ADSORPTION OF POLAR AND NONPOLAR VAPORS ON SELECTED ADSORBENTS: EXPERIMENTAL CHALLENGES AND THEIR SOLUTION

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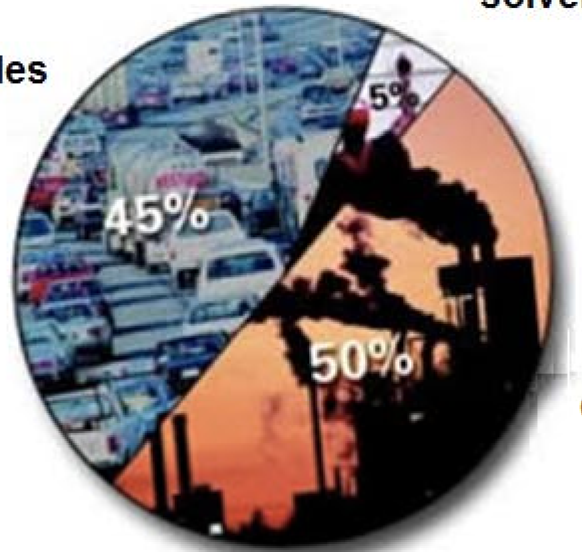
VOC – Volatile Organic Compounds

Emissions are dangerous for human and nature

Motor vehicles



SOURCES OF VOC

Consumer solvents

Industrial/ Commercial Processes

Sorption of vapors are extremely relevant in industrial processes

- purification of exhaust
- drying processes
- usage in thermal energy storage

Material Characterization and Selection

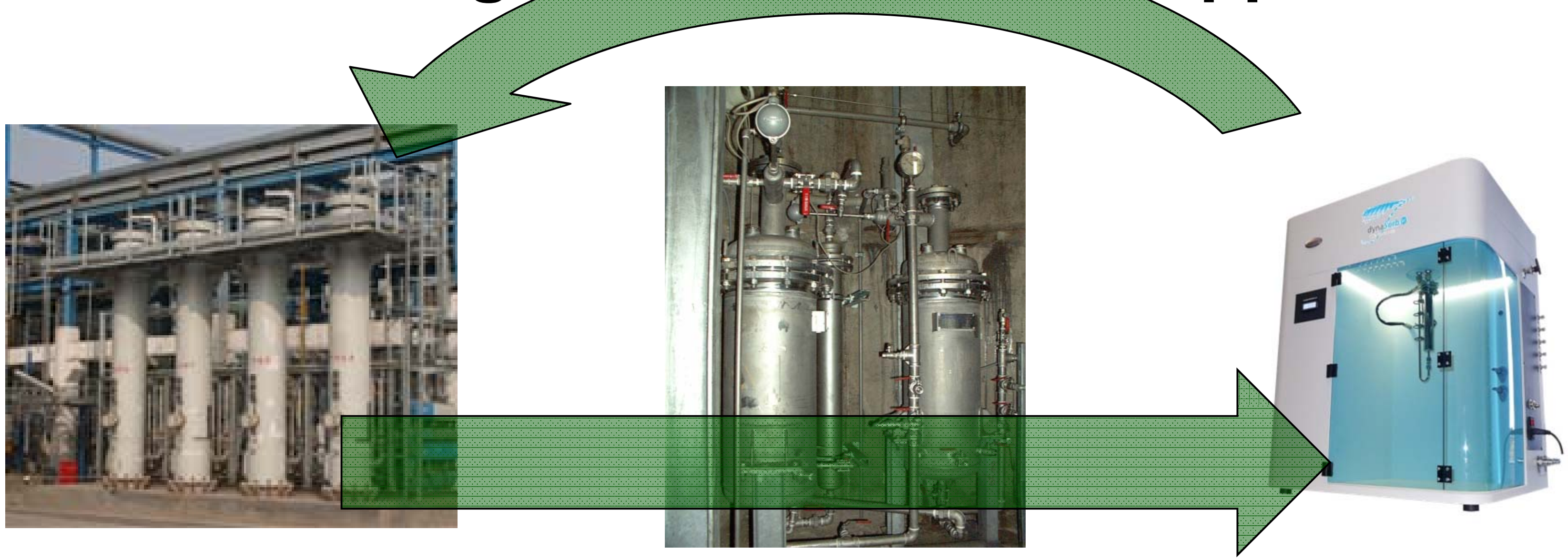
→ Designing industrial processes

→ Downscaling the process to lab-scale

→ Different methods to provide data basis:

Volumetry, Gravimetry and Breakthrough Measurements

→ Modeling/Simulation of new applications

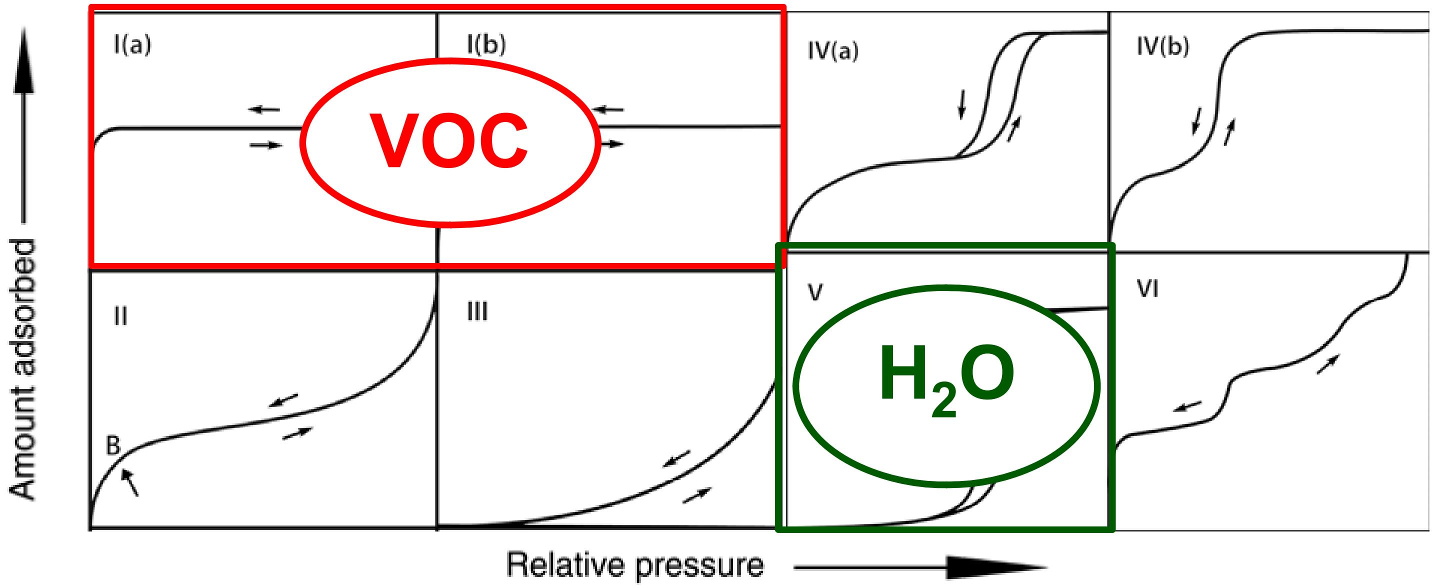


Characterization – Isotherms and Models

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

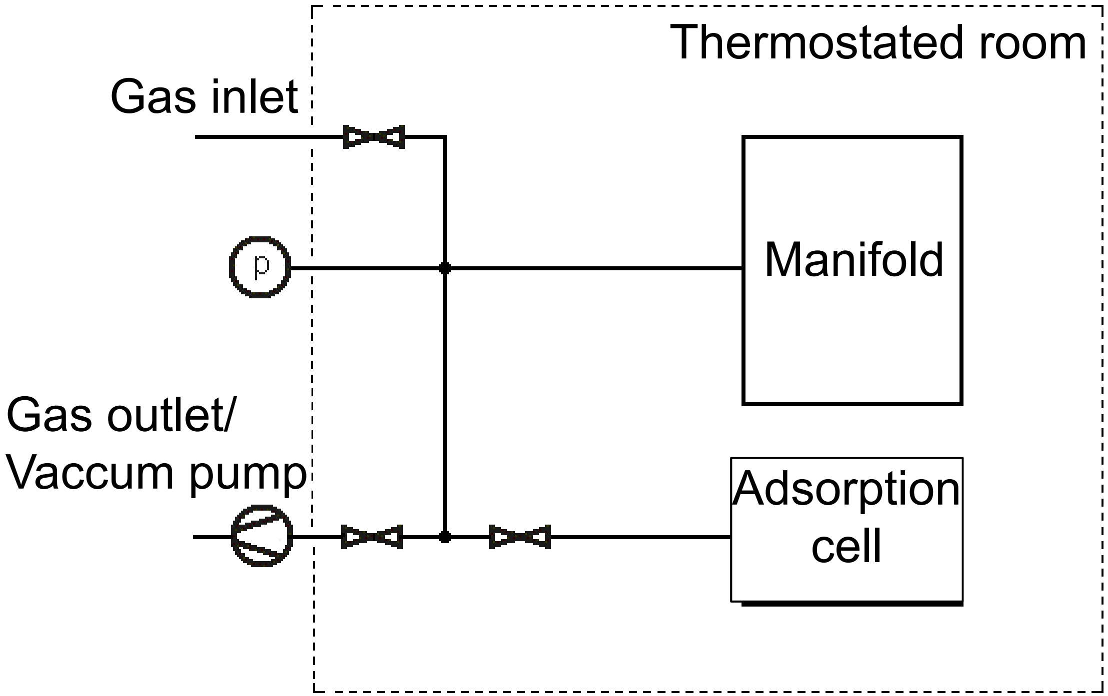
→Material selection for specific application

→Targeted modification of material surface



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

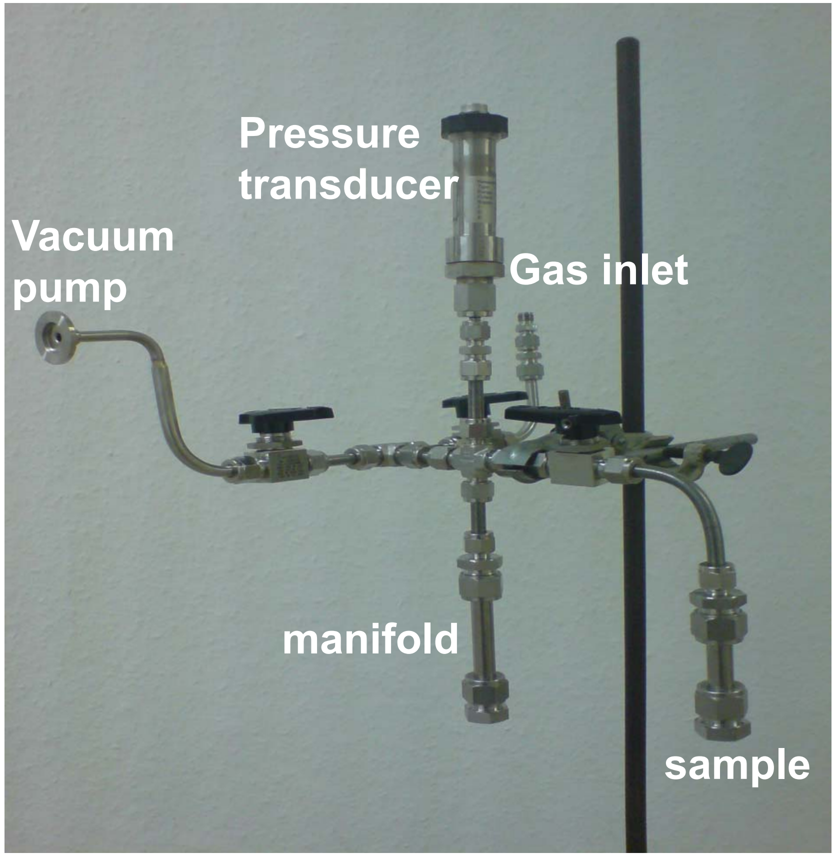
Static Methods I – Volumetry



Static Methods I – Volumetry

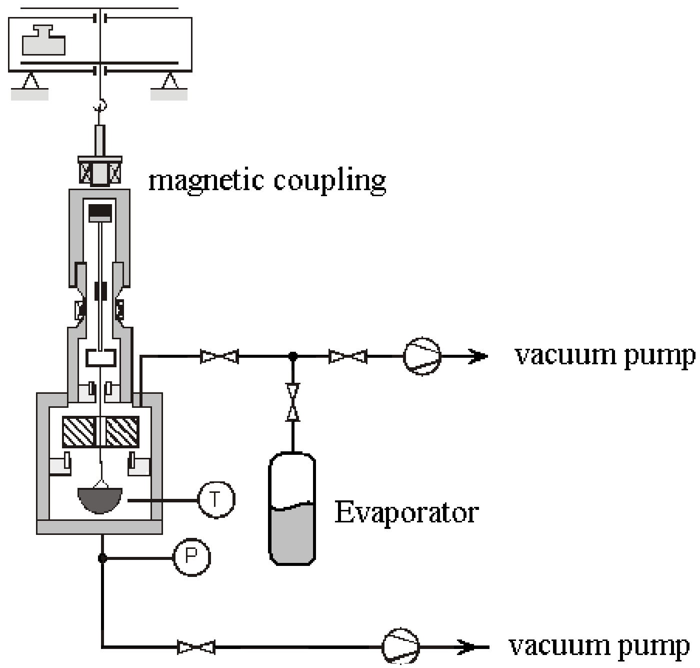
Advantages:

- Robust, small, cheap design
- Measurements with corrosive and toxic gases, e.g. SO_3, H_2S
- Measurements with small sample quantity (< 0,5 g)
  → new adsorbents
- Determination of adsorbed amount via mass balance



Static Methods II – Gravimetry

- registration of change in weight
  due to pressure modification
- pressure increase → adsorption
- pressure drop → desorption
- correlation weight - pressure
  → isotherm



