SEMPA®

Thin Film Solutions

Portfolio

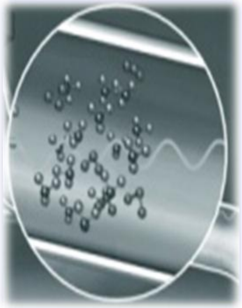
Chemical supply

systems

Bulk and

special gas

distribution



Engineering,

design and

development

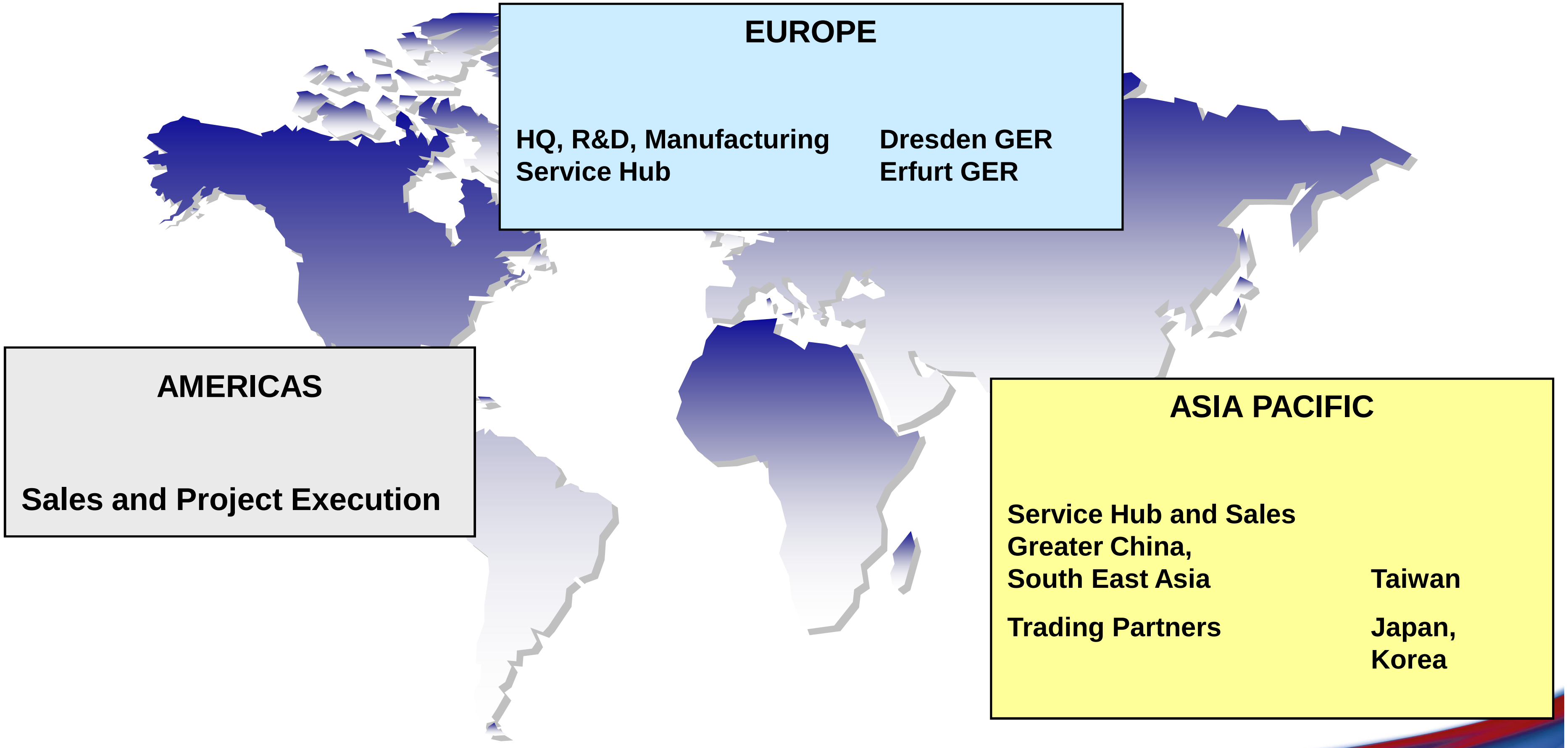
Service and

operation

Process vacuum

and exhaust systems

Global Structure



EUROPE

HQ, R&D, Manufacturing	Dresden GER
Service Hub	Erfurt GER

AMERICAS

Sales and Project Execution

ASIA PACIFIC

Service Hub and Sales Greater China, South East Asia	Taiwan
Trading Partners	Japan, Korea

Thin-Film Solutions

- HiBarSens

- Special equipment for thin film deposition (excerpt…)
  - DEZn supply for ZnO TCO layers
  - TMAl supply for AlOx backside passivation
  - PECVD for barrier layers – HMDSO…
  - Enabling III/V on Si
  - Special liquid Indium-MO source supply systems for IGZO
  - LED supply systems for MO-III (TMGa)
  - ….

