Oxygen and Water Vapour Permeation Measurements for Packagings and Technical Films

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Content from:
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Fraunhofer IVV

Structure

- Some necessary Basics
- Oxygen Permeation
- Water Vapour Permeation
- Conclusions

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- **Some necessary Basics**
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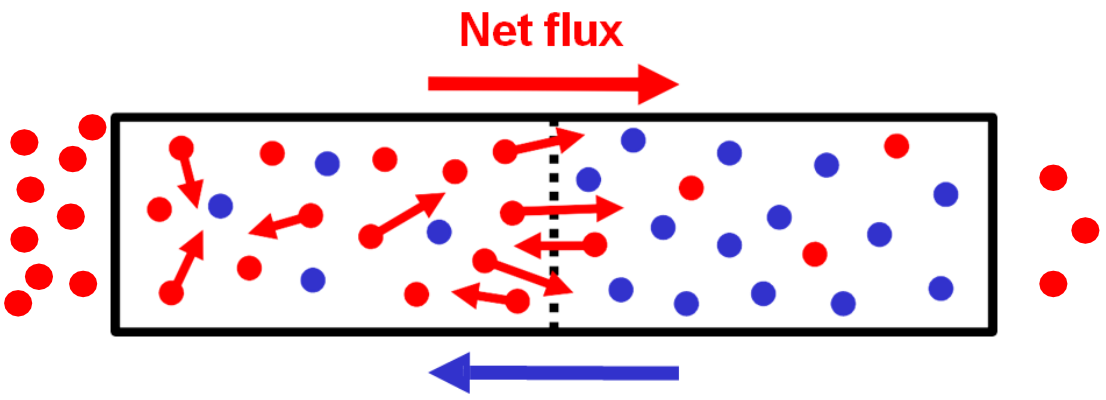
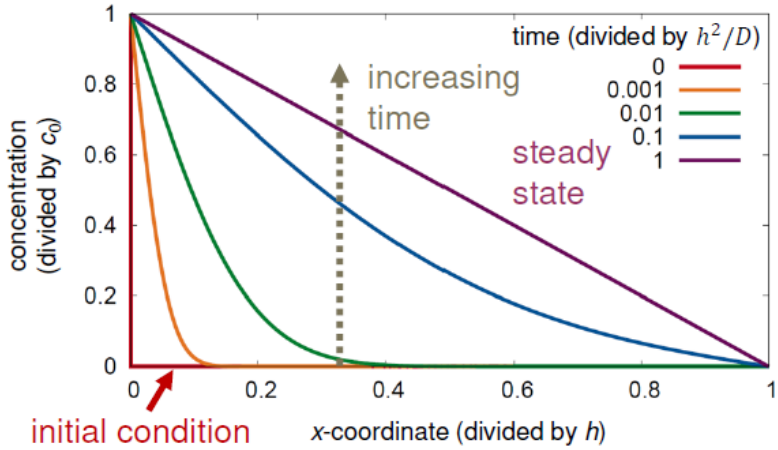
Permeation



