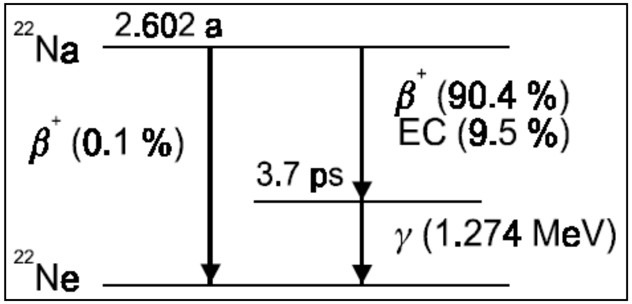
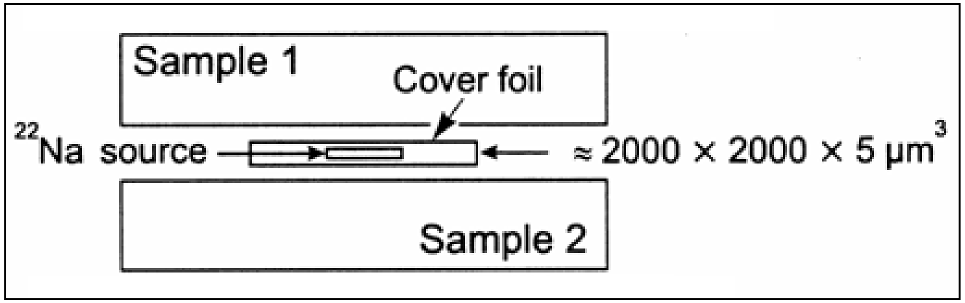
2015 Frontiers of Characterization and Metrology for Nanoelectronics

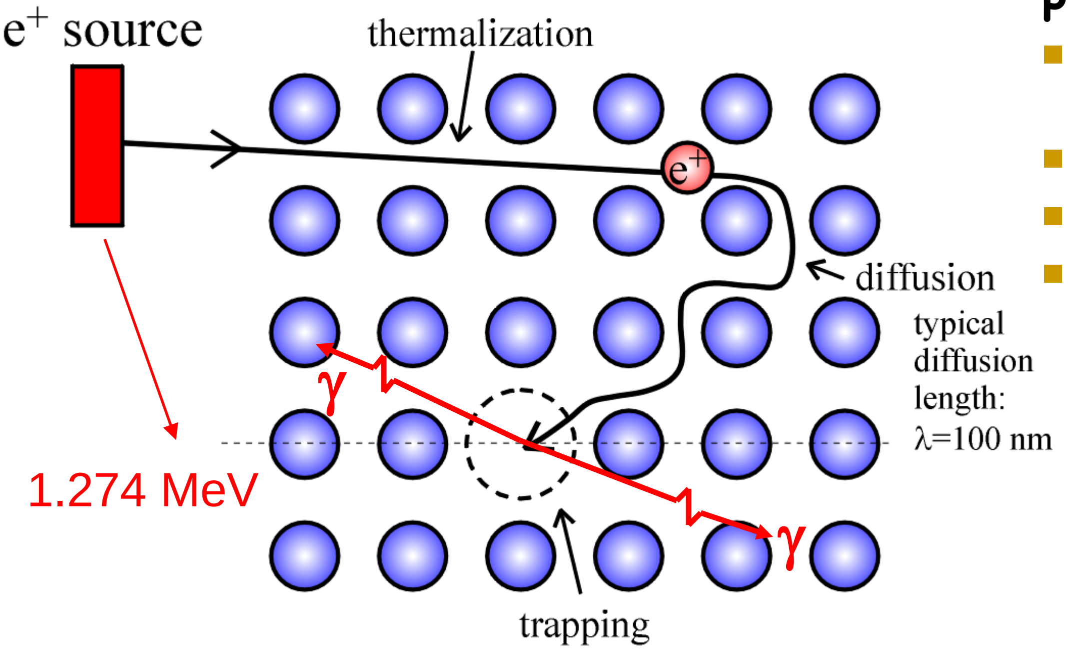
Positron Annihilation Spectroscopy Measurements for Porosimetry

R. Krause-Rehberg, Dept. of Physics, University Halle

Positron Annihilation Lifetime Spectroscopy - PALS







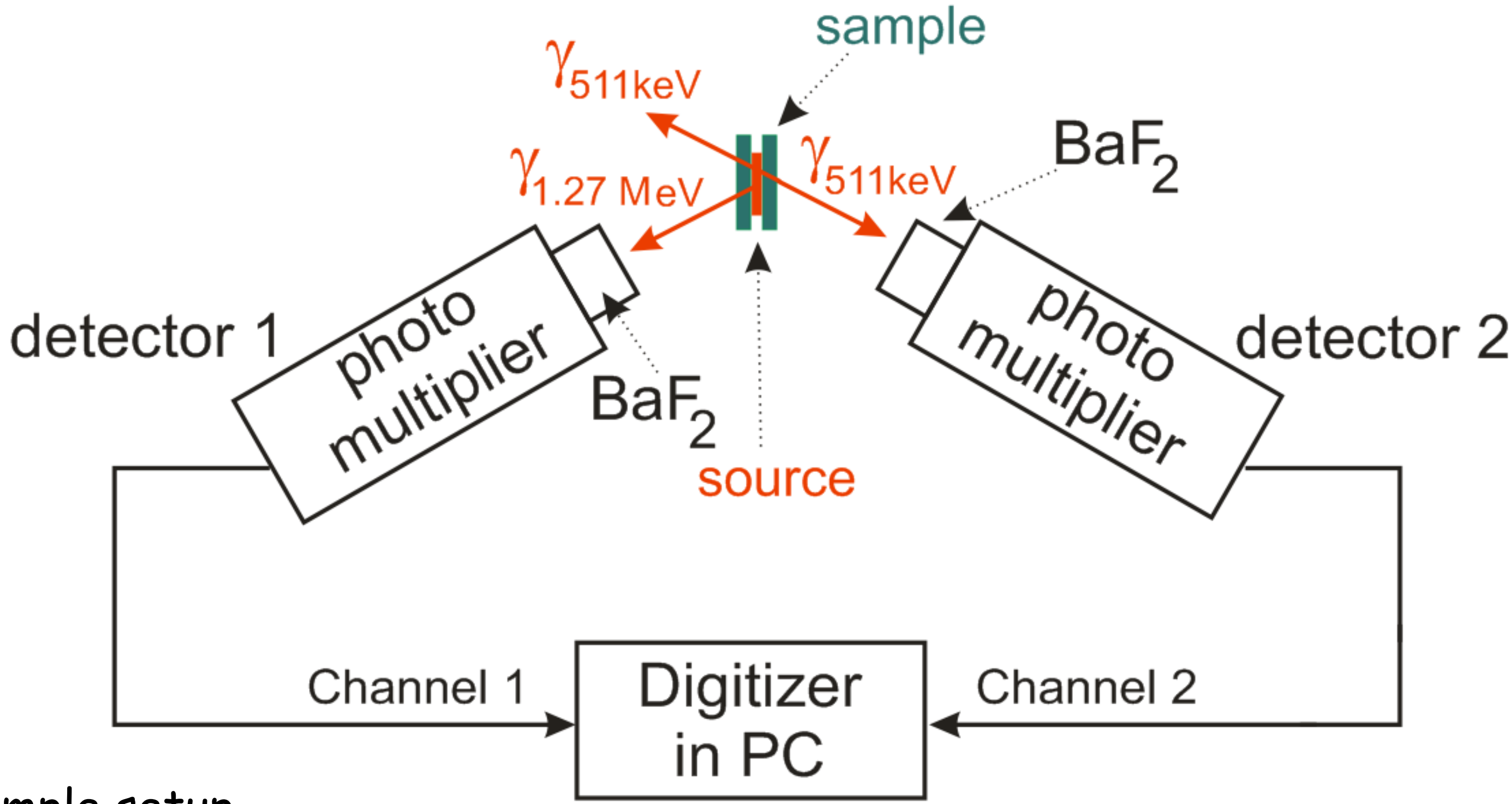
positrons:

- thermalize (reach thermal energies)
- diffuse
- being trapped
- and annihilate

When trapped in vacancies:

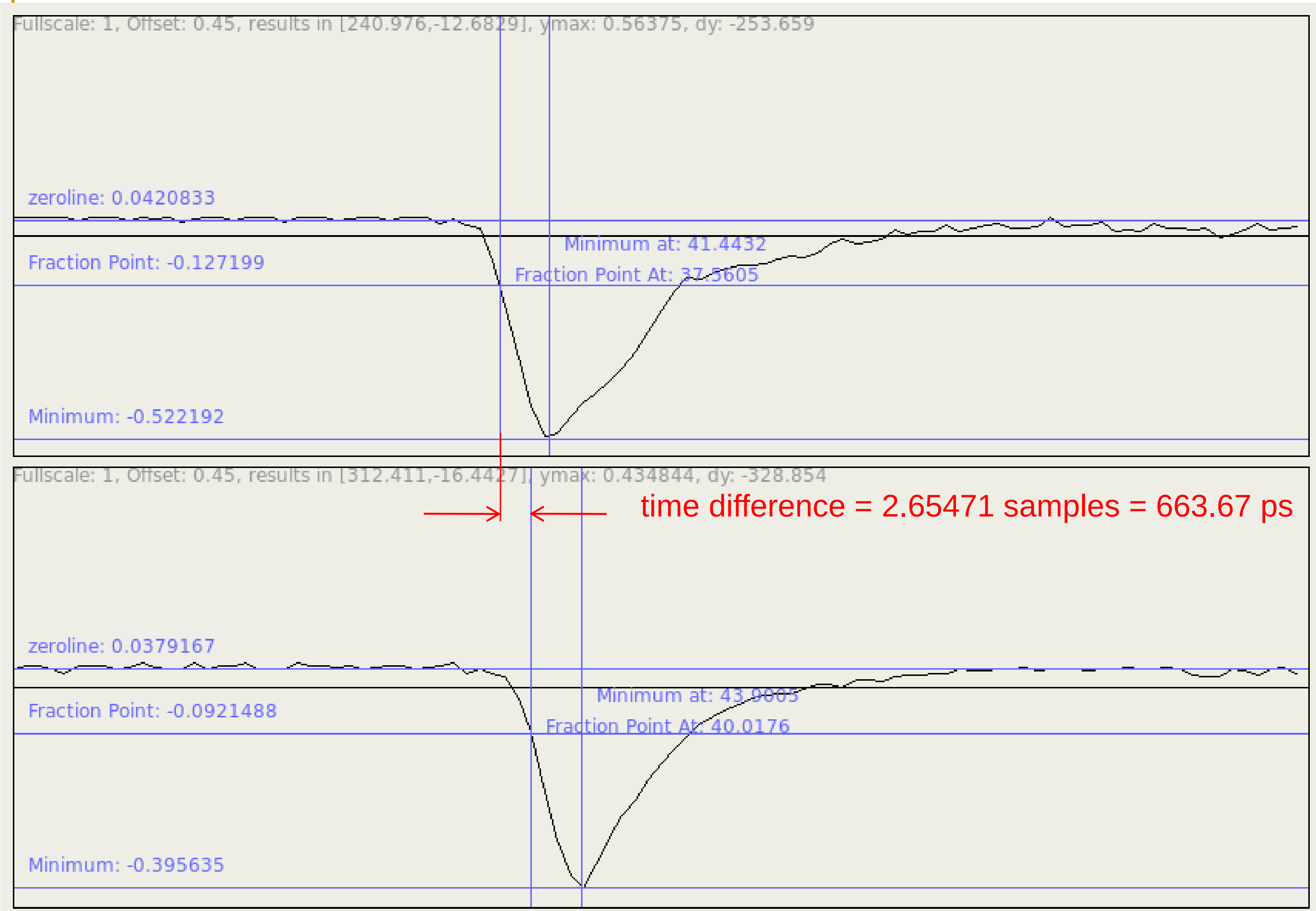
- Lifetime increases due to smaller electron density in open volume

Digital lifetime measurement



- simple setup
- timing very accurate
- each detector for start & stop (double statistics)

