

Microcomputer program for analysis of positron annihilation lifetime spectra

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Abstract

A user friendly program (LT) for analysis of the lifetime spectra has been designed for personal computers. The program is compared with other existing programs such as POSITRONFIT, CONTIN and MELT. LT enables one to analyse both discrete and continuous spectra as well as mixed- partially linear and partially continuous spectra. The searched parameters are found by using a fully automatic procedure and/or by a nonlinear optimising procedure, starting from a set of chosen parameters. The program is tested for series of simulated data as well as some chosen experimental ones, especially for the two polymers PTFE and hard polyethylene. The analysis of these polymer spectra is carried out on the basis of the log-normal distribution model and a new model of the lifetime spectrum developed by Dauwe et al., recently adapted to LT.

1. Introduction

There are two general approaches to the problem of the experimental data analysis:

- *convolution* of the assumed physical model function with appropriate instrument functions to construct the theoretical curve and its fitting to the experimental one to obtain the optimum values of the model parameters,
- *deconvolution* of the experimental curve from the instruments functions to set apart the physical meaning information.

Both of them are applied to the positron annihilation lifetime data analysing. Such programs as POSITRONFIT [1] or RESOLUTIONS [2] represent the first approach whereas CONTIN [3,4] or MELT [5] the other one, i.e. they transform the experimental data into a continuous lifetime distribution function.

In this paper the computer program LT v.3.0 is described. The program enables one to analyse both discrete and continuous lifetime spectra as well as mixed, partially linear and partially continuous spectra. It comprises the two ways of analysis mentioned above (Section 3) employing two different procedures: the linear-log procedure for deconvolution of the data and an iterative fitting procedure based on a given model of the lifetime spectrum.

The deconvolution methods are more convenient for operation and, because of their model-independence, more ob-

jective. However, generally, the extraction of the physical valuable information from the experimental data needs to solve the inverse problem for a Fredholm integral of the first kind (additionally convoluted with the instrumental resolution function) [6]. Such a problem is very ill-posed, therefore its solution is sensitive to the noise imposed to the experimental data and one obtains a set of feasible solutions rather than a unique one. To choose a physically acceptable solution from this set, the programs employ some special criteria. In the MELT program it is the maximum entropy principle, the principle of parsimony (see. p. 500 in Ref. [3]) in CONTIN or the condition of the best correlation of a linear regression in the linear-log procedure of the LT program (Section 3). Sometimes the criteria could be insufficient to select the unique solution. For example for the PTFE spectrum, analysed in Ref. [3], there arose a problem of distinction, on the basis of goodness-of-fit, between the five-peak and four-peak solution for the lifetime distribution determined by CONTIN. So the author made use of the lifetime resolution factor calculated from the expression developed by Schrader and Usmar [6]. The ratio (1.72) of the closest lifetime values in the five-peaks solution was smaller than the calculated factor (2.2)¹. To verify the validity of the five-peaks solution, the author suggested to increase the

¹ This value estimated by the Schrader and Usmar expression seems to be too large, because both MELT and the deconvolution program in LT are able to separate two peaks with the ratio of their lifetime values equal to 1.5 (for a spectrum of much lower statistic than the spectrum of PTFE, see Section 4).

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information content of the data by increasing the counts in the experiment. Of course such a method is time consuming and effects in the data error connected with the instrumental drift so it cannot be used without any limitation.

Another way of increasing the solution uniqueness is a considerable reduction of the number of degrees of freedom of the fitting procedure for the price of its model-independence. The results of CONTIN (see, e.g. Fig. 3c) suggest that the lifetime distribution function can be approximately described as a sum of Gaussians in logarithmic scale of lifetimes. Such a model has been introduced into the fitting procedure. A spectrum consisting of n components is now described by n parameters more than an analogical spectrum with the same number of discrete components. These new parameters are the widths of the particular Gaussian peaks in the lifetime distribution function. Usually, on the basis of prior expectations, some of the widths can be fixed at a value of zero. This way the number of the new degrees of freedom increases only a little in relation to their number for analogical discrete lifetime spectrum.

All the computer programs mentioned here make use of the fact that an elementary lifetime component is an exponential function. Recently a new model with non-exponential decay component of the lifetime spectrum has been developed by Dauwe et al. [18]. The model has been adopted to the LT and some first results obtained by means of the model are presented in Section 6.

The LT v.3.0 is a new and developed version of the program. Its first version was described in Ref. [7]. The earlier designed versions have been presented at several Polish seminars on positron annihilation and are used in some Polish laboratories for at least three years so the LT has been very well checked and tested now [8].

Below, after a brief description of LT, some of its results are given and compared with similar results obtained by means of other existing programs.

2. The theoretical model

The shape of the theoretical lifetime curve is determined on the basis of the following assumptions:

- A lifetime spectrum is a sum of several components and extends over a constant background of spectrum B. Each of the components is either an exponential decay curve (*a simple component*) or a more complicated function (*a complex component*).

