International Standard 5794/1

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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

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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.

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Rubber compounding ingredients — Silica, precipitated, hydrated — Part 1 : Non-rubber tests

1 Scope and field of application

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

ISO 5974/2 specifies methods of test for precipitated hydrated silica in compounded rubber.

2 References

ISO 787, *General methods of test for pigments and extenders*

— *Part 2 : Determination of matter volatile at* 105 °C.

— *Part 9 : Determination of pH value of an aqueous suspension.*

— *Part 10 : Determination of density — Pyknometer method.*

— *Part 18 : Determination of residue on sieve by a mechanical flushing procedure.*

ISO 842, *Raw materials for paints and varnishes — Sampling.*

ISO 3262, *Extenders for paints.*

ISO 4652, *Rubber compounding ingredients — Carbon black — Determination of specific surface area — Nitrogen adsorption methods.*

3 Definition

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 842.

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 dried sample, % (m/m)	ISO 3262, clause 17, except that in the expression of results the denominator shall be M_0, where M_0 is the mass in grams of the test portion taken in sub-clause 11.2 of ISO 3262, not the mass of ignited residue obtained in 11.2.
Colour	ISO 3262, clause 7
Residue on sieve (nominal aperture size 45 µm) :	
— for silica in powder form	ISO 3262, clause 8
— for silica in other forms	ISO 787/18
Matter volatile at 105 °C (loss on heating)	ISO 787/2 (Use a test portion of 2 g weighed to the nearest 0,1 mg)
Loss on ignition at 1 000 °C on dried sample	ISO 3262, clause 11
pH of slurry	ISO 787/9
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 annex D
Density, g/cm^3	ISO 787/10

Annex A

Determination of total copper content

(This annex forms an integral part of the Standard.)

A.1 Principle

A test portion is digested with hydrofluoric acid and sulfuric acid and the silicon is volatilised 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 for the determination of copper contents up to 125 mg/kg, and there is provision for extending the range to 1 250 mg/kg.

A.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

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

A.2.1 Acetylene, compressed gas supply.

A.2.2 Air, compressed gas supply.

A.2.3 Hydrochloric acid, 10 % (m/m) solution.

Dilute 35 % (m/m) hydrochloric acid solution (20 cm^3) (ϱ_{20} = 1,18 g/cm^3) with water (50 cm^3).

A.2.4 Hydrofluoric acid, 40 % (m/m) solution (ϱ_{20} = 1,13 g/cm^3).

A.2.5 Sulfuric acid, 98 % (m/m) solution (ϱ_{20} = 1,84 g/cm^3).

A.2.6 Copper, standard solution corresponding to 1 g of Cu per cubic decimetre.

Dissolve 1,000 ± 0,001 g of high purity copper turnings in a mixture of 10 cm^3 of water and 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3) in a 100 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 µg of copper.

A.2.7 Copper, standard solution corresponding to 50 mg of Cu per cubic decimetre.

Pipette 50,0 cm^3 of the standard copper solution (A.2.6) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), make up to the mark with water and mix.

1 cm^3 of this standard solution contains 50 µg of copper.

A.2.8 Copper, standard solution corresponding to 10 mg of Cu per cubic decimetre.

Pipette 50,0 cm^3 of the standard copper solution (A.2.7) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), make up to the mark with water and mix.

1 cm^3 of this standard solution contains 10 µg of copper.

NOTE — Commercially available standard copper solutions may be used, if preferred, instead of A.2.6, A.2.7 and A.2.8.

A.3 Apparatus

Usual laboratory equipment and

A.3.1 Platinum dish, of capacity approximately 35 cm^3.

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

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

A.4 Procedure

A.4.1 Test portion

Weigh, to the nearest 0,001 g, 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 cm^3 volumetric flasks, transfer the volumes of the standard copper solution (A.2.8) indicated in table 2, dilute to the mark with water and mix.

Table 2 — Standard calibration solutions for determination of copper

Volume of standard copper solution (A.2.8)	Corresponding copper content
cm^3	$\mu g/cm^3$
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 each of the standard calibration solutions, in turn, 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 abscissae and the corresponding values of absorbance as ordinates.

