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Understanding Surface Energy

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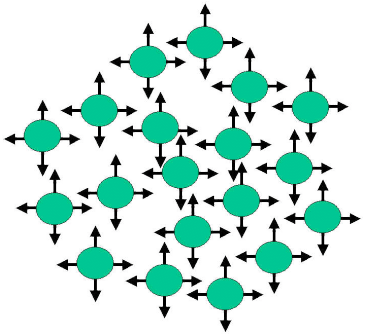
Surface Measurement Systems Ltd.

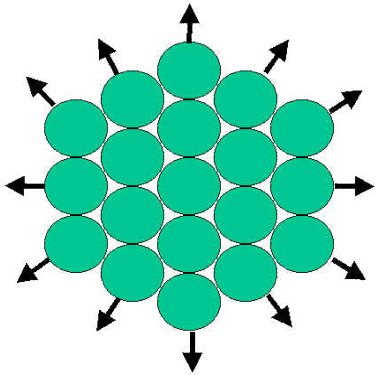
6th October 2015

What is the SE; Why it is important to measure and How it can be measured?

Basics



Atoms in the centre of a material are surrounded by other atoms



some of the surface electrons could interact with atoms surrounding the material.

To quantify the ability of the surface to react.

1st Law: "all systems try to reach their lowest energy levels." - metals' surface oxidation

Surface Energy

Materials with high surface energy are easier to wet and adhere to than those with low surface energy.

Surface energy components according by Fowkes:

- Dispersive component – physical long range interactions, measured by the series of n-alkanes
- Lewis acid-base component– chemical short range interactions, measured by two mono-functional polar solvents

$$\gamma_s^T = \gamma_s^d + \gamma_s^{ab} \qquad [J/m^2]$$

γ_l - Surface tension of liquid

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Introduction of the SE

The surface energy is a very informative and important parameter of solids.

1st development for surface energy and acid/base interactions** of IGC was for polymers and composite materials.

Knowledge of surface energetics is important in the **formulation design** of multi-component systems and the prediction of **processing performance**.

Ability to measure the surface energy of various materials is essential for ensuring **compatibility** between the given base material and the top coating one wishes to apply onto it or other materials one wishes to attach to it.

*Laub, R.J. and Pecsok, R.L., Physicochemical Applications of Gas Chromatography. 1978, New York: John Wiley & Sons.

** Schultz, J., Lavielle, L., and Martin, C., The role of the interface in carbon fibre epoxy composites. J. of Adhesion, 1987. 23(1): p45-60.

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Examples for Importance of Surface Energy

1. Paper Industry

printing quality strongly influenced by the structural and chemical properties of the paper surface