- The *simple component* C is described by two parameters: its fraction f and lifetime τ :

$$C = \frac{f}{\tau} \exp\left(-\frac{t}{\tau}\right). \quad (1)$$

- The *complex component* is built-up from a continuous sum of the decay curves given with a log-normal distribution; i.e. a Gaussian distribution in a logarithmic scale of lifetimes. It is a function of three parameters: the centre of

the Gaussian distribution τ , variation of the distribution σ and fraction of the component f :

$$C = \frac{1}{\sqrt{2\pi}\sigma} \int_0^\infty \frac{d\lambda}{\lambda} \exp\left\{-\frac{\ln^2(\lambda\tau)}{2\sigma^2}\right\} f\lambda \exp(-\lambda t). \quad (2)$$

- Each of the components is smeared by a resolution curve R ; i.e. a pure Gaussian:

$$R = G(\text{FWHM}, t) \quad (3)$$

or a Gaussian convoluted with two exponential functions:

$$R = \int_{-\infty}^0 dt_1 \exp\left(-\frac{t_1}{\tau_1}\right) \times \int_0^\infty dt_2 \exp\left(-\frac{t_2}{\tau_2}\right) G(\text{FWHM}, t - t_1 - t_2), \quad (4)$$

where FWHM is the full width at half maximum, τ_1 and τ_2 some time constants².

In Fig. 1 a prompt curve, measured with ^{60}Co , is presented. This curve was fitted once by the pure Gaussian (3) and the second time by the function (4). One can see, that the second fit is much better. The same was observed for the real resolution functions of the concrete lifetime spectra.

- The *simple component* (1), convoluted with the R function given by Eq. (3), is expressed by [1]:

$$F(f, \tau, t_k) = \frac{f}{2} [Y(\tau, t_k) - Y(\tau, t_{k+1}) - \Phi(t_{k+1}/s) + \Phi(t_k/s)], \quad (5)$$

where t_k is the mean time related to the k th channel and

$$s = \frac{\text{FWHM}}{2\sqrt{\ln 2}},$$

$$Y(\tau, t) = \exp\left(-\frac{s^2}{4\tau^2}\right) \Phi\left(\frac{s}{2\tau} - \frac{t}{s}\right) \exp\left(-\frac{t}{\tau}\right), \quad (5a)$$

$$\Phi(x) = 1 - \text{erf}(x).$$

- For the second form of R (Eq. (4)), the *simple component* is described by the following expression:

$$f [F(\alpha, \tau, t_k) + F(\alpha_1, \tau_1, -t_k) + F(\alpha_r, \tau_r, t_k)], \quad (6)$$

where

$$\alpha = \frac{\tau^2}{(\tau + \tau_1)(\tau - \tau_r)},$$

$$\alpha_1 = \frac{\tau_1^2}{(\tau + \tau_1)(\tau_r + \tau_1)}, \quad \alpha_r = \frac{\tau_r^2}{(\tau_r - \tau)(\tau_r + \tau_1)},$$

² In the newest version of LT one more function of type (4) can be used to approximate a considerably asymmetric prompt peak.

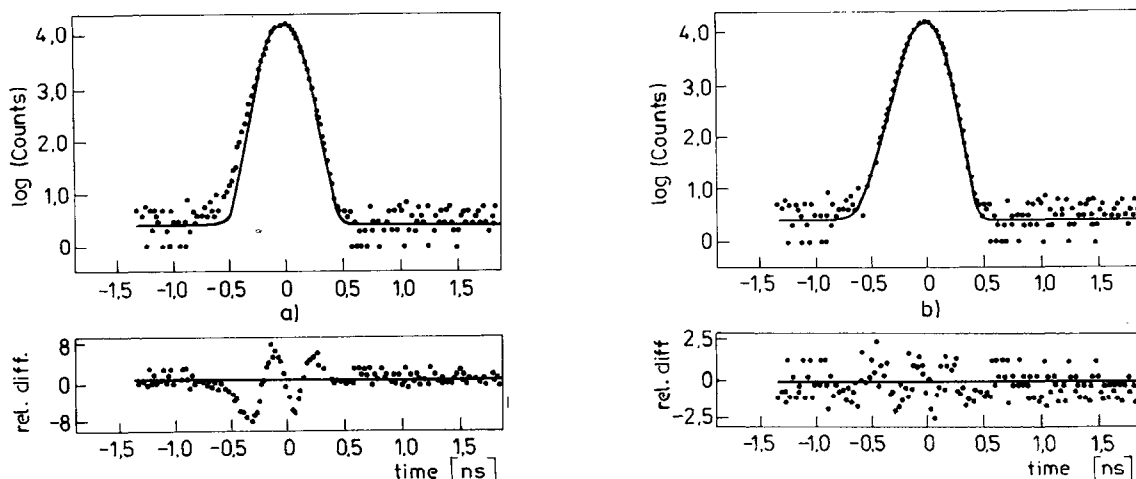


Fig. 1. A prompt curve measured with ^{60}Co in a fast-slow system with plastic scintillators and fitted: (a) by a Gaussian function (3), (FWHM = 257.9 ps); (b) by a modified Gaussian function (4), (FWHM = 225.8 ps, $\tau_1 = 53.5$ ps, $\tau_r = 31.8$ ps).

This formula has been calculated as a convolution of the C function (Eq. (1)) with the R function (Eq. (4)).

– Taking into consideration the R function, the shape of the *complex component* can be determined from the integral (2), in which the expression (5) or (6) substitutes for the term $f\lambda\exp(-\lambda t)$. In LT the integral is calculated by numerical integration.

3. Methods of the calculations

The program contains two procedures of calculations; one of them carries out the deconvolution of the experimental data whereas the other searches for the model's optimum parameters by means of a nonlinear fitting procedure.

The fitting procedure MINSQ [9] has been adapted into the LT program. The procedure is employed in both of the numerical methods described below.

