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Third edition
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Rubber compounding ingredients — Determination of multipoint nitrogen surface area (NSA) and statistical thickness surface area (STSA)

Ingrédients de mélange du caoutchouc — Détermination de la surface par adsorption d'azote (NSA) et de la surface par épaisseur statistique (STSA) par méthode multipoints

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This third edition cancels and replaces the second edition (ISO 18852:2012), which has been technically revised with the following changes:

- Clause 6: deletion of the description of what operators do not have to do; specification of what operators have to do. The verification of measured values was moved to Clause 8 for measurement procedure;
- Clauses 7 and 10: addition of explanations for operators to carry out the procedure easily;
- Clause 8: the description for selecting data points has been modified;
- the specification of sample mass has been moved to Clause 7 for sample preparation, and the previous Clause 9 was deleted.

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

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard 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 to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies a method for the determination of the nitrogen surface area (NSA) of carbon blacks and other rubber compounding ingredients, like silicas and zinc oxides, based on the Brunauer, Emmett and Teller (BET) theory of gas adsorption using a multipoint determination as well as the determination of the statistical thickness surface area (STSA), otherwise known as the external surface area. STSA, however, is not applicable to silica and zinc oxide.

The method can also be used for verifying “single-point” procedures described in ISO 4652 and other standards.

2 Normative references

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

ISO 4652:2012, *Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Single-point procedures*

ISO 5794-1:2010, *Rubber compounding ingredients — Silica, precipitated, hydrated — Part 1: Non-rubber tests*

3 Principle

A sample of carbon black, silica, zinc oxide, etc., is placed in a cell of known volume and degassed. Known volume of nitrogen gas is dosed into the cell that is kept at the temperature of liquid nitrogen. The pressure in the cell decreases to the equilibrium due to the adsorption by the sample. The adsorbed amount at the equilibrium is derived from the difference between the amount of the dosed gas and that of remainder in the cell. The pressure is measured together with the temperature in the system, and the volume of the system is measured with a gas that does not adsorb such as helium before the test. NSA is determined by the BET analysis on the adsorption amount obtained, and STSA is determined by t-plot analysis.

4 Apparatus

4.1 Automatic volumetric adsorption measurement apparatus, consisting of a pressure gauge or transducer, a calibration volume, a Dewar flask and all other accessories required for the analysis.

The pressure gauge or transducer shall have the ±0,25 % accuracy of full scale at the range from 0 kPa to 133 kPa.

Calibration volume is where the volume of the nitrogen to be adsorbed is measured and shall have a known internal volume with a valve or stopcock. It shall have been calibrated by its manufacturer prior to testing.

Sample port volume is where the adsorption to samples takes place, and the pressure at adsorption equilibrium described in Clause 3 is the pressure of this part. A connector connects the apparatus with an adsorption cell.

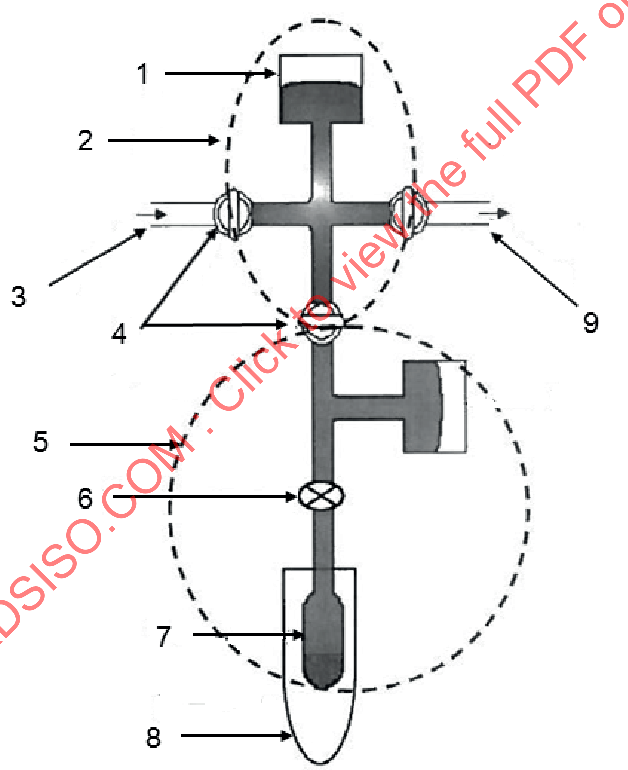
NOTE Commercially, there are two types of the apparatus with different calibration method for the volume of the adsorption cell; those which a calibration factor is applied to the volume of the blank cell determined prior to testing, and those which the volume of the cell with a sample is directly measured during testing (with or without parallel measurement of the volume of another blank cell). Either type is suitable.

