INTERNATIONAL STANDARD

ISO 4652

Third edition
2020-07

Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Single-point procedures

Ingrédients de mélange du caoutchouc — Noir de carbone — Détermination de la surface spécifique par méthodes par adsorption d'azote — Modes opératoires à un point de mesure

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 4652:2020
https://standards.iteh.ai/catalog/standards/sist/5228f9f3-becc-4dea-aa46-
6ccde38b03b1/iso-4652-2020

iTeh STANDARD PREVIEW
(standards.iteh.ai)

COPYRIGHT PROTECTED DOCUMENT

Contents

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document 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 third edition cancels and replaces the second edition (ISO 4652:2012), which has been technically revised. The main changes compared to the previous edition are as follows:

— the former method A has been updated as an automatic volumetric method (method B);

— the former method B has been removed;

— the former methods C and D have been updated as an automatic gas chromatography method (method A);

— 4.4 has been clarified;

— Annex B on precision data has been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The specific surface area of carbon black is an important element which categorizes the type of carbon black. In this document, nitrogen adsorption at the relative pressure of 0,3 is measured to determine the specific surface area (the single-point method). The single-point method can be a reasonable alternative for process management and shipping management after testing with the multi-point method in ISO 18852, because the measurement time is shorter and relative magnitude of the specific surface area among the samples is kept.

The multi-point method determines specific surface area on the basis of monolayer amount of nitrogen adsorbed (V_m) which is derived by Formula (1):

$$V_m = 1/(M + B) \tag{1}$$

where

> M is the slope of the BET plot (see ISO 9277);
>
> B is the intercept of the BET plot (see ISO 9277),

The single-point method simplifies this technique by assuming the intercept (B) as zero and calculating the slope (M) with the straight line joining the origin and the point at the relative pressure of 0,3. Therefore, the monolayer amount and specific surface area determined by the single-point method is always lower than those determined by the multi-point method.

Although most of the operation is done automatically, the operator should be familiar with the operation and follow the instruction manual.

ISO 4652:2020
https://standards.iteh.ai/catalog/standards/sist/5228f9f3-becc-4dea-aa46-
6ccde38b03b1/iso-4652-2020

Rubber compounding ingredients — Carbon black — Determination of specific surface area by nitrogen adsorption methods — Single-point procedures

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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.

1 Scope

This document specifies two methods for the determination of the specific surface area of types and grades of carbon black for use in the rubber industry:

— method A: automatic gas chromatography method (carrier gas method);

— method B: automatic volumetric method.

Somewhat different results might be obtained from the two methods. The degassing procedure differs between method A and method B, and it is important to investigate the possibility of correcting the results by using standard reference blacks.

The results might also differ from those obtained using the multipoint method specified in ISO 18852, which is the preferred method.

These methods are not applicable to porous carbon blacks.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Method A: Automatic gas chromatography (carrier gas method)

4.1 Principle

The mixed gas of helium and nitrogen (volume fraction 70 % and 30 %, respectively) is dosed to the degassed sample at the temperature of liquid nitrogen. The nitrogen in the mixed gas is adsorbed on the surface of a test portion of carbon black, so that the composition of the gas changes. The nitrogen is then desorbed by warming the test portion and the ratio of the mixed gas changes again. Since the thermal conductivity varies depending on the mixed gas concentration, it is possible to determine the amount of absorbed nitrogen gas using the thermal conductivity detector (TCD) of the system. Almost all the operations are automatically performed.

4.2 Apparatus

4.2.1 Automatic gas chromatography specific surface area measurement system, incorporating a thermal conductivity detector as well as the following devices.

— Dewar flask, for liquid nitrogen, of a size to contain the liquid nitrogen and capable to keep the adsorption cell cooled for a predetermined time.

WARNING — Use caution. Gloves and safety glasses should be worn as the temperature of the liquid nitrogen is −196 °C.

— Heating device, capable of maintaining the temperature of 300 °C ± 10 °C, for degassing the test portion.

— Air blower.

