Working with Vapors and Low Concentrations in Breakthrough Experiments

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The presentation will begin shortly.
Please be patient while other attendees log in.

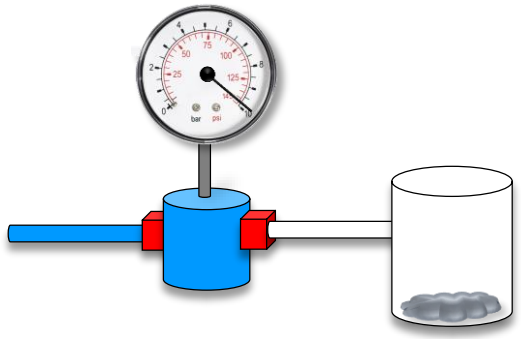
Outline

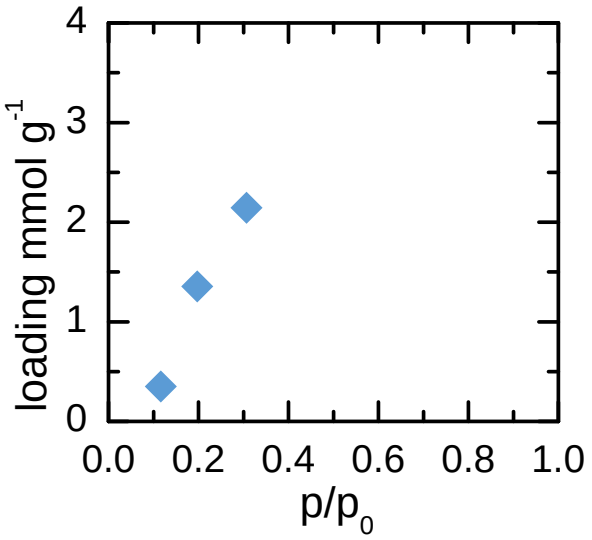
1. **Breakthrough Curve Theory**
2. **The mixSorb L Vapor Option**
3. **mixSorb L Adsorber Sizes**
4. **Examples**
   - I. Water Breakthrough Curves
     on Zeolite, Silica Gel and Activated Carbon
   - II. Removing CO_2 from Air
     with Zeolites
   - III. Breakthrough Curves in Presence of Water
   - IV. Organic Vapors
     on Activated Carbon
   - V. Investigating the Surface Hydrophobicity
     with 1,4-Dioxane, Cyclohexane and 2-Propanol
   - VI. Applying Liquid Mixtures
5. **Conclusions & Questions**

2. Breakthrough Curve Theory

Static Volumetric Measurements

- Sorption takes place in enclosed chamber
- Pressure is recorded over time
- Pure Gases only





$$n_{\mathrm{ads},i} = n_{\mathrm{dosed},i} - n_{\mathrm{free},i}$$

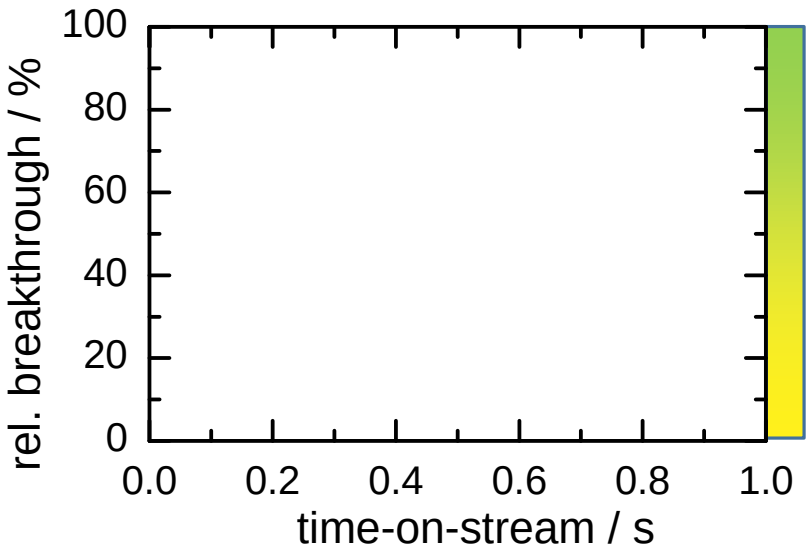
$$n_{\mathrm{dosed},i} = \frac{p_{\mathrm{Dose},i}\, V_{\mathrm{Dose}}}{RT}$$

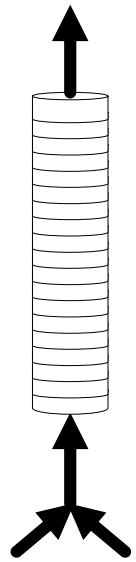
$$n_{\mathrm{free},i} = \frac{p_{\mathrm{Cell},i}\, (V_{\mathrm{Dose}} + V_{\mathrm{Cell}})}{RT}$$

$$n_{\mathrm{ads}} = \sum_{0}^{i} n_{\mathrm{ads},i}$$

Breakthrough Experiment

- Sorption takes place in open system
- Pressure is constant
- Outlet composition is recorded over time
- Gas Mixtures only





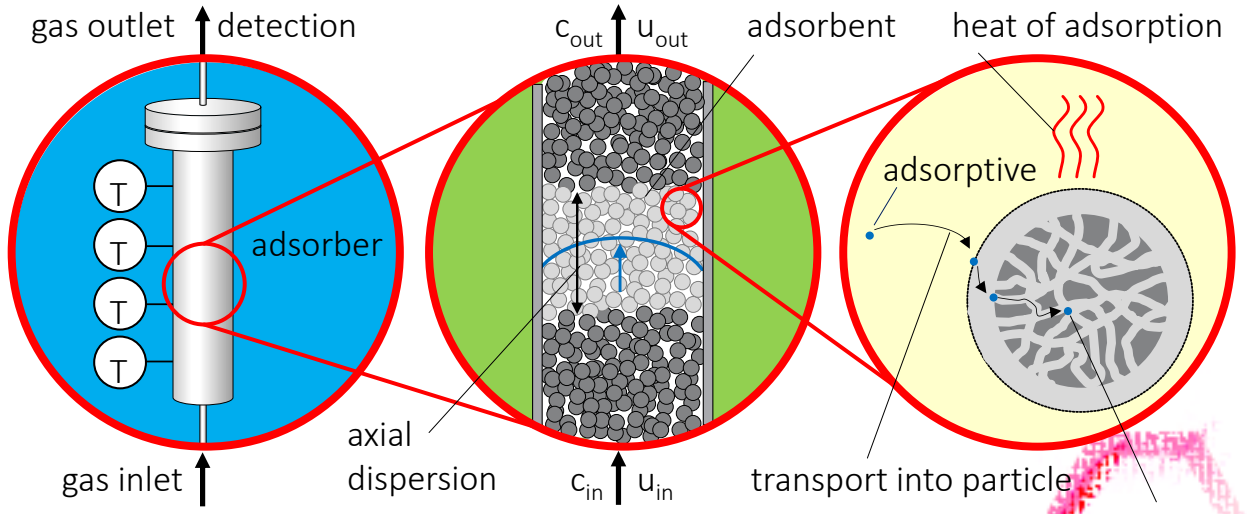
$$n_{\mathrm{adsorbed}} = \int \dot{n}_{\mathrm{in}}(t)\mathrm{d}t - \int \dot{n}_{\mathrm{out}}(t)\mathrm{d}t$$

$$n_{\mathrm{adsorbed}} = \int \dot{V}_{\mathrm{in}}(t)\frac{y_{\mathrm{in}}(t)}{V_{\mathrm{m}}}\mathrm{d}t - \int \dot{V}_{\mathrm{out}}(t)\frac{y_{\mathrm{out}}(t)}{V_{\mathrm{m}}}\mathrm{d}t$$

2. Breakthrough Curve Theory

Breakthrough Curves

- Not all Gas Flow Experiments are Breakthrough Experiments!
- Requirement: **Fixed Adsorber Bed**
  → gas must not pass the sample without **interaction**!



- What is the result of a breakthrough experiment?

  ✓ **Time** until 5 %, 50 % ,… of breakthrough is the **cycle or production time**

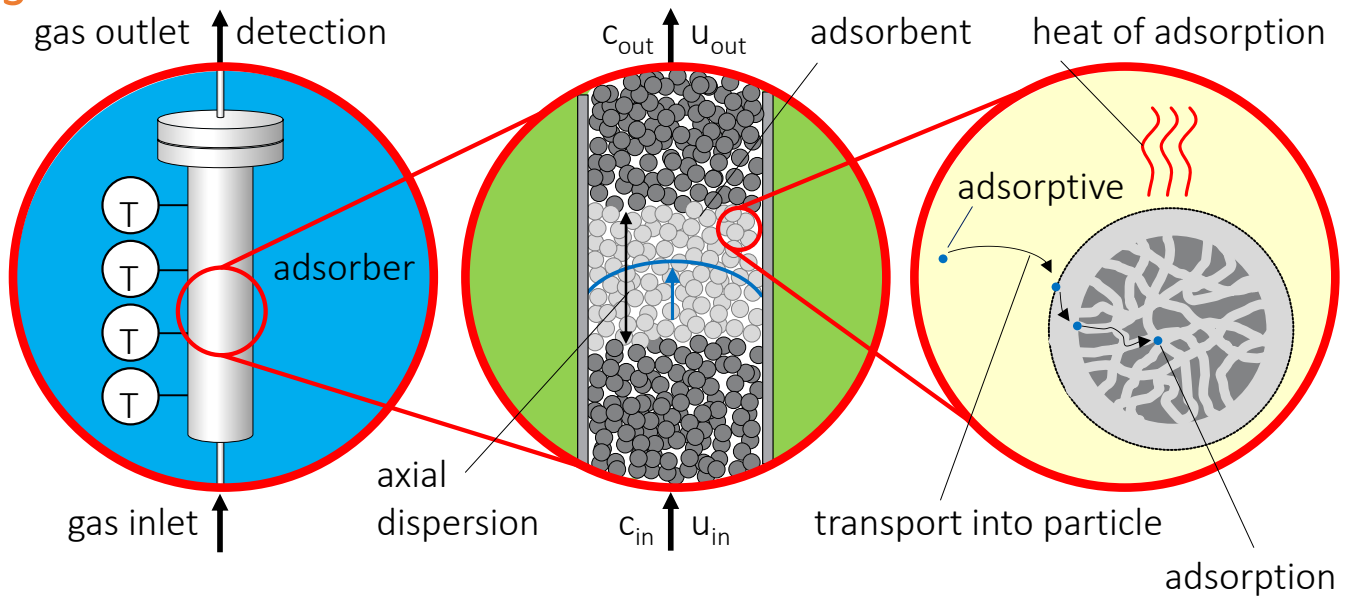
  ✓ **Integration** of the **full curve** gives **saturation capacity** of a gas on the adsorbent (**equilibrium**)

  ✓ **Integration** until cycle time gives **technically usable sorption capacity**

  ✓ **Shape of the curve** contains information about **kinetics/mass transfer**

2. Breakthrough Curve Theory

Breakthrough Curves



Macroscopic

- Size of Adsorber
- Shape of Adsorber

Mesoscopic

- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

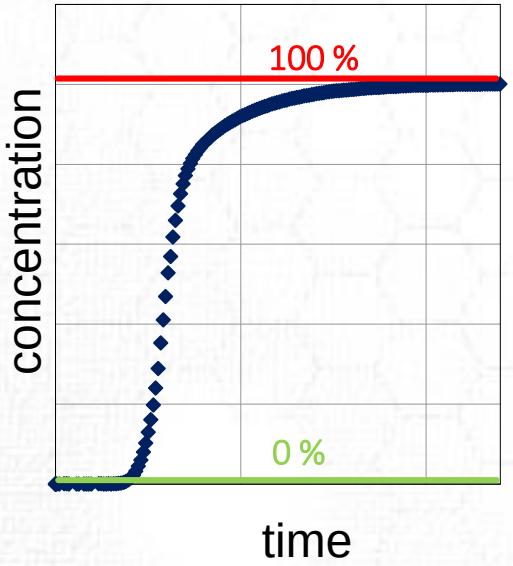
Microscopic

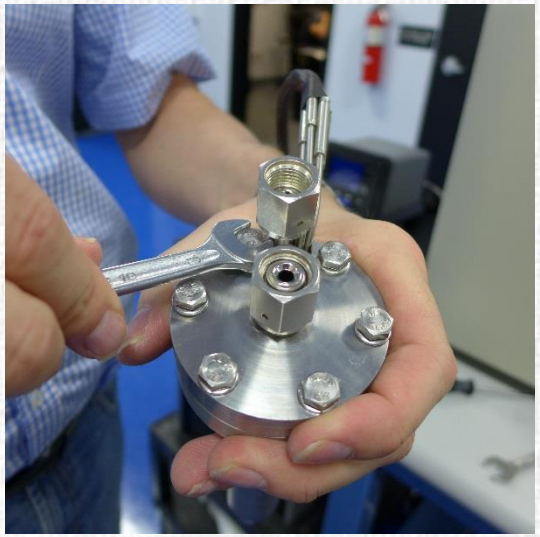
- Textural Properties
- Surface Characteristics
- Accessibility

2. Breakthrough Curve Theory

Procedure

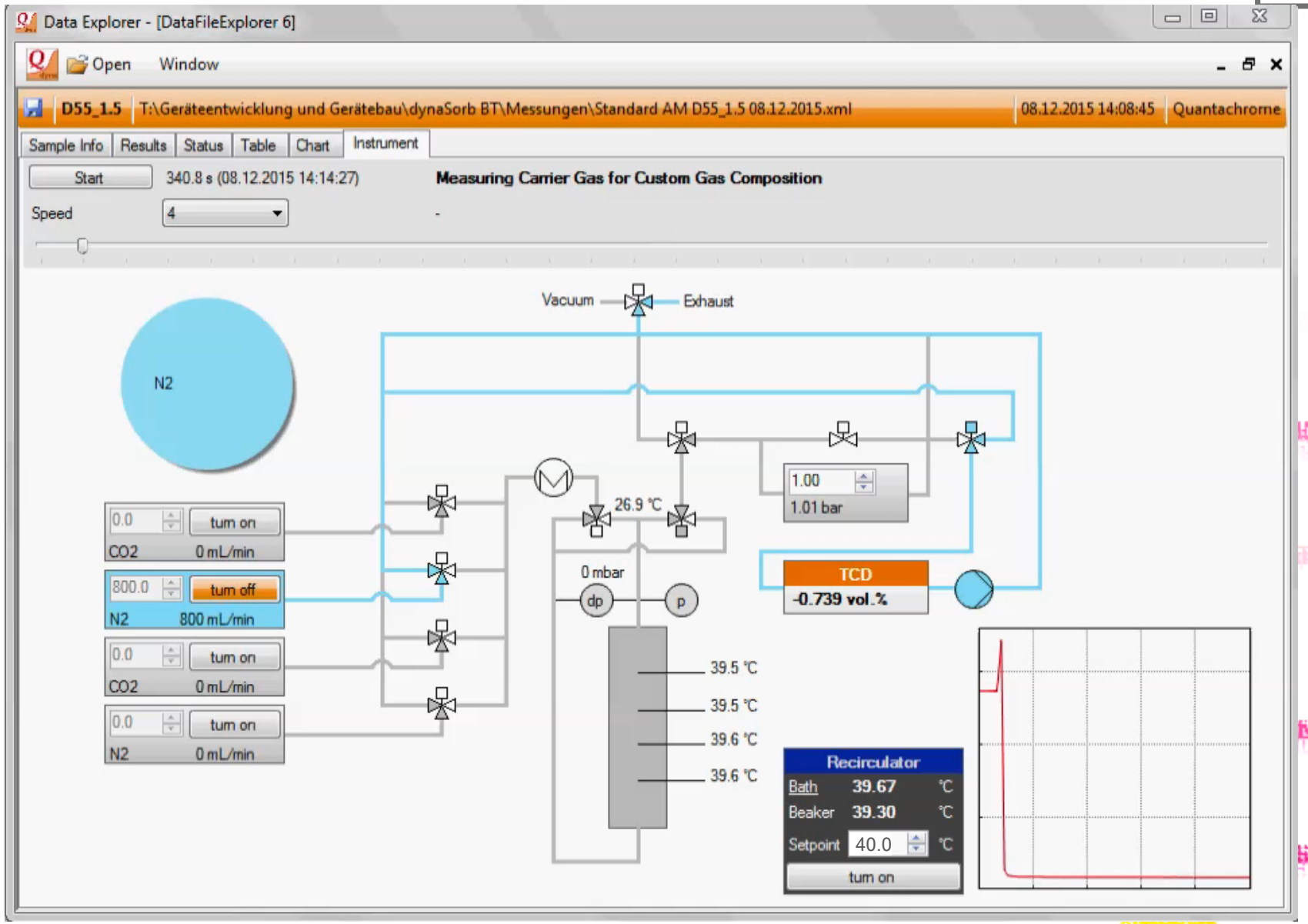
1. Determining **100 %** and **0 %** Breakthrough Signal in **Bypass**
2. Introducing **Carrier Gas** to the Sample Cell (Adsorber)
3. Pressurizing the Adsorber
4. Waiting for **stable** Pressure and Temperatures
5. Introducing additionally **CO_2** to create the **Gas Mixture**
6. Monitoring Adsorber **Temperatures** along the Sample Bed and **Gas Composition** at the Adsorber Outlet
7. Finishing Experiment when Temperatures and TCD Signal are **stable**





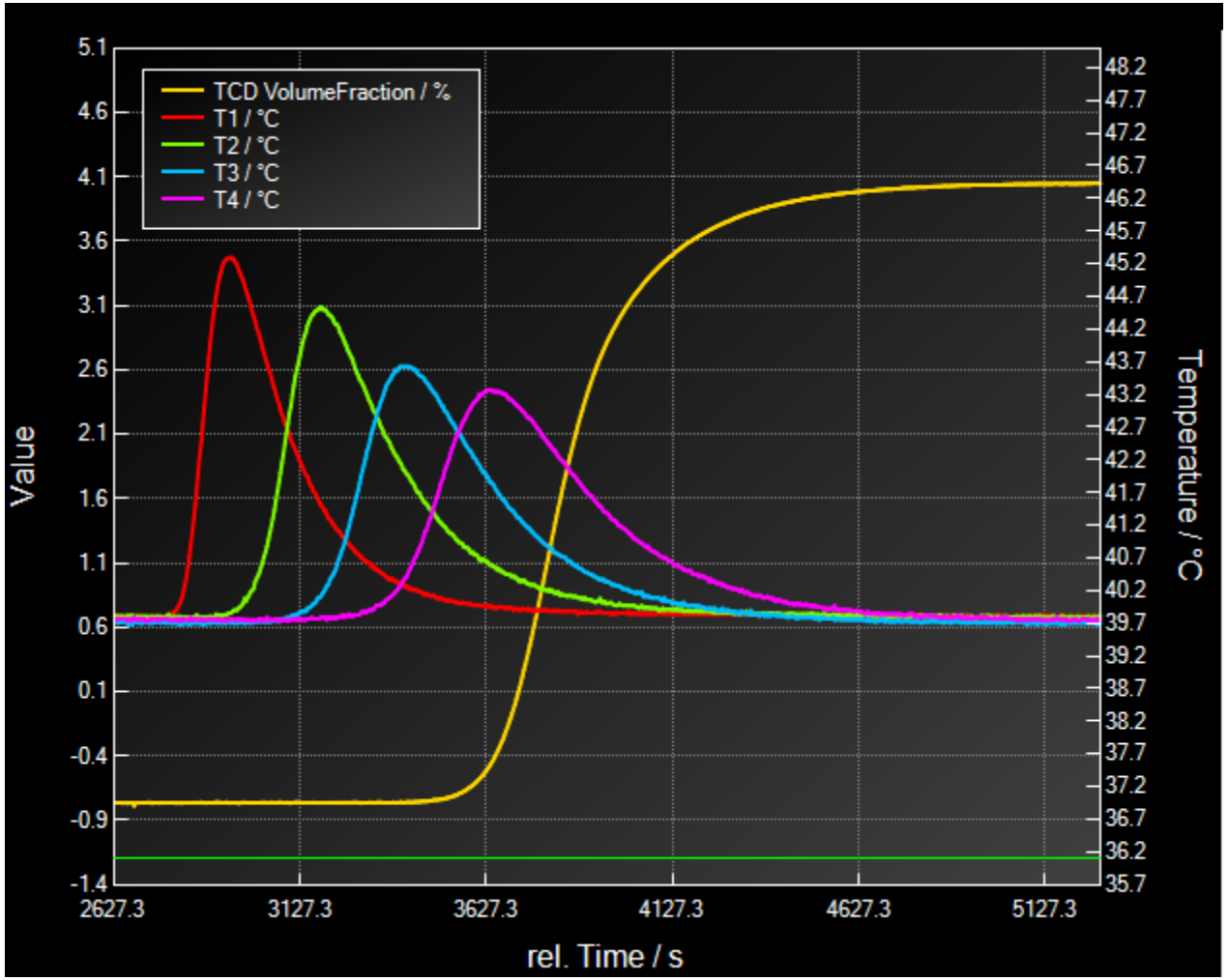
2. Breakthrough Curve Theory

Watch a Measurement



2. Breakthrough Curve Theory

Resulting Curves



- 40 °C, 2 L min^{-1}
- 5 bar (pressurization with N_2)
- Inlet compositions: **5 % CO_2 in N_2**

- Temperature Maxima Decrease in Flow Direction
  → Increasing Dispersion
- Area under Temperature Curves increases in Flow Direction
  → Transfer of heat through gas flow

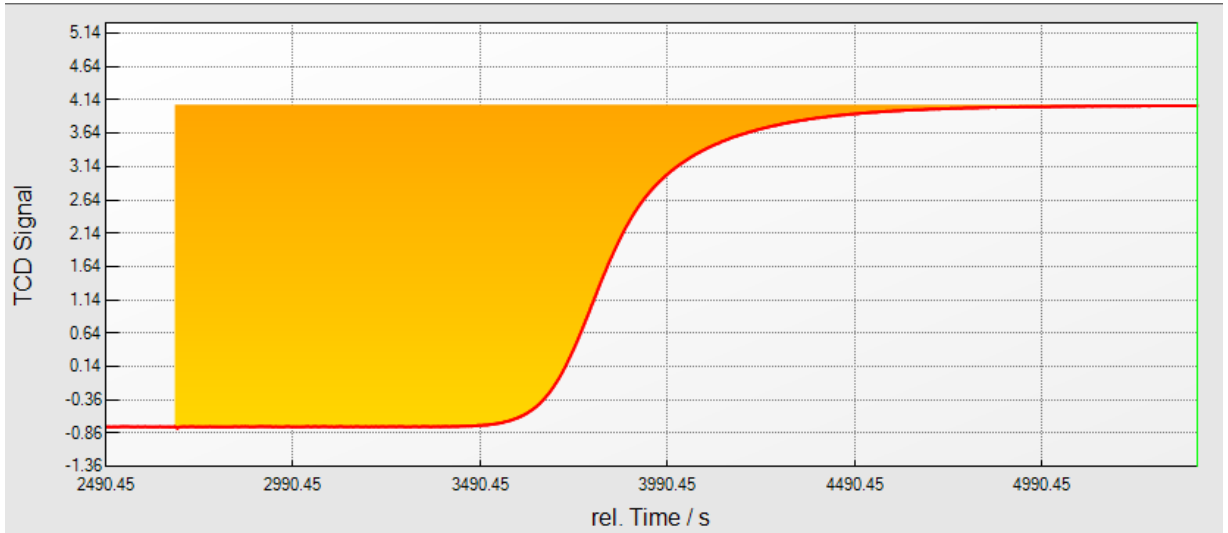
2. Breakthrough Curve Theory

Calculating Loadings

$$n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t)\mathrm{d}t - \int \dot{n}_{\text{out}}(t)\mathrm{d}t$$

$$n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t)\frac{y_{\text{in}}(t)}{V_{\text{m}}}\mathrm{d}t - \int \dot{V}_{\text{out}}(t)\frac{y_{\text{out}}(t)}{V_{\text{m}}}\mathrm{d}t$$

