Dynamische Sorptionsuntersuchungen am System VOC/Aktivkohle

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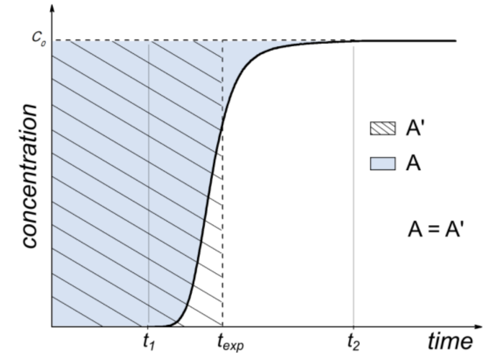
Outline

- Effects influencing breakthrough curve measurements

  → Dosage of organics

  → Requirements

  → Limitations

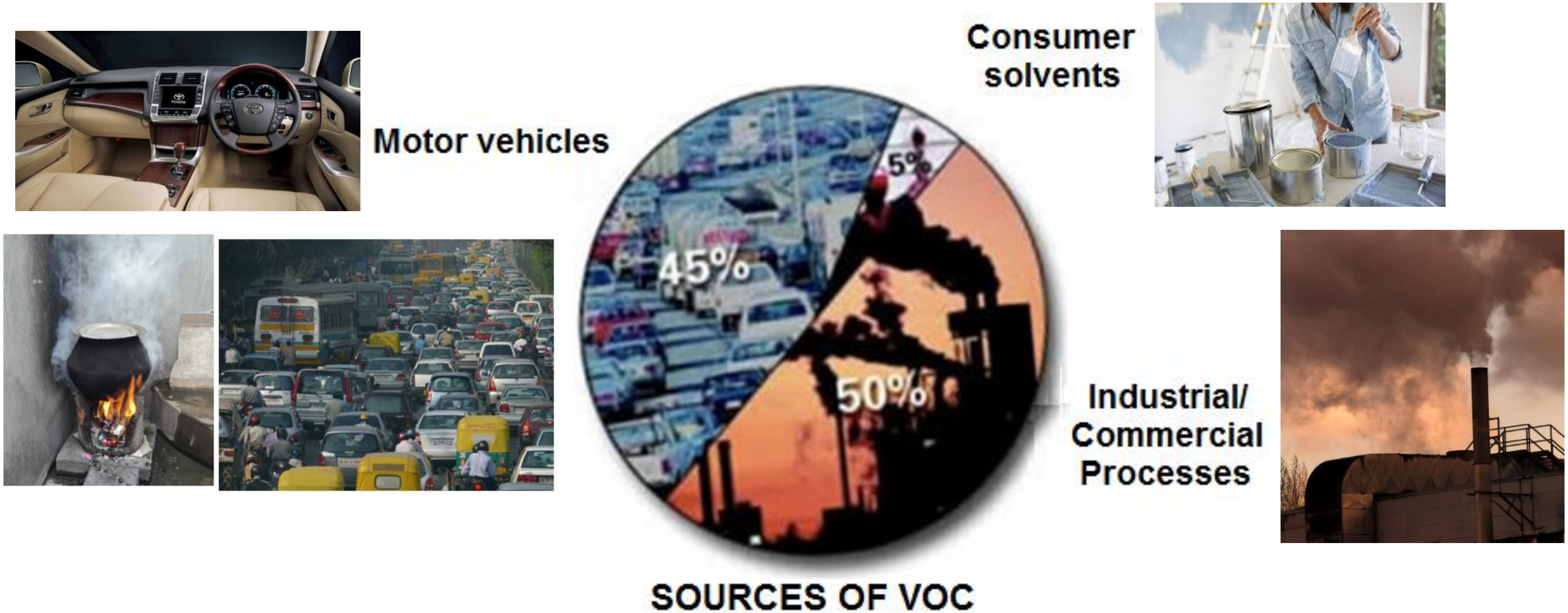


- Example I (VOC separation from biomass plant)

- Example II (VOC/humidity on AC)

VOC – Volatile Organic Compounds

Vaporizable, carbon-containing compounds



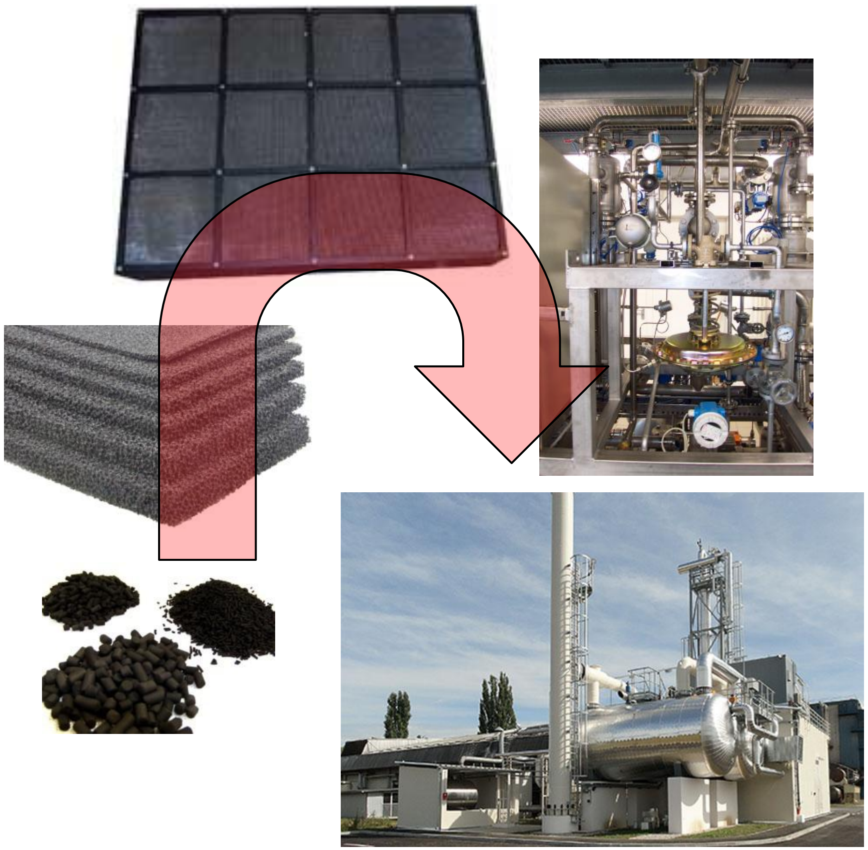
Contamination leads to massive health issues like

