International Standard 8556

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Aluminium ores — Determination of phosphorus content — Molybdenum blue spectrophotometric method

Minerais alumineux — Dosage du phosphore — Méthode spectrophotométrique au bleu de molybdène

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Foreword

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Aluminium ores — Determination of phosphorus content — Molybdenum blue spectrophotometric method

1 Scope and field of application

This International Standard specifies a molybdenum blue spectrophotometric method for the determination of phosphorus in aluminium ores and minerals.

The method is applicable to materials having phosphorus contents, expressed as diphosphorus pentoxide between 0,01 and 5 % (m/m).

The arsenic content of the sample does not affect the determination.

2 Reference

ISO 8558, *Aluminium ores — Preparation of predried test samples.*

3 Principle

Decomposition of a test portion, by either

a) treatment with a mixture of hydrochloric acid, nitric acid and sulfuric acid;

NOTE — This method is recommended for ores containing Gibbsite and/or Boehmite and when the residue from the dissolution of the test portion after silica volatilization is less than 1 % of the test portion.

or

b) sintering with sodium peroxide followed by a brief fusion. Dissolution of the melt with sulfuric acid.

NOTE — This method is recommended for ores containing Diaspore and when the residue from the dissolution of the test portion is greater than 1 % of the mass of the test portion.

Dehydration of silica, dissolution of salts, filtration and ignition of the impure silica. Removal of the silica by evaporation with hydrofluoric and sulfuric acids. Fusion with sodium carbonate and sodium tetraborate, dissolution with hydrochloric acid and combination with the main solution.

Addition of molybdate to convert the phosphate to molybdophosphate complex, and reduction to molybdenum blue with ascorbic acid. Spectrophotometric measurement of the absorbance of the molybdenum blue complex at approximately 710 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical reagent grade, and only distilled water or water of equivalent purity.

4.1 Sodium peroxide (Na_2O_2), powder.

NOTE — Sodium peroxide should be protected against humidity and should not be used once it has begun to agglomerate.

4.2 Sodium carbonate/sodium tetraborate flux.

Mix intimately 3 parts by mass of anhydrous sodium carbonate (Na_2CO_3) with 1 part by mass of anhydrous sodium tetraborate ($Na_2B_4O_7$).

4.3 Sulfuric acid, ϱ_{20} 1,84 g/ml, diluted 1 + 1.

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4.5 Hydrofluoric acid, 40 % (m/m) (ϱ_{20} 1,13 g/ml) or 48 % (m/m) (ϱ_{20} 1,18 g/ml).

4.6 Hydrobromic acid, 40 % (m/m) (ϱ_{20} 1,38 g/ml) or 47 % (m/m) (ϱ_{20} 1,48 g/ml).

4.7 Acid mixture

Measure into a 1 litre beaker 225 ml water and add cautiously, with mixing, 175 ml of sulfuric acid (4.3). Cool well and add 150 ml hydrochloric acid (ϱ_{20} 1,19 g/ml) and 50 ml of nitric acid (ϱ_{20} 1,41 g/ml).

Prepare this solution fresh for each series of tests, and discard any unused solution, flushing copiously with water.

4.8 Ascorbic acid ($C_6H_8O_6$), 2 g/l solution.

Prepare this solution fresh on the day of use.

4.9 Disodium disulfite ($Na_2S_2O_5$), 150 g/l solution.

Prepare this solution fresh on the day of use.

4.10 Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), 50 g/l solution.

4.11 Bismuth, solution.

Dissolve 4,25 g of bismuth sulfate $[Bi_2(SO_4)_3]$ (specification 90 %) or 2,80 g of bismuth oxycarbonate (90 % Bi_2O_3) in 280 ml of sulfuric acid (4.3) and heat until the salt is dissolved completely. Cool to room temperature, transfer to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this solution contains 2,5 mg of Bi_2O_3.

4.12 Phosphorus, standard solution corresponding to 0,02 g of P_2O_5 per litre.

Dry several hundred milligrams of potassium dihydrogen orthophosphate (KH_2PO_4) at 105 °C to constant mass and allow to cool in a desiccator.

