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# International Standard



# 4686

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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

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## Iron ores — Determination of silicon content — Reduced molybdosilicate spectrophotometric method

*Minerais de fer — Dosage du silicium — Méthode spectrophotométrique au molybdosilicate réduit*

First edition — 1980-02-01

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UDC 553.31 : 543.42 : 546.28

Ref. No. ISO 4686-1980 (E)

**Descriptors** : iron ores, chemical analysis, determination of content, silicon, spectrophotometric analysis, test results.

## 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.

International Standard ISO 4686 was developed by Technical Committee ISO/TC 102, *Iron ores*, and was circulated to the member bodies in June 1978.

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It has been approved by the member bodies of the following countries :

<u>ISO 4686:1980</u>		
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Austria	Iran	South Africa, Rep. of
Bulgaria	Italy	Sweden
Canada	Japan	Turkey
Chile	Korea, Dem. P. Rep. of	United Kingdom
Czechoslovakia	Mexico	USA
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Germany, F. R.	Poland	

No member body expressed disapproval of the document.

# Iron ores — Determination of silicon content — Reduced molybdosilicate spectrophotometric method

## 1 Scope and field of application

This International Standard specifies a reduced molybdosilicate spectrophotometric method for the determination of the silicon content of iron ores.

This method is applicable to a concentration range of 0,1 to 5,0 % (*m/m*) of silicon in natural iron ores, and iron ore concentrates and agglomerates, including sinter products, especially for ores containing fluorine.

The fluorine content of the sample does not affect the determination.

## 2 References

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples.*

ISO 3081, *Iron ores — Increment sampling — Manual method.*

ISO 3083, *Iron ores — Preparation of samples.*

## 3 Principle

Decomposition of the test portion by fusion with sodium tetraborate or a fusion mixture (carbonate and tetraborate) and treatment with dilute nitric acid.

Addition of molybdate to convert the silicate into a molybdosilicate complex and reduction to molybdenum blue with ascorbic acid.

Spectrophotometric measurement of the absorbance of the molybdenum blue complex at a wavelength of approximately 600 nm.

## 4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

**4.1 Sodium tetraborate** ( $\text{Na}_2\text{B}_4\text{O}_7$ ), anhydrous.

**4.2 Potassium nitrate** ( $\text{KNO}_3$ ).

To be used as in note 2 in 7.3.1.

**4.3 Fusion mixture.**

Mix 100 g of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ )/anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ ) mixture (1 + 1) with 30 g of anhydrous sodium tetraborate (4.1) and 0,5 g of potassium nitrate (4.2).

**4.4 Nitric acid**, ( $\rho$  1,4 g/ml), diluted 1 + 9.

**4.5 Ammonium molybdate** [ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ] solution 120 g/l.

**4.6 Oxalic acid** ( $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) solution 50 g/l.

**4.7 Sulphuric acid**, ( $\rho$  1,84 g/ml), diluted 1 + 3.

**4.8 Ascorbic acid** ( $\text{C}_6\text{H}_8\text{O}_6$ ) solution 20 g/l.

Prepare this solution fresh on the day of use.

**4.9 Hydrogen peroxide**, solution 3 % (*V/V*).

To be used as in note 5 in 7.3.1.

**4.10 Silicon**, standard solution, corresponding to 0,050 g of Si per litre.

Calcine an appropriate quantity of silicon dioxide at 1 050 °C, cool, and weigh  $53,5 \pm 0,1$  mg into a platinum crucible. Add 400 mg of iron(III) oxide and 4 g of sodium tetraborate (4.1) or fusion mixture (4.3) and mix.

Heat the mixture gently up to a temperature of 1 100 °C (see 7.3.1) until a clear melt is obtained.

Cool and dissolve in 200 ml of the nitric acid solution (4.4), transfer to a 500 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,050 mg of Si.

**4.11 Background solution.**

In parallel with the standard solution (4.10), prepare a background solution from 4 g of sodium tetraborate (4.1) or fusion mixture (4.3) and 400 mg of iron(III) oxide as described in 4.10, but without any addition of silicon dioxide.

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## 5 Apparatus

Ordinary laboratory apparatus and

### 5.1 Platinum crucibles.

### 5.2 Furnace, capable of heating to 1 100 °C.

### 5.3 Spectrophotometer, suitable for measurement of absorbance in the region of 600 nm.

## 6 Sampling and samples

For analysis, a laboratory sample of minus 100 µm particle size which has been taken in accordance with ISO 3081<sup>1)</sup> and prepared in accordance with ISO 3083<sup>1)</sup> shall be used. In the case of ores having high contents of combined water and/or oxidizable compounds, the particle size shall be minus 160 µm.