Cancer, Liver and kidney damage

Central nervous system damage

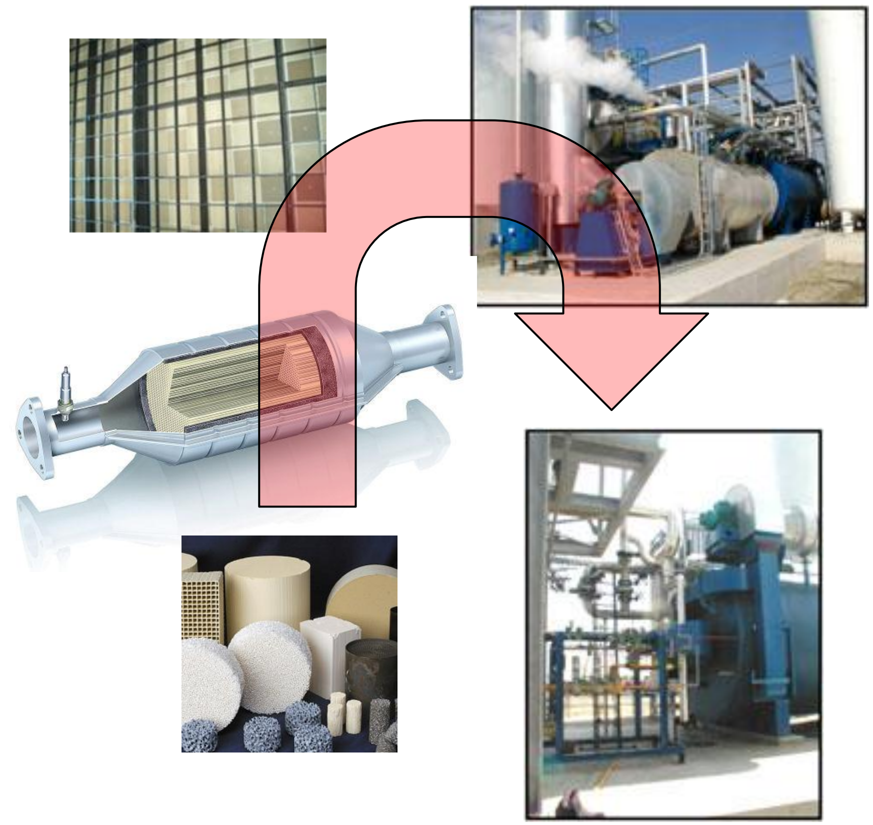
Overview – examples for VOC separation

Sorption with activated carbon



→ Breakthrough Testing

Thermal or catalytic decomposition



Overview – Principle of Breakthrough Measurement

Dosage system

Mass flow controller bubbler

Thermostated unit

Reactor/Adsorber

Glass or metal version

Detector

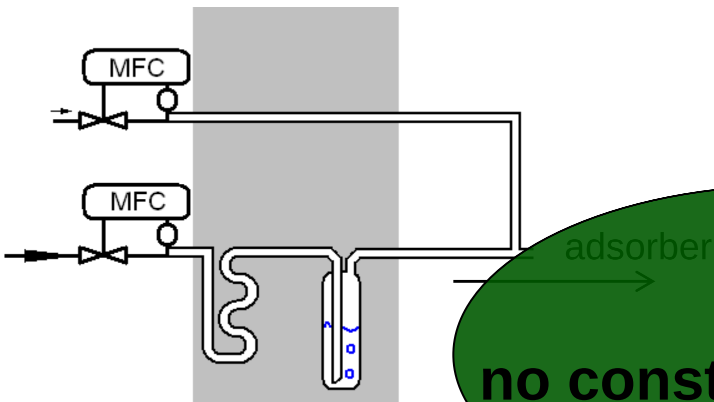
FID, MS, IR, electrochemical, others

Off-gas treatment (optional)

Dosage system – Example I

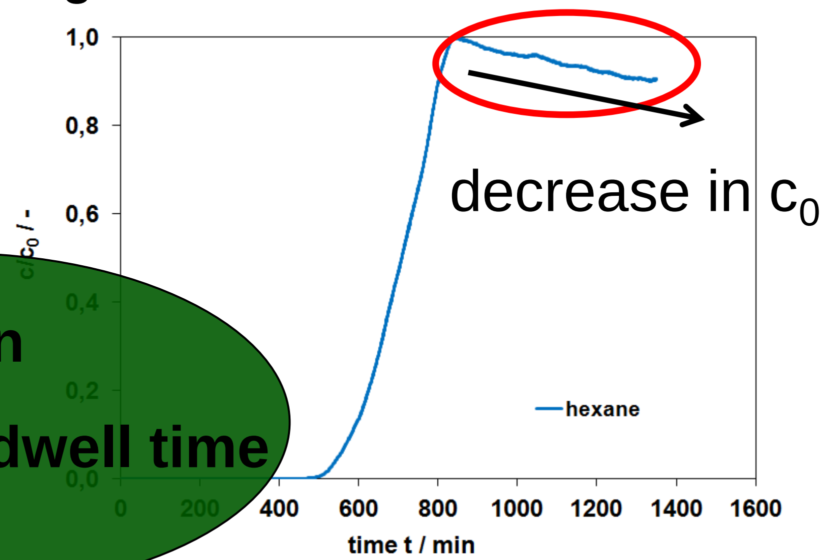
Providing a saturated inert gas flow by

- Bubbling with inert gas through one bubbler



often

no constant dwell time

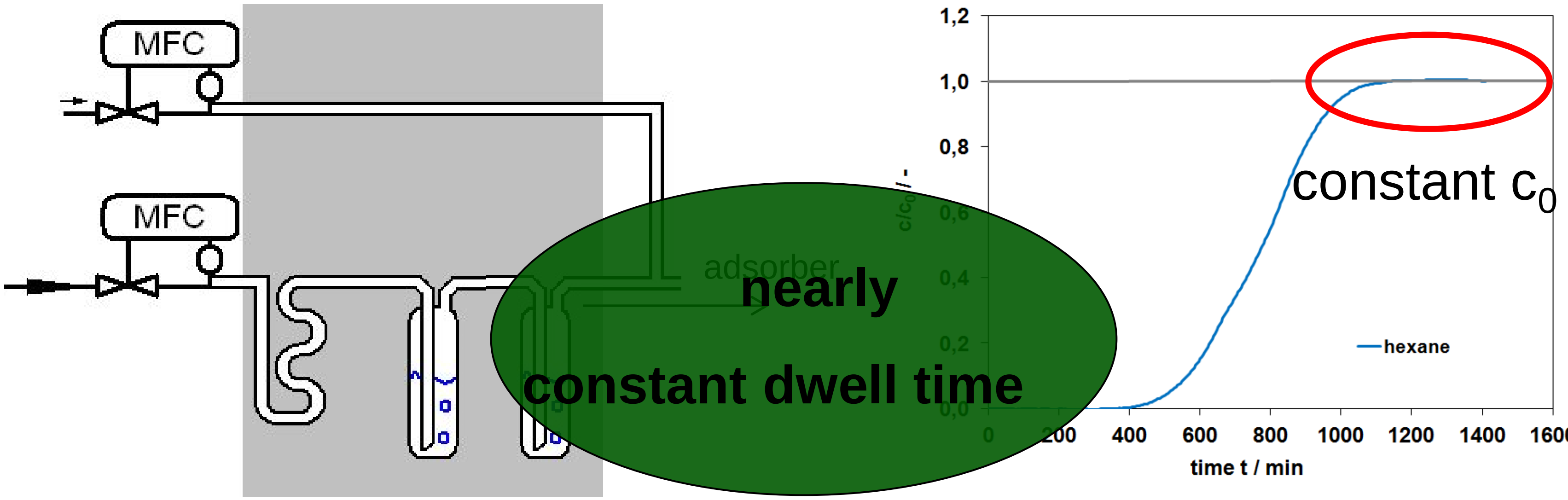


Pro	**Contra**
- No heater needed	- Only for pure organics
- Easy handling	- c_0 depends on fill level

Dosage system – Example II

Providing a saturated inert gas flow by

- Bubbling with inert gas through two bubbler



Pro

- No heater needed

- Nearly constant c_0

Contra

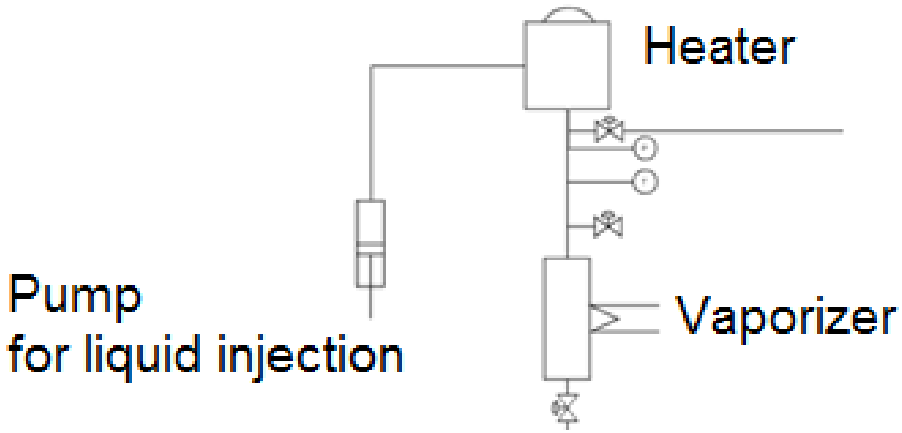
- Only for pure organics

- More complex handling

Dosage system – Example III

Providing a saturated inert gas flow by

- Heater/vaporizer – direct injection



Pro

- Miscible liquid mixtures possible
- Direct control of c_0

Contra

- Heater is needed
- Complex equipment

Dosage system – limitations

→ Larger concentration is limited due to the c_{sat} of the used solvent/VOC (depends on T and p)