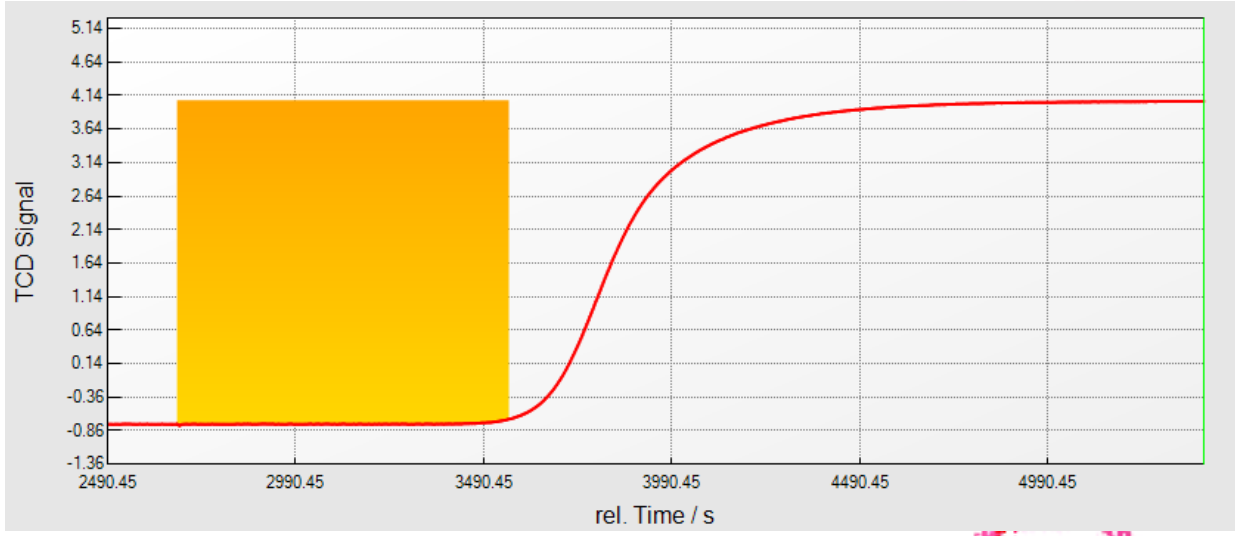
Integrating over the full Curve



Saturation Capacity

dq = 0.611 mmol g^{-1}

Integrating over the Curve to *e.g.* 1 % Breakthrough



Technically Usable Sorption Capacity

dq = 0.445 mmol g^{-1}

2. The dynaSorb BT Vapor Option

dynaSorb BT

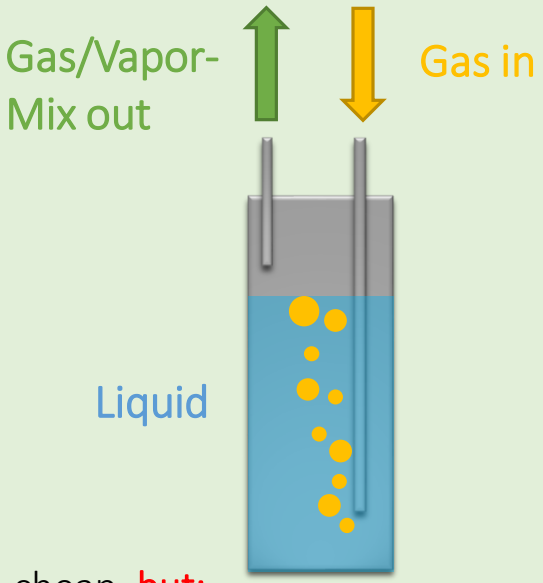
- Fully automated Breakthrough Analyzer
- **Integrated Gas Mixing – Including Vapors**
- Up to 40 L/min Gas Flow, up to **10 bar**
- Up to **4 mass flow controllers (MFCs)**
- Up to 2 **Evaporators**, each capable to supply vapor mixtures

- Monitoring of gas composition by **TCD** at the Outlet or Bypass
- You can attach any additional Analytical Device (e.g. **Mass Spec**) at the **sample port**
- Option: Triggering Pfeiffer Mass Spectrometer (Thermostar, Omnistar)
- dynaSim Simulation Software

2. The mixSorb L Vapor Option

Evaporators

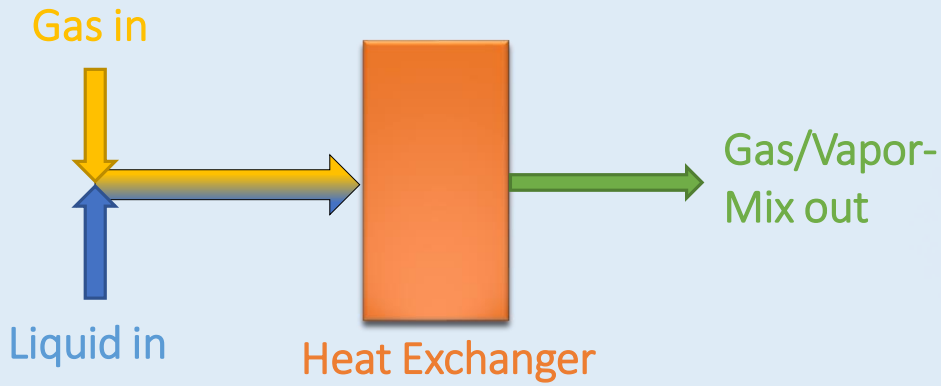
Saturator, “Bubbler”



- Easy, cheap, but:
- Performance highly dependent on **temperature** and **pressure**
- No liquid mixtures
- Unstable long-time performance
- Vapor concentration undetermined

- Can be easily used for low flow rates

Controlled Evaporation



- More complex, but:
- Performance independent on **temperature** and **pressure**
- liquid mixtures possible
- Vapor concentration defined by **liquid flow rate and gas flow rate**

- Preferred for high flow rates and long measurement times

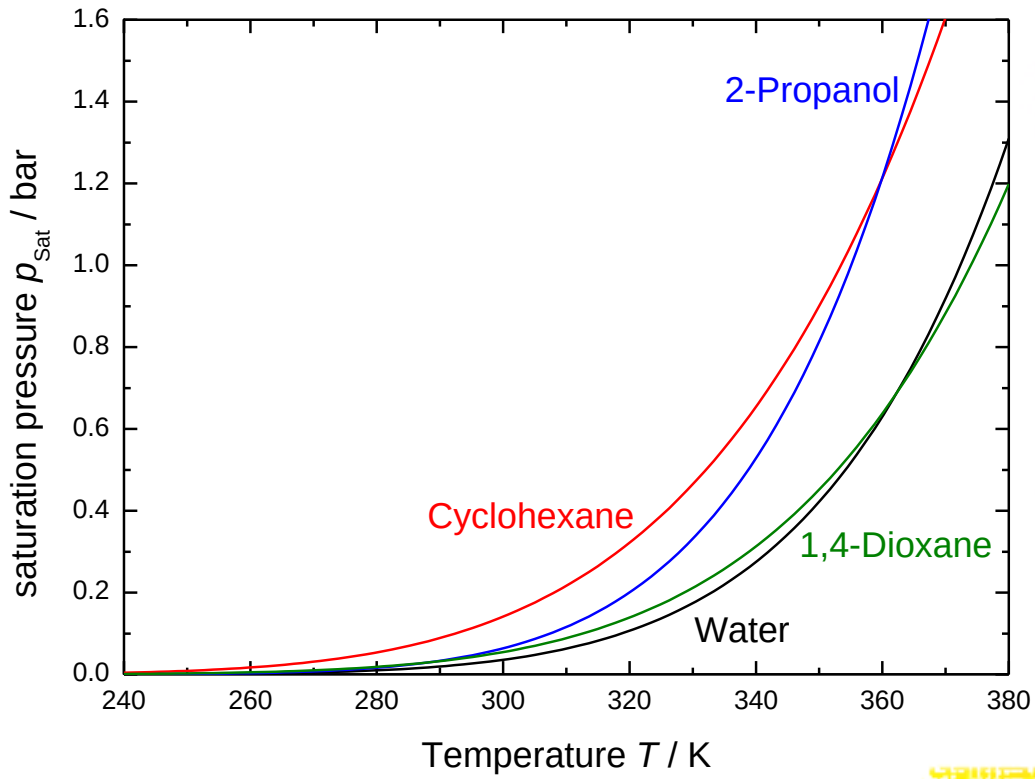
2. The mixSorb L Vapor Option

Estimation of **saturation pressure** of liquids important for:

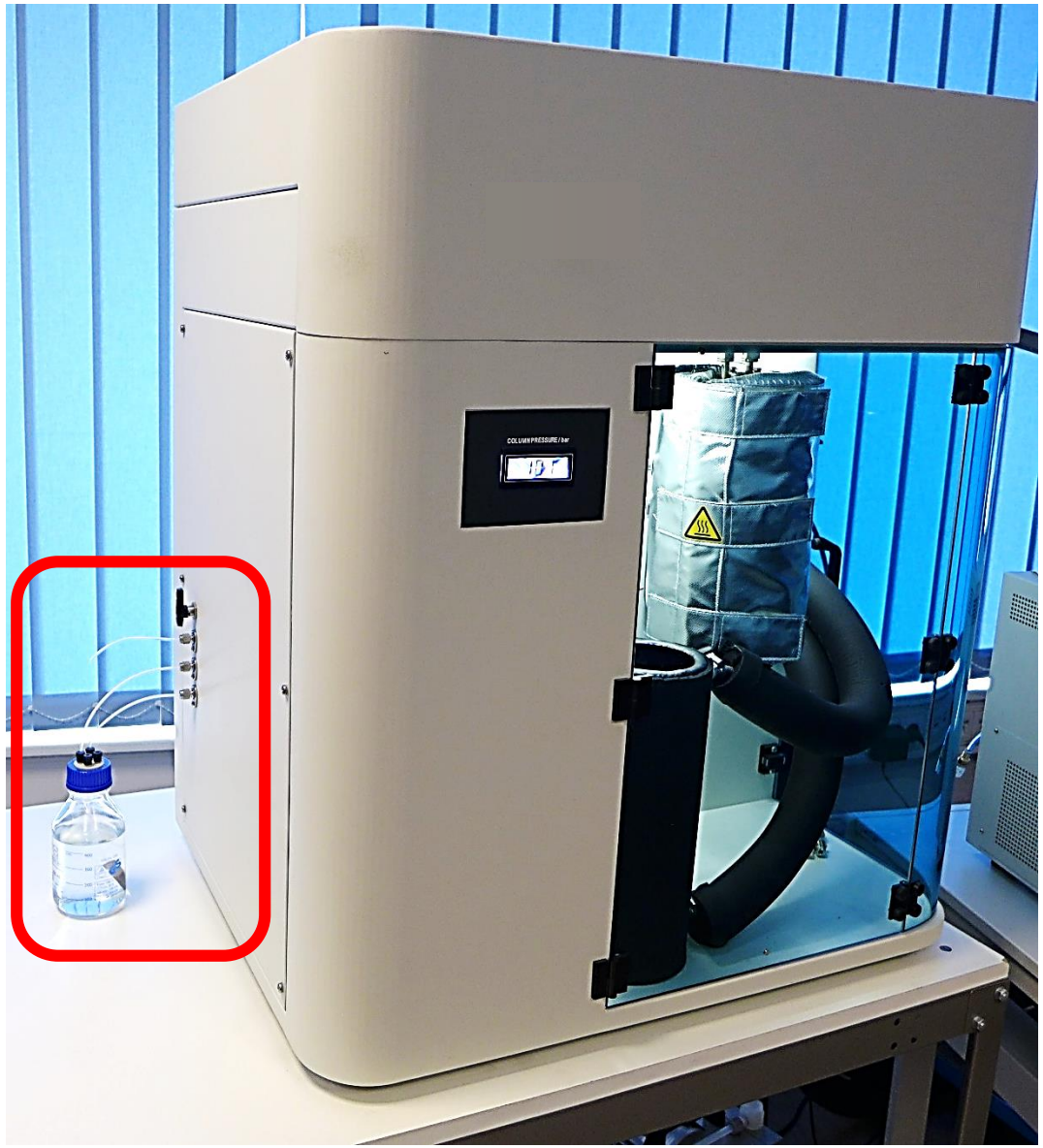
- Calculation or **Relative Humidity**
- Calculation of **Dew Point**
- Preventing **condensation**

Component	Molar Mass / g mol^{-1}	A	B	C
Water	18.00	5.2093	1733.926	-39.485
Cyclohexane	84.16	3.96988	1203.526	-50.287
2-Propanol	60.10	4.8610	1357.427	-75.815
1,4-Dioxane	88.11	4.58135	1570.093	-31.297

Antoine equation	$\log(p_{\text{sat}}) = A - \frac{B}{C+T}$
Relative Humidity	$RH = \frac{p_i}{p_{\text{sat}}}$
Dalton's law	$p_i = p_{\text{total}} \cdot y_i$
Volume Fraction	$y_i = \frac{\frac{\dot{m}}{M} \cdot V_m}{\dot{V}_{\text{total}}}$
Molar Volume (0 °C, 1 atm)	$V_m = 22.414 \frac{L}{mol}$



2. The mixSorb L Vapor Option



Liquids

- Clean, evaporable liquids or liquid mixtures (miscible)
- Only non-corrosive liquids
- No salts, No ionic liquids, No residue forming fluids
- No decomposable liquids

Gases

- Gas should not chemically react with liquid
- Under Vapor Performance: minimum 400 mL min^{-1} gas flow through evaporator
- Maximum 10,000 mL min^{-1} gas flow through evaporator port

Liquid dosing system

- High precision **Coriolis-type** Mass Flow Controller
- Flow range: **0.4…20 g h^{-1}**
- Pressurized with an HPLC pump

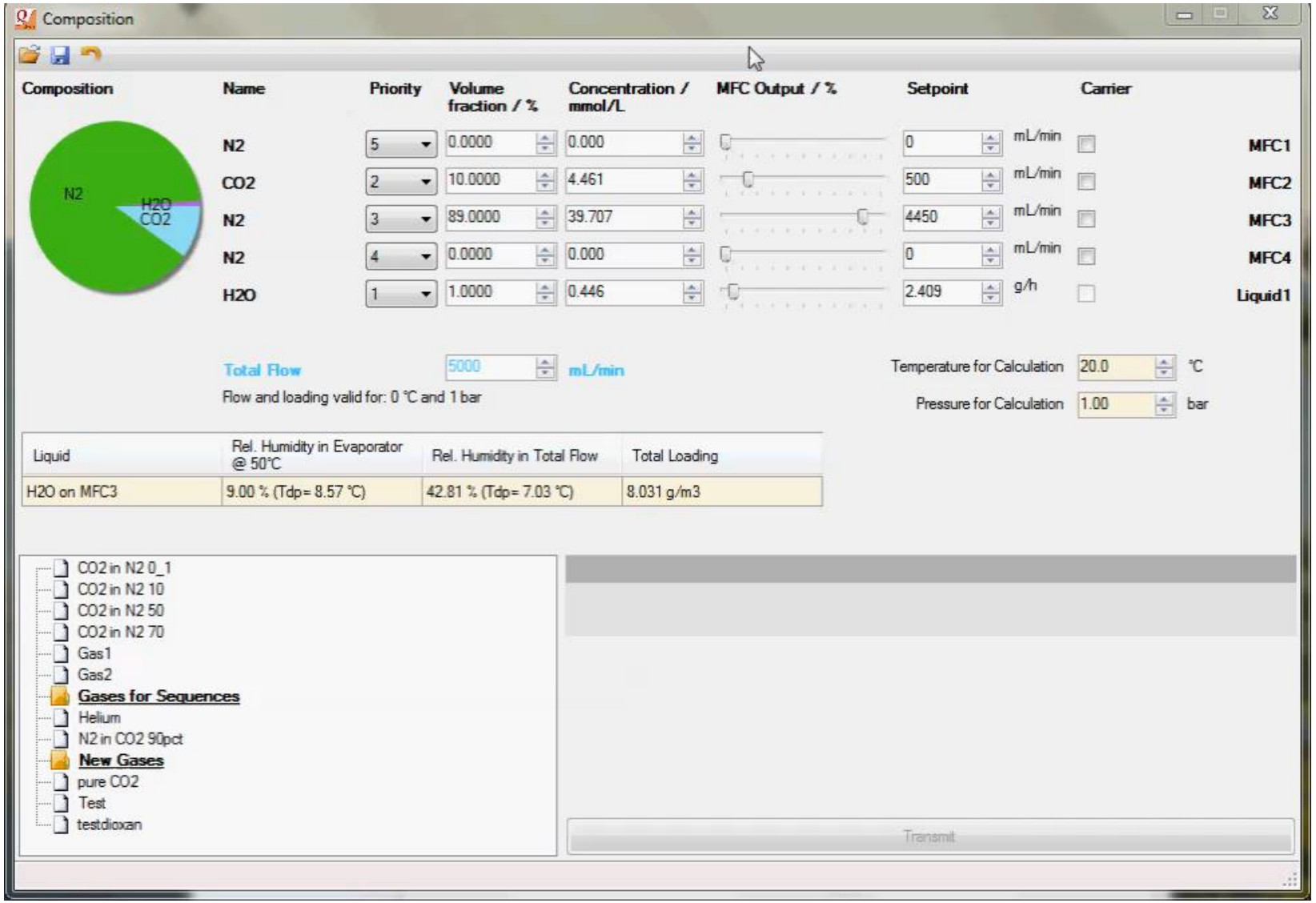
Heat exchanger

- Temperature range: **20…180 °C**

Manifold Heating

- Temperature range: **20…55 °C**

2. The mixSorb L Vapor Option

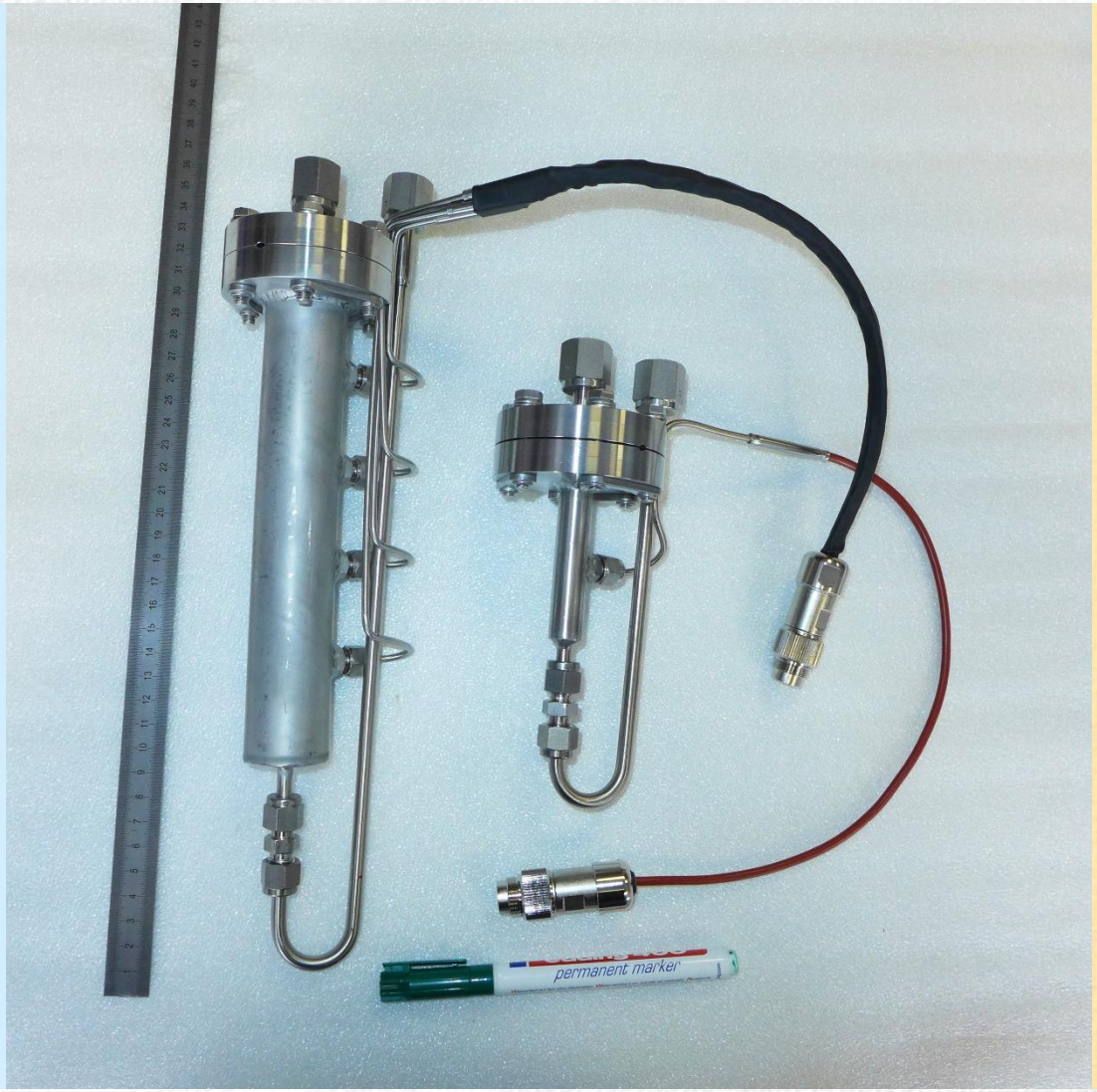


3. mixSorb L Adsorber Sizes

The mixSorb L is available with **2 different Adsorber sizes**

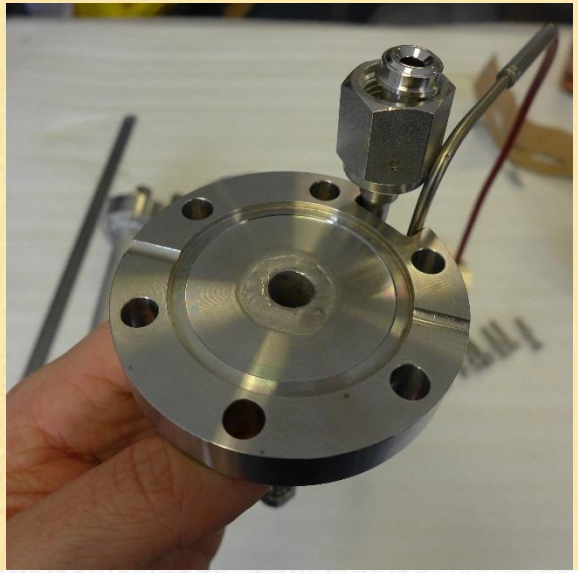
Standard Adsorber

- Inner Diameter:
  30 mm
- Bed height:
  180 mm
- Sample Volume:
  130 cm³
- **4** temperature probes



