International Standard 6994

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Aluminium ores — Determination of aluminium content — EDTA titrimetric method

Minerais alumineux — Dosage de l'aluminium — Méthode titrimétrique à l'EDTA

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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 aluminium content — EDTA titrimetric method

1 Scope and field of application

This International Standard specifies an EDTA titrimetric method for the determination of the aluminium content of aluminium ores.

The method is applicable to products having aluminium contents, expressed as aluminium oxide (Al_2O_3), in the range 30 to 65 % (m/m).

2 Reference

ISO 8557, *Aluminium ores — Determination of hygroscopic moisture in analytical samples — Gravimetric method.*

3 Principle

Decomposition of the test portion by either

a) treatment with hydrochloric, nitric and sulfuric acids;

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 brief fusion and 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 after silica volatilization is greater than 1 % of the test portion.

or

c) fusion with sodium tetraborate/sodium carbonate flux followed by dissolution of the melt with sulfuric acid.

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

Removal of silica by filtration to give a solution containing aluminium and other elements. Measurement of an aliquot portion and precipitation of aluminium and other elements except chromium, manganese and vanadium, by ammonium benzoate in acid solution. Filtration and dissolution of the precipitated benzoates in acid followed by precipitation of elements except aluminium by sodium hydroxide. Filtration of the precipitate followed by acid dissolution, reprecipitation with sodium hydroxide and filtration to recover coprecipitated aluminium. Addition of an excess of EDTA to the combined filtrates and determination of aluminium content by back titration of the excess EDTA with zinc sulfate solution using xylenol orange as indicator.

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 (Na_2O_2), powdered.

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) and 1 part by mass of anhydrous sodium tetraborate ($Na_2B_4O_7$).

4.3 Ammonium acetate, 250 g/l solution.

Dissolve 250 g of ammonium acetate in 900 ml of water and adjust the pH to 6 by the addition of glacial acetic acid (ϱ 1,050 g/ml). Dilute to 1 litre.

4.4 Ammonium benzoate, 100 g/l solution.

NOTE — To obtain a clear solution after warming, it may be necessary to add up to 5 ml of ammonia solution (4.6). Filter if necessary to remove any particulate residue.

4.5 Hexamethylenetetramine (hexamine), 250 g/l solution.

Dissolve 25 g of hexamethylenetetramine in 70 ml of water and dilute to 100 ml.

4.6 Ammonia solution, (ϱ 0,9 g/ml), diluted 1+1.

4.7 Glacial acetic acid, (ϱ 1,050 g/ml).

4.8 Hydrochloric acid (ϱ 1,17 g/ml), diluted 2+3.

4.9 Sodium hydroxide, 160 g/l solution.

This solution shall be stored in a plastic bottle.

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

4.11 Sulfuric acid (ϱ 1,84 g/ml), diluted 1+3.

4.12 Sulfuric acid (ϱ 1,84 g/ml), diluted 1+9.

4.13 Hydrofluoric acid, 40 % (m/m), (ϱ 1,13 g/ml).

4.14 Sodium sulfate, ($Na_2SO_4 \cdot 10H_2O$), 100 g/l solution.

4.15 Potassium permanganate, 1 g/l solution.

4.16 Acid mixture.

Measure into a 1 litre beaker 225 ml of water and add cautiously, with stirring, 175 ml of sulfuric acid (ϱ 1,84 g/ml). Cool to room temperature and add 150 ml of hydrochloric acid (ϱ 1,17 g/ml) and 50 ml of nitric acid (ϱ 1,42 g/ml).

This solution shall be prepared for each series of determinations and any unused solution discarded.

4.17 Standard aluminium solution.

Dissolve approximately 1,00 g, weighed to the nearest 0,000 1 g, of aluminium metal (not less than 99.9 %) in 60 ml of the hydrochloric acid (4.8), heating if necessary. Cool and dilute to the mark in a 1 000 ml one-mark volumetric flask.

Calculate the equivalent aluminium oxide concentration a of the standard solution, in grams per litre, using the equation

$$a = m_1 \times 1{,}889\,5 \times \frac{P}{100}$$

where

m_1 is the mass of aluminium metal, in grams;

P is the purity of aluminium used, in per cent.

4.18 Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), approximately 0,05 mol/l (18,6 g/l) standard volumetric solution.

4.19 Zinc sulfate, standard volumetric solution, $c(ZnSO_4 \cdot 7H_2O)$ = 0,05 mol/l.

Dissolve 14,5 g of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in water, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume and mix.

4.19.1 Standardization procedure

4.19.1.1 Titration of EDTA solution with standard zinc sulfate solution

Using a pipette, add 50 ml of the EDTA solution (4.18) to a 500 ml beaker and add 250 ml of water. Add 0,3 ml of the methyl orange indicator (4.20) and, if necessary, add the ammonia solution (4.6) drop by drop until the colour just changes to yellow.

Add 20 ml of the ammonium acetate solution (4.3) and adjust to pH 5,7 ± 0,1, using either the ammonia solution (4.6) or the glacial acetic acid (4.7). Add 0,5 ml of the xylenol orange indicator (4.21) and titrate to the end-point (colour change yellow to purple) with zinc sulfate solution (4.19). Record the titre (V_1).

4.19.1.2 Determination of the equivalence factor for zinc sulfate solution

Pipette 50 ml (V_3) of the standard aluminium solution (4.17) into a 500 ml beaker, and add 200 ml of water.

With a pipette, add 50 ml of the EDTA solution (4.18), and 0,3 ml of the methyl orange indicator (4.20). Add the ammonia solution (4.6) drop by drop until the colour just changes.

