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Brunauer–Emmett–Teller (BET) surface area analysis: brief theory and instrumentation

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13 July 2019

Outline

1. Definition-discovery & what technique does
2. Definition-theory of BET, adsorption vs. desorption and adsorbates
3. Types of pores
4. Equipment
5. Sample preparation
6. Results obtained from instrument/software

Definition

- **Discovered by Stephen Brunauer, Paul Hugh Emmett and Edward Teller in 1938**
- **Studies physical adsorption of gas molecules on a solid surface**
- **Can therefore be used to study surface area & pore size distribution in given material**
- **Depends on T, P, surface energy distribution and surface area**

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Surface area	BET, Langmuir, Temkin, Freundlich	Can be calculated from section of isotherm (generally P/P_0=0.05-0.35)
Total Pore Volume	Kelvin equation	Generally carried out at P/P_0 = 0.99 – 0.998 although theoretically all pores should be full at P/P_0=0.995
Mesopore volume, area, and distribution	BJH, Dollimore-Heal	Requires full adsorption and desorption isotherms
Micropore distribution	Dubinin-Radushkevich and Astakhov, Horvath-Kawazoe, Saito-Foley, Cheng-Yang, MP method	Requires full adsorption isotherm
Pore size modeling	Density Functional Theory	Requires full adsorption isotherm
Surface energy	Density Functional Theory	Requires full adsorption isotherm

Definition

- **Gases that adsorb onto material surface are called adsorbates**
- **These gases should not chemically react with material surfaces**
- **Most common adsorbate is N_2**
  - **Ar, CO, CO_2, and O_2 may also be used**
  - **Volume of gas adsorbed is measured at boiling point of nitrogen (-196 ºC)**

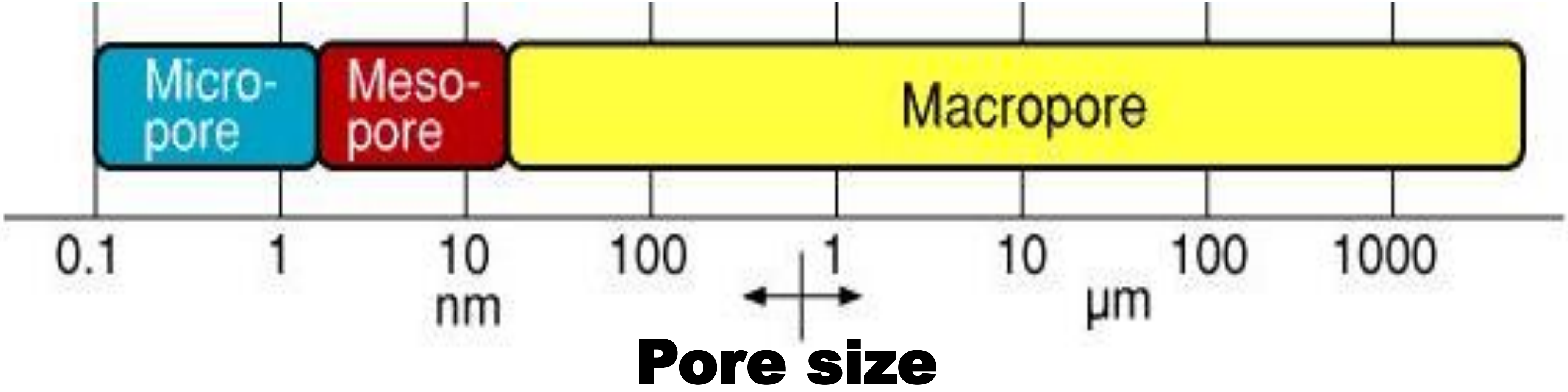
Definition

- **Adsorption vs. desorption:**
  - **Adsorption is the sticking of gas molecules onto the surface of a solid**
  - **Desorption is the removal of gas molecules from the surface of a solid**
  - **These include surfaces inside open pores**

Definition

- When the interaction between a surface and an adsorbate is relatively weak only **physisorption** takes place
- When electrons available for chemical bond formation on surface atoms, **chemisorption** occurs
  - activation energy-adsorbate molecules must overcome an energy barrier

