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ISO RECOMMENDATION
R 808

CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

PHOTOMETRIC DETERMINATION OF SILICON

(Silicon content between 0.02 and 0.4 %)

1st EDITION
August 1968

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BRIEF HISTORY

The ISO Recommendation R 808, *Chemical analysis of aluminium and aluminium alloys – Photometric determination of silicon (Silicon content between 0.02 and 0.4 %)*, was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys*, the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question by the Technical Committee began in 1957 and led, in 1965, to the adoption of a Draft ISO Recommendation.

In December 1966, this Draft ISO Recommendation (No. 1129) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina	India	South Africa,
Austria	Ireland	Rep. of
Belgium	Israel	Spain
Bulgaria	Italy	Sweden
Canada	Japan	Switzerland
Chile	Korea, Rep. of	Turkey
Czechoslovakia	Netherlands	United Kingdom
France	New Zealand	U.S.A.
Germany	Norway	U.S.S.R.
Hungary	Poland	Yugoslavia

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in August 1968, to accept it as an ISO RECOMMENDATION.

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CHEMICAL ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS
PHOTOMETRIC DETERMINATION OF SILICON
(Silicon content between 0.02 and 0.4 %)

1. SCOPE

This ISO Recommendation describes a photometric method for the determination of silicon in aluminium and in 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 ISO Recommendation these special cases are not treated.

2. PRINCIPLE

- 2.1 Attack of the sample with sodium hydroxide and oxidation with hydrogen peroxide.
- 2.2 Acidification with nitric and hydrochloric acids.
- 2.3 Formation of the yellow silico-molybdic complex (at a pH of approximately 0.9) on an aliquot of the principal solution.
- 2.4 Increase of the acidity with sulphuric acid and reduction to the blue silico-molybdic complex (using a reducing solution based on 1-amino-2-naphthol-4-sulphonic acid or, alternatively, ascorbic acid solution).
- 2.5 Photometric measurement at a wavelength of about 810 nm.

3. REAGENTS

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

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

Dilute 17 ml of hydrogen peroxide 36 % ($d = 1.12$) with water and make up the volume to 100 ml.

- 3.2 *Sulphurous acid solution*

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

- 3.3 *Basic solution for plotting the calibration graph*

Into a plastic vessel (e.g. polythene) of suitable capacity (e.g. 400 ml), introduce 40.0 ml of sodium hydroxide solution (3.7), add approximately 200 ml of water, and acidify by means of 54.0 ml of nitric acid (3.8) and 40.0 ml of hydrochloric acid (3.9). After cooling, transfer the solution to a 500 ml volumetric flask and make up to volume with water.

3.4 Molybdate solution

Either :

3.4.1 Sodium molybdate solution, 145 g per litre.

Dissolve 145 g of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in approximately 700 ml of warm water. Cool, filter if necessary through a medium texture filter, collect the filtrate in a 1000 ml volumetric flask and wash with cold water. Make up to volume with water and transfer to a polythene 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 solution, 106 g per litre, stabilized at pH 7.2.

In a vessel of suitable capacity (e.g. 600 ml glass beaker), dissolve 53 g of ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] in approximately 250 ml of water. Add approximately 30 ml of sodium hydroxide solution (3.7), mix, cool to room temperature, if necessary, and make up the volume to approximately 350 ml with water. Add, dropwise 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 polythene vessel.

3.5 Tartaric acid solution, 200 g per litre.

Dissolve 200 g of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) in water and make up the volume to 1000 ml.

3.6 Reducing solution

Either :

3.6.1 Solution of 1-amino-2-naphthol-4-sulphonic acid

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 ($\text{Na}_2\text{S}_2\text{O}_5$) 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 1000 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 one month old.

Or :

3.6.2 Ascorbic acid solution, 20 g per litre.

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 solution, 8 N

Dissolve 320 g of sodium hydroxide with water in a container not attacked by sodium hydroxide (e.g. 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 plastic containers is recommended.

Cool and transfer to a polythene bottle provided with a mark at 1000 ml; make up to volume with water and mix. Check the concentration of the solution by titrating it with nitric acid solution 8 N (3.8), using 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 nitric acid (3.8).

3.8 Nitric acid, 8 N

Dilute 540 ml of nitric acid, $d = 1.40$ (approximately 15 N), to 1000 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 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

Dilute 352 ml of hydrochloric acid, $d = 1.19$ (approximately 12.5 N), to 1000 ml with water. Check the strength by titrating it with 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 sodium hydroxide solution (3.7).

