Introduction to Surface Area Analysis

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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
Outline

- Why determine surface area?
- Surface area and size
- Determining surface area
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 $\rightarrow$ Large surface area

Effect of Particle Size on Surface Area
Solid, Perfectly Spherical Silica

Surface area of 1 kg of particles, $m^2$

- Disneyland
- football field
- parking space

Diameter, $\mu m$

Ludox SM  |  Silica Fume
Small Size $\rightarrow$ Large Surface Area

- Density = 1 gram/mL
- Density = 4 gram/mL

1 Kg of material has this area

- Diameter, microns
- Specific Surface Area, m²/gram

- Parking space
- House (2000 ft²)
- Olympic pool
- Football field
- Horiba building, Irvine
- Boeing Everett Factory
- Disneyland
- Very large oil tanker length × width
- International airport runway
Surface Area and Size

\[ S = 4\pi (d/2)^2 \]

\[ V = \frac{4}{3} \pi (d/2)^3 \]

\[ D_V = \frac{\sum V_i d_i}{\sum V_i} \]

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

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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- Determining surface area
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\textsubscript{2} as a function of pressure.
Surface area

EQUIPOTENTIAL SURFACES

EQUIVALENT MONOLAYER

$W_t$

$W_m$

$P/P_0$

Type 2
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).
Once that determination has been accomplished, a SINGLE POINT MEASUREMENT is quite satisfactory for many (90–95%) practical cases.
Monolayer volume

BET equation

\[ Y = m \times x + b \]

\[ \frac{P}{P_0} = \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right)^{1/m} + \frac{1}{W_m C} \]

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

Intercept \( b \)
Slope \( m \)
Monolayer volume

BET equation

\[ Y = m \times x + b \]

\[ \frac{P}{P_0} \left( \frac{1 - P}{P_0} \right) = \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right) + \frac{1}{W_m C} \]

\[ W_m = \frac{1}{b + m} \]

\[ C = \frac{m + b}{b} \]

We use \( W_m \) to get surface area.

Intercept \( b \)

Slope \( m \)
Monolayer volume

- Measuring for BET equation

\[
\frac{P}{P_0} \left(1 - \frac{P}{P_0}\right) = \frac{C - 1}{W_m C} \left(\frac{P}{P_0}\right) + \frac{1}{W_m C}
\]

- \(P = N_2\) partial pressure = controlled by instrument (MFC)
- \(P_0 = N_2\) equilibrium vapor pressure = known
- \(W = \text{mass adsorbed } N_2 = \text{measured from desorbed volume of nitrogen}\)
- \(W_m = \text{mass of } N_2\) monolayer = found from equation
- \(C = \text{BET constant} = \text{found from equation}\)
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\textsubscript{2} pressure.

References:
Monolayer mass, Single Point

BET equation

\[
\frac{P}{P_0} - \frac{1}{P/P_0} = \frac{C-1}{W_mC(P/P_0)} + \frac{1}{W_mC}
\]

\[C \to \infty \quad \frac{1}{W_mC} \to 0 \quad (C-1) \to C\]

\[W\left(1 - \frac{P}{P_0}\right) = W_m\]

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 = $6.02 \times 10^{23}$ molecules/mol
$A_x$ = 16.2 x $10^{-20}$ m²/molecule
Single point measurement errors

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

![Graph showing the relationship between BET constant ($c$) and error (%), with two curves for $P/P_0 = 0.1$ and $P/P_0 = 0.3$.](image)
Getting to single point when life is bad

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

\[ V_m = V_a \left(1 - \frac{P}{P^0}\right) \]
i.e. \[ V_m = \frac{1}{\text{slope}} \]

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.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Multi-point BET (m²/g)</th>
<th>Uncorrected single-point (m²/g)</th>
<th>Uncorrected difference (%)</th>
<th>Corrected single-point (m²/g)</th>
<th>Corrected difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.923</td>
<td>4.241</td>
<td>-13.9</td>
<td>4.948</td>
<td>0.51</td>
</tr>
<tr>
<td>2</td>
<td>4.286</td>
<td>3.664</td>
<td>-14.5</td>
<td>4.275</td>
<td>-0.26</td>
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<tr>
<td>3</td>
<td>8.056</td>
<td>6.867</td>
<td>-14.8</td>
<td>8.011</td>
<td>-0.56</td>
</tr>
<tr>
<td>4</td>
<td>5.957</td>
<td>5.194</td>
<td>-12.8</td>
<td>6.060</td>
<td>+1.73</td>
</tr>
</tbody>
</table>
Sampling matters!

- Not all of sample brought to lab is analyzed

<table>
<thead>
<tr>
<th>Bulk or process stream</th>
<th>Gross sample</th>
<th>Laboratory sample</th>
<th>Test sample</th>
<th>Measurement sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^n$ kg</td>
<td>&gt;kg</td>
<td>&lt;kg</td>
<td>g</td>
<td>mg</td>
</tr>
</tbody>
</table>

- 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

<table>
<thead>
<tr>
<th>Method</th>
<th>Relative Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone &amp; Quartering</td>
<td>6.81</td>
</tr>
<tr>
<td>Scoop Sampling</td>
<td>5.14</td>
</tr>
<tr>
<td>Table Sampling</td>
<td>2.09</td>
</tr>
<tr>
<td>Chute Riffler</td>
<td>1.01</td>
</tr>
<tr>
<td>Spin Riffling</td>
<td>0.125</td>
</tr>
</tbody>
</table>

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

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

Add sample to cell using a funnel
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.
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

<table>
<thead>
<tr>
<th></th>
<th>2207</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>174.07</td>
</tr>
<tr>
<td>Test 2</td>
<td>179.15</td>
</tr>
<tr>
<td>Test 3</td>
<td>171.93</td>
</tr>
<tr>
<td>Average</td>
<td>172.2</td>
</tr>
<tr>
<td>S.D.</td>
<td>1.77</td>
</tr>
<tr>
<td>COV</td>
<td>1.0%</td>
</tr>
</tbody>
</table>
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 m²/g

- By flowing gas BET: 3.5 m²/g
  - Diameter is close to microscope resolution limit (0.5 microns)
  - Surface roughness
Repeatability

Two different ceramic powders, run repeats.

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>90.53</td>
<td>3.69</td>
</tr>
<tr>
<td>Test 2</td>
<td>88.21</td>
<td>3.59</td>
</tr>
<tr>
<td>Test 3</td>
<td>88.18</td>
<td>3.58</td>
</tr>
<tr>
<td>Average</td>
<td>88.97</td>
<td>3.62</td>
</tr>
<tr>
<td>S.D.</td>
<td>1.34</td>
<td>0.0608</td>
</tr>
<tr>
<td>COV</td>
<td>1.5%</td>
<td>1.6%</td>
</tr>
</tbody>
</table>
Another sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass, g</th>
<th>Mass loss on degassing, %</th>
<th>Specific Surface Area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A, Split 1</td>
<td>0.4372</td>
<td>8.0</td>
<td>3.52</td>
</tr>
<tr>
<td>Sample A, Split 2</td>
<td>0.5018</td>
<td>8.9</td>
<td>3.41</td>
</tr>
</tbody>
</table>

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

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

Outgassing station

Analysis stations

Liquid nitrogen bath
Thank you
Thank you