
**Rubber compounding ingredients —
Silica, precipitated, hydrated —**

**Part 1:
Non-rubber tests**

*Ingrédients de mélange du caoutchouc — Silices hydratées
précipitées —*

Partie 1: Essais sur le produit brut



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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. Each 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5794-1 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This fourth edition cancels and replaces the third edition (ISO 5794-1:2005), of which it constitutes a minor revision comprising the following changes:

- the distilled or deionized water used for the tests has been replaced throughout the document by grade 3 water as defined in ISO 3696;
- the way in which the silica content is calculated (see Table 1) has been simplified;
- for the sieve specified in F.3.2, an alternative sieve height (45 mm) has been included in addition to the sieve height of 25 mm originally specified.

This fourth edition also incorporates the Technical Corrigenda ISO 5794-1:2005/Cor.1:2006 and ISO 5794-1:2005/Cor.2:2007.

ISO 5794 consists of the following parts, under the general title *Rubber compounding ingredients — Silica, precipitated, hydrated*:

- *Part 1: Non-rubber tests*
- *Part 2: Evaluation procedures in styrene-butadiene rubber*

Rubber compounding ingredients — Silica, precipitated, hydrated —

Part 1: Non-rubber tests

WARNING — Persons using this part of ISO 5794 should be familiar with normal laboratory practice. This part of ISO 5794 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and ensure compliance with any national regulatory conditions.

1 Scope

This part of ISO 5794 specifies methods of test for characterizing precipitated hydrated silica for use as a rubber compounding ingredient. A definition of precipitated hydrated silica is given.

ISO 5794-2 specifies the test formulation, mixing equipment, mixing procedure and methods of test for use in determining the physical properties of styrene-butadiene rubber compounded with precipitated hydrated silica.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

ISO 787-2, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C*

ISO 787-8, *General methods of test for pigments and extenders — Part 8: Determination of matter soluble in water — Cold extraction method*

ISO 787-9, *General methods of test for pigments and extenders — Part 9: Determination of pH value of an aqueous suspension*

ISO 787-10, *General methods of test for pigments and extenders — Part 10: Determination of density — Pycnometer method*

ISO 787-18, *General methods of test for pigments and extenders — Part 18: Determination of residue on sieve — Mechanical flushing procedure*

ISO 1124, *Rubber compounding ingredients — Carbon black shipment sampling procedures*

ISO 3262-1:1997, *Extenders for paints — Specifications and methods of test — Part 1: Introduction and general test methods*

ISO 3262-19:2000, *Extenders for paints — Specifications and methods of test — Part 19: Precipitated silica*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 18852, *Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
precipitated hydrated silica
 material composed of amorphous particles obtained from soluble silicates by precipitation from aqueous solution

4 Sampling

Sampling shall be carried out in accordance with ISO 15528.

5 Methods of test

The properties of precipitated hydrated silica shall be determined by the methods of test referred to in Table 1.

Table 1 — Methods of test

Property	Method of test
Silica content of ignited sample, % (by mass)	ISO 3262-19:2000, Clause 6
Colour	ISO 3262-1:1997, 5.1
Residue on sieve (nominal aperture size 45 µm) for silica in powder form for silica in other forms	ISO 3262-19:2000, Clause 8 ISO 787-18
Volatile matter at 105 °C (loss on heating)	ISO 787-2 (Use a test portion of 2 g weighed to the nearest 0,1 mg.)
Density, Mg/m ³	ISO 787-10
Loss on ignition at 1 000 °C of dried sample	ISO 3262-1:1997, 5.2
pH of slurry	ISO 787-9
Water-soluble matter	ISO 787-8
Total copper content, mg/kg	See Annex A
Total manganese content, mg/kg	See Annex B
Total iron content, mg/kg	See Annex C
Specific surface area, m ² /g	See Annexes D, E
Granule size distribution, %	See Annex F
CTAB surface area, m ² /g	See Annex G

6 Test report

The test report shall include the following information:

- a) a reference to this part of ISO 5794;
- b) all details necessary for complete identification of the material tested;
- c) the results of the tests:
 - 1) silica content,
 - 2) colour,
 - 3) residue on sieve (and the test method used),
 - 4) volatile matter at 105 °C,
 - 5) density,
 - 6) loss on ignition at 1 000 °C,
 - 7) pH of slurry,
 - 8) water-soluble matter,
 - 9) total copper content,
 - 10) total manganese content,
 - 11) total iron content,
 - 12) specific surface area by nitrogen adsorption (and the test method used),
 - 13) granule size distribution (fraction retained on the 75 µm and 300 µm screens, and the fines content),
 - 14) specific surface area by CTAB adsorption,
- d) any unusual observations noted during the test;
- e) any deviations from the test method and the reason for them;
- f) any tests performed not covered by this part of ISO 5794;
- g) the date of the test.

Annex A (normative)

Determination of total copper content

A.1 Principle

A test portion is digested with hydrofluoric acid and sulfuric acid and the silicon is volatilized as silicon tetrafluoride.

Any metals in the digested test portion are dissolved in hydrochloric acid, then the solution is diluted and aspirated into the flame of an atomic absorption spectrometer set at a wavelength of 324,7 nm.

The method is applicable to the determination of copper contents up to 125 mg/kg, and there is provision for extending the range to 1 250 mg/kg.

WARNING — All recognized health and safety precautions should be taken when performing this method of analysis.

A.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be grade 3 water as defined in ISO 3696:1987.

A.2.1 Acetylene, compressed-gas supply.

A.2.2 Air, compressed-gas supply.

A.2.3 Hydrochloric acid, 10 % (by mass) solution.

Dilute 20 cm³ of 35 % (by mass) hydrochloric acid solution ($\rho_{20} = 1,18 \text{ Mg/m}^3$) with 50 cm³ of water.

A.2.4 Hydrofluoric acid, 40 % (by mass) solution ($\rho_{20} = 1,13 \text{ Mg/m}^3$).

A.2.5 Sulfuric acid, 98 % (by mass) solution ($\rho_{20} = 1,84 \text{ Mg/m}^3$).

A.2.6 Nitric acid, 68 % (by mass) solution ($\rho_{20} = 1,42 \text{ Mg/m}^3$).