3.1. Deconvolution of the experimental curve by the linear-log method

For $t \gg s$ (practically for $t > 2\text{FWHM}$) $\Phi(t)$ is a hardly changeable function of t , so the difference of the Φ 's in Eq. (5) can be estimated by zero. Additionally assuming $\tau > s$ the function Φ in Eq. (5a) becomes almost equal to 2. This way formula (5) turns out to be:

$$\begin{aligned} F(f, \tau, t_k) &= f \exp\left(\frac{s^2}{4\tau^2}\right) \left[\exp\left(-\frac{t_k}{\tau}\right) - \exp\left(-\frac{t_{k+1}}{\tau}\right) \right] \\ &= \frac{f}{\tau} \exp\left(\frac{s^2}{4\tau^2}\right) \exp\left(-\frac{t_k}{\tau}\right) \Delta t \\ &= f\lambda\Delta t \exp\left(-\frac{\lambda^2(\text{FWHM})^2}{16\ln 2}\right) \exp(-\lambda t_k), \quad (7) \end{aligned}$$

where Δt is the width of a channel.

Therefore the measured spectrum, for large t , can be regarded as a sum of the exponential functions and well known linear-log fit method can be used for its decomposition. (The linear-log fit used to be employed widely as a graphical method, before the computer calculations became commonly used.) In the LT program the method runs entirely automatically according to the following steps:

- 1) Reading the experimental data and approximate value of FWHM (optionally the two other approximate values of parameters τ_1 and τ_r – see expression (6)).

- 2) Cutting-off the constant background, determined from the experimental points lying on the background level; a *remainder* is obtained.

- 3) Fitting of a straight line to the logarithm of the *remainder*. The fitting is carried out within a proper range. The first point of the range is matched in such a way, that the correlation of the fit would be the best. The last point of the range is determined by the channel in which the *remainder* is still so big, that it considerably differs from the statistical noise.

- 4) Determination of f and $\lambda^{-1} = \tau$ by comparison of the fitted straight line with logarithm of Eq. (7).

- 5) Calculation of $F(f, \tau, t_k)$ and its subtracting from the previous *remainder* (a new *remainder* is obtained).

- 6) Repeating of the steps from 2 to 4 until the *remainder* contains only statistical noise within the whole range from 2 FWHM to the end of the data.

- 7) Analysis of the experimental data by means of the mentioned searching procedure with the results of the linear-log method as the starting parameters. The set of the starting parameters contains the following data:

- previously determined f 's and τ 's,
- if the sum Σ of previously determined f 's is less than 100% then one more pair of f and τ ($f = 100\% - \Sigma$ and $\tau = \frac{1}{2}\text{FWHM}$),
- background level B and zero of time (as a number of channel) T_0 , the resolution curve parameters: FWHM and

optionally τ_1 and τ_2 ; sometimes f 's and τ 's for *source components* (if they are known before calculations. In this case the algorithm is modified in step 1).

During the calculations the number of components is optimised. If two of the found components have very close τ 's they are joined into one resulting component.

3.1.1. Constraints

As it previously was mentioned, the analysing method can be used without any limitations on the parameter values. However, when some of the parameter values have been (exactly or approximately) known from the theoretical predictions or earlier measurements then one can establish these values at the beginning of calculations. This method enables the following values to be established (as free or fixed parameters):

- Contribution of source, lifetimes and relative intensities for *source components*.
- Resolution curves parameters.
- Background and zero time channel.

The deconvolution procedure gives the final results for discrete lifetime spectra with several (≤ 4) well-separated components. It optimises the component number, the values of lifetimes and fractions related to each of them as well as the background level and the resolution curve parameters' values. For complicated spectra (some components with a small intensity, components of close lifetime values or spectra with the continuous distribution of the lifetimes) the mentioned procedure can be treated as a preliminary one. Its results can be used (after an optional modification) as a good starting parameters set for the nonlinear fitting procedure.

3.2. Fitting of the model by the nonlinear optimising method

The method enables fitting spectra which are a sum of the *simple components* (1) as well as the *complex components* (2) convoluted with the resolution curve and the background.

This method can be employed

- after the previously described one, or
- independently of it, if the number of components and values of the model's variables are known quite well before any calculations. This takes place, for example, when a series of spectra with continuously changing parameters is analysed, because then the results for the previous spectrum can play a part of the starting parameters for the next one.

The set of the starting parameters (directly typed or obtained as the result of preceding calculations) can be edited before the procedure runs

3.2.1. Editing of the starting parameters values

The following editor's operations are possible:

- Correction of a chosen parameter value.
- Deleting or adding a component.

Table 1

The values of lifetimes for the free positrons annihilation for some annealed metal found by LT

Metal	Lifetime [ps] (by LT)	Ref. data [13]
Iron	104 \pm 1	106
Copper	114.5 \pm 0.8	112
Nickel	108 \pm 2	110

– Transforming a *simple component* into a *complex one* by choosing σ (Eq. (2)) unequal to zero.

– Splitting a component into two components of the same mean lifetime as the lifetime of the component undergoing splitting.

– Joining two components into one “mean component”.

– Compressing many chosen *simple components* into one *complex component*.

3.2.2. Constraints

Preferred solutions can be achieved by putting some limitations on the starting parameters' set. The method enables:

- to fix any of the models' variables (in case of the fraction f its relative value is fixed),
- to separate the *source components* and fitting them as a whole.