A.4.4 Determination

A.4.4.1 Preparation of the test solution

Add 10 cm^3 of the hydrofluoric acid solution (A.2.4) and 0,5 cm^3 of sulfuric acid solution (A.2.5) to the test portion (A.4.1) in the 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 cm^3 of the hydrochloric acid solution (A.2.3) and transfer to a 10 cm^3 volumetric 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 (A.4.4.1) and the blank test solution (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 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 cm^3 of the test solution to 50 cm^3 with water, repeat the measurement 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.

The total copper content of the sample, expressed in milligrams per kilogram, is given by the formula.

$$\frac{10\,(M_1 - M_2)}{m}$$

where

M_1 is the copper content, in micrograms per cubic centimetre, of the test solution;

M_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 formula by 10.

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

A.6 Test report

The test report shall include the following information :

a) all details required for complete identification of the sample;

b) the test conditions;

c) the result obtained for each sample;

d) any deviations from the procedure specified which might have affected the results;

e) a reference to annex A of this International Standard.

Annex B

Determination of total manganese content

(This annex forms an integral part of the Standard.)

B.1 Principle

The principle is the same as for the determination of total copper content (see clause A.1) except that the absorbance of the test solution is measured at 279,5 nm and is compared with the absorbance of standard calibration manganese solutions.

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

B.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

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

B.2.1 Acetylene.

See annex A, sub-clause A.2.1.

B.2.2 Air.

See annex A, sub-clause A.2.2.

B.2.3 Hydrochloric acid solution.

See annex A, sub-clause A.2.3.

B.2.4 Hydrofluoric acid solution.

See annex A, sub-clause A.2.4.

B.2.5 Sulfuric acid solution.

See annex A, sub-clause A.2.5.

B.2.6 Manganese, standard solution corresponding to 1 g of Mn per cubic decimetre.

Dissolve 1,000 ± 0,001 g of high purity, oxide-free manganese in a mixture of 50 cm^3 of water and 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3) 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 µg of manganese.

B.2.7 Manganese, standard solution corresponding to 50 mg of Mn per cubic decimetre.

Pipette 50,0 cm^3 of the standard manganese solution (B.2.6) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), dilute to the mark with water and mix.

1 cm^3 of this standard solution contains 50 µg of manganese.

B.2.8 Manganese, standard solution corresponding to 10 mg of Mn per cubic decimetre.

Pipette 50,0 cm^3 of the standard manganese solution (B.2.7) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), make up to the mark with water and mix.

1 cm^3 of this standard solution contains 10 µg of manganese.

NOTE — Commercially available standard manganese solutions may be used, if preferred, instead of B.2.6, B.2.7 and B.2.8.

B.3 Apparatus

As specified in annex A, clause A.3.

B.4 Procedure

B.4.1 Test portion

See annex A, sub-clause A.4.1

B.4.2 Blank test

See annex A, sub-clause 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 cm^3 volumetric flasks, transfer the volumes of the standard manganese solution (B.2.8) indicated in table 3, dilute to the mark with water and mix.

Table 3 — Standard calibration solutions for determination of manganese

Volume of standard manganese solution (B.2.8)	Corresponding manganese content
cm^3	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 each of the standard calibration solutions, in turn, 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 abscissae and the corresponding values of absorbance as ordinates.

B.4.4 Determination

B.4.4.1 Preparation of the test solution

See annex A, sub-clause A.4.4.1.

B.4.4.2 Spectrometric measurements

Aspirate the test solution (B.4.4.1) and the blank test solution (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 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 cm^3 of the test solution to 50 cm^3 with water, repeat the measurement 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.

The total manganese content of the sample, expressed in milligrams per kilogram, is given by the formula

$$\frac{10\,(M_3 - M_4)}{m}$$

where

M_3 is the manganese content, in micrograms per cubic centimetre, of the test solution;

M_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 formula by 10.

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

B.6 Test report

The test report shall include the following information :

a) all details required for complete identification of the sample;

b) the test conditions;

c) the result obtained for each sample;

d) any deviations from the procedure specified which might have affected the results;

e) a reference to annex B of this International Standard.

Annex C

Determination of total iron content

(This annex forms an integral part of the Standard.)