A.2.7 Copper, standard solution corresponding to 1 g of Cu per cubic decimetre.

Dissolve 1,000 g $\pm$ 0,001 g of high-purity copper turnings in a mixture of 10 cm³ of water and 5 cm³ of nitric acid (A.2.6) in a 100 cm³ beaker. Boil under a fume hood to expel oxides of nitrogen. Cool, transfer to a 1 dm³ volumetric flask, make up to the mark with water and mix. 1 cm³ of this standard solution contains 1 000 μg of copper.

A.2.8 Copper, standard solution corresponding to 50 mg of Cu per cubic decimetre.

Pipette 50,0 cm³ of the 1 g/dm³ standard copper solution (A.2.7) into a 1 dm³ volumetric flask, add 5 cm³ of nitric acid (A.2.6), make up to the mark with water and mix. 1 cm³ of this standard solution contains 50 μg of copper.

A.2.9 Copper, standard solution corresponding to 10 mg of Cu per cubic decimetre.

Pipette 50,0 cm³ of the 50 mg/dm³ standard copper solution (A.2.8) into a 250 cm³ volumetric flask, add 1 cm³ of nitric acid (A.2.6), make up to the mark with water and mix. 1 cm³ of this standard solution contains 10 µg of copper.

NOTE Commercially available standard copper solutions may be used, if preferred, instead of the solutions described in A.2.7, A.2.8 and A.2.9.

A.3 Apparatus

Usual laboratory equipment, plus the following:

A.3.1 Platinum dish, of capacity approximately 35 cm³.

A.3.2 Atomic absorption spectrometer, fitted with an air/acetylene burner.

A.3.3 Analytical balance, capable of weighing to 0,1 mg.

A.4 Procedure

A.4.1 Test portion

Weigh, to the nearest 0,1 mg, approximately 2 g of sample into the platinum dish (A.3.1).

A.4.2 Blank test

Carry out a blank test simultaneously with the determination, using the same reagents and same procedures, but omitting the test portion.

A.4.3 Preparation of the calibration graph

A.4.3.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard copper solution (A.2.9) indicated in Table A.1, dilute to the mark with water and mix.

Table A.1 — Standard calibration solutions for determination of copper

Volume of standard copper solution (A.2.9) cm ³	Corresponding copper content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

A.4.3.2 Spectrometric measurements

Aspirate in turn each of the standard calibration solutions prepared in A.4.3.1 into the flame of the atomic absorption spectrometer (A.3.2) and record their absorbances at a wavelength of 324,7 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

A.4.3.3 Plotting the graph

Plot a graph having, for example, the copper contents, in micrograms per cubic centimetre, as the abscissae and the corresponding values of absorbance as the ordinates.

A.4.4 Determination

A.4.4.1 Preparation of the test solution

Add 10 cm³ of hydrofluoric acid solution (A.2.4) and 0,5 cm³ of sulfuric acid solution (A.2.5) to the test portion prepared in A.4.1, in the platinum dish (A.3.1).

Place the dish and contents on a heated sand tray and evaporate under a fume hood until the evolution of dense white fumes ceases.

Dissolve any residue in 5 cm³ of hydrochloric acid solution (A.2.3) and transfer to a 10 cm³ volumetric flask, rinsing the dish with two 1 cm³ portions of water and adding the rinsings to the flask. Make up to the mark with water, and transfer the solution to a dry polyethylene bottle.

A.4.4.2 Spectrometric measurements

Aspirate the test solution prepared in A.4.4.1 and the blank test solution (see A.4.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 324,7 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest copper content, dilute 5 cm³ of the test solution to 50 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

A.5 Expression of results

By reference to the calibration graph, determine the copper contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total copper content of the sample, $w(\text{Cu})$, expressed in milligrams per kilogram, from the equation

$$w(\text{Cu}) = 10(\rho_1 - \rho_2)/m$$

where

ρ_1 is the copper content, in micrograms per cubic centimetre, of the test solution;

ρ_2 is the copper content, in micrograms per cubic centimetre, of the blank test solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in A.4.4.2, multiply the right-hand side of the equation by 10.

Express the result to the nearest 0,1 mg/kg.

Annex B (normative)

Determination of total manganese content

B.1 Principle

The principle is the same as for the determination of total copper content (see Annex A), except that the absorbance of the test solution is measured at 279,5 nm and is compared with the absorbance of manganese standard calibration solutions. The method is applicable to the determination of manganese contents up to 125 mg/kg, and there is provision for extending the range to 1 250 mg/kg.

WARNING — All recognized health and safety precautions should be taken when performing this method of analysis.

B.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be grade 3 water as defined in ISO 3696:1987.

B.2.1 Acetylene, as specified in A.2.1.

B.2.2 Air, as specified in A.2.2.

B.2.3 Hydrochloric acid solution, as specified in A.2.3.

B.2.4 Hydrofluoric acid solution, as specified in A.2.4.

B.2.5 Sulfuric acid solution, as specified in A.2.5.

B.2.6 Nitric acid solution, as specified in A.2.6.

B.2.7 Manganese, standard solution corresponding to 1 g of Mn per cubic decimetre.

Dissolve $1,000 \text{ g} \pm 0,001 \text{ g}$ of high-purity, oxide-free manganese in a mixture of 50 cm^3 of water and 5 cm^3 of nitric acid (B.2.6) in a 400 cm^3 beaker. Boil under a fume hood to expel oxides of nitrogen. Cool, transfer to a 1 dm^3 volumetric flask, make up to the mark with water and mix.

1 cm^3 of this standard solution contains $1\,000 \text{ }\mu\text{g}$ of manganese.

B.2.8 Manganese, standard solution corresponding to 50 mg of Mn per cubic decimetre.

Pipette $50,0 \text{ cm}^3$ of the 1 g/dm^3 standard manganese solution (B.2.7) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (B.2.6), dilute to the mark with water and mix.

1 cm^3 of this standard solution contains $50 \text{ }\mu\text{g}$ of manganese.

B.2.9 Manganese, standard solution corresponding to 10 mg of Mn per cubic decimetre.

