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Jag J. Singh,
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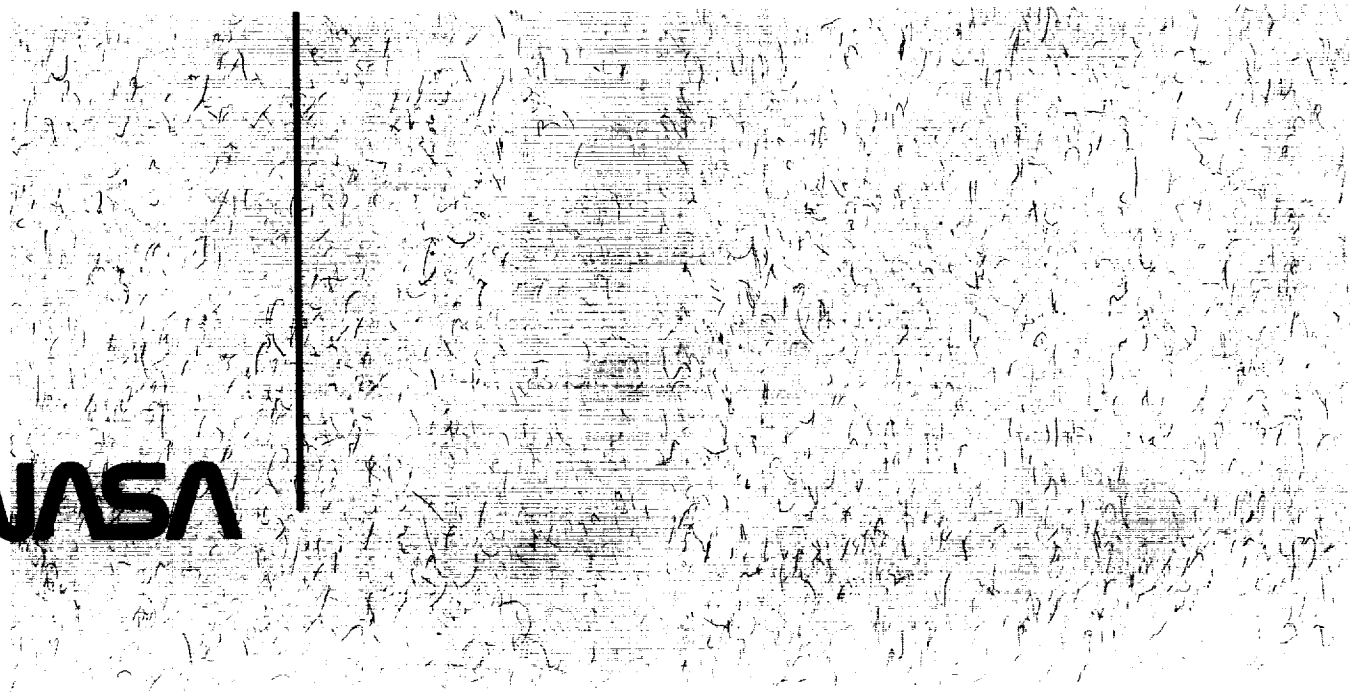

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Analysis of Positron Lifetime Spectra in Polymers

Jag J. Singh
Langley Research Center
Hampton, Virginia

Gerald H. Mall
Computer Sciences Corporation
Hampton, Virginia

Danny R. Sprinkle
Langley Research Center
Hampton, Virginia

National Aeronautics
and Space Administration

Scientific and Technical
Information Division

Summary

A new procedure for analyzing multicomponent positron lifetime spectra in polymers has been developed. It requires initial estimates of the lifetimes and intensities of various components, which are readily obtainable by a standard spectrum stripping process. These initial estimates, after convolution with the timing-system-resolution function, are then used as the inputs for a nonlinear least-squares analysis to compute the estimates that conform to a global-error minimization criterion. The convolution integral uses the full experimental resolution function, in contrast to the previous studies in which analytical approximations of it were utilized. These concepts have been incorporated into a generalized computer program for analyzing positron lifetime spectra (PAPLS) in polymers. The validity of this program has been tested by using several artificially generated data sets. These data sets were also analyzed with the widely used POSITRONFIT program. In almost all cases, the PAPLS program gives closer fits to the input values. The new procedure has been applied to the analysis of several lifetime spectra measured in metal-ion containing Epon 828 samples. The results are described in this report.

Introduction

Positrons are slowed down quickly (refs. 1 to 4) upon entering a condensed medium such as polymers. After thermalization, they may annihilate as free positrons or after being trapped in microvoids or at defect sites on molecular chains. Some of the trapped positrons also loosely bind with the molecular electrons to form positronium (Ps) atoms. (See refs. 3 to 8.) Depending on the final states of the positrons they annihilate at different times. The lifetime of the positron can thus provide valuable information about the electronic and physical structure of the bulk material and the various defects or impurities in it.

Positron lifetime studies make use of radioactive sources that emit a gamma ray almost simultaneously with the positron. The widely used Na^{22} source emits a 1.28-MeV photon within 3 psec of the emission of the preceding positron. The detection of this gamma photon marks the zero time (reference time) for a lifetime measurement, since the thermalization time for the positrons in polymers is much less than their subsequent lifetime and can usually be ignored. (See refs. 9 to 11.) The annihilation of the positron is signalled by the detection of one of the two annihilation photons produced in the $[e^+ + e^- \rightarrow 2h\nu$ (511 keV each)] process. The time interval between these two signals is a measure of the positron lifetime and is commonly measured by fast timing systems. The two widely used timing systems are described in references 12 to 15.

A typical lifetime spectrum of positrons annihilating in polymers (refs. 7 and 16 to 19) is expected to consist of at least three exponentially decaying components, each characterized by a mean lifetime and a relative probability amplitude. The three components are short-lifetime (resulting from prompt positron and parapositronium decays), intermediate-lifetime (resulting from trapped positron decays), and long-lifetime (resulting from orthopositronium decays). Quite often, the lifetime spectra in polymers have been analyzed by considering only two components, representing the mean lives of the "shorter" and "longer" components, for reasons of simplicity and/or expediency. (See refs. 7 and 20 to 28.) However, a detailed analysis that provides at least three components is preferable, since the annihilations of all the positron groups are dependent on their local atomic environments and can thus provide more detailed information about the host-material defect structure.

Observed spectra are subject to a finite time resolution of the lifetime measurement system. Data events which would theoretically fall into a certain time interval (channel) actually exhibit a near Gaussian distribution over many channels depending on the timing-system resolution. In previous studies, the timing-system-resolution function has been approximated by an analytical expression for reasons of simplicity and convenience of analysis. However, the resolution function does not lend itself to a complete description by a reasonable analytical expression. It would therefore be preferable to use the full experimental resolution function for deconvolving the lifetime spectra.

The purpose of this report is to develop a procedure for resolving a multicomponent experimental spectrum into individual lifetime components while imposing as few constraints and assumptions as possible. This procedure has been incorporated into a computer program for analyzing positron lifetime spectra (PAPLS) in polymers. This program has been used to analyze lifetime spectra observed in metal-ion containing Shell Epon 828 epoxy samples, and the results are compared with those obtained with the previously developed analysis techniques. This procedure is adaptable for other types of condensed matter within which positronium is likely to be formed.

Problem Statement

The lifetime spectra of positrons annihilating in a molecular solid consist of several components. It is often convenient to group the several lifetimes into three broad categories. (See ref. 29.) The shortest lifetime component (0.1 to 0.5 nsec) includes prompt free-positron decay and parapositronium decay. The intermediate lifetime component (0.5 to 0.9 nsec) is believed to arise from the annihilation of trapped positrons. The longest lifetime component (1 to 4 nsec) arises from pick-off annihilation of orthopositronium atoms. Each of the annihilation processes contributes a decaying exponential, with a characteristic decay constant, to the spectrum. In the previous studies of positron annihilation spectroscopy (PAS) in molecular solids (refs. 2, 7, and 21 to 28), it has often been convenient to resolve the experimental lifetime spectra into two components. This procedure has been justified on the basis of the arguments that the long-life component, which results from the pick-off annihilation of the triplet positronium and is the most sensitive indicator of the host-material properties, can be easily deconvolved from the rest of the spectrum; the short and intermediate lifetime components are then lumped together into a compound short-life component. It would, however, be more appropriate if all the positron groups could be deconvolved (refs. 16 to 19) particularly since the other groups are also dependent on the atomic environment of the trapped positrons and can provide some very useful information about the host defect structure.

For a three-component system, the lifetime spectrum can be written as the sum of three exponentials as follows:

$$n(t) = \sum_{i=1}^{3} A_i e^{-\lambda_i t} + B = A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t} + A_3 e^{-\lambda_3 t} + B \quad (1)$$

where A_i and λ_i represent zero-time amplitudes and decay constants, respectively, and B is a constant background.

When experimental ($n(t)$ versus t) data are displayed on a semilog format, the spectrum appears to be a sum of three straight lines—each representing an exponential decay. The three groups are easily discernible if λ_1, λ_2, and λ_3 are sufficiently different from each other and if their relative probabilities are comparable. In that case, the spectrum can be decomposed into individual components rather easily. Sometimes, though, the λ_i values are not sufficiently different, and the longer lived components are weaker; then, the spectrum analysis is a difficult problem.

The theoretical spectrum defined by equation (1) must be modified for the finite time resolution of the lifetime measurement system. Data events which would theoretically fall in a certain time interval (channel) actually exhibit a near Gaussian distribution whose effective full width at half maximum (FWHM) equals the timing-system resolution. The form of the time-resolution function can be determined by measuring a prompt spectrum, such as that obtained from detecting the near-simultaneous 1.17-MeV and 1.33-MeV gamma photons from a Co^{60} source, with the same experimental settings for electronics that are used in the actual lifetime experiment. Zero time is determined by the centroid of this prompt spectrum. Incorporation of the finite-resolution function into equation (1) modifies the lifetime spectrum as follows:

$$n(t) = \int_{-\infty}^{+\infty} R(t - t') n(t')\, dt' \quad (2)$$

where $R(t - t')$ represents the timing-system resolution-function and t' is the time variable, which differs from t by an integral number of time channels.

In previous studies, the resolution function has been assumed to be Gaussian; therefore, a direct analytical deconvolution of the observed data was possible. This approximation, however, tended to introduce systematic errors and to give poorer fits to the lifetime values. To improve on this situation, several authors have used modified Gaussian representations of the resolution function. Lichtenberger et al. (ref. 30) used a double-sided exponential function, whereas Hall et al. (ref. 31) used a side-sloped function to represent the resolution function. Eldrup et al. (refs. 7 and 8) and Kirkegaard et al. (ref. 32), on the other hand, assume the time-resolution function to be a sum of three Gaussian functions rather than a single Gaussian. Use of these various forms of analytical approximations improves the quality of the fits without complicating the solution of the convolution integral.

However, it has long been recognized that the experimental resolution functions of the fast timing systems used in PAS studies have slowly decaying characteristics which do not admit to simple analytical representations. To overcome the limitations imposed by imperfect analytical representation of the resolution function, actual experimental resolution functions are used as the smearing functions. An additional argument in support of this procedure arises from the fact that each timing system has its own unique resolution function. Even though this

approach makes the analysis procedure slightly more tedious, it is better suited for analyzing experimental spectra with inadequate statistics, as is often the case with the more promising types of polymers such as PMR-15, LARC-TPI, and other high-temperature polyimides.

The use of the actual experimental resolution function, rather than an approximate analytical representation of it, constitutes the major point of difference between the present and previous investigations. However, because of the numerical representation of the resolution function, it is not possible to analytically convolve the instrumental resolution effects into the theoretical spectrum. They have to be incorporated numerically as illustrated in the following example.

Assume that a lifetime spectrum has the following three components:

$$\tau_1 = 457 \text{ psec}; \quad I_1 = 79.7\%$$
$$\tau_2 = 917 \text{ psec}; \quad I_2 = 5.3\%$$
$$\tau_3 = 2300 \text{ psec}; \quad I_3 = 15.0\%$$

where τ_i is the lifetime of the ith component and I_i is the intensity of the ith component. Also assume that the timing-system resolution is 250 psec, the time channel width is 61.23 psec, and the total counting time is such that the peak channel count is 10^5 and the background count is 10. Figure 1 shows the histogram that is observed with a perfect system. Random statistical fluctuations have been included in this calculated histogram. A timing system with a finite resolution will smear this histogram into a spectrum shown in figure 2. The total counts which fall in any one channel for a perfect system are spread over an experimental distribution defined by the Co^{60} spectrum. This smearing process is repeated for each time channel in the theoretical histogram. Finally, the sums of all redistribution counts in the individual channels are recorded to give the computed spectrum (fig. 2) that would be observed with a finite-resolution timing system.

Close comparison of figures 1 and 2 shows that the first 10 or so channels are severely disturbed by the finite-resolution effects. Channels higher than 10 are essentially undisturbed, which indicates that the counts gained from the neighboring channels neutralize the losses to the neighboring channels that resulted from the finite-resolution effects. Figure 2 also shows that the peak in the synthesized smeared spectrum is about 100 psec to the right of the time zero (t_z) (reference) channel. This information can also be used to help locate the zero of the time scale in subsequent analyses. Figure 3 shows an actual experimental lifetime spectrum of positrons in an epoxy target. Obviously, the spectra shown in figures 2 and 3 are similar.

In the following sections, a procedure for resolving the experimental lifetime spectrum into three or more components is described. Previous attempts to develop procedures and programs for analyzing multicomponent positron lifetime spectra are described in references 32 to 34.

Spectrum Analysis

Procedure

The analysis procedure is described by referring to the experimental data shown in figure 3(b). The data have been plotted on a semilog paper in order to simplify the discussion. A cursory examination of this figure shows that it has three distinct components superimposed on a constant background. The stripping process starts by subtracting the background, which can be easily determined by averaging about 50 channels to the far right where no genuine positron decay events contribute to the observed data. Figure 4(a) shows the spectrum remaining after the background is subtracted. (The time-scale origin t_z has been shifted to channel zero and the abscissa has been expanded for the sake of clarity and for convenience of discussion.) Attention is first focused on the longest lifetime component (i.e., the third component). The first and second components do not seem to make any contributions to the data beyond channel 150. It would therefore appear that data in channels 150 to 180 are solely attributable to the third component, the initial estimate of which can be obtained by a least-squares fit to the data in these channels. After subtracting the third component from the background-free spectrum, the remaining spectrum (fig. 4(b)) has two distinct components. The counts in channels 40 to 60 are reasonably free from the effects of the first component. A least-squares fit to the data in channels 40 to 60 then provides the necessary initial information about the second component. Figure 4(c) illustrates the fit for the second component. The spectrum remaining after subtracting the second component is then solely attributable to the first component. Figure 4(d) shows this residual spectrum. Analysis of the residual spectrum then provides an initial estimate for the first component in the spectrum. Figure 4(e) illustrates the fit for the first component. After obtaining initial estimates for the three components, the finite-resolution effects are included in each component as discussed in the preceding section. The sum of these modified components gives the initial computed least-squares spectrum for comparison with the experimental spectrum.

Figure 4(f) illustrates the initial computed spectrum. This initial computed spectrum is then reiterated until the difference between the computed and the experimental spectra is minimized. The final comparison between the fitted and experimental spectra is shown in figure 4(g). A computer program developed by using these procedures is described in appendixes A and B.

Test of New Method

To validate the computational procedure described in appendixes A and B, several artificial sets of data with random fluctuations were first constructed. An experimentally observed Co^{60} spectrum was used to convolve the input sum of exponentials for simulation of the true experimental data. These simulated spectra were then analyzed using the same procedure as for the actual data. A second experimental Co^{60} spectrum was used as the input for the resolution function for PAPLS and POSITRONFIT analyses. Typical results for two such cases are summarized in tables I to III.

It is apparent from the results summarized in tables II and III that the present method deconvolves the artificial spectra correctly. It is also apparent that PAPLS provides closer fits to the input values for almost all the parameters than the POSITRONFIT program, particularly in the case of intensity values for the three components. Figures 5(a) and 5(b) illustrate the comparison between the fits predicted by PAPLS and POSITRONFIT programs, respectively, for case 1.

Applications

The PAPLS program has been applied in the analysis of positron lifetime spectra observed in metal-ion containing Epon 828 epoxy samples. The target specifications and experimental lifetime spectra observed in them are listed in appendix C. The same spectra were also analyzed using the POSITRONFIT program for the purpose of comparison. The results of this analysis are also included in table IV. A comparison of the two sets of values shows that while they are in general agreement, certain differences do exist. For example, most of the POSITRONFIT lifetime values are slightly higher than the values given by the PAPLS program.[1] Similarly, the intensities of all the POSITRONFIT shortest lifetime components are higher, whereas the intensities of the intermediate lifetime components are lower than the corresponding PAPLS values. These differences are attributable to the fact that the PAPLS program uses the exact resolution function, whereas the POSITRONFIT program assumes it to be a Gaussian or sum of Gaussians. The resolution function is not rigorously representable by a sum of Gaussians or Gaussians and exponentials.

Because of the manner in which t_z is calculated in PAPLS, it takes considerably longer to complete a PAPLS analysis than a POSITRONFIT analysis. Overall, however, the PAPLS program is more accurate, because it uses an exact resolution function rather than an approximate analytical representation.

Concluding Remarks

A new technique for analyzing multicomponent positron lifetime spectra in polymers has been developed. It utilizes the actual experimental timing-system-resolution function, rather than an analytical approximation, for deconvolving the experimental spectra. These concepts have been incorporated into a computer program for analyzing positron lifetime spectra (PAPLS) in polymers and other condensed media where positronium is likely to be formed. The validity of this program has been tested using several artificially generated data sets with random statistical fluctuations. Typically, the fitted parameters agree with the input values within ± 2 percent. These same data sets were also analyzed using the widely used POSITRONFIT program for the purpose of comparison. In almost all cases, the present technique gives closer fits to the input values. Both PAPLS and POSITRONFIT have been used to analyze several lifetime spectra measured in metal-ion containing Epon 828 epoxy samples. Even though the results obtained by the two programs are essentially equal, the PAPLS results are considered more accurate, because PAPLS does not make an a priori assumption about the nature of the life timing-system-resolution function.

NASA Langley Research Center
Hampton, Virginia 23665-5225
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[1] The PAPLS program gives slightly higher τ_2 and τ_3 values in Epon 828 containing 0.1 mole fraction of Cr $(DMSO)_6$ $(ClO_4)_3$.

Appendix A
Computer Program (PAPLS)

The computer program for analyzing positron lifetime spectra (PAPLS) is written in FORTRAN Version 5 language for the Control Data CYBER 170 series digital computer system with the Network Operating System (NOS 2.4). Machine dependence is limited to the use of several library routines (matrix inversion and graphics routines), and the program should be readily adaptable to other computer systems. All routines not included in the program are described in the code. The program requires approximately 70 000 octal locations of core storage, and a typical analysis requires approximately 100 central processing unit (CPU) seconds.

It is assumed in the program that the positron lifetime spectrum can be described by the equation

$$n_k = \left[\sum_{j=0}^{\infty} W_{j,k} \sum_{i=1}^{3} A_i e^{-\lambda_i (t_j - t_z)} \right] + B \qquad \text{(A1)}$$

where n_k is the number of counts in channel k, A_i is the amplitude at time zero t_z of each component, $\lambda_i = 1/\tau_i$, τ_i is the lifetime of each component, t_j is the time corresponding to channel j, B is a constant background, and the values of $W_{j,k}$ are normalized weights representing the resolution function smearing between channels j and k. In this expression, the values of the amplitudes A_i are zero for $t < t_z$. The number of components is arbitrary, but the particular version of the program being described has three components. The weights $W_{j,k}$ may be defined by using either an experimental resolution function or an analytical representation. The program defaults to a Gaussian time function if an experimental spectrum is not provided. The default weights are computed by

$$W_{j,k} = \frac{1}{\sigma\sqrt{\pi}} e^{-(t_j - t_k)^2/\sigma^2} \qquad \text{(A2)}$$

where σ is the standard deviation.

The process of obtaining a solution begins by first eliminating the background from the spectrum. The background is obtained by averaging counts over several channels (the default is 51 channels) at the high end of the spectrum. Thus, it is important that enough channels are provided so that the contribution of genuine positron decay events is negligible within the region used for background averaging.

Before applying the least-squares technique, described in detail in appendix B, to equation (A1) with B subtracted from both sides of the expression, it is necessary to estimate initial values for A_i and λ_i. Rather crude estimates are usually sufficient when the experimental data are relatively noise free. A stripping process is used to obtain these estimates. For this purpose, equation (A1) is approximated by the following simplistic expression:

$$\ln(n - B) = \ln(A_1) - \lambda_1 t + \ln(A_2) - \lambda_2 t + \ln(A_3) - \lambda_3 t \qquad \text{(A3)}$$

At this point of the solution process, it is further assumed that the resolution is perfect and that the t_z is exactly at the center of a channel a fixed number of channels (the default is 2 channels) to the left of the observed spectrum maximum.