C.1 Principle

The principle is the same as for the determination of total copper content (see clause A.1) except that the absorbance of the test solution is measured at a wavelength of 248,3 nm and is compared with the absorbances of standard calibration iron solutions.

The method is applicable for the determination of iron contents up to 125 mg/kg and the there is provision for extending the range to 2500 mg/kg.

C.2 Reagents and materials

All reagents shall be of recognized analytical grade. The water used shall be distilled water or water of equivalent purity.

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

C.2.1 Acetylene.

See annex A, sub-clause A.2.1.

C.2.2 Air.

See annex A, sub-clause A.2.2.

C.2.3 Hydrochloric acid solution.

See annex A, sub-clause A.2.3.

C.2.4 Hydrofluoric acid solution.

See annex A, sub-clause A.2.4.

C.2.5 Sulfuric acid solution.

See annex A, sub-clause A.2.5.

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

Dissolve 1,000 ± 0,001 g of high purity iron in a mixture of 10 cm^3 of water and 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3) in a 100 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 µg of iron.

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

Pipette 50,0 cm^3 of the standard iron solution (C.2.6) into a 1 dm^3 volumetric flask, add 5 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), dilute to the mark with water and mix.

1 cm^3 of this standard solution contains 50 µg of iron.

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

Pipette 50,0 cm^3 of the standard iron solution (C.2.7) into a 250 cm^3 volumetric flask, add 1 cm^3 of nitric acid (ϱ_{20} = 1,42 g/cm^3), make up to the mark with water and mix.

1 cm^3 of this standard solution contains 10 µg of iron.

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

C.3 Apparatus

As specified in annex A, clause A.3.

C.4 Procedure

C.4.1 Test portion

See annex A, sub-clause A.4.1

C.4.2 Blank test

See annex A, sub-clause 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 cm^3 volumetric flasks, transfer the volumes of the standard iron solution (C.2.8) indicated in table 4, dilute to the mark with water and mix.

Table 4 — Standard calibration solutions for determination of iron

Volume of standard iron solution (C.2.8)	Corresponding iron content
cm^3	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, in turn, 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 abscissae and the corresponding values of absorbance as ordinates.

C.4.4 Determination

C.4.4.1 Preparation of the test solution

See annex A, sub-clause A.4.4.1.

C.4.4.2 Spectrometric measurements

Aspirate the test solution (C.4.4.1) and the blank test solution (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 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 cm^3 of the test solution to 100 cm^3 with water, repeat the measurement 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.

The total iron content of the sample, expressed in milligrams per kilogram, is given by the formula.

$$\frac{10\,(M_5 - M_6)}{m}$$

where

M_5 is the iron content, in micrograms per cubic centimetre, of the test solution;

M_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 formula by 20.

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

C.6 Test report

The test report shall include the following information :

a) all details required for complete identification of the sample;

b) the test conditions;

c) the result obtained for each sample;

d) any deviations from the procedure specified which might have affected the results;

e) a reference to annex C of this International Standard.

Annex D

Determination of specific surface area — Method using an Areameter apparatus

(This annex forms an integral part of the Standard.)

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 feed pressure and the mass of the test portion.

The method is similar to that described in ISO 4652, clause 4 (method B).

D.2 Materials

D.2.1 Nitrogen, in a cylinder, or other source of prepurified nitrogen, of recognized analytical quality.

D.2.2 Liquid nitrogen.

D.3 Apparatus

D.3.1 Adsorption apparatus[1] (see figure 1), comprising a reference flask (7) and a sample flask (8) mounted with gas-tight connections.

These connections are provided with one valve each (1 and 2) by means of which the flasks can be connected with the atmosphere. The gas to be adsorbed is fed into each flask through the connection pieces.

D.3.1.1 The flasks are made of glass which is resistant to sudden changes of temperature and have a volume of approximately 100 cm^3. The volume difference between the two flask necks shall not exceed 0,1 %.

The flask necks are made of calibrated precision glass tubes with an inside diameter of 5 ± 0,02 mm. This ensures that several flasks can be used as sample or reference flasks without needing to adjust the equalizing volume for every combination.

