



Manganese ores — Determination of chromium content — Diphenylcarbazide photometric method and silver persulphate titrimetric method

Minerais de manganèse — Dosage du chrome — Méthode photométrique à la diphenylcarbazide et méthode titrimétrique au persulfate d'argent

Second edition — 1981-12-15

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Foreword

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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 619 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 619-1975), which had been approved by the member bodies of the following countries:

Austria	Hungary	South Africa, Rep. of
Chile	India	Spain
Czechoslovakia	Italy	Switzerland
Egypt, Arab Rep. of	Korea, Rep. of	Turkey
France	Netherlands	United Kingdom
Germany, F.R.	Poland	USSR
Greece	Romania	Yugoslavia

No member body had expressed disapproval of the document.

Manganese ores — Determination of chromium content — Diphenylcarbazide photometric method and silver persulphate titrimetric method

1 Scope and field of application

This International Standard specifies two methods for the determination of chromium in manganese ores:

- **Method I:** diphenylcarbazide photometric method, which is applicable to manganese ores having chromium contents less than 0,1 % (*m/m*);
- **Method II:** silver persulphate titrimetric method, which is applicable to manganese ores having chromium contents greater than 0,1 % (*m/m*).

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: Diphenylcarbazide photometric method

3.1 Principle

Fusion of a test portion with sodium carbonate and sodium peroxide and extraction of the fused mass in water.

NOTE — If the vanadium content exceeds 0,1 % (*m/m*), its effect can be eliminated by extraction of the hydroxyquinolate of vanadium with chloroform (see the note in 3.5.2.4).

Formation of a red-violet coloured complex by oxidation of diphenylcarbazide with chromate ions.

Photometric measurement of the complex at a wavelength of 520 to 530 nm.

1) At present at the stage of draft.

2) Hitherto expressed as "6 N solution".

3) Hitherto expressed as "2 N solution".

3.2 Reagents

3.2.1 Sodium carbonate, anhydrous.

3.2.2 Sodium peroxide.

3.2.3 Ethanol.

3.2.4 Chloroform.

3.2.5 Sulphuric acid, solution, $c(1/2 \text{ H}_2\text{SO}_4) = 6 \text{ mol/l}$.²⁾

3.2.6 Sulphuric acid, solution, $c(1/2 \text{ H}_2\text{SO}_4) = 2 \text{ mol/l}$.³⁾

3.2.7 Ammonium persulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, 250 g/l solution.

Prepare this solution at the time of use.

3.2.8 Diphenylcarbazide, 1 g/l solution.

Prepare this solution at the time of use, as follows.

Dissolve 0,1 g of diphenylcarbazide in 10 ml of 80 % (*m/m*) acetic acid and dilute with water to 100 ml.

3.2.9 8-Hydroxyquinoline, 25 g/l solution in acetic acid solution, $c(\text{CH}_3\text{COOH}) = 2 \text{ mol/l}$.³⁾

3.2.10 Silver sulphate (Ag_2SO_4), 2,5 g/l solution.

3.2.11 Chromium, standard solution corresponding to 0,1 g of Cr per litre.

Dissolve 0,282 8 g of potassium dichromate, recrystallized and dried at a temperature of 180 to 200 °C, in a small quantity of water in a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,000 1 g of chromium.

3.2.12 Methyl orange, 1 g/l solution.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Nickel or corundum crucibles.

3.3.2 Muffle furnace, capable of being controlled at 700 to 800 °C.

3.3.3 Photoelectric absorptiometer, fitted with a green (wavelength 520 to 530 nm) filter.

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 about 1 g of the test sample into a nickel or corundum crucible (3.3.1).

3.5.2 Determination

3.5.2.1 Add to the test portion (3.5.1) in the nickel or corundum crucible, 8 g of a 1 + 1 mixture of the sodium carbonate (3.2.1) and the sodium peroxide (3.2.2), mix thoroughly, cover the crucible with a lid and fuse the mixture in the muffle furnace (3.3.2) at a temperature of 700 to 800 °C for 15 to 20 min.

3.5.2.2 After the fused mass has cooled, extract it in 200 ml of hot water (60 to 70 °C), heat the solution to boiling, allow to boil 15 to 20 min, add the ethanol (4.3), drop by drop, and boil until the green colour disappears.

3.5.2.3 Cool the solution, transfer it with the precipitate to a 250 ml one-mark volumetric flask, dilute to the mark and mix with water; allow the residue to settle and filter the solution through a dry beaker, rejecting the first 10 to 15 ml of filtrate.

