# Positron Lifetime Spectroscopy on controlled Pore Glass Porosimetry and Pore Size Distribution

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**Keywords:** porous glass, mesopores, pore size distribution, positronium.

**Abstract.** Positron annihilation lifetime spectroscopy (PALS) is used to study a series of controlled pore glasses (CPG). The lifetime spectra were decomposed into four components using the routine LifeTime, version 9.0 (LT9). The largest lifetime $\tau_4$, which is attributed to the annihilation of ortho-positronium (*o*-Ps) localized at mesopores, varied at 300 K between 21 and 131 ns. The size of mesopores (mean free path), $D$, was determined by $N_2$ adsorption and Hg intrusion techniques to vary between 1.8 and 56 nm. It is shown that the Tao-Eldrup model extended to cylinders of infinite length and diameter $d = D$ describes well the experiment for an overlap parameter $\delta$ fitted to be $\delta = 0.193$ nm. The spectra were also analyzed allowing a distribution of *o*-Ps lifetimes. A method is developed to calculate the pore size distribution $n(d)$ from the $\tau_4$ distribution. This method is of particular interest since PALS is very sensitive to pores being too small to be exactly analyzed by conventional porosimetry.

## Introduction

Mesoporous glasses (pore size 2 - 50 nm) are of interest for various applications (low-dielectric thin films, catalysis, molecular filters). For their utilization it is necessary to characterize their properties, especially the pore size, using capable methods. Positronium annihilation lifetime spectroscopy (PALS) provides just in the range 0.5 - 10 nm a high sensitivity to the pore size and furthermore allows a non-destructive measurement, also on closed pore systems. In dielectric amorphous materials, electrons and a part of the implanted positrons may form a bound state called positronium (Ps) [1]. The long-living triplet spin state of Ps (*ortho*-positronium, *o*-Ps) is a suitable probe for measuring the pore sizes. In vacuum, *o*-Ps decays with a mean lifetime of 142 ns via emission of 3 γ rays. But in matter the lifetime of *o*-Ps can be reduced markedly by pick-off annihilation, a quenching process of the *o*-Ps caused by interaction with electrons of suitable spin (opposite direction to the Ps's positron spin) leading to a 2 γ decay. Ps formed near the pore or at its internal surface will be localized at the pore. So the pick-off lifetime of *o*-Ps is a function of the pore size $D$, which can be calculated directly from the lifetime using the extended Tao-Eldrup (ETE) model [2,3].

The aim of this work is to find a calibration curve for the dependence of the longest lifetime on the pore size and furthermore we spent particular attention for getting information on the pore size distributions.

**The Calibration Curve**

The experiments were done as described in [4]. Figure 1 shows the mean $o$-Ps lifetime $\tau_4$ as a function of the pore size $D = 4V/S$ (mean free path) from porosimetry for the CPG's at room temperature (300 K). The line corresponds to theoretical results of the ETE model for infinitely long cylinders of diameter $d = D$ with the overlap value $\delta$ as a parameter. $\delta$ was determined so that the sum of the squares of deviations between experiment and theory weighted with the error of experiments gives a minimum value. The estimated $\delta = 0.193$ nm for cylindrical geometry is in agreement with the data of Ciesielski et al. [5], $\delta = 0.19$ nm, obtained for porous Vycor glass while Zaleski et al. [6] determined recently $\delta = 0.18$ nm for mesoporous silica sieves MCM-41. This data can be used as a CPG calibration curve for the correlation of the $o$-Ps lifetime attributed to mesopores and the pore size $D$. At room temperature the extended TE model is a useful porosimetry tool for a characterization of porous media. As already mentioned the given pore sizes were obtained using $N_2$ adsorption and mercury intrusion technique. The disadvantage of those techniques is their limitation for pore diameters larger than 3.9 nm (mercury intrusion) and 2 nm ($N_2$ adsorption). So especially for characterizing small pores PALS is more reliable compared to the conventional techniques.

