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INTERNATIONAL STANDARD 808

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Aluminium and aluminium alloys — Determination of silicon — Spectrophotometric method with the reduced silicomolybdic complex

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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.

Prior to 1972, the results of the work of the Technical Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, International Standard ISO 808 replaces ISO Recommendation R 808-1968 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

Argentina
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South Africa, Rep. of
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Turkey
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Yugoslavia

No Member Body expressed disapproval of the Recommendation.

Printed in Switzerland

Aluminium and aluminium alloys – Determination of silicon – Spectrophotometric method with the reduced silicomolybdic complex

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a photometric method for the determination of silicon in aluminium and aluminium alloys.

The method is applicable to the determination of silicon content between 0,02 and 0,4 %.

The method does not apply to the special cases of aluminium alloys containing tin or bismuth. In this International Standard these special cases are not treated.

2 PRINCIPLE

Attack of the sample with sodium hydroxide and oxidation with hydrogen peroxide. Acidification with nitric and hydrochloric acids. Formation of the yellow silicomolybdic complex (at a pH of approximately 0,9) on an aliquot of the test solution.

Increase of the acidity with sulphuric acid and reduction to the blue silicomolybdic complex (using a reducing solution based on 1-amino-2-naphthol-4-sulphonic acid or, alternatively, ascorbic acid solution).

Photometric measurement at a wavelength of about 810 nm.

3 REAGENTS

For the preparation of solutions and during the analysis use doubly distilled water.

3.1 **Hydrogen peroxide**, 6 % (*V/V*) (approximately 20 volumes).

Dilute 17 ml of hydrogen peroxide 36 % (*V/V*) (ρ 1,12 g/ml) with water and make up the volume to 100 ml.

3.2 **Sulphurous acid** solution.

Pass a current of sulphur dioxide gas (SO_2) through water until saturation point is reached.

3.3 **Basic solution** for plotting the calibration curve

Into a plastics vessel (for example polyethylene) of suitable capacity (for example 400 ml), introduce 40,0 ml of the sodium hydroxide solution (3.7), add approximately 200 ml of water, and acidify by means of 54,0 ml of the nitric acid (3.8) and 40,0 ml of the hydrochloric acid (3.9). After cooling, transfer the solution to a 500 ml volumetric flask and make up to volume with water.

3.4 **Molybdic solution**

Use either of the solutions indicated below

3.4.1 **Sodium molybdate,** 145 g/l solution.

Dissolve 145 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) in approximately 700 ml of warm water. Cool, filter if necessary through a medium texture filter, collect the filtrate in a 1 000 ml volumetric flask and wash with cold water. Make up to volume with water and transfer to a polyethylene vessel. Check the pH of this solution; if it is higher than 8, discard the solution and prepare a fresh one using purer sodium molybdate.

Or :

3.4.2 **Ammonium molybdate,** 106 g/l solution, stabilized at pH 7,2.

In a vessel of suitable capacity (for example 600 ml glass beaker), dissolve 53 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in approximately 250 ml of water. Add approximately 30 ml of the sodium hydroxide solution (3.7), mix, cool to room temperature, if necessary, and make up the volume to approximately 350 ml with water. Add, drop by drop and while stirring, sufficient sodium hydroxide solution (3.7) to bring the pH to about 7,2, using a pH meter. Filter through a sintered glass filter, collect the filtrate in a 500 ml volumetric flask and wash with water. Make up to volume with water, mix and transfer to a polyethylene vessel.

3.5 Tartaric acid, 200 g/l solution.

Dissolve 200 g of tartaric acid ($C_4H_6O_6$) in water and make up the volume to 1 000 ml.

3.6 Reducing solution

Either :

3.6.1 1-amino-2-naphthol-4-sulphonic acid solution.

Dissolve 7 g of anhydrous sodium sulphite (Na_2SO_3) in 100 ml of water, then add 1,5 g of 1-amino-2-naphthol-4-sulphonic acid and stir the solution until dissolution is complete. Dissolve separately 90 g of sodium metabisulphite ($Na_2S_2O_5$) in approximately 800 ml of water. Mix the two solutions, then filter through a medium texture filter, collecting the filtrate and the washings in a 1 000 ml volumetric flask. Make up to volume with water, mix and transfer the solution to a flask of amber glass. Use a solution less than 1 month old.

