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METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF CALCIUM OXIDE CONTENT AND MAGNESIUM OXIDE CONTENT

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BRIEF HISTORY

The ISO Recommendation R 552, *Methods of Chemical Analysis of Manganese Ores—Determination of Calcium Oxide Content and Magnesium Oxide Content*, was drawn up by Technical Committee ISO/TC 65, *Manganese Ores*, the Secretariat of which is held by the Komitet Standartov, Mer i Izmeritel'nyh Priborov pri Sovete Ministrov SSSR (GOST).

Work on this question by the Technical Committee began in 1957 and led, in 1959, to the adoption of a Draft ISO Recommendation.

In November 1962, this Draft ISO Recommendation (No. 541) 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:

Australia
Austria
Burma
Chile
Czechoslovakia
France
Germany
Hungary
India
Iran
Ireland
Italy
Japan
Poland
Romania
Spain
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 December 1966, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 552 December 1966

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF CALCIUM OXIDE CONTENT AND MAGNESIUM OXIDE CONTENT

(Atomic mass Ca : 40.08 ; molecular mass CaO : 56.08)

(Atomic mass Mg : 24.32 ; molecular mass MgO : 40.32)

This ISO Recommendation contains four parts:

I. INTRODUCTION

1. GENERAL INSTRUCTIONS

1.1 In the following analysis, use a sample for chemical analysis of air-dried manganese ore, which has been crushed to a size not exceeding 0.10 mm and checked on a sieve of appropriate size.

Simultaneously with the collection of samples for the determination of calcium oxide and magnesium oxide, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of calcium oxide and that of magnesium oxide in ore which is absolutely dry by multiplying the numerical results of these determinations by the conversion factor K, as found from the following formula:

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

where A = hygroscopic moisture content, per cent.

1.2 The determination of calcium oxide and magnesium oxide in manganese ore is carried out by simultaneously analysing three samples of ore with two blank determinations to enable a corresponding correction in the result of the determinations to be made.

Simultaneously and under the same conditions, carry out a check analysis of a standard sample of manganese ore for calcium oxide and magnesium oxide.

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

The following conditions should be observed:

The maximum difference between the highest and the lowest results should not exceed double the absolute value of the permissible tolerance on the result of the analysis (for the corresponding interval of calcium oxide content and magnesium oxide content), shown in the tables under clauses 5.2, 10.2 and 14.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for calcium and magnesium oxides should not differ from the result shown in the certificate by more than the ± value of the permissible tolerance (for the corresponding interval of calcium and magnesium oxide content), shown in the tables under clauses 5.2, 10.2 and 14.2, " Accuracy of method ".

For the analysis take a standard sample of the type of ore to which the sample being analysed belongs.

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

1.4 Deionized water should be used during the procedure and for the preparation of solutions.

1.5 Meanings of the following 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. means that	the first figure gives the number of parts by volume of concentrated acid or some other solution, and the second figure gives the number of parts by volume of water.

1.6 Indications as to the concentration of solutions show the quantity of solute (in grammes) in the corresponding volume of the solvent.

1.7 The following symbols and abbreviations are used:

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

II. GRAVIMETRIC OXALATE METHOD OF DETERMINATION OF CALCIUM OXIDE CONTENT

2. PRINCIPLE OF METHOD

After the separation of silicic acid, manganese hydroxide, ferric hydroxide, aluminium hydroxide, etc., calcium is precipitated by ammonium oxalate solution and the precipitate ignited to oxide. Calcium oxide content in manganese ore is found by the weighing of its precipitate.

3. REAGENTS REQUIRED

3.1 *Ammonium persulphate* ($(NH_4)_2S_2O_8$), CP.
3.2 *Ammonium chloride*, CP.
3.3 *Sodium carbonate, anhydrous*, CP.
3.4 *Hydrochloric acid*, CP (*d* 1.19).
3.5 *Hydrochloric acid*, CP, diluted (1: 4).
3.6 *Hydrochloric acid*, CP, diluted (1: 50).
3.7 *Sulphuric acid*, CP (*d* 1.84).
3.8 *Hydrofluoric acid*, PFA, 40%.
3.9 *Ammonia*, CP, solution, free from carbonates (*d* 0.91).
3.10 *Hydrogen peroxide*, CP, 30% (perhydrol).
3.11 *Ammonium chloride*, CP, solution (20 g/l).
3.12 *Ammonium oxalate*, CP, solution (40 g/l).
3.13 *Ammonium oxalate*, CP, solution (1 g/l).
3.14 *Sodium carbonate*, CP, solution (10 g/l).
3.15 *Methyl-red, alcohol solution* (1 g/l).

4. PROCEDURE

4.1 Introduce 1 g of manganese ore into a 100 ml beaker and dissolve while heating in 10 to 15 ml of hydrochloric acid (*d* 1.19). Evaporate the solution until dry, add 10 ml of hydrochloric acid (*d* 1.19) to the dry residue and again evaporate until dry, keeping the dry residue for 40 to 60 min at a temperature of 120 to 130 °C.

