International Standard 4294

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Manganese ores and concentrates — Determination of copper content — Extraction-spectrometric and spectrometric methods

Minerais et concentrés de manganèse — Dosage du cuivre — Méthodes spectrométriques avec et sans extraction

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Foreword

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Manganese ores and concentrates — Determination of copper content — Extraction-spectrometric and spectrometric methods

1 Scope and field of application

This International Standard specifies the following methods for the determination of the copper content of manganese ores and concentrates

method A: extraction-spectrometric method, applicable to products having copper contents up to 0,5 % (*m/m*);

method B: spectrometric method, applicable to products having copper contents from 0,1 to 1 % (*m/m*).

It should be read in conjunction with ISO 4297.

2 References

ISO 4296, *Manganese ores — Sampling —*

Part 1: Increment sampling.

Part 2: Preparation of samples.

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

3 Method A: Extraction-spectrometric method for copper contents up to 0,5 % (*m/m*)

3.1 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids, and evaporation of the solution to dryness. Dissolution of the dry residue in hydrochloric acid. Separation of the insoluble residue by filtration, ignition of the filter with the residue and treatment with sulfuric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in water and combination of the solution obtained with the main solution. Addition, to an aliquot portion of the resulting solution, of ammonium citrate solution, Na_2EDTA solution, ammonium hydroxide solution to adjust the pH to 8,5, and sodium diethyldithiocarbamate solution.

Extraction of the copper-diethyldithiocarbamate complex with chloroform. Spectrometric measurement.

3.2 Reactions

The method is based on the interaction of copper(II) ions with sodium diethyldithiocarbamate, resulting in the formation of a yellow or brown colour complex depending on the concentration of copper.

The influence of iron and other accompanying components is eliminated by binding them into soluble complexes with ammonium citrate and Na_2EDTA solution.

3.3 Reagents

3.3.1 Chloroform.

3.3.2 Sodium carbonate, anhydrous.

3.3.3 Nitric acid, ϱ 1,40 g/ml.

3.3.4 Hydrofluoric acid, ϱ 1,14 g/ml.

3.3.5 Hydrochloric acid, ϱ 1,19 g/ml.

3.3.6 Hydrochloric acid, diluted 1 + 19.

3.3.7 Sulfuric acid, diluted 1 + 1.

3.3.8 Ammonium hydroxide, diluted 1 + 1.

3.3.9 Ammonium citrate [$(NH_4)_2C_6H_5O_7$], 100 g/l solution.

3.3.10 Sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NS_2Na \cdot 3H_2O$), 1 g/l solution.

Prepare fresh as required.

3.3.11 Disodium dihydrogen ethylenedinitrilotetraacetate (Na_2EDTA), 100 g/l solution.

Dissolve 10 g of Na_2EDTA in 100 ml water while heating slightly, and filter.

3.3.12 Copper, standard solution, corresponding to 0,004 g of Cu per litre.

3.3.12.1 Copper, stock solution, 0,1 g/l.

Dissolve 0,1 g of metallic copper [purity 99,95 % (*m/m*)] in 10 ml of nitric acid (diluted 1 + 1), boil until free from nitrogen oxides, cool, add 10 ml of sulfuric acid (3.3.7), evaporate to

dense white fumes of sulfuric acid, cool, add water and heat to dissolve the salts. Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

3.3.12.2 Preparation

Transfer 10 ml of copper stock solution (3.3.12.1) to a 250 ml one-mark volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 0,004 mg of Cu.

3.4 Apparatus

Usual laboratory apparatus and

3.4.1 Platinum crucible.

3.4.2 Spectrometer, with selectors for continuous or discontinuous variation, suitable for measurements at 436 nm, with matching cells.

3.5 Sample

For the sampling of manganese ores, see ISO 4261/1. For the preparation of samples, see ISO 4296/2.

3.6 Procedure

3.6.1 Test portion

Weigh a mass of the test sample, chosen from table 1, in accordance with the expected copper content.

3.6.2 Decomposition of test portion

Place the test portion (3.6.1) in a 300 ml beaker, dissolve in 15 to 25 ml of the hydrochloric acid (3.3.5) while heating, then add 1,5 to 2,0 ml of the nitric acid (3.3.3). Boil the solution and evaporate to dryness. Moisten the dry residue with 10 ml of the hydrochloric acid (3.3.5) and evaporate again. Repeat the evaporation with 10 ml of the same hydrochloric acid. Dissolve the dry residue in 10 ml of the hydrochloric acid (3.3.5) and 40 ml of water while heating. Heat the solution to boiling and filter through a medium-texture filter paper containing a small quantity of paper pulp. Wash the beaker and the precipitate on the filter four or five times with the hydrochloric acid (3.3.6) and several times with hot water. Reserve the filtrate as the main solution.