4. Some results for the experimental data

Earlier versions of the LT program were used for data analysis, e.g. in Refs. [10,11]. In Ref. [7] calculations for polycrystalline ice at -10°C (the testing data for POSITRONFIT are from Ref. [1], see p. 251) were performed. The analysis was carried out at the same conditions (the same set of the guessed parameters values, numbers of the fixed parameters, and range of the data) as those in Ref. [1]. One can see that both methods gave almost identical results (compare Ref. [1] p. 253 and Ref. [7] p. 148).

The LT program was also tested on some positron lifetime spectra measured for pure polycrystalline annealed metals with source in Kapton foils. According to the result of Ref. [12] the positron lifetime in Kapton was assumed to be 386 ps and fixed during the fitting procedure. The results compared with data from Refs. [13] are presented in Table 1.

4.1. Comparison with the MELT program

The linear-log procedure of the LT program was compared with the MELT program for simulated data. The data were created alike the spectra from Ref. [5]³ (series A to

³ Calculations were carried out for the original data which had been used by Shukla et al. [5], and there was no substantial differences between the results obtained for the original data and the data simulated in the present work. The original data were sent to us by Dr. Shukla.

Table 2
Comparison the LT and MELT results for the same simulated spectra

Series	Method	First comp.	Second comp.	Third comp.	Fourth comp.
A	simulation	100	250	600	1000
		25	25	25	25
	MELT	103.1(0.6)	254.9(4.3)	559.3(14.1)	947.8(6.4)
		25.7(0.35)	23.94(0.36)	20.92(0.80)	29.87(0.94)
	LT	99.2(4.3)	249.5(13.7)	591.3(23.3)	996.8(8.1)
B	simulation	150	250		
		50	50		
	MELT	148.2(4.0)	242.4(4.0)		
		46.7(3.3)	53.3(3.3)		
	LT	143.4(4.0)	246.6(2.6)		
C	simulation	150	220		
		50	50		
	MELT	150.4(9.0)	213.3(6.1)		
		46.4(10.7)	53.6(10.7)		
	LT	143.0(7.9)	216.0(4.8)		
D	simulation	150	190		
		50	50		
	MELT	105.5	172.6		
		5.1	94.9		
	LT	166.2	252.7		
		94.4	5.6		

D). Some of the assumed values of the model parameters for each series are given in Table 2. Additional parameters were: time calibration 58 ps/channel, FWHM = 270 ps, background $B = 100$ counts, and the number of the total counts under a spectrum – 20 M (for spectrum A) and 2M (for spectra B–D). Analysis was performed fully automatically. All of the model parameters, i.e. f 's, τ 's, FWHM, B and T_0 , and number of the components were searched for. In Table 2, there are the results of the calculations compared with the values achieved with the MELT program.

One can see, that both programs give very similar values of the lifetime parameters, which suggests that the results of an analysis depend more on the experimental data (their statistics and type) than on the method using for the analysis. However, it seems, that the present program has some advantages over the MELT program. They are:

- calculating without any steering parameters,
- optimising the T_0 and FWHM parameters (MELT determines these parameters only with finite accuracy).

5. Spectra with continuous lifetime distribution

It is well known, see e.g. Ref. [14], that in porous materials, e.g. polymers, zeolites, pressed powders, positrons form hydrogen-like atoms – positroniums – which localise in the pores of the material. The lifetime of the triplet positronium species (o-Ps) increases with increasing pore size, therefore the lifetime spectrum reflects the free volume

Table 3
Parameters found by LT for simulated data of the first series with the automatic linear-log procedure

Total area [counts]	First comp. τ [ps] f [%]	Second comp. τ [ps] f [%]	Third comp. τ [ps] f [%]	FWHM [ps]	χ^2
Model	125 10	400 60	1000 30	300	
2M	178(12) 15.5(1)	449(8) 64.1(1.1)	1240(13) 20.3(0.6)	296	0.975
4M	180(10) 15.7(1)	449(6) 63.8(0.8)	1233(10) 20.4(0.5)	296	1.003
8M	160(7) 14.0(0.6)	444(4) 65.7(0.5)	1245(7) 20.3(0.3)	297.9	1.003
16M	158(4) 14.0(0.3)	444(2) 65.6(0.3)	1241(5) 20.3(0.2)	299.0	1.025
32M	129(5) 10.6(0.4)	408(5) 63.0(0.9)	986(34) 1682(84) 21.4(0.6) 5.0(1.2)	299.7	0.999

size distribution in the continuous lifetime distribution (the *complex component*) [15]. However, the spectrum contains some other components related with the free positron annihilations, the singlet positronium species (p-Ps) decays so extraction of the complex component from all of the components is rather a difficult problem. Below, we will investigate the possibility of a valid analysis of some complex spectra by performing several tests for simulated ones.

5.1. Tests for simulated data

The tests were performed for two series of simulated spectra. The first series was calculated for the following values of the model parameters: two *simple components* 125 ps (10%), 400 ps (60%) and one *complex component* $\tau = 1000$ ps, $\sigma = 0.30$ (30%), FWHM = 300 ps and $B = 0.005\%$ of the total count s . It consisted of five spectra with total counts of 2M, 4M, 8M, 16M and 32M. The simulated spectra were calculated with high accuracy (the numerical integration, needed for determination of the *complex components*, was carried out with higher accuracy than the common calculations in the LT program), in 2048 channels with 25 ps/channel and then an appropriate Poisson noise was added.