Pipette $50,0 \text{ cm}^3$ of the 50 mg/dm^3 standard manganese solution (B.2.8) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (B.2.6), make up to the mark with water and mix.

1 cm^3 of this standard solution contains $10 \text{ }\mu\text{g}$ of manganese.

NOTE Commercially available standard manganese solutions may be used, if preferred, instead of the solutions described in B.2.7, B.2.8 and B.2.9.

B.3 Apparatus

As specified in A.3.

B.4 Procedure

B.4.1 Test portion

See A.4.1.

B.4.2 Blank test

See A.4.2.

B.4.3 Preparation of the calibration graph

B.4.3.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard manganese solution (B.2.9) indicated in Table B.1, dilute to the mark with water and mix.

Table B.1 — Standard calibration solutions for determination of manganese

Volume of standard manganese solution (B.2.9) cm ³	Corresponding manganese content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

B.4.3.2 Spectrometric measurements

Aspirate in turn each of the standard calibration solutions prepared in B.4.3.1 into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 279,5 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

B.4.3.3 Plotting the graph

Plot a graph having, for example, the manganese contents, in micrograms per cubic centimetre, as the abscissae and the corresponding values of absorbance as the ordinates.

B.4.4 Determination

B.4.4.1 Preparation of the test solution

See A.4.4.1.

B.4.4.2 Spectrometric measurements

Aspirate the test solution prepared in B.4.4.1 and the blank test solution (see B.4.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 279,5 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest manganese content, dilute 5 cm³ of the test solution to 50 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

B.5 Expression of results

By reference to the calibration graph, determine the manganese contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total manganese content of the sample, $w(\text{Mn})$, expressed in milligrams per kilogram, from the equation

$$w(\text{Mn}) = 10(\rho_3 - \rho_4)/m$$

where

ρ_3 is the manganese content, in micrograms per cubic centimetre, of the test solution;

ρ_4 is the manganese content, in micrograms per cubic centimetre, of the blank test solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in B.4.4.2, multiply the right-hand side of the equation by 10.

Express the result to the nearest 0,1 mg/kg.

Annex C (normative)

Determination of total iron content

C.1 Principle

The principle is the same as for the determination of total copper content (see Annex A), except that the absorbance of the test solution is measured at a wavelength of 248,3 nm and is compared with the absorbances of iron standard calibration solutions.

The method is applicable to the determination of iron contents up to 125 mg/kg, and there is provision for extending the range to 2 500 mg/kg.

WARNING — All recognized health and safety precautions should be taken when performing this method of analysis.

C.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be grade 3 water as defined in ISO 3696:1987.

C.2.1 Acetylene, as specified in A.2.1.

C.2.2 Air, as specified in A.2.2.

C.2.3 Hydrochloric acid solution, as specified in A.2.3.

C.2.4 Hydrofluoric acid solution, as specified in A.2.4.

C.2.5 Sulfuric acid solution, as specified in A.2.5.

C.2.6 Iron, standard solution corresponding to 1 g of Fe per cubic decimetre.

Dissolve 1,000 g $\pm$ 0,001 g of high-purity iron in a mixture of 10 cm³ of water and 5 cm³ of hydrochloric acid (C.2.3) in a 100 cm³ beaker. Boil under a fume hood until dissolution is complete. Cool, transfer to a 1 dm³ volumetric flask, make up to the mark with water and mix.

1 cm³ of this standard solution contains 1 000 μ g of iron.

C.2.7 Iron, standard solution corresponding to 50 mg of Fe per cubic decimetre.

Pipette 50,0 cm³ of the 1 g/dm³ standard iron solution (C.2.6) into a 1 dm³ volumetric flask, add 5 cm³ of hydrochloric acid (C.2.3), dilute to the mark with water and mix.

1 cm³ of this standard solution contains 50 μ g of iron.

C.2.8 Iron, standard solution corresponding to 10 mg of Fe per cubic decimetre.

Pipette 50,0 cm³ of the 50 mg/dm³ standard iron solution (C.2.7) into a 250 cm³ volumetric flask, add 1 cm³ of hydrochloric acid (C.2.3), make up to the mark with water and mix.

1 cm³ of this standard solution contains 10 μ g of iron.

NOTE Commercially available standard iron solutions may be used, if preferred, instead of the solutions described in C.2.6, C.2.7 and C.2.8.

C.3 Apparatus

As specified in A.3.

C.4 Procedure

C.4.1 Test portion

See A.4.1.

C.4.2 Blank test

See A.4.2.

C.4.3 Preparation of the calibration graph

C.4.3.1 Preparation of standard calibration solutions

Into a series of six 50 cm³ volumetric flasks, transfer the volumes of 10 mg/dm³ standard iron solution (C.2.8) indicated in Table C.1, dilute to the mark with water and mix.

Table C.1 — Standard calibration solutions for determination of iron

Volume of standard iron solution (C.2.8) cm ³	Corresponding iron content µg/cm ³
0,5	0,1
2,5	0,5
5,0	1,0
10,0	2,0
15,0	3,0
25,0	5,0

C.4.3.2 Spectrometric measurements

Aspirate each of the standard calibration solutions prepared in C.4.3.1 into the flame of the atomic absorption spectrometer and record their absorbances at a wavelength of 248,3 nm, following the instructions of the instrument manufacturer.

Aspirate water into the flame after each measurement.

C.4.3.3 Plotting the graph

Plot a graph having, for example, the iron contents, in micrograms per cubic centimetre, as the abscissae and the corresponding values of absorbance as the ordinates.

C.4.4 Determination

C.4.4.1 Preparation of the test solution

See A.4.4.1.

C.4.4.2 Spectrometric measurements

Aspirate the test solution prepared in C.4.4.1 and the blank test solution (see C.4.2) into the flame of the atomic absorption spectrometer and measure their absorbances at 248,3 nm, following the instructions of the instrument manufacturer. Repeat this procedure and record the mean values of the absorbance of the test solution and the blank test solution.

Aspirate water into the flame after each measurement.

If the absorbance of the test solution is greater than that of the standard calibration solution having the highest iron content, dilute 5 cm³ of the test solution to 100 cm³ with water, repeat the measurements and take the dilution into account in the expression of results.