Screenshot of two digitized anode pulses



Fullscale: 1, Offset: 0.45, results in [240.976,-12.6829], ymax: 0.56375, dy: -253.659

zeroline: 0.0420833

Fraction Point: -0.127199

Minimum at: 41.4432

Fraction Point At: 37.5605

Minimum: -0.522192

Fullscale: 1, Offset: 0.45, results in [312.411,-16.4427], ymax: 0.434844, dy: -328.854

time difference = 2.65471 samples = 663.67 ps

zeroline: 0.0379167

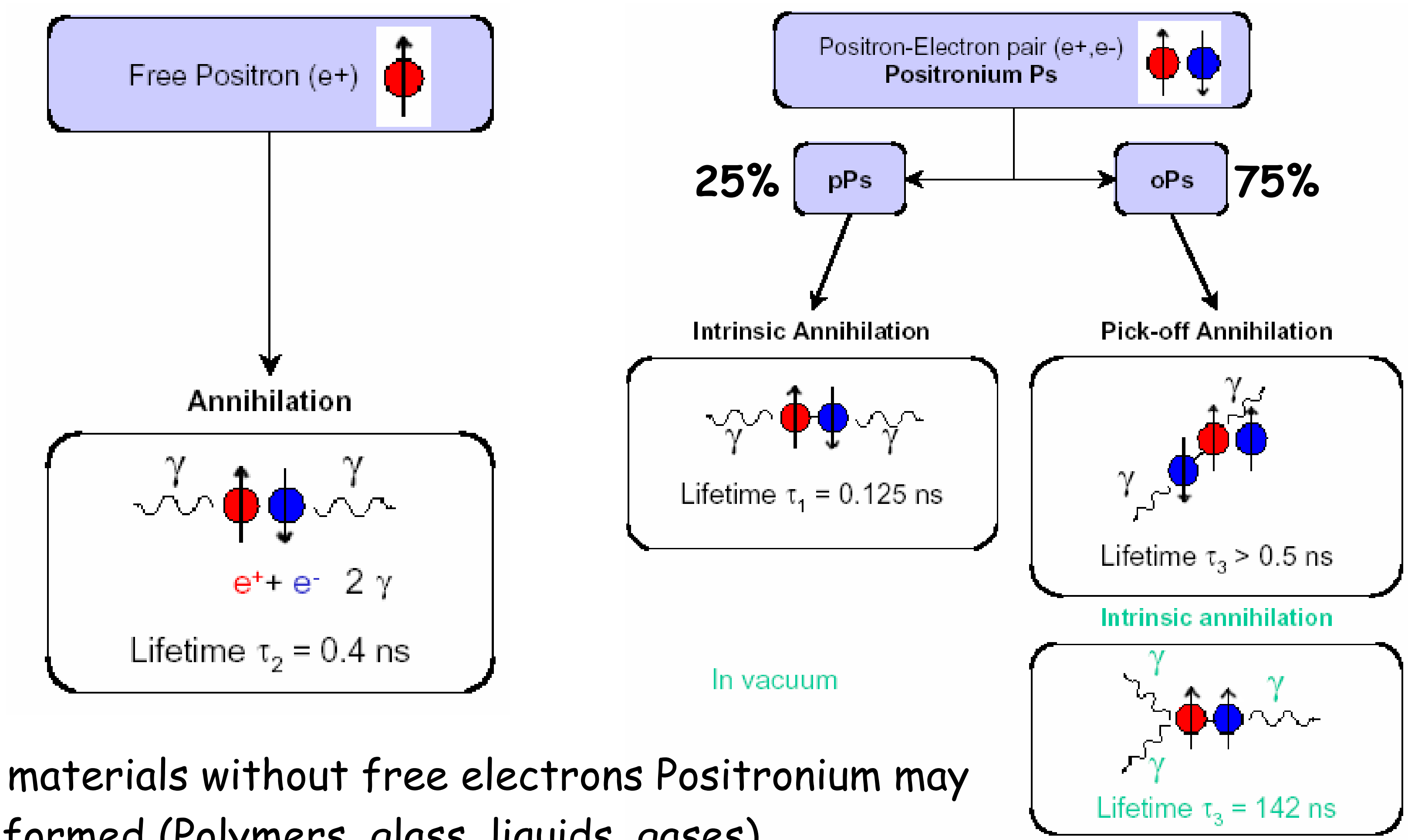
Minimum at: 43.9005

Fraction Point: -0.0921488

Fraction Point At: 40.0176

Minimum: -0.395635

Principles of PALS: ortho-Positronium



Free Positron (e+)

Annihilation

$e^+ + e^-$ 2 γ

Lifetime $\tau_2 = 0.4$ ns

Positron-Electron pair (e+,e-)
Positronium Ps

25% pPs

oPs **75%**

Intrinsic Annihilation

Lifetime $\tau_1 = 0.125$ ns

Pick-off Annihilation

Lifetime $\tau_3 > 0.5$ ns

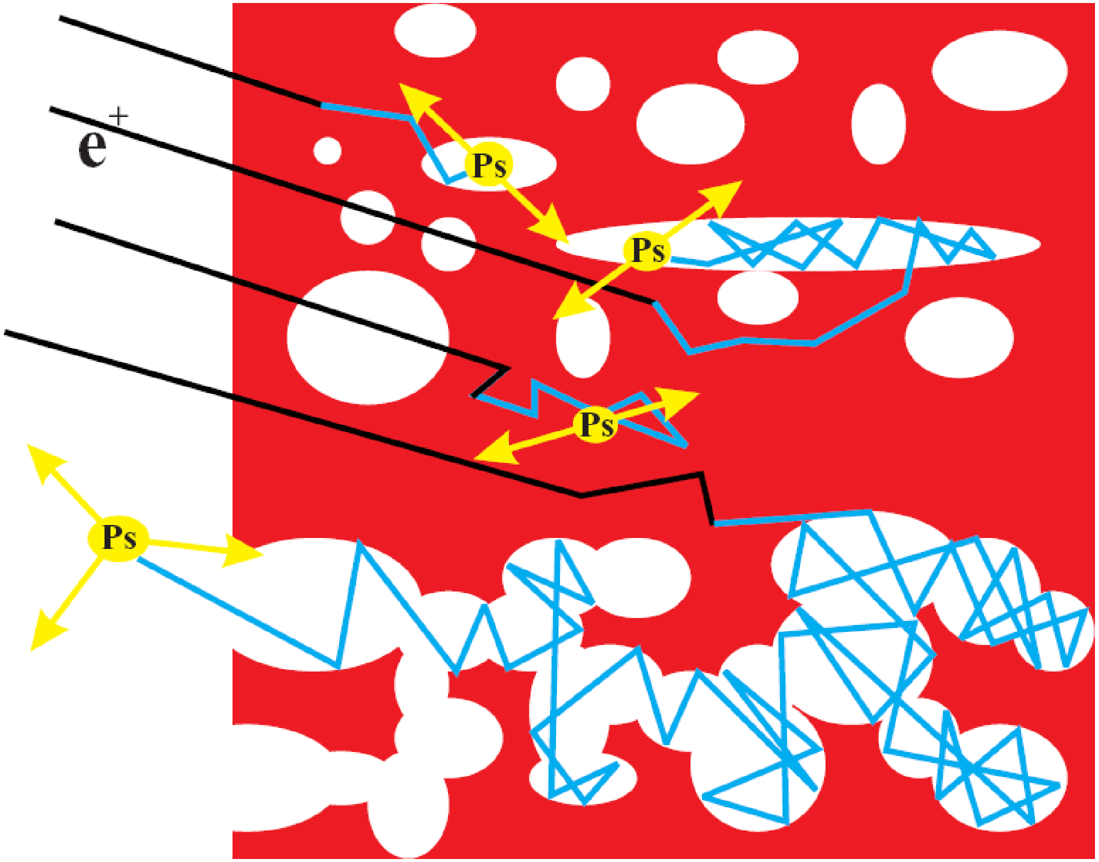
In vacuum

Intrinsic annihilation

Lifetime $\tau_3 = 142$ ns

- In materials without free electrons Positronium may be formed (Polymers, glass, liquids, gases).

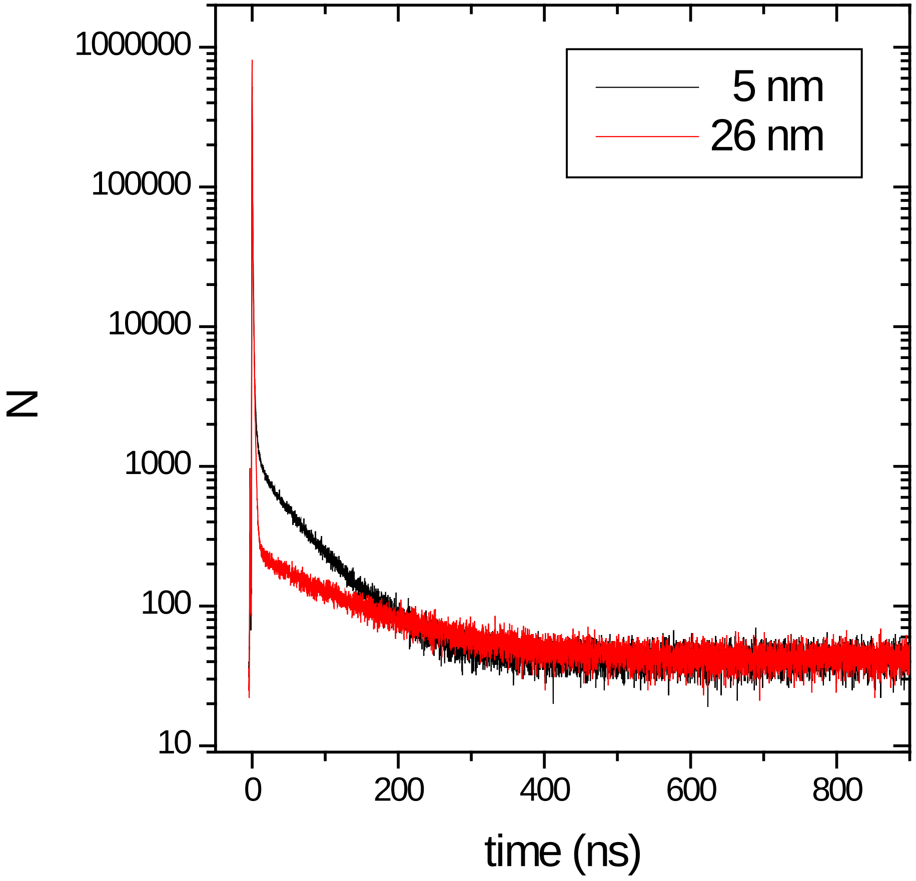
Principles of PALS: pick-off Annihilation



pick-off annihilation:

- o-Ps is converted to p-Ps by capturing an electron with anti-parallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size 0.5 ns ... 142 ns
- lifetime can be extracted from spectra

Principles of PALS: typical spectrum

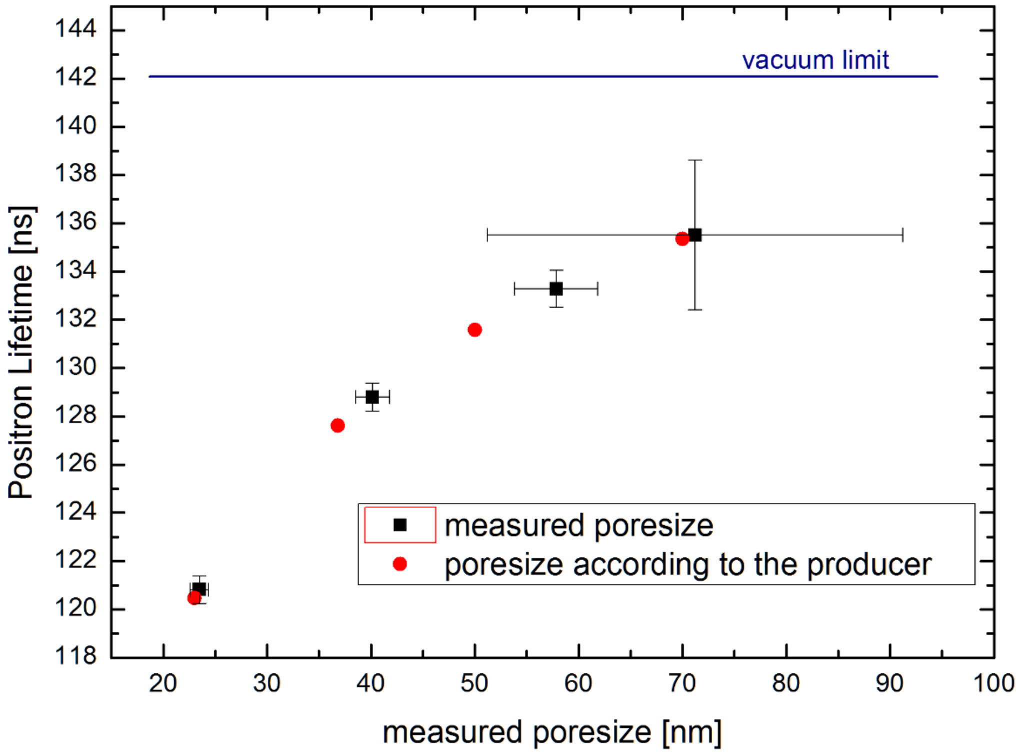


typical lifetime spectrum for porous glass:

- 4 exponential decay components
- p-Ps -> 0.125 ns
- free positrons ~ 0.5 ns
- o-Ps in amorphous region of glass ~ 1.5 ns
- o-Ps in pores

