

Positron annihilation lifetime spectroscopy study of thermal processing and rehydration of dry leek (*Allium porrum* L.)

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Abstract. New application of positron annihilation lifetime spectroscopy (PALS) to development of food processing techniques is tested. Dehydrated leeks were an object of the study. Three experiments were performed consisting of evacuating air and volatile compounds from the sample, applying thermal treatment and rehydrating the sample. Distinct changes in positron lifetime spectra allowed the monitoring of alterations in the sample structure. The most likely origin of the particular components present in the spectra was able to be proposed from these data. Changes of the components were ascribed to the various processes occurring in the samples.

Key words: positron annihilation • lifetime spectroscopy • food processing • rehydration • leek (*Allium porrum* L.)

Introduction

Positron annihilation lifetime spectroscopy (PALS) is a technique that allows the structural analysis of matter at the micro- and mesoscopic scale. Positron lifetime spectra reveal information about the size and concentration of free volumes present in a material. Taking into account the possibility of measuring the lifetime of positronium (hydrogen-like bound state of positron and electron), which can be formed in most non-conducting solids, free volumes ranging in size from angstroms to tens of nanometres can be studied. Results of these measurements are averaged over several cubic millimetres of a sample giving mean information free of local fluctuations. Since it is based on the properties of subatomic particles and takes advantage of nuclear methods, PALS is suitable for taking measurements under various conditions, such as widely fluctuating temperatures, pressure and humidity. It has been successfully applied to the investigation of a range of substances, such as metals, polymers and porous materials. Increases in knowledge and understanding of positron and positronium physics and chemistry will allow for the future application of PALS to new fields of research such as food processing, as indicated by several pioneering works [10, 16].

To test the applicability of PALS in research for development of food processing, leeks were chosen as the subject of the study. Leek (*Allium porrum* L.) is an herbaceous biennial plant closely related to onion and garlic. The leaves of leeks can be eaten cooked, usually in soups (famous since Nero, Caesar of Rome), or it can be added to salads. Consumption of *Allium* species gives numerous health benefits [21]. Leeks are one of

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the most commercially important field vegetable crops in eastern Asia and in Europe. The largest producer of leeks in the world today is Indonesia, followed by Turkey, France and Belgium. Poland is the sixth largest producer of leeks in the world [8].

Once harvested, leeks are perishable and must be either consumed rapidly or preserved. One of the most popular procedures for leek preservation is drying. Decrease of water activity in the material reduces microbiological activity and minimizes physical and chemical changes during storage. Drying brings a substantial reduction in mass and volume, minimizing the cost associated with packaging, storage and transportation [7]. Rehydration is necessary before further processing and consumption of dry leeks. During the rehydration process there is a loss of soluble compounds from the dried leeks as plant tissues absorb water and simultaneously loose these compounds due to changes in the nature of chemical compounds and the internal structure of the plant tissue [19]. Therefore, rehydration is not simply a reverse process to drying; e.g. product obtained as a result of drying is unable to absorb the same amount of water as it has lost. The rehydration of products having agricultural origins is often a subject of study for the purpose of improving food-processing techniques. The aim of this work is to test whether PALS is a suitable tool for studying changes of the internal structure of leeks during heating or the rehydration process.

Experimental

Fresh leeks were purchased from a local market in Lublin, Poland. The leaves of the leeks were divided into three parts: white, light green and green. Only white and green parts were used in further investigation, in order to observe the differences between parts devoted mostly to the photosynthetic (green) and storage (white) activities of a plant. The leek samples were air-dried for 24 h. Drying temperature was stabilized at 373 ± 5 K in order to maximize nutrient and enzyme retention while keeping the drying process within a reasonable time frame [1]. Dried samples were ground for 2 min in a mix mill. For PALS measurements, about 1 g of powdered sample forming an 11 mm thick layer was placed on the bottom of a cylindrical container with a diameter of 16 mm. A vacuum on the order of 1 Pa could be obtained in a hermetic chamber. The copper-made container was thermally insulated, allowing the temperature of a sample to be controlled to within 0.1 K. One part of the experiment consisted of adding water to a sample. This was done by pouring water on the top surface of a sample's layer, followed by sealing the chamber in order to avoid water vaporization.