Pore classification



- **Microporus <2nm**
- **Mesoporus 2-50nm**
- **Macroporous >50nm**

Definition

- **Assumptions:**

1. **Homogeneous surface**- adsorption occurs across entire surface with no preference for one or more sites
    - Each site is either unoccupied or occupied by a single adsorbate molecule
    - Once adsorbed, molecule can act as sorption site for another gas molecule

Definition

- **Assumptions:**

2. All sites on the surface are equal

3. No lateral interactions between molecules

4. Adsorbate molecule is immobile

5. The rate of adsorption is equal to the rate of desorption

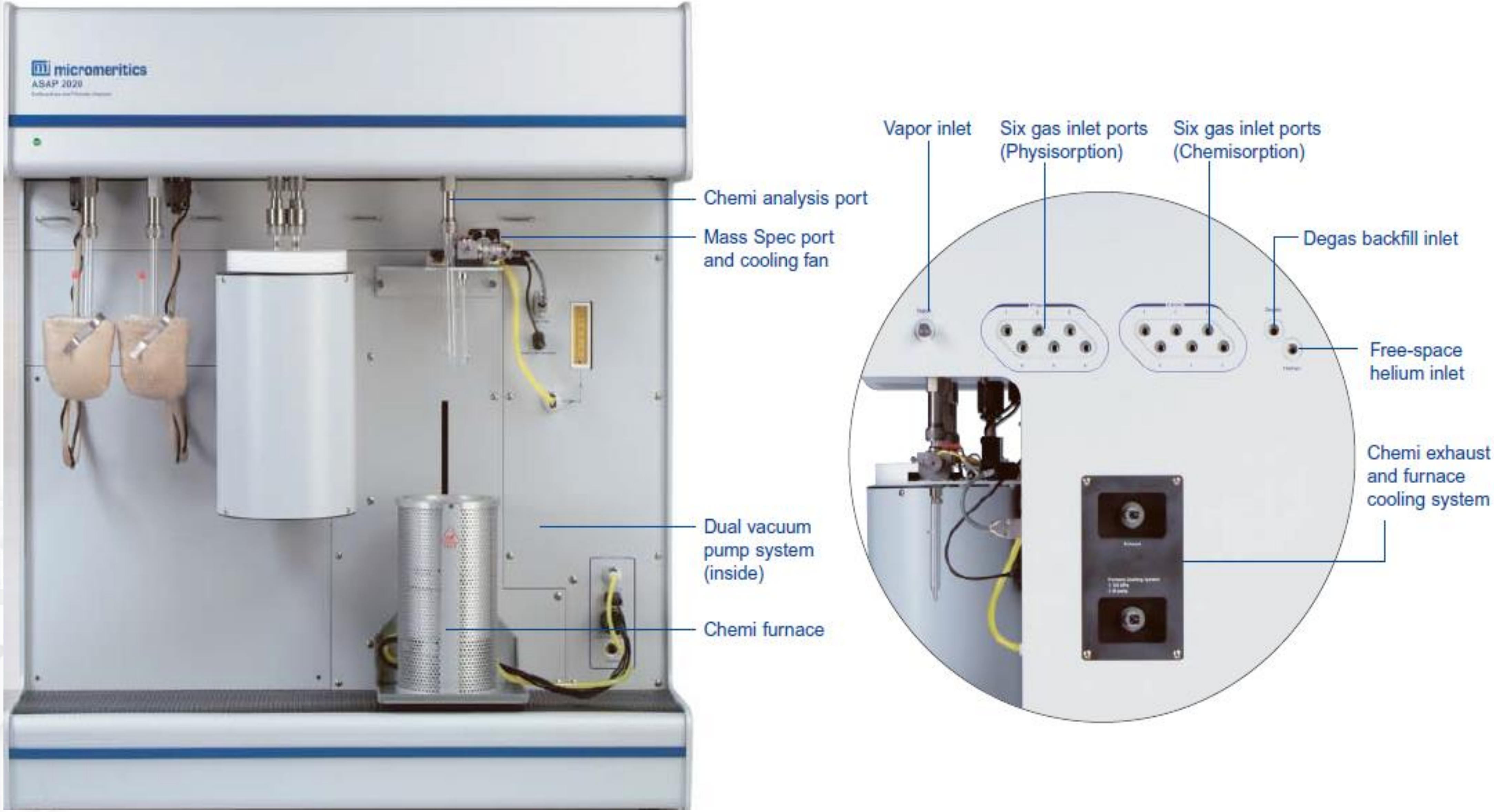
Equipment

micromeritics
ASAP 2020
Surface Area and Porosity Analyzer

Equipment


ASAP 2020
Programmable two-station degas system
Isothermal jacket
Vacuum cold trap
Long-duration Dewar (more than 72 hours)

