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Magnesium and magnesium alloys – Determination of silicon – Spectrophotometric method with the reduced silicomolybdic complex

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FOREWORD

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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 1975 replaces ISO Recommendation R 1975-1971 drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

Australia
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Norway
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No Member Body expressed disapproval of the Recommendation.

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Magnesium and magnesium alloys — Determination of silicon — Spectrophotometric method with the reduced silicomolybdic complex

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a spectrophotometric method using the reduced silicomolybdic complex for the determination of silicon in magnesium and magnesium alloys.

This method is applicable to the determination of silicon content between 0,01 and 0,6 %.

The method does not apply to the special case of magnesium alloys containing rare earths or thorium (this case is being studied).

2 PRINCIPLE

Attack by sulphuric acid in the presence of bromine water. Complexing of the silicon by potassium fluoride and decomplexing by boric acid.

Formation of the oxidized silicomolybdic complex (yellow) under clearly defined conditions of acidity.

Selective reduction of the complex in a sulphuric acid medium of high acidity and in the presence of tartaric acid.

Spectrophotometric measurement of the blue-coloured complex at a wavelength of about 810 nm.

3 REAGENTS

For the analysis, use only doubly distilled water.

Keep all the reagent solutions, with the exception of the bromine water (3.1), in plastics bottles.

3.1 Bromine water saturated at ambient temperature.

3.2 Sulphuric acid, ρ 1,29 g/ml, approximately 10 N solution.

Carefully add 280 ml of sulphuric acid (ρ 1,84 g/ml), approximately 35,6 N, to approximately 700 ml of water. After cooling, make up the volume to 1 000 ml and mix.

3.3 Sulphuric acid, ρ 1,03 g/ml, approximately 1 N solution.

Dilute 100 ml of the sulphuric acid (3.2) with water and make up the volume to 1 000 ml.

3.4 Magnesium, 10 g/l solution.

Weigh, to within 0,01 g, 10 g of pure magnesium (purity greater than 99,9 %) and place in a tall-form beaker of suitable capacity (for example 600 ml). Add approximately 200 ml of water and, in small portions, 120 ml of the sulphuric acid (3.2). When the reaction is completed, boil the solution for 5 min. Cool and transfer quantitatively to a 1 000 ml volumetric flask. Make up to volume and mix.

3.5 Potassium fluoride, 50 g/l solution.

Dissolve 50 g of potassium fluoride (KF) in water, filter if necessary, and make up the volume to 1 000 ml.

3.6 Boric acid, solution saturated at 20 °C (approximately 40 g/l).

Dissolve 40 g of boric acid (H_3BO_3) in hot water, dilute to approximately 900 ml, cool and make up the volume to 1 000 ml.

3.7 Molybdic solution

Use either of the solutions indicated below :

3.7.1 Sodium molybdate, 195 g/l solution.

Dissolve 19,5 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in hot water, and after cooling make up the volume to 100 ml.

The pH of this solution should be about 7.

3.7.2 Ammonium molybdate, 140 g/l solution.

Dissolve 14,0 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in lukewarm water, and make up the volume to 100 ml.

Prepare these solutions immediately before use.

3.8 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.

3.9 Ascorbic acid, 20 g/l solution.

Dissolve 2 g of ascorbic acid ($C_6H_8O_6$) in water, and make up the volume to 100 ml.

Use a freshly prepared solution.

3.10 Silicon standard solution, containing 0,100 g of silicon (Si) per litre.

In a platinum crucible weigh, to the nearest 0,000 2 g, 0,214 0 g of pure silica (SiO_2) finely ground, previously calcined at 1 000 °C to constant mass and cooled in a desiccator.

Add to the crucible 2 g of a mixture of equal parts of anhydrous sodium carbonate and anhydrous potassium carbonate. Mix carefully, preferably with a platinum spatula, and fuse carefully until a transparent mass is obtained. Allow to cool, dissolve the fused mass in hot water and transfer the solution to a plastics beaker.

Dilute to approximately 700 ml, cool, transfer the solution to a 1 000 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,10 mg of Si.

NOTE — Avoid contact between platinum containers and refractory materials. In order to isolate them from the furnace plate, use, for example, platinum supports.

