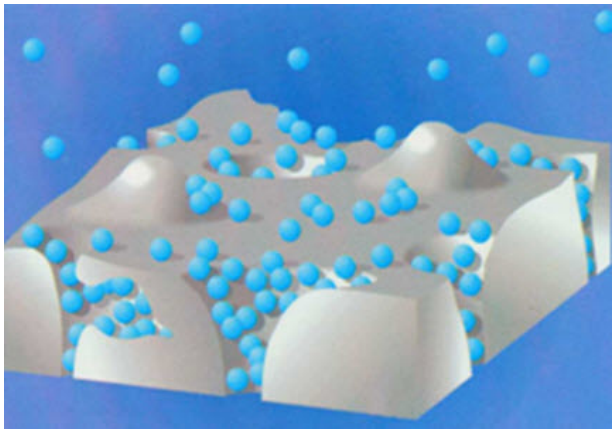
Introduction to Surface Area Analysis



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HORIBA Scientific
www.horiba.com/us/particle

Outline

- Why determine surface area?
- Surface area and size
- Determining surface area

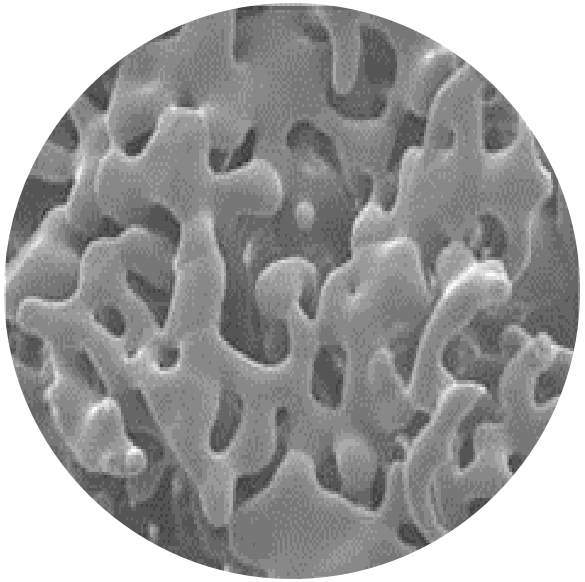
Why surface area?

Surface area directly correlates with desired properties.

- Reactivity
- Dissolution
- Catalysis
- Separation

Applications

- Catalysts
- Adsorbents
- Pigments
- Pharmaceutical products
- Chromatographic carriers
- Sintered materials
- Building materials
- Ceramics
- Filters



Chemical reactions

When a solid is involved in a chemical reaction, either as a reagent or a catalyst, the surface area is the only accessible area for the reaction.

Dramatic example: dust explosions!

Dissolution

- Dissolution of materials (e.g., API's) depends on surface area.
- Noyes–Whitney Equation

$$\frac{dm}{dt} = A\frac{D}{d}(C_s - C_b)$$

m = mass dissolved material
t = time
A = Surface area of interface
D = Diffusion coefficient
d = Boundary layer thickness
C_s = Concentration of substance on surface
C_b = Concentration of substance in solvent

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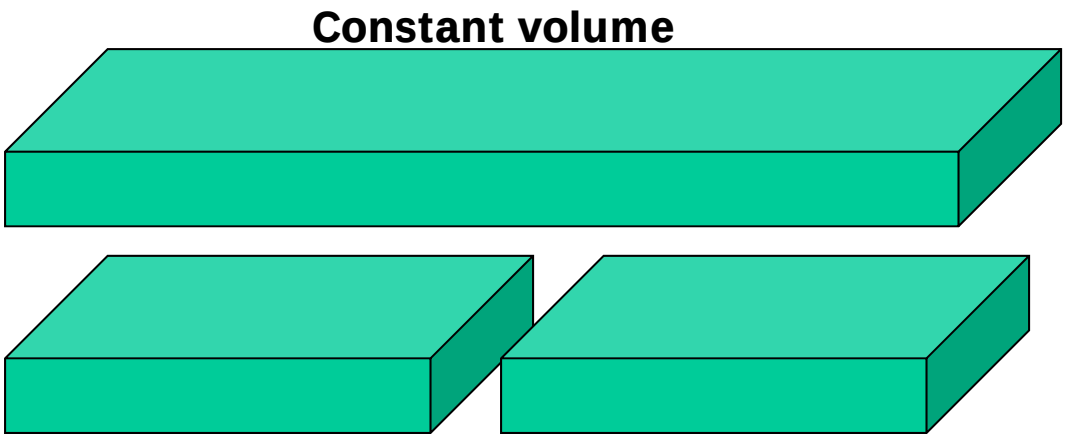
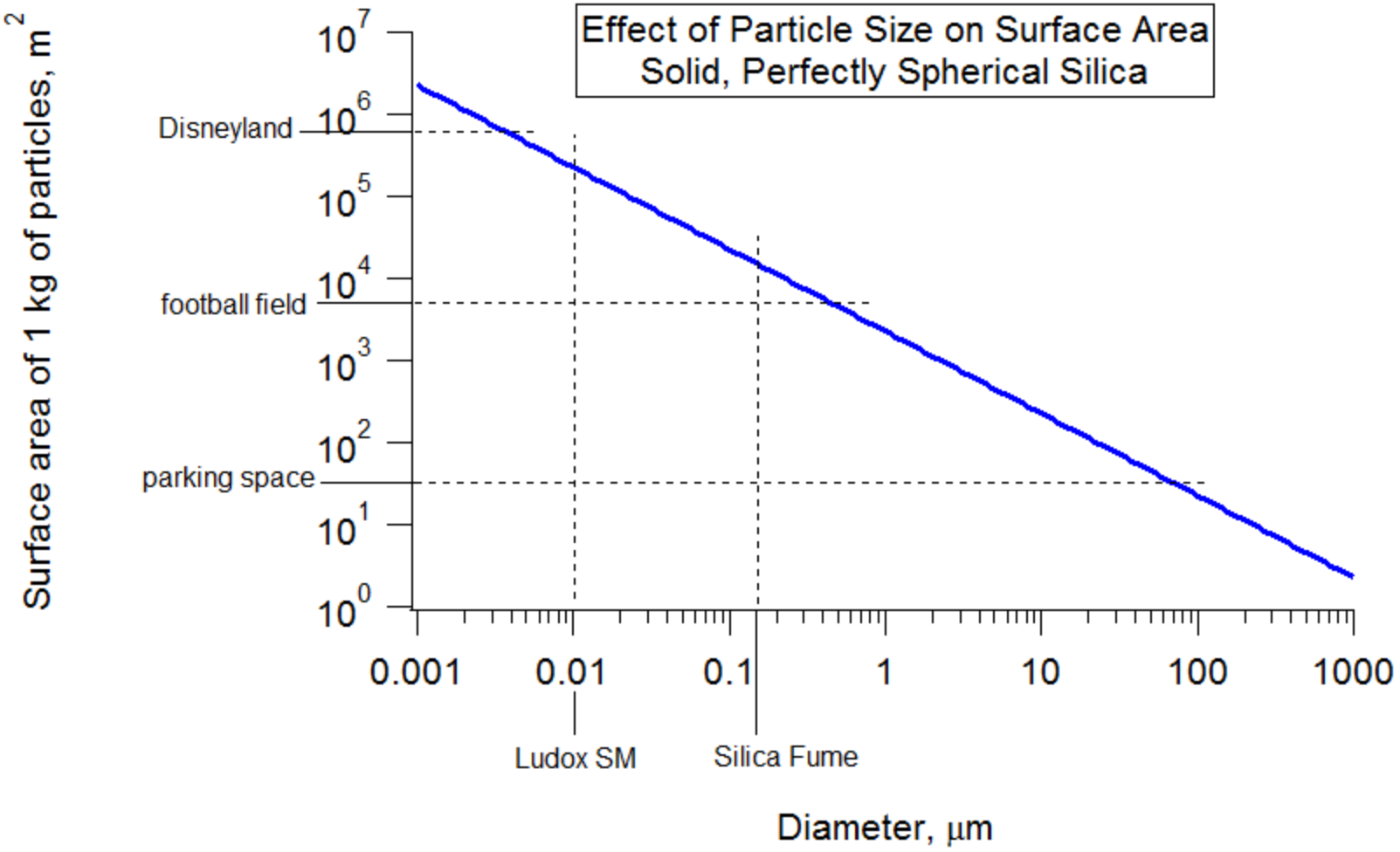
Surface area vs. particle size

When a particle of a given volume is broken into two parts as shown in the figure, total volume does not change. The total surface area, however, does change. It INCREASES by the amount of the two newly–exposed edges.

