SLOVENSKI STANDARD

SIST ISO 320:2001

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Manganove rude - Doloļ evanje ģvepla - Gravimetrijska metoda z barijevim sulfatom in titrimetrijska metoda z ģveplovim dioksidom po zgorevanju

Manganese ores -- Determination of sulphur content -- 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

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International Standard 320

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Manganese ores — Determination of sulphur content — 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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 320 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

This second edition was submitted directly to the ISO Council, in accordance with clause 5.10.1 of part 1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 320-1975), which had been approved by the member bodies of the following countries :

Austria
Bulgaria
Chile
Czechoslovakia
Finland
France
Germany, F. R.
Hungary
India
Ireland
Italy
Japan
Netherlands
Poland
Portugal
Romania
South Africa, Rep. of
Spain
United Kingdom
USSR

No member body had expressed disapproval of the document.

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INTERNATIONAL STANDARD ISO 320-1981 (E)

Manganese ores — Determination of sulphur content — 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 :

— **Methods I and II** : barium sulphate gravimetric methods, which are applicable to manganese ores having sulphur contents greater than 0,01 % (m/m);

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

This International Standard should be read in conjunction with ISO 4297.

2 References

ISO 4296/1, *Manganese ores — Sampling — Part 1 : Increment sampling.*[1]

ISO 4296/2, *Manganese ores — Sampling — Part 2 : Preparation of samples.*[1]

ISO 4297, *Manganese ores and concentrates — Methods of chemical analysis — General instructions.*

3 Method I : Gravimetric method (first variant)

3.1 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.

3.2 Reagents

3.2.1 Sodium carbonate, anhydrous.

3.2.2 Sodium peroxide.

3.2.3 Fusion mixture, consisting of 30 g of anhydrous sodium carbonate, 25 g of magnesium oxide and 2 g of potassium chlorate. Finely grind potassium chlorate with a small quantity of the anhydrous sodium carbonate (3.2.1) in a porcelain mortar. Then add the remaining quantity of sodium carbonate and magnesium oxide and mix well.

3.2.4 Ethanol.

3.2.5 Sodium carbonate, 10 g/l solution.

3.2.6 Hydrochloric acid, diluted 1 + 1.

3.2.7 Barium chloride, 100 g/l solution.

3.2.8 Washing solution.

Add 10 ml of barium chloride solution (3.2.7) to 10 ml of hydrochloric acid (3.2.6) and dilute to 1 litre with water.

3.2.9 Silver nitrate, 1 g/l solution.

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

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Platinum crucible (for procedure A) or

3.3.2 Nickel crucible (for procedure B).

3.3.3 Muffle furnace.

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[1] At present at the stage of draft.

3.4 Sample

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

Use a test sample which has been crushed to a size not exceeding 100 µm (checked on a sieve of appropriate aperture size) and air-dried under laboratory conditions.

3.5 Procedure

3.5.1 Test portion

Weigh 3 to 5 g of the test sample.

3.5.2 Determination

3.5.2.1 Procedure A

3.5.2.1.1 Transfer the test portion (3.5.1) to the platinum crucible (3.3.1), add 4 to 7 g of the fusion mixture (3.2.3) and carefully mix. Place the crucible in the muffle furnace (3.3.3) and heat at 800 to 900 °C for 20 to 30 min.

Cool, 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, remove the crucible from the beaker and rinse with water.

3.5.2.1.2 If the solution is tinted to a green colour by a manganate, reduce the latter by adding a few drops of the ethanol (3.2.4) and heating until complete decolorization is achieved.

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

3.5.2.1.4 Pour 50 ml of hot (60 to 70 °C) sodium carbonate solution (3.2.5) into the beaker with the residue, boil for 5 to 10 min, and filter the solution through the same filter paper. 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 the hydrochloric acid solution (3.2.6) in the presence of the methyl red solution (3.2.10), subsequently adding to the solution an excess of 1 to 1,5 ml of the same acid.

