
International Standard



317

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Manganese ores and concentrates — Determination of arsenic content — Spectrometric method

Minerais et concentrés de manganèse — Dosage de l'arsenic — Méthode spectrométrique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 317 was developed by Technical Committee ISO/TC 65, *Manganese and chromium ores*, and was circulated to the member bodies in February 1983.

It has been approved by the member bodies of the following countries:

Australia	France	Poland
Austria	Germany, F.R.	Romania
Brazil	India	South Africa, Rep. of
Bulgaria	Italy	Thailand
China	Japan	United Kingdom
Czechoslovakia	Mexico	USSR

No member body expressed disapproval of the document.

This International Standard cancels and replaces ISO Recommendation R 317-1963, of which it constitutes a technical revision.

Manganese ores and concentrates — Determination of arsenic content — Spectrometric method

1 Scope and field of application

This International Standard specifies a spectrometric method for the determination of the arsenic content of manganese ores and concentrates.

The method is applicable to products having an arsenic content of 0,001 to 0,2 % (*m/m*).

This International Standard should be read in conjunction with ISO 4297.

2 References

ISO 4296/1, *Manganese ores — Sampling — Part 1: Increment sampling*.

ISO 4296/2, *Manganese ores — Sampling — Part 2: Preparation of samples*.

ISO 4297, *Manganese ores and concentrates — Methods of chemical analysis — General instructions*.

3 Principle

Decomposition of a test portion by treatment with hydrochloric, nitric and sulfuric acids and double evaporation to fumes of sulfuric acid. Reduction of As(V) by hydrazine sulfate to As(III). Distillation of the As(III) in the presence of potassium bromide and hydrochloric acid.

Evaporation of the distillate with nitric acid to dryness, the dry residue being heated at 120 to 130 °C for 40 to 60 min.

Addition of ammonium molybdate solution in 3 mol/l perchloric acid and ascorbic acid to the dry residue. Spectrometric determination.

4 Reactions

The method is based on the formation of a coloured heteropolyacid by As(V) followed by its reduction to a blue

arsenomolybdate complex with ascorbic acid in 2,5 to 4 mol/l perchloric acid solution.

Arsenic previously reduced to oxidation state III is separated from the accompanying elements by distillation from 6 to 9 mol/l hydrochloric acid. Then the As(III) is oxidized to As(V) with nitric acid.

5 Reagents

5.1 Potassium bromide.

5.2 Hydrazine sulfate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{SO}_4$).

5.3 Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), 5 g/l solution.

The solution shall be freshly prepared.

5.4 Sulfuric acid (ρ 1,84 g/ml), diluted 1 + 1.

5.5 Hydrochloric acid (ρ 1,19 g/ml), diluted 1 + 3.

5.6 Nitric acid, ρ 1,42 g/ml.

5.7 Acid mixture, made up of 3 parts by volume hydrochloric acid (ρ 1,19 g/ml) and 1 part by volume nitric acid (5.6).

5.8 Perchloric acid, $c(\text{HClO}_4) = 3$ mol/l.

5.9 Ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$], solution.

Dissolve 8,1 g of ammonium molybdate in 250 ml of water while heating. Transfer 350 ml of perchloric acid (ρ 1,51 g/ml) into a beaker of capacity 1 000 ml containing 300 ml of water, and add gradually, while mixing, cooled ammonium molybdate solution. Transfer the solution to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

This solution remains stable for more than 2 months.

5.10 Arsenic, standard solution corresponding to 1 g of As per litre.

Dissolve 1,320 4 g of arsenic trioxide in 10 ml of sodium hydroxide 100 g/l solution, transfer to a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

1 ml of this standard solution contains 1 mg of As.

5.11 Arsenic, standard solution corresponding to 0,01 g of As per litre.

Pipette 10 ml of standard arsenic solution (5.10) into a one-mark volumetric flask of capacity 1 000 ml, dilute with water to the mark and mix.

This solution should be freshly prepared.

1 ml of this standard solution contains 0,01 mg of As.

6 Apparatus

Usual laboratory apparatus and

6.1 Apparatus for distillation of arsenic (see the figure).

NOTES

1 Prior to first use the distillation apparatus and receiver beaker shall be cleaned with chromic acid cleaning mixture and rinsed well with water to ensure that all internal surfaces are film wettable. This condition shall be maintained as necessary. Ground glass joints shall be cleaned to remove organic lubricants and then lubricated with the minimum quantity of sulfuric acid (ρ 1,84 g/ml).

2 Apparatus used after the distillation stage (the receiver beaker and, where applicable, pipettes and volumetric flasks) should be given the following special cleaning treatment.