4.2 Adsorption cell (hereinafter called "cell"), made of glass and capable of maintaining a vacuum at a pressure 2,7 Pa or below when connected to the adsorption apparatus.

A stopper or valve needs to be attached in order to avoid adsorption after drying.

4.3 Analytical balance, with 0,1 mg sensitivity.

4.4 Degassing station and heating mantle, capable of maintaining the temperatures in Table 1 together with vacuum suction or purge gas flow in order to perform degassing procedure specified in Clause 7.



Key

1	pressure gauge or transducer	6	connector
2	calibration volume	7	adsorption cell
3	gas dosed	8	Dewar flask
4	valve	9	to vacuum pump
5	sample port volume		

Figure 1 — Diagram of adsorption measurement apparatus

5 Reagents

5.1 Liquid nitrogen, 99,9 % or higher purity.

5.2 Ultra-high-purity nitrogen gas, 99,995 % or higher purity.

5.3 Ultra-high-purity helium gas, 99,99 % or higher purity.

NOTE Helium is used for the calibration of the volume of the automatic volumetric adsorption measurement apparatus since it does not adsorb to the cell or sample.

6 Preparation of automatic volumetric adsorption measurement apparatus

6.1 Turn on the automatic volumetric adsorption measurement apparatus and computer.

6.2 Connect the cylinders of helium and nitrogen to the automatic volumetric adsorption measurement apparatus with gas tubes, and check if the secondary pressure of the regulator is as specified by the manufacturer of the apparatus.

6.3 Check if there is no leakage between the connected tubes.

6.4 Carry out gas purging for the tubes to the apparatus when the cylinders are replaced or the apparatus is not used for a month or longer.

6.5 Verify periodically that the error sources in the apparatus have been appropriately minimised in accordance with the user's manual.

7 Sample preparation

7.1 General

Prior to the determination of NSA or STSA, adsorbed contaminants such as atmospheric molecules shall be removed from the sample surface (= degassing). The degassing conditions vary by the material measured and shall be as given in Table 1.

Table 1 — Degassing condition

Material	Temperature °C	Time, minimum h	Reference
Carbon black	300 ± 10	0,5	ISO 4652-1:2012, 3.6.1.2, 4.4, 5.5.6, 6.7.4, and 6.7.5
Silica	155 ± 5	1,0	ISO 5794-1:2010, D.4.6 and E.3.2
Zinc oxide (Type A or B) [a]	300 ± 10	0,5	
Zinc oxide (Type C)[a]	155 ± 5	1,0	ISO 5794-1:2010, D.4.6

[a] The various zinc oxide grades are listed in Table D.1 of ISO 9298:1995.

7.2 Vacuum suction method

7.2.1 After degassing a blank cell by vacuum suction, fill the cell with nitrogen gas (5.2) or helium gas (5.3) of atmospheric pressure. Insert a glass rod into the adsorption cell stem, if recommended by the manufacturer of the apparatus, to reduce the dead volume. Disconnect the cell from the adapter and promptly seal it with a stopper or valve. Weigh the cell to the nearest 0,1 mg and record the mass m1.

