INTERNATIONAL STANDARD 619

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

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

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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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 65 has reviewed ISO Recommendation R 619 and found it technically suitable for transformation. International Standard ISO 619 therefore replaces ISO Recommendation R 619-1967 to which it is technically identical.

ISO Recommendation R 619 was 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	Poland	U.S.S.R.
Greece	Romania	Yugoslavia

No Member Body expressed disapproval of the Recommendation.

No Member Body disapproved the transformation of ISO/R 619 into an International Standard.

Printed in Switzerland

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

1 SCOPE AND FIELD OF APPLICATION

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

Method I : a diphenylcarbazide photometric method, applicable to manganese ores the chromium content of which is less than 0,1 % (*m/m*);

Method II : a silver persulphate volumetric method, applicable to manganese ores the chromium content of which is greater than 0,1 % (*m/m*).

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.* [1)]

METHOD I — DIPHENYLCARBAZIDE PHOTOMETRIC METHOD

3 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 %, its effect can be eliminated by extraction of 8-hydroxyquinolate of vanadium with chloroform (see the note in 7.5.4).

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.

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 dichromate.

4.2 Sodium carbonate, anhydrous.

4.3 Sodium peroxide.

4.4 Ethanol.

4.5 Chloroform.

4.6 Sulphuric acid, 6 N solution.

4.7 Sulphuric acid, 2 N solution.

4.8 Acetic acid, 80 % (*m/m*).

4.9 Acetic acid, 2 N solution.

4.10 Ammonium persulphate $[(NH_4)_2S_2O_8]$ freshly prepared 250 g/l solution.

4.11 Diphenylcarbazide, freshly prepared solution.

Dissolve 0,1 g of diphenylcarbazide in 10 ml of acetic acid (4.8) and dilute with water to 100 ml.

4.12 8-hydroxyquinoline, 25 g/l solution in acetic acid (4.9).

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

4.14 Standard chromium solution.

Dissolve 0,282 8 g of potassium dichromate (4.1), recrystallized and dried at a temperature of 180 to 200 °C, in a small quantity of water in a 1 l volumetric flask, dilute with water to the mark and mix.

1 ml of the solution contains 0,000 1 g of chromium.

4.15 Methyl orange, 1 g/l solution.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Nickel or corundum crucibles.

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.*

5.2 Muffle furnace, capable of being maintained at 700 to 800 °C.

5.3 Photoelectric absorptiometer fitted with a green (wavelength 520 to 530 nm) light-filter.

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 analysis 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 chromium content and of the type of ore to which the sample being analysed belongs.

7.4 Test portion

Weigh, to the nearest 0,000 2 g, about 1 g of the test sample into a nickel or corundum crucible (5.1).

7.5 Determination

7.5.1 To the test portion (7.4) in the nickel or corundum crucible, add 8 g of a 1 : 1 mixture of sodium carbonate (4.2) and sodium peroxide (4.3), mix thoroughly, cover the crucible with a lid and fuse the mixture in the muffle furnace (5.2) at a temperature of 700 to 800 °C for 15 to 20 min.

7.5.2 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 for 15 to 20 min, add ethanol (4.4) drop by drop and boil until the green colouring disappears.

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

7.5.4 Transfer a 10 ml aliquot portion of the filtrate to a 100 ml beaker, neutralize with sulphuric acid solution (4.7) in the presence of methyl orange (4.15) until the yellow colour changes to orange, and mix for 2 min.

NOTE — When vanadium content exceeds 0,1 % place the aliquot portion after the process of neutralization in a 100 ml separating funnel, add 0,2 to 0,3 ml of the acetic acid solution of 8-hydroxyquinoline (4.12) and 3 to 5 ml of chloroform (4.5), 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 completed, filter the solution, containing chromium, through a filter wetted with water. Wash the filter five or six times with warm water (40 to 50 °C) and resume the determination, starting with 7.5.5.

7.5.5 Add 2 ml of sulphuric acid (4.6) and 4 ml of silver sulphate solution (4.13) to the solution and heat to boiling.

Add 2 ml of ammonium persulphate solution (4.10) to the boiling solution and continue boiling for 10 min. Cool the solution, transfer it to a 50 ml volumetric flask, add 5 ml of the diphenylcarbazide solution (4.11), mix for 20 to 30 s, dilute with water to the mark, mix again and carry out the photometric measurement using the green light-filter. If vanadium is present, the photometry should be carried out in 10 to 15 min.