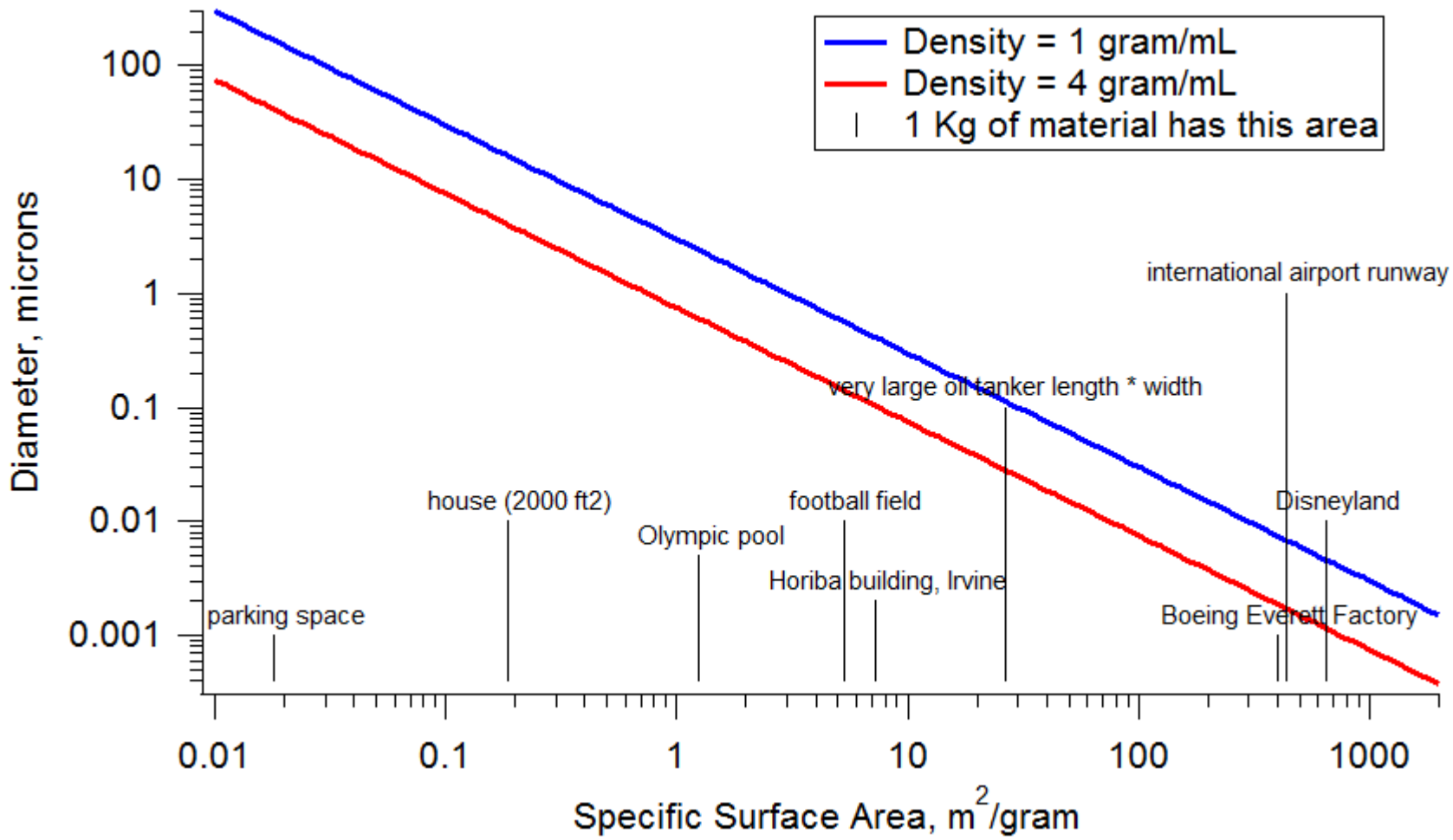


This simple illustration demonstrates relationship between surface area and particle size. As ratio of surface area to volume increases, surface phenomena come into play. For this reason, measurement of surface area becomes much more important for small particles.

Small size -> Large surface area



Small Size -> Large Surface Area

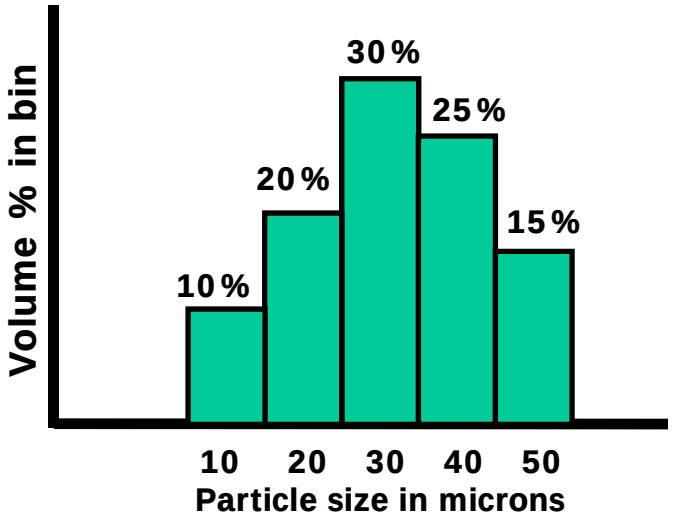


Surface Area and Size

$$S = 4\pi(d/2)^2$$

$$V = \tfrac{4}{3}\pi(d/2)^3$$

$$D_V = \frac{\sum V_i d_i}{\sum V_i}$$

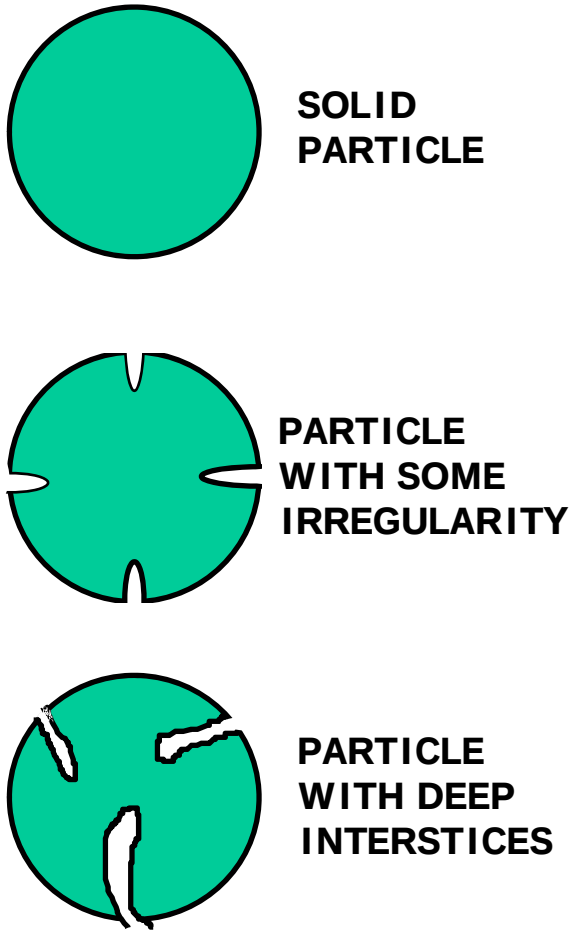


$$D_S = \frac{\sum S_i d_i}{\sum S_i} = \frac{\sum S_i d_i}{\sum S_i} = \frac{\sum (6V_i / d_i) d_i}{\sum (6V_i / d_i)} = \frac{\sum V_i}{\sum (V_i / d_i)}$$

Surface area mean size can be arithmetically calculated from a measured volume based particle size distribution.

Surface roughness

- Surface area measurement using nitrogen adsorption detects total surface area of the particles.
- Conventional particle sizing detects only the overall structure of the particles.
- All of these particles will produce same result using conventional particle size measurement techniques.
- Nitrogen adsorption methods will yield progressively higher results for particles with greater irregularities.



Surface area and shape

- We can use a size analyzer, but eventually prefer to measure surface area directly.
- Specific surface area for a given size changes according to shape
- Another way to think about determining particle shape or surface roughness