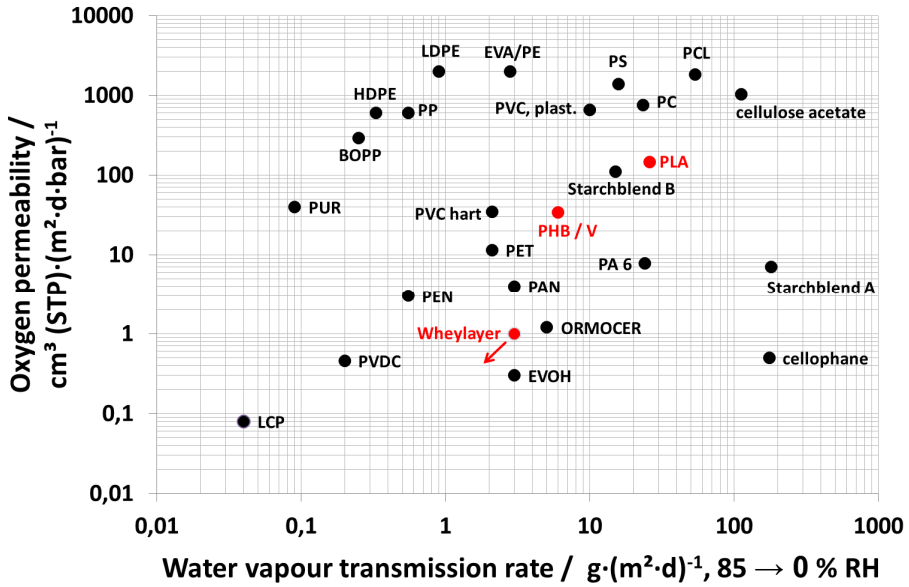
$$P = S \cdot D$$

Lag time

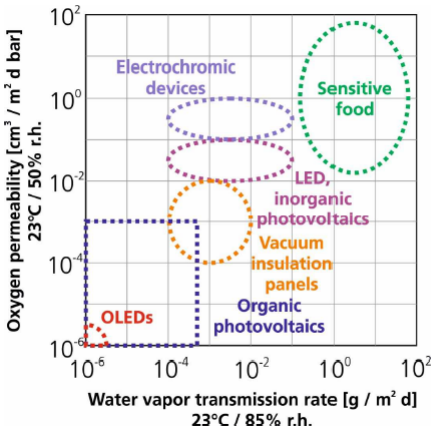


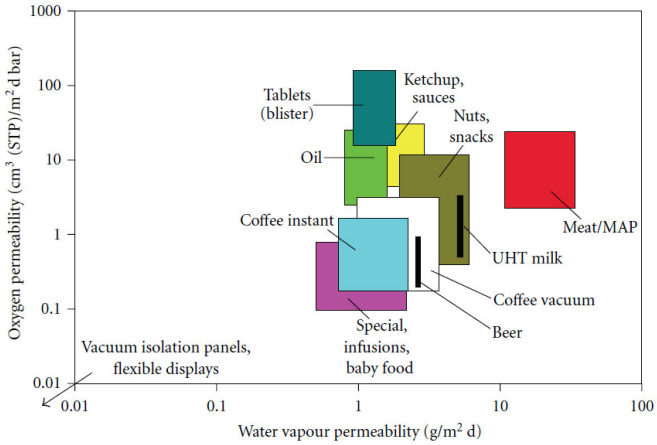
$$\vartheta = \frac{h^2}{6\,D}$$

Permeabilities, monomaterial, 100 µm, 23 °C

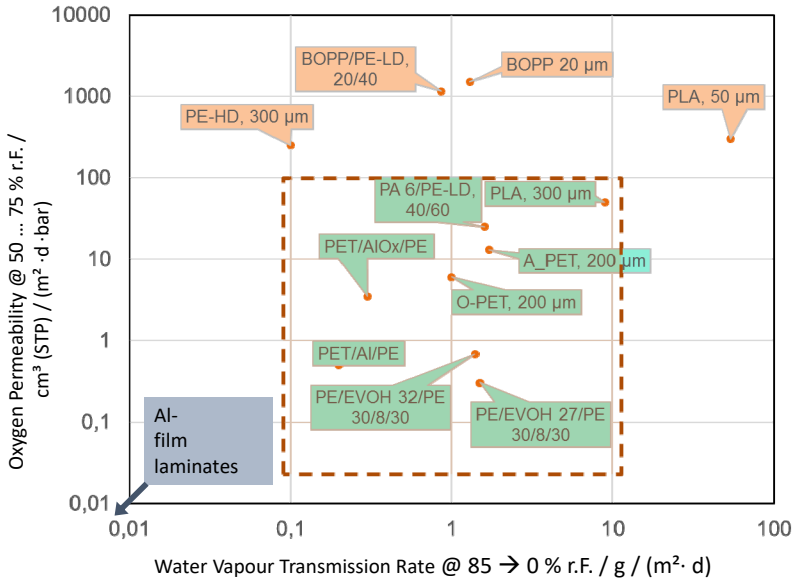


Barrier requirements





Barrier materials on the market



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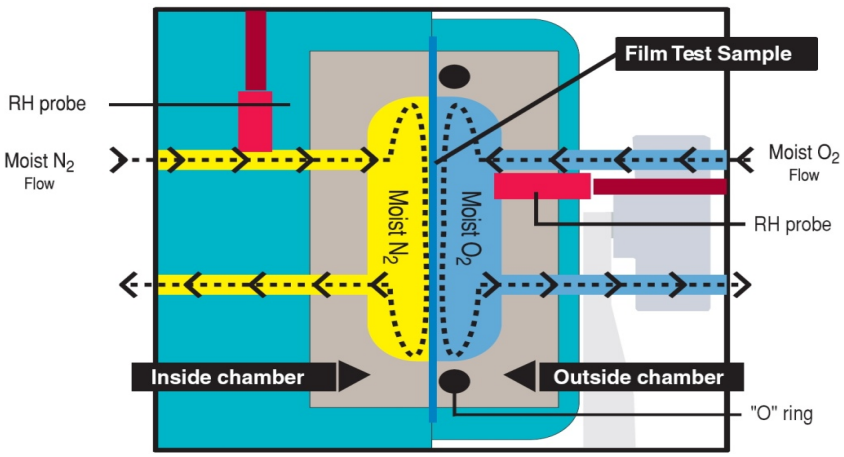
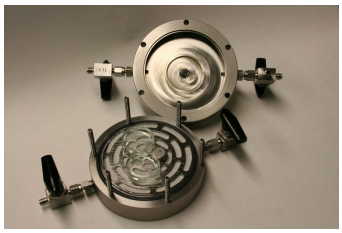
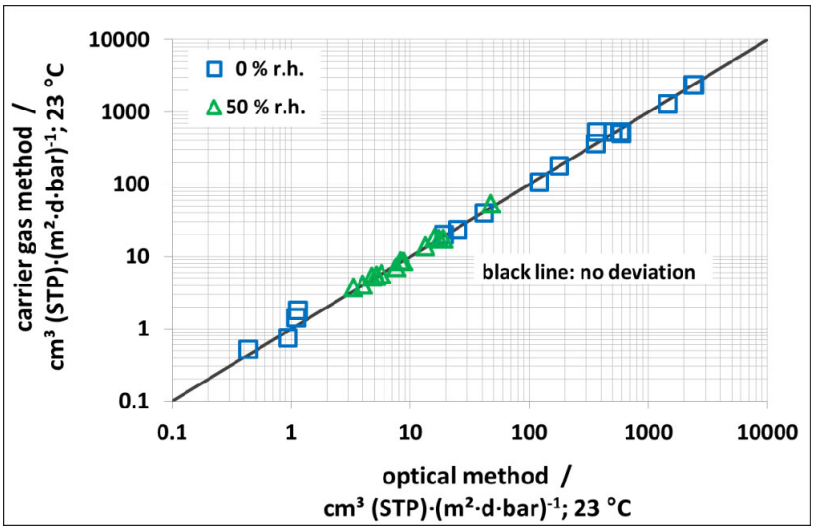
Electrochemical method



