Positron annihilation is used for decades for the study of open-volume lattice defects, such as vacancies, voids, dislocations, and grain boundaries. A positron and an electron can also form positronium (Ps). In two states: the singlet state (para-Ps; antiparallel spin) annihilates with a lifetime of 125 ps, independent of the ambient host material. In the triplet state (ortho-Ps; parallel spin) the lifetime in vacuum is 142 ns. When o-Ps is formed in a porous material, the lifetime is shortened by the pick-off annihilation process. Here, the positron picks up an electron from the pore wall material with antiparallel spin and forms, thus, p-Ps which annihilates almost instantaneously. This process depends on the number of wall contacts, and therefore, the o-Ps lifetime is a direct measure of the pore size. The pore size distribution can also be determined. The method is non-destructive and can be used for open and closed pore systems. The sensitivity limits are 0.2 ... 40 nm.

Positrons can be obtained from radioactive $^{22}$Na (2.6 a half life). The positrons thermalize and diffuse a short path through the sample material. The lifetime can be measured as time difference between the 1.274 MeV quantum ($\beta^+$ decay) and the 0.511 MeV quantum (positron annihilation).

Positrons of $^{22}$Na sources have a high energy (up to 540 keV) and penetrate as deep as 1mm into the sample. Thus, they can be moderated to form a monoenergetic positron beam of a few keV which can be accelerated to obtain depth profiles of the layer.

Positronium formation

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

\[ \text{Pick-off annihilation:} \]
- o-Ps is converted to p-Ps by capturing an electron with antiparallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size: 9.5 ns ... 142 ns
- lifetime can be extracted from spectra
- Also in closed pore systems

\[ \text{o-Ps lifetime} = f(\text{pore size}) \]
- quantum-mechanical models

\[ \text{Tao-Edrup-Model} \]
- acceptable for pore size up to 2 nm in diameter
- extended Tao-Edrup-Model
- acceptable for pore size up to 100 nm in diameter

\[ \text{vacuum limit} = 142 \text{ ns} \]

\[ \text{sensitivity range:} 2 \text{A} - 40 \text{nm} \]