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

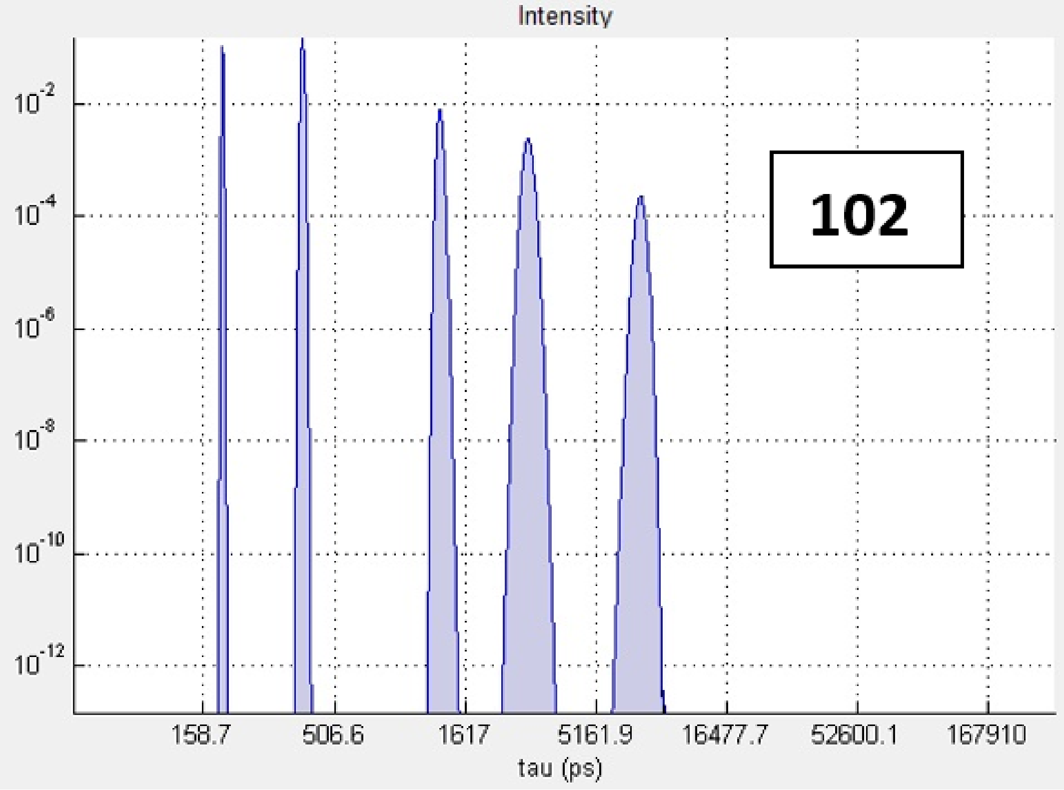
PALS: detection limits



- lower detection limit: open volume of 2Å diameter
- e.g. open volume between polymer chains

- upper limit: ≈ 60 nm diameter
- physical limit: vacuum lifetime of o-Ps = 142 ns
- upper limit depends also on corresponding intensity

New Analysis Technique: MELT



porous polymer

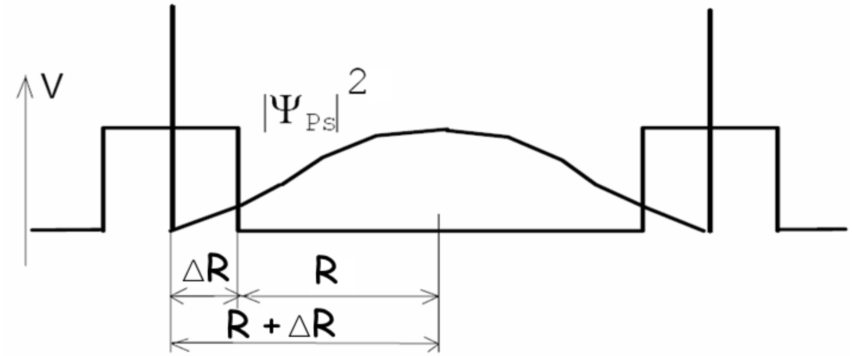
MELT[1] = Maximum Entropy for Lifetime Analysis

- number of components must not be known
- output is intensity versus lifetime
- pore size distribution can be determined
- disadvantage: very high statistics necessary (> 10^7 counts)

---

[1] A. Shukla et al., 1997, Materials Science Forum, 255-257, 233

The TE model



- Annihilation rate: $\dfrac{1}{\tau_{o-Ps}} = \lambda_{o-Ps}$

$$= \lambda_{2\gamma} + \lambda_{3\gamma}$$

$$= \lambda_{2\gamma}^{0}(P) + \lambda_{3\gamma}^{0}(1-P) \cong \lambda_{2\gamma}^{0}(P)$$

$$\lambda_{2\gamma}^{0} = \frac{\lambda_S + 3\lambda_T}{4} = \lambda_A \approx 2ns^{-1}$$

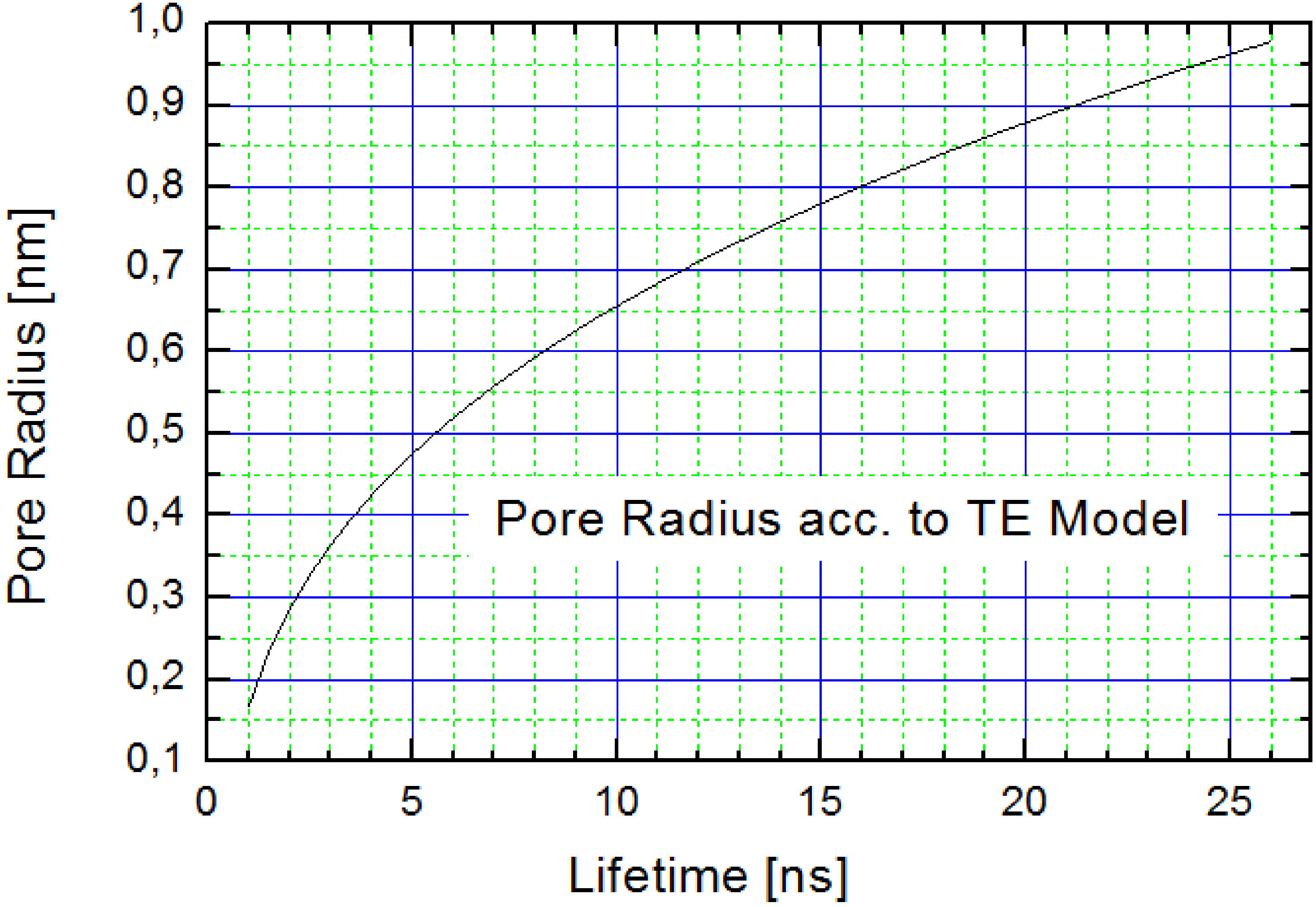
- Pore size < 1 nm -> $\lambda_{3\gamma}$ neglected, only pick off annihilation

$$\lambda_{TE}(R) = \lambda_A\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]$$

- ΔR = 0.166 nm determined by Eldrup and Jean
- Pore size > 1 nm ->$\lambda_{3\gamma}$ cannot be neglected, temperature dependence of o-Ps lifetime (excited states)

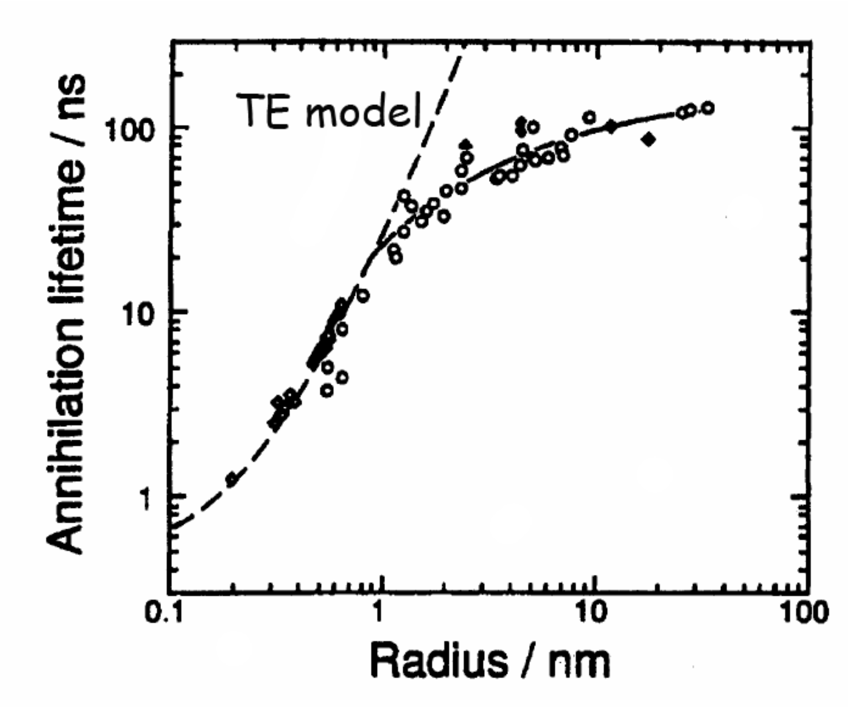
Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

The TE model (valid until 1 nm radius)