C.5 Expression of results

By reference to the calibration graph, determine the iron contents corresponding to the absorbances of the test solution and the blank test solution.

Calculate the total iron content of the sample, $w(\text{Fe})$, expressed in milligrams per kilogram, from the equation

$$w(\text{Fe}) = 10(\rho_5 - \rho_6)/m$$

where

ρ_5 is the iron content, in micrograms per cubic centimetre, of the test solution;

ρ_6 is the iron content, in micrograms per cubic centimetre, of the blank test solution;

m is the mass, in grams, of the test portion.

If the test solution was diluted as described in C.4.4.2, multiply the right-hand side of the equation by 20.

Express the result to the nearest 0,1 mg/kg.

Annex D (normative)

Determination of specific surface area

D.1 Principle

Two flasks of equal volume — one containing the test portion, the other empty — are filled with nitrogen under atmospheric pressure at room temperature. Both flasks are then cooled by immersion in liquid nitrogen.

At this temperature, the test portion adsorbs nitrogen, whereby a pressure difference is created between the flask containing the test portion and the reference flask. The pressure difference is measured by means of a differential pressure gauge. The specific surface area is calculated from the measured pressure difference, the nitrogen-gas feed pressure and the mass of the test portion. The method is similar to that described in ISO 4652-1:1994, Clause 4 (method B).

WARNING — All recognized health and safety precautions should be taken when performing this method of analysis.

D.2 Materials

D.2.1 Nitrogen gas, in a cylinder, or other source of pre-purified nitrogen, of recognized analytical quality.

D.2.2 Liquid nitrogen.

D.3 Apparatus

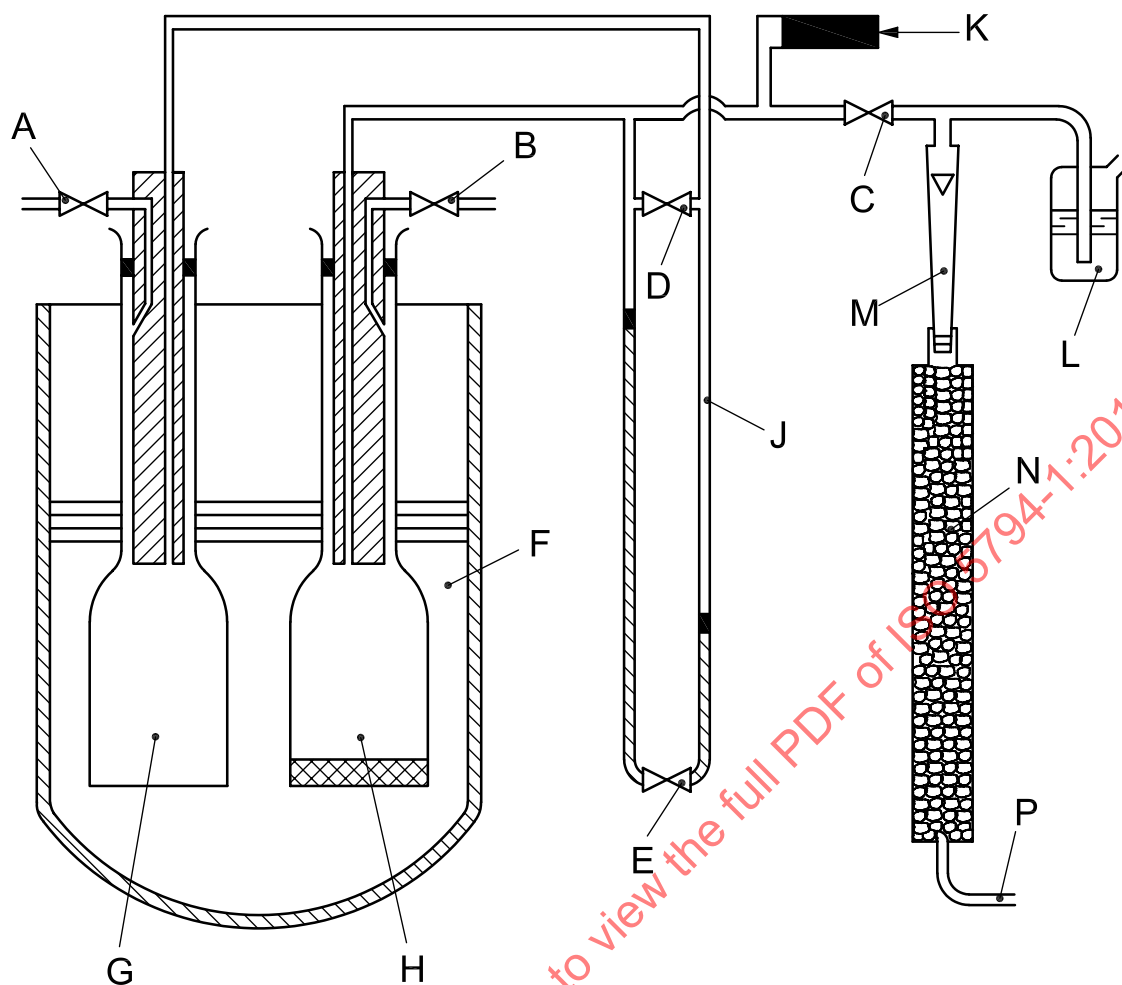
D.3.1 Adsorption apparatus¹⁾ (see Figure D.1), comprising a reference flask (G) and a sample flask (H) mounted with gastight connections. These connections are provided with one valve each (A and B) by means of which the flasks can be connected to the atmosphere. The gas to be adsorbed is fed into each flask through the connection pieces.

The flasks are made of glass which is resistant to sudden changes of temperature, and have a volume of approximately 100 cm³. The volume difference between the two flasks shall not exceed 0,1 %. The flask necks are made of calibrated precision glass tubing with an inside diameter of 5 mm ± 0,02 mm. This ensures that several flasks can be used as sample or reference flasks without having to adjust the compensation volume for each different combination.