4.2 Pour 10 to 15 ml of hydrochloric acid (*d* 1.19) onto the dry residue, moderately heat for 3 to 5 min, then add 30 to 40 ml of hot water, heat to boiling, filter off the insoluble residue through a filter of average density and collect the filtrate in a 350 to 500 ml beaker. Wash the residue on the filter three to four times with hot hydrochloric acid, diluted (1 : 50), and then six to eight times with hot water. Transfer the filter with the residue into a platinum crucible, dry and ignite at a temperature of 500 to 600 °C. After cooling moisten the residue with two or three drops of water, add two or three drops of sulphuric acid (*d* 1.84), 5 to 7 ml of hydrofluoric acid (40%) and evaporate until dry. Ignite the dry residue at a temperature of 500 to 600 °C, cool, mix with 2 to 4 g of sodium carbonate (anhydrous), cover the crucible with a lid and fuse at a temperature of 900 to 1000 °C for 20 to 25 min. Place the crucible with the fusion into a 100 to 150 ml beaker, pour 50 to 60 ml of hot water, heat to a complete decomposition of the fusion, wash the crucible and the lid with water, take them out of the beaker and boil the solution for 2 to 3 min. Filter off the solution through a filter containing a small quantity of paper pulp and wash the residue on the filter with the sodium carbonate solution (10 g/l).

4.3 Dissolve the washed residue on the filter in 10 to 15 ml of hot hydrochloric acid, diluted (1 : 4), wash the filter three to four times with hot water and add this solution to the major fraction.

4.4 Evaporate the combined solutions to a volume of 100 to 150 ml, add 5 g of ammonium chloride, two or three drops of methyl-red and ammonia (d 0.91) until the colour of the solution changes into yellow. Add to the solution two or three drops of hydrochloric acid (d 1.19), 3 to 4 g of ammonium persulphate, 4 to 6 ml of ammonia (d 0.91), heat to boiling and boil to a complete coagulation of the residue. In order to ensure a full precipitation of manganese it is necessary that the excess of ammonia be maintained in the solution all the time. Filter off the residue of hydroxides on a rapid filter, wash five to six times with hot neutral ammonium chloride solution (20 g/l) and wash it off with water into the beaker in which the precipitation took place. Dissolve the residue on the filter in 30 to 35 ml of hot hydrochloric acid, diluted (1 : 4), containing ten drops of hydrogen peroxide.

4.5 The residue having been dissolved, wash the filter three to four times with hydrochloric acid, diluted (1 : 50), then four to five times with hot water and discard the filter. Add to the solution obtained 5 g of ammonium chloride and repeat the precipitation of hydroxides by means of ammonia in the presence of ammonium persulphate as described above. Filter off the residue, wash eight to ten times with hot neutral ammonium chlorate solution (20 g/l) and discard it. Add the filtrate to the main solution.

4.6 Evaporate the combined filtrates up to 200 ml and neutralize with ammonia (d 0.91) until the colour of methyl-red indicator changes. If the residue of aluminium and manganese hydroxides appears, filter it off, wash with neutral ammonium chloride solution (20 g/l) and evaporate the solution once again up to 200 ml. Pour hydrochloric acid (d 1.19) to the solution until acid reaction is obtained and then add 2 to 3 ml of hydrochloric acid in excess.

Heat the solution to boiling, then while stirring carefully pour 40 ml of hot ammonium oxalate solution (40 g/l) and several drops of ammonia (d 0.91) until the colour of the indicator changes, boil for 1 to 2 min, and allow to stand for 12 hours.

4.7 Filter off the residue of calcium oxalate on a dense filter, wash the beaker and the filter with the residue eight to ten times using cold ammonium oxalate solution (1 g/l). Keep the filtrate for the determination of magnesium oxide. Dissolve the residue on the filter in 20 ml of hydrochloric acid, diluted (1 : 4), collecting the solution into the beaker in which the precipitation of calcium took place. Wash the filter six to eight times with hydrochloric acid, diluted (1 : 50).

Dilute the solution with water up to 100 to 150 ml and repeat (under the same conditions) the precipitation of calcium with 15 to 20 ml of ammonium oxalate solution. Allow the residue to stand for 3 to 4 hours and then filtrate on a dense filter; wash eight to ten times with cold ammonium oxalate solution (1 g/l). Add the filtrate from the residue of calcium oxalate to the basic filtrate, containing magnesium (see above).

4.8 Place the filter with the residue into an ignited and weighed platinum crucible, ignite carefully at a temperature of 1000 to 1100 °C to constant mass, then cool and weigh. Weigh quickly in the crucible covered with a lid.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of calcium oxide is calculated from the following formula:

$$\text{CaO} = \frac{A \times 100}{G} \text{ per cent}$$

where A = mass of calcium oxide, expressed in grammes;

G = mass of test sample of ore, expressed in grammes.

