# InfraSORP - Speeding up Characterization of Functional Materials by Optical Calorimetry


Dr. Nicole Klein

nicole.klein@iws.fraunhofer.de

+49 351 83391 3719

Department of Chemical Surface and Reaction Technology

Fraunhofer Institute for Material and Beam Technology IWS

Dresden / Germany



LEIPZIGER SYMPOSIUM
DYNAMISCHE SORPTIONSVERFAHREN
30.05.2017





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# Outline

- Motivation
- Demands on screening device
- Measuring principle of optical calorimetry
- Adsorption screening by optical calorimetry
- Application
- Conclusion

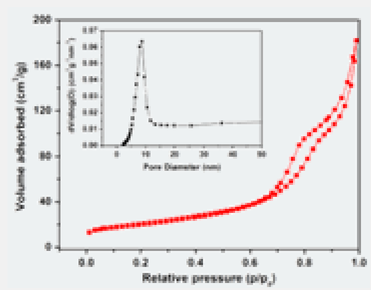
# Motivation

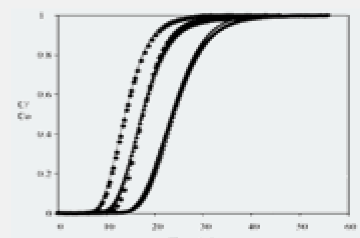
**Porous material**

Activated carbon
Zeolites
MOFs

**Characterization**

Common methods
are <u>time-consuming</u>



**Application**

Toxic Gas Adsorption
Separation
Air Purification
Catalysis

**Speed-up by optical calorimetry**

# Demands on a screening device

**Screening** - engl. „to screen“: check, select, filter

Quick

5 minutes

Minimal effort

Ambient conditions

Simple handling

Parallelization

12 samples parallel

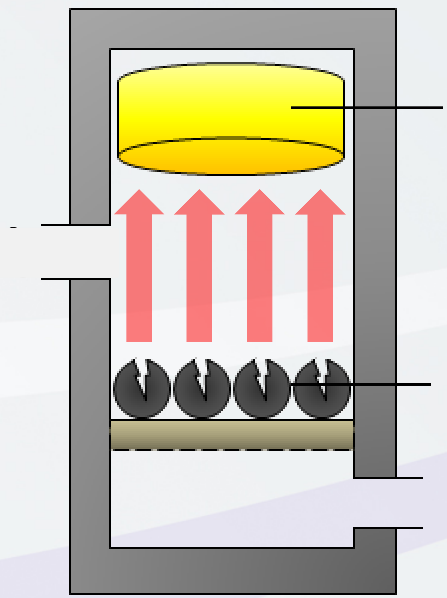
High sample throughput

Automatization

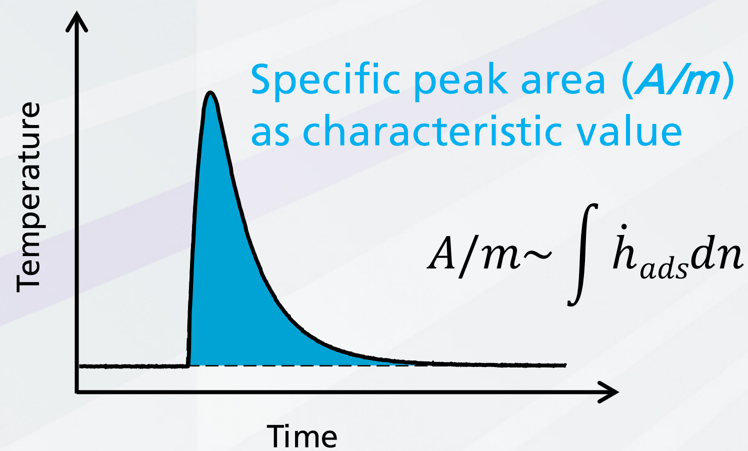
Screening of functional materials
by optical calorimetry

# Measuring principle of optical calorimetry

**InfraSORP – Single cell setup**




**Thermal Response**

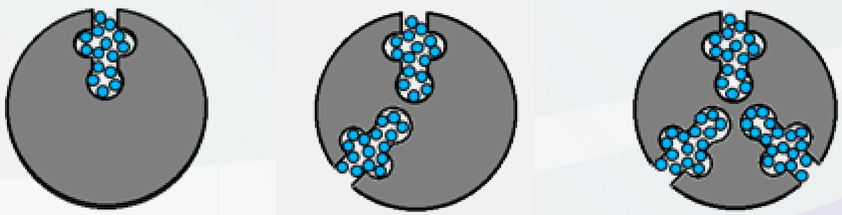


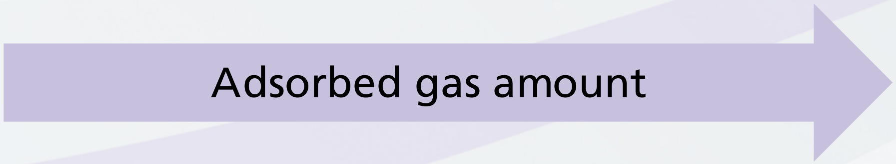

adsorption at ambient conditions
→ suitable test gas: *n*-butane, $CO_2$, $NH_3$, …

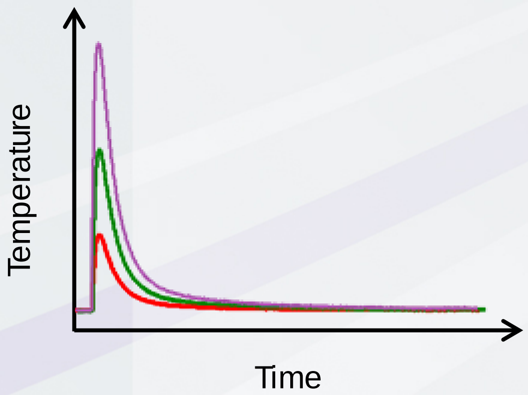
Accessible Information:

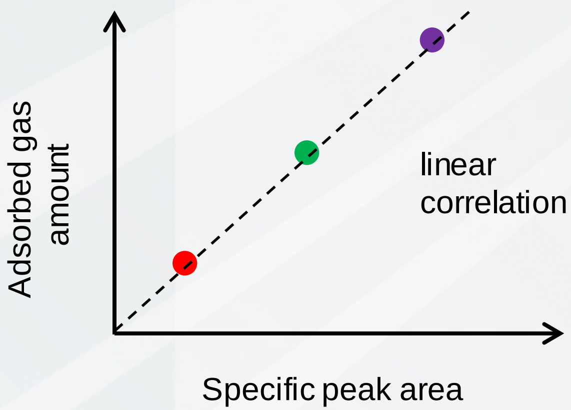
- Adsorption capacity
- Heat of adsorption
- Adsorption kinetics
- Heat transfer properties

# Measuring principle of optical calorimetry





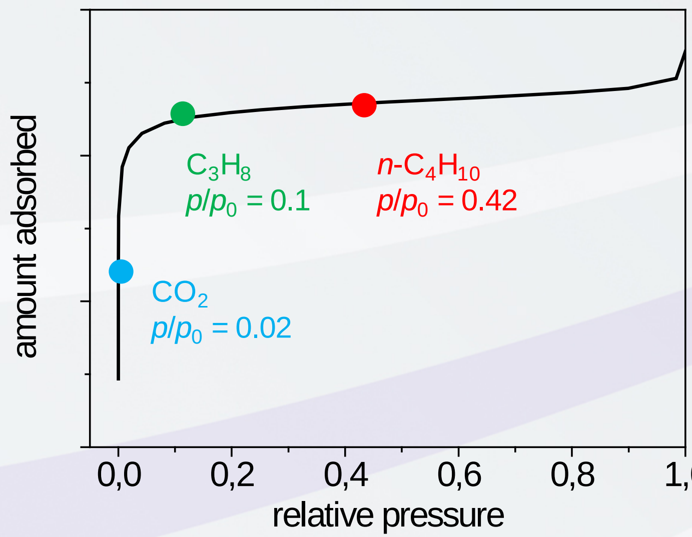



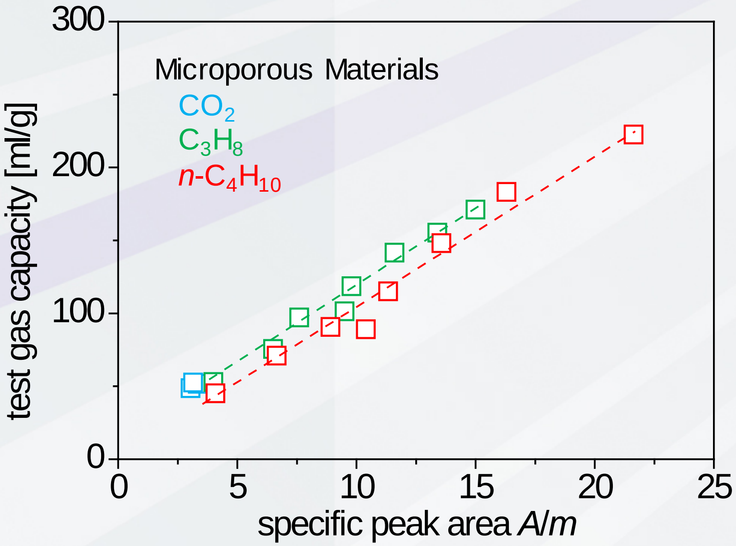
# Adsorption screening by optical calorimetry

## Adsorption capacity

InfraSORP measurement at ambient conditions (298 K, 1 bar)




Direct proportionality between test gas capacity and thermal response signal




P. Wollmann, M. Leistner, S. Kaskel et al. *Chem. Commun.* **2011**, *47*, 5151-5153.
M. Leistner, W. Grählert, S. Kaskel *Chem. Ing. Tech.* **2013**, *85*, 747 – 752.





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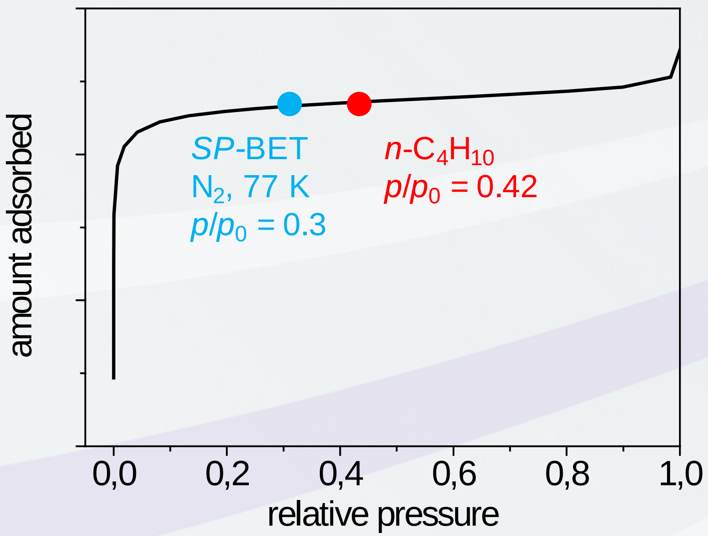
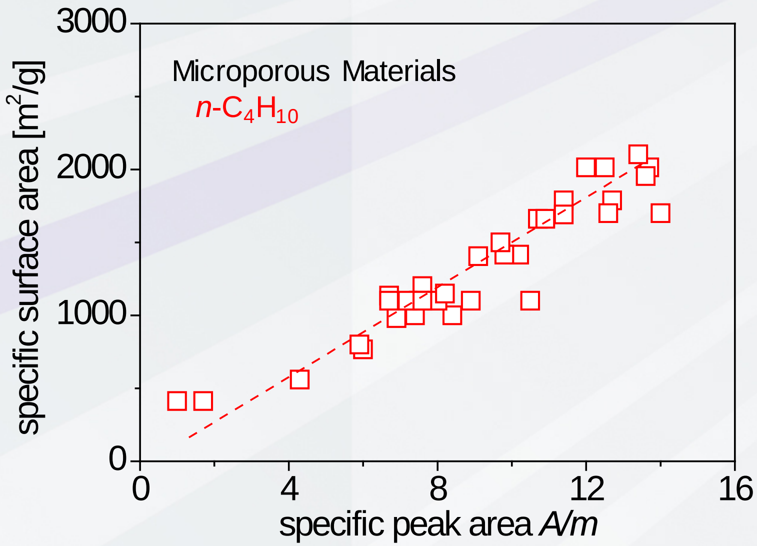
# Adsorption screening by optical calorimetry

