UDC 669.74

Ref. No.: ISO/R 619 - 1967 (E)

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 619

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF CHROMIUM CONTENT

1st EDITION
September 1967

For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 619, *Methods of Chemical Analysis of Manganese Ores — Determination of Chromium Content*, was drawn up by Technical Committee ISO/TC 65, *Manganese Ores*, the Secretariat of which is held by Komitet Standartov Mer i Izmeritel'nyh Priborov pri Sovete Ministrov S.S.S.R. (GOST).

Work on this question by the Technical Committee began in 1954 and led, in 1964, to the adoption of a Draft ISO Recommendation.

In April 1965, this Draft ISO Recommendation (No. 778) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies:

Argentina
Austria
Chile
Czechoslovakia
France
Germany
Greece
Hungary
India
Italy
Korea, Rep. of
Netherlands
Poland
Romania
Spain
Switzerland
Turkey
U.A.R.
United Kingdom
U.S.S.R.
Yugoslavia

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in September 1967, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 619 September 1967

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF CHROMIUM CONTENT

(Atomic mass Cr: 52.01; molecular mass Cr_2O_3: 152.02)

This ISO Recommendation contains three parts:

I. INTRODUCTION

1. GENERAL INSTRUCTIONS

1.1 In the following analysis use a sample for chemical analysis of air-dried manganese ore, sampled and prepared in accordance with ISO Recommendation R 309, *Methods of Sampling Manganese Ores.*

Simultaneously with the collection of test samples for the determination of chromium, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of chromium in ore on the dry basis by multiplying the numerical results of the determination of chromium by the conversion factor K, as found from the following formula:

$$K = \frac{100}{100-A}$$

where

A is the percentage hygroscopic moisture content.

1.2 The determination of chromium in manganese ore should be carried out by analysing three parallel-weighed test samples of the ore together with two blank tests to allow the necessary corrections to be made to the results of the determination.

Simultaneously and under the same conditions, carry out a check analysis of a standard sample of manganese ore for the determination of its chromium content. The standard sample for analysis should be taken from the same type of ore as that from which the analysed sample was taken.

The arithmetical mean of the three results should be accepted as the final result.

The following conditions should be observed:

The difference between the highest and the lowest results should not exceed double the absolute value of the permissible tolerance for the corresponding interval of chromium content shown in the Tables under clauses 5.2 and 10.2, "Accuracy of method".

The average result of the simultaneous check analysis of the standard sample of manganese ore for chromium content should 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 tables under clauses 5.2 and 10.2, "Accuracy of method".

1.3 The test samples should be weighed to an accuracy of ± 0.0002 g.

1.4 Double distilled or de-ionized water should be used during the procedure and for preparation of the solutions.

1.5 Meanings of particular expressions:

hot water (or solution)	implies a temperature of the liquid of 60 to 70 °C;
warm water (or solution)	implies a temperature of the liquid of 40 to 50 °C;
diluted 1:1, 1:2, 1:5, etc.	the first figure gives the number of parts by volume of concentrated acid or some other solution; the second figure gives the number of parts by volume of water.

1.6 Indications as to the concentrations of solutions show the quantity of solute, in grammes, in the corresponding volume of the solvent.

1.7 The following abbreviations and symbols are used:

CP	chemically pure
d	relative density
g	gramme
g/l	grammes per litre
l	litre
ml	millilitre
nm	nanometre
N	standard solution of normal concentration
PFA	pure for analysis.

II. PHOTOMETRIC METHOD OF DETERMINATION OF CHROMIUM CONTENT BY USING DIPHENYLCARBAZIDE

(For chromium content below 0.1 %)

2. PRINCIPLE OF METHOD

A test sample of ore is fused with sodium carbonate and sodium peroxide and the fused mass is extracted in water.*

Chromium is determined in the solution by the photometric method based on the oxidation of diphenylcarbazide with chromate ions with the formation of a compound of red-violet colour.

---

* If the vanadium content exceeds 0.1 %, its effect can be eliminated by extraction of 8-hydroxyquinolate of vanadium with chloroform (see the Note under clause 4.4).

3. REAGENTS

3.1 *Potassium dichromate*, CP.

3.2 *Sodium carbonate*, CP, anhydrous.

3.3 *Sodium peroxide*, CP.

3.4 *Ethanol*, PFA.

3.5 *Chloroform*, CP.