Outline

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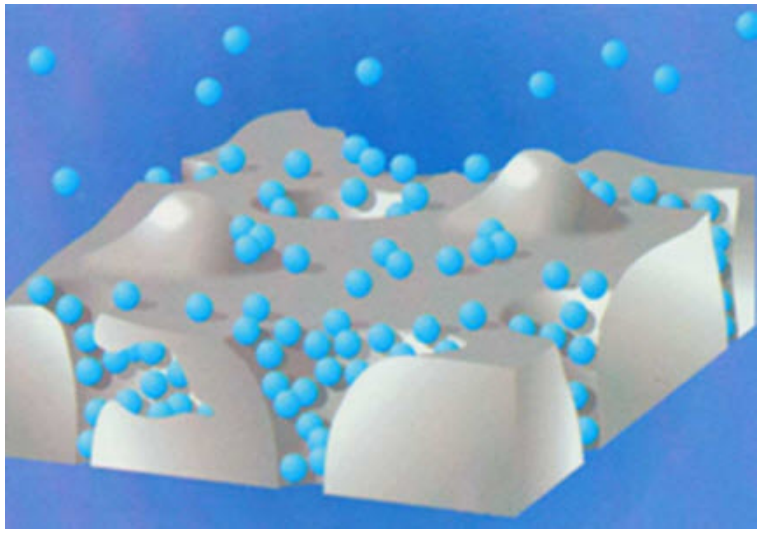
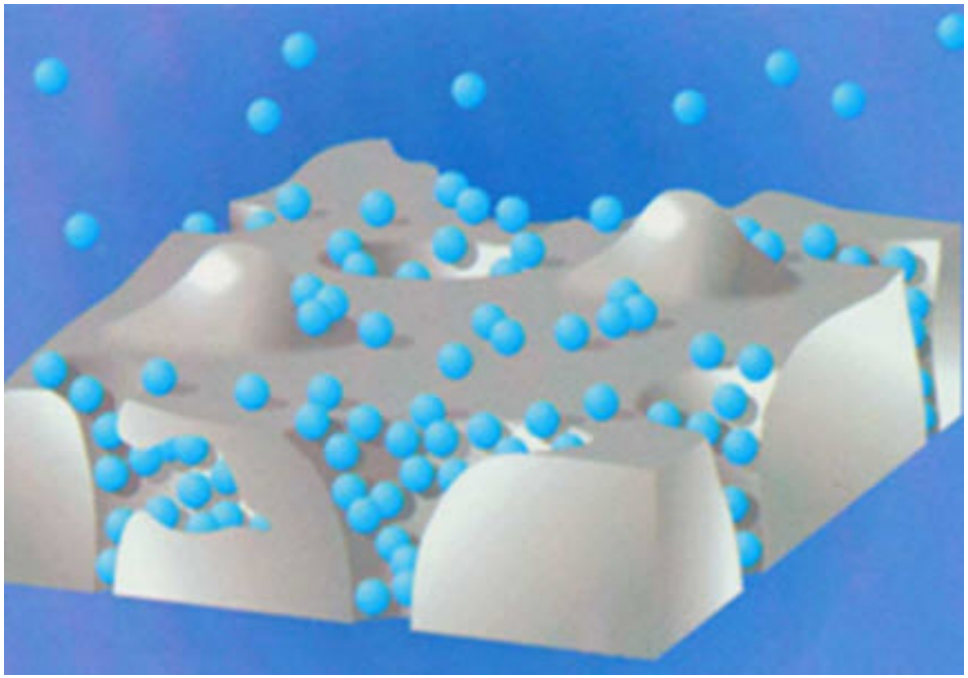
Nitrogen adsorption

To find surface area, “simply” determine amount of N_2 adsorbed to the surface in a single layer. Use the projected surface area of each molecule times the number of molecules to find surface area.

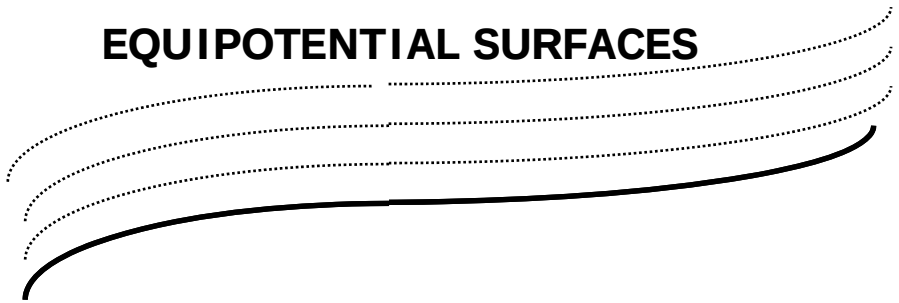


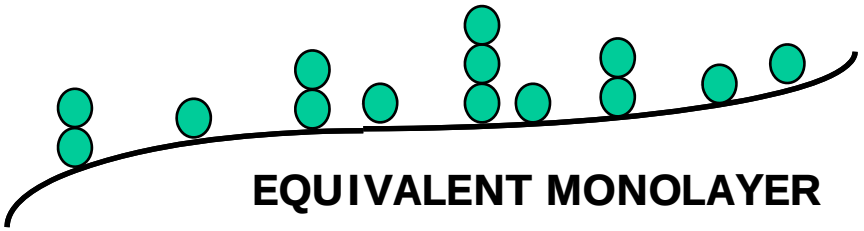
Really?

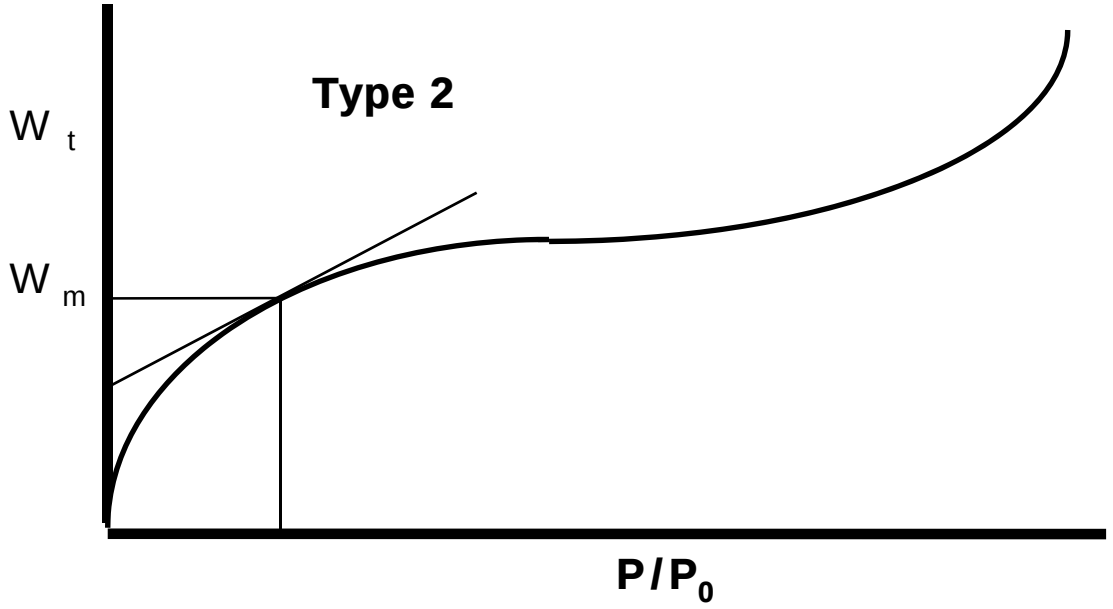
Need a single layer, but how do we find a single layer? Need to look at adsorbed N_2 as a function of pressure.



Surface area

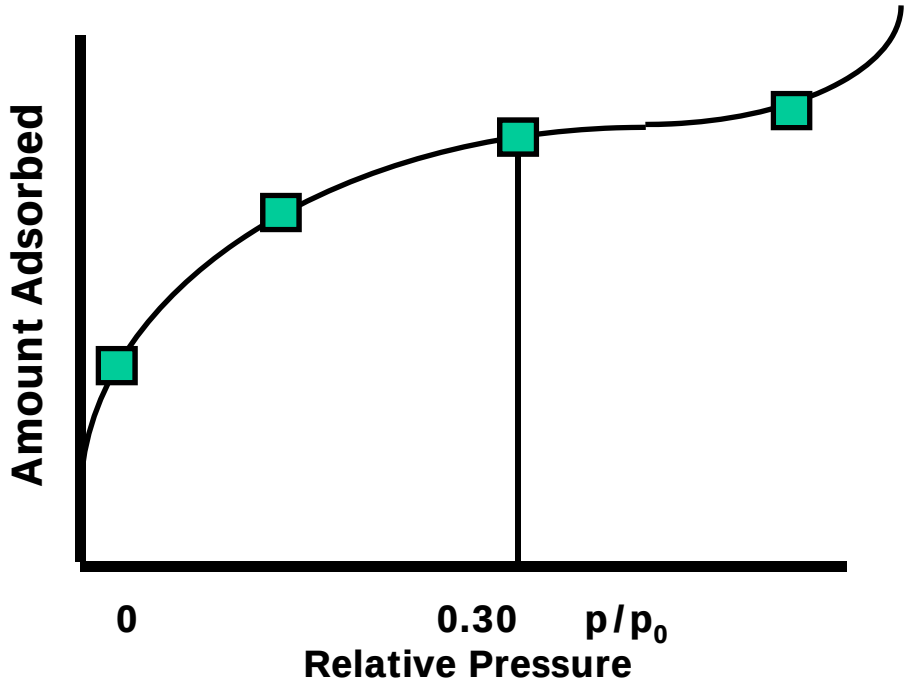






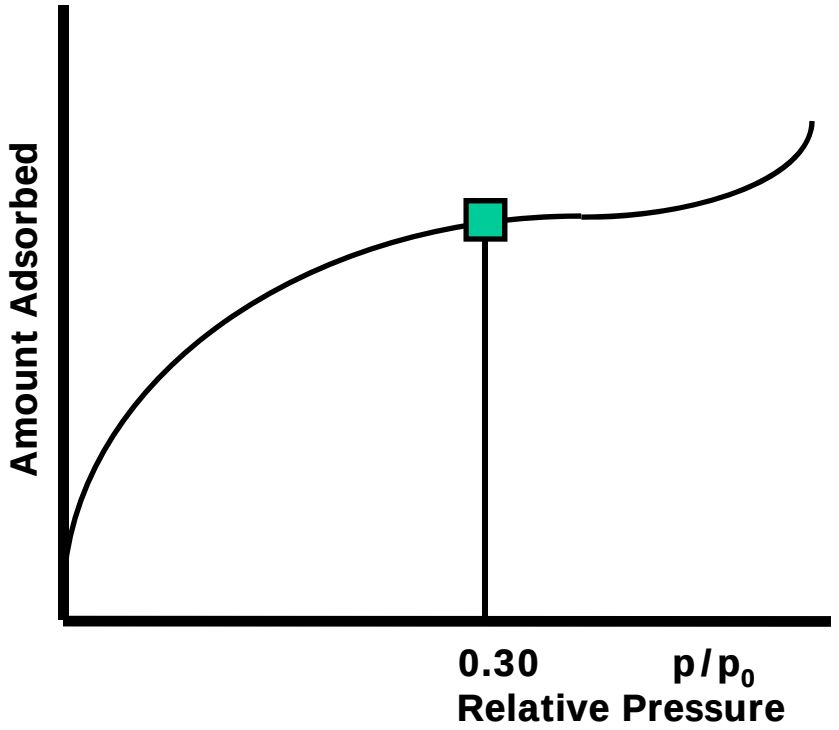
Multi-point method

- Used for unknown materials to determine behavior of the material.
- Measure multiple points to two parameters (a material constant and the surface area).



