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Understanding bulk and surface properties of complex solid state materials through Vapor Sorption Techniques

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Surface Measurement Systems

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OUTLINE

Material Characterisation by Sorption Processes

1. How it compares to other characterization techniques
2. Types of sorption processes and what they measure

Dynamic Vapour Sorption Technique

1. DVS Introduction
2. Water Sorption and Stability (coffee granules, freeze-dried antigen)
3. Diffusion / Permeability Studies (biofilms)

Inverse Gas Chromatography Technique

1. IGC-SEA Introduction
2. BET Specific Surface Area
3. Surface Energy Distribution

Characterization of Solids

Energy as a Probe

Spectroscopy

-Light, x-rays, lasers, etc.

-Analytical and structural information

Heat as a Probe

-Calorimetry

-Thermodynamic information

Energy

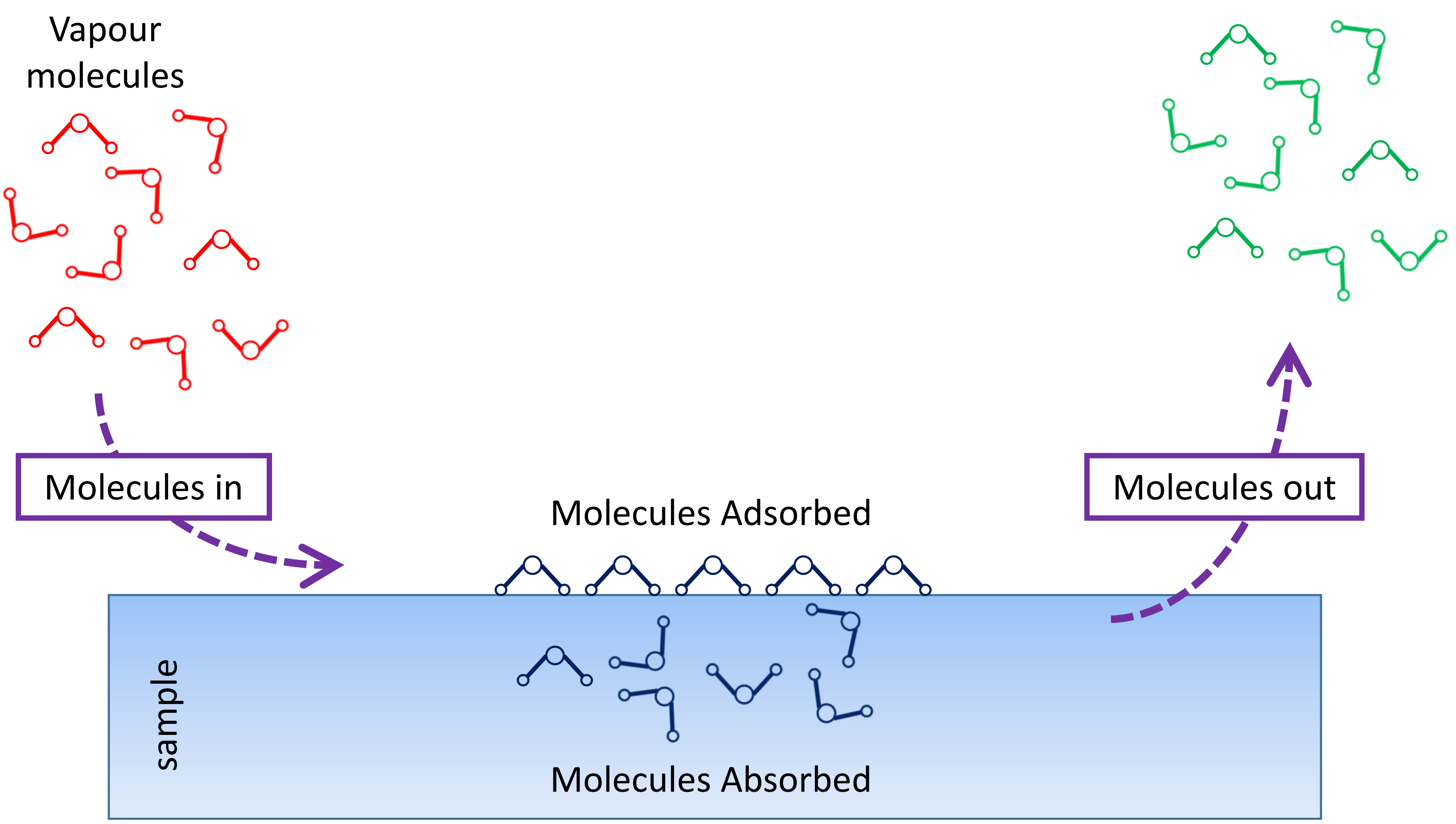
Molecules as a Probe

-Sorption techniques

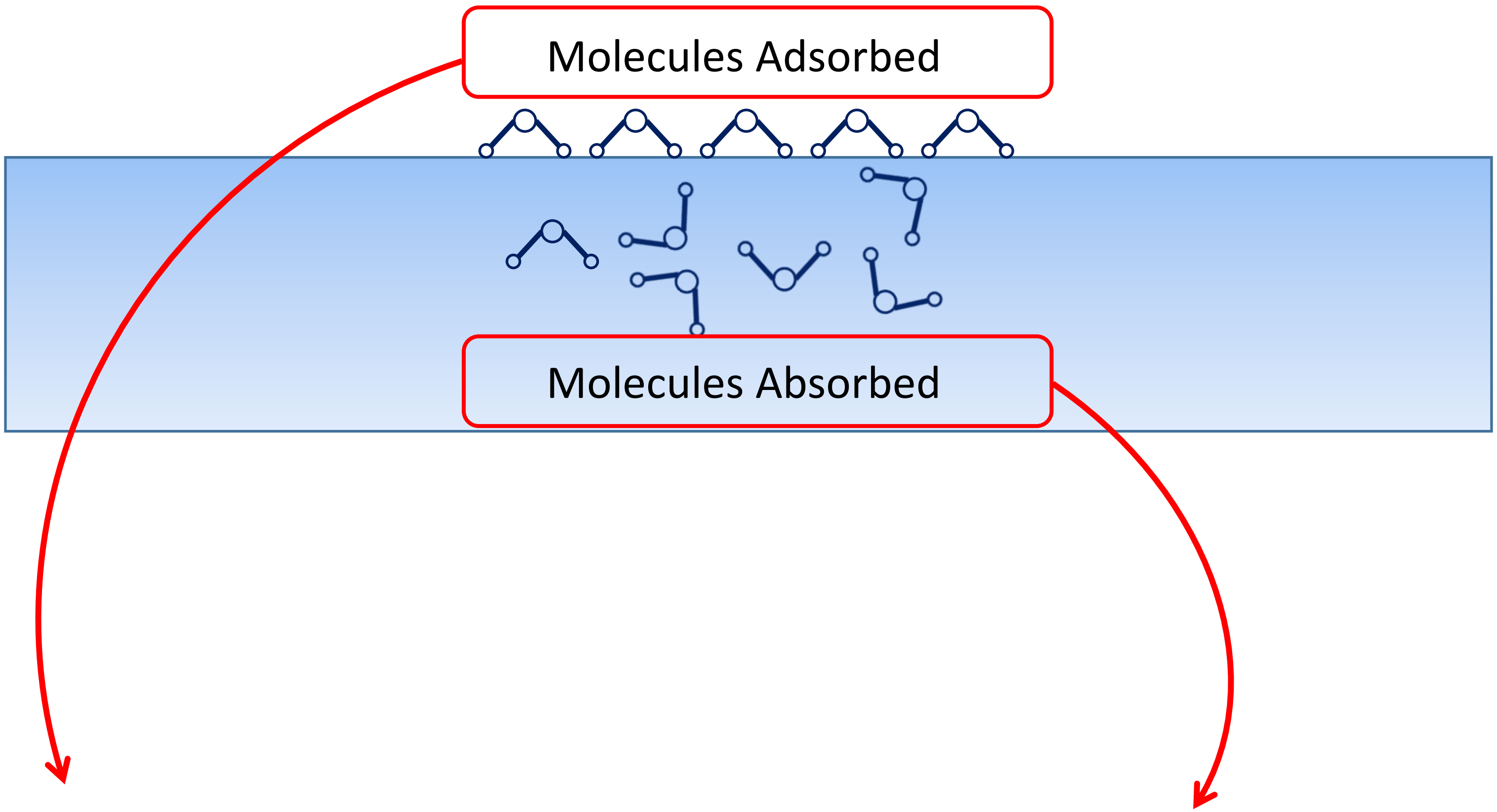
-Thermodynamic, chemical, and structural Information