The longest lifetime component is first addressed by examining only the data in a range where the contribution from the other two components has decayed to a negligible value (the default range is from channel 100 to channel 130 to the right of t_z). The data in these channels are least-squares fitted to a straight line to provide the initial estimates for A_3 and λ_3. Using these values, the third component is subtracted from equation (A3). The intermediate lifetime component is next considered by examining only the data in a range where the short lifetime component has decayed to a small value (the default range is from channel 38 to channel 58 to the right of t_z). As before, a straight line fit yields the initial estimates for A_2 and λ_2. The intermediate lifetime component is next subtracted from equation (A3). Finally, initial estimates for A_1 and λ_1 are obtained by a straight line fit to the remaining data. The default range for this fit is from channel 11 through channel 20 to the right of t_z.

With these six values used as initial estimates, an iterative process is initiated to determine the solution of equation (A1). The first step is to hold these six values constant and find the value of t_z, which minimizes the sum of the squares of the residuals. The entire range of data is used starting eight channels to the left of the peak. The initial estimates for A_i and λ_i are then used with this value of t_z, and the least-squares technique is employed to generate new values for A_i and λ_i. For this portion of the solution, the range of data used does not include data from eight channels to the left of the peak to three channels to the right of the peak. The improved values of A_i and λ_i are then held fixed, and t_z is once more adjusted to minimize the sum of the squares of the residuals. This iterative process continues until $\Delta t_z < 10^{-3}$ channel, where Δt_z is the change in t_z from one iteration to the next.

The resulting seven values of A_i, λ_i, and t_z are then used as initial estimates for one final iterative

procedure. This procedure is identical to the previous step, except that all the data are used when employing the least-squares technique.

Program Input

All program control input is provided through the NAMELIST name INDAT. A summary of the input variables is provided below. (Default values are provided in parentheses.)

NDIV (51):
Number of channels at high end of spectrum to be used in obtaining average background.

BKG (computed on basis of NDIV):
Average background. If specified, it will override the computed value.

TSF (61.27):
Time-scale factor in psec per channel.

NPO (120,38,11):
Array that provides channel offsets for defining regions used in obtaining initial estimates.

NPL (30,20,9):
Array that provides interval lengths for defining regions used in obtaining initial estimates. Defaults are based on the default value of TSF.

IDCHAN (-2):
Correction factor to compensate for apparent shift in peak location that results from time-resolution function. In general, the true value of t_z is to the left of the peak in the experimental data. An examination of the program output should verify that the computed and experimental data peak in the same channel; if not, an appropriate value of IDCHAN will correct for this.

IGAUSS (1):
Flag to indicate if a Gaussian time-resolution function is to be used in fit. If IGAUSS = 0, no time resolution function is used.

SIGINV (0.135621):
Value of $1/\sigma^2$, where σ is standard deviation of Gaussian time-resolution function.

ITERMX (30):
Maximum number of iterations to be allowed in least-squares fit.

IPRFLG (0,0,1,0,0,1):
Array controlling quantity of printed output. Each of six flags controls a specific output item. If the flag is "1," the item is printed. If the flag is "0," the item is not printed. The flags correspond to the following output items:

1. Raw data
2. Background corrected data
3. Initial-estimate fit results
4. Spectrum with initial fit subtracted
5. Fit using initial estimates
6. Final fit

IPLFLG (1,0,1,1,1,1):
Array that controls the quantity of graphic output. Each of six flags controls a specific plot. If the flag is "1," the plot is generated. If the flag is "0," the plot is not generated. The flags correspond to the same items as those for IPRFLG.

IPEEK (0,0):
Array used to simply examine data. If IPEEK(1) $\neq$ 0, the program produces a plot of the log of the data versus channel number; the plot begins with channel number IPEEK(1) to the right of the peak and continues through channel number IPEEK(2) to the right of the peak. No fit is attempted. This feature is useful for determining the ranges used for obtaining initial estimates.

In addition to program control input, the program reads the spectrum from TAPE1. The first record on this file should contain the number of channels and a data identification label in I4, A7 format. No more than 800 channels are allowed. The remaining records on this file contain integer counts for the number of channels specified in list-directed format. When an experimental resolution function spectrum is provided, these data complete the contents of TAPE1, which is also in list-directed format.

Program Output

The bulk of the program output is controlled by user-defined flags as indicated in the section "Program Input." The initial output (fig. A1) is always produced and provides an echo of the input spectrum with the data identification label, the number of channels, the value of the average background, and the number of channels used to compute the average background. If desired, the raw data are then output, as illustrated in figure A2, and give the time in psec, the counts, and the log of the counts for each channel. The data that are corrected for background may also be printed in the same four-column format. Data relating to the spectrum peak are then output, as shown in figure A3, and give the maximum value of the background-corrected spectrum, the channel where the peak occurs, and the channel corresponding to t_z. For each component, a summary of the initial-estimate calculations can be produced as shown in figure A4. This summary identifies the component, the channel range used to obtain the estimates, and the values (with errors in parentheses) for the slope λ, lifetime TAU, intercept $\ln(A)$,

and the area under the resulting curve. Also output are the fit standard deviation, the number of iterations required for convergence, and an error code. If this error code is not zero, the solution did not converge. For each component, the spectrum that results from subtracting the initial-estimate curve can also be output in a form similar to that in figure A2. After initial estimates have been determined for all six unknowns, the spectrum calculated from these values can be output for comparison with the experimental data. A sample of this output is included as figure A5; the sample provides the channel number, time (in psec), experimental data, and the fitted spectrum by using initial estimates. These data can be examined to verify the experimental data and the fit peak in the same channel. If not, the input variable IDCHAN requires adjustment. Sample output corresponding to the final-fit values is illustrated in figure A6. For each component, values are given (with errors in parentheses) for the slope λ, lifetime TAU, intensity $\left(\text{Area}_i \Big/ \sum_{j=1}^{3} \text{Area}_j\right)$, intercept $\ln(A)$, and the area under the resulting curve. Values are also provided for the fit standard deviation, the number of iterations required for convergence, and an error code. The final output is similar to figure A5, where the calculated spectrum is obtained using the final-fit values.

In addition to the printed output, the program produces graphic output, all of which is controlled by user-defined flags. The plots corresponding to the six flags are shown in figure A7. Results similar to figures A7(c) and A7(d) are produced for each component.