**Pore size distribution**

In order to get information on the size distribution of mesopores we have used the routine LT9.0 in its distribution mode. The routine LT9.0 assumes that the function $\alpha_4(\lambda)$ follows a log normal distribution where $\alpha_4(\lambda)$ is the distribution of the o-Ps annihilation rate in the pores [7]. From $\alpha_4(\lambda)$ the lifetime distributions $\alpha_4(\tau) = \alpha_4(\lambda)\lambda^2$ and its mean (first momentum), $\langle\tau_4\rangle$, and standard deviation (square-root of second momentum), $\sigma_4$, can be calculated.
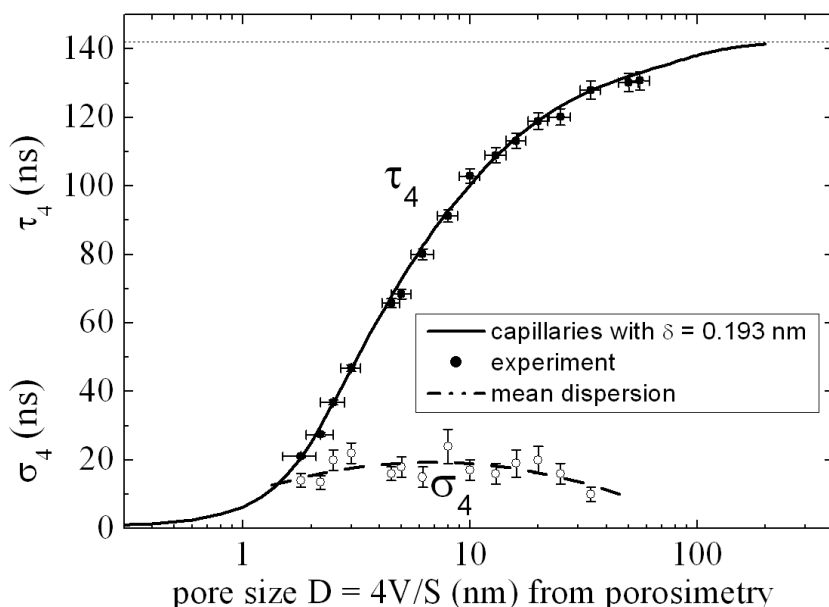


**Fig. 1:** The mean o-Ps lifetime $\tau_4$ as a function of the pore size $D$ (mean free path $D = 4V/S$) from porosimetry for CPG. The closed circles represent our experimental data at 300 K, the line correspond to the best fit of our experimental data on theoretical results of the ETE model for capillaries with $\delta = 0.193$ nm (here $D = d$ is the diameter of the cylindrical capillaries). $\sigma_4$ is the mean dispersion (square-root of variance) of the o-Ps lifetime distribution. For mean lifetimes $\tau_4$ larger than 100 ns the value of $\sigma_4$ could not be correctly determined.

We have analyzed truncated spectra, as frequently done in the literature [3]. We assumed a single component with distributed lifetimes, fixed the time zero of the spectrum to the value from the complete analysis, and determined the parameter $\tau_4$ and $\sigma_4$. The spectrum cut-off on the side of small delays was changed from 10 ns upwards. While $\tau_4$ remained almost unaffected, $\sigma_4$ decreased with increasing cut-off. For delays between 20 and 40 ns the analyzed values of $\sigma_4$ stabilize. These values are used for the further discussion. For mean lifetimes $\tau_4 > 100$ ns the value of $\sigma_4$ exhibited dramatically increasing statistical errors since the flat lifetime curve merges more and more with the background from random coincidence events. Therefore, we limited this analysis to the data from the range $\tau_4 < 100$ ns. The analyzed lifetime distributions show mass centers $\langle\tau_4\rangle$ which agree with the lifetimes $\tau_4$ from the

discrete term analysis within the statistical error limits. The standard deviations of the distributions, $\sigma_4$, are shown in Fig.1. They show only a weak variation with the pore size $D$.

Four samples with pore sizes $D = 4V/S$ of 1.8 nm, 2.5 nm, 4.5 nm, and 6.2 nm (from porosimetry) are chosen for analyzing the pore size distribution. The corresponding $\tau_4/\sigma_4$ values are 21.1/14.8, 46.9/17.6, 65.9/18.9, and 80.0/19.3 (all values in ns). These width parameters $\sigma_4$ which are used for calculation of distributions are values obtained from smoothing the experimental data by fitting a quadratic function (dash-dotted line in Fig.1). The lifetime distributions are of roughly Gaussian shape with a tail at the side of larger lifetimes. The routine LT assumes that $\alpha_4(\lambda)$ follows a logarithmic Gaussian function which determines the shape of $\alpha_4(\tau) = \alpha_4(\lambda)\lambda^2$. One problem of this kind of analysis is that the fitting procedure does not take into account that $\tau_4$ can not exceed 142 ns. Therefore, the tail of the distributions in case of larger lifetimes can be overestimated and also exceed the physical limit of the $o$-Ps lifetime in vacuum. From the distribution of $o$-Ps lifetimes, $\alpha_4(\tau)$, one can calculate the distribution of the hole diameters n($d$) taking into account the non-linear character of this transformation [8,9] n($d$) $= \alpha_4(\tau)\, d\tau_4/dd$. For this calculation we need an analytical function which describes the dependency $\tau_4 = \tau_4(d)$ and which can be differentiated. For this purpose we fitted a numerical calibration curve for $\delta = 0.193$ nm and 300 K.

