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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 322

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF COPPER

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BRIEF HISTORY

The ISO Recommendation R 322, *Methods of Chemical Analysis of Manganese Ores—Determination of Copper*, 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.

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. 255) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

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

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 July 1963, to accept it as an ISO RECOMMENDATION.

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METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF COPPER

(Atomic mass Cu : 63.54; molecular mass CuO : 79.54)

This ISO Recommendation contains three parts:

- I. Introduction section 1,
- II. Gravimetric method of copper determination in the form of salicylaldoxime complex, for copper content exceeding 0.05 per cent sections 2 to 5,
- III. Colorimetric method with diethyl-dithiocarbamate, for copper content below 0.05 per cent sections 6 to 9.

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

Calculate the content of copper in ore which is absolutely dry, by multiplying the numerical results of the determination of copper 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 copper 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 copper 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 copper content), shown in the tables under clauses 5.2 and 9.2, "Accuracy of method".

The average result of the simultaneous check analysis of the standard sample of manganese ore for copper content should not differ from the result shown in the certificate by more than the $\pm$ value of the permissible tolerance (for the corresponding interval of copper content), shown in the tables under clauses 5.2 and 9.2, "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:

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

II. GRAVIMETRIC METHOD OF COPPER DETERMINATION IN THE FORM OF SALICYLALDOXIME COMPLEX FOR COPPER CONTENT EXCEEDING 0.05 PER CENT

2. PRINCIPLE OF METHOD

The method is based on the formation by copper ions of insoluble salicylaldoxime complex in acetate medium with pH 5-6. Copper is separated from all accompanying interfering elements (manganese and others) by precipitation with sodium thiosulphate solution.

3. REAGENTS REQUIRED

- 3.1 *Ammonium hydroxide*, PFA, solution (*d* 0.91).
- 3.2 *Nitric acid*, PFA (*d* 1.40).
- 3.3 *Sulphuric acid*, PFA (*d* 1.84).
- 3.4 *Sulphuric acid*, PFA, diluted 1:1.
- 3.5 *Sulphuric acid*, PFA, diluted 1:9.
- 3.6 *Hydrochloric acid*, PFA (*d* 1.19).
- 3.7 *Hydrofluoric acid*, PFA, 40 per cent.
- 3.8 *Tartaric acid*, PFA, solution (100 g/l).
- 3.9 *Acetic acid*, PFA, 98 per cent.
- 3.10 *Potassium pyrosulphate*, PFA.
- 3.11 *Methyl red indicator*, alcoholic solution (1 g/l).
- 3.12 *Sodium thiosulphate* ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), CP, solution (300 g/l).
- 3.13 *Salicylaldoxime*, PFA, alcoholic solution (10 g/l).
- 3.14 *Ethyl alcohol* (95°).
- 3.15 *Standard copper solution*. Dissolve 0.1000 g of metallic copper, PFA, in 10 ml of nitric acid, diluted 1:1, add 10 ml of sulphuric acid, diluted 1:1, and evaporate the solution until fumes of sulphur trioxide appear. Transfer the solution obtained to a 1 litre graduated flask; dilute with water up to the mark, and mix; 1 ml of the solution contains 0.0001 g of copper.

4. PROCEDURE

- 4.1 Weigh 2 g of manganese ore into a beaker of 500 ml capacity, and dissolve, while heating, in 25 ml of hydrochloric acid (*d* 1.19). When solution is complete, add 20 ml of sulphuric acid, diluted 1:1, and evaporate until fumes of sulphur trioxide appear. Cool the solution,

and dissolve the salts in 50 ml of water, filter, and wash the residue on the filter with hot water. Place the filter with the residue in a platinum crucible, ignite at a temperature of 500 to 600 °C. Cool and moisten the residue with a few drops of water, add 1 or 2 drops of sulphuric acid (*d* 1.84) and 5 to 6 ml of hydrofluoric acid, and evaporate until dry. Fuse the residue with 1 g of potassium pyrosulphate, place the fusion in a beaker of 150 ml capacity, extract in 40 to 50 ml of sulphuric acid, diluted 1:9, and add to the original solution. Dilute the solution with water to 350 ml, heat to boiling, and precipitate the copper with 25 to 30 ml of sodium thiosulphate solution (300 g/l), boiling continuously until the solution becomes quite clear (for 15 to 20 min); then filter it through a medium filter.