Small Adsorber

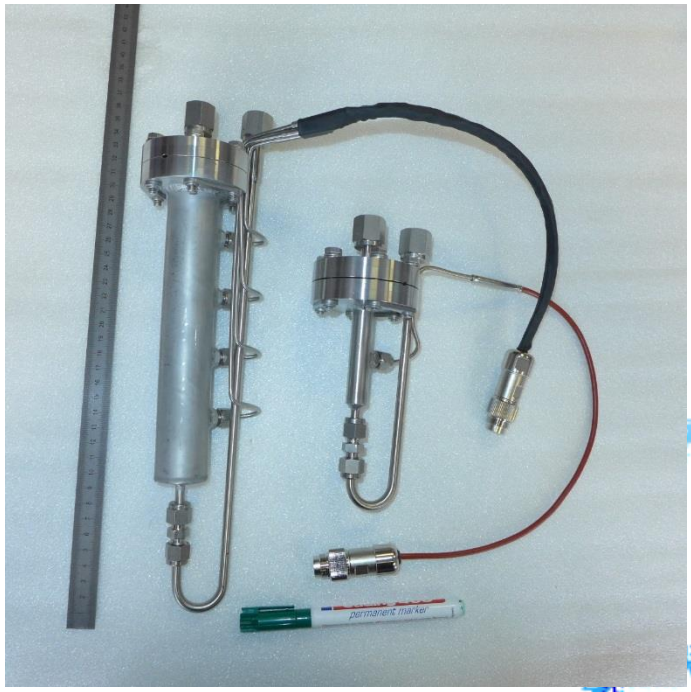
- Inner Diameter:
  10 mm
- Bed height:
  60 mm
- Sample Volume:
  5 cm³
- **1** temperature probe



3. mixSorb L Adsorber Sizes

Selecting the right Adsorber:

- Use the **Standard Adsorber** whenever possible
  - → **Larger amount** of sample → larger measurement **effect**
  - → Four temperature probes instead of one
  - → More realistic fixed bed → Upscaling possible
- The small Adsorber is designed to enable measurement with **low gas concentrations** on high-performance materials.
  - → Measurements can take up to **several days or weeks** with the Standard Adsorber
  - → Reduction of the sample mass **shortens measurement times** drastically.
  - → The small Adsorber is **not designed for powder samples and samples with low performance**.
- Particle sizes for both Adsorbers should be **> 0.1 mm**



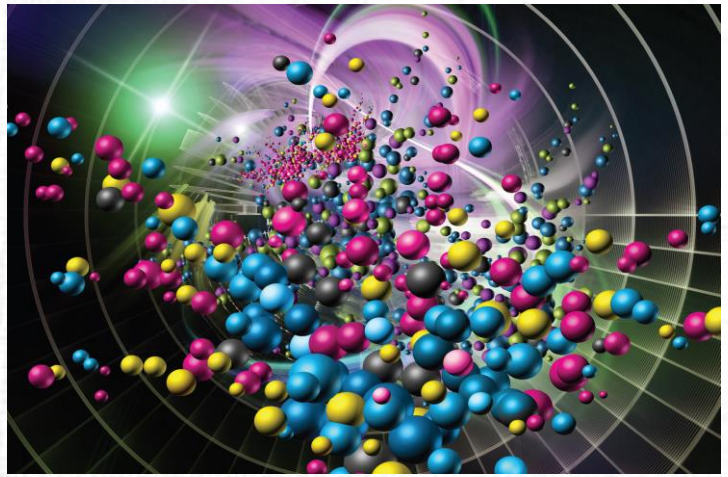
4. Examples – I Water Breakthrough Curves

Breakthrough Curves of H_2O / N_2: Applications

Air separation is important for O_2 and N_2 production [production of inert gases, medical applications, steel industry,…]

Important to **remove Water** and CO_2 in Air **before**:

- Cryogenic Air Separation:
  - → Water would plug the piping by freezing.
- Air separation with Pressure Swing Adsorption (PSA) on Zeolites
  - → Water has strong affinity to surface (stronger than N_2 and O_2)
  - → Water is not as effectively desorbed upon pressure reduction → Build-up Effects
  - → Decreasing efficiency over time
  - → Thermal regeneration is expensive

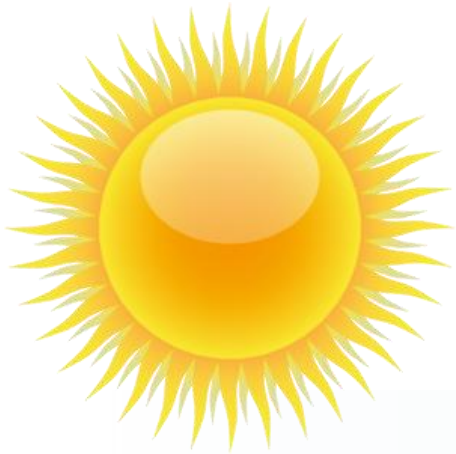


Verborgene Adsorption – TSA-Anlagen in industriellen Gasaufbereitungsprozessen Benedikt Schürer, Linde AG, Engineering Division, Pullach, Deutschland ProcessNet Dechema Jahrestreffen 2017

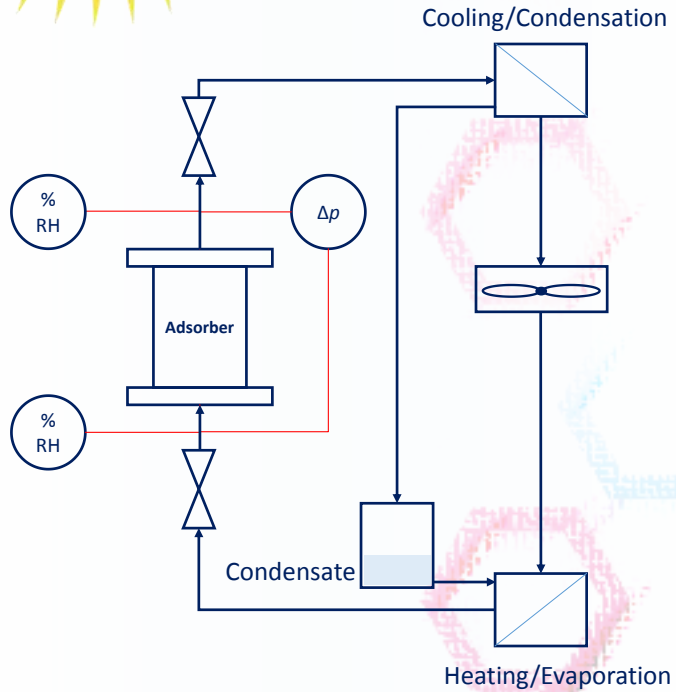
4. Examples – I Water Breakthrough Curves

Breakthrough Curves of H_2O / N_2: Applications (II)

Utilizing the Heat of Adsorption



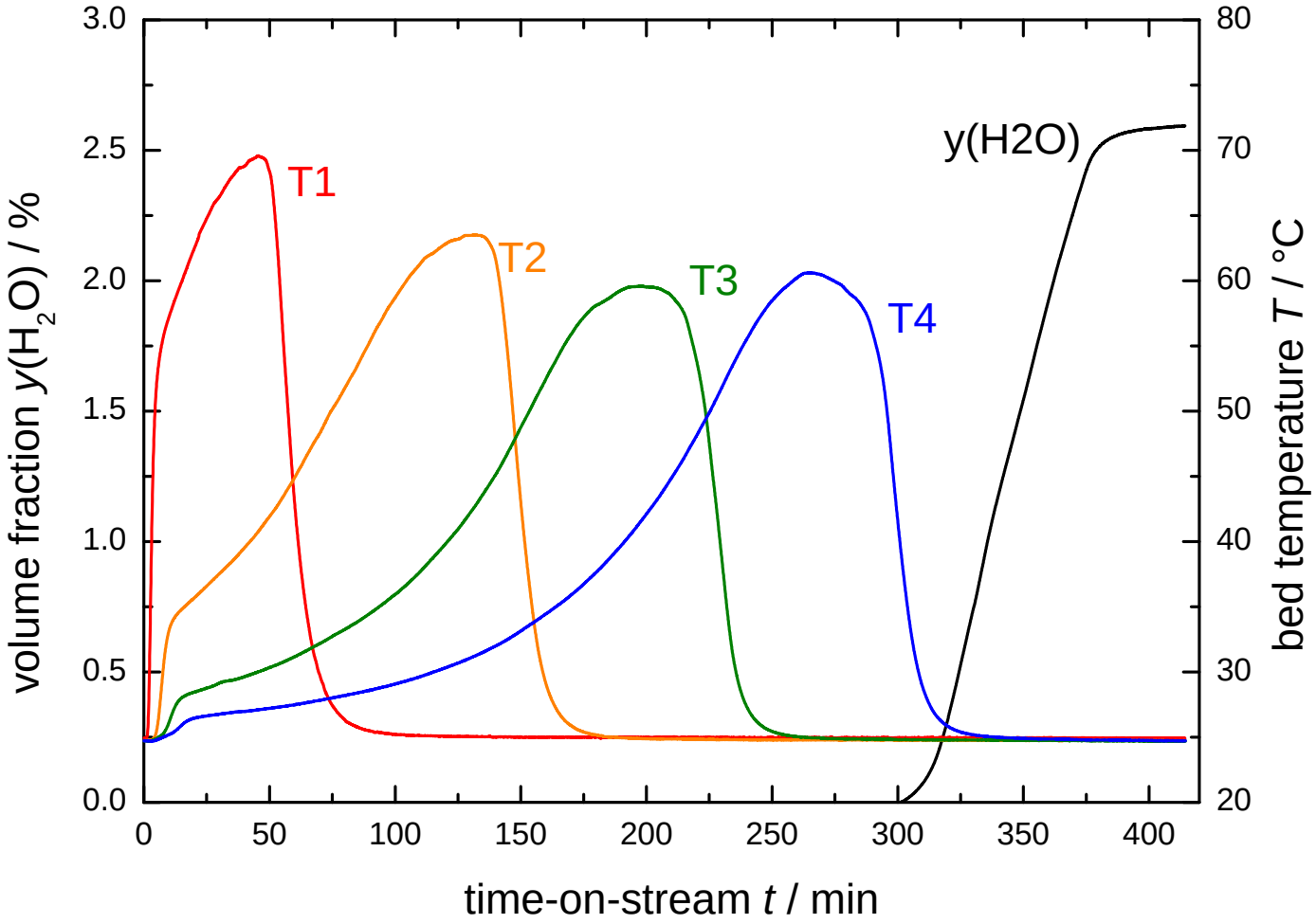
- Energy Storage
  - → Adsorption of water vapor → releasing heat of adsorption. Control heat output with **dosing of water**
  - → Regeneration with e.g. thermal **solar energy** (roof top)
  - → Can be used for cooling as well
- Adsorption Chiller
  - → Using adsorption of a vapor as driving force for **evaporation of a liquid reservoir**
  - → **Enthalpy of vaporization** is used to cool
  - → Cycling **Adsorption/Evaporation** vs. **Desorption/Condensation** with two separate units.



→Investigating Cycles of Adsorption of H_2O in N_2

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Zeolite 13X



- Experimental conditions of a simple breakthrough experiment after Activation at **400 °C for 4 h**
- 25 °C, Flow rate 4 L min^{-1}
- Pressure: 1 bar
- Standard Adsorber with 80 g of sample
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

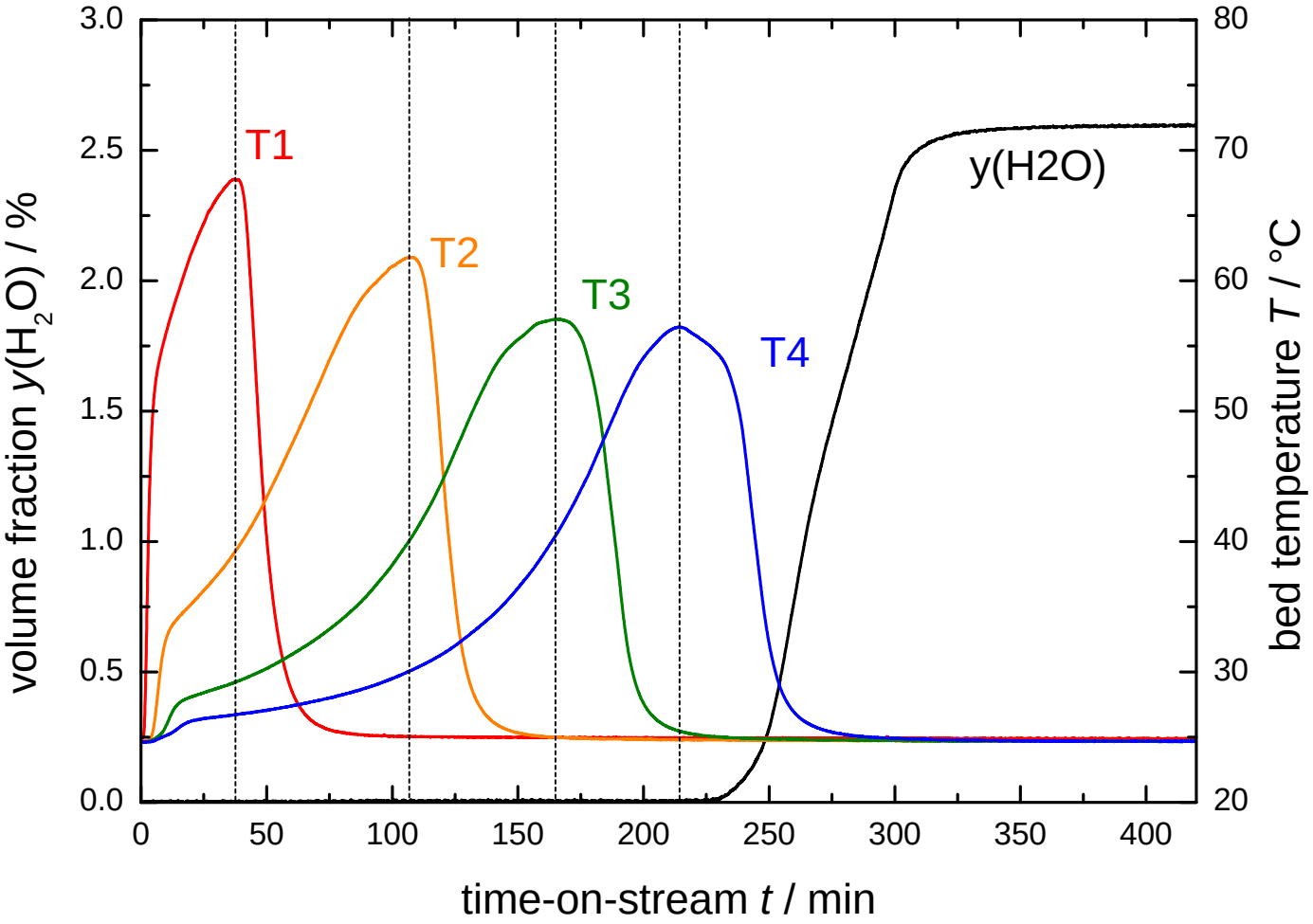
→ High temperatures during adsorption

→ Loading: **18.9 mmol g^{-1}**

→ **Regeneration at 130 °C for 3.5 h**

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Zeolite 13X



- Sample regenerated at **130 °C for 3.5 h**
- Same experimental conditions
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

→ Loading: **15.4 mmol g^{-1} → lower**

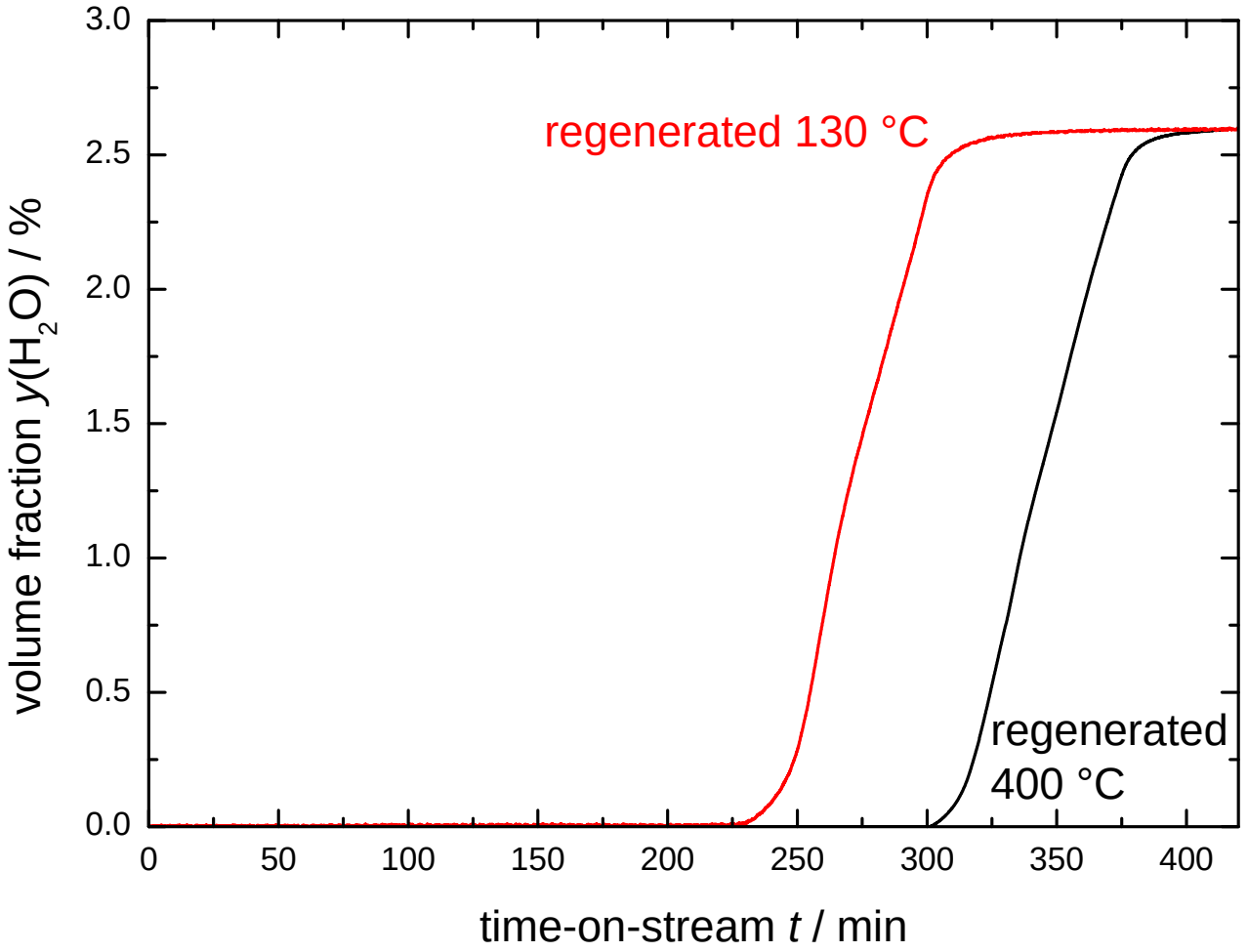
→ Unsymmetrical temperature profiles

→ Residual loading before experiment not equally distributed

→ Overlay

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Zeolite 13X



- Loadings:
  18.9 mmol g^{-1} (activated at 400 °C) vs.
  15.4 mmol g^{-1} (regenerated at 130 °C)
- Breakthrough Curve shifted to the left
- Breakthrough curves still have similar shapes

→ Zeolite requires harsh regeneration

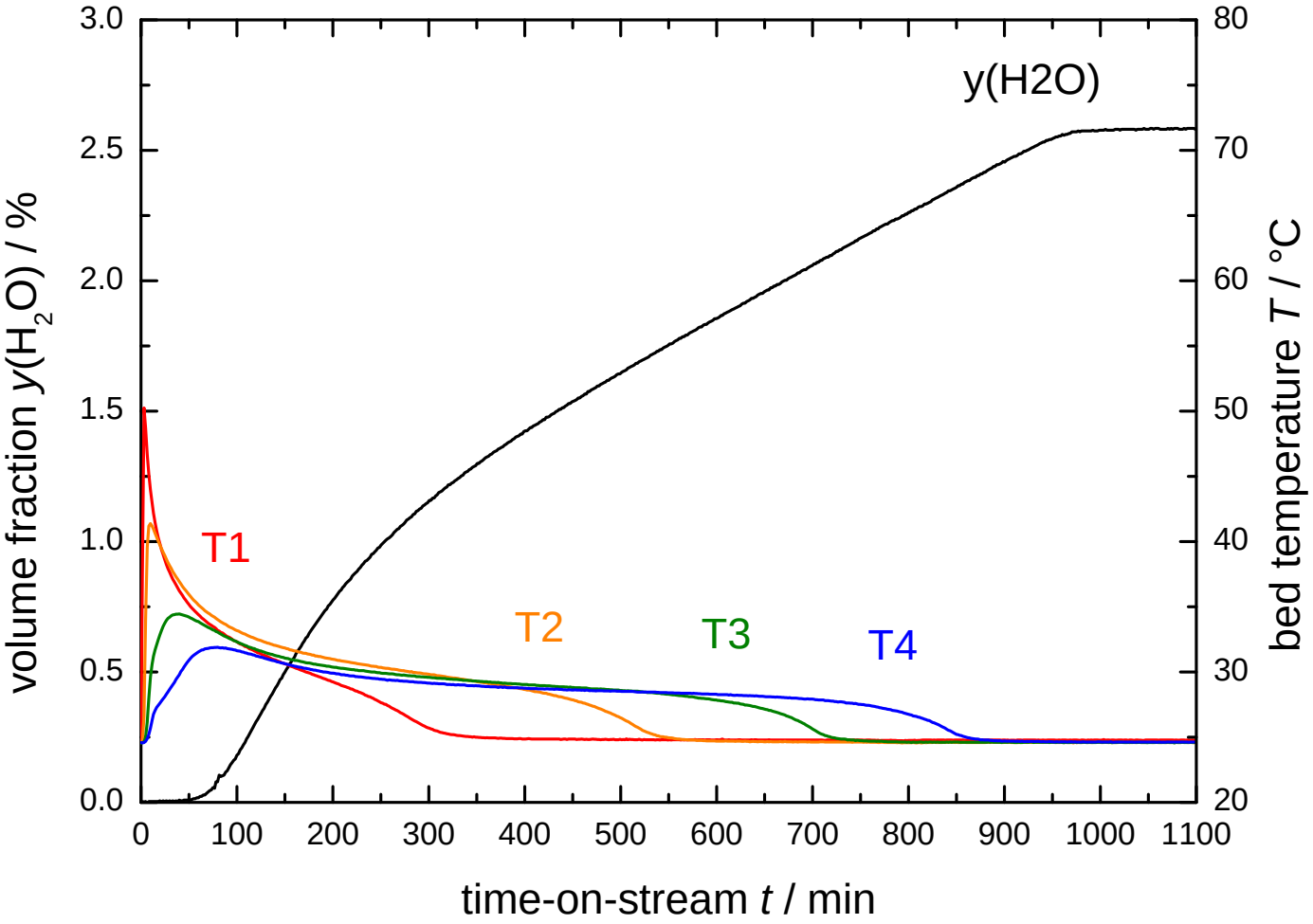
→ High temperatures

→ Steep Breakthrough Curves indicate steep isotherms

→ High affinity to water

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Silica Gel



- Experimental conditions of a simple breakthrough experiment after Activation at **350 °C for 4 h**
- 25 °C, Flow rate 4 L min^{-1}
- Pressure: 1 bar
- Standard Adsorber with 80 g of sample
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

