International Standard ISO 6995

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Aluminium ores — Determination of titanium content — 4,4′-Diantipyrylmethane spectrophotometric method

Minerais alumineux — Dosage du titane — Méthode spectrophotométrique au diantipyrylméthane-4,4′

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Foreword

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Aluminium ores — Determination of titanium content — 4,4'-Diantipyrylmethane spectrophotometric method

1 Scope and field of application

This International Standard specifies a 4,4'-diantipyrylmethane spectrophotometric method for the determination of the titanium content of aluminium ores.

The method is applicable to ores containing between 0,5 and 8 % (*m/m*) of titanium dioxide.

2 Reference

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Decomposition of the test portion by:

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 mass 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 after silica volatilization for acid decomposition is greater than 1 % of the mass of the test portion;

or

c) Fusion with sodium tetraborate/sodium carbonate flux followed by treatment with sulfuric acid.

NOTE — This method is suitable for all types of ores.

Dehydration of silica, dissolution of salts, and filtration and ignition of the residue. Removal of the silica by evaporation with hydrofluoric and sulfuric acids. Fusion of the residue with sodium carbonate/sodium tetraborate flux, dissolution of the melt with sulfuric acid and addition to the main solution.

Reduction of the iron with ascorbic acid; colour development with 4,4'-diantipyrylmethane and measurement of the absorbance at about 390 nm.

4 Reagents

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

4.1 Sodium peroxide.

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 3 parts by mass of anhydrous sodium carbonate and 1 part by mass of anhydrous sodium tetraborate.

4.3 Hydrofluoric acid, 40 % (*m/m*), ϱ_{20} 1,13 g/ml.

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

4.5 Sulfuric acid, ϱ_{20} 1,84 g/ml, diluted 1 + 9.

4.6 Hydrochloric acid, ϱ_{20} 1,17 g/ml, diluted 1 + 1.

4.7 Acid mixture.

Measure into a one-litre beaker 225 ml of water and add cautiously, with mixing, 175 ml of sulfuric acid (ϱ_{20} 1,84 g/ml). Cool to room temperature and add 150 ml of hydrochloric acid (ϱ_{20} 1,17 g/ml) and 50 ml of nitric acid (ϱ_{20} 1,42 g/ml).

Prepare this solution fresh for each series of determinations and discard any unused solution.

4.8 Ascorbic acid, 100 g/l solution.

Prepare this solution as required.

4.9 4,4'-Diantipyrylmethane, 15 g/l solution.

Dissolve 15 g of 4,4'-diantipyrylmethane ($C_{23}H_{24}N_4O_2$) in 1 l of sulfuric acid solution (ϱ_{20} 1,84 g/ml, diluted 1 + 49).

Prepare fresh as required.

4.10 Ammonium iron(III) sulfate solution.

Dissolve 6 g of ammonium iron(III) sulfate — 24 water [$Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$] in 1 litre of water containing 10 ml of the sulfuric acid solution (4.5).

4.11 Titanium, standard solution, corresponding to 1,0 g of TiO_2 per litre.

One of the following methods may be used:

a) Weigh, to the nearest 0,001 g, 0,300 g of high purity (99,9 %) titanium metal into a conical flask, add 50 ml of water and 50 ml of the sulfuric acid solution (4.4) and heat to dissolve the metal. Oxidize the solution until the purple colour disappears by adding, drop by drop, nitric acid solution (ϱ_{20} 1,42 g/ml, diluted 1 + 4). Cool and transfer quantitatively to a 500 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

b) Weigh, to the nearest 0,001 g, 0,500 g of high purity (99,9 %) titanium dioxide (previously ignited in a platinum crucible at 950 to 1 000 °C for 30 min and dried at 105 ± 5 °C) into a 250 ml conical flask. Add 8 g of ammonium sulfate and 25 ml of sulfuric acid (ϱ_{20} 1,84 g/ml). Insert a short-stemmed glass funnel in the neck of the flask and heat cautiously with frequent agitation to incipient boiling. Continue heating until complete dissolution has been effected and no unattacked material remains on the walls of the flask. Cool to ambient temperature and add 200 ml of cold water in one portion without mixing.

Mix when the addition is complete, cool, transfer quantitatively to a 500 ml one-mark volumetric flask using 100 ml of the sulfuric acid solution (4.5) and dilute to the mark with water.