An example is shown in Figure 1.
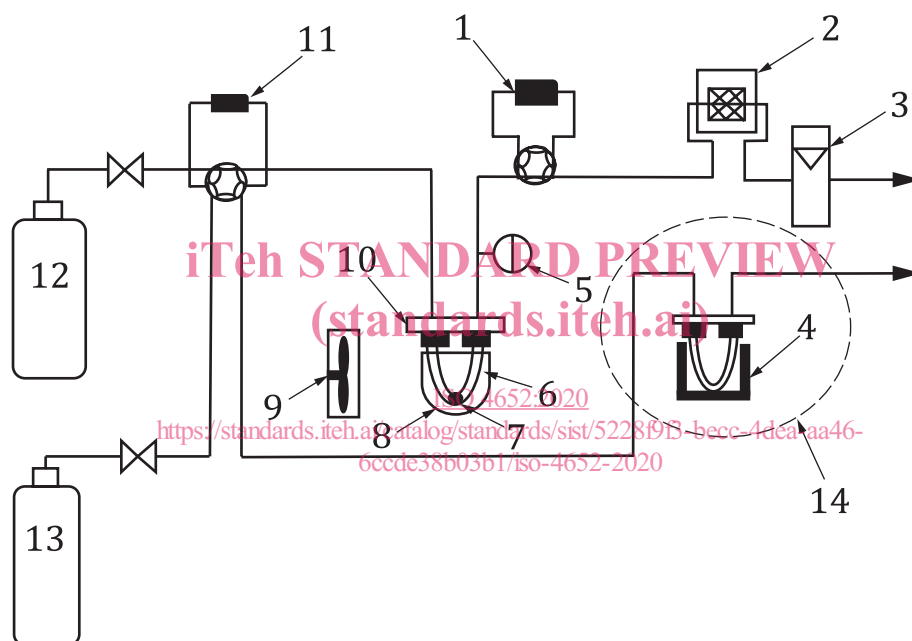
Key

1	buffer	8	Dewar flask
2	thermal conductivity detector	9	air blower
3	flowmeter	10	connector
4	heating device	11	calibration loop
5	pressure gauge	12	mixed gas cylinder
6	adsorption cell (sample tube)	13	nitrogen cylinder
7	sample	14	degassing holder for the test portion

Figure 1 — Apparatus of automatic gas chromatography

4.2.2 Sample tubes, U-tube type, made of heat-resistant glass, of a size to fit the automatic gas chromatography specific surface area measurement system used.

4.2.3 Pressure regulators, for helium-nitrogen mixed gas (4.3.1) and nitrogen gas (4.3.2).

4.2.4 Analytical balance, accurate to 0,1 mg.

4.2.5 Pipe cleaner.

4.3 Reagents

4.3.1 Helium-nitrogen mixed gas.

The volume mixing ratio of helium and nitrogen is 7:3, and it is kept in a pressure vessel.

4.3.2 Nitrogen gas, of purity greater than 99,999 5 %.

4.3.3 Standard reference black.

4.4 Preparation of the sample portion

Pellets of carbon black may not be crushed. Unagitated, unpelletized carbon black may be densified if desired.

Prepare a test portion by roughly weighing the mass of test portion given in Table 1. If the approximate specific surface area of the sample is not known, preliminary test may be carried out to determine the mass of the test portion. The final mass of the test portion to be used for the calculation is weighed and determined in 4.6.7, 5.5.2.2 and 5.5.3.5 of each procedure.

NOTE   Generally a good precision is obtained when the mass of the test portion corresponds to the specific surface area between 10 m² and 20 m² as given in Table 1.

Table 1 — Recommended test portion masses

Carbon black series	Specific surface area m²/g	Mass of test portion g
Higher grade than N100	>200	0,05
N100	120 to 150	0,08 to 0,14
N200	100 to 120	0,1 to 0,16
N300	70 to 100	0,14 to 0,20
N500	40 to 60	0,25 to 0,33
N600	25 to 40	0,4 to 0,5
N700–N900	10 to 25	1,0

4.5 Degassing of sample

4.5.1   To determine the specific surface area, it is necessary to degas the contaminating molecules adsorbed on the sample surface before measurement. Connect an empty sample tube to the degassing holder. After the nitrogen gas is introduced into the sample tube, the tube is removed from the holder and promptly sealed with a lid or valve, and the mass in grams (m_1) is recorded to the nearest 0,1 mg.

4.5.2   Put the prepared test portion (see 4.4) in the adsorption cell. Drop the specimen clinging on the tube wall into the bottom with the pipe cleaner.