5.2 Accuracy of method

The permissible tolerances, per cent (absolute value), are given in the table below:

Calcium oxide content		Permissible tolerance (in absolute value)
from	to	
	0.3%	± 0.02%
0.3%	0.5%	± 0.03%
0.5%	1.0%	± 0.04%
1.0%	5.0%	± 0.06%

III. VOLUMETRIC PERMANGANATE METHOD OF DETERMINATION OF CALCIUM OXIDE CONTENT

(Calcium oxide content exceeds 0.5%)

6. PRINCIPLE OF METHOD

After the separation of silicic acid and manganese, ferric and aluminium hydroxides, etc., calcium is precipitated with ammonium oxalate solution, and the determination is completed by using the volumetric permanganate method.

7. REAGENTS REQUIRED

7.1 Same reagents as for the gravimetric method of determination of calcium.

7.2 *Sodium oxalate* (anhydrous), CP.

7.3 *Sulphuric acid*, CP, diluted (1 : 10.)

7.4 *Titration solution of potassium permanganate* 0.05 to 0.1 N: 3.16 g of potassium permanganate, CP, are dissolved in 1 litre of distilled water. Allow the solution to stand for 6 days in a closed vessel and then siphon or filter it through a glass wool layer and ignited asbestos into a dark glass flask without disturbing the residue of manganese dioxide on the bottom of the flask.

The solution in the flask should be protected from dust and air and kept in a cool place. The titre of the solution is determined not earlier than the next day after its filtration. The titre of potassium permanganate solution is determined against sodium oxalate, anhydrous, CP, or against the standard sample of manganese ore, using for this purpose not less than three test samples and the mean of the three most closely coinciding results is found.

8. DETERMINING THE TITRE OF POTASSIUM PERMANGANATE SOLUTION

8.1 Against sodium oxalate

Place 0.05 to 0.1 g of sodium oxalate, anhydrous, CP, (previously dried at a temperature of 110 to 120 °C) into a 500 ml flask, add 200 ml of sulphuric acid, diluted (1 : 10), heat the solution on a water bath up to a temperature of 75 to 80 °C and then titrate with potassium permanganate solution until a stable pink colour appears, which does not disappear for 1 to 2 min.

The titre of potassium permanganate solution, expressed in grammes of calcium oxide (T), is calculated from the formula:

$$T = \frac{G \times 0.4185}{V}$$

where G = mass of test samples of sodium oxalate, expressed in grammes;

0.4185 = factor of conversion of the titre of potassium permanganate solution (expressed against sodium oxalate) to the titre of calcium oxide;

V = volume, in millilitres, of potassium permanganate solution used for the titration of the test sample of sodium oxalate.

8.2 Against the standard sample

To determine the titre of the solution of potassium permanganate take the standard sample of manganese ore having approximately the same content of calcium oxide and other elements as that of the sample being analysed and pass it through all the stages of the analysis (see section 9 " Procedure ").

The titre of the solution of potassium permanganate for calcium oxide expressed in grammes of calcium oxide (T) is found from the following formula:

$$T = \frac{A \times G}{V \times 100}$$

where A = percentage of calcium oxide in the standard sample of ore;

G = mass of the standard sample of ore, expressed in grammes;

V = volume, in millilitres, of the solution of potassium permanganate, used for the titration of oxalic acid, equivalent to calcium oxide contained in the given weighed quantity of the standard sample of ore.

9. PROCEDURE

9.1 The residue of calcium oxalate, obtained under the same conditions as described in the gravimetric method, is filtered off on a dense filter, washed five to six times with warm ammonium oxalate solution (1 g/l) and then with cold water until oxalate-ion is completely removed.

In order to ensure a full removal of oxalate-ion, add 1 to 2 ml of sulphuric acid, diluted (1 : 10), to 3 to 5 ml of filtrate, heat up to a temperature of 75 to 80 °C and add one drop of 0.1 N solution of potassium permanganate. Stability of pink colouring for 1 to 2 min shows that the removal is complete.

9.2 Make a little aperture in the filter and wash off the residue with a water jet into a 500 ml vessel (flask or beaker) in which the precipitation of calcium took place. To dissolve the residue remaining on the filter wash the filter eight to ten times with hot sulphuric acid, diluted (1 : 10), and then four to five times with hot water, allowing the liquid to flow into the same vessel. Add hot water to the solution up to the volume of 200 ml, heat to a temperature of 75 to 80 °C and titrate with 0.05 to 0.1 N potassium permanganate solution until a light-pink colour persists for 1 to 2 min. The temperature of the solution during the titration should be maintained at 75 to 80 °C.

9.3 After the stable light-pink colour appears, drop the filter paper into the solution and slightly heat again. If the pink colouring disappears, continue the titration until the pink colour persists for 0.5 to 1 min.