Or :

3.6.2 Ascorbic acid, 20 g/l solution.

Dissolve 2 g of ascorbic acid in water and make up the volume to 100 ml. Use a freshly prepared solution.

3.7 Sodium hydroxide, 8 N solution.

Dissolve 320 g of sodium hydroxide with water in a container not attacked by sodium hydroxide (for example a nickel basin).

NOTE – Make sure that the sodium hydroxide contains as little silica as possible. For this reason the use of sodium hydroxide supplied in plastics containers is recommended.

Cool and transfer to a polyethylene bottle provided with a mark at 1 000 ml; make up to volume with water and mix. Check the concentration of the solution by titrating it with the nitric acid solution (3.8), using the methyl red solution (3.14) as indicator.

If necessary, adjust the concentration of the sodium hydroxide solution so that 10,0 ml of this solution corresponds to 10,0 ± 0,1 ml of the nitric acid (3.8).

3.8 Nitric acid, 8 N solution.

Dilute 540 ml of nitric acid (ρ 1,40 g/ml), approximately 15 N, to 1 000 ml with water. Check the strength of the solution by titrating 10,600 g of anhydrous sodium carbonate (Na_2CO_3) previously dried in a hot air oven (at approximately 110 °C) and using the methyl red solution (3.14) as indicator.

The theoretical quantity of 8 N nitric acid for the above quantity of anhydrous sodium carbonate is 25 ml. If necessary, adjust the concentration of the nitric acid solution by adding water or acid so that the solution corresponds to the strength of 8 N.

3.9 Hydrochloric acid, 4,4 N solution.

Dilute 352 ml of hydrochloric acid (ρ 1,19 g/ml), approximately 12,5 N, to 1 000 ml with water. Check the strength by titrating it with the sodium hydroxide solution (3.7) and, if necessary, adjust the concentration so that 20,0 ml of the hydrochloric acid solution corresponds to 11,0 ± 0,1 ml of the sodium hydroxide solution (3.7).

3.10 Sulphuric acid, 8 N solution.

Carefully add 225 ml of sulphuric acid (ρ 1,84 g/ml), approximately 35,6 N, to water, cool and make up the volume to 1 000 ml. Check the strength by titrating it with the sodium hydroxide solution (3.7) and if necessary adjust the concentration so that 10,0 ml of the sulphuric acid solution corresponds to 10,0 ± 0,1 ml of the sodium hydroxide solution (3.7).

3.11 Silicon, 0,1 g/l standard solution (1 ml contains 0,1 mg of silicon).

Either :

3.11.1 In a large platinum crucible with a lid, fuse 0,214 0 g of pure silica (SiO_2), previously calcined at 1 000 °C to constant mass, with 2 g of a mixture of equal parts of sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3).

NOTE – Avoid contact between the platinum crucible and refractory materials (for example use triangles or supports of platinum or nickel-chromium).

Continue the fusion until a clear melt is obtained. Cool, dissolve the fused mass with warm water and transfer the solution to a polyethylene beaker. Dilute to approximately 700 ml with water, transfer the solution to a 1 000 ml volumetric flask, make up to volume with water and mix.

Or :

3.11.2 In a plastics beaker of suitable capacity (for example approximately 500 ml) place 0,670 2 g of sodium fluorosilicate (Na_2SiF_6) and add approximately 400 ml of warm water. Cover with a plastics lid and heat on a water bath until the salt appears dissolved. Continue heating for another 30 min, stirring occasionally with a polyethylene rod. Then cool to room temperature, transfer to a 1 000 ml volumetric flask, make up to volume with water and mix.

Immediately transfer the solution (3.11.1 or 3.11.2) to a polyethylene bottle.

3.12 Silicon, 0,01 g/l standard solution (1 ml contains 0,01 mg of silicon).

Take 50,0 ml of silicon standard solution (3.11), place this in a 500 ml volumetric flask and make up to volume with water. Prepare just before use.

Transfer the solution to a polyethylene vessel.