## Specific surface area

InfraSORP measurement at ambient conditions (298 K, 1 bar)




Direct correlation between *SP*-BET surface area and specific peak area




**Determination of the specific surface area within 5 min**


P. Wollmann, M. Leistner, S. Kaskel et al. *Chem. Commun.* **2011**, *47*, 5151-5153.
M. Leistner, W. Grählert, S. Kaskel *Chem. Ing. Tech.* **2013**, *85*, 747 – 752.



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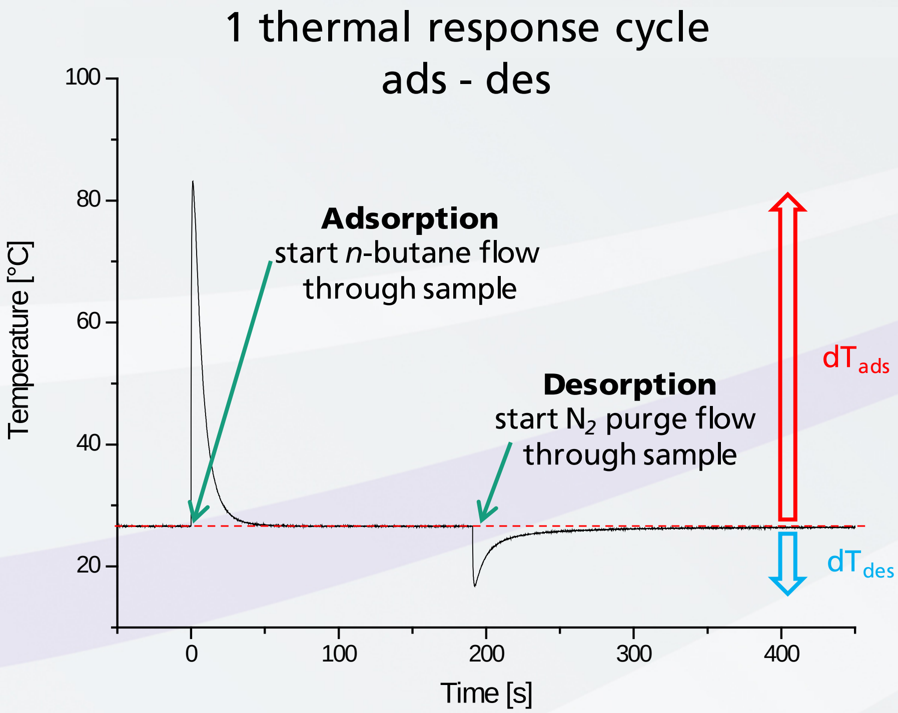
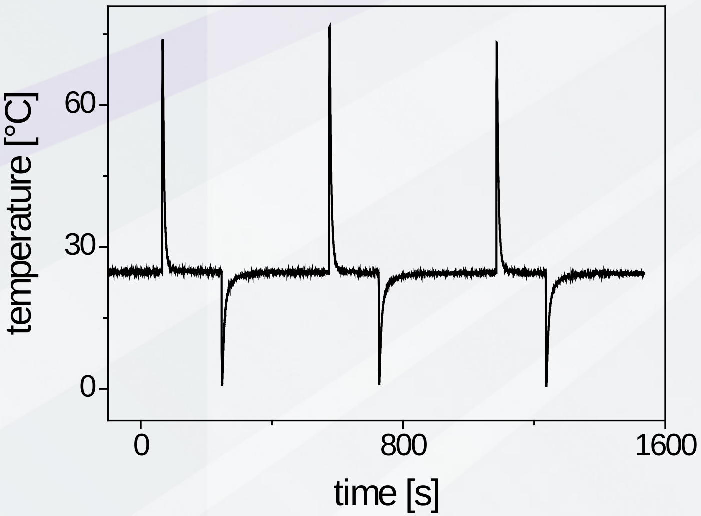
# Adsorption screening by optical calorimetry

