International Standard ISO 4293

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Manganese ores and concentrates — Determination of phosphorus content — Extraction-molybdovanadate photometric method

Minerais et concentrés de manganèse — Dosage du phosphore — Méthode photométrique au molybdovanadate avec extraction

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Foreword

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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.

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

Austria
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France
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Germany, F.R.

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Manganese ores and concentrates — Determination of phosphorus content — Extraction-molybdovanadate photometric method

1 Scope and field of application

This International Standard specifies an extractionmolybdovanadate photometric method for the determination of the phosphorus content of manganese ores and concentrates.

The method is applicable to products having phosphorus contents from 0,02 to 0,5 % (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.*[1]

ISO 4296/2, *Manganese ores — Sampling — Part 2 : Preparation of samples.*[1]

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

3 Principle

Decomposition of a test portion by treatment with hydrochloric and nitric acids. Separation of silicon by evaporation to fumes of perchloric acid. Dissolution of the salts in water, separation of the insoluble residue by filtration, the filtrate being reserved as the main solution.

Ignition of the filter with the residue and treatment with sulphuric and hydrofluoric acids. Fusion of the ignited residue with sodium carbonate. Dissolution of the melt in hydrochloric acid and combination of the solution obtained with the main solution. Evaporation of the solution to fumes of perchloric acid. Conversion of the phosphorus to phosphovanadomolybdate complex.

Elimination of the interference by iron and arsenic by addition of citric acid. Extraction of the phosphovanadomolybdate into *iso*butyl methyl ketone with citric acid present to complex arsenic and iron.

Photometric measurement using a spectrophotometer or a photoelectric absorptiometer.

4 Reagents

4.1 Sodium carbonate, anhydrous.

4.2 Hydrochloric acid, ϱ 1,19 g/ml.

4.3 Hydrochloric acid, diluted 1 + 1.

4.4 Hydrochloric acid, diluted 1 + 50.

4.5 Nitric acid, ϱ 1,40 g/ml.

4.6 Perchloric acid, ϱ 1,51 g/ml.

4.7 Sulphuric acid, diluted 1 + 1.

4.8 Hydrofluoric acid, ϱ 1,14 g/ml.

4.9 Ammonium vanadate (NH_4VO_3), 2,50 g/l solution.

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[1] At present at the stage of draft.

4.10 Ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], 150 g/l solution.

4.11 Citric acid [$C_3H_4(OH)(COOH)_3$], 500 g/l solution.

4.12 *Iso*butyl methyl ketone ($C_6H_{12}O$).

4.13 Phosphorus, standard solution, corresponding to 0,1 g of P per litre.

Place 0,439 4 g of potassium orthophosphate (KH_2PO_4) (high purity) previously dried at 105 °C for 1 to 2 h into a 1 000 ml one-mark volumetric flask, dissolve in 100 ml of water, dilute to the mark and mix.

1 ml of this standard solution contains 0,1 mg of P.

4.14 Phosphorus, standard solution corresponding to 0,05 g of P per litre.

Transfer 50 ml of the standard phosphorus solution (4.13) to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,05 mg of P.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrophotometer or **photoelectric absorptiometer.**

5.2 Platinum crucible.

6 Sample

For increment 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 size), and air-dried under laboratory conditions.

7 Procedure

7.1 Decomposition of test portion

Place 0,5 g of the test sample in a 300 ml beaker, add 25 ml of the hydrochloric acid (4.2), 5 ml of the nitric acid (4.5) and dissolve while heating. When solvent action ceases, add 10 ml of the perchloric acid (4.6) and evaporate to fuming. Cool, add 25 ml of water, and heat to boiling. Filter off the insoluble residue on a rapid filter paper containing a small quantity of paper pulp and receive the filtrate in a 300 to 500 ml conical flask. Wash the residue on the filter three or four times with the hydrochloric acid solution (4.4) and then several times with hot water. Reserve the filtrate as the main solution.

If the test material does not contain insoluble phosphates, discard the filter with the residue obtained.