Single-point method

- Once that determination has been accomplished, a SINGLE POINT MEASUREMENT is quite satisfactory for many (90-95%) practical cases.



Monolayer volume

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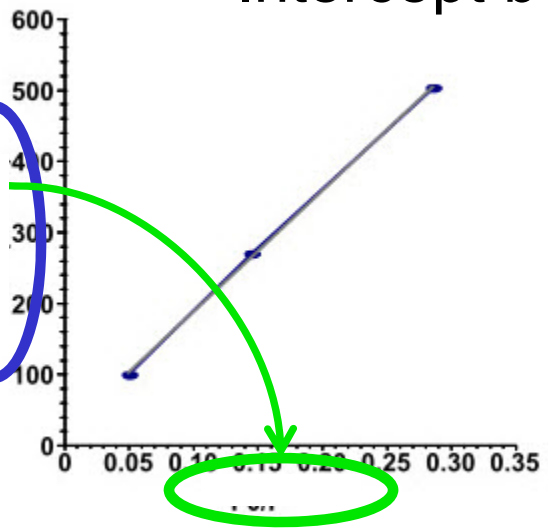
BET equation

$$Y = m \quad x + b$$

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

Slope m

Intercept b



P = N_2 partial pressure
P_0 = N_2 equilibrium vapor pressure
W = mass adsorbed N_2
W_m = mass of N_2 monolayer
C = BET constant

Monolayer volume

BET equation

$$Y = m\ x + b$$

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

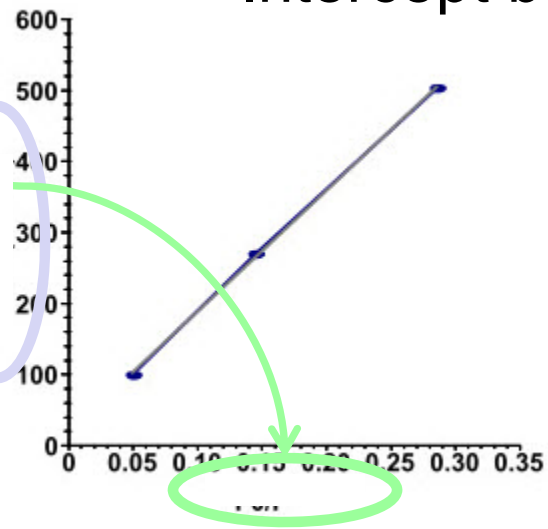
Intercept b

Slope m

$$W_m = \frac{1}{b+m}$$

We use W_m to get surface area.

$$C = \frac{m+b}{b}$$



Monolayer volume

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Measuring for BET equation

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

P = N_2 partial pressure = controlled by instrument (MFC)
P_0 = N_2 equilibrium vapor pressure = known
W = mass adsorbed N_2 = measured from desorbed volume of nitrogen
W_m = mass of N_2 monolayer = found from equation
C = BET constant = found from equation

Single Point Measurement

- The single-point method B.E.T. method is applicable to many, but not all samples.
- For unknown materials, the multi-point method is best. However, for most materials, the single point method applies. Single point is preferred because it is much simpler and faster to use.
- Measure at a single N_2 pressure.

- References:
- Brunauer,S., Emmett, P., and Teller, E., J. Amer. Chem. Soc. 60, 309 (1938)
- Gregg, S.J., and Sing, K.S.W., Adsorption, Surface Area & Porosity, Academic Press, (1967)

Monolayer mass, Single Point

BET equation

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

$$C \to \infty \qquad \frac{1}{W_m C} \to 0 \qquad (C-1) \to C$$

$$W\left(1-P/P_0\right) = W_m$$

Measure W at one value of P/P_0 and obtain W_m.

Getting surface area from W_m

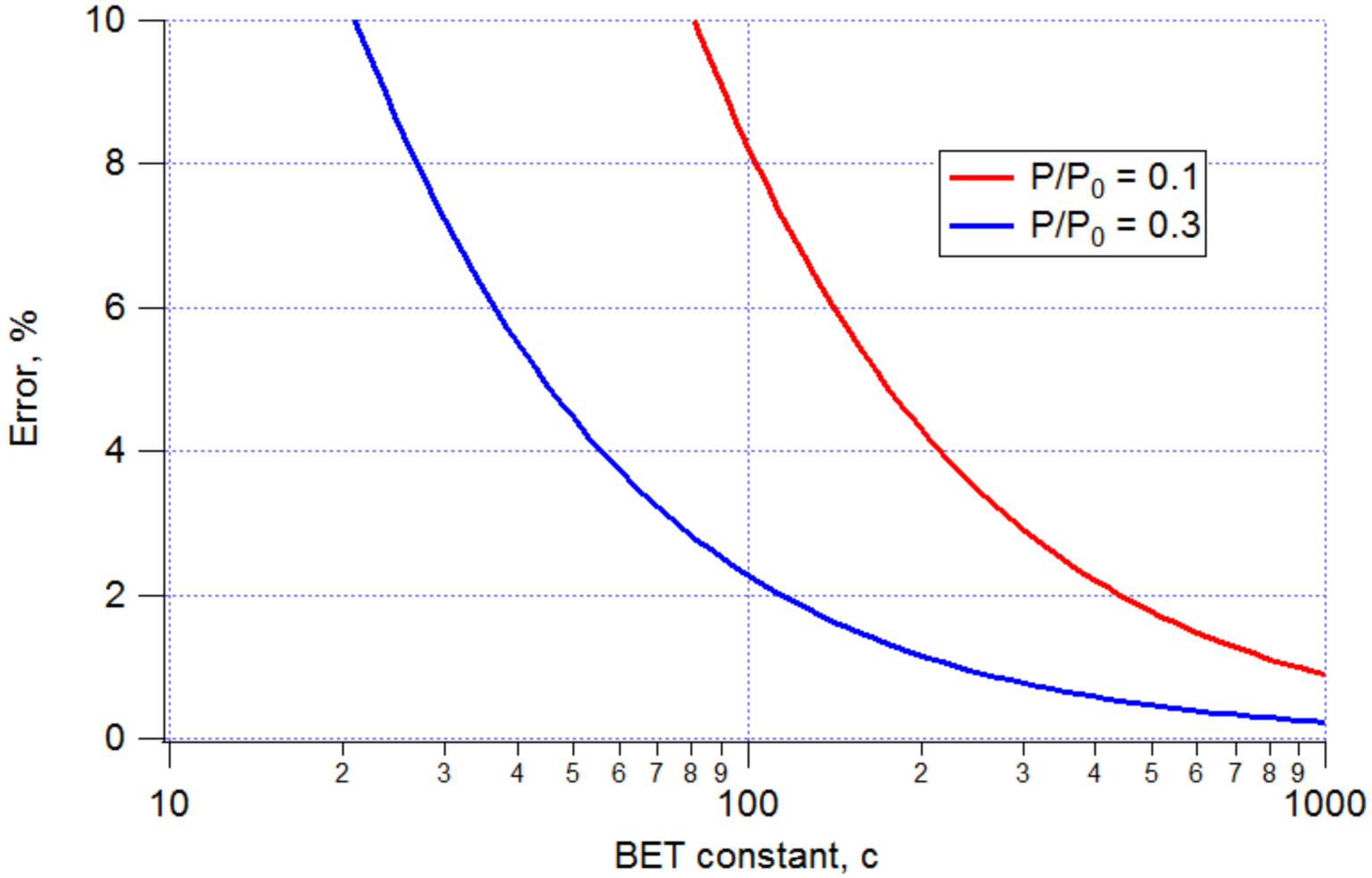
- We obtain W_m from linear plot (multipoint) or single point.
- Use W_m (quantity of N_2) and cross sectional area of N_2 to determine surface area:

$$S_t = \frac{W_m N_A A_x}{M_w}$$

S_t=Total surface area
W_m = Mass of N_2 monolayer
M_w = Molecular weight of N_2 = 28 g/mol
N_A = Avagadro's Number = 6.02 x 10^{23} molecules/mol
A_x = 16.2 x 10^{-20} m^2/molecule

Single point measurement errors

If we know c, we can predict error in single point results.



Getting to single point when life is bad

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Single-point method offers the advantage of simplicity and speed, with acceptable accuracy.

$$V_m = V_a\left(1 - P/P^o\right) \qquad \text{i.e. } V_m = 1/slope$$

A relative pressure of 0.3 gives good general agreement with the multi-point method.