3.11 Silicon standard solution, containing 0,010 g of silicon (Si) per litre.

Transfer 50,0 ml of the silicon standard solution (3.10) to a 500 ml volumetric flask, make up to volume and mix.

1 ml of this standard solution contains 0,01 mg of Si.

Prepare this solution immediately before use.

4 APPARATUS

4.1 Ordinary laboratory apparatus

The glassware shall be carefully washed with a hot sulphuric/chromic acid mixture, copiously rinsed with water and finally with doubly distilled water (do not dry). Platinum containers (crucibles, dishes, etc.) shall be cleaned with fused sodium carbonate, washed with boiling hydrochloric acid, then copiously washed with doubly distilled water.

4.2 pH meter, fitted with a glass electrode.

4.3 Spectrophotometer.

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, to the nearest 0,001 g, 1 g of the test sample (5.2) for silicon contents between 0,01 and 0,05 %, or 0,5 g for silicon contents between 0,05 and 0,6 %.

6.2 Preparation of the calibration curve

In view of the fact that the interference from magnesium is in proportion to the quantity of magnesium present, it is necessary to plot two calibration curves. The curve in the presence of 0,02 g of magnesium is identical, for low silicon contents, with the calibration curve plotted in the absence of magnesium; for this reason it can also serve as the blank test.

6.2.1 *Preparation of standard matching solutions* (related to spectrophotometric measurements carried out with an optical path of 1 cm).

6.2.1.1 TEST PORTION OF 1 g

Into each of a series of six plastics beakers of suitable capacity (for example 250 ml), place the 100,0 ml of the magnesium solution (3.4), containing 1 g of magnesium, and then respectively the volumes of the silicon standard solution (3.10 or 3.11) indicated in table 1 :

TABLE 1

Volume of silicon standard solution		Corresponding mass of silicon
(3.11)	(3.10)	
ml	ml	mg
0*	–	0
5,0	–	0,05
10,0	–	0,10
25,0	–	0,25
–	5,0	0,50
–	7,5	0,75

* Compensation solution.

Then add to each beaker 5 ml of the potassium fluoride solution (3.5), stir with a plastics rod and allow to stand for 15 to 20 min at a temperature of between 60 and 70 °C.

Add 50 ml of the boric acid solution (3.6) and stir.

Cool to ambient temperature, transfer the solutions to 250 ml volumetric flasks, make up to volume and mix.

6.2.1.2 TEST PORTION OF 0,5 g AND BLANK TEST

Into each of a series of six plastics beakers of suitable capacity (for example 250 ml), place 50,0 ml of the magnesium solution (3.4), containing 0,5 g of magnesium,

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

and 23,0 ml of the sulphuric acid (3.2) and finally the volumes of silicon standard solution (3.10) indicated in table 2 :

TABLE 2

Volume of silicon standard solution (3.10)	Corresponding mass of silicon
ml	mg
0*	0
2,5	0,25
5,0	0,50
12,5	1,25
25,0	2,50
37,5	3,75

* Compensation solution.

Dilute, if necessary, to 100 ml, then add to each beaker 5 ml of the potassium fluoride solution (3.5), stir with a plastics rod and allow to stand for 15 to 20 min at a temperature of between 60 and 70 °C. Add 50 ml of the boric acid solution (3.6) and stir. Cool to ambient temperature, transfer the solutions to 250 ml volumetric flasks, make up to volume and mix.

NOTE — In order to avoid hydrolysis of the silicon solutions, it is necessary to prepare them immediately before use.

6.2.2 *Preliminary test for the checking and correction of pH to be carried out for each check solution for the two calibration curves*

6.2.2.1 TEST PORTION OF 1 g

In a beaker of suitable capacity (for example 150 ml) place 50,0 ml of the solution obtained by the procedure described in 6.2.1.1 and 5 ml of the molybdic solution (3.7.1 or 3.7.2) and stir. Check the pH value with the pH meter (4.2) : this value should be between 1,35 and 1,50 when the sodium molybdate solution (3.7.1) is used, or between 1,20 and 1,30 when the ammonium molybdate solution (3.7.2) is used. If it is not, correct the pH by slowly adding from a burette or graduated pipette, drop by drop and stirring after each addition, the necessary quantity of the sulphuric acid solution (3.3).

