

Surface Properties of Graphene, Carbon Blacks and Carbon Fibers by IGC (Inverse Gas Chromatography)

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In practice: powders are difficult

- Within specification, but somehow different
- Surface modification, treatments, batch-to-batch
- Graphene, carbon nanotubes, carbon blacks, graphites, carbon fibres...
- General problem: Fillers, mineral oxides, pigments, construction materials, battery materials, catalysts, adsorbents, excipients, food, fibres



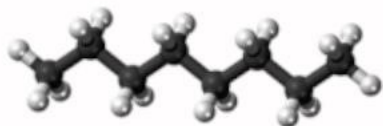
Need for

highly sensitive, quantitative
and reproducible characterization
of surface **interaction** properties

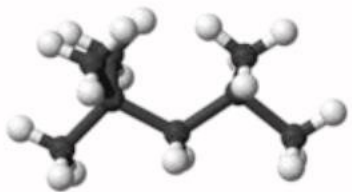
beyond BET(N₂), SEM images, XPS, applications...

Principle: interaction by gas probes

- Any type of gaseous molecular probe (apolar, polar, ...) – usually set of 15+
- Concentration range: „infinite dilution (ID)“ or „finite concentration (FC)“



n-alkanes apolar, linear flexible

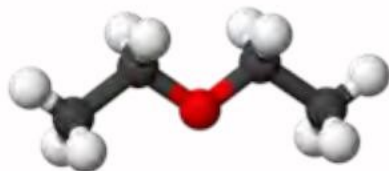


2,2,4-trimethylpentan,
isooctane

apolar, bulky



CHCl₃, chloroform
polar, electron pair acceptor
(Lewis acid)



diethylether
polar, electron pair donor
(Lewis base)



Interactions of the „unknown“ surface with the known gas probes

- Quantitative properties!
- Disperse surface energy, nanoroughness, polarity, acid/base, adsorption isotherm, heterogeneity

Unique IGC setup: automated, flexible



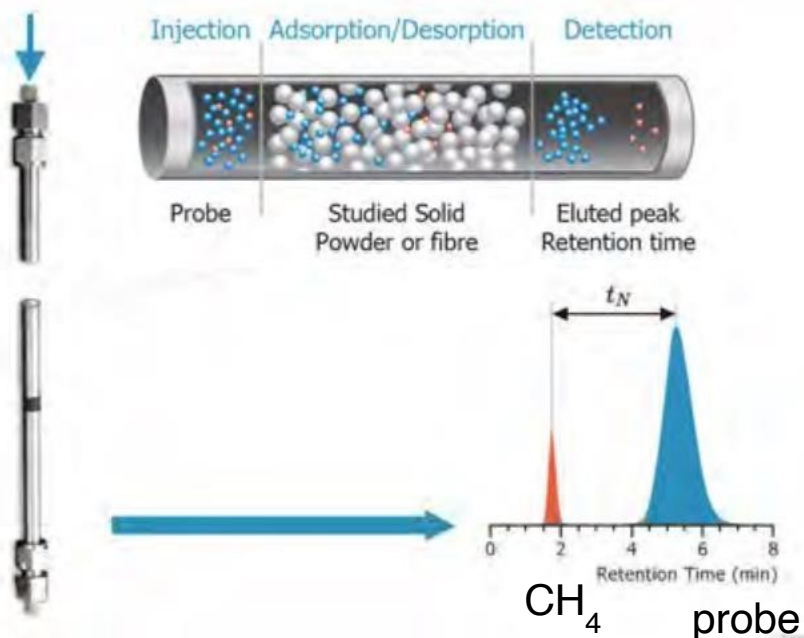
Our Instruments
Clear setup, flexible



Wide
concentration
range:
headspace or
liquid injection

Sample and Experiment
50 - 3'000 mg, 15+ probing gases

Inert gas + „probe molecules“



interaction strengths

Automation
Proprietary software

Control software (or
manual operation)