Figure 2 shows the obtained distribution (pdf) n(d) of pore diameters d for selected samples. The arrows show the $d$-values directly calculated from the mean $o$-Ps lifetime, $d = d(\tau_4)$. n($d$) should be considered as an apparent distribution which comes from the true variation in the diameter of cylindrical pores but contains also the effect of the irregular, non-linear character of pores. The long tail in the distribution for larger pores should be considered as overestimation which comes from an overestimation of $\alpha_4(\tau)$ and from the nonlinear character of the $\tau_4$ vs. $d$ relation for larger lifetimes. For two samples we also show the (volume weighted) pore size distribution obtained from the Barrett-Joyner-Halenda-method (N₂ adsorption) [10]. For comparison those curves are normalized to the same height. The BJH-curve for the 2.5 nm sample shows general agreement to the pore size distribution obtained from PALS.
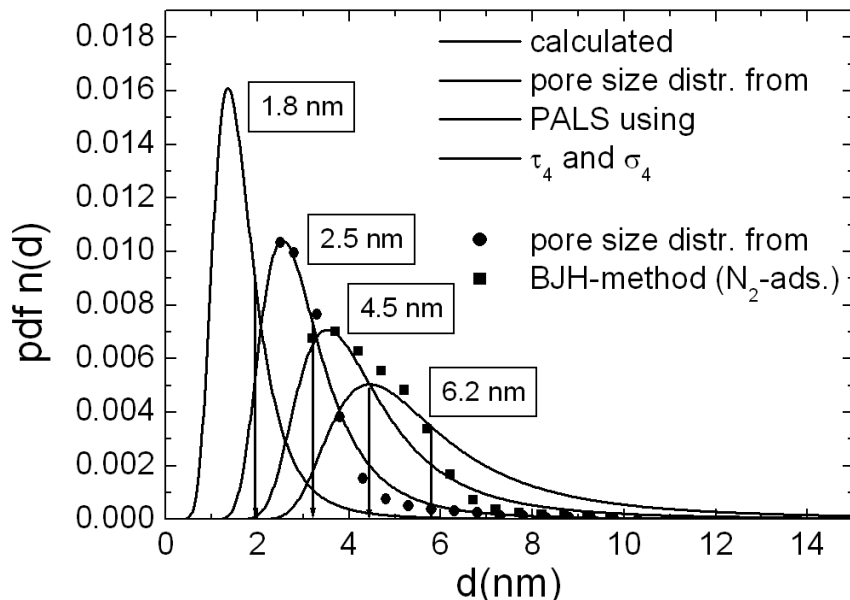


**Fig. 2:** Distribution n($d$) of pore diameters $d$ for selected samples. The distribution is normalized to 1. The arrows show the $d$-values directly calculated from the mean o-Ps lifetime, $d = d(\tau_4)$, (1.77 nm, 3.09 nm, 4.38 nm, and 5.8 nm). The porosimetry delivered pore sizes D = 4V/S of 1.8 nm, 2.5 nm, 4.5 nm, and 6.2 nm. The closed symbols show the pore size distribution obtained from the BJH-method and the adsorption branch of the isotherm for the 2.5 nm and 4.5 nm samples.

For the 4.5 nm sample the pore size distribution obtained from PALS is narrower compared to the BJH-method. Also the longer tail in the PALS distribution is obvious. The BJH-method is limited to a minimum pore size of 2 nm, so it is not possible to use this method for micropores. This limitation leads also to the problem that the distribution can only be measured particularly, as shown in Fig. 2. However, PALS is not limited and a powerful tool to measure pore size distributions for micropores and smaller mesopores.

**Summary**

The lifetime of *o*-Ps annihilating from localized states at mesopores of controlled pore glasses can be described by the extended Tao-Eldrup (ETE) model assuming a cylindrical pore geometry (diameter *d*, infinite length). The pore size determined as mean free path, *D*, by $N_2$ adsorption and Hg intrusion techniques varied between 1.8 and 56 nm. Correspondingly, the mean *o*-Ps lifetime increased from 21 and 131 ns. From a last-squares fit to the experimental data the overlap parameter $\delta$ of the ETE model was determined to be $\delta$ = 0.193±0.005 nm at 300 K assuming *d* = *D*. An analytic (modified logistic) function fitted to the theoretical ETE model curve can be used for the calculation of the pore size directly from the *o*-Ps lifetime. This analytic calibration curve makes the application of PALS as routine porosimetry tool easier. In this context the particular sensitivity of PALS for small pores is to emphasize. Using the calibration curve the *o*-Ps lifetime distribution, analyzed in this work by employing the routine LifeTime9.0, can be converted into a pore size distribution.

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**Positron and Positronium Chemistry**
10.4028/www.scientific.net/MSF.607


**Positron Lifetime Spectroscopy on Controlled Pore Glass Porosimetry and Pore Size Distribution**
10.4028/www.scientific.net/MSF.607.169

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