Correction of single point "error" at P/P_0 = 0.3 by multiplying the single point BET value by C/C-2 decreases the difference.

Sample No.	Multi-point BET (m^2/g)	Uncorrected single-point (m^2/g)	Uncorrected difference (%)	Corrected single – point (m^2/g)	Corrected difference (%)
1	4.923	4.241	-13.9	4.948	0.51
2	4.286	3.664	-14.5	4.275	-0.26
3	8.056	6.867	-14.8	8.011	-0.56
4	5.957	5.194	-12.8	6.060	+1.73

Sampling matters!

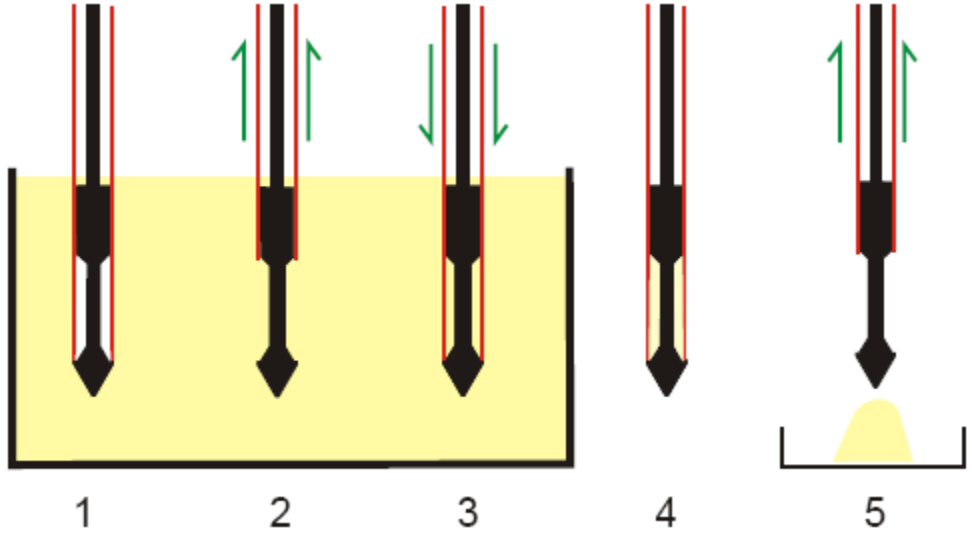
- Not all of sample brought to lab is analyzed

Bulk or process stream	Gross sample	Laboratory sample	Test sample	Measurement sample
10^n kg	>kg	<kg	g	mg

- Must sub-divide sample
- How to introduce representative sample into instrument?

Sampling from Drums

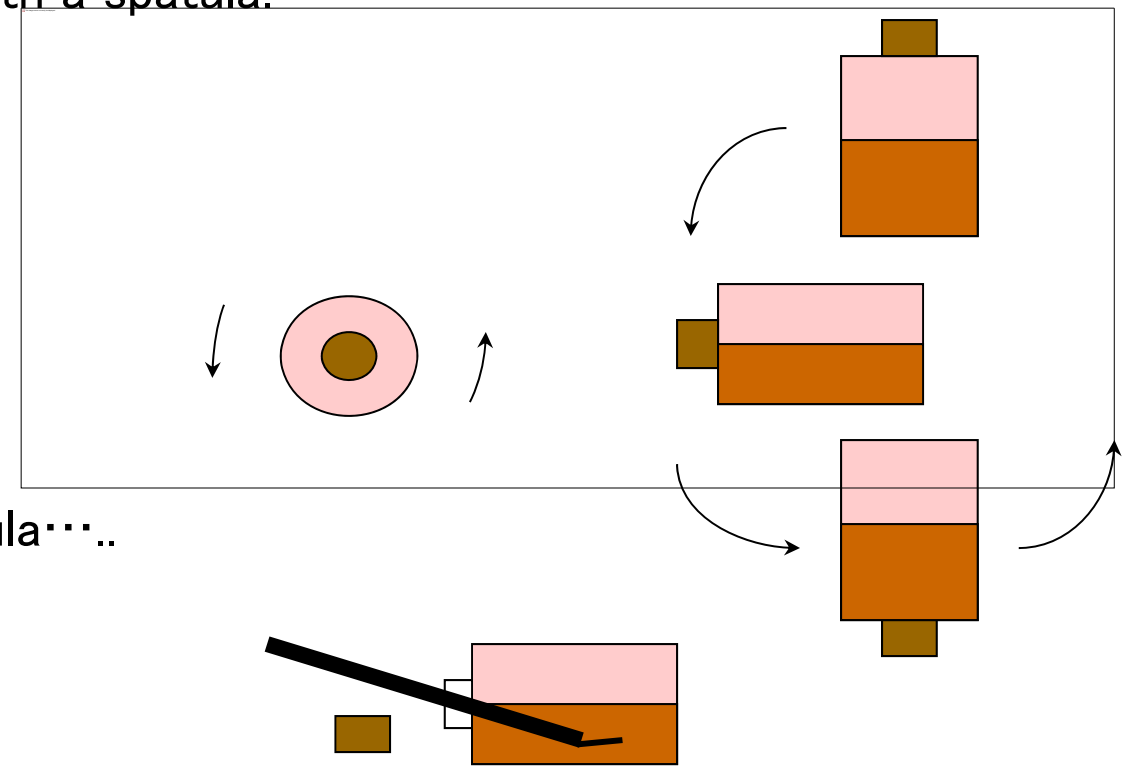
Powder Thief



www.samplingsystems.com

Grab Sampling from Bottle

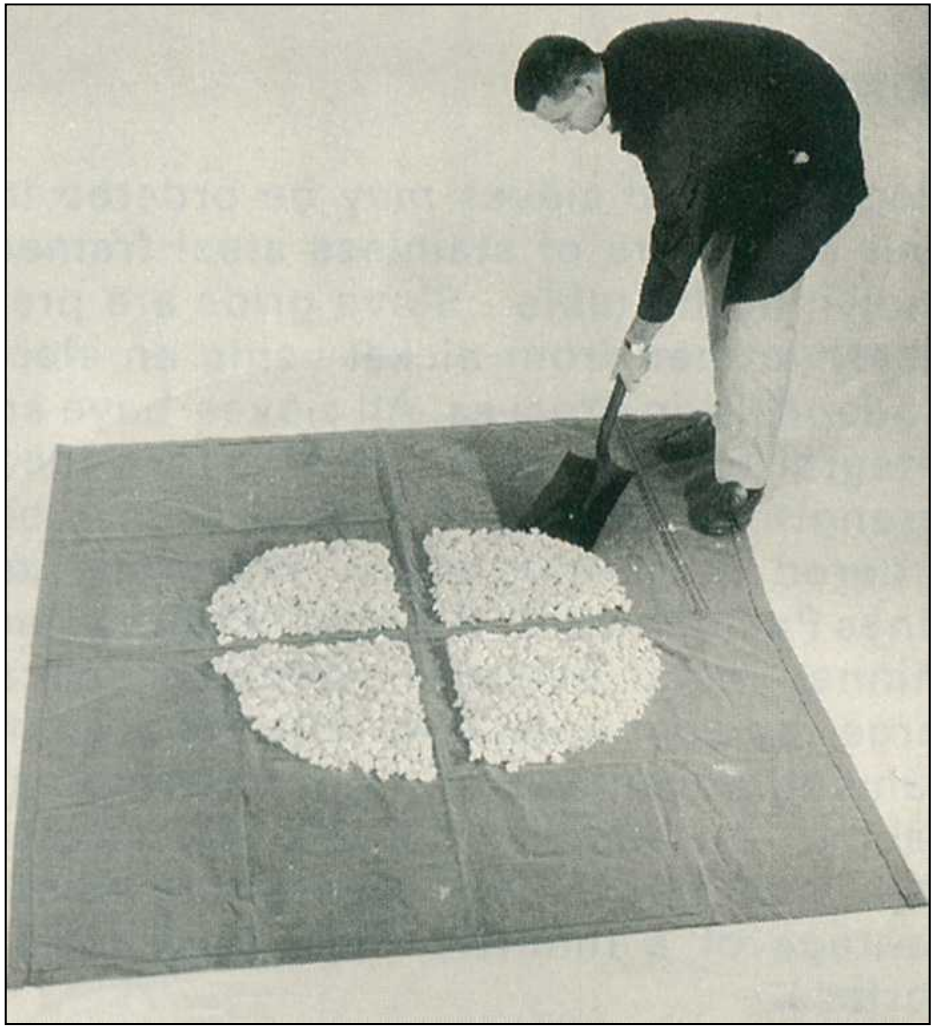
When a powder is stored in a container, it can be mixed by rolling and tumbling the container. The container should not be more than half to two-thirds full. It is important to perform this action before "grabbing" a sample with a spatula.



Then pull sample with a spatula…..