Positron lifetime spectra were registered using a fast-slow coincidence spectrometer with BaF_2 scintillation counters. A positron source 0.3 MBq of ^{22}Na , enclosed in a 8 μm thick Kapton envelope was used. The source was placed on the container symmetry axis, 5 mm from the top surface of a sample in such a way that the Kapton foil did not disturb water transport. The lifetime spectra were initially processed by MELT program [17], which requires large numbers of collected events to give reliable results. For this purpose, 8×10^6

coincidences were collected over the course of 15 h. Basing on the reference spectrum of well-annealed silicon ($\tau = 216$ ps), resolution function was approximated by two Gaussians with FWHM 262 ps (93%) and 212 ps (7%) shifted by 167 ps. The correction for annihilation in the Kapton envelope was found to be 15%, with the lifetime 382 ps. Knowing the complexity of the spectra (Fig. 1), some simplifications were made in order to observe relative changes of the spectra parameters. The LT 9.2 program [12] was used for this purpose. Only three components were assumed in fitted model: the short-lived component belonged to *para*-positronium (*p*-Ps), medium-lived one – averaged annihilation of free positrons (e^+) and the longest-lived one – averaged *ortho*-positronium (*o*-Ps) components. Changes that occurred from raising the temperature of a sample were observed collecting 2×10^6 coincidences (3 h in one temperature), and rehydration – collecting 6×10^5 coincidences (1 h).

Results and discussion

Bayesian methods of positron lifetime spectra analysis provided by MELT revealed complex structure of leek spectra (Fig. 1). It is to be expected that there are various kinds of organic material forming dry remnants of leek

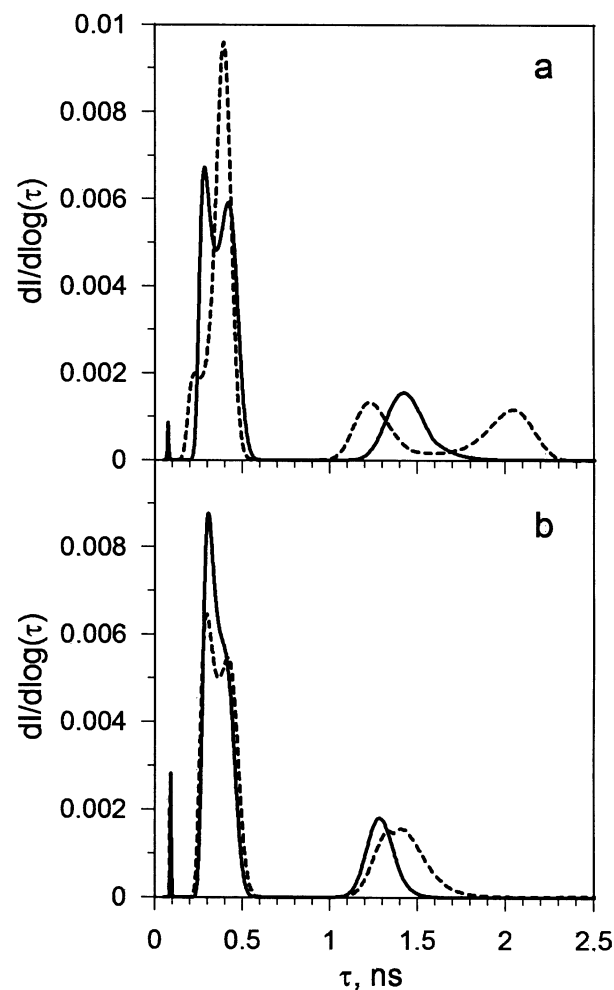


Fig. 1. Distribution of positron lifetime for green part (a) and white part (b) of dehydrated leek leaf obtained from the spectra measured in air (solid line) and in vacuum (dashed line).