D.3.1.2 A U-tube is mounted between the two flasks, and the legs of the pressure gauge are connected by capillary tubes to the two adsorption flasks. By means of valve 4, the two adsorption vessels can be either separated from one another or connected to one another via their capillary tubes. Using valve 5, both liquid legs of the differential pressure gauge can be separated or joined together. The measuring fluid is dibutylphthalate.

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

The gas is allowed into the equipment through valve 3. If valves 1, 2 and 4 are open, the gas flows through both flasks. If valves 1 and 4 are closed, the reference flask is shut off and only the sample flask is rinsed with the gas.

During measurement, only part of the volume enclosed by valves 1, 2 and 3 is cooled to the measuring temperature by the liquid nitrogen. The remaining volume, at room temperature, may be only 10 % of the total volume. The connections to the adsorption flasks are therefore capillaries which almost completely fill out 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 control purposes are given in clause D.7.

D.3.2 Regulating thermostat[2], permitting maintenance of the adsorption flasks (with the test portions) at a constant temperature, and either rinsing with dry nitrogen or evacuation.

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

D.3.4 Drying oven, capable of being controlled at 105 ± 2 °C.

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

1) A suitable adsorption apparatus is available commercially. Details may be obtained from the Secretariat of ISO/TC 45 (BSI) or ISO Central Secretariat. Other equipment may be used provided it complies with the specified requirements.

2) A suitable thermostat is available commercially. Details may be obtained from the Secretariat of ISO/TC 45 (BSI) or ISO Central Secretariat. Other equipment may be used provided it complies with the specified requirements.

D.4 Preparation of the sample

D.4.1 The maximum indication (400 mm) on the differential pressure gauge corresponds to a surface area of approximately 50 m^2. The mass of the test portion must therefore be adjusted so that Δh on 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 masses of test portion shall be performed to establish the most suitable mass of test portion.

NOTE — As a guide, table 5 gives masses of test portion according to specific surface area.

Table 5 — Mass of test portion according to specific surface area

Specific surface area	Mass of test portion
m^2/g	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 Dry the sample for 2 h in the drying oven (D.3.4), controlled at 105 ± 2 °C. Transfer a suitable amount of sample to the previously tared sample flask by means of a funnel, introducing the test portion into the flask in such a manner that no material adheres to the walls of the neck.

Determine the mass of sample by difference, carrying out both weighings to the nearest 0,1 mg.

D.4.3 Before the determination, remove as much as possible of the matter that has already been adsorbed from the surface of the test portion. Carry out desorption by rinsing in a flow of nitrogen. This desorption shall be carried out in a thermoregulator at 150 to 160 °C (preferably 155 to 160 °C), the desorption time being 65 ± 5 min. The nitrogen flow in the sample flask shall be adjusted to 75 cm^3/min.

D.4.4 After desorption, cool the test portion to room temperature under a flow of nitrogen and stopper and store the flasks until required for the determination.

D.5 Procedure

D.5.1 Connect the sample flask containing the prepared test portion to the nitrogen source and open valves 2 and 3.

D.5.2 Open valves 4, 1 and 5 and place the flasks in a water bath controlled at 23 ± 2 °C.

D.5.3 After 10 to 15 min, determine the pressure difference in the flasks by closing valves 1, 2, 3 and 4. If a pressure difference exists, reopen the valves in the order 4, 3, 2 and 1 and continue rinsing with nitrogen. Close valves 1, 2, 3 and 4 when the pressure is equal.

D.5.4 When pressure equilibrium is attained, close valve 5 and stop the nitrogen flow by closing the valves.

D.5.5 Wipe off the water drops and immerse the flasks in the liquid nitrogen bath (D.4.3.5) to the lower mark on the neck and, after 1 min, open valve 5 very slowly.

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

D.5.7 Close valve 5 and open valve 4. Replace the cold bath with a water bath controlled at approximately 40 °C. After a few minutes, start the nitrogen flow and open valves 3, 2, 1 and 5 in that order.

D.5.8 As soon as the connections have reached room temperature, close valves 1, 4 and 5 and disconnect the sample flask.