Program Listing

```
      PROGRAM PAPLS(OUTPUT,INPUT,TAPE5=INPUT,TAPE6=OUTPUT,
     1 TAPE1)
C*********************************************************************
C                                                                     *
C         PAPLS IS A COMPUTER PROGRAM FOR ANALYZING POSITRON          *
C         LIFETIME SPECTRA. THE CURRENT VERSION OF THE PROGRAM        *
C         IS LIMITED TO THREE COMPONENTS, BUT MINOR CODING            *
C         CHANGES WOULD BE REQUIRED TO ENABLE THE PROGRAM             *
C         TO PROCESS MORE OR FEWER COMPONENTS. AN ADVANTAGE           *
C         OF PAPLS OVER OTHER PROGRAMS OF A SIMILAR NATURE            *
C         IS ITS HANDLING OF THE TIME RESOLUTION FUNCTION.            *
C         THE RESOLUTION FUNCTION IS DESCRIBED IN TABULAR             *
C         FORM, THUS ALLOWING ANY ANALYTIC (OR NON-ANALYTIC)          *
C         REPRESENTATION. FOR A NON-ANALYTIC FUNCTION, A LOW          *
C         LEVEL OF NOISE IN THE REPRESENTATION OF THE TIME            *
C         RESOLUTION IS REQUIRED FOR RELIABLE PROGRAM                 *
C         EXECUTION.                                                  *
C                                                                     *
C*********************************************************************
      COMMON/INDAT/ICNT(800),NPTS,NPTSS,BKG,NDIV,IMAXC,TSF,IDCHAN,
     1 IPRFLG(10),IPLFLG(10),NPO(4),NPL(4),LABEL,CFRAC
      COMMON/PEEK/IPEEK(2)
      COMMON/GAUSDAT/AMP,SIGINV,IGAUSS,GAUSS(91)
      COMMON/OTDAT/SLOPEX(4),XOFFX(4),ESLOPE(4),EXOFF(4),
     1 NP1ST(4),NPLST(4),TAU(4),ETAU(4),AREA(4),EAREA(4)
      COMMON/FITDAT/XX(800),YY(800)
      COMMON/PRDAT/DATAX(800),DATAY(800),DATAXT(800),DATAYL(800)
      COMMON/CLCDAT/X(800),Y(800),YL(800)
      COMMON/CHARS/MSGPR(4)
      DIMENSION SOL(7),E(7)
      COMMON/NEWCOM/SOL,E,ITER2,IERR,STD
      DIMENSION Z(800)
      DATA MSGPR/6H FIRST,6HSECOND,6H THIRD,6HFOURTH/
      DATA SLOPEX,XOFFX/8*0./
      DATA NPASS/0/
    1 FORMAT(1H1,5X,'.....INPUT SPECTRUM (',A7,')'//)
    2 FORMAT(5I10)
    3 FORMAT(1HO,5X,'NUMBER OF CHANNELS IN DATA FILE = ',I5)
    4 FORMAT(1HO,5X,'BACKGROUND AVG. = ',1PE13.5,5X,'NDIV = ',I5)
    5 FORMAT(1HO,5X,'NUMBER OF COMPONENTS TO FIT = ',I5)
    6 FORMAT(1H1,5X,'RAW SPECTRUM'//
     1 5X,'CHANNEL',10X,'TIME(PS)',10X,'COUNTS',10X,'LOG(COUNTS)'//)
    7 FORMAT(1X,F10.0,7X,1PE13.5,5X,1PE13.5,5X,1PE13.5)
    8 FORMAT(1H1,5X,'BACKGROUND CORRECTED SPECTRUM'//
     1 5X,'CHANNEL',10X,'TIME(PS)',10X,'COUNTS',10X,'LOG(COUNTS)'//)
    9 FORMAT(1H1,5X,'SPECTRUM MAXIMUM = ',1PE13.5/
     1 1HO,5X,'CHANNEL NUMBER CORRESPONDING TO SPECTRUM MAXIMUM = ',
     2 I5/1HO,5X,'CORRECTED CHANNEL = ',I5)
   10 FORMAT(1HO,5X,'SPECTRUM MAXIMUM = ',1PE13.5/
     1 1HO,5X,'CHANNEL NUMBER CORRESPONDING TO SPECTRUM MAXIMUM = ',
     2 I5/1HO,5X,'CORRECTED CHANNEL = ',I5)
   11 FORMAT(1H1,5X,'SPECTRUM CORRECTED FOR ',A6,' FIT'//
     1 5X,'CHANNEL',10X,'TIME(PS)',10X,'COUNTS',10X,'LOG(COUNTS)'//)
```

```
   12 FORMAT(1H1,5X,A6,' FIT   (FROM',I5,' TO',I5,')'///
     1 10X,'SLOPE = ',1PE16.8,1X,
     2 '(',1PE16.8,')'//10X,'TAU = ',1PE16.8,1X,'(',
     3 1PE16.8,')'//10X,'INTERCEPT = ',1PE16.8,1X,'(',
     4 1PE16.8,')'//10X,'AREA = ',1PE16.8,1X,'(',
     5 1PE16.8,')'//10X,'STANDARD DEVIATION = ',1PE16.8//
     6 10X,'ITERATIONS = ',I5//10X,'IERR = ',I5///)
   13 FORMAT(1H1,5X,'FITTED SPECTRUM'//
     1 5X,'CHANNEL',10X,'TIME(PS)',10X,'COUNTS',10X,'    FIT    '//)
   14 FORMAT(1H1,5X,'NONLINEAR FIT'///
     1 10X,'    SLOPE = ',3(1PE14.6,1X,'(+',1PE14.6,')',3X)/
     A 1H+,21X,3(16X,'_',18X)/
     2 10X,'      TAU = ',3(1PE14.6,1X,'(+',1PE14.6,')',3X)/
     A 1H+,21X,3(16X,'_',18X)/
     3 10X,'INTERCEPT = ',3(1PE14.6,1X,'(+',1PE14.6,')',3X)/
     A 1H+,21X,3(16X,'_',18X)/
     4 10X,'     AREA = ',3(1PE14.6,1X,'(+',1PE14.6,')',3X)/
     A 1H+,21X,3(16X,'_',18X)/
     5 10X,'INTENSITY = ',3(1PE14.6,1X,'(+',1PE14.6,')',3X)/
     A 1H+,21X,3(16X,'_',18X)/
     6 10X,'       TO = ',1PE14.6,1X,'(+',1PE14.6,')'/
     A 1H+,21X,1(16X,'_',18X)/
     7 10X,'STANDARD DEVIATION = ',1PE14.6//
     8 10X,'ITERATIONS = ',I5,',',I5//
     8 10X,'       ICT = ',I5//
     9 10X,'IERR = ',I5///)
   15 FORMAT(1HO,5X,'LINEAR FIT STANDARD DEVIATION = ',1PE16.8,
     1 5X,'VARIANCE = ',1PE16.8)
   16 FORMAT(1HO,5X,'NONLINEAR FIT STANDARD DEVIATION = ',1PE16.8,
     1 5X,'VARIANCE = ',1PE16.8)
   17 FORMAT(1HO,5X,'TOTAL COUNTS = ',I10)
   18 FORMAT('  GTOT = ',E16.8)
C-------------------------------------------------------------------
C
C         SUBROUTINE PSEUDO INITIALIZES THE PLOT VECTOR FILE.
C         THIS SUBROUTINE IS DOCUMENTED IN "LANGLEY GRAPHICS
C         SYSTEM", CENTRAL SCIENTIFIC COMPUTING COMPLEX
C         DOCUMENT G-3
C
C-------------------------------------------------------------------
      CALL PSEUDO
C+++++
C
C         READ INPUT DATA
C
C+++++
      ICT = 0
      CALL DATRD
      WRITE(6,1) LABEL
      WRITE(6,2) (ICNT(I),I=1,NPTS)
      ISUMCT = 0.
      DO 20 I=1,NPTS
      ISUMCT = ISUMCT + FLOAT(ICNT(I))
   20 CONTINUE
      WRITE(6,17) ISUMCT
      WRITE(6,3) NPTS
```

```
      WRITE(6,4) BKG,NDIV
      NFIT = 0
      DO 30 I=1,4
      IF(NPL(I).NE.0) NFIT = NFIT + 1
   30 CONTINUE
      WRITE(6,5) NFIT
C+++++
C
C          STORE SPECTRUM IN DATAY
C          STORE LOG(SPECTRUM) IN DATAYL
C          STORE CHANNEL NUMBER IN DATAX
C          STORE TIME(PS) IN DATAXT
C
C+++++
      CNTTOT = 0.
      DO 40 I=1,NPTS
      CNTTOT = CNTTOT + ICNT(I)
      DATAY(I) = FLOAT(ICNT(I))
      DATAYL(I) = 0.
      IF(DATAY(I).GE.1.) DATAYL(I) = ALOG(DATAY(I))
      DATAX(I) = FLOAT(I)
      DATAXT(I) = DATAX(I)*TSF
   40 CONTINUE
C+++++
C
C          WRITE OUT RAW DATA IF REQUESTED
C
C+++++
      IF(IPRFLG(1).EQ.0) GO TO 60
      WRITE(6,6)
      DO 50 I=1,NPTS
      WRITE(6,7) DATAX(I),DATAXT(I),DATAY(I),DATAYL(I)
   50 CONTINUE
   60 CONTINUE
C+++++
C
C          PLOT RAW SPECTRUM IF REQUESTED
C
C+++++
      IF(IPLFLG(1).EQ.0) GO TO 70
      CALL DATPLT(DATAX,DATAYL,1,SLOPE,XOFF,NPL(1),
     1 NPO(1),MFIT)
   70 CONTINUE
      IF(IPEEK(1).NE.0) GO TO 400
C+++++
C
C          ELIMINATE BACKGROUND
C
C+++++
      DO 80 I=1,NPTS
      DATAY(I) = DATAY(I) - BKG
      DATAYL(I) = 0.
      IF(DATAY(I).GE.1.) DATAYL(I) = ALOG(DATAY(I))
   80 CONTINUE
C+++++
C
```

```
C          WRITE OUT BACKGROUND CORRECTED DATA IF REQUESTED
C
C+++++
      IF(IPRFLG(2).EQ.0) GO TO 100
      WRITE(6,8)
      DO 90 I=1,NPTS
      WRITE(6,7) DATAX(I),DATAXT(I),DATAY(I),DATAYL(I)
   90 CONTINUE
  100 CONTINUE
C+++++
C
C          PLOT BACKGROUND CORRECTED DATA IF REQUESTED
C
C+++++
      IF(IPLFLG(2).EQ.0) GO TO 110
      CALL DATPLT(DATAX,DATAYL,2,SLOPE,XOFF,NPL(1),
     1 NPO(1),MFIT)
  110 CONTINUE
C+++++
C
C          LOCATE CHANNEL CONTAINING SPECTRUM MAXIMUM
C
C+++++
      YMAX = 0.
      DO 120 I=1,NPTS
      IF(DATAY(I).LT.YMAX) GO TO 120
      YMAX = DATAY(I)
      IMAX = I
  120 CONTINUE
C+++++
C
C          SET CORRECTED CHANNEL AND SHIFT DATA
C          STORE DATA IN CALCULATION ARRAYS
C
C+++++
      IMAXC = IMAX + IDCHAN
      NPTSS = NPTS - IMAXC + 1
      DO 130 I=1,NPTSS
      X(I) = FLOAT(I-1)
      Y(I) = DATAY(I+IMAXC-1)
      YL(I) = DATAYL(I+IMAXC-1)
  130 CONTINUE
      IF(IPRFLG(1)+IPRFLG(2).EQ.0) WRITE(6,10) YMAX,IMAX,IMAXC
      IF(IPRFLG(1)+IPRFLG(2).NE.0) WRITE(6,9) YMAX,IMAX,IMAXC
C+++++
C
C          CALCULATE GAUSS WEIGHTS
C
C+++++
      ICOR = IMAXC - 46
      GTOT = 0.
      IF(IGAUSS.EQ.2) GO TO 150
      DO 140 I=38,54
      XI = FLOAT(I+ICOR)
      GAUSS(I) = AMP*EXP(-SIGINV*(XI - FLOAT(IMAXC))**2)
```

```
      GTOT = GTOT + GAUSS(I)
  140 CONTINUE
      GO TO 170
  150 CONTINUE
      DO 160 I=38,54
      GTOT = GTOT + GAUSS(I)
  160 CONTINUE
      GO TO 190
  170 CONTINUE
      IF(IGAUSS.EQ.1) GO TO 190
      DO 180 I=1,91
      GAUSS(I) = 0.
  180 CONTINUE
      GAUSS(46) = 1.
  190 CONTINUE
      WRITE(6,18) GTOT
C+++++
C
C          LOOP THROUGH DESIRED FITS
C
C+++++
      MFIT = 0
      DO 240 K=1,4
      IF(NPL(K).EQ.0) GO TO 240
      MFIT = MFIT + 1
      CALL LSQ2(NPL(K),X(NPO(K)),YL(NPO(K)),SLOPE,XOFF,
     1 ITER,IERR,STD,E1,E2)
      SLOPEX(MFIT) = SLOPE
      XOFFX(MFIT) = XOFF
      ESLOPE(MFIT) = E1
      EXOFF(MFIT) = E2
      TAU(MFIT) = -1./SLOPE
      TAU(MFIT) = TAU(MFIT)*TSF
      ETAU(MFIT) = E1/SLOPE**2
      ETAU(MFIT) = ETAU(MFIT)*TSF
      AREA(MFIT) = TAU(MFIT)*EXP(XOFF)
      EAREA(MFIT) = ETAU(MFIT)*EXP(XOFF)
     1 + EXOFF(MFIT)*TAU(MFIT)
      NP1ST(MFIT) = NPO(K)
      NPLST(MFIT) = NPO(K) + NPL(K)
C+++++
C
C          WRITE OUT FIT RESULTS IF REQUESTED
C
C+++++
      IF(IPRFLG(3).EQ.0) GO TO 200
      WRITE(6,12) MSGPR(MFIT),NP1ST(MFIT),NPLST(MFIT),SLOPE,E1,
     1 TAU(MFIT),ETAU(MFIT),XOFF,E2,AREA(MFIT),EAREA(MFIT),STD,
     2 ITER,IERR
  200 CONTINUE
C+++++
C
C          PLOT THE FIT IF REQUESTED
C
C+++++
```

```
      IF(IPLFLG(3).NE.0) CALL DATPLT(X,YL,5 SLOPE,
     1 XOFF,NPL(K),NPO(K),MFIT)
C+++++
C
C          SUBTRACT OUT THIS RESULT
C
C+++++
      FN = EXP(XOFF)
      DO 210 I=1,NPTSS
      Y(I) = Y(I) - FN*EXP(SLOPE*X(I))
      IF(Y(I).LT.0.) Y(I) = 0.
      YL(I) = 0.
      IF(Y(I).GT.1.) YL(I) = ALOG(Y(I))
  210 CONTINUE
C+++++
C
C          WRITE OUT CORRECTED SPECTRUM IF REQUESTED
C
C+++++
      IF(IPRFLG(4).EQ.0) GO TO 230
      WRITE(6,11) MSGPR(K)
      DO 220 I=1,NPTSS
      IF(I.LT.IMAXC)
     1WRITE(6,7) DATAX(I),DATAXT(I),DATAY(I),DATAYL(I)
      J = I - IMAXC + 1
      IF(I.GE.IMAXC)
     1WRITE(6,7) DATAX(I),DATAXT(I),Y(J),YL(J)
  220 CONTINUE
C+++++
C
C          PLOT THE CORRECTED SPECTRUM IF REQUESTED
C
C+++++
      IF(IPLFLG(4).EQ.0) GO TO 230
      CALL DATPLT(X,YL,3,SLOPE,XOFF,NPL(K),
     1 NPO(K),MFIT)
  230 CONTINUE
  240 CONTINUE
  250 CONTINUE
      NPASS = NPASS + 1
C+++++
C
C          RESTORE DATA
C
C+++++
      DO 260 I=1,NPTS
      DATAY(I) = DATAY(I) + BKG
      DATAYL(I) = 0.
      IF(DATAY(I).GE.1.) DATAYL(I) = ALOG(DATAY(I))
  260 CONTINUE
C+++++
C
C          COMPUTE FITTED SPECTRUM
C
C+++++
```

```
      DO 290 I=1,NPTS
      ZZZ = 0.
      YY(I) = 0.
      XX(I) = FLOAT(I)
      IF(I.LT.IMAXC) GO TO 280
      ARGX = DATAX(I) - (FLOAT(IMAXC) + CFRAC)
      IF(I.EQ.IMAXC) ARGX = 0.5*(0.5 - CFRAC)
      IF(ARGX.LT.0.) ARGX = 0.
      DO 270 KK=1,MFIT
      ZZZ = ZZZ + EXP(XOFFX(KK))*EXP(SLOPEX(KK)*ARGX)
  270 CONTINUE
      IF(I.EQ.IMAXC) ZZZ = (0.5 - CFRAC)*ZZZ
  280 CONTINUE
      ZZZ = ZZZ + BKG
      IF(ZZZ.LE.1.) GO TO 290
      YY(I) = ALOG(ZZZ)
  290 CONTINUE
      IF(IGAUSS.EQ.0) GO TO 330
      IBEG = IMAXC - 8
      IEND = NPTS-10
      DO 310 I=IBEG,IEND
      GCOR = 0.
      DO 300 K=38,54
      INDX = I+46-K
      IF(INDX.LE.0) GO TO 300
      YDATA = EXP(YY(INDX)) - BKG
      GCOR = GCOR + GAUSS(K)*YDATA
  300 CONTINUE
      Z(I) = GCOR + BKG
      Z(I) = ALOG(Z(I))
  310 CONTINUE
      DO 320 I=IBEG,IEND
      YY(I) = Z(I)
  320 CONTINUE
  330 CONTINUE
      STDTMP = 0.
      VARTMP = 0.
      NBEG = IMAXC - 6
      DO 340 I=NBEG,NPTS
      STDTMP = STDTMP + (EXP(YY(I)) - FLOAT(ICNT(I)))**2
      OBSRV = 1.
      IF(ICNT(I).NE.0) OBSRV = 1./FLOAT(ICNT(I))
      VARTMP = VARTMP + OBSRV*(EXP(YY(I)) - FLOAT(ICNT(I)))**2
  340 CONTINUE
      STDTMP = SQRT(STDTMP/FLOAT(NPTS-NBEG))
      VARTMP = VARTMP/(FLOAT(NPTS-NBEG+1 - 7))
      IF(NPASS.EQ.1) STDLIN = STDTMP
      IF(NPASS.EQ.1) VARLIN = VARTMP
      IF(NPASS.EQ.2) STDNLIN = STDTMP
      IF(NPASS.EQ.2) VARNLIN = VARTMP
C+++++
C
C         WRITE OUT THE FITTED SPECTRUM IF REQUESTED
C
C+++++
```

```
      IF(IPRFLG(NPASS+4).EQ.0) GO TO 360
      WRITE(6,13)
      DO 350 I=1,NPTS
      FIT = EXP(YY(I))
      WRITE(6,7) DATAX(I),DATAXT(I),DATAY(I),FIT
  350 CONTINUE
  360 CONTINUE
      FITMAX = EXP(YY(IMAXC))
      RELMAX = DATAY(IMAXC)
      RATMAX = RELMAX/FITMAX
      IF(NPASS.EQ.1) WRITE(6,15) STDLIN,VARLIN
      IF(NPASS.EQ.2) WRITE(6,16) STDNLIN,VARNLIN
C+++++
C
C         PLOT THE FITTED SPECTRUM IF REQUESTED
C
C+++++
      IF(IPLFLG(NPASS+4).EQ.0) GO TO 370
      CALL DATPLT(DATAX,DATAYL,4*NPASS,SLOPE,XOFF,NPL(1),
     1 NPO(1),MFIT)
  370 CONTINUE
      IF(NPASS.EQ.2) GO TO 400
C+++++
C
C         DETERMINE NONLINEAR FIT
C
C+++++
      SOL(1) = EXP(XOFFX(1))
      SOL(1) = SOL(1)*RATMAX
      SOL(2) = -SLOPEX(1)
      SOL(3) = EXP(XOFFX(2))
      SOL(3) = SOL(3)*RATMAX
      SOL(4) = -SLOPEX(2)
      SOL(5) = EXP(XOFFX(3))
      SOL(5) = SOL(5)*RATMAX
      SOL(6) = -SLOPEX(3)
      SOL(7) = 0.5
      DO 380 I=1,NPTS
      DATAY(I) = DATAY(I) - BKG
  380 CONTINUE
      SOL1 = SOL(1)
      SOL2 = SOL(2)
      SOL3 = SOL(3)
      SOL4 = SOL(4)
      SOL5 = SOL(5)
      SOL6 = SOL(6)
      SOL7 = SOL(7)
  390 CONTINUE
      SOL(1) = SOL1
      SOL(2) = SOL2
      SOL(3) = SOL3
      SOL(4) = SOL4
      SOL(5) = SOL5
      SOL(6) = SOL6
      SOL(7) = SOL7
```

```
      CALL LSQ6(NPTS,X,DATAY,SOL,E,ITER1,IERR,STD,IMAXC,
     1 NPO,NPL,CFRAC,ICT)
      SOL1 = SOL(1)
      SOL2 = SOL(2)
      SOL3 = SOL(3)
      SOL4 = SOL(4)
      SOL5 = SOL(5)
      SOL6 = SOL(6)
      SOL7 = SOL(7)
      SLOPEX(1) = - SOL(2)
      SLOPEX(2) = - SOL(4)
      SLOPEX(3) = - SOL(6)
      ESL1 = E(2)
      ESL2 = E(4)
      ESL3 = E(6)
      EXO1 = ALOG(E(1))
      EXO2 = ALOG(E(3))
      EXO3 = ALOG(E(5))
      SOL(2) = SOL(3)
      SOL(3) = SOL(5)
      SOL(4) = CFRAC
      SOL(5) = -SLOPEX(1)
      SOL(6) = -SLOPEX(2)
      SOL(7) = -SLOPEX(3)
      CFRACO = CFRAC
      CALL LSQ1
      XOFFX(1) = ALOG(SOL(1))
      XOFFX(2) = ALOG(SOL(2))
      XOFFX(3) = ALOG(SOL(3))
      TZERO = FLOAT(IMAXC) + SOL(4) + 0.5
      ETZERO = E(4)
      CFRAC = SOL(4)
C+++++
C
C          WRITE OUT FINAL FIT IF REQUESTED
C
C+++++
      IF(IPRFLG(3).EQ.0) GO TO 250
      SLOPE1 = SLOPEX(1)
      SLOPE2 = SLOPEX(2)
      SLOPE3 = SLOPEX(3)
      XOFF1 = XOFFX(1)
      XOFF2 = XOFFX(2)
      XOFF3 = XOFFX(3)
      TAU1 = -1./SLOPE1
      TAU1 = TAU1*TSF
      TAU2 = -1./SLOPE2
      TAU2 = TAU2*TSF
      TAU3 = -1./SLOPE3
      TAU3 = TAU3*TSF
      ETAU1 = ESL1/SLOPE1**2
      ETAU1 = ETAU1*TSF
      ETAU2 = ESL2/SLOPE2**2
      ETAU2 = ETAU2*TSF
      ETAU3 = ESL3/SLOPE3**2
```

```
      ETAU3 = ETAU3*TSF
      AREA1 = TAU1*EXP(XOFF1)
      AREA2 = TAU2*EXP(XOFF2)
      AREA3 = TAU3*EXP(XOFF3)
      EAREA1 = ETAU1*EXP(EXO1) + EXO1*TAU1
      EAREA2 = ETAU2*EXP(EXO2) + EXO2*TAU2
      EAREA3 = ETAU3*EXP(EXO3) + EXO3*TAU3
      AREAT = AREA1 + AREA2 + AREA3
      EAREAT = EAREA1 + EAREA2 + EAREA3
      XINT1 = AREA1/AREAT
      XINT2 = AREA2/AREAT
      XINT3 = AREA3/AREAT
      EINT1 = EAREA1/AREAT + EAREAT*AREA1/AREAT**2
      EINT2 = EAREA2/AREAT + EAREAT*AREA2/AREAT**2
      EINT3 = EAREA3/AREAT + EAREAT*AREA3/AREAT**2
      WRITE(6,14) SLOPE1,ESL1,SLOPE2,ESL2,SLOPE3,ESL3,
     1 TAU1,ETAU1,TAU2,ETAU2,TAU3,ETAU3,
     2 XOFF1,EXO1,XOFF2,EXO2,XOFF3,EXO3,
     3 AREA1,EAREA1,AREA2,EAREA2,AREA3,EAREA3,
     4 XINT1,EINT1,XINT2,EINT2,XINT3,EINT3,
     5 TZERO,ETZERO,STD,ITER1,ITER2,ICT,IERR
      DELTO = CFRAC - CFRACO
      IF(ICT.NE.0) DELTO = 4.*DELTO
      CFRAC = CFRACO + DELTO
      IF(ABS(CFRAC - CFRACO).LE.0.001) ICT = ICT + 1
      IF(ABS(CFRAC - CFRACO).GT.0.001
     1 .OR.ICT.LT.2) GO TO 390
      GO TO 250
  400 CONTINUE
C-----------------------------------------------------------------------
C
C          SUBROUTINE CALPLT CLOSES THE PLOT VECTOR FILE.
C          THIS SUBROUTINE IS DOCUMENTED IN "LANGLEY GRAPHICS
C          SYSTEM", CENTRAL SCIENTIFIC COMPUTING COMPLEX
C          DOCUMENT G-3
C
C-----------------------------------------------------------------------
      CALL CALPLT(0.,0.,999)
      STOP
      END
      SUBROUTINE DATPLT(X,Y,ICODE,SLOPE,XOFF,NPLA,NPOA,NFIT)
C
C          SUBROUTINE DATPLT GENERATES GRAPHIC OUTPUT OF THE
C          PROGRAM RESULTS. SEVERAL SUBROUTINES USED BY
C          DATPLT ARE DOCUMENTED IN "LANGLEY GRAPHICS
C          SYSTEM", CENTRAL SCIENTIFIC COMPUTING COMPLEX
C          DOCUMENT G-3.
C
      COMMON/PRDAT/DATAX(800),DATAY(800),DATAXL(800),DATAYL(800)
      COMMON/PEEK/IPEEK(2)
      COMMON/OTDAT/SLOPEX(4),XOFFX(4),ESLOPE(4),EXOFF(4),
     1 NP1ST(4),NPLST(4),TAU(4),ETAU(4),AREA(4),EAREA(4)
      COMMON/INDAT/ICNT(800),NPTS,NPTSS,BKG,NDIV,IMAXC,TSF,IDCHAN,
     1 IPRFLG(10),IPLFLG(10),NPO(4),NPL(4),LABEL,CFRAC
      DIMENSION JMESS(4),KMESS(3)
```

```
      COMMON/FITDAT/XX(800),YY(800)
      DIMENSION X(800),Y(800)
      DIMENSION MESS(2)
      DIMENSION MESS1(4)
      DATA IENT/0/
      DATA JMESS/10HFIRST FIT ,10HSECOND FIT,10HTHIRD FIT ,
     1 10HFOURTH FIT/
      DATA KMESS/10HOR FIRST  ,10HOR SECOND ,10HOR THIRD  /
      NPST = NPTS
      IF(IPEEK(1).EQ.0) GO TO 20
      YMAX = 0.
      DO 10 I=1,NPST
      IF(Y(I).LT.YMAX) GO TO 10
      YMAX = Y(I)
      IMAX = I
   10 CONTINUE
      NPST = IPEEK(2) - IPEEK(1) + 1
   20 CONTINUE
      IF(ICODE.EQ.3.OR.ICODE.EQ.5) NPST = NPTSS
      IENT = IENT + 1
C-----------------------------------------------------------------------
C
C         SUBROUTINE NFRAME IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND EXECUTES A FRAME ADVANCE
C
C-----------------------------------------------------------------------
      IF(IENT.GT.1) CALL NFRAME
C-----------------------------------------------------------------------
C
C         SUBROUTINE CALPLT IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND MOVES THE PEN TO A NEW LOCATION WITH PEN
C         UP OR DOWN. CALPLT CAN ALSO ESTABLISH A NEW PLOT
C         ORIGIN
C
C-----------------------------------------------------------------------
      CALL CALPLT(1.5,1.5,-3)
      MESS(1) = 10HLN (COUNTS
      MESS(2) = 10H)
      IF(ICODE.EQ.1) MESS1(1) = 10HRAW SPECTR
      IF(ICODE.EQ.1) MESS1(2) = 10HUM
      IF(ICODE.EQ.2) MESS1(1) = 10HSPECTRUM M
      IF(ICODE.EQ.2) MESS1(2) = 10HINUS BACKG
      IF(ICODE.EQ.2) MESS1(3) = 10HROUND
      IF(ICODE.EQ.3) MESS1(1) = 10HSPECTRUM C
      IF(ICODE.EQ.3) MESS1(2) = 10HORRECTED F
      IF(ICODE.EQ.3) MESS1(3) = KMESS(NFIT)
      IF(ICODE.EQ.3) MESS1(4) = 10HFIT
      IF(ICODE.EQ.4.OR.ICODE.EQ.8) MESS1(1) = 10HFITTED SPE
      IF(ICODE.EQ.4.OR.ICODE.EQ.8) MESS1(2) = 10HCTRUM
      IF(ICODE.EQ.5) MESS1(1) = JMESS(NFIT)
      INDX1 = 1