NOTE — When using a hot-plate, ensure that it is at maximum temperature so that incipient boiling is reached in the minimum time.

c) Weigh, to the nearest 0,001 g, 2,215 g of potassium titanium oxalate dihydrate [$K_2TiO(C_2O_4)_2.2H_2O$] into a 250 ml conical flask; add 25 ml of sulfuric acid (ϱ 1,84 g/ml) and gradually heat to boiling. Boil for 10 min, cool well and pour the solution into 300 to 400 ml of water. Cool and transfer quantitatively to a 500 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

4.12 Titanium, standard solution corresponding to 25 mg of TiO_2 per litre.

Pipette 5,0 ml of the standard titanium solution (4.11) into a 200 ml one-mark volumetric flask, dilute to the mark with the sulfuric acid solution (4.5) and mix thoroughly.

Prepare this solution immediately before use.

5 Apparatus

Ordinary laboratory glassware and apparatus, and

5.1 Muffle furnaces, adjustable from 480 °C to greater than 1 000 °C.

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

5.3 Platinum/gold alloy (95/5) crucibles or equivalent, approximately 25 ml capacity, for the fusion decomposition in 7.5.1.3.

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

5.5 Spectrophotometer, suitable for measurement of absorbance at about 390 nm.

5.6 Desiccator, containing phosphorus(V) oxide as desiccant.

6 Sampling and preparation of samples

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

7 Procedure

7.1 Number of determinations

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

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

7.2 Test portion

Weigh, to the nearest 0,000 1 g, approximately 1 g of test sample.

7.3 Blank test

In parallel with the decomposition of the test portion, prepare a blank solution according to the method of decomposition, but omitting 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

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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.*

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.

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. If the decomposition is to be based on fusion, proceed as specified in 7.5.1.3.

7.5.1.1 Acid decomposition

Transfer the test portion (7.2) to a 400 ml beaker. Moisten with water and add 60 ml of the acid mixture (4.7). Cover the beaker and heat at 80 °C to decompose the sample.

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

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 hot-plate set to produce in the solution a temperature of 210 ± 10 °C.

NOTE — Determine the temperature setting by using a separate test beaker containing a partial-immersion thermometer in a 10 mm depth of sulfuric acid.

7.5.1.2 Alkali sinter decomposition

Transfer the test portion (7.2) to a dry zirconium crucible (5.2), add 10 g of the sodium peroxide (4.1) and mix intimately using a dry metal spatula. Place the crucible and contents in a muffle furnace (5.1), maintained 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 melt while swirling for a total time of 2 min.

Allow the crucible to cool to ambient temperature (a metal block can be used to expedite this process) and place it on its side in a 400 ml beaker. Cover and add cautiously at the rear of the crucible 140 ml of the sulfuric acid solution (4.5). Add 20 ml of the sulfuric acid solution (4.4) 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 hot-plate set to produce in the solution a temperature of 210 ± 10 °C.

7.5.1.3 Fusion decomposition

Transfer the test portion (7.2) to a dry platinum/gold crucible (5.3, see the note), add 2 g of the sodium carbonate/sodium tetraborate flux (4.2) and mix intimately using a dry metal spatula. Cover with a platinum lid and place in a muffle furnace (5.1), maintained at 480 to 500 °C, for 5 min, then transfer to a muffle furnace, maintained at 900 to 950 °C, for 10 min.

NOTE — A platinum crucible may be used, but care should be taken to ensure that the hot fusion mixture does not "creep" over the side of the crucible. Consequently, it would be preferable to use a larger platinum crucible, e.g. 30 ml.

Allow the crucible to cool and place it on its side in a 400 ml beaker. Add 40 ml of water and 35 ml of the sulfuric acid solution (4.4), cover and digest to leach the contents of the crucible. Remove the crucible when the contents are completely leached and rinse well into the main solution.

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 hot-plate set to produce in the solution a temperature of 210 ± 10 °C.

7.5.2 Dissolution and filtration

Cool the solution from 7.5.1.1, 7.5.1.2 or 7.5.1.3 to ambient temperature, cautiously add 130 ml of water and heat to 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 aliquot portions of hot water. Reserve the filtrate and washings for use in 7.5.3. Retain the filter paper and residue and continue according to 7.5.3.

NOTE — With high titanium contents, it may be necessary to increase the volume of wash solution.

7.5.3 Treatment of the residue

Transfer the filter paper and residue from 7.5.2 to a pre-ignited tared platinum crucible (5.4). Dry and char slowly and then ash the filter paper by increasing the temperature to 600 to 700 °C for 30 min in a muffle furnace (5.1). Allow the crucible to cool and moisten the residue with a few drops of water. Add 5 drops of the sulfuric acid solution (4.4) and, depending on the silica content, 5 to 15 ml of the hydrofluoric acid (4.3). Evaporate carefully to dryness in a fume cupboard to expel silica and sulfuric acid. Allow the crucible to cool, and weigh. Determine the mass of residue to ensure that the conditions of 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 a muffle furnace (5.1), roll 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 solution (4.5) and warm to dissolve the fused mass. Transfer the solution to the reserved filtrate (7.5.2), rinsing the crucible with water. Cool to ambient temperature, dilute to the mark with water and mix. Prepare test solutions in accordance with table 1.

