# Texture characteristic of membrane materials – ASAP, BET

## Theory

Specific surface (surface area) is used for the characterization of many materials. There are various techniques how measure the specific surface solids. Gas adsorption (i.e. the condensation of molecules on the mineral surface) determines surface area from the relationship between applied pressure and volume of gas forced into the specimen (water vapor is included in this group). Another technique is the absorption of molecules from solution into a solid surface, in particular, dyes such as methylene blue.

The Brunauer, Emmett and Teller (BET) gas adsorption theory is the foundation for the measurement of surface area in high specific materials. Brunauer et. al. derived an isotherm for the adsorption of multimolecular layers of gas on a solid adsorbent similar to Langmuir`s derivation for a unimolecular layer. The BET equations represent the general shape of actual experimental isotherms, and from these isotherms the volume of gas required to form a unimolecular layer of gas on adsorbents can be computed. Surface area is determined using the following relationship:

$$\frac{p}{a.(p_0 - p)} = \frac{1}{a_m.C} + \frac{C-1}{a_m.C}.\frac{p}{p_0}$$

where $p$ is the applied pressure, $p_0$ is the saturation pressure, $a$ is the amount of substance in 1 gram sample (units – mol/g) of adsorbed at $p/p_0$, $a_m$ is the amount of substance in 1 gram sample (units – mol/g) for one monolayer of surface coverage, and $C$ is related to the heat of adsorption in the first and subsequent adsorbed layers. When you use $X = p/p_0$, then

$$\frac{X}{a.(1 - X)} = \frac{1}{a_m.C} + \frac{C-1}{a_m.C}.X$$

Plots of $\frac{X}{a.(1-X)}$ versus $X$ yield a straight line, from which the slope and intercept can be used to determine $a_m$ and $C$. The surface area $S_g$ of the specimen is

$$S_g = a_m.A_{N.}N_a$$

where $A_N$ is the cross-sectional area of the adsorbate molecule (for nitrogen is $1{,}62.10^{-19}$ m$^2$) and $N_a$ is the Avogadro constant.

## Experiment

**Preparation of sample**

*Material*: $TiO_2$-membrane

*Procedure*: Weight ca. 0,2 g membrane and insert to the sample tube.

**A) 1st point plot of BET, $x_{N2}$( mole fraction of nitrogen) = 0.2, X ($p/p_0$)=0.2**

**1) Measurement**

The sample tube with $TiO_2$-membrane insert into instrument. Regulate flow nitrogen to 58.9 and hydrogen to 37.97. This is $X$ = 0.2. Wait 10 minutes. Install cold trap. The adsorption peak is detected on strip chart recorder. Wait 5 minutes. Press key "START. Lift down cold trap. The desorption peak is detected on strip chart recorder. Wait 5 minutes. Press key "STOP" (result).Write result "area of peak" from integrator. This measurement repeats 2x and calculates average area of peak.

**2) Calibration**

Change sample tube for batch meter. Wait 10 minutes. Press key "START". Fill the syringe nitrogen (5.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key "STOP". Write result "area of peak" from integrator.

Press key "START". Fill the syringe nitrogen (7.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key "STOP". Write result "area of peak" from integrator.

Press key "START". Fill the syringe nitrogen (10.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key "STOP". Write result "area of peak" from integrator.

**B) 2nd point plot of BET, $x_{N2}$( mole fraction of nitrogen) = 0.3, X ($p/p_0$)=0.3**

**1) Measurement**

The sample tube $TiO_2$-membrane insert into instrument. Regulate flow nitrogen to 90.9 and hydrogen to 33.4. This is $X$ = 0.3. Wait 10 minutes. Install cold trap. The adsorption peak is detected on strip chart recorder. Wait 5 minutes. Press key "START. Lift down cold trap. The desorption peak is detected on strip chart recorder. Wait 5 minutes. Press key "STOP" (result).