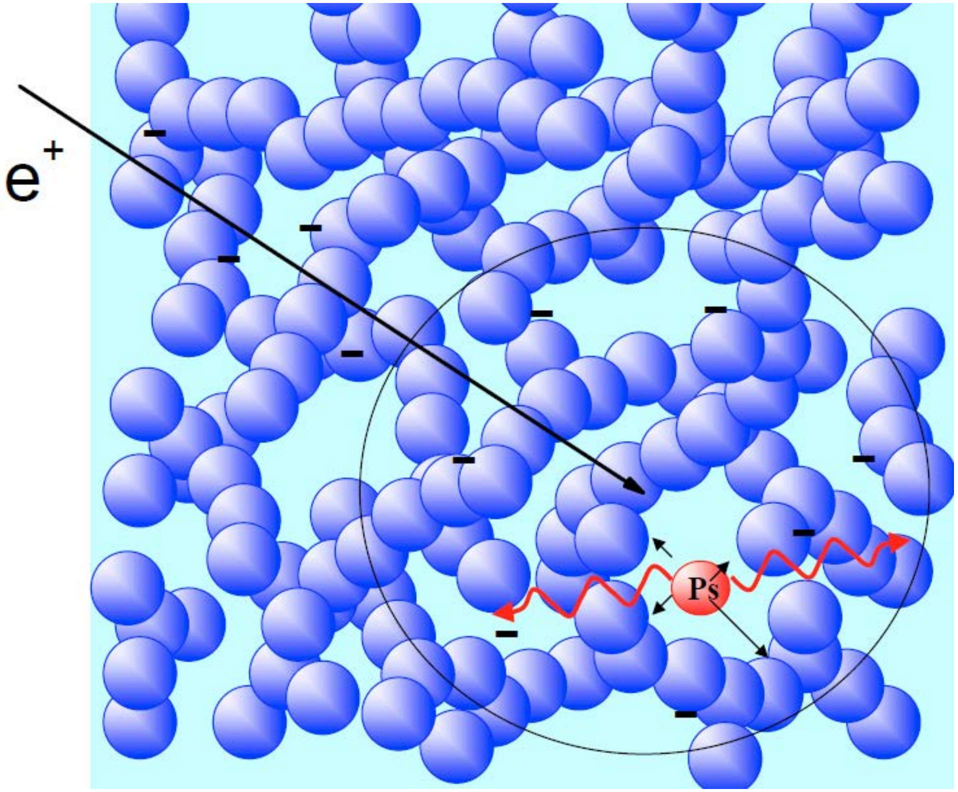


Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

The TE model

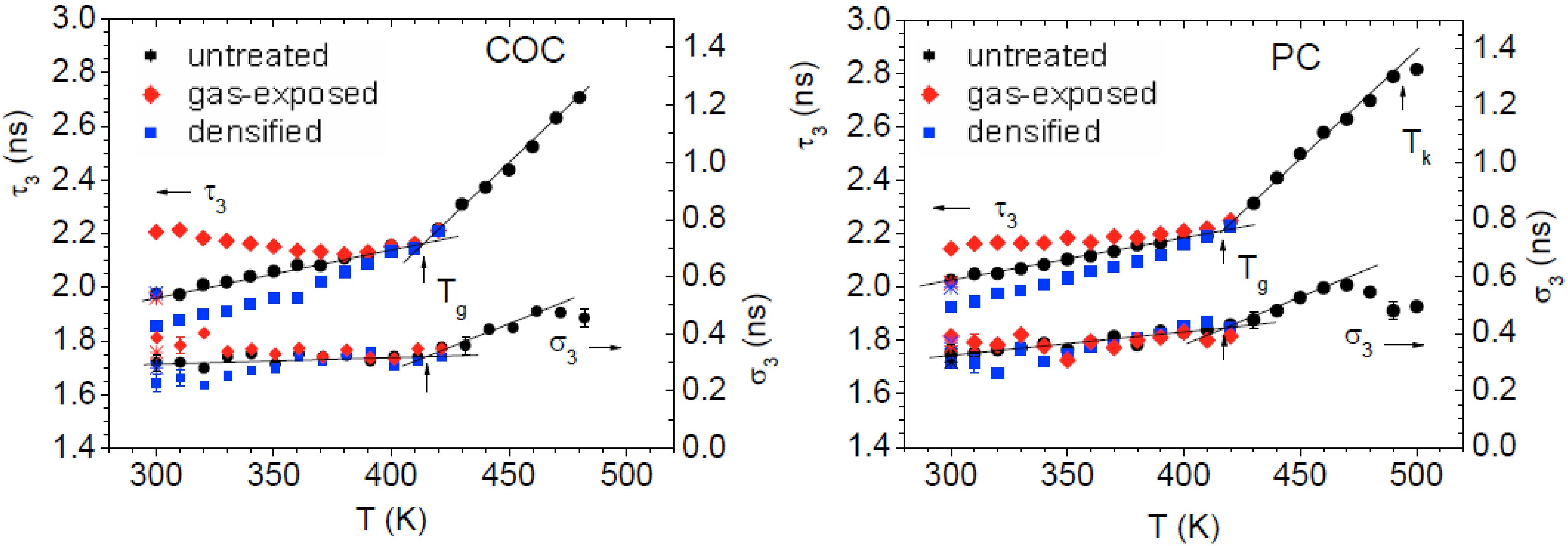


- TE model valid for r > 2nm
- very successful for open-volume characterization in polymers



Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

Polymer research



PALS study of different polymers under CO_2 gas exposure and pressure densified (200 MPa)

G. Dlubek et al., Macromol. Chem. Phys. 2008, 209, 1920–1930 and e-Polymers 2007, no. 108

Polymer research

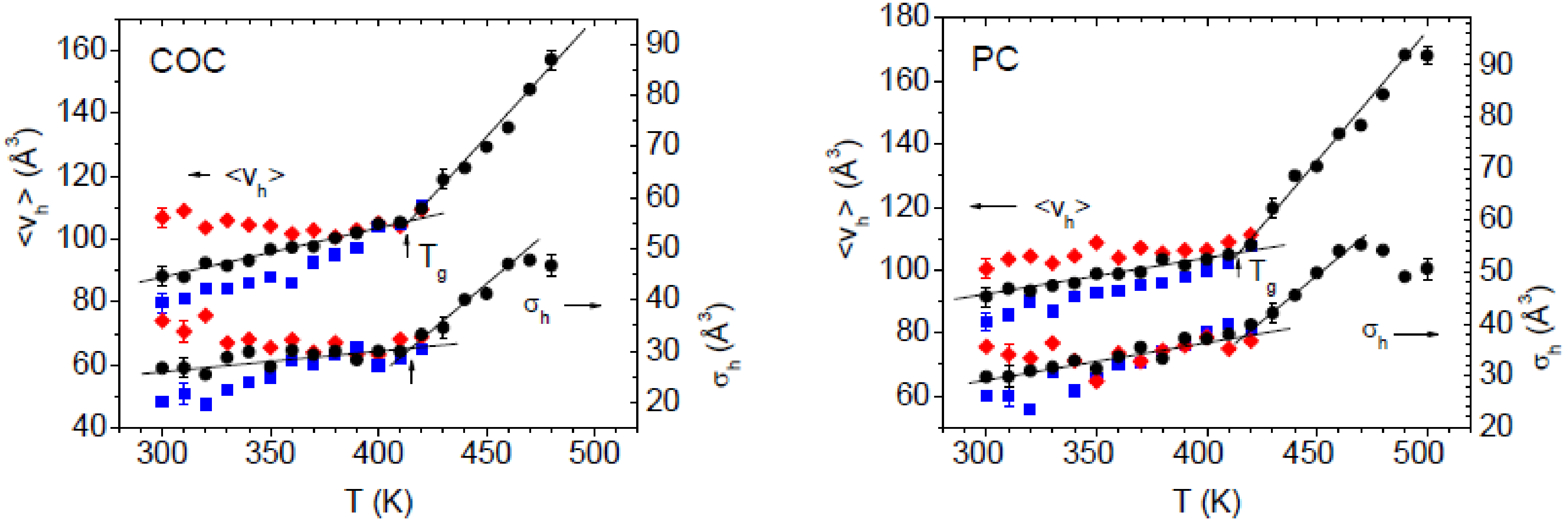
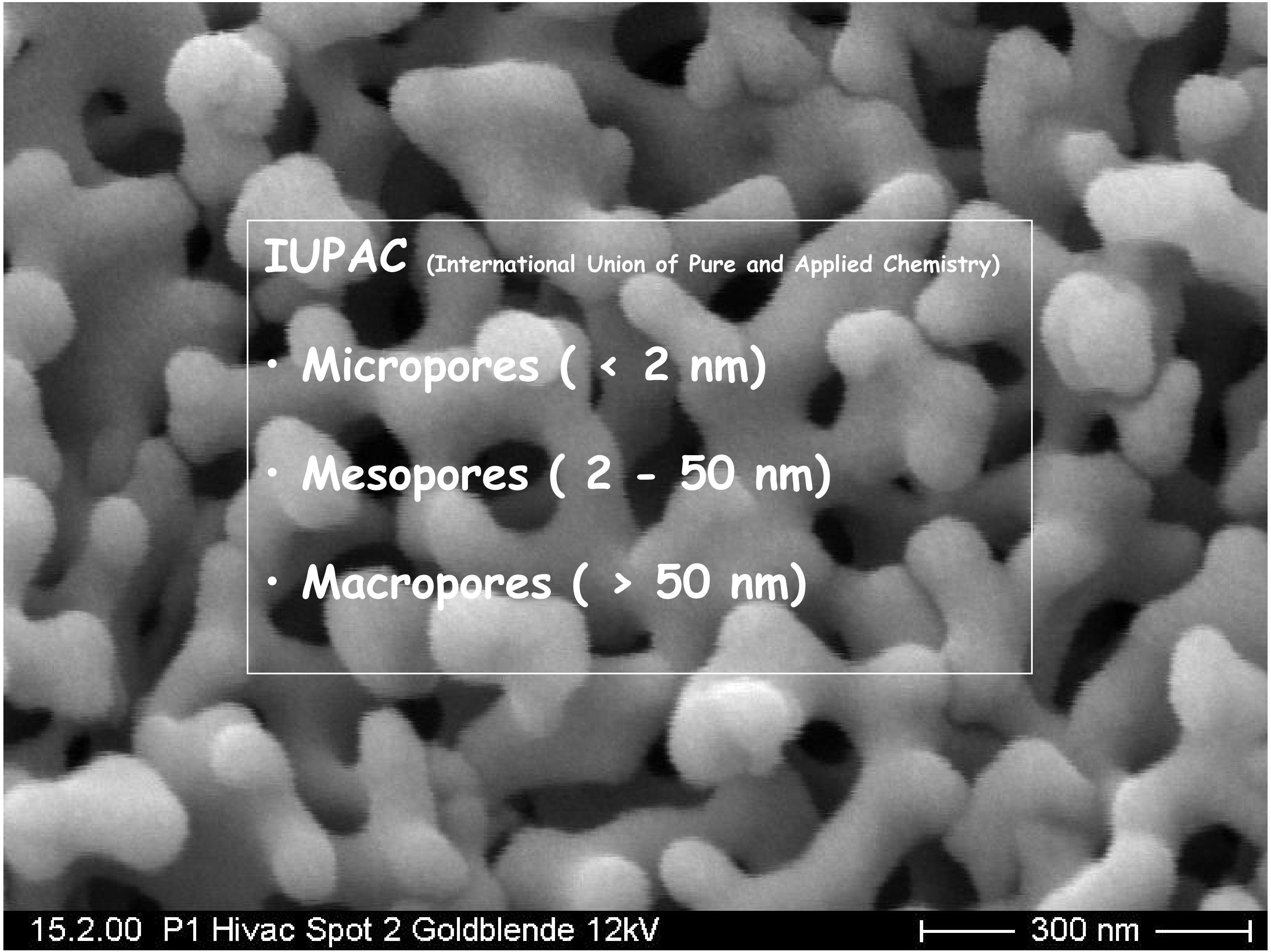


Fig. 5. The mean, $\langle v_h \rangle$, and the mean dispersion, σ_h, of the hole volume as a function of temperature *T* for untreated (black), densified at 200 MPa (blue), and CO_2 gas-exposed and degassed (red) COC and PC.

G. Dlubek et al., Macromol. Chem. Phys. 2008, 209, 1920–1930 and e-Polymers 2007, no. 108

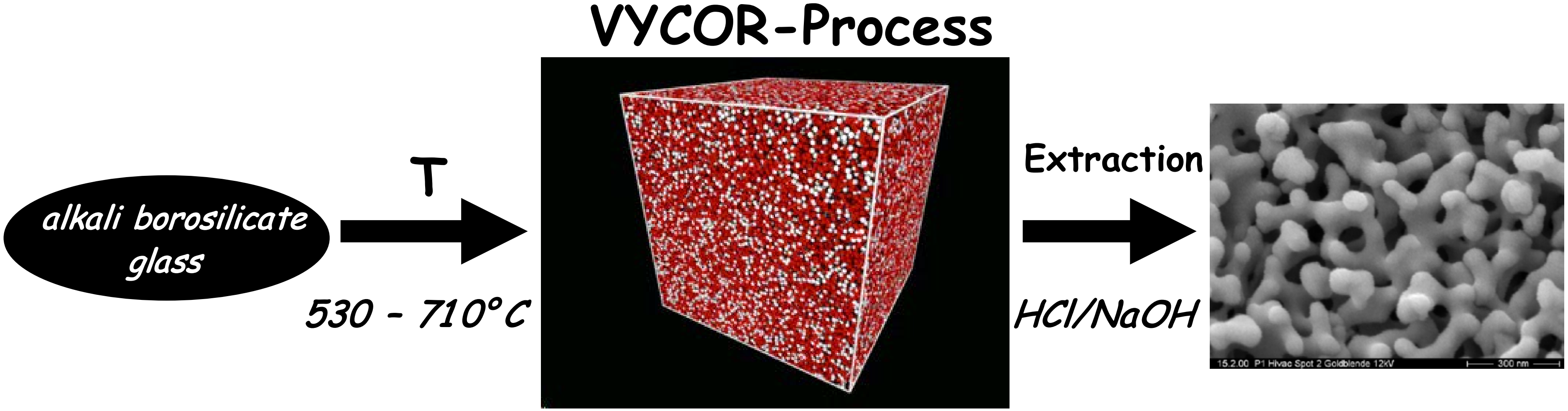
Mesopores - Controlled pore glasses



IUPAC (International Union of Pure and Applied Chemistry)