      IF(IPEEK(1).NE.0) INDX1 = IMAX + IPEEK(1)
      INDX2 = NPST
      IF(IPEEK(1).NE.0) INDX2 = IMAX + IPEEK(2)
      YSV = DATAYL(INDX1)
```

```
      DATAYL(INDX1) = 0.
C-----------------------------------------------------------------------
C
C         SUBROUTINE ASCALE IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND COMPUTES A SCALING FACTOR FOR AN ARRAY
C         OF DATA. ASCALE ALSO DETERMINES THE DATA MINIMUM
C
C-----------------------------------------------------------------------
      IF(IENT.EQ.1) CALL ASCALE(DATAYL(INDX1),3.,NPST,1,10.)
      DATAYL(INDX1) = YSV
      IF(IENT.EQ.1) YMIN = DATAYL(INDX2+1)
      IF(IENT.EQ.1) YSF = DATAYL(INDX2+2)
      Y(INDX2+1) = YMIN
      Y(INDX2+2) = YSF
      ISF = ALOG10(X(NPST)/10.)
      SF = 10.**ISF
      VP = X(NPST)/SF
      IVP = VP
      IVP = IVP + 1
      VMAX = IVP*SF
      VMAX = VMAX/10.
      X(NPST+1) = 0.
      X(NPST+2) = VMAX
      MESS2 = 7HCHANNEL
C-----------------------------------------------------------------------
C
C         SUBROUTINE NOTATE IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND DRAWS ALPHANUMERIC INFORMATION
C
C-----------------------------------------------------------------------
      CALL NOTATE(4.5,7.1,0.2,LABEL,0.,7)
      IF(ICODE.EQ.5) GO TO 30
      IF(ICODE.EQ.4.OR.ICODE.EQ.8) GO TO 50
C-----------------------------------------------------------------------
C
C         SUBROUTINE AXES IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND DRAWS A LINE, ANNOTATES THE VALUE OF A
C         VARIABLE AT SPECIFIED INTERVALS WITH TIC MARKS
C         AND PROVIDES AN AXIS IDENTIFICATION LABEL
C
C-----------------------------------------------------------------------
      CALL AXES(0.,0.,0.,10.,X(NPST+1),X(NPST+2),1.,0.,
     1 MESS2,0.2,-7)
      CALL AXES(0.,0.,90.,8.,Y(INDX2+1),Y(INDX2+2),1.,0.,
     1 MESS(1),0.2,11)
      IF(ICODE.EQ.1) CALL NOTATE(4.5,7.5,0.2,MESS1,0.,12)
      IF(ICODE.EQ.2) CALL NOTATE(4.5,7.5,0.2,MESS1,0.,25)
      IF(ICODE.EQ.3) CALL NOTATE(4.5,7.5,0.2,MESS1,0.,33)
      IF(ICODE.EQ.4.OR.ICODE.EQ.8)
     1CALL NOTATE(4.5,7.5,0.2,MESS1,0.,15)
      IF(ICODE.EQ.8) CALL NOTATE(3.5,7.5,0.2,6HFINAL,0.,5)
C-----------------------------------------------------------------------
C
C         SUBROUTINE LINPLT IS A PART OF THE LANGLEY GRAPHICS
C         SYSTEM AND DRAWS A LINE BETWEEN AND/OR DRAWS A NASA
```

```
C          STANDARD SYMBOL AT EACH SUCCESSIVE DATA POINT IN AN
C          ARRAY
C
C-----------------------------------------------------------------------
      CALL LINPLT(X,Y(INDX1),NPST,1,-1,22,1,0)
   30 CONTINUE
      IF(ICODE.LE.4) GO TO 60
      NP = NPLA + NPOA
      DO 40 I=1,NP
      XX(I) = FLOAT(I - 1)
      YY(I) = SLOPE*XX(I) + XOFF
   40 CONTINUE
      XX(NP+1) = 0.
      ISF = ALOG10(XX(NP)/10.)
      SF = 10.**ISF
      VP = XX(NP)/SF
      IVP = VP
      IVP = IVP + 1
      VMAX = IVP*SF
      VMAX = VMAX/10.
      XX(NP+2) = VMAX
      YY(NP+1) = YMIN
      YY(NP+2) = YSF
      XSV1 = X(NP+1)
      XSV2 = X(NP+2)
      YSV1 = Y(NP+1)
      YSV2 = Y(NP+2)
      X(NP+1) = XX(NP+1)
      X(NP+2) = XX(NP+2)
      Y(NP+1) = YY(NP+1)
      Y(NP+2) = YY(NP+2)
      CALL AXES(0.,0.,0.,10.,X(NP+1),X(NP+2),1.,0.,
     1 MESS2,0.2,-7)
      CALL AXES(0.,0.,90.,8.,Y(NP+1),Y(NP+2),1.,0.,
     1 MESS(1),0.2,11)
      CALL NOTATE(4.5,7.5,0.2,MESS1,0.,10)
      CALL LINPLT(X,Y,NP,1,-1,22,1,0)
      CALL LINPLT(XX,YY,NP,1,0,0,0,0)
      XXP = XX(NPOA)/XX(NP+2)
      YYP = YY(NPOA)/YY(NP+2)
C-----------------------------------------------------------------------
C
C          SUBROUTINE PNTPLT IS A PART OF THE LANGLEY GRAPHICS
C          SYSTEM AND DRAWS A NASA STANDARD SYMBOL CENTERED ON
C          A GIVEN COORDINATE
C
C-----------------------------------------------------------------------
      CALL PNTPLT(XXP,YYP,3,2)
      XXP = XX(NP)/XX(NP+2)
      YYP = YY(NP)/YY(NP+2)
      CALL PNTPLT(XXP,YYP,3,2)
      X(NP+1) = XSV1
      X(NP+2) = XSV2
      Y(NP+1) = YSV1
      Y(NP+2) = YSV2
```

```
      GO TO 60
   50 CONTINUE
      Y(NPST+1) = YMIN
      Y(NPST+2) = YSF
      CALL AXES(0.,0.,0.,10.,X(NPST+1),X(NPST+2),1.,0.,
     1 MESS2,0.2,-7)
      CALL AXES(0.,0.,90.,8.,Y(NPST+1),Y(NPST+2),1.,0.,
     1 MESS(1),0.2,11)
      IF(ICODE.EQ.8) CALL NOTATE(3.5,7.5,0.2,5HFINAL,0.,5)
      CALL NOTATE(4.5,7.5,0.2,MESS1,0,15)
      CALL LINPLT(X,Y,NPST,1,-1,22,1,0)
      YY(NPST+1) = YMIN
      YY(NPST+2) = YSF
      XX(NPST+1) = X(NPST+1)
      XX(NPST+2) = X(NPST+2)
      CALL LINPLT(XX(1),YY(1),NPST,1,0,0,0,0)
   60 CONTINUE
      RETURN
      END
      SUBROUTINE DATRD
C
C         SUBROUTINE DATRD READS THE EXPERIMENTAL DATA AND
C         THE OPERATION INSTRUCTIONS
C
      COMMON/INDAT/ICNT(800),NPTS,NPTSS,BKG,NDIV,IMAXC,TSF,IDCHAN,
     1 IPRFLG(10),IPLFLG(10),NPO(4),NPL(4),LABEL,CFRAC
      COMMON/MXNIT/ITERMX
      COMMON/PEEK/IPEEK(2)
      COMMON/GAUSDAT/AMP,SIGINV,IGAUSS,GAUSS(91)
      NAMELIST/ INDAT/BKG,NDIV,TSF,IDCHAN,NPO,NPL,IPRFLG,IPLFLG,
     1  AMP,SIGINV,IGAUSS,IPEEK,ITERMX,CFRAC
    1 FORMAT(I4,A7)
      REWIND 1
      READ(1,1) NPTS,LABEL
      READ(1,*) (ICNT(I),I=1,NPTS)
      BKG = 0.
      NDIV = 51
      N1 = NPTS - NDIV + 1
      DO 10 I=N1,NPTS
      BKG = BKG + FLOAT(ICNT(I))
   10 CONTINUE
      BKG = BKG/FLOAT(NDIV)
      TSF = 61.57
      IDCHAN = -2
      NPO(1) = 120
      NPL(1) = 30
      NPO(2) = 38
      NPL(2) = 20
      NPO(3) = 11
      NPL(3) = 9
      NPO(1) = NPO(1) - IDCHAN
      NPO(2) = NPO(2) - IDCHAN
      NPO(3) = NPO(3) - IDCHAN
      NPO(4) = 0
      NPL(4) = 0
```

```
      DO 20 I=1,10
      IPRFLG(I) = 0
      IPLFLG(I) = 1
   20 CONTINUE
      IPRFLG(3) = 1
      IPRFLG(6) = 1
      IPLFLG(2) = 0
      AMP = 0.22387
      SIGINV = 0.15745
      IGAUSS = 1
      ITERMX = 30
      CFRAC = -0.5
      IPEEK(1) = 0
      IPEEK(2) = 0
      READ(5,INDAT,END=30)
   30 IF(EOF(5).NE.0) GO TO 40
   40 CONTINUE
      IF(IGAUSS.EQ.0) AMP = 0.
      IF(IGAUSS.NE.2) GO TO 50
      READ(1,*) (GAUSS(KK),KK=38,54)
   50 CONTINUE
      WRITE(6,INDAT)
      RETURN
      END
      SUBROUTINE LSQ2(N,X,Y,SLOPE,XOFF,ITER,IERR,STD,E1,E2)
C
C         SUBROUTINE LSQ2 OBTAINS THE LEAST-SQUARE FIT OF
C         A STRAIGHT LINE TO A PORTION OF THE EXPERIMENTAL
C         DATA IN THE LOG DOMAIN
C
      DIMENSION X(30),Y(30),ARAY(2),R(100),B(2,3),C(2)
      DIMENSION KARY(7),ERROR(2)
      DATA ERROR/2*1.E-5/
      IERR = 0
      XOFF = 0.
      SLOPE = 20.
      ITER = 0
   10 CONTINUE
      DO 20 I=1,2
      DO 20 J=1,3
      B(I,J) = 0.
   20 CONTINUE
      ITER = ITER + 1
      DO 50 I=1,N
      ARAY(1) = X(I)
      ARAY(2) = 1.
      FX = SLOPE*X(I) + XOFF
      R(I) = Y(I) - FX
      ISUM = 1
      DO 40 K=1,2
      B(K,ISUM) = B(K,ISUM) + ARAY(ISUM)**2
      B(K,3) = B(K,3) + ARAY(K)*R(I)
      IF(ISUM.EQ.2) GO TO 40
      JM1 = ISUM
      ISUM = ISUM + 1
```

```
      DO 30 J=ISUM,2
      B(K,J) = B(K,J) + ARAY(JM1)*ARAY(J)
   30 CONTINUE
   40 CONTINUE
   50 CONTINUE
      DO 70 I=1,2
      IM1 = I - 1
      IF(I.EQ.1) GO TO 70
      DO 60 J=1,IM1
      B(I,J) = B(J,I)
   60 CONTINUE
   70 CONTINUE
      KARY(1) = 10
      KARY(2) = 2
      KARY(3) = 3
      KARY(4) = 0
      KARY(5) = 2
      KARY(6) = 0
      KARY(7) = 0
C-----------------------------------------------------------------------
C
C         SUBROUTINE MATOPS OBTAINS THE INVERSE OF A MATRIX AND THE
C         SOLUTION OF A SET OF LINEAR EQUATIONS. THIS SUBROUTINE IS
C         DOCUMENTED IN "MATHEMATICAL AND STATISTICAL SOFTWARE AT
C         LANGLEY", CENTRAL SCIENTIFIC COMPUTING COMPLEX DOCUMENT
C         N2-3A
C
C-----------------------------------------------------------------------
      CALL MATOPS(KARY,B,DET,DUMMY)
      DO 80 I=1,2
      C(I) = B(I,3)
   80 CONTINUE
      IF(SLOPE.EQ.0.) GO TO 110
      TEST = ABS(C(1)/SLOPE)
      IF(TEST.GT.ERROR(1)) GO TO 150
   90 IF(XOFF.EQ.0.) GO TO 120
      TEST = ABS(C(2)/XOFF)
      IF(TEST.GT.ERROR(2)) GO TO 150
  100 CONTINUE
      GO TO 130
  110 IF(ABS(C(1)).GT.ERROR(1)) GO TO 150
      GO TO 90
  120 IF(ABS(C(2)).GT.ERROR(2)) GO TO 150
      GO TO 100
  130 CONTINUE
      SLOPE = SLOPE + C(1)
      XOFF = XOFF + C(2)
      STD = 0.
      DO 140 IJ=1,N
      STD = STD + R(IJ)**2
  140 CONTINUE
      STD = STD/FLOAT(N-2)
      E1 = B(1,1)*STD
      E2 = B(2,2)*STD
      E1 = SQRT(E1)
```

```
      E2 = SQRT(E2)
      STD = FLOAT(N-2)*STD
      STD = SQRT(STD/FLOAT(N))
      RETURN
  150 IF(ITER.GT.30) GO TO 160
      SLOPE = SLOPE + C(1)
      XOFF = XOFF + C(2)
      GO TO 10
  160 IERR = 1
      GO TO 130
      END
      SUBROUTINE LSQ6(NPTS,X,Y,SOL,E,ITER,IERR,STD,IMAXC,
     1 NPO,NPL,CFRAC,ICT)
C
C          SUBROUTINE LSQ6 LOCATES THE AMPLITUDES AND LIFETIMES
C          FOR FIXED ZERO TIME THAT MINIMIZE THE STANDARD
C          DEVIATION BETWEEN THE ANALYTIC APPROXIMATION AND THE
C          EXPERIMENTAL DATA
C
      DIMENSION NPL(4),NPO(4)
      DIMENSION FXC(800),DER(6,800)
      DIMENSION X(800),Y(800)
      COMMON/MXNIT/ITERMX
      COMMON/GAUSDAT/AMP,SIGINV,IGAUSS,GAUSS(91)
      DIMENSION E(6)
      DIMENSION R(800)
      DIMENSION SOL(6)
      DIMENSION ARAY(25),B(6,7),C(25)
      DIMENSION KARY(7),ERROR(25)
      DATA ERROR/25*1.E-5/
      DATA EPS/1.E-5/
      DATA NENTRY/0/
      ITER = 0
      IERR = 99
      E(1) = 1.
      E(2) = 1.
      E(3) = 1.
      E(4) = 1.
      E(5) = 1.
      E(6) = 1.
      NENTRY = NENTRY + 1
      IF(NENTRY.EQ.1) RETURN
      IERR = 0
      IPT = IMAXC + 3
      IF(ICT.EQ.1) IPT = IMAXC - 6
      ITER = 0
   10 CONTINUE
      DO 20 I=1,6
      DO 20 J=1,7
      B(I,J) = 0.
   20 CONTINUE
      ITER = ITER + 1
      NVAR = 6
      NXO = IMAXC
      XO = FLOAT(IMAXC)
```

```
      NPTSP = NPTS + 20
      DO 30 JJ=1,NPTSP
      IF(JJ.LT.NXO-16) GO TO 30
      ARGX = FLOAT(JJ) - (XO + CFRAC)
      IF(JJ.EQ.NXO) ARGX = 0.5*(0.5 - CFRAC)
      IF(ARGX.LT.0.) ARGX = 0.
      ARG = SOL(2)*ARGX
      C1 = 0.
      IF(ARG.LT.670.) C1 = EXP(-ARG)
      DER(1,JJ) = C1
      DER(2,JJ) = -SOL(1)*ARGX*DER(1,JJ)
      ARG = SOL(4)*ARGX
      C2 = 0.
      IF(ARG.LT.670.) C2 = EXP(-ARG)
      DER(3,JJ) = C2
      DER(4,JJ) = -SOL(3)*ARGX*DER(3,JJ)
      ARG = SOL(6)*ARGX
      C3 = 0.
      IF(ARG.LT.670.) C3 = EXP(-ARG)
      DER(5,JJ) = C3
      DER(6,JJ) = -SOL(5)*ARGX*DER(5,JJ)
      FXC(JJ) = SOL(1)*DER(1,JJ) + SOL(3)*DER(3,JJ) + SOL(5)*DER(5,JJ)
      IF(JJ.EQ.NXO) FXC(JJ) = (0.5 - CFRAC)*FXC(JJ)
      IF(JJ.LT.NXO) FXC(JJ) = 0.
      IF(JJ.LT.NXO) DER(1,JJ) = 0.
      IF(JJ.LT.NXO) DER(3,JJ) = 0.
      IF(JJ.LT.NXO) DER(5,JJ) = 0.
   30 CONTINUE
      DO 80 I=1,NPTS
      R(I) = 0.
      FX = 0.
      DO 40 JJ=1,6
      ARAY(JJ) = 0.
   40 CONTINUE
      IF(I.LT.IPT) GO TO 80
      NST = I-8
      NEND = I + 8
      KK = 37
      DO 50 JJ=NST,NEND
      KK = KK + 1
      ARAY(1) = ARAY(1) + DER(1,JJ)*GAUSS(KK)
      ARAY(2) = ARAY(2) + DER(2,JJ)*GAUSS(KK)
      ARAY(3) = ARAY(3) + DER(3,JJ)*GAUSS(KK)
      ARAY(4) = ARAY(4) + DER(4,JJ)*GAUSS(KK)
      ARAY(5) = ARAY(5) + DER(5,JJ)*GAUSS(KK)
      ARAY(6) = ARAY(6) + DER(6,JJ)*GAUSS(KK)
      FX = FX + FXC(JJ)*GAUSS(KK)
   50 CONTINUE
      R(I) = Y(I) - FX
      ISUM = 1
      DO 70 K=1,NVAR
      B(K,ISUM) = B(K,ISUM) + ARAY(ISUM)**2
      B(K,NVAR+1) = B(K,NVAR+1) + ARAY(K)*R(I)
      IF(ISUM.EQ.NVAR) GO TO 70
      JM1 = ISUM
```

```
      ISUM = ISUM + 1
      DO 60 J=ISUM,NVAR
      B(K,J) = B(K,J) + ARAY(JM1)*ARAY(J)
   60 CONTINUE
   70 CONTINUE
   80 CONTINUE
      DO 100 I=1,NVAR
      IM1 = I - 1
      IF(I.EQ.1) GO TO 100
      DO 90 J=1,IM1
      B(I,J) = B(J,I)
   90 CONTINUE
  100 CONTINUE
      KARY(1) = 10
      KARY(2) = 6
      KARY(3) = 7
      KARY(4) = 0
      KARY(5) = NVAR
      KARY(6) = 0
      KARY(7) = 0
C-----------------------------------------------------------------------
C
C          SUBROUTINE MATOPS OBTAINS THE INVERSE OF A MATRIX AND THE
C          SOLUTION OF A SET OF LINEAR EQUATIONS. THIS SUBROUTINE IS
C          DOCUMENTED IN "MATHEMATICAL AND STATISTICAL SOFTWARE AT
C          LANGLEY", CENTRAL SCIENTIFIC COMPUTING COMPLEX DOCUMENT
C          N2-3A
C
C-----------------------------------------------------------------------
      CALL MATOPS(KARY,B,DET,DUMMY)
      DO 110 I=1,NVAR
      C(I) = B(I,NVAR+1)
  110 CONTINUE
      DO 120 K=1,NVAR
      TST = ABS(C(K))
      IF(ABS(SOL(K)).GT.EPS) TST = ABS(C(K)/SOL(K))
      IF(TST.GT.ERROR(K)) GO TO 170
  120 CONTINUE
      DO 130 IJ=1,NVAR
      SOL(IJ) = SOL(IJ) + C(IJ)
  130 CONTINUE
  140 CONTINUE
      STD = 0.
      DO 150 IJ=1,NPTS
      IF(IJ.LT.IPT) GO TO 150
      STD = STD + R(IJ)**2
  150 CONTINUE
      STD = STD/FLOAT(NPTS-NXO-2)
      DO 160 IJ=1,NVAR
      E(IJ) = SQRT(ABS(B(IJ,IJ))*STD)
  160 CONTINUE
      STD = FLOAT(NPTS-NXO-2)*STD
      STD = SQRT(STD/FLOAT(NPTS-NXO))
      RETURN
  170 IF(ITER.GT.ITERMX) GO TO 200
```

```
      RATMAX = 0.
      DO 180 IJ=1,NVAR
      RAT = ABS(C(IJ)/SOL(IJ))
      IF(RAT.GT.RATMAX) RATMAX = RAT
  180 CONTINUE
      FRAC = 1.
      IF(RATMAX.GT.0.4) FRAC = 0.4/RATMAX
      DO 190 IJ=1,NVAR
      SOL(IJ) = SOL(IJ) + FRAC*C(IJ)
  190 CONTINUE
      GO TO 10
  200 IERR = 1
      GO TO 140
      END
      SUBROUTINE LSQ1
C
C          SUBROUTINE LSQ1 LOCATES THE VALUE OF ZERO TIME FOR
C          FIXED AMPLITUDES AND LIFETIMES WHICH MINIMIZES THE
C          STANDARD DEVIATION BETWEEN THE ANALYTIC APPROXIMATION
C          AND THE EXPERIMENTAL DATA
C
      COMMON/MXNIT/ITERMX
      COMMON/FUNCOM/R(800),XO,NXO
      COMMON/GAUSDAT/AMP,SIGINV,IGAUSS,GAUSS(91)
      DIMENSION E(7)
      DIMENSION SOL(7)
      COMMON/NEWCOM/SOL,E,ITER,IERR,STD
      COMMON/PRDAT/DATAX(800),DATAY(800),DATAXL(800),DATAYL(800)
      COMMON/CLCDAT/X(800),Y(800),YL(800)
      COMMON/INDAT/ICNT(800),NPTS,NPTSS,BKG,NDIV,IMAXC,TSF,IDCHAN,
     1 IPRFLG(10),IPLFLG(10),NPO(4),NPL(4),LABEL,CFRAC
      DATA EPS/1.E-5/
      DATA NENTRY/0/
      NENTRY = NENTRY + 1
      IERR = 0
      ITER = 0
      NXO = IMAXC
      XO = FLOAT(IMAXC)
      CALL FUNX(STDO,SOL)
      DELX = 0.05
      IF(NENTRY.GT.1) DELX = 0.01
      SOL(4) = SOL(4) + DELX
      CALL FUNX(STD,SOL)
      IF(STD.GE.STDO) DELX = -DELX
      STDO = STD
      SOL(4) = SOL(4) + DELX
   10 CONTINUE
      ITER = ITER + 1
      CALL FUNX(STD,SOL)
      IF(STD.GE.STDO) GO TO 20
      STDO = STD
      SOL(4) = SOL(4) + DELX
      GO TO 10
   20 TST = ABS(STDO - STD)/STDO
      IF(TST.LT.EPS) GO TO 30
```

```
      SOL(4) = SOL(4) - 2.0*DELX
      DELX = 0.5*DELX
      STDO = 1.E99
      GO TO 10
   30 CONTINUE
      STD = 0.
      DO 40 IJ=1,NPTS
      IF(IJ.LT.NXO) GO TO 40
      STD = STD + R(IJ)**2
   40 CONTINUE
      STD = STD/FLOAT(NPTS-NXO-2)
      E(4) = ABS(DELX)
      RETURN
      END
      SUBROUTINE FUNX(STD,SOL)
C
C         SUBROUTINE FUNX CALCULATES THE STANDARD DEVIATION
C         BETWEEN THE ANALYTIC APPROXIMATION AND THE EXPERIMENTAL
C         DATA. THE THREE AMPLITUDES ARE IN SOL(1), SOL(2),
C         AND SOL(3). THE ZERO TIME IS IN SOL(4). THE THREE
C         LAMBDAS (1/TAU) ARE IN SOL(5), SOL(6), AND SOL(7).
C
      COMMON/FUNCOM/R(800),XO,NXO
      COMMON/PRDAT/DATAX(800),DATAY(800),DATAXT(800),DATAYL(800)
      DIMENSION SOL(7)
      COMMON/GAUSDAT/AMP,SIGINV,IGAUSS,GAUSS(91)
      COMMON/INDAT/ICNT(800),NPTS,NPTSS,BKG,NDIV,IMAXC,TSF,IDCHAN,
     1 IPRFLG(10),IPLFLG(10),NPO(4),NPL(4),LABEL,CFRAC
      DIMENSION CONT(800)
      NPTSP = NPTS + 20
      DO 10 JJ=1,NPTSP
      IF(JJ.LT.NXO-20) GO TO 10
      ARG = SOL(5)*(FLOAT(JJ) - (XO + SOL(4)))
      IF(JJ.EQ.NXO) ARG = SOL(5)*0.5*(0.5 - SOL(4))
      C1 = 0.
      IF(ARG.LT.670.) C1 = EXP(-ARG)
      ARG = SOL(6)*(FLOAT(JJ) - (XO + SOL(4)))
      IF(JJ.EQ.NXO) ARG = SOL(6)*0.5*(0.5 - SOL(4))
      C2 = 0.
      IF(ARG.LT.670.) C2 = EXP(-ARG)
      ARG = SOL(7)*(FLOAT(JJ) - (XO + SOL(4)))
      IF(JJ.EQ.NXO) ARG = SOL(7)*0.5*(0.5 - SOL(4))
      C3 = 0.
      IF(ARG.LT.670.) C3 = EXP(-ARG)
      CONT(JJ) = SOL(1)*C1 + SOL(2)*C2 + SOL(3)*C3
      IF(JJ.EQ.NXO) CONT(JJ) = (0.5 - SOL(4))*CONT(JJ)
      IF(JJ.LT.NXO) CONT(JJ) = 0.
   10 CONTINUE
      DO 30 I=1,NPTS
      FX = 0.
      IF(I.LT.NXO-8) GO TO 30
      NST = I-8
      NEND = I + 8
      KK = 37
      DO 20 JJ=NST,NEND
```

```
      KK = KK + 1
      FX = FX + CONT(JJ)*GAUSS(KK)
   20 CONTINUE
      R(I) = DATAY(I) - FX
   30 CONTINUE
      STD = 0.
      DO 40 IJ=1,NPTS
      IF(IJ.LT.NXO-8) GO TO 40
      STD = STD + R(IJ)**2
   40 CONTINUE
      RETURN
      END
```

```
    0        0        0        0        0
    0        0        1        4        0
    1        2        5        4        1
    3        3        4        6        7
    7        5        7        3       10
    6        5        6        7       11
   11        9        5        9       13
    6        5       10        6        6
   11       11        2        8       11
   18       23       12       12       17
   14       14       12        5       12
   15       12       18       14       20
   11       17       12       10        9
   16       15       17        8       13
   14       16       16       16       16
   12       18       13       11       13
   12       16        9       12       14
   23       14       16       15       13
   24       13       15       20       24
  104      379     1627     5549    17239
42056    80360   122509   152716   160866
152636   134497   115315    97223    82396
69670    60471    51668    45037    39372
34291    30716    27085    24209    21504
19336    17210    15327    14182    12738
11623    10827     9787     9075     8404
 7740     7123     6843     6381     5945
 5570     5427     5157     4921     4531
    .        .        .        .        .
    .        .        .        .        .
    .        .        .        .        .
   18       14       16       13       13
    7       12       16       12       13
   14       11       17       17       11
    8       13       13        9       21

 TOTAL COUNTS =     1872471

 NUMBER OF CHANNELS IN DATA FILE =    650

 BACKGROUND AVG. =   1.29020E+01      NDIV =     51

 NUMBER OF COMPONENTS TO FIT =      3
```