→ Smaller temperatures peaks

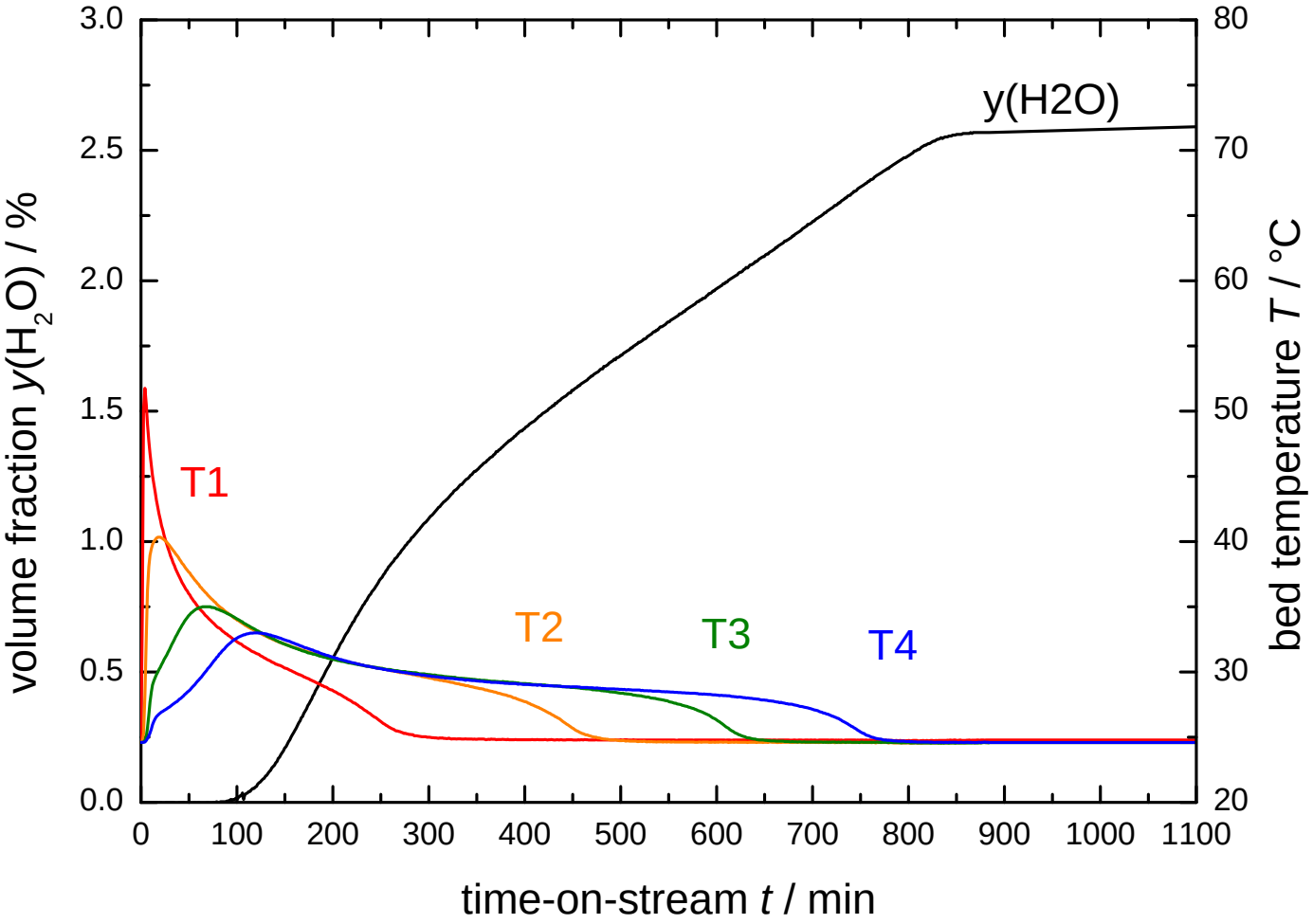
→ Much longer measurement

→ Loading: **25.9 mmol g^{-1}**

→ **Regeneration at 130 °C for 3.5 h**

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Silica Gel



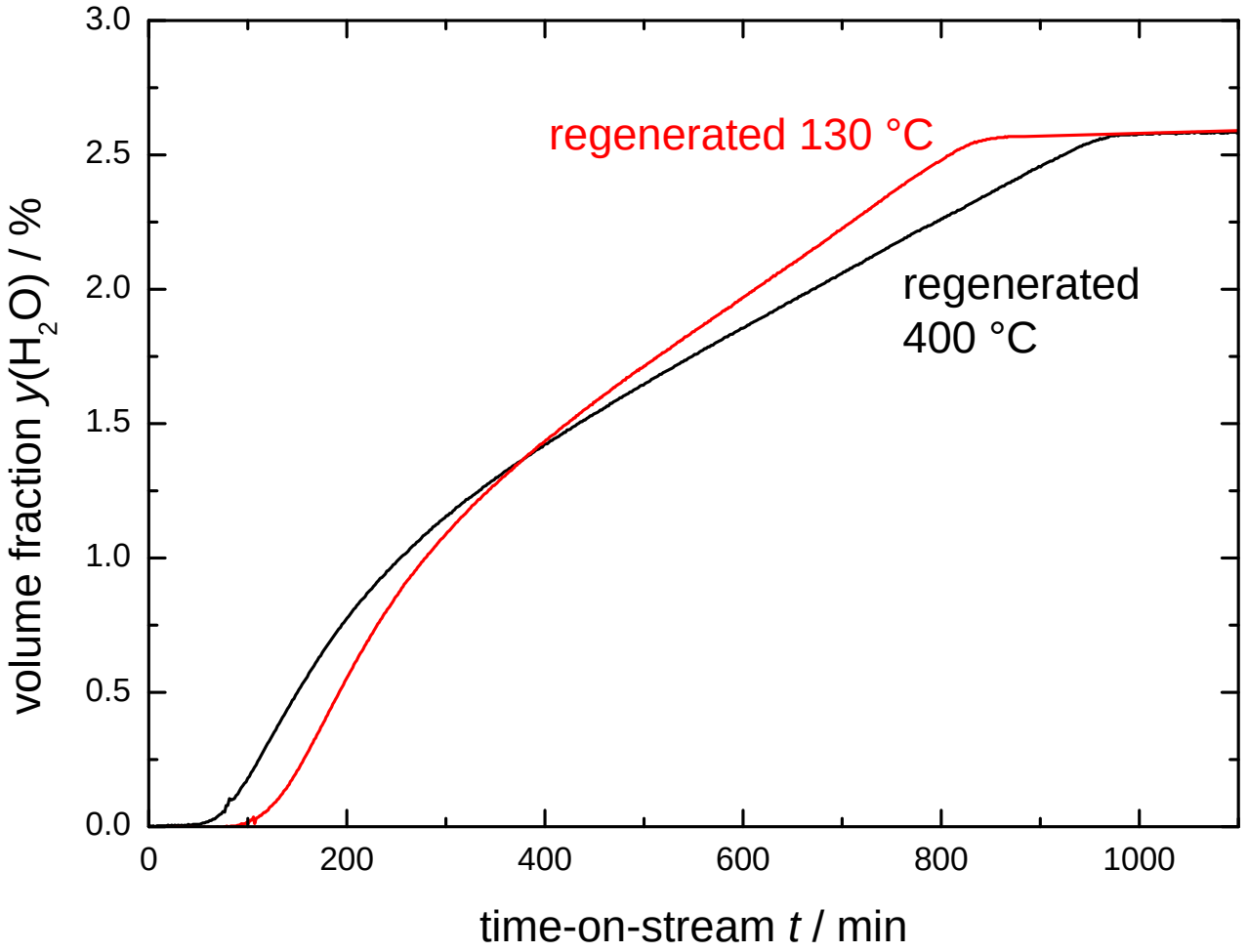
- Sample regenerated at **130 °C for 3.5 h**
- Same experimental conditions
- Inlet composition: **5 g h^{-1} H_2O in N_2** (volume fraction $y(H_2O)$ = **2.59 %**, Relative humidity approx. **80 % @ 25 °C**)

→ Loading: **25.1 mmol g^{-1}**
→ **almost identical**

→ Overlay

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Silica Gel



- Loadings:
  25.9 mmol g^{-1} (activated at 350 °C) vs.
  25.1 mmol g^{-1} (regenerated at 130 °C)
- Breakthrough Curve changed slope
- Changing surface chemistry until stable in cycles

→ **Regeneration** much **easier**, efficient

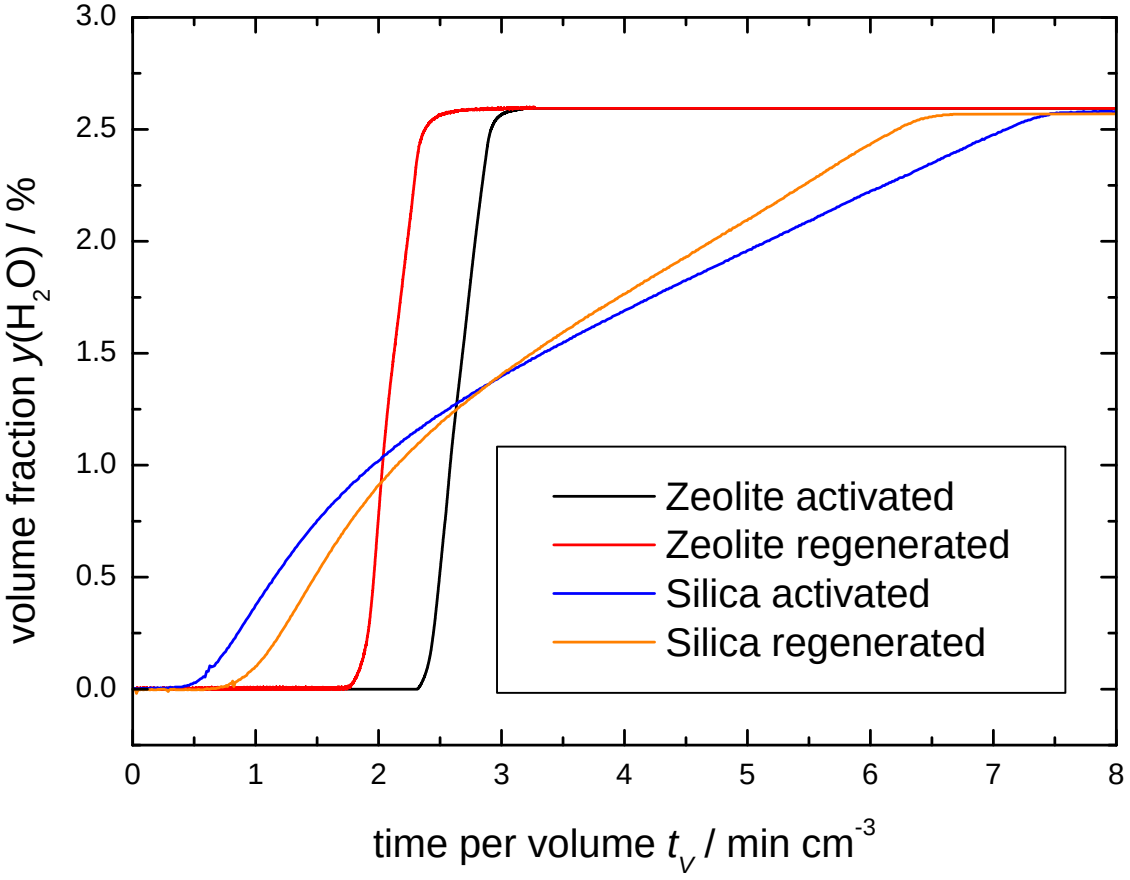
→ No high temperature required

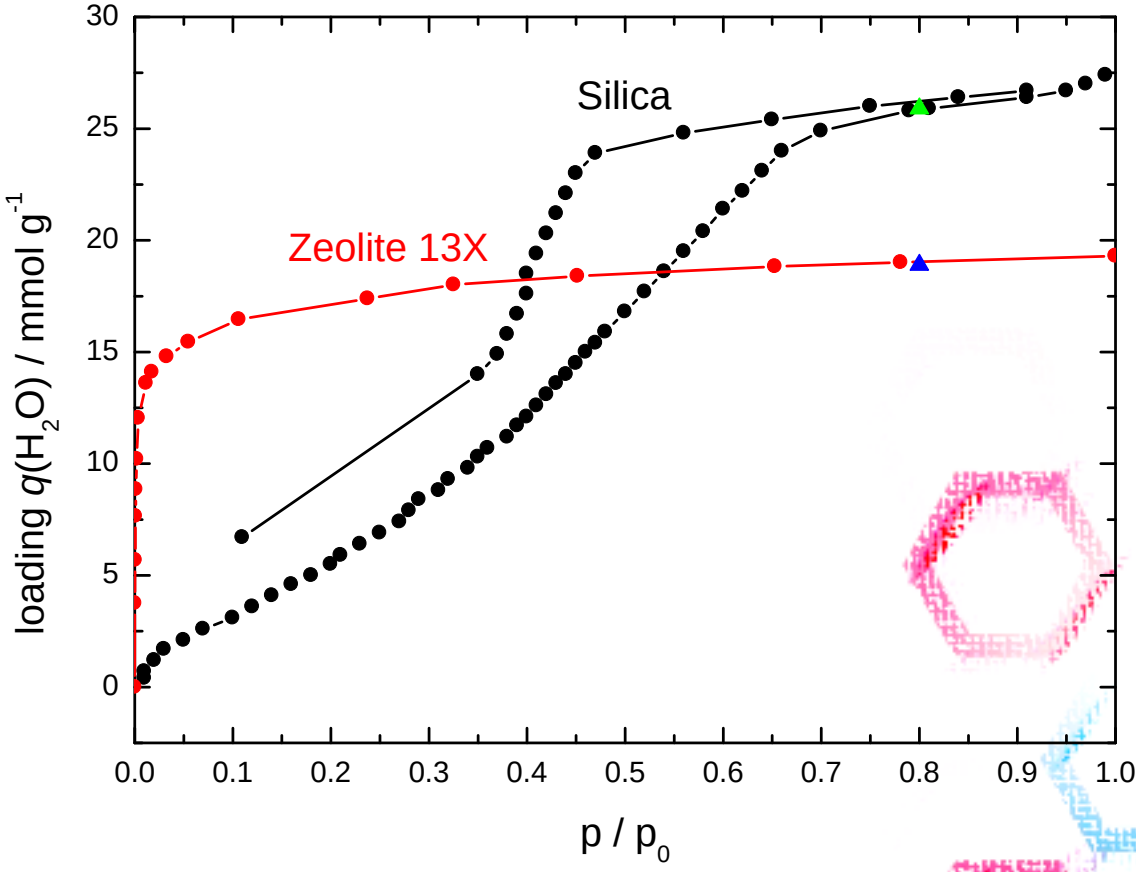
→ Regeneration possible by **Pressure Reduction**

→ **But**: Breakthrough occurs earlier!

4. Examples – I Water Breakthrough Curves

Breakthrough Curve of H_2O / N_2 on Zeolite 13X and Silica Gel





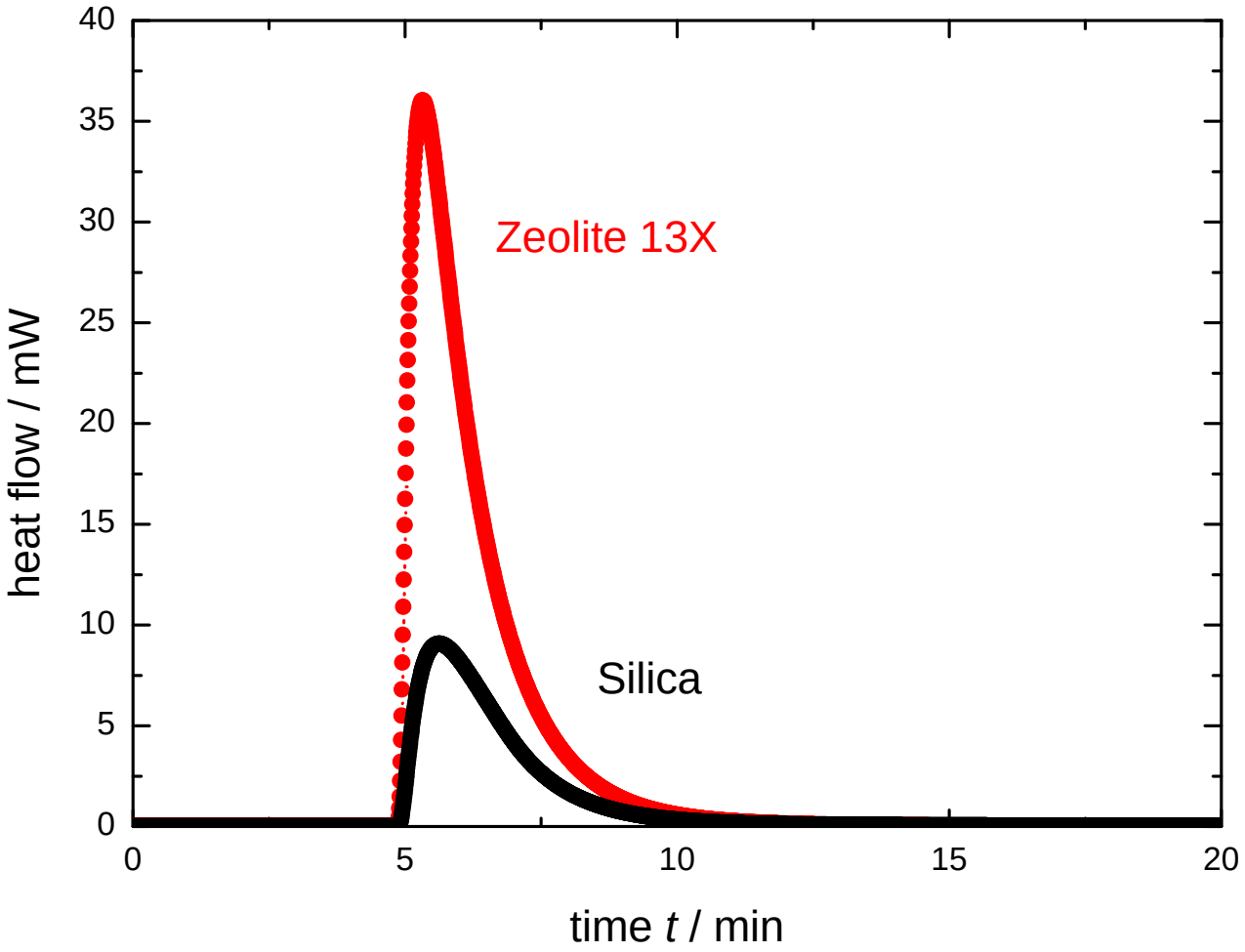
- Materials behave differently in Adsorption/Desorption Cycles
- Good Agreement with Isotherm data (right hand side)

→ **Can we use these curves to get information about stored energy and heating power?**

4. Examples – I Water Breakthrough Curves

Immersion Calorimetry

- Determining the Heat of Adsorption in Liquid Phase



»Enthalpy of Adsorption = Wetting + Condensation«

$$h_A = h_W + h_C$$

Enthalpy of wetting

Zeolite: 550 J g^{-1} (g of Adsorbent)

Silica Gel: 140 J g^{-1}(g of Adsorbent)

Zeolite: 1600 J g^{-1} (g of water)

Silica Gel: 300 J g^{-1} (g of water)

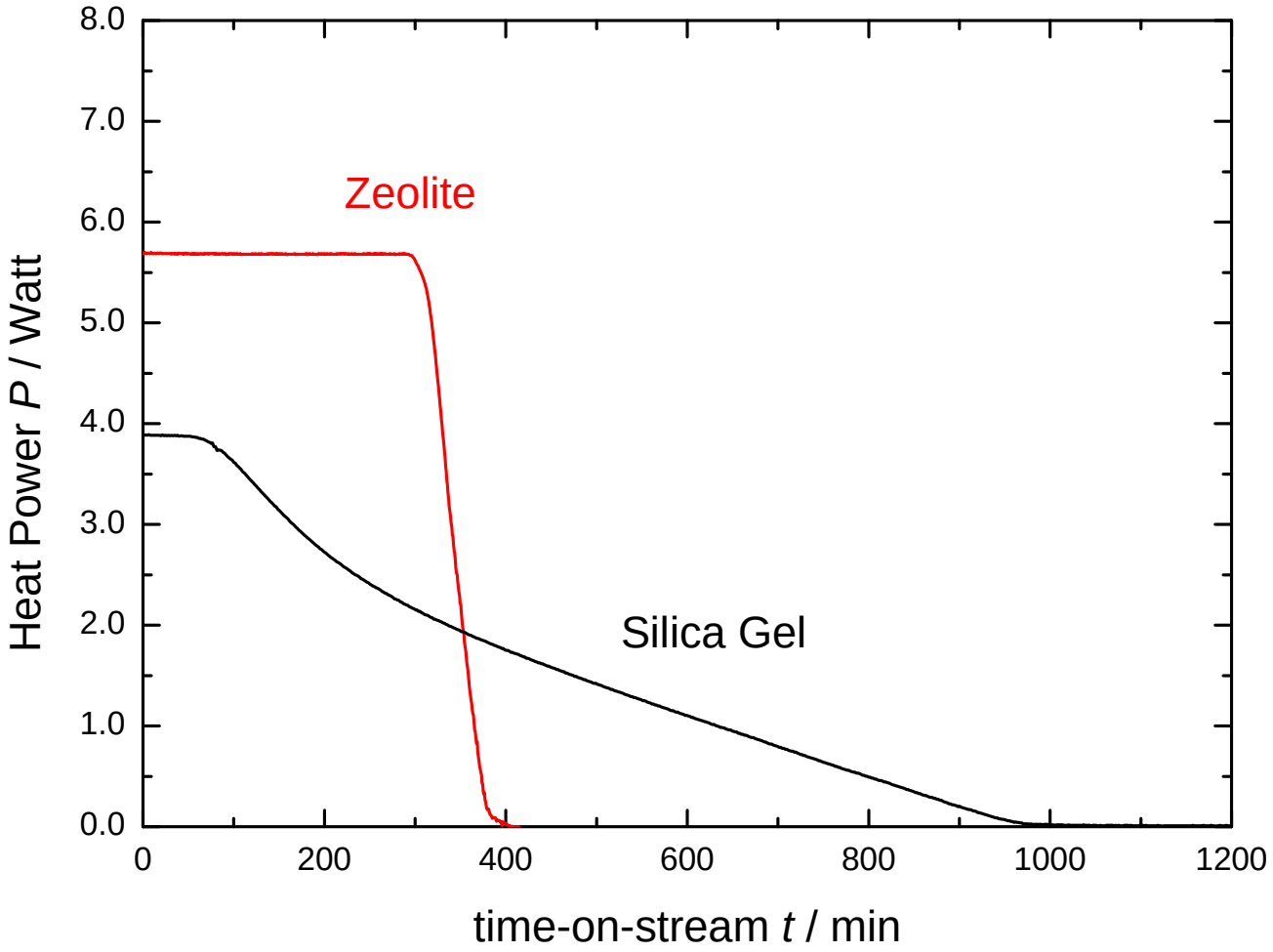
(re-calculated according to water isotherms)