→ be sure that no condensation can occur **(heating up tubes)**

→ Low concentration is limited due to the c_{sat} of the used solvent/VOC (dilution; lower T possible)

→ normally dilution down to 1:500 works (dilution depends also on overall flow)

→ Dilution below 1:500 – **use premixed testing gases !!!**

Reactor/Adsorber

Reactor differs in size and geometry

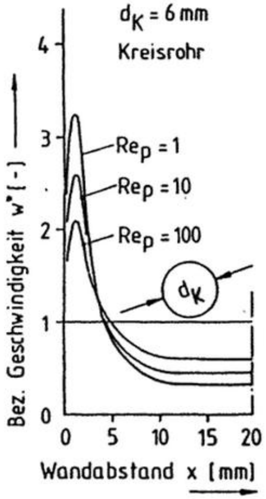
→ $d_{bed} : d_{Particle} > 10:1$

→ $h_{bed} : d_{bed} > 3:1$

Early breakthrough on wall

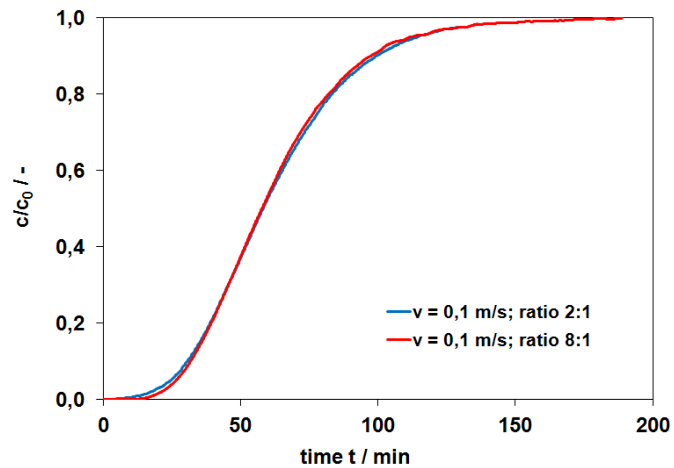
→ curve flattens

d_{bed} = 40 mm



Minimization of

Bypass flow



To do:

- Check bed parameters depending on particle size
- Check bed length and velocity for pressure drop

H.W. Kajszika, Adsorptive Abluftreinigung und Lösemittelrückgewinnung durch Inertgasregenerierung, Utz Verlag, 1998.

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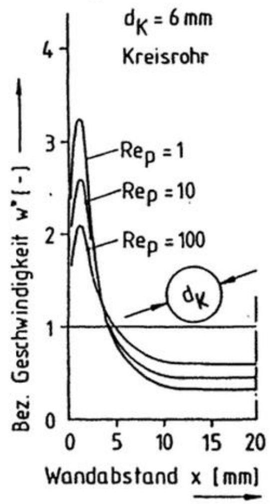

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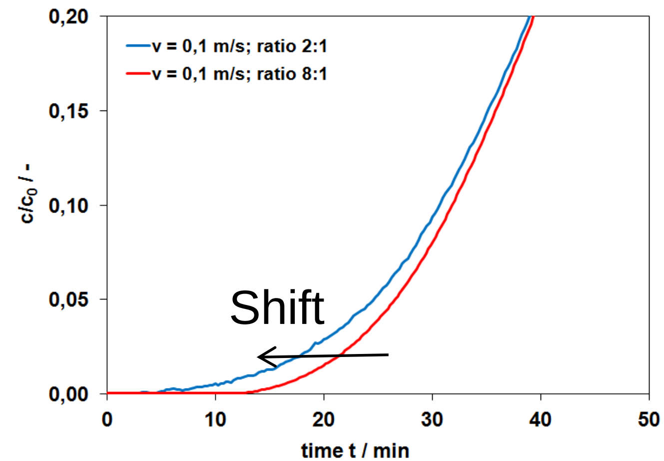

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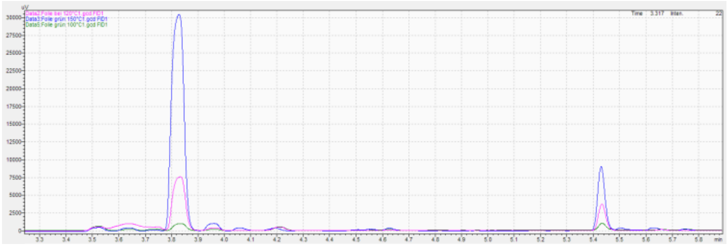
Detector

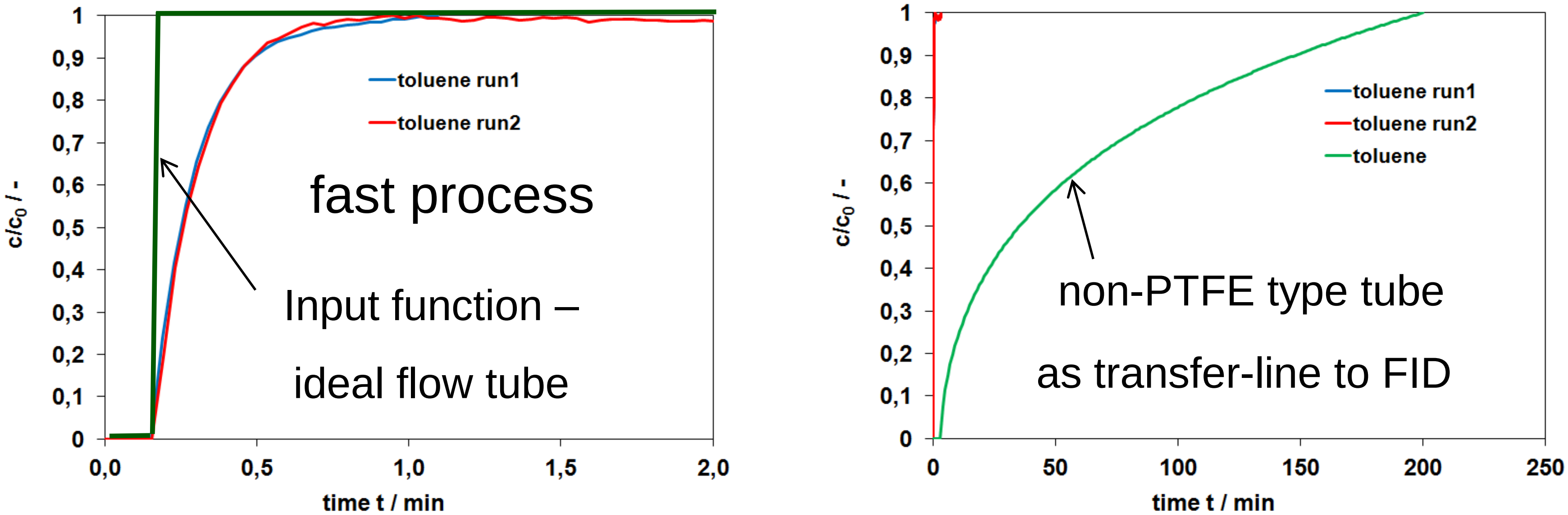
Depends on analytical question

- Number of compounds
- Concentration range (**detection limit depends on scope**, but should be at least 100-1000 times lower as c_0)
- Check **time resolution** for online GC systems or ECD
- Coupled systems possible → be sure if the **overall flow is large enough for all analytical devices** (e.g. aspirated IR or µGC)



