

Characterization of Column Packings for High-Performance Liquid Chromatography by Positron Annihilation Lifetime Spectroscopy

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High-performance liquid chromatography (HPLC) belongs to the most common separation methods applied in the analysis of complex mixtures of both low-molecular and macromolecular substances. HPLC separation of sample components usually takes place within a bed of microparticles arranged either in a column or in a thin layer. Various organic and inorganic materials are used as the HPLC column packings, however, silica gels with chemically bonded alkyl groups clearly dominate. Besides chemical nature of column packings, their chromatographic performance is strongly affected also by numerous physical characteristics, especially by diameter, volume, and shape of their pores. Therefore, evaluation of pore structure of chromatographic materials is object of numerous studies. Various physicochemical methods are applied for this purpose, mainly mercury porometry, low-temperature nitrogen adsorption (LTNA), and size-exclusion chromatography. The results are, however, often rather ambiguous, especially in the case of alkyl-bonded phases possessing long alkyl groups [1–5], which are the most important HPLC column packings. It is of interest to extend the choice of methods appropriate for this purpose, to allow comparisons of column packings from different points of view.

We propose the use of positron annihilation lifetime spectroscopy for the assessment of pore diameters of HPLC column packings. We tested its applicability with both bare and alkyl-bonded silica gels. The preliminary results are presented in this paper.

When positrons from a radioactive source enter molecular solids three different processes can be

observed, each with a different lifetime [6]. The shortest lifetime in the range of 100–200 ps is attributed to the annihilation of positron with an electron of the opposite spin (*p*-Ps). The second lifetime between 200 ps and 500 ps is attributed to the annihilation of free or trapped positrons in the solid. The third lifetime τ_3 is the annihilation of semi-stable species called *ortho*-positronium (*o*-Ps), consisting of a positron bound to an electron with the same spin. This latter process can give important information on structure of molecular solids. The binding energy of Ps (6.8 eV *in vacuo*) is reduced in solid dielectrics and thus Ps tends to localize in their free volume (voids, pores, cavities, *etc.*). The vacuum lifetime of *o*-Ps (142 ns) is reduced because *o*-Ps can pick off an electron of opposite spin from surroundings. The lifetime reduction depends markedly on the average electron density in the walls of pores and thus information on their sizes can be deduced from the *o*-Ps lifetimes. The positron annihilation lifetime spectroscopy is routinely used to study bulk polymers where Ps lifetimes of 2 to 3 ns are indicative of small sub/nm voids [7–9].

The quantum-mechanical model for the probability of annihilation of *o*-Ps trapped in small pores was described by *Eldrup et al.* [10] and *Nakanishi* with *Jean* [11]. It consists of a spherical potential well, in which the single particle states of Ps atom are calculated. Only the ground state in the well is considered and the pick-off annihilation depends both on the overlap of the positron from *o*-Ps atom and the molecular-electron wave function. This overlap is significant only when the Ps is in close proximity to the pore walls.

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The radius of "effective" free volume sphere R_h can be calculated from o -Ps lifetime τ_3 according to the equation

$$\tau_3 = \frac{1}{2} \cdot \left[1 - \frac{R_h}{R_h + \Delta} + \frac{1}{2\pi} \sin \left(2\pi \frac{R_h}{R_h + \Delta} \right) \right]^{-1}$$

where Δ has been determined from the experimental values of τ_3 for molecular solids of known pore size to be $\Delta = 0.166$ nm [11]. Finally, the volume of the free volume hole was calculated using $V_h = (4\pi R_h^3/3)$.

This standard scheme is certainly an approximation because the positronium as an inserted probe detects the empty space as many isolated irregularly shaped, local free volumes of atomic and molecular dimension.

For very long lifetimes, for example in the case of high-porosity powders of silica this standard model is not valid. The average o -Ps lifetimes are within a few percent of vacuum value of 142 ns and cavities are very large, about tens of nm. For such large cavities significant fractions of the Ps atoms will be in excited states of the potential well due to high density of states. The energy difference between levels is much lower than the thermal energy kT . Each Ps atom continuously samples the Boltzman population distribution of the particle energy levels (the Ps is always assumed to be in its atomic ground state). The introduction of lifetime averaged over as many excited states as necessary is an essential point; it is a second rank problem what geometry is most appropriate for particular case (sphere, cylinder, cube, *etc.*) [12, 15, 16]. The calculations of the Ps lifetime based on this physical idea were proposed in several papers of *Goworek et al.* [12] and *Gidley et al.* [13].

In this work, the o -Ps lifetimes measured in silica gel have been converted to pore dimensions using the calculations reported by *Zaleski* and *Goworek* [12].

Measurements were performed with the equipment built in the Institute of Physics, Slovak Academy of Sciences. The samples of bare and bonded silica gels (KROMASIL) were obtained from Eka Chemicals, Bohus, Sweden. Their strictly spherical particles had outer diameter of 10 μ m. Diameter D of pores in bare silica gel was determined by the supplier using LTNA

and mercury porometry. It was 10 nm. Bare silica gel was bonded by alkyl groups of various lengths. The corresponding materials are designated C1, C4, C8, and C18, respectively. In fact, C1 designation belongs to trimethylsilyl groups, C18 designates dimethyloctadecylsilyl groups, *etc.*

Two disc-shaped containers filled successively with specific silica gel samples were placed on either side of Na-22 positron source. This was 4 MBq activity spot sandwiched between 6 μ m Kapton foils. During the low-temperature measurements from 14 K up to 300 K sample assemblies were fixed at the end of the cold finger of closed-cycle helium gas cryocooler with the automatic temperature regulation. The measured samples were initially cooled to 14 K in about 2 h and data were taken after allowing the sample to achieve thermal equilibrium. Sample temperature was then stepwise increased for 15 min to allow equilibration. Lifetime data were taken for each equilibrium temperature. The process of increasing sample temperature, equilibration, and data acquisition was repeated until the highest temperature was achieved. In all cases, the measuring time was 2 h or longer. Several measurements were also performed in air at room temperature, at atmospheric or lowered pressure.

