

JACEK FILIPECKI^{1, A, E-F}, AGNIESZKA KOCELA^{1, A-D}, WITOLD KORZEKWA^{2, D-E}

Study of Free Volumes of Polymer Hydrogel and Silicone-Hydrogel Contact Lenses by Means of the Positron Annihilation Lifetime Spectroscopy Method

Badanie wolnych objętości polimerowych hydrożelowych i silikonowo-hydrożelowych soczewek kontaktowych metodą spektroskopii czasów życia anihilujących pozytonów

¹ Jan Długosz University in Częstochowa, Institute of Physics, Częstochowa, Poland

² Komed Clinic, Częstochowa, Poland

A – research concept and design; B – collection and/or assembly of data; C – data analysis and interpretation; D – writing the article; E – critical revision of the article; F – final approval of the article

Abstract

Background. Polymer materials based on hydrogel and silicone-hydrogel materials are commonly used in ophthalmology. It is important to research the structure of these materials, mainly the prevalence of free volumes.

Objectives. The study has been conducted in order to determine the presence of free volume gaps in the structure of polymer hydrogel and silicone-hydrogel contact lenses. In addition, to demonstrate differences in the occurrence of free volumes between types of represented contact lenses.

Material and Methods. Three different hydrogel and three different silicone-hydrogel polymer contact lenses were used as research material. The study was done by means of positron annihilation lifetime spectroscopy (PALS).

Results. As a result of the performed measurements, a graphical curve resulted which describes the relationship between the number of the annihilation acts in the time function. The study revealed the existence of three τ_1 , τ_2 and τ_3 components. Significant changes were observed in the ortho-positronium long life component τ_3 and their intensities between the examined polymer contact lenses.

Conclusions. The conducted study using the Tao-Eldrup model indicates the presence of free volume holes in all research materials. The results lead to the following connection: contact lenses of higher oxygen permeability coefficient (silicone-hydrogel contact lenses) have more and larger free volumes than contact lenses of less oxygen permeability coefficient (hydrogel contact lenses) (*Polim. Med.* 2014, 44, 4, 255–260).

Key words: positron annihilation, free volumes, biopolymers, contact lenses.

Streszczenie

Wprowadzenie. Soczewki kontaktowe oparte na budowie polimerów hydrożelowych i silikonowo-hydrożelowych są powszechnie stosowane w okulistyce. Ważnym aspektem staje się badanie struktury wewnętrznej tych materiałów.

Cel pracy. Badania zostały przeprowadzone w celu wykazania występowania swobodnych objętości w strukturze wewnętrznej polimerowych hydrożelowych i silikonowo-hydrożelowych soczewek kontaktowych. Dodatkowo wykazano różnice w występowaniu wolnych objętości między typami badanych soczewek.

Materiał i metody. Trzy różne hydrożelowe soczewki kontaktowe oraz trzy różne silikonowo-hydrożelowe soczewki kontaktowe zostały zastosowane jako materiał badawczy. Badania struktury wewnętrznej próbek były przeprowadzone z użyciem spektroskopii czasów życia anihilujących pozytonów (PALS).

Wyniki. W wyniku przeprowadzonych pomiarów uzyskano krzywe opisujące ilość zliczeń aktów anihilacji par pozyton-elektron w materiale w funkcji czasu. Badania wykazały istnienie w widmie czasów życia pozytonów trzech składowych τ_1 , τ_2 , i τ_3 . Istotne zmiany były obserwowane w długo żyjących składowych ortopozytu τ_3 i jej natężeń między badanymi polimerowymi soczewkami kontaktowymi.

Wnioski. Przeprowadzone badania wskazują na istnienie we wszystkich badanych materiałach swobodnych objętości. Wyniki wykazały następujące zależności: soczewki kontaktowe o większym współczynniku tlenoprzepuszczalności (soczewki silikonowo-hydrożelowe) mają więcej wolnych objętości, a także o większych rozmiarach niż soczewki kontaktowe o mniejszym współczynniku tlenoprzepuszczalności (soczewki hydrożelowe) (*Polim. Med.* 2014, 44, 4, 255–260).

Słowa kluczowe: soczewki kontaktowe, biopolimery, wolne objętości, anihilacja pozytonów.