cells. This fact is reflected by a broad distribution (from 200 ps to over 500 ps) and the complex structure of free positron components observed in air. The lifetime of free positrons yields information about the mean electron density of the material averaged over the diffusion range of thermalized positrons. This component is usually assumed to be purely exponential, i.e. a component possessing a positron lifetime without any distribution that would be presented in Fig. 1 as the delta function. However, the distribution of e^+ lifetime was introduced already in the lifetime spectra of polymers [4, 5], where its presence was explained as a result of the distribution of free volume sizes. Although there was no explanation given about how these two quantities are connected, it is undoubtedly a result of the heterogeneity of such an amorphous medium. Positrons have different possible sites for annihilation in such a medium. Sites with a higher electron density would be more preferential for positrons and hence their lifetime should be shorter there, but still it is possible that positrons annihilate with longer lifetimes in sites with lower electron density. This is probably the origin of the distribution of e^+ lifetime. However, in highly heterogeneous material, positrons after thermalization in a region with lower electron density could never reach a region with higher electron density if its diffusion length is smaller than the size of a region with a lower electron density. Such a situation would also result in the distribution of e^+ lifetime if the differences in electron density were not large, or even in the appearance of two separate components otherwise. In the case of organic materials the diffusion length is on the order of tens of nanometres [2, 3], and while there should be various organic structures present in dry leek (e.g. cell walls, nucleus, mitochondrion and chloroplast), each of them is hundreds of nanometres large even after drying. Such structures, made of various molecules having various mean electron densities, form 'domains' resulting in a complex (not purely exponential) e^+ component.

Bimodal distribution of this lifetime obtained by MELT (Fig. 1) is of uncertain reliability because of known MELT problem consisting of the possibility of splitting the broad lifetime distribution into two separate peaks [6]. However, the distribution of free positron lifetimes is undoubtedly asymmetric and the shape of the distribution changes between various samples under various conditions. In order to explain this behaviour, as a starting point we take two different e^+ lifetimes (about 300 ps and 450 ps) contributing to this component and ascribe to them two kinds of organic material forming the dry remnants of leeks: cell interiors and cell walls. In air, the short-lived part of e^+ component dominates in both green and white samples. Long-lived parts of the component increase after evacuating air ($p \approx 1$ Pa), especially in green samples where it exceeds several times the short-lived part. Such behaviour can be explained by the pumping out of volatile compounds [15, 24] from the cell interiors of the sample. Based on this hypothesis, long-lived parts of e^+ component can be ascribed mostly to cell wall materials, while short-lived ones would originate from other elements of leek cells. This interpretation leads to the conclusion that a larger amount of volatile compounds is removed from the green parts of leeks in a vacuum, because the difference

between PALS spectra before and after evacuation is more distinct in green samples than in white samples. This conclusion is confirmed by the results of mass loss measurements: green sample mass decreases by 6.3%, while white sample mass decreases by 4.2% only.

Changes of e^+ component during evacuating the samples are followed by o -Ps component (Fig. 1). Initially (i.e. in air), mean lifetime of o -Ps in the white part of a leek is about 1.25 ns, which is 0.13 ns shorter than in the green part, inducing slightly smaller free volumes. When air is evacuated, the lifetime of this component in white samples becomes longer in conjunction with the increase of width of its distribution. This is the result of emptying additional free volumes present in the sample. This effect is in agreement with the previous hypothesis that free volumes were initially partially filled with organic material, which was subsequently removed during air evacuation. Also in the case of o -Ps component, changes caused by air evacuation are much more distinct in green samples – two o -Ps components with lifetimes about 1.2 ns and 2.0 ns appear instead of one. This effect is similar to that in white samples, but the evacuation seems to be much more complete. It is difficult to identify the origin of each component based only on PALS results. Changes of o -Ps components are distinct compared to e^+ components, allowing the determination (based on performing simplified analysis by LT) that the time needed for the complete evacuation of volatile compounds from leeks is less than 1 h.