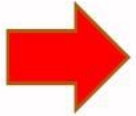
Data interpretation
and handling



Content

- Introduction

- ▶ Difficult powders
- ▶ IGC principles
- ▶ IGC setup and experiences



- Examples

- ▶ Carbon Blacks
- ▶ Graphene
- ▶ Carbon on/in porous carrier
- ▶ Carbon Fibres

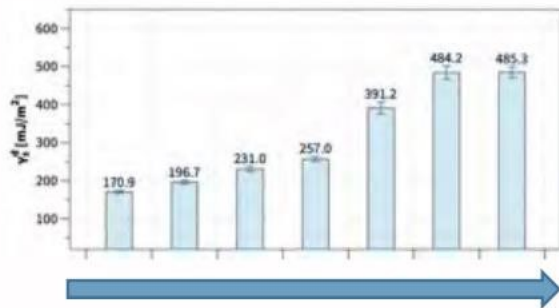
- Summary

- ▶ ... and Q&A

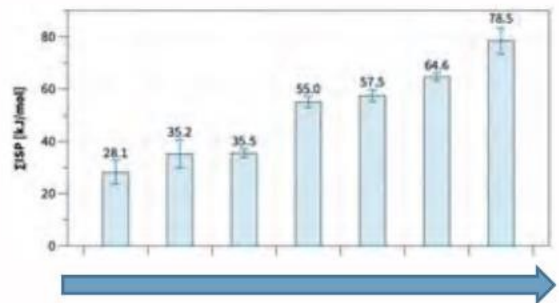
Carbon blacks

Industrial case: comparison of different carbon blacks (purchased and treated)

