furnace (5.3) 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 (60 to 70 °C). Heat until the extraction is complete, after which take the crucible out and rinse with water.

7.5.1.2 If the solution is tinted to a green colour by a manganate, reduce the latter by adding a few drops of ethanol (4.6) and heating until complete decolorization is achieved.

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

7.5.1.4 Pour 50 ml of hot (60 to 70 °C) sodium carbonate solution (4.7) into the beaker with the residue, boil for 5 to 10 min, and filter the solution through the same filter. Repeat this operation two or three times. Wash off the residue from the beaker onto the filter, and wash four times with hot sodium carbonate solution. Carefully neutralize the filtrate, the volume of which should be about 250 to

300 ml, with hydrochloric acid (4.8) in the presence of methyl red (4.12), subsequently adding to the solution an excess of 1 to 1,5 ml of the same acid.

7.5.1.5 Heat the solution to boiling point and then add, drop by drop, 10 to 15 ml of hot (60 to 70 °C) barium chloride solution (4.9), 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 h.

7.5.1.6 Filter and collect the precipitate on a fine filter containing a small quantity of paper pulp, and use a jet of cold washing solution (4.10) for washing off the residue from the beaker.

Wash the precipitate on the filter three or four times with the washing solution, and then with warm water (40 to 50 °C) until chloride ions are completely absent from the washings (test reaction with silver nitrate solution (4.11)).

7.5.1.7 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 to an accuracy of ± 0,000 2 g.

#### 7.5.2 Procedure B

7.5.2.1 Transfer the test portion (7.4) to the nickel crucible (5.2), add 3 to 5 g of sodium carbonate (4.2) and 3 to 5 g of sodium peroxide (4.4) and carefully mix.

7.5.2.2. Place the crucible in the muffle furnace (5.3) 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 (60 to 70 °C) over the beaker.

Carry out the additional operations (from the reaction of reduction of manganate with ethanol) in accordance with procedure A (7.5.1.2 to 7.5.1.7).

## 8 EXPRESSION OF RESULTS

### 8.1 Method of calculation

The sulphur content of the absolutely dry ore, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 0,137 4 \times 100}{m_0} \times \frac{100}{100 - A}$$

where

$m_0$  is the mass, in grams, of the test portion;

$m_1$  is the mass, in grams, of the barium sulphate;

0,137 4 is the conversion factor for barium sulphate to sulphur;

A is the hygroscopic moisture content of the test sample, as a percentage by mass, determined in accordance with ISO 310.

Take as the result the arithmetic mean of the three determinations provided that the requirement of repeatability (see 8.2) is satisfied.

## 8.2 Repeatability

The difference between the highest and the lowest results shall 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 table below.

Sulphur content, %		Permissible tolerance, % (in absolute value)
from	to	
0,010	0,030	± 0,001
(over) 0,030	0,050	± 0,002
" 0,050	0,100	± 0,003
" 0,100	0,200	± 0,006

The average result of the simultaneous check analysis of the standard sample of manganese ore for sulphur content shall not differ from the result shown in the certificate by more than the  $\pm$  value of the permissible tolerance (for the corresponding interval of sulphur content) shown in the table.

## 9 TEST REPORT

The test report shall include the following information :

- indications necessary for the identification of the sample;
- reference to this International Standard;
- results of the analysis;
- the reference number of the results;
- any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the results.

## METHOD II — GRAVIMETRIC METHOD (SECOND VARIANT)

### 10 PRINCIPLE

Dissolution of a test portion in hydrochloric acid in the presence of potassium chlorate. Precipitation of the sulphate ions in the form of barium sulphate.