Transfer the filter containing the residue to a platinum crucible, dry and ignite at 600 to 700 °C. Cool the crucible, moisten the residue with 2 or 3 drops of water, add 1 ml of the sulfuric acid (3.3.7), 5 ml of the hydrofluoric acid (3.3.4) and evaporate until the fuming of the sulfuric acid ceases. Ignite the residue at 500 to 600 °C. Cool, add 1 g of the sodium carbonate (3.3.2) and fuse at 950 to 1 000 °C. Dissolve the melt in 50 ml of warm water with addition of 1 ml of the hydrochloric acid (3.3.5). Add the solution thus obtained to the main solution. Evaporate the solution to 50 to 60 ml, cool and transfer to a 100 or 250 ml one-mark volumetric flask (see table 1), make up to the mark with water and mix.

Table 1

Expected copper content	Mass of test portion	Dilution	Aliquot portion of solution	Copper content of aliquot portion of solution
% (m/m)	g	ml	ml	µg
⩾0,002 5 to 0,005	1,0	100	25	6,25 to 12,5
>0,005 to 0,01	1,0	100	10	5,0 to 10,0
>0,01 to 0,03	0,5	100	10	5,0 to 15,0
>0,03 to 0,05	0,5	100	5	7,5 to 12,5
>0,05 to 0,10	0,5	100	2	5,0 to 10,0
>0,10 to 0,50	0,5	250	2	4,0 to 20,0

3.6.3 Extraction

Take an aliquot portion of the solution according to table 1, add 5 ml of the ammonium citrate solution (3.3.9) and 10 ml of the Na_2EDTA solution (3.3.11), mix, then add the ammonium hydroxide (3.3.8) to adjust the pH to 8,5, using a universal indicator test paper. Transfer the solution to a 200 to 250 ml separating funnel, dilute to 70 ml with water, then add 5 ml of the sodium diethyldithiocarbamate solution (3.3.10) and extract with 10 ml of the chloroform (3.3.1), shaking the funnel vigorously for not less than 3 min. Allow the organic layer to settle and draw it off into a 25 ml one-mark volumetric flask.

Add a further 5 ml of the chloroform to the aqueous layer in the separating funnel and repeat the extraction. Combine the extracts. Make up the solution in the volumetric flask to the mark with chloroform and mix.

3.6.4 Spectrometric measurement

Transfer the solution to a 10 to 50 mm cell, filtering through a dry, medium-texture filter paper to separate particles of water.

Measure the absorbance of the solution using a spectrometer (3.4.2) with selectors for continuous variation at 436 nm or a spectrometer (3.4.2) with a filter having maximum transmission near 430 nm, against the chloroform (3.3.1) as reference.

3.6.5 Preparation of calibration graph

Introduce, using a burette, into each of a series of seven 100 ml beakers, 0,0; 0,5; 1,5; 2,5; 3,5; 4,5; and 5,5 ml of copper standard solution (3.3.12), corresponding to 0,000; 0,002; 0,006; 0,010; 0,014; 0,018; and 0,022 mg of copper. Add 5 ml of the ammonium citrate solution (3.3.9), 10 ml of the Na_2EDTA solution (3.3.11) and 20 ml of water, while stirring. Add ammonium hydroxide (3.3.8) to adjust the pH to 8,5, using a universal indicator test paper. Transfer each solution to a 200 to 250 ml separating funnel, dilute with water to 70 ml, add

5 ml of the sodium diethyldithiocarbamate solution (3.3.10) and 10 ml of the chloroform (3.3.1), then stopper and shake vigorously for not less than 3 min. Allow the organic layer to settle and draw it off into a 25 ml one-mark volumetric flask.

To the aqueous layer in the separating funnel, add again 5 ml of the chloroform (3.3.1) and repeat the extraction. Combine the extracts. Make up the solution in the volumetric flask to the mark with chloroform and mix.

Measure the absorbance of each solution as specified in 3.6.4.