HiBarSens

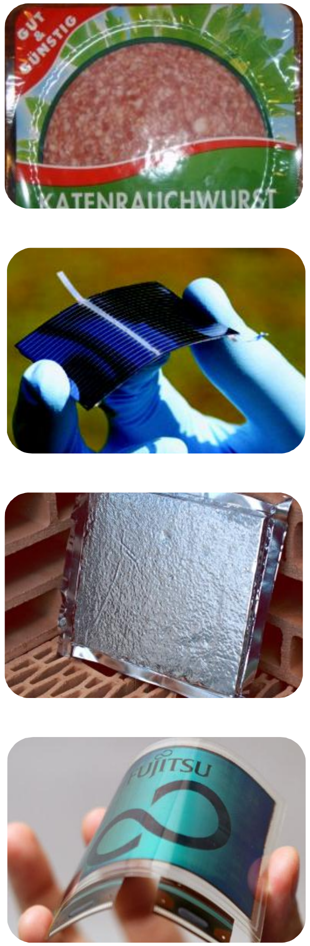
HBS 18-1

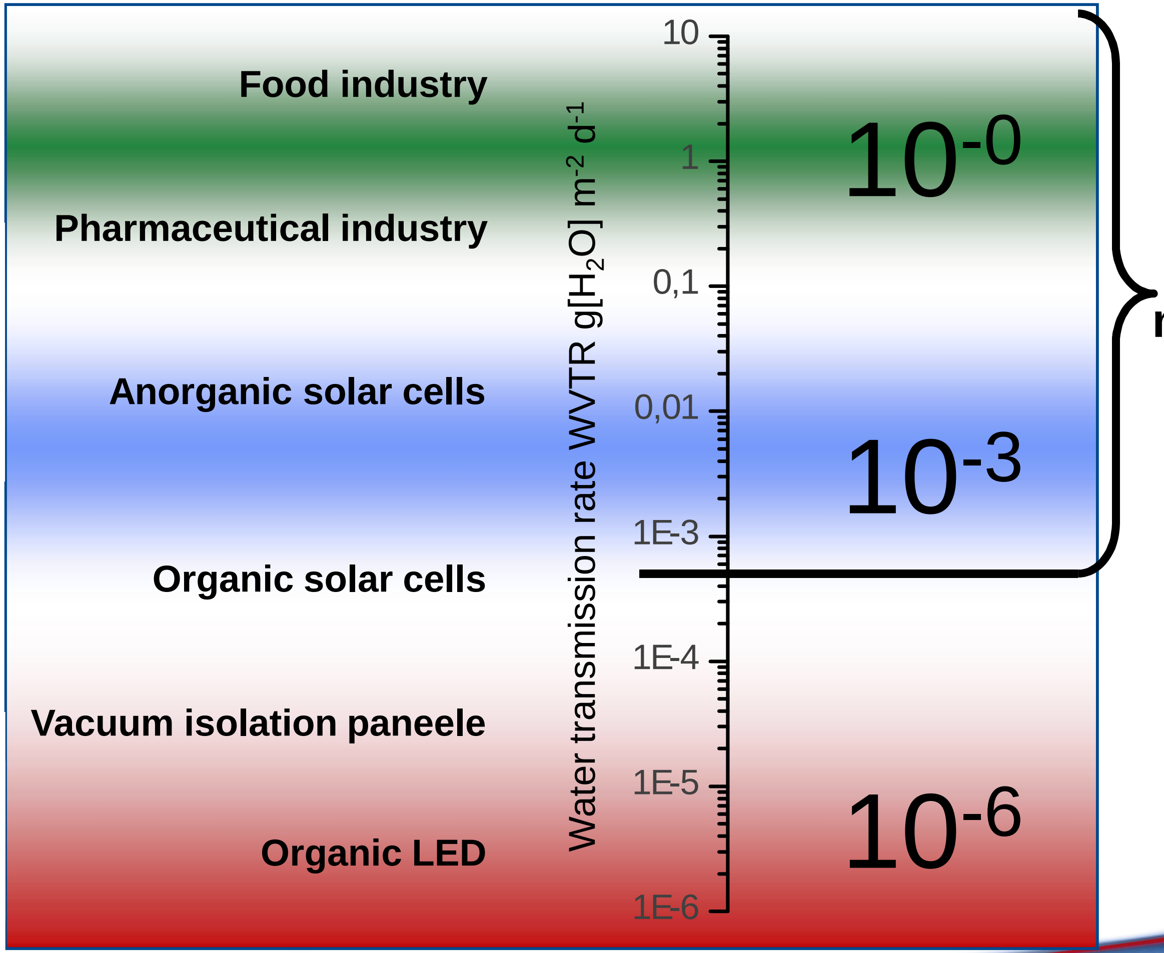
Water Vapor

Permeation

Measurement System

Summary: Starting point

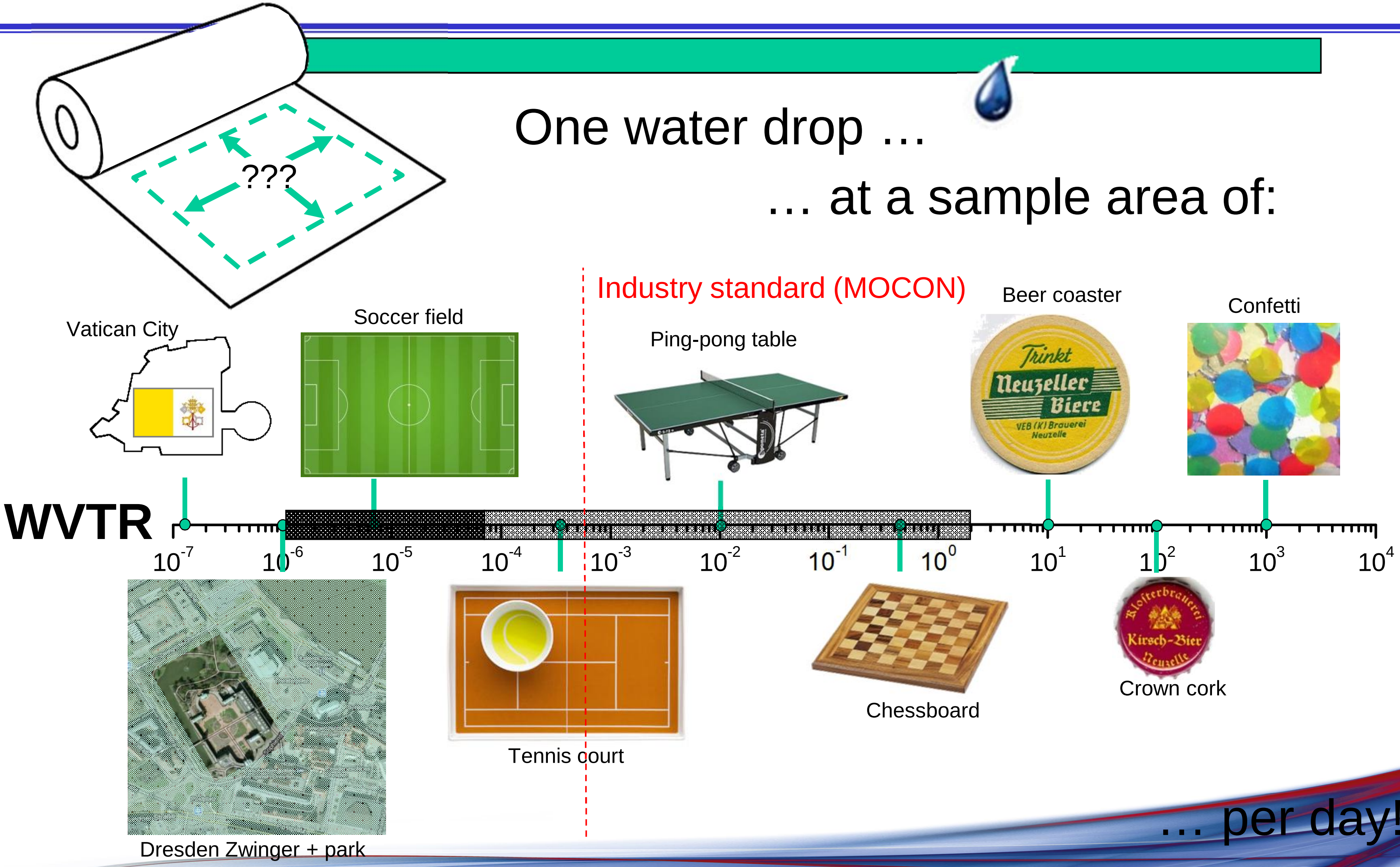




currently measurable by standard methods

?

WVTR of 10^{x} g m^{-2} d^{-1} is equivalent to:

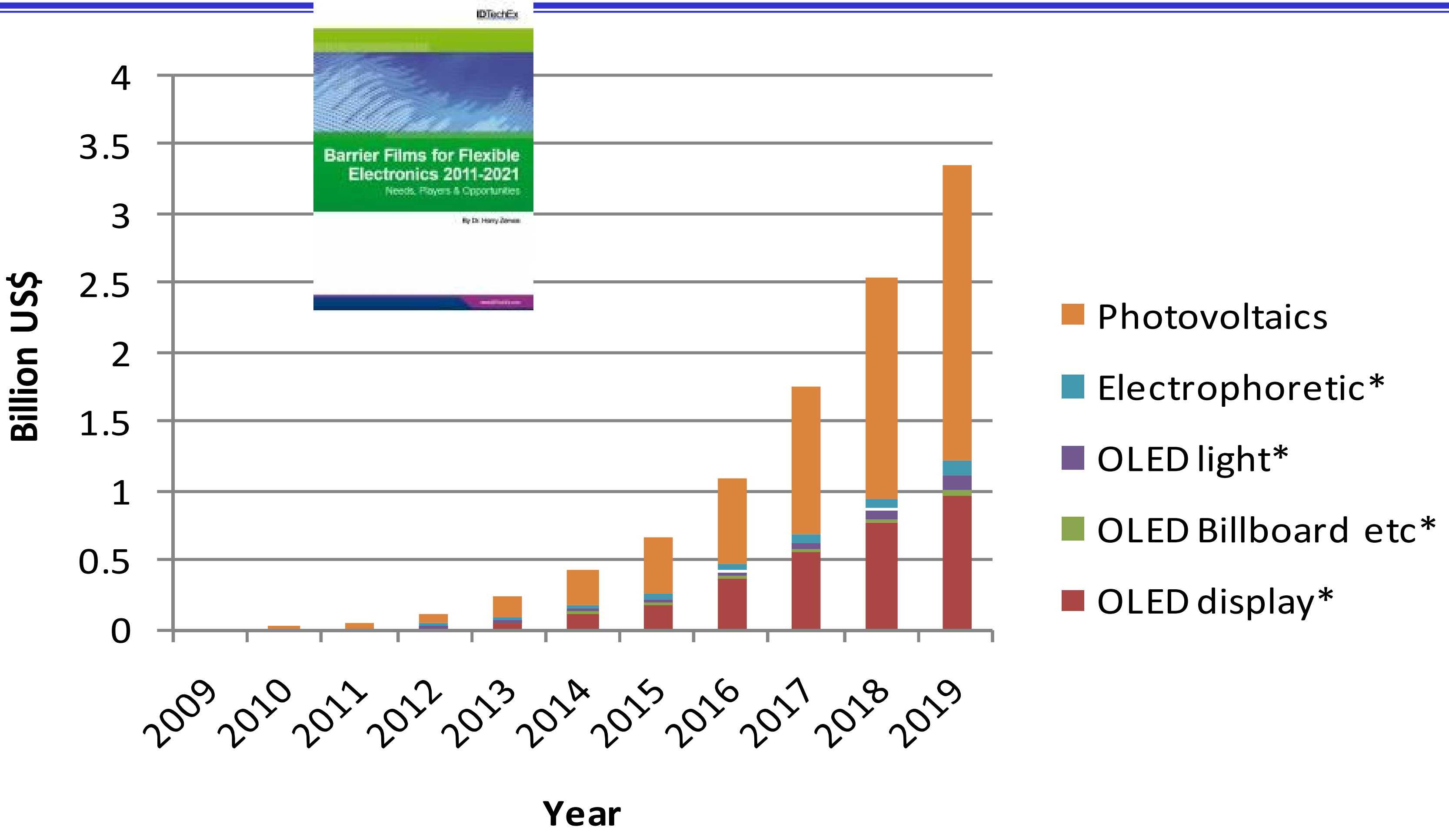


One water drop …

… at a sample area of:

… per day!

