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ISO RECOMMENDATION

R 321

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF PHOSPHORUS

1st EDITION
July 1963

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BRIEF HISTORY

The ISO Recommendation R 321, *Methods of Chemical Analysis of Manganese Ores—Determination of Phosphorus*, was drawn up by the 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.

Work on this question by the Technical Committee began in 1954 and led, in 1957, to the adoption of a Draft ISO Recommendation.

In October 1958, this Draft ISO Recommendation (No. 254) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

Austria
Bulgaria
Burma
Chile
Czechoslovakia
France
Germany
Hungary
Ireland
Italy
Japan
Netherlands
Poland
Portugal
Republic of South Africa
Romania
Spain
United Kingdom
U.S.S.R.

One Member Body opposed the approval of the Draft: India.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in July 1963, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 321 July 1963

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF PHOSPHORUS

(Atomic mass P: 30.975; molecular mass P_2O_5: 141.95)

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 phosphorus, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of phosphorus in ore which is absolutely dry by multiplying the numerical results of the determination of phosphorus 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 phosphorus 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 determination to be made.

Simultaneously and under the same conditions, carry out a check analysis of a standard sample of manganese ore, for phosphorus content.

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 phosphorus 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 phosphorus 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 phosphorus 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 Distilled 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:

cm	centimetre
d	relative density
g	gramme
g/l	grammes per litre
ml	millilitre
mm	millimetre
nm	nanometre
PFA	pure for analysis

II. GRAVIMETRIC METHOD
OF PHOSPHORUS DETERMINATION IN THE FORM OF BLUE SALT

2. PRINCIPLE OF METHOD

After removal of arsenic and separation of silicic acid, the phosphorus is precipitated in the form of ammonium phospho-molybdate. This complex salt is dissolved in ammonia; the solution is evaporated in a weighed porcelain dish, heated until the residue of ammonium phospho-molybdate ($P_2O_5 \cdot 24\,MoO_3$) is formed, and then weighed.

3. REAGENTS REQUIRED

3.1 *Ammonium hydroxide*, PFA (*d* 0.91).

3.2 *Ammonium hydroxide*, PFA, diluted 1 : 1.

3.3 *Ammonium nitrate*, PFA.

3.4 *Ammonium bromide* (NH_4Br), PFA.

3.5 *Hydroxylamine hydrochloride* ($NH_2OH \cdot HCl$), neutral, PFA, solution (150 g/l).

3.6 *Nitric acid*, PFA (*d* 1.40).

3.7 *Hydrochloric acid*, PFA (*d* 1.19).

3.8 *Hydrochloric acid*, PFA, diluted 1 : 100.

3.9 *Hydrofluoric acid*, PFA (40 per cent).

3.10 *Ammonium nitro-molybdate solution.*

Prepare the two following solutions:

First solution. Dissolve 36 g of molybdic acid, PFA, in 35 ml of ammonia (*d* 0.91) and 50 ml of water;

Second solution. Pour carefully 115 ml of ammonia (*d* 0.91), stirring continually, into 575 ml of nitric acid, diluted 1 : 1, and add 230 ml of water.

Cool the two solutions and mix them, adding slowly the first solution to the second and shaking vigorously to dissolve the white turbidity. Care should be taken to ensure that there is no rise in the temperature of the solution. Keep the ammonium nitro-molybdate solution in an open flask for 48 hours, after which it is ready for use. Filter the solution before using.

3.11 *Sodium nitrite* ($NaNO_2$), PFA, solution (50 g/l).

3.12 *Sodium carbonate*, PFA (anhydrous).

3.13 *Washing solution.* 10 ml of nitric acid (*d* 1.40) and 10 g of ammonium nitrate are dissolved in 1 litre of water.

4. PROCEDURE

4.1 Weigh 1 to 2 g of manganese ore into a 300 ml beaker, and dissolve in 40 ml of acid mixture made up as follows: 3 parts of hydrochloric acid (*d* 1.19) and 1 part of nitric acid (*d* 1.40). After the sample has been dissolved, evaporate the solution until dry. Moisten the residue with 5 ml of hydrochloric acid (*d* 1.19), then add 0.5 to 1 g of ammonium bromide, and again evaporate the solution until dry, to remove arsenic. Repeat this operation twice, after which, keep the dry residue at 120 to 130 °C for 40 to 60 min.

4.2 Add 20 ml of hydrochloric acid (*d* 1.19) to the residue, and heat for 2 to 3 min until the salts are dissolved. Add 40 to 50 ml of hot water, heat the solution to boiling and filter the insoluble residue. Wash the residue on the filter with hydrochloric acid, diluted 1 : 100, 3 to 4 times, and then with hot water, 6 to 8 times. Evaporate the filtrate to 50 to 70 ml.

4.3 Place the filter and residue in a platinum crucible, and ignite.

Moisten the residue with water; add 2 ml of nitric acid (*d* 1.40) and 4 to 6 ml of hydrofluoric acid, and evaporate until dry. Repeat twice the procedure of adding nitric acid and evaporating. Gently ignite the residue, add 1 g of anhydrous sodium carbonate, and fuse the whole at 900 to 1000 °C.

