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CHEMICAL ANALYSIS OF MAGNESIUM AND ITS ALLOYS
DETERMINATION OF SILICON
SPECTROPHOTOMETRIC METHOD
WITH THE REDUCED SILICOMOLYBDIC COMPLEX

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BRIEF HISTORY

The ISO Recommendation R 1975, *Chemical analysis of magnesium and its alloys – Determination of silicon – Spectrophotometric method with the reduced silicomolybdic complex*, 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 led to the adoption of Draft ISO Recommendation No. 1975, which was circulated to all the ISO Member Bodies for enquiry in May 1970. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia	India	Spain
Austria	Iran	Sweden
Belgium	Israel	Switzerland
Canada	Italy	Thailand
Chile	Japan	U.A.R.
France	Netherlands	United Kingdom
Germany	New Zealand	U.S.A.
Greece	Norway	
Hungary	South Africa, Rep. of	

No Member Body opposed the approval of the Draft.

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

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CHEMICAL ANALYSIS OF MAGNESIUM AND ITS ALLOYS
DETERMINATION OF SILICON
SPECTROPHOTOMETRIC METHOD
WITH THE REDUCED SILICOMOLYBDIC COMPLEX

1. SCOPE

This ISO Recommendation describes 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 contents between 0.01 and 0.6 %.

Special cases

Alloys containing rare earths or thorium (this case is being studied).

2. PRINCIPLE

- 2.1 Attack by sulphuric acid in the presence of bromine water. Complexing of the silicon by potassium fluoride and decomplexing by boric acid.
- 2.2 Formation of the oxidized silicomolybdic complex (yellow) under clearly defined conditions of acidity.
- 2.3 Selective reduction of the complex in a sulphuric acid medium of high acidity and in the presence of tartaric acid.
- 2.4 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 plastic bottles.

- 3.1 *Bromine water* saturated at ambient temperature.
- 3.2 *Sulphuric acid* ($d = 1.29$), approximately 10 N.
Carefully add 280 ml of sulphuric acid ($d = 1.84$), approximately 35.6 N, to approximately 700 ml of water. After cooling, make up the volume to 1000 ml and mix.
- 3.3 *Sulphuric acid* ($d = 1.03$), approximately 1 N.
Dilute 100 ml of the sulphuric acid (3.2) with water and make up the volume to 1000 ml.

3.4 Magnesium solution, 10 g/l.

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 sulphuric acid (3.2). When the reaction is completed, boil the solution for 5 minutes. Cool and transfer quantitatively to a 1000 ml volumetric flask. Make up to volume and mix.

3.5 Potassium fluoride solution, 50 g/l.

Dissolve 50 g of potassium fluoride (KF) in water, filter if necessary, and make up the volume to 1000 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 1000 ml.

3.7 Molybdic solution

Use either of the solutions indicated below :

3.7.1 Sodium molybdate solution, 195 g/l.

Dissolve 19.5 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) 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 solution, 140 g/l.

Dissolve 14.0 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in lukewarm water, and make up the volume to 100 ml.

Prepare these solutions immediately before use.

3.8 Tartaric acid solution, 200 g/l.

Dissolve 200 g of tartaric acid ($C_4H_6O_6$) in water, and make up the volume to 1000 ml.

3.9 Ascorbic acid solution, 20 g/l.

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 Standard silicon solution containing 0.100 g of silicon (Si) per litre.

In a platinum crucible weigh, to the nearest 0.0002 g, 0.2140 g of pure silica (SiO_2) finely ground, previously calcined at 1000 °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 plastic beaker.

Dilute to approximately 700 ml, cool, transfer the solution to a 1000 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 Standard silicon solution containing 0.010 g of silicon (Si) per litre.

Transfer 50.0 ml of standard silicon 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 should 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.) should 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***
- 5.2 **Test sample**

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

6. PROCEDURE

6.1 Sample

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 Plotting 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 check 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 plastic beakers of suitable capacity (for example 250 ml), place 100.0 ml of the magnesium solution (3.4), containing 1 g of magnesium, and then respectively the volumes of the standard silicon solution (3.10 or 3.11) indicated in the following table :

Volume of standard silicon 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

* Compensating solution.

* The ISO Recommendation concerning sampling from supply batches will be studied as soon as ISO/TC 69, *Applications of statistical methods*, has specified the general procedures to be adopted.

Then add to each beaker 5 ml of the potassium fluoride solution (3.5), stir with a plastic rod and allow to stand for 15 to 20 minutes 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 plastic beakers of suitable capacity (for example 250 ml), place 50.0 ml of the magnesium solution (3.4), containing 0.5 g of magnesium, and 23.0 ml of the sulphuric acid (3.2) and finally the volumes of standard silicon solution (3.10) indicated in the following table :

Volume of standard silicon 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

* Compensating solution.

Dilute, if necessary, to 100 ml, then add to each beaker 5 ml of the potassium fluoride solution (3.5), stir with a plastic rod and allow to stand for 15 to 20 minutes 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 clause 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 sodium molybdate solution (3.7.1) is used, or between 1.20 and 1.30 when 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 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 clause 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 clause 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 clause 6.2.1.1) and then add the quantity of the sulphuric acid solution (3.3) used for the correction of the pH (see clause 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 minutes. Then add 5 ml of tartaric acid solution (3.8), 10 ml of sulphuric acid (3.2) and finally 5 ml of ascorbic acid solution (3.9). Mix and make up to volume.

The six solutions contain respectively 0 (compensating 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 clause 6.2.1.2). Then add 40 ml of water and then the quantity of sulphuric acid (3.3) used for the correction of the pH in the corresponding preliminary test (see clause 6.2.2.2). Then continue as indicated in clause 6.2.3.1. The six check solutions contain respectively 0 (compensating 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 minutes, but within 40 minutes, make the spectrophotometric measurements (see clauses 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 adjusting the apparatus to zero optical density against the compensating 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 expressed in milligrammes of the quantities of silicon (Si) contained in 100 ml of check solution, and as ordinates the corresponding values of the optical density.

6.3 Determination

6.3.1 Preparation of the test solution. The test portion, the quantities of bromine water (3.1) and of 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 following table :

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.