2. Building Industry

to evaluate adhesion of bituminous crack sealant to aggregates

3. Medical Care

to bond a resin to a tooth

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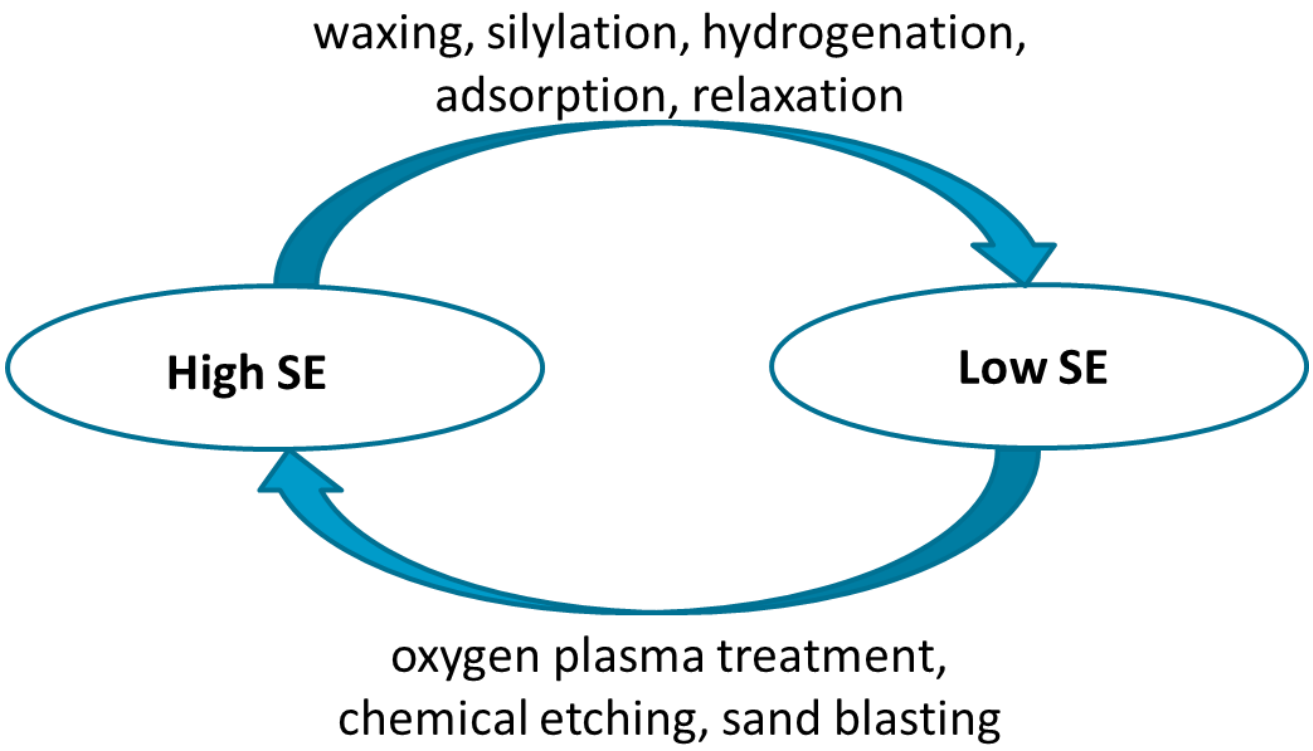
Modify Surface Energy

Investigation the influence of surface treatments

Common industrial process for tuning the surface energy of materials to application needs.



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Pharmaceutical Powders*

Selected chemical and solid-state material properties, usually constitute the critical variables of a pharmaceutical manufacturing process

Spectroscopic properties	Measured by electronic transmission (UV-Vis Spectra,) vibrational transitions (IR and Raman Spectra), rotational transitions (far-IR or microwave spectra), as well as nuclear spin transitions (NMR spectra)
Thermodynamic properties	Measured as melting point, enthalpy, entropy, free energy, solubility
Kinetic properties	Measured as dissolution rate, rates of solid state reactions, stability
Packing properties	Measured as unit cell volume
Mechanical properties	Measured as hardness, tensile strength, compatibility, tableting, flowability
Surface properties	Measured as surface free energy, interfacial tensions, and crystal habits

* *Dilip M. Parikh, American Pharmaceutical Society (2006)* An Overview of the Properties of Pharmaceutical Powders and their Effects on Processibility

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Pharmaceutical Powders*

- Tablet strength is controlled by formation of intermolecular forces over the areas of contact between the particles. The strength of these bonding forces is **controlled by surface energy**.*
- Knowledge of the wettability and surface energy of pharmaceutical solids is important in the design of pharmaceutical formulations.*
- If the surface energies of the individual compounds are known, the **work of adhesion or cohesion** can be obtained.

* *Dilip M. Parikh, American Pharmaceutical Society (2006)* An Overview of the Properties of Pharmaceutical Powders and their Effects on Processibility

