

# ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

## ISO RECOMMENDATION R 323

METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES  
DETERMINATION OF LEAD

1st EDITION

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## BRIEF HISTORY

The ISO Recommendation R 323, *Methods of Chemical Analysis of Manganese Ores—Determination of Lead*, 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. 256) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

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

Two Member Bodies opposed the approval of the Draft:

France, 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.

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## METHODS OF CHEMICAL ANALYSIS OF MANGANESE ORES

## DETERMINATION OF LEAD

(Atomic mass Pb : 207.21; molecular mass PbO : 223.21)

This ISO Recommendation contains three parts:

- |  |                   |
|--|-------------------|
| I. Introduction . . . . .  | section 1,        |
| II. Gravimetric method of lead determination in the form of lead molybdate, for lead content over 0.1 per cent . . . . . | sections 2 to 5,  |
| III. Volumetric cerium method (ceric sulphate standardization), for lead content below 0.1 per cent . . . . .            | sections 6 to 10. |

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

Calculate the content of lead in ore which is absolutely dry by multiplying the numerical results of the determination of lead 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 lead 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 lead 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 lead 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 lead 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 lead content), shown in the tables under clauses 5.2 and 10.2, "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  $\pm 0.0002$  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
<b>g</b>	gramme
<b>g/l</b>	grammes per litre
<b>mg</b>	milligramme
<b>ml</b>	millilitre
<b>mm</b>	millimetre
<b>PFA</b>	pure for analysis

**II. GRAVIMETRIC METHOD OF LEAD DETERMINATION  
IN THE FORM OF LEAD MOLYBDATE  
FOR LEAD CONTENT OVER 0.1 PER CENT**

**2. PRINCIPLE OF METHOD**

The method consists in the separation of lead from the accompanying elements in the form of lead sulphide, the solution of the latter in ammonium acetate, and the subsequent precipitation of the lead with ammonium molybdate.

**3. REAGENTS REQUIRED**

- 3.1 *Ammonium nitrate*, PFA, solution (20 g/l).
- 3.2 *Ammonium acetate*, PFA, solution (300 g/l).
- 3.3 *Ammonium chloride*, PFA, solution (150 g/l).
- 3.4 *Ammonium molybdate*, PFA, solution (50 g/l).
- 3.5 *Ammonium hydroxide*, PFA (*d* 0.91).
- 3.6 *Ammonium sulphate*, PFA, solution (100 g/l).
- 3.7 *Ferrous sulphide* (FeS), PFA (to obtain hydrogen sulphide).
- 3.8 *Nitric acid*, PFA (*d* 1.40).
- 3.9 *Sulphuric acid*, PFA (*d* 1.84).
- 3.10 *Sulphuric acid*, PFA, diluted 1 : 50.
- 3.11 *Hydrochloric acid*, PFA (*d* 1.19).
- 3.12 *Hydrochloric acid*, PFA, diluted 1 : 1.
- 3.13 *Citric acid*, PFA, solution (200 g/l).
- 3.14 *Copper sulphate*, PFA, solution (10 g/l).
- 3.15 *Sodium chloride*, PFA, solution (150 g/l).
- 3.16 *Sodium sulphide* (Na<sub>2</sub>S), PFA, solution (50 g/l).
- 3.17 *Hydrogen peroxide*, PFA, 30 per cent (perhydrol).
- 3.18 *Ethyl alcohol*, PFA.

**4. PROCEDURE**

- 4.1 Weigh 5 g of manganese ore into a 300 ml beaker, and digest by heating in 30 ml of hydrochloric acid (*d* 1.19). Add, drop by drop, 3 to 5 ml of nitric acid (*d* 1.40), boil for 5 min, and evaporate until dry. Add 15 ml of hydrochloric acid (*d* 1.19) to the dry residue, and again evaporate until dry. Add to the residue 20 ml of hydrochloric acid (*d* 1.19), heat for 2 to 3 min, add 40 to 50 ml of hot water, 10 ml of ammonium acetate solution (300 g/l) and 5 ml of citric acid solution (200 g/l), heat to boiling, and boil for 5 min.
- 4.2 Filter the insoluble residue, and wash 6 to 8 times with hot water.\* Add ammonium hydroxide (*d* 0.91) to the filtrate until precipitation of the hydroxides occurs. Carefully dissolve the

\*The residue may be used for determination of silicon dioxide content.

precipitate in hydrochloric acid, diluted 1 : 1, using not more than 3 to 4 ml excess, add 1 ml of copper sulphate solution (10 g/l), heat to boiling, pass hydrogen sulphide for a period of 20 min, dilute with water to 350 to 400 ml, and again pass hydrogen sulphide for a period of 20 min.

