SLOVENSKI STANDARD
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Kromove rude in koncentrati - Doloļ evanje silicija - Molekulsko absorbcijska spektrometrijska metoda

Chromium ores and concentrates -- Determination of silicon content -- Molecular absorption spectrometric method and gravimetric method

Minerais et concentrés de chrome -- Dosage du silicium -- Méthode par spectrométrie d'absorption moléculaire et méthode gravimétrique

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International Standard 5997

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Chromium ores and concentrates — Determination of silicon content — Molecular absorption spectrometric method and gravimetric method

Minerais et concentrés de chrome — Dosage du silicium — Méthode par spectrométrie d'absorption moléculaire et méthode gravimétrique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been established 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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 5997 was prepared by Technical Committee ISO/TC 65, *Manganese and chromium ores*.

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Chromium ores and concentrates — Determination of silicon content — Molecular absorption spectrometric method and gravimetric method

1 Scope and field of application

This International Standard specifies the following methods for the determination of the silicon content of chromium ores and concentrates :

- **method A** : molecular absorption spectrometric method, applicable to products having silicon contents from 0,05 to 0,5 % (m/m);
- **method B** : gravimetric method, applicable to products having silicon contents from 0,5 to 15 % (m/m).

This International Standard should be read in conjunction with ISO 6629.

2 Reference

ISO 6629, *Chromium ores and concentrates — Methods of chemical analysis — General instructions.*

3 Method A — Spectrometric method for silicon contents from 0,05 to 0,5 % (m/m)

3.1 Principle

Decomposition of a test portion by fusing with fusion mixture. Dissolution of the melt in water.

Adjustment of pH of the solution with hydrochloric acid. Reaction of the silica with ammonium molybdate and reduction with ascorbic acid in the presence of citric acid.

Spectrometric measurement at the wavelength 810 nm or 620 to 640 nm.

3.2 Reactions

The method is based on the interaction of silicic acid with ammonium molybdate with the formation of a yellow silicomolybdate heteropolyacid which is reduced with ascorbic acid to a blue silicomolybdate complex.

3.3 Reagents

3.3.1 Fusion mixture.

Mix 100 g of sodium carbonate anhydrous, 50 g of sodium tetraborate (previously ignited till foaming ceases) and 0,5 g of potassium nitrate and thoroughly grind in a corundum or hard steel mortar.

3.3.2 Ammonium molybdate, 50 g/l solution.

Keep the solution in a polyethylene container. In case of need, the reagent shall be previously recrystallized. For this transfer 250 g of the reagent to a 600 ml beaker and dissolve in 400 ml of water while heating at 70 to 80 °C. Filter the solution through a close-texture filter paper, add 300 ml of ethanol [96 % (m/m)] while mixing and allow to stand for 1 h until the precipitate coagulates.

Filter the precipitate with suction on a medium-texture filter paper, wash two or three times with ethanol and dry in the air.

3.3.3 Hydrochloric acid, ϱ 1,19 g/ml, diluted 1 + 3.

3.3.4 Mixture of acids.

Dissolve 5 g of citric acid and 1 g of ascorbic acid in 100 ml of water.

Prepare the mixture fresh.

3.3.5 Silicon, standard solution corresponding to 50 mg of Si per litre.

Weigh 0,107 0 g of silicon dioxide, calcined at 1 000 to 1 100 °C to constant mass, into a platinum crucible, add 2 g of fusion mixture (3.3.1), mix with a platinum wire, cover with a platinum lid and fuse at 1 000 to 1 100 °C. Transfer the crucible with the melt to a 1 000 ml beaker. Dissolve the melt in 100 to 150 ml of 10 g/l sodium carbonate solution while heating gently. Cool the solution, dilute with 10 g/l sodium carbonate solution to about 750 ml, transfer to a 1 000 ml one-mark volumetric flask, dilute with 10 g/l sodium carbonate solution to the mark and mix.

Keep the solution in polyethylene containers.

Pipette 25 ml of this solution to a 500 ml beaker, dilute with water to 350 to 400 ml, acidify with hydrochloric acid (3.3.3) to adjust to pH 1,5 to 1,7, using the pH meter (3.4.3), transfer to a 500 ml one-mark volumetric flask, dilute with water to the mark and mix.