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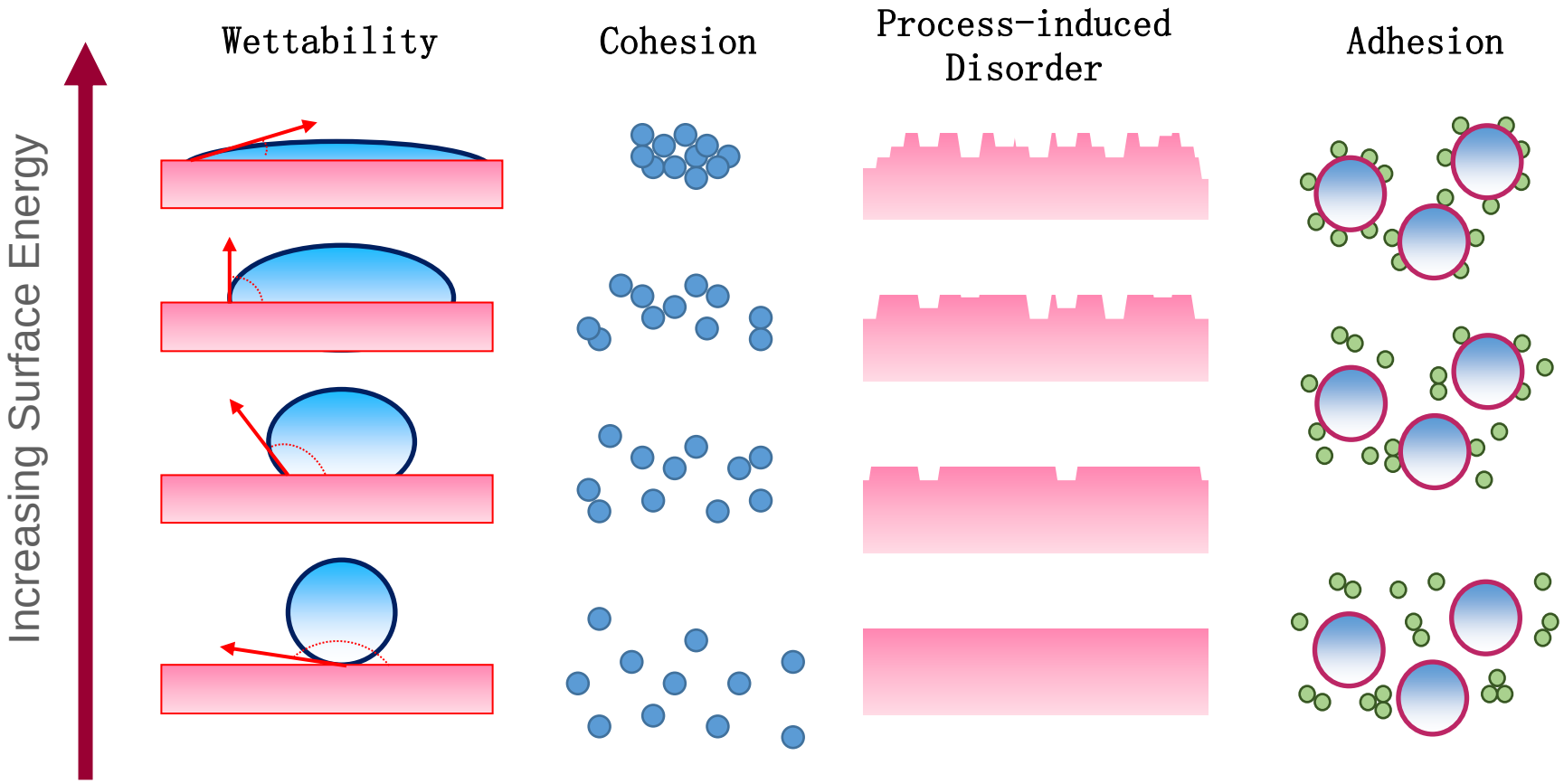