Dead time correction

- Dead time or volume – time is needed for flowing the bed up to the detection unit



- Avoid interaction between VOC and tubes/fitting/sealing
- Avoid back mixing in the whole system

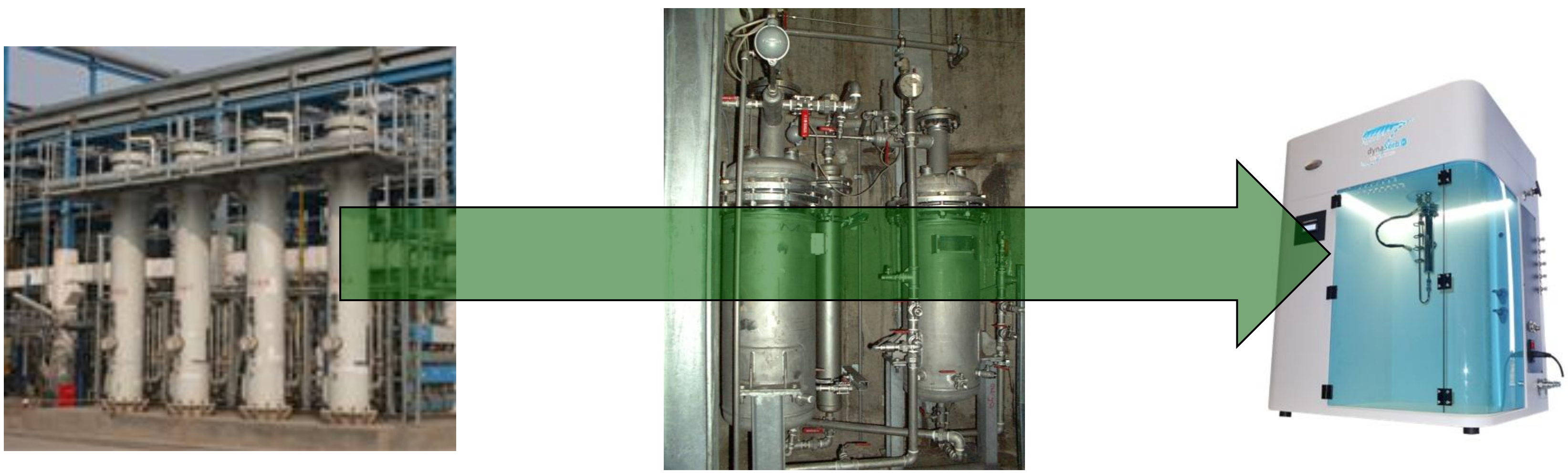
Summary I

→ Breakthrough measurements can be a complex scenario

→ Modular concept ensure high flexibility

→ Check process conditions and select equipment, but

Down-scaling your process, be careful



Example I - Biomass gasification

- Gasification of lignocellulosic biomass, mostly:

wood chips

cereal or maize straw

- Biomass → Gasification → Purification → Turbine/ Power plant
- Gasification agents: Air, O_2, Steam, (CO_2)
- Product gas contains: H_2 35-45%, CO_2 20-25%, CO 19-25%, CH_4 9-11%, C_xH_{2x+y} 3-4%, impurities like benzene, toluene, styrene, …

Adsorptive Purification – Lab test

Characterization of activated carbon

Isotherms

Static method

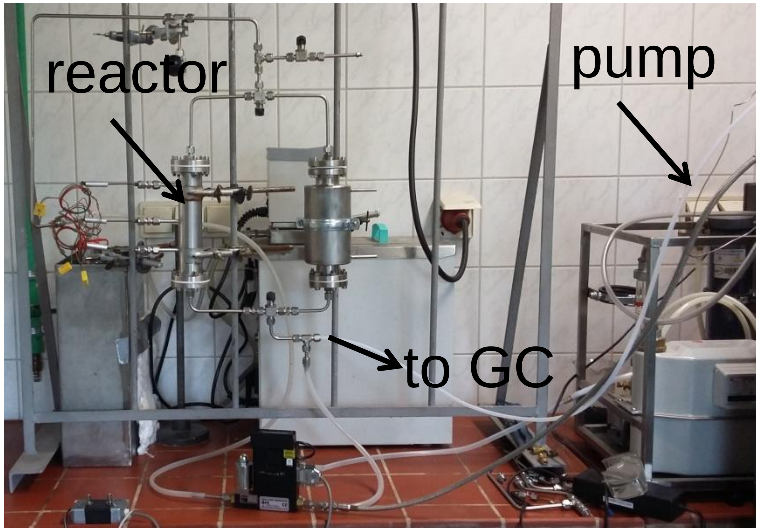
Hexane

Cyclohexane

Benzene

Toluene

Breaktrough experiments



Dynamic experiment (fixed bed)

Experimental section: Breakthrough Curves

DynaSorb BT:

→ Dynamic method

→ Fully automated

→ Different adsorber sizes available

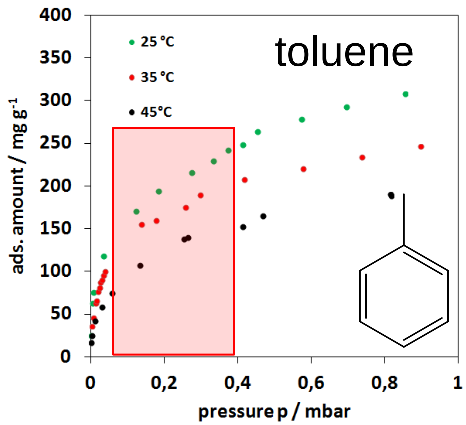
→ Temperature measurement inside the adsorber bed

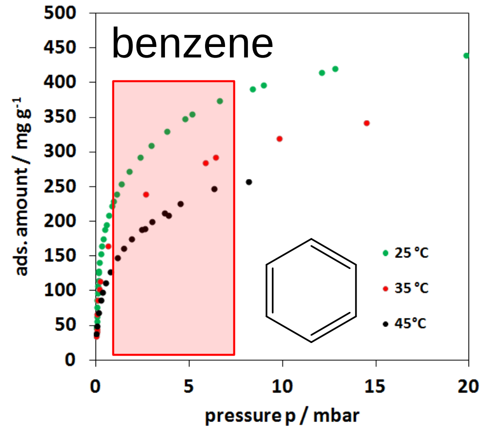
→ Data collecting and data evaluation tools (with simulation according LDF-approach)

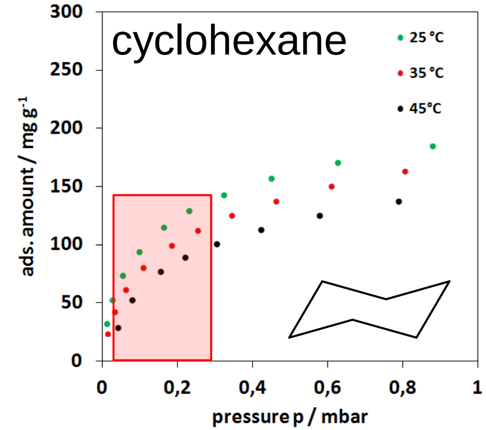
Quantachrome
Your partner in particle characterization