Figure A1. Input spectrum.

RAW SPECTRUM

CHANNEL	TIME(PS)	COUNTS	LOG(COUNTS)
1.	6.15700E+01	.00000E+00	.00000E+00
2.	1.23140E+02	.00000E+00	.00000E+00
3.	1.84710E+02	.00000E+00	.00000E+00
4.	2.46280E+02	.00000E+00	.00000E+00
5.	3.07850E+02	.00000E+00	.00000E+00
6.	3.69420E+02	.00000E+00	.00000E+00
7.	4.30990E+02	.00000E+00	.00000E+00
8.	4.92560E+02	1.00000E+00	.00000E+00
9.	5.54130E+02	4.00000E+00	1.38629E+00
10.	6.15700E+02	.00000E+00	.00000E+00
11.	6.77270E+02	1.00000E+00	.00000E+00
12.	7.38840E+02	2.00000E+00	6.93147E-01
13.	8.00410E+02	5.00000E+00	1.60944E+00
14.	8.61980E+02	4.00000E+00	1.38629E+00
15.	9.23550E+02	1.00000E+00	.00000E+00
16.	9.85120E+02	3.00000E+00	1.09861E+00
17.	1.04669E+03	3.00000E+00	1.09861E+00
18.	1.10826E+03	4.00000E+00	1.38629E+00
19.	1.16983E+03	6.00000E+00	1.79176E+00
20.	1.23140E+03	7.00000E+00	1.94591E+00
21.	1.29297E+03	7.00000E+00	1.94591E+00
22.	1.35454E+03	5.00000E+00	1.60944E+00
23.	1.41611E+03	7.00000E+00	1.94591E+00
24.	1.47768E+03	3.00000E+00	1.09861E+00
25.	1.53925E+03	1.00000E+01	2.30259E+00
26.	1.60082E+03	6.00000E+00	1.79176E+00
27.	1.66239E+03	5.00000E+00	1.60944E+00
28.	1.72396E+03	6.00000E+00	1.79176E+00
29.	1.78553E+03	7.00000E+00	1.94591E+00
30.	1.84710E+03	1.10000E+01	2.39790E+00
31.	1.90867E+03	1.10000E+01	2.39790E+00
32.	1.97024E+03	9.00000E+00	2.19722E+00
.	.	.	.
.	.	.	.
.	.	.	.

Figure A2. Sample raw spectrum output.

```
SPECTRUM MAXIMUM =    1.60853E+05
CHANNEL NUMBER CORRESPONDING TO SPECTRUM MAXIMUM =    105
CORRECTED CHANNEL =    103
```

Figure A3. Sample peak output.

```
FIRST FIT    (FROM  137 TO  167)

    SLOPE =  -3.54o9o816E-02 (  3.11o94633E-03)
    TAU =    1.73584868E+03 (  1.52540054E+02)
    INTERCEPT =    9.46815652E+00 (  4.69875567E-01)
    AREA =    2.24636328E+07 (  1.97483780E+0o)
    STANDARD DEVIATIUN =    1.42757049E-01
    ITERATIONS =       2
    IERR =       0
```

Figure A4. Sample fit output (initial estimate).

FITTED SPECTRUM

CHANNEL	TIME(PS)	COUNTS	FIT
.	.	.	.
.	.	.	.
.	.	.	.
97.	5.97229E+03	3.79000E+02	2.00127E+02
98.	6.03386E+03	1.62700E+03	1.12727E+03
99.	6.09543E+03	5.59900E+03	4.94789E+03
100.	6.15700E+03	1.72390E+04	1.64066E+04
101.	6.21857E+03	4.20560E+04	4.13228E+04
102.	6.28014E+03	8.03600E+04	8.02398E+04
103.	6.34171E+03	1.22509E+05	1.22844E+05
104.	6.40328E+03	1.52716E+05	1.53020E+05
105.	6.46485E+03	1.60866E+05	1.61664E+05
106.	6.52642E+03	1.52636E+05	1.52155E+05
107.	6.58799E+03	1.34497E+05	1.33946E+05
108.	6.64956E+03	1.15315E+05	1.14537E+05
109.	6.71113E+03	9.72230E+04	9.72127E+04
110.	6.77270E+03	8.23960E+04	8.26306E+04
111.	6.83427E+03	6.96700E+04	7.05282E+04
112.	6.89584E+03	6.04710E+04	6.04883E+04
113.	6.95741E+03	5.16680E+04	5.21369E+04
114.	7.01898E+03	4.50370E+04	4.51665E+04
115.	7.08055E+03	3.93720E+04	3.93276E+04
116.	7.14212E+03	3.42910E+04	3.44189E+04
117.	7.20369E+03	3.07160E+04	3.02755E+04
118.	7.26526E+03	2.70850E+04	2.67643E+04
119.	7.32683E+03	2.42090E+04	2.37760E+04
120.	7.38840E+03	2.15040E+04	2.12237E+04
121.	7.44997E+03	1.93360E+04	1.90331E+04
122.	7.51154E+03	1.72100E+04	1.71451E+04
123.	7.57311E+03	1.53270E+04	1.55111E+04
124.	7.63468E+03	1.41820E+04	1.40907E+04
125.	7.69625E+03	1.27380E+04	1.28506E+04
126.	7.75782E+03	1.16230E+04	1.17635E+04
127.	7.81939E+03	1.08270E+04	1.08063E+04
128.	7.88096E+03	9.78700E+03	9.96017E+03
129.	7.94253E+03	9.07500E+03	9.20912E+03
130.	8.00410E+03	8.40400E+03	8.53980E+03
.	.	.	.
.	.	.	.
.	.	.	.

NONLINEAR FIT STANDARD DEVIATION = 1.05934364E+02

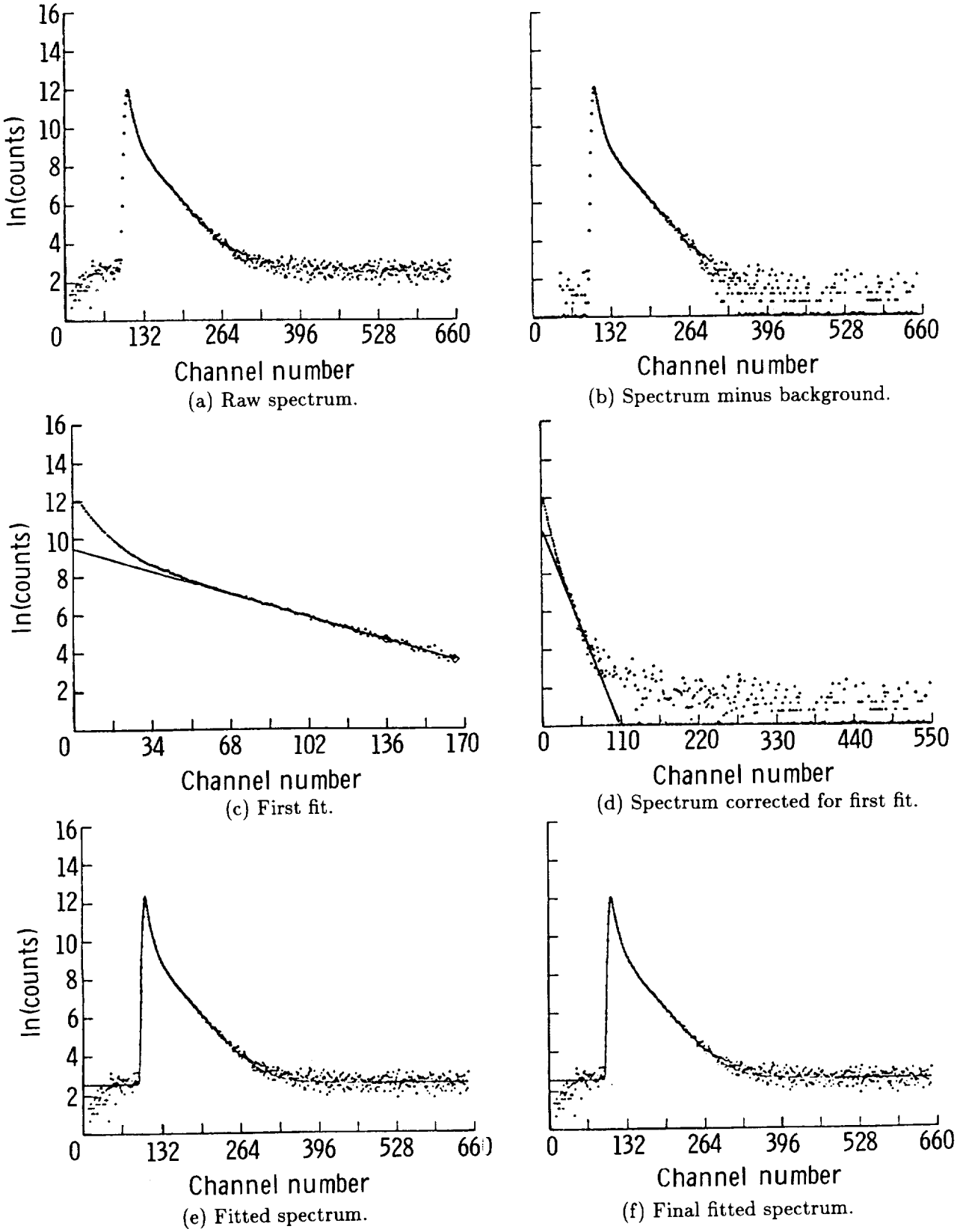
VARIANCE = 1.80950085E+00

Figure A5. Sample fitted spectrum output (initial estimate).

```
NONLINEAR FIT

      SLOPE =  -3.556485E-02 (± 1.049433E-03)   -1.177839E-01 (± 7.178350E-03)   -2.256389E-01 (± 4.318354E-03)
        TAU =   1.731204E+03 (± 5.108365E+01)    5.227371E+02 (± 3.185826E+01)    2.728696E+02 (± 5.222271E+00)
  INTERCEPT =   9.509106E+00 (± 6.935311E+00)    1.118825E+01 (± 9.204537E+00)    1.218858E+01 (± 9.272345E+00)
       AREA =   2.333997E+07 (± 6.451731E+04)    3.778151E+07 (± 3.215507E+05)    5.362752E+07 (± 5.809341E+04)
  INTENSITY =   2.034002E-01 (± 1.349553E-03)    3.292535E-01 (± 4.076657E-03)    4.673463E-01 (± 2.315232E-03)
         TO =   1.031930E+02 (± 7.812500E-05)
STANDARD DEVIATION =   7.703474E+03
ITERATIONS =     9,   30
       ICT =     1
IERR =     0
```

Figure A6. Sample results from final fit.



(a) Raw spectrum.

(b) Spectrum minus background.

(c) First fit.

(d) Spectrum corrected for first fit.

(e) Fitted spectrum.

(f) Final fitted spectrum.

Figure A7. Sample graphic output.

Appendix B

Least-Squares Solution

The solution of equation (A1) consists of seven parameters: A_1, A_2, A_3, λ_1, λ_2, λ_3, and t_z, where A_i is the amplitude of the ith component, t_z is time zero, $\lambda_i = 1/\tau_i$, and τ_i is the lifetime of the ith component. The method of least squares has been used to obtain the solution. This method is extremely sensitive to the initial estimated values of the seven parameters; accordingly, a multistep procedure is employed to obtain crude initial estimates and then refine them. This procedure is described in appendix A.

In general, equation (A1) can be written as follows:

$$n_k = F_k(t_j, A_1, A_2, A_3, \lambda_1, \lambda_2, \lambda_3) + \varepsilon_k \qquad \text{(B1)}$$

where the measurement error in channel k is given by ε_k. Expanding equation (B1) in a Taylor series and dropping higher order terms yields the following linear approximation:

$$\begin{aligned} n_k = (n_k)_0 &+ \frac{\partial F_k}{\partial A_1}(A_1 - A_{1,0}) + \frac{\partial F_k}{\partial A_2}(A_2 - A_{2,0}) \\ &+ \frac{\partial F_k}{\partial A_3}(A_3 - A_{3,0}) + \frac{\partial F_k}{\partial \lambda_1}(\lambda_1 - \lambda_{1,0}) \\ &+ \frac{\partial F_k}{\partial \lambda_2}(\lambda_2 - \lambda_{2,0}) \\ &+ \frac{\partial F_k}{\partial \lambda_3}(\lambda_3 - \lambda_{3,0}) + \varepsilon_k \end{aligned} \qquad \text{(B2)}$$

Equation (B2) can be simplified with the following definitions:

$$b_{k,1} = \frac{\partial F_k}{\partial A_1} \qquad b_{k,2} = \frac{\partial F_k}{\partial A_2} \qquad b_{k,3} = \frac{\partial F_k}{\partial A_3}$$

$$b_{k,4} = \frac{\partial F_k}{\partial \lambda_1} \qquad b_{k,5} = \frac{\partial F_k}{\partial \lambda_2} \qquad b_{k,6} = \frac{\partial F_k}{\partial \lambda_3}$$

$$\Delta\alpha_1 = A_1 - A_{1,0} \qquad \Delta\alpha_2 = A_2 - A_{2,0} \qquad \Delta\alpha_3 = A_3 - A_{3,0}$$

$$\Delta\alpha_4 = \lambda_1 - \lambda_{1,0} \qquad \Delta\alpha_5 = \lambda_2 - \lambda_{2,0} \qquad \Delta\alpha_6 = \lambda_3 - \lambda_{3,0}$$

The simplified equation (B2) takes the form:

$$\Delta n_k = \sum_{l=1}^{6} b_{k,l}\Delta\alpha_l + \varepsilon_k \qquad \text{(B3)}$$

or, in matrix notation,

$$Z_k = B_k\Delta\alpha + e_k \qquad \text{(B4)}$$

where

$$Z_k = \Delta n_k,$$

$$\boldsymbol{\Delta\alpha} = \begin{bmatrix} \Delta\alpha_1 \\ \Delta\alpha_2 \\ \vdots \\ \Delta\alpha_6 \end{bmatrix},$$

$$B_k = \left[b_{k,1},\ b_{k,2},\ b_{k,3},\ \ldots,\ b_{k,6}\right],$$

and

$$\boldsymbol{e}_k = [\varepsilon_k]$$

Thus, for N channels, there are N matrix equations, which may be written as

$$\bar{Z} = \bar{B}\Delta\alpha + \bar{e} \qquad \text{(B5)}$$

where

$$\bar{\boldsymbol{Z}} = \begin{bmatrix} Z_1 \\ Z_2 \\ \vdots \\ Z_N \end{bmatrix} \quad \bar{\boldsymbol{B}} = \begin{bmatrix} B_1 \\ B_2 \\ \vdots \\ B_N \end{bmatrix} \quad \bar{\boldsymbol{e}} = \begin{bmatrix} e_1 \\ e_2 \\ \vdots \\ e_N \end{bmatrix}$$

The sum of the squares of the residuals

$$\bar{e}^T\bar{e} = (\bar{Z} - \bar{B}\Delta\alpha)^T(\bar{Z} - \bar{B}\Delta\alpha) \qquad \text{(B6)}$$

is a minimum for that value of $\Delta\alpha$ for which the first variation with respect to $\Delta\alpha$ of equation (B6) vanishes if the second variation with respect to $\Delta\alpha$ is positive. Both these conditions are satisfied for

$$\Delta\alpha' = \left(\bar{B}^T\bar{B}\right)^{-1}\bar{B}^T\bar{Z} \qquad \text{(B7)}$$

The value of $\Delta\alpha$ obtained from equation (B7) is used to determine new values of A_i and λ_i, and this iteration process continues until $\Delta\alpha' \to 0$. This process leads to the best values of A_i and λ_i.

The derivatives included in equation (B2) are readily determined from equation (A1) and are given

by the following expressions:

$$\left.\begin{aligned}
\frac{\partial F_k}{\partial A_1} &= \sum_{j=0}^{\infty} W_{j,d} e^{-\lambda_1 (t_j - t_z)} \\
\frac{\partial F_k}{\partial A_2} &= \sum_{j=0}^{\infty} W_{j,d} e^{-\lambda_2 (t_j - t_z)} \\
\frac{\partial F_k}{\partial A_3} &= \sum_{j=0}^{\infty} W_{j,k} e^{-\lambda_3 (t_j - t_z)} \\
\frac{\partial F_k}{\partial \lambda_1} &= -\sum_{j=0}^{\infty} W_{j,k} (t_j - t_z) A_1 e^{-\lambda_1 (t_j - t_z)} \\
\frac{\partial F_k}{\partial \lambda_2} &= -\sum_{j=0}^{\infty} W_{j,k} (t_j - t_z) A_2 e^{-\lambda_2 (t_j - t_z)} \\
\frac{\partial F_k}{\partial \lambda_3} &= -\sum_{j=0}^{\infty} W_{j,k} (t_j - t_z) A_3 e^{-\lambda_3 (t_j - t_z)}
\end{aligned}\right\} \quad \text{(B8)}$$

Appendix C

Positron Lifetime Measurements in Epoxy Samples

As part of an ongoing study for elucidating the role of metal ions in controlling free volume in polymers, the following chromium compounds were introduced in Epon 828 epoxy resin. The metal-complex concentration in each case was 1 for every 10 repeat units of the host epoxy.

1. Chromic acetate $[Cr(Ac)_3]$
2. Chromic perchlorate $[Cr(DMSO)_6\ (ClO_4)_3]$
3. Chromous chloride $[CrCl_2]$

The samples were prepared in the form of 1-in-diameter by 0.1-in-thick discs. Positron lifetime spectra were measured in these samples by using a standard fast-fast coincidence measurement system. (See refs. 12 to 15.) The experimental lifetime spectra are listed in table CI. These spectra have been analyzed using the program for analyzing positron lifetime spectra (PAPLS) and POSITRONFIT program. The results of these analyses have been summarized in tables I to III in the text.