The interest in structural studies concerning amorphous polymer materials has been growing along with the development of the science of modern biomedical materials. The goal of this work is the analysis of positron annihilation lifetime spectroscopy (PALS) as a tool for studying changes of nanostructures in contact lenses.

The driving force of the evolution of the materials used for manufacturing contact lenses is the need to keep the influence of the material on cornea physiology to a minimum. The cornea of our eye, like our entire body, needs an adequate amount of water to function correctly. As it does not have its own blood vessels, it takes oxygen directly from the atmosphere. It is obvious, therefore, that the moment we put a lens on the cornea, it will reduce the amount of available oxygen.

The basic difference between the materials currently used to manufacture contact lenses (Fig. 1) and the materials of the preceding generation (Fig. 2) is several times higher oxygen permeability. Therefore, the lenses made of modern, silicon-based materials are much safer and healthier for the eyes. Modern silicon-based contact lenses have such a high oxygen permeability that one can safely sleep in them all night. The more oxygen, the healthier the eyes, the fewer irritations and the longer

wearing time. The eyes of active people, those working in air-conditioned conditions or with computers need particularly large amounts of oxygen [1, 2].

Apart from high oxygen permeability, silicone-hydrogel lenses are marked by lower water content. Lower water content in a lens means lower evaporation, i.e. lower loss of water. The less water evaporates from a lens, the less tears the lens must absorb from the eye to replace it. Apart from this significant progress, there is still the problem of the reduction of the amount of oxygen available for the cornea, which often results in pathological changes in the cornea [3, 4].

Positron annihilation is a process involving transformation of the entire mass of both particles and their kinetic energy into gamma ray photon energy. This is why the examination of the photons created in the annihilation process provides information about the state of the annihilating electron positron pair. The process of annihilation of a particle with an antiparticle is possible only when all the conservation laws are satisfied, i.e. conservation of energy, linear momentum and angular momentum, electrical charge and charge parity. Annihilation of a particle and an antiparticle results in concurrent emission of even ($^2\gamma$) or odd ($^3\gamma$) gamma quantum numbers.