A U-tube is mounted between the two flasks, and the arms of the pressure gauge are connected by capillary tubes to the two adsorption flasks. By means of valve D, the two adsorption vessels can be either separated from one another or connected to one another via their capillary tubes. Using valve E, the two liquid arms of the differential pressure gauge can be separated or joined together. The measuring fluid is dibutyl phthalate.

The two arms of the differential pressure gauge are made of calibrated precision glass tubing with an inside diameter of 5 mm ± 0,02 mm. Therefore, any change in volume during gas adsorption can be sufficiently accurately calculated. The feed capillary to the sample flask, owing to its short length, is considered as a compensation volume which is adjusted during preparation of the equipment (see D.7).

1) A suitable adsorption apparatus is the Areameter, available from Juwe GmbH, Fuggerstr. 6, D-41352 Korschenbroich, Germany. This information is given for the convenience of users of this part of ISO 5794 and does not constitute an endorsement by ISO of the apparatus named. Other apparatus may be used provided it complies with the specified requirements.

**Key**

A to E	valves	K	compensation volume
F	cold bath	L	safety valve
G	reference flask	M	flow meter
H	sample flask	N	drying tower
J	differential pressure gauge	P	nitrogen inlet

Figure D.1 — Areameter adsorption apparatus

The gas is introduced into the equipment through valve C. If valves A, B and D are open, the gas flows through both flasks. If valves A and D are closed, the reference flask is shut off and only the sample flask is purged with the gas.

When a measurement is made, only part of the volume enclosed by valves A, B and C is cooled to the measurement temperature by the liquid nitrogen. The remaining volume, which will be at or near room temperature, shall not be more than 10 % of the total volume. The connections to the adsorption flasks are therefore capillaries which almost completely fill the necks of the flasks. In this manner, the volume of gas at room temperature is kept to a minimum.

NOTE Procedures for commissioning new equipment and for carrying out checks are given in D.7.

D.3.2 Control thermostat²⁾, designed to ensure that the adsorption flasks are kept at a constant temperature, and either purged with nitrogen gas or evacuated.

D.3.3 Analytical balance, accurate to 0,1 mg.

D.3.4 Drying oven, capable of maintaining a temperature of $105\text{ °C} \pm 2\text{ °C}$.

D.3.5 Cold bath, containing liquid nitrogen (D.2.2).

D.4 Preparation of the test portion

D.4.1 The maximum reading (400 mm) of the differential pressure gauge corresponds to a surface area of approximately 50 m^2 . The mass of the test portion shall therefore be adjusted so that the difference in liquid levels, Δh , in the differential pressure gauge is as great as possible and at least 50 mm. If the approximate specific surface area is not known, preliminary tests with various test-portion masses shall be performed to establish the most suitable mass for the test portion.

NOTE Table D.1 gives, as a guide, the test-portion masses most suitable for various specific surface areas.

Table D.1 — Test-portion masses suitable for various specific surface areas

Specific surface area m^2/g	Mass of test portion g
20	0,6 to 0,8
30	0,4, to 0,6
40	0,3 to 0,5
80	0,2 to 0,3
120	0,15 to 0,2
140	0,1 to 0,15
> 200	< 0,1

D.4.2 Transfer a suitable amount of silica without pre-drying to a previously tared sample flask by means of a funnel. Introduce the test portion into the flask in such a manner that no material adheres to the walls of the neck. In order to avoid electrostatic charge causing the silica to adhere to the neck of the flask, discharge the flask by putting it on a grounded copper plate before and after weighing.

D.4.3 Determine the mass of the test portion by difference, carrying out both weighings to the nearest 0,1 mg.

D.4.4 In order to determine the actual silica content, the mass of the test portion in the flask shall be corrected for the moisture content. For this purpose, determine the moisture content immediately after weighing the silica into the Areameter flask, using a separate silica test portion, as follows. Weigh, to the nearest 0,1 mg, 2 g of the silica under test into a weighing bottle with a ground-glass stopper. With the weighing bottle open, dry the test portion for 2 h at $105\text{ °C} \pm 2\text{ °C}$ in the oven (D.3.4). Stopper the hot weighing bottle in the oven and allow it to cool to room temperature in a desiccator. Weigh the stoppered weighing bottle plus contents to the nearest 0,1 mg. Calculate the moisture content of the test portion by difference.

2) A suitable thermostat is that designed for the Areameter, available from Juwe GmbH, Fuggerstr. 6, D-41352 Korschenbroich, Germany. This information is given for the convenience of users of this part of ISO 5794 and does not constitute an endorsement by ISO of the apparatus named. Other apparatus may be used provided it complies with the specified requirements.

D.4.5 Before determining the surface area, remove as much adsorbed matter as possible from the surface of the test portion by purging in a flow of nitrogen.

D.4.6 Carry out this desorption in a thermostat-controlled enclosure at 150 °C to 160 °C (preferably 155 °C to 160 °C) for a period of 60 min ± 5 min. Adjust the thermostat thermometer to a height 3 cm above the bottom of the flask. Adjust the nitrogen flow through the flask to 75 cm³/min.

D.4.7 After desorption, allow the test portion to cool to room temperature under a flow of nitrogen, and stopper and store the flask until required for the determination.

D.5 Procedure

D.5.1 Connect flask H containing the prepared test portion to the nitrogen supply and open valves B and C, allowing nitrogen to flow into the flask with valves D, A and E closed.

D.5.2 Open valves D, A and E and place both reference and sample flask in a water bath maintained at 23 °C ± 2 °C, maintaining the flow of nitrogen.

D.5.3 After 10 min to 15 min, determine the pressure difference in the flasks by closing valves A, B, C and D. If a pressure difference exists, re-open the valves in the order D, C, B and A, and continue purging with nitrogen. Close valves A, B, C and D when the pressures are equal.

D.5.4 When pressure equilibrium has been attained, close valve E and stop the nitrogen flow by closing the supply valves.

D.5.5 Wipe the water drops off the flasks, immerse the flasks in the liquid-nitrogen bath (D.3.5) to the lower mark on the neck and, after 1 min, open valve E very slowly.

D.5.6 When the resulting pressure difference has stabilized, read the difference in heights of the liquid in the U-tube arms to the nearest 0,5 mm.