## 7 Procedure

Carry out the analysis generally in duplicate, independently, on one ore sample.

NOTE — The expression "independently" implies the change of the person carrying out the analysis. If the same person must carry out the analysis, the procedure shall be carried out at different times.

Simultaneously with the analysis, determine the hygroscopic moisture in accordance with ISO 2596.

### 7.1 Test portion

Weigh, to the nearest 0,000 2 g, approximately 0,5 g of the test sample obtained in accordance with clause 6.

### 7.2 Blank test and check test

In each run, one analysis of a certified reference material of the same type of ore and one blank test shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions.

NOTE — The certified reference material should be of the same type as the sample to be analysed. Such certified reference material 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.

When the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and that the reagents used are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

## 7.3 Determination

### 7.3.1 Decomposition of the test portion

Mix the test portion (7.1) with 4 g of sodium tetraborate (4.1) or fusion mixture (4.3) in a platinum crucible (5.1). (See notes 1 and 2.)

Cover the platinum crucible and heat gently in a furnace (5.2) up to a temperature of 1 100 °C. Maintain this temperature until the test portion is completely dissolved. (See note 3.)

Cool the platinum crucible (see note 4), place it in a 600 ml glass beaker containing 200 ml of nitric acid (4.4), and dissolve the cooled melt at a temperature below 90 °C. (See note 5.)

Cool the solution, wash into a 500 ml volumetric flask, dilute to volume with water and mix. (This solution is the test solution.)

### NOTES

1 To minimize corrosive attack on the platinum crucible, it is recommended that 2 g of sodium tetraborate (4.1) or fusion mixture (4.3) be pre-melted in the crucible and swirled while cooling to cover the lower walls of the crucible. The remaining 2 g of sodium tetraborate (4.1) or fusion mixture (4.3) is mixed with the test portion on the surface of the cooled melt and then fused.

2 When fusing with sodium tetraborate (4.1), 0,1 g of potassium nitrate (4.2) should be added to samples containing reducing elements or sulfides in order to accelerate the decomposition and to prevent any attack on the crucible.

3 Swirling the melt during the heating period greatly helps dissolution of the test portion. In general, 15 min will be sufficient; however, the fusion must be continued until the test portion is completely dissolved.

4 In order to accelerate the subsequent dissolution of the cooled melt, it is recommended that the melt be gently swirled during cooling, to enable it to solidify as a thin uniform film on the inner wall of the crucible. The application of slight heat during the swirling may help this process.

5 Higher manganese contents of the sample may cause cloudiness. In this case, add a few drops of hydrogen peroxide solution (4.9) and heat to boiling for the minimum time required to decompose the excess hydrogen peroxide.

### 7.3.2 Preparation of blank test solution

In parallel with the fusion of the test portion, make a second fusion using all the reagents and following the same procedure as given in 7.3.1, but omitting the test portion.

Dissolve the cooled melt, treat in the same way as the test solution, dilute in a volumetric flask to 500 ml with water and mix.

1) A further International Standard now in preparation (ISO 3082) will specify mechanical methods of increment sampling and will also specify methods for preparation of samples.

### 7.3.3 Spectrophotometric determination

Transfer 5,0 ml of the test solution and 5,0 ml of the blank test solution (7.3.2), respectively, to 100 ml volumetric flasks. Then add 2 ml of nitric acid (4.4) and 5,0 ml of ammonium molybdate solution (4.5).

Mix the solutions thoroughly and allow to stand for 5 min.

Add the following reagents, in quick succession, shaking well after each addition : 10,0 ml of oxalic acid solution (4.6), 5,0 ml of sulfuric acid (4.7) and 5,0 ml of ascorbic acid solution (4.8). The maximum time allowed for the complete addition shall not exceed 3 min. After the final thorough mixing, allow the solutions to stand for 1 min, dilute to the mark with water and mix.

After a further 5 min, measure, in cells of a suitable optical pathlength, the absorbance of the test solution and of the blank test solution, against water as the reference. The portion of the absorption curve suitable for measurement is located between 550 and 630 nm. Correct the absorbance of the test solution with the absorbance of the blank test solution.