The simulated data were analysed in two ways:

1) By means of the linear-log deconvolution procedure.

The results of the calculations are given in Table 3. The obtained fits were very good, with variances between 0.98 and 1.03. The value of B deviated by less than 1 from its real value and T_0 by less than 0.2 of a channel. For the data from 2M to 16M counts, the program detected three components. The lifetimes and fractions related to the first and the second components differed from the assumed ones but for the

Table 4

Parameters found by LT for simulated data of the first series with the nonlinear fitting procedure. Parameters from Table 3 were the starting parameters for this procedure

Total area [counts]	First comp. τ [ps] f [%]	Second comp. τ [ps] f [%]	Third comp. τ [ps] f [%] σ	FWHM [ps]	χ^2
Model	125 10	400 60	1000 30 0.300	300	
2M	93(16) 8.4(0.3)	380(5) 57.8(0.5)	936(10) 33.9(0.5) 0.332(0.008)	302.5	0.910
4M	123(14) 9.1(0.8)	390(9) 58.5(1.9)	959(48) 32.4(1.9) 0.316(0.032)	299.1	0.943
8M	130(12) 10.2(0.8)	405(8) 61.3(1.3)	1033(37) 28.5(1.4) 0.280(0.026)	298.7	0.956
16M	121(6) 10.1(0.4)	401(5) 60.8(0.7)	1018(20) 29.1(0.8) 0.286(0.015)	300.9	0.973
32M	125(5) 10.1(0.3)	399(5) 59.6(0.5)	994(13) 30.3(0.5) 0.303(0.009)	300.0	0.998

smoothest (32M) spectrum the results nearly approached the correct values. In this case four components were found; the *complex component* was represented by two *simple* ones. Their total fraction was 26.4% and mean lifetime 1119 ps.

2) *By the fitting procedure.* In this analysis two *simple components* and one *complex component* were assumed. The starting parameters for this method were the results of the linear-log method (complemented by a σ parameter). Although the obtained fits are only a bit better than the previous ones (Table 4), one can see, that now the parameter values are much better, especially for spectra with more than 2M counts.

From the analysis it follows, that for a spectrum with a *complex component* of fraction $\geq 30\%$, the determination of the lifetime distribution parameters (at least its first and second moment) is possible, if the total number of counts is greater than 2M. This conclusion is a little more optimistic than the conclusion arising from the results of Ref. [16], devoted to the determination of the lifetime distribution in an epoxy polymer with the CONTIN program. (The spectrum of this polymer contains only one complex component similar to our simulated data.) The authors found out, that CONTIN gives valid information about the lifetime distribution for spectra with statistics over 10M. In Ref. [17] a physical meaningful solution was obtained for spectra of lysozyme (one *complex component* with a fraction of about 20%) with 1.8M counts, which better agrees with our conclusion.

Table 5

Comparison the fit variances obtained for the model with the fixed correct values of parameters and the same model with the free parameters

Total [counts]	Exact parameters	Free parameters
5M	1.0084	1.0072
80M	0.9517	0.9509

Some polymers give more complicated spectra with at least two *simple* and two *complex components*, e.g. polytetrafluoroethylen (PTFE), e.g. Refs. [3,4]. To check the validity of solutions for such a type of spectrum, we simulated data for the model parameters similar to those expected for PTFE and then analysed them with the LT program. The following values of the model parameters were assumed:

– $\tau_1 = 125$ ps, $f_1 = 10\%$, $\tau_2 = 400$ ps, $f_2 = 60\%$ (for the *simple components*),

– $\tau_3 = 1000$ ps, $f_3 = 15\%$, $\sigma_3 = 0.30$, $\tau_4 = 3000$ ps, $f_4 = 15\%$, $\sigma_3 = 0.30$ (for the *complex components*) and

– FWHM = 300 ps and $B = 0.005\%$ of the total counts.

There were generated two spectra in 2048 channels with a scale of 25 ps per channel with statistics of 5M and 80M counts. Both were analysed in two ways:

1) All of the model parameters except the global size of the spectrum were fixed with their exact values.

2) Only the FWHM was fixed. All of the other parameters were free.

From these tests the following conclusions have arisen:

– At a common spectrum statistics the determination of the lifetime distributions could be a very ambiguous problem, what is caused not by the method employed to the data analysis but because of the loss of information, due to the statistical noise. This becomes obvious if you compare the fit variances for the exact spectra with the fitted ones (Table 5). It turned out, that for the 5M as well as the 80M spectrum procedure 2 gave a slight better fit variance than procedure 1, which made use of the exact values of the model parameters.

– When the dispersion of a *complex component* is small and its intensity is also tiny (in our case about 15%) its width (lifetime dispersion) could be immeasurable, hardly measurable or quite well measurable. It depends on the position of the component on the lifetime scale but first of all on the spectrum statistics. In our case, the third component's width is impossible to determine at 5M counts and hardly determined at 80M counts, but the σ parameter of the fourth component is close its correct value, even at 5M counts (Table 6).