	Zeolite 13X	Silica Gel
h_W / J g^{-1} (H_2O)	1600	300
h_C / J g^{-1} (H_2O)	2500	2500
h_A / J g^{-1} (H_2O)	**4100**	**2800**

4. Examples – I Water Breakthrough Curves

Heat Power Comparison

- Comparing the Heating Power during Adsorption

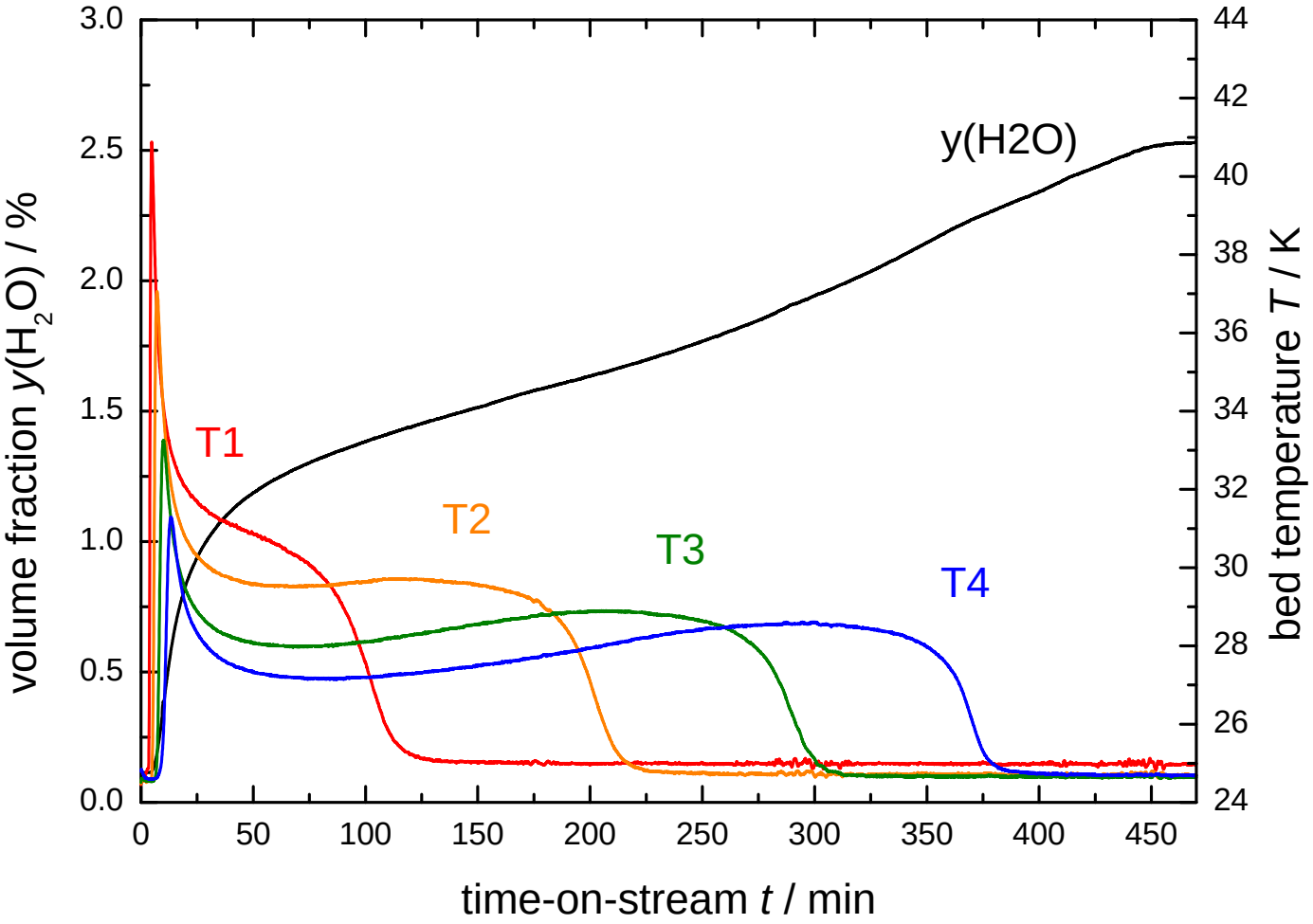


$$P = (1 - \text{rel. Breakthrough}) \times \frac{5\,\frac{\text{g}}{\text{h}}}{3600\,\frac{\text{s}}{\text{h}}} \times h_A$$

- Zeolite: More Heating Power, but over short duration → abrupt drop
- Silica Gel: Less Heating Power, continuously decreasing → longer duration

4. Examples – I Water Breakthrough Curves

For Comparison: Breakthrough Curve of H_2O / N_2 on Activated Carbon



- 25 °C, 4 L min^{-1}
- 1 bar
- Inlet composition:
  5 g h^{-1} H_2O in N_2
  (volume fraction y(H_2O) = 2.59 %, RH approx. 80%)
- Shape of curves can be explained by **adsorption** and **condensation** in the pores.
- Fast breakthrough due to hydrophobic surface
- Similar to Silica Gel, but Condensation is more pronounced

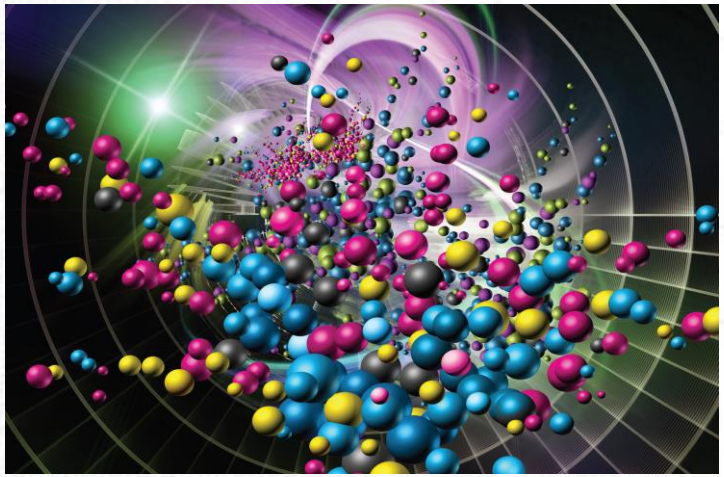
4. Examples – II Removing CO_2 from Air

Breakthrough Curves of CO_2 / N_2: Applications

Air separation is important for O_2 and N_2 production [production of inert gases, medical applications, steel industry,…]

Important to **remove** Water and **CO_2** in Air **before**:

- Cryogenic Air Separation:
  - → CO_2 would plug the piping by freezing.
- Air separation with Pressure Swing Adsorption (PSA) on Zeolites
  - → CO_2 has strong affinity to surface (stronger than N_2 and O_2)
  - → CO_2 is not as effectively desorbed upon pressure reduction → Build-up Effects
  - → Decreasing efficiency over time

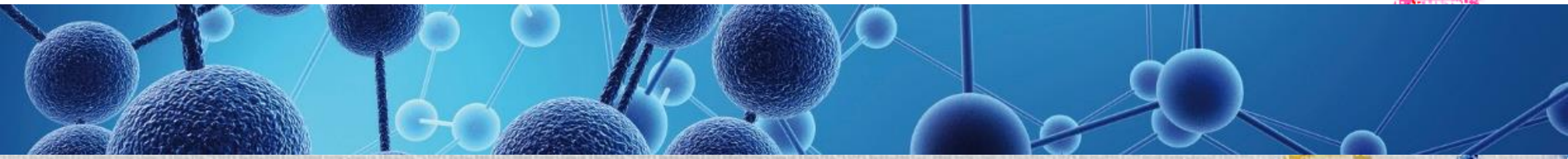


Verborgene Adsorption – TSA-Anlagen in industriellen Gasaufbereitungsprozessen Benedikt Schürer, Linde AG, Engineering Division, Pullach, Deutschland ProcessNet Dechema Jahrestreffen 2017

4. Examples – II Removing CO_2 from Air

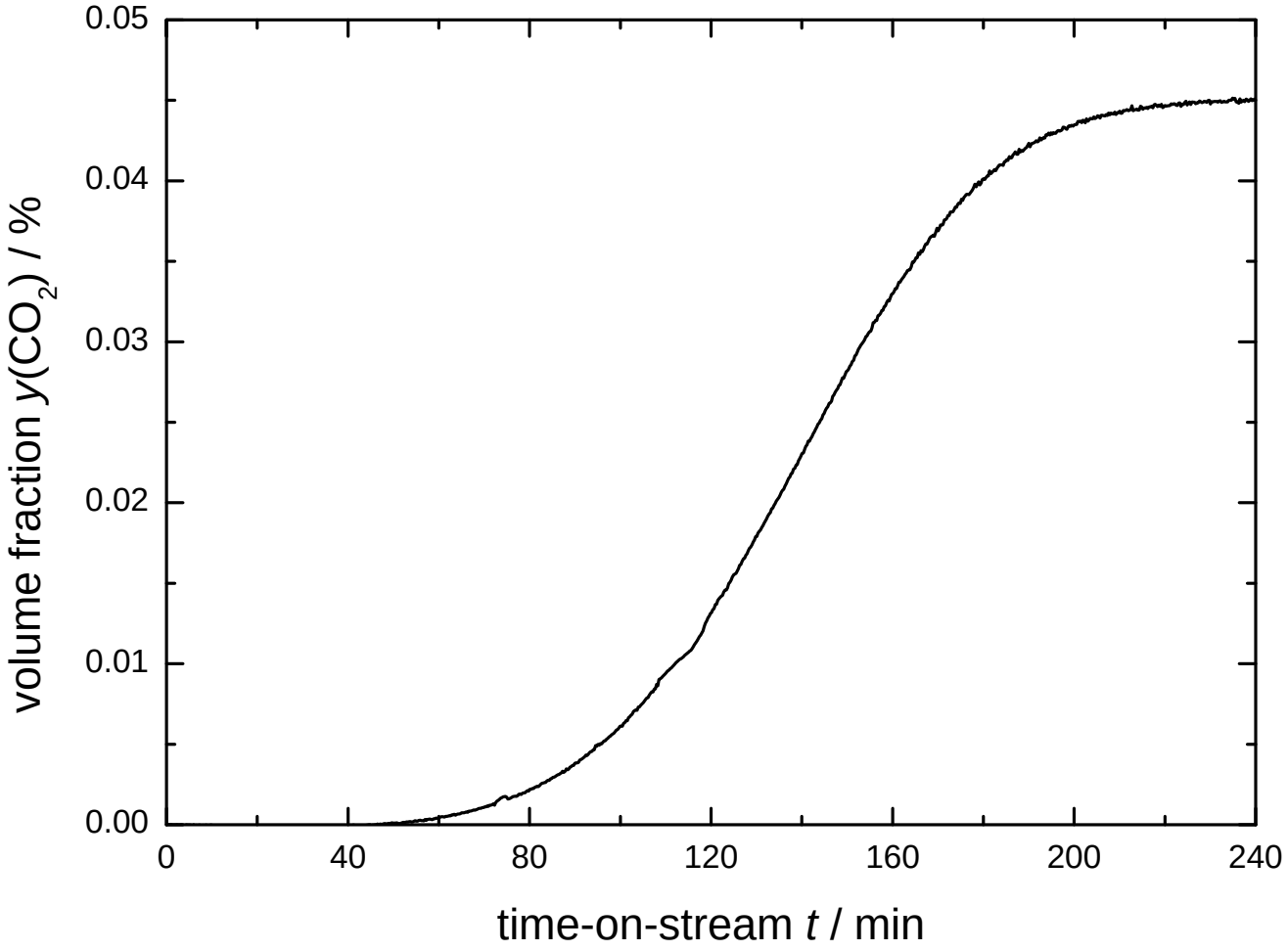
Breakthrough Curve of 450 ppm CO_2 in N_2 on Zeolite 13X

- Pressure: **6 bar**
- Gas Flow: **20 L min^{-1} → High Flow Application**
  → 0.47 m s^{-1} superficial flow velocity (at STP)
  Typical superficial flow velocities in the industry are around **0.4 m s^{-1}**
- Zeolite, 55 g
- Temperature: **25 °C**
- Inlet composition: **450 ppm CO_2, balance: N_2** (9 mL min^{-1} CO_2, 19991 mL min^{-1} N_2)
- For Measurements with such low concentrations, a **Mass Spec is recommended**
- **Pfeiffer ThermoStar Mass Spec** attached and synchronized
- Mass Spec Data were then imported in dynaWin and used for calculations



4. Examples – II Removing CO_2 from Air

Breakthrough Curve of 450 ppm CO_2 in N_2 on Zeolite 13X



Integration gives **loading**:
0.419 mmol g^{-1}

With the low concentrations and the very high flow rates, the breakthrough curve is not as steep as usual with Zeolites.

→ Measurements with very low concentrations are possible with the dynaSorb BT

4. Examples – III Breakthrough Curves in the Presence of Water

Breakthrough Curves in presence of Humidity: Applications

Most processes and application are running in the presence of water (humidity)

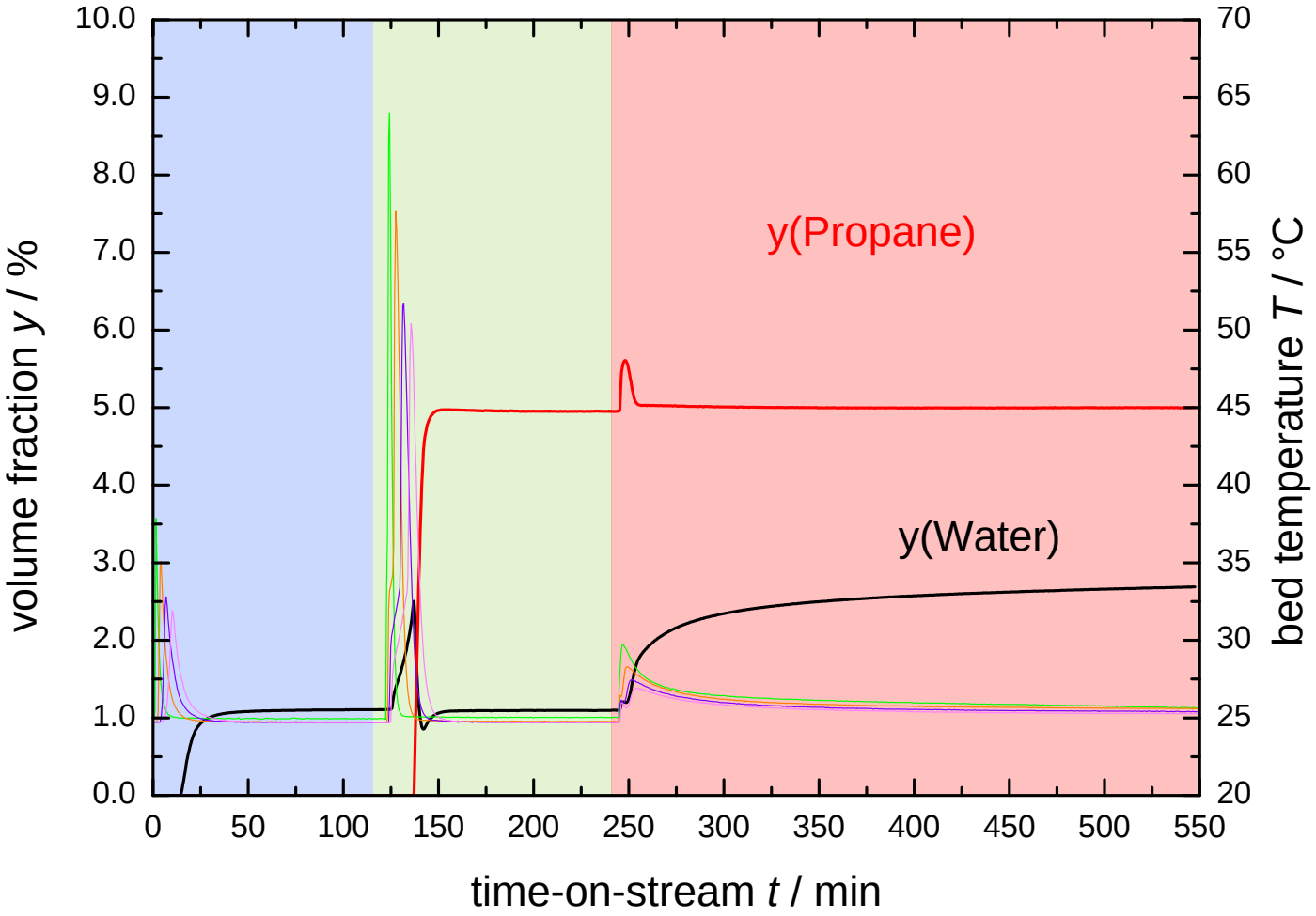
- The presence of water can have an major impact on the separation performance of adsorbents (*e.g.* on Zeolites)
- Purification of waste air, indoor air cleaning, gas masks
- Characterization under application-related conditions!

- **Example:** Adsorption of Propane in the presence of Water on **Activated Carbon** (about 55 g)
- **25 °C, Flow rate 4 L min^{-1}**
- Pressure: **1 bar**, Standard Adsorber
- Using **Mass Spectrometer** as Analytical Device

4. Examples – III Breakthrough Curves in the Presence of Water

Co-Adsorption of Propane and Water

Three Segments → Sequence of Breakthrough Experiments



Segment 1

volume fraction $y(H_2O)$ = **0.95 %**,
Relative humidity approx. **30 % @ 25 °C**

Segment 2

volume fraction $y(C_3H_8)$ = **5.00 %,**
volume fraction $y(H_2O)$ = 0.95 %,
Relative humidity approx. 30 % @ 25 °C

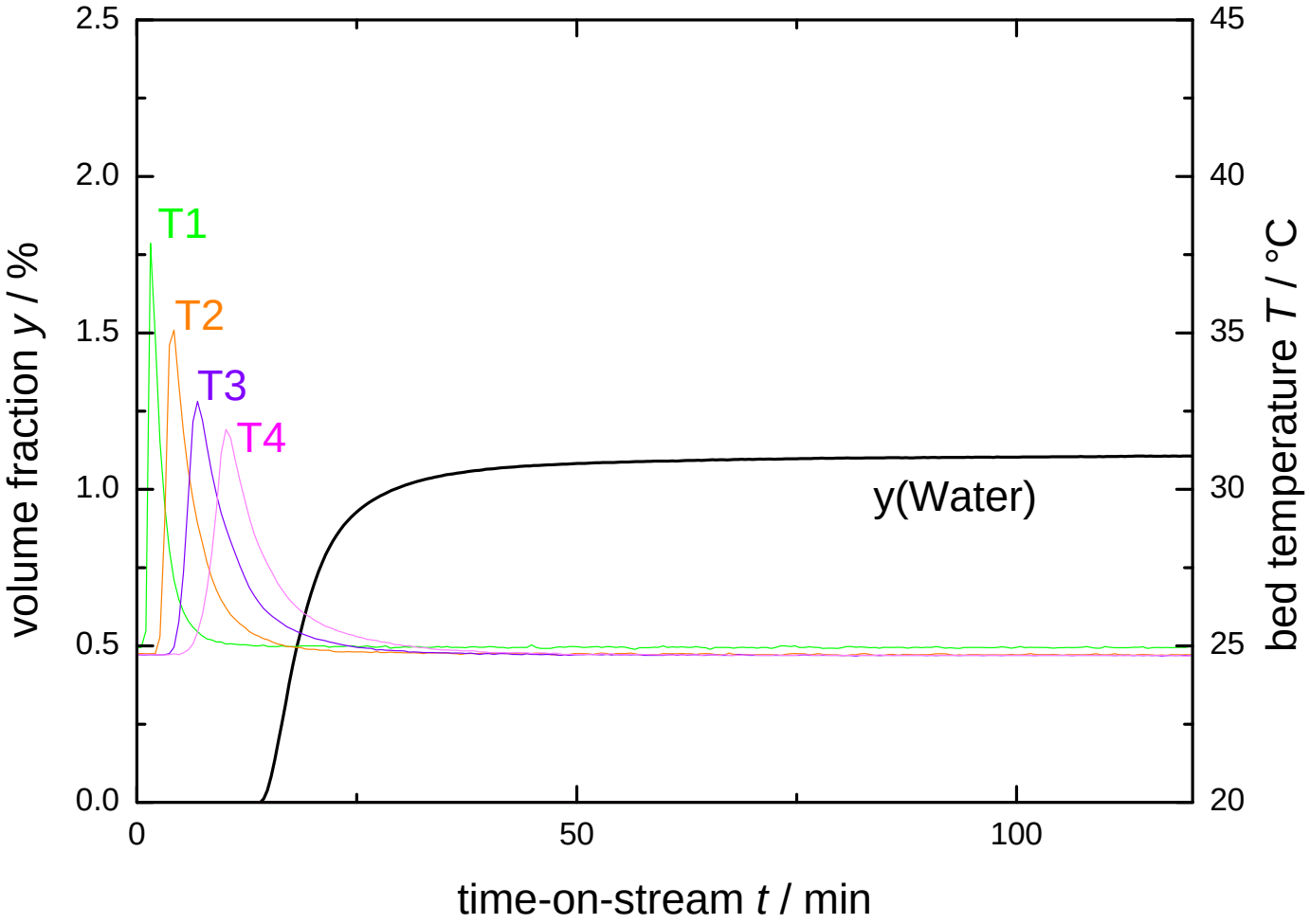
Segment 3

volume fraction $y(C_3H_8)$ = 5.00 %,
volume fraction $y(H_2O)$ = **2.70 %**,
Relative humidity approx. **85 % @ 25 °C**

