Positron Annihilation – a powerful Method for open and closed Porosimetry

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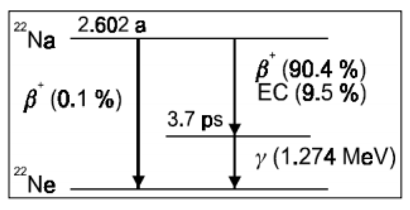
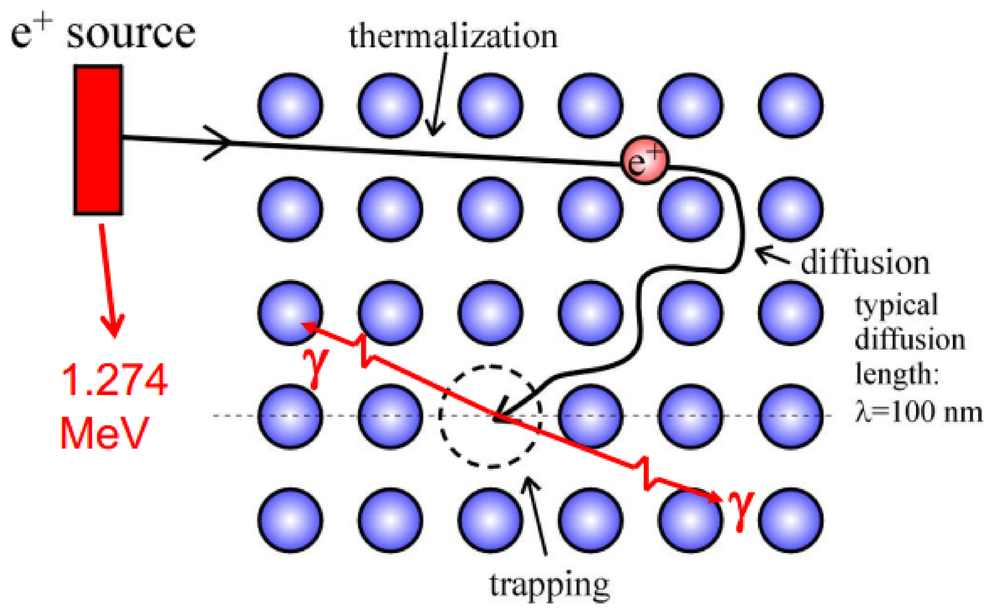
Positrons are obtained in from weak radioactive sources of 22-Na. In porous systems, positronium as bound state between a positron and an electron can be formed. Para-positronium (p-Ps), as the singlet state (opposite spins) annihilates in 125 ps and does not carry any information about the host system. However, 75% of the positronium is generated as ortho-positronium (triplet state) with parallel spins. The lifetime in vacuum is 142 ns. In a pore, o-Ps will be bounced between the pore walls. At the wall, o-Ps can exchange the electron of the parallel spin to an electron of opposite spin, and thus form p-Ps, which annihilates very fast. This process is called **pick-off annihilation**. It may shorten the positronium lifetime to values between 0.7 and 142 ns depending on the pore size. Thus, Ps lifetime spectroscopy can be used for porosimetry in the range from 0.5 to about 50 nm . From a possible distribution of the lifetimes, also the pore size distribution can be reconstructed. The method can be applied for open- and closed-pore systems. Typical applications are the investigation of open volume between polymer chains and molecules of ionic liquids; porous membranes and powders, such as zeolites; and porous layers (100nm … 5µm). Also thin porous layers (< 1 µm) can be characterized.