5.2. Experimental support

To compare the LT program with the well known CONTIN program, an analysis of exactly the same data, which

Table 6

Parameters found by LT for simulated data of the second series with the nonlinear fitting procedure

Total area [counts]	First comp. τ [ps] f [%]	Second comp. τ [ps] f [%]	Third comp. τ [ps] f [%] σ	Fourth comp. τ [ps] f [%] σ	χ^2
Model	125 10	400 60	1000 15 0.300	3000 15 0.300	
5M	127(7) 10.5(1.1)	411(12) 62.8(4.7)	1113(122) 10.5(5.6) 0(1.4)	2899(413) 16.1(3.5) 0.32(0.08)	1.007
80M	127(2) 10.3(0.4)	405(3) 61.5(1.7)	1031(29) 11.9(2.1) 0.15(0.1)	2884(138) 16.2(1.3) 0.32(0.03)	0.951

had been used by Gregory in Refs. [3,4]⁴, was carried out. The data consist of:

– A spectrum of single crystals of molybdenum, measured at a temperature of 5.3°C, with about 2.2M total counts. In the experiment a positron source ²²Na, put between two Al-foils of 7 μ m, was employed. These reference data enabled the CONTIN program to avoid direct determination of the prompt curve shape. In the present analysis the data allowed to establish the prompt and source parameters.

– A spectrum of PTFE measured with the statistics 6.6M counts. The measurement conditions and source were identical with those for the reference material.

During the analysis of the reference data by LT, $\tau_{M0} = 123$ ps for free annihilations in molybdenum was assumed, i.e. an identical value with that, which had been assumed in Ref. [3]. Unfortunately, the second lifetime $\tau_{A1} = 166$ ps (free annihilations in Al) seems to be incorrect. At this value the spectrum could not be well fit in any way (the best chi-square was 2.05, Fig. 2a). However, an excellent fit was obtained after freeing τ_{A1} ($\chi^2 = 1.098$, Fig. 2b) and the following values of changeable parameters were obtained:

– For the prompt parameters: FWHM = 294.7(1.9) ps, $\tau_1 = 60.54(0.73)$ ps and $\tau_r = 54.7(3.0)$ ps.

– For the source parameters: contribution = 30.4(1.4)% (what is close to the value of 33%, calculated by Gregory and Sue [3]), $\tau_{A1} = 252.1(6.9)$ ps, $\tau_{s2} = 792.1(128)$ ps, $f_{s2} = 1.93\%$ of the source contribution. The existence of the second source component was also observed by Gregory in his paper, but there had been assumed another value $\tau_{s2} = 400$ ps.

Here, in the analysis of the PTFE spectrum, the two *simple* and two *complex components* were taken into consideration. The parameters τ_1 , τ_r , τ_{A1} , τ_{s2} and f_{s2} were fixed at those values, which had been found in the reference data analysis. Also the *source contribution* was fixed at the value of 23% (according to the Gregory calculations [3]). The rest of the

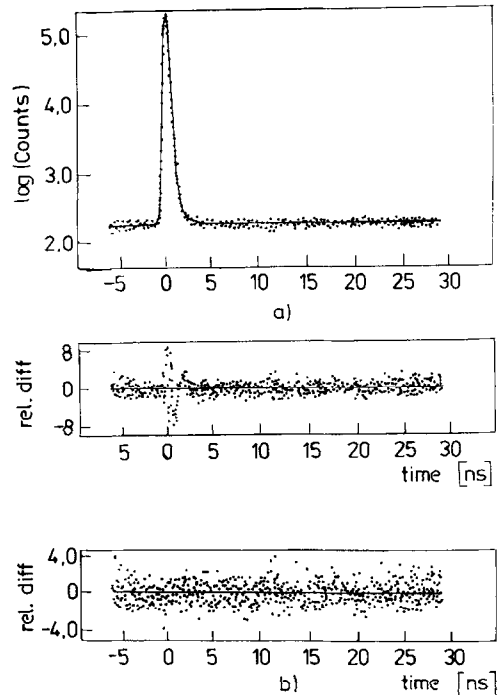


Fig. 2. The spectrum of Mo, measured with ²²Na between 7 μ m of Al foils (reference data from Ref. [3]). (a) The fit and the weighted residuals for lifetimes parameters given from Ref. [3]. (b) the weighted residuals for free lifetimes parameters (only $\tau_{M0} = 123$ ps was fixed).

parameters – FWHM and the sample parameters – was free. The achieved fit (with $\chi^2 = 1.050$) is presented in Fig. 3a. The determined value of FWHM = 295.07(0.59) is equal (in the error range) to the one obtained for the reference data. The other parameters are presented in Table 7.

The annihilation rate distribution related to the PTFE spectrum calculated by the LT and CONTIN programs is presented in Figs. 3b and 3c. The peak width connected with the fourth component was found almost equal to 0, although the starting value of σ was 0.4.

The resultant τ 's connect the first component to annihilations from the p-positronium state, the second to the free annihilations, the third and fourth components to two different states of o-Ps. A possible physical interpretation of these components is carried out in the next section.

6. Positronium thermalisation model adapted to the LT program

Recently a new model function for the lifetime analysis of slowly thermalising orthopositronium has been developed [18]. The model has been adapted to the LT program and tested for several simulated spectra and some experimental ones [19]. The authors of Ref. [18] employed the model to explain the lifetime spectra for pressed fine powder of alumina (Al₂O₃). The annihilation rate distribution predicted

⁴ The data were used with the agreement of their owner.