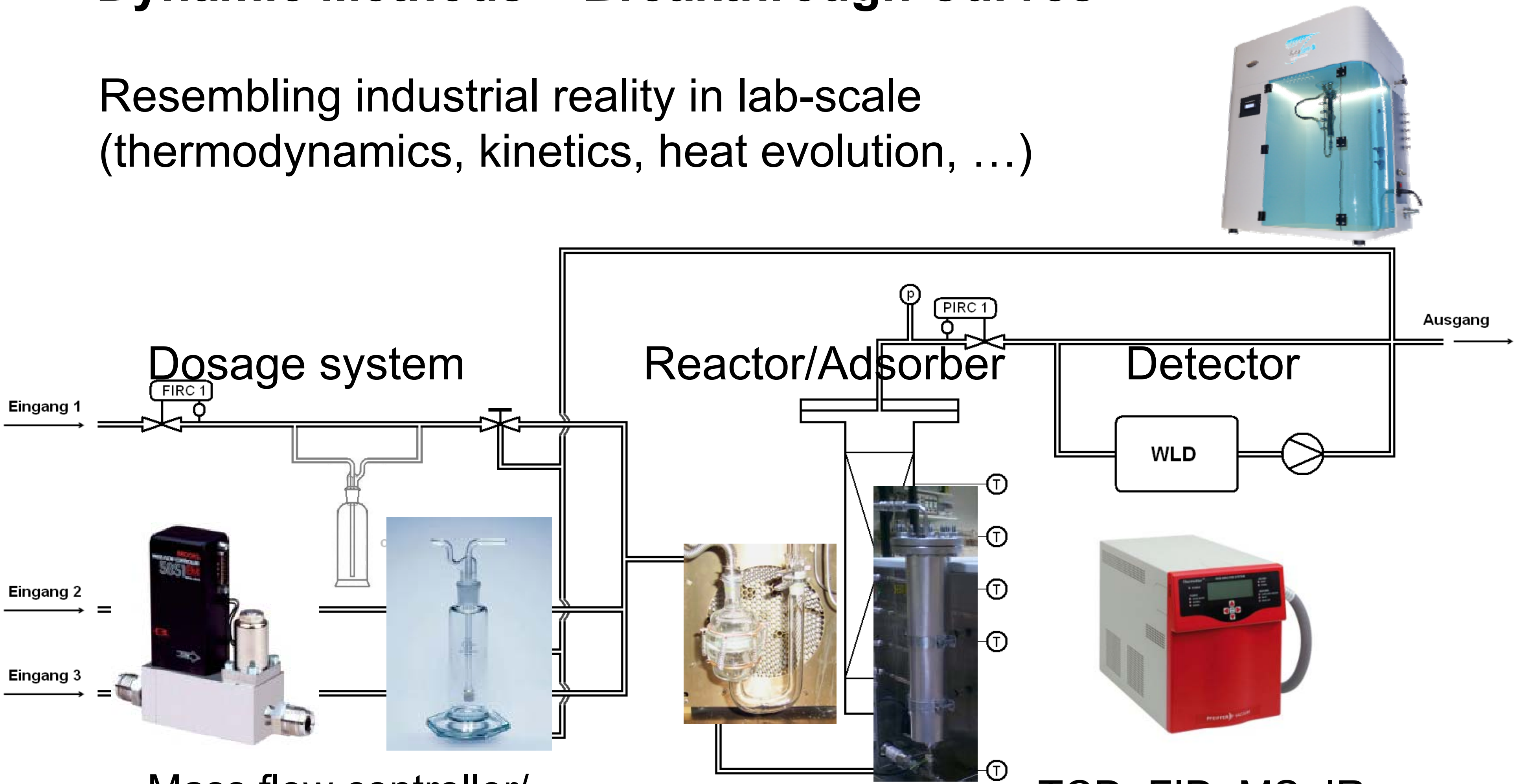
Stepwise dosage of pure vapor

- Degassing of liquid
- Flushing the pipes

Advantages:
- More accurate
- Fast equilibration
- Very low concentration possible

Dynamic Methods – Breakthrough Curves

Resembling industrial reality in lab-scale
(thermodynamics, kinetics, heat evolution, …)