3.13 Silicon, 0,002 g/l standard solution (1 ml contains 2 μg of silicon).

Take 100,0 ml of silicon standard solution (3.12), place this in a 500 ml volumetric flask and make up to volume with water. Prepare just before use.

Transfer the solution to a polyethylene vessel.

3.14 Methyl red, 0,02 % (V/V) solution.

Dissolve 0,02 g of methyl red in 60 ml of ethanol, 95 % (V/V) approximately, and dilute to 100 ml with water.

4 APPARATUS

4.1 Ordinary laboratory apparatus

Glass vessels shall not be used with alkaline solutions. The glassware shall be carefully washed with a hot chromic mixture, thoroughly rinsed in water and finally in doubly distilled water (do not wipe).

The platinum vessels (crucibles, dishes, etc.) shall be cleaned by fusing in them pure sodium carbonate and then washing with boiling hydrochloric acid and rinsing thoroughly with doubly distilled water.

NOTE — The use of graduated pipettes or burettes of polyethylene is advisable for measuring the volumes of sodium hydroxide solution. It is nevertheless possible to use glass graduated pipettes or burettes which shall be washed immediately after use with water then with hydrochloric acid of moderate concentration and, finally, with distilled water.

4.2 Spectrophotometer (wavelength approximately 810 nm).

5 SAMPLING

5.1 Laboratory sample[1]

5.2 Test sample

Chips not more than 1 mm thick obtained by milling or drilling.

6 PROCEDURE

6.1 Test portion

Weigh 0,25 g of the test sample (5.2) with an accuracy of ± 0,001 g.

6.2 Preparation of the calibration curve

Into a series of nine 100 ml volumetric flasks, introduce 25,0 ml of the basic solution (3.3), then into five of them respectively, 0 (compensation solution), 5,0 – 10,0 – 15,0 and 20,0 ml of silicon standard solution (3.13), and into the four remaining flasks respectively 5,0 – 10,0 – 15,0 and 20,0 ml of silicon standard solution (3.12). The flasks contain, therefore, respectively, 0 – 10 – 20 – 30 – 40 – 50 – 100 – 150 and 200 μg of silicon. Using a graduated pipette or a burette, add to each flask the quantity of water necessary to make up the volume to 65 ml, then add 5 ml of the molybdate solution (3.4), stir and allow to stand for exactly 10 min. Then add 5 ml of the tartaric acid solution (3.5), 15,0 ml of the sulphuric acid (3.10) and finally 5 ml of the reducing solution (3.6). Mix, make up to volume with water and mix again.

After 10 min, but not more than 40 min, carry out the photometric measurements (temperature between 20 and 30 °C) at the maximum of the absorption curve (wavelength of approximately 810 nm), after having adjusted the instrument to zero absorbance against the compensation solution (zero term).

NOTE — In order to obtain good results it is necessary to take into account in the calculation the calibration of the cells used for photometric measurements.

Plot a graph having, for example, the values of absorbance as ordinates and the corresponding concentrations of silicon as abscissae. The calibration graph will pass through the origin.

6.3 Blank test

At the same time and following the same procedure, carry out a blank test using all reagents, but reducing to 13,5 ml the quantity of the nitric acid (3.8) used for acidification of the alkaline solution (the quantity of the hydrochloric acid (3.9) remains 10,0 ml).

NOTE — The reagents and the doubly distilled water used for the analysis should be of sufficient purity to give the blank test a very low value for the absorbance (for example, this value should not exceed one-fifth of the value of the actual absorbance of the test on the sample, measured with the same optical path as that used for the blank test).

6.4 Determination

6.4.1 *Attack of the test portion*

Introduce the test portion into a platinum vessel (crucible or dish) of suitable capacity (for example 100 ml), and add 10,0 ml of the sodium hydroxide solution (3.7). Cover the vessel with a platinum lid and heat gently, without bringing to the boil, in order to complete the attack. Add approximately 2 ml of the hydrogen peroxide (3.1) and heat gently. Move the lid of the platinum vessel slightly and evaporate with precaution to a syrupy consistency.