Prior to first use, chromic acid treatment shall be followed by rinsing with water, then treatment with nitric acid (5.6) diluted 1 + 10. Allow the nitric acid solution to stand in the vessel for several hours.

Such vessels shall be reserved for arsenic determinations and labelled accordingly. In routine use, the standing time in dilute nitric acid can be reduced to 30 min.

3 Detergents which may contribute to interferences from phosphates shall not be used in this procedure.

6.2 Spectrometer with selectors for continuous variation suitable for measuring absorbance at 840 nm or for discontinuous variation suitable for measuring absorbance at 630 to 700 nm.

7 Sample

For the sampling of manganese ores, see ISO 4296/1. For the preparation of samples, see ISO 4296/2.

Use a test sample which has been crushed to a size not exceeding 100 μm (checked on a sieve of appropriate aperture size) and air dried under laboratory conditions.

8 Procedure

8.1 Test portion

Weigh a mass of the test sample chosen from table 1 in accordance with the expected arsenic content.

8.2 Blank test

Carry out a blank test through all stages of the analysis.

8.3 Decomposition of test portion

Place the test portion (8.1) in a wide-necked flask of capacity 100 to 120 ml, moisten with a few drops of water and dissolve in 10 ml of the acid mixture (5.7) and 10 ml of sulfuric acid (5.4), to decompose the ore.

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

NOTE — To avoid loss of arsenic(V) chloride, the time allowed for fuming of the sulfuric acid should be kept to a minimum.

8.4 Distillation of arsenic

Cool the contents of the flask and transfer the solution into a 100 to 120 ml distillation flask containing 50 to 60 ml of hydrochloric acid (5.5). Add 0,5 g of hydrazine sulfate (5.2) and 0,5 g of potassium bromide (5.1). Heat the solution in the flask to boiling and distil the arsenic in the form of arsenic trichloride at about 108 °C until two-thirds of the original volume of the solution are distilled over. Collect the distillate in a beaker of capacity 100 ml containing 10 ml of nitric acid (5.6). Place the receiver in a cold water-bath.

Table 1

Expected arsenic content % (m/m)	Mass of test portion g	Dilution ml	Aliquot ml	Arsenic content in the solution measured mg
$\geq 0,001$ to 0,005	1	—	—	$\geq 0,010$ to 0,050
$> 0,005$ to 0,01	0,5	—	—	$> 0,025$ to 0,050
$> 0,01$ to 0,05	0,5	100	20	$> 0,010$ to 0,050
$> 0,05$ to 0,1	0,2	100	20	$> 0,020$ to 0,040
$> 0,1$ to 0,2	0,2	100	10	$> 0,020$ to 0,040