## Cycling

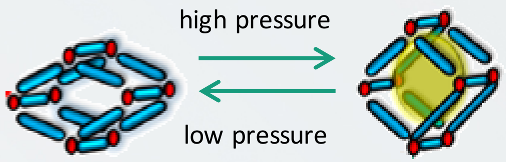


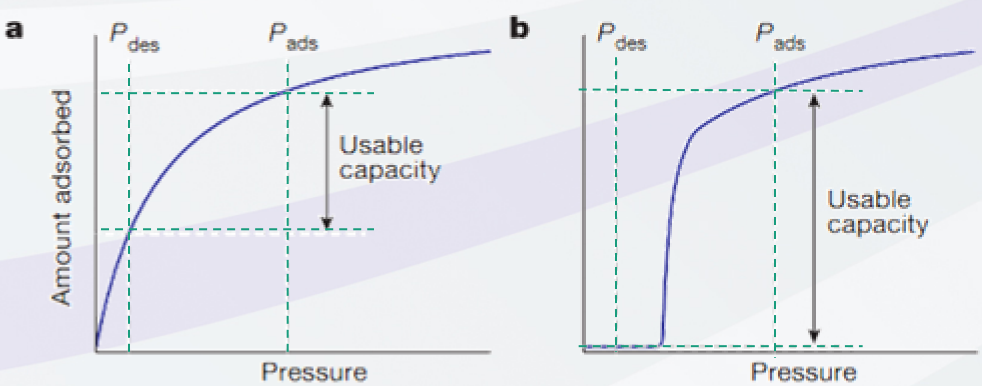
# Application

## Cycling stability studies of flexible MOFs

Gate opening effect of flexible MOFs

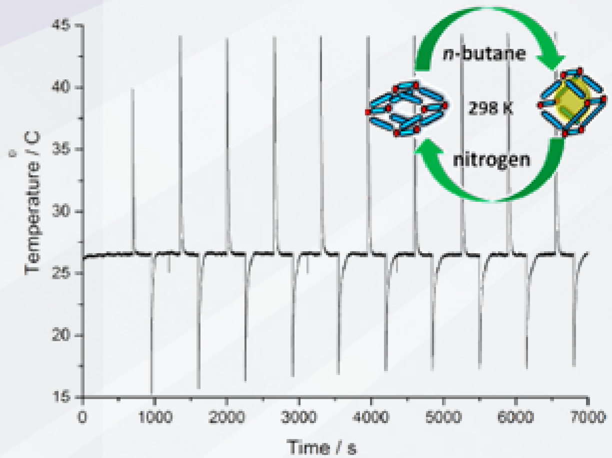



Flexible MOFs as promising materials for PSA




Necessity of cycling stability of flexible MOFs in PSA application

→ fast cycling stability studies by optical calorimetry




**100 cycles in 16 hours**

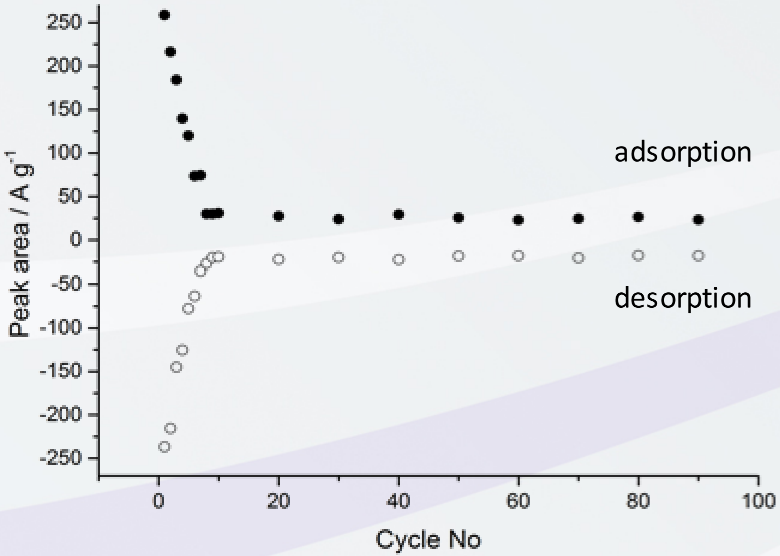
J. Long and coworkers *Nature* **2015**, *527*, 357
V. Bon, N. Kavoosi, I. Senkovska, S. Kaskel, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 22292 - 22300