3.5.2.4 Transfer a 10 ml aliquot portion of the filtrate to a 100 ml beaker, neutralize with the sulphuric acid solution (3.2.6) in the presence of the methyl orange (3.2.12) until the yellow colour changes to orange, and mix for 2 min.

NOTE — If vanadium content exceeds 0,1 % (*m/m*), place the aliquot portion after neutralization in a 100 ml separating funnel, add 0,2 to 0,3 ml of the 8-hydroxyquinoline solution (3.2.9) and 3 to 5 ml of the chloroform (3.2.4), shake vigorously for 1 to 2 min and allow to settle for 2 to 3 min.

Drain off the chloroform layer into a separate vessel and discard. Repeat the extraction with chloroform two or three times in order to ensure a more complete extraction of vanadium hydroxyquinolate. When the extraction is complete, filter the solution, containing chro-

mium, through a filter wetted with water. Wash the filter five or six times with warm water (40 to 50 °C) and resume the determination, from 3.5.2.5.

3.5.2.5 Add 2 ml of the sulphuric acid solution (3.2.5) and 4 ml of the silver sulphate solution (3.2.10) to the solution and heat to boiling.

Add 2 ml of the ammonium persulphate solution (3.2.7) to the boiling solution and continue boiling for 10 min. Cool the solution, transfer it to a 50 ml one-mark volumetric flask and add 5 ml of the diphenylcarbazide solution (3.2.8). Mix for 20 to 30 s, dilute with water to the mark, mix again and carry out the photometric measurement using the green filter. If vanadium is present, the photometric measurement should be carried out in 10 to 15 min.

3.5.2.6 Determine the percentage of chromium in the test sample, from the absorbance of the solution being tested, using either of the following methods:

a) Calibration graph method

Take appropriate volumes of the standard chromium solution (3.2.11), covering both the limits (maximum and minimum) and the intermediate contents of chromium in the given type of ore, and carry out all the stages of the analysis on them, including determination of the absorbance, in parallel with the sample being analysed. Plot a graph of measured absorbance against the chromium contents of the volumes of standard chromium solution taken.

b) Comparison method

Take a definite volume of the standard chromium solution (3.2.11) corresponding approximately to the chromium content of the sample being analysed and, in parallel with the latter, carry out all the stages of the analysis on it, including determination of the absorbance.

3.6 Expression of results

3.6.1 Calculation

The chromium (Cr) content, expressed as a percentage by mass on the dry basis, is given:

a) for the calibration graph method, by the value read directly from the calibration curve multiplied by the factor *K*, or

b) for the comparison method, by the formula

$$\frac{D_x \times m_1 \times 100}{D_{st} \times m_0} \times K$$

where

D_x is the absorbance of the solution being analysed;

D_{st} is the absorbance of the standard chromium solution;

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

m_1 is the mass, in grams, of chromium in the volume of standard chromium solution used for the determination;

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

3.6.2 Permissible tolerances on results of duplicate determinations

Chromium content, % (m/m)		Permissible tolerance, % (m/m)
from	to	
	0,005	0,000 5
0,005	0,010	0,001 0
0,010	0,050	0,002 0
0,050	0,100	0,003 0

4 Method II: Silver persulphate titrimetric method

4.1 Principle

Oxidation of chromous ions to chromate ions in an acid medium by ammonium persulphate in the presence of silver nitrate as a catalyst.

Reduction of the chromate ions with ammonium iron(II) sulphate and titration of the excess of the latter with standard volumetric potassium permanganate solution.

4.2 Reagents

4.2.1 Sodium carbonate, anhydrous.

4.2.2 Sodium peroxide.

4.2.3 Ethanol.

4.2.4 Phosphoric acid, ρ 1,70 g/ml.

4.2.5 Sulphuric acid, diluted 1 + 1.

4.2.6 Ammonium persulphate, 250 g/l solution.

4.2.7 Sodium chloride, 50 g/l solution.

4.2.8 Ammonium iron(II) sulphate, 12 g/l solution.

Dissolve 12 g of ammonium iron(II) sulphate hexahydrate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ in 1 l of sulphuric acid, diluted 5 + 95.

4.2.9 Silver nitrate, 2,5 g/l solution.

4.2.10 Potassium permanganate, standard volumetric solution, $c(1/5 \text{ KMnO}_4) = 0,03 \text{ mol/l.}^{1)}$

4.2.10.1 Preparation of the solution

Dissolve 0,95 g of potassium permanganate in 1 l of water. Allow the solution to stand for 6 days and then, without disturbing any precipitated manganese dioxide which may have formed, syphon or filter the solution through a layer of glass wool and ignited asbestos into a dark glass flask.