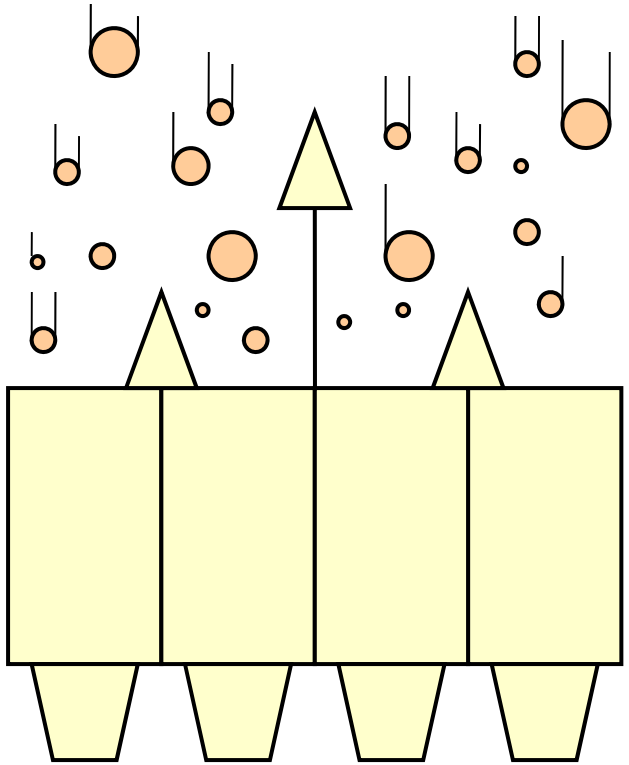
Technique: Coning & Quartering

- Pile of powder is divided into 4 sections.
- Two diagonal sections are discarded, and two are retained and mixed together.
- Mixture is again divided into 4 sections, and two diagonal sections are mixed.
- Process is repeated until remaining sample is correct amount for analysis.
- Can be carried out with very small sample amount or very large samples.



Technique: Chute Riffling

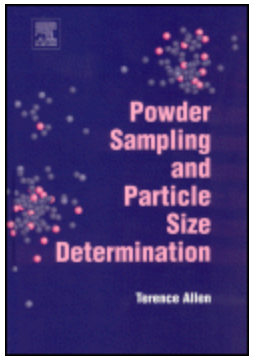
Chute splitting allows sample to vibrate down a chute to vanes which separate the mass into two portions. Each portion moves further where they each are divided into two parts, now giving four parts. This may be continued until usually 8 or 16 portions are obtained.



Sampling Technique Error Levels

Standard Deviation (σ) in % Sugar–Sand Mixture

SCOOP SAMPLING	6.31
TABLE SAMPLING	2.11
CHUTE RIFFLER	1.10
SPINNING RIFFLER	0.27



Density of sand and sugar respectively 2.65 and 1.64 g/ml

Reference: Allen, T. and Khan, A.A. (1934), Chem Eng, 238, CE 108–112

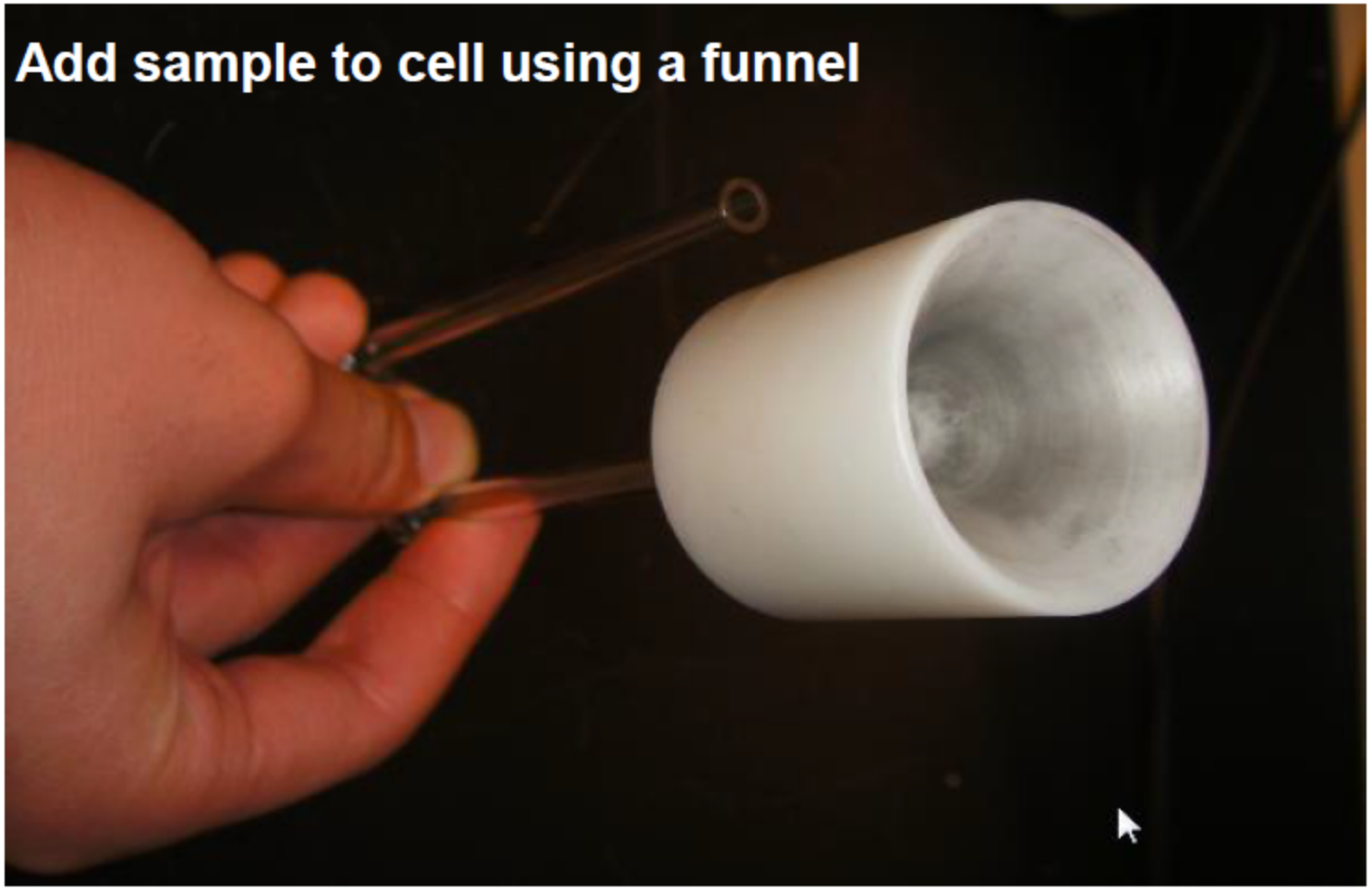
Method	Relative Standard Deviation (%)
Cone & Quartering	6.81
Scoop Sampling	5.14
Table Sampling	2.09
Chute Riffling	1.01
Spin Riffling	0.125

Weighing out sample

- Frequent source of error.
- Use a balance with four places.
- Carefully determine and record mass of empty sample cell. You will need this value after measurement.

Add sample

- Record mass of cell+sample



Degassing

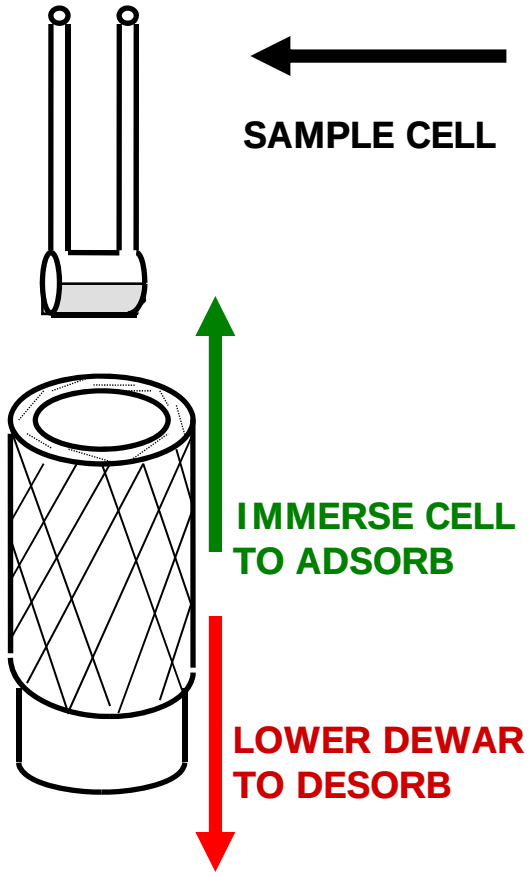
- Material in Sample Cell must be OUTGASSED
  - Sample cell containing sample must be heated to over 100 C° for at least 20 to 30 minutes to drive off impurities that adhere to surfaces.