4.5.3   The sample tube with the sample (4.5.2) is connected to the degassing holder, and the nitrogen gas of the appropriate flow rate (which does not scatter the sample) is introduced.

4.5.4   While introducing the gas, heat the sample at 300 °C ± 10 °C by the heater for 15 min, then allow it to cool to the room temperature to terminate the degassing process.

4.6 Measurement procedure

4.6.1 After setting the degassed sample tube to the measurement unit and distributing helium-nitrogen mixture gas (4.3.1), ensure that the baseline of the thermal conductivity detector is stable. Set the baseline to zero.

4.6.2 After circulating helium-nitrogen mixture gas for a few minutes, the thermal conductivity detector is turned on.

4.6.3 Cool the sample tube with the sample in the liquid nitrogen in the Dewar flask.

4.6.4 The baseline of the thermal conductivity detector becomes stable when the adsorption has been completed. Remove the sample tube out of the liquid nitrogen and warm it with the air blower to the room temperature.

To operate efficiently, degassing of the next sample portion may be done in parallel with the adsorption and desorption process.

4.6.5 The peak area of the desorption is stored in the device or in the control computer.

4.6.6 Calibrate the thermal conductivity detector for the next portion.

Calibration is intended to introduce a known volume of nitrogen gas, a method using a syringe and a volume-tested calibration loop. In either case, high purity nitrogen is used after desorption measurement. Calibration is performed for each measurement, but it is also possible to use the values which are determined by measuring thermal conductivity of high purity nitrogen gas in advance.

NOTE   In the fully automatic measuring devices, the procedures 4.6.1 to 4.6.6 are performed entirely automatically.

4.6.7 Remove the sample tube from the measurement unit and wipe the water droplets, and measure the mass in grams (m_2) to the nearest 0,1 mg. The mass of the sample in grams (m_3) can be calculated by Formula (2).

$$m_3 = m_2 - m_1 \qquad\qquad (2)$$

where

m_1 is the total mass of the adsorption cell, the nitrogen gas and the stopper or valve, in grams;

m_2 is the total mass of the adsorption cell, the nitrogen gas, the sample and the stopper or valve, in grams;

m_3 is the sample mass, in grams.

4.7 Validation

It is recommended to validate the device with standard reference black (SRB) periodically.

The specific surface area of the SRB corresponding to the varieties is measured by performing the procedures in 4.5 and 4.6 and applying Formulae (3) and (4). When the difference between the measured value and the nominal value exceeds ±1,2 m^2/g, calculate the correction factor, K, and apply it to the test measurement in accordance with 4.8.2.

4.8 Expression of results

4.8.1 Results without correction

Nitrogen adsorption specific surface area, S_A, is calculated by Formulae (3) and (4). The measurement results shall be rounded to one decimal place.

$$V_m = \frac{V_a\left(1 - \dfrac{P}{P_0}\right)}{m_3} = \frac{0,7 \cdot V_a}{m_3} \tag{3}$$

$$S_A = \frac{V_m}{22\,700} \times L \times \sigma \times 10^{-18} \tag{4}$$

where

V_m is the volume of nitrogen which covers a monomolecular layer, in cm^3/g;

V_a is the adsorbed volume of nitrogen measured, in cm^3/g;

P is the equilibrium pressure, in Pa;

P_0 is the saturation vapour pressure of nitrogen, in Pa;

m_3 is the sample mass, in grams;

S_A is the nitrogen adsorption specific surface area, in m^2/g;

L is the Avogadro constant ($6,022 \times 10^{23}$);

σ is the cross-sectional area of nitrogen molecule ($0,162\ nm^2$).

NOTE   22 700 is the molar volume of nitrogen gas at the standard state (100 kPa and 273,15 K), in cm^3.

4.8.2 Results with correction

The correction coefficient (K) is calculated by Formula (5). Perform the correction of the measurement results by Formula (6).

$$K = \frac{S_{SRB}}{S_m} \tag{5}$$

$$S'_A = S_A \times K \tag{6}$$

where

K is the correction coefficient;

S_{SRB} is the nominal nitrogen absorption specific surface area value of SRB, in m^2/g;

S_m is the measured nitrogen absorption specific surface area value of SRB, in m^2/g;

S'_A is the corrected measurement result, in m^2/g;

S_A is the measured nitrogen absorption specific surface area value of the sample, in m^2/g.

Report S'_A as a corrected test result.