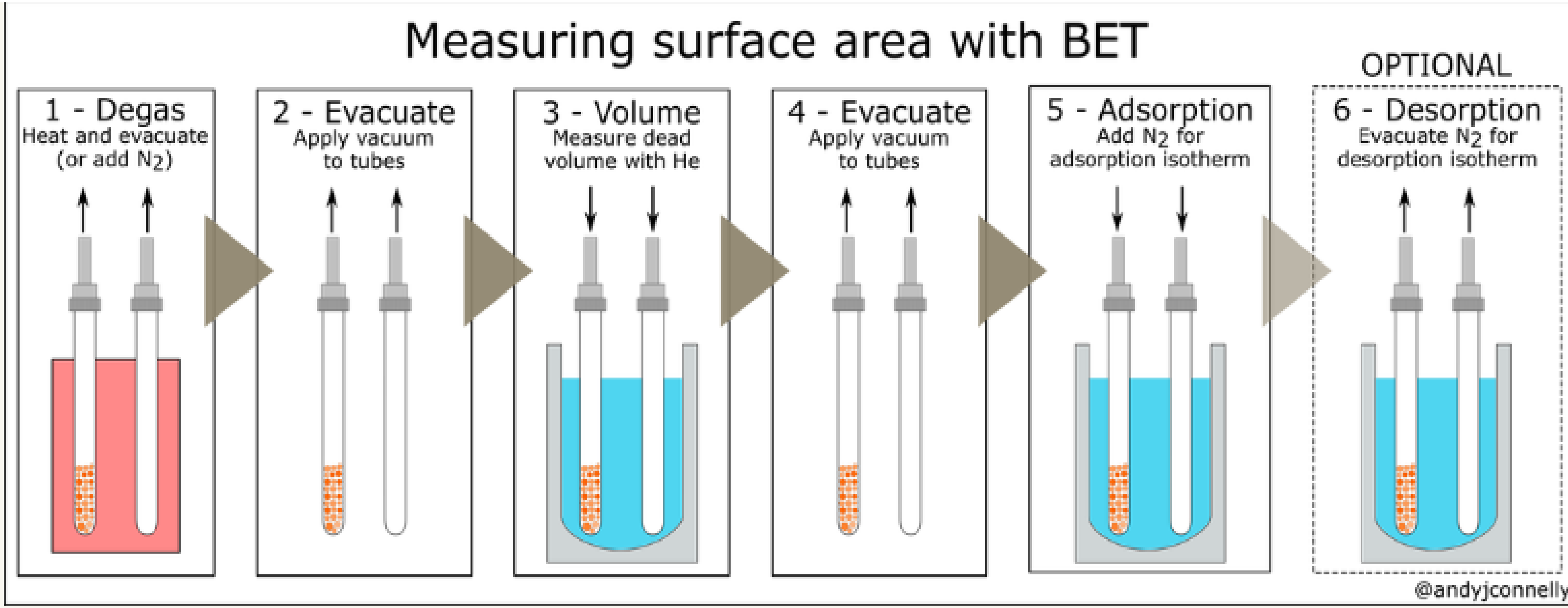
Equipment


micromeritics
ASAP 2020
Chemi analysis port
Mass Spec port and cooling fan
Dual vacuum pump system (inside)
Chemi furnace
Vapor inlet
Six gas inlet ports (Physisorption)
Six gas inlet ports (Chemisorption)
Degas backfill inlet
Free-space helium inlet
Chemi exhaust and furnace cooling system

Sample preparation

- Clean, pure & dry sample
- Measurement of sample mass
- Degassing the sample using heat & vacuum
- Heating releases water vapor
- Measuring adsorption
- Analyzing measurement