3.6 *Sulphuric acid*, CP (6N).

3.7 *Sulphuric acid*, CP (2N).

3.8 *Acetic acid*, 80%.

3.9 *Acetic acid*, 2N.

3.10 *Ammonium persulphate* $(NH_4)_2S_2O_8$, CP, aqueous solution (250 g/l), freshly prepared.

3.11 *Diphenylcarbazide*, CP, freshly prepared solution; 0.1 g of diphenylcarbazide is dissolved in 10 ml of acetic acid (3.8) and diluted with water to 100 ml.

3.12 *8-hydroxyquinoline*, CP, solution (25 g/l) in acetic acid (3.9).

3.13 *Silver sulphate* Ag_2SO_4, CP, aqueous solution (2.5 g/l).

3.14 *Standard solution of chromium.* Dissolve 0.2828 g of potassium dichromate, CP, (3.1), recrystallized and dried at a temperature of 180 to 200°C, in a small quantity of water in a 1 litre volumetric flask, dilute with water up to the mark and stir; 1 ml of the solution contains 0.0001 g of chromium.

3.15 *Methyl-orange*, aqueous solution (1 g/l).

4. PROCEDURE

4.1 Weigh accurately about 1 g of the manganese ore into a nickel or corundum crucible, add 8 g of sodium carbonate (3.2) and sodium peroxide (3.3) mixture (1: 1), mix thoroughly, cover the crucible with a lid and fuse the mixture in a muffle furnace at a temperature of 700 to 800 °C for 15 to 20 minutes.

4.2 After the fused mass has cooled, extract it in 200 ml of hot water, heat the solution to boiling, allow to boil for 15 to 20 minutes, add ethanol (3.4) drop by drop and boil until the green colouring disappears.

4.3 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.

4.4 Transfer a 10 ml aliquot portion of the filtrate into a 100 ml beaker, neutralize with 2N sulphuric acid solution (3.7) in the presence of methyl-orange (3.15) until the yellow colour changes to orange and mix for 2 minutes.

NOTE. — When vanadium content exceeds 0,1% place the aliquot part after the process of neutralization into a 100 ml separating funnel, add 0.2 to 0.3 ml of the acetic acid solution of 8-hydroxyquinoline (3.12) and 3 to 5 ml of chloroform (3.5), shake vigorously for 1 to 2 minutes and allow to settle for 2 to 3 minutes.

Drain off the chloroform layer into a separate vessel and discard. Repeat the extraction with chloroform 2 to 3 times in order to ensure a more complete extraction of vanadium hydroxyquinolate. The extraction being completed, the solution, containing chromium, is filtered through a filter wetted with water. Wash the filter 5 or 6 times with warm water and resume the determination, starting with clause 4.5.

4.5 Add 2 ml of sulphuric acid (3.6) and 4 ml of silver sulphate solution (3.13) to the solution and heat to boiling.

Add 2 ml of ammonium persulphate solution (3.10) to the boiling solution and continue boiling for 10 minutes. Cool the solution, transfer it to a 50 ml volumetric flask, add 5 ml of the diphenylcarbazide solution (3.11), mix for 20 to 30 seconds, dilute with water to the mark, mix again and carry out the photometric determination with a green light filter (wave-length 520 to 530 nm). If vanadium is present the photometry should be carried out in 10 to 15 minutes.

4.6 Simultaneously take through all the stages of the analysis a quantity of the standard solution of chromium (3.14) of approximately the same chromium content as the ore being analysed.

For this test, place the exact quantity of the standard solution of chromium into a nickel or corundum crucible and introduce all the reagents in the same quantities that are used for the determination of chromium in the ore being analysed.

4.7 The percentage content of chromium is determined from the optical density found for the solution being tested by the calibration curve method or by the comparative method.

(*a*) *Calibration curve method*

To construct the calibration curve, take corresponding volumes of the standard solution of chromium (3.14), covering both the limits (maximum and minimum) and the intermediate degrees of its concentration in the given type of ore, and take them through all the stages of the analysis, including the determination of the optical density, parallel with the sample being analysed.

The calibration curve is constructed on the basis of the values of the optical density of the standard solutions. The percentage chromium content is determined from the calibration curve on the basis of the optical density of the solution of the sample.