- Micropores (< 2 nm)
- Mesopores (2 - 50 nm)
- Macropores (> 50 nm)

Controlled pore glasses - CPG



VYCOR-Process

alkali borosilicate glass

T

530 - 710°C

Extraction

HCl/NaOH

d_p 1 to 110 nm

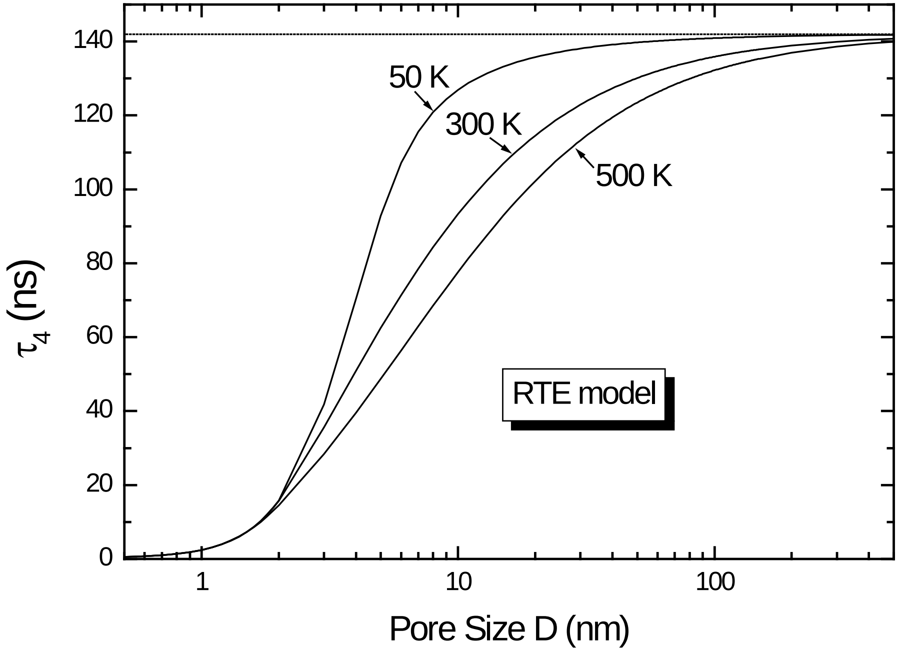
- spinodal phase separation
- decomposition is initiated by heat treatment
- alkali rich borate phase <-> pure silica
- alkali phase soluable in acid -> silica network
- pore size depends on basic material
- shape depends on duration and T of heat treatment

F. Janowski, D. Enke in F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH, Weinheim, **2002**, 1432-1542.

Model for R > 1 nm - RTE

- Rectangular TE model = RTE model (for 3D cubic pores):

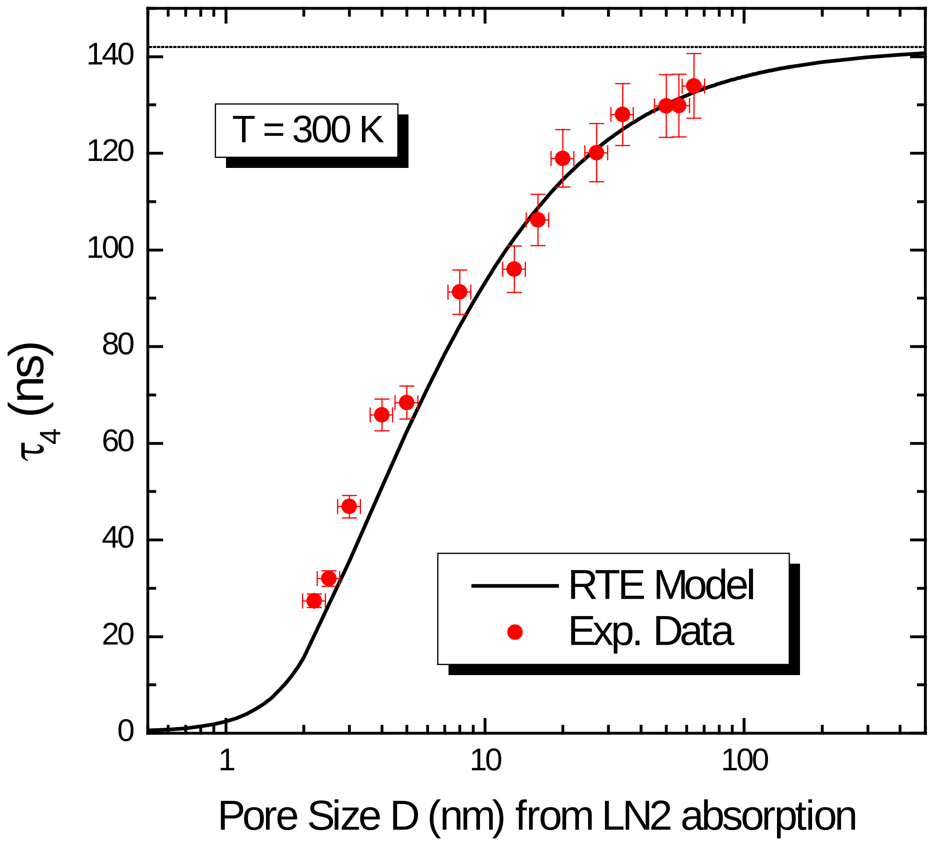
$$\lambda_{RTE}(D,T) = \lambda_A - \frac{\lambda_S - \lambda_{3\gamma}}{4}\left[1 - \frac{2\delta}{D} + \frac{\sum_{i=1}^{\infty} \frac{1}{i\pi}\sin\left(\frac{2i\pi\delta}{D}\right)e^{\left(\frac{-\beta i^2}{D^2kT}\right)}}{\sum_{i=1}^{\infty} e^{\left(\frac{-\beta i^2}{D^2kT}\right)}}\right]^3$$



- Boltzmann statistics ascribes explicit temperature dependence to the lifetime
- Rectangular geometry -> prevention of complicated Bessel functions
- δ= 0.18 nm analogous to TE model

D. W. Gidley, T. L. Dull, W. E. Frieze, J. N. Sun, A. F. Yee, *J. Phys. Chem. B* **2001**, *105*, 4657.

The experiments at room temperature



- we measured porous glass in a broad pore size range
- pore size obtained by N_2-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

The RTE model

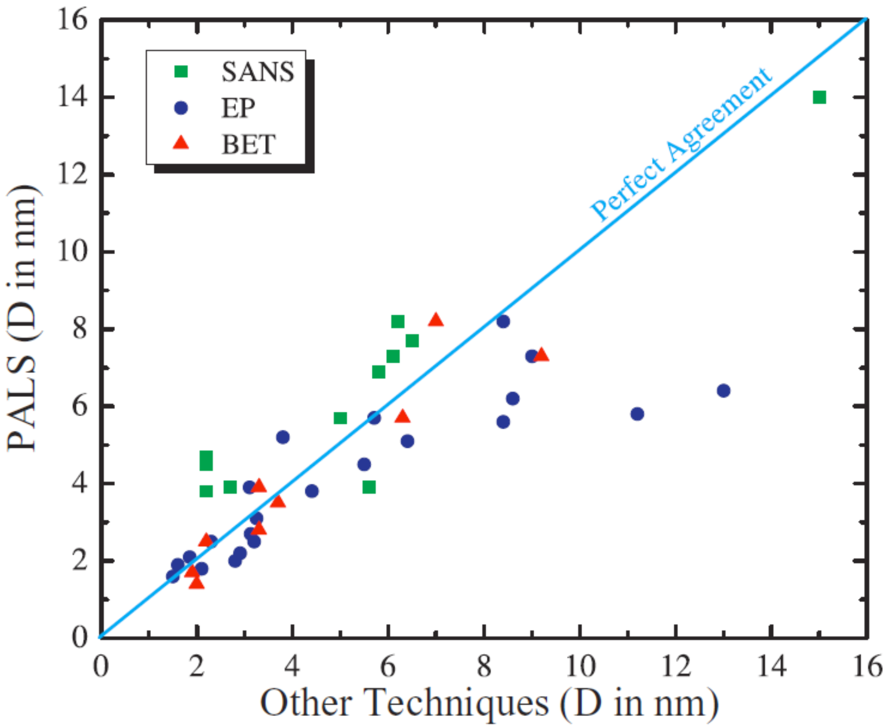


Figure 5 (*Top*) Pore size calibration calculated at different temperatures versus mean-free path. (*Bottom*) Recent round-robin comparisons of PALS pore diameters with those measured by small-angle neutron scattering (SANS), ellipso-metric porosimetry (EP), and gas absorption (BET).

D.W. Gidley et al., Annu. Rev. Mater. Res. 2006. 36:49–79

Small pores in the wall of larger pores

Microporous and Mesoporous Materials 182 (2013) 136–146

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

ELSEVIER

Transformation of porous glasses into MCM-41 containing geometric bodies

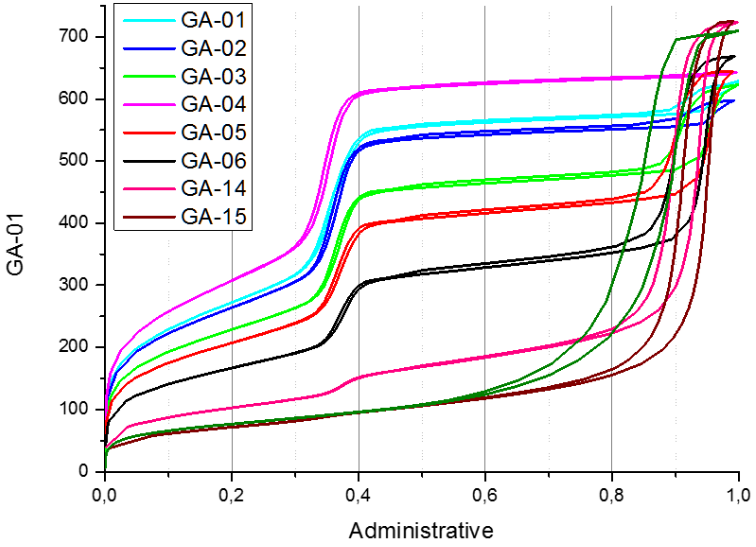
CrossMark

Hans Uhlig [a,*], Marie-Luise Gimpel [a], Alexandra Inayat [b], Roger Gläser [a], Wilhelm Schwieger [b], Wolf-Dietrich Einicke [a], Dirk Enke [a]

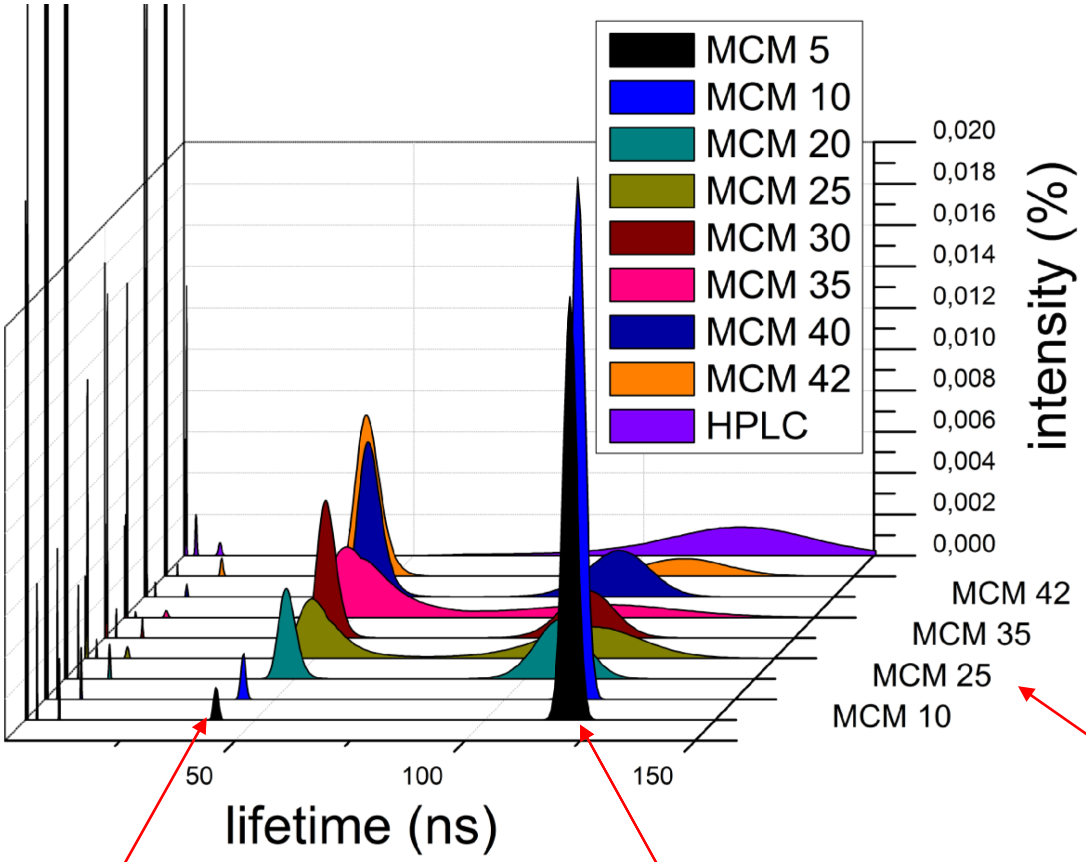
[a] *University of Leipzig, Institute of Chemical Technology, Linnéstr. 3, 04103 Leipzig, Germany*
[b] *University of Erlangen-Nuremberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany*