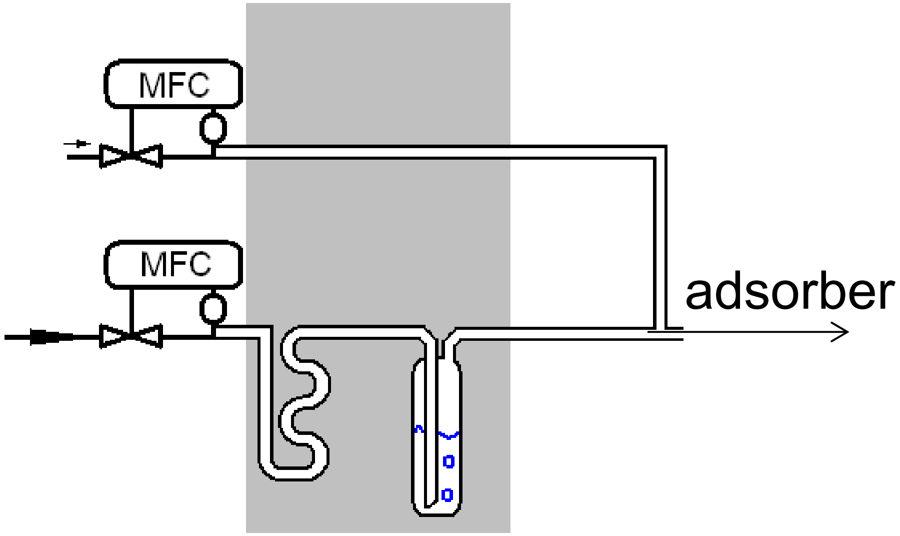
Mass flow controller/
bubbler

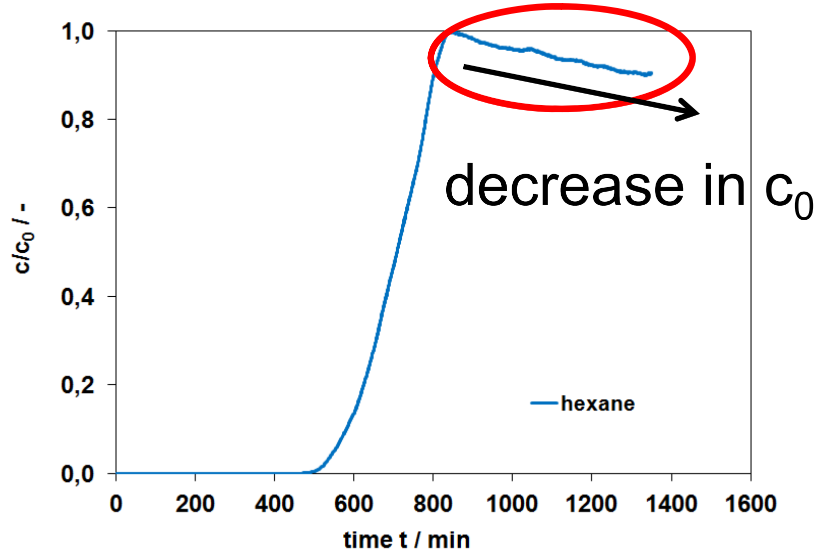
Glass or metal
version

TCD, FID, MS, IR,
electrochemical, others

Dosage system – Example I

Providing a saturated gas flow by bubbling with inert gas through one bubbler





Pro

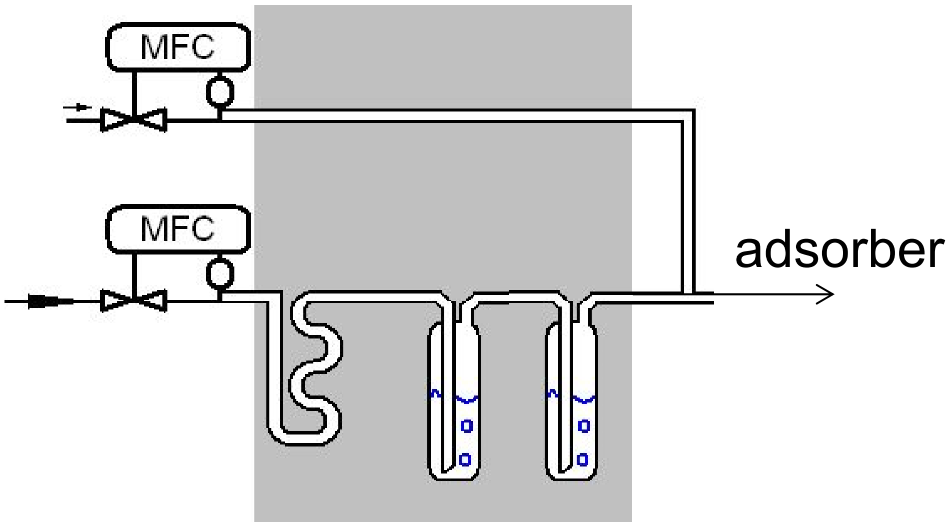
- No heater needed
- Easy handling

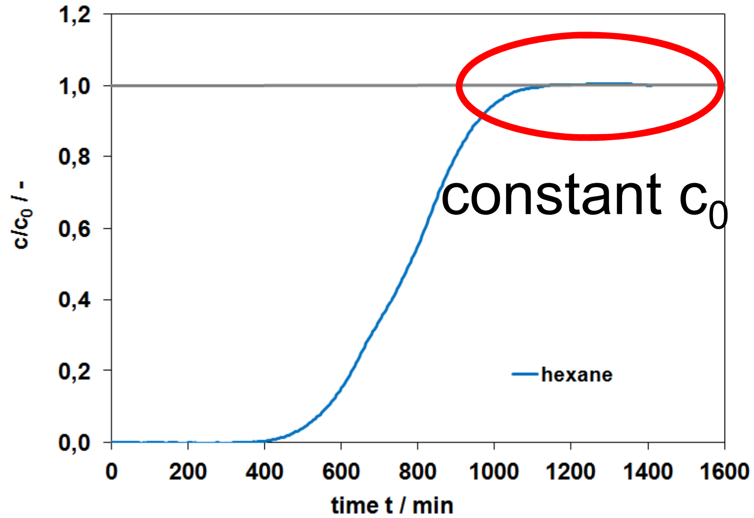
Contra

- Only for pure organics
- c_0 depends on fill level and T

Dosage system – Example II

Providing a saturated gas flow by bubbling with inert gas through two bubbler





Pro

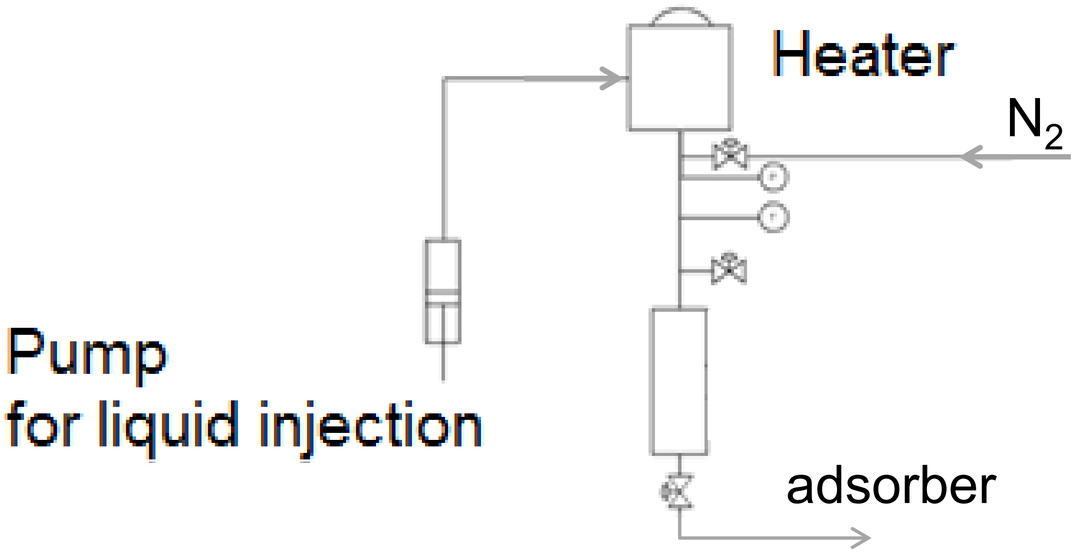
- No heater needed
- Nearly constant c_0

Contra

- Only for pure organics
- More complex handling

Dosage system – Example III

Providing a saturated gas flow by vaporizer – direct injection



Pro

- Miscible liquid mixtures possible
- Direct control of c_0

Contra

- Heater is needed
- Complex equipment

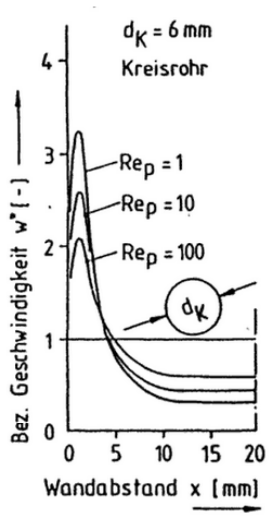
Reactor/Adsorber

Choose a reactor regarding particle size

→ $d_{bed} : d_{Particle} > 10:1$

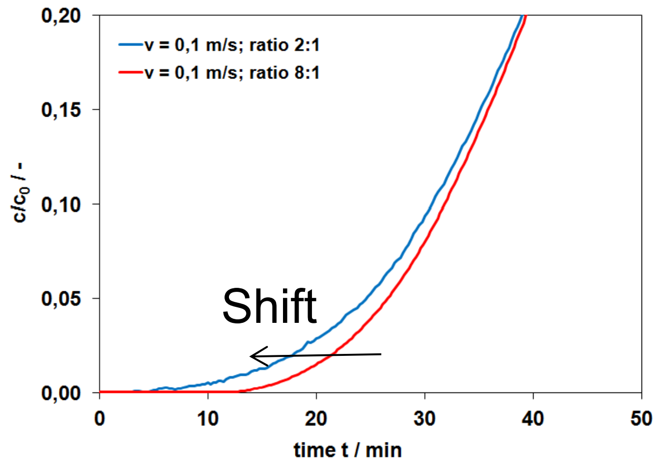
→ $h_{bed} : d_{bed} > 3:1$

d_{bed} = 40 mm



Minimization of Bypass flow

Early breakthrough on wall → curve flattens



To do:

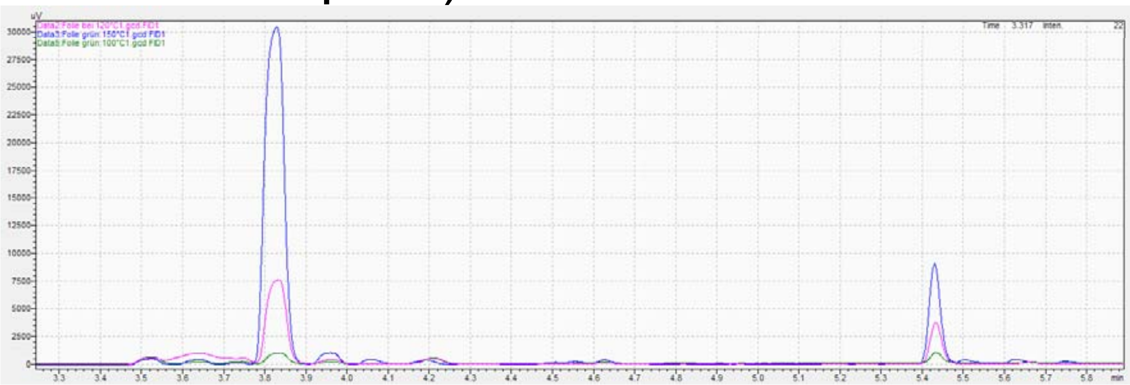
- Check bed parameters depending on particle size
- Check bed length and velocity for pressure drop