7.2.2 Weigh a sample dried in advance so that the NSA of the sample is equivalent to 20 m^2 to 50 m^2, and put it in the cell. Drop the sample clinging on the cell stem into the cell with a pipe cleaner.

7.2.3 Connect the cell containing a sample to the degassing station and degas under vacuum suction with heating in accordance with the operating instructions.

7.2.4 After degassing, fill the cell with the gas, of atmospheric pressure, used in 7.2.1. Disconnect the cell from the adapter and promptly seal it with a stopper or valve. Weigh the cell to the nearest 0,1 mg and record the mass m_2.

7.2.5 Calculate the sample mass as follows:

$$m_0 = m_2 - m_1 \quad (1)$$

where

m_0 is the sample mass, expressed in grams;

m_2 is the mass of the cell, glass rod, gas in the cell, sample and stopper or valve, expressed in grams;

m_1 is the mass of the cell, glass rod, gas in the cell and stopper or valve, expressed in grams.

7.3 Purge gas flow method

7.3.1 Connect a blank cell to the adapter and open the valve connected to the cell. Insert a gas tube for nitrogen gas (5.2) or helium gas (5.3) to the bottom of the cell and fill the cell with the gas. Disconnect the cell from the adapter and promptly seal it with a stopper or valve. Weigh the cell to the nearest 0,1 mg and record the mass m_1.

7.3.2 Weigh a sample dried in advance so that the NSA of the sample is equivalent to 20 m^2 to 50 m^2, and put it in the cell. Drop the sample clinging on the cell stem into the cell with a pipe cleaner.

7.3.3 Connect the cell containing a sample to the adapter and open the valve connected to the cell. Insert the gas tube used in 7.3.1 again to the bottom of the cell and apply an appropriate amount of gas flow so that the sample is not stirred up. While applying the gas, heat the sample in accordance with a condition in Table 1 until the mass becomes constant.

The degassing time might vary significantly from sample to sample, and a reasonable margin of excess time is recommended.

7.3.4 After degassing, disconnect the cell from the adapter and promptly seal it with a stopper or valve. Weigh the cell to the nearest 0,1 mg and record the mass m_2.

7.3.5 Calculate the sample mass m_0 as given in 7.2.5.

8 Measurement procedure

8.1 Measurement

8.1.1 Since most of the operations are conducted automatically, it is important to become thoroughly familiar with the procedures and to follow carefully the operating instructions.

8.1.2 Determine the saturation vapour pressure of the liquid nitrogen (5.1) in a Dewar flask by measuring its temperature. This pressure is affected by the purity of the liquid nitrogen and the ambient pressure. Impurities dissolved in the liquid nitrogen such as oxygen usually cause the temperature of the liquid nitrogen to increase, thus the saturation vapour pressure increases by some kilopascals.

NOTE Some apparatuses are capable of measuring the saturation vapour pressure automatically.

8.1.3 Input relative-pressure range, number of data points (see 8.2), saturation vapour pressure, sample mass and other information to the computer in accordance with the operating instructions. This relative pressure is expressed as a fraction of saturation vapour pressure P_0 and measured pressure P (P/P_0).

8.1.4 Check if there is no defect on the O-ring before measurement.

NOTE If this procedure is not done appropriately, a leakage which leads to an underestimation of the value might occur during the measurement.

8.1.5 Connect the cell containing the degassed sample (Clause 7) to the adapter. A glass rod may be inserted into the cell stem in order to decrease the volume of the cell and eventually to improve precision.

NOTE While the cell stem is in contact with the liquid nitrogen, the level of the liquid nitrogen might affect the cell stem. Hence, some error to the measurement might occur.