Market forecast for ultra barrier films



Harry Zervos: "Barrier Films for Flexible Electronics: Needs, Players &Opportunities". IDTechEx Ltd., December 2008)

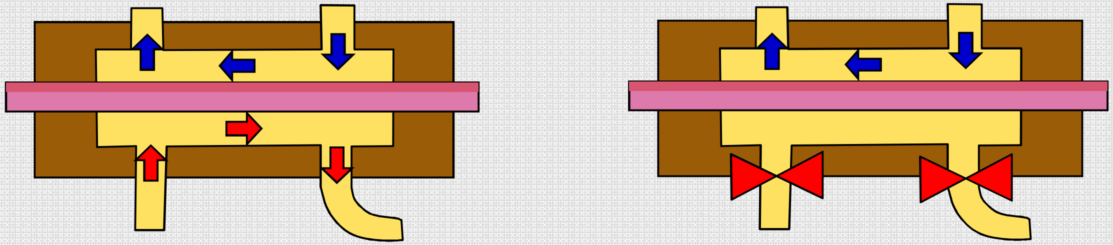
BASICS

Measuring modes: dynamic vs. static

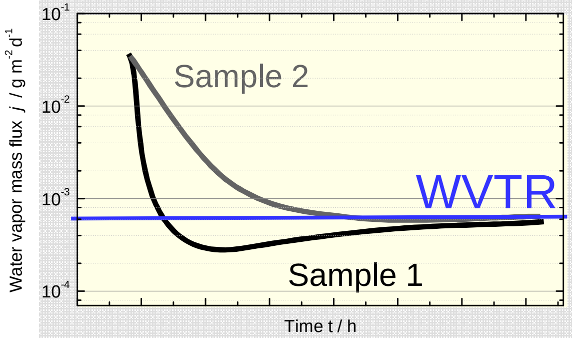
- Measuring setup:

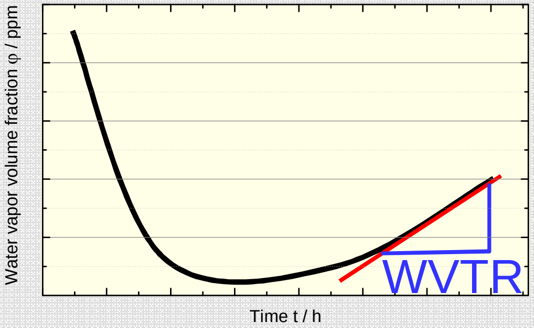
dynamic (isostatic)

static (quasi isostatic)



- Typical chart





- Calculation of WVTR

$$WVTR = \frac{\dot{V}_{Purge} \cdot M_{H_2O}}{R \cdot T \cdot A_{sample}} \cdot p \cdot \frac{\varphi}{1-\varphi}$$

$$WVTR - \dot{n}_{sorp} = \frac{V_{cell}}{R \cdot T} \cdot \frac{M_{H_2O}}{A_{sample}} \cdot \frac{p \cdot \Delta\varphi}{\Delta t}$$

φ … Water vapor volume fraction (measured by LDS)

The LASER as a sensor

- Tunable diode laser absorption spectroscopy (TDLAS)

  Limit of Detection LOD(H_2O): 100 ppb m

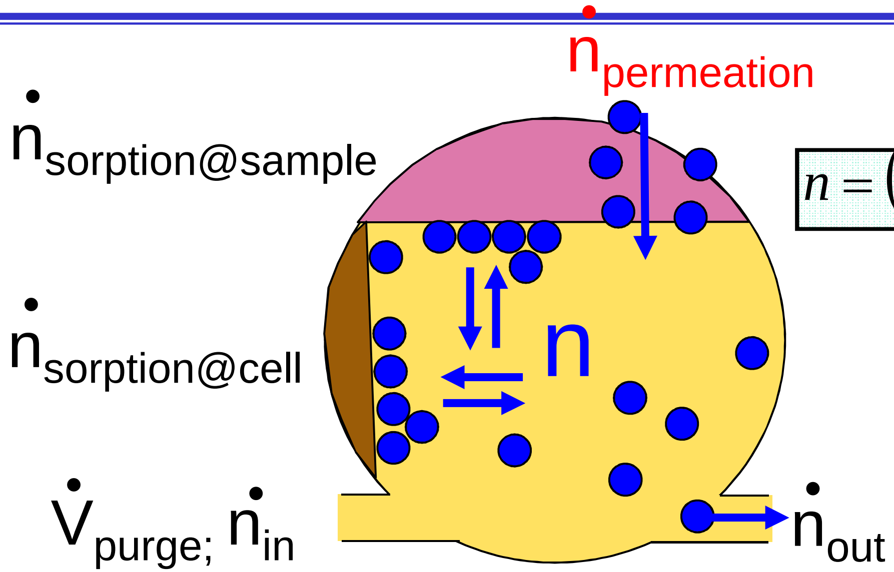
- Measuring setup:

	dynamic	static
Sample size	100 cm^2	
Chamber volume	0,1 l	
Accumulation time	-	10 h
Purge flow	0,01 slm	-
Optical path length	1 m	
	~ 10^{-5} g m^{-2} d^{-1}	~ 10^{-6} g m^{-2} d^{-1}

!Theoretical estimations!

- WVTR < 10^{-4} g m^{-2} d^{-1} are measurable

Balance equation for dynamic



n = amount of substance (moisture)

General balance equation

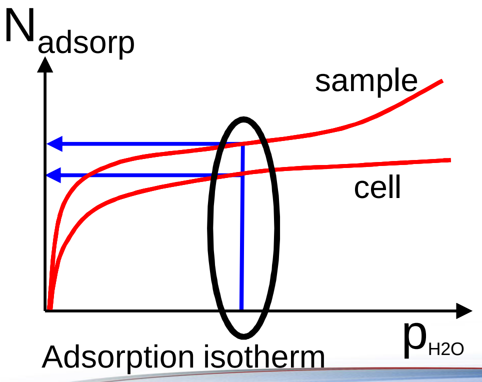
$$n = \left(\dot n_{in} + \dot n_{perm} + \dot n_{sorpt} + \dot n_{leak} - \dot n_{out}\right)\cdot \Delta t + n_o$$