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

Detector

Depends on analytical question

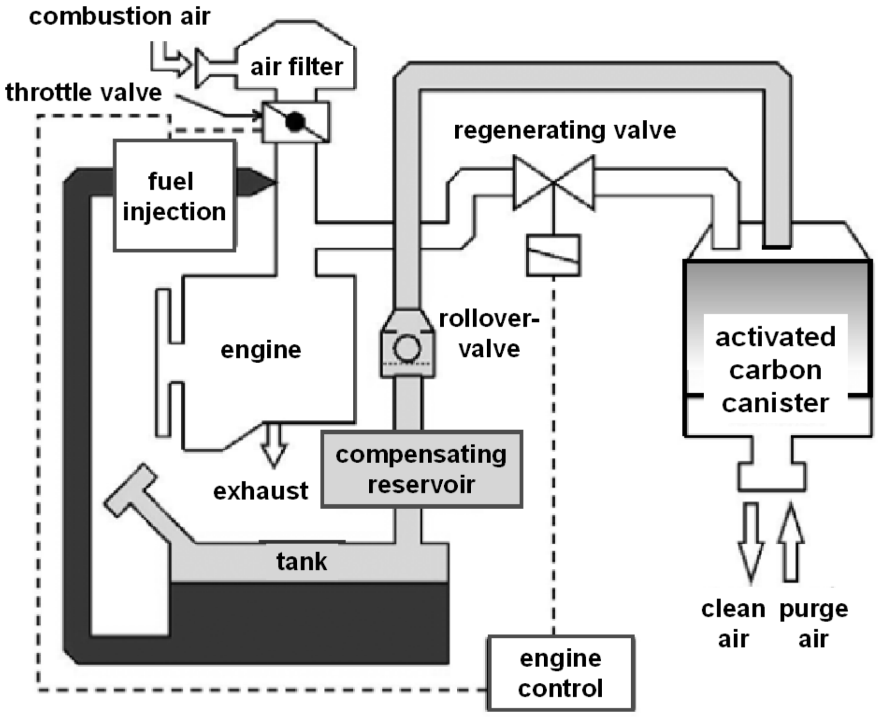
- Number of compounds
- Concentration range (**detection limit depends on scope**, but should be at least 100-1000 times lower as c_0)
- Check **time resolution** for online GC systems or ECD
- Coupled systems possible → be sure if the **overall flow is large enough for all analytical devices** (e.g.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



Example I – Vapors on Activated Carbons

→ Adsorption studies using **static method** for the optimization of fuel vapor retention systems

→ statements for capacity of AC-containers if Bio-components (-ethanol) were added to gasoline



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Example I – Vapors on Activated Carbons

gasoline is a complex mixture of hydrocarbons

➔difficult to describe/model

➔search for an appropriate model fluid

⇓

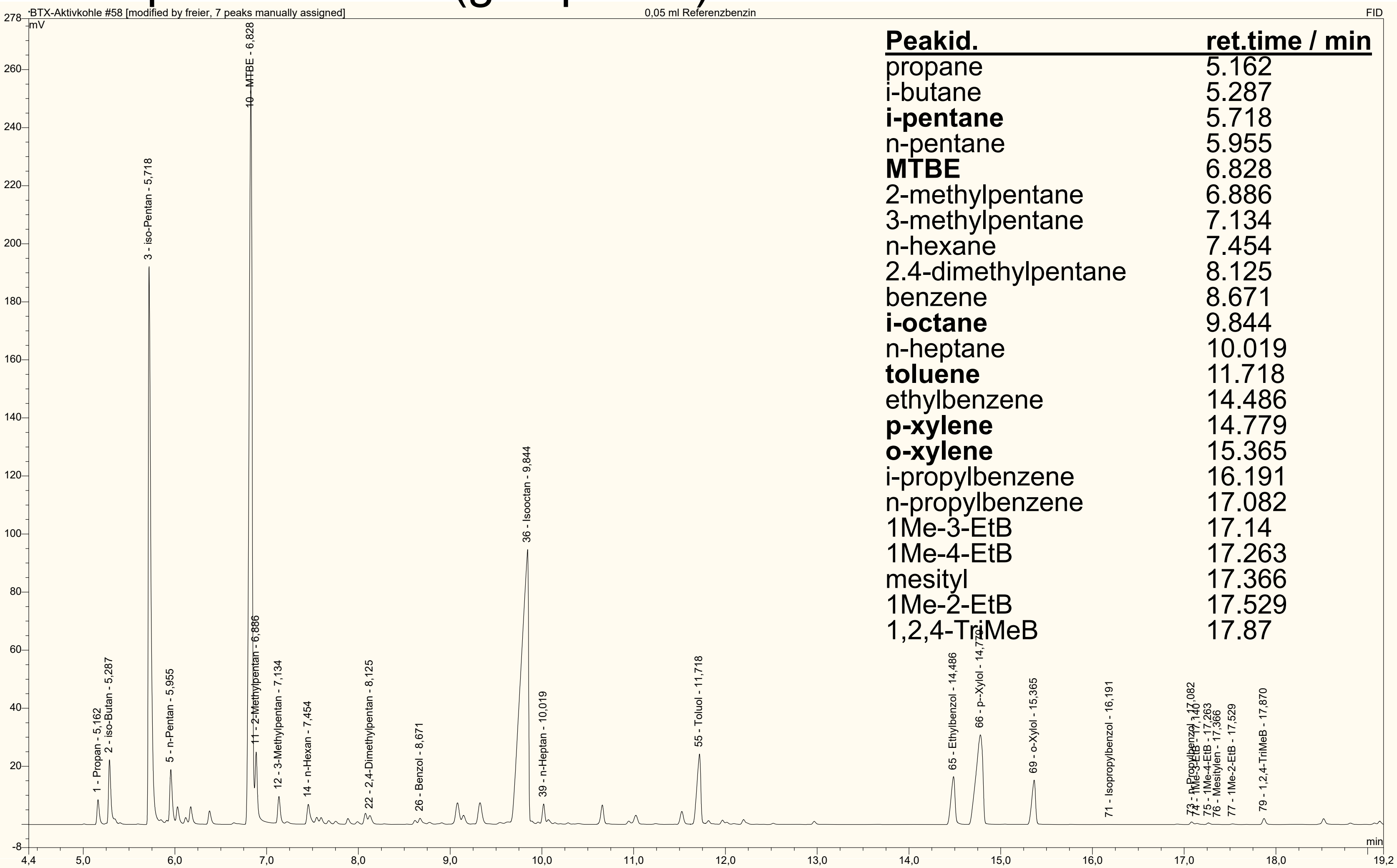
analysis of gasoline

a) Headspace-GC (gas phase)

b) GC – FID (liquid phase)

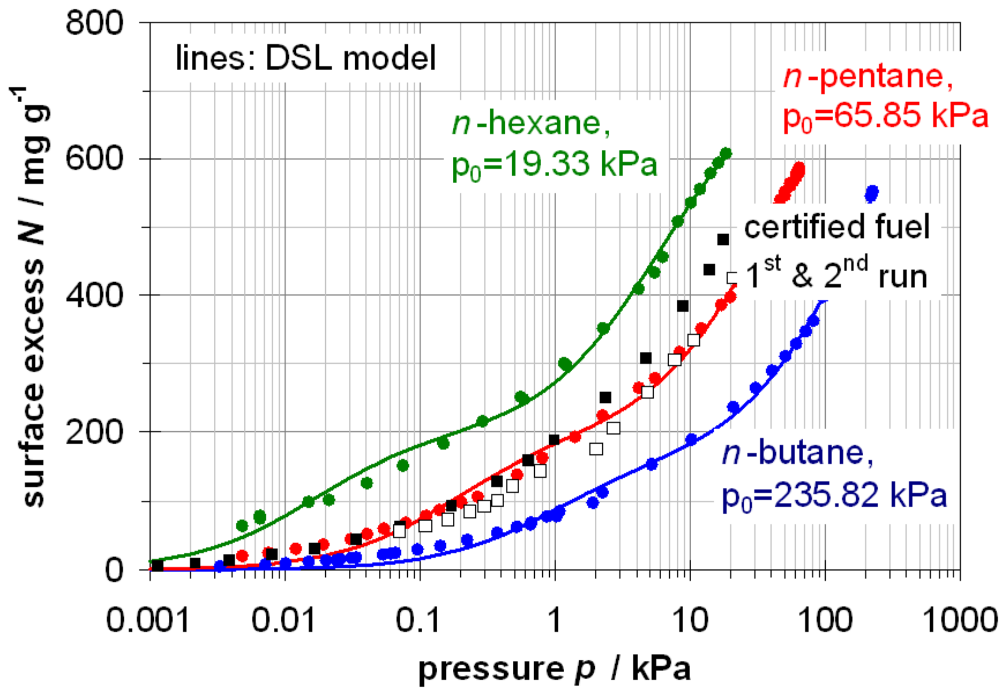
Example I – Vapors on Activated Carbons

Headspace-GC-FID (gas phase)



