INTERNATIONAL STANDARD

ISO 23604

First edition
2022-11

Method of determining specific surface area of coal

Méthode de détermination de la surface spécifique du charbon

Reference number
ISO 23604:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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 *Coalbed methane (CBM)*, ISO/TC 263.

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.

Method of determining specific surface area of coal

1 Scope

This document provides a method for determining the specific surface area of solid materials using gas adsorption.

This document is applicable to the determination of specific surface area of coal, and other powder and porous materials including nano-powders and nano-grade porous materials with a determination range of 0,001 m^2/g to 1 000 m^2/g.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 9277, *Determination of the specific surface area of solids by gas adsorption — BET method*

3 Terms and definitions

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

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

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

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

3.1
surface area
extent of accessible surface area as determined by a given method under stated conditions

[SOURCE: ISO 15901-1:2016, 3.30]

3.2
adsorption
enrichment of the adsorptive gas at the external and accessible internal surfaces of a solid material

[SOURCE: ISO 15901-2:2022, 3.2, modified — "material" added to the definition]

3.3
adsorbate
adsorbed gas

[SOURCE: ISO 15901-2:2022, 3.1]

3.4
saturation vapour pressure
vapour pressure of the bulk liquefied adsorptive gas at the temperature of *adsorption* (3.2)

[SOURCE: ISO 15901-2:2022, 3.20 modified — "gas" added to the definition]

3.5
relative pressure
ratio of the equilibrium adsorption pressure, p, to the *saturation vapour pressure* (3.4), p_0, at analysis temperature

[SOURCE: ISO 15901-2:2022, 3.19]

3.6
adsorption amount
amount of gas adsorbed by the adsorbent under the equilibrium adsorption pressure at given temperature

3.7
adsorption isotherm
curve obtained by plotting the amount of gas adsorbed against the equilibrium pressure or relative pressure at a constant temperature

3.8
specific surface area
surface area of a solid substance per unit mass (or unit volume)

3.9
micropore
pore with width about 2 nm or less

[SOURCE: ISO 15901-2:2022, 3.13]

4 Principles

The principle of determination of specific surface area by gas adsorption is based on the adsorption properties of gases on solid surfaces. Under a certain pressure and ultra-low temperature, the physical adsorption of the sample particles (adsorbent) for gas molecules (adsorbate) is reversible, and there is a determinate equilibrium adsorption corresponding to a certain pressure. Therefore, the specific surface area of the sample can be equivalently determined by measuring the equilibrium adsorption on the basis of a theoretical model.

5 Reagents and materials

5.1 **Helium**, purity no less than 99,99 %.

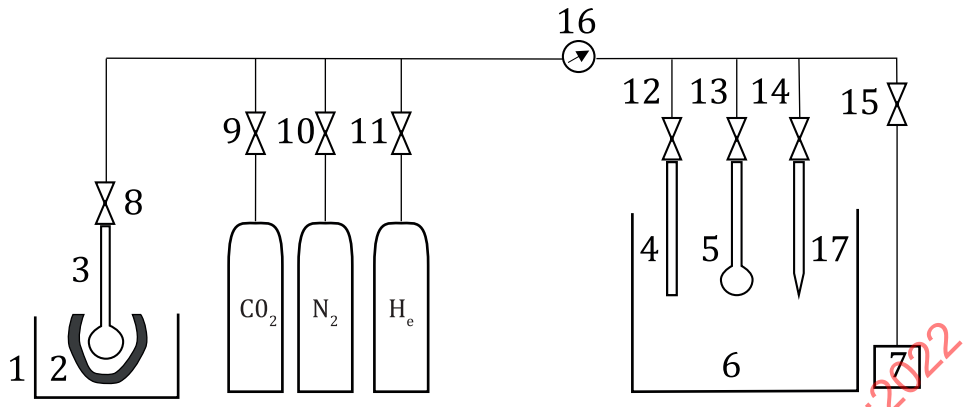
5.2 **Nitrogen**, purity no less than 99,99 %.

5.3 **Liquid nitrogen,** temperature at 77 K.

5.4 **Carbon dioxide**, purity no less than 99,9 %.

5.5 **Standard sieves(number of mesh)**, 60 and 35.

5.6 Specific surface area analyser (see Figure 1).



Key

1	degasser
2	heating mantle
3 and 5	sample tube
4	manifold
6	dewar bottle
7	vacuum pump
8–15	solenoid valves
16	pressure gauge
17	liquid nitrogen probe/water probe

Figure 1 — Specific surface area analyser

6 Sample preparation

6.1 Fresh coal samples shall be selected for the determination, or otherwise the oxide layer of coal samples shall be removed.