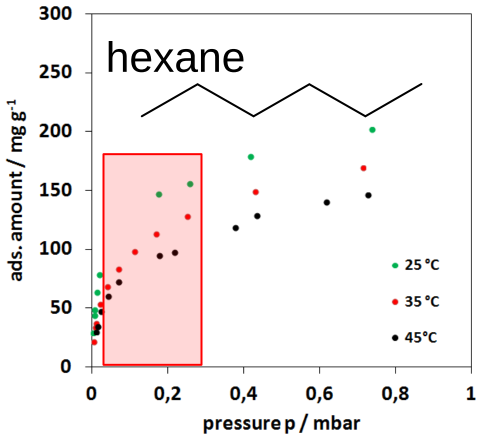
DynaSorb BT

Adsorptive Purification – Lab test: isotherms

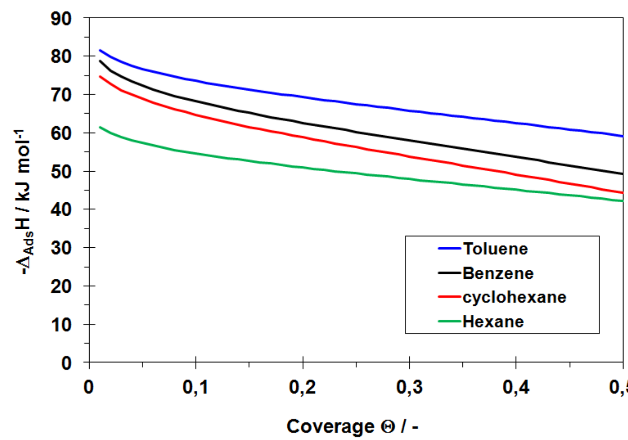








- Affinity: toluene > benzene > cyclohexane > hexane

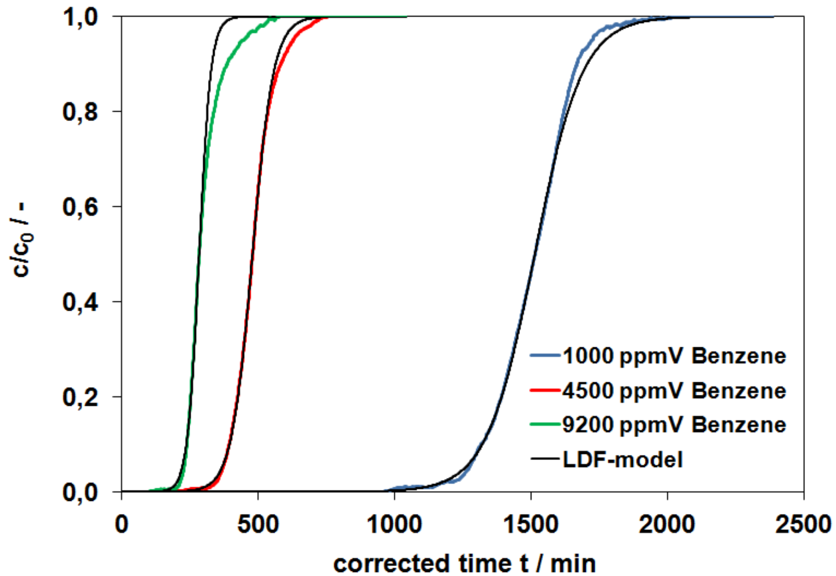


relevant concentration range

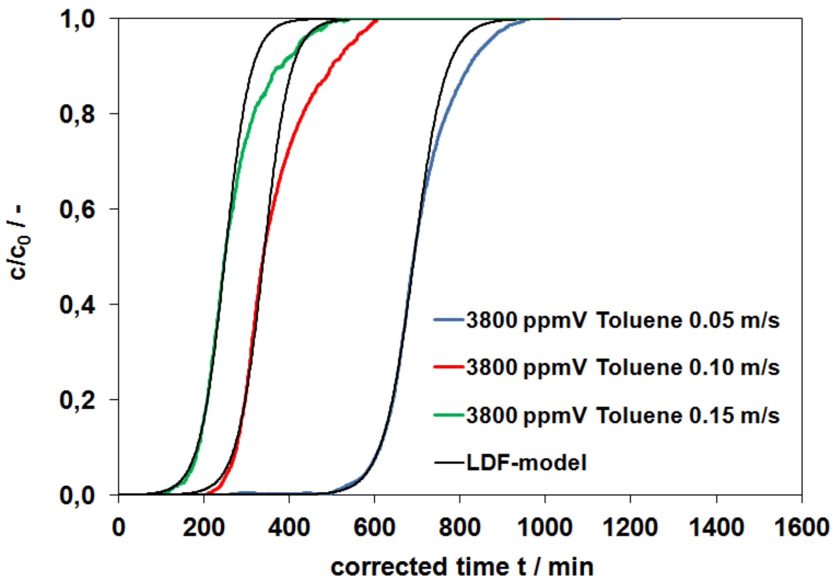
Adsorptive Purification – Lab test: breakthrough curves

- Breakthrough of pure vapors benzene and toluene at 35 °C

Variation of c



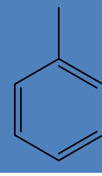
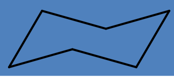
Variation of velocity



- Lower concentration leads to larger breakthrough time
- Higher velocity leads to decrease in breakthrough time

Adsorptive Purification – Lab test: breakthrough curves

- Determination of k_{LDF} from breakthrough experiments at 35 °C

pure components (constant velocity)	toluene 	benzene 	cyclohexane 	hexane 
~ 1000 ppm k_{LDF} / 10^{-4} s^{-1}	1.75	1.73	1.94	4.33
~ 4500 ppm k_{LDF} / 10^{-4} s^{-1}	4.60	4.21	4.27	8.64
~ 9000 ppm k_{LDF} / 10^{-4} s^{-1}	6.88	7.57	6.72	10.67
Lorimier et al. 2005	3.2 – 5.8			

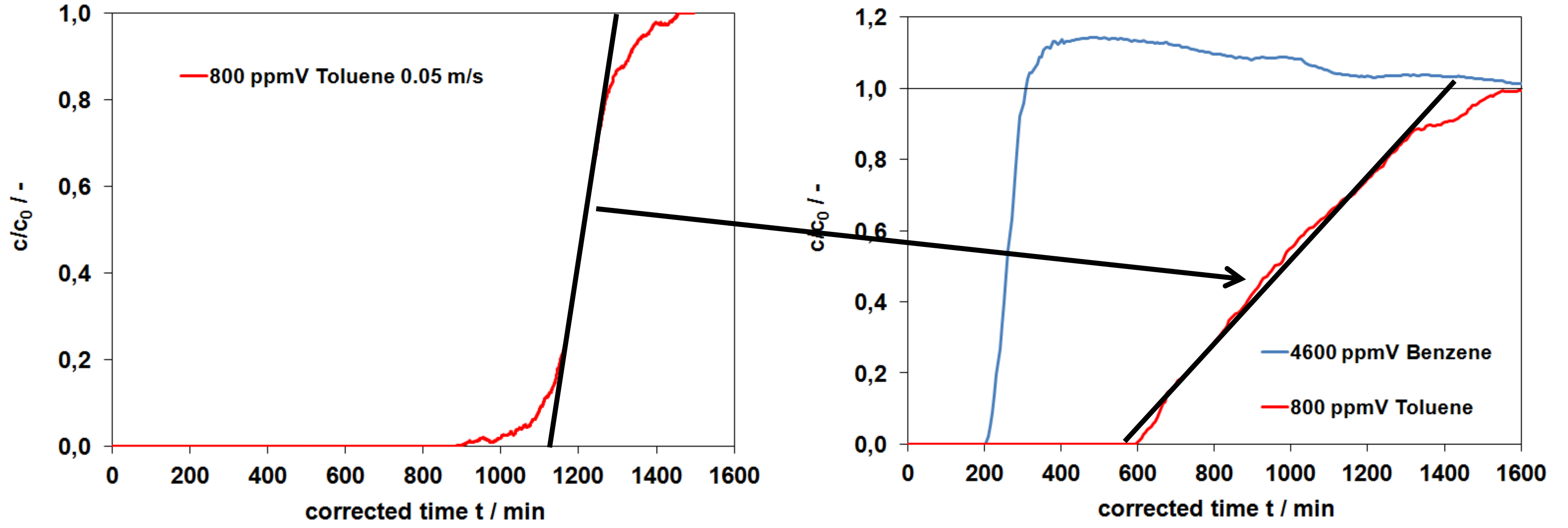
- k_{LDF} depends on molecular size:

  hexane > benzene > toluene/cyclohexane

C. Lorimier, A. Subrenat, L. LeCoq, P. Le Chloirec, Environ. Technol. 26 (2005), 1217-1230.

Adsorptive Purification – Lab test: breakthrough curves

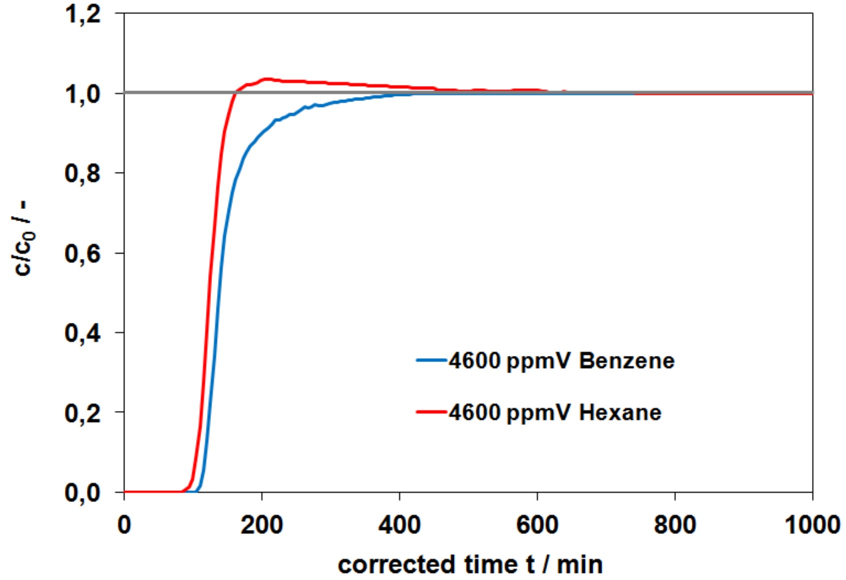
- Breakthrough of mixed vapors benzene/toluene at 35 °C

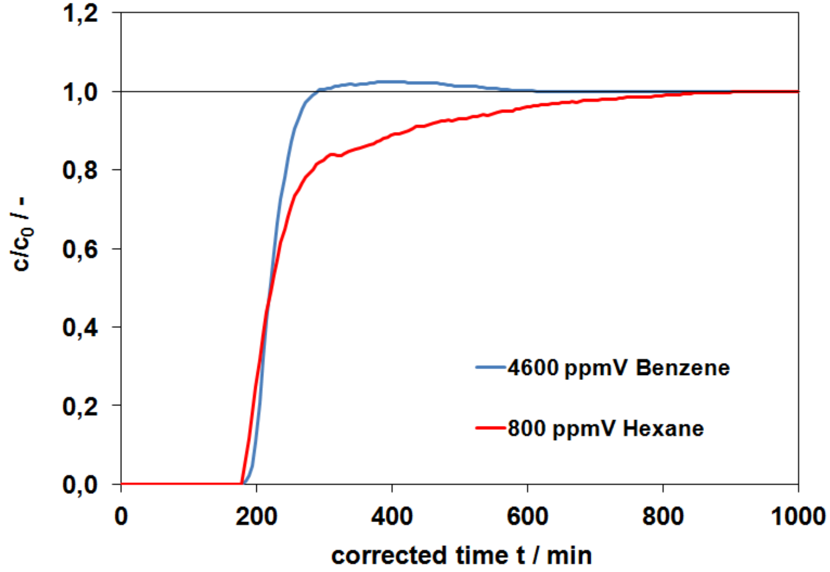


- Benzene is displaced by toluene
- Slope of toluene breakthrough flattens

Adsorptive Purification – Lab test: breakthrough curves

- Breakthrough of mixed vapors benzene/hexane at 35 °C





- Benzene is displaced by hexane at low hexane concentration
- Traceable concentration effects