Matter

Molecules as a Probe



Molecules as a Probe - Interactions



Adsorption

- Physisorption
- Chemisorption

Absorption

- Bulk absorption
- Absorption into lattice structure

Molecules as a Probe - Interactions

Adsorption

- Physisorption
- Chemisorption

- **Weak interactions**
- **Probe molecules not chemically bound to surface**
- **Reversible sorption**

Associated properties measured:

- Structural: surface area, pore size, surface roughness
- Chemical Interactions: surface sorption capacity, surface energy, hydrophilicity, Lewis acidity-basicity, surface heterogeneity
- Thermodynamic: heat of sorption, free energy

Molecules as a Probe - Interactions

Adsorption

- Physisorption
- Chemisorption →

- **Usually strong interactions**
- **Probe molecules are covalently bound to surface**
- **Can be reversible or irreversible sorption**

Associated properties measured:

- Titrate acid-base sites
- Active surface area
- Catalyst Dispersion

Molecules as a Probe - Interactions

Absorption

- Bulk absorption
- Absorption into lattice structure

- **Penetrate surface**
- **Desorption is often diffusion limited**
- **Reversible or irreversible sorption**

Associated properties measured

- Structural: vapor-induced phase changes (glass transition, crystallization, deliquescence), glass transition temperatures, crosslink density
- Chemical: total sorption capacity, solubility parameters
- Kinetic: diffusion coefficients, solid-solid phase transformation, drying kinetics

Molecules as a Probe - Interactions

Absorption

- Bulk absorption
- Absorption into lattice structure →

- **Solvate formation**
- **Reversible or irreversible solvate formation**

Associated properties measured

- Structural: stoichiometric hydrate/solvate, channel hydrate/solvate
- Kinetic: hydrate/solvate formation/loss kinetics

Dynamic Vapor Sorption (DVS)

DVS Introduction (Dynamic Vapour Sorption)

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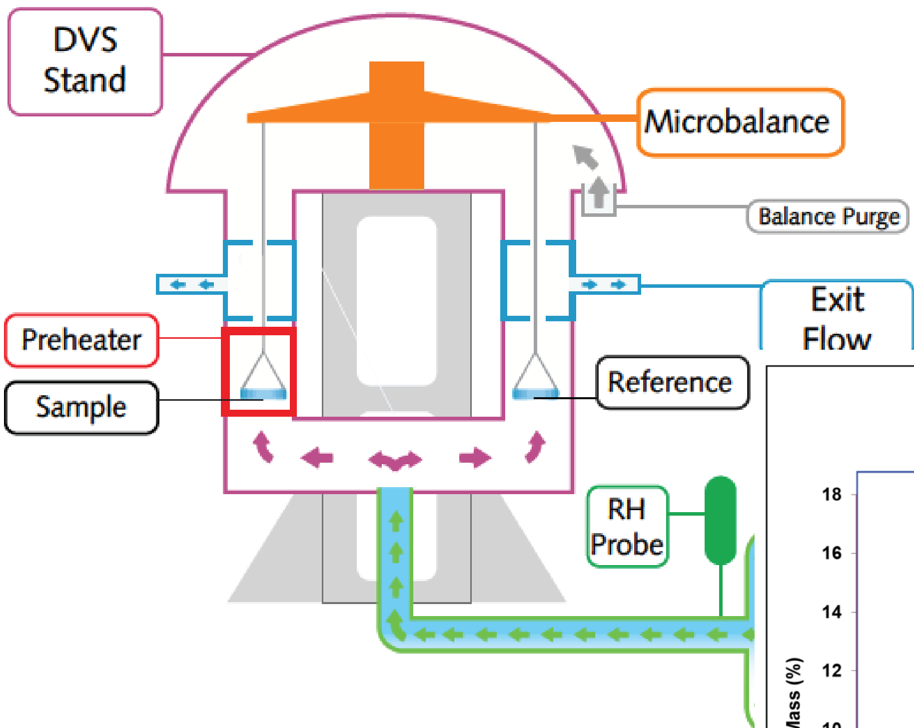
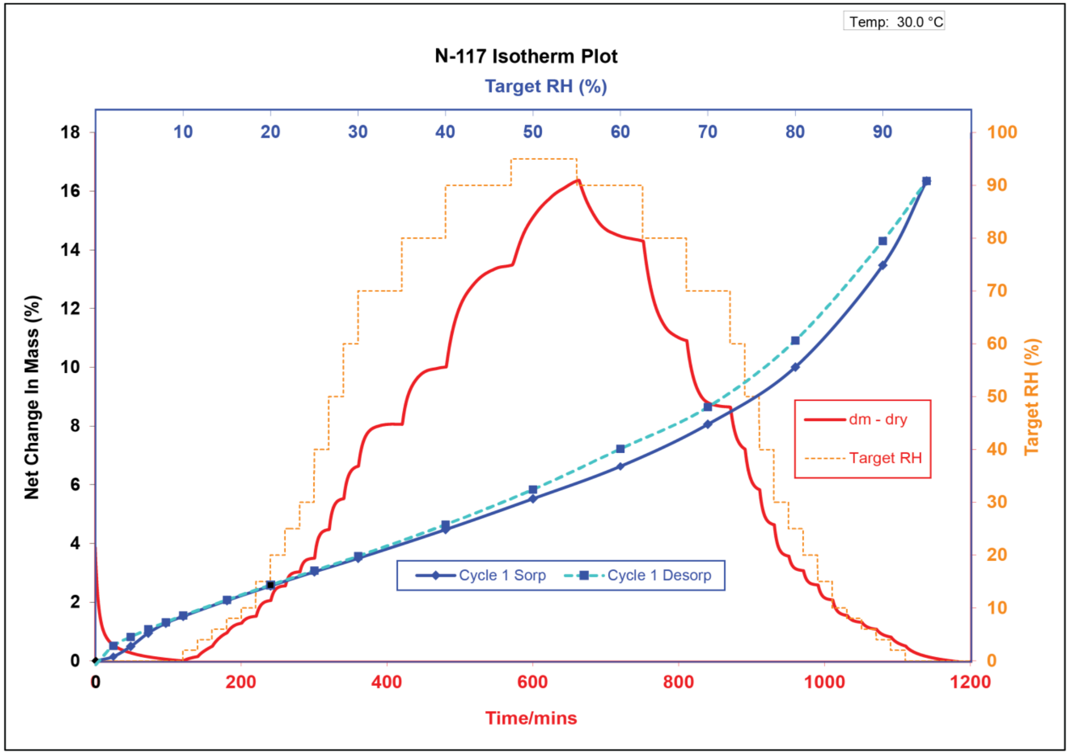
DVS Schematic