Table 1 — Intermediate dilutions

TiO_2 content	Volume of aliquot portion	Final volume
% (*m*/*m*)	ml	ml
0,5 to 2,0	25,00	50,00
2,0 to 4,0	25,00	100,00
4,0 to 8,0	25,00	200,00

7.5.4 Spectrophotometric determination

Pipette a 5 ml aliquot portion of the test solution or diluted test solution, prepared in accordance with 7.5.3, and of the blank test solution, prepared similarly, into separate 50 ml one-mark volumetric flasks. Add 5 ml of the ammonium iron(III) sulfate solution (4.10) to each flask. Add 5 ml of the ascorbic acid solution (4.8), mix and allow to stand for 10 min. Add 10 ml of the hydrochloric acid solution (4.6), mix well, then add 15 ml of the 4,4′-diantipyrylmethane solution (4.9). Dilute to the mark and mix.

Allow to stand for 60 min and measure at the peak absorbance at about 390 nm in a 10 mm cell using water as the reference solution.

7.6 Calibration graph

Pipette aliquot portions of the standard titanium solution (4.12) as shown in table 2 into separate 50 ml one-mark volumetric flasks. Add 5 ml of the ammonium iron(III) sulfate solution (4.10), 5 ml of the ascorbic acid solution (4.8), mix and allow to stand for 10 min. Add 10 ml of the hydrochloric acid solution (4.6), mix well, then add 15 ml of the 4,4′-diantipyrylmethane solution (4.9). Dilute to the mark and mix.

Table 2 — Mass of TiO_2 in titanium solutions

Volume of standard titanium solution (4.12)	Mass of TiO_2
ml	µg
0,0	0
2,0	50
4,0	100
6,0	150
8,0	200

Allow to stand for 60 min and measure at the peak absorbance at about 390 nm in a 10 mm cell using water as the reference solution.

Plot the absorbance of each calibration solution against the quantity of titanium dioxide, in micrograms.

8 Expression of results

8.1 Calculation of titanium dioxide content

The titanium content, expressed as a percentage by mass of titanium dioxide in the test sample, is given by the formula

$$\frac{m_2 - m_{2b}}{m_1} \times 10^{-4}$$

where

m_1 is the mass, in grams, of the test portion, corrected for the intermediate dilutions;

m_2 is the mass, in micrograms, of TiO_2 in the aliquot portion of the test solution;

m_{2b} is the mass, in micrograms, of TiO_2 in the aliquot portion of the blank solution.

8.2 General treatment of results

8.2.1 Precision

The precision of this method, as determined in an international test programme, is expressed in terms of repeatability, reproducibility and reproducibility index in table 3.

Table 3 — Precision data for titanium determinations

Sample	Mean TiO_2 content	Components of standard deviation		Reproducibility index
	% (m/m)	r	R	$2s$
MT/12/6	1,29	0,01	0,05	0,10
MT/12/2	2,59	0,03	0,06	0,15
MT/12/1	3,22	0,03	0,13	0,26
MT/12/5	5,27	0,04	0,12	0,25

where

r is the repeatability;

R is the reproducibility.

8.2.2 Acceptance of analytical values (see ISO 5725)

The analytical value for the test sample shall be accepted when the analytical value obtained for the corresponding certified reference material agrees with the certified value within the limit of the reproducibility index contained in table 3, and when the difference between the two values for the test sample does not exceed 2,77 r as calculated from the appropriate value of r given in table 3.

When the analytical value obtained for the certified reference material is outside the reproducibility index, an analysis shall be carried out simultaneously on one test sample and one certified reference material, with one blank test. The analytical value obtained for the certified reference material shall be examined for the acceptance of the value for the test sample, as above. If the value obtained for the certified reference material is again outside the limits, the procedure shall be repeated with a different reference material of the same type of ore until two acceptable values for the test sample are obtained.

When the range (absolute difference) of the two values for the test sample is greater than 2,77 r additional analyses shall be carried out on one test sample with one blank test simultaneously with an analysis of a certified reference material of the same type of ore. Acceptance of such additional values for the test sample shall be subject, in each case, to the acceptability of the value obtained for the certified reference material.