3.5.2.1.5 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 (3.2.7), 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.

3.5.2.1.6 Filter and collect the precipitate on a fine filter containing a small quantity of paper pulp, and use a jet of the cold washing solution (3.2.8) 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 (3.2.9)].

3.5.2.1.7 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. Allow the crucible with the residue to cool in a desiccator and then weigh.

3.5.2.2 Procedure B

3.5.2.2.1 Transfer the test portion (3.5.1) to the nickel crucible (3.3.2), add 3 to 5 g of the sodium carbonate (3.2.1) and 3 to 5 g of the sodium peroxide (3.2.2) and carefully mix.

3.5.2.2.2 Place the crucible in the muffle furnace (3.3.3) and incinerate for 20 to 30 min, at 550 to 600 °C. Cool, 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 (3.5.2.1.2 to 3.5.2.1.7).

3.6 Expression of results

3.6.1 Calculation

The sulphur (S) content, expressed as a percentage by mass, is given by the formula

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

where

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

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

K is the conversion factor for the expression of the sulphur content on the dry basis;

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

3.6.2 Permissible tolerances on results of duplicate determinations

Sulphur content, % (m/m)		**Permissible tolerance, % (m/m)**
from	to	
0,010	0,030	0,001
0,030	0,050	0,002
0,050	0,100	0,003
0,100	0,200	0,006

4 Method II : Gravimetric method (second variant)

4.1 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.

4.2 Reagents

4.2.1 Potassium chlorate.

4.2.2 Sodium carbonate, anhydrous.

4.2.3 Hydrochloric acid, ϱ 1,19 g/ml.

4.2.4 Hydrochloric acid, diluted 1 + 1.

4.2.5 Hydrofluoric acid, 40 % (m/m) solution.

4.2.6 Nitric acid, ϱ 1,40 g/ml.

4.2.7 Barium chloride, 100 g/l solution.

4.2.8 Barium nitrate, 10 g/l solution.

4.2.9 Sodium carbonate, 10 g/l solution.

4.2.10 Washing solution.

Add 10 ml of the hydrochloric acid (4.2.3) to 10 ml of the barium chloride solution (4.2.7) and dilute to 1 litre with water.

4.2.11 Silver nitrate, 1 g/l solution.

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

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Hot-plate or **water-bath.**

4.3.2 Platinum crucibles.

4.4 Sample

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

Use a test sample which has been crushed to a size not exceeding 100 µm (checked on a sieve of appropriate aperture size) and air-dried under laboratory conditions.

4.5 Procedure

4.5.1 Test portion

Weigh 2 to 5 g of the test sample into a 300 ml beaker.

4.5.2 Determination

4.5.2.1 Add to the beaker containing the test portion (4.5.1) 1 to 2 g of the potassium chlorate (4.2.1) and dissolve the mixture in 20 to 30 ml of the hydrochloric acid (4.2.3), heating moderately.

4.5.2.2 When the test portion is dissolved, add 3 to 5 ml of the barium chloride solution (4.2.7), and evaporate the liquid until dry.

4.5.2.3 Moisten the dry residue with 4 to 5 ml of the hydrochloric acid solution (4.2.4), moderately heat in 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). When the salts are dissolved, filter off the residue on a fine filter.

Wash the residue with the washing solution (4.2.10). Place the filter with the residue in one of the platinum crucibles, moisten with 5 to 10 drops of the barium nitrate solution (4.2.8) and carefully ignite at 500 to 600 °C. Moisten the ignited and cooled residue with 10 to 12 drops of the nitric acid (4.2.6), add 10 to 15 ml of the hydrofluoric acid solution (4.2.5), evaporate until dry, and heat to 500 to 600 °C.

4.5.2.4 Fuse the residue in the crucible with 3 to 4 g of the sodium carbonate (4.2.2) 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 (4.2.9).