1 ml of this standard solution contains 0,005 0 mg of Si.

3.4 Apparatus

Ordinary laboratory apparatus and

3.4.1 Platinum crucible, with platinum lid and platinum wire.

3.4.2 Spectrometer with a radiation selector for continuous variation, or

3.4.3 Spectrometer with a radiation selector for discontinuous variation.

3.4.4 pH meter.

3.5 Procedure

3.5.1 Test portion

Weigh 0,1 g of the test sample.[1]

3.5.2 Blank test

Carry out the blank test through all stages of the analysis.

3.5.3 Decomposition of test portion

Transfer the test portion (3.5.1) into a platinum crucible (3.4.1), add 2 g of fusion mixture (3.3.1), mix with a platinum wire (3.4.1), cover with a platinum lid (3.4.1) and fuse at 1 000 to 1 100 °C. Cool the crucible containing the melt and transfer into a 250 ml fluoroplastic beaker. Dissolve the melt while heating gently in 70 to 80 ml of water (if necessary, filter the solution). Cool the solution, acidify with hydrochloric acid (3.3.3) to adjust to pH 1,5 to 1,7, using the pH meter (3.4.4), transfer to a 100 ml one-mark volumetric flask, dilute with water to the mark and mix.

3.5.4 Preparation of test solution

Pipette suitable aliquot portions of the solution, the volume of which will depend upon the expected silicon content of the sample (see table 1) into two 100 ml one-mark volumetric flasks.

Table 1

Expected silicon content	Aliquot portion
% (*m*/*m*)	ml
0,05 to 0,25 0,25 to 0,5	10 5

Add 1,5 ml of hydrochloric acid (3.3.3) and 60 to 65 ml of water to each flask. Add 5 ml of ammonium molybdate solution (3.3.2) to one of the flasks, mix and allow the solutions to stand for 10 min.

Add 5 ml of mixture of acids (3.3.4) to both flasks, dilute with water to the mark, mix and allow to stand for 15 min.

3.6 Spectrometric measurement

Measure the absorbance of each solution using the spectrometer (3.4.2) at 810 nm or the spectrometer (3.4.3) at 620 to 640 nm in 20 to 50 mm cells against the solution to which ammonium molybdate solution has not been added as reference.

3.7 Preparation of calibration graph

Introduce, using a burette, into each of a series of six 100 ml one-mark volumetric flasks 0,0; 2,0; 4,0; 6,0; 8,0; and 10,0 ml of the standard silicon solution (3.3.5), corresponding to 0,0; 0,005; 0,010; 0,015; 0,020; and 0,025 mg of Si. Add 1,5 ml of hydrochloric acid (3.3.3), 60 to 65 ml of water, and 5 ml of ammonium molybdate solution (3.3.2), mix and allow the solutions to stand for 10 min. Then add 5 ml of mixture of acids (3.3.4), dilute with water to the mark, mix and allow to stand for 15 min.

Measure the absorbance of each solution as specified in 3.6 using the compensation solution as reference.

Prepare a calibration graph by plotting the absorbance values against the nominal silicon content.

3.8 Expression of results

3.8.1 Calculation

Convert the absorbance reading for the test solution to silicon content by means of the calibration graph (3.7) deducting the absorbance reading for the blank test.

The silicon (Si) content, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 100}{m_2 \times 1\,000} \times K$$

$$= \frac{m_1}{m_2 \times 10} \times K$$

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[1] Sampling and sample preparation of chromium ores will be the subject of ISO 6153 and ISO 6154, respectively.

where

m_1 is the mass, in milligrams, of silicon in the aliquot portion of the test solution, obtained from the calibration graph;

m_2 is the mass, in grams, of the test portion corresponding to the aliquot portion of the test solution;

K is the conversion factor for the expression of the silicon content on the dry basis.

3.8.2 Permissible tolerances on results of duplicate determinations

Table 2

Silicon content	Permissible tolerance
% (m/m)	% (m/m)
0,05 to 0,25 0,25 to 0,50	0,02 0,05

4 Method B — Gravimetric method for silicon contents from 0,5 to 15 % (m/m)

4.1 Principle

Decomposition of a test portion, by either method 1, or method 2.