Table CI. Experimiental Lifetime Spectra Observed in Epon 828 Epoxy Sample Containing 0.1 Mole Fraction of Transition Metal Compounds

(a) $Cr(Ac)_3$

85640	0	0	0	0	0	0	0
0	1	2	1	1	1	1	1
2	0	2	0	5	4	0	0
2	4	5	6	5	2	6	3
6	6	3	4	5	3	4	4
5	3	3	4	9	7	6	3
6	12	8	6	7	10	9	9
12	7	11	16	5	11	6	10
4	9	6	10	10	5	7	9
6	11	9	9	16	9	7	6
7	10	11	7	5	8	6	8
5	12	9	6	14	9	16	22
51	235	939	3467	11143	25965	48945	73446
91292	95598	90162	78976	67947	57663	49008	41536
35696	30604	26904	23266	20652	18178	15907	14229
12580	11396	10186	9117	8407	7534	6821	6286
5811	5439	4998	4614	4314	3947	3753	3587
3525	3121	3131	2969	2706	2619	2528	2328
2375	2126	2079	2027	1915	1787	1698	1573
1626	1470	1406	1311	1325	1247	1142	1160
1104	1091	1042	927	963	932	859	847
801	783	761	736	690	694	639	626
620	611	555	531	534	471	485	493
497	406	413	424	410	390	405	309
345	308	327	303	293	273	294	264
259	248	237	214	220	227	180	205
218	177	187	184	180	191	172	158
156	141	138	127	137	110	140	131
103	115	116	93	113	94	95	95
88	68	86	71	80	84	75	67
61	61	73	53	61	57	67	54
58	55	47	46	51	30	43	50
36	35	39	52	41	29	31	29
36	38	36	31	20	29	31	26
17	24	28	35	36	22	22	24
15	29	22	28	25	26	23	19
23	23	21	17	19	22	19	26
18	10	21	20	18	11	26	21
19	12	15	11	16	12	14	17
16	15	14	13	13	10	16	6
13	18	20	13	14	15	12	17
8	11	12	7	13	10	11	17
10	13	11	10	11	9	8	13
19	10	5	7	10	9	11	5
8	8	13	11	4	9	3	10
11	9	11	9	8	6	8	6
6	13	9	9	7	9	12	7
8	6	11	6	12	8	10	5
9	10	8	10	19	5	9	5
8	10	11	13	9	9	8	5
6	14	5	10	9	8	2	8
3	9	10	5	7	10	8	6
4	9	6	8	5	10	10	11
6	3	9	2	6	12	2	6
6	6	10	8	10	10	7	6
9	6	11	9	6	8	8	8
6	10	5	9	9	6	10	9
7	6	13	13	7	7	9	14
7	12	8	8	8	7	8	12
8	8	11	7	10	5	11	10

Table CI. Continued

(b) $Cr(DMSO)_6\ (ClO_4)_3$

85364	0	0	0	0	0	0	1
2	3	1	2	0	1	1	0
1	4	3	4	5	0	3	2
2	5	5	6	8	6	5	3
5	2	4	3	6	5	6	5
7	3	7	7	1	8	4	4
8	5	10	7	5	8	13	15
10	8	9	11	7	9	9	6
5	9	11	4	7	9	9	6
8	7	8	15	4	12	11	11
9	14	8	7	6	10	7	12
10	10	6	14	7	10	13	15
77	242	972	3619	11029	26962	51125	77254
96094	102257	96753	85425	73481	61416	52216	43964
38232	32262	28756	24449	21391	18693	16612	14761
12941	11659	10281	9238	8202	7381	6814	6101
5642	5161	4800	4389	3904	3744	3501	3278
3208	2853	2807	2635	2566	2332	2222	2084
1932	1954	1848	1728	1645	1588	1463	1380
1377	1277	1253	1186	1141	1099	1077	980
955	958	890	897	825	814	748	721
683	711	656	639	629	592	561	536
554	479	501	456	451	469	427	391
410	380	395	362	340	333	310	321
315	295	269	250	240	243	231	257
202	204	181	179	201	182	182	183
175	145	163	164	143	142	131	130
114	123	107	115	86	99	109	114
107	110	95	89	96	78	98	78
68	75	75	67	75	68	52	61
52	58	49	58	49	47	44	48
50	57	45	37	40	37	40	33
33	31	33	36	25	25	33	25
34	38	27	31	30	23	33	29
19	25	14	23	27	25	21	24
19	18	20	34	22	22	23	14
26	27	16	26	24	22	11	9
16	14	16	8	19	15	18	17
11	9	15	10	19	14	13	14
10	11	15	14	10	11	8	11
14	11	8	14	10	5	18	12
10	12	10	13	12	9	12	10
9	10	12	14	9	6	6	10
17	5	13	11	10	11	9	9
10	7	5	10	6	8	10	10
6	5	7	8	4	11	9	7
6	8	10	9	12	11	10	6
7	9	13	14	7	7	7	5
10	9	10	3	6	13	6	11
6	10	10	8	7	4	9	12
6	5	5	13	12	12	16	5
14	10	4	2	9	9	6	7
5	8	11	15	9	6	9	10
10	3	13	11	13	11	9	4
11	10	9	7	14	7	15	8
9	3	10	8	5	13	12	13
12	8	4	2	5	10	7	3
7	7	6	7	10	6	6	8
12	4	9	4	2	3	11	12
11	10	6	9	8	7	6	10

Table CI. Concluded

(c) $CrCl_2$

1	4	0	1	2	5	4	1
3	3	4	6	7	7	5	7
3	10	6	5	6	7	11	11
9	5	9	13	6	5	10	6
6	11	11	2	8	11	18	23
12	12	17	14	14	12	5	12
15	12	18	14	20	11	17	12
10	9	16	15	17	8	13	14
16	16	16	16	12	18	13	11
13	12	16	9	12	14	23	14
16	15	13	24	13	15	20	24
104	379	1627	5599	17239	42056	80360	122509
152716	160866	152636	134497	115315	97223	82396	69670
60471	51668	45037	39372	34291	30716	27085	24209
21504	19336	17210	15327	14182	12738	11623	10827
9787	9075	8404	7740	7123	6843	6381	5945
5570	5427	5157	4921	4531	4413	4099	4007
4005	3580	3537	3224	3189	3069	2805	2734
2578	2370	2378	2249	2236	2076	1994	1937
1840	1755	1721	1641	1641	1560	1439	1407
1360	1322	1262	1167	1158	1157	1112	1072
1023	971	1008	885	915	873	827	785
777	684	712	686	648	677	617	597
581	518	515	507	526	489	452	406
411	406	412	399	390	381	308	351
318	311	297	286	269	286	251	236
219	238	227	232	203	229	214	196
205	175	165	189	147	156	188	134
160	135	145	135	121	125	127	118
103	102	106	106	104	89	111	98
101	90	73	66	79	69	80	67
65	79	80	61	84	57	50	67
52	52	45	55	49	50	64	57
46	50	48	46	42	39	39	42
38	40	36	28	38	31	25	29
34	37	24	27	35	25	28	33
25	22	31	30	22	36	30	19
32	21	25	28	22	24	28	16
22	23	21	24	19	24	15	29
15	24	19	15	21	24	28	24
27	16	18	17	20	24	19	20
16	19	22	20	21	13	18	18
22	20	16	16	14	20	19	16
11	15	15	13	12	22	16	19
14	21	16	11	18	26	14	17
13	16	9	10	9	17	18	14
16	11	21	19	27	23	24	15
14	15	16	9	23	14	12	17
12	17	12	12	14	8	18	13
21	16	15	24	17	15	16	12
11	7	21	10	19	8	17	10
11	16	11	13	9	22	14	14
13	16	15	11	14	11	11	17
19	11	14	15	21	9	8	14
15	16	15	10	10	17	9	19
9	9	9	15	16	13	11	13
15	13	14	20	10	15	17	13
16	17	18	15	8	14	11	9
13	14	13	13	10	10	11	15

References

1. Goldanskii, V. I.: Physical Chemistry of the Positron and Positronium. *At. Energy Review,* vol. 6, no. 1, 1968, pp. 3–148.
2. Hamielec, A. E.; Eldrup, M.; Mogensen, O.; and Jansen, P.: Positron Annihilation Techniques (PAT) in Polymer Science and Engineering. *Reviews in Macromolecular Chemistry, Volume 10,* George B. Butler, Kenneth F. O'Driscoll, and Mitchel Shen, eds., Marcel Dekker, Inc., 1973, pp. 305–337.
3. West, R. N.: Positron Studies of Condensed Matter. *Advan. Phys.,* vol. 22, no. 3, May 1973, pp. 263–383.
4. Siegel, R. W.: Positron Annihilation Spectroscopy. *Annual Review of Materials Science, Volume 10,* Robert A. Huggins, Richard H. Bube, and David A. Vermilyea, eds., Annual Reviews, Inc., 1980, pp. 393–425.
5. Goldanskii, V. I.: The Quenching of Positronium and the Inhibition of Its Formation (Role of Phase Transitions, Magnetic and Chemical Factors). *Positron Annihilation,* A. T. Stewart and L. O. Roellig, eds., Academic Press, Inc., 1967, pp. 183–255.
6. Mogensen, O. E.: Spur Reaction Model of Positronium Formation. *J. Chem. Phys.,* vol. 60, no. 3, Feb. 1, 1974, pp. 998–1004.
7. Eldrup, M.; Shantarovich, V. P.; and Mogensen, O. E.: Inhibition of Ps Formation by Strong Ps Quenchers. *Chem. Phys.,* vol. 11, no. 1, Oct. 1975, pp. 129–142.
8. Eldrup, M.; Mogensen, O. E., and Evans, J. H.: A Positron Annihilation Study of the Annealing of Electron Irradiated Molybdenum. *J. Phys. F: Met. Phys.,* vol. 6, no. 4, Apr. 1976, pp. 499–521.
9. Bhatki, K. S.; Pradhan, S. D., and Thosar, B. V.: Further Studies on Positron Lifetimes in γ-Irradiated Teflon in Low Dose Range. *Phys. Status Solidi (a),* vol. 47, no. 2, June 16, 1978, pp. 691–698.
10. Paulin, R.: Implantation of Fast Positrons in Solids. *Positron Solid-State Physics,* W. Brandt and A. Dupasquier, eds., North-Holland Publ. Co., 1983, pp. 565–580.
11. Siegel, R. W.; Fluss, M. J.; and Smedskjaer, L. C.: The Application of Positron Annihilation in Materials Science. Argonne National Lab. paper presented at the Fifth Riso International Symposium on Metallurgy and Materials Science (Roskilde, Denmark), Sept. 3–7, 1984.
12. Bell, R. E.; and Jørgensen, M. H.: Mean Lives of Positrons in Aluminum and the Alkali Metals. *Canadian J. Phys.,* vol. 38, no. 5, May 1960, pp. 652–664.
13. Gedcke, D. A.; and McDonald, W. J.: Design of the Constant Fraction of Pulse Height Trigger for Optimum Time Resolution. *Nucl. Instrum. & Methods,* vol. 58, no. 2, Jan. 1968, pp. 253–260.
14. Bedwell, Michael O.; and Paulus, Thomas J.: A Constant Fraction Differential Discriminator for Use in Fast Timing Coincidence Systems. *IEEE Trans. Nucl. Sci.,* vol. NS-26, no. 1, Feb. 1979, pp. 422–427.
15. Hardy, W. H., II; and Lynn, K. G.: A New Approach to Timing: The Fast-Fast System. *IEEE Trans. Nucl. Sci.,* vol. NS-23, no. 1, Feb. 1976, pp. 229–233.
16. Stevens, J. R.: Positron Annihilation. Polymers—Part A: *Molecular Structure and Dynamics,* R. A. Fava, ed., Volume 16 of Methods of Experimental Physics, Academic Press, Inc., 1980, pp. 371–403.
17. Bertolaccini, M.; Bisi, A.; Gambarini, G.; and Zappa, L.: Relaxed Positronium in Polymers. *J. Phys. C:* Solid State Phys., vol. 7, no. 21, Nov. 7, 1974, pp. 3827–3832.
18. Kerr, Donald P.: Positron Annihilation in Teflon and Polyethylene. *Canadian J. Phys.,* vol. 52, no. 11, June 1, 1974, pp. 935–939.
19. Bertolaccini, M.; Bisi, A.; Gambarini, G.; and Zappa, L.: Positrons Trapped in Polyethylene: Electric Field Effect. *Appl. Phys.,* vol. 17, no. 2, Oct. 1978, pp. 203–205.
20. Merrigan, Joseph A.; Green, James H.; and Tao, Shu-Jen: Positron Annihilation. Part IIID—X-Ray, Nuclear, Molecular Beam, and Radioactivity Methods, Physical Methods of Chemistry, Arnold Weissberger and Bryant W. Rossiter, eds., Volume I of *Techniques of Chemistry,* Wiley-Interscience, c.1972, pp. 501–586.
21. Nicholas, J. Blair; Wild, Ralph E.; Bartal, Lawrence J.; and Ache, Hans J.: Effect of Complex Formation on the Reactions of Positronium Atoms With Inorganic Ions. *Phys. Chem.,* vol. 77, no. 2, 1973, pp. 178–182.
22. Singh, K. P.; Singru, R. M.; and Rao, C. N. R.: Positron Lifetime Studies in Organic Media. *J. Phys. B.:* At. & Mol. Phys., vol. 4, no. 2, Feb. 1971, pp. 261–268.
23. Chuang, S. Y.; Tao, S. J.; and Wilkenfeld, J. M.: Ortho-Positronium Annihilation and the Glass Transition of Nylon 6. *J. Appl. Phys.,* vol. 43, no. 2, Feb. 1972, pp. 737–739.
24. West, D. H. D.; McBrierty, V. J.; and Delaney, C. F. G.: Positron Decay in Polymers: Molecular Weight Dependence in Polystyrene. *Appl. Phys.,* vol. 7, no. 3, July 1973, pp. 171–174.
25. Eldrup, M.; Huang, Y. M.; and McKee, B. T. A.: Estimates of Uncertainties in Analysis of Positron Lifetime Spectra for Metals. *Appl. Phys.,* vol. 15, no. 1, Jan. 1978, pp. 65–71.
26. Singh, Jag J.; Holt, William H.; and Mock, Willis, Jr.: *Moisture Determination in Composite Materials Using Positron Lifetime Technique.* NASA TP-1681, 1980.
27. Singh, Jag J.; St. Clair, Terry L.; Holt, William H.; and Mock, Willis, Jr.: Moisture Dependence of Positron Annihilation Spectra in Nylon-6. *Nucl. Instrum. & Methods Phys. Res.,* vol. 221, no. 2, Apr. 1, 1984, pp. 427–432.
28. Singh, Jag J.; Stoakley, Diane M.; Holt, William H.; Mock, Willis M., Jr.; and Teter, Joseph P.: Effects of Transition Metal Ions on Positron Annihilation Characteristics in Epoxies. *Nucl. Instrum. & Methods Phys. Res.,* vol. B26, no. 4, June 1987, pp. 598–602.

29. Hautojärvi, P., ed.: *Positrons in Solids*. Springer-Verlag, 1979.
30. Lichtenberger, P. C.; Stevens, J. R.; and Newton, T. D.: Analysis of Counting Distributions With a Complex Exponential Character. *Canadian J. Phys.*, vol. 50, no. 4, Feb. 15, 1972, pp. 345–351.
31. Hall, Thomas M.; Goland, A. N.; and Snead, C. L., Jr.: Applications of Positron-Lifetime Measurements to the Study of Defects in Metals. *Phys. Review B*, third ser., vol. 10, no. 8, Oct. 15, 1974, pp. 3062–3074.
32. Kirkegaard, P.: Positronfit Extended: A New Version of a Program for Analysing Positron Lifetime Spectra. *Comput. Phys. Commun.*, vol. 7, no. 7, July 1974, pp. 401–409.
33. Tao, S. J.: Methods of Data Reduction in Analyzing Positron Annihilation Lifetime Spectra. *IEEE Trans. Nucl. Sci.*, vol. NS-15, no. 1, Feb. 1968, pp. 175–187.
34. West, D. H. D.: Incremental Least Squares and the Approximate Separation of Exponentials. *Nucl. Instrum. & Methods*, vol. 136, no. 1, July 1, 1987, pp. 137–143.

Table I. Summary of Input Parameters

$$\begin{bmatrix} \tau_i = \text{Lifetime of } i\text{th component} \\ I_i = \text{Intensity of } i\text{th component} \\ t_z = \text{Time zero} \end{bmatrix}$$

Case 1	Case 2
$\tau_1 =$ 300 psec; $I_1 = 70\%$ $\tau_2 =$ 700 psec; $I_2 = 15\%$ $\tau_3 = 2100$ psec; $I_3 = 15\%$	$\tau_1 =$ 300 psec; $I_1 = 85\%$ $\tau_2 =$ 700 psec; $I_2 = 10\%$ $\tau_3 = 2100$ psec; $I_3 = 5\%$
t_z = Channel 50.300 Background counts = 10.00	

Table II. Summary of Results Obtained for Case 1

$$\begin{bmatrix} \tau_i = \text{Lifetime of } i\text{th component} \\ I_i = \text{Intensity of } i\text{th component} \\ t_z = \text{Time zero} \end{bmatrix}$$

PAPLS results	POSITRONFIT results
$\tau_1 = 298 \pm 1$ psec; $I_1 = 70.49 \pm 0.02\%$ $\tau_2 = 672 \pm 16$ psec; $I_2 = 15.14 \pm 0.02\%$ $\tau_3 = 2080 \pm 22$ psec; $I_3 = 14.37 \pm 0.02\%$	$\tau_1 = 310 \pm 2$ psec; $I_1 = 73.80 \pm 0.89\%$ $\tau_2 = 771 \pm 39$ psec; $I_2 = 12.39 \pm 0.67\%$ $\tau_3 = 2128 \pm 19$ psec; $I_3 = 13.81 \pm 0.33\%$
t_z = Channel 50.320 Background counts = 10.27 Standard deviation = 27.46	t_z = Channel 50.285 Background counts = 9.89 Standard deviation = 85.06

Table III. Summary of Results Obtained for Case 2

$$\begin{bmatrix} \tau_i = \text{Lifetime of } i\text{th component} \\ I_i = \text{Intensity of } i\text{th component} \\ t_z = \text{Time zero} \end{bmatrix}$$

PAPLS results	POSITRONFIT results
$\tau_1 = 298 \pm 1$ psec; $I_1 = 84.44 \pm 0.04\%$ $\tau_2 = 643 \pm 23$ psec; $I_2 = 10.52 \pm 0.03\%$ $\tau_3 = 2021 \pm 59$ psec; $I_3 = 5.04 \pm 0.02\%$	$\tau_1 = 308 \pm 1$ psec; $I_1 = 87.64 \pm 0.64\%$ $\tau_2 = 778 \pm 42$ psec; $I_2 = 7.95 \pm 0.49\%$ $\tau_3 = 2144 \pm 41$ psec; $I_3 = 4.45 \pm 0.22\%$
t_z = Channel 50.321 Background counts = 10.27 Standard deviation = 27.64	t_z = Channel 50.288 Background counts = 9.87 Standard deviation = 98.97

Table IV. Comparison of POSITRONFIT and PAPLS Programs for Lifetime Spectra Analysis

[Target system: Epon 828 + Me^{x+}; τ_i = Lifetime of ith component;
I_i = Intensity of ith component; σ = Standard deviation; t_z = Time zero]

Target system	POSITRONFIT				PAPLS			
	$\frac{\tau_1(\text{psec})}{I_1(\%)}$	$\frac{\tau_2(\text{psec})}{I_2(\%)}$	$\frac{\tau_3(\text{psec})}{I_3(\%)}$	σ (counts)	$\frac{\tau_1(\text{psec})}{I_1(\%)}$	$\frac{\tau_2(\text{psec})}{I_2(\%)}$	$\frac{\tau_3(\text{psec})}{I_3(\%)}$	σ (counts)
Epon 828 containing 0.1 mole fraction of $Cr(Ac)_3$	$\frac{289\pm6}{52.1\pm3.2}$	$\frac{554\pm27}{27.5\pm3.0}$	$\frac{1734\pm12}{20.4\pm0.4}$	104.70	$\frac{273\pm5}{46.7\pm0.2}$	$\frac{523\pm32}{33.0\pm0.4}$	$\frac{1731\pm51}{20.3\pm0.1}$	105.93
	Average background = 12.72 counts/channel t_z = Channel 103.17				Average background = 12.90 counts/channel t_z = Channel 103.19			
Epon 828 containing 0.1 mole fraction of $Cr(DMSO)_6$ $(ClO_4)_3$	$\frac{302\pm8}{56.7\pm4.9}$	$\frac{552\pm39}{26.2\pm4.6}$	$\frac{1728\pm18}{17.1\pm0.5}$	100.32	$\frac{290\pm7}{54.5\pm0.7}$	$\frac{556\pm62}{29.2\pm1.1}$	$\frac{1762\pm108}{16.3\pm0.4}$	98.81
	Average background = 7.0 counts/channel t_z = Channel 103.16				Average background = 8.35 counts/channel t_z = Channel 103.19			
Epon 828 containing 0.1 mole fraction of $Cr(Cl_2)$	$\frac{314\pm5}{63.8\pm2.1}$	$\frac{713\pm55}{17.5\pm1.5}$	$\frac{1787\pm24}{18.8\pm0.8}$	58.68	$\frac{301\pm5}{58.4\pm0.6}$	$\frac{606\pm80}{21.5\pm0.8}$	$\frac{1734\pm85}{20.1\pm0.3}$	78.20
	Average background = 6.93 counts/channel t_z = Channel 103.11				Average background = 8.16 counts/channel t_z = Channel 103.11			