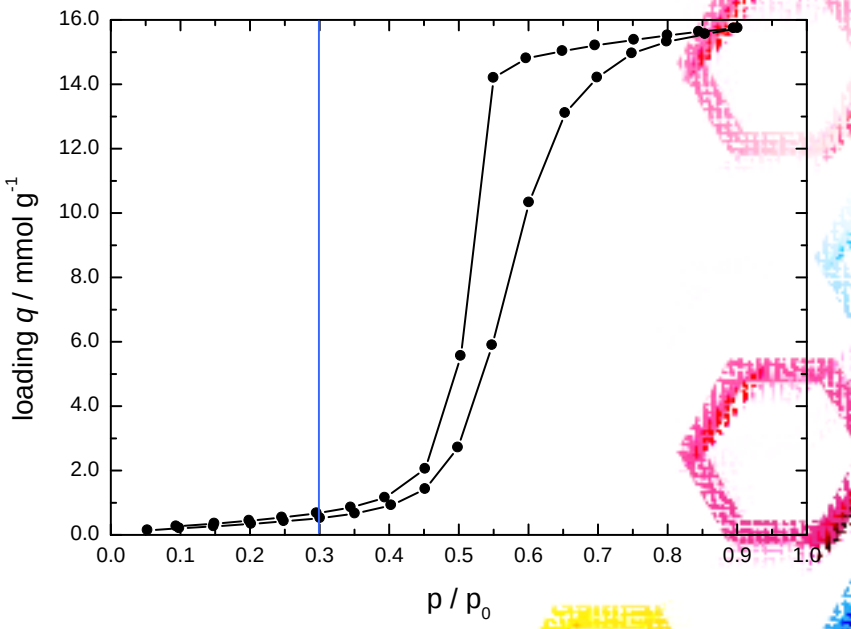
4. Examples – III Breakthrough Curves in the Presence of Water

Co-Adsorption of Propane and Water

Segment 1 → Breakthrough of RH 30% @ 25 °C



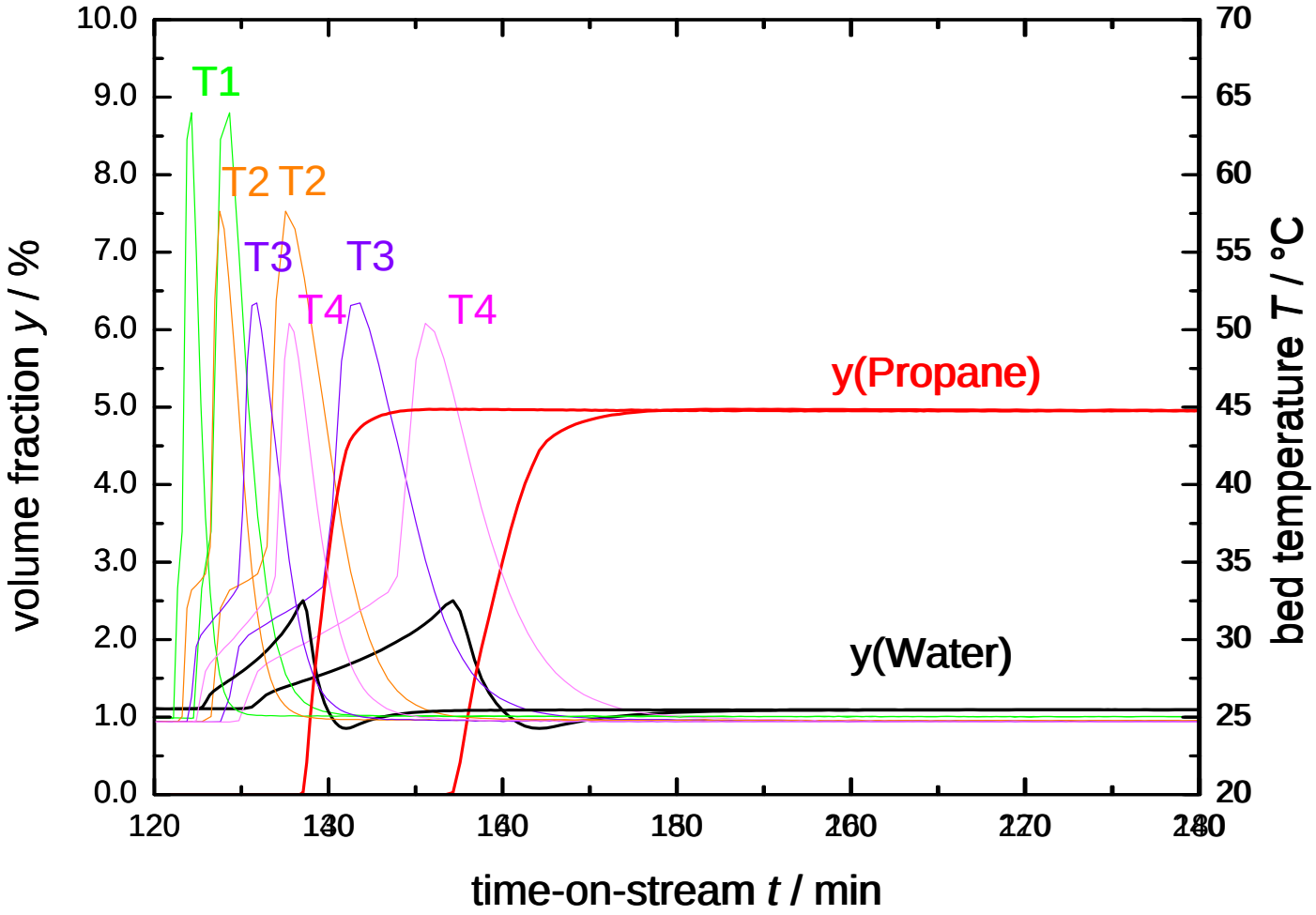
- Breakthrough Curve and Temperature Curves show regular shape
- No distinct Condensation observable
- Loading: $q(H_2O) = 0.64$ mmol g^{-1}
- Very Good Agreement with Water Isotherm measure on ASiQ



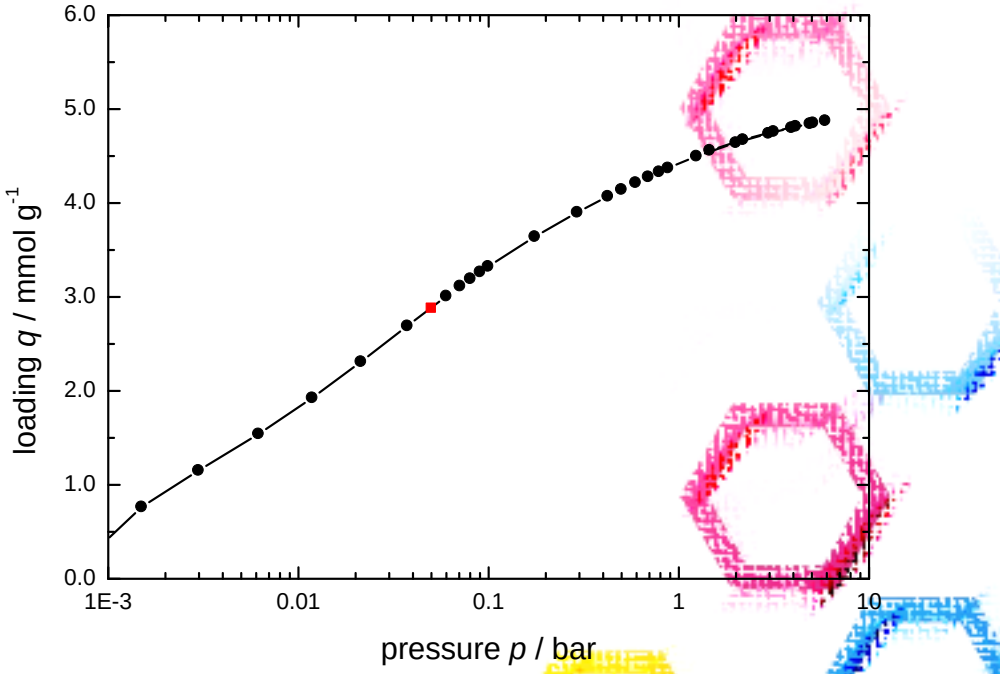
4. Examples – III Breakthrough Curves in the Presence of Water

Co-Adsorption of Propane and Water

Segment 2 → Breakthrough of Propane in N_2 with RH 30% @ 25 °C



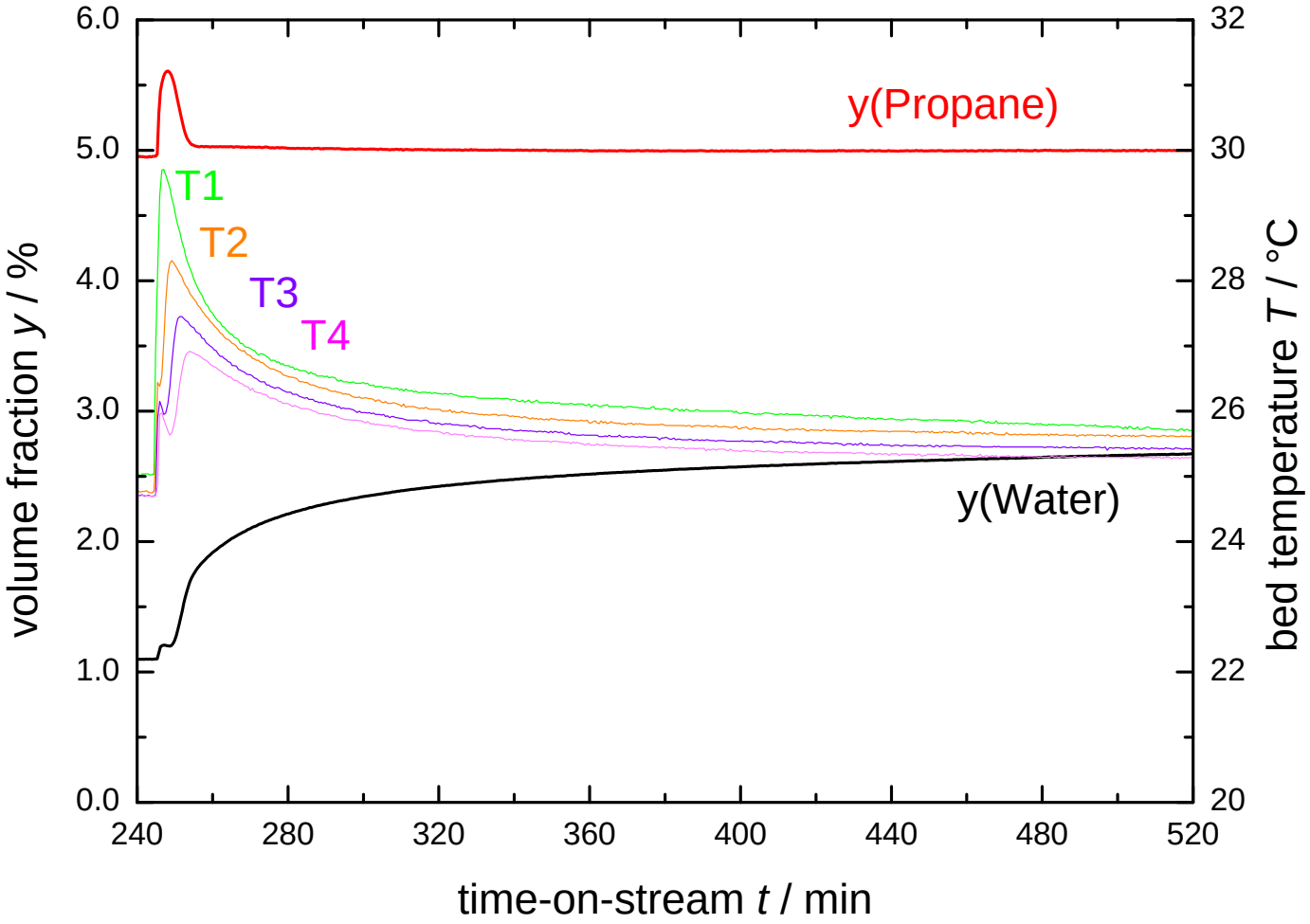
- Water gets displaced
- Distinct Temperature Curves
- Loading: $q(C_3H_8)$ = **2.84 mmol g^{-1}**
- Very Good Agreement with Loading at dry conditions (not shown): **2.88 mmol g^{-1}** and iSorb measurements



4. Examples – III Breakthrough Curves in the Presence of Water

Co-Adsorption of Propane and Water

Segment 3 → Increasing RH to 85 % in the presence of Propane



- **Displacement** of Propane (»red peak«)
- Not equilibrated after 5 h
  →Very slow process
- Condensation of water in the pores

Result similar as the Water on Activated Carbon Breakthrough Curve.

4. Examples – IV Organic Vapors on Activated Carbons

Breakthrough Curves with Organic Vapors

Removing Solvent Vapors and VOC (Volatile Organic Compounds) from air

- Pharmaceutical Industry
- Pigment, Toner, Color, Paint Manufacturers
- Solvent Recovery
- VOCs in atmosphere lead to the formation of ground-near Ozone

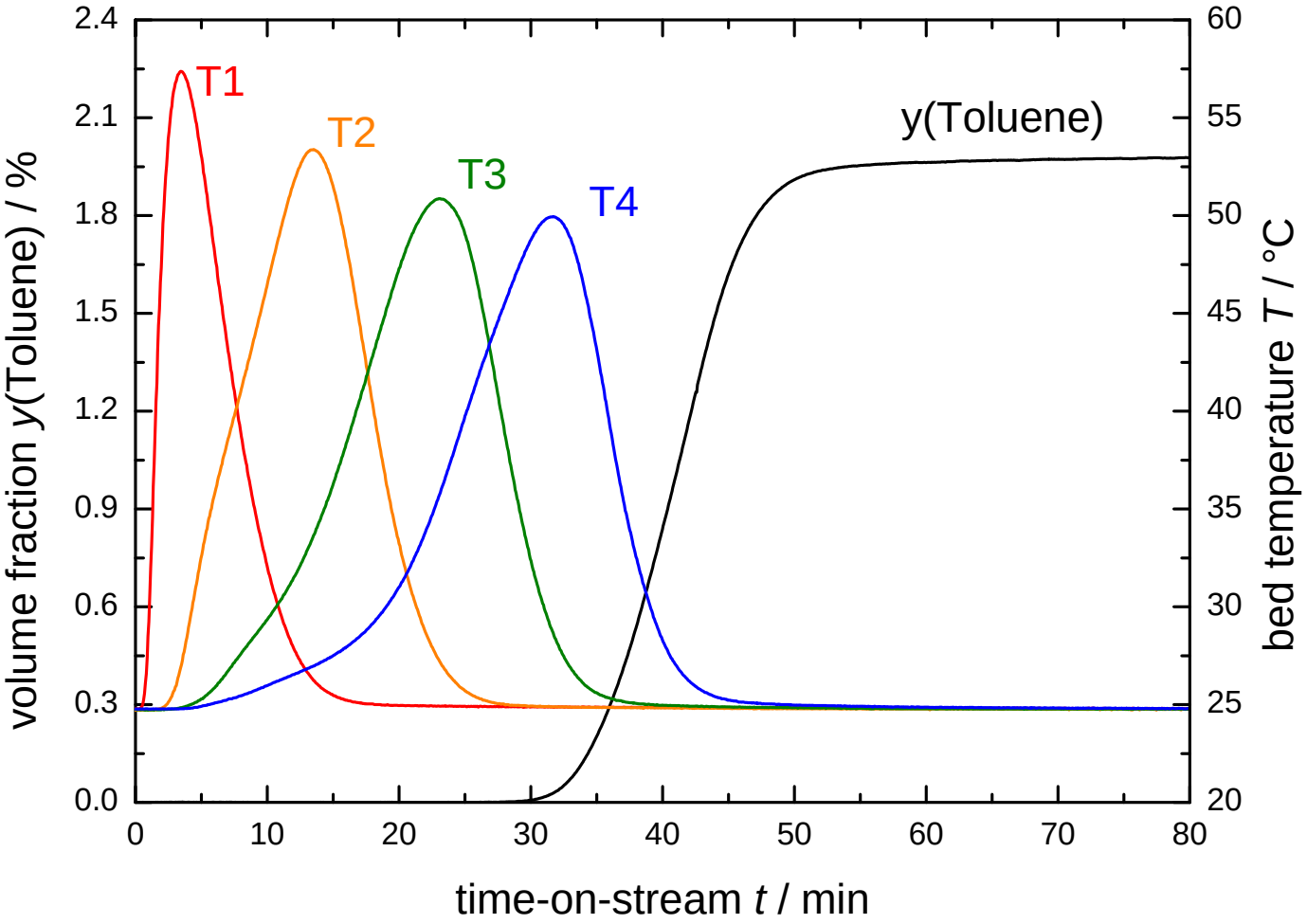
Removing Hydrocarbon Vapors to prevent **condensation** from

- Synthesis Gas (CO + x H_2)
- Natural Gas

http://www.silica.berlin/de/products-de/natural-gas-conditioning-de.html

4. Examples – IV Organic Vapors on Activated Carbons

Breakthrough Curve of Toluene/N_2



- Activated Carbon D55/1.5
- 25 °C, 4 L min^{-1}
- Inlet composition: **20 g h^{-1}** Toluene in N_2 (volume fraction *y*(Toluene) = **2.0 %, p/p_0= 0.53** (@ 25 °C)

→ Large temperature peaks

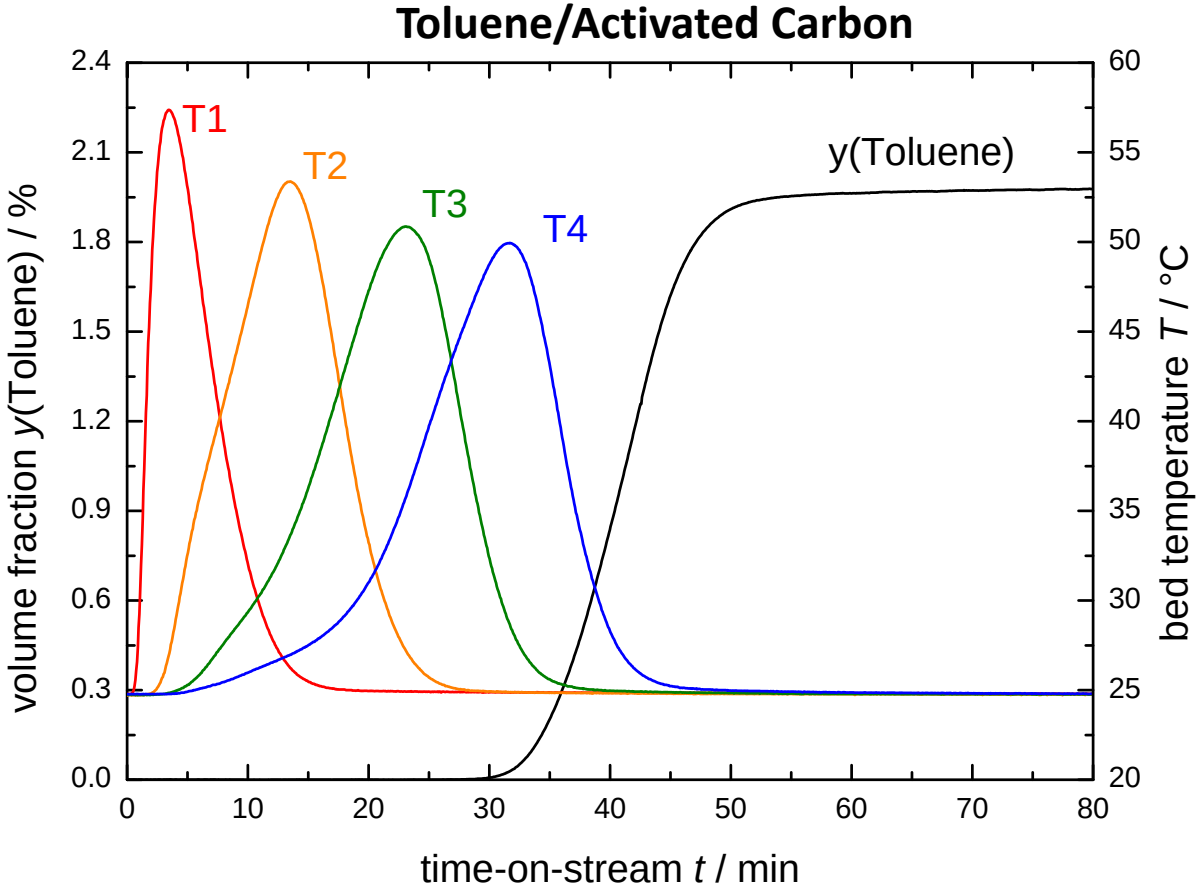
→ Steep Breakthrough Curve

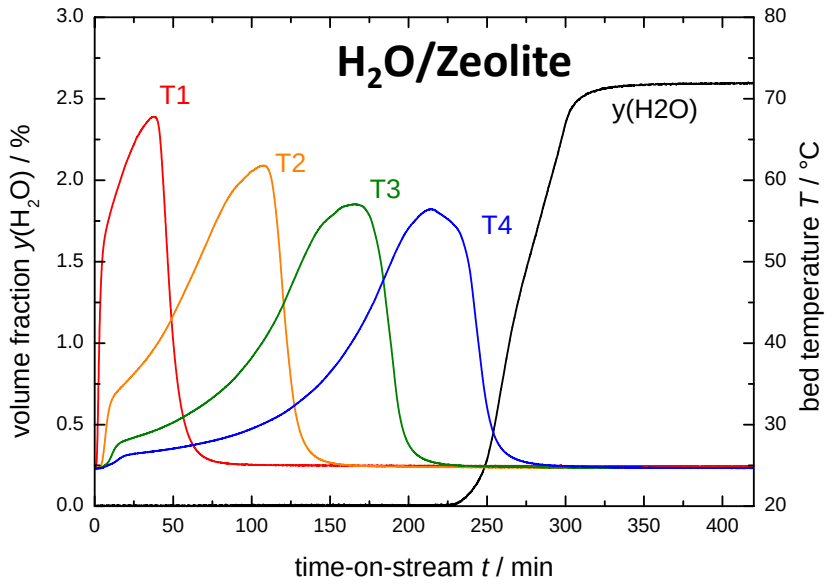
→ Loading: **2.1 mmol g^{-1}**

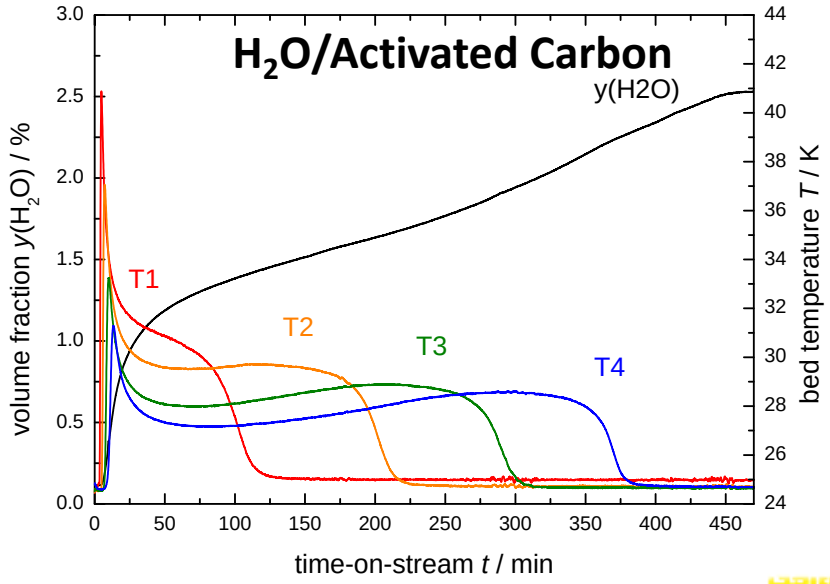
→ More similar to **H_2O/Zeolite** than H_2O/Activated Carbon