Method 1 : Decomposition by fusion with sodium peroxide, followed by treatment with hydrochloric and perchloric acids.

Method 2 : Decomposition by treatment with nitric and perchloric acids.

Separation of the silicic acid by fuming with perchloric acid and filtration. Ignition of the residue and weighing. Treatment of the ignited residue with hydrofluoric and sulfuric acids, ignition and reweighing.

4.2 Reagents

4.2.1 Sodium peroxide.

CAUTION — Wear safety glasses during fusion. Keep away from humidity. Do not allow to come into contact with organic materials to avoid possible explosion hazards.

4.2.2 Sodium carbonate, anhydrous.

4.2.3 Sulfuric acid, ϱ 1,84 g/ml, diluted 1 + 1.

4.2.4 Perchloric acid, ϱ 1,50 g/ml.

CAUTION — Risk of poisoning by inhalation, swallowing or contact with the skin. Handle in an efficient fume cupboard, away from exposed flames, etc. Avoid inhalation of fumes and contact with skin, eyes and clothing.

4.2.5 Hydrochloric acid, ϱ 1,19 g/ml.

4.2.6 Hydrochloric acid, diluted 1 + 4.

4.2.7 Hydrochloric acid, diluted 1 + 9.

4.2.8 Hydrochloric acid, diluted 1 + 100.

4.2.9 Hydrofluoric acid, ϱ 1,13 g/ml, 40 % (m/m) solution.

4.2.10 Nitric acid, ϱ 1,4 g/ml.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Iron or **nickel crucible,** with a nickel rod.

4.3.2 Platinum crucible.

4.3.3 Muffle furnace, capable of being maintained at 1 000 to 1 100 °C.

4.4 Procedure

4.4.1 Test portion

Weigh a mass of the test sample[1] chosen from table 3 in accordance with the expected silicon content.

Table 3

Expected silicon content	Mass of test portion
% (m/m)	g
0,5 to 2,5 2,5 to 15,0	1,0 0,5

4.4.2 Blank test

Carry out the blank test through all stages of the analysis.

4.4.3 Decomposition of test portion

If the decomposition is to be based on method 1, proceed as instructed in 4.4.3.1. If the decomposition is to be based on method 2, proceed as instructed in 4.4.3.2.

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[1] Sampling and sample preparation of chromium ores will be the subject of ISO 6153 and ISO 6154, respectively.

4.4.3.1 Place the test portion (4.4.1) in an iron or nickel crucible (4.3.1) and add 8 to 10 g of sodium peroxide (4.2.1).

Mix the content of the crucible with a nickel rod (4.3.1), cover with a layer of sodium peroxide (4.2.1) (1 to 2 g) and fuse at 800 to 850 °C, regularly mixing the contents of the crucible by swirling.

Cool the crucible, place it into a 500 ml fluoroplastic beaker and cover it with a polyethylene watch-glass, leach the melt with 150 to 200 ml of water. Wash the watch-glass and the crucible with hot water and remove the crucible from the beaker. Carefully add hydrochloric acid (4.2.5) to the contents of the beaker until iron hydroxides dissolve, transfer the solution to a 600 ml glass beaker, add 60 ml of perchloric acid (4.2.4), mix and heat to white fumes of perchloric acid. Continue heating to maintain this stage until crystallization of salts begins.

Cool the solution, pour carefully down the inside wall of the beaker 30 ml of hydrochloric acid (4.2.7), followed by 150 to 200 ml of water and heat to dissolve the salts.

Collect the precipitate on a close-texture filter paper containing a small amount of ashless paper pulp. Rinse the beaker with hot hydrochloric acid (4.2.8) using a rubber-tipped glass rod for removing all adhering particles of silicic acid. Wash the residue 10 to 12 times with hot hydrochloric acid (4.2.8) and then two or three times with hot water. Collect the filtrate and washings in a 600 ml beaker. Preserve the residue on the filter. Add 10 ml of perchloric acid (4.2.4) to the filtrate and evaporate to white fumes of perchloric acid. Continue to heat to maintain this stage until crystallization of salts begins. Cool the solution, add 40 to 50 ml of hot water, mix and heat to dissolve the salts. Filter the residue and wash the filter as before.