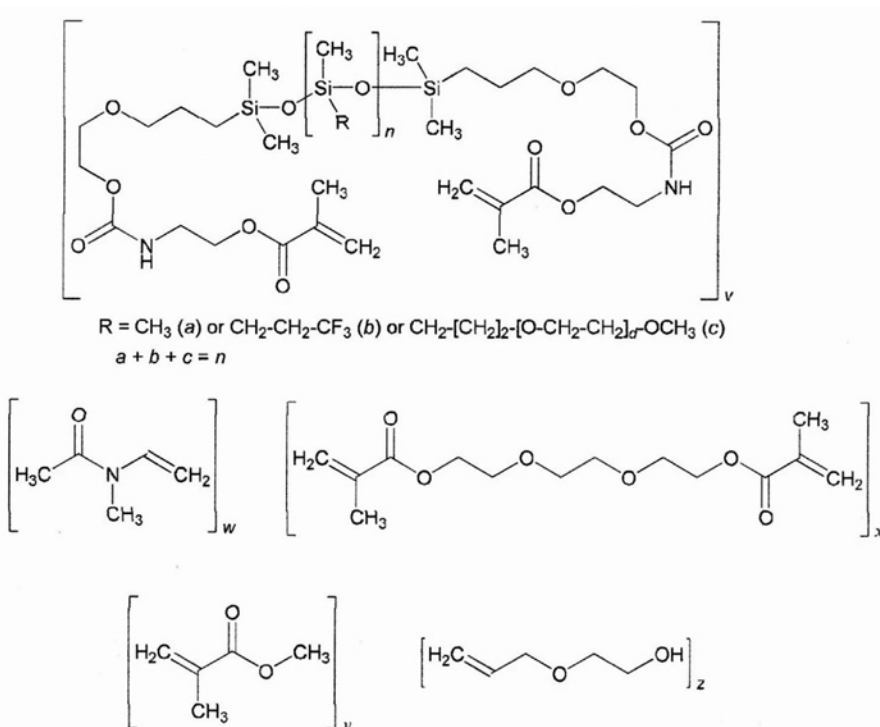


Fig. 1. The structural formula of the silicone-hydrogel material

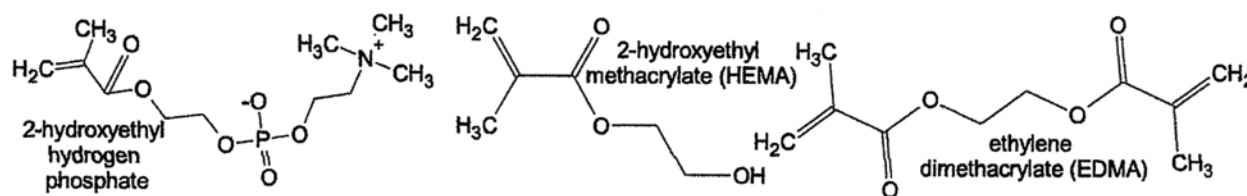


Fig. 2. The structural formula of the hydrogel material

Apart from the free annihilation, there is also electron-positron annihilation when a positron and an electron create a hydrogen-like atom called positronium P_s . The annihilation of high-energy positrons in matter is preceded by the phenomenon of thermalization, which involves a fast loss of positron energy due to the scattering and excitation of the medium. Thermalization is extremely important when the source of the positrons is the β^+ disintegration of atomic nuclei. When losing the last 10–50 eV of its energy, a positron covers the distance of the same length and then a reaction of positronium formation may occur with one of the freed electrons that, in a way, accompany the positron [5, 6].

Two kinds of positronium can be distinguished, due to the different arrangement of spins: para-positronium $p-P_s$ with anti-parallel spins and ortho-positronium $o-P_s$ with parallel spins. Positron and positronium properties depend on their interaction with the surrounding medium. One of the observed phenomena is a shortening of the mean lifetime of the annihilating ortho-positronium, called $o-P_s$ quenching. The basic quenching process is the “pick-off” annihilation process. It is associated with the fact that the positronium which is part of $o-P_s$ combines directly with an electron of opposed spin coming from one of the atoms present in the vicinity of the positronium, which results in a two photon annihilation [7–9].

In this paper, the Tao-Eldrup model was used to describe the interdependence between the $o-P_s$ lifetime and the size of a free volume [10, 11]. It assumes that a positronium is localized in a single ball-shaped potential well. In order to simplify the calculations, Tao suggested replacement of the finite potential well with the infinite potential well extended by the ΔR value. The value ΔR of the parameter must be adjusted so as not to affect the probability of finding a positronium outside an R radius sphere. Further theoretical deliberations show that the τ_3 lifetime as a function of free volume of the R radius can be described by the formula [10, 12, 13]:

$$\tau_3 = 0.5 \times \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \quad (1)$$

Where $\Delta R = 0.166$ nm is an empirical expression of electron layer thickness.

As described in earlier publications [12–15], after empirical solving of the above equation and determin-

ing R , the V_f size of the free volume can be calculated by the following formula:

$$V_f = \frac{4}{3} \pi R^3 \quad (2)$$

The relationship between the free volume of the polymer and the fractional free volume is determined by the following semi-empirical formula:

$$f_v = CV_f I^3 \quad (3)$$

where:

V_f – size of the free volume;

I_3 – intensity of the long-life component in the positron life time spectrum expressed in [%];

C – is an empirical parameter determined to be 0.0018 from the specific volume data [5].

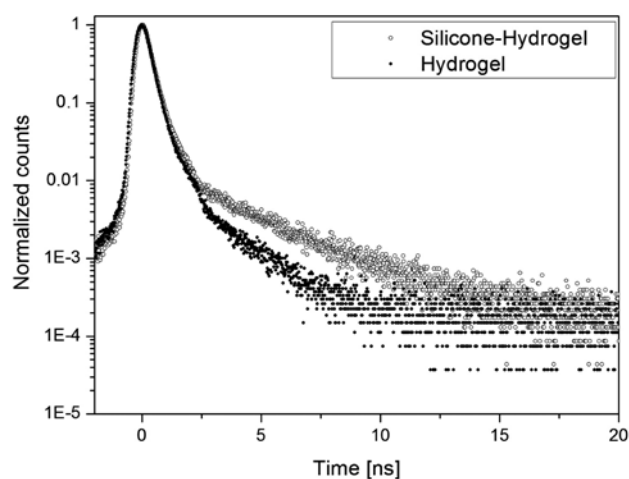
Material and Methods

Looking for new materials for advanced medical use, i.e. biomaterials, is in the sphere of interest of a large number of scientists, including physicists, chemists and biologists, and their interdisciplinary attitude towards the issue is evolving. In fact, the modern polymer materials used in contact lens production are hydrogel and silicone-hydrogel materials, and their chemical and biological properties must be bio-compatible with the human body. The goal of this study was to make an attempt at a comparative analysis of hydrogel and silicone-hydrogel contact lenses by means of positron annihilation lifetime spectroscopy (PALS). Contact lenses manufactured by two leading companies, Cooper Vision and Johnson & Johnson, were used in the study. More specific parameters are listed in Table 1.