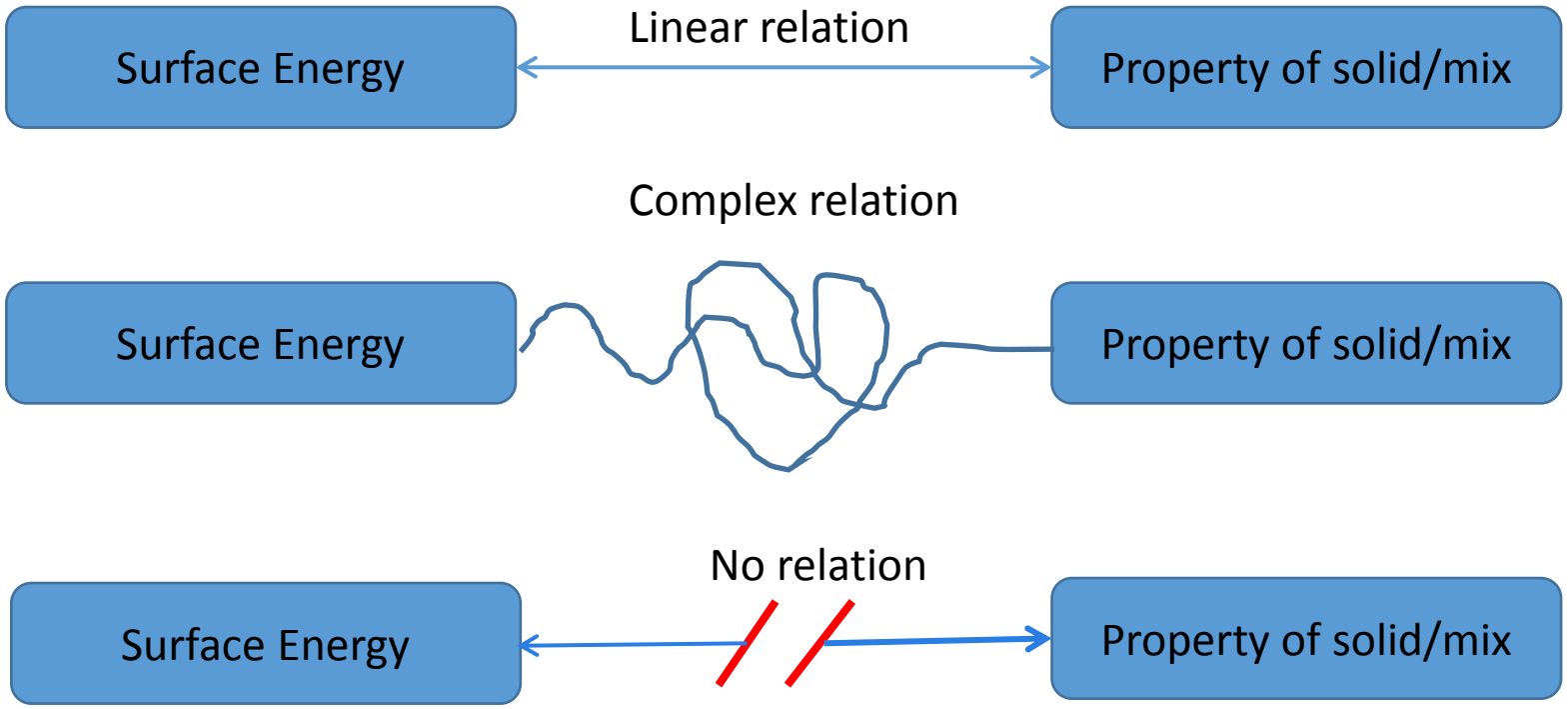
Relationship with other properties