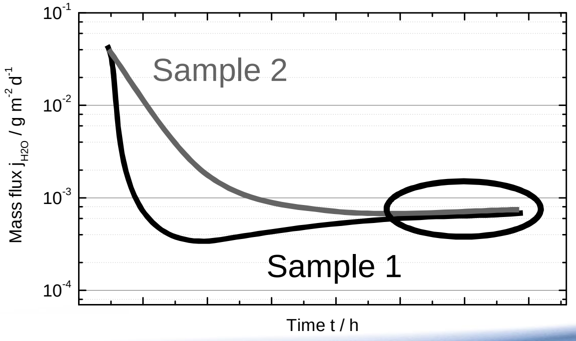
Steady-state conditions

$$\dot n_{sorption} = \dot n_{desorption} - \dot n_{adsorption} = 0$$

$$p - p_0 = 0$$

$$n - n_0 = \left(\dot n_{perm} - \dot n_{out}\right)\cdot \Delta t = const.$$



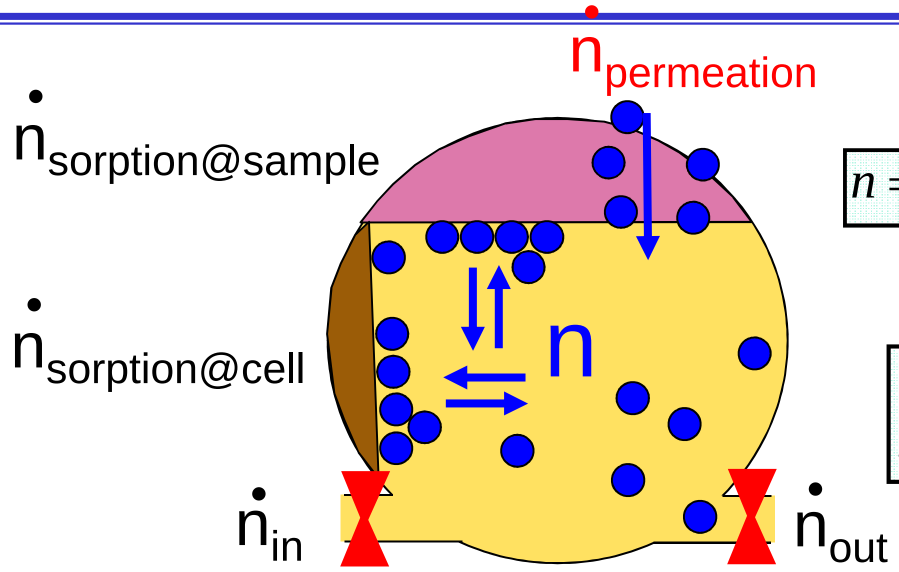


Calculation of WVTR

$$n = \left(\dot n_{perm} - \dot n_{out}\right)\cdot \Delta t + n_o$$

$$WVTR = \frac{\dot V_{Purge}\cdot M_{H_2O}}{R\cdot T\cdot A_{Sample}}\cdot p\cdot \frac{\varphi}{1-\varphi}$$

Balance equation for static setup



n = amount of substance (moisture)

General balance equation

$$n = \left(\dot n_{in} + \dot n_{perm} + \dot n_{sorpt} + \dot n_{leak} - \dot n_{out}\right)\cdot \Delta t + n_o$$

„non constant“ conditions

$$\dot n_{in} = \dot n_{out} = 0;\quad \dot n_{perm} = const$$

$$\dot n_{sorption} = \dot n_{adsorption} - \dot n_{desorption} > 0; \qquad p - p_0 > 0$$

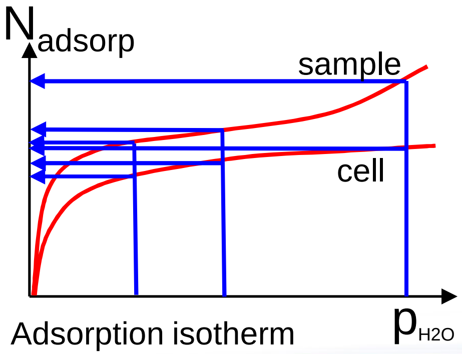
Calculation of WVTR

$$n = \left(\dot n_{perm} + \dot n_{sorpt}\right)\cdot \Delta t + n_o$$

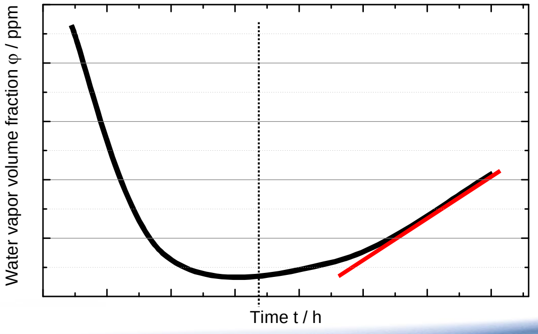
$$WVTR = \dot n_{perm}\frac{M_{H_2O}}{A_{Sample}} = \frac{\Delta n}{\Delta t}\cdot\frac{M_{H_2O}}{A_{Sample}}$$

$$WVTR = \frac{V_{cell}}{R\cdot T}\cdot\frac{M_{H_2O}}{A_{Sample}}\cdot\frac{p\cdot\Delta\varphi}{\Delta t}$$

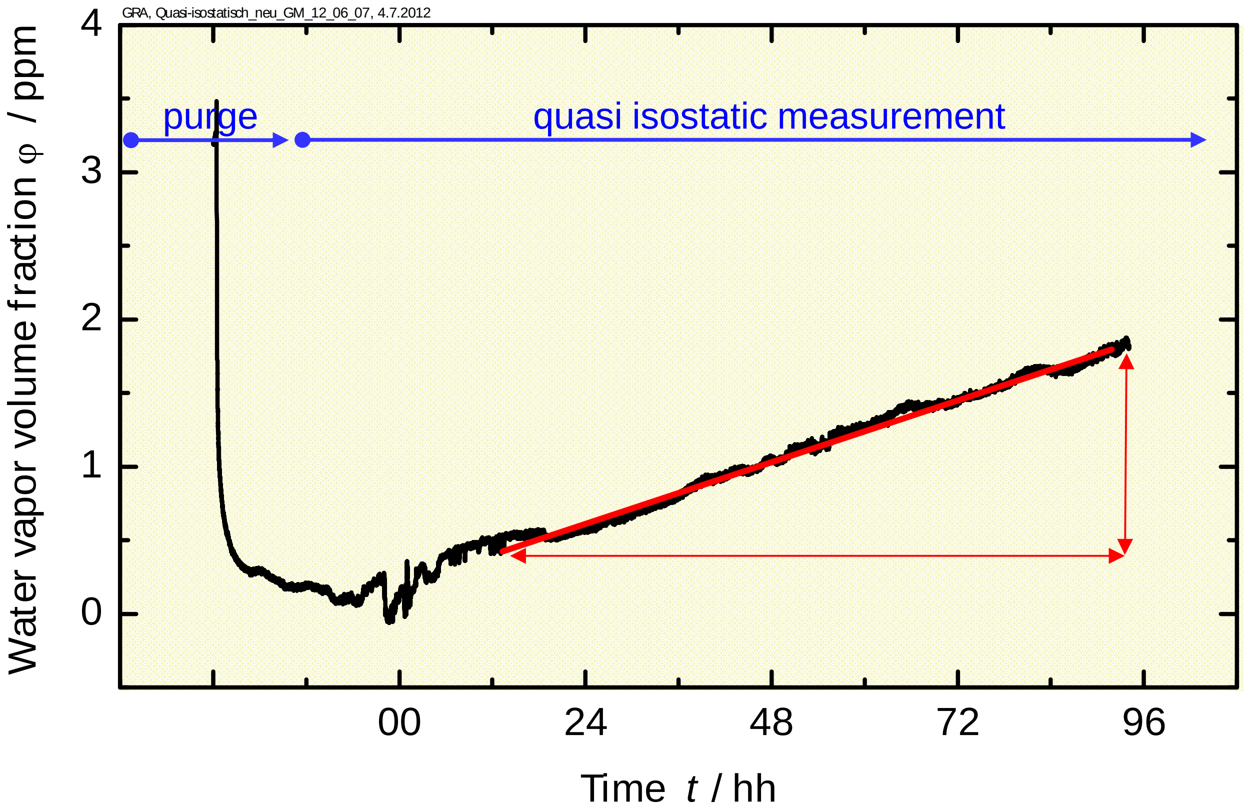
$$WVTR - \dot n_{sorp} = \frac{V_{cell}}{R\cdot T}\cdot\frac{M_{H_2O}}{A_{Sample}}\cdot\frac{p\cdot\Delta\varphi}{\Delta t}$$



Adsorption isotherm



Static measurement: Background level

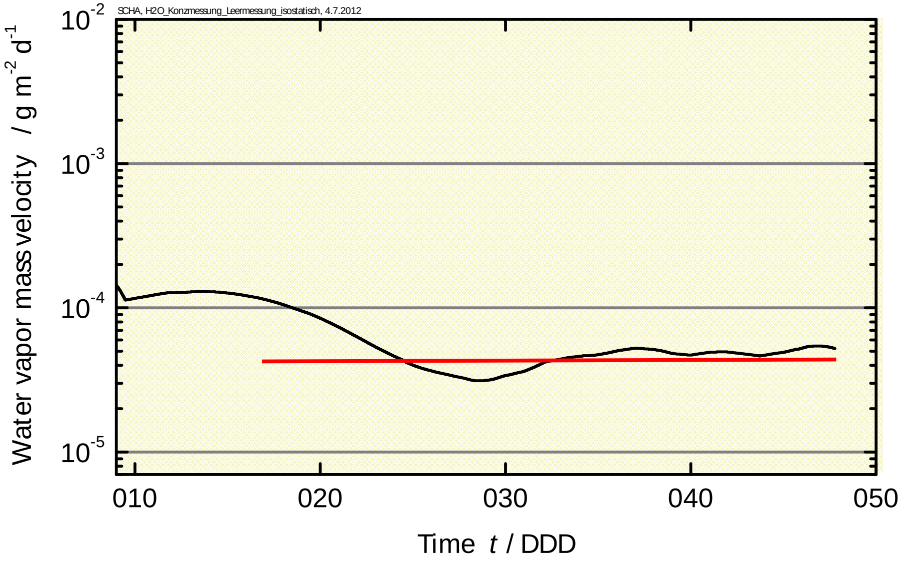


Measured background level
(sample: stainless steel)
@ 38°C / 90% r.H.