The purpose of the next experiment was to determine the influence of high temperatures on leek structure. Both white and green samples were heated from room temperature to 450 K. During the first part of the experiment, the chamber containing a sample was continuously pumped while the temperature was increased incrementally. Keeping the pressure at a level of several Pa assured that the volatile products of thermal decomposition were instantly removed. The obtained dependences of o -Ps component parameters vs. temperature for both white and green samples are very similar (Fig. 2). The only differences between both temperature dependences were a several-percent larger value in both lifetime and intensity in the case of green sample. Below 400 K, changes of spectrum parameters are insignificant. The lifetimes are completely temperature independent and the intensities relative decrease less than 20%. Above 400 K, the lifetimes start rising quite rapidly and the slope of the intensity decrease becomes steeper. Changes in both lifetime and intensity for each temperature are irreversible, i.e. cooling the sample down to 300 K from any higher temperature does not cause any change of positron lifetime spectrum compared to the spectrum obtained at higher temperatures. Increase of the lifetimes indicates enlargement of free volumes in the structure of leeks. On the other hand, a decrease of the intensities means that the specific surface of free volume is reduced. Combining these data one can conclude that among all free volumes of various sizes present in the sample, smaller free volumes are being closed while larger ones remain open. It is unlikely that the changes are a result of o -Ps quenching by carbon black appearing as the by-product of decomposition of organic material at high temperatures [23]. Such decomposition of organic material,

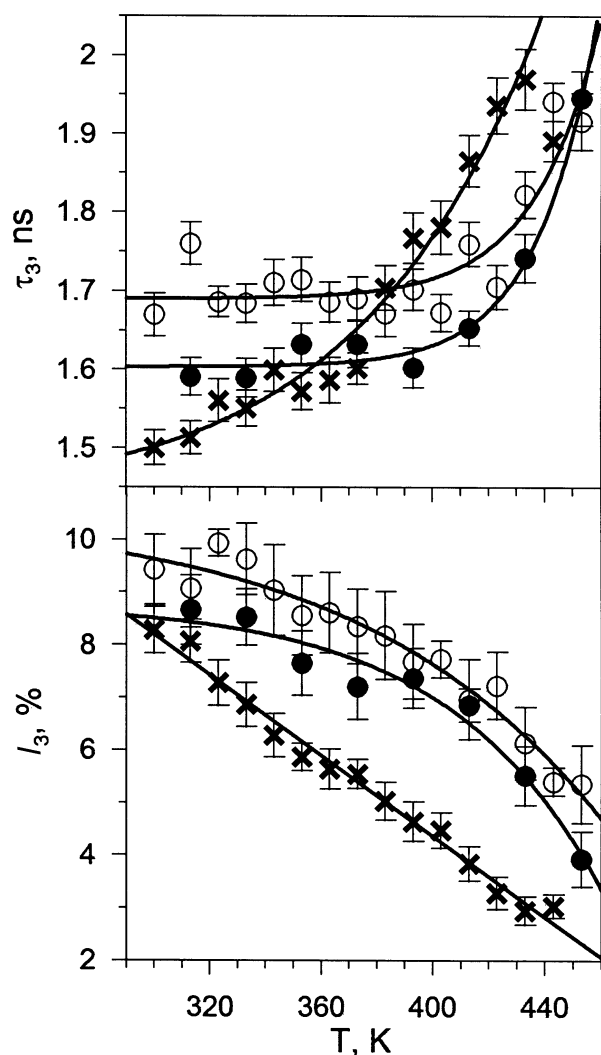


Fig. 2. Temperature dependence of *ortho*-positronium lifetime (τ_3) and intensity (I_3) for: green part (open circles) and white part (full circles) of dehydrated leek leaf heated in continuously pumped chamber; white part of dehydrated leek leaf heated in sealed chamber (crosses). The exponential lines serve as eye-guides only.

e.g. hydrocarbon chains, occurs at temperatures above 520 K and requires the presence of oxygen [13], which was initially removed from all the samples in the present experiment. Thus, there are two possible causes of such behaviour: either smaller free volumes are being filled by products of thermal decomposition or their walls are being decomposed, resulting in destruction of the structures where they are located.