- 4.2 Wash the residue on the filter 8 to 10 times with warm water, place it in a porcelain crucible, and ignite at a temperature of 500 to 600 °C. Then, while heating, dissolve the residue in the crucible in 3 to 5 ml of nitric acid (*d* 1.40).

Transfer the solution into a 300 ml beaker, add 35 to 40 ml of ammonium hydroxide (*d* 0.91), filter off the trace amount of precipitated hydroxides, wash 8 to 10 times with hot water, and discard.

Add to the filtrate 2 to 3 ml of tartaric acid solution (100 g/l), 3 or 4 drops of methyl red indicator (1 g/l) and then acetic acid (98 per cent) until the colour changes. Cool the solution, add 50 ml of salicylaldoxime alcoholic solution (10 g/l), mix, and allow to stand for 5 to 6 hours. Filter the precipitate into a weighed crucible-filter, and wash 12 to 15 times with water and once or twice with alcohol. Dry the crucible-filter with the precipitate at a temperature of 110 to 120 °C to constant weight, cool in a desiccator, and weigh.

5. EXPRESSION OF RESULTS

5.1 Method of calculation

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

$$\text{Cu} = \frac{A \times 0.1894 \times 100}{G} \text{ per cent}$$

where

A = mass of dried precipitate of salicylaldoxime of copper, in grammes;

0.1894 = conversion factor for salicylaldoxime of copper to copper;

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:

Copper content		Permissible tolerance (in absolute value)
from	to	
0.05 per cent	0.10 per cent	± 0.005 per cent
(over) 0.10 per cent	0.20 per cent	± 0.0075 per cent
„ 0.20 per cent	0.30 per cent	± 0.010 per cent
„ 0.30 per cent	0.40 per cent	± 0.012 per cent
„ 0.40 per cent	0.50 per cent	± 0.015 per cent
„ 0.50 per cent		± 0.020 per cent

III. COLORIMETRIC METHOD WITH DIETHYL-DITHIOCARBAMATE FOR COPPER CONTENT BELOW 0.05 PER CENT

6. PRINCIPLE OF METHOD

The method is based on the formation of a yellow complex of copper and diethyl-dithiocarbamate, at pH 9. Copper is separated from all the accompanying interfering elements, mostly manganese, with sodium thiosulphate or with hydrogen sulphide in a weak acid solution. The yellow complex of copper diethyl-dithiocarbamate is extracted with carbon tetrachloride, after which the colorimetric determination is carried out.

7. REAGENTS REQUIRED

- 7.1 *Ammonium hydroxide*, PFA (*d* 0.91).
- 7.2 *Sodium diethyl-dithiocarbamate*, PFA, solution (1 g/l).
- 7.3 *Hydrochloric acid*, PFA, distilled (*d* 1.16).
- 7.4 *Hydrochloric acid*, PFA, distilled, diluted 1:20.
- 7.5 *Nitric acid*, PFA distilled (*d* 1.35).
- 7.6 *Nitric acid*, PFA, distilled, diluted 1:1.
- 7.7 *Sulphuric acid*, PFA, diluted 1:1.
- 7.8 *Sulphuric acid*, PFA (*d* 1.84).
- 7.9 *Hydrofluoric acid*, PFA (40 per cent).
- 7.10 *Sodium thiosulphate* ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), CP, solution (300 g/l).
- 7.11 *Potassium pyrosulphate*, PFA.
- 7.12 *Sodium citrate*, PFA, solution (100 g/l).
- 7.13 *Standard solution of copper*. Dissolve by heating 0.1 g of metallic copper, PFA, in 10 ml of nitric acid, diluted 1:1, add 10 ml of sulphuric acid, diluted 1:1, and evaporate the solution until sulphur trioxide fumes appear. After cooling, dissolve the salts in water. Transfer the solution obtained to a measuring flask of 1 litre capacity, dilute with water up to the mark, and mix thoroughly. 1 ml of the solution contains 0.0001 g of copper.
- 7.14 *Mercuric chloride* (HgCl_2), PFA, solution (50 g/l).
- 7.15 *Phenolphthalein*, PFA, alcoholic solution (1 g/l).
- 7.16 *Carbon tetrachloride*, PFA, distilled.
- 7.17 Use cationed water for the preparation of the solutions of the reagents and for the analysis.