Protect the solution in the flask from dust and gases and keep it in a cool place.

Determine the titre of the solution but not before the day after filtering.

4.2.10.2 Standardization of the solution against sodium oxalate (theoretical titre)

Weigh about 0,05 g of anhydrous oxalate, dried to constant mass at a temperature of 110 to 120 °C, into a 250 ml one-mark volumetric flask and add 100 ml of sulphuric acid, diluted 1 + 9. Heat the solution to a temperature of 70 to 80 °C and titrate with the potassium permanganate solution (4.2.10.1) until a light pink colour, stable for about 1 min, is obtained.

Carry out the standardization using at least three test portions of sodium oxalate.

The titre T of the potassium permanganate solution is given by the formula

$$T = \frac{m \times 0,258 7}{V}$$

where

m is the mass, in grams, of the test portion of sodium oxalate;

V is the volume, in millilitres, of the potassium permanganate solution used;

0,258 7 is the factor to relate the concentration of the potassium permanganate solution to the mass of chromium, as determined by the sodium oxalate method.

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

1) Hitherto expressed as "0,03 N standard volumetric solution".

4.2.11 Methyl orange, 1 g/l solution.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Nickel or corundum crucibles.

4.3.2 Muffle furnace, capable of being controlled at 650 to 750 °C.

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 about 1 g of the test sample into a nickel or corundum crucible (4.3.1).

4.5.2 Determination

4.5.2.1 Add to the test portion (4.5.1) in the nickel or corundum crucible, 8 g of a 1 + 1 mixture of the sodium carbonate (4.2.1) and the sodium peroxide (4.2.2), mix, cover the crucible with a lid and fuse the mixture in the muffle furnace (4.3.2) at a temperature of 650 to 750 °C for 15 to 20 min.

4.5.2.2 After the fused mass has cooled, extract it in 200 ml of hot water (60 to 70 °C), heat to boiling, add the ethanol (4.2.3), drop by drop, and boil for 15 to 20 min until the green colour disappears.

Cool the solution, transfer it with precipitate to a 500 ml one-mark volumetric flask, dilute to the mark with water, mix and allow to stand until the supernatant liquid becomes clear.

4.5.2.3 Filter the solution through a dry filter into a dry beaker, rejecting the first portion of the filtrate. Transfer a 250 ml aliquot portion of the filtrate (corresponding to 0,5 to 1,0 g of the ore) to a 500 ml conical flask, add 2 or 3 drops of the methyl orange solution (4.2.11) and neutralize with the sulphuric acid solution (4.2.5) until the colour changes. Add 10 ml of the sulphuric acid solution in excess and 10 ml of the phosphoric acid (4.2.4).

4.5.2.4 Heat the solution to boiling, add 10 ml of the silver nitrate solution (4.2.9) and 30 ml of the freshly prepared ammonium persulphate solution (4.2.6) and boil for 8 to 10 min. Add to the boiling solution 5 ml of the sodium chloride solution (4.2.7) and boil until the solution becomes clear.

4.5.2.5 Cool the solution to a temperature of 15 to 20 °C and add from a burette 15 ml of the ammonium iron(II) sulphate solution (4.2.8), mix thoroughly and titrate the excess ammonium iron(II) sulphate with the standard volumetric potassium permanganate solution (4.2.10) until a light pink colour, stable for about 1 min, is obtained.

4.5.2.6 Simultaneously, determine the relation between the ammonium iron(II) sulphate solution and the standard volumetric potassium permanganate solution, using for this purpose the same number of millilitres of the ammonium iron(II) sulphate solution as was added to the solution of ore for the reduction of chromium. Carry out the determination not less than three times and take the mean value.

4.6 Expression of results

4.6.1 Calculation

The chromium (Cr) content, expressed as a percentage by mass on the dry basis, is given by the formula

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

where

T is the titre of the standard volumetric potassium permanganate solution used (see 4.2.10.2);

V_1 is the volume, in millilitres, of the standard volumetric potassium permanganate solution used in the titration of the ammonium iron(II) sulphate solution (see 4.5.2.6);

V_2 is the volume, in millilitres, of the standard volumetric potassium permanganate solution used in the back titration (see 4.5.2.5);

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

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

4.6.2 Permissible tolerances on results of duplicate determinations

Chromium content, % (m/m)		Permissible tolerance, % (m/m)
from	to	
0,10	0,20	0,015
0,20	0,50	0,020
0,50	—	0,025