OX-TRAN® Model 2/21, Brochure, Mocon®

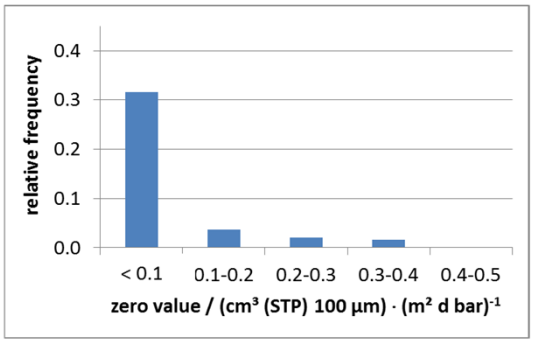
Optical method

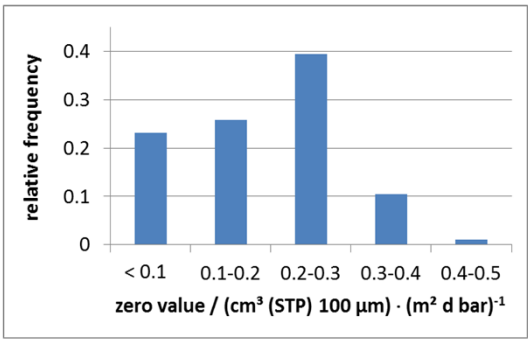




Polymer Testing 63 (2017) 126-132

Optical method



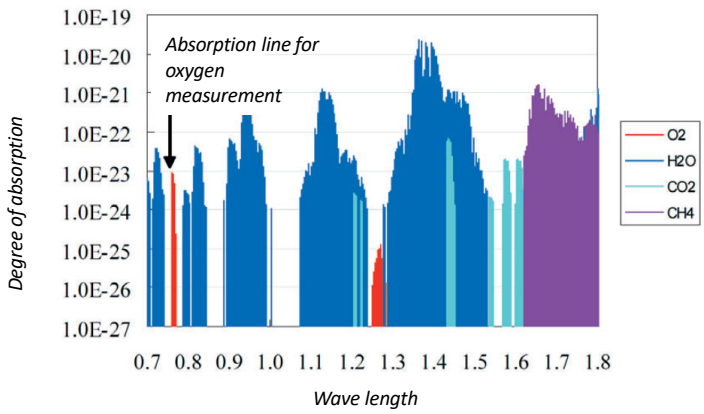


a) Carrier gas method according to DIN53380-3 (Mocon Oxtran 2/20), 181 samples

b) Optical method according to DIN53380-5, 190 samples

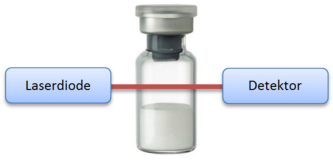
Polymer Testing 63 (2017) 126-132

Laser Method

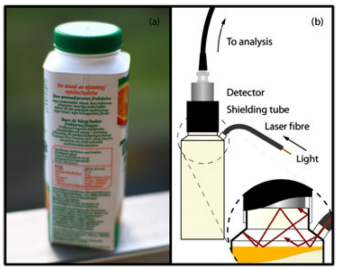


Absorption wave lengths of some known gases. Particularly, the absorption spectra do not overlap with the one of oxygen

Vaisala, Germany



WILCO AG, Switzerland



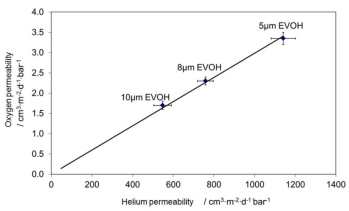
Lewander, M., et al., 2011. 24(5): p. 271-280.

He-Permeation

Time lag / min	O_2	CO_2	He
LDPE	0.6	0.8	0.04
PVC	23	111	0.10
PET	62	335	0.14

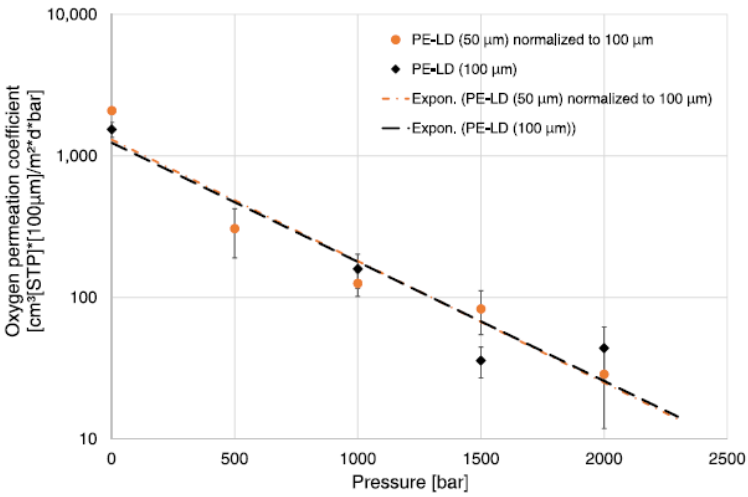
Film thickness: 100 µm
Source: K. Müller, VDI-Wissensforum, Bonn, 13.06.2012