8.1.6 Start the measurement. Adsorbed amount is calculated at the input relative pressures (see 8.1.3) by the apparatus.

8.2 Selection of data points and determination of nitrogen surface area (NSA)

8.2.1 General

NSA is usually determined by making the BET plot and selecting a certain range of data points from the plot. The selection of data points shall be done in accordance with Procedure A (8.2.2) or B (8.2.3). Relative pressure range and the number of data points to perform adsorption measurement (8.1.3) shall also be determined as specified in the procedures.

8.2.2 Procedure A

Procedure A is the standard method that generates high precision and shall be applied when the relative pressure range of data points to be used for determining NSA or STSA of a sample is unknown.

Measure the adsorbed amount at relative pressures equally distributed in the range from 0 to 0,5. A minimum of 10, and preferably 20 or more data points shall be obtained. The type of adsorption isotherm may be determined at this point.

For calculating NSA, prepare a BET plot based on the measured amount of gas adsorbed by using an appropriate tool, for example, the function in the software of an automatic volumetric adsorption measurement apparatus.

Select a range with the best linearity on the BET plot and calculate NSA. The usual relative-pressure range for determining NSA is from 0,05 to 0,3. It, however, is recommended to adjust the range depending on the adsorbed amount measured since the end point tends to be shifted downward as NSA increases.

For calculating STSA, see 9.3 and 9.4.

NOTE An adsorption isotherm with more data points is more accurate, but more time is required for the measurement.

8.2.3 Procedure B

Procedure B is a simplified method and it may be applied when the range of data points to be used for determining NSA or STSA of a sample is already known by Procedure A.

Measure the adsorbed amount at relative pressures of two or more data points in the known range.

Prepare a BET plot and calculate NSA as given in 8.2.2.

For calculating STSA, see 9.3 and 9.4

8.3 Verification of measured values

8.3.1 In order to verify the NSA measured, calculation of the BET constant is advisable. For carbon blacks, the value of the BET constant usually falls between +75 and +250.

In case of porous carbon blacks, the BET constant becomes negative if the calculation is carried out with a relative pressure range from 0,05 to 0,3. In this case, fix a measurement ranges as up to the relative pressure at which the term V (1-P/P_0) indicates a maximum value (where V and P/P_0 denote adsorbed amount measured and relative pressure, respectively), and a re-measurement or re-calculation shall be carried out within the range where the BET constant is not negative (see ISO 9277:2010, Annex C for details).

8.3.2 In order to guarantee the precision of measurements, carry out periodical verifications with a certified reference material[1] or an in-house reference material. In-house reference materials should be verified against certified reference materials. If the measured values are out of the uncertainty range, go through the procedures in 7.2, 7.3 and 8.1 to 8.3 again. If the deviation still persists, consult with the manufacturer of the apparatus.

9 Determination of statistical thickness surface area (STSA)

9.1 General

STSA of carbon black that excludes the internal surface of pores is one of the crucial factors for determining the properties of rubber compounds with carbon black. STSA is determined through a t-plot analysis, which is to exclude the internal surface area of pores of 0,86 nm or smaller from the total surface area by using the adsorbed amount of nitrogen measured in the sample and statistical thickness of a reference adsorbent.

NOTE 1 Appropriate data for statistical thickness of reference adsorbent are usually available from the manufacturers of volumetric adsorption measurement apparatus or past literatures.

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[1] Certified reference materials are provided by certified reference material producer, and those for NSA are available from the following institutions: Bundesanstalt für Materialforschung und – prüfung (BAM)Division I. 1 Inorganic Chemical Analysis; Reference MaterialsBranch Adlershof, Richard-Willstätter-Straße 11, D-12489 Berlin, GermanyEuropean Commission – Joint Research CentreInstitute for Reference Materials and Measurements (IRMM) Reference Materials Unit, attn. reference materials salesRetieseweg 111, B-2440 GEEL, BelgiumStandard Reference Materials ProgramNational Institute of Standards and Technology (NIST)100 Bureau Drive, Stop 2322Gaithersburg, MD 20899-2322, USAThis information is given for the convenience of users of this standard and does not constitute an endorsement by ISO of their products

NOTE 2 The STSA excludes the internal surface of pores of smaller than 2 nm. The size of pores to be excluded is subject to the range of relative pressure in the determination. The setting of the relative pressure in this International Standard (0,2 to 0,5) is to exclude pores of up to 0,86 nm, but the exclusion of larger pores is feasible by expanding the range of relative pressure. For example, the relative pressure between 0,6 and 0,9 is necessary in order to exclude pores of 1,4 nm or smaller.