Write result “area of peak” from integrator. This measurement repeats 2x and calculates average area of peak.

**2) Calibration**

Change sample tube for batch meter. Wait 10 minutes. Press key “START Fill the syringe nitrogen (5.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key “STOP”. Write result “area of peak” from integrator.

Press key “START”. Fill the syringe nitrogen (7.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key “STOP”. Write result “area of peak” from integrator.

Press key “START”. Fill the syringe nitrogen (10.0 $cm^3$). Dose gaseous nitrogen in batch meter. The peak is detected on strip chart recorder. Wait 5 minutes. Press key “STOP”. Write result “area of peak” from integrator.

**C) Calculate surface area, $S_g$.**

A) Relative pressure 0,2

Calibration:

“Area of peak” corresponds to the volume of nitrogen. (For example 7.0 $cm^3$ of nitrogen= designated area of peak).You need to do the calibration equation.

Measurement:

The volume of adsorbed nitrogen of sample will determined from average area of peak.

Volume of adsorbed nitrogen to calculate the amount of substance. (from ideal gas equation of state). ($a_{0,2}$). This value is converted to one gram. (units – mol/g)

B) Relative pressure 0,3

Calibration:

“Area of peak” corresponds to the volume of nitrogen. (For example 7.0 $cm^3$ of nitrogen= designated area of peak).

Measurement:

The volume of adsorbed nitrogen of sample will determined from average area of peak.

Volume of adsorbed nitrogen to calculate the amount of substance (from ideal gas equation of state). ($a_{0,3}$). This value is converted to one gram. (units – mol/g).

C) BET equation

Substitute values $a_{0,2}$ and $a_{0,3}$ in the BET equation. The value of X is the corresponding relative pressure.

Plots of $\frac{X}{a.(1-X)}$ versus $X$ yield a straight line, from which the slope and intercept can be used to determine $a_m$ and $C$. The surface area $S_g$ of the specimen is

$$S_g = a_m.A_{N.}N_a$$

where $A_N$ is the cross-sectional area of the adsorbate molecule (for nitrogen is $1{,}62.10^{-19}$ $m^2$) and $N_a$ is the Avogadro constant.

**D) Compared with measurements ASAP**

Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry analyzer uses the gas sorption technique to generate high-quality data for research and quality control applications. The ASAP 2020 is used to monitor catalysts converting a stream of feedstock chemicals into a product, activated carbon used for the recovery of precious metals from a mining process solution, a pharmaceutical tablet as it undergoes dissolution and absorption at just the right dosing rate, and production of ceramics made from an exacting combination of finely powdered raw materials.

All ASAP 2020 Models includes:

- Single and Multipoint BET surface area
- Langmuir surface area
- Temkin and Freundlich isotherm analyses
- Pore volume and pore area distributions in the mesopore and macropore ranges by the BJH method using a variety or thickness equations including a user - defined, standart isotherm
- Pore volume and total pore volume in a user - defined pore size range
- Micropore distribution by the MP method and total micropore volume by the t-Plot and α Plot methods
- F-Ratio plots that illustrate the difference between theoretical and experimental isotherm data
- Heat of adsorption

With the Micropore option, the report set is expanded to include high-resolution distributions of micropore volume and area by pore size using the methods of:

- Dubinin – Radushkevich
- Dubinin- Astakhov
- Horvath-Kavazoe

## Experiment

**Preparation of sample**

*Material*: $TiO_2$-membrane

*Procedure*: Weight ca. 0,2 g sample and insert to the sample tube.

**1) Measurement**

The sample tube insert into instrument – degas port. Setup conditions analyze. (degas conditions, T-300 $^0$C, time 300 minutes, measurement conditions – five points BET method). Starts up degas. Wait to end degas. The sample tube insert into instrument -measurement port. Start up measurement. Wait to end measurement. Determine from results surface area and compare with previous measurements.

## Develop protocol and send in a week.