(*b*) *Comparative method*

Take a specified volume of the standard solution of chromium (3.14) corresponding to the same chromium content as in the sample being analysed and, parallel with the latter, take it through all the stages of the analysis including the determination of the optical density.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of chromium (Cr) is calculated

(*a*) from the calibration curve, graphically,

(*b*) by the comparative method, from the following formula:

$$\mathrm{Cr} = \frac{D_x\, C_{st} \times 100}{D_{st}\, G}\ \%$$

where

D_x is the optical density of the solution being analysed;

C_{st} is the quantity of the standard solution used, expressed in grammes of chromium;

D_{st} is the optical density of the standard solution of chromium;

G is the mass of the test sample of ore, corresponding to the aliquot portion of the solution taken for the photometric determination expressed in grammes.

5.2 Accuracy of method

The permissible tolerances, expressed as percentages (absolute value), are given in the Table below.

Chromium content		Permissible tolerance (absolute value)
from (over)	to	
	0.005 %	± 0.0005 %
0.005 %	0.010 %	± 0.0010 %
0.010 %	0.050 %	± 0.0020 %
0.050 %	0.100 %	± 0.0030 %

III. VOLUMETRIC METHOD OF DETERMINATION OF CHROMIUM CONTENT USING SILVER PERSULPHATE

(For chromium content over 0.1 %)

6. PRINCIPLE OF METHOD

The method is based on the oxidation of chromous ions to chromate ions in an acid medium with ammonium persulphate in the presence of silver nitrate as a catalyst.

Chromate ions are reduced with ferrous ammonium sulphate and the excess of the latter is titrated with potassium permanganate solution.

7. REAGENTS

7.1 *Potassium permanganate*, CP

7.2 *Sodium carbonate*, CP, anhydrous

7.3 *Sodium oxalate*, CP, anhydrous

7.4 *Sodium peroxide*, PFA

7.5 *Ethanol*, PFA

7.6 *Phosphoric acid*, PFA, (*d* 1.70)

7.7 *Sulphuric acid*, PFA (*d* 1.84), diluted 1 : 1

7.8 *Sulphuric acid*, PFA (*d* 1.84), diluted 1 : 9

7.9 *Sulphuric acid*, PFA (*d* 1.84), diluted 5 : 95

7.10 *Ammonium persulphate*, CP, aqueous solution (250 g/l)

7.11 *Sodium chloride*, PFA, aqueous solution (50 g/l)

7.12 *Ferrous ammonium sulphate* [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], CP.
Dissolve 12 g of the salt in 1 litre of sulphuric acid (7.9).

7.13 *Silver nitrate*, CP, aqueous solution (2.5 g/l).

7.14 *Standard solution of potassium permanganate* (approximately 0.03 N). Dissolve 0.95 g of potassium permanganate (7.1) in 1 litre 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.

The strength of the solution should be determined not earlier than the next day after filtering.

7.15 *Methyl-orange,* aqueous solution (1 g/l).

8. STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION AGAINST SODIUM OXALATE

(Theoretical titre)

8.1 Weigh accurately about 0.05 g of sodium oxalate (7.3), dried to a constant mass at a temperature of 110 to 120 °C, into a 250 ml volumetric flask, add 100 ml of dilute sulphuric acid (7.8); heat the solution to a temperature of 70 to 80 °C and titrate with the potassium permanganate solution (7.14) until a light pink colour appears which remains unchanged for about 1 minute.

8.2 The titre of the potassium permanganate solution (T), expressed in grammes of chromium, is calculated from the following formula:

$$T = \frac{G \times 0.2587}{V}$$

where

G is the mass of test sample of sodium oxalate, expressed in grammes;

0.2587 is the factor for conversion of the strength of the potassium permanganate solution to the quantity of chromium, as determined by sodium oxalate method;

V is the volume of the potassium permanganate solution taken for titration of the test sample of sodium oxalate, expressed in millilitres.

8.3 The concentration of the potassium permanganate solution should be established with not less than three test samples of sodium oxalate, and the mean of three closely coinciding results should be retained.

9. PROCEDURE

9.1 Weigh accurately about 1 g of manganese ore into a nickel or corundum crucible, add 8 g of sodium carbonate (7.2) and sodium peroxide (7.4) mixture (1: 1), mix, cover the crucible with a lid and fuse the mixture in a muffle furnace at a temperature of 650 to 750 °C for 15 to 20 minutes.