## 11 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

11.1 Potassium chlorate.

11.2 Sodium carbonate, anhydrous.

11.3 Hydrochloric acid,  $\rho$  1,19 g/ml.

11.4 Hydrochloric acid, diluted 1 : 1.

11.5 Hydrofluoric acid, 40 % (m/m).

11.6 Nitric acid,  $\rho$  1,40 g/ml.

11.7 Barium chloride, 100 g/l solution.

11.8 Barium nitrate, 10 g/l solution.

11.9 Sodium carbonate, 10 g/l solution.

11.10 Washing solution.

Add 10 ml of hydrochloric acid (11.3) to 10 ml of barium chloride solution (11.7) and dilute with water to 1 l.

11.11 Silver nitrate, 1 g/l solution.

11.12 Methyl red indicator, 1 g/l alcoholic solution.

## 12 APPARATUS

Ordinary laboratory apparatus and

12.1 Hot-plate or water-bath.

12.2 Platinum crucible.

## 13 SAMPLE

Use a test sample which has been crushed to a size not exceeding 0,10 mm (checked on a sieve of appropriate size) and air-dried under laboratory conditions (see ISO . . .).

## 14 PROCEDURE

### 14.1 Number of analyses

Carry out the determination simultaneously on three test portions taken from the same test sample.

### 14.2 Blank test

In parallel with the determination and under the same conditions, carry out a blank test in duplicate, to enable a corresponding correction in the result of the determination to be made.

**14.3 Check test**

In parallel with the determination and under the same conditions, carry out a check analysis of a standard sample of manganese ore of known sulphur content and of the type of ore to which the sample being analysed belongs.

**14.4 Test portion**

Weigh, to the nearest 0,000 2 g, 2 to 5 g of the test sample into a 300 ml beaker.

**14.5 Determination**

**14.5.1** Add to the beaker containing the test portion (14.4) 1 to 2 g of potassium chlorate (11.1) and dissolve the mixture in 20 to 30 ml of hydrochloric acid (11.3), heating moderately.

**14.5.2** The sample having dissolved, add 3 to 5 ml of barium chloride solution (11.7), and evaporate the liquid until dry.

**14.5.3** Moisten the dry residue with 4 to 5 ml of hydrochloric acid (11.4), 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 (60 to 70 °C). After the salts have dissolved, filter off the residue on a slow filter.

Wash the residue with the washing solution (11.10). Place the filter with the residue in a platinum crucible, moisten with 5 to 10 drops of barium nitrate solution (11.8) and carefully ignite at 500 to 600 °C. Moisten the ignited and cooled residue with 10 to 12 drops of nitric acid (11.6), add 10 to 15 ml of hydrofluoric acid (11.5), evaporate until dry, and heat to 500 to 600 °C.

**14.5.4** Fuse the residue in the crucible with 3 to 4 g of sodium carbonate (11.2) at 950 to 1 000 °C. Place the crucible with the melt in a 150 ml beaker, and extract in 50 ml of hot water (60 to 70 °C), 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 eight to ten times with hot (60 to 70 °C) sodium carbonate solution (11.9).

**14.5.5** Discard the filter with the residue, and carefully neutralize the solution (whose volume is about 300 ml) with hydrochloric acid (11.3) in the presence of methyl red (11.12), 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 (60 to 70 °C) barium chloride solution (11.7).

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 h.

Filter off the precipitate on a thick filter, wash five or six times with the washing solution (11.10) and then with warm water (40 to 50 °C) until the chloride ions are

completely removed (test reaction with silver nitrate solution (11.11)).

**14.5.6** 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 to an accuracy of ± 0,000 2 g.

**15 EXPRESSION OF RESULTS**

**15.1 Method of calculation**

The sulphur content of the absolutely dry ore is given, as a percentage by mass, by the formula

$$\frac{m_1 \times 0,137 4 \times 100}{m_0} \times \frac{100}{100 - A}$$

where

$m_0$  is the mass, in grams, of the test portion;

$m_1$  is the mass, in grams, of the barium sulphate;

0,137 4 is the conversion factor for barium sulphate to sulphur;

A is the hygroscopic moisture content of the test sample, as a percentage by mass, determined in accordance with ISO 310.