Degassing

- Need to heat sample under inert gas to drive off moisture and volatile components.
- Very sample dependent.
- High temperatures can affect some materials.
- Low temperatures require a longer time.
- Good degassing will make the results independent of sample history (e.g., humidity during manufacturing).
- Typically 1–2 hours at 200–300 C
- Inorganic oxides 120 to 150 C (NIST practice guide)
- Microporous carbons and zeolites: 300 C

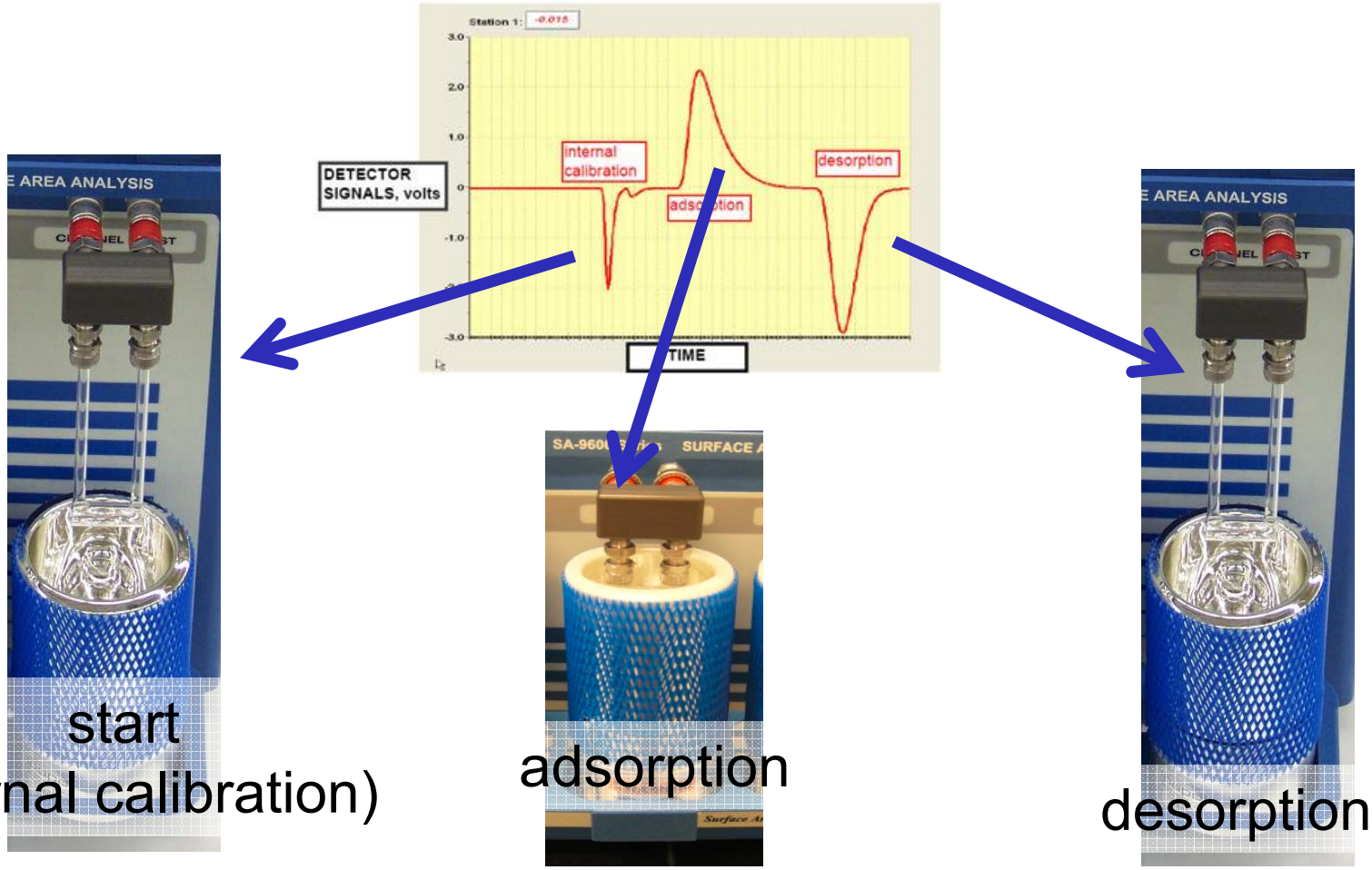
Measurement

- Sample cell is partially filled with sample material, immersed into liquid nitrogen to cool sample so nitrogen gas will condense on particle surfaces.
  - Adsorption Phase: Nitrogen gas condenses on particle surfaces, resulting in a LOSS of gas.
  - Desorption Phase: Nitrogen gas evaporates from particle surfaces, resulting in a GAIN of gas.



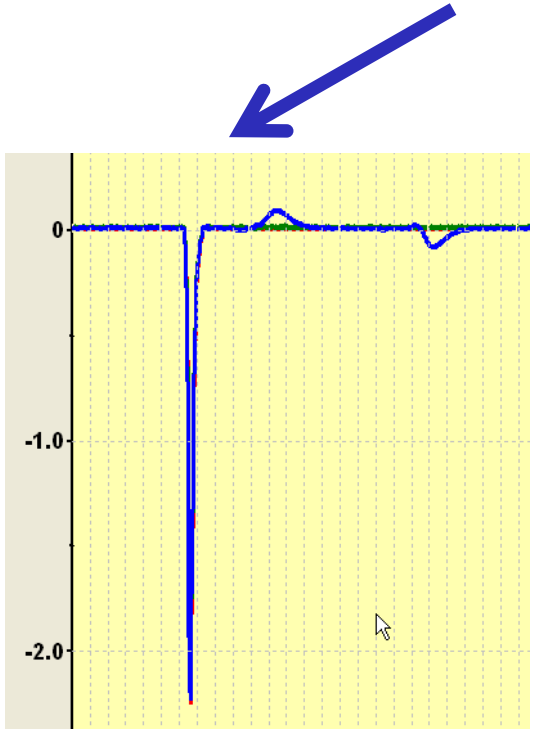
W, mass adsorbed

To measure adsorbed mass we can measure loss of N_2 flowing across surface (adsorption process) or "extra" N_2 that appears as N_2 flows across surface (desorption process).



Comparison

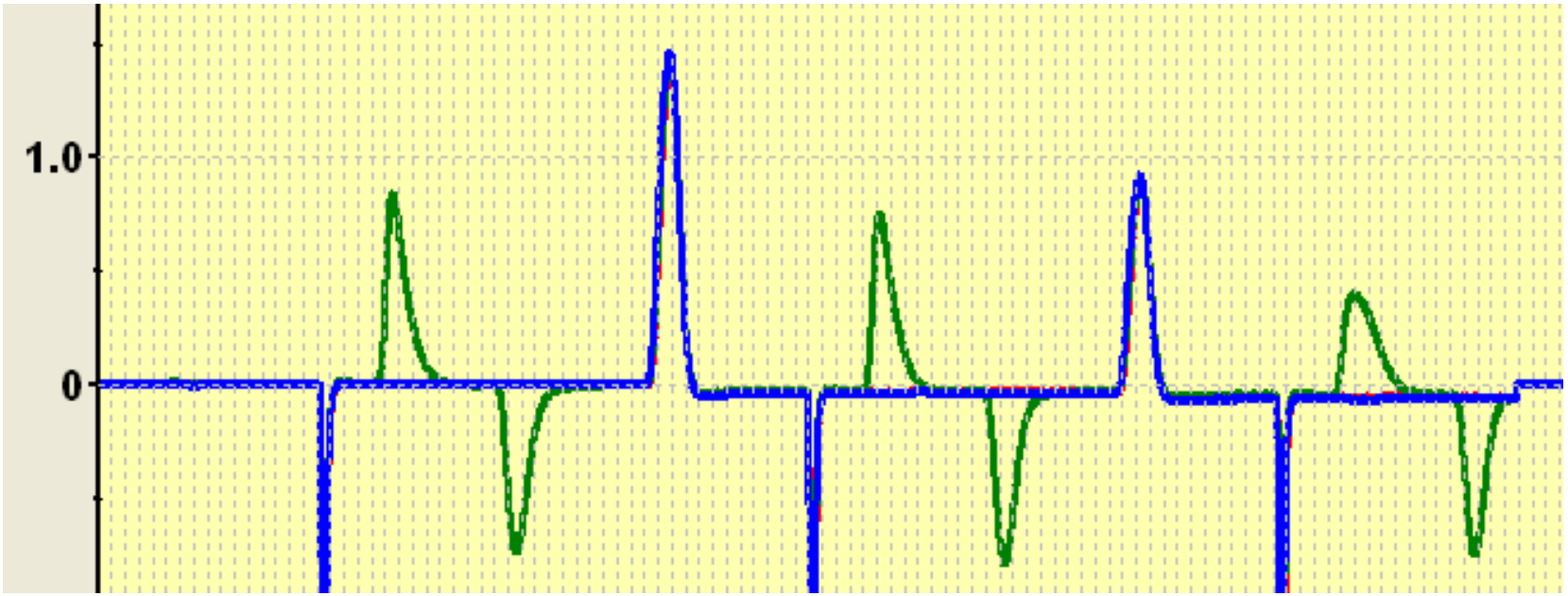
Small surface area



Large surface area

Multi-point

Make measurement at different N2 concentrations. Note baseline steps.



End of measurement

- Weigh after degassing (very important)
- Did you keep your tare value?
- Mass determination is a major source of uncertainty. For 0.1 gram of sample an weighing error of 0.001 gram (1 milligram) will give a 1% error in results.