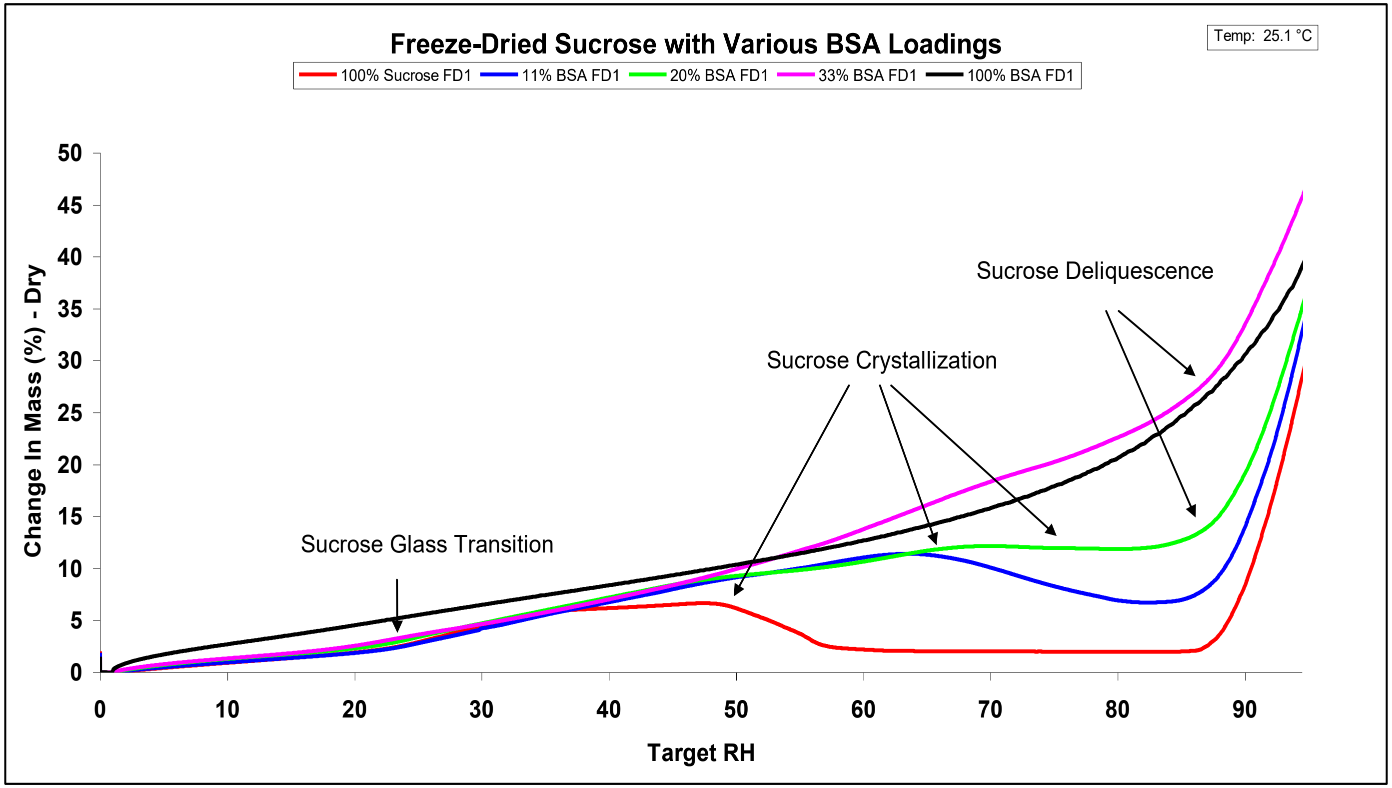
DVS Typical Data



Moisture sorption/desorption **kinetics** (bottom and left axis) and **isotherms** (top and left axis) for a proton exchange membrane at 30°C.

Water sorption and stability

Solid-moisture interactions are important and allow a unique understanding of bulk and surface properties of complex solid state materials



Bovine Serum Albumin (BSA) acting as a stabilising agent

Ref: SMS DVS AppNote 33: Impact of Protein Concentration on the Moisture-Induced Phase Transitions of Protein-Sugar Formulations

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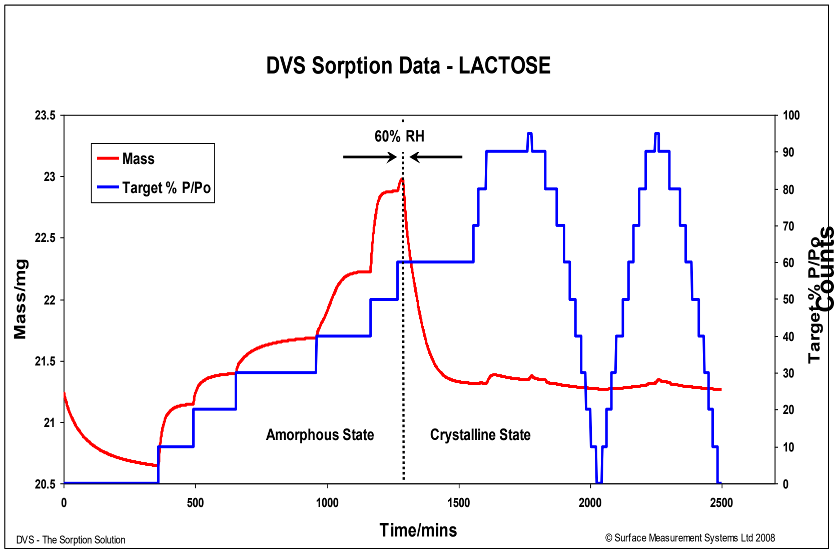
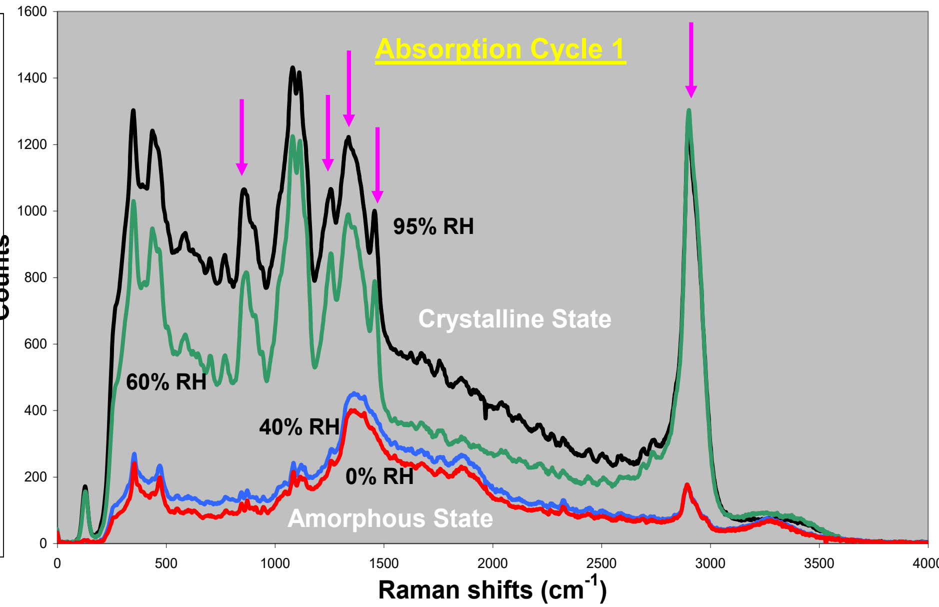
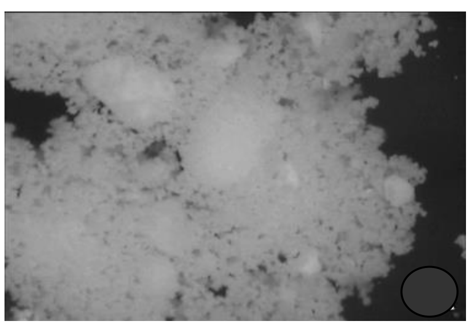
Water sorption and stability