$\mathrm{WVTR_{qis}} = 2{,}5 \times 10^{-6}\ \mathrm{g\ m^{-2}\ d^{-1}}$

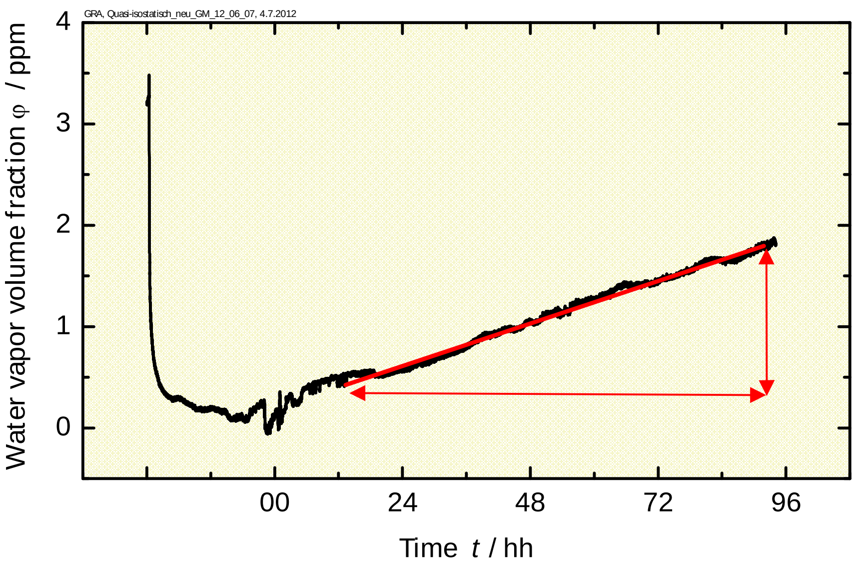
Dynamic vs. Static: background level

Dynamic setup



WVTR$_{qis}$ = 5x 10^{-5} g m^{-2} d^{-1}

Static setup

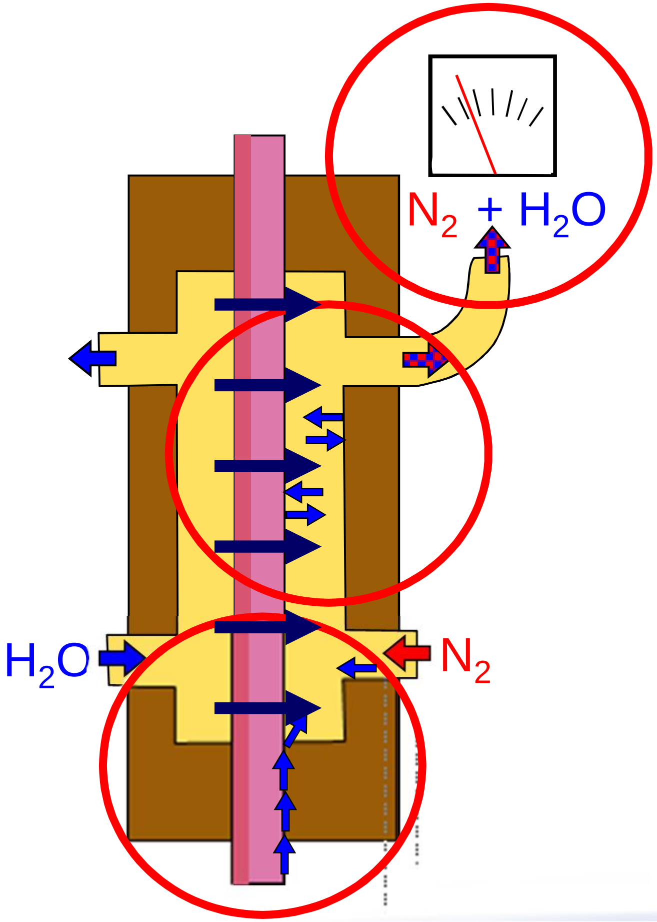


WVTR$_{qis}$ = 2,5x 10^{-6} g m^{-2} d^{-1}

Measured background level (sample: stainless steel) @ 38°C / 90% r. H.