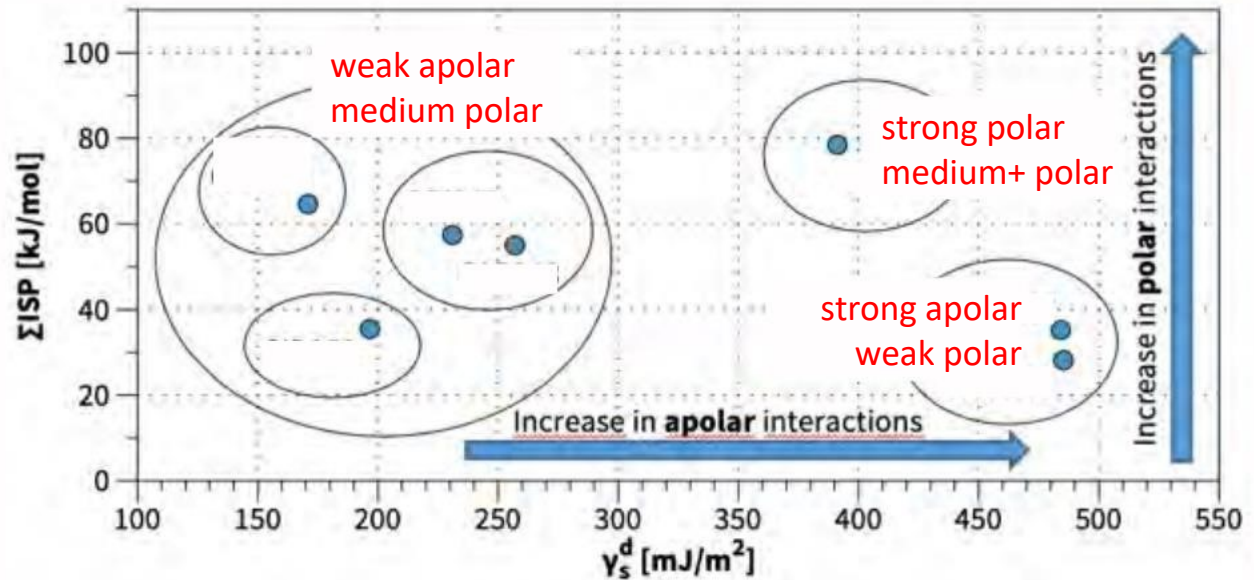
Disperse (apolar) surface energy



Overall polar interactions



Clear classification of the different carbon blacks

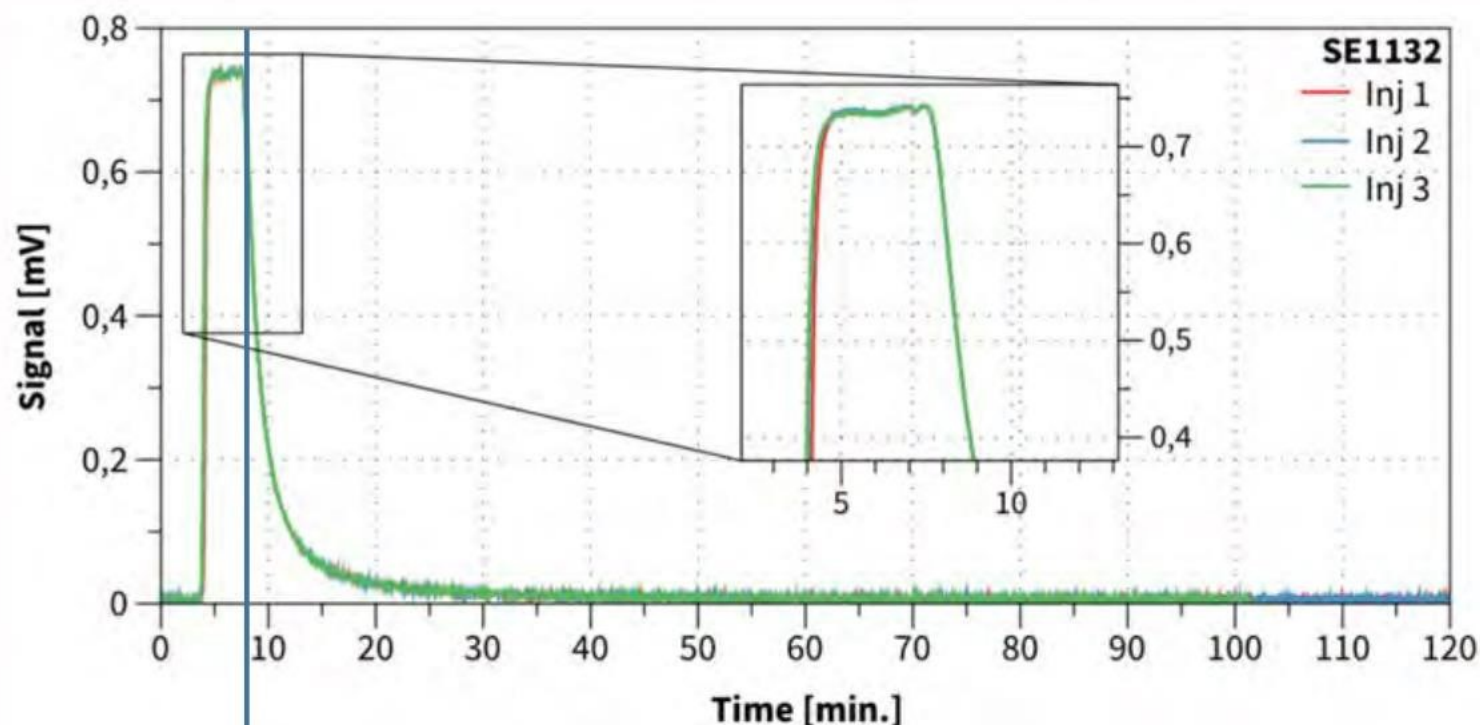


- Improved understanding of the properties
- Better interpretation of the application results
- Further optimisation of carbon black selection and use

Principle: Adsorption capacity and surface heterogeneity

A constant flow saturates the surface at a given p/p^0

- Injection of 10 μL at 0,025 $\mu\text{L/s}$ (duration: 6 min 40 s)
- Amazing reproducibility of the chromatograms (Inj 1, 2, 3)



Backbone of our new IGC instrument



Isotherms, quantities (BET) and elution profile (heterogeneity)