Film thickness: 100 µm	He-Perm. / $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$	O_2-Perm. / $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$	Permselectivity He / O_2
LDPE (*)	3600	1700	2
PET	580	12	50
EVOH (**)	55	0.2	330

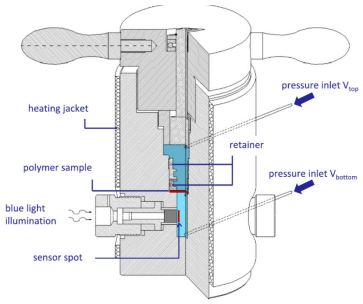


PET thickness: 50 µm	He-Perm. / $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$	O_2-Perm. / $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot bar^{-1}$	Permselectivity He / O_2
PET	1200	23	50
PET / Al	18	0.4	45
PET / SiO_x	810	0.3	2700

High Pressure Method



Film thickness (μm)	Pressure (bar)	Oxygen permeation coefficient $\left[\frac{cm^3[STP]}{m^2\ d\ bar}[100\ \mu m]\right]$	95% confidence interval
100	1	1540	165
	500	...	...
	1000	160	44
	1500	36	6
	2000	44	13
50	1	2090	75
	500	307	146
	1000	126	24
	1500	83	20
	2000	29	17



J. Chem. Phys. 143, 114201 (2015); https://doi.org/10.1063/1.4931399

Testing devices, oxygen permeability

System	Producer	Measurement range film / cm³/(m²·d·bar)	Measurement range packaging / cm³/(Pck· d·bar)	Temperature / °C	Humidity / % rel. h.
Manometric	PBI Dansensor	1 - 10^4	not possible		not recommended
Manometric	Brugger	1 - $3\cdot10^4$	not possible	-20 - 60, extern	not recommended
Electrochemical	Mocon	$5\cdot10^{-3}$ - $2\cdot10^2$	$5\cdot10^{-5}$ - 1	5 - 50; 10 - 40	0 or 35 – 90
Electrochemical	Systech	$8\cdot10^{-3}$ - $4\cdot10^2$	$4\cdot10^{-5}$ - 2	5 - 50	0 - 95
Electrochemical	Extra Solution	$5\cdot10^{-3}$ - $2\cdot10^4$	$5\cdot10^{-4}$ - $5\cdot10^2$	10 - 50	0 - 95, only O_2-side
Zirkonium-sensor	PBI DanSensor	10^{-1} - 10^4	not possible	5 - 60; (< 30°C extern)	2 - 90, (20 - 40)
Luminescense	PreSens	10^{-1} - 10^7	-	any	any

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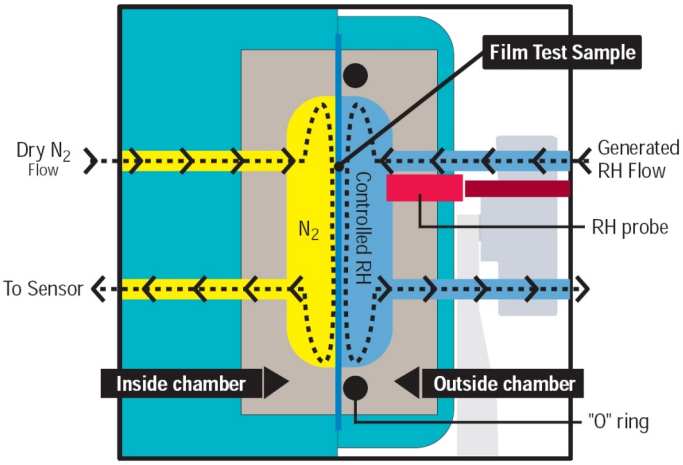
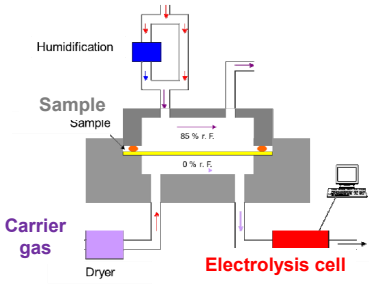
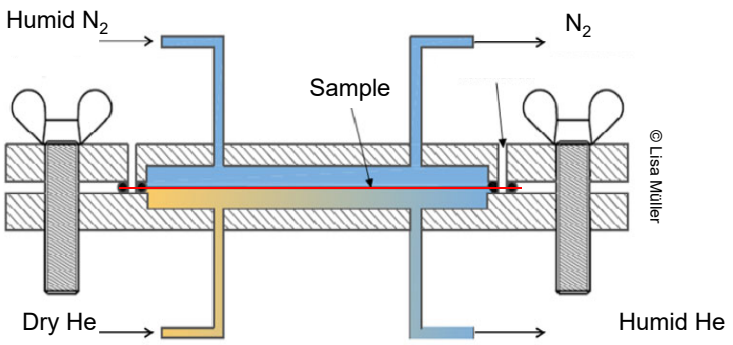
Coulometric method