PPRODUCT IMPLEMENTATION

Sensitivity of a WVTR measurement

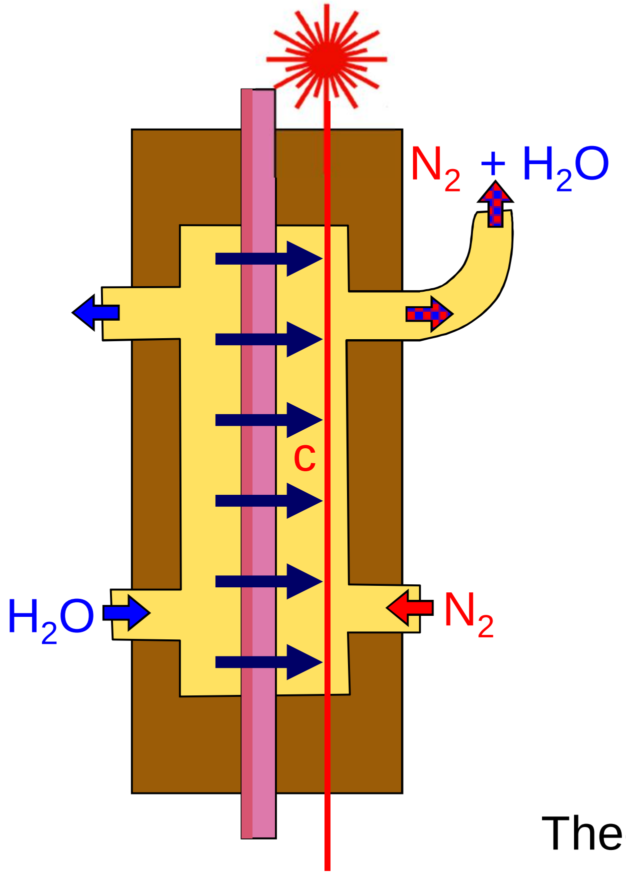


Sensor sensitivity

Adsorption / desorption of moisture

Sealing of the test cell

Parameters for tuning the sensitivity



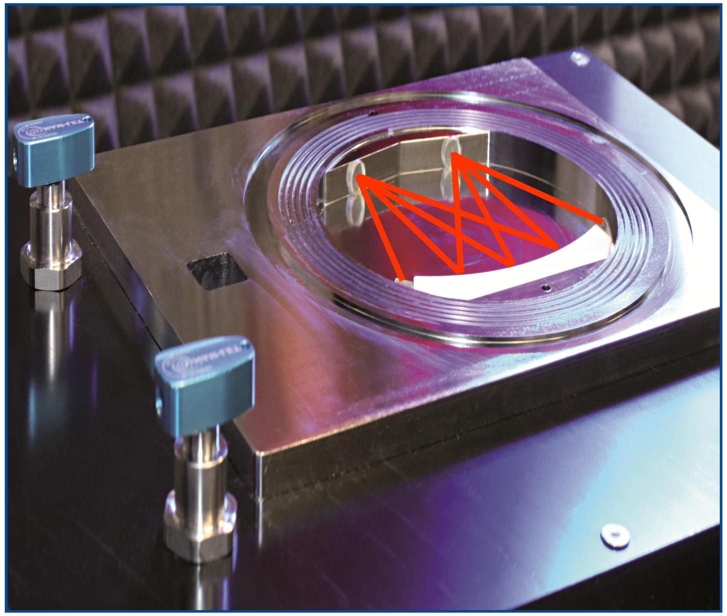
dynamic setup

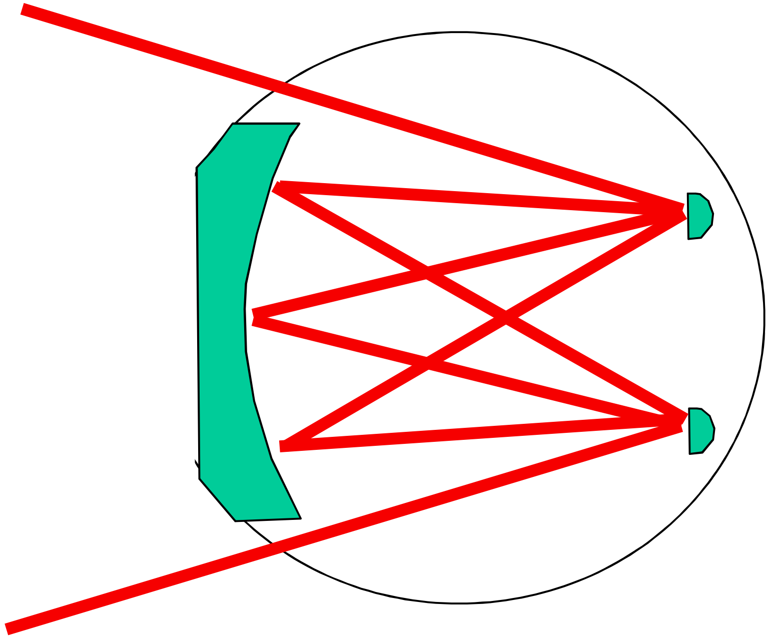
- Optical path length
- Carrier gas flow → c
- Sample area → c
- Selection of absorption line

$$-\ln\frac{I(\lambda)}{I_o(\lambda)} = \varepsilon_\lambda \cdot \textcircled{c} \cdot d$$

Theoretical sensitivity **LOD = 150 ppb m**

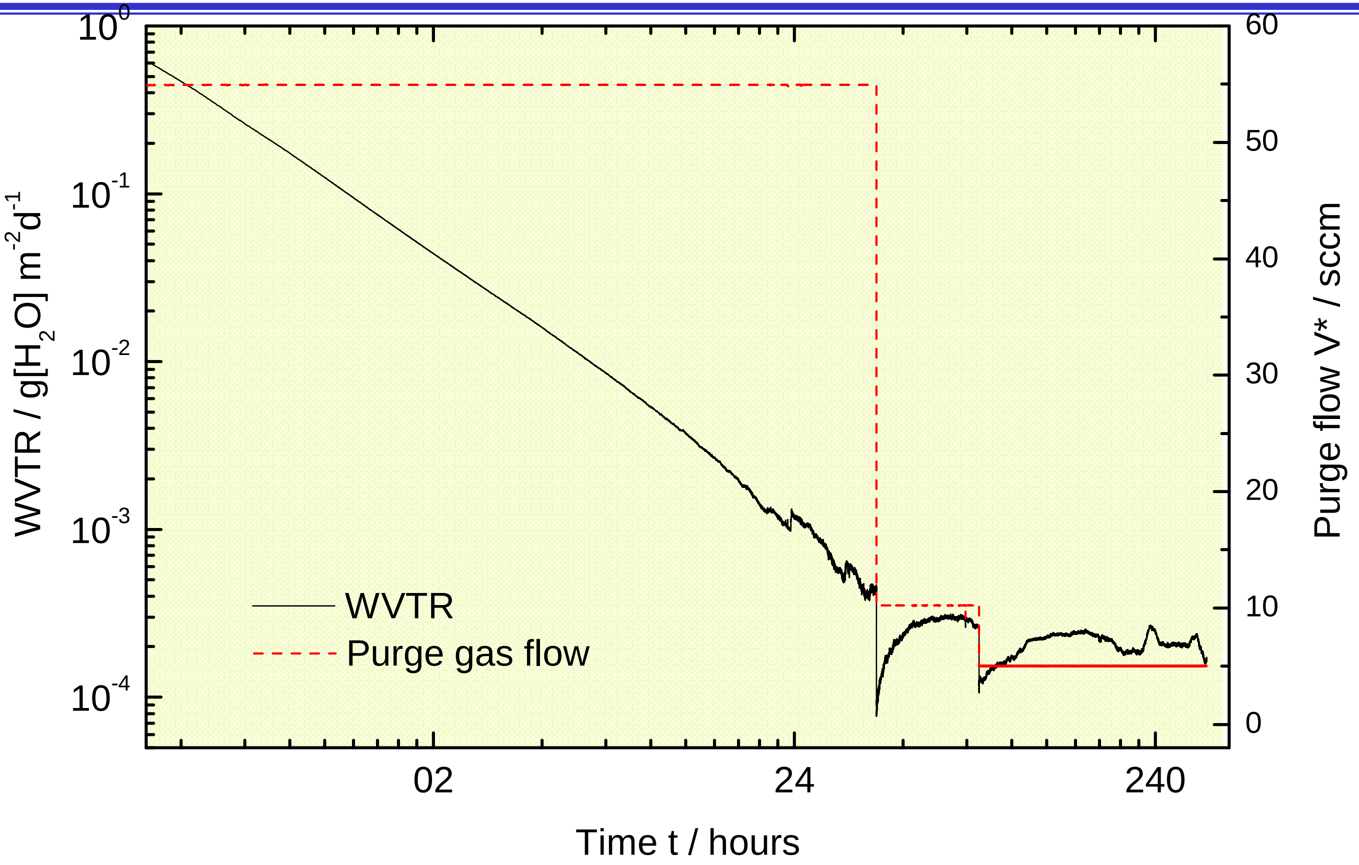
Tuning sensitivity: optical path length





Multipath design in HiBarSens®
2 m optical path length by multi 20 reflections

Tuning sensitivity: Carrier gas flow



Carrier gas flow
3 sccm - 50 sccm

Boost the sensitivity
by factor 16!

Sensitivity of WVTR measurement

Sensor sensitivity: the laser as a sensor

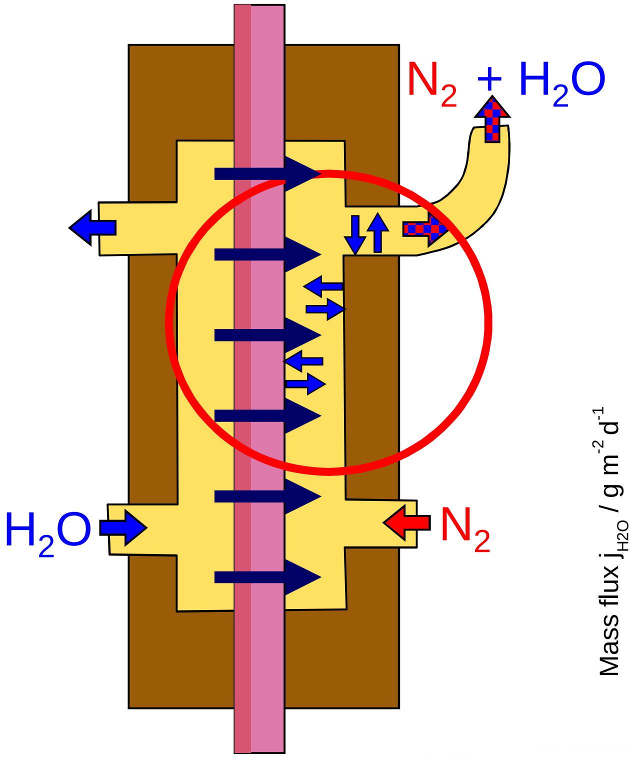
Further advantages

- High dynamic range: ppb - % (10^{-5} – 1 g m^{-2} d^{-1})
- Very high selectivity
- Immune to high concentrated moisture
- Long time stable, no drift, no hysteresis
- Low-maintenance
- Change of target permeate by change of the laser diode
- Allows the realization of a compact design
- Easy to use

Tunable Diode Absorption Spectroscopy (TDLAS) is a non-invasive, high sensitive, high selective sensor for detection of moisture traces!