Carbon blacks: Adsorption Energy Distribution

Additional evaluation: adsorption isotherms

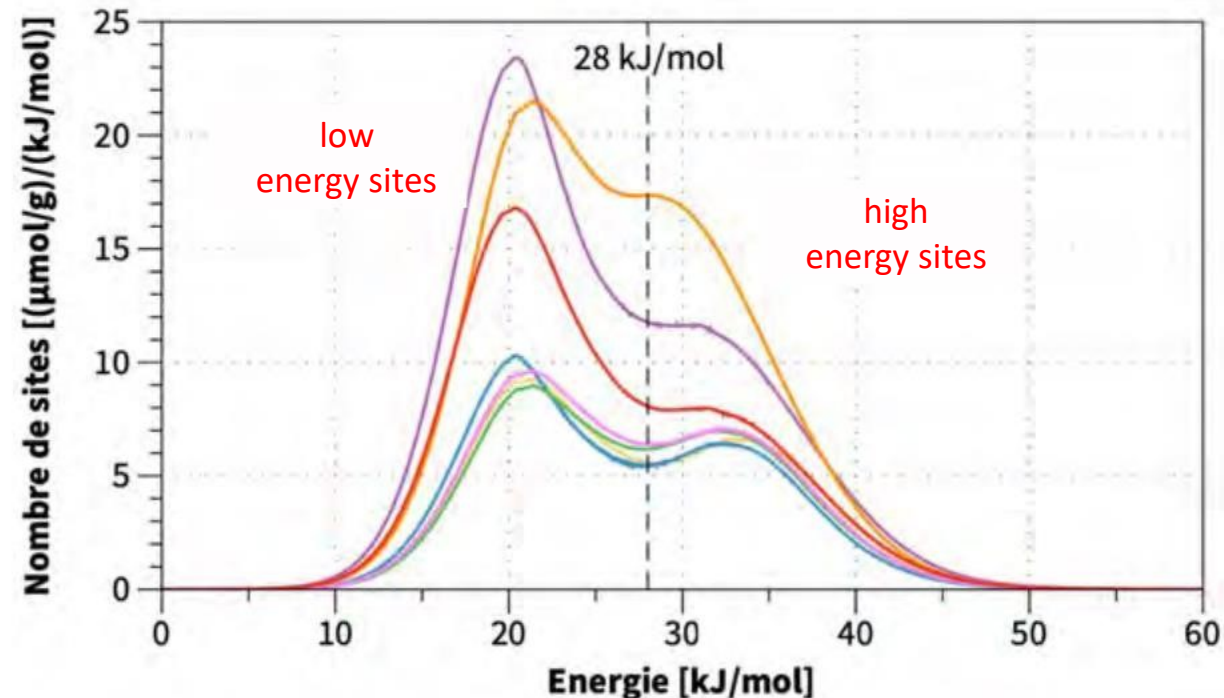
by full surface coverage using n-heptane and desorption profile (IGC-FC)

- Differentiation of sample qualities

- Specific surface area (BET) in m^2/g using any gas probe
- Irreversible adsorption
- Surface heterogeneity (AEDF)

Based on the complete surface coverage and NOT on a “nominal surface coverage” undefined in a peak

Adsorption energy distribution function (AEDF) using n-heptane



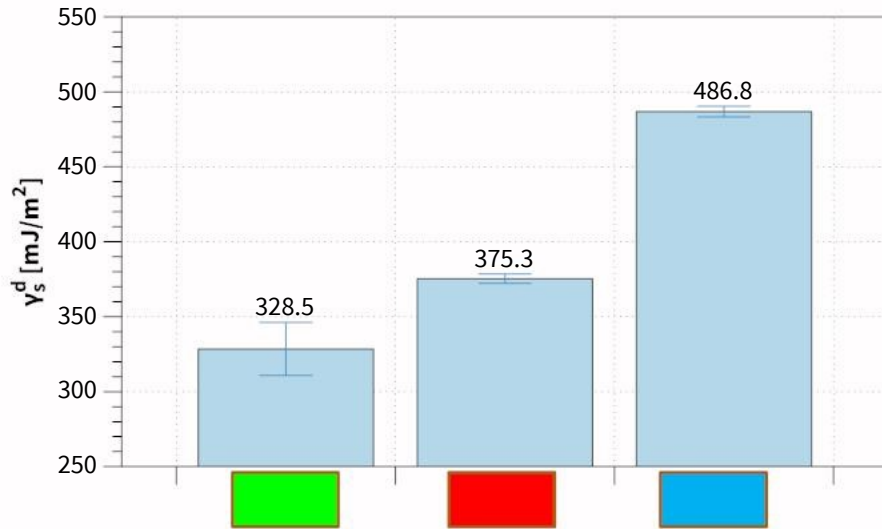
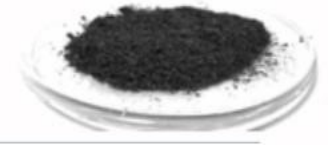
Example: Graphen