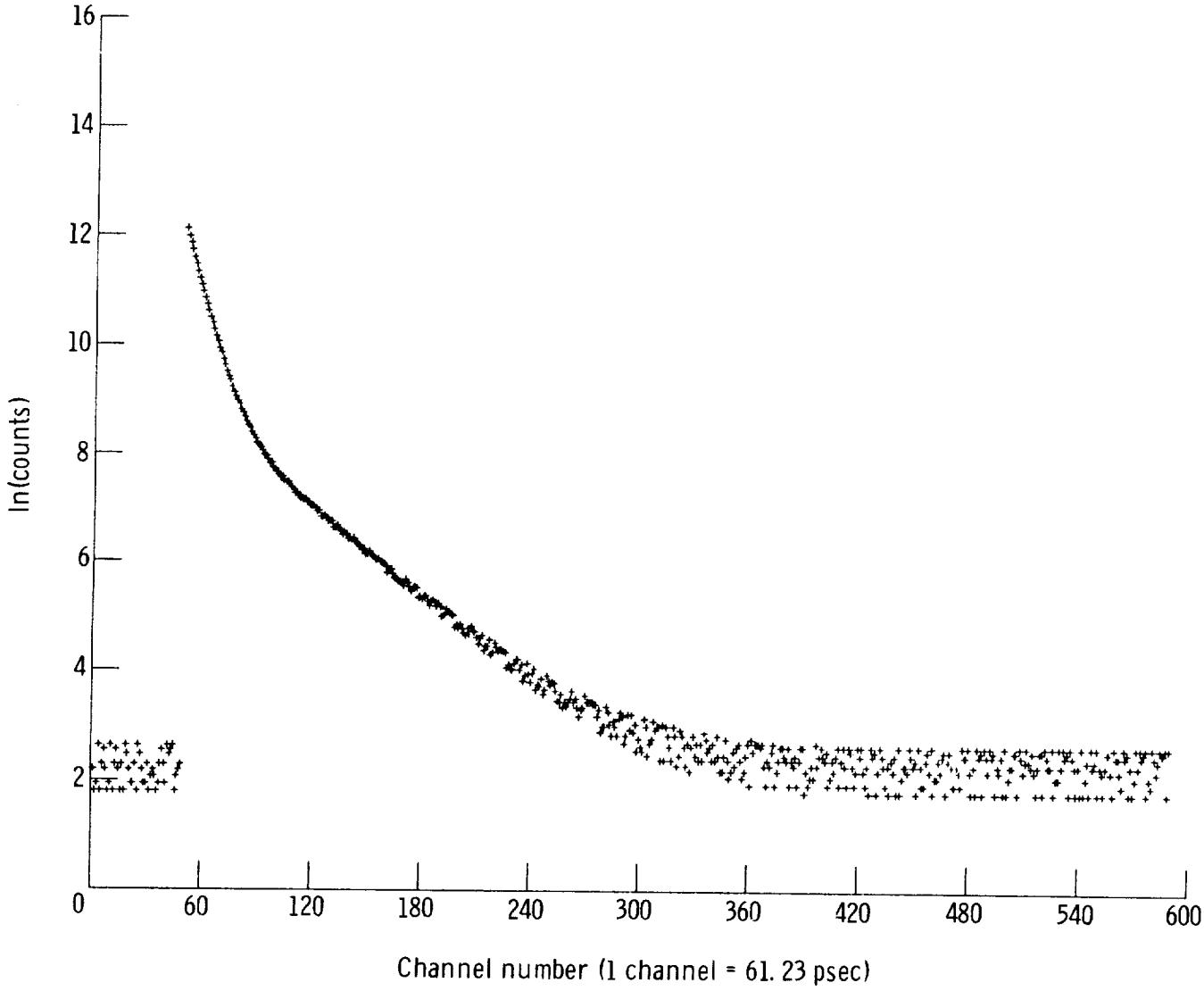


Figure 1. Computer-generated spectrum with background counts added.

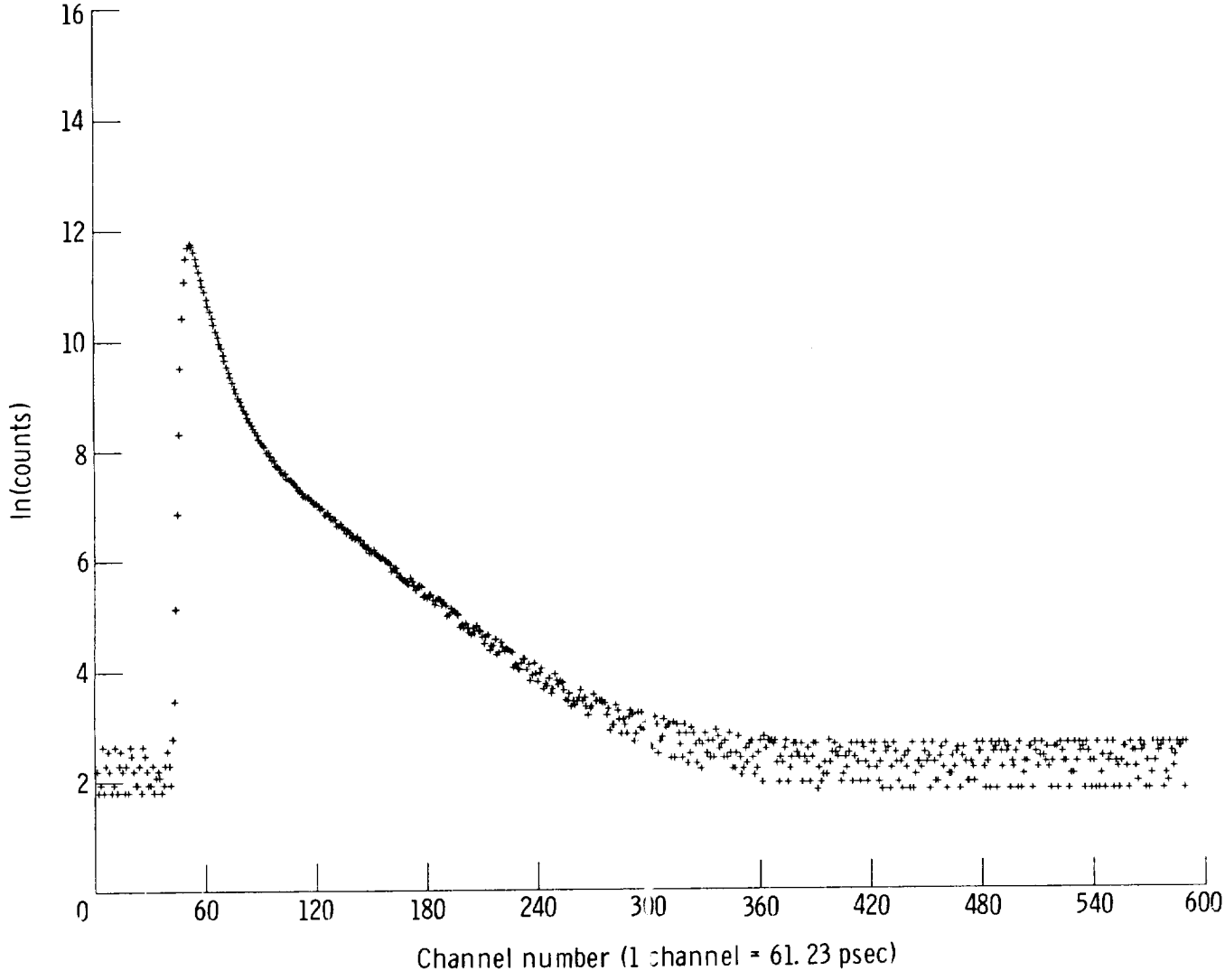
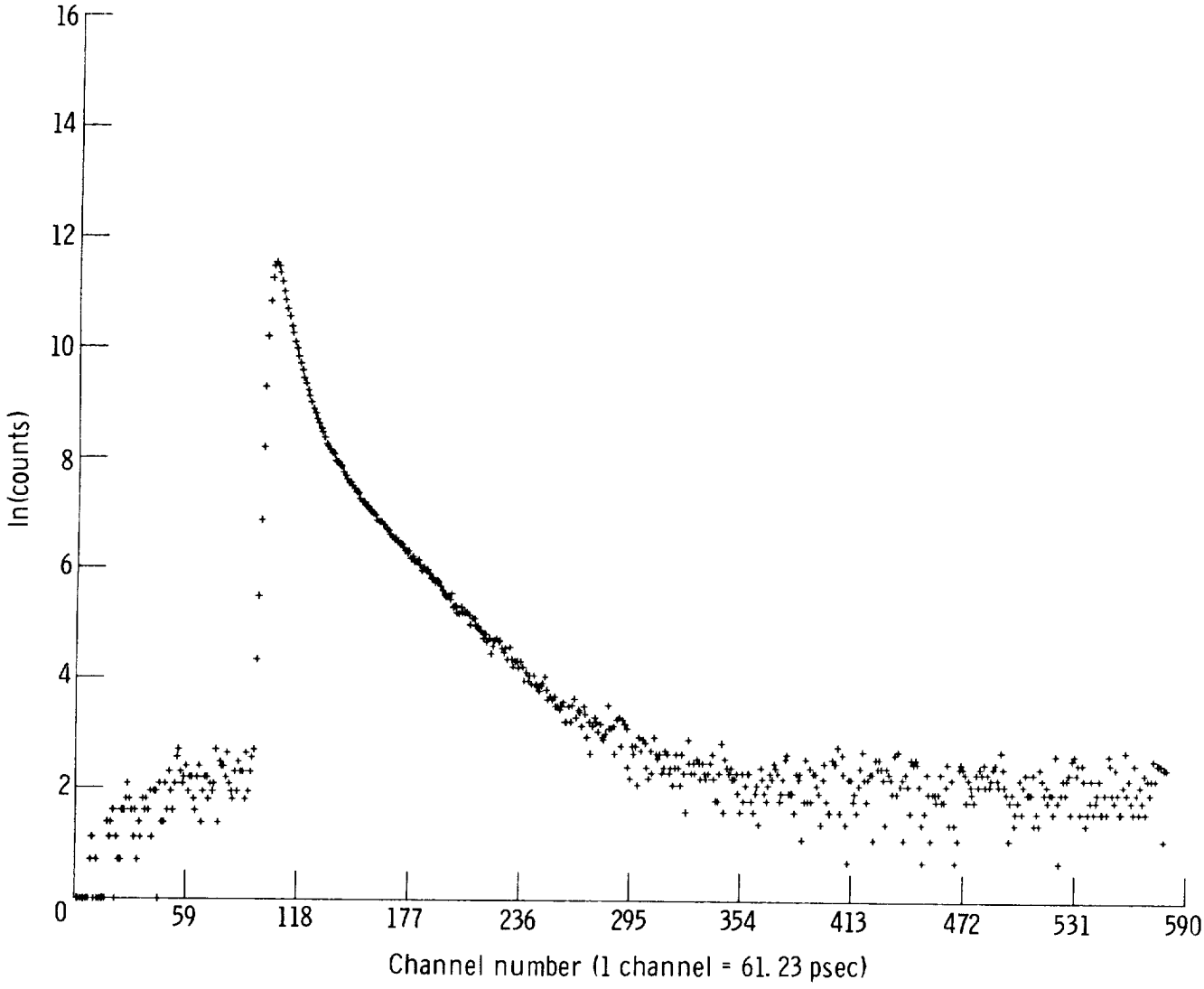
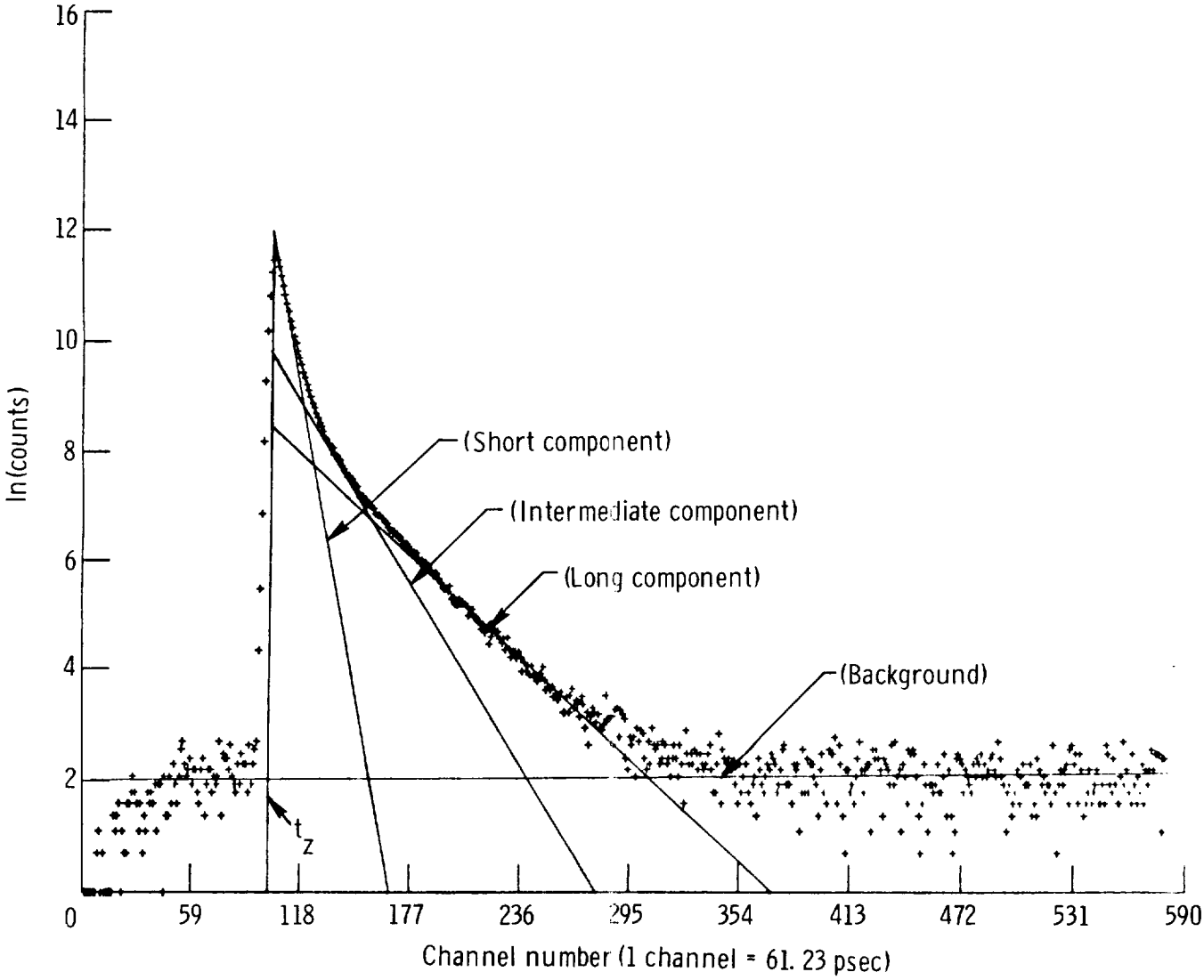


Figure 2. Computer-generated spectrum that shows effect of finite resolution of counting system.



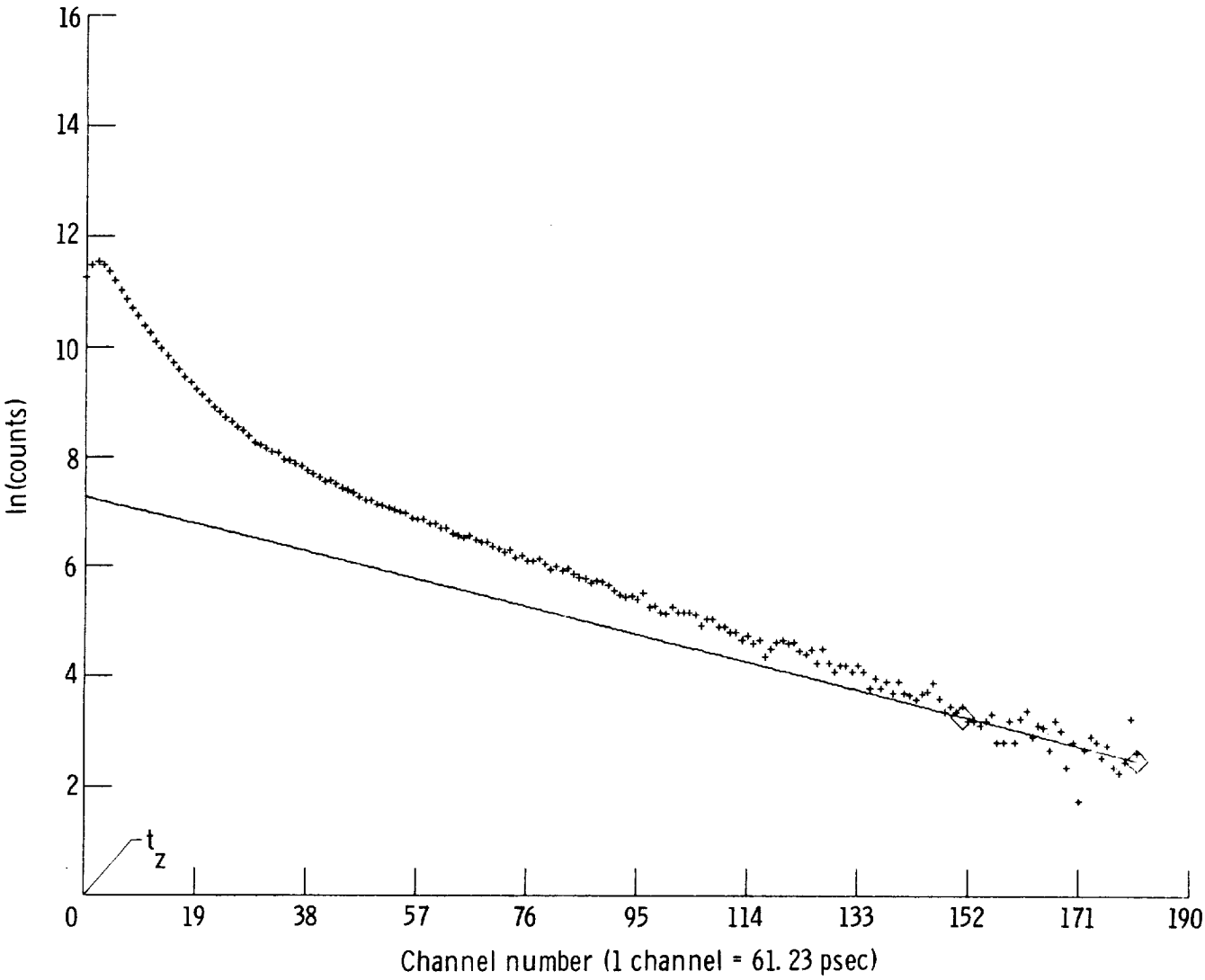
(a) Composite spectrum.

Figure 3. Typical positron lifetime spectrum in an epoxy target.



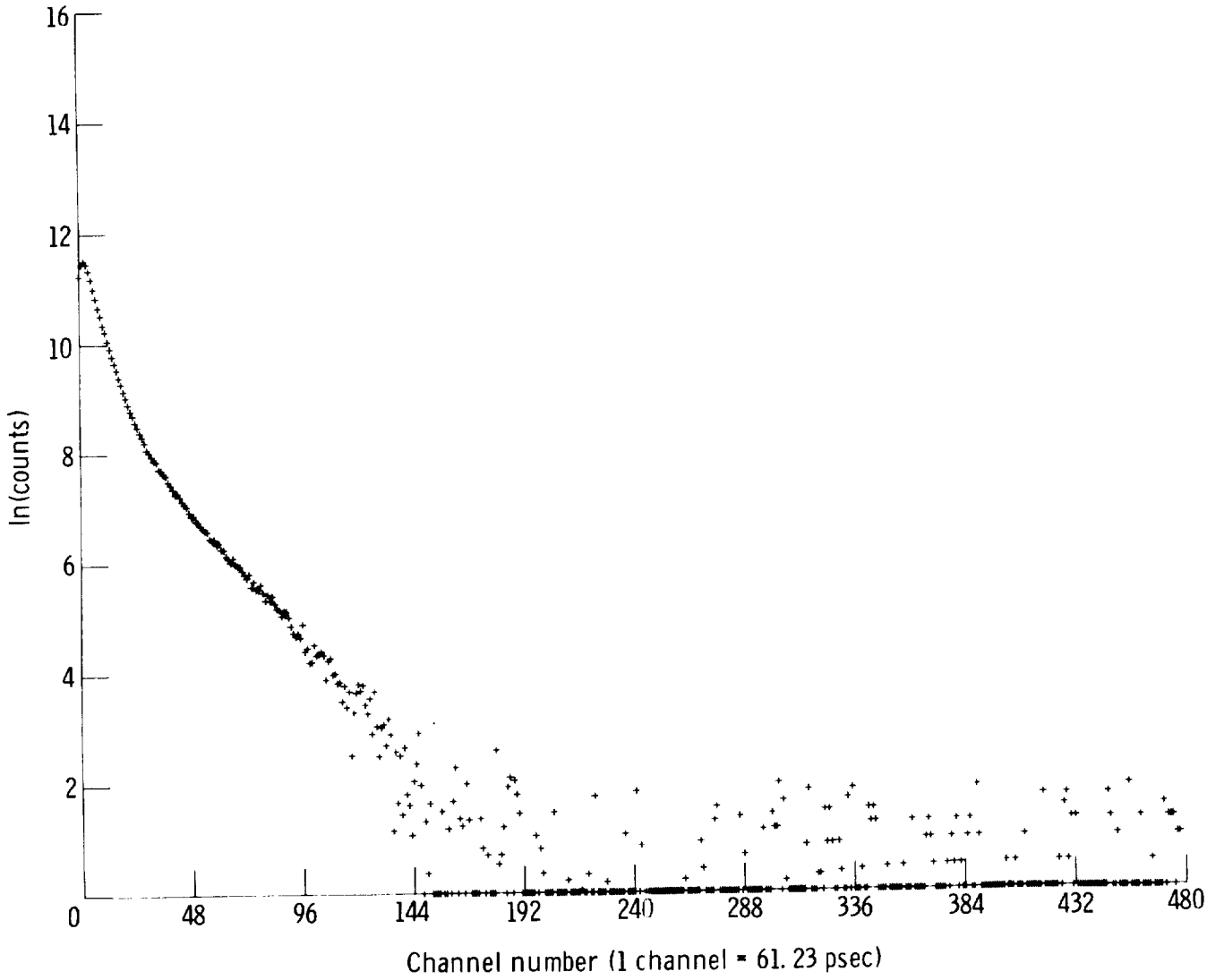
(b) Spectrum resolved into three components; t_z = time zero.

