Protocol
Specific Surface Area (BET method)

1. Method

The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. The observations are interpreted following the model of Brunauer, Emmett and Teller (BET Method).

2. Equipment

- Instrument: Micromeritics Gemini 2375;
- Flowing-gas degassing unit Micromeritics FlowPrep 060, set-up at adequate temperature based on the nature of the sample (be careful, the unit is by default set at 200 [°C]!). The drying temperature needed for an unknown material must be determined by a preliminary thermal analysis (thermogravimetric analysis TGA);
- Analytical balance (precision 0.1 [mg]);
- Spatula for powder samples;
- Test tube suitable for the instrument;
- Stopper for the test tube;
- Support for test tube.

3. Protocol

Preparation of samples

- If this is the first measurement of the day to be carried out, install three empty test tubes (with lids) in the flowing-gas degassing unit and let them dry with flowing nitrogen for 1 [h] or until constant weight. Remove the test tubes from the oven and leave for cooling for 5 [min]. One test tube is to be used for the analysis and the other two for calibrating the P_0;
- Weigh one empty test tube together with its rack and stopper using the analytical balance (accuracy 0.1 [mg]). Carefully write down the result W_T [g];
- With the spatula add a sufficient amount of powder to the test tube (the total surface available should range from 5 and 10 [m^2]);
- Weigh the test tube containing the powder together with its support and stopper (accuracy 0.1 [mg]). Carefully write down the result W_B [g];
- Place the test tube and lid in the flowing-gas degassing unit for the time necessary based on the nature of the sample. Remove the test tube from the oven and leave for cooling for 5 [min]. Place the test tube (with lid) on its rack and weigh (accuracy 0.1 [mg]). Carefully write down the result W_C [g];
- The mass of powder to insert to the measuring system is calculated from:

$$W_P = W_C - W_T [g]$$

Operations

- While the sample is being dried and degassed in the flowing-gas degassing unit, install the two other test tubes onto the instrument in order to perform the P_0 (measurement of saturation pressure;

- Fill in the Dewar with nitrogen and place it on the platform below the two test tubes;
- Press the white key on the keyboard (2nd function) then "P_0/." then "Enter" – the calibration takes about 10-15 [min]; P_0 is automatically registered.
- Replace the right test tube on instrument with the sample test tube;
- Control the level of nitrogen in the Dewar and fill in with extra liquid nitrogen if necessary;
- Press the white key on the keyboard (2nd function) then "Analyse/4 [1]" then "Enter"
    - "Sample ID": type the sample number then press "Enter";
    - "Mass": type the mass W_P then press "Enter";
    - "Saturation pressure 738.52 mmHg" press "Enter";
    - "Evacuation rate 50mmHg/min" press "Enter"; [2]
    - Press "Enter" to start;
    - One standard measurement takes between 50 and 60 [min].
- Once the measurement has started, open "Gemini.ht"
    - Go to the "Transfert" menu, select "Capturer le texte", then Browse to select the folder in which the measurement will be saved. Name the sample Powder-Lotn°-BET-Experimentn°-Operator.txt, then OK.
    - Once the measurement is finished, go to the "Transfert" menu, select "Capturer le texte", and "Arrêter"
- Once the measurement is finished and saved, remove the powder from the test tube, wash the tube with water using the ultrasonic bath, rinse with ethanol and dry at 60 [°C] in the oven.

4. Presentation of the results, data storage and data treatment

Data storage
- Copy the file Powder-Lotn°-BET-Experimentn°-Operator.txt Go to \\Ltppc40\powderfiles. Copy the folder *Powderfiles*. Paste it in your project folder, and change its name into Powder-Lotn°.
- Paste the TXT file in the folder Project/Powder-Lotn°/BET/Data.

Data treatment
- Go to \\Ltppc40\powderfiles. In the folder Project/Powder-Lotn°, open the Excel sheet "Powdersheet.xls"
- Click on the *BET* button, and follow the instructions given in the Excel sheet

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[1] Choose the programme parameters for measurements: range of P/P_0 + parameters for data collection + BET mode (see. 6.N2 adsorption program).

[2] The evacuation rate can be modified depending on the particle size and state of agglomeration. For powders with apparent densities <0.5 the evacuation rate may have to be decreased to prevent transfer of the powder towards the vaccum system. For powders with apparent densities >1.5 the evacuation rate can be increased.

5. Calculation of d$_{BET}$

The d$_{BET}$ is an average surface diameter calculated from the measurement of the specific surface area assuming the particles are spherical and monodisperse.

It is calculated using the formula d$_{BET}$ [µm]=6/(S×ρ)

with S = BET specific surface area [m^2/g] and ρ = theoretical density [g/cm^3]

6. N2 adsorption program

5 points BET-standard = programme 1

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Analysis conditions                      H and J parameter 3:   0.333
Evacuation time:        1                Minimum thickness:     3.5
Free space:             Measure          Maximum thickness:     5
Sample density:         1                Area Correction:       1
Pressure table?         Replace          Total Pore volume?     None
First rel. pressure:    0.05             Report BJH?            No
Last rel. pressure:     0.3              Minimum diameter:      17
Number of points:       5                Maximum diameter:      3000
Adsorb pressure 1:      0.05             Report isotherm?       Adsorption
Adsorb pressure 2:      0.1125           Thickness curve?       Hasley
Adsorb pressure 3:      0.175            Halsey parameter 1:    3.54
Adsorb pressure 4:      0.2375           Halsey parameter 2:    5
Adsorb pressure 5:      0.3              Halsey parameter 3:    0.333
                                         Molecular area:        0.0015468
Number of points:       0                Density conversion:    0.0015468
                                         Non ideality:          5
Analysis mode?          Equilibrate
Equilibration time:     5                Data transmission
Scan rate:              10               Baud rate?             9600
                                         Data bits?             8
Report options                           Stop bits?             1
Report destination?     printer          Parity?                None
Transmission format?    Spreadsheet      Xon/Xoff protocol?     Diabled
Area points from:       0.04
Area points to:         0.31             System options
Report BET multi-pt?    Yes              Language?              English
Report Langmuir?        No               ID for Setup 1:
Report BET 1-pt?        No               Instrument ID:         3691
Report t-method?        No               Date (DD/MM/YY):       date
t-method range from:    0                Time (HH:MM:SS):       time
t-method range to:      0.7              Request sample ID?     Yes
Thickness curve?        Harkins &        Request sample wt?     Yes
                        Jura             Request sat. prs.?     Yes
H and J parameter 1:    13.99            Volume correction:     0
H and J parameter 2:    0.034
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