The positron annihilation lifetime spectra (PALS) were obtained by conventional fast-fast coincidence method using plastic scintillators coupled to Phillips XP2020 photomultipliers. The time resolution (FWHM) was about 350 ps.

A standard three- or four-component analysis of spectra was carried out using the well-known PATFIT software package. Source correction as well as correction on aluminium containers was taken into account.

The summaries of PALS results are shown in Tables 1 and 2. Table 1 contains values of τ_3 , I_3 , and diameter of pores D deduced from τ_3 measured at room temperature with the samples in rotary pump vacuum. The diameters are calculated for two different assumptions about pore geometry, the spherical D_{SH} and cylindrical D_{CY} ones. In Table 2 the data on o -Ps behaviour in air at room temperature and at atmospheric pressure are presented in similar way.

The mean pore diameter of bare HPLC silica gel estimated from PALS is 8.62 nm considering the spher-

Table 1. Lifetimes τ_3 and Intensities I_3 of o -Ps in Bare Silica Gel and in Samples Bonded with Alkyl Groups of Different Lengths CX

Sample	τ_3 /ns	I_3 /%	D_{SH} /nm	D_{CY} /nm
Silica gel S	96.8(1.1)	14.0(0.1)	8.62	7.58
SC1	96.4(0.6)	15.2(0.1)	8.56	7.56
SC4	89.6(0.1)	16.9(0.1)	7.14	6.36
SC8	85.9(0.4)	17.0(0.1)	6.62	5.82
SC18	83.6(0.5)	17.1(0.1)	6.26	5.50

The measurements were performed at room temperature in vacuum. The diameter of pores was deduced from τ_3 using *Zaleski's* tables [12].

Table 2. Lifetimes τ_3 and Intensities I_3 of *o*-Ps in Bare Silica Gel and in Samples Bonded by Alkyl Groups CX

Sample	τ_3 /ns	I_3 /%	D_{SH} /nm	D_{CY} /nm
Silica gel S	57.8(0.6)	14.4(0.1)	3.68	3.56
SC1	53.5(0.5)	14.9(0.1)	3.46	3.26
SC4	54.4(0.5)	18.2(0.1)	3.50	3.36
SC18	49.5(0.4)	18.5(0.1)	3.22	3.04

The measurements were performed at room temperature in air. The diameter of pores was deduced from τ_3 using Zaleski's calculations [12].

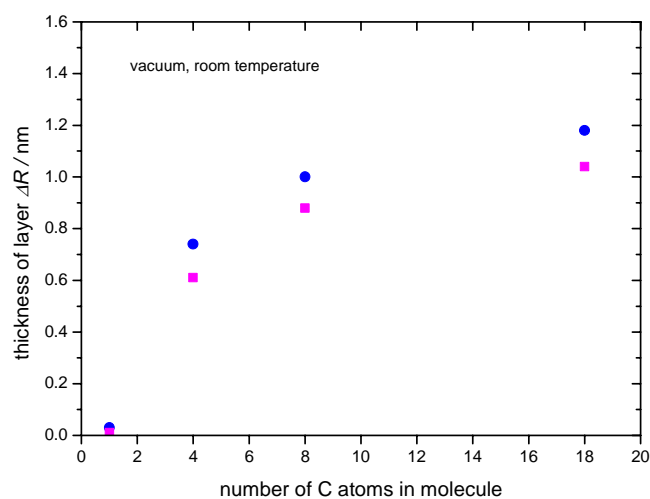


Fig. 1. Dependence of bonded layer thickness in silica gel pores on the alkyl group length. ● Sphere, ■ cylinder.

ical hole model or 7.58 nm for pores of cylindrical shape. We can say that the diameter of pores, D_h is approximately 8.0 nm. This value is in good agreement with $D = 10.0$ nm provided by supplier of samples and obtained by the LTNA method.

In their very recent publication, Dutta *et al.* [14] observed similar agreement between diameters from PALS and LTNA method for noncrystalline polymerized silicic acid powder with estimated pore size $D = 6.034$ nm.

The evolution of pore diameters in dependence on the bonded alkyl group is presented in Fig. 1. Logically, pore diameters decrease with increasing length of alkyl groups, however, it seems that longer alkyls are no more stretched and assume a more or less collapsed conformation. Thickness of collapsed C18 chains is approximately 1 nm. This confirms the conclusion drawn by Rustamov *et al.* [5] that in dry state the alkyl chains are partially collapsed on the surface and the thickness of C18 layer is approximately 0.7 nm.

The results demonstrate that *o*-Ps lifetime provides reasonable information on the pore sizes for both bare and alkyl-bonded silica gels. In this way, PALS can furnish additional data on the porous structure of HPLC column packings and on its changes in the course of chemical and physical modifications. Data

on the pore diameters for alkyl-bonded silica gels in the presence of organic liquids will be especially valuable because in this case the LTNA method cannot be used. These values will enable conclusions on the alkyl groups conformation, including their collapse in the presence of polar additives, for example water. Work in this direction is in progress in our laboratories.

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