Example II – Effect of humidity to sorption of VOC

Important case of application: Effects of humidity

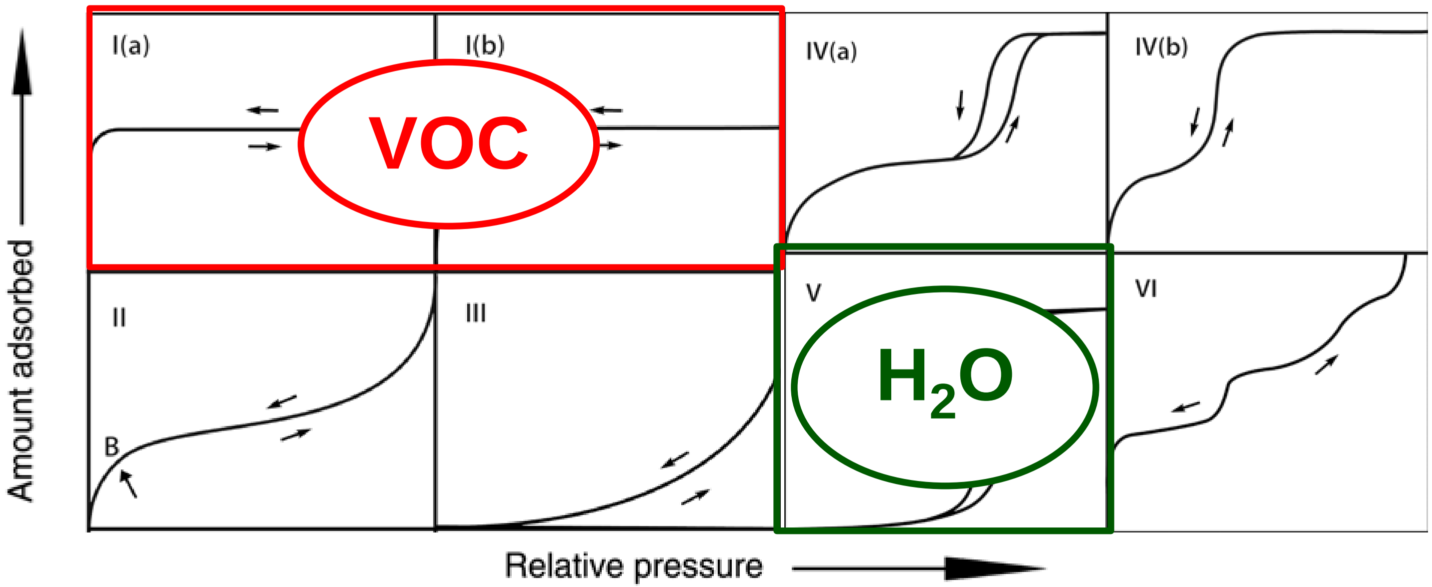
- Waste air/exhaust air cleaning

→ Humidity depends on conditions at location

http://www.silica.berlin/de/

Example II – VOC vs. H_2O sorption on AC

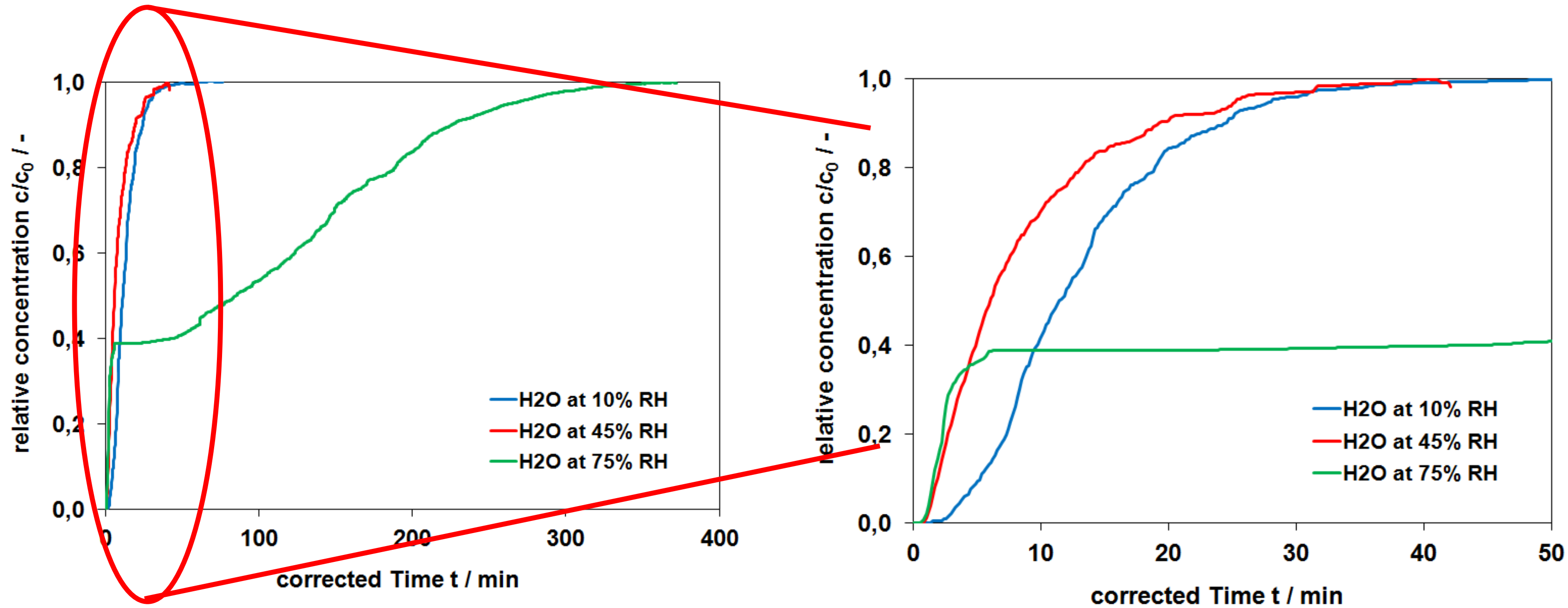
- Completely different sorption behaviour due to difference in physico-chemical properties



IUPAC Technical Report, Pure Appl. Chem. 2015; 87(9-10), 1051-1069

Breakthrough curve – H_2O

H_2O breakthrough at different concentrations

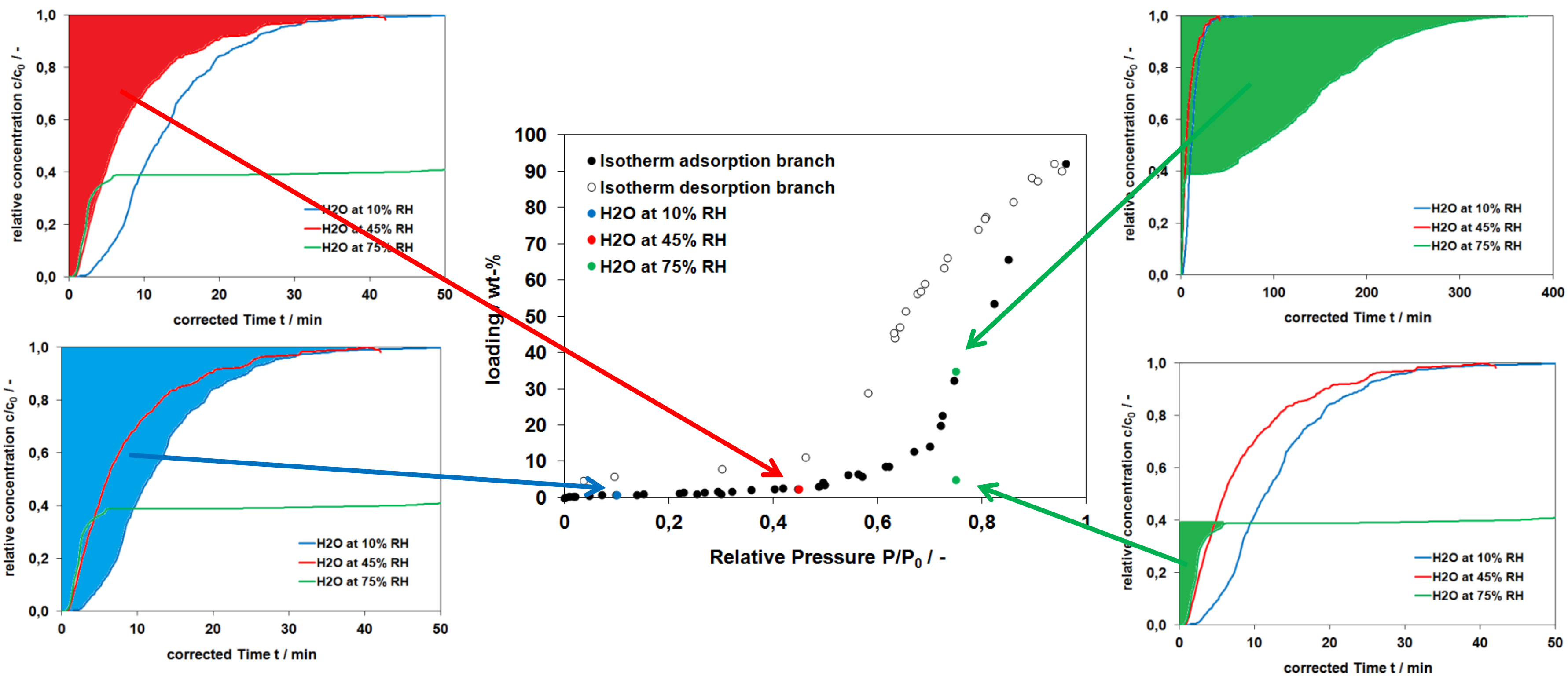


→ H_2O breakthrough below inflection point of isotherm shows typical shape, at higher concentration a stepwise curve is observed due to capillary condensation