Sample preparation

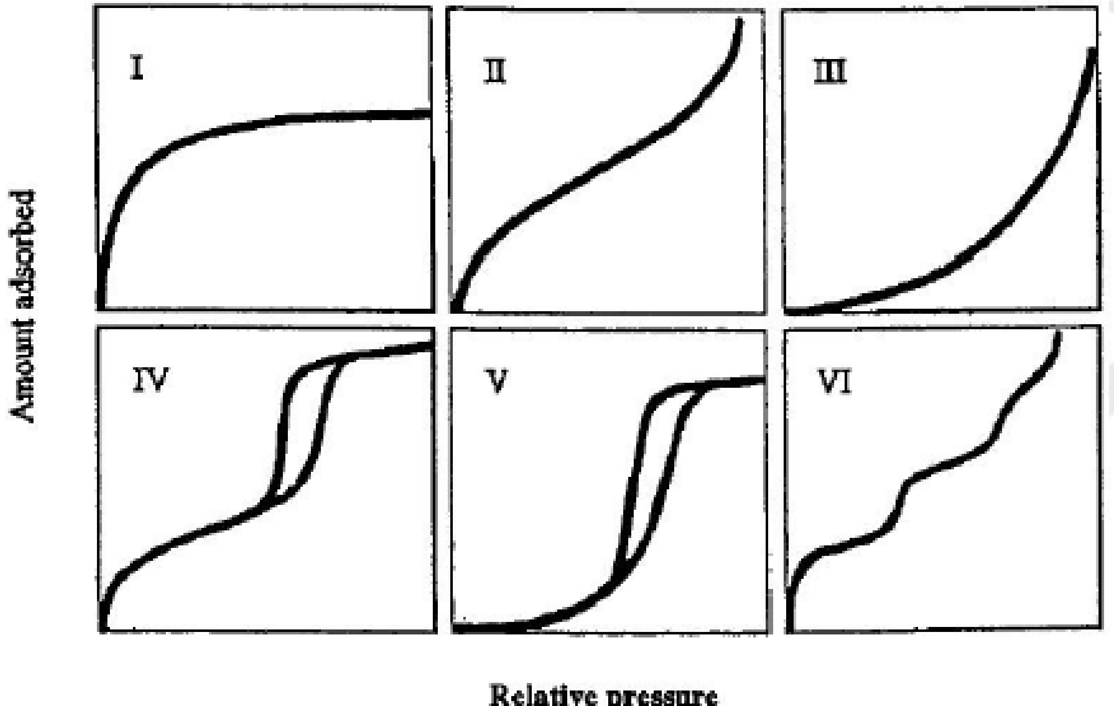


Isotherms

- 6 isotherms & BET applicable to:

type II (disperse, nonporous or macroporous solids)

type IV (mesoporous solids; pore diameter 2-50 nm)



The BET linear equation

$$\frac{1}{W\left(\left(P_0/P\right)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right)$$