Positron annihilation lifetime measurements were carried out at room temperature with an ORTEC spectrometer [14] based on the “start-stop” principle. The time resolution of the FWHM system was 0.270 ps (as monitored with a ^{60}Co source). Each sample was made of a layer of contact lenses which was 10mm in diameter and 1.2 mm thick. The examined sample, together with a sodium Na^{22} source of positrons of 4×10^5 Bq activity, formed the “sandwich” type system. An example of the experimental curves of the positron annihilation lifetime spectrum in hydrogel and silicone-hydrogel contact lens samples is shown in Fig. 3.

Table 1. Comparison of hydrogel and silicone-hydrogel lenses

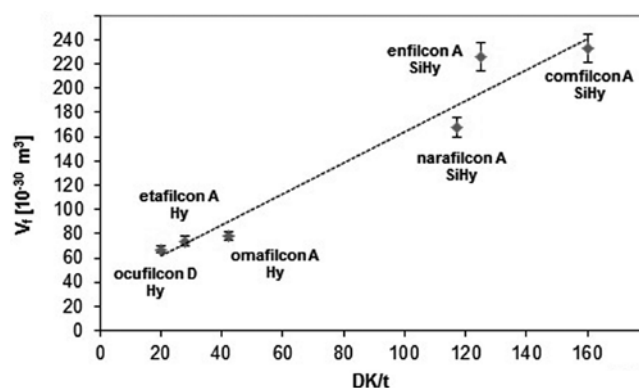
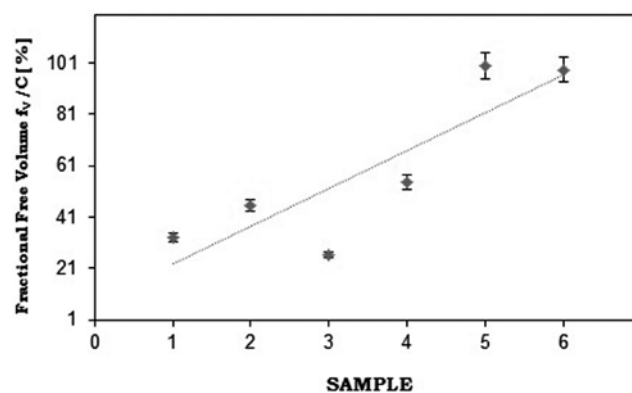
Sample	Material	Water Content (%)	Oxygen Permeability: Dk/t
BIOMEDICS EVO 55	Ocufilecon D (hydrogel)	55	20
ACUVUE MOIST	Etafilecon A (hydrogel)	58	28
PROCLEAR SPHERE	Omafilecon A (hydrogel)	62	42
ACUVUE TRUEYE	Narafilecon A (silicone-hydrogel)	46	117
AVAIRA ASPHERIC TRIALS	Enfilecon A (silicone-hydrogel)	46	125
BIOFINITY TRIAL	Comfilecon A (silicone-hydrogel)	48	160

**Fig. 3.** A comparison between the curves of positron lifetime's spectra of the measured samples of the silicone-hydrogel and hydrogel contact lenses

Results

The results of calculating the mean values of positron lifetimes in the examined samples revealed the existence of component τ_3 in the positron lifetime spectrum (Table 2). The errors obtained result from mathematical analysis. The positron lifetime values τ_3 *o*-P_s (the pick-off process) and their intensities I_3 , as well as the hole radius R , the sizes of the free volume V_f and fractional of the free volume f_v are listed in Table 3. The fraction of free volume f_v is proportionate to $V_f I_3$, because C in the equation (3) is constant. Due to the significant effect of oxygen permeability parameters on the correct functioning of the human cornea, we compared the mean sizes of free volumes V_f dependent on their oxygen permeability Dk/t (Fig. 4) and values of the fraction of free values f_v depending on oxygen permeability Dk/t (Fig. 5).