D.5.7 Close valve E. Replace the liquid-nitrogen bath (D.3.5) with a water bath maintained at approximately 40 °C. After a few minutes, start the nitrogen flow and open valves D, C, B, A and E in that order.

D.5.8 When the connections have reached room temperature, close valves A, D and E and disconnect the sample flask with valves B and C open.

D.6 Expression of results

D.6.1 Method of calculation

Calculate the specific surface area, S_m , in square metres per gram, using the equation

$$S_m = 1,174 \times 10^{-7} \left[\frac{(1,05 \times 10^5) - p}{m} \right] \times \left[(13,71 + 6,656 \times 10^{-5} p) \Delta h + \frac{m}{\rho} \left(\frac{p}{77,6} - \frac{p_B}{295} \right) \right]$$

where

p is the equilibrium pressure, in pascals, given by

$$p = \frac{109,6 p_B}{393,1 + (9,82 \times 10^{-3} \Delta h)} - 10,29 \Delta h$$

m is the mass, in grams, of the test portion corrected for the moisture content of the sample;

Δh is the difference, in millimetres, in the heights of the liquid in the U-tube arms;

p_B is the atmospheric pressure, in pascals;

ρ is the density, in megagrams per cubic metre, of the test sample, assumed to be equal to 2,0 Mg/m³.

NOTE For specific surface areas greater than 1 m²/g, the term

$$\frac{m}{\rho} \left(\frac{p}{77,6} - \frac{p_B}{295} \right)$$

may be ignored.

Express the result to the nearest 1 m²/g.

D.6.2 Calculation using a nomogram

Calculation may be simplified by the use of a nomogram (see Figure D.2).

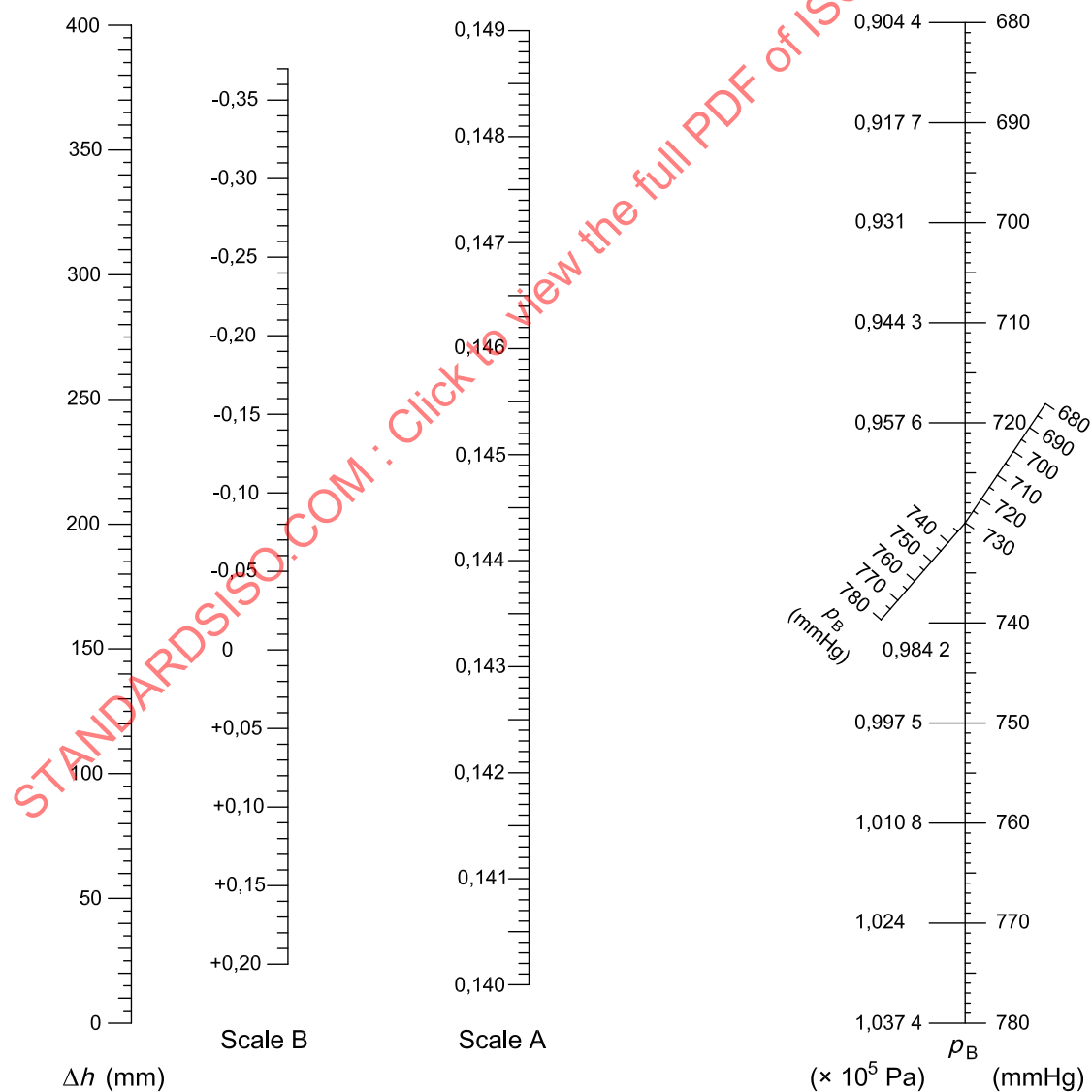


Figure D.2 — Nomogram

Place a straight edge over the nomogram to join the measured value of Δh on the Δh scale with the measured value of p_B on the vertical p_B scale. Record the value at the point of intersection of the line and scale A.

Place a straight edge over the nomogram to join the measured value of Δh on the Δh scale with the measured value of p_B on the inclined, reduced p_B scale. Record the value at the point of intersection of the line and scale B.

The specific surface area, in square metres per gram, is given by the equation

$$S_m = \frac{A \times \Delta h}{m} + \frac{B}{\rho \times p}$$

where

A and B are the values derived from the nomogram as described above;

Δh , m , ρ and p are as defined in D.6.1.

Express the result to the nearest 1 m²/g.