Dissolve 0,192 g of dried salt in water, transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix. Transfer 25,0 ml of this solution to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,02 mg of P_2O_5.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Dishes, of inert material of sufficient size to take the required quantity of sample at a layer density of 5 mg/mm^2.

5.2 Oven, electrically heated, with a temperature-control device capable of maintaining a temperature of 105 ± 5 °C.

NOTE — The oven should be checked by placing the usual number of drying dishes in position in the oven and then measuring the temperature in the vicinity of each dish to ensure that the required temperature is maintained throughout the oven, not just in the neighbourhood of the controlling element.

5.3 Muffle furnace, adjustable from 480 °C to greater than 1 000 °C.

5.4 Zirconium crucibles, approximately 40 ml capacity, for sinter decomposition.

5.5 Platinum crucibles, for treatment of the residue in 7.5.3.

5.6 Desiccator, containing either fresh magnesium perchlorate or activated alumina as desiccant.

NOTES

1 Activated alumina should be activated by heating at 300 ± 10 °C overnight.

2 When discarding magnesium perchlorate, flush down the sink using copious quantities of water.

5.7 Spectrophotometer, suitable for measurement of absorbance in the region of 710 nm.

6 Sampling and samples

6.1 Samples

Laboratory samples shall be taken and ground to pass a 150 µm test sieve in accordance with the methods specified in the relevant standards.[1)]

6.2 Preparation of the test sample

Prepare the test sample by drying it in an oven, following the procedure specified in ISO 8558.

7 Procedure

7.1 Number of determinations

Carry out the analysis in duplicate and independently on one ore sample.

NOTE — The expression "independently" implies the change of the person carrying out the analysis. If the same person must carry out the analysis, the procedure should be carried out at a different time.

7.2 Test portion

Weigh, to the nearest 0,001 g, approximately 1 g of the test sample obtained in accordance with clause 6.

7.3 Blank test

In parallel with the decomposition of the test portion, prepare a blank solution according to the method of decomposition, but with the omission of the test portion. When the analysis is carried out on several samples at the same time, the blank value may be represented by one test provided that the procedure is the same and the reagents used are from the same bottles.

7.4 Check test

In each run, one analysis of a certified reference material of the same type of ore shall be carried out in parallel, and under the same conditions, with the analysis of one ore sample.

NOTE — The certified reference material should be of the same type as the sample to be analysed. Such certified reference material cannot, however, be considered as being of the same type if the properties of the sample to be analysed differ from those of the certified reference material to such an extent that the analytical procedure must be changed substantially.

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1) Where no International Standards exist, the relevant standards shall be the national standards. Two International Standards on this subject are currently in preparation : ISO 6137, *Aluminium ores — Method of sampling*, and ISO 6140, *Aluminium ores — Preparation of samples.*

7.5 Determination

7.5.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as specified in 7.5.1.1. If the decomposition is to be based on alkali sintering, proceed as specified in 7.5.1.2.

7.5.1.1 Acid attack

Transfer the test portion (7.2) to a 400 ml beaker. Moisten with water and add as a freshly prepared mixture, 60 ml of the acid mixture (4.7). Cover the beaker and heat at approximately 80 °C to decompose the sample (see note 1).

When the evolution of brown fumes ceases, carefully rinse the cover and wall of the beaker. Evaporate the uncovered solution to dense fumes of sulfuric acid. Replace the cover and heat strongly for 60 min on a hotplate set to produce in the solution a temperature of 210 ± 10 °C (see note 2).

NOTES

1 With samples of high iron content [> 15 % (*m/m*) Fe_2O_3], the initial heating should be conducted for an extended period.

2 Determine the temperature setting using a separate test beaker containing a partial immersion thermometer in a 10 mm depth of sulfuric acid (ϱ_{20} 1,84 g/ml).

7.5.1.2 Alkali sinter attack

CAUTION — Protective goggles must be used during the following attack.