Similar results, according to the free volumes in relation to oxygen permeability Dk/t for similar contact

**Fig. 4.** Average sizes of free volumes V_f depending on oxygen permeability Dk/t**Fig. 5.** The fraction of free volumes f_v/C for the measured samples of the silicone-hydrogel and hydrogel contact lenses. (1 – Ocufilecon D; 2 – Etafilecon A; 3 – Omafilecon A; 4 – Narafilecon A; 5 – Enfilecon A; 6 – Comfilecon A)

lenses (Hilafilcon B and Balafilcon A), were found by Sane and Tuomisto [16]. In addition, these researchers also conducted measurements of PALS for *in vitro* studies on mammalian cells (porcine lenses) to establish similar relationship changes of the ortho-positronium component τ_3 [17].

Table 2. Mean values of positron lifetime τ_3 and their intensity

SAMPLE	τ_3 (ns)	I_3 (%)
BIOMEDICS EVO 55 (Ocufileon D)	1.668 ± 0.030	8.51 ± 0.17
ACUVUE MOIST (Etafileon A)	1.746 ± 0.041	10.64 ± 0.22
PROCLEAR SPHERE (Omafileon A)	1.803 ± 0.044	5.80 ± 0.23
ACUVUE TRUEYE (Narafileon A)	2.709 ± 0.061	5.59 ± 0.27
AVAIRA ASPHERIC TRIALS (Enfileon A)	3.244 ± 0.079	7.59 ± 0.31
BIOFINITY TRIALS (Comfileon A)	3.289 ± 0.079	7.25 ± 0.30

Table 3. Mean values of positron lifetime τ_3 , their intensity I_3 the hole radius R, the sizes of the free volume V_f and fractional of the free volume f_v

SAMPLE	τ_3 (ns)	I_3 (%)	R (nm)	V_f (10^{-30} m^3)	f_v (%)
BIOMEDICS EVO 55 (Ocufileon D)	1.668	8.51	0.252	67	33
ACUVUE MOIST (Etafileon A)	1.746	10.64	0.260	74	46
PROCLEAR SPHERE (Omafileon A)	1.803	5.80	0.266	78	26
ACUVUE TRUEYE (Narafileon A)	2.709	5.59	0.343	168	55
AVAIRA ASPHERIC TRIALS (Enfileon A)	3.244	7.59	0.378	226	100
BIOFINITY TRIALS (Comfileon A)	3.289	7.25	0.382	233	98

Discussion

Changes in the values of τ_3 lifetimes and their intensity I_3 are displayed also as changes of free volumes V_f and fraction of free volumes f_v (Figs. 4 and 5). The figures show that there are significant differences of the V_f values in the examined contact lenses. This fact could be due to oxygen permeability, which is also much higher for the silicone-hydrogel lenses. Taking into consideration the defined V_f values (equation 2) and f_v values (equation 3), it can be observed that the differences in V_f are responsible for changes in size of the free volumes, whereas the differences in f_v are responsible for the changing number of the occurring free volumes. On the grounds of the performed measurements, it can be found that sizes and numbers of free volumes are higher for the silicone-hydrogel lenses. The high coefficient of oxygen permeability in the silicone-hydrogel lenses may also indicate larger sizes of V_f free volumes and the fraction of free volumes f_v that can be found in these lenses. From the point of view of the physiology of the eye, the oxygen permeability coefficient is the

most important parameter describing a contact lens. The more oxygen reaches the eye, the healthier the eye. Contact lenses that let more oxygen reach the cornea significantly reduce the risk of infections, are safer for the user of the lenses and are more comfortable to use.

Structural studies of changes in free volumes were carried out on 6 different hydrogel and silicone-hydrogel polymer materials of the contact lenses with the use of the positron annihilation lifetime spectroscopy method.

Analysis was carried out of the third positron lifetime component τ_3 and of its corresponding intensity I_3 , which reflect the sizes of the occurring free volumes and their number in the examined materials. The results of the measurements show that the formation of free volume gaps takes place in all the examined lenses. The sizes of the V_f free volumes and fraction of free volumes f_v for the silicone-hydrogel lenses are higher than those for hydrogel lenses.

The combination of the results of the study with oxygen permeability makes it possible to formulate the following connection: contact lenses of higher Dk/t coefficient have more and larger free volumes.