9.2 Procedure

Measure the adsorbed amount of nitrogen as specified in 8.1 and 8.2 (Procedure A or B).

In Procedure A, the procedures for determining NSA and STSA can be carried out simultaneously.

Procedure B is a simplified one that is applicable when the range of data points to be used for determining STSA of a sample is already known by Procedure A. This procedure can be carried out separately from the determination of NSA. Determine STSA after determining the adsorbed amount at relative pressures of three or more data points in the known range and assessing its linearity.

9.3 Calculation of STSA

9.3.1 Carry out a t-plot analysis at the relative pressure between 0,2 and 0,5, and obtain a regression line. Using the slope of the line, calculate the STSA.

9.3.2 Install the program of t-plot analysis after consulting with the manufacturer of the apparatus. Persons using the program shall be familiar with the instruction of the program.

9.4 Verification of measured values

In order to guarantee the precision of measurements, carry out periodical verifications with a certified reference material or an in-house reference material. In-house reference materials should be verified against certified reference materials. If the measured values are out of the uncertainty range, go through the procedures in 7.2, 7.3, 9.2, and 9.3 again. If the deviation still persists, consult with the manufacturer of the apparatus.

10 Precision

See Annex A.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 18852;

b) all details necessary for complete identification of the sample;

c) a full description of conditions for sample preparation;

d) an indication of the procedure used [NSA or STSA (Procedure A or B)];

e) the test result, reported to the nearest 0,1 × 10^3 m^2/kg (0,1 m^2/g);

f) the number of data points used to obtain the result and the corresponding relative-pressure range;

g) the date of the test;

h) the operator.

Annex A
(informative)

Precision

A.1 General

A.1.1 These precision statements have been prepared in accordance with ISO/TR 9272:2005, level 2 method. Refer to this TR for terminology and other statistical details.

A.1.2 The precision results in this clause give an estimate of the precision of this test method with the materials used in the particular interlaboratory programme described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols of the test method.

A.1.3 For carbon blacks, a type 1 interlaboratory test programme was conducted as detailed in Table A.1. Both repeatability and reproducibility represent short-term (daily) testing conditions.

Table A.1 — Interlaboratory test programme for carbon blacks

Nominal test period	Material	Number of laboratory
April 2012	SRB-E8 (NSA)	6
April 2012	SRB-E8 (STSA)	6
June 2012	Porous carbon black (NSA)	6

A.2 Precision for multipoint nitrogen surface area (NSA) of carbon black

The results of the precision calculations are given in Table A.2.

Table A.2 — Precision for multipoint nitrogen surface area (NSA) of carbon black

Material	**Mean surface area** m^2/g	**Within laboratory**			**Between laboratories**		
		s_r m^2/g	r m^2/g	**(r)** %	s_R m^2/g	R m^2/g	**(R)** %
SRB-E8 (N660)	36,25	0,005	0,142	0,4	0,481	1,36	3,8

NOTE The symbols used are as follows:

s_r is the repeatability standard deviation;

r is the repeatability, in measurement units;

(r) is the repeatability, in percent (relative);

s_R is the reproducibility standard deviation;

R is the reproducibility, in measurement units;

(R) is the reproducibility, in percent (relative).

The precision for the mean value of multipoint nitrogen surface area (NSA) is as follows:

a) *Repeatability* — The repeatability (r) has been established as 0,4 %. Any other value in Table A.2 may be used as an estimate of repeatability, as appropriate. Two single test results that differ by