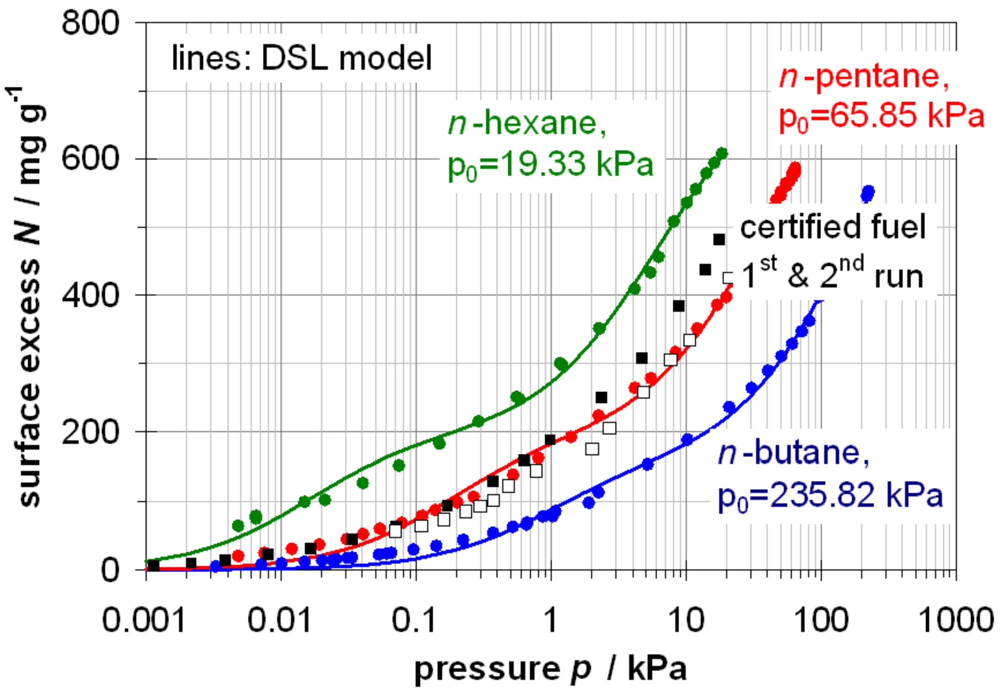
Peakid.	ret.time / min
propane	5.162
i-butane	5.287
i-pentane	5.718
n-pentane	5.955
MTBE	6.828
2-methylpentane	6.886
3-methylpentane	7.134
n-hexane	7.454
2.4-dimethylpentane	8.125
benzene	8.671
i-octane	9.844
n-heptane	10.019
toluene	11.718
ethylbenzene	14.486
p-xylene	14.779
o-xylene	15.365
i-propylbenzene	16.191
n-propylbenzene	17.082
1Me-3-EtB	17.14
1Me-4-EtB	17.263
mesityl	17.366
1Me-2-EtB	17.529
1,2,4-TriMeB	17.87

Example I – Vapors on Activated Carbons



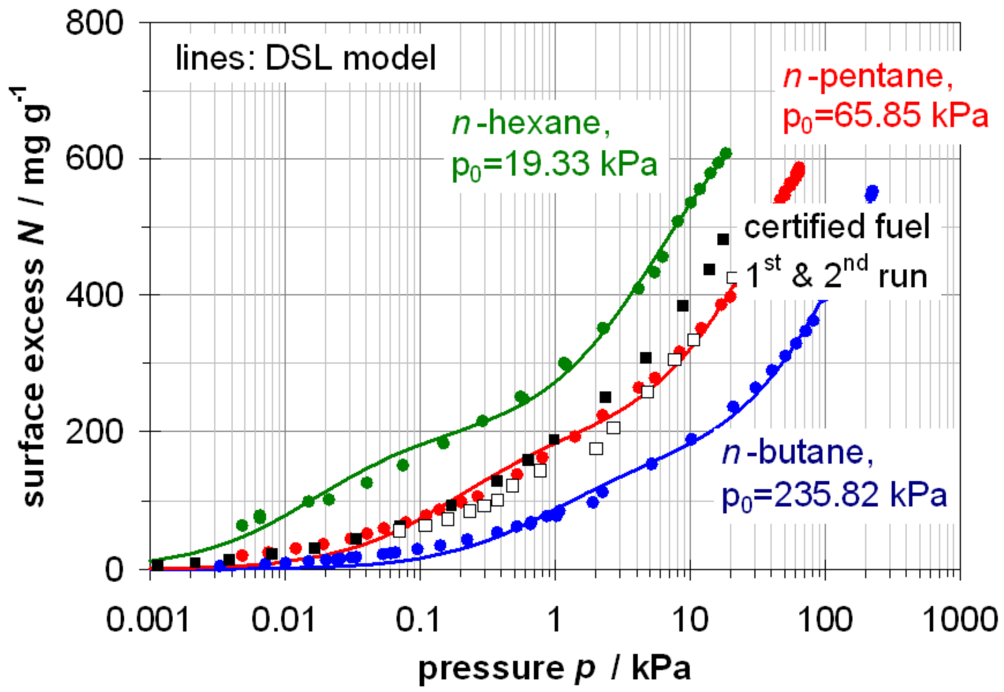
- comparison of adsorption isotherms of accredited fuel with *n*-alkanes to find an appropriate model fluid for gasoline
- the adsorption isotherm of gasoline corresponds with *n*-pentane

Example I – Vapors on Activated Carbons



- measurement of *n*-butane, *n*-pentane and *n*-hexane up to its saturation pressure at 297 K