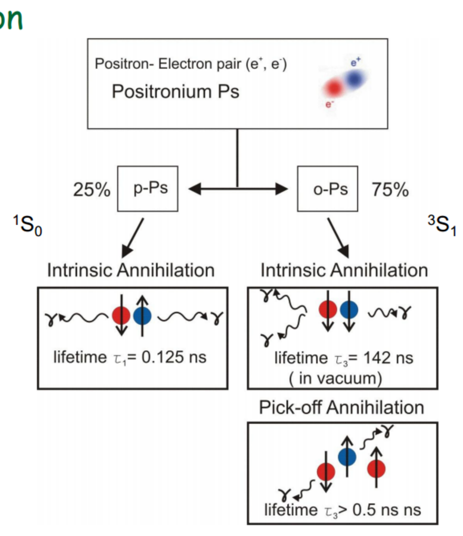
Positron Lifetime Spectroscopy

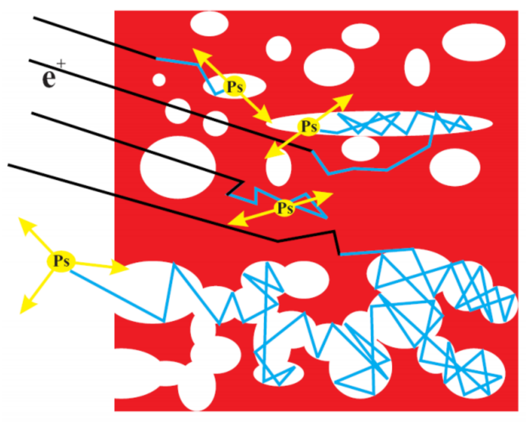




Positronium formation

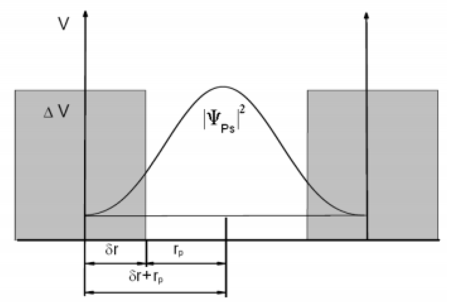
- in materials without free electrons
- polymers, glass, liquids, gases, …
- Positronium is formed
- Lightest atom: bound state between electron and positron
- Ortho-Ps lifetime is measure for open volume
- Pick-off annihilation



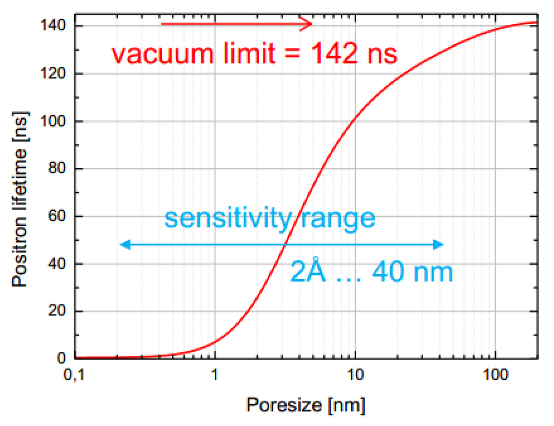


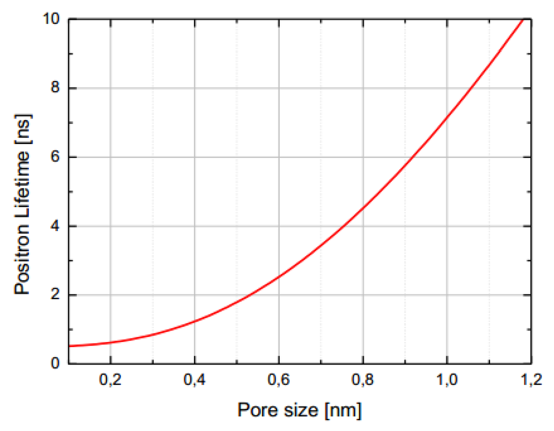
pick-off annihilation:

- 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
- Also in closed pore systems