D.7 Notes on procedure — Preparation of the Areameter

D.7.1 General

When commissioning new equipment or when checking existing equipment, carry out the following tests to check whether the compensation volume (K in Figure D.1) is correctly adjusted and that the apparatus is leak-proof.

D.7.2 Volume-equalization test

It is essential for this test that valve D be gastight (see D.7.3).

Connect the empty adsorption flasks to the apparatus, aligning the upper marks on the flask necks with the lower gasket. Then open all the valves and purge the apparatus with nitrogen. Use a flow rate of 2,8 cm³/s $\pm$ 0,15 cm³/s.

While purging, keep the flasks immersed in a water bath at 23 °C $\pm$ 2 °C to the lower mark on the flask necks, so that both flasks attain the same temperature. When this can be assumed to have taken place (allow at least 10 min), seal the apparatus from the atmosphere and separate the flasks from each other by closing valves A, B, C and D in that order. Closing valve D may cause a minor pressure difference. If this pressure difference changes within the next 2 min, complete temperature equilibrium has not been reached between the adsorption flasks. In this case, re-open valves D, C, B and A in that order and again purge the apparatus with nitrogen. Repeat the test after a few minutes. When temperature equilibrium has been reached, close valve E. Remove the water bath, wipe off the adhering water drops and immerse the flasks to the lower mark on the flask necks in a cold bath of boiling nitrogen.

As soon as the flasks have assumed the temperature of the boiling nitrogen (for empty flasks, after approximately 1 min), open valve E very slowly. If the volumes of the sample flask and the reference flask are correctly balanced, there will be no pressure difference between them. In this case, close valve E again and re-open valve D. Then remove the cold bath and replace by a water bath at approximately 40 °C to thaw out the flasks. Remove the warm-water bath as soon as the flasks have reached approximately room temperature. After a few minutes, re-open valves C, B and A in that order, and purge the apparatus with nitrogen.

Cooling and heating the flasks may result in high pressure differences for short periods. This could cause the dibutyl phthalate in the U-tube to enter other parts of the apparatus. It is therefore important that valve E be kept open at the times indicated.

If a pressure difference should arise during the preparation of the apparatus, change the compensation volume (K in Figure D.1) at room temperature in such a way that the volumes on both sides of the differential pressure gauge are equal. Check the volume balance by repeating the above test.

D.7.3 Leak test

If balancing the volumes at the temperature of boiling nitrogen results in a continuously increasing, or very considerable, pressure difference (greater than 400 mm) after valve E has slowly been opened, this is evidence of leaks from the apparatus to the atmosphere (i.e. through valves A, B and C).

The gastightness of valve D cannot be checked by means of the pressure difference, and this valve must therefore be tested separately. To do this, immerse the flasks in the cold bath, close valves B, C and D and open valves A and E. By means of valve A, produce a difference in liquid heights of approximately 300 mm and close valve A.

This difference in height shall not change by more than 1 mm within 10 min.

D.7.4 Operational check

Check the correct operation of the apparatus initially, and periodically during use, by measurement of the surface area of a silica of known specific surface area. The specific surface area of the reference material shall have been measured using the same method.

D.7.5 Maintenance

Replace the dibutyl phthalate in the U-tube if it becomes polluted, or at least once a year. Also replace exhausted silica gel in the drying tower.

Annex E (normative)

Determination of the specific surface area by multipoint nitrogen adsorption test (BET test)

E.1 Scope

E.1.1 This annex specifies a method for the determination of the surface area of precipitated hydrated silicas based on the Brunauer, Emmett and Teller (BET) theory of gas adsorption using multipoint determinations. The test method described in ISO 18852 specifies the sample preparation and treatment, instrument calibration, required accuracy and precision of experimental data, and calculation of the surface area from the data obtained.

E.1.2 The method is used to determine the nitrogen surface area of precipitated silicas with specific surface areas in the range of 1 hm^2/kg to 50 hm^2/kg (10 m^2/g to 500 m^2/g).

E.2 Significance and use

E.2.1 This method is used to measure the surface area of precipitated hydrated silicas that is available to the nitrogen molecule.

E.2.2 Silicas, like other solids, adsorb nitrogen under specified conditions. With increasing partial pressure, coverage of the silica surface increases and, at a certain stage, a monolayer of nitrogen molecules is formed.

NOTE The quantity in this hypothetical monomolecular layer is calculated using the BET equation. Combining this with the area occupied by the nitrogen molecule yields the total surface area of the solid.

E.2.3 The method measures the estimated quantity of nitrogen in the monomolecular layer by adsorption at liquid nitrogen temperature and at several (at least five) partial pressures of nitrogen.

E.2.4 Before a surface area determination can be made, it is necessary that the silica be stripped of any material which may already be adsorbed on the surface. The stripping of adsorbed foreign material (by heating under vacuum while maintaining the hydration of the silica) eliminates two potential errors. The first error is associated with the mass of the foreign material. The second error is associated with the surface area occupied by the foreign material.

E.3 Procedure

E.3.1 Sampling shall be carried out in accordance with ISO 15528.

E.3.2 Carry out the determination by the procedure described in ISO 18852 except that, before starting the determination, the sample shall be pre-dried at $110\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$. When drying hydrated silica, it shall be ensured that the moisture level does not drop below 1 % (preferably staying in the 2 % to 6 % range) because electrostatic build-up makes it difficult to handle and transfer the powder.

E.3.3 The suitability of the statistical thickness surface area (STSA) method for hydrated silicas has not been established yet.

Annex F (normative)

Determination of granule size fractions of granulated precipitated silica

F.1 Principle

This test method covers a procedure to measure the granule size fractions of granulated precipitated silica. It describes the test equipment, sample treatment and evaluation of test results.

A test portion of granulated silica is put on a stack of defined sieves and is shaken for 5 min. The amount of silica passing through all sieves or remaining on the various sieves is determined.

The method is applicable to all granulated silicas.

F.2 Sampling

Samples shall be taken in accordance with ISO 15528 or ISO 1124.

F.3 Apparatus

F.3.1 Sieve shaker³⁾.