Dilute, if necessary, so that the final volume of the solution (after the addition of the sulphuric acid solution) is approximately 65 ml and again check the pH. Note the volume of the sulphuric acid solution (3.3) used for the correction of the pH.

6.2.2.2 TEST PORTION OF 0,5 g AND BLANK TEST

In a beaker of suitable capacity (for example 150 ml) place 10,0 ml of the solution obtained by the procedure described in 6.2.1.2, add 40 ml of water and 5 ml of the molybdic solution (3.7.1 or 3.7.2) and then check and correct the pH as indicated in 6.2.2.1.

6.2.3 *Development of the colour*

6.2.3.1 TEST PORTION OF 1 g

Into each of a series of six 100 ml volumetric flasks, place 50,0 ml of the corresponding check solution (see 6.2.1.1) and then add the quantity of the sulphuric acid solution (3.3) used for the correction of the pH (see 6.2.2.1) and dilute, if necessary, to approximately 60 ml. Then add to each flask 5 ml of the molybdic solution (3.7.1 or 3.7.2), mix and allow to stand for 10 min. Then add 5 ml of the tartaric acid solution (3.8), 10 ml of the sulphuric acid (3.2) and finally 5 ml of the ascorbic acid solution (3.9). Mix and make up to volume.

The six solutions contain respectively 0 (compensation solution) — 0,010 — 0,020 — 0,050 — 0,100 and 0,150 mg of silicon (Si) and 0,2 g of magnesium.

6.2.3.2 TEST PORTION OF 0,5 g AND BLANK TEST

Into each of a series of six 100 ml volumetric flasks, place 10,0 ml of the corresponding check solution (see 6.2.1.2). Then add 40 ml of water and then the quantity of the sulphuric acid (3.3) used for the correction of the pH in the corresponding preliminary test (see 6.2.2.2). Then continue as indicated in 6.2.3.1. The six check solutions contain respectively 0 (compensation solution) — 0,010 — 0,020 — 0,050 — 0,100 and 0,150 mg of silicon (Si) and 0,02 g of magnesium.

6.2.4 *Spectrophotometric measurements*

After 10 min, but within 40 min, carry out the spectophotometric measurements (see 6.2.3.1 and 6.2.3.2) (temperature between 20 and 30 °C) using the spectrophotometer (4.3) at a wavelength of approximately 810 nm, after having adjusted the instrument to zero absorbance against the compensation solution.

NOTE — The cells used for the spectrophotometric measurements should be accurately calibrated.

6.2.5 *Plotting of the calibration curves*

Plot two curves (6.2.5.1 for the 1 g test portion and 6.2.5.2 for the 0,5 g test portion respectively), plotting for example, as abscissae the values, in milligrams, of the quantities of silicon (Si) contained in 100 ml of standard matching solution, and as ordinates the corresponding values of absorbance.

6.3 Determination

6.3.1 *Preparation of the test solution*

The test portion, the quantities of the bromine water (3.1) and of the sulphuric acid (3.2) to be used in the attack of the test portion, the dilution of the test solution and the aliquot to be taken in relation to the silicon content to be determined, are indicated, for guidance, in the table 3 :

TABLE 3

Presumed silicon content	Mass of test portion	Volumes of reagents for the attack		Final volume of the test solution	Aliquot for the colour reaction	
		Bromine water (3.1)	Sulphuric acid (3.2)		Volume to be taken	Corresponding presumed mass of silicon
%	g	ml	ml	ml	ml	mg
0,01 to 0,05	1	75	12,0	250	50,0	0,020 to 0,100
0,05 to 0,6	0,5	50	30,0	250	10,0	0,010 to 0,120

NOTE — The quantity of the sulphuric acid solution (3.2) to be taken for the attack has been calculated so as always to obtain the same acidity for the aliquot taken for the colour reaction.