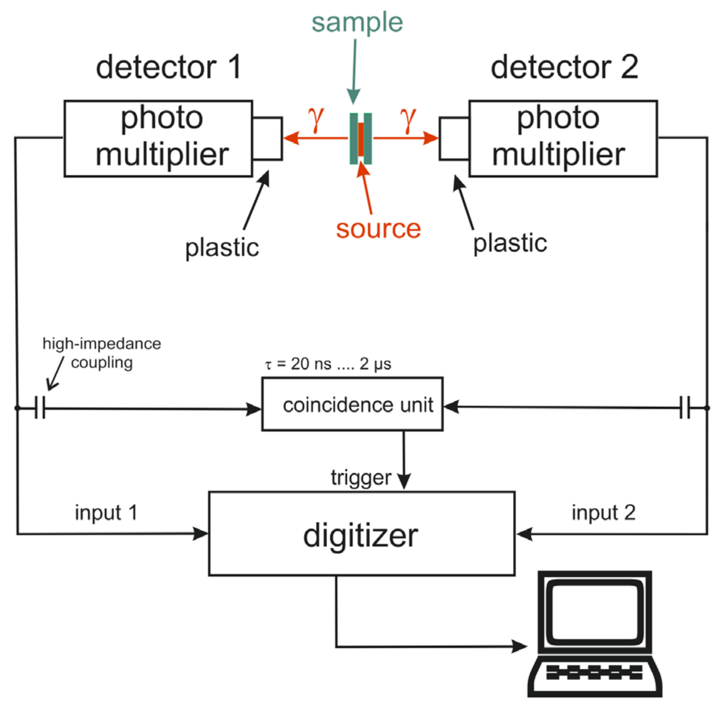
- Tao-Eldrup-Model
  - acceptable for pore size up to 2 nm in diameter
- extended Tao-Eldrup-Model
  - acceptable for pore size up to 100 nm in diameter