6.2 If salinity of formation water is higher than 5 000 mg/l, the coal sample shall be cleaned to remove salt.

6.3 The coal sample is broken into certain particle range and then divided into several samples with equal reliability.

6.4 Smash and screen the sample and take 5 g to 10 g of the sample with particle sizes of 0,28 mm to 0,45 mm. Put it into the sample bag labelled with the information including sampling date, well number, depth and layer as well as sample number.

6.5 Air-dry the prepared samples at room temperature or in a thermostat. The temperature of the thermostat shall not exceed 40 °C. The dried samples shall be sealed and put into a desiccator for later use.

7 Experiments and calculations

7.1 Degas the sample tube degassing

7.1.1 Install the sample tube into the degasser (see Figure 1), which is then heated to 100 °C to 150 °C and vacuum-degassed.

7.1.2 After the vacuum degree of the degasser reaches below 1,33 Pa, continue vacuum degassing for 30 min and turn off the heating mantle (see Figure 1). Cool the system down to room temperature and backfill the sample tube with nitrogen to the atmospheric pressure.

7.1.3 Take off the sample tube, plug the nozzle and weigh it, and take the mass as m_1.

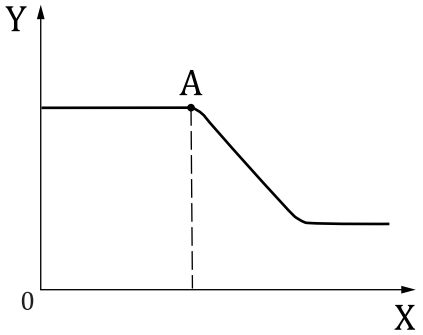
7.2 Sample pretreatment

7.2.1 Degassing of samples

The amount of prepared samples is determined by lithology: 2 g to 5 g shall be used for coal rock, tight sandstone, limestone and gypsum rock, and 1 g to 3 g for mudstone and shale. Put the weighed sample into the sample tube that is then installed onto the degassing device. Select the appropriate heating temperature (100 °C to 300 °C) according to the physical properties of the coal sample, and execute vacuum degassing. After the vacuum degree of the degassing device system reaches below 1,33 Pa, continue vacuum degassing for 4 h, and turn off the heating mantle. Cool the system down to room temperature and backfill the sample tube with nitrogen to atmospheric pressure. Take off the sample tube, seal it with the original plug. Weigh the plug-on sample tube and take the resultant mass as m_2. Therefore, the sample mass $m = m_2 - m_1$.

7.2.2 Heating temperature selection

The sample shall be degassed at high temperature and a vacuum degree less than 1,33 Pa to remove physically adsorbed substances, but irreversible surface structure changes (such manifesting as colour changes) shall be avoided. The maximum heating temperature can be determined by thermogravimetry analysis (TG). Specifically, TG is a thermal analysis method to measure the relationship between the mass and temperature of a substance at a certain heating rate (generally 10 °C/min). The heating temperature of a sample generally does not exceed the initial pyrolysis temperature of the substance (Point A in Figure 2).



Key

X temperature (°C)

Y relative mass change (%)

A pyrolysis temperature (°C)

Figure 2 — Thermogravimetric analysis curve

7.3 Determination of free space volume

7.3.1 Zero the pressure sensor and check for gas leakage in the analyser.

7.3.2 Put the sample-loaded sample tube that has been degassed into the analysis device, and lower it down into the Dewar bottle filled with liquid nitrogen so as to keep the sample at least 5 cm below the liquid nitrogen level.

7.3.3 Fill the manifold with helium until the pressure reaches 7,99 × 10^4–11,99 × 10^4 Pa. Record the present system pressure, p_1, and the manifold temperature, t_1 (pre-equilibrium).

7.3.4 Fill the sample tube with helium, and 5 minutes after equilibrium, record the system pressure, p_2, the manifold temperature, t_2, and the liquid nitrogen temperature, t_s (post-equilibrium).

7.3.5 Calculate the free space volume using Formula (1).

$$V_S = \frac{t_s V_d}{p_2}\left[\frac{p_1}{t_1} - \frac{p_2}{t_2}\right] \tag{1}$$

where

V_S is the free space volume, expressed in m^3;

V_d is the manifold volume, expressed in m^3;

p_1 is the pre-equilibrium system pressure, expressed in Pa;

p_2 is the post-equilibrium system pressure, expressed in Pa;

t_s is the liquid nitrogen temperature, expressed in K;

t_1 is the pre-equilibrium manifold temperature, expressed in K;

t_2 is the post-equilibrium manifold temperature, expressed in K.