In order to test which of the hypotheses of those presented above is more reliable, a second part of the experiment was performed. A white sample was placed inside the measurement chamber, which was evacuated to about 1 Pa only at room temperature and then the chamber was sealed. As a result of further heating, the pressure inside the chamber increased due to the constant emission of volatile products of thermal decomposition. Pressure in the chamber exceeded atmospheric pressure at about 430 K. Relation between *o*-Ps component parameters and temperature obtained during this part of experiment is distinctly different from the relation for the sample heated in a continuously pumped chamber (Fig. 2). The lifetime begins to increase at much lower

temperatures. The increase is initially slow, but it speeds up at a temperature about 30 K lower than that during continuous evacuation. However, an increase of the lifetime at high temperatures ($T > 400$ K) seems to be slightly slower in a sealed chamber. Similar differences were observed regarding the intensity – the decrease is faster below, but it becomes slower above 400 K. As a result, dependence of the intensity vs. temperature is almost linear. Increase of the lifetime and decrease of the intensity at 440 K is greater in a sealed chamber than during continuous evacuation: the intensity falls to 3% and the lifetime reaches about 2 ns. These results lead to the conclusion that the products of thermal decomposition fill small free volumes much faster if their removal from the sample is not forced by pumping. The influence of blocking small free volumes upon changes of *o*-Ps lifetime and intensity is quite clearly visible below 400 K. However, it is still questionable whether the disappearance of small free volumes at temperatures above 400 K is caused by this process alone.

Dehydrated leeks usually need to be wetted before consumption. This process was also studied by PALS. In Fig. 3 changes of *o*-Ps lifetime and intensity during rehydration of a white sample is shown. The sample was

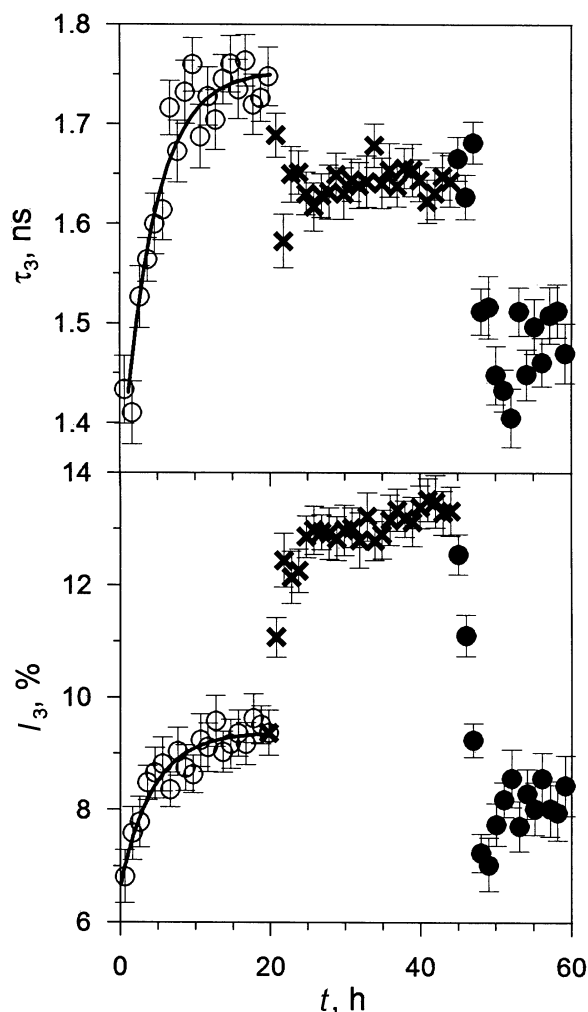


Fig. 3. Changes of *ortho*-positronium lifetime (τ_3) and intensity (I_3) observed during: rehydration of white part of dehydrated leek leaf using 1:2 mass ratio of water to leek (open circles), then 1:1 mass ratio (crosses) followed by dehydration in vacuum (full circles).