Sample	Amount of tenside solution in ml	new sample name
GA-01	40	MCM-40
GA-02	35	MCM-35
GA-03	30	MCM-30
GA-04	42	MCM-42
GA-05	25	MCM-25
GA-06	20	MCM-20
GA-14	10	MCM-10
GA-15	5	MCM-05

LN2 adsorption



data analysis by MELT



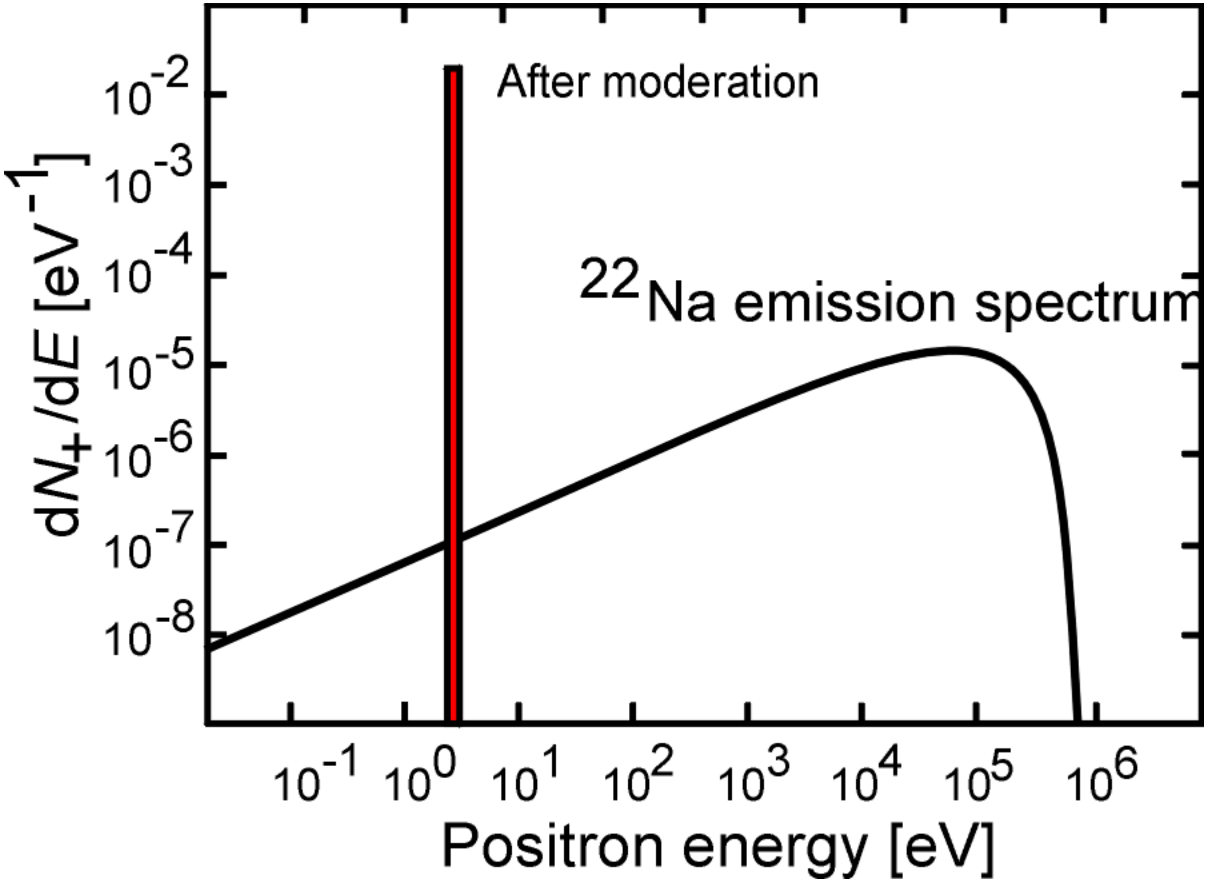
- solvent (MCM) was added into a larger pore system
- large pores: 15 nm
- small pores are formed in the walls: 4 nm

amount of solvent

4 nm pores

15 nm pores

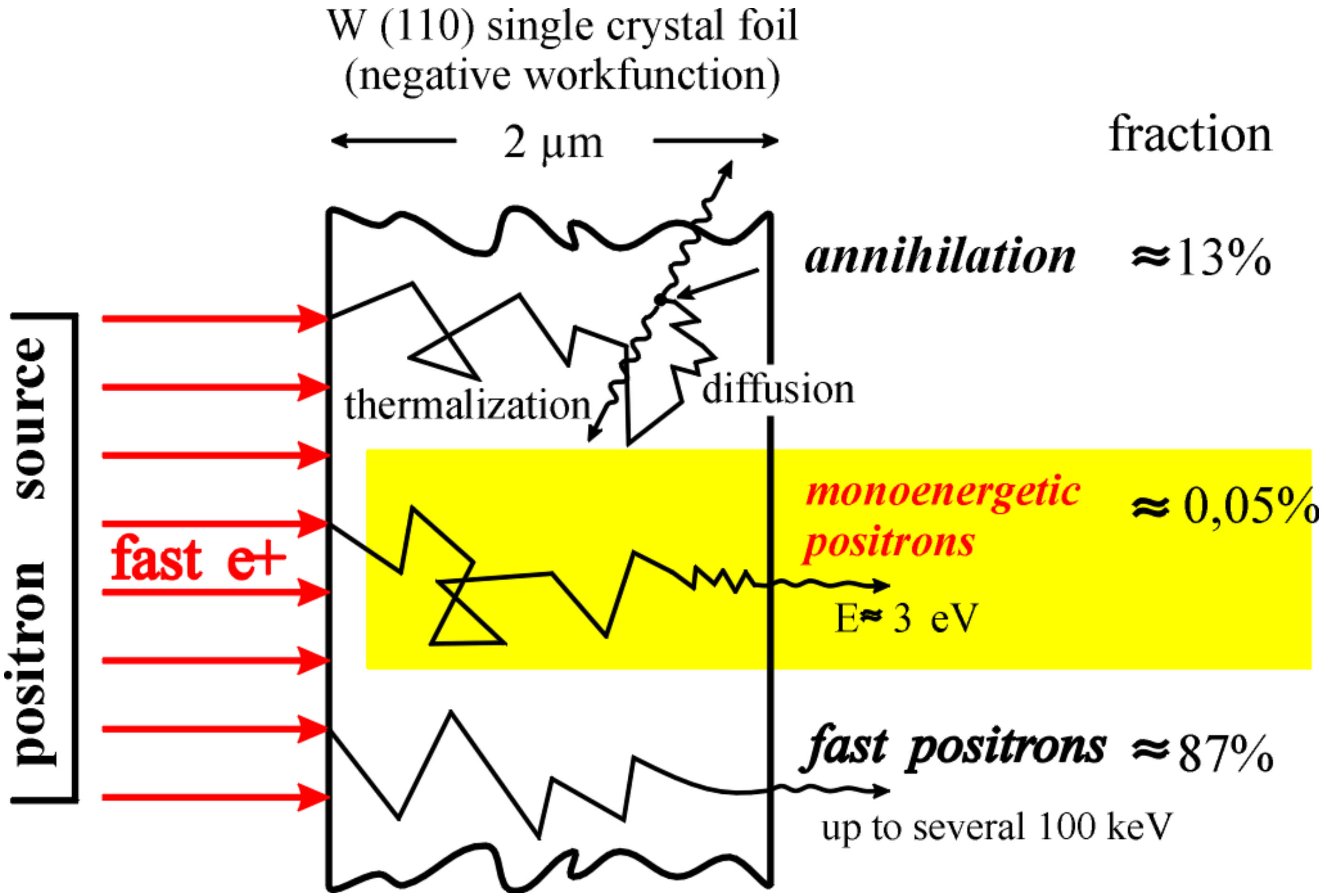
The Slow-Positron Beam Technique



- broad positron emission spectrum from beta sources
- deep implantation into solids
- no use for study of defects in thin layers
- moderation necessary

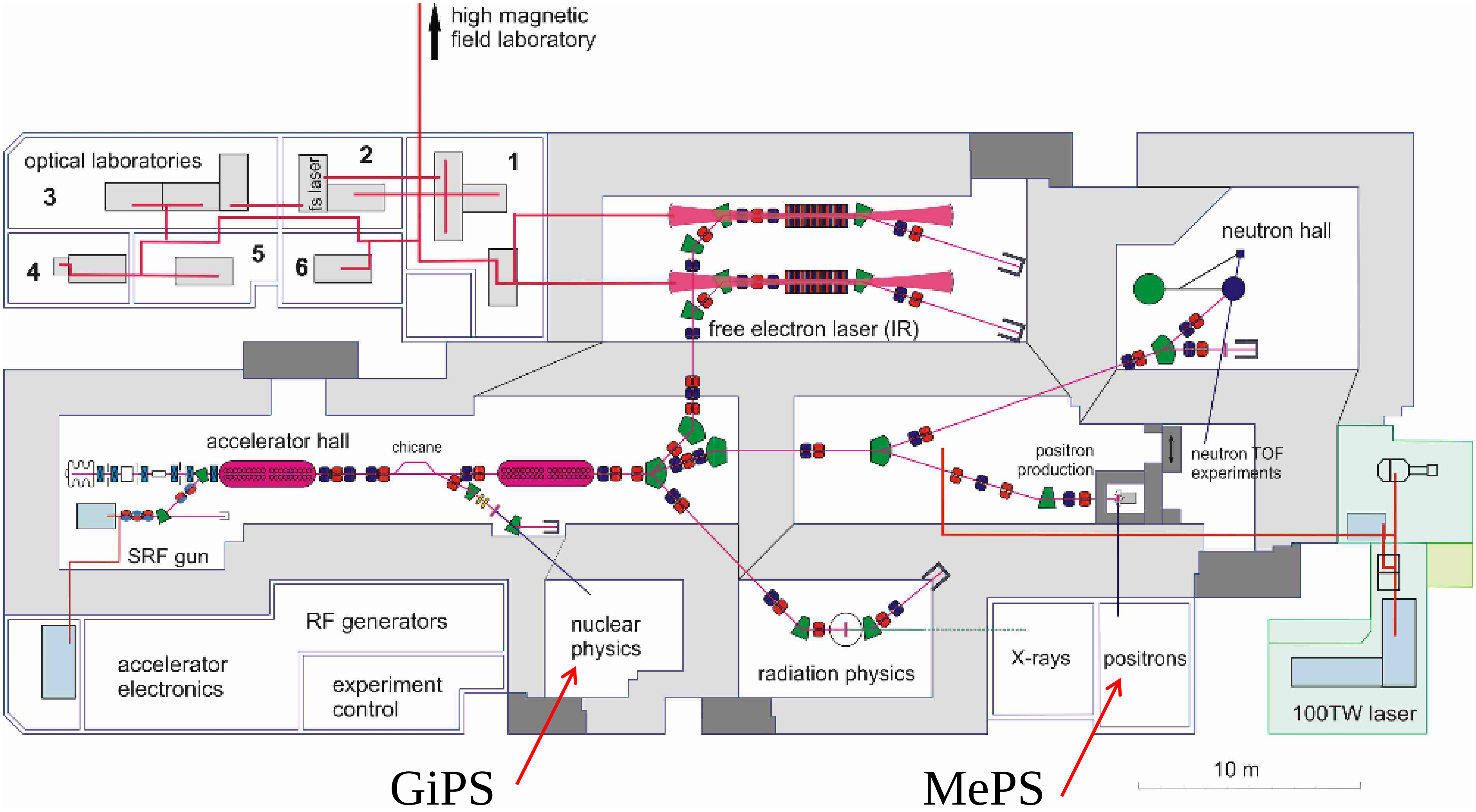
Mean implantation depth of un-moderated positrons (1/e): Si: 50µm