Breakthrough curve – H_2O

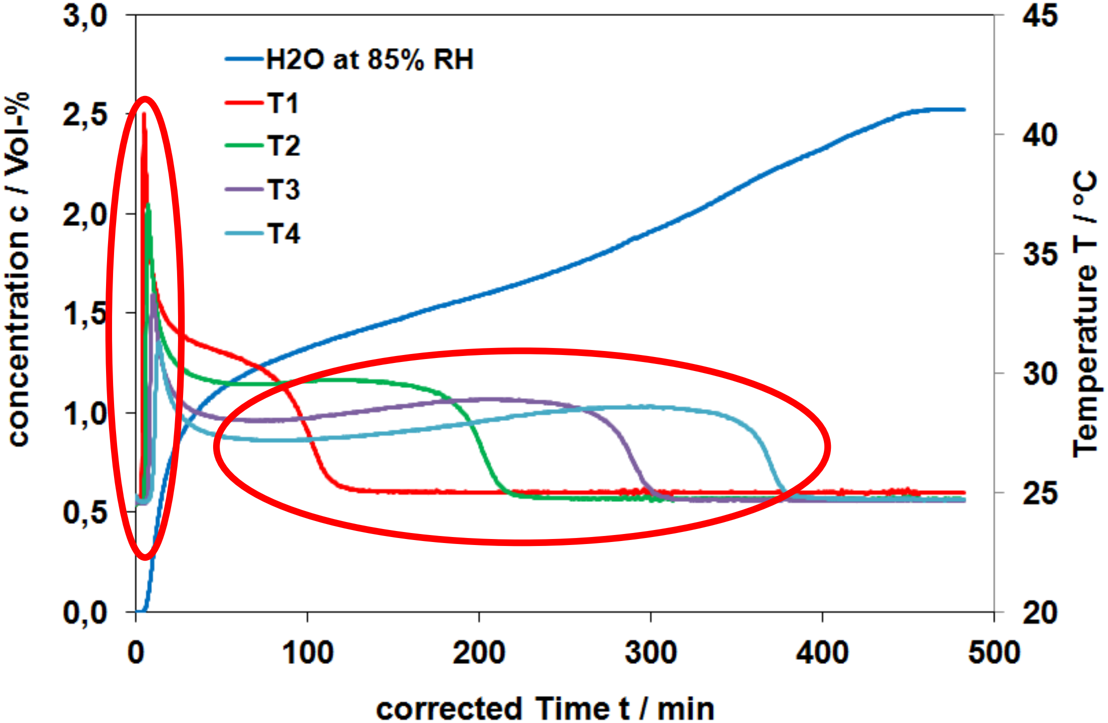
Below 45% RH

Above 45% RH



Breakthrough curve – H_2O (low affinity towards AC?)

Type V isotherm is coupled with a low affinity?

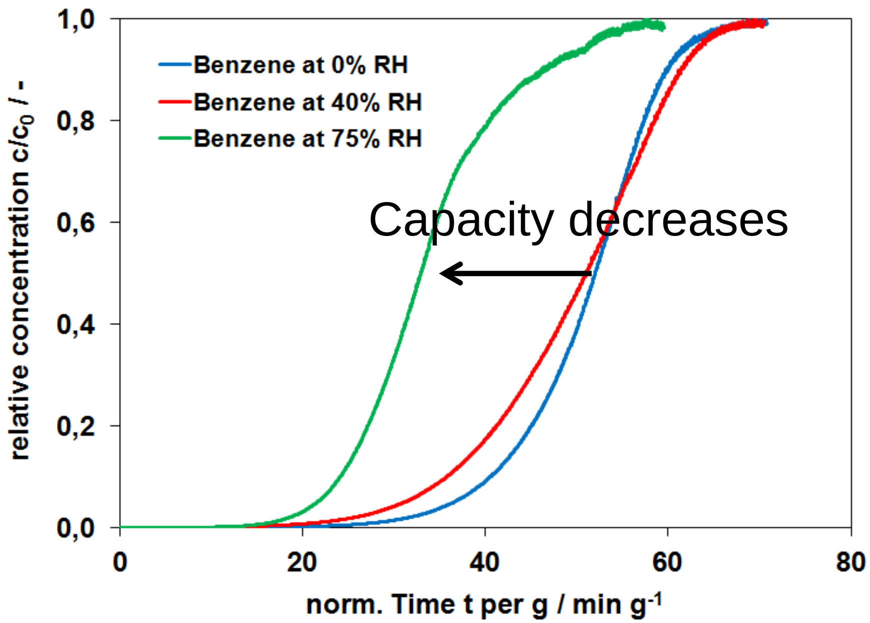


→ Strong heat detection during first adsorption due to large interaction of H_2O with ash content of carbon

→ Second heat peak is provided by heat of vaporization

Breakthrough curve – Benzene

Benzene capacity is influenced by humidity

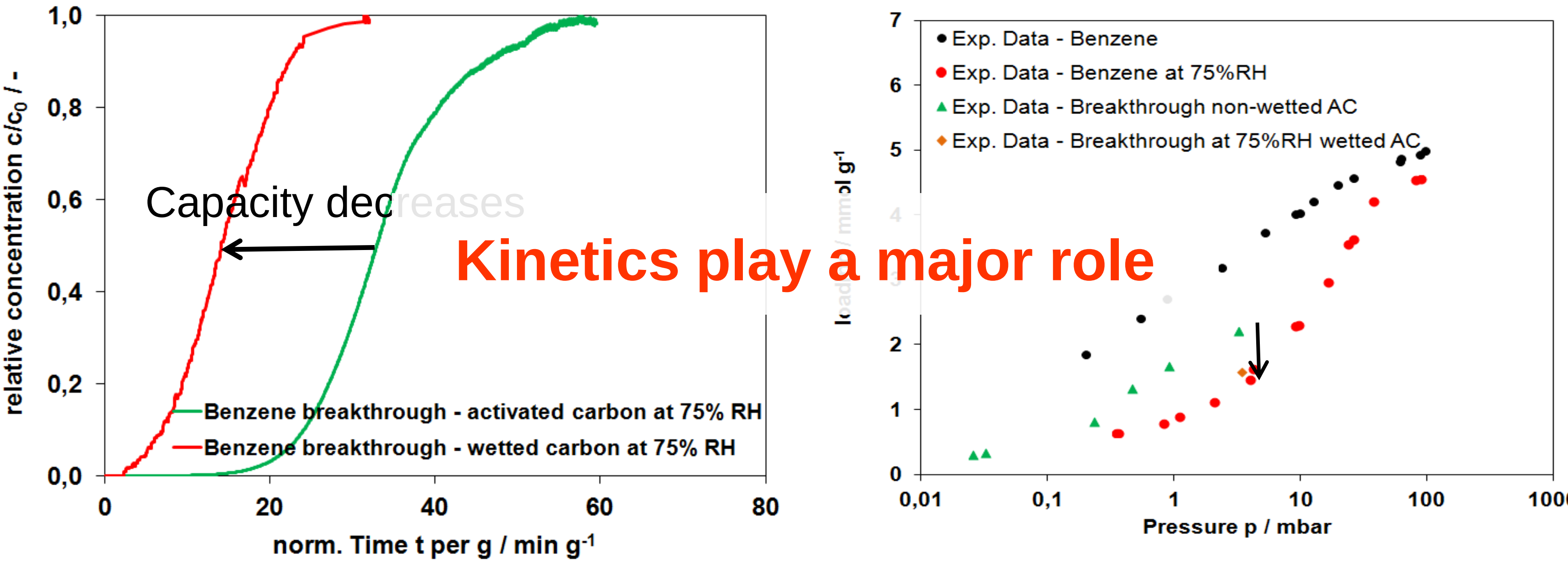


→ Benzene breakthrough flattens for low H_2O concentrations

→ Benzene capacity decreases with increasing H_2O content

Breakthrough curve – effect of pre-wetting

Benzene capacity is influenced by pre-wetting of the AC in dynamic (breakthrough) experiment



Kinetics play a major role

→ Capacity of benzene decreases after pre-wetting the AC

→ Long equilibration time for H_2O sorption (due to capillary condensation) leads to an unachievable equilibrium case

Summary II

- Breakthrough test ideal for Process Down-Scaling

  → Check general experimental conditions

- Studying sorption under real conditions

  → Kinetics

  → Thermodynamics

  → Detection of heat effects

  → Competitive sorption (complex mixtures possible)

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Zentrales Innovationsprogramm Mittelstand

DFG Deutsche Forschungsgemeinschaft

Quantachrome
Your partner in particle characterization

DBFZ

SILICA

INDUCON

http://research.uni-leipzig.de/inc http://www.dynamicsorption.com/

Many thanks for your attention!

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