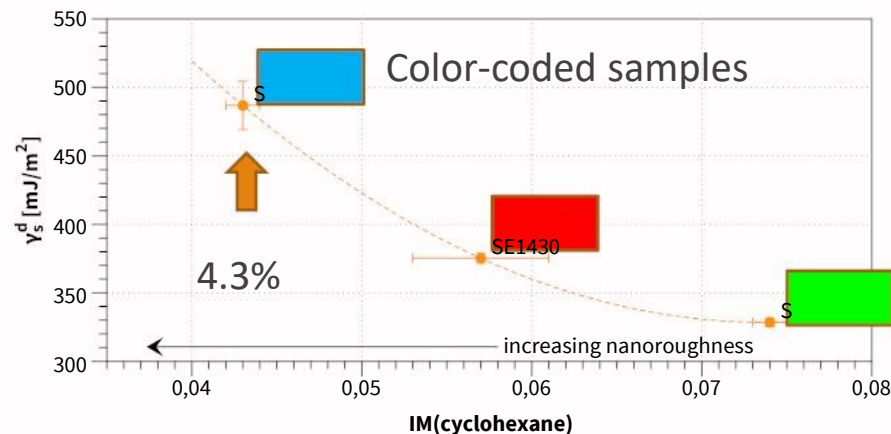
Technical samples,
different surface properties, e.g. oxidation

3 Graphene samples
kindly provided by
The Sixth Element
(Changzhou)
Materials
Technology Co, Ltd.

3 Technical Graphene Samples

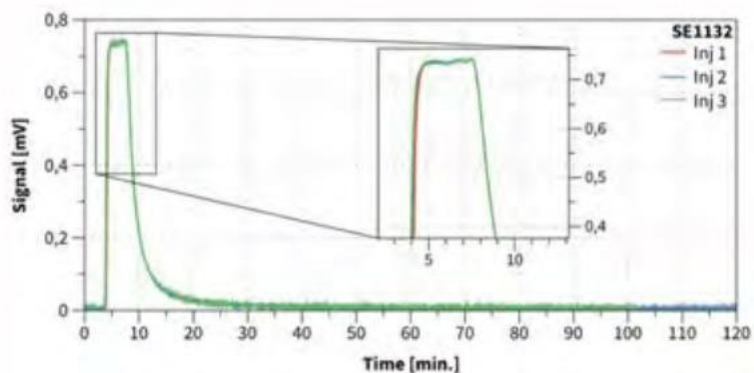


- Significant differences in dispersive surface energy (interaction with alkanes)



- Very strong size exclusion (nanoroughness):
 - $IM(\text{cyclohexane}) = 0.043$
 - Retention time is only 4.3% of n-hexane