Transfer the test portion (7.2) to a dry zirconium crucible (5.4), add 10 g of the sodium peroxide (4.1) and mix intimately with a dry metal spatula. Place in the muffle furnace (5.3), controlled at 480 to 500 °C, for 45 min. Remove the crucible and contents from the furnace and heat over a burner to melt the sinter (about 30 s). Continue heating the molten state, with swirling, for a total time of 2 min.

Allow the crucible to cool (a metal block can be used to expedite this process). If necessary, clean the base of the crucible by wiping with a damp filter paper. Then, place it, lying on its side, in a 400 ml beaker, cover, and add cautiously to the beaker 140 ml of the sulfuric acid (4.4). Add 20 ml of the sulfuric acid (4.3) and digest to leach the contents of the crucible. Remove the crucible when the contents are completely leached and rinse well into the solution in the beaker.

Carefully rinse the cover and wall of the beaker. Evaporate the uncovered solution to dense fumes of sulfuric acid. Replace the cover and heat strongly for 60 min on a hotplate set to produce in the solution a temperature of 210 ± 10 °C.

NOTE — Determine the temperature setting using a separate test beaker containing a partial immersion thermometer in a 10 mm depth of sulfuric acid (ϱ_{20} 1,84 g/ml).

7.5.2 Dissolution and filtration

Cool the solution from 7.5.1.1 or 7.5.1.2 to room temperature, cautiously add 130 ml of water and heat at 80 to 90 °C for at least 40 min with stirring to completely dissolve the salts. Filter while hot through a medium-texture filter paper, collecting the filtrate in a 250 ml one-mark volumetric flask. Rinse the beaker with water and, using a rubber tipped glass rod, clean the beaker and transfer the residue quantitatively to the paper. Wash the paper and residue five times with 5 to 10 ml portions of hot water. Reserve the filtrate and washing. Retain the filter paper and residue and continue according to 7.5.3.

7.5.3 Treatment of the residue

Transfer the filter paper and residue from 7.5.2 to a pre-ignited, tared platinum crucible (5.5). Dry and char slowly and then ash the filter paper by increasing the temperature to 600 to 700 °C in the muffle furnace. Allow the crucible to cool and moisten the residue with a few drops of water. Add 5 drops of the sulfuric acid (4.3) and, depending on the silica content, 5 to 15 ml of the hydrofluoric acid (4.5). Evaporate carefully in a fume cupboard to dryness to expel silica and sulfuric acid. Allow the crucible to cool in the desiccator (5.6) and weigh it. Determine the mass of the residue to ensure that the requirements of the clause 3 are met.

Add 0,7 ± 0,1 g of the flux (4.2). Fuse at above 1 000 °C for 4 to 5 min in the muffle furnace, swirl the melt briefly then return to the furnace for 1 to 2 min.

Allow the crucible to cool, add 10 ml of the sulfuric acid (4.4) and warm to dissolve the fused mass. Transfer the solution to the reserved filtrate (7.5.2), rinsing the crucible with water. Cool to room temperature, dilute to the mark with water and mix. This is the test solution.

7.5.4 Treatment of the test solution

For P_2O_5 contents in the range 0,01 to 1 % (*m/m*), pipette aliquot portions directly from the test solution.

For P_2O_5 contents in the range 1 to 5 % (*m/m*), pipette 10 ml of the test solution into a 100 ml one-mark volumetric flask, dilute to volume with water and mix. This is the diluted test solution.

Transfer to a 150 ml beaker the aliquot portion of test solution (or diluted test solution) taken in accordance with table 1 and add, if necessary, any further sulfuric acid (4.3) as specified in this table.

Table 1 — Aliquot portions of test solution required

P_2O_5 content % (*m/m*)	**Solution to be used**	**Aliquot portion** ml	**Additional acid (4.3)** ml
0,01 to 0,5	Test solution	20	0
0,5 to 1,0	Test solution	10	1,25
1,0 to 5,0	Diluted test solution	20	2,25

Add 5 ml of the hydrobromic (4.6) (see the note), heat the solution until dense white fumes are evolved, then cool and add 50 ml of water. Heat to boiling to facilitate dissolution of the salts, then evaporate to approximately 30 ml.