Moderation of Positrons

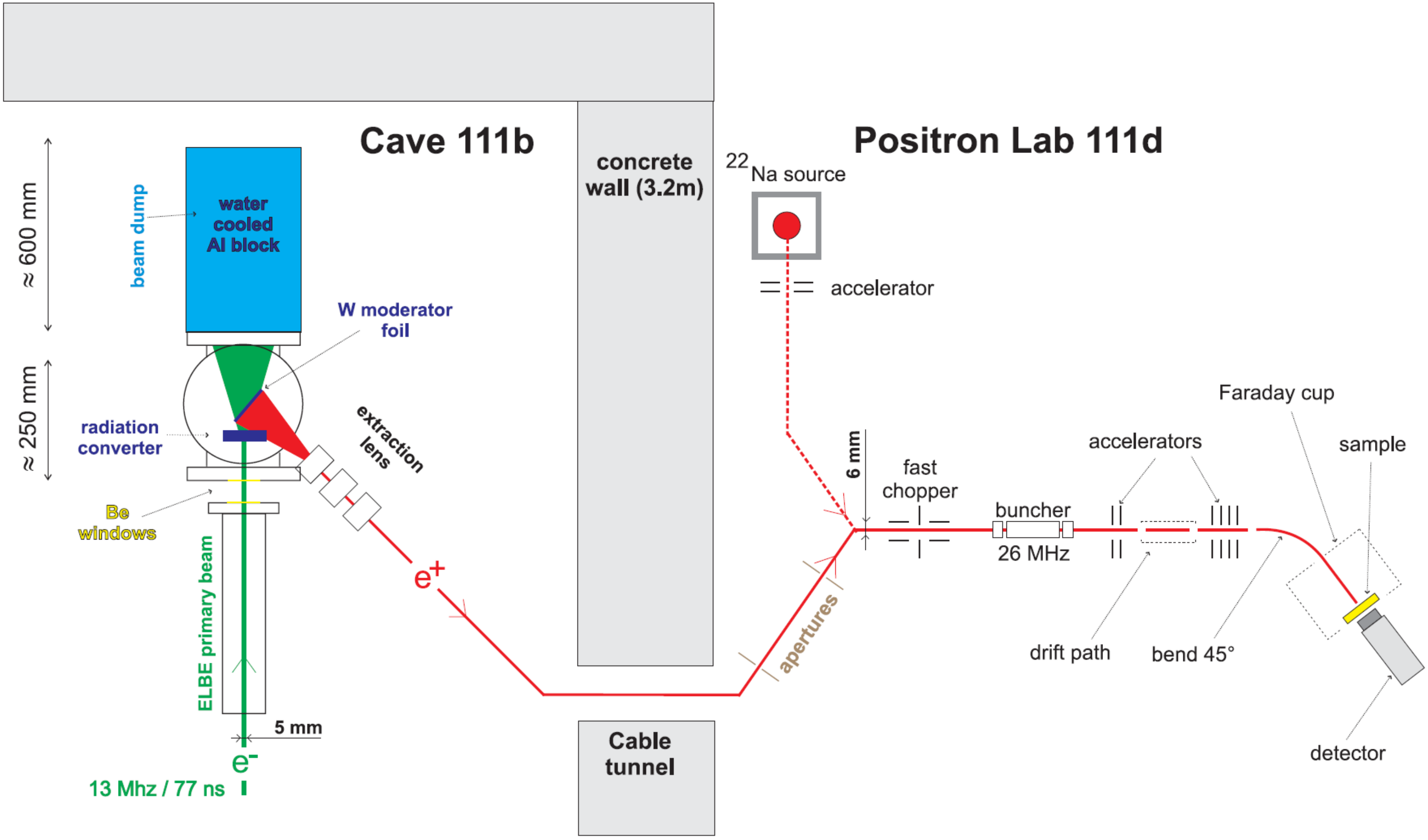


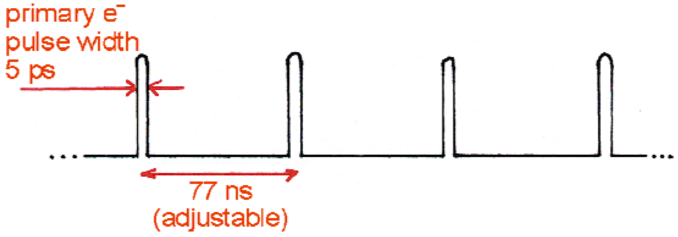
moderation efficiency: ≈10^{-4}

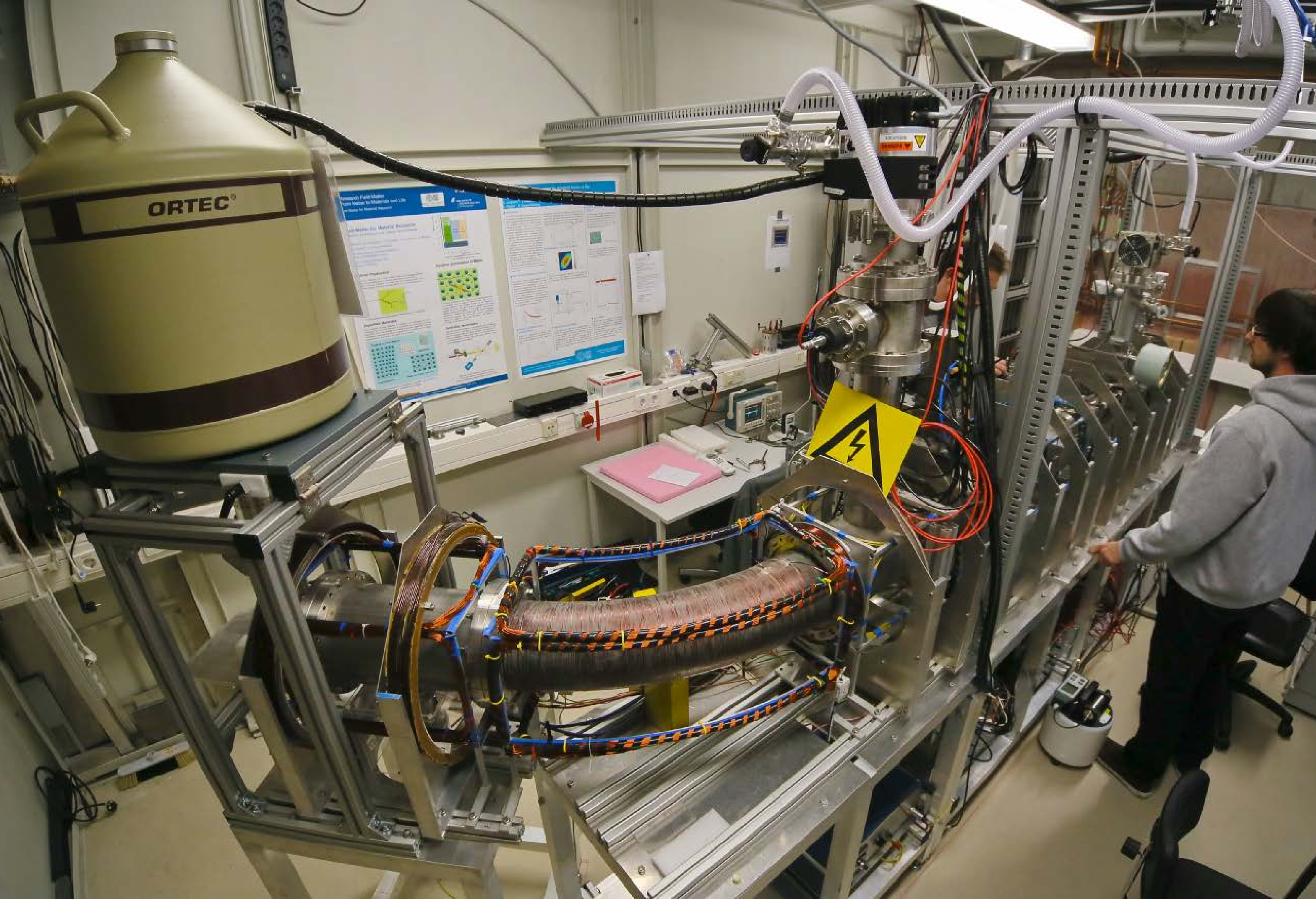
HZDR Dresden-Rossendorf: Ground map of the ELBE hall



MePS scheme


Cave 111b
Positron Lab 111d
concrete wall (3.2m)
≈ 600 mm
≈ 250 mm
beam dump
water cooled Al block
W moderator foil
radiation converter
extraction lens
Be windows
ELBE primary beam
5 mm
e-
13 Mhz / 77 ns
e+
Cable tunnel
22Na source
accelerator
apertures
6 mm
fast chopper
buncher
26 MHz
accelerators
drift path
bend 45°
Faraday cup
sample
detector


primary e- pulse width 5 ps
77 ns (adjustable)



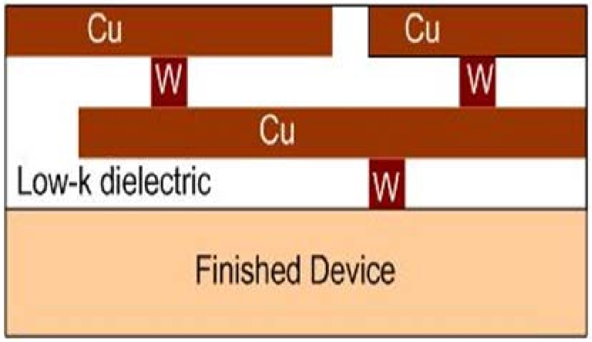
MePS system @ ELBE, 26. November 2013

Low-K dielectric layers

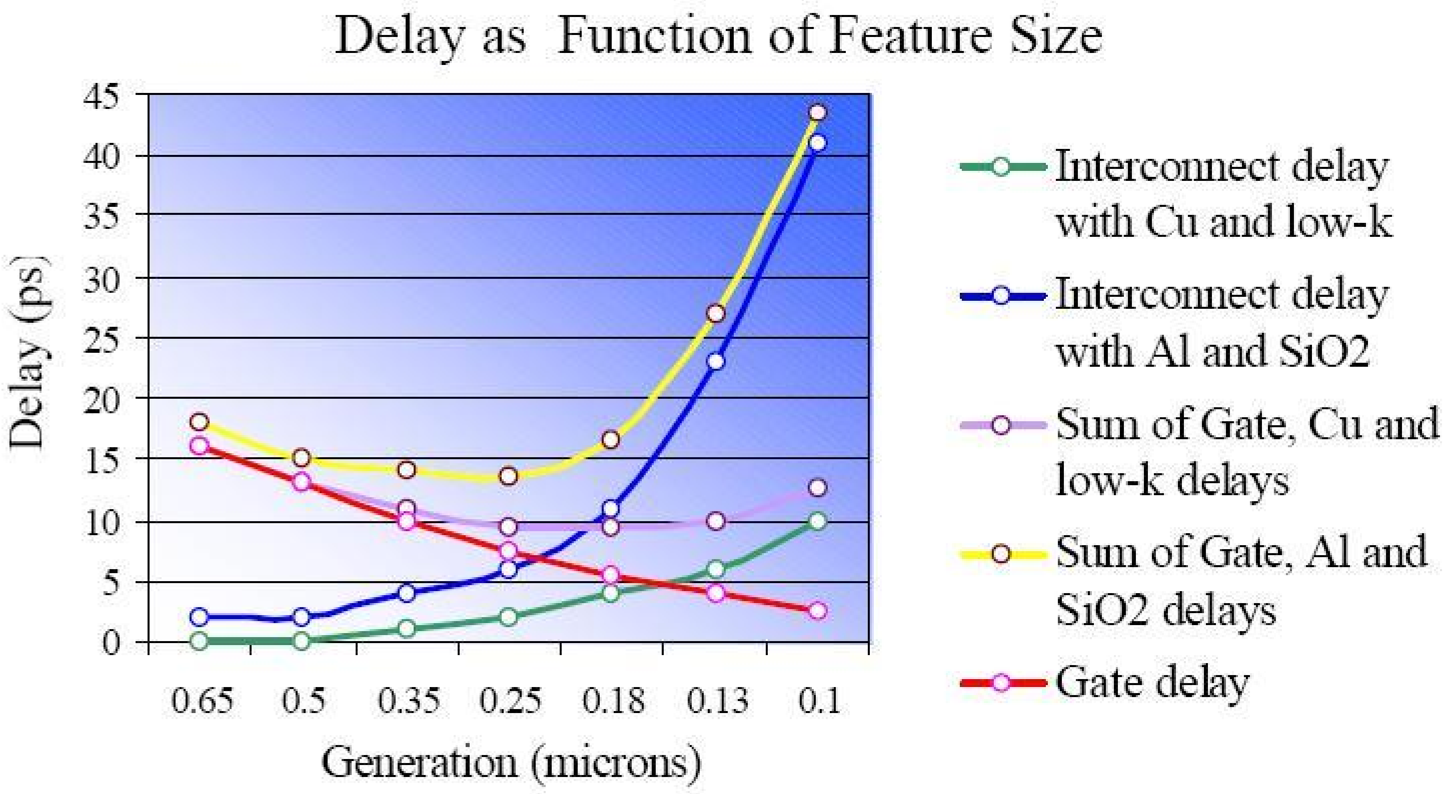
- modern ultra-large scale microprocessors suffers from long relaxation times
- information transport is limited by product R × C
- R has been decreased: Copper technology (instead of Al)
- C is relatively high when SiO_2 is used as isolation layer; ε_r=4