4. Examples – IV Organic Vapors on Activated Carbons

Breakthrough Curves of Toluene/N_2 and H_2O/N_2







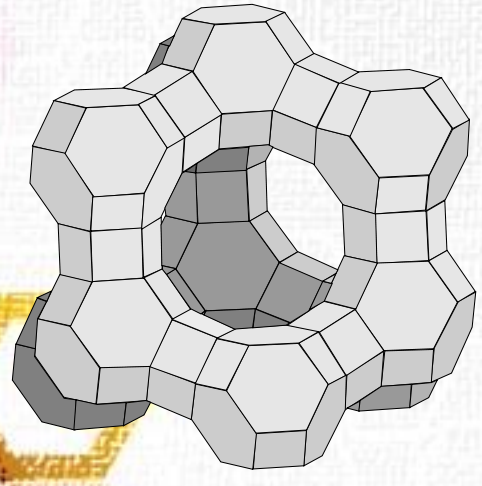
4. Examples – V Investigating the Surface Hydrophobicity

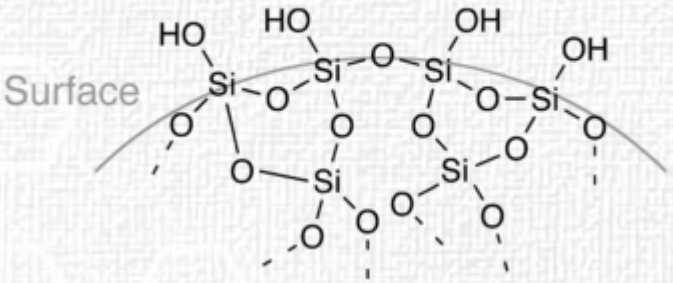
Different Surface Chemistry

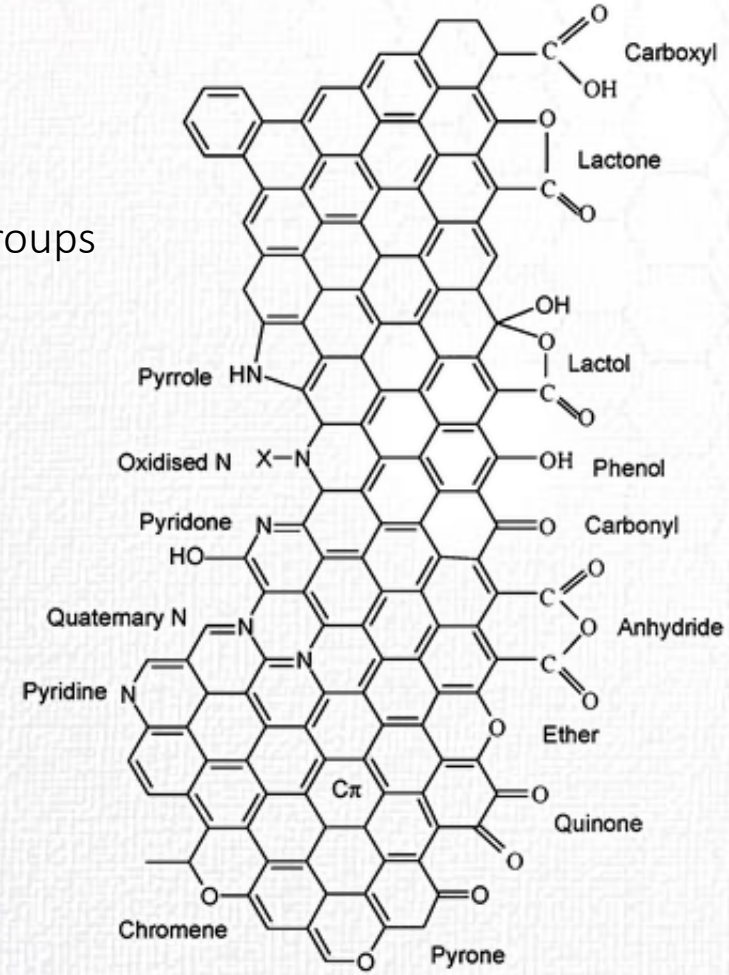
Different Adsorbents have different Surface Properties

- Hydroxyl Groups on Silica Gel
- Charged/Polar Surface Properties on Zeolites
- Organic Hydroxyl, Aldehyde, Ketone, Acidic, Aliphatic and Aromatic Groups on Activated Carbons

→ Investigating the Adsorption of organic Vapors with different Polarity







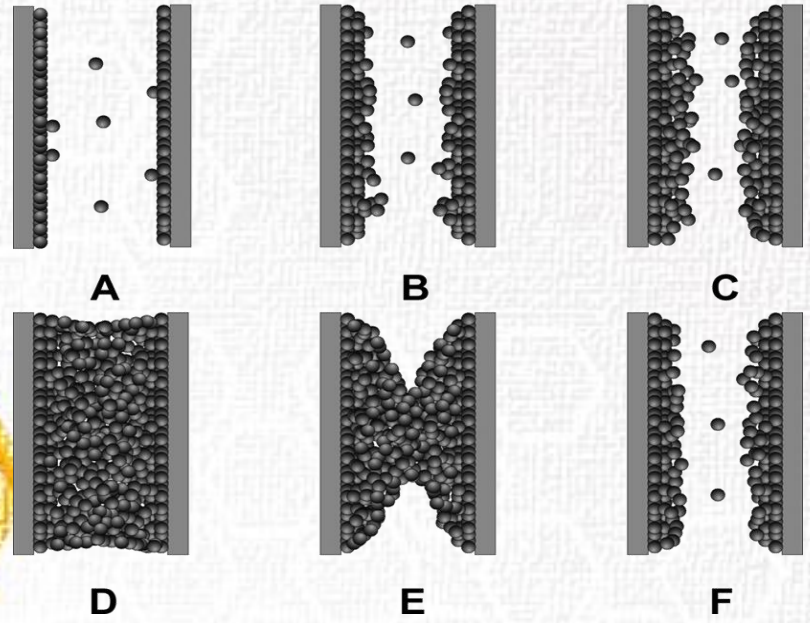
J. Mater. Chem. A, 2013,1, 9351-9364

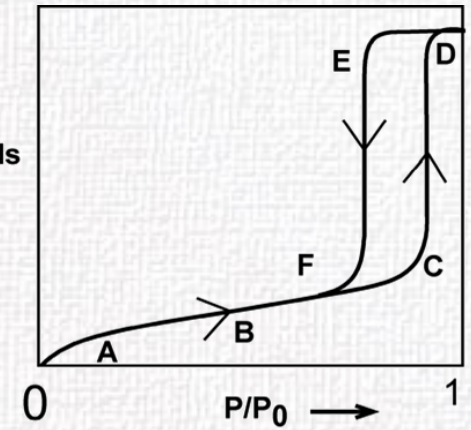
4. Examples – V Investigating the Surface Hydrophobicity

Adsorptives with different Polarity

Using Different Adsorptives with **different Polarity**

- **Elutropic Series**
- Elutropic Index is Empirical Value from **Chromatography**
- To see the Solid-Gas interaction → Measure at **low p/p_0**
  Otherwise: Pore Filling –Adsorbate interaction
- Select different Solvents and measure at equal p/p_0
  → **Different concentrations!**



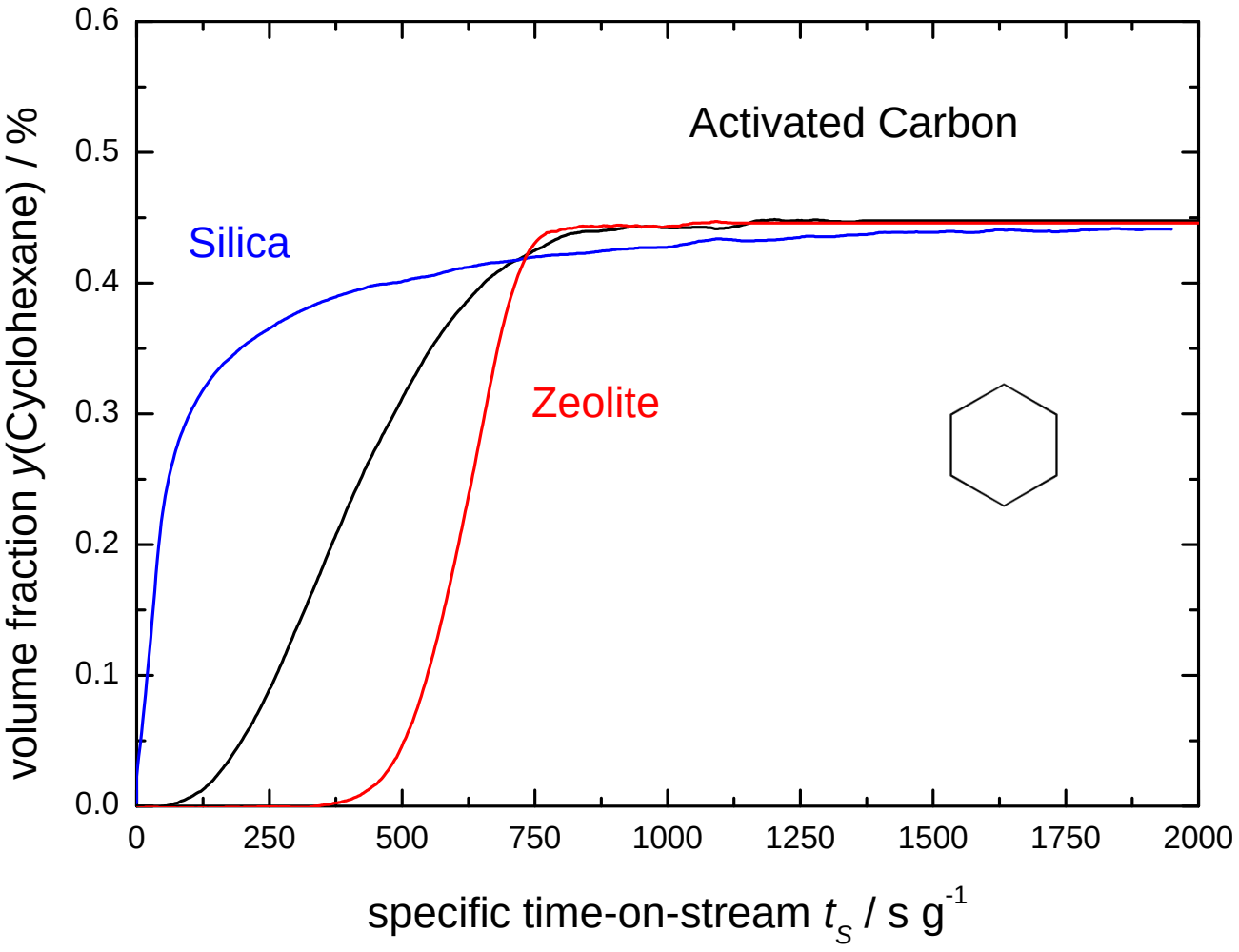


Compound	E
n-Hexane	0.00
Cyclohexane	**0.03**
Toluene	0.22
Benzene	0.25
Diethylether	0.29
Chloroform	0.31
Acetone	0.43
1,4-Dioxane	**0.43**
Tetrahydrofuran	0.48
2-Propanol	**0.60**
Ethanol	0.68
Methanol	0.73
Water	1.00

Katie Cychosz, »Interpretation of Data, Surface&Pores«, Quantachrome, 2011

4. Examples – V Investigating the Surface Hydrophobicity

Breakthrough Curves with Cyclohexane/N_2

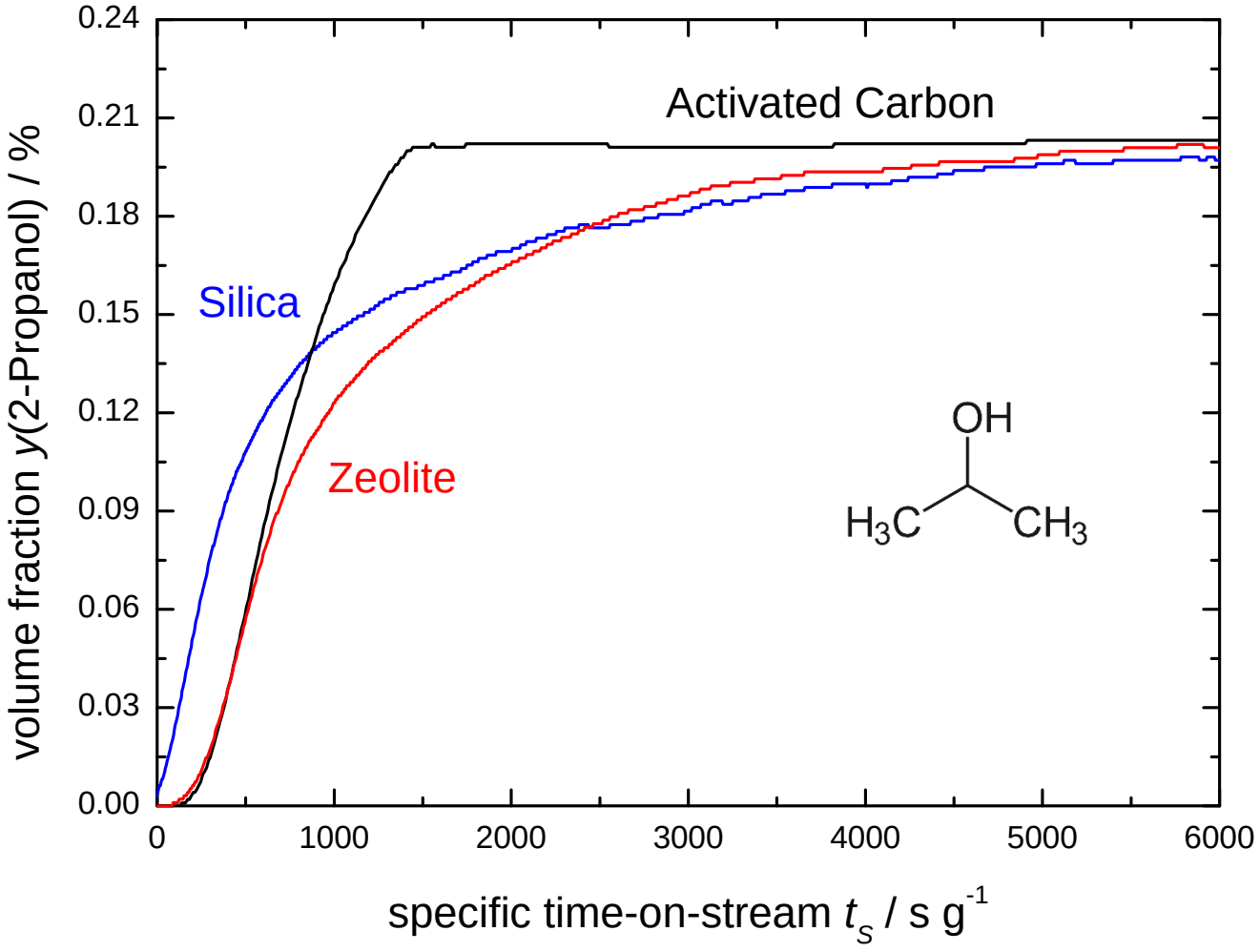


- 25 °C, Flow rate 1 L min^{-1}
- Pressure: 1 bar
- **Small** Adsorber with approx. 3 g of sample
- **1 g h^{-1} Cyclohexane in N_2**
  volume fraction *y*(Cyclohexane) = **0.44 %**,
  p/p_0 = **0.033 @ 25 °C**

Asorbent	Loading / mmol g^{-1}
Activated Carbon	1.34
Silica	0.54
Zeolite 13X	2.02

4. Examples – V Investigating the Surface Hydrophobicity

Breakthrough Curves with 2-Propanol/N_2



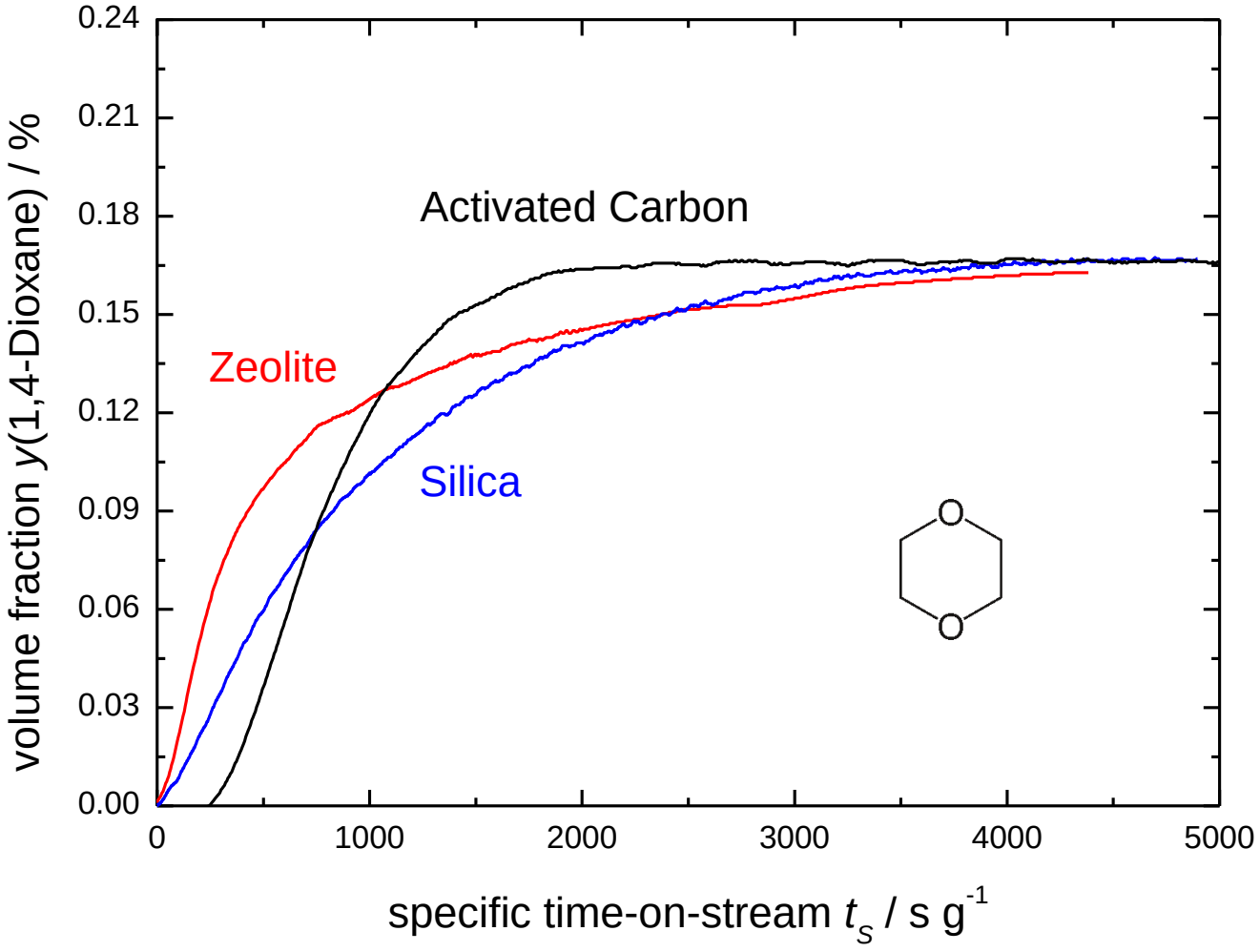
- 25 °C, Flow rate 2 L min^{-1}
- Pressure: 1 bar
- **Small** Adsorber with approx. 3 g of sample
- **0.645 g h^{-1} 2-Propanol in N_2**
  volume fraction *y*(2-Propanol) = **0.2 %**,
  p/p_0 = **0.033 @ 25 °C**

Asorbent	Loading / mmol g^{-1}	Factor (Cyclohexane)
Activated Carbon	2.10	1.56
Silica	2.88	5.33
Zeolite 13X	3.41	1.69

- Does the smaller size of 2-Propanol play a role?