W= weight of gas adsorbed

P/P_0 =relative pressure

Wm = weight of adsorbate as monolayer

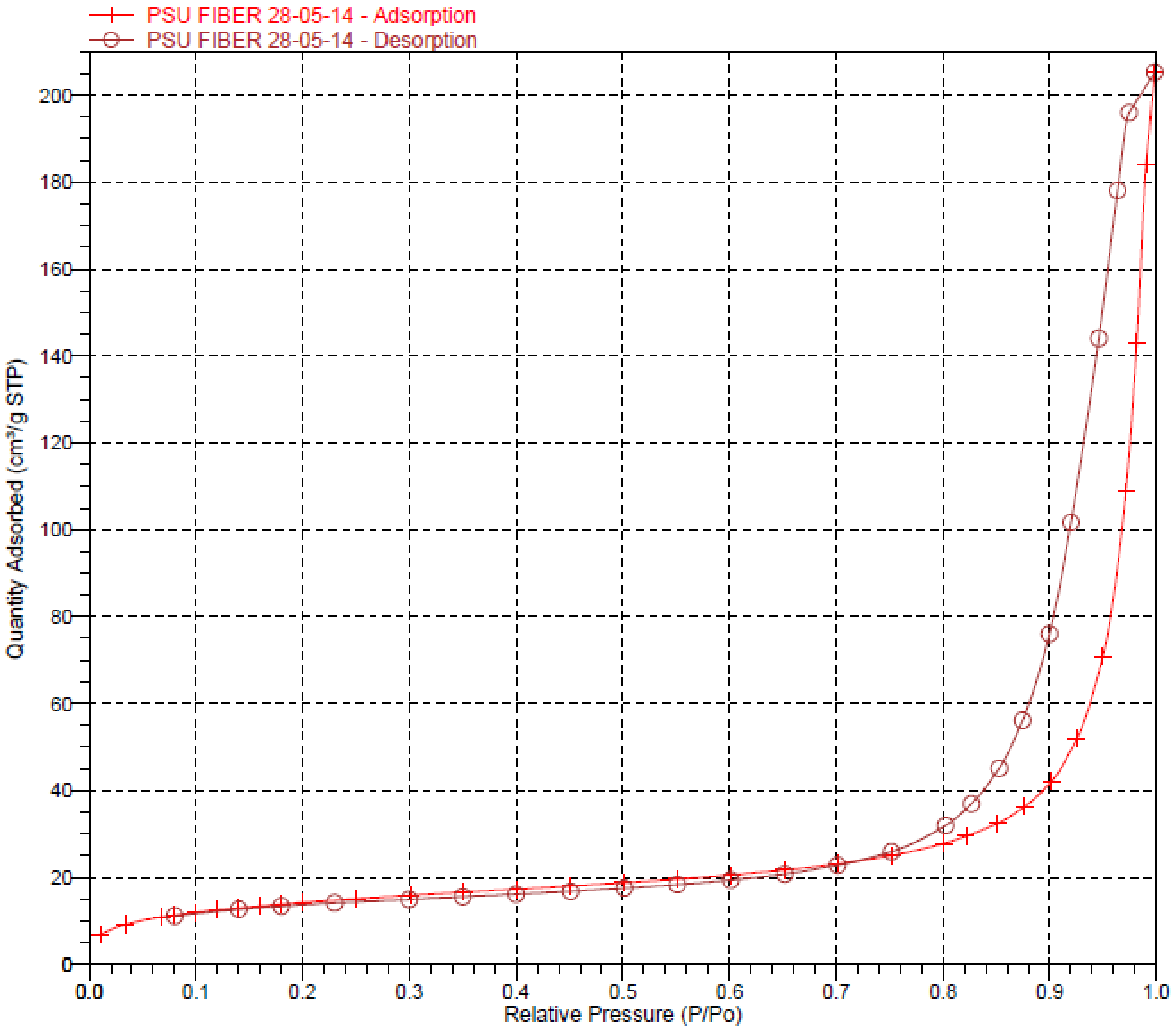
C = BET constant

Results obtained

Isotherm Tabular Report

Relative Pressure (P/Po)	Absolute Pressure (mmHg)	Quantity Adsorbed (cm^3/g STP)	Elapsed Time (h:min)	Saturation Pressure (mmHg)
0.651836196	473.429138	20.7401	07:35	
0.601228584	436.672791	19.3545	07:38	
0.551034638	400.216888	18.2998	07:42	
0.501234484	364.046997	17.4776	07:46	
0.451258022	327.749054	16.7214	07:49	
0.399832030	290.398315	16.0543	07:53	
0.349851051	254.097092	15.4635	07:56	
0.299844400	217.777222	14.8354	07:59	
0.229961637	167.021317	14.0502	08:02	
0.179915174	130.672531	13.2939	08:06	
0.140199811	101.827232	12.5832	08:09	
0.080126871	58.196209	11.0801	08:13	

Results obtained



Results obtained

BET Surface Area Report

BET Surface Area: 49.5820 ± 0.7249 m^2/g
Slope: 0.087270 ± 0.001264 g/cm^3 STP
Y-Intercept: 0.000528 ± 0.000221 g/cm^3 STP
C: 166.425263
Qm: 11.3898 cm^3/g STP
Correlation Coefficient: 0.9991614
Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (P/Po)	Quantity Adsorbed (cm^3/g STP)	1/[Q(Po/P - 1)]
0.068087909	10.8554	0.006731
0.079936541	11.2290	0.007737
0.099916081	11.8922	0.009334
0.119986694	12.4611	0.010942
0.139950966	12.8949	0.012619
0.159806150	13.3244	0.014275
0.179918207	13.7578	0.015947
0.199958369	14.1398	0.017676
0.250164656	15.0133	0.022222
0.301304540	15.7727	0.027341

Conclusions

- **BET can be used for:**

1. **Fibers**
2. **Nanocatalysts (chemisorption)**
3. **Nanotubes**
4. **Polymer membranes**

References

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https://andyjconnelly.wordpress.com/2017/03/13/bet-surface-area/