Graphene: specific surface area and heterogeneity



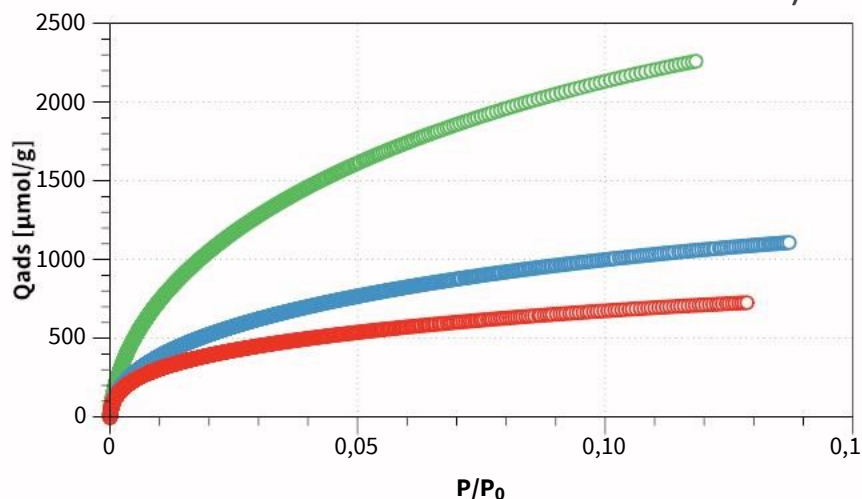
- Benzene as probe (44,1 Å²)



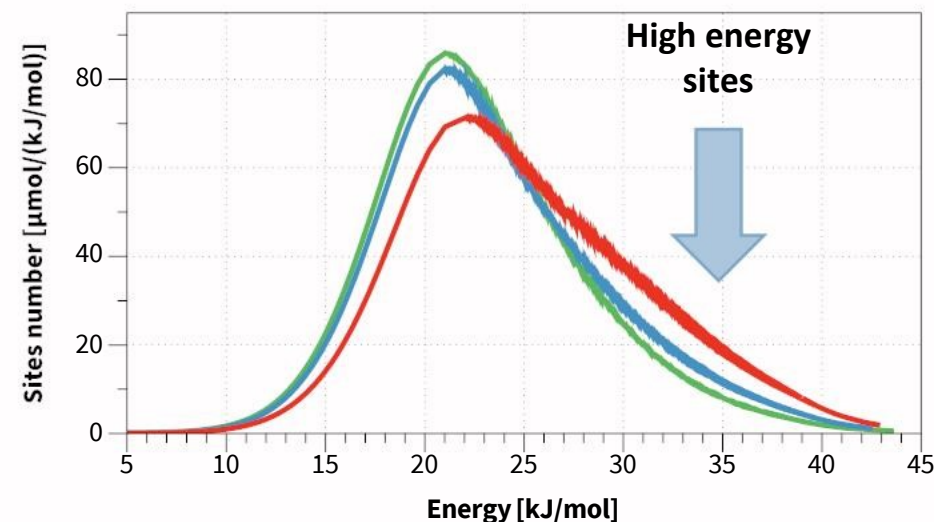
- Specific surface area (BET)

Sample	Q _{ads} [μmol/g]	S _{BET} [m ² /g]	C _{BET} [n.u.]
SE1132	1134.9 ± 8.2	301.3 ± 2.2	34.1 ± 0.9
SE1233	2471.7 ± 19.1	656.2 ± 5.1	31.8 ± 0.5
SE1430	735.0 ± 20.9	195.1 ± 5.5	44.3 ± 3.3

FACP
(Frontal Analysis by
Concentration Point)