4. Examples – V Investigating the Surface Hydrophobicity

Breakthrough Curves with 1,4-Dioxane/N_2

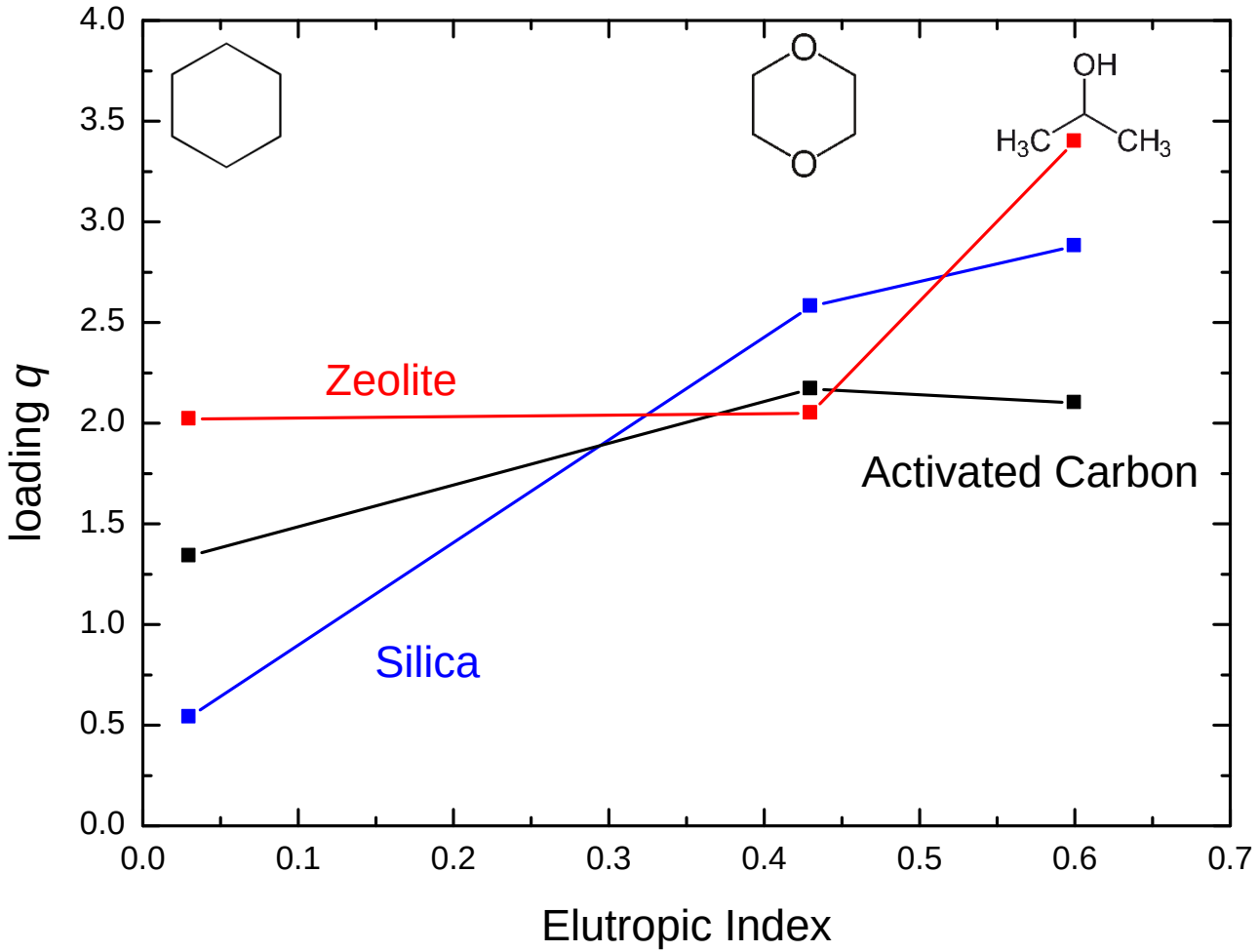


- 25 °C, Flow rate 2 L min^{-1}
- Pressure: 1 bar
- **Small** Adsorber with approx. 3 g of sample
- **0.782 g h^{-1} 1,4-Dioxane in N_2**
  volume fraction *y*(1,4-Dioxane) = **0.16 %**,
  p/p_0 = **0.033 @ 25 °C**

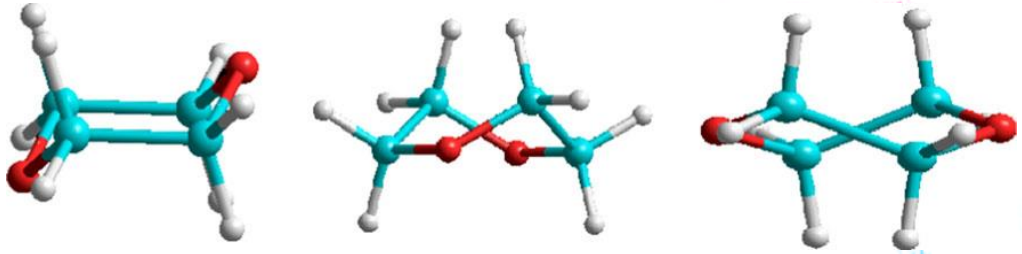
Asorbent	Loading / mmol g^{-1}	Factor (Cyclohexane)
Activated Carbon	2.17	1.62
Silica	2.58	4.78
Zeolite 13X	2.05	1.01

4. Examples – V Investigating the Surface Hydrophobicity

Comparison: Loading vs. Elutropic Index



- Silica appears to be least hydrophobic
- Maybe concentration still to high for Activated Carbon and Zeolite
  → Pore Filling?
- Conformation Changes of Cyclohexane and 1,4-Dioxane possible



→ **Further comprehensive investigations necessary**

R. Barata-Morgado *et al.*, *Theor Chem Acc* **2013**, *132*, 1157.

4. Examples – VI Applying Liquid Mixtures

Breakthrough Curves with Organic Vapor Mixtures

Removal of Solvent Mixtures

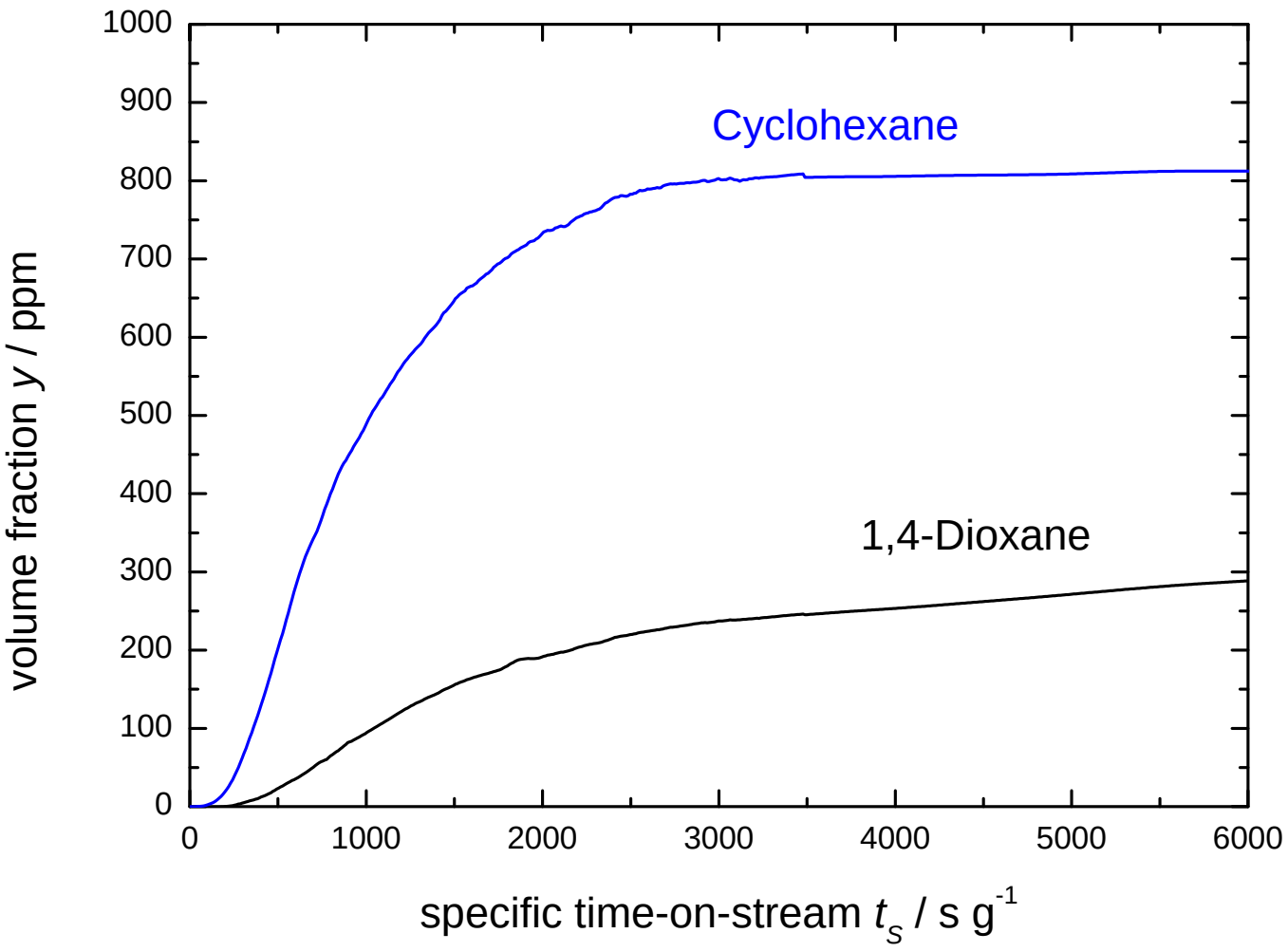
- Pharmaceutical Industry
- Pigment, Toner, Color, Paint Manufacturers
- Solvent Recovery

→ **Do the different Adsorptives influence each other?**

- Zeolite 13X and Activated Carbon D55/1.5
- 25 °C, Flow rate 2 L min^{-1}
- Pressure: 1 bar
- Small Adsorber with approx. 3 g of sample
- **800 ppm Cyclohexane + 300 ppm 1,4-Dioxane**
  (0.5 g h^{-1} Mix: 125.5 g Cyclohexane + 49 g 1,4-Dioxane)
- Mass Spectrometer

4. Examples – VI Applying Liquid Mixtures

Cyclohexane/1,4-Dioxane on Activated Carbon D55/1.5

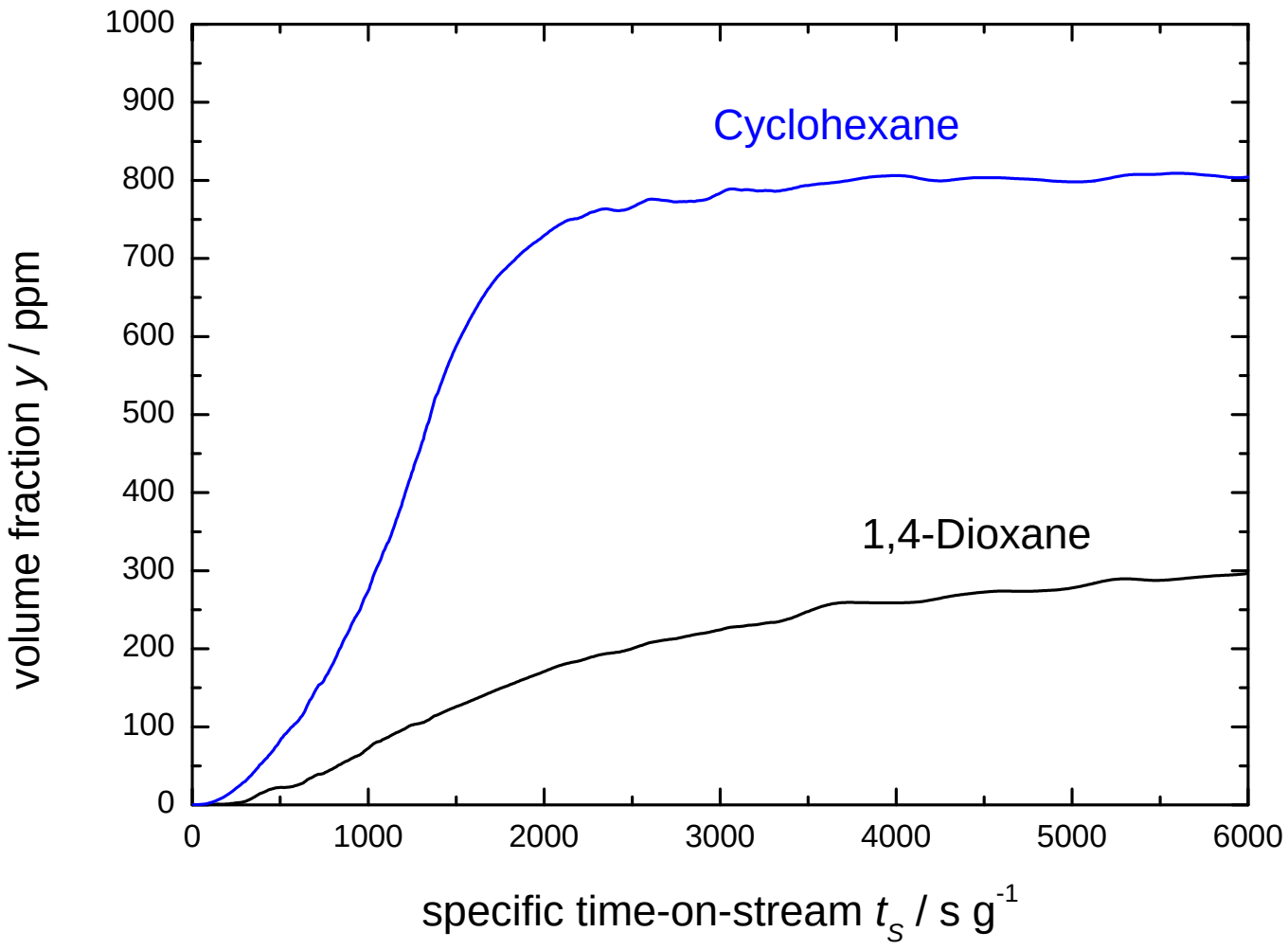


- Very long experiments
  - → Small Adsorber very useful for low concentrations
- No spontaneous Breakthrough
- Short technically usable sorption capacity BUT: Very high flow velocity at a very small fixed bed!
  - → very short residence time
- Small Adsorber only for equilibrated data!
- Loadings

Adsorptive	Loading / mmol g^{-1}
Cyclohexane	0.011
1,4-Dioxane	0.009

4. Examples – VI Applying Liquid Mixtures

Cyclohexane/1,4-Dioxane on Zeolite 13X



- Very long experiments
  - → Small Adsorber very useful for low concentrations
- No spontaneous Breakthrough
- Short technically usable sorption capacity BUT: Very high flow velocity at a very small fixed bed!
  - → very short residence time
- Small Adsorber only for equilibrated data!
- Loadings

Adsorptive	Loading / mmol g^{-1}
Cyclohexane	0.014
1,4-Dioxane	0.009

5. Conclusions

Characterization under application-related conditions!

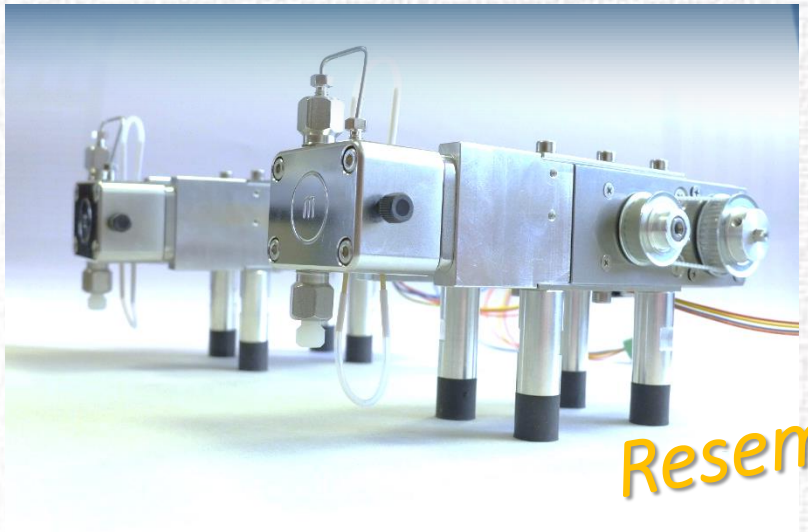
- mixSorb L is very versatile instrument for application-related studies
- Vapor Option
  - ✓ **Vapor Sorption, determine Isotherms, Mixture Isotherms**
  - ✓ Breakthrough curves of other Adsorptives in the Presence of Water
  - ✓ Adsorption Studies of Organic Vapors: VOC adsorption
- Broad Concentration Range (from ppm to high %)
  - ✓ Different Massflow Controllers
  - ✓ Different Adsorber Sizes → Reasonable measurement time
- Mass Spectrometer allows experiments with more complex gas/vapor mixtures

  → investigation of competitive adsorption possible

Thank You!

Thank you for your attention!

mixSorb L Liquid Compression Pumps



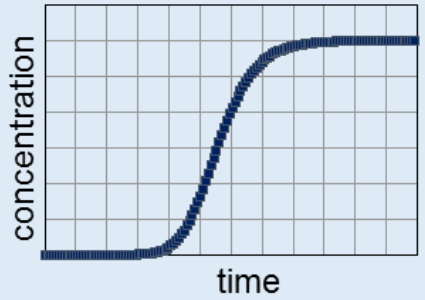
Star Wars® Imperial Walker »AT-AT«

Resemblance…

2. Gas Flow Methods

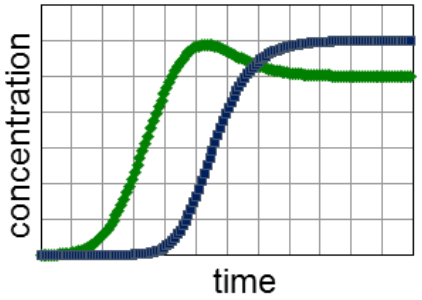
mixSorb L

Standard Breakthrough Curves



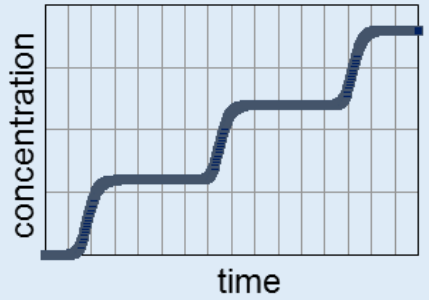
- Breakthrough time
- Mass Transfer
- Technically usable Sorption Capacity
- Modelling

Multicomponent Adsorption



- Competitive Adsorption
- Displacement

Isotherms



- Saturation Capacity
- Isotherms (single or **mixture**)

Cycle stability testing

- Regenerability
- Cycle-Stability

PSA-Emulation

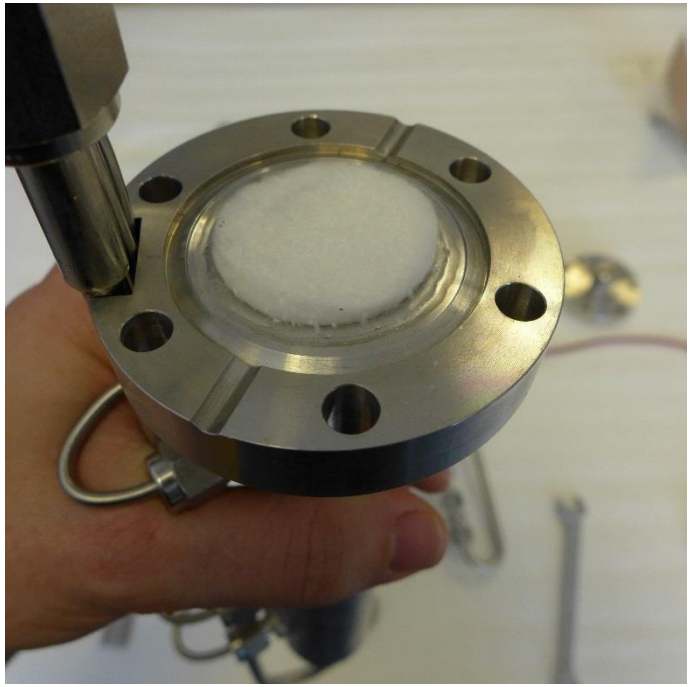
- Emulation of PSA
- Down-Scaling

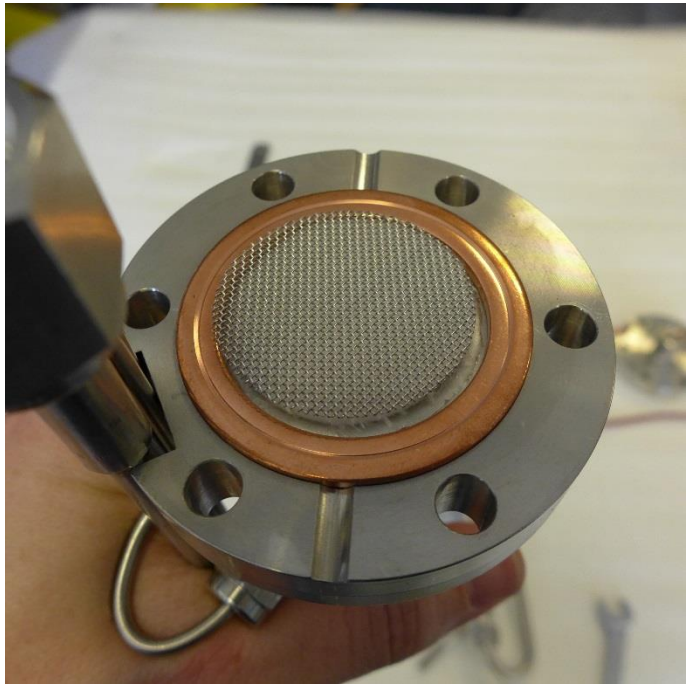
Chromatography

- Chromatographic parameters

3. mixSorb L Adsorber Sizes

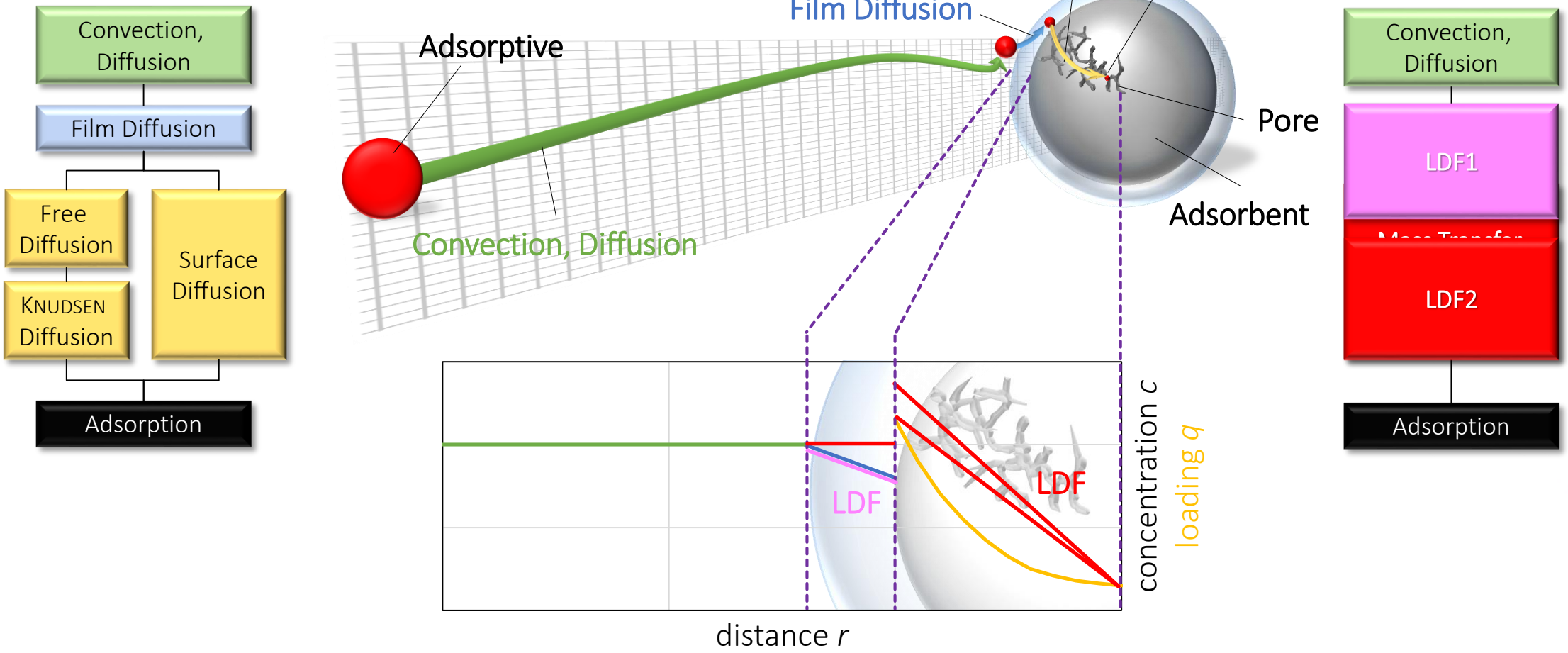
mixSorb L Adsorber Packing:





4. Simulation

Mass Transfer coefficient k_{LDF}



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W. Kast, *Adsorption aus der Gasphase: Ingenieurwissenschaftliche Grundlagen und technische Verfahren*, 1.Aufl., VCH Wiley Verlag, Weinheim, **1988**.