7.4 Determination of adsorption isotherms

7.4.1 Vacuum the instrument pipe and sample pipe, remove the helium gas, and make the vacuum degree below 1,33 Pa.

7.4.2 Fill the analyser with a certain amount of nitrogen, and when the pressure change does not exceed 13,3 Pa within 5 mins after some period of time for adsorption, it can be considered that the adsorption equilibrium has been reached. Record the system pressure p, manifold temperature, t, liquid nitrogen temperature, t'_s, and saturation vapour pressure, p_0, of nitrogen after adsorption equilibrium. Calculate the adsorption amount, V_a, per unit mass according to Formula (2).

$$V_a = \frac{V - 273,2p\Big/\left[1,013\times10^4\left(V_s/t'_s + V_d/t\right)\right]}{m} \tag{2}$$

where

V_a is the adsorption amount per unit mass after reaching adsorption equilibrium, expressed in cm^3/g;

V is the amount of filled gas, expressed in cm^3/g;

m is the mass of samples, expressed in g;

p is the post-equilibrium system pressure, expressed in Pa;

t is the post-equilibrium manifold temperature, expressed in K;

t'_s is the post-equilibrium liquid nitrogen temperature, expressed in K.

7.4.3 Refill the analyser with a certain amount of nitrogen and repeat 7.4.2. Repeat this process for at least 15 pressure points within p/p_0 = 0,01–0,995.

7.4.4 Gradually reduce the relative pressure from p/p_0 = 0,995 for the desorption branch test. At least 20 points should be measured within p/p_0 = 0,995–0,25.

7.4.5 As per the analysis requirement, if the specific surface area value is only demanded, tests can be ended after measuring 5–7 adsorption points within p/p_0 = 0,05–0,35. Subsequently, the amount of single molecule adsorption can be calculated using Formula (3). Formula (5) can be used to calculate the specific surface area.

7.5 Monolayer saturated adsorption, V_m

7.5.1 Calculation of V_m by adsoprtion isotherm

V_m can be obtained from the isotherm adsorption line using the BET equation. Determination of the specific surface area of solids by the BET volumetric method is based on the BET adsorption theory. The basic assumption is that after a layer of molecules has been adsorbed on the solid surface via physical adsorption, adsorption can continue in the multi-layer form, due to the Van der Waals force of the gas itself. When adsorption reaches equilibrium, the amount of gas adsorbed is equal to the sum of the adsorbed amounts of each layer. The BET equation derived from this assumption is as follows:

$$\frac{P}{V_a(P_0-P)}=\frac{1}{V_m C}+\frac{C-1}{V_m C}(p/p_0) \tag{3}$$

where

P is the equilibrium pressure, expressed in MPa;

P_0 is the saturated vapour pressure of adsorbate at adsorption temperature, expressed in MPa;

V_m is the monolayer adsorption capacity of gas when the adsorbed monolayer fully occupies the solid surface, expressed in cm^3/g;

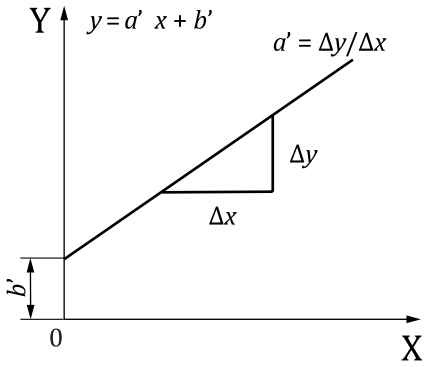
C is a constant associated with the temperature, adsorption heat, and condensation heat.

The X-axis on the isothermal adsorption line is between 0,05 and 0,35 and at least 5 points can be arbitrarily taken. p/p0 is the abscissa and $\frac{p/p_0}{V_a(1-p/p_0)}$ is the ordinate, 5 points are fitted into a straight line. The slope is A'(A' = $\frac{C-1}{V_m C}$), the intercept is B'(B' = $\frac{1}{V_m C}$), and the adsorption capacity is Vm($V_m = \frac{1}{B'C}$).