# Application

## Cycling stability studies of flexible MOFs

Multiple *n*-butane adsorption/desorption cycling

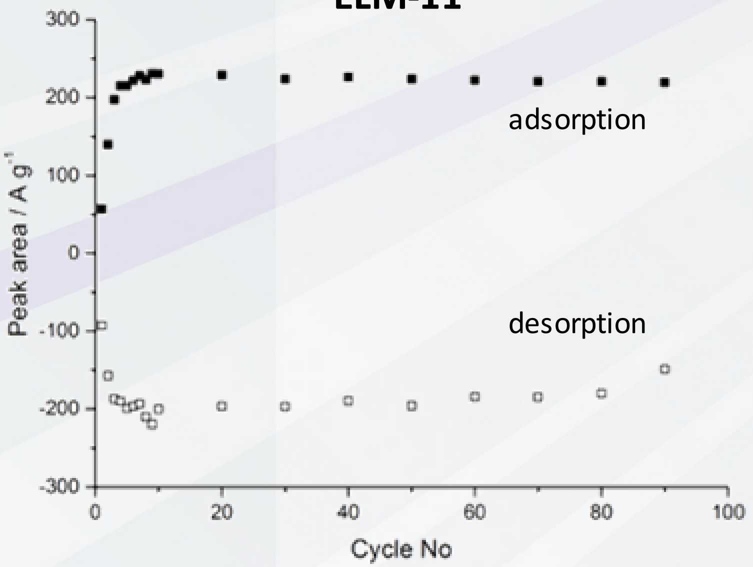
**DUT-8**




Capacity loss during the first cycles

→ Not suitable for PSA

**ELM-11**




Constant capacity of ELM-11

→ Suitable for PSA

V. Bon, N. Kavoosi, I. Senkovska, S. Kaskel, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 22292 - 22300

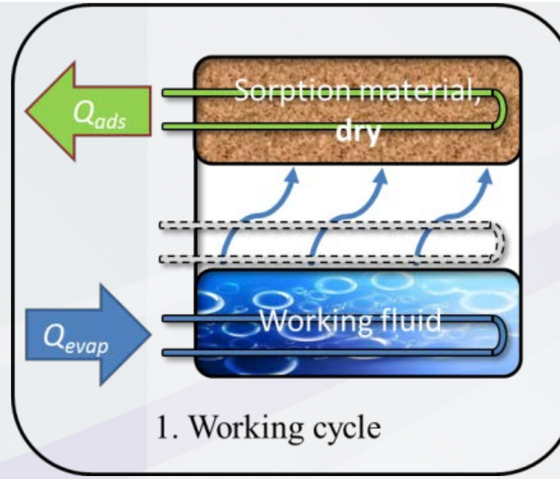
# Application

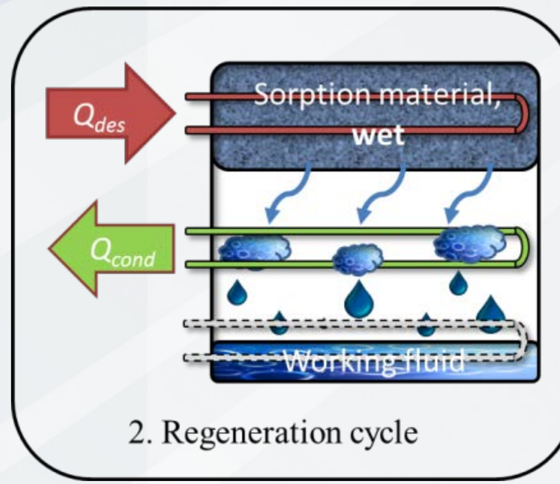
## Adsorption Heat Pumps: Heat and humidity management

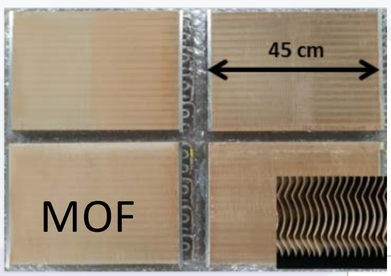
- Sorption-based heat-pumps feature a 2-phase process

  1. Working Cycle: evaporation and adsorption → e.g. cold production

  2. Regeneration Cycle: desorption and condensation → e.g. driving heat uptake




Heat exchange module

Fa. Vaillant, Invensor, Bosch

MIL-101, Al-fumarate etc.


J.-S. Chang et al., The Chemistry of MOFs, S. Kaskel (Ed.), Wiley VCH, **2016;** C. Serre, G. Maurin et al., *Angew. Chem. Int. Ed.*, 54: 3664–3668; F. Jeremias et al. *New J. Chem*. **2014**, 38, 1846 – 1852; C. Janiak, S. K. Henninger et al. *Eur. J. Inorg. Chem*. **2012**, 2625 – 2634; *Eur. J. Inorg. Chem.* **2011**, 471–474; G. Férey et al., Chem. Soc. Rev., 37 (2008) 191.

# Application

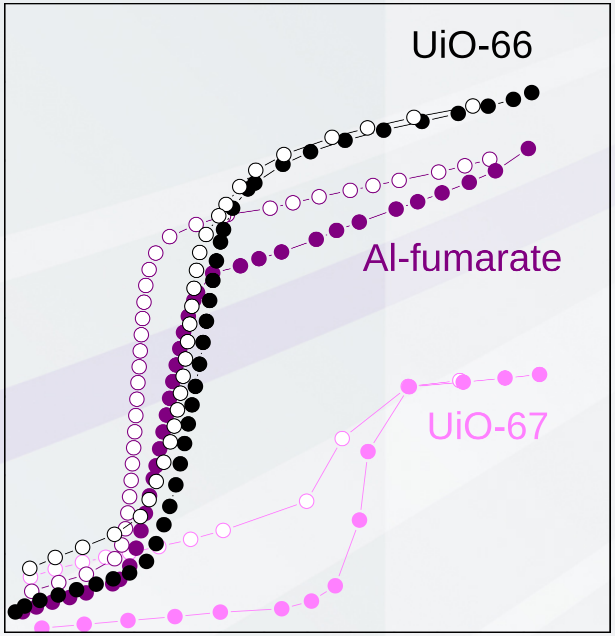
## Adsorption Heat Pumps: Heat and humidity management

**Why MOFs?**

- High capacities
- Stepwise adsorption isotherm → favorable for application!
- High working capacity
- Adjustable $p/p_0$ range, beneficial for regeneration cycle

**$H_2O$ isotherms, 298 K**

(3.2 kPa = 100 % humidity)




Kuesgens, P.; Rose, M.; Senkovska, I.; Froede, H.; Henschel, A.; Siegle, S.; Kaskel, S.: "Characterization of metal-organic frameworks by water adsorption", Microporous Mesoporous Mater. **(2009)**, 120(3), 325-330.





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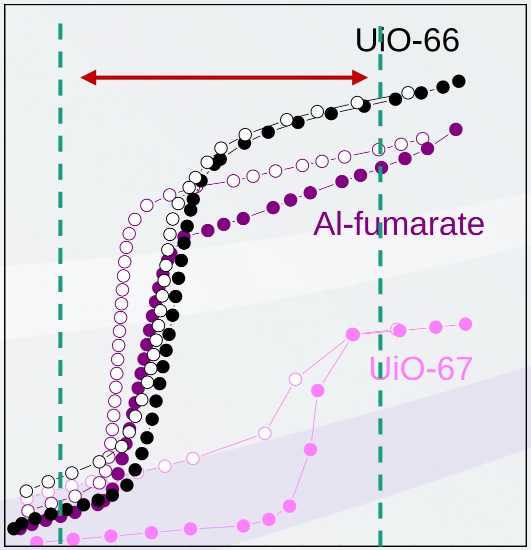
# Application