rehydrated in two stages, each time 0.5 cm³ of water (1:2 mass ratio of water to leek) was added to the sample and next the changes in positron lifetime spectra were observed for about 20 h. During the first stage, a slow (time constant 4.3 h) increase of both the lifetime and the intensity was observed. Most likely, water was slowly penetrating the sample during this time. Additional larger free volumes were created, as indicated by both the 3% bigger intensity and 0.3 ns longer lifetime. These free volumes are very likely located inside or between cellular structures (e.g. vacuole). Their appearance might be caused by changes occurring in these structures due to being filled with water. When both lifetime and intensity reached saturation values, the next dose of water was added to the sample starting a second stage of rehydration. This time changes of *o*-Ps component parameters were about two times faster. Like previously, the intensity rose. It reached a value two times larger than before rehydration in saturation. Just the opposite, the lifetime decreases by 0.1 ns when more water is added to the sample. In order to determine if this unexpected change is a result of the appearance of additional components which would indicate the existence of a two phase (water + leek) system, or just a reduction of the lifetime of a single component, distribution of lifetimes obtained by MELT for dehydrated leek, leek after second stage of rehydration and water were compared. The results are presented in Fig. 4. Distribution of lifetimes for pure liquid water reveals that there is a single *o*-Ps component with lifetime about 2 ns. As opposed to solids (e.g. dry leeks), in liquid there is no pre-existing free volume of appropriate size, but it is created by positronium itself [9]. The lifetime in a liquid is determined mainly by the surface tension of the liquid [14, 20]. A tail extending from *e*⁺ component in the direction of longer lifetimes is undoubtedly the result of non-exponential shapes of components caused by Ps oxidation and *ortho-para* conversion, occurring in the terminal part of the *e*⁺ track in water [18]. Positron lifetime spectrum of rehydrated leeks is surprisingly simple. There is no sign of distortion caused by *ortho-para* conversion. The slightly asymmetrical shape of

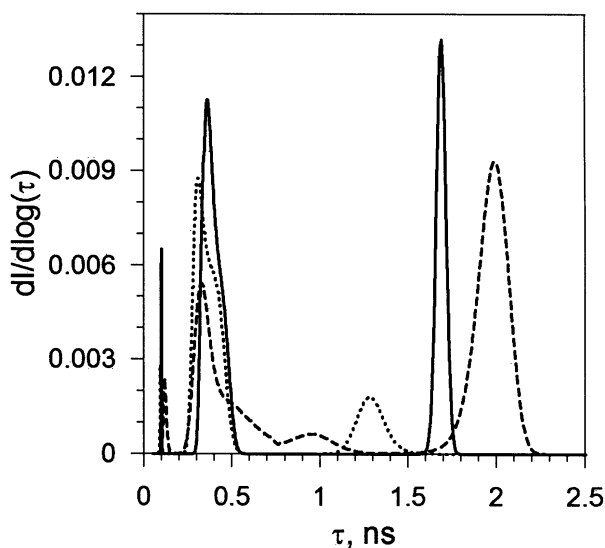


Fig. 4. Distribution of positron lifetime for white part of dehydrated leek leaf in air (dotted line), rehydrated leek leaf (solid line) and water (dashed line).