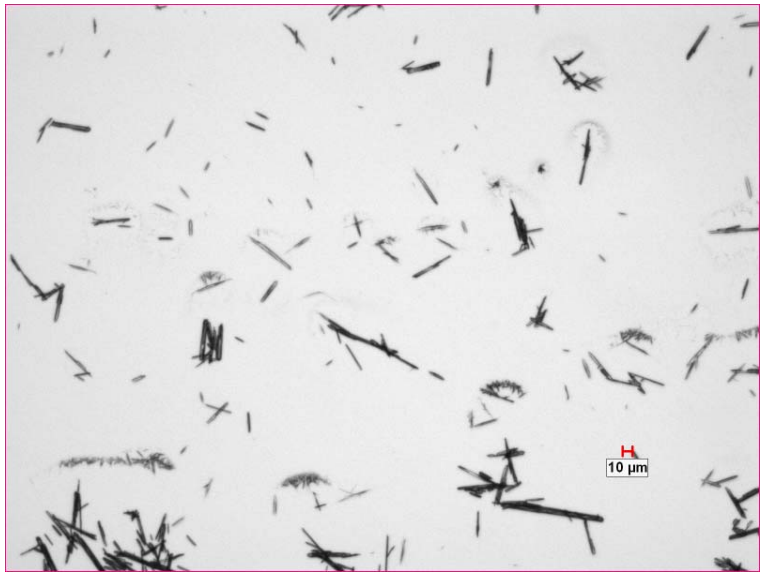
Standards

- NIST 2207
- Certified mean value of single point surface area is 174.2

	2207
Test 1	174.07
Test 2	179.15
Test 3	171.93
Average	172.2
S.D.	1.77
COV	1.0%

Real sample

- Needle-like material
- By microscopy:
  - Length: 50 microns
  - Diameter: 2 microns
  - Density: 1.4 g/cc
  - Estimate specific surface area of 1.5 m^2/g



- By flowing gas BET: 3.5 m^2/g
  - Diameter is close to microscope resolution limit (0.5 microns)
  - Surface roughness

Repeatability

Two different ceramic powders, run repeats.

	P1	P2
Test 1	90.53	3.69
Test 2	88.21	3.59
Test 3	88.18	3.58
Average	88.97	3.62
S.D.	1.34	0.0608
COV	1.5%	1.6%

Another sample

Sample	Mass, g	Mass loss on degassing, %	Specific Surface Area, m^2/g
Sample A, Split 1	0.4372	8.0	3.52
Sample A, Split 2	0.5018	8.9	3.41

This sample had a bigger than usual loss of mass on degassing. So degassing is particularly important.

Advantages

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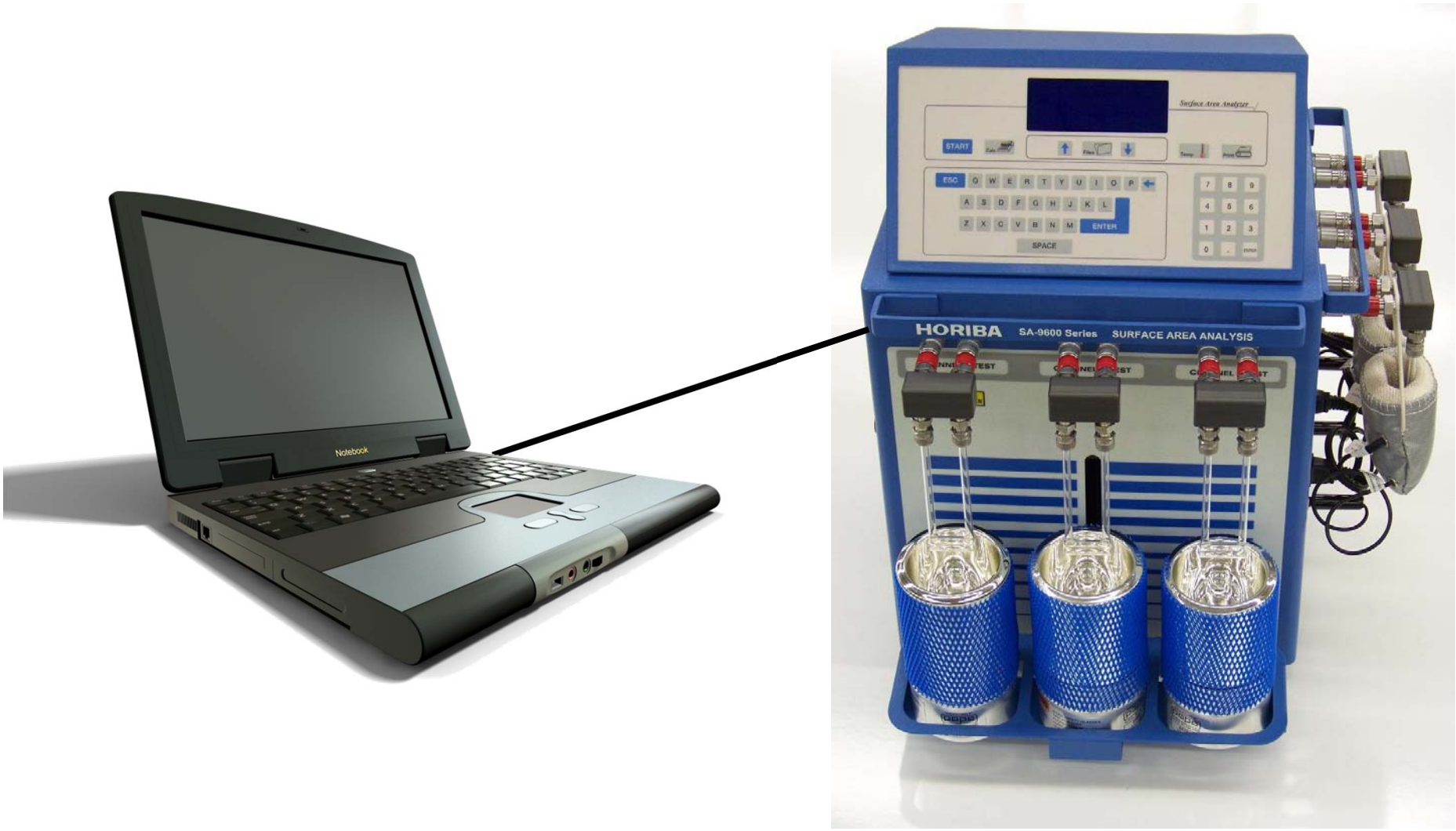
Flowing gas BET advantages

- Fast (5 to 10 minutes)
- Repeatable
- Accurate
- Direct measurement of surface area

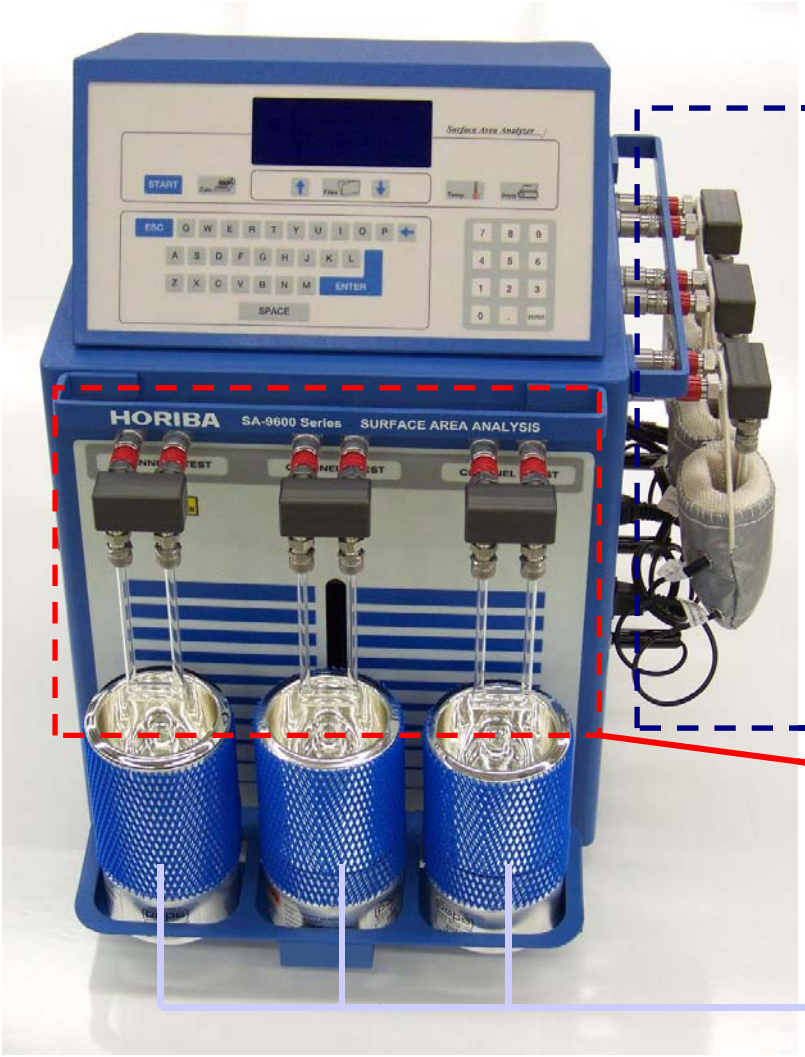
The SA-9600 surface area analyzer



SA-9600 single station

- 2 Outgassing Stations
- 1 Analysis Station

SA-9603 multi-station



Thank you

Thank you

ありがとうございました

Cảm ơn

Dziękuję

ขอบคุณครับ

谢谢

Gracias

Grazie

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Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka

Danke

Merci

Obrigado

감사합니다

Большое спасибо