DVS Data



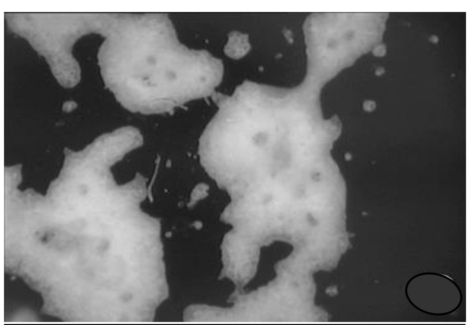
Raman Data





Amorphous State

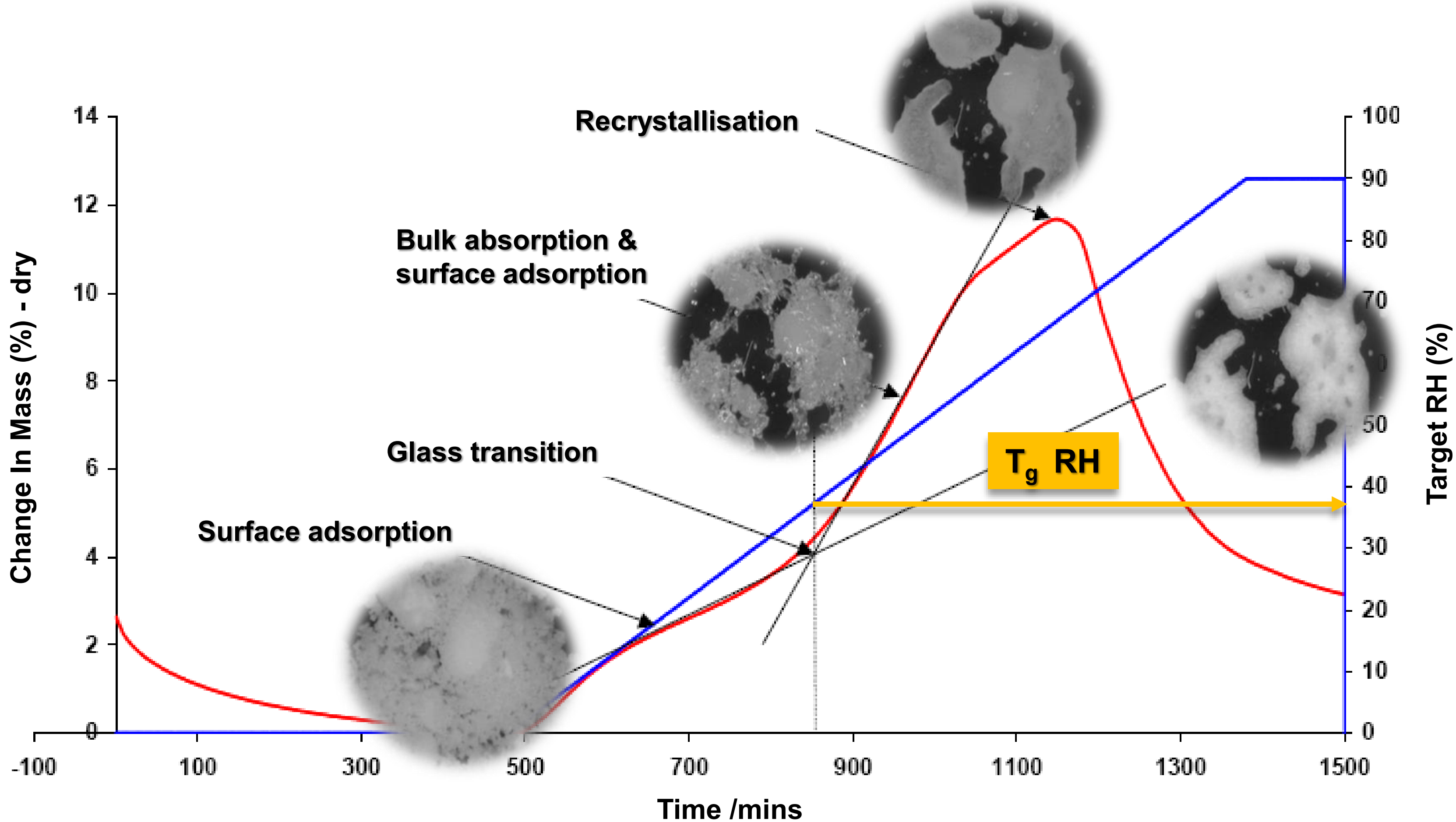
Video Images



Crystalline State

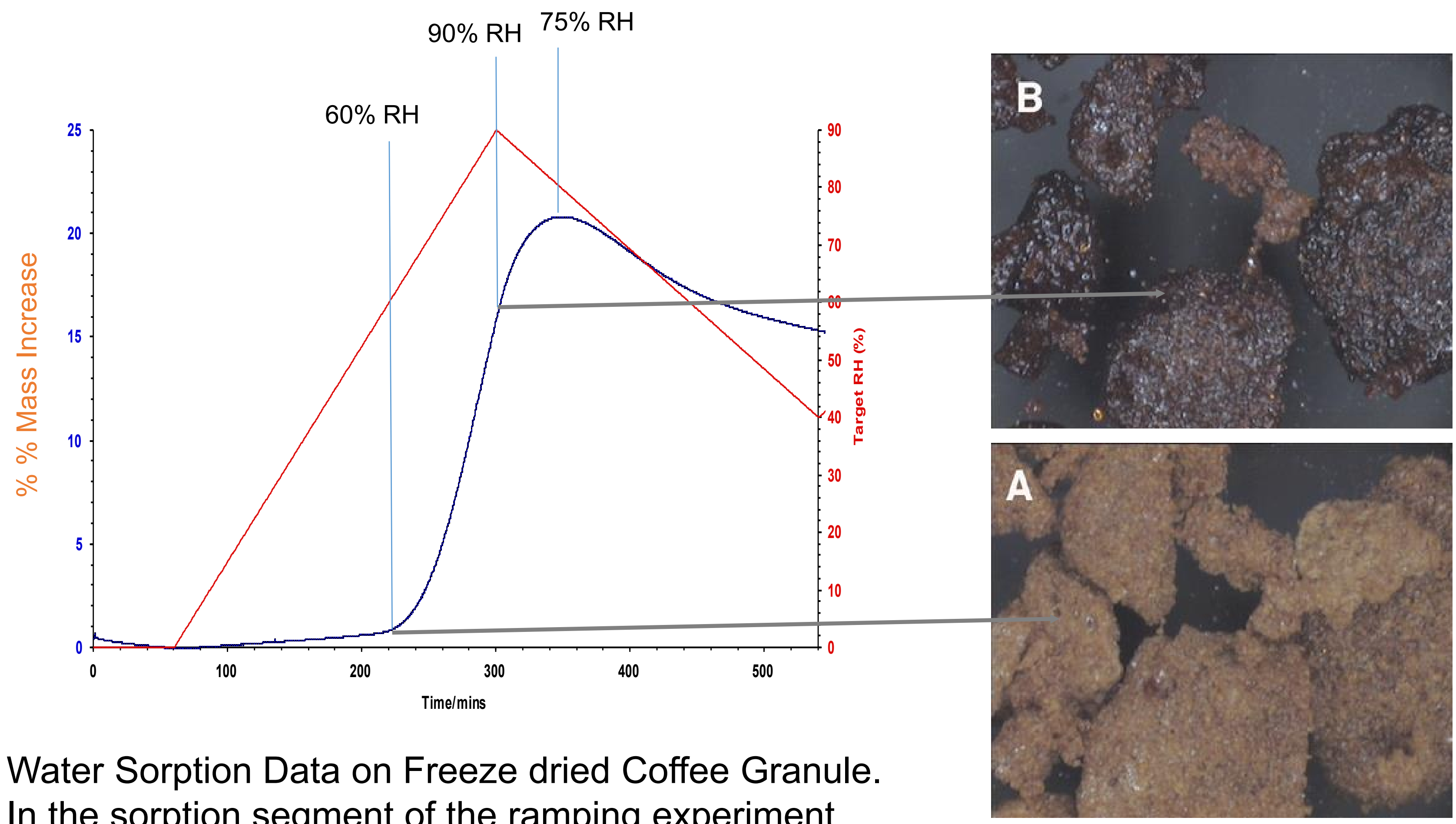
Water sorption and stability
(vapour-induced phase transitions)

Glass Transition and Crystallisation



- RH ramping experiment (similar to DSC temperature ramp) can reveal phase transition points i.e. when products cake, clump or deliquesce
- Gravimetric data clearly shows moisture-induced glass transition- change in slope

Moisture Sorption of Coffee



Water Sorption Data on Freeze dried Coffee Granule. In the sorption segment of the ramping experiment very little moisture uptake is observed below 60% RH. Desorption segment shows a maximum at 75% RH.