7.5.2 Calculation of V_m by the Langmuir equation

In the actual test process, usually 3 to 5 values of the adsorption capacity, V_a, of tested samples under different equilibrium pressures, P, are measured. Then p/p_0 is plotted as the X-axis and $(p/p_0)/V_a$, as the Y-axis, of which the resultant line is linearly fitting using the Langmuir equation. A linear equation

$y = A'x + B$ with the slope A' ($A' = 1 / V_m$) and intercept B' ($B' = b'/ V_m$) is obtained, as shown in Figure 3. The values of slope A' and intercept B' can be obtained by the Langmuir equation plotting or least square method, and thus the single-layer capacity V_m can be derived, as shown in Figure 1.



Key

X p/p_0

Y $(p/p_0)/V_a$

Figure 3 — Langmuir line

The Langmuir equation:

$$\frac{(p/p_0)}{V_a} = \frac{b'}{V_m} + \frac{1}{V_m}(p/p_0) \tag{4}$$

where b' is langmuir constant.

The X-axis on the isothermal adsorption line is between 0,05 and 0,35, and at least 5 points can be arbitrarily taken. With p/p_0 as the abscissa and $\frac{p/p_0}{V_a}$ as the ordinate, 5 points are fitted into a straight line. The slope is $A'(A' = \frac{1}{V_m})$, the intercept is $B'(B' = \frac{b'}{V_m})$, and the adsorption capacity is $V_m(V_m = \frac{1}{A'})$.

7.6 Specific surface area calculation

When nitrogen is used as the adsorption gas, the experimental process shall be carried out according to ISO 9277. The specific surface area of the solid substance can be calculated by the following formula:

$$S_g = \frac{V_m N_A A_m}{2\,240m} \times 10^{-18} \tag{5}$$

where

S_g is the specific surface area of tested samples, expressed in m^2/g;

V_m is the monolayer adsorption capacity of the nitrogen under the standard conditions, expressed in ml;

A_m is the equivalent maximum cross-sectional area of nitrogen molecules ($A_m = 0{,}162\ nm^2$);

m is the mass of tested samples, expressed in g;

N_A is the Avogadro's constant ($6{,}02 \times 10^{23}$).

7.7 Determination of micropores total volume

7.7.1 Micropore filling theory

It is difficult to analyse the pore size and pore volume of micropore materials such as coal with nitrogen. This is because the filling of pores with pore sizes from 0,5 nm to 1 nm by nitrogen gas occurs only at relative pressures between 10^{-7} and 10^{-5}, in which case, the diffusion rate and the adsorption equilibrium process are very slow. On the other side, diffusion is limited by extremely low pressure, which prevents nitrogen molecules from entering the finest micropores and consequently adsorption isotherm anomaly and underestimated pore volumes. Given these, carbon dioxide is used as the adsorbate for adsorption at 273,15 K to overcome the above disadvantages. The saturation vapour pressure of carbon dioxide at this temperature is about 3,485 Pa, and thus it can be used to detect micropores. Compared with cryogenic nitrogen adsorption, there is no obvious diffusion limit, so the equilibrium can be reached quickly.

It is in the form of micropore filling that carbon oxide adsorption occurs at relative pressures less than 0,03, regardless of being mono- or multi- layered. Therefore, at low relative pressures, the specific surface area can be calculated on the basis of the pore filling theory, namely the D-A/D-R model, using the measured adsorption data of carbon dioxide. This approach characterizes the specific surface area of pores with pore sizes less than 2 nm, which can better reflect the adsorption capacity of coal rock.

7.7.2 DR-DA equation

The adsorption isotherm of pure gas on microporous adsorbent can be described by the Polanyi theory. In the case of that the adsorbate/adsorbent system is affected by the special chemical properties of the adsorbent, the system can be characterized by the adsorption potential E. On the basis of Polanyi theory[3], Dubinin et al. studied the micropore adsorption and established the micropore filling theory[4] (Dubinin-Polanyi theory). The adsorbed molecules do not cover the pore surface, and instead fill the micropore space. The filling degree of micropores is defined as in Formula (6):

$$\theta = \frac{W}{W_0} \tag{6}$$

where

W_0 is the total volume of micropores;

W is the volume filled at relative pressures p/p_0;

θ is micropore filling degree.

Assuming the pore distribution conforms to the Gaussin function, as shown in Formulae (7) to (9):

$$\theta = \exp\left[-k\left(\frac{A}{\beta}\right)^2\right] \tag{7}$$

$$A = RT1n\frac{p_0}{p} \tag{8}$$