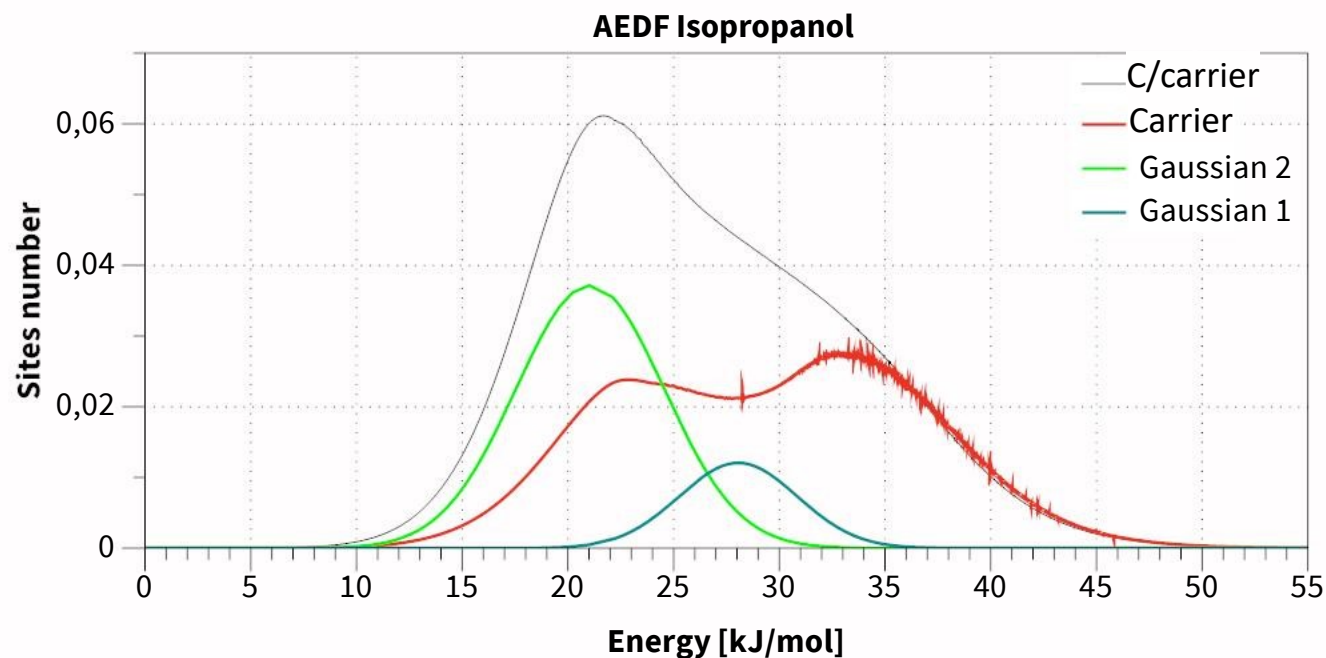


- Adsorption Energy Distribution (AEDF)



Example: Battery material - Carbon on/in porous carrier

- Question: specific surface area of carbon on/in porous carrier
- **Method: IGC-FC (finite concentration) using isopropanol**
- Differentiation between C and carrier
 - What are the specific surface areas?



Example: Carbon Fibers



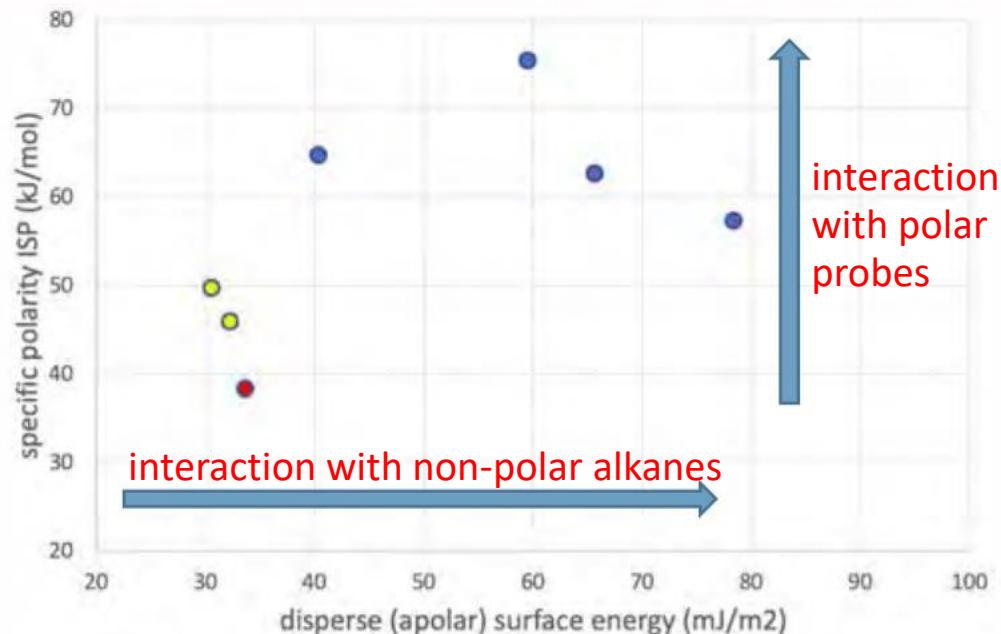
Customer samples
for analysis by IGC

(picture for illustration only)

