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**Method of determining specific  
surface area of coal**

*Méthode de détermination de la surface spécifique du charbon*

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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](http://www.iso.org/directives)).

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This document was prepared by Technical Committee *Coalbed methane (CBM)*, ISO/TC 263.

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# 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<sup>2</sup>/g to 1 000 m<sup>2</sup>/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]

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## 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 %.

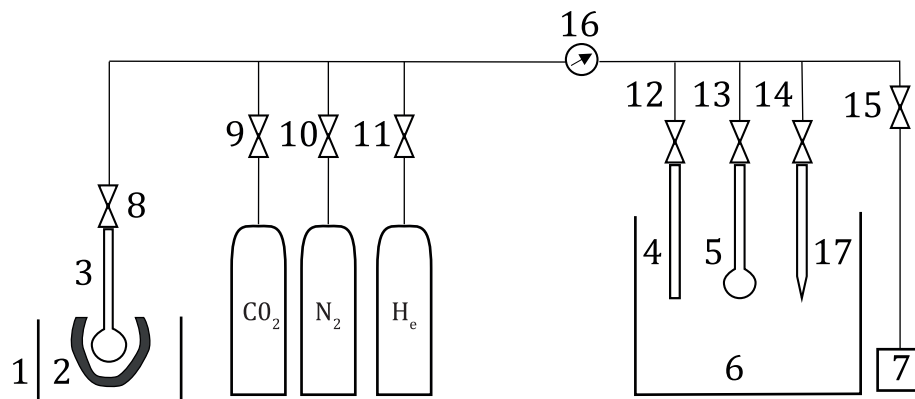
5.2 **Nitrogen**, purity no less than 99,99 %.

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**

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## 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  $m_1$ .

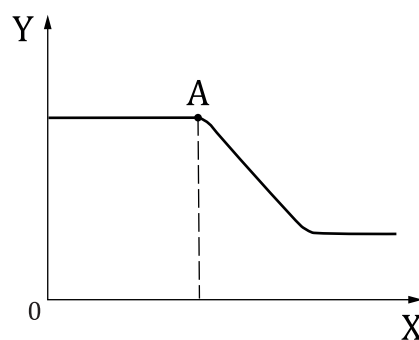
### 7.2 Sample pretreatment

#### 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 as 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  $7,99 \times 10^4$ – $11,99 \times 10^4$  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 \(1\)](#).

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

where

$V_S$  is the free space volume, expressed in m<sup>3</sup>;

$V_d$  is the manifold volume, expressed in m<sup>3</sup>;

$p_1$  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 \(2\)](#).

$$V_a = \frac{V - 273,2p / \left[ 1,013 \times 10^4 \left( V_s / t'_s + V_d / t \right) \right]}{m} \quad (2)$$

where

$V_a$  is the adsorption amount per unit mass after reaching adsorption equilibrium, expressed in cm<sup>3</sup>/g;

$V$  is the amount of filled gas, expressed in cm<sup>3</sup>/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 adsorption 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  $\text{cm}^3/\text{g}$ ;
- $C$  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.  $p/p_0$  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  $V_m(V_m = \frac{1}{B'C})$ .

**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