7.5.6 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 curve method*

To construct the calibration curve, take corresponding volumes of the standard chromium solution (4.14), covering both the limits (maximum and minimum) and the intermediate contents of chromium in the given type of ore, and take them through all the stages of the analysis, including the determination of the absorbance, parallel with the sample being analysed.

b) *Comparison method*

Take a specified volume of the standard chromium solution (4.14) corresponding approximately to the chromium content of the sample being analysed and, parallel with the latter, take it through all the stages of the analysis including the determination of the absorbance.

8 EXPRESSION OF RESULTS

8.1 Method of calculation

The chromium content of the absolutely dry ore is calculated, as a percentage by mass, either

a) as the value read directly from the calibration curve and multiplied by the factor $100/(100 - A)$

b) by the comparison method, using the formula

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

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;

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 chromium content) shown in the table below.

Chromium content, %		Permissible tolerance, % (in absolute value)
from (over)	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

The average result of the simultaneous check analysis of the standard sample of manganese ore for chromium 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 chromium content) shown in the table.

9 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 II – SILVER PERSULPHATE VOLUMETRIC METHOD

10 PRINCIPLE

Oxidation of chromous ions to chromate ions in an acid medium with 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.

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 permanganate.

11.2 Sodium carbonate, anhydrous.

11.3 Sodium oxalate, anhydrous.

11.4 Sodium peroxide.

11.5 Ethanol.

11.6 Phosphoric acid, ρ 1,70 g/ml.

11.7 Sulphuric acid, ρ 1,84 g/ml.

11.8 Sulphuric acid, diluted 1 : 1.

11.9 Sulphuric acid, diluted 1 : 9.

11.10 Sulphuric acid, diluted 5 : 95.

11.11 Ammonium persulphate, 250 g/l solution.

11.12 Sodium chloride, 50 g/l solution.

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

Dissolve 12 g of ammonium iron(II) sulphate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ in 1 l of sulphuric acid (11.10).

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

11.15 Potassium permangante, standard volumetric solution, approximately 0,03 N.

11.15.1 *Preparation of the solution*

Dissolve 0,95 g of potassium permanganate (11.1) in 1 l of water. Allow the solution to stand for 6 days and then, without disturbing any precipitated manganese dioxide which may be formed, syphon or filter the solution through a layer of glass wool and ignited asbestos into a dark glass flask.

The solution in the flask should be protected from dust and gases and kept in a cool place.

Determine the strength of the solution not earlier than the next day after filtering.

11.15.2 *Standardization of the solution against sodium oxalate (theoretical titre)*

Weigh, to the nearest 0,000 2 g, about 0,05 g of sodium oxalate (11.3), dried to constant mass at a temperature of 110 to 120 °C, into a 250 ml volumetric flask and add 100 ml of dilute sulphuric acid (11.9); heat the solution to a temperature of 70 to 80 °C and titrate with the potassium permanganate solution (11.15.1) until a light pink colour appears which remains unchanged for about 1 min.

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

The titre 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;

0,258 7 is the factor for conversion of the strength of the potassium permanganate solution to the mass of chromium, as determined by the sodium oxalate method;

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

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

11.16 Methyl orange, 1 g/l solution.

12 APPARATUS

Ordinary laboratory apparatus and

12.1 Nickel or corundum crucibles.

12.2 Muffle furnace, capable of being maintained at 650 to 750 °C.

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 analysis 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 chromium 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, about 1 g of the test sample into a nickel or corundum crucible (12.1).

14.5 Determination

14.5.1 To the test portion (14.4) in the nickel or corundum crucible, add 8 g of sodium carbonate (11.2) and sodium peroxide (11.4) mixture (1 : 1), mix, cover the crucible with a lid and fuse the mixture in the muffle furnace (12.2) at a temperature of 650 to 750 °C for 15 to 20 min.

14.5.2 After cooling the fused mass, extract it in 200 ml of hot water (60 to 70 °C), heat to boiling, add ethanol (11.5) drop by drop and boil for 15 to 20 min until the green colour disappears.

After cooling the solution, transfer it complete with precipitate to a 500 ml volumetric flask, dilute with water up to the mark, mix and allow to stand until the supernatant liquid becomes clear.

14.5.3 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 (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 (11.16) and neutralize with dilute sulphuric acid (11.8), until the colour changes, add 10 ml of sulphuric acid in excess and 10 ml of phosphoric acid (11.6).