Relationship with other properties

BUT it is not correlate linearly with everything



Note: Does not mean that the surface energy value is wrong or not useful

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How we can measure?

- Contact Angle (CA) technique
- Atomic Force Microscope (AFM)
- Washburn capillary rise technique
- **Invers Gas Chromatography (IGC)**
- Wetting Balance

IGC is the most commonly successfully used technique for surface energy analysis of powders and fibres.

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SEA vs. CA and AFM

Surface Energy Analyzer (SEA)	Contact Angle (CA)	Atomic Force Microscopy (AFM)
Powder, fibres, nano particles, granules, films and semi -solids	Flat, smooth, homogenous and inert macroscopic substrate	Thin flat, molecular level
Surface heterogeneity	Specific point of the flat surface	Three way (x, y, z)
Very good reproducibility (RSD%=1)	varying	Scatter and irreproducible
Vary conditions (temperature and RH)	one - ambient condition	Strict controlled- low humidity level, controlled and known loads

Comparison Table available online on SMS website

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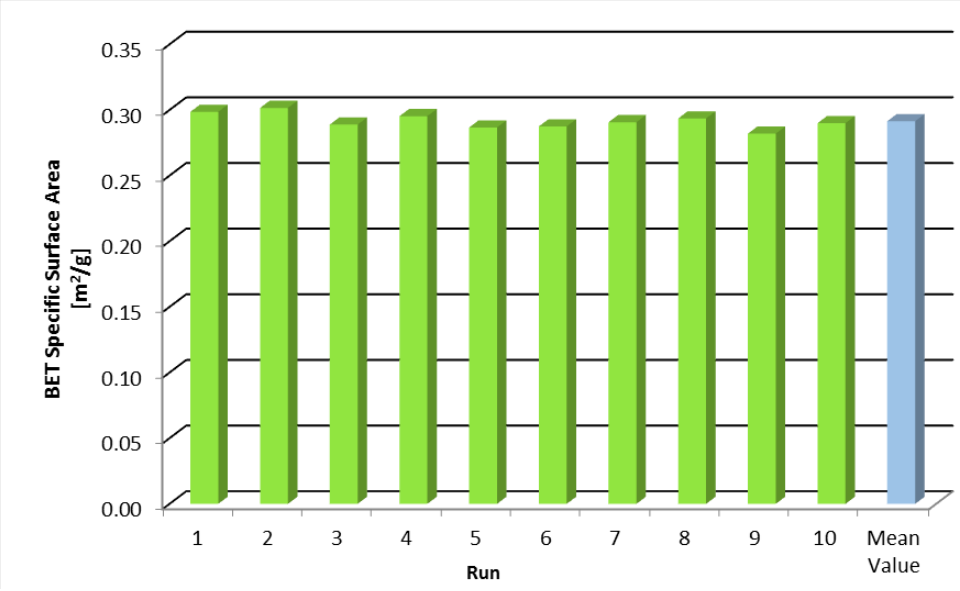
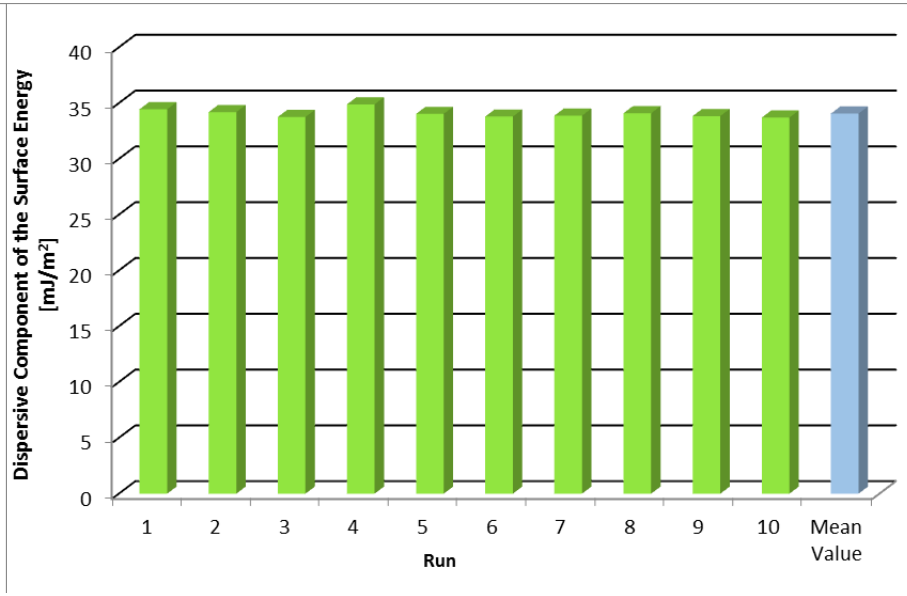
Reliability of the iGC-SEA results

Uncertainty of the measurement





Experiment to experiment				
	Mean value	R^2	SD	**RSD**
BET SSA By IGC-SEA	0.2876 – 0.2788 m^2/g	0.9993-0.9996	0.0027 – 0.0060 m^2/g	**0.94 - 2.16%**
y_d by Peak Max by IGC-SEA	34.43 – 34.15 mJ/m^2	0.9998-1.0000	0.15 – 0.38 mJ/m^2	**0.45 – 1.10%**
y_d by Peak COM by IGC-SEA	38.74 – 39.16 mJ/m^2	0.9994-0.9996	0.14 – 0.27 mJ/m^2	**0.37 – 0.69%**

Reference: SMS - TN807 Repeatability Part 1

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IGC Introduction

- Gas phase sorption technique
- Inverse Gas Chromatography (IGC) principles*: 1st developed in 1950s.
- Focus of physicochemical studies on the kinetic information and thermodynamic quantities from sorption equilibria.
- Earlier work for catalytic materials, e.g. activated carbon, alumina and silica.
- Powerful physico-chemical characterization tool for **powders, fibres, films, particulates, semi-solids**.
- 1st development for surface energy and acid/base interactions** was for polymers and composite materials.