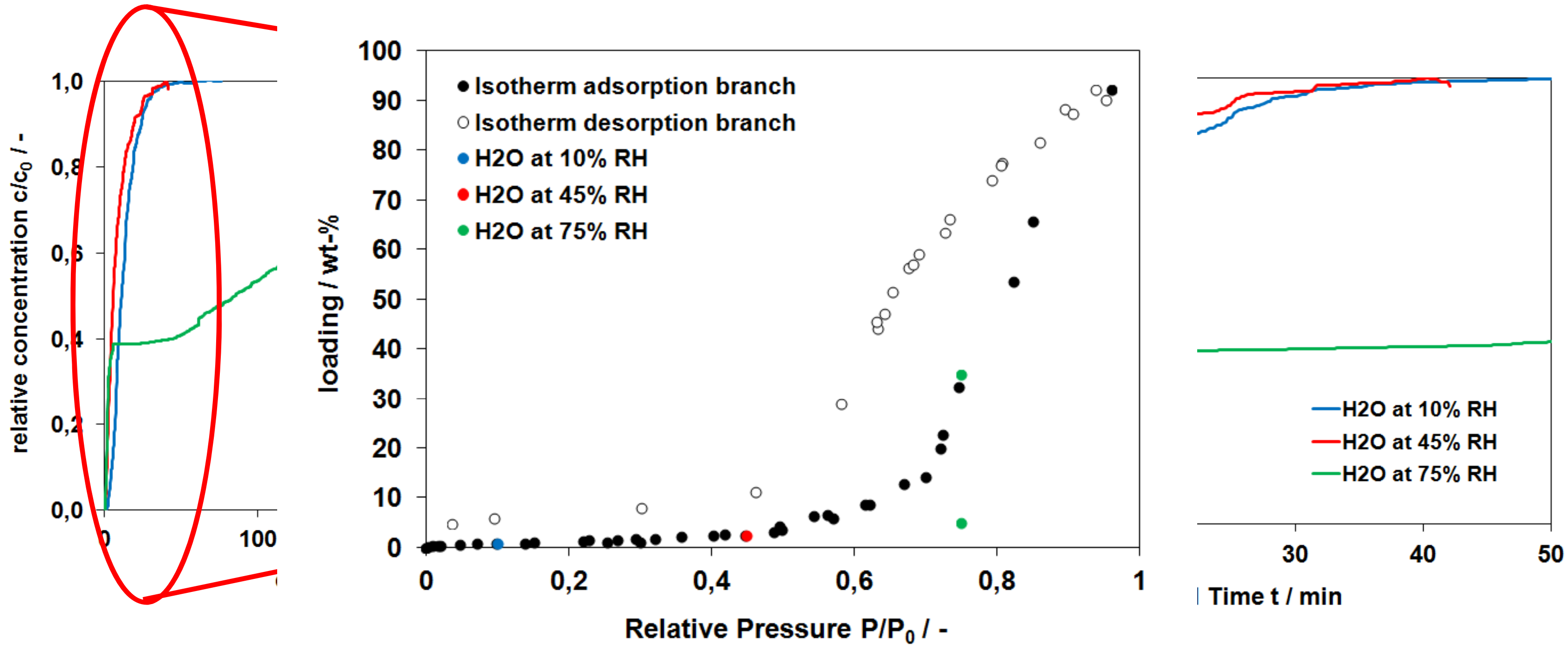
Example I – Vapors on Activated Carbons



→ stripping effect of fluid mixture

Example II – Breakthrough curves: VOC vs. H_2O on AC

H_2O breakthrough at different concentrations

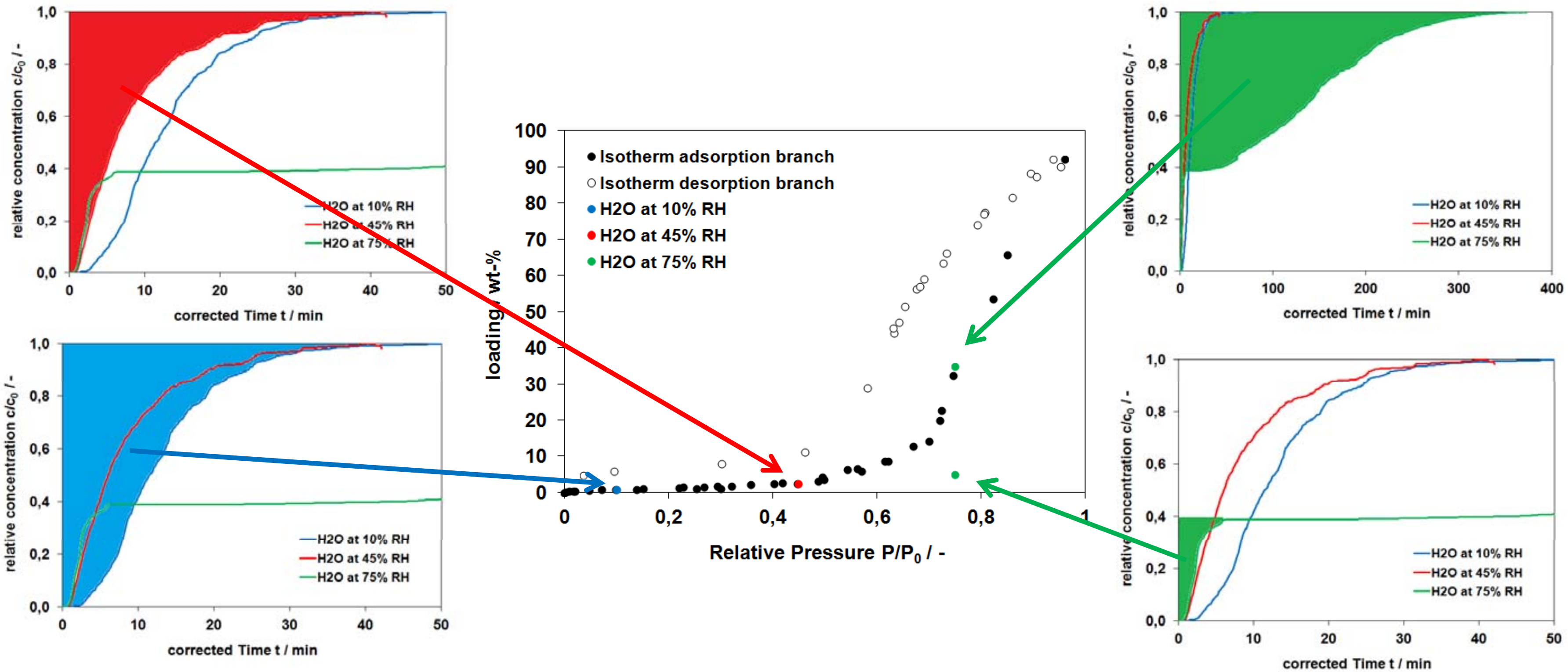


→ H_2O breakthrough below inflection point of isotherm shows typical shape, at higher concentration a stepwise curve is observed due to capillary condensation