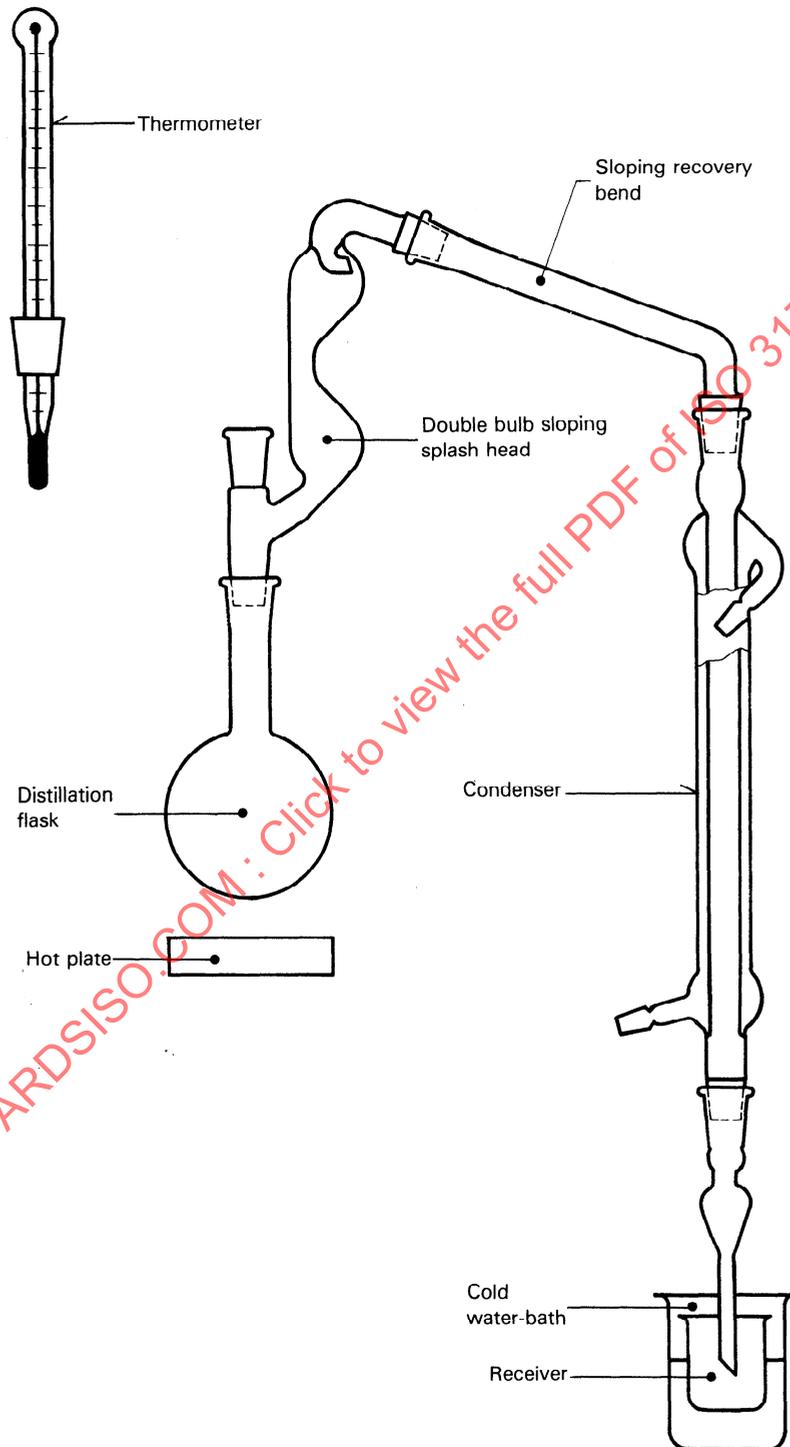


Figure — Apparatus for the distillation of arsenic

8.5 Preparation of the solution for spectrometric measurement

Heat the distillate and boil for about 5 min. Cool and transfer the distillate to a one-mark volumetric flask of capacity 100 ml, if necessary, and take the aliquot (see table 1). Add to the aliquot 5 ml of nitric acid (5.6).

Evaporate the distillate or the aliquot to dryness. Heat the dry residue at 120 to 130 °C for 40 to 60 min. Add to the dry residue 20 ml of ammonium molybdate solution (5.9), 1 ml of ascorbic acid solution (5.3), and mix and heat on a water-bath with boiling water for 10 to 15 min. Cool the solution and transfer to a one-mark volumetric flask of capacity 50 ml, wash the sides of the beaker with perchloric acid solution (5.8), dilute with the same solution to the mark and mix.

8.6 Spectrometric measurement

Measure the absorbance of the solution in a cell, using the spectrometer (6.2) at 840 nm or at 630 to 700 nm, against water as reference.

8.7 Preparation of comparison solution

Transfer a known volume of the standard arsenic solution (5.11) of a concentration approaching that of the test solution into three wide-neck conical flasks of capacity 100 ml, add 10 ml of acid mixture (5.7), 10 ml of sulfuric acid (5.4) and treat the solutions obtained as described in 8.3 to 8.6.

9 Expression of results

9.1 Calculation

Convert the net absorbance reading for the test solution (obtained by subtracting the absorbance reading of the blank test solution from that of the test solution), to arsenic content by means of the comparison method (8.7).

The arsenic (As) content, expressed as a percentage by mass, is given by the formula

$$\frac{A_1 m_1 \times 100}{A_2 m_0 \times 1\,000} \times K = \frac{A_1 m_1}{A_2 m_0 \times 10} \times K$$

where

A_1 is the absorbance value for the test solution after deducting the absorbance value for the blank solution;

A_2 is the mean absorbance value for three standard comparison solutions after deducting the absorbance value for the blank solution;

m_0 is the mass, in grams, of the test portion, corresponding to the test solution or to the aliquot portion;

m_1 is the mass, in milligrams, of arsenic in the standard comparison solution;

K is the conversion factor for the expression of the arsenic content on the dry basis.

9.2 Permissible tolerances on results of parallel determinations

Table 2

Values as percentages by mass

Arsenic content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
> 0,001 to 0,002 5	0,001 5	0,001
> 0,002 5 to 0,005	0,002 5	0,002
> 0,005 to 0,01	0,004	0,003
> 0,01 to 0,02	0,006	0,005
> 0,02 to 0,05	0,008	0,007
> 0,05 to 0,10	0,015	0,01
> 0,10 to 0,20	0,025	0,02