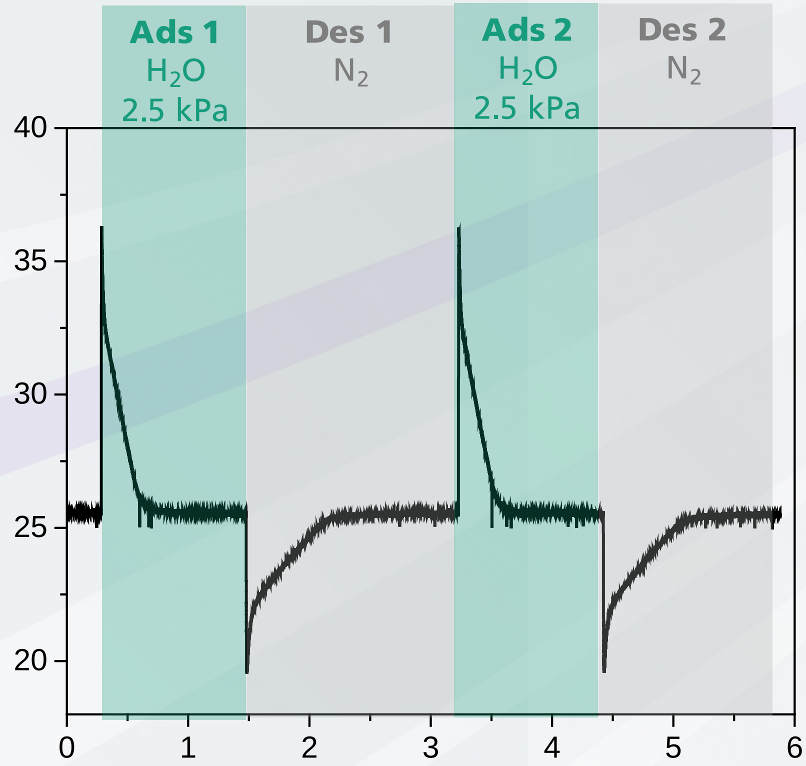
## Adsorption Heat Pumps: Heat and humidity management

### Water cycling stability studies

$H_2O$ isotherms, 298 K




Thermal response measurement
298 K, 1 atm




unpublished



M. Wöllner: Rapid Water Adsorption Cycling of Metal-Organic Frameworks by InfraSORP Technology, JFA, 8.3.2017

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# Application

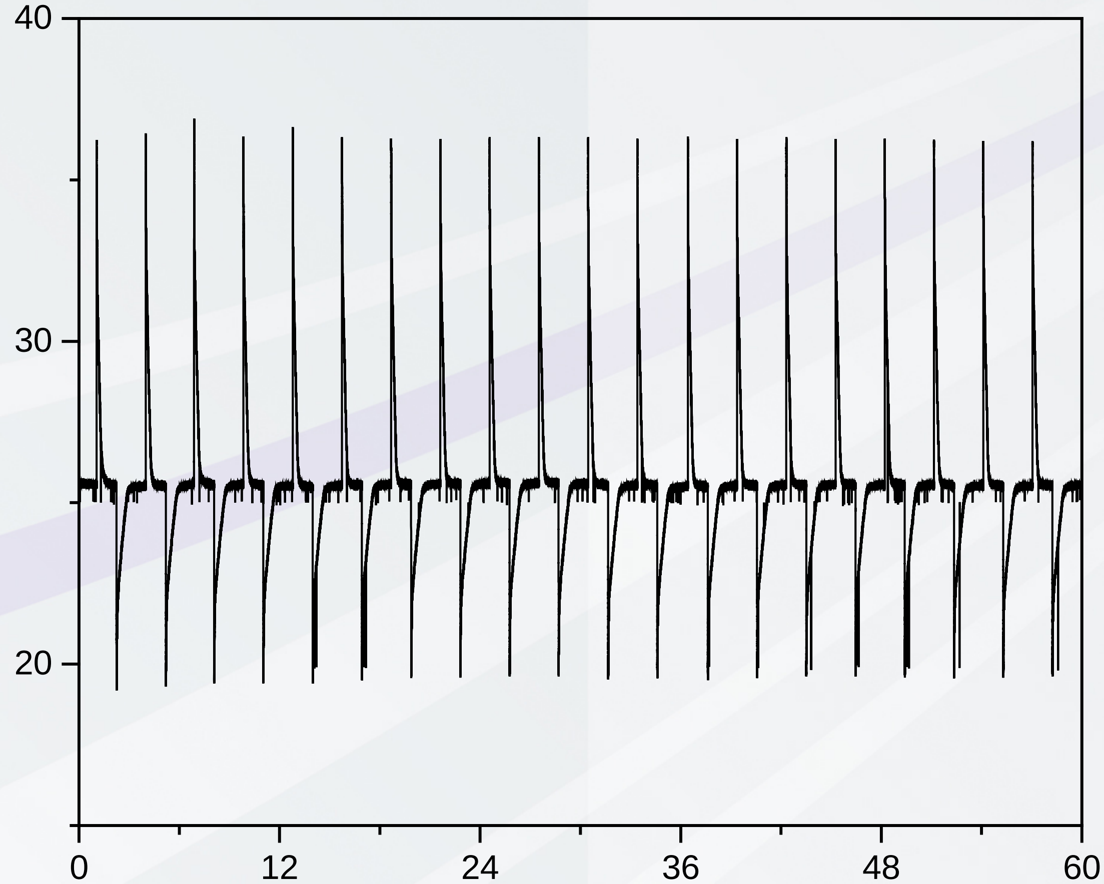
## Adsorption Heat Pumps: Heat and humidity management

**Water cycling stability studies**

**Al-fumarate**

2.5 kPa water vapor, 298 K

- Constant thermal response signal over 20 cycles → moisture stable
- 20 adsorption-desorption cycles in around 2.5 days
- Al-fumarate: among the stable MOFs