NOTE — As an indication of the sensitivity of the method, the following information is provided : 0,250 mg Si/100 ml determined with a mercury vapour lamp and an Hg 578 filter results in an absorbance of 0,55 for an optical pathlength of 1 cm.

### 7.4 Plotting of the calibration curve

In order to plot the calibration curve, measure aliquots of the standard silicon solution (4.10) and make up to 5,0 ml with appropriate quantities of the background solution (4.11) in accordance with table 1.

NOTE — During the preparation of the test solution and calibration solutions, the same fusion reagents should be used.

Table 1 — Aliquots

Standard Si solution (4.10) ml	Background solution (4.11) ml	Mass of Si in 5 ml aliquot mg	% Si (0,50 g sample)
0,00	5,0	0,00	0,0
0,10	4,9	0,005 0	0,10
0,20	4,8	0,010	0,20
0,50	4,5	0,025	0,50
1,00	4,0	0,050	1,00
3,00	2,0	0,150	3,00
5,00	0,0	0,25	5,00

Treat these solutions as indicated in 7.3.3 correcting the absorbances with the absorbance obtained for the zero calibration solution. Plot the absorbance calculated for an optical pathlength of 1 cm on the abscissa against the known mass of silicon on the ordinate. The slope  $Z$  of the curve serves to calculate the silicon content as a percentage by mass.

## 8 Expression of results

### 8.1 Calculation of silicon content

The silicon content, as a percentage by mass, is calculated from the formula

$$\text{Si \% (m/m)} = \frac{E \times Z \times 10}{m} \times K$$

where

$E$  is the absorbance of the test solution corrected with the absorbance of the blank test solution (7.3.2) and reduced to an optical pathlength of 1 cm;

$Z$  is the slope of the calibration curve, in

$$\frac{\text{mg Si in 100 ml}}{\text{absorbance/cm}}$$

$m$  is the mass, in grams, of the test portion;

$K$  is the conversion factor found from the formula

$$K = \frac{100}{100 - A}$$

where  $A$  is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 2596.

### 8.2 General treatment of results

#### 8.2.1 Acceptance of analytical values

The analytical values for the test sample shall be accepted when the respective analytical values obtained for the corresponding certified reference material agree with the certified value within the limit of permissible tolerance for certified reference materials, and when the difference between the two values for the test sample does not exceed the permissible tolerance for test samples (table 2).

When the analytical value obtained for the certified reference material is outside the limit of the permissible tolerance (table 2, second column), 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 limit, 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 outside the limit of the permissible tolerance (table 2, third column), additional analyses shall be carried out on one test sample with one blank test, as required by the procedure specified in annex A, 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.

### 8.2.2 Calculation of final result

The arithmetical mean of the acceptable values of the test sample is the final result.

The arithmetical mean of the acceptable analytical values, calculated to the fourth decimal place, is to be 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 is a figure 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 is no figure 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 is increased by one if it is 1, 3, 5, 7 or 9.

### 8.3 Permissible tolerances

The permissible tolerances described in 8.2.1 are shown in table 2.<sup>1)</sup>

Table 2 — Permissible tolerances within laboratories

Silicon content Si (%)	Certified reference material Si (%) 1,96 $s_w$	Test sample Si (%)	
		2,77 $s_w$	3,31 $s_w$
0,1 to 0,2	± 0,030	0,042	0,050
0,2 to 1,0	± 0,045	0,062	0,075
1,0 to 5,0	± 0,085	0,120	0,143

### 8.4 Oxide factor

$$\text{SiO}_2 (\%) = 2,139 \times \text{Si} (\%)$$

## 9 Test report

The test report shall include the following information :