Carbon Fibres

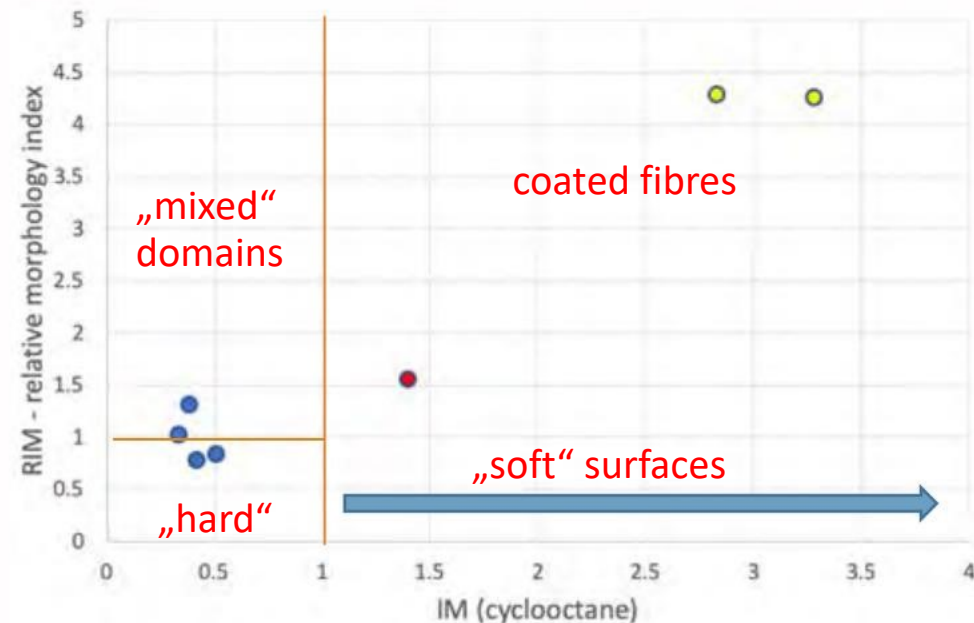
Demand: effect of sizing, surface treatment, compatibility towards polymer matrix

Quantification of polar and non-polar interaction strength



Sizing – dissolution behaviour

Use of cyclooctane, isooctane and n-alkanes



Note: cyclooctane dissolves easily in organic layers and indicates thereby organic coatings or amorphous regions (soft surfaces)

Summary

- Challenge:
Surface interaction properties of powders ??

- IGC Setup and 20 years experience



- Examples:

- ▶ Carbon Blacks
- ▶ Graphene
- ▶ Carbon on/in porous carrier
- ▶ Carbon Fibres

- ▶ Sensitive, quantitative, reproducible characterisations

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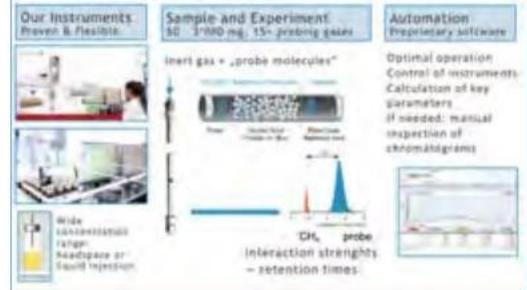


Need for

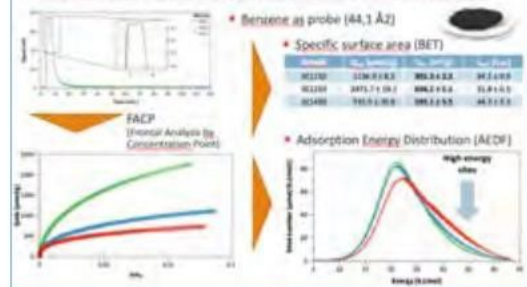
highly sensitive, quantitative and reproducible characterization of surface interaction properties

beyond BET(N₂), SEM images, XPS, applications...

Practical setup of IGC



Graphene: specific surface area and heterogeneity



Clear classification of the different carbon blacks