Take as the result the arithmetic mean of the three determinations provided that the requirement of repeatability (see 15.2) is satisfied.

**15.2 Repeatability**

The maximum difference between the highest and the lowest results shall 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 table below.

Sulphur content, %		Permissible tolerance, % (in absolute value)
from	to	
0,010	0,030	± 0,001
(over) 0,030	0,050	± 0,002
" 0,050	0,100	± 0,003
" 0,100	0,200	± 0,006

The average result of the simultaneous check analysis of the standard sample of manganese ore for sulphur content shall 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 table.

## 16 TEST REPORT

The test report shall include the following information :

- a) indications necessary for the identification of the sample;
- b) reference to this International Standard;
- c) results of the analysis;
- d) the reference number of the results;
- e) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the results.

## METHOD III – SULPHUR DIOXIDE TITRIMETRIC METHOD AFTER COMBUSTION

### 17 PRINCIPLE

Burning of a test portion either in a current of oxygen at 1 350 to 1 400 °C, or in a current of carbon dioxide at 1 200 to 1 250 °C, the sulphur being evolved as sulphur dioxide (SO<sub>2</sub>) which is carried by the current of oxygen or carbon dioxide into an absorption vessel containing water. Titration of the sulphurous acid formed in the reaction with standard volumetric iodine solution in the presence of starch as indicator.

### 18 REAGENTS

During the analysis, use only reagents of recognized analytical reagent grade and only distilled water or water of equivalent purity.

**18.1 Calcium chloride**, anhydrous in granular form.

**18.2 Potassium hydroxide** in stick form.

**18.3 Potassium hydroxide**, 300 g/l solution.

**18.4 Sulphuric acid**,  $\rho$  1,84 g/ml.

**18.5 Iodine**, 0,005 N standard volumetric solution.

#### 18.5.1 Preparation of the solution

Place 0,635 g of crystalline iodine and 1,3 g of potassium iodide in a 100 ml beaker and dissolve in 50 ml of water. Dilute the solution with water to 1 l.

#### 18.5.2 Standardization of the solution

Take three test portions from a standard sample of manganese ore having a known sulphur content approximately the same as that of the sample to be analysed, and pass them through all the stages of the analysis (21.5).

The titre of the iodine solution is given by the formula

$$T = \frac{B \times m}{V \times 100}$$

where

$T$  is the titre of the iodine solution expressed as grams of sulphur corresponding to 1 ml of the solution;

$B$  is the sulphur content, as a percentage by mass, of the standard sample of manganese ore;

$m$  is the mass, in grams, of the test portion of the standard sample;

$V$  is the volume, in millilitres, of the iodine solution used in the titration.

Take as the titre the average of three closely coinciding results.

**18.6 Starch** indicator solution, 5 g/l.

Grind 0,5 g of soluble starch in a mortar, mix with 20 ml of water and pour in a thin stream into a vessel containing 80 ml of boiling water.

### 19 APPARATUS

The apparatus shall be constituted as shown in the figure.

The oxygen (or carbon dioxide) required for the determination is passed from the cylinder (A) via the reducing valve (B), into the wash bottles (C) and (D) containing potassium hydroxide solution (18.3) and sulphuric acid (18.4) respectively, and into the drying tower (E), the lower half of which is filled with pieces of potassium hydroxide (18.2), and the upper half with dry calcium chloride (18.1), above which is a glass wool filter.

Should the test portion be heated in a stream of carbon dioxide, the wash bottles (C) and (D) can be dispensed with, and the drying tower (E) filled with anhydrous magnesium perchlorate, or with calcium chloride.

The purified and dried oxygen is led through rubber tubing to the porcelain combustion tube (F), 19 to 20 mm in diameter, in the electric furnace (G).

The gaseous products of combustion together with the surplus oxygen or carbon dioxide are led from the combustion tube (F) via the outflow tube (H) to the absorption vessel (I), 250 mm high and 30 mm in diameter, half-filled with the aqueous starch solution (18.6), tinted by the iodine to a pale-blue colour. A similar absorption vessel (J) placed beside it and filled with the same solution serves as a duplicate.