Acknowledgment. The authors have no commercial interests in any of the contact lenses and material used in this paper. We wish to thank the Cooper Vision firm for donating the lenses used in this work.

References

- [1] **Tranoudis I., Efron N.:** In-eye performance of soft contact lenses made from different materials. *Contact Lens Anterior Eye* 2004, 27, 133–148.
- [2] **Guillon M., Maissa C.:** Bulbar conjunctival staining in contact lens wearers and non lens wearers and its association with symptomatology. *Contact Lens Anterior Eye* 2005, 28, 67–73.
- [3] **Pult H., Purslow C., Berry M., Murphy P.J.:** Clinical tests for successful contact lens wear: relationship and predictive potential. *Optometry & Vision Science* 2008, 85, 924–929.
- [4] **Wolffsohn J.S., Hunt O.A., Basra A.K.:** Simplified recording of soft contact lens fit. *Contact Lens Anterior Eye* 2009, 32, 37–42.
- [5] **Pathrick R.A.:** Positron annihilation – a probe for nanoscale voids and free volume. *Prog. Polymer Sci* 1997, 22, 1–47.
- [6] **Jean Y.C.:** NATO Advanced Research Workshop, Advances with Positron Spectroscopy of Surfaces, Italy, Yarennna, 1993.
- [7] **Shao-Jie W., Yin-Hua X., Zhong-Xun T., De-Chong T.:** Section J29: Positron annihilation study of structural relaxation and crystallization of amorphous alloys. [In:] *Positron annihilation*. Eds.: Jain P.C., Singru R.M., Gopinathan K.P. World Scientific Publishing Co. Pte. Ltd., Singapore 1985, 924–927.
- [8] **Dryzek J.:** Wstęp do spektroskopii anihilacji pozytonów w ciele stałym (Introduction to positron annihilation spectroscopy in solids). Jagiellonian University, Kraków 1997.
- [9] **Brandt W., Berko S., Walker W.W.:** Positronium decay in molecular substances. *Phys. Rev.* 1960, 120, 1289–1295.
- [10] **Tao S.J.:** Positron annihilation in molecular substances. *J. Chem. Phys.* 1972, 56, 5499–510.
- [11] **Eldrup M., Lighbody D., Sherwood J.N.:** Positron annihilation in polymers. *Chem. Phys.* 1981, 63, 51–62.
- [12] **Liao Kuo-Sung, Chen Hongmin, Awad Somia, Yuan Jen-Pwu, Hung Wei-Song, Lee Kuier-Rarn, Lai Juin-Yih, Hu Chien-Chieh, Jean Y.C.:** Determination of Free-Volume Properties in Polymers Without Orthopositronium Components in Positron Annihilation Lifetime Spectroscopy. *Macromolecules* 2011, 44, 6818–6826.
- [13] **Jean Y.C., Van Horn J. David, Hung Wei-Song, Kuier-Rarn L.:** Perspective of Positron Annihilation Spectroscopy in Polymers. *Macromolecules* 2013, 46, 7133–7145.
- [14] **Filipecki J., Golis E., Reben M., Filipecka K., Kocela A., Wasylak J.:** Positron life time spectroscopy as a method to study of the defect degree materials with disordered structure. *Optoelectron. Adv. Mat.* 2013, 7, 1029–1031.
- [15] **Kansy J.:** Microcomputer program for analysis of positron annihilation lifetime spectra. *Nucl. Instr. Meth. Phys. Res. A* 1996, 374, 235–244.
- [16] **Sane P., Tuomisto F., Holopainen J.M.:** Void volume variations in contact lens polymers. *Contact Lens & Anterior Eye* 2011, 34, 2–6.
- [17] **Sane P., Tuomisto F., Wiedmer S.K., Nyman T., Vattulainen I., Holopainen J.M.:** Temperature-induced structural transition in-situ in porcine lens – Changes observed in void size distribution. *Biochimica et Biophysica Acta* 2010, 1798, 958–965.

Address for correspondence:

Jacek Filipecki
Department of Structural Research and Medical Physics
Institute of Physics
Jan Długosz University in Częstochowa
Armii Krajowej 13/15
42-200 Częstochowa
Poland
E-mail: j.filipecki@ajd.czystochowa.pl

Conflict of interest: None declared

Received: 16.09.2014

Revised: 13.11.2014

Accepted: 04.12.2014