Mocon®



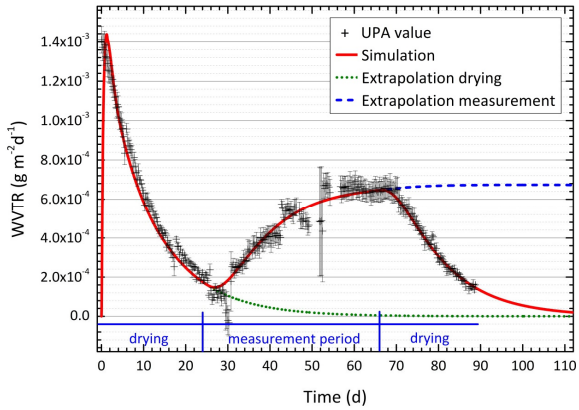
Ultra permeation measurement device, Fraunhofer IVV



30 measuring cells

Ref. of Figures: S. Kiese

Simulation, WVTR by UPA: Laminate Structure



Numerical simulation: FEM
COMSOL Multiphysics 4.4

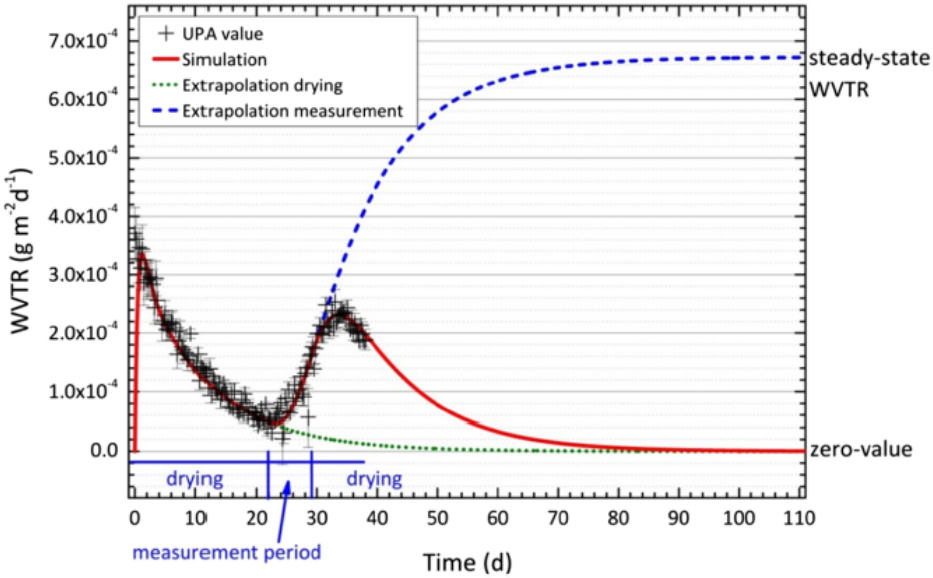
38°C / 36% RH	D_{eff} ($m^2 \cdot s^{-1}$)	S_{eff} ($mol \cdot m^{-3} \cdot Pa^{-1}$)
PET	$9.2 \cdot 10^{-13}$	$6.2 \cdot 10^{-2}$
ORM	$2.1 \cdot 10^{-13}$	1.3
Adh	$8.0 \cdot 10^{-12}$	$2.9 \cdot 10^{-1}$
	P_{eff} ($mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$)	
SiO_x	$7.2 \cdot 10^{-20}$	

→ Prediction of the steady-state WVTR values
→ Reduction of long permeation measurement times for multilayer structures

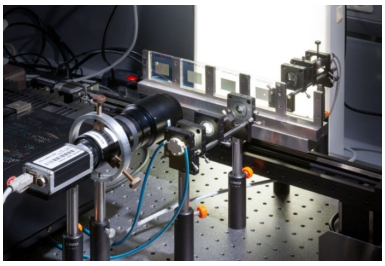
D_P has no influence → S_P changes **time-lag**
D_B *and* S_B of inorganic barrier layer can be changed → same P_B → **steady-state**

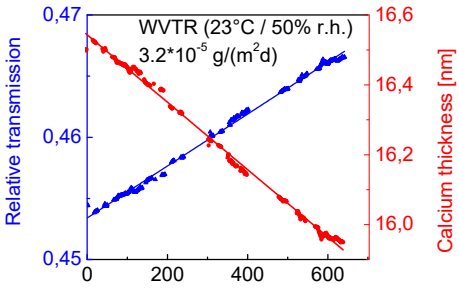
Kiese S., et al., Review of Scientific Instruments 88 (2017) 025108; Kiese S., et al., Thin Solid Films, (2019)

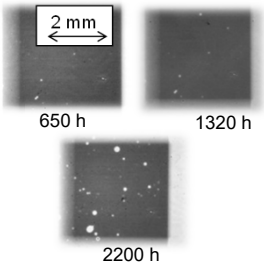
Simulation, WVTR by UPA: Laminate Structure