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

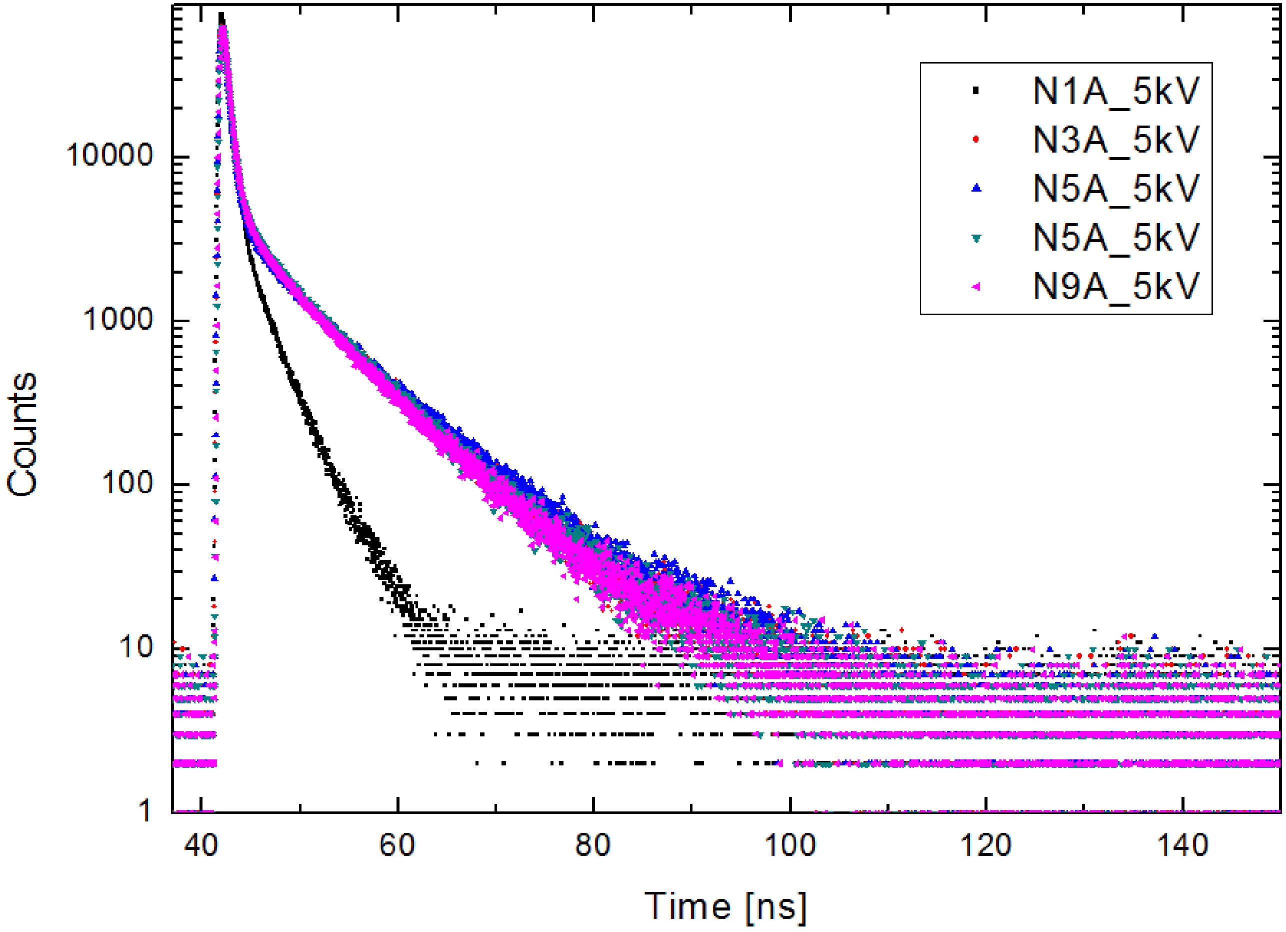
- low-k (small ε_r = 2…2.5) layers may help
- these are layers with micropores with pore size of d≈1 nm with high porosity
- problem for characterization: closed porosity



Low-K dielectric layers

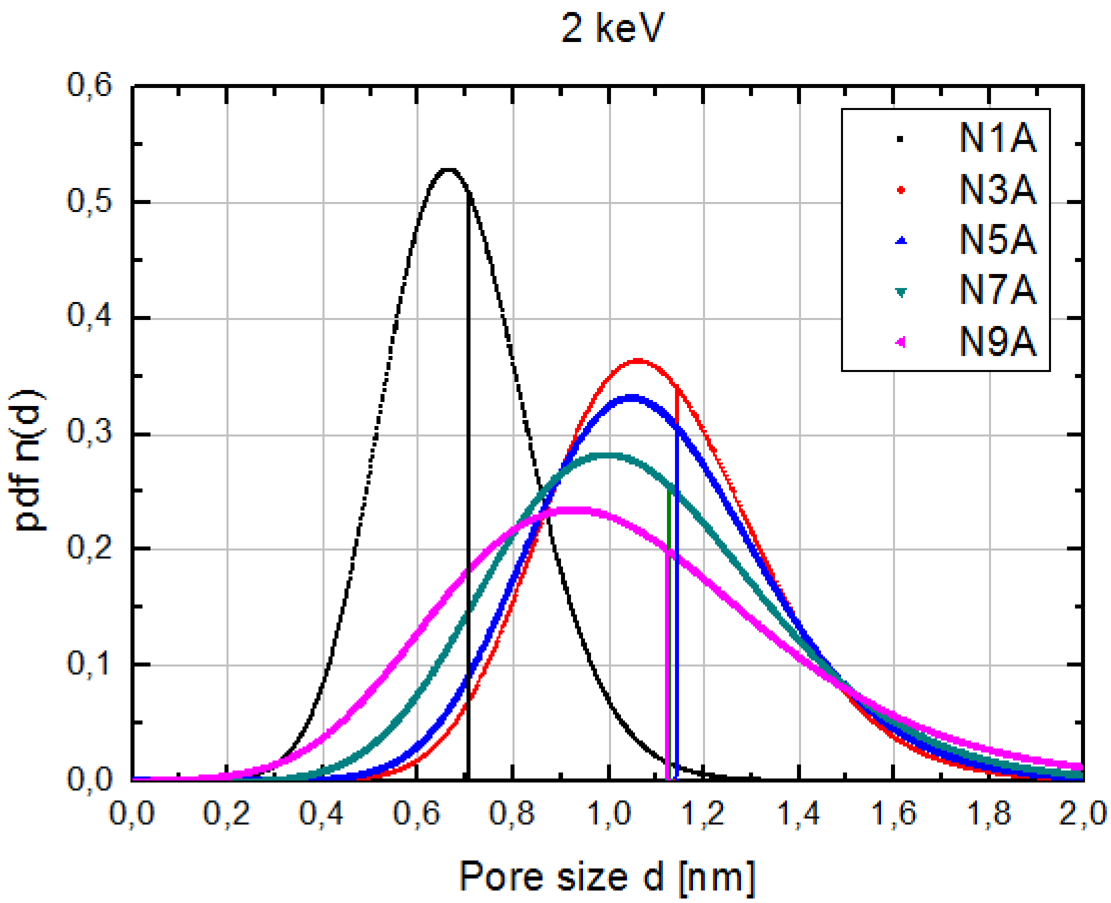


Low-K dielectric layers



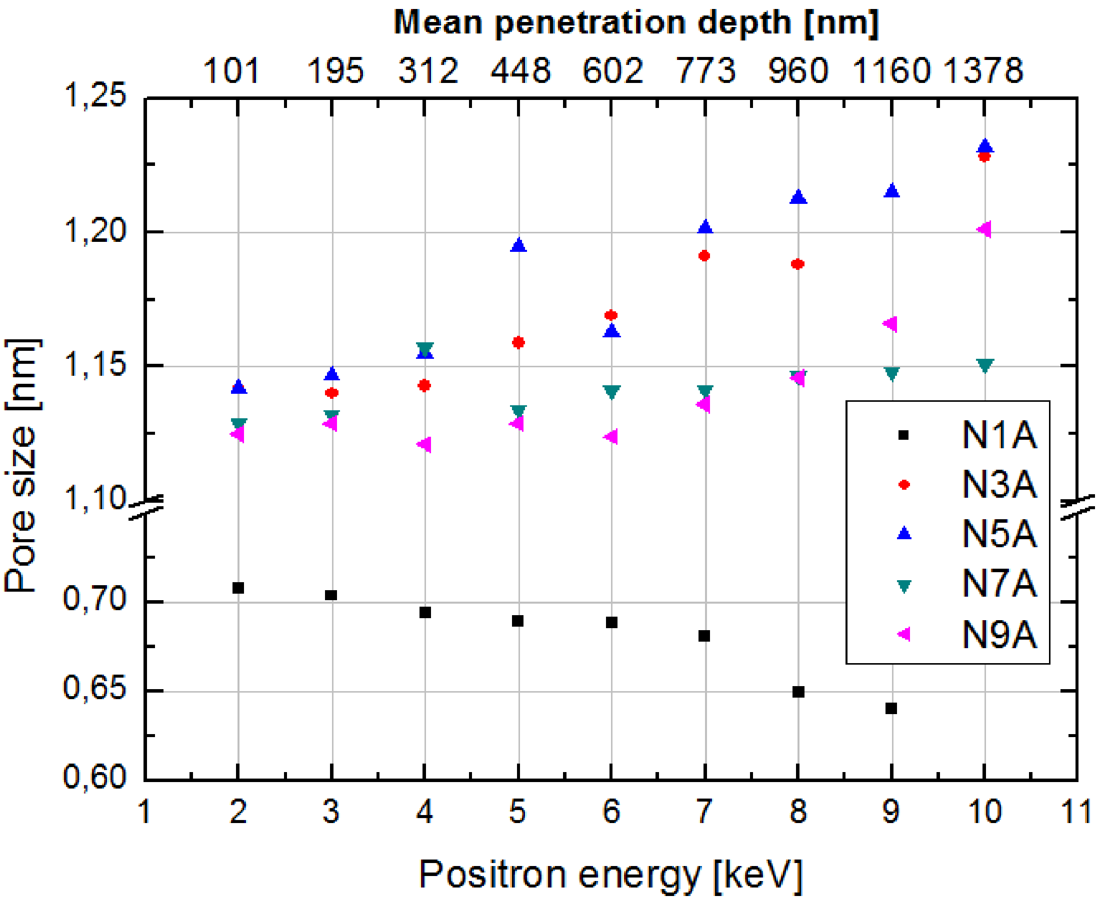
- Positrons are ideal tool for closed porosity in low-k layers
- Lifetime spectra of differently treated low-K layers
- Treatment:
  - untreated porous layer
  - plasma treatment for compactation
  - TiN cap layer

Low-K dielectric layers



- dispersion of lifetime gives the size distribution of the pore system

Low-K dielectric layers



- monoenergetic positrons can be used to depth scan the layer
- monoenergetic positrons are obtained by moderation

Summary

- PALS is a useful porosimetry tool
  - very sensitive method for **small pores (0.3 to 10 nm)**
  - upper sensitive limit ≈ 60 nm
  - **non-destructive** method
  - Works in open and **closed pore** systems
  - applicable also for **thin layers** (50 … 2000 nm)

HZDR Dresden-Rossendorf 21.-23. October 2015

Workshop

Methods of Porosimetry and Applications

The workshop will treat aspects of the different methods of porosimetry, such as N_2-Adsorption, Hg intrusion, SAXS, SANS and Positron Annihilation. Tutorial talks will be given about these topics. The limitations and possible applications of these techniques will be discussed. The workshop will be organized at the Institute of Radiation Physics at HZDR in Dresden-Rossendorf.

Dr. A. Wagner

Prof. D. Enke

Prof. R. Krause-Rehberg

UNIVERSITÄT LEIPZIG

Helmholtz-Zentrum Dresden-Rossendorf

Martin-Luther-Universität Halle-Wittenberg

> *“A theory is something nobody believes,*
> *except the person who made it.*
> *An experiment is something everybody*
> *believes, except the person who made it.”*
>
> *Albert Einstein (American German 1879-1955)*

Acknowledgement

Uni Halle	**HZDR**
Stefan Thränert	Andreas Wagner
Dirk Enke	Maik Butterling
Marco Jungmann	Wolfgang Anwand
Maik Butterling	
Steve Zieger	
Thomas Cudrig	
Mohamed Elsayed	….and more