NOTE — The hydrobromic acid is used to remove arsenic. If the arsenic content is considered to be insignificant, then the hydrobromic acid addition and fuming can be omitted.

7.5.5 Spectrophotometric measurement

Transfer the solution to a 100 ml one-mark volumetric flask, rinsing the beaker with water. (The total volume must not exceed 50 ml.) Add 10 ml of the disodium disulfite solution (4.9), mix and place in a boiling water bath for exactly 5 min. Add 10 ml of the bismuth solution (4.11) and cool to 30 to 35 °C. Add 5 ml of the sodium molybdate solution (4.10) directly into the centre of the solution without allowing any contact with the inner wall of the flask. Rinse the neck with 5 ml of water, mix, and then immediately add 10 ml of the ascorbic acid solution (4.8). Dilute to the mark with water and mix.

Allow to stand for 25 min at room temperature, then measure the absorbance of the test solution against the water in cells of suitable path length. If the absorbance of the blank exceeds 0,1, check the reagents for phosphorus contamination and replace or purify as necessary.

NOTE — Usually 10 mm optical path length will be preferred. If the absorbance value is less than 0,05, a 20 mm cell is recommended.

The absorption peak suitable for measurement is located in the vicinity of 710 nm.

7.6 Preparation of the calibration graph

Transfer suitable increments, 0 — 5,00 — 10,00 — 15,00 and 20,00 ml, of the phosphorus standard solution (4.12) to 100 ml beakers.

Add 2,5 ml of the sulfuric acid (4.3), 40 ml of water and boil gently for 5 min. Cool partially, then transfer the solutions to 100 ml one-mark volumetric flasks, rinsing the beakers with water but keeping the final volume below 50 ml.

Add 10 ml of the disodium disulfite solution (4.9), then proceed with the formation and subsequent spectrophotometric measurement of the molybdenum blue complex as specified in 7.5.5. Prepare the calibration graph by plotting the relationship between the quantity of diphosphorus pentoxide, expressed in milligrams to three significant figures, and the absorbance, on the basis of an optical pathlength of 10 mm.

NOTE — As a guide to performance of the method, the following information is provided :

> 0,200 mg of P_2O_5 in the final solution when measured at 710 nm using an optical pathlength of 10 mm and corrected for the zero calibration blank, gave an absorbance of 0,440.

8 Expression of results

8.1 Calculation of the phosphorus content

Calculate the phosphorus content, expressed as a percentage by mass of diphosphorus pentoxide, using the following formula

$$\frac{m_2}{m_1} \times \frac{25}{V} \times f$$

where

m_1 is the mass, in grams, of the test portion (7.2);

m_2 is the mass, in milligrams, of diphosphorus pentoxide contained in the aliquot portion of test solution, or diluted test solution, (7.5.4) determined by using the calibration graph, after correcting for the blank and, if necessary, to a basis of an optical pathlength of 10 mm;

f is the dilution factor, equal to 10, if diluted test solution has been used;

V is the volume of the aliquot portion of test solution, or diluted test solution (7.5.4).

8.2 General treatment of results

8.2.1 Precision

A planned trial was carried out by nine countries with a total of thirteen laboratories participating. Two determinations were carried out on each of four samples. The repeatability, reproducibility and reproducibility index have been calculated and are presented in table 2.

8.2.2 Acceptance of analytical values

The analytical value for the test sample shall be accepted when the analytical value obtained for the corresponding certified

Table 2 — Precision data for phosphorus determinations

Sample	Mean P_2O_5 content % (m/m)	Components of standard deviation		Reproducibility index 2 s
		s_w	s_b	
MT/12/6	0,056	0,005	0,003	0,011
MT/12/9	0,381	0,007	0,013	0,030
MT/12/12	0,558	0,007	0,008	0,021
MT/12/7	3,692	0,057	0,080	0,196

s_w is the within-laboratory standard deviation;

s_b is the between-laboratories deviation.