Optical calcium test







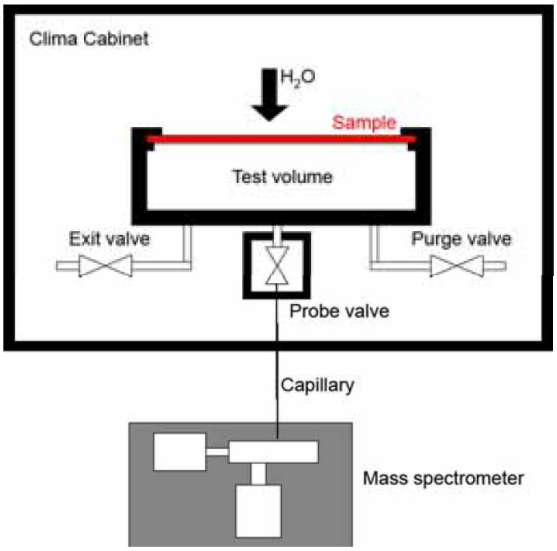
- Detection of transmission increase using photodiode or CCD camera, calculation of thickness from Lambert-Beer's-Law

$$d_{Ca} \propto OD = log_{10}\left(\frac{I_{incident}}{I_{transmitted}}\right)$$

- Intrinsic WVTR measurement on „defect-free" area or by image analysis methods (greyscale histogram)
- **Sample size:** ~ few cm²
- **Limit of Detection**: 10^{-6} g/(m²d)
- long measurement time (1 nm Ca-degradation needs $1.4 \cdot 10^{-3}$ g_{H2O}/m^2 ➔ 1400 days for 10^{-6} g/(m²d))

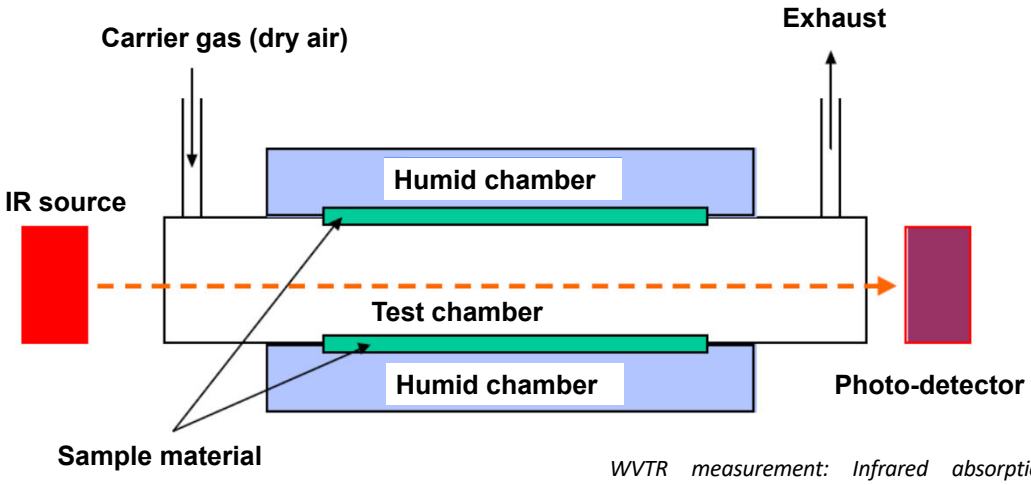
C. Boeffel, Fraunhofer IAP

Mass spectrometric method



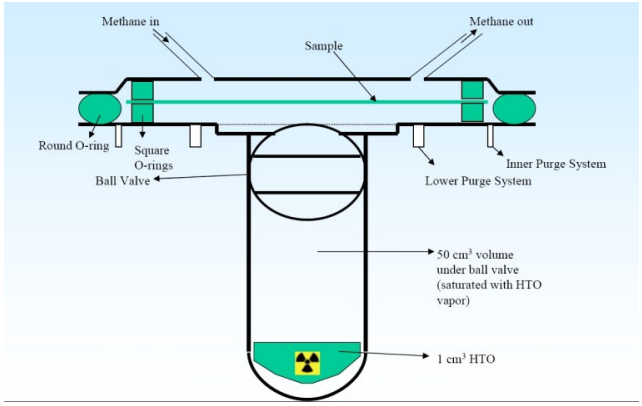
Permeation of water vapour, P. Hülsmann et al., Presentation, 1. Hamburger Verpackungsgespräche, 2009

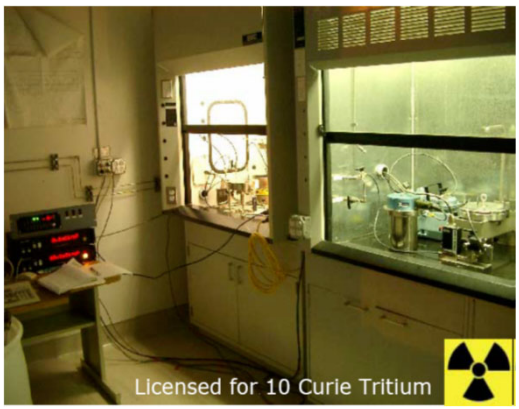
Laser light absorption



WVTR measurement: Infrared absorption, B. Duncan et al., Review of Measurement and Modelling of Permeation and Diffusion in Polymers, NPL Report DEPC MPR 012, 2005