7.2 Treatment of residue

Transfer the filter and residue to the platinum crucible (5.2), ash and ignite at 500 to 600 °C. Allow the crucible to cool, moisten the residue with 2 or 3 drops of water, add 2 or 3 drops of the sulphuric acid solution (4.7), 5 to 7 ml of the hydrofluoric acid (4.8) and evaporate to dryness. Ignite the dry residue at 500 to 600 °C, cool, add 1 or 2 g of the sodium carbonate (4.1) and fuse the residue at 900 to 1 000 °C for 15 to 20 min. Place the crucible with the melt in a 100 ml beaker, add 20 ml of the hydrochloric acid solution (4.3), and heat to dissolve the melt completely. Remove the crucible from the beaker and rinse it with water. Boil the solution obtained and combine it with the main solution (see 7.1).

7.3 Extraction of phosphovanadomolybdate complex

Evaporate the combined solution until white dense fumes of perchloric acid appear from the top of the flask, cool, add 25 ml of water, then 5 ml of the nitric acid (4.5), and boil for 5 min.

For phosphorus contents greater than 0,08 % (*m*/*m*), transfer the combined solution to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer a 20 ml aliquot into a 125 ml conical flask, add 9 ml of the perchloric acid (4.6) and evaporate to dense fumes of perchloric acid. After cooling the solution, add 25 ml of water, 5 ml of the nitric acid (4.5) and boil for 5 min.

Allow the solution to cool to ambient temperature, add 10 ml of the ammonium vanadate solution (4.9) and 15 ml of the ammonium molybdate solution (4.10), then allow to stand for 7 min for colour development of the complex.

If more than 0,5 % (*m*/*m*) titanium is present in the sample, complete colour development is obtained by increasing the standing time to 1 h.

Transfer the solution to a 100 ml separating funnel, add 10 ml of the citric acid solution (4.11), mix and immediately add 40 ml of the *iso*butyl methyl ketone (4.12) by means of a burette. Shake the funnel for 30 s.

Allow the two layers to separate and discard the lower (aqueous) layer. Dry the inside of the stem of the separating funnel with a small piece of filter paper. Filter off the organic layer through a dry rapid paper into a small dry beaker.

7.4 Photometric measurement

Measure the absorbance of the solutions using the spectrophotometer or the photo-electric absorptionmeter (5.1) at a wavelength 425 nm in a 10 mm cell, using the *iso*butyl metyl ketone as a reference solution.

7.5 Blank test

Carry out a blank test throughout the analysis.

7.6 Preparation of calibration graph

Weigh 0,25 g of metallic manganese of high purity into each of a series of seven 300 ml beakers, add 25 ml of the hydrochloric acid (4.2) and dissolve while heating. To the resultant solutions add, by means of a burette, 0 — 1,0 — 2,0 — 4,0 — 6,0 — 8,0 — 10,0 ml of the standard phosphorus solution (4.14), corresponding to 0 — 0,05 — 0,10 — 0,20 — 0,30 — 0,40 — 0,50 mg of phosphorus, respectively. Then add 5 ml of the nitric acid (4.5) and 10 ml of the perchloric acid (4.6) and evaporate to dense fumes of perchloric acid. After cooling the solution, add 25 ml of water, 5 ml of the nitric acid (4.5) and boil for 5 min.

Allow the solution to cool to ambient temperature, add 10 ml of the ammonium vanadate solution (4.9), 15 ml of the ammonium molybdate solution (4.10) and allow to stand for 7 min for colour development of the complex. Continue in accordance with 7.3 from "Transfer the solution to a 100 ml separating funnel...".

Prepare a calibration graph by plotting the mean values of the absorbance against the known phosphorus contents, deducting the absorbance reading for the compensation solution.

8 Expression of results

8.1 Calculation

Convert the absorbance reading for the test solution to phosphorus content by means of the calibration graph (7.6), deducting the absorbance reading for the blank.

The phosphorus (P) content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 100}{m_0 \times 1\ 000} \times K$$

$$= \frac{m_1}{m_0 \times 10} \times K$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in milligrams, of phosphorus, obtained from the calibration graph;

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

8.2 Permissible tolerances on results of parallel determinations

Phosphorus content	Permissible tolerance	
	Three parallel determinations	Two parallel determinations
% (m/m)	% (m/m)	% (m/m)
From 0,02 to 0,05	0,010	0,008
From 0,05 to 0,10	0,015	0,013
From 0,10 to 0,15	0,020	0,017
From 0,15 to 0,25	0,025	0,020
From 0,25 to 0,50	0,040	0,035
From 0,50 to 1,0	0,050	0,040

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