In-situ video images at (A) 60% RH and (B) 90% RH.

Ref: SMS DVS AppNote 08: Moisture Sorption of Coffee Granules Studied using the DVS-µScope

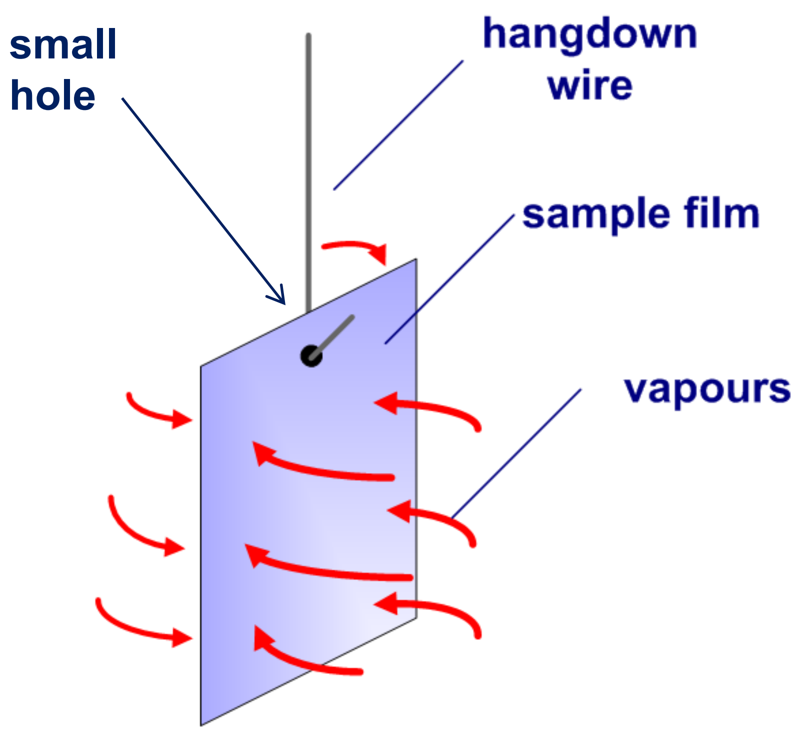
Moisture Sorption of Freeze-dried Influenza Antigen

Moisture levels in vial storage can rise over time and reduce the dry state glass transition temperature (T_g) thus increasing the chance of exceeding it causing a complete/partial melt or collapse reverting back to its liquid solution.

Higher moisture could lead to cake collapse, degradation and loss in biological potency.

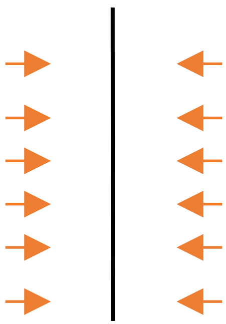
Ref: Duralliu, A., Matejtschuk, P., & Williams, D. R. (2018). Humidity induced collapse in freeze dried cakes: a direct visualization study using DVS. *European Journal of Pharmaceutics and Biopharmaceutics*, *127*, 29-36.

Diffusion Constants in Thin Films and Coatings

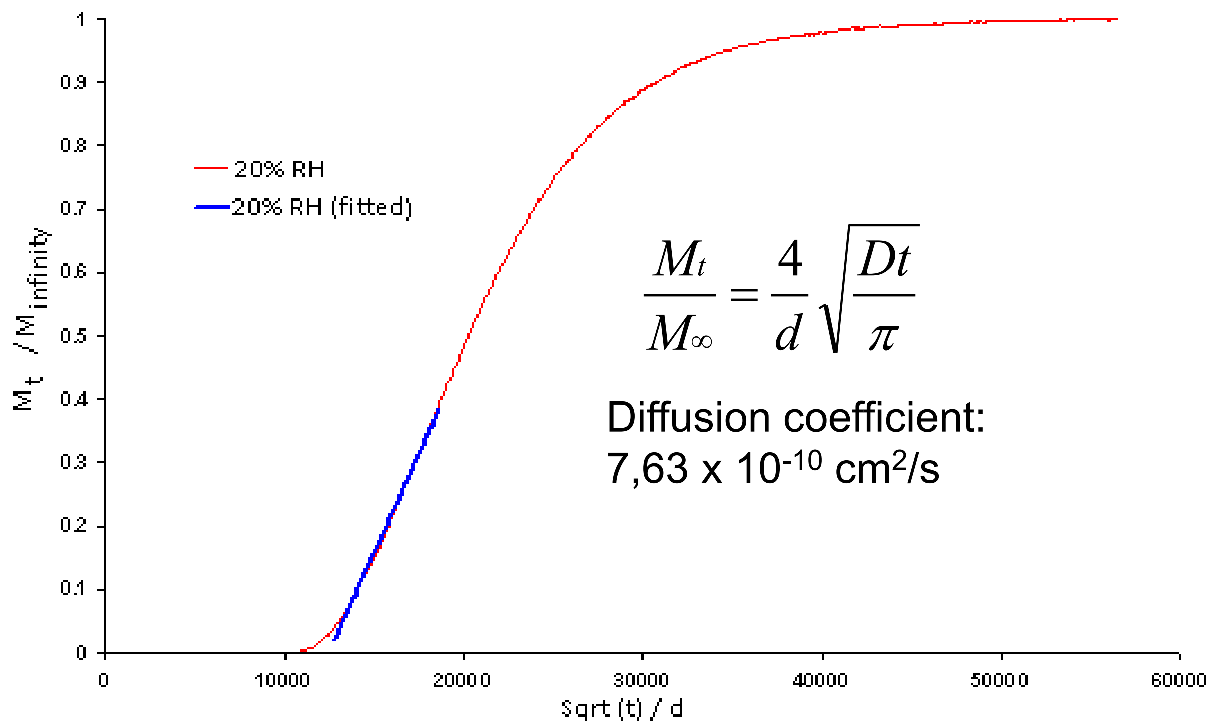


Diffusion Constants in Thin Films and Coatings

Polyimide films



Two Sided Diffusion Experiment



$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}}$$

Diffusion coefficient:
7,63 x 10^{-10} cm^2/s

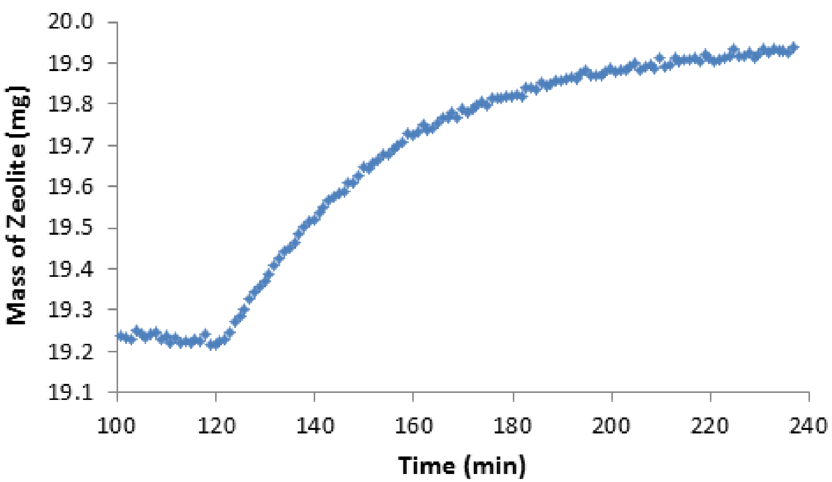
Diffusion plot for 0% RH to 20% RH step in humidity on a 7.5mm polyimide film

M_t = amount adsorbed at time t,
M_∞ = amount adsorbed at thermodynamic equilibrium,
D = diffusion constant.