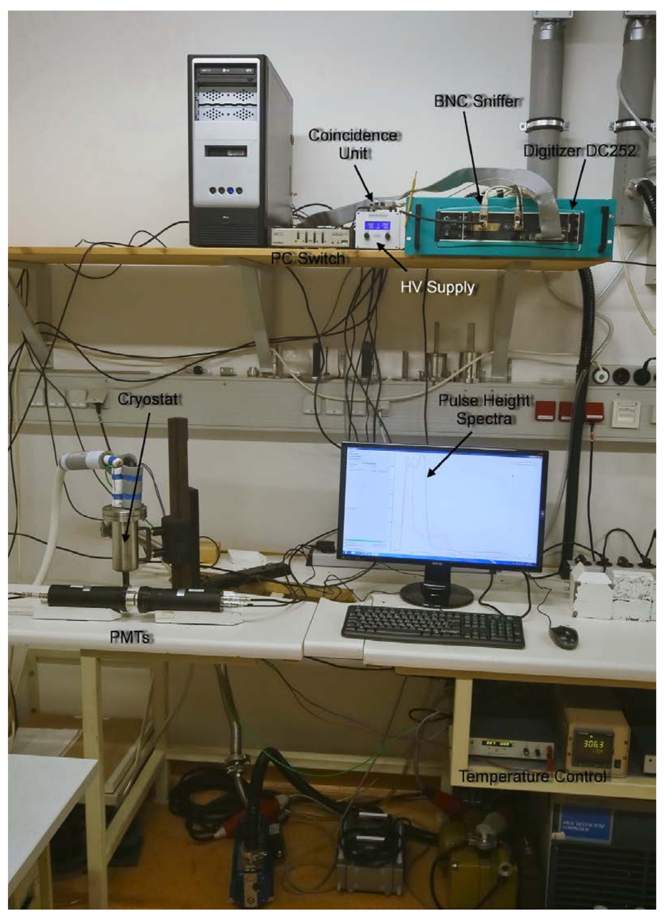


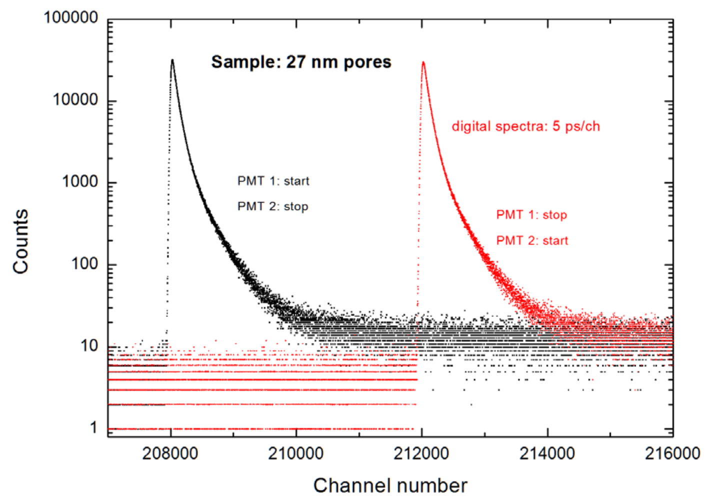


Digital Positron Lifetime Spectrometer

The positron lifetime is measured as time difference of the appearance of the 1.27 MeV "Birth"-quantum and the 0.511 MeV annihilation quanta. The source must be weak enough so that the simultaneous appearance of two positrons is highly unlikely.







The completed spectrometer with cryostat, vacuum system and temperature control unit. Two lifetime spectra taken in a porous sample (pore diameter 27 nm) are shown as example.

Example:

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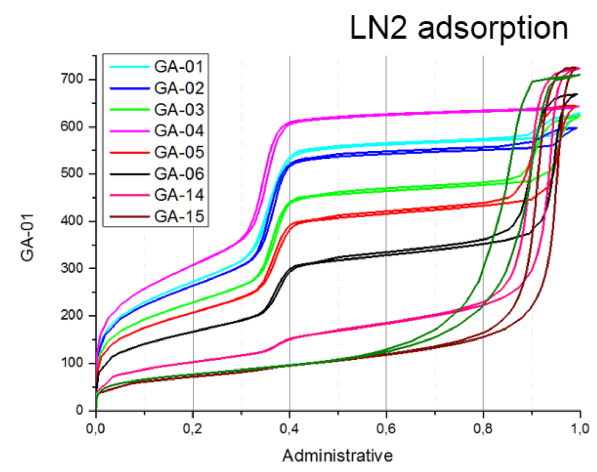
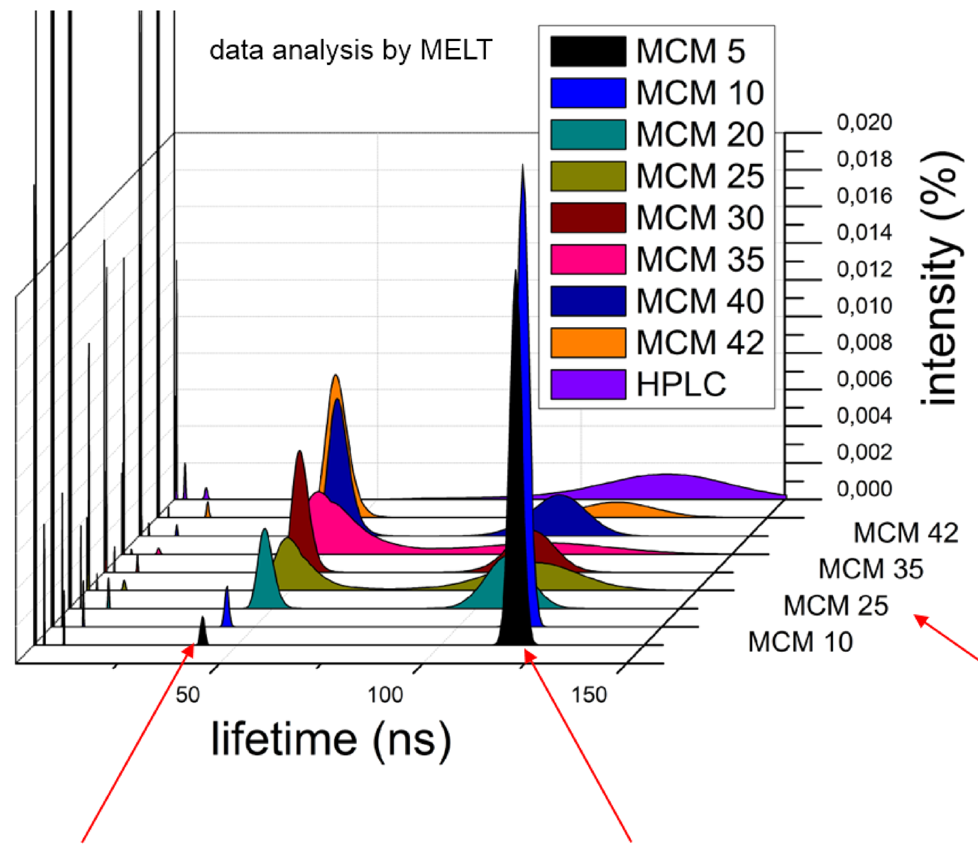
Transformation of porous glasses into MCM-41 containing geometric bodies