3.10 Sulphuric acid, 8 N

Carefully add 225 ml of sulphuric acid, $d = 1.84$ (approximately 35.6 N), to water, cool and make up the volume to 1000 ml. Check the strength by titrating it with 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 Standard silicon solution, 0.1 g per litre (1 ml contains 0.1 mg of silicon).

Either :

- 3.11.1 In a large platinum crucible with a lid, fuse 0.2140 g of pure silica (SiO_2), previously calcined at 1000°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, transfer the solution to a 1000 ml volumetric flask, make up to volume with water and mix.

Or :

- 3.11.2 In a plastic beaker of suitable capacity (e.g. approximately 500 ml) place 0.6702 g of sodium fluorosilicate (Na_2SiF_6) and add approximately 400 ml of warm water. Cover with a plastic lid and heat on a water bath until the salt appears dissolved. Continue heating for another 30 minutes, stirring occasionally with a polythene rod. Then cool to room temperature, transfer to a 1000 ml volumetric flask, make up to volume with water and mix.

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

3.12 Standard silicon solution, 0.01 g per litre (1 ml contains 0.01 mg of silicon).

Take 50.0 ml of standard silicon 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 polythene vessel.

3.13 Standard silicon solution, 0.002 g per litre (1 ml contains 2 µg of silicon).

Take 100.0 ml of standard silicon 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 polythene vessel.

3.14 Methyl red solution, 0.02 %.

Dissolve 0.02 g of methyl red in 60 ml of ethanol (95 % approximately) and dilute to 100 ml with water.

4. APPARATUS

4.1 Ordinary laboratory apparatus

All volumetric apparatus (flasks, burettes, pipettes) should comply with national standards. Glass vessels should not be used with alkaline solutions. The glassware should 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.) should 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 polythene is advisable for measuring the volumes of sodium hydroxide solution. It is nevertheless possible to use glass graduated pipettes or burettes which should 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

See the appropriate national standard on sampling.

5.2 Test sample

Chips not more than 1 mm thick should be obtained from the laboratory sample by milling or drilling.

6. PROCEDURE

6.1 Calibration graph

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 (compensating solution), 5.0, 10.0, 15.0 and 20.0 ml of standard silicon solution (3.13), and into the four remaining flasks respectively 5.0, 10.0, 15.0 and 20.0 ml of standard silicon 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 molybdate solution (3.4), stir and allow to stand for exactly 10 minutes. Then add 5 ml of tartaric acid solution (3.5), 15.0 ml of sulphuric acid (3.10) and finally 5 ml of reducing solution (3.6). Mix, make up to volume with water and mix again.

After 10 minutes, but not more than 40 minutes, carry out the photometric measurements (temperature between 20 and 30 °C) at the maximum of the absorption curve (wavelength of approximately 810 nm), setting the apparatus to zero optical density against the compensating 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.

Draw a graph plotting, for example, the values for the optical density as ordinates and the corresponding concentrations of silicon as abscissae. The calibration graph will pass through the origin.

6.2 Test portion

Weigh 0.25 g of the test sample (5.2) with an accuracy of ± 0.001 g.

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 nitric acid (3.8) used for acidification of the alkaline solution (the quantity of 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 optical density (for example, this value should not exceed one-fifth of the value of the actual optical density 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 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 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 minutes, *making absolutely certain that boiling of the solution is avoided.*

6.4.2 *Preparation of the principal solution.* Cool and transfer, while stirring (use a polythene 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 nitric acid (3.8), 10.0 ml of 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 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 sulphurous acid solution (3.2) to complete the solution of manganese hydroxide; then boil gently for 10 to 15 seconds.

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 *Colour reaction.* 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.

Silicon content	Principal solution	Blank test solution
% (m/m)	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 molybdate solution (3.4), mix and allow to stand for 10 minutes. Then add tartaric acid solution (3.5), sulphuric acid (3.10) and the reducing solution (3.6) as indicated in clause 6.1.

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 sulphuric acid (3.10), 5 ml of tartaric acid solution (3.5), 5 ml of molybdate solution (3.4) and, finally, 5 ml of 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 optical density at the wavelength used for measurement of the test solution.

6.4.5 *Photometric measurements.* After 10 minutes, but not more than 40 minutes, carry out photometric measurements (temperature between 20 and 30 °C) at the maximum of the absorption curve (wavelength of approximately 810 nm), having set the apparatus to zero optical density against doubly distilled water.

Let Δ_E and Δ_B be respectively the optical densities corresponding to the sample solution and the blank test solution.