Cool (if necessary, plunge the base of the platinum vessel into cold water), wash the lid and the walls of the vessel with the smallest possible quantity of warm water (for example approximately 30 ml), then heat gently, avoiding boiling, to detach from the bottom and the walls of the platinum vessel all the solidified mass. Remove the source of heat. Dilute to approximately 75 to 80 ml with warm water and heat for 15 to 20 min, **making absolutely certain that boiling of the solution is avoided.**

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[1] The sampling of aluminium and aluminium alloys will form the subject of a future International Standard.

6.4.2 *Preparation of the test solution*

Cool and transfer, while stirring (use a polyethylene or platinum rod), the alkaline solution (6.4.1) into a glass beaker of suitable capacity (for example 400 ml) containing 17,0 ml of the nitric acid (3.8), 10,0 ml of the hydrochloric acid (3.9) and approximately 50 ml of lukewarm water.

NOTE — When transferring the alkaline solution, care should be taken to avoid any contact of the solution with the glass walls of the beaker.

Wash the platinum vessel and the lid with warm water and add the washings to the acid solution contained in the glass beaker. If manganese hydroxide separates out and adheres to the walls of the platinum vessel, transfer into the vessel a little of the acid solution, add several drops of the sulphurous acid solution (3.2) and mix.

Then again transfer the solution to the glass beaker and wash the platinum vessel with warm water. Adjust the volume of the acid solution to approximately 180 ml, heat almost to boiling point and, if necessary, add several drops of the sulphurous acid solution (3.2) to complete the solution of manganese hydroxide; then boil gently for 10 to 15 s.

Cool, then transfer the clear solution to a 250 ml volumetric flask. Make up to volume and mix.

NOTE — In the presence of noticeable quantities of titanium, the solution is cloudy; in this case, filter the solution through a close texture filter and collect the filtrate in a 250 ml volumetric flask, washing the filter with hot water and collecting the washings in the same flask.

6.4.3 *Development of the colour*

Taking into account the presumed silicon content of the test sample and also the characteristics of the apparatus used, take for the colour reaction the quantities of principal solution indicated in the table below (as examples).

If the aliquot taken is less than 50 ml, add to the same volumetric flask the quantity of solution of the blank test necessary to make up the volume to 50 ml, in order that the colour reaction may be carried out under the same conditions of acidity.

Presumed silicon content	Principal solution	Blank test solution
%	ml	ml
0,02 to 0,20	50	0
0,20 to 0,40	25	25

Transfer the aliquot and also the complementary volume, if any, of the blank solution to a 100 ml volumetric flask. Add 15 ml of water, 5 ml of the molybdate solution (3.4), mix and allow to stand for 10 min. Then add the tartaric acid solution (3.5), the sulphuric acid (3.10) and the reducing solution (3.6) as indicated in 6.2.

6.4.4 *Check test*

In order to ensure that the excess molybdenum(VI) of the reagent has not been reduced, carry out the following check test :

Into a 100 ml volumetric flask introduce an aliquot of the principal solution of the same volume as that used for the colour reaction (together with the additional volume of the blank test solution, if any) and in the following order add 15,0 ml of the sulphuric acid (3.10), 5 ml of the tartaric acid solution (3.5), 5 ml of the molybdate solution (3.4) and, finally, 5 ml of the reducing solution (3.6). Mix and make up to volume with water. Within the adopted time limit for photometric measurement of the test solution, the check test solution should remain colourless and should have a negligible absorbance at the wavelength used for measurement of the test solution.

6.4.5 *Photometric measurements*

After 10 min, but not more than 40 min, carry out the photometric measurements (temperature between 20 and 30 °C) at the maximum of the absorption curve (wavelength of approximately 810 nm), after having adjusted the instrument to zero absorbance against doubly distilled water.

Let Δ_E and Δ_B be respectively the values of absorbance corresponding to the test solution and the blank test solution.

7 EXPRESSION OF RESULTS

Calculate the difference ($\Delta_E - \Delta_B$) and, by means of the calibration graph, determine the corresponding mass of silicon.

Calculate the silicon content, as a percentage by mass, from the formula

$$\text{Si}\ \%\ (m/m) = \frac{m_1 \times R}{10\, m_0}$$

where

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

m_1 is the mass, in milligrams, of silicon contained in the aliquot from the test solution;

R is the ratio of the volume of the test solution to the volume of the aliquot taken for the colour reaction.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.