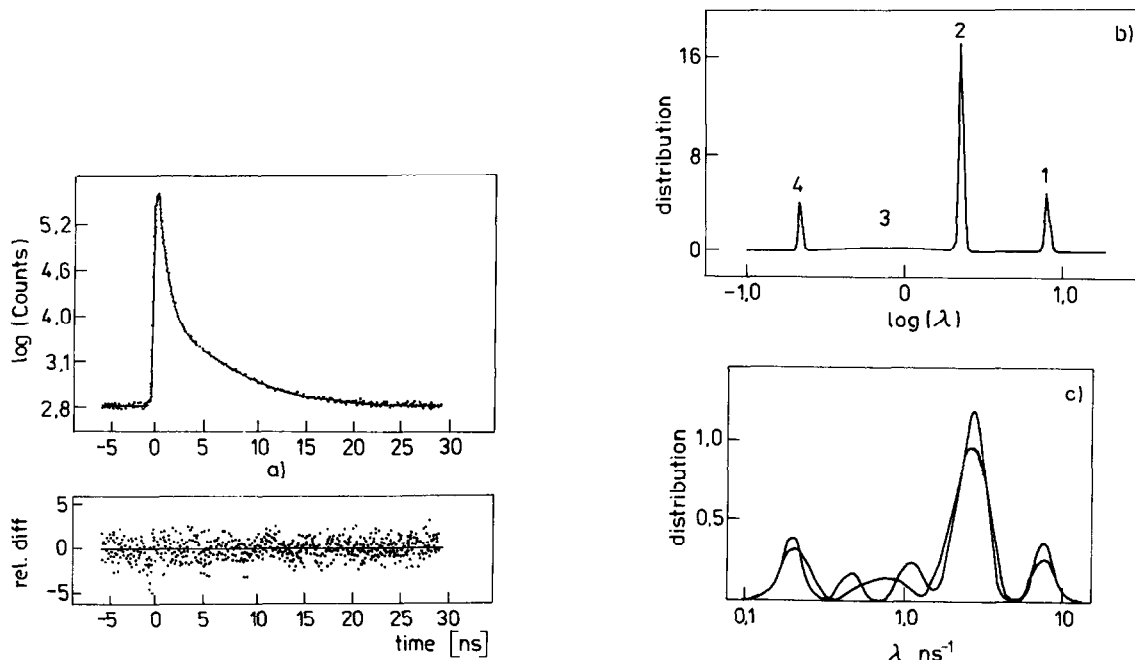


Fig. 3. The spectrum of PTFE in 5.3°C (data from Ref. [3]), measured at the same conditions as the reference data. The source contribution was taken from Ref. [3]. The prompt and source parameters were fixed to be equal to those found for the reference data. (a) The fit and the weighted residuals. (b) Distribution of the annihilation rate obtained by LT (in reality the widths of the peaks 1 and 2 were exactly equal to 0 and peak 4 was almost equal to 0, but for the graphical needs some small widths of these peaks have been assumed). (c) Distribution of the annihilation rate obtained by CONTIN [3].

Table 7

Lifetime parameters in PTFE at 5.3°C. Comparison between LT and CONTIN

Component number	Analysis with LT program			Analysis with CONTIN (Gregory [3]) components	
	Lifetime [ps]	Fraction [%]	Dispersion	Mean lifetime	Fraction
1	122.6(0.74)	15.92(0.030)	–	128	10.6
2	430.7(0.48)	56.00(0.033)	–	417	64.3
3	1326(4.9)	14.81(0.032)	0.435(0.007)	1346	9.4
4	4263(12)	13.27(0.01)	0.01(0.09)	4042	15.7

by the model is like that obtained for PTFE, which suggested that, maybe, the behaviour of a positronium in the free volumes in polymers is similar to the behaviour of a positronium in the space between the fine particles of alumina. The hypothesis has been checked here for two polymers PTFE (Gregory's data) and a spectrum of hard polyethylene.

Before the results are presented, some information about the model and its functioning in the LT program will be given.

6.1. The model assumptions

– A positron can be emitted from the bulk into a free space as a hot o-positronium with energy of about 1 eV.

– The o-positronium can decay in a three-photons process with mean rate $\lambda_0 = 1/142 \text{ ns}^{-1}$ or in a two-photons process after a conversion to the p-state, while a collision with the inner surface of the free space. The rate of the process is

equal to:

$$\lambda_q = \frac{\nu}{\delta} \mu, \quad (8)$$

where μ is the decay probability per collision, ν the Ps velocity and δ the mean free path of the Ps in the space.

– Due to the elastic collisions with the surface the o-Ps loses its kinetic energy and gradually thermalises, therefore its annihilation rate decreases.

The assumption leads to the following non-exponential model function:

$$A(t) = N_0 \exp[-(\lambda_0 + p_1)t] \{ \lambda_0 + \eta_{23} p_1 [\lambda(t) - \lambda_0] \} \times \left[\frac{1 - K}{1 - K \exp(-p_3 t)} \right]^{2p_1/p_3}, \quad (9)$$

where

$$\lambda(t) = \lambda_0 + \frac{1 + K \exp(-p_3 t)}{1 - K \exp(-p_3 t)}, \quad K = \frac{p_2 - p_1}{p_2 + p_1} \quad (10)$$

is the annihilation rate at a moment t , $p_1 = \lambda_q(\infty)$ the rate of the ortho–para conversion after the thermalisation process, $p_2 = \lambda_q(0)$ the initial value of the rate, $p_3 = (1/T_{1/2}) \ln(2-K)$, $T_{1/2}$ the time needed to reduce the annihilation rate to the value $\lambda_0 + (p_2 + p_1)/2$, η_{23} the ratio of detection efficiency for photons from two-photons and tree-photons decay.