e⁺ component rather resembles the one observed in dehydrated leeks than in water. It means that there are still 'domains' with different mean electron density where free positrons annihilate. There is a single *o*-Ps component with a mean lifetime 0.3 ns shorter than in pure water and a quite narrow distribution of lifetimes. The absence of *o*-Ps components with mean lifetimes equal to 2 ns means that there are no reservoirs of pure liquid water left within positron range. We can conclude from these data that water was absorbed by the cells of the leek. On the other hand, because the volume of water added during the second stage of rehydration was almost half of the volume occupied by the sample, it is reasonable to assume that *o*-Ps forms and annihilates mostly in liquid filling cells of leek. Probably, this liquid is an aqueous solution of the same kind of organic material remaining in the cells, the removal of which was observed during evacuation of the samples. Somewhat confusing is the fact that *o*-Ps lifetime is shorter in the solution than in water. Usually surface tension of aqueous solutions of organic compounds is smaller than in pure water [11, 22], and should result in larger values of the lifetime. Thus, observed lifetime shortening suggests that some inorganic solutes are present in the liquid. Contrary to the doubts concerning *o*-Ps lifetime presented above, an increase in the intensity after the second stage of rehydration is consistent with the hypothesis that positronium annihilates mostly in liquid. Positronium can form anywhere in a liquid, unlike in a solid, where it needs to find existing free volume. Therefore, the appearance of volumes filled with a liquid gives additional opportunity of Ps formation that is reflected in larger *o*-Ps intensity.

After 45 h of wetting, the sample was dehydrated again by pumping water out at room temperature. During the first 3 h, only *o*-Ps intensity decreased, while the lifetime remained at a constant level. When the intensity reached the level observed for dry sample, the lifetime decreased rapidly to the same value it had before rehydration. These changes can be explained in the following way: the initial decrease of the intensity probably reflects a shrinking of the leeks cells due to the decreased amount of liquid inside them. Constant value of the lifetime indicates that *o*-Ps still annihilates mostly in the aqueous solution, because free volumes in solid parts of leek cell structure are blocked by the liquid. When water is completely removed, these free volumes are emptied and the lifetime specific for their size is observed again.

Conclusions

A highly complex structure of positron lifetime spectra was found in dehydrated leek samples, confirming heterogeneity of the material. Exposure of the samples to vacuum, high temperature or humidity results in distinct changes of the spectra in every case. These changes reflect modifications to the structure of samples. Even without exact knowledge of their origin, it is possible to derive from PALS data information potentially useful for the food processing industry. For instance, a threshold temperature above which degradation of the sample occurs under particular conditions (e.g.

pressure) can be found. Obtained this way, knowledge of the thermal decomposition processes of leeks may be useful when devising methods of leek preparation at high temperatures, e.g. drying leeks for storage. Another example of practical importance is examination of the rehydration process by PALS. In this case, the amount of water and time necessary to complete the process can be determined.

Besides deducing the degree of modification of sample structure from relative changes in positron lifetime spectra collected in varying conditions, one can hypothesize about the origin of the changes. Even moderately precise knowledge of structure transformations taking place during the experiment enable identification of where positrons or positroniums annihilate. Such reasoning was performed for all three experiments described above: evacuation of air and volatile compounds from the sample, thermal treatment and rehydration of the samples. From all the discussions, we can describe a simplified model of a leek consisting mostly of solid cellular walls and volatile compounds from the remnants of leek cell interior. Inside, or in the vicinity of, the walls free spaces suitable for trapping positronium exist. These free volumes may be filled as result of various treatments of the sample, e.g. by products of thermal degradation of the sample, or by water added to the sample. The reverse process is also possible, i.e. the fillers may be removed, usually by exposing the sample to vacuum. The free volumes reappear in a vacuum, except at high temperatures. The structure of the walls is probably damaged above approximately 400 K. The interpretation of PALS results presented above seems to be consistent, but it should be verified by other methods if PALS is going to be used for studies of plant material. Detailed knowledge of changes occurring on a microscopic scale, which can possibly be obtained by PALS, may help in developing food preparation techniques that minimize nutrient and enzyme loss.

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