4.4 Extract the fusion in 50 to 60 ml of hot water, and wash the crucible with water. Boil the solution for 5 to 10 min, and then filter; wash the filter with water, and add the filtrate to the original solution.

4.5 Evaporate the combined solutions until crystallization of the salts begins. Add 10 to 15 ml of nitric acid (*d* 1.40) to the solution and evaporate to syrupy condition. Repeat the evaporation with 10 to 15 ml of nitric acid (*d* 1.40), add 10 ml of nitric acid (*d* 1.40), and dilute with 40 to 50 ml of water. If the manganese dioxide precipitates in the solution, dissolve it by adding 2 or 3 drops of sodium nitrite solution (50 g/l) to the boiling solution. Boil the solution until the nitric oxides are completely dispelled, cool, and neutralize with ammonia until the hydroxides precipitate. Dissolve the precipitate with a few drops of nitric acid (*d* 1.40), adding an excess of 1 to 2 ml of the acid.

4.6 To reduce pentavalent vanadium, add 2 ml of hydroxylamine solution (150 g/l), and then 10 g of ammonium nitrate. Heat to a temperature of 40 to 50 °C; precipitate with 80 ml of ammonium nitro-molybdate solution, stir, and allow to stand for 5 or 6 hours for complete precipitation of ammonium phospho-molybdate.

4.7 Filter off the precipitate of ammonium phospho-molybdate on a slow filter. When filtering is complete, wash the sides of the beaker with the washing solution 4 or 5 times, pouring the solution on the filter. Wash the residue 8 to 10 times with washing solution, and dissolve it in 10 ml of ammonia, diluted 1 : 1, on the filter.

Collect the solution in the beaker in which the precipitation has been carried out. Wash the filter 3 or 4 times with hot water. To ensure a complete extraction of the residue, again wash the filter with 10 ml of ammonium hydroxide, diluted 1 : 1, and then 4 or 5 times with hot water. Evaporate the solution to a volume of 3 to 5 ml, and add 2 ml of ammonium hydroxide, diluted 1 : 1. Transfer the solution to a weighed porcelain dish of 6 cm diameter, carefully wash the sides of the beaker, and evaporate the solution until dry. Carefully ignite the dish containing the dry residue at 400 to 450 °C until all the residue becomes blue, cool it in a desiccator, and weigh.

NOTES

1. If the ore sample contains a considerable amount of organic matter, it is ignited for 15 to 20 min, at 600 to 700 °C, before being dissolved. The sample is then placed in a beaker and dissolved.

2. The method recommended may also be applied to the analysis of ores containing lead.

3. Alternatively, for the determination of phosphorus, the filtrate remaining after the determination of silicic acid may be used (see ISO Recommendation R 311, *Methods of chemical analysis of manganese ores. Determination of silicon dioxide*).

5. EXPRESSION OF RESULTS

5.1 Method of calculation

The percentage content of phosphorus is calculated from the following formula:

$$\mathrm{P} = \frac{A \times 0.017\,24 \times 100}{G} \text{ per cent}$$

where

A = weight of residue, in grammes;

0.017 24 = conversion factor for ammonium phospho-molybdate ($P_2O_5 \cdot 24\ MoO_3$) to phosphorus;

G = mass of sample of ore, in grammes.

5.2 Accuracy of method

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

Phosphorus content from (over)	to	Permissible tolerance (in absolute value)
	0.050 per cent	± 0.0015 per cent
0.050 per cent	0.100 per cent	± 0.0025 per cent
0.100 per cent	0.300 per cent	± 0.0045 per cent
0.300 per cent	0.500 per cent	± 0.0075 per cent

III. VOLUMETRIC METHOD

6. PRINCIPLE OF METHOD

After removal of arsenic and separation of silicic acid, phosphorus is precipitated in the form of ammonium phospho-molybdate, which is dissolved in a standard solution of sodium hydroxide, the excess of which is titrated with a standard nitric acid solution.

7. REAGENTS REQUIRED

7.1 *Ammonium hydroxide*, PFA (*d* 0.91).

7.2 *Ammonium hydroxide*, PFA, diluted 1 : 1.

7.3 *Ammonium nitrate*, PFA.

7.4 *Ammonium bromide*, PFA.

7.5 *Hydroxylamine hydrochloride* ($NH_2OH{\cdot}HCl$), neutral, PFA, solution (150 g/l).

7.6 *Nitric acid*, PFA (*d* 1.40).

7.7 *Hydrochloric acid*, PFA (*d* 1.19).

7.8 *Hydrochloric acid*, PFA, diluted 1 : 100.

7.9 *Hydrofluoric acid*, PFA (40 per cent).

7.10 *Ammonium nitro-molybdate solution.*

Prepare the following two solutions:

First solution. Dissolve 36 g of molybdic acid, PFA, in 35 ml of ammonia (*d* 0.91) and 50 ml of water.