Example II – Breakthrough curves: VOC vs. H_2O on AC

Below 45% RH

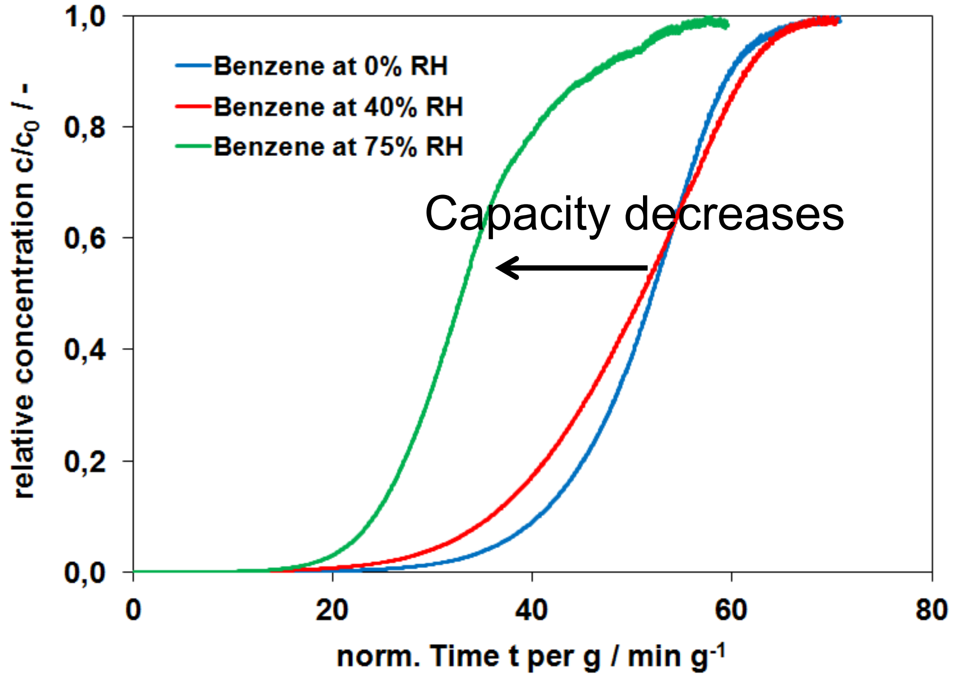
Above 45% RH



→ Equilibrium takes place for pure H_2O breakthrough

Example II – Breakthrough curves: VOC vs. H_2O on AC

Benzene capacity is influenced by humidity

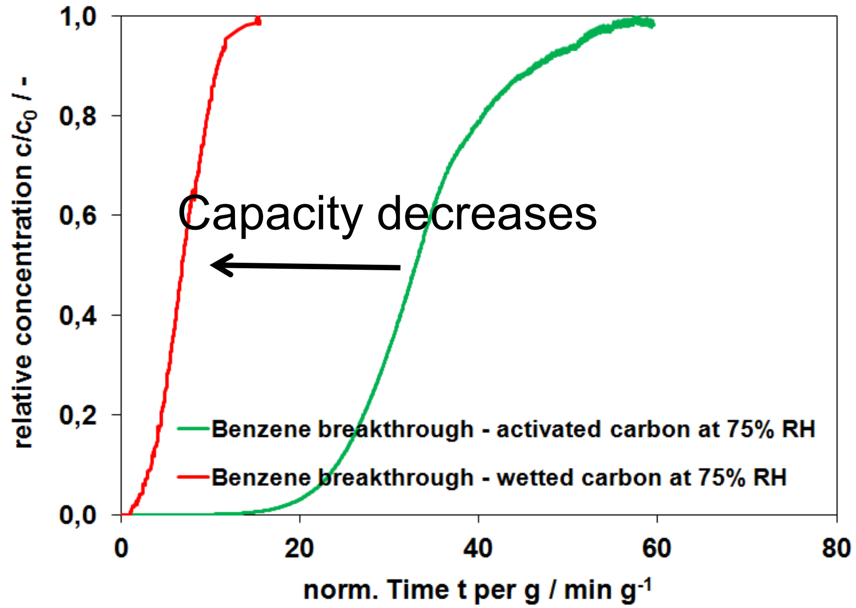


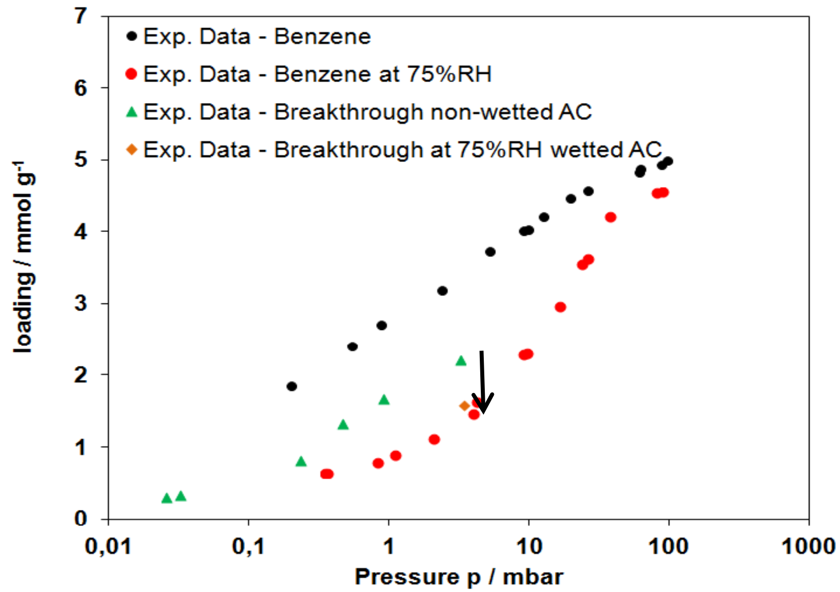
→ Benzene breakthrough flattens for low H_2O concentrations

→ Benzene capacity decreases with increasing H_2O content

Example II – Breakthrough curves: VOC vs. H_2O on AC

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





→ Capacity of benzene decreases after pre-wetting the AC

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

Summary

- Downscaling industrial processes to lab-scale and material characterization for specific new application or improvement
- Different methods are available to collect sorption data (equilibrium, kinetics, heat evolution, etc.)
- Breakthrough measurements represent industrial processes best

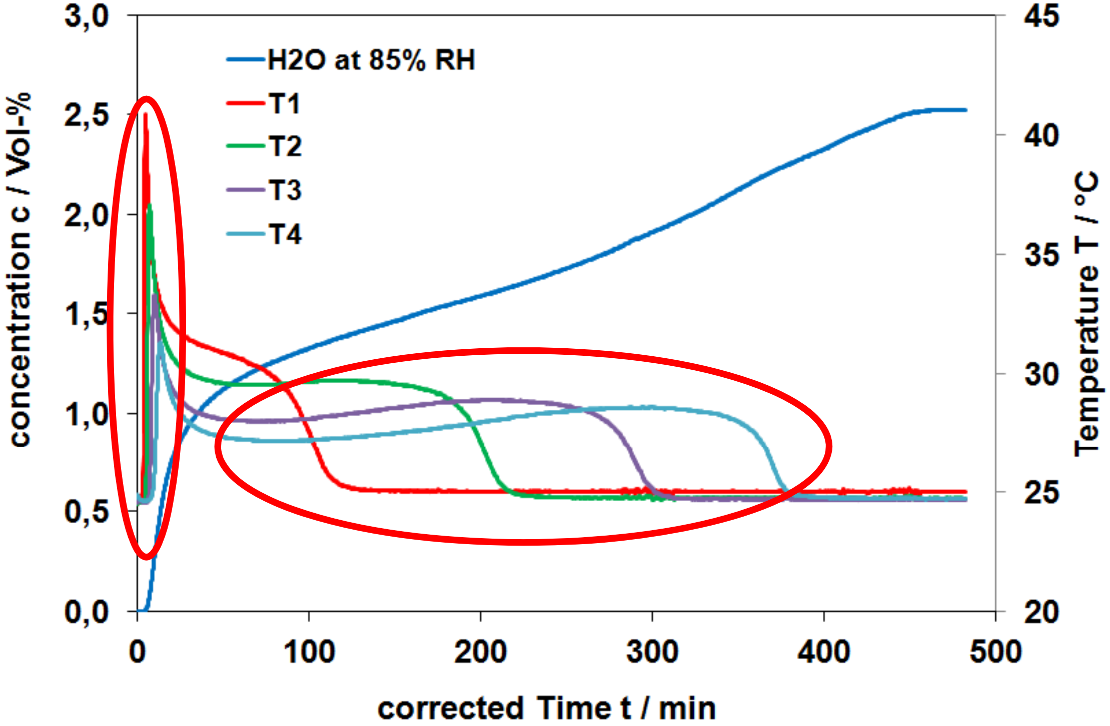
  BUT: consider several experimental challenges:

  - Sample preparation (heating, pre-wetting, …)
  - Dosage System (concentration, stripping effects, condensation)
  - Reactor (particle size ↔ dimension)
  - Detector (detection limit, selectivity, …)

→ **Modular concept ensures high flexibility**

Breakthrough curve of H_2O (low affinity towards AC?)

Type V isotherm is coupled with low affinity?



→ Detection of high temperature during first adsorption due to large interaction between H_2O and ash content of carbon

→ Second heat peak is provided by heat of condesation

INC Team

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Many thanks for your attention!