Figure 3. Concluded.



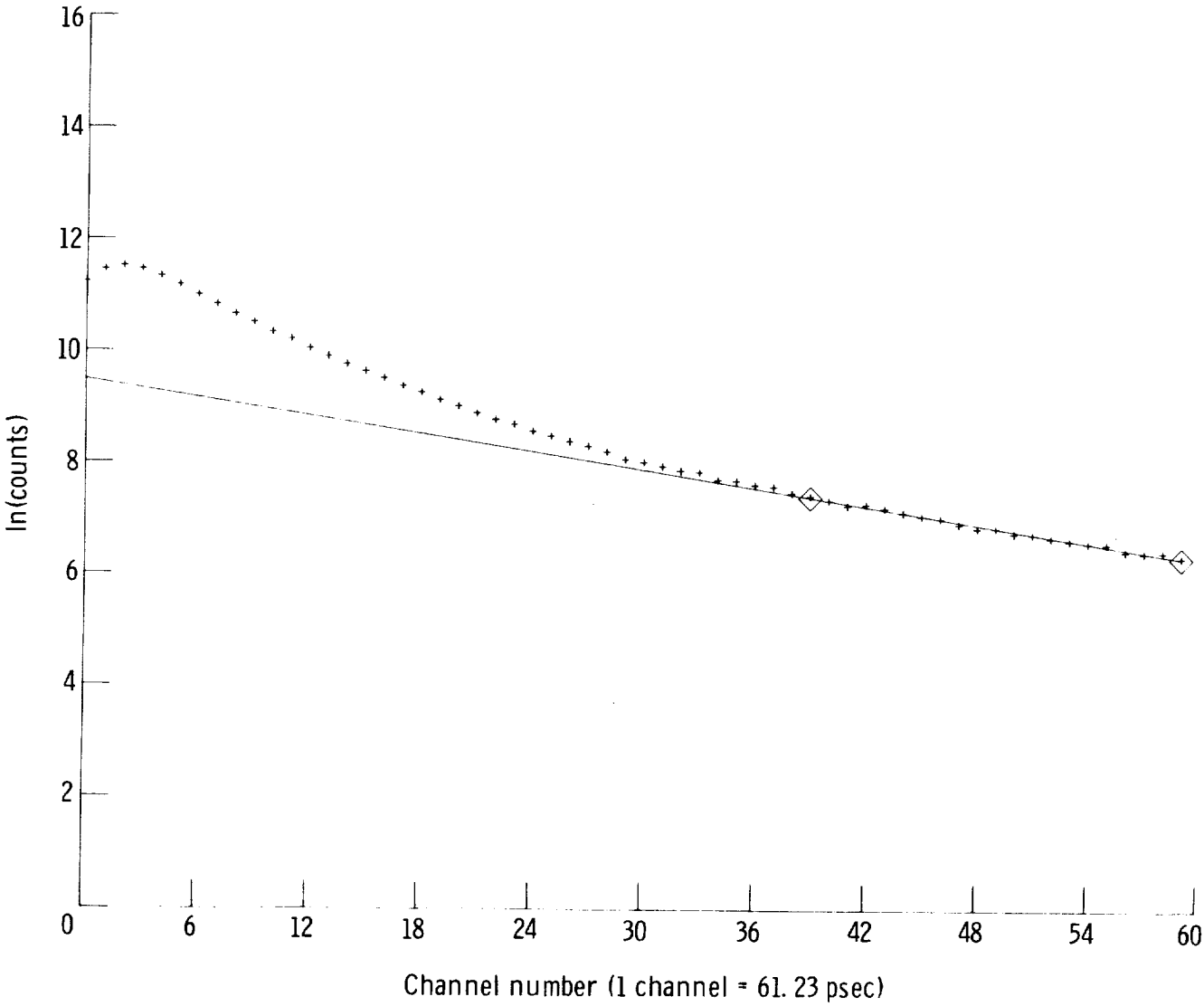
(a) Experimental spectrum, minus background, showing third component; t_z = time zero.

Figure 4. Analysis procedure for a positron lifetime spectrum.



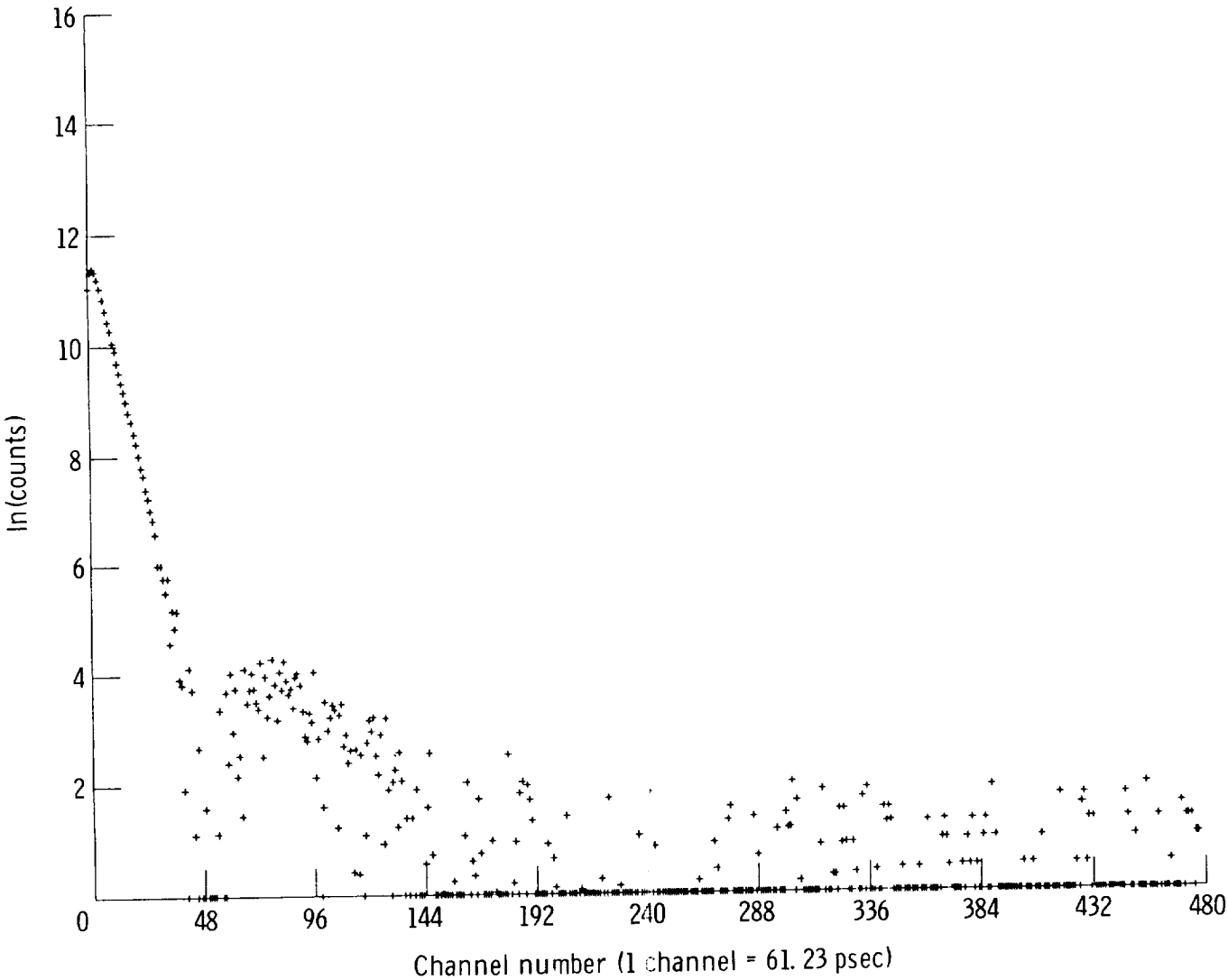
(b) Experimental spectrum, minus background and third component, showing second component clearly.

Figure 4. Continued.



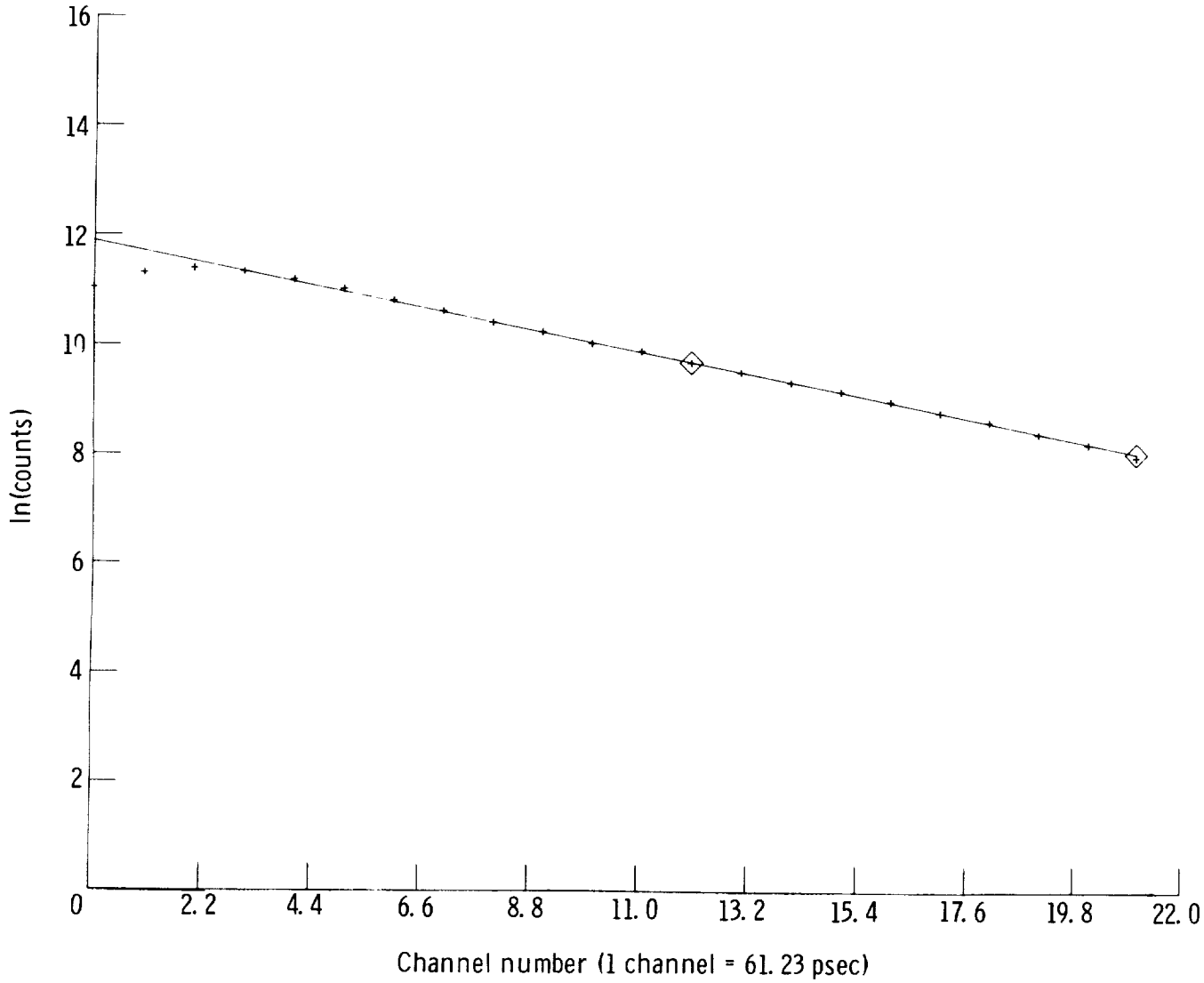
(c) Experimental spectrum showing second component fit.

Figure 4. Continued.



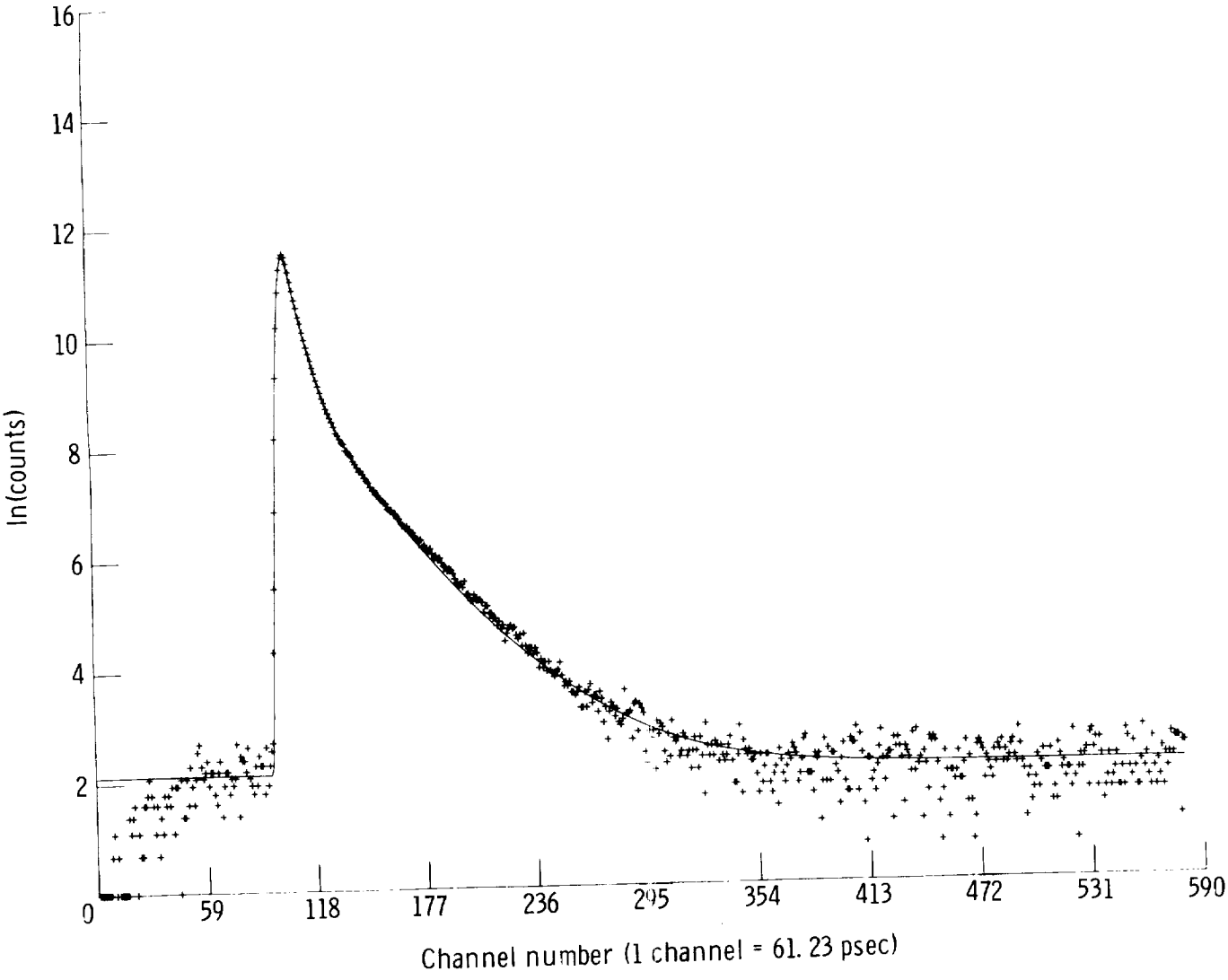
(d) Experimental spectrum minus background, and second and third components.

Figure 4. Continued.



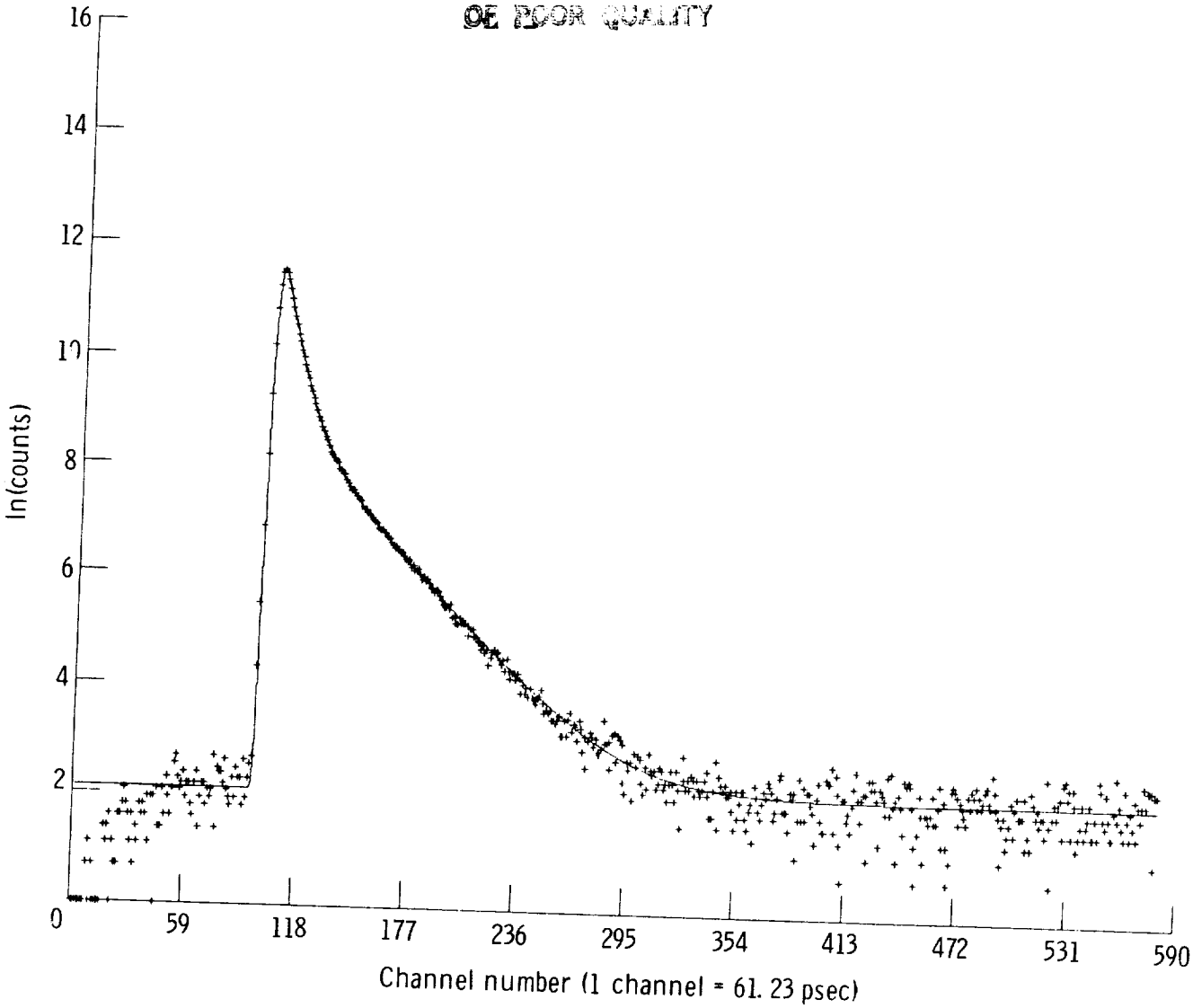
(e) Residual spectrum showing first component fit.

Figure 4. Continued.