Sensitivity of WVTR measurement

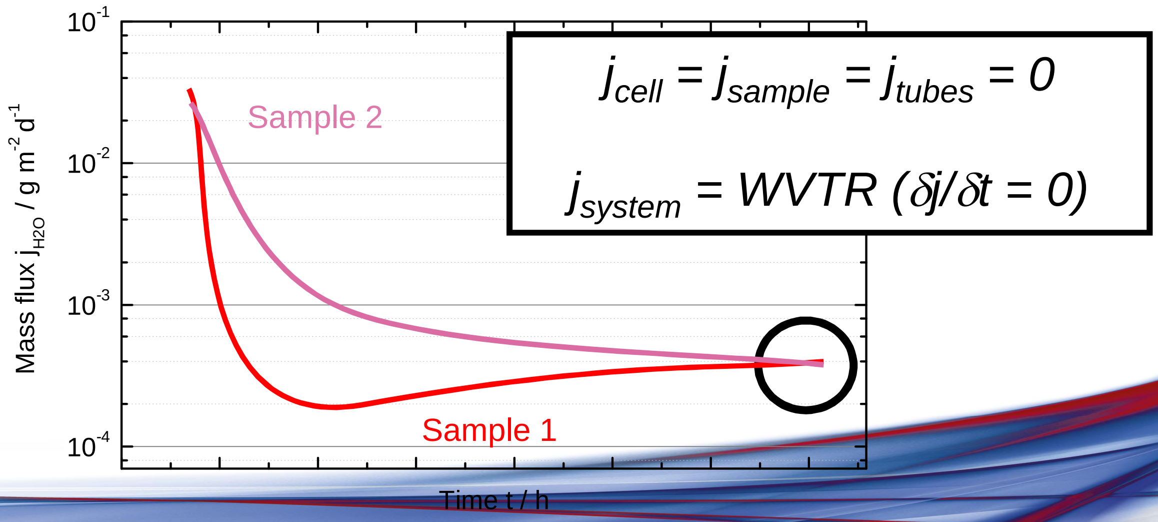
Adsorption / desorption of moisture



Mass flux

$$j_{system} = WVTR + j_{cell} + j_{sample} + j_{tubes}$$

$$j_x\left[\frac{g}{m^2 \cdot d}\right] = \frac{\Delta m_{H_2O}[g]}{A_x\,[m^2]\cdot \Delta t[d]}$$

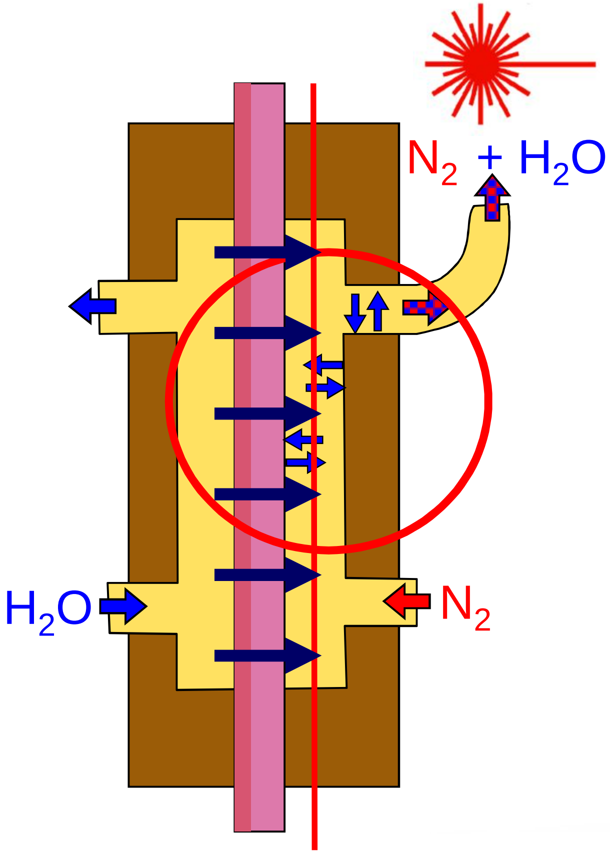


$$j_{cell} = j_{sample} = j_{tubes} = 0$$

$$j_{system} = WVTR\ (\delta j/\delta t = 0)$$

Sensitivity of WVTR measurement

Adsorption / desorption of moisture



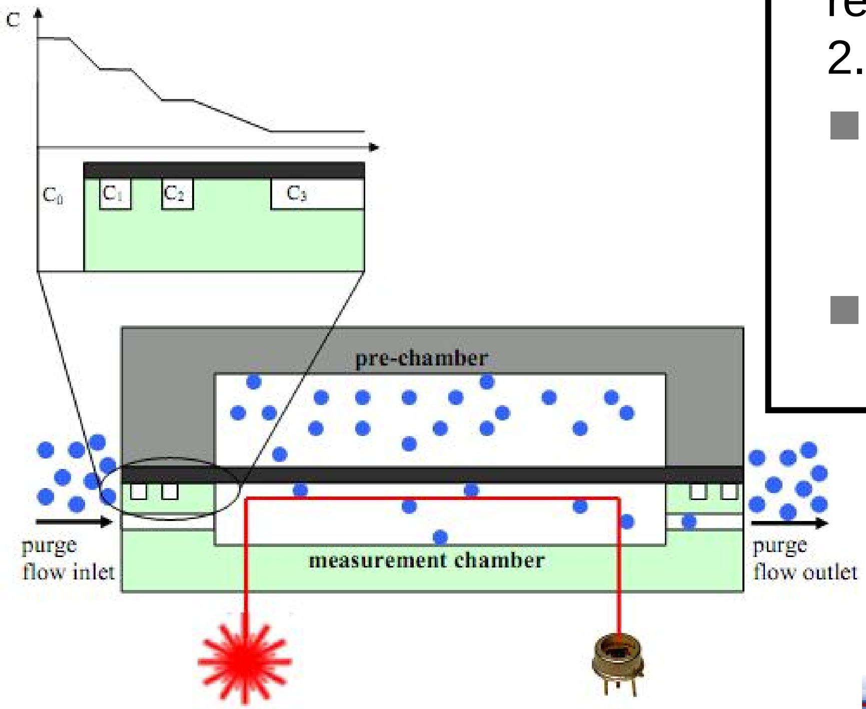
- Steady state conditions are required
  - As small as possible surface area of the cell in contact with moisture
  - Ultra smooth surfaces
  - Avoid any problematic materials inside the cell
  - Highest temperature stability
- HiBarSens - realization
  - Volume and surface vs. sample area optimized cell design
  - Electro-polished surfaces
  - Temperature stability < 0,5°C
  - Sensor is placed inside the test cell

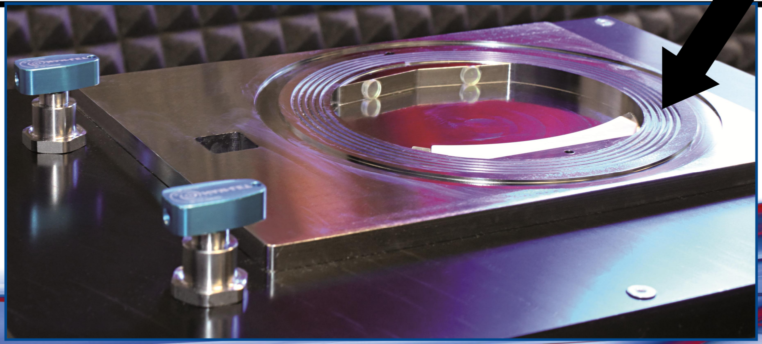
Sensitivity of WVTR measurement

Sealing of test (measuring) cell

Mass flux: $j_{system} = WVTR + j_{cell} + \ldots + j_{leakage}$

- Sample clamping has to follow the requirement for leakage rates of 2.4E-9 mbar*l/s
  - Substitution of the classical concept (polymer O-rings) by the concept of an “active sealing”
  - Purge channels prevent ambient moisture diffusion into the cell

