INTERNATIONAL STANDARD ISO 4294

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

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

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

First edition — 1978-08-15

UDC 553.32 : 546.56 : 543.4

Ref. No. ISO 4294-1978 (E)

Descriptors : manganese ores, chemical analysis, determination of content, copper, spectrophotometric analysis.

Price based on 5 pages

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 4294 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in May 1977.

It has been approved by the member bodies of the following countries :

Australia	Hungary	Romania
Bulgaria	India	South Africa, Rep. of
Czechoslovakia	Italy	Turkey
France	Mexico	U.S.S.R.
Germany, F.R.	Poland	Yugoslavia

No member body ~~of the following country~~ expressed disapproval of the document ~~on technical grounds~~.

Japan

This International Standard cancels and replaces ISO Recommendation R 322-1963, of which it constitutes a technical revision.

Printed in Switzerland

INTERNATIONAL STANDARD ISO 4294-1978 (E)

AMENDMENT SLIP
Published 1978-10-15

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

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

MODIFICATION TO FOREWORD *(Inside front cover)*

The ISO member body for Japan has now withdrawn its disapproval of this International Standard. Japan should therefore be included in the list of countries whose member bodies have approved the document.

Manganese ores and concentrates — Determination of copper content — Extraction-photometric and photometric 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-photometric method, applicable to products having copper contents up to 0,5 % (*m/m*);

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

It should be read in conjunction with ISO 4297.

2 REFERENCE

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

3 METHOD A — EXTRACTION-PHOTOMETRIC 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, the residue being discarded or decomposed by fusion with sodium peroxide if it is suspected to contain a significant amount of copper. Addition, to an aliquot portion of the filtrate, of ammonium citrate solution, EDTA solution, ammonium hydroxide solution to adjust the pH to 8,5, and sodium diethyldithiocarbamate solution.

Extraction of the copper-diethyldithiocarbamate complex with chloroform. Photometric 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 the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA).

3.3 Reagents

3.3.1 Ammonium hydroxide solution, diluted 1 + 1.

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

3.3.3 Nitric acid, ρ 1,40 g/ml.

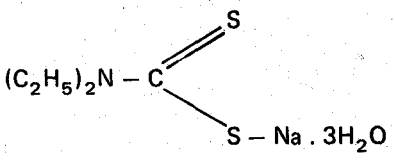
3.3.4 Nitric acid, diluted 1 + 1.

3.3.5 Sulphuric acid, diluted 1 + 1.

3.3.6 Hydrochloric acid, ρ 1,19 g/ml.

3.3.7 Hydrochloric acid, diluted 5 + 95.

3.3.8 Sodium diethyldithiocarbamate trihydrate :



1 g/l solution.

Prepare fresh as needed.

3.3.9 (Ethylenedinitrilo)tetraacetic acid (EDTA), disodium salt, 100 g/l solution.

Dissolve 10 g of EDTA, disodium salt, in 100 ml of water while heating slightly, and filter.

3.3.10 Chloroform.

3.3.11 Copper, 0,1 g/l standard solution.

Dissolve 0,1 g of metallic copper (purity 99,95 %) in 10 ml of the nitric acid (3.3.4), boil until free from nitrogen oxides, cool, add 10 ml of the sulphuric acid (3.3.5), evaporate to dense white fumes of sulphuric acid, cool, add water and heat to dissolve the salts. Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,1 mg of copper.

3.3.12 Copper, 0,004 g/l standard solution.

Transfer 10 ml of the standard copper solution (3.3.11) to a 250 ml one-mark volumetric flask, dilute with water to the mark and mix.

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

3.3.13 Sodium peroxide.

3.4 Apparatus

Ordinary laboratory apparatus and

3.4.1 Spectrophotometer or **photocolorimeter.**

3.5 Procedure

3.5.1 *Test portion*

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

3.5.2 *Decomposition of test portion*

Place the test portion (3.5.1) in a 300 ml beaker, dissolve in 15 to 25 ml of the hydrochloric acid (3.3.6), 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 (3.3.6) 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 (3.3.6) 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 (3.3.7) and several times with hot water. Discard the filter (see note) and evaporate the filtrate to 60 to 70 ml; cool, transfer to a 100 ml or 250 ml volumetric flask (see table 1), dilute with water to the mark and mix.

NOTE — If any residue is suspected to contain a significant amount of copper, ignite the residue, fuse it with 3 to 5 g of sodium peroxide (3.3.13) and dissolve the melt in warm water with addition of dilute hydrochloric acid; combine the solution with the main solution.

3.5.3 *Extraction*

Take an aliquot portion of the solution according to table 1, add 5 ml of the ammonium citrate solution (3.3.2) and 10 ml of the EDTA solution (3.3.9), mix, then add the ammonium hydroxide solution (3.3.1) 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 (3.3.8) and extract with 10 ml of the chloroform (3.3.10), 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. Dilute the solution in the volumetric flask with chloroform to the mark and mix.