D.6 Expression of results

D.6.1 Method of calculation

Calculate the specific surface area, S_m, in square metres per gram, from the formula

$$S_m = 1{,}187 \times 10^{-7} \left[\frac{(1{,}044 \times 10^5) - p}{m}\right] \times \left[\left(13{,}645\,8 + (6{,}65 \times 10^{-5}\, p)\right) \Delta h + \frac{1}{p\varrho}\left(\frac{p}{77{,}6} - \frac{p_B}{295}\right)\right]$$

where

p is the equilibrium pressure, in pascals :

$$p = \frac{105{,}55\, p_B}{393{,}11 + (0{,}004\,9\, \Delta h)} - 10{,}2\, \Delta h$$

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

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

p_B is the atmospheric pressure, in pascals;

ϱ is the density, in grams per cubic centimetre, of the test sample, (assumed to be equal to 2,0 g/cm^3).

NOTE — For specific surface areas greater than 1 m^2/g, the term $\frac{1}{p\varrho}\left(\frac{p}{77{,}6} - \frac{p_B}{295}\right)$ may be ignored.

Express the result to the nearest 1 m^2/g.

D.6.2 Calculation using a nomogram

The calculation may be simplified by the use of a nomogram (see figure 2).

Draw a straight line connecting the measured value of Δh on the vertical 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.

Draw a straight line connecting the measured value of Δh on the vertical 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 formula

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

where

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

Δh, m, ϱ and p have the same meanings as in D.6.1.

Express the result to the nearest 1 m^2/g.

D.7 Notes on procedure — Preparation of the Areameter

D.7.1 General

When commissioning new equipment or for control purposes, carry out tests to check whether the equalizing volume (see 10 in figure 1) is correctly adjusted and whether the apparatus is leakproof.

D.7.2 Test for volume equalization

The volume equalization balance pre-supposes the tightness of valve 4 (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 valves and rinse the apparatus with nitrogen. The flow rate should be 2,8 ± 0,15 cm^3/s.

While rinsing, immerse the flasks in a water bath at 23 ± 2 °C to the lower mark on the flask neck, so that both flasks may attain the same temperature. As soon as equality of temperature is expected (after at least 10 min), seal the apparatus from the atmosphere and separate the flasks from each other by closing valves 1, 2, 3 and 4 in that order. Closing valve 4 may cause a minor pressure differential. If this pressure differential changes within the next 2 min, complete temperature balance has not been achieved within the adsorption flasks. In this case, reopen valves 4, 3, 2 and 1 in that order and again rinse the apparatus with nitrogen. Repeat the test after a few minutes. When temperature balance is achieved, again close valve 5. Remove the water bath, wipe off the adhering water drops and immerse the flasks to the lower marks 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 5 very slowly. If the volumes of the sample flask and the reference flask are correctly balanced, no pressure difference will be present. In this case, again close valve 5 and reopen valve 4. Then remove the cold bath and replace by a water bath at approximately 40 °C to thaw the flasks. Remove the warm water bath as soon as the flasks have reached approximately room temperature. After a few minutes reopen valves 3, 2 and 1 in that order and rinse the apparatus with nitrogen.

Cooling and heating of the flasks may result in greater pressure differentials for a short time. This could cause the dibutylphthalate in the U-tube to enter other parts of the apparatus; valve 5 must, therefore, be open during the indicated stages.

If a pressure differential should arise during the preparation of the apparatus, change the equalizing volume (see 10 in figure 1) at room temperature in such a way that the volumes on both sides of the differential pressure gauge are equal. For control of the volume balance, repeat the above test.

D.7.3 Leak test

If balancing the volumes at the temperature of boiling nitrogen shows continuously increasing, or very considerable, pressure differentials (greater than 400 mm) after valve 5 has slowly been opened, this is evidence of leaks from the apparatus to the atmosphere (i.e. valves 1, 2 and 3).

The tightness of valve 4 cannot be checked by pressure differential and must be tested separately. To do this, immerse the flasks in the cold bath, close valves 2, 3 and 4 and open valves 1 and 5. By means of valve 1, produce a pressure differential giving a difference in liquid heights of 300 mm and again close valve 1.

The difference in height should not change by more than 1 mm within 10 min.

D.7.4 Operational test

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

D.7.5 Maintenance

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