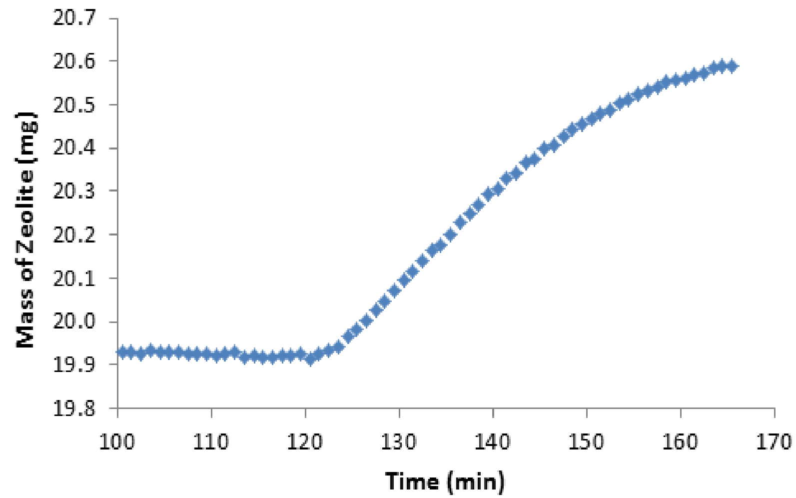
This equation is generally valid for values of M_t/M_∞ <0.4, where a plot of M_t/M_∞ against $t^{1/2}/d$ should be linear

Case Study on Biofilms
(Moisture permeability rates)

Change in mass of zeolite in response to 90%RH (at 120th minute)



CarboSil®
100μm thickness



Polyurethane
40μm thickness

Sample	Diffusion Rate [mg/min]	Water Vapor Flux [g/(hr·m²)]
CarboSil®	0.0150 ± 0.0046	57.36 ± 18.70
Polyurethane	0.0220 ± 0.0026	84.14 ± 11.16

Ref: SMS DVS AppNote 52: Vapour Permeability of Porous Materials using Payne Diffusion Cell

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Inverse Gas Chromatography Surface Energy Analyzer (iGC-SEA)

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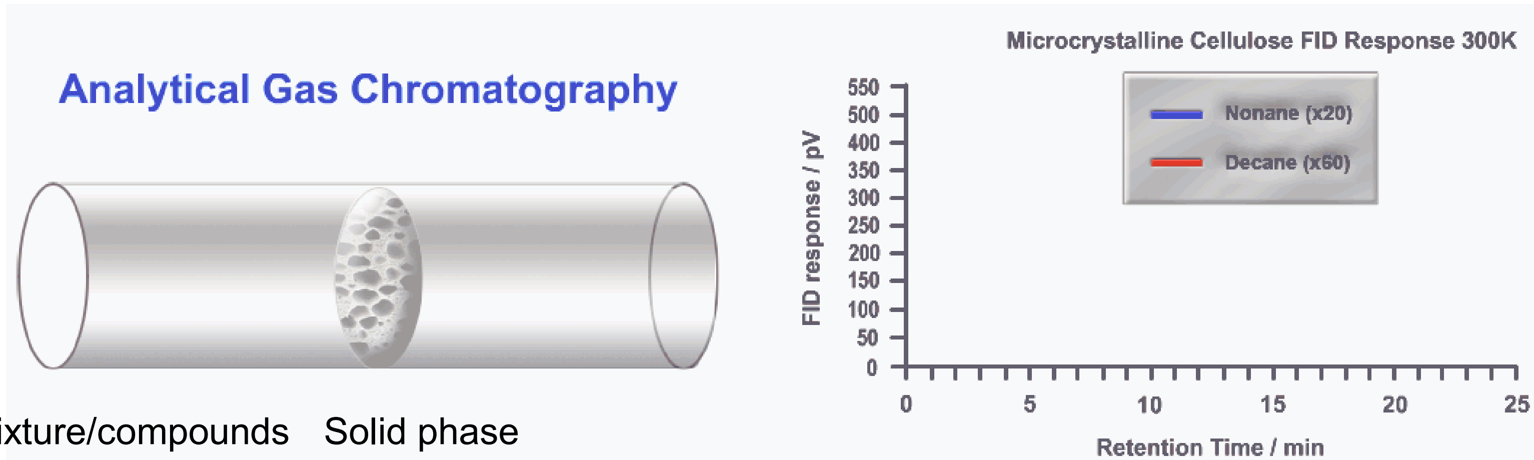
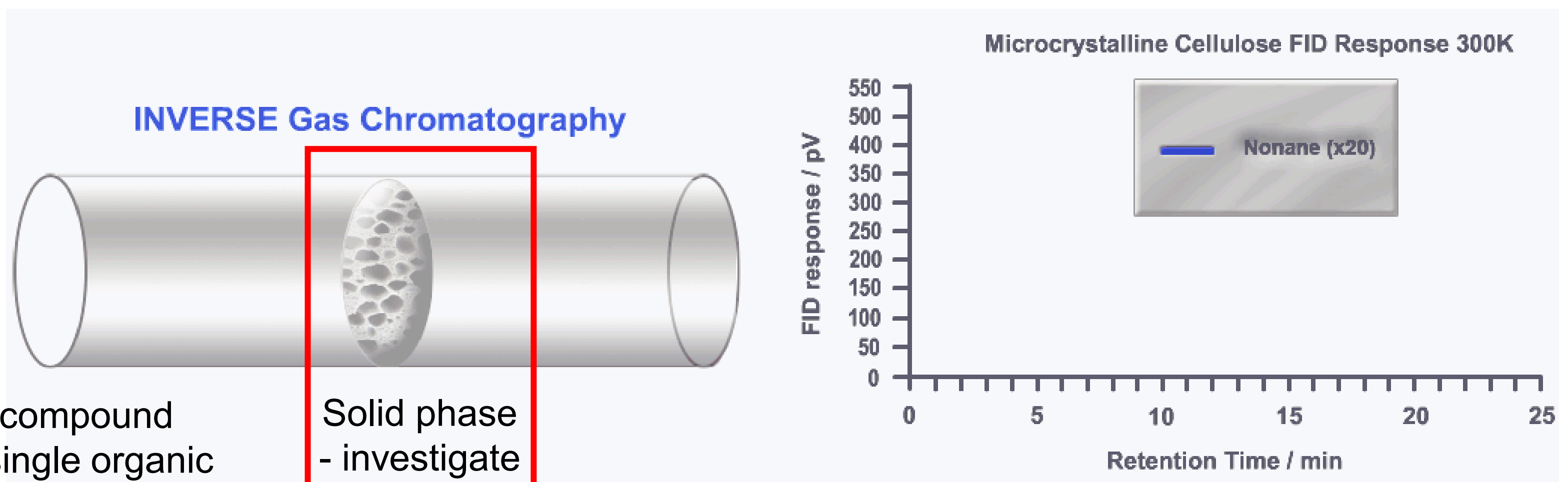
IGC SEA Introduction (Inverse Gas Chromatography)



Injected mixture/compounds - investigate

Solid phase **Known**

Quality and **quantity** information of injected compounds from the peaks



Injected compound **Known** – single organic vapours

Solid phase - investigate

Physicochemical properties of the solid

Animation by L. Teng, Surface Measurement Systems

Properties measured by SEA

The SEA provides unique access to the following physico-chemical properties of a wide range of solid materials in a controlled humidity environment:

- Dispersive and Polar Surface Energies
- Surface Energy heterogeneity mapping
- Heats and Entropies of Adsorption
- Acid/Base Interactions and Specific pair Interaction Parameter (I_{sp})
- Sorption Isotherms
- BET SSA - Specific Surface Area
- Phase Transitions
- Permeability, Solubility and Diffusion
- Competitive (Multicomponent) Adsorption
- Thermodynamic Work of Cohesion and Adhesion
- Constantly extend the applications – future applications e.g. Chemisorption

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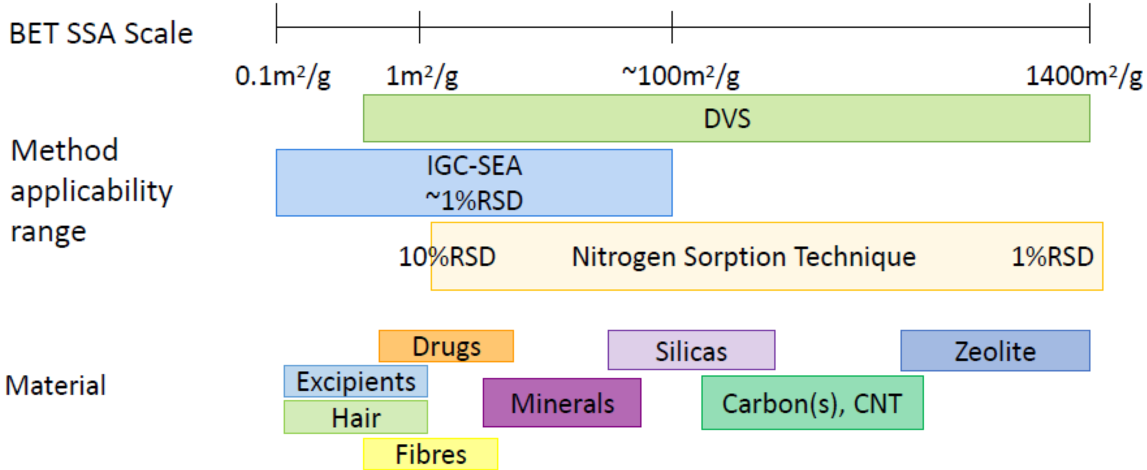
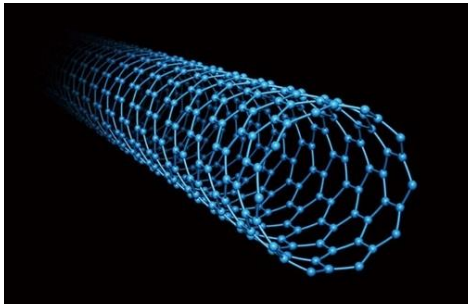
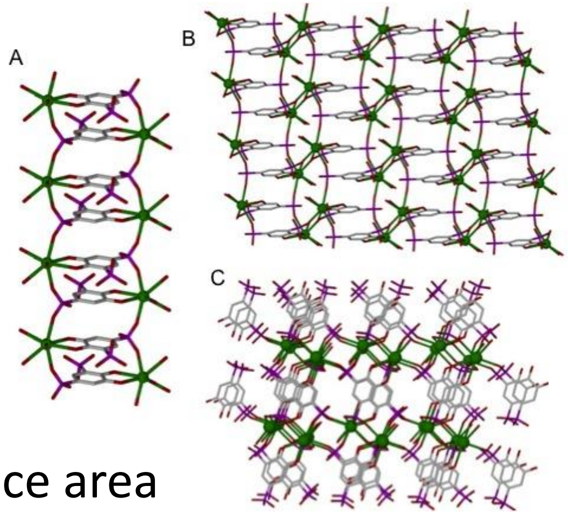
Importance of Surface Area



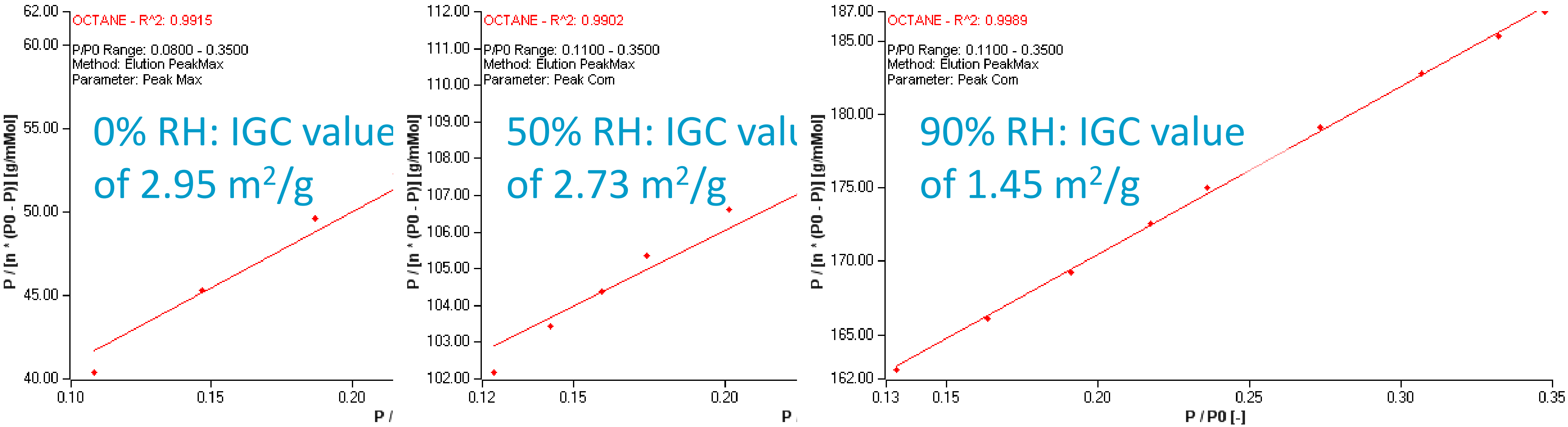


	DVS	IGC-SEA	N2 Technique
Measurement temperature	20-400°C	20-150°C	-196°C (77K)
Applied adsorbate	Organic vapors	Organic vapors	Nitrogen/Krypton
Measurements pressure	~Ambient / Vacuum	Ambient	Vacuum

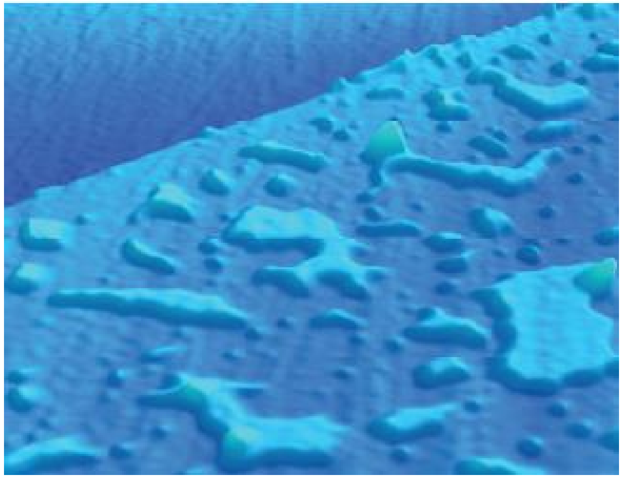


- It is important to have an appreciation of the physical dimensions of particulate materials and how their surface area changes due to different processes. For example the surface area for spherical particles with a radius of 1nm = 3000 m^2/gm, 1µm = 3 m^2/gm, and 100µm = 0.01 m^2/gm.

Impact of Humidity on Surface Area



- As humidity increases, measured BET surface area decreases
- Water competing for sites or blocking available surface area
- Example AFM image on Graphene: JACS, 2011, 133(8), 2334-2337.



