International Standard ISO 6607

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Aluminium ores — Determination of total silicon content — Combined gravimetric and spectrophotometric method

Minerais alumineux — Dosage du silicium total — Méthodes gravimétrique et spectrophotométrique combinées

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Foreword

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INTERNATIONAL STANDARD **ISO 6607-1985 (E)**

Aluminium ores — Determination of total silicon content — Combined gravimetric and spectrophotometric method

1 Scope and field of application

This International Standard specifies a combined gravimetric method and spectrophotometric method for the determination of the total silicon content in aluminium ores.

The method is applicable to ores containing between 1 and 25 % (*m*/*m*) of silicon dioxide.

2 References

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

ISO 6995, *Aluminium ores — Determination of titanium content — 4,4'-Diantipyrylmethane spectrophotometric method.*

3 Principle

Decomposition of the 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 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) The fusion method given in 3c) and sub-clause 7.5.1.3 of ISO 6995.

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

Treatment of an aliquot portion of the main solution with excess sodium hydroxide and heating to depolymerize the silica in solution. Acidification with sulfuric acid and adjustment to pH 1,40, followed by addition of ammonium molybdate. Destruction of molybdophosphoric and molybdoarsenic acids with further sulfuric acid, reduction of the β-molybdosilicic acid to the blue complex and measurement of the absorbance at about 810 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 flux.

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 + 3.

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

4.7 Sulfuric acid, ϱ_{20} = 1,84 g/ml, diluted 1 + 39.

4.8 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). Mix.

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

4.9 Ascorbic acid, 50 g/l solution.

Dissolve 5 g of ascorbic acid in 100 ml of water.

Prepare this solution daily.

4.10 Ammonium molybdate, 100 g/l solution.

Dissolve 100 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 1 litre of water.

Discard the solution when precipitation has commenced.

4.11 Sodium hydroxide, 160 g/l solution.

Dissolve 160 g of sodium hydroxide in 1 litre of water in a plastics beaker.

Store in a plastics bottle.

4.12 Silica, standard solution corresponding to 400 mg of SiO_2 per litre.

Ignite pure silica at 1 000 °C for 1 h and cool in a desiccator. Weigh, to the nearest 0,001 g, 0,400 g of the ignited silica into a platinum crucible. Add 4,0 g of anhydrous sodium carbonate, mix thoroughly using a metal spatula and fuse carefully for 10 min at 1 000 °C.

Cool and transfer to a 400 ml plastics beaker. Add 200 ml of hot water and stir to complete dissolution of the melt.

Cool and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

Transfer immediately into a plastics bottle.

4.13 Silica, standard solution corresponding to 4 mg of SiO_2 per litre.

Pipette 10 ml of the standard silica solution (4.12) into a 1 000 ml one-mark volumetric flask, dilute to the mark and mix thoroughly.

Prepare this solution immediately before use.

4.14 Calibration blank solution

Prepare a calibration blank solution by following the steps set out in 4.12 and 4.13, but omitting the silica.

4.15 Phenolphthalein, indicator solution.

Dissolve 0,05 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml.

5 Apparatus

Ordinary laboratory apparatus and scratch-free unetched glassware, and

5.1 Platinum crucible, of capacity approximately 30 ml, with lid.

5.2 One-mark pipettes, 5, 10, 15, 20 and 25 ml, class A.

5.3 Plastics beakers, of capacity approximately 150 ml.

5.4 Laboratory muffle furnace, capable of being maintained at 480 to 1 100 °C, with provision for a flow of air through the heated cavity.

5.5 Zirconium crucible, of capacity approximately 40 ml.

5.6 pH-meter.

5.7 Spectrophotometer, for measuring absorbance at about 810 nm.

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

6 Sampling and preparation of 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]

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 has to carry out the analysis, the procedure shall be carried out at different times.

7.2 Test portion

Weigh, to the nearest 0,001 g, approximately 1 g of test sample and record the mass (m_1).

7.3 Blank test

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

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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*.

but with the omission of the test portion. When the analysis is carried out on several samples at the same time, then 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 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.

7.5 Gravimetric determination of silicon

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 decomposition

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 (4.8). 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 the dry zirconium crucible (5.5), add 10 g of the sodium peroxide (4.1) and mix intimately using a dry metal spatula. Place the crucible and contents in the muffle furnace (5.4), 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 room temperature (a metal block may 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 (4.6). 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.

7.5.2 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 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 of hot water. Reserve the filtrate and washings for use in 7.5.4. Retain the filter paper containing the impure silica and continue according to 7.5.3.

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

7.5.3 Treatment of impure silica

Transfer the paper containing the impure silica to the pre-ignited tared platinum crucible (5.1). Dry and char slowly and then ash completely by increasing the temperature to 600 to 700 °C.

Cover the crucible and ignite in the muffle furnace (5.4), maintained at 1 075 ± 25 °C, for 30 min and allow to cool in air for 1 to 2 min.

Place in the desiccator (5.8). Allow to cool to room temperature and weigh.

NOTE — The time allowed for cooling should be approximately 10 min.

Repeat the ignition, cooling and weighing steps until the mass is constant to within 0,000 5 g. Record the mass of the crucible and content (m_2).

Add water, drop by drop, to the residue in the crucible until it is completely wetted. Add 8 drops of the sulfuric acid solution (4.4) followed by 5 ml of the hydrofluoric acid (4.3). Heat cautiously and evaporate until dense white fumes cease to be evolved.

Heat gently over a low flame then cover the crucible and ignite in the muffle furnace (5.4), maintained at 1 075 ± 25 °C, for 15 ± 2 min. Allow to cool in air for 1 to 2 min.