F.3.2 Sieves, nominally 200 mm diameter, 25 mm or 45 mm high, of woven metal wire cloth, conforming to ISO 565, having apertures of 300 μm (US standard sieve No. 50) and 75 μm (US standard sieve No. 200).

Other sizes may be added by agreement between the interested parties.

F.3.3 Analytical balance, capable of weighing to 0,001 g.

F.4 Procedures

F.4.1 Weigh, to the nearest 0,01 g, the bottom receiver pan, the 75 μm sieve and the 300 μm sieve.

F.4.2 Weigh, to the nearest 0,01 g, approximately 100 g of the silica sample. Alternatively, 10 g may be used.

F.4.3 Stack the sieves in the following order from bottom to top:

- bottom receiver pan;
- 75 μm sieve;
- 300 μm sieve.

3) A Ro-Tap sieve shaker is satisfactory for this purpose. It is available from W.S. Tyler, 8570 Tyler Boulevard, Mentor, Ohio 44060, USA. This information is given for the convenience of users of this part of ISO 5794 and does not constitute an endorsement by ISO of the apparatus named. Other types of apparatus may be used if they can be shown to lead to the same results.

F.4.4 Transfer the silica sample to the top sieve and install the top sieve cover.

F.4.5 Transfer the sieve assembly to the sieve shaker. Raise the sieve assembly to the holding clamp at the top of the apparatus and tighten with the wing nuts.

F.4.6 Place the hammer in the operating position.

F.4.7 Set the timer of the equipment to 5 min and switch on.

F.4.8 The equipment is switched off automatically after reaching the shaking time set.

F.4.9 Weigh the silica retained on the sieves and in the bottom receiver pan.

F.5 Calculation of test results

The silica in the bottom receiver pan constitutes the fines content. All results shall be expressed as a percentage of the silica test-portion mass determined in F.4.2.

Silica retained = (Vessel + silica) – Empty vessel

$$w_1 = \frac{\text{Mass of silica retained on 300 } \mu\text{m screen}}{\text{Mass of test portion}} \times 100$$

$$w_2 = \frac{\text{Mass of silica retained on 75 } \mu\text{m screen}}{\text{Mass of test portion}} \times 100$$

$$\text{Fines} = \frac{\text{Mass of silica retained in bottom pan}}{\text{Mass of test portion}} \times 100$$

Annex G (normative)

Determination of CTAB surface area

G.1 Scope

This annex specifies a method for determining the hexadecyltrimethyl ammonium bromide (CTAB) surface area which reflects the external, i.e. non-porous, surface area of the silica.

G.2 Principle

A solution of CTAB is added to a test portion of silica. Under agitation, a suspension is generated, leading to adsorption of CTAB by the silica surface.

After separation of the liquid phase, the non-adsorbed CTAB is determined by turbidity titration.

G.3 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be grade 3 water as defined in ISO 3696:1987.

G.3.1 Buffer solution of pH 9,6, $c(\text{H}_3\text{BO}_3) = 0,05 \text{ mol/dm}^3$.

To a 1 000 cm³ volumetric flask containing 500 cm³ of water, add 3,101 g of boric acid, 3,708 g of potassium chloride and, with a burette, 36,85 cm³ of 1 M sodium hydroxide. After the solids have dissolved, fill the volumetric flask to 1 000 cm³ with water and homogenize with a magnetic stirrer.

G.3.2 Hexadecyltrimethyl ammonium bromide (CTAB) solution, $c(\text{CTAB}) = 0,015 \text{ mol/dm}^3$.

In a 1 000 cm³ volumetric flask containing 350 cm³ of buffer solution (G.3.1) and approximately 500 cm³ of water, dissolve 5,50 g of reagent-grade CTAB, purity > 99 %. Fill up to the mark with water and warm the solution to a temperature of 27 °C to 37 °C to facilitate dissolution. Cool to a temperature between 22 °C and 25 °C before using.

Do not store the solution or allow it to cool below 22 °C since this will result in slow crystallization of the CTAB.

G.3.3 Sodium di(2-ethylhexyl) sulfosuccinate (aerosol OT) solution, $c(\text{aerosol OT}) = 0,003 \text{ mol/dm}^3$.

Dissolve 1,730 g of aerosol OT in 1 000 cm³ of water by stirring vigorously with a magnetic stirrer for 48 h. Allow to stand an additional 12 days before use.

Cap the solution tightly and store in a cool place. Since aerosol OT solution may be subject to slow biodegradation, do not store the solution for more than 2 months.

Once opened, keep solid aerosol OT in a desiccator.

G.4 Apparatus

G.4.1 Automatic titration equipment, with a) a photoelectric detector or photometer measuring the light transmittance at a wavelength of 550 nm, and b) a 20 cm³ burette.

G.4.2 Analytical balance, 0,1 mg sensitivity.

G.4.3 Magnetic stirrer.

G.4.4 Magnetic spinbar.

G.4.5 Microfiltration membrane filter discs, 47 mm diameter, pore size 0,1 µm.

G.4.6 Filter holder.

G.4.7 Sampling cylinder, 30 cm³, stainless steel, suitable for 0,7 MPa (7 bar) pressure.

G.4.8 Centrifuge.

G.4.9 Centrifuge tubes.

G.4.10 Syringe.

G.4.11 Filter for syringe, pore size preferably 0,45 µm.

G.4.12 Glass vials.

G.4.13 Pipettes, 5 cm³, 10 cm³, 30 cm³, class A.

G.4.14 Gravity-convection drying oven, capable of maintaining a temperature of 105 °C ± 1 °C.

G.4.15 Volumetric flasks, 1 000 cm³.

G.4.16 Titration beakers.

G.4.17 Combined glass/calomel electrode.

G.4.18 pH-meter (if automatic titrator is not used for pH adjustment).

G.4.19 Mortar and pestle.

G.4.20 Sieve, 150 µm, with receiver pan.

G.5 Sample preparation

The silica is tested without prior drying. Powder the granulated silica gently with a mortar and pestle and then pass it through a 150 µm sieve.

G.6 Procedure

G.6.1 Test portion

Weigh, to the nearest 0,1 mg, a test portion of the sieved silica into a glass vial and record the mass. Appropriate test portions may be selected as indicated in Table G.1.