The model is described by five parameters. In Ref. [18] the following quantities as the model parameters have been chosen: $\lambda_{\text{therm}} = \lambda_0 + \lambda_q(\infty)$, $\lambda_{\text{hot}} = \lambda_0 + \lambda_q(0)$, $T_{1/2}$, η_{12} , and N_0 .

6.2. The model in the LT program

It turned out, that formula (9) can be well approximated by a sum of exponential functions and the coefficients before the exponents can be expressed by appropriate functions of the model parameters [20]. This form of the formula allowed us to easily include the model into the LT program. In the program, the function (9) is convoluted with the resolution curve (4) and integrated over the range of a channel. For spectra obtained for two-photons decay only, the parameter and in this case formula (9) gives:

$$A(t) = N_0 \exp[-(\lambda_0 + p_1)t] [\lambda(t) - \lambda_0] \times \left[\frac{1-K}{1-K \exp(-p_3 t)} \right]^{2p_1/p_3}, \quad (11)$$

and is expressed by four parameters only.

Formula (11) was fitted to the spectrum of PTFE (Gregory's data). The results are given in Table 8. The fit was very good ($\chi^2 = 1.064$).

The previous analysis of PTFE with log-normal distribution (see Section 5) found the fourth component as a *simple one* (the distribution width almost equal 0) and only the third component as a *complex one*. A possible explanation of these facts can be carried over on the basis of the discussed model. Function (11) can be easily transform into the sum of two components:

$$A(t) = N_0 [E(t) + R(t)]. \quad (12)$$

The first component, $E(t) = \exp[-(\lambda_0 + p_1)t]$, is discrete and relates to peak no. 4 in Fig. 3b, while the other one, which can be represented by a quasi-continuous sum of exponential functions, relates to the wide peak no. 3 in the Fig. 3b.

The small width of the first component (previously determined in the log-normal model distribution procedure) suggests that the mean free path of Ps (see formula (8)) is almost constant.

From formula (8), initial energy of Ps can be evaluated:

$$E_0 = \left[\frac{\lambda_q(0)}{\lambda_q(\infty)} \right]^2 \frac{3}{2} kT, \quad (13)$$

what gives $E_0 = 1.15$ eV for initial energy of a hot Ps in PTFE.

Table 8

Lifetime parameters in PTFE at 5.3°C found with the model [18]. The contribution of source was taken according to the calculations from Ref. [3]. The prompt parameters and the rest of the source parameters were fixed at the values obtained from the analysis of the reference data. f_{s2} was calculated in relative to the source distribution. "Sample" fractions are normalised to 100%

Prompt parameters:	
FWHM [ps]	295.1
τ_1 [ps]	60.54
τ_r [ps]	54.7
Source parameters:	
contribution [%]	33
τ_{A1} [ps]	252.1
τ_{s2} [ps]	792
f_{s2} [%]	1.93
Sample parameters:	
Model Dauwe et al. [18]	
f [%]	34.45(0.84)
τ_{therm} [ps]	4000(85)
τ_{hot} [ps]	723(47)
$T_{1/2}$ [ps]	469(30)
Rest of the components	
f_1 [%]	16.6(0.57)
τ_1 [ps]	115(2.3)
f_2 [%]	48.95(0.73)
τ_2 [ps]	363(2)

An additional test of the model was made with a spectrum of hard polyethylene. The spectrum was measured with statistics 3M in room temperature. The source of ^{22}Na was spotted between two 8.0 μm foils of Kapton. In the numerical analysis with LT, the lifetime for positrons in Kapton was assumed to be 386 ps [12]. The contribution of the source was calculated by computer simulations, which employed the value of the absorption coefficient for ^{22}Na positrons in Kapton determined in Ref. [12]. Results of this analysis are gathered in Table 9. The fit was carried out in full range of the experimental data and the fit variance achieved the very good value 1.14.

Using the found values and formula (12), one can calculate the initial energy of the hot positronium in hard polyethylene to be equal to 0.12 eV.

7. Additional information about LT

The LT v.3.0 program has been designed in the Borland PASCAL 7.0 programming language for PC microcomputers with 4 MB RAM and system DOS. The program is built in a windows environment, the basis is the Turbo Vision framework so it possesses a familiar look and is user friendly. A typical calculation (on a 50 MHz PC 486DX) takes less than half a minute for a spectrum with *simple components* only and for a spectrum with a continuous lifetime distribution, several minutes.

Table 9

Lifetime parameters in hard polyethylene found with the model in Ref. [18]. The contribution of the source was taken according to the calculations performed on the basis of data from Ref. [12]. "Sample" fractions are normalised to 100%

Prompt parameters:	
FWHM [ps]	295.2(0.4)
τ_1 [ps]	45.9
τ_r [ps]	50.0
Source parameters:	
contribution [%]	24.4
τ_{Al} [ps]	386
τ_2 [ps]	–
f_2 [%]	–
Sample parameters:	
Model Dauwe et al. [18]	
f [%]	24.23(0.3)
τ_{thrm} [ps]	2553(66)
τ_{hot} [ps]	1405(37)
$T_{1/2}$ [ps]	1472(176)
Rest of the components	
f_1 [%]	10.85(0.36)
τ_1 [ps]	117.9(2.9)
f_2 [%]	64.92(0.38)
τ_2 [ps]	329.0(1.7)

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