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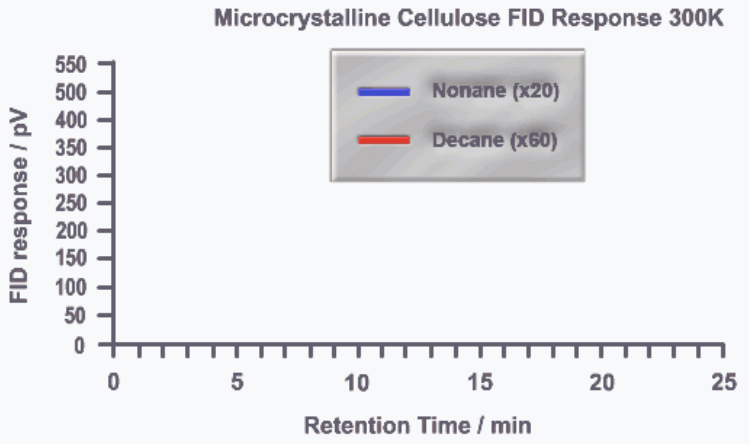
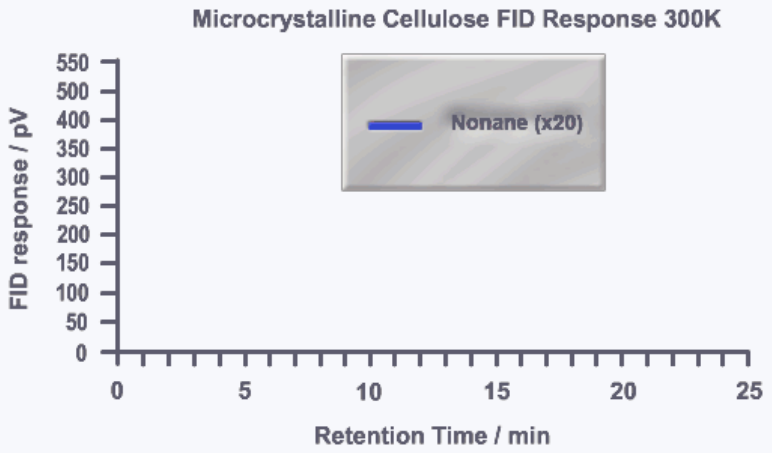
IGC Principles

Analytical Gas Chromatography



INVERSE Gas Chromatography



Animation by L. Teng, Surface Measurement Systems

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Properties measured by IGC-SEA

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

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iGC-SEA Introduction

- 2nd generation chromatographic sorption instrument
- **Compact design** - Reduced footprint: 450 mm (18”) x 450 mm (18”) x 700 mm (27.5”)
- 12 vapor reservoirs (50 ml)
- 2 column oven design: **20 to 150 ˚C**
- Flame Ionization Detector (FID)
- **User Friendly** Control and Analysis **Software**
- **Background Humidity Controller**

Safety Features:
Hydrogen Leak & Organic Vapor Leak Detectors

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Applications

- **Surface treatment studies**
- **Evaluation of the pre-treatments**
- Batch-to batch variation study
- **Formulation design**
- Surface characterization
- **Influence of humidity for BET Surface Area**

And about hundred publications so far.

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Every Colleagues at Surface Measurement Systems

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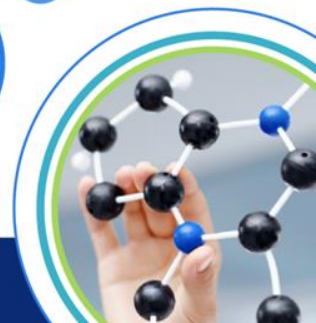
Thank you for your attention!



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