4.5.2.5 Discard the filter with the residue, and carefully neutralize the solution (the volume of which shall be about 300 ml) with the hydrochloric acid (4.2.3) in the presence of the methyl red (4.2.12), 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 (4.2.7).

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 and collect the precipitate on a fine filter, wash five or six times with the washing solution (4.2.10) and then with warm water (40 to 50 °C) until the chloride ions completely removed [test reaction with silver nitrate solution (4.2.11)].

4.5.2.6 Place the filter containing the barium sulphate precipitate in a platinum or porcelain crucible which has been dried and weighed. Carefully ignite and heat at 600 to 700 °C.

Allow the crucible with the residue to cool in a desiccator and then re-weigh.

4.6 Expression of results

4.6.1 Calculation

The sulphur (S) content, expressed as a percentage by mass, is given by the formula

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

where

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

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

K is the conversion factor for the expression of the sulphur content on the dry basis;

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

4.6.2 Permissible tolerances on results of duplicate determinations

Sulphur content, % (m/m) from	to	**Permissible tolerance** % (m/m)
0,010	0,030	0,001
0,030	0,050	0,002
0,050	0,100	0,003
0,100	0,200	0,006

5 Method III : Sulphur dioxide titrimetric method after combustion

5.1 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_2) 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.

5.2 Reagents

5.2.1 Calcium chloride, anhydrous in granular form.

5.2.2 Potassiun hydroxide, in stick form.

5.2.3 Potassium hydroxide, 300 g/l solution.

5.2.4 Sulphuric acid, ϱ 1,84 g/ml.

5.2.5 Iodine, standard volumetric solution, $c(1/2\ I_2) = 0{,}005$ mol/l.

5.2.5.1 Preparation of the solution

Place 0,635 g of crystalline iodine and 1,3 g of potassium iodine in a 100 ml beaker and dissolve in 50 ml of water. Dilute the solution to 1 000 ml with water.

5.2.5.2 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 carry out all the stages of the analysis (see 5.5.2) on them.

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, expressed 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.

Take as the titre the average of the three results.

5.2.6 Starch, 5 g/l indicator solution.

Triturate 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.

5.3 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 the potassium hydroxide solution (5.2.3) and sulphuric acid (5.2.4) respectively, and into the drying tower (E), the lower half of which is filled with pieces of the potassium hydroxide (5.2.2), and the upper half with the dry calcium chloride (5.2.1) 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 the calcium chloride (5.2.1).

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 starch solution (5.2.6), 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 iodine solution (5.2.5).

The electric furnace (G) with silit [silicon carbonitride (Si_2NC_2)] 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.

5.4 Sample

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

Use a sample which has been crushed to a size not exceeding 100 µm (checked on a sieve of appropriate aperture size) and air-dried under laboratory conditions.

5.5 Procedure

5.5.1 Test portion

Weigh 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, and tared, 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

5.5.2 Determination

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

5.5.2.2 Fill the absorption vessel (I) and the vessel serving as the duplicate (J) to half of their capacity with the aqueous starch solution (5.2.6), tinted by the iodine solution (5.2.5) to a pale-blue colour.

5.5.2.3 Place the boat with the test portion (5.5.1) in the porcelain tube in the hottest part 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 iodine solution, by passing it from the burette (K) 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.

5.6 Expression of results

5.6.1 Calculation

The sulphur (S) content, expressed as a percentage by mass, is given by the formula

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

where

T is the titre of the iodine solution (see 5.2.5.2);

V_1 is the volume, in millilitres, of iodine solution used in the blank test;

V_2 is the volume, in millilitres, of iodine solution used in the determination;

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

K is the conversion factor for the expression of the sulphur content on the dry basis.

5.6.2 Permissible tolerances on results of duplicate determinations

Sulphur content, % (*m*/*m*)		Permissible tolerance, % (*m*/*m*)
from	to	
0,010	0,030	0,001
0,030	0,050	0,002
0,050	0,100	0,003
0,100	0,200	0,006