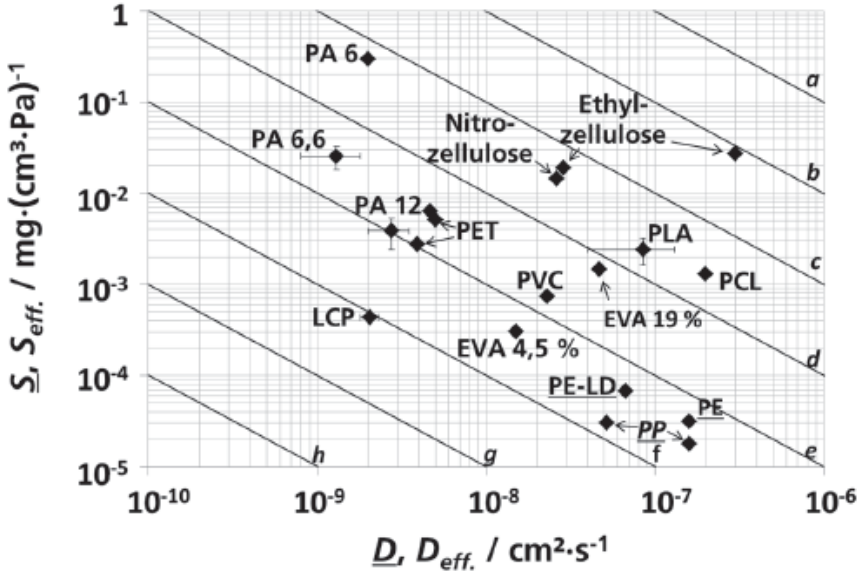
Radioactive method, tritium test



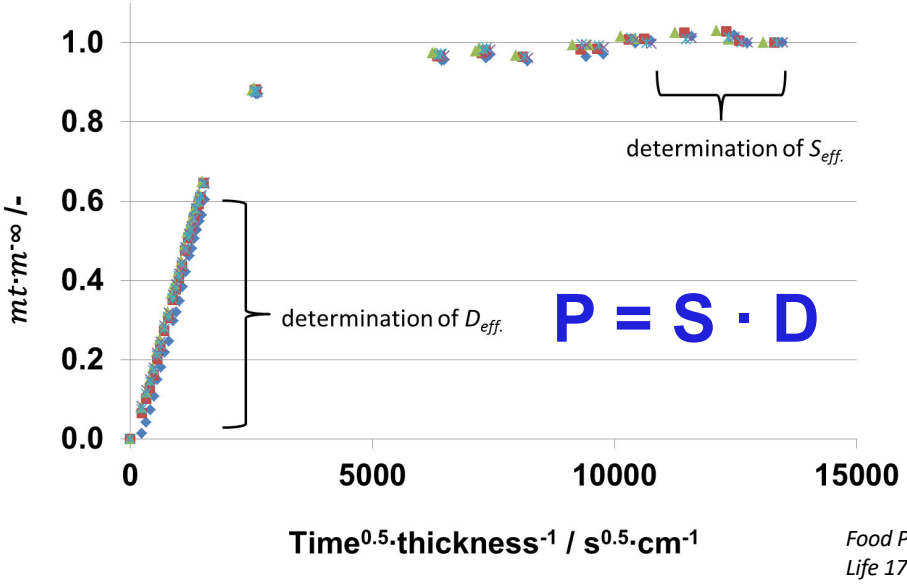


R. Dunkel, Method of measuring ultra-low water vapor permeation for OLED displays (General Atomics)

Sorption method

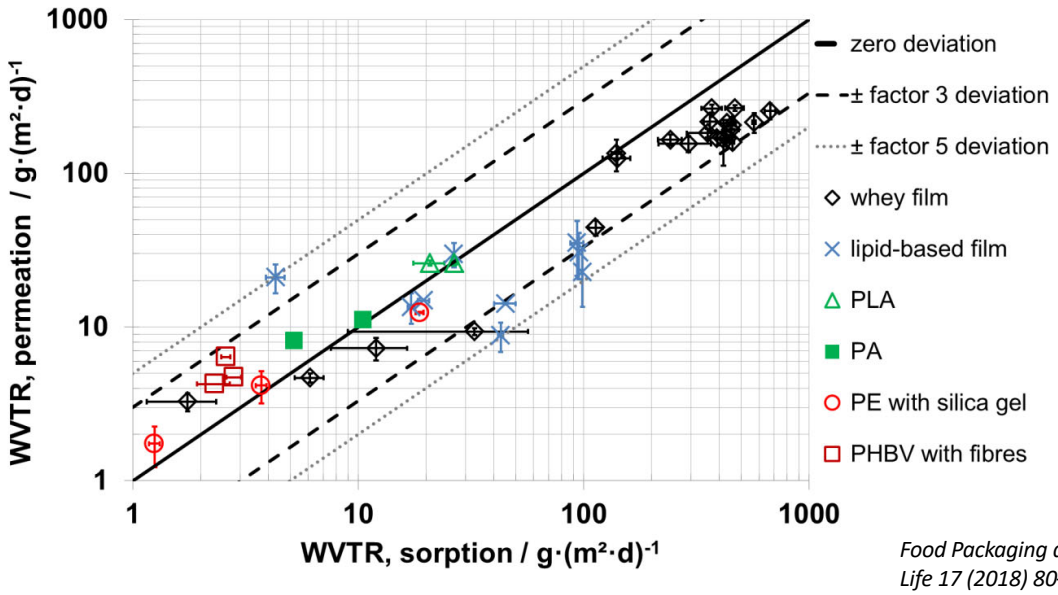


Sorption method



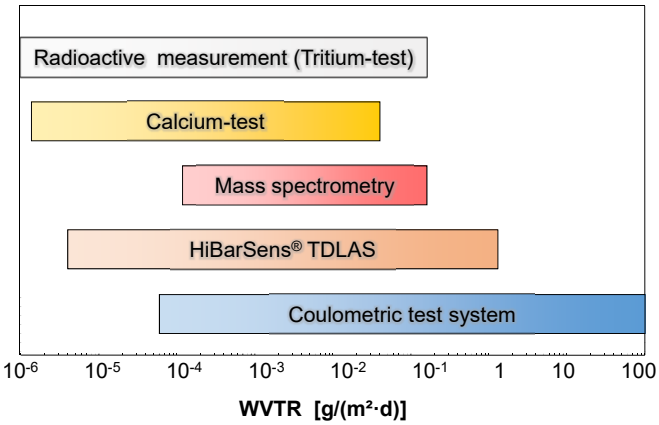
Food Packaging and Shelf Life 17 (2018) 80–84

Sorption method



Food Packaging and Shelf Life 17 (2018) 80–84

Testing methods water vapour permeation



Test conditions

- 23°C / 85% RH: ambient
- 38°C / 90% RH: tropical
- 60°C / 90% RH: accelerated aging
- 85°C / 85% RH: damp-heat-test

None of the methods simulate a real device test!

Contribution from C. Boeffel, Fraunhofer IAP

Testing devices water vapour permeation

System	Producer	Measurement range film [g/(m²· d)]	Measurement range / packaging [g/(pck·d)]	Temperature [°C]	Humidity [% r. h.]
Gravimetric	Cups	$5\cdot10^{-1}$ - $2.5\cdot10^{2}$	$5\cdot10^{-3}$ - ?	~10 - ~50	any