Prepare a calibration graph by plotting the absorbance values against the nominal copper contents of the solutions.

3.7 Expression of results

3.7.1 Calculation

Convert the absorbance reading for the test solution to copper content by means of the calibration graph (3.6.5), deducting the absorbance reading for the blank.

The copper (Cu) content is given, as a percentage by mass, by the formula

$$\frac{m_1 \times 100}{m_0 \times 1\,000} \times K = \frac{m_1}{m_0 \times 10} \times K$$

where

m_0 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

m_1 is the mass, in milligrams, of copper in the aliquot portion of the test solution, obtained from the calibration graph;

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

3.7.2 Permissible tolerances on results of parallel determinations

Table 2

Copper content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
0,002 5 to 0,006	0,000 8	0,000 7
0,006 to 0,01	0,001	0,000 8
0,01 to 0,03	0,002	0,002
0,03 to 0,05	0,004	0,003
0,05 to 0,1	0,006	0,005
0,1 to 0,2	0,01	0,008
0,2 to 0,3	0,02	0,02
0,3 to 0,5	0,04	0,03

4 Method B: Spectrometric method for copper contents from 0,1 to 1 % (m/m)

4.1 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids and evaporation of the solution to dryness. Dissolution of the dry residue in hydrochloric acid. Separation of the insoluble residue by filtration, ignition of the filter with the residue and treatment with sulfuric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in water and combination of the solution obtained with the main solution. Addition, to an aliquot portion of the resulting solution, of ammonium citrate solution and ammonium hydroxide, to adjust the pH to 6.

Addition of hydroxylammonium chloride solution and 2,2'-bicinchoninic acid solution. Spectrometric measurement at 540 nm.

4.2 Reactions

The method is based on the interaction of copper (I) ions with 2,2'-bicinchoninic acid at pH 6, forming a stable coloured complex.

The influence of iron and other accompanying components is eliminated by binding them into soluble complexes with ammonium citrate.

4.3 Reagents

4.3.1 Sodium carbonate, anhydrous.

4.3.2 Hydrofluoric acid, ϱ 1,14 g/ml.

4.3.3 Nitric acid, ϱ 1,40 g/ml.

4.3.4 Hydrochloric acid, ϱ 1,19 g/ml.

4.3.5 Hydrochloric acid, diluted 1 + 19.

4.3.6 Sulfuric acid, diluted 1 + 1.

4.3.7 Ammonium hydroxide, diluted 1 + 1.

4.3.8 Ammonium citrate $[(NH_4)_2C_6H_5O_7]$, 100 g/l solution.

4.3.9 Hydroxylammonium chloride $(NH_3OH^+Cl^-)$, 100 g/l solution.

4.3.10 2,2'-Bicinchoninic acid, 1 g/l solution.

Dissolve 1 g of 2,2'-bicinchoninic acid (4,4'-dicarboxy-2,2'-biquinoline) in 1 litre of 20 g/l potassium hydroxide solution.

4.3.11 Copper, standard solution, corresponding to 0,005 g of Cu per litre.

4.3.11.1 Copper, stock solution, 0,1 g/l.

Weigh 0,1 g of metallic copper [purity 99,95 % (*m/m*)] into a 100 to 200 ml beaker, add 10 ml of nitric acid (diluted 1 + 1) and dissolve while heating, then boil until free from nitrogen oxides, and cool. Add 10 ml of sulfuric acid (4.3.6), evaporate to sulfuric acid fumes, cool, and dissolve the salts in water while heating. Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

4.3.11.2 Preparation

Transfer 5 ml of copper stock solution (4.3.11.1) to a 100 ml one-mark volumetric flask, make up to the mark with water and mix.

1 ml of this standard solution contains 0,005 mg of Cu.

4.4 Apparatus

Usual laboratory apparatus and

4.4.1 Platinum crucible.

4.4.2 Spectrometer, with selectors for continuous or discontinuous variation, suitable for measurements at 540 nm, with matching cells.

4.5 Sample

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

4.6 Procedure

4.6.1 Test portion

Weigh a mass of the test sample, chosen from table 3, in accordance with the expected copper content.

4.6.2 Decomposition of test portion

Place the test portion (4.6.1) in a 300 ml beaker, add 15 ml of the hydrochloric acid (4.3.4) and dissolve while heating. Then add 1 to 1,5 ml of the nitric acid (4.3.3), boil the solution and evaporate to dryness. Moisten the dry residue with 10 ml of the hydrochloric acid (4.3.4) and again evaporate to dryness.