# Application

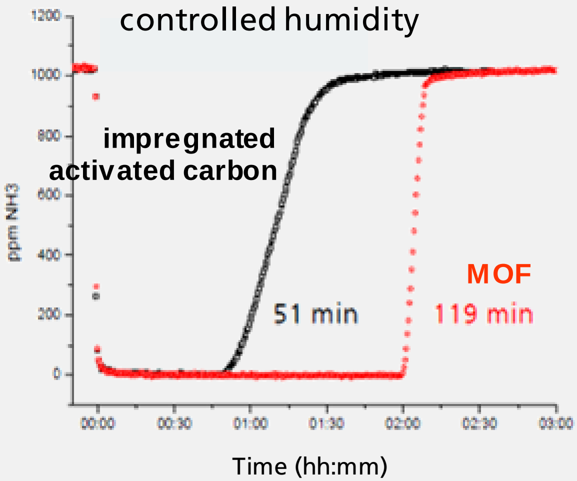
## MOFs for the Adsorption of TICs

MOFs as adsorbent material for toxic gas adsorption



Common characterization by breakthrough experiments

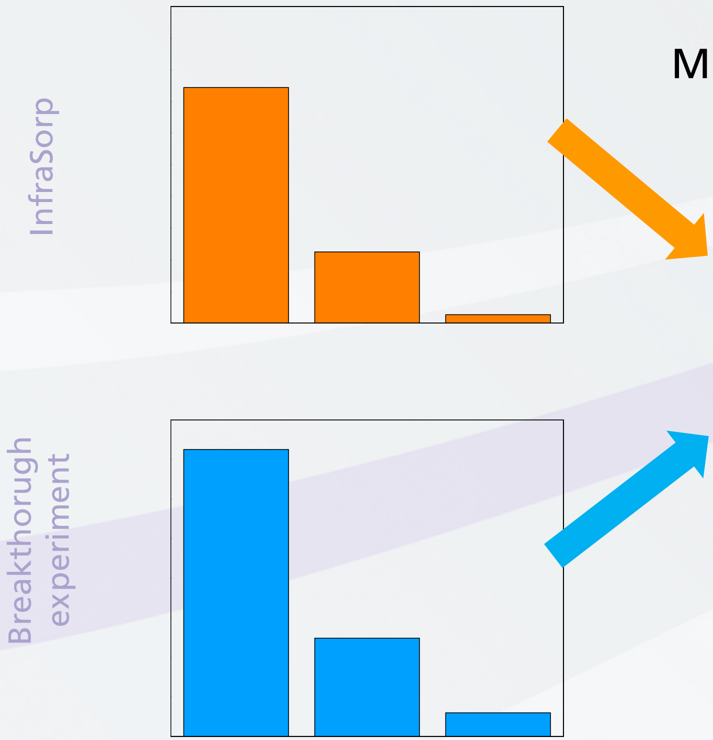
**1000 ppm $NH_3$, 293 K**
controlled humidity



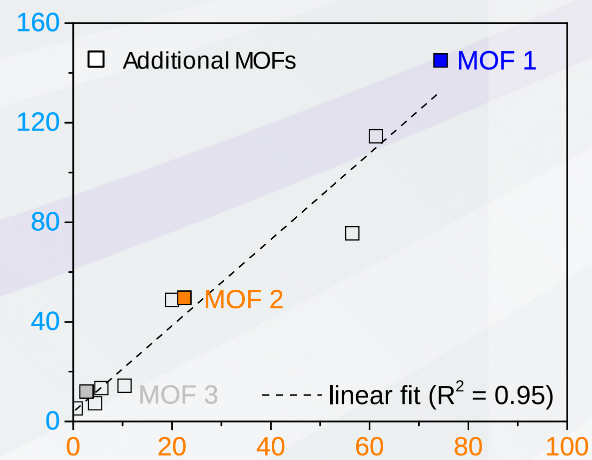

disadvantage: time-consuming

Solution: OPTICAL CALORIMETRY?