Above the absorption vessel is a burette (K) containing the standard volumetric iodine solution (18.6).

The electric furnace (G) with silit heaters is fed with alternating current through the transformer (L) fitted with a thermo-regulator.

To avoid over-heating of the ends of the porcelain tube (F), the butt ends of the furnace are covered with asbestos board (N). The ends of the tube shall protrude to 150 to 200 mm from the butt sides. The ends of the tube shall be cooled outside with moistened strips of cotton fabric at the places where they are stoppered.

## 20 SAMPLE

Use a sample which has been crushed to a size not exceeding 0,10 mm (checked on a sieve of appropriate size) and air-dried under laboratory conditions (see ISO . . .).

## 21 PROCEDURE

### 21.1 Number of analyses

Carry out the determination simultaneously on three test portions taken from the same test sample.

### 21.2 Blank test

In parallel with the determination and under the same conditions, carry out a blank test in duplicate, to enable a corresponding correction in the result of the determination to be made.

### 21.3 Check test

In parallel with the determination and under the same conditions, carry out a check analysis of a standard sample of manganese ore of known sulphur content and of the type of ore to which the sample being analysed belongs.

### 21.4 Test portion

Weigh to the nearest 0,000 2 g, into a porcelain weighing boat previously ignited at 1 350 to 1 400 °C in a current of oxygen, or at 1 200 to 1 250 °C in a current of carbon dioxide, a mass of the test sample depending upon its sulphur content, as follows :

up to 0,02 % sulphur : 1,0 g  
0,02 % sulphur and over : 0,5 g

### 21.5 Determination

21.5.1 Before combustion, ensure that the apparatus is gas-tight.

21.5.2 Before commencement, fill the absorption vessel (I) and the vessel with solution serving as a duplicate (J) to half of their capacity with the aqueous starch solution (18.6), tinted by the standard volumetric iodine solution (18.5) to a pale-blue colour.

21.5.3 Place the boat with the test portion (21.4) in the hottest portion of the porcelain tube of the furnace. Quickly stopper the tube, and pass through a current of oxygen (or carbon dioxide) at a rate of 4 l/min. When the

sulphurous gas, in its passage from the furnace into the absorption vessel, begins to decolorize the lower part of the liquid, add to it, drop by drop, the standard volumetric iodine solution, by passing it from the burette at such a speed as will ensure that the liquid remains pale blue in colour the whole time. The ignition of the test portion is considered finished when the pale-blue colour of the solution in the absorption vessel remains unchanged for 2 min during the continuous passage of a current of oxygen (or of carbon dioxide), without further addition of the iodine solution.

## 22 EXPRESSION OF RESULTS

### 22.1 Method of calculation

The sulphur content of the absolutely dry ore is given, as a percentage by mass, by the formula

$$\frac{T (V_2 - V_1) \times 100}{m_0} \times \frac{100}{100 - A}$$

where

*T* is the titre of the standard volumetric iodine solution (see 18.5.2);

*V*<sub>1</sub> is the volume, in millilitres, of standard volumetric iodine solution used in the blank test;

*V*<sub>2</sub> is the volume, in millilitres, of standard volumetric iodine solution used in the determination;

*m*<sub>0</sub> is the mass, in grams, of the test portion;

*A* is the hygroscopic moisture content of the test sample, as a percentage by mass, determined in accordance with ISO 310.

Take as the result the arithmetic mean of the three determinations provided that the requirement of repeatability (see 22.2) is satisfied.

### 22.2 Repeatability

The difference between the highest and the lowest results shall 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 table below.

Sulphur content, %		Permissible tolerance, % (in absolute value)
from	to	
0,010	0,030	± 0,001
(over) 0,030	0,050	± 0,002
" 0,050	0,100	± 0,003
" 0,100	0,200	± 0,006