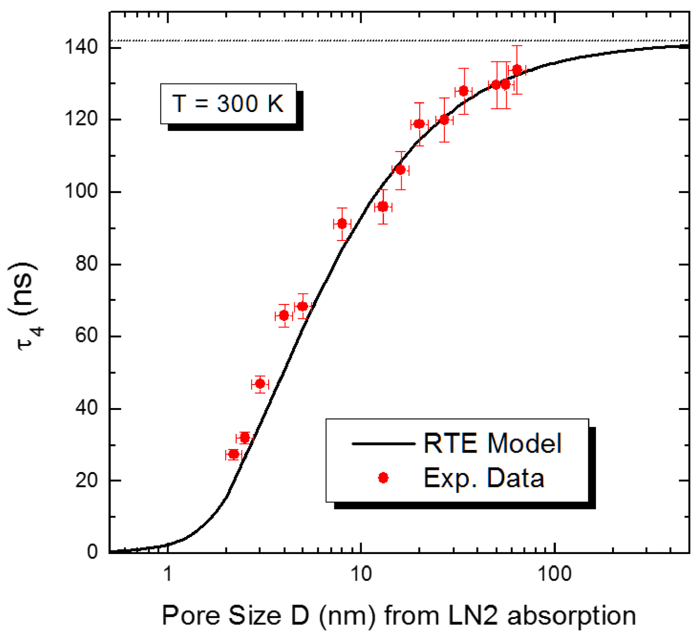
Hans Uhlig, Marie-Luise Gimpel, Alexandra Inayat, Roger Gläser, Wilhelm Schwieger, Wolf-Dietrich Einicke, Dirk Enke





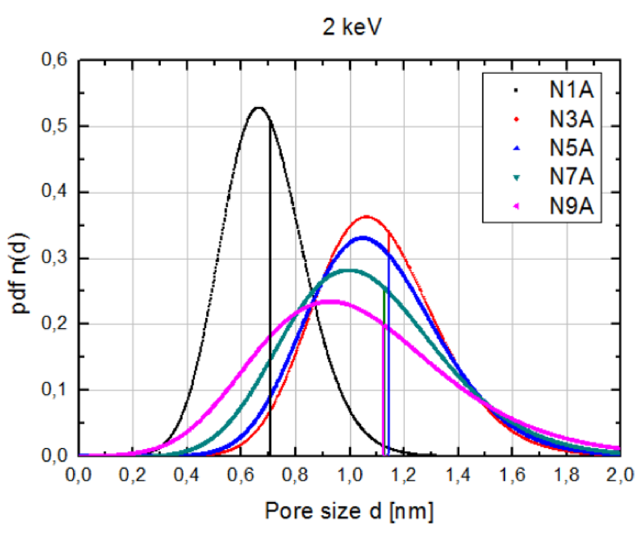
- solvent (MCM) was added into a larger pore system
- large pores: 15 nm
- small pores are formed in the walls: 4 nm

Example: pores in controlled pore glass (CPG)

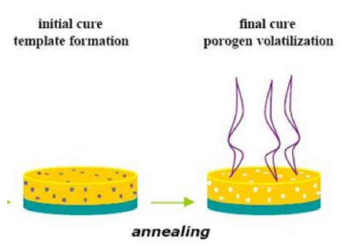


- we measured porous glass in a broad pore size range
- pore size obtained by N_2-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

Example: thin porous layers in low-K dielectric films



- dispersion of lifetime gives the size distribution of the pore system
- N1A: incomplete curing - some porogen left



You are welcome to join our workshop at HZDR in September!

Poster is available at http://positron.physik.uni-halle.de

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