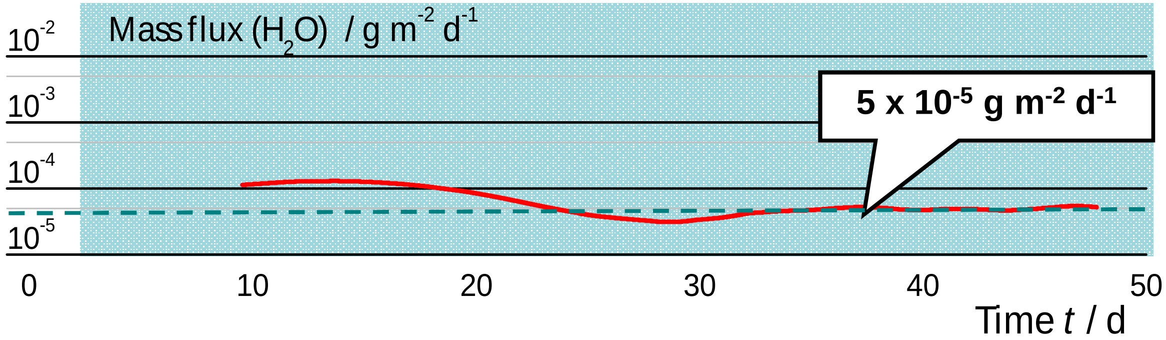




HiBarSens® at work

Measured background level

(sample: stainless steel)

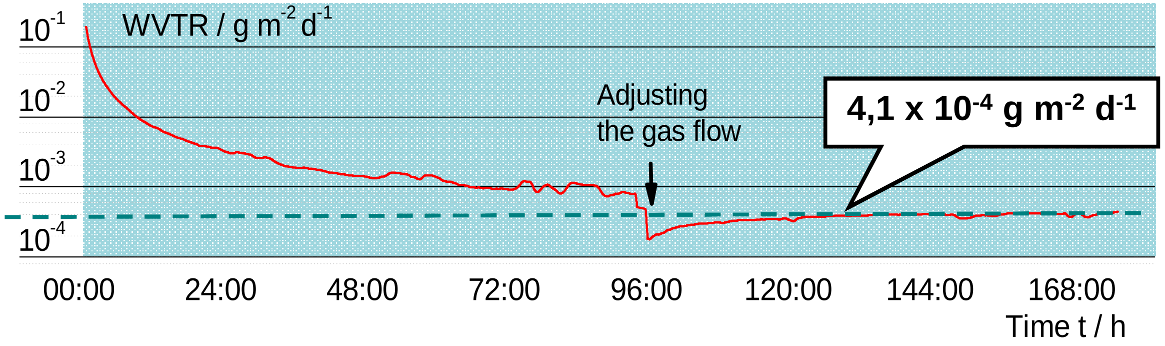


5 x 10^{-5} g m^{-2} d^{-1}

WVTR-measurement

of ultra barrier sample

(Fraunhofer POLO)

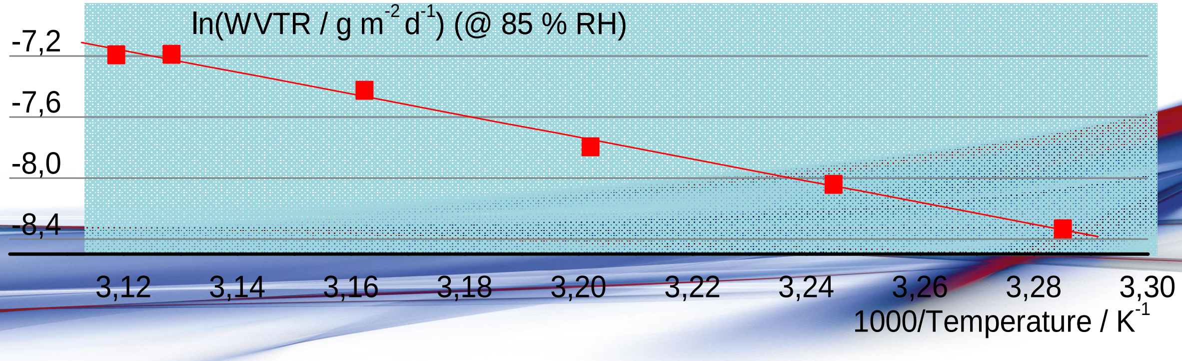


Adjusting the gas flow

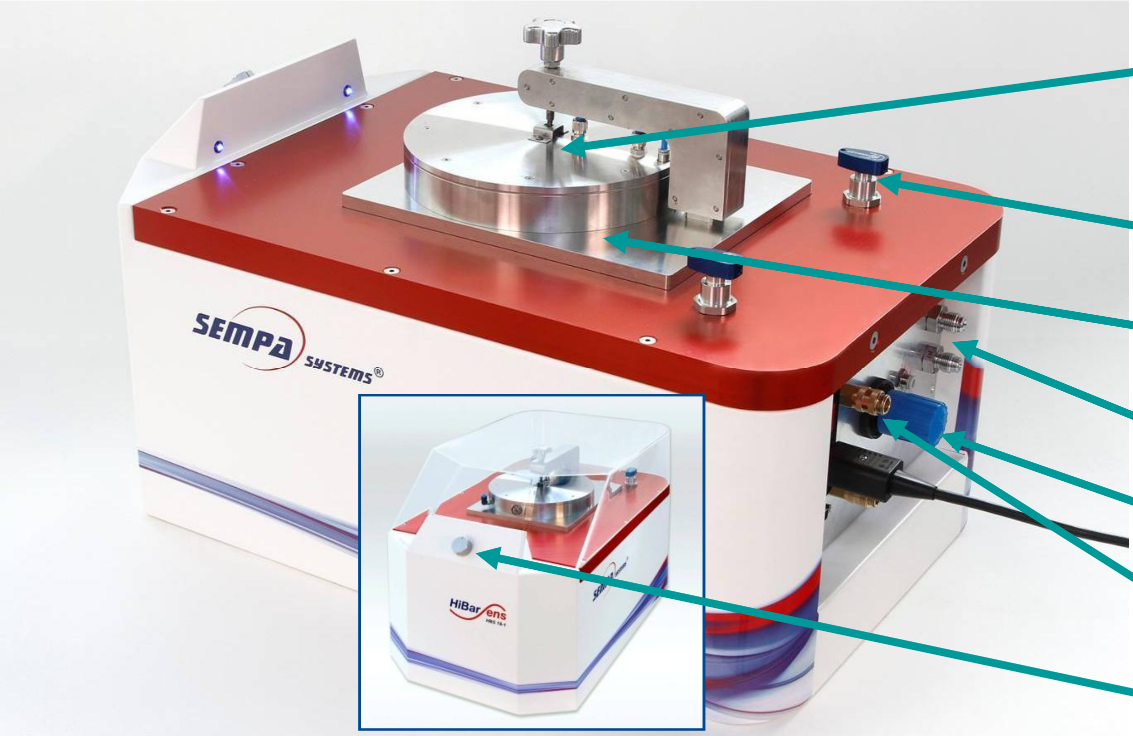
4,1 x 10^{-4} g m^{-2} d^{-1}

Temperature dependence of ultra barrier sample

(for photovoltaic)



compact & easy to use device



Permeation cell
- tempered
- integrated moisture generator
- Gentle clamping of the test sample

Purifier valve

Sample

N_2 purge gas in /out

Rel. Humidity controller

Connectors for thermostat

Flow controller

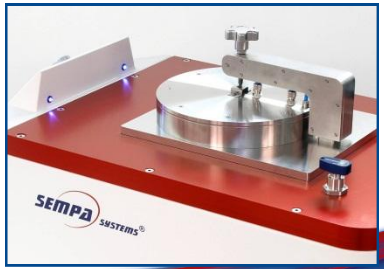
Place sample → Close test cell → Measurement: Adjust rel. Humidity purge flow, temperature → Print report

Summary

■ HiBarSens	laser based sensor technology for highly sensitive determination of water vapor transmission rates of ultra barrier samples
■ HiBarSens	provides reliable measurements of WVTR down to 10^{-5} g m^{-2} d^{-1} with the potential to 10^{-6} g m^{-2} d^{-1}
■ HiBarSens	is available as a compact, easy to use table top device

HiBarSens
HBS 18-1

PERMALYZER



Acknowlegment

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Fraunhofer
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Harald Beese

Wulf Grählert