

SI -1 Specific Surface Area Measurement

SI-1.1 BET Method (used by Yu et al. (2017))

The BET method was developed by Brunauer, Emmett and Teller in 1938 and enables specific surface area measurement by gas adsorption. The protocol which was used is the one described by Alcade et al. (2013). It is based on the determination of gas quantity necessary to cover the external surface and internal pores of a solid by a complete monolayer. The method is applicable on powdered solid sample which particle diameter does not exceed 2 mm and which specific surface area is greater than 0.2 m²·g⁻¹.

The sample is placed in an oven at 105°C, crushed and put into a glass sample holder. In order to empty the sample porosity of water and air that it may contain and enable fixation of N₂ gas, the powdered sample is degassed at 105°C for 120 minutes and cooled in a bath of liquid nitrogen at a temperature of 77 K, to avoid gas condensation with increasing temperature.

Helium, a gas that will not fix on the sample surface, is injected into the sample holder to measure the volume which is not occupied by the sample. After helium evacuation, nitrogen is injected by successive steps, enabling the apparatus to measure the pressure in the sample holder. The partial pressure regularly measured and in the range of 0 to 0.995 enables to determine the quantity of adsorbed nitrogen. Results are processed using the equation of Brunauer, Emmett and Teller:

$$\frac{\frac{P_s}{P_0}}{n_a(1-\frac{P_s}{P_0})} = \frac{1}{n_m C} + \left(\frac{C-1}{n_m C}\right) P_s/P_0 \quad (SI- 1)$$

where P_s [Pa] is the pressure of adsorption gas in equilibrium with the adsorbate gas, P_0 [Pa] is the saturation vapour pressure of the adsorption gas, P_s/P_0 [-] is the relative pressure of the adsorption gas, n_a [mol·g⁻¹] is the specific adsorbed gas quantity, n_m [mol·g⁻¹] is the molecular coverage capacity, quantity of adsorbed gas necessary to cover a unit surface with a complete monolayer and C [-] is the BET constant.

Graphically, the quantity $\frac{\frac{P_s}{P_0}}{n_a(1-\frac{P_s}{P_0})}$ is represented in function of relative pressure P_s/P_0 . When

P_s/P_0 is in the range 0.05 to 0.35, equation (AI-1) is a linear function $y= ax+b$

With slope $a = \left(\frac{c-1}{n_m c}\right)$ (SI- 2)

and y-intercept $b = \frac{1}{n_m c}$ (SI-3)

Thus, BET constant writes :

$$C = \frac{a}{b} + 1 \quad (SI- 4)$$

And the monolayer volume is given by:

$$V_M = \frac{1}{a+b} \quad (SI- 5)$$

The corresponding specific surface area is deduced with the following relation

$$A_s = \frac{V_M}{V_m M_{sample}} S_{Adsorbate} NA \quad (SI- 6)$$

where A_s [$m^2 \cdot g^{-1}$] is the specific surface area of the solid, V_M [cm^3] is the volume of the adsorbed gas monolayer, $S_{Adsorbate}$ [m^2] is the area of the efficient section per adsorbate molecule, V_m [$22414 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $P = 1 \text{ atm}$ and $T = 25^\circ\text{C}$] is the volume of a molecular gram, M_{sample} [g] is the mass of the sample after degassing, and NA [$6.022 \cdot 10^{23} \text{ atomes} \cdot \text{mol}^{-1}$] is the Avogadro constant.

SI-1.2 BJH Method (used by Yu et al. (2017))

The BJH technique enables to obtain specific surface area and pore size distribution. The theory was proposed by Barrett, Joy and Halenda in 1951. Its principle is based on the analysis of isotherm of adsorption and desorption of nitrogen at 77 K, showing a hysteresis loop. In this method, calculation of the specific surface area is done on the desorption part which is supposed to be the most representative of the equilibrium between gaseous nitrogen and condensed nitrogen by capillarity. Pores are considered to be filled at the equilibrium pressure for which a saturation plateau or an

inflexion point can be seen. According to Brunauer classification , the shape of the hysteresis loop gives information on pore size and shape.

SI-2 Grain density determination (used by Yu et al. (2017))

Grain density is determined using helium pycnometry. The apparatus is an AccuPyc II 1340. Protocol is described in Alcade et al. (2013). The technique enables to measure volumetric mass of a bulk or powdered solid, of regular or irregular shape from the measure of real volume V_s of a dried sample (but it does include closed porosity), which mass M_s is known by weighing on a precision balance.

Sample is placed in a helium cell which volume V_{cell} is known, at a known pressure P_1 and known ambient temperature T_a .

The apparatus consists in two cells: the measuring cell and the expansion cell. The sample volume should neither be less than 10% of the measuring cell neither superior than 90% of it. Valve is closed and expansion cell with known volume V_{exp} is put into contact with helium with known pressure P_a and temperature T_a . Then, valve is open and the two cells are communicating with a pressure of equilibrium P_2 .



Figure 1: AccuPyc II 1340 Helium-Pycnometer

According to the ideal gas law:

$$P_1(V_{cell} - V_{sample}) = n_{cell}RT_a \quad SI- 7$$

$$P_a V_{exp} = n_{exp}RT_a \quad SI- 8$$

$$P_2(V_{cell} - V_{sample} + V_{exp}) = (n_{cell} + n_{exp})RT_a \quad SI- 9$$

By replacing the right member of equation AII-3 by the left member of AII-1 and AII-2, the following equation is obtained:

$$V_{sample} = V_{cell} - P_2 - P_a P_1 - P_2 V_{exp} \quad SI- 10$$

The sample grain density ρ_s is given by:

$$\rho_s = \frac{M_s}{V_s} \quad SI- 11$$

SI-3 Calculation of uncertainties

The uncertainty of each parameter in the calculation of the permeability have been considered to determine the uncertainty of permeability results in Hassler cell. For used instruments, uncertainties are calculated using the formula

$$Uncertainty = \sqrt{(instrument\ uncertainty)^2 + (Stdev\ of\ repeated\ measurements)^2} \quad (SI- 12)$$

Where the instrument uncertainty is given by the manufacturer, and standard deviation is calculated based on three repeated measurements. For example, the uncertainties of the imposed upstream and downstream pressures are calculated following the same formula.

The uncertainty of a member of a used equation is calculated using Gauss's formula which takes into account the uncertainty of each member of the equation. For example the mean pressure is defined as $P_m = (P_u + P_d)/2$ and its uncertainty is determined using this formula:

$$\sigma^2 P_m = \sigma^2 P_u \left(\frac{\partial P_m}{\partial P_u} \right)^2 + \sigma^2 P_d \left(\frac{\partial P_m}{\partial P_d} \right)^2$$

Where σ is the error on the mean pressure (P_m), the upstream pressure (P_u) and the downstream pressure (P_d) pressures. $\left(\frac{\partial P_m}{\partial P_u}\right)$ is the derivative of the mean pressure with respect to the upstream pressure, and $\left(\frac{\partial P_m}{\partial P_d}\right)$ is the derivative of the mean pressure with respect to the downstream pressure.