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METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES
DETERMINATION OF ARSENIC

1st EDITION
July 1963

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BRIEF HISTORY

The ISO Recommendation R 317, *Methods of Chemical Analysis of Manganese Ores—Determination of Arsenic*, 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. 250) 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
India
Ireland
Italy
Japan
Netherlands
Poland
Portugal
Republic of South Africa
Romania
Spain
United Kingdom
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.

ISO Recommendation R 317 July 1963

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

DETERMINATION OF ARSENIC

(Atomic mass As: 74.91)

This ISO Recommendation contains two 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 arsenic, take three more test samples for the determination of hygroscopic moisture.

Calculate the content of arsenic in ore which is absolutely dry by multiplying the numerical results of the determination of arsenic 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 arsenic 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 arsenic 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 arsenic content), shown in the table under clause 5.2, " Accuracy of method ".

The average result of the simultaneous check analysis of the standard sample of manganese ore for arsenic 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 arsenic content), shown in the table under clause 5.2, " 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.

The following symbols and abbreviations are used:

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

II. COLORIMETRIC METHOD OF ARSENIC DETERMINATION IN THE FORM OF A BLUE ARSENO-MOLYBDATE COMPLEX

2. PRINCIPLE OF METHOD

The method is based on the separation of arsenic from the accompanying elements by distilling it off from a hydrochloric solution in the presence of the reducers, hydrazine sulphate and potassium bromide. The reduced arsenic is oxidized with nitric acid until it becomes pentavalent; the pentavalent arsenic and molybdic acid form a yellow arseno-molybdate complex. The complex is reduced with hydrazine, which results in the formation of a blue arseno-molybdate complex; the latter is analysed by the colorimetric method.

3. REAGENTS REQUIRED

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

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, 5 N.

3.6 *Potassium bromide* (KBr), PFA.

3.7 *Molybdate-hydrazine solution.* This is prepared from the following two solutions:

A. 1 g of ammonium molybdate, PFA, is dissolved in 100 ml of 5 N sulphuric acid, and
B. 0.15 g of hydrazine sulphate, PFA, is dissolved in 100 ml of water.

For the preparation of the working solution, take 10 ml of the solution *A*, dilute it with water to 90 ml, add 1 ml of the solution *B* and dilute with water to 100 ml. The working solution should be prepared before starting the analysis.

3.8 *Acid mixture* : 3 volumes of hydrochloric acid (*d* 1.19) and 1 volume of nitric acid (*d* 1.40).

3.9 *Standard solution of arsenic A.* Dissolve 0.132 g of arsenic trioxide (As_2O_3), PFA, in 5 ml of a 5 per cent solution of caustic soda, add 30 ml of water, slightly acidify with hydrochloric acid, transfer to a 100 ml measuring flask and add water until it reaches the mark. 1 ml of the solution contains 1 mg of arsenic.

Standard solution of arsenic B. Measure off with a microburette 1 ml of the solution *A* into a 100 ml measuring flask, and add water until it reaches the mark. 1 ml of the solution contains 0.01 mg of arsenic.

4. PROCEDURE

4.1 Weigh 0.1 to 1 g of manganese ore into a porcelain dish of 9 cm diameter and dissolve it in 10 ml of the acid mixture and 10 ml of sulphuric acid, diluted 1 : 1.

When the decomposition of ore is complete, evaporate the solution until sulphur trioxide fumes appear. Cool the solution, wash the sides of the dish with a small quantity of water, and evaporate again until sulphur trioxide fumes appear.

4.2 Cool the contents of the dish, carefully add 15 ml hydrochloric acid (*d* 1.19) and transfer the solution obtained into a 150 ml distilling flask (see Figure, page 8). Wash off the salts remaining on the sides of the dish with 10 to 15 ml of water, introduce into the flask 0.5 g of hydrazine sulphate and 0.5 g of potassium bromide, and distil over the arsenic in the form of arsenic trichloride, by distilling off $^2/_3$ of the original volume of the solution.

4.3 Collect the distillate in a 100 ml receiver-flask, which contains 10 ml of water. Add 10 ml of nitric acid (*d* 1.40) to the distillate and evaporate to dryness. Heat the dry residue at 120 to 130 °C for 40 to 60 min; cool, add 20 ml of molybdate-hydrazine solution, and heat in a water bath at 90 to 95 °C for 15 to 20 min. Cool the solution, and transfer to a 100 ml receiver-flask. Wash the sides of the flask with the molybdate-hydrazine solution, and dilute with the same solution up to the mark, mix, and carry out the colorimetric determination, using a red light-filter (wavelength 600 to 710 nm).

4.4 The percentage of arsenic is determined by the calibration method or by the comparison method from the optical density of the solution being tested.

(a) Calibration curve method

To construct the calibration curve, take corresponding volumes of the standard solution of arsenic, covering both the extreme limits (maximum and minimum) and the intermediate degrees of arsenic concentration in the given type of ore, and take them through all the stages of the analysis simultaneously with the sample being analysed.

The percentage of arsenic in the sample being analysed is determined, from the calibration curve, on the basis of the optical density of the solution.

(b) Comparison method

Take a known volume of the standard solution of arsenic of a concentration approaching that of the sample being analysed, and pass it through all the stages of the analysis simultaneously with the sample.

NOTES

1. If the ore being analysed is not completely attacked in the acid mixture, add 0.5 of sodium fluoride.

2. Depending on the percentage of arsenic, the mass of the test sample should be determined as follows:

Arsenic content from (over)	Arsenic content to	Test sample of ore
per cent	per cent	Grammes
	0.02	1
0.02	0.05	0.5
0.05	0.10	0.2
0.10		0.1