3.5.4 *Photometric measurement*

Transfer the solution to a 1 to 5 cm cell, filtering through a dry, medium-texture filter paper to separate particles of water.

Measure the absorbance of the solution using the spectrophotometer at 436 nm or photocolorimeter (3.4.1) with a filter having maximum transmission near 430 nm, against the chloroform (3.3.10) as reference.

3.5.5 *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 the standard copper 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 (3.3.2), 10 ml of the EDTA solution (3.3.9) and 20 ml of water, while stirring. Add the ammonium hydroxide solution (3.3.1) to adjust the pH to 8,5, using a universal indicator test paper. Transfer each solution to

TABLE 1

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

a 200 to 250 ml separating funnel, dilute with water to 70 ml, add 5 ml of the sodium diethyldithiocarbamate solution (3.3.8) and 10 ml of the chloroform (3.3.10), 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 (3.3.10) and repeat the extraction. Combine the extracts. Dilute the solution in the volumetric flask with chloroform to the mark and mix.

Measure the absorbance of each solution as specified in 3.5.4.

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

3.6 Expression of results

3.6.1 *Calculation*

Convert the absorbance reading for the test solution to copper content by means of the calibration graph (3.5.5), deducting the absorbance reading for the blank.

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

$$\frac{m_1 \times 100}{m_2 \times 1\,000} \times K$$

$$= \frac{m_1}{m_2 \times 10} \times K$$

where

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

m_2 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

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

3.6.2 *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 – PHOTOMETRIC 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, the residue being discarded. Addition, to an aliquot portion of the filtrate, of ammonium citrate solution and ammonium hydroxide solution, to adjust the pH to 6.

Addition of hydroxylammonium chloride solution and 2,2′-bicinchoninic acid solution.

Photometric 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 Ammonium hydroxide solution, diluted 1 + 1.

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

4.3.3 Hydroxylammonium chloride ($NH_2OH.HCl$), 100 g/l solution.

4.3.4 Hydrochloric acid, ρ 1,19 g/ml.

4.3.5 Hydrochloric acid, diluted 5 + 95.

4.3.6 Nitric acid, ρ 1,40 g/ml.

4.3.7 Nitric acid, diluted 1 + 1.

4.3.8 Sulphuric acid, diluted 1 + 1.

4.3.9 Potassium hydroxide, 20 g/l solution.

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

Dissolve 1 g of 2,2′-bicinchoninic acid [2,2′-(4,4′-quinoline carboxylic acid)] in 1 litre of the potassium hydroxide solution (4.3.9).

4.3.11 Copper, 0,1 g/l standard solution.

Weigh 0,1 g of metallic copper (purity 99,95 %) into a 100 to 200 ml beaker, add 10 ml of the nitric acid (4.3.7) and dissolve while heating, then boil until free from nitrogen oxides, and cool. Add 10 ml of the sulphuric acid (4.3.8),

evaporate to sulphuric acid fumes, cool, and dissolve the salts in water while heating. Cool the solution, transfer to a 1 000 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,1 mg of copper.

4.3.12 Copper, 0,005 g/l standard solution.

Transfer 5 ml of the standard copper solution (4.3.11) to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

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

4.4 Apparatus

Ordinary laboratory apparatus and

4.4.1 Spectrophotometer or **photoelectric colorimeter** fitted with a filter having maximum transmission at 540 nm.

4.5 Procedure

4.5.1 *Test portion*

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

TABLE 3

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

4.5.2 *Decomposition of test portion*

Place the test portion (4.5.1) 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 (4.3.6), 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. 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. Discard the filter with the precipitate. Evaporate the filtrate to about 50 to 60 ml, cool, transfer to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

4.5.3 *Preparation of solution for photometric 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 (4.3.2) and mix, then add the ammonium hydroxide solution (4.3.1) 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 (4.3.3), 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, dilute with water to the mark and mix.

4.5.4 *Photometric measurement*

Measure the absorbance of the solution using the spectrophotometer or photoelectric colorimeter at 540 nm, with a 2 cm cell, against the blank test solution as reference.

4.5.5 *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 (4.3.12), 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 (4.3.2) to each beaker and mix. Add the ammonium hydroxide solution (4.3.1) to adjust the pH to 6, using an indicator test paper, then add 5 ml of the hydroxylammonium chloride solution (4.3.3) and 2 ml of the 2,2′-bicinchoninic acid solution (4.3.10), while stirring. Transfer the solutions to 50 ml volumetric flasks, dilute with water to the mark and mix.

Measure the absorbance of the solutions as specified in 4.5.4, 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.

4.6 Expression of results

4.6.1 *Calculation*

Convert the absorbance reading for the test solution to copper content by means of the calibration graph (4.5.5).

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

$$\frac{m_3 \times 100}{m_4 \times 1\,000} \times K$$

$$= \frac{m_3}{m_4 \times 10} \times K$$

where

m_3 is the mass, in milligrams, of copper in the aliquot portion of the test solution, obtained from the calibration graph;

m_4 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

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

4.6.2 *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