Combine the residue thus obtained with the main residue of silicic acid. Retain the filter papers with residues and continue according to 4.4.4.

4.4.3.2 Place the test portion (4.4.1) in a 250 ml beaker and moisten with 5 ml of water. Add 50 to 70 ml of perchloric acid (4.2.4) and 5 ml of nitric acid (4.2.10). Cover the beaker with a watch-glass, heat to white fumes of perchloric acid and continue heating to oxidize chromium.

NOTE — Evaporation should not be taken completely to dryness because of the hazard involved in heating perchlorate salts.

Remove the watch-glass and carefully add hydrochloric acid (4.2.5), drop by drop, along the walls of the beaker until brown fumes of chromyl chloride cease to evolve, chromium being reduced to the trivalent state. Replace the watch-glass on the beaker and continue to heat the solution to oxidize chromium completely. Repeat the distillation of chromyl chloride until the test portion is completely decomposed. Replace the watch-glass on the beaker and continue to heat until the atmosphere in the beaker is clear. Maintain this stage until most of the perchloric acid has evaporated, but avoid evaporation to dryness.

CAUTION — While working with chromyl chloride avoid poisoning by inhalation, swallowing or contact with the skin. Handle in an efficient fume cupboard, away from exposed flames, etc. Avoid inhalation of fumes and contact with skin, eyes and clothing.

Allow the beaker to cool, add 50 ml of hydrochloric acid (4.2.6), agitate and heat gently to dissolve the soluble salts. Add about 50 ml of hot water and stir, collect the precipitate on a close-texture filter paper containing a small amount of ashless paper pulp. Rinse the beaker with hot hydrochloric acid (4.2.8) using a rubber-tipped glass rod for removing all adhering particles of silicic acid. Wash the residue with hot hydrochloric acid (4.2.8) until free from iron salts and finally two or three times with hot water. Discard the filtrate and washings.

Place the residue with the filter paper in a platinum crucible (4.3.2), dry, ashify the filter paper and ignite at 750 to 800 °C. Allow the crucible to cool, add 2 to 3 g of sodium carbonate (4.2.2), mix with a spatula and ignite at 900 to 1 000 °C to effect complete fusion.

Allow the crucible to cool, then place it in the original beaker. Cover the beaker with a watch-glass. Add 50 ml of hydrochloric acid (4.2.6), heat gently to dissolve the melt, rinse the crucible with water and remove it from the beaker.

Add 30 ml of perchloric acid (4.2.4), partially remove the cover from the beaker and heat until the dense white fumes of perchloric acid appear.

Cover the beaker completely and continue heating, until the atmosphere in the beaker is clear. Maintain this stage until most of the perchloric acid has evaporated, but avoid evaporation to dryness.

Allow the beaker to cool and add 50 ml of hydrochloric acid (4.2.6). Agitate and heat gently to dissolve the soluble salts, then rinse the walls of the beaker and dilute to about 100 ml with hot water.

Filter the solution through a close-texture filter paper containing a small amount of ashless paper pulp. Rinse the beaker with hot hydrochloric acid (4.2.8) using a rubber-tipped glass rod for removing all adhering particles of silicic acid. Wash the residue 10 to 12 times with hot hydrochloric acid (4.2.8), then two or three times with hot water. Retain the filter paper with residue and continue according to 4.4.4.

4.4.4 Treatment of residue

Place the residue (4.4.3) with the filter paper in a platinum crucible, dry, ashify the paper and ignite in the muffle furnace (4.3.1) at 1 000 to 1 100 °C to constant mass.

Allow to cool in a desiccator and weigh.

Moisten the residue with a few drops of sulfuric acid (4.2.3), add 3 to 5 ml of hydrofluoric acid solution (4.2.9).

Heat gently to remove silicic acid and sulfuric acid. Finally, ignite the crucible for 15 min in the muffle furnace at 1 000 to 1 100 °C.

Allow to cool in a desiccator and weigh. Repeat the treatment with sulfuric and hydrofluoric acids until constant mass is obtained.