- a) reference to this International Standard;
- b) details necessary for the identification of the sample;
- 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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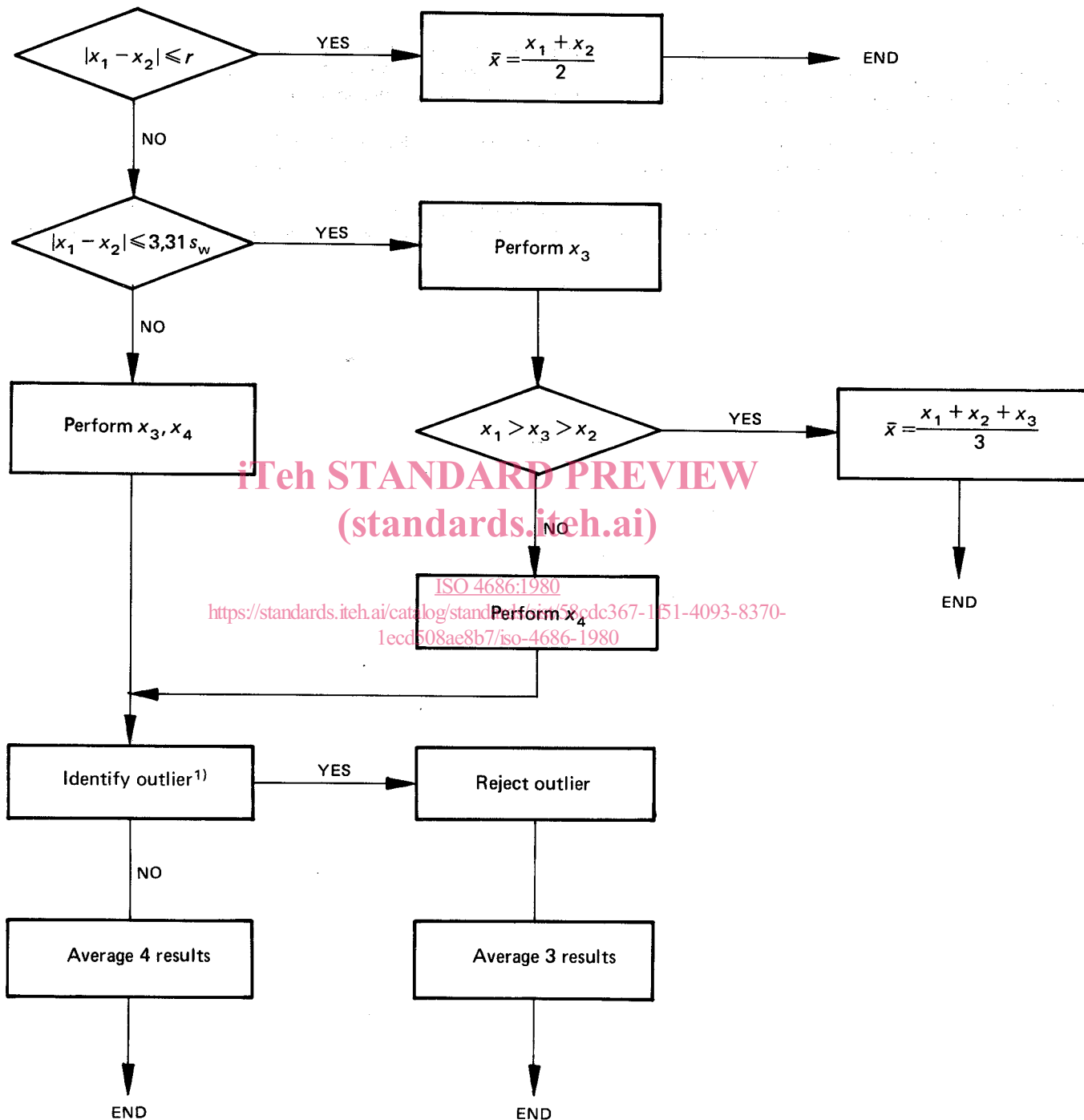
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1) The derivation of the figures in the table is given in annex B.

### Annex A

## Flowsheet on the procedure for the acceptance of analytical values for test samples



$r$  = repeatability  
 $= 2,77 s_w$   
 $\bar{x}$  = average

1) Use Dixon's criteria for outlier.

## Annex B

### Derivation of permissible tolerances

The standard deviations within laboratories ( $s_w$ ) were derived from a comparison of the results of international analytical trials carried out in 1970/1971 on five iron ore samples : Palabora ore (0,192 % Si), Philippine iron sand (1,069 % Si), Swedish ore (3,93 % Si), UK sinter (7,87 % Si), Krivoj Rog ore (12,95 % Si). The results of these trials were reported in document 102/2N 225 E, June 1971.

The permissible tolerances for the certified reference material (table 2, second column) are calculated by multiplying the standard deviations by the statistical factor 1,96 and relate to the upper limit of each range of contents respectively.

The permissible tolerances for the test sample (table 2, third column) are calculated by multiplying the standard deviations by the statistical factors 2,77 and 3,31 ( $n = 2$  with 95 % confidence) and relate to the upper limit of each range of contents respectively.

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