Gravimetric	MRS-Seitter	1 mg, resolution of balance	restricted	~ 23 - 40, + cooling	40-85 - 0
Electrolytic	Systech	$2\cdot10^{-3}$ - $2.8\cdot10^{2}$	10^{-5} - $5\cdot10^{-1}$	5 - 50	any
Electrolytic	Brugger	$5\cdot10^{-3}$ - ~5	not possible	"-20 - 60, (extern)	100 - 0 (any)
Electrolytic	Mocon	$5\cdot10^{-5}$ - 5	possible	5 - 50	100 - 0
Capacitive, dew point monitor	ExtraSolution	$2\cdot10^{-3}$ - $5\cdot10^{2}$	not possible	10 - 50	5-95 - 0
Capacitive	Dansensor	$3\cdot10^{-2}$ - 10^{4}	not possible	5 - 70, (< 30 extern)	50-95 - 0
IR-sensor	Mocon	$5\cdot10^{-3}$ - 10	$3\cdot10^{-5}$ - $5\cdot10^{-2}$	5 - 50, 10 - 40	max. 90-0, 100-0
GC	Fraunhofer	$2\cdot10^{-5}$ - …	-	23 - 80	15-90
Ca-Test	Several	10^{-6} …	-	23 - 80	≤ 100
Laser absorption	Sempa	10^{-6} …	-	-	-
Tritium test	-	$2\cdot10^{-7}$ - …	-	-	-

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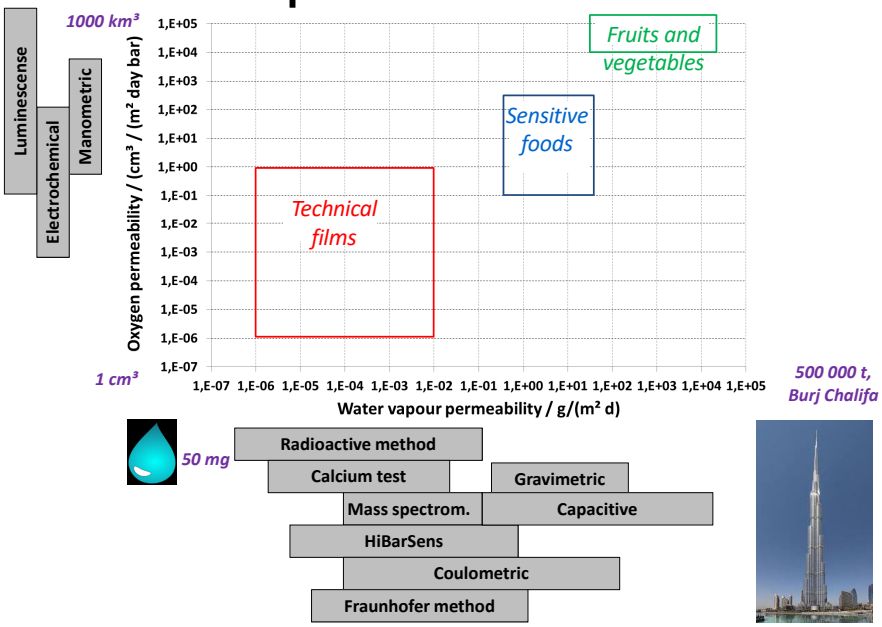
Comparison of Methods



“Paralysis by Analysis”

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