Second solution. Pour carefully 115 ml of ammonia (*d* 0.91), stirring continually, into 575 ml of nitric acid, diluted 1 : 1, and add 230 ml of water.

Cool the two solutions and mix them, adding slowly the first solution to the second, and shaking vigorously to dissolve the white turbidity. Care should be taken to ensure that there is no rise in the temperature of the solution. Keep the ammonium nitro-molybdate solution in an open flask for 48 hours, after which it is ready for use. Filter the solution before using.

7.11 *Sodium nitrite* ($NaNO_2$), PFA, solution (50 g/l).

7.12 *Sodium carbonate*, PFA (anhydrous).

7.13 *Washing solution.* 10 ml of nitric acid (*d* 1.40) and 10 g of ammonium nitrate are dissolved in 1 litre of water.

7.14 *Phenolphthalein*, alcohol solution (5 g/l).

7.15 *Standard solution of nitric acid.* 50 ml of nitric acid (*d* 1.40) diluted with water to 10 litres; 1 ml of nitric acid solution corresponds approximately to 0.0001 g of phosphorus.

7.16 *Standard solution of sodium hydroxide.* Dissolve 33 g of sodium hydroxide, PFA, in 10 litres of cold water, which has been previously boiled. Add 5 or 6 ml barium hydroxide solution (10 g/l), and allow to stand for 48 hours. Decant transparent solution carefully through a siphon tube into another flask. After the solution is fully decanted, seal the flask with a bung, the hole of which is fitted with a soda-lime tube. 1 ml of sodium hydroxide solution corresponds approximately to 0.0001 g of phosphorus. Determine the titre of sodium hydroxide solution against the standard sample of ore.

7.17 *Potassium nitrate* (KNO_3), PFA, 2 per cent neutral solution.

8. STANDARDIZATION OF SODIUM HYDROXIDE SOLUTION

8.1 Against standard sample of ore

8.1.1 To determine the titre of the sodium hydroxide solution, take three test samples of the standard sample of manganese ore, having approximately the same phosphorus content as that of the sample being analysed, and pass them through all the stages of analysis.

8.1.2 The titre of the sodium hydroxide solution is found from the following formula:

$$T = \frac{A\ G}{(V - (V_1\ C)) \times 100}$$

where T = titre of sodium hydroxide solution, expressed in grammes of phosphorus;

A = phosphorus content in the standard sample of ore, per cent;

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

V = number of millilitres of sodium hydroxide used in dissolving the ammonium phospho-molybdate precipitate;

V_1 = number of millilitres of nitric acid used for titrating the excess of sodium hydroxide;

C = correlation between standard solutions of sodium hydroxide and nitric acid.

9. PROCEDURE

9.1 Weigh 1 to 2 g of manganese ore into a 300 ml beaker, and dissolve in 40 ml of acid mixture made up as follows: 3 parts of hydrochloric acid (*d* 1.19) and 1 part of nitric acid (*d* 1.40). After the sample has been dissolved, evaporate the solution until dry. Moisten the residue with 5 ml of hydrochloric acid (*d* 1.19), then add 0.5 to 1 g of ammonium bromide, and again evaporate the solution until dry, to remove arsenic. Repeat this operation twice, after which keep the dry residue at 120 to 130 °C for 40 to 60 min.

9.2 Add 20 ml of hydrochloric acid (*d* 1.19) to the residue, and heat for 2 to 3 min until the salts are dissolved. Add 40 to 50 ml of hot water, heat to boiling, and filter off the insoluble residue. Wash the residue on the filter with hydrochloric acid, diluted 1 : 100, 3 or 4 times, and then wash with hot water, 6 to 8 times. Evaporate the filtrate to 50 to 70 ml.

9.3 Place the filter and the residue in a platinum crucible, and ignite. Moisten the residue with water; add 2 ml of nitric acid (*d* 1.40) and 4 to 6 ml of hydrofluoric acid, and evaporate until dry. Repeat twice the procedure of adding nitric acid and evaporating. Gently ignite the residue, add 1 g of anhydrous sodium carbonate, and fuse the whole at 900 to 1000 °C.

9.4 Extract the fusion in 50 to 60 ml of hot water, and wash the crucible with water. Boil the solution for 5 to 10 min, and then filter; wash the filter with water, and add the filtrate to the original solution.

9.5 Evaporate the combined solutions until crystallization of salts begins. Add 10 to 15 ml of nitric acid (*d* 1.40) to the solution, and evaporate to syrupy condition. Repeat the evaporation with 10 to 15 ml of nitric acid (*d* 1.40), add 10 ml of nitric acid (*d* 1.40), and dilute with 40 to 50 ml of water. If the manganese dioxide precipitates, dissolve it by adding 2 or 3 drops of sodium nitrite solution (50 g/l) to the boiling solution. Boil the solution until the nitric oxides are completely dispelled, cool, and neutralize with ammonium hydroxide until the hydroxides precipitate. Dissolve the precipitate with a few drops of nitric acid (*d* 1.40), adding an excess of 1 or 2 ml of the acid.