Place in the desiccator. Allow to cool to room temperature and weigh.

Repeat the acid treatment, fuming and ignition steps until the mass is constant to within 0,000 5 g. Record the mass of the crucible and contents (m_3).

NOTE — If the mass remains constant at a value greater than 0,01 g more than the mass of the crucible when the acid decomposition procedure is used, then the alternative sinter decomposition should be used.

7.5.4 Treatment of the residue

To the residue remaining from 7.5.3, add 0,7 ± 0,1 g of the flux (4.2). Fuse at above 1 000 °C for about 4 to 5 min in the muffle furnace (5.4). Remove the crucible, 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 (4.6) and warm to dissolve the fused mass. Transfer to the reserved solution (7.5.2) in the 250 ml one-mark volumetric flask and rinse the crucible with water, transferring the rinsings to the reserved solution. Cool to room temperature, dilute to the mark with water and mix. This is the test solution.

7.6 Spectrophotometric determination of residual silica

Unless otherwise specified, the following steps shall be carried out on both the test solution and the blank test solution.

Pipette (5.2) a 10 ml aliquot portion of each solution into a plastics beaker (5.3). Add 1 drop of the phenolphthalein solution (4.15), neutralize with the sodium hydroxide solution (4.11) and add 2 ml in excess. Dilute to 25 ml.

Heat on a water bath at 70 °C for about 15 min and cool.

Neutralize with the sulfuric acid solution (4.6). Add 7 ml of the sulfuric acid solution (4.7) and dilute to 50 ml. Check that the pH is 1,4 ± 0,1, adjusting if necessary with sodium hydroxide or sulfuric acid solution.

From this step to the development of the colour, maintain the temperature of the solutions in the range 15 to 25 °C.

Add 2,0 ml of the ammonium molybdate solution (4.10), to each solution, mix thoroughly and allow to stand for 10 min.

Add 20 ml of the sulfuric acid solution (4.5) to each solution, mix and allow to stand for 10 min.

Add 5 ml of the ascorbic acid solution (4.9) to each solution and transfer to separate 100 ml one-mark volumetric flasks. Rinse the beakers several times with small amounts of water and add the washings to the flasks. Dilute immediately to the mark and mix. Allow the colour to develop for 1 h.

Measure the absorbances of the solutions at about 810 nm using water as the reference solution and record them as

T Absorbance of the test solution

B Absorbance of blank test solution

Calculate and record the absorbance equivalent to the silica in solution as

$$A = T - B$$

7.7 Calibration

Into six separate 150 ml plastics beakers (5.3), pipette 0, 5, 10, 15, 20 and 25 ml aliquot portions respectively of the standard silica solution (4.13) as shown in table 1. Into the same six beakers, add the respective 25, 20, 15, 10, 5 and 0 ml aliquot portions of the calibration blank solution (4.14) in accordance with table 1.

Table 1 — Calibration solutions

Volume of standard silica solution (4.13)	Volume of calibration blank solution (4.14)	Mass of silica in 100 ml
ml	ml	µg
0	25	0
5	20	20
10	15	40
15	10	60
20	5	80
25	0	100

Treat each standard solution according to the procedure specified in 7.6 for the test aliquot portions.

Measure the absorbances of the solutions using water as the reference and record them as

$A_0, A_5, A_{10}, A_{15}, A_{20}, A_{25}$.

Prepare a calibration graph by plotting absorbance against mass of silica as follows:

Absorbance	Silica µg
$A_0 - A_0$	0
$A_5 - A_0$	20
$A_{10} - A_0$	40
$A_{15} - A_0$	60
$A_{20} - A_0$	80
$A_{25} - A_0$	100

8 Expression of results

8.1 Calculation of total silica content

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

$$\text{Total silica } \% \ (m/m) = \% \ (m/m) \text{ Gravimetric silica} + \% \ (m/m) \text{ Residual silica}$$

$$= \frac{(m_2 - m_3) - (m_{2b} - m_{3b})}{m_1} \times 100 + \frac{m_{SiO_2} \times 0{,}002\,5}{m_1}$$

where

m_1 is the mass, in grams, of test portion taken;

m_2 is the mass of crucible and contents, in grams, after ignition (7.5.3);

m_3 is the mass of crucible and contents, in grams, after treatment with hydrofluoric acid (7.5.3);

m_{2b} is the mass of crucible and contents, in grams, after ignition for the blank determination;

m_{3b} is the mass of crucible and contents, in grams, after treatment with hydrofluoric acid for the blank determination;

m_{SiO_2} is the mass of silica, in micrograms, obtained from the calibration graph.

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 2.

Table 2 — Precision data for silicon determinations

Sample	Mean SiO_2 content	Components of standard deviation		Reproducibility index
	% (m/m)	r	R	$2s$
MT/12/2	1,53	0,035	0,072	0,16
MT/12/1	2,57	0,034	0,025	0,085
MT/12/4	5,04	0,045	0,070	0,17
MT/12/6	21,59	0,059	0,19	0,39

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 2, 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 2.

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.

8.2.3 Calculation of final result

The final result is the arithmetical mean of the acceptable analytical values calculated to four decimal places and rounded off to the second decimal place as follows:

a) when the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;

b) when the figure in the third decimal place is 5 and there are figures other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) when the figure in the third decimal place is 5 and there are no figures other than 0 in the fourth decimal place, the 5 is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8, and increased by one if it is 1, 3, 5, 7 or 9.

9 Test report

The test report shall include the following information:

a) details necessary for the identification of the sample;

b) reference to this International Standard;

c) results of the analysis;

d) reference number of the results;

e) any characteristics noticed during the determination and any operations not specified in this International Standard which may have had an influence on the results.

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