Add 20 ml of the ammonium acetate solution (4.3) and a boiling aid. Boil for 10 min and cool. Adjust to pH 5,7 ± 0,1, as in 4.19.1.1. Add 0,5 ml of the xylenol orange indicator (4.21) and titrate to the end-point with the zinc sulfate solution (4.19). Record the titre (V_2).

Calculate the equivalence factor A of the zinc sulfate solution, using the formula

$$1 \text{ ml zinc sulfate solution } (A) \equiv \frac{V_3\, a}{V_1 - V_2} \text{ mg of } Al_2O_3$$

where a is the mass, in grams, of aluminium oxide per litre of standard aluminium solution (4.17).

4.20 Methyl orange indicator, 0,1 g/l solution.

4.21 Xylenol orange indicator, 1 g/l solution.

Prepare each month and store in a dark bottle.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Dishes, of inert material and 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 and mechanical convection, 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 Platinum/gold (95/5) crucibles, of approximately 25 ml capacity for the fusion decomposition in 7.6.1.3.

5.4 Zirconium crucibles, of approximately 40 ml capacity for the sinter decomposition in 7.6.1.2.

5.5 Platinum crucibles.

5.6 Filter papers.

5.6.1 Medium-textured filter papers.

NOTE — Whatman 540 grade have been found suitable.

5.6.2 Fast, hardened, ashless filter papers.

NOTE — Whatman 541 grade have been found suitable.

6 Sampling and samples

6.1 Sampling

Laboratory samples shall be taken and ground to pass a 150 µm test sieve by the procedures specified in the relevant standards.[1]

6.2 Preparation of the test sample

Take approximately 10 g of the laboratory sample and place in the sample dish (5.1). Spread the sample evenly to give a layer density of approximately 5 mg/mm^2 and allow the sample to equilibrate with the laboratory atmosphere for a minimum of 2 h.

7 Procedure

7.1 Number of determinations

Carry out the analysis in duplicate and independently on one 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 should be carried out at different times.

7.2 Test portion

Weigh, to the nearest 0,000 1 g, approximately 1 g of air-equilibrated sample and record the mass (m).

NOTE — For ores containing more than 55 % (m/m) of aluminium oxide, the mass of the test portion should be 0,9 g.

7.3 Determination of hygroscopic moisture content

Simultaneously with the weighing of the test portion, weigh two test portions for the determination of hygroscopic moisture and carry out the determinations by the procedure specified in ISO 8557.

7.4 Blank test

In parallel with the decomposition of the test portion, prepare a blank test solution appropriate 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 test value may be represented by one test, provided that the procedure is the same and the reagents used are from the same bottles.

7.5 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 materials 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.

7.6 Preparation of the test solution

7.6.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as specified in 7.6.1.1. If the decomposition is to be based on alkali sintering, proceed as specified in 7.6.1.2. If the decomposition is to be based on fusion, proceed as specified in 7.6.1.3.

7.6.1.1 Acid decomposition

Transfer the test portion (7.2) to a 400 ml beaker. Moisten with water and add 60 ml of acid mixture (4.16). Cover the beaker and heat at approximately 80 °C to decompose the sample (see note 1).

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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.*

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*) of Fe_2O_3], the initial heating should be conducted for an extended period.

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

7.6.1.2 Alkali sinter decomposition

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 a muffle furnace 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 room temperature (a metal block may be used to expedite this process). If necessary, clean the base of the crucible by wiping with a damp filter paper. Place the crucible on its side in a 400 ml beaker, cover and add cautiously to the beaker 140 ml of the sulfuric acid (4.12). Add 20 ml of the sulfuric acid (4.10) 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 by using a separate test beaker containing a partial immersion thermometer in a 10 mm depth of sulfuric acid (ϱ 1,84 g/ml).

7.6.1.3 Fusion decomposition

Transfer the test portion (7.2) to a dry platinum/gold crucible (5.3) (see note 1), add 2 g of the sodium carbonate/sodium tetraborate flux (4.2) and mix intimately with a dry metal spatula. Cover with a platinum lid and place in a furnace at 480 to 500 °C for 5 min, then transfer to a furnace at 1 000 °C for 15 min.

Allow the crucible to cool and place it on its side in a 400 ml beaker. Add 70 ml of the sulfuric acid (4.11), 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. Completely 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 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).

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

7.6.2 Dissolution and filtration

Cool the solution from 7.6.1.1, 7.6.1.2 or 7.6.1.3, to room temperature, then 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. Add a small quantity of ashless pulp with stirring and filter while hot through a medium-textured filter paper, (5.6.1) 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. Retain the filter paper and residue and continue according to 7.6.3.

7.6.3 Treatment of the residue

Transfer the filter paper and residue from 7.6.2 to a pre-ignited tared platinum crucible. 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. Allow the crucible to cool and moisten the residue with a few drops of water. Add 5 drops of the sulfuric acid solution (4.10) and 8 ml of the hydrofluoric acid (4.13). Evaporate carefully to dryness in a fume cupboard to expel silica and sulfuric acid. Heat gently over a low flame, then to red heat, allow the crucible to cool, and weigh. Determine the mass of residue to ensure that the requirements 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, roll the melt briefly then return to the furnace for 1 to 2 min.

NOTE — If necessary for complete attack, a gas burner may be beneficial.

Allow the crucible to cool, add 10 ml of the sulfuric acid solution (4.12), cover and warm to dissolve the fused mass. Transfer the solution to the reserved filtrate (7.6.2), rinsing the crucible with water. Cool to room temperature, dilute to the mark with water and mix. This is the test solution.