## Adsorption of $NH_3$ (5000 ppm)




MOF 1 > MOF 2 > MOF 3




**MOF 2**

$A/m$ = 23 Ks/mg

$C_{ads,fit}$ = 43 mg/g
$C_{ads,exp}$ = 50 mg/g

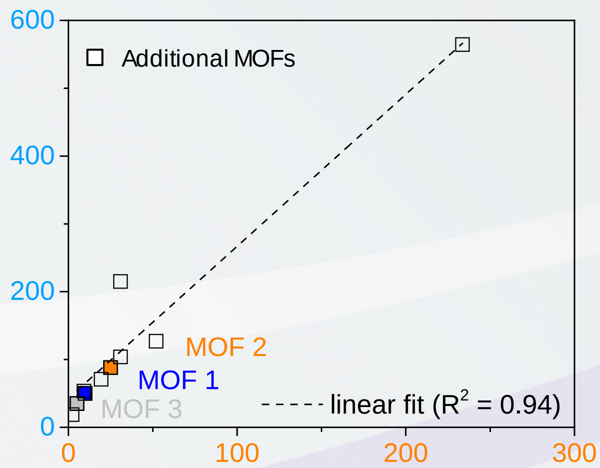
InfraSORP: 5 min
Breakthrough: 1.5 h

**20 times faster by using optical calorimetry**

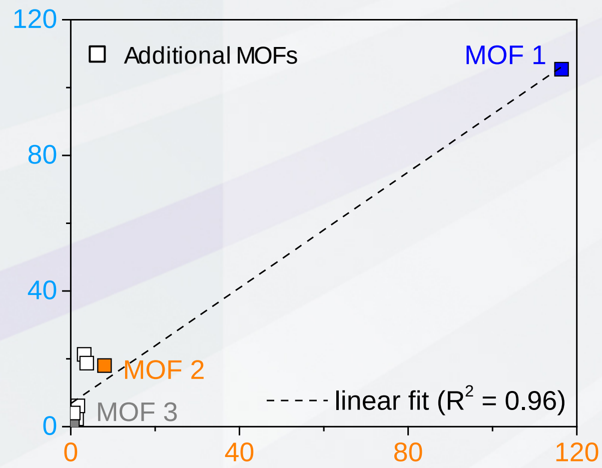
# Application

## MOFs for the Adsorption of TICs

### Adsorption of $NO_2$ (5000 ppm)




### Adsorption of $H_2S$ (5000 ppm)




**MOF 2**

$C_{ads,fit}$ = 94 mg/g
$C_{ads,exp}$ = 88 mg/g

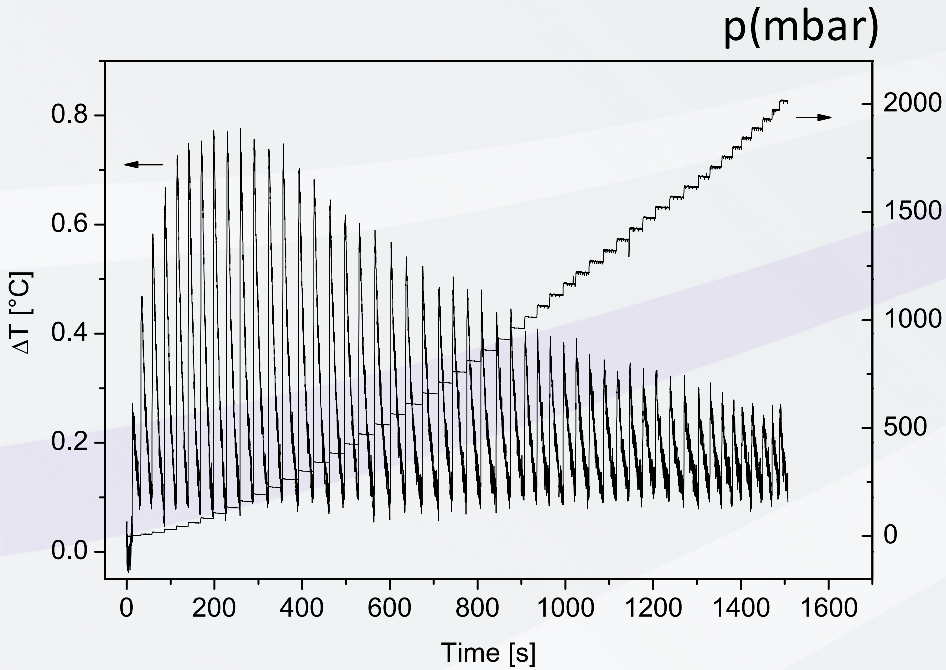
$C_{ads,fit}$ = 14 mg/g
$C_{ads,exp}$ = 18 mg/g

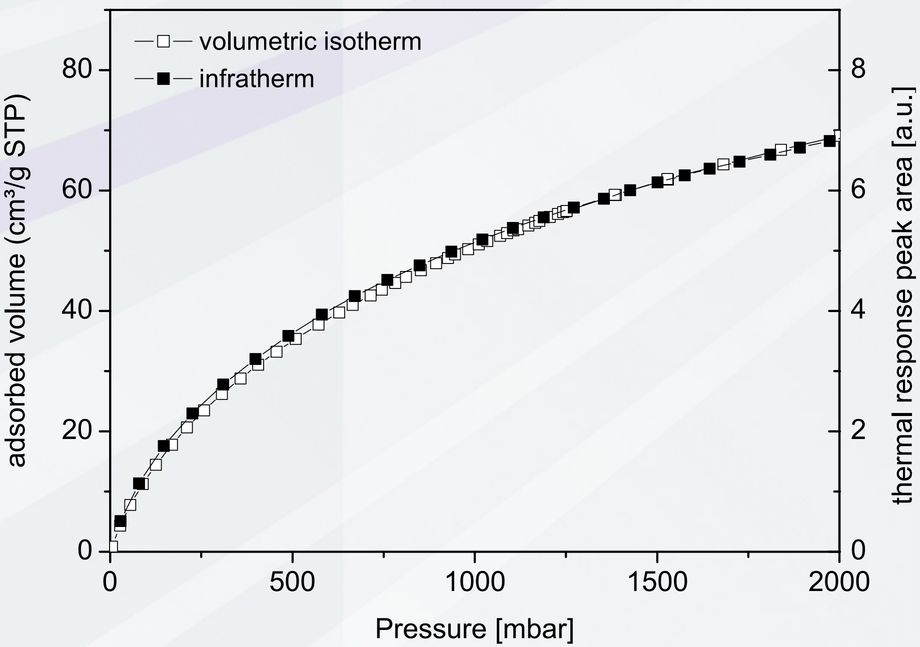
F. Sandra et al. *Ind. Eng. Chem Res.* **2015**, *54*, 6677 – 6682.

# Isotherm measurement by InfraSorp:
## Infratherm

### An optically measured Adsorption Isotherm:

- Static mode
- Step wise pulsing
- Peak area is plotted vs. equil. pressure




M. Leistner, W. Grählert, S. Kaskel, Chem. Ing. Tech. 2013;85:747-752





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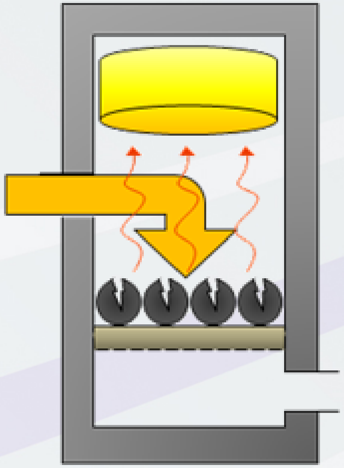
# Conclusion

## Optical calorimetry "InfraSORP"



### Characterization

- adsorption capacity
- specific surface area
- pore structure
- adsorption kinetic
- cycle stability
- chemisorption

### Application

- Catalysis
- Gas Separation
- Toxic Gas Adsorption
- Cycling stability
- Quality Control

### Advantages of optical calorimetry

+ simple (conditions, adsorptives)
+ small sample amount
+ automation and parallelization
+ quick (measurement in 5 min)





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# InfraSORP - Speeding up Characterization of Functional Materials by Optical Calorimetry

## Thank you for your attention!

Dr. Nicole Klein
Fraunhofer IWS
Winterbergstraße 28
01277 Dresden, Germany

Telefon +49 351 83391-3719
Fax +49 351 83391-3300
E-Mail nicole.klein@iws.fraunhofer.de


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