Let stand for 10 to 12 hours, then filter on a close filter containing a small quantity of paper pulp; wash 5 or 6 times with water saturated with hydrogen sulphide, until removal of iron ions is complete. Discard the filtrate.

**4.3** To remove arsenic and antimony, wash the precipitate with sodium sulphide solution (50 g/l).

Place the filter with residue in the beaker in which the precipitation took place, dissolve it in 15 to 20 ml of acid mixture (2 parts of sulphuric acid ( $d$  1.84), and 1 part of nitric acid ( $d$  1.40)), loosen the filter with a glass rod, and evaporate until fumes of sulphur trioxide appear. The contents of the beaker should be colourless. Cool the beaker, add 200 ml of cold water and 10 to 15 ml of ammonium sulphate solution (100 g/l), heat to boiling, cool, add 40 to 50 ml of ethyl alcohol, and stir; settle the precipitate for 10 to 12 hours, filter off on a close filter containing a small quantity of paper pulp; wash with sulphuric acid, diluted 1 : 50, and discard the filtrate.

Place the filter with the residue in the beaker in which the precipitation of lead sulphate took place, add 25 to 30 ml of ammonium acetate solution (300 g/l), loosen the filter with a glass rod, heat to boiling, and boil for 10 to 15 min.

Filter the hot solution through a close filter, wash the sides of the beaker 2 or 3 times and the residue on the filter 4 or 5 times with hot water, and discard the filter and residue. Add to the filtrate 25 ml of sodium chloride solution (150 g/l), heat to boiling point, add slowly, and while stirring, 15 to 20 ml of ammonium molybdate solution (50 g/l), and boil for 15 to 20 min.

Allow the residue to settle on a hot plate for 2 hours, then filter it off on a close filter, and wash 8 to 10 times with a hot solution of ammonium nitrate (20 g/l).

Place the filter with the residue in a weighed porcelain crucible, ignite carefully at a temperature of 450 to 550 °C, cool, and weigh.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation

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

$$\text{Pb} = \frac{A \times 0.5644 \times 100}{G} \text{ per cent}$$

where  $A$  = mass of lead molybdate residue, in grammes;

0.5644 = conversion factor for lead molybdate to lead oxide;

$G$  = 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:

Lead content		Permissible tolerance (in absolute value)
from (over)	to	
	0.30 per cent	± 0.010 per cent
0.30 per cent	0.50 per cent	± 0.020 per cent

**III. VOLUMETRIC CERIUM METHOD  
(CERIC SULPHATE STANDARDIZATION)  
FOR LEAD CONTENT BELOW 0.1 PER CENT**

**6. PRINCIPLE OF METHOD**

- 6.1 This method is based on the separation of lead from barium and other elements, using ammonium hydroxide in the presence of ammonium salts to form a number of hydroxides.
- 6.2 The lead is precipitated in the form of a sulphate, strontium being used as a collector. The sulphates are changed into carbonates and the lead is precipitated in the form of a chromate in an acetate medium.
- 6.3 The chromate is reduced with a solution of ferrous ammonium sulphate, the surplus of the latter being titrated with a solution of ceric sulphate in the presence of methyl-orange indicator.

**7. REAGENTS REQUIRED**

- 7.1 *Ammonium hydroxide*, PFA, solution ( $d$  0.91).
- 7.2 *Ammonium nitrate*, PFA, solution (500 g/l).
- 7.3 *Ammonium nitrate*, PFA, solution (10 g/l).
- 7.4 *Ferrous ammonium sulphate* ( $\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), PFA, 0.005 N solution.
- 7.5 *Ferric nitrate* ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), PFA, solution (15 g/l).
- 7.6 *Nitric acid*, PFA ( $d$  1.40).
- 7.7 *Nitric acid*, PFA, diluted 1 : 2.
- 7.8 *Hydrochloric acid*, PFA, distilled, diluted 1 : 1.
- 7.9 *Sulphuric acid*, PFA, diluted 1 : 3.
- 7.10 *Sulphuric acid*, PFA, diluted 1 : 100.
- 7.11 *Hydrofluoric acid*, PFA (40 per cent).
- 7.12 *Potassium nitrate* ( $\text{KNO}_3$ ), PFA.
- 7.13 *Acetic acid*, PFA (80 per cent).
- 7.14 *Potassium dichromate*, PFA, solution (50 g/l).
- 7.15 *Methyl-orange indicator*, PFA, solution (0.1 g/l).
- 7.16 *Sodium nitrite* ( $\text{NaNO}_2$ ), PFA, solution (50 g/l).
- 7.17 *Sodium carbonate*, PFA, anhydrous.