Table 3

Expected copper content	Mass of test portion	Aliquot portion of solution	Copper content of aliquot portion of solution
% (*m/m*)	g	ml	µg
⩾ 0,1 to 0,2	0,5	5	25 to 50
> 0,2 to 0,5	0,3	5	30 to 75
> 0,5 to 1,0	0,2	5	50 to 100

Repeat the evaporation with 10 ml of the same hydrochloric acid. Dissolve the dry residue in 10 ml of the hydrochloric acid (4.3.4) and 40 ml of water while heating. Heat the solution to boiling and filter through a medium-texture filter paper containing a small quantity of paper pulp. Wash the beaker and the precipitate on the filter with the hydrochloric acid (4.3.5) four or five times and with hot water six to eight times. Reserve the filtrate as the main solution.

Transfer the filter containing the residue to a platinum crucible, dry and ignite at 600 to 700 °C. Cool the crucible, moisten the residue with 2 or 3 drops of water, add 1 ml of the sulfuric acid (4.3.6), 5 ml of the hydrofluoric acid (4.3.2) and evaporate until the fuming of the sulfuric acid ceases. Ignite the residue at 500 to 600 °C. Cool, add 1 g of the sodium carbonate (4.3.1) and fuse at 950 to 1 000 °C. Dissolve the melt in 50 ml of warm water with addition of 1 ml of the hydrochloric acid (4.3.4). Add the solution thus obtained to the main solution. Evaporate the solution to 50 to 60 ml, cool and transfer to a 100 ml one-mark volumetric flask, make up to the mark with water and mix.

4.6.3 Preparation of solution for spectrometric measurement

Take an aliquot portion of the solution according to table 3, transfer it to a 100 ml beaker, add 5 ml of the ammonium citrate solution (4.3.8) and mix, then add the ammonium hydroxide (4.3.7) to adjust the pH to 6, using an indicator test paper. To reduce the copper(II) ions to copper(I) ions, add 5 ml of the hydroxylammonium chloride solution (4.3.9), while stirring. Add 2 ml of the 2,2'-bicinchoninic acid solution (4.3.10) and mix. Transfer the solution to a 50 ml one-mark volumetric flask, make up to the mark with water and mix.

4.6.4 Spectrometric measurement

Measure the absorbance of the solution using the spectrometer (4.4.2) at 540 nm, with a 20 mm cell, against the blank test solution as reference.

4.6.5 Preparation of calibration graph

Introduce, using a burette, into each of a series of seven 100 ml beakers, 0,0; 4,0; 8,0; 12,0; 16,0; 20,0; and 24,0 ml of the standard copper solution (4.3.11), corresponding to 0,00; 0,02; 0,04; 0,06; 0,08; 0,10; and 0,12 mg of copper. Add 5 ml of the ammonium citrate solution (4.3.8) to each beaker and mix. Add the ammonium hydroxide (4.3.7) to adjust the pH to 6, using an indicator test paper, then add 5 ml of the hydroxylammonium chloride solution (4.3.9) and 2 ml of the 2,2'-bicinchoninic acid solution (4.3.10), while stirring. Transfer the solutions to 50 ml one-mark volumetric flasks, make up to the mark with water and mix.

Measure the absorbance of the solutions as specified in 4.6.4, against the solution containing no standard copper solution as reference.

Prepare a calibration graph by plotting the absorbance values against the nominal copper contents of the solutions.

4.7 Expression of results

4.7.1 Calculation

Convert the absorbance reading for the test solution to copper content by means of the calibration graph (4.6.5).

The copper (Cu) content is given, as a percentage by mass, by the formula

$$\frac{m_1 \times 100}{m_0 \times 1\,000} \times K = \frac{m_1}{m_0 \times 10} \times K$$

where

m_0 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

m_1 is the mass, in milligrams, of copper in the aliquot portion of the test solution, obtained from the calibration graph;

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

4.7.2 Permissible tolerances on results of parallel determinations

Table 4

Copper content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (*m*/*m*)	% (*m*/*m*)	% (*m*/*m*)
⩾ 0,1 to 0,2	0,01	0,008
> 0,2 to 0,3	0,02	0,02
> 0,3 to 0,5	0,04	0,03
> 0,5 to 1,0	0,06	0,05

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