Place the test portion in a tall-form beaker of suitable capacity (for example 250 ml). Add the bromine water (3.1) then, in small portions, cooling as necessary, the sulphuric acid solution (3.2) in the quantities indicated in table 3. If, during the attack of the test portion, the orange coloration due to the bromine disappears, or if there is separation of a residue (consisting essentially of unattacked copper), add a further 10 ml of the bromine water (3.1), taking this into account when carrying out the blank test. When the test portion is completely dissolved, boil the solution until the excess of bromine is eliminated. Adjust the volume to approximately 100 ml with water, then transfer the solution to a plastics beaker and add 5 ml of the potassium fluoride solution (3.5), stir with a plastics rod and allow to stand for 15 to 20 min at a temperature of between 60 and 70 °C.

Then add 50 ml of the boric acid solution (3.6) and mix. Cool to ambient temperature, transfer the solution to a 250 ml volumetric flask, make up to volume and mix. Transfer the solution to a plastics container.

NOTE — In order to avoid the hydrolysis of the silicon, prepare the test solution immediately before use.

6.3.2 *Preliminary check of pH*

Take two aliquots of the test solution (6.3.1), as indicated in table 3, and place them respectively in a beaker of suitable capacity (for example 100 ml) and a 100 ml volumetric flask and, if necessary, dilute to 50 ml.

To the aliquot placed in the beaker, add 5 ml of the molybdic solution (3.7.1 or 3.7.2) and mix.

Check the value of the pH with the pH meter (4.2) and, if necessary, correct it as described in 6.2.2.1.

6.3.3 *Development of the colour*

To the corresponding aliquot placed in the 100 ml volumetric flask (see 6.3.2), add the quantity of the sulphuric acid (3.3) established by the preliminary test for checking and correction of pH (see 6.3.2); if necessary, dilute to approximately 60 ml and shake. Add 5 ml of the molybdic solution (3.7.1 or 3.7.2), mix and allow to stand for 10 min.

Then add 5 ml of the tartaric acid solution (3.8), 10 ml of the sulphuric acid solution (3.2) and finally 5 ml of the ascorbic acid solution (3.9). Mix and make up to volume.

6.3.4 *Check test*

In order to check if the Mo(VI) of the excess reagent has not been reduced, perform the following check test :

In a 100 ml volumetric flask place an aliquot of the test solution (see 6.3.1) of the same volume as that used for the colour reaction, and add the quantity of the sulphuric acid solution (3.3) established by the preliminary test for checking and correcting the pH (see 6.3.2), 10,0 ml of the sulphuric acid (3.2), 5 ml of the tartaric acid solution (3.8), 5 ml of the molybdic solution (3.7.1 or 3.7.2) and 5 ml of the ascorbic acid solution (3.9). Mix and make up to volume. Within the time limits fixed for the spectrophotometric measurement of the test solution, the check solution should remain uncoloured and should have a negligible optical density at the wavelength at which the measurement is made on the test solution.

6.3.5 *Spectrophotometric measurements* (see note to 6.2.4)

After 10 min, but within 40 min, carry out the spectrophotometric measurements on the test solution and the blank test solution as described in 6.2.4, after having adjusted the instrument to zero absorbance against water.

6.3.6 *Blank test*

Perform a blank test in parallel with the analysis, using the same procedure as that used for the analysis and the following quantities of reagents :

- for a 1 g test portion : bromine water (3.1) 75 ml
  sulphuric acid (3.2) 5 ml
- for a 0,5 g test portion : bromine water (3.1) 50 ml
  sulphuric acid (3.2) 25 ml.

7 EXPRESSION OF RESULTS

By means of the calibration curve 6.2.5.1 or 6.2.5.2 (depending on the test portion) determine the quantity of silicon corresponding to the value of the spectrophotometric measurement of the aliquot of the test solution. Using the calibration curve 6.2.5.2, determine the quantity of silicon corresponding to the value of spectrophotometric measurement of the corresponding aliquot of the blank test solution.

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

$$\text{Si \% } (m/m) = \frac{(m_1 - m_2) \times R}{m_0 \times 10}$$

where

m_0 is the mass, in grams, of the test portion (see 6.1);

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

m_2 is the mass, in milligrams, of silicon found in the aliquot of the blank test solution (see 6.3.6);

R is the ratio of the volume of 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.