Comparison of morphology for SD and FD materials

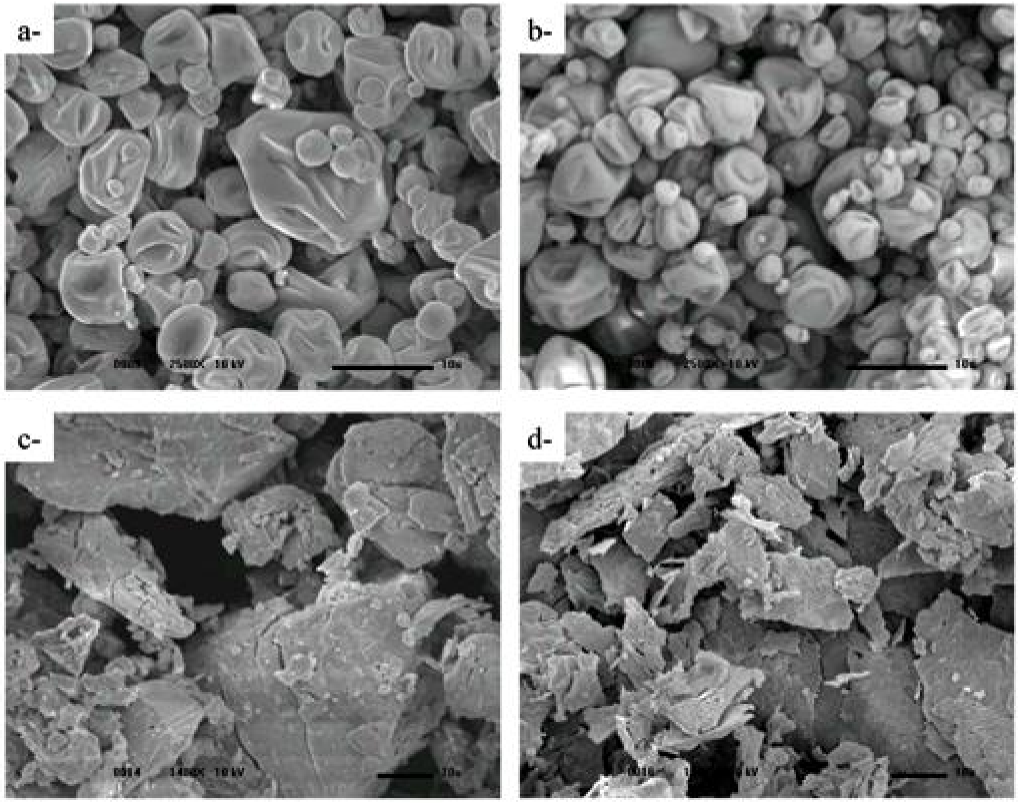


Figure 1 - SEM micrographs of microcapsules: **a**- spray-dried gum arabic:sucrose (8:2) , **b**- spray-dried gum arabic:sucrose (8:2) + lycopene, both with magnification of 2500x, **c**- freeze-dried β-CD, **d**- freeze-dried lycopene-β-CD complex, both with magnification of 1400x.

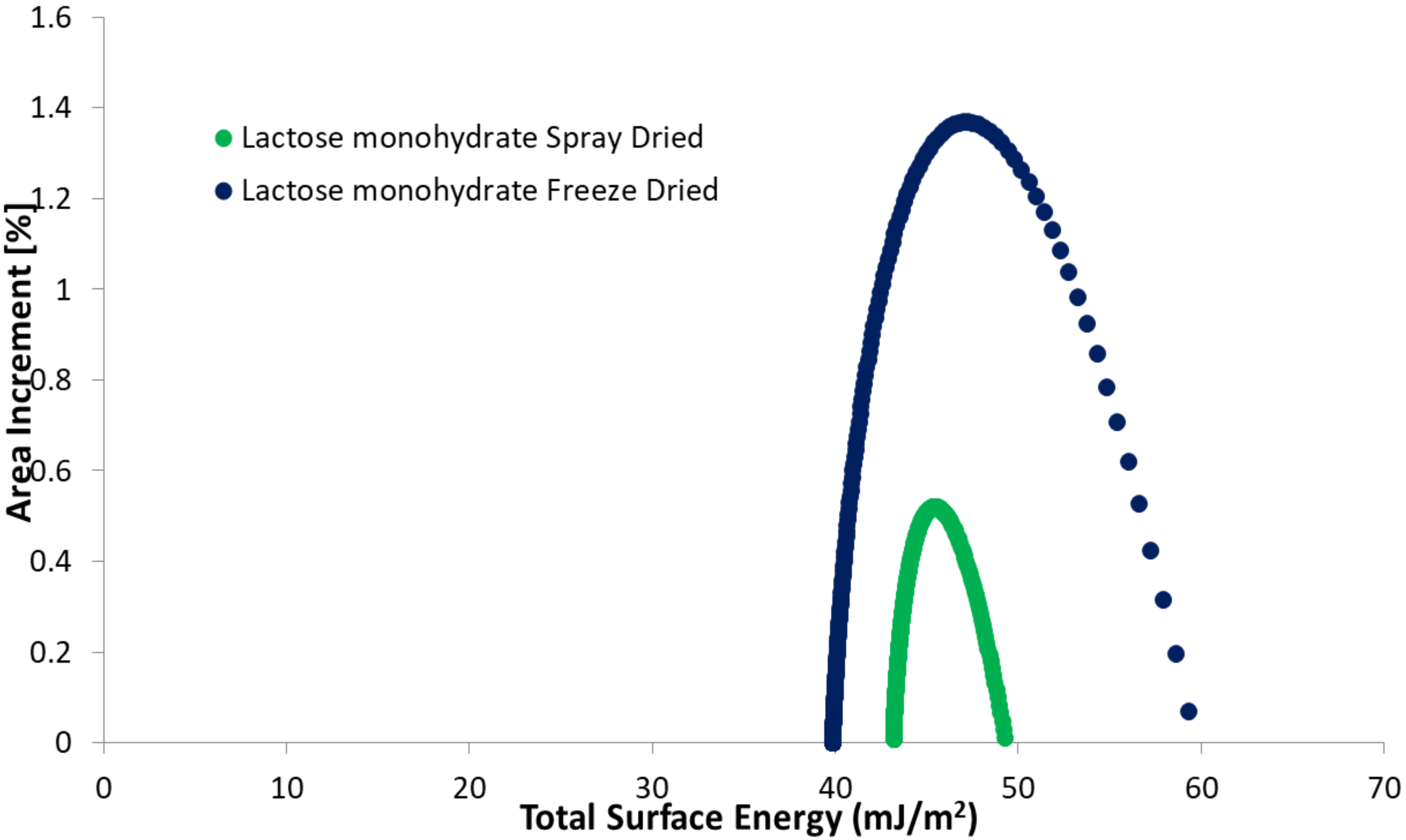
SD sample:
mostly spherical particles and smaller particle size distribution

FD sample:
Different shapes and sizes particles

Ref: Itaciara Larroza Nunes; Adriana Zerlotti Mercadante, Food Science and Technology, Encapsulation of lycopene using spray-drying and molecular inclusion processes, ISSN 1516-8913

Total surface energy distribution

- The SD sample has more homogenous surface due to the more uniform particle size and shape.
- The FD sample exhibits a wide variation of surface energy.



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Thank you for your attention!

We'd also like to invite you to our upcoming two-day virtual conference, **Sorption Science Symposium Online 2021**. Taking place in two weeks' time on 22 & 23 September, the event will offer a dedicated sorption science agenda exploring the latest case studies and applications in DVS and iGC. This will be combined with the opportunity to engage directly with speakers, and a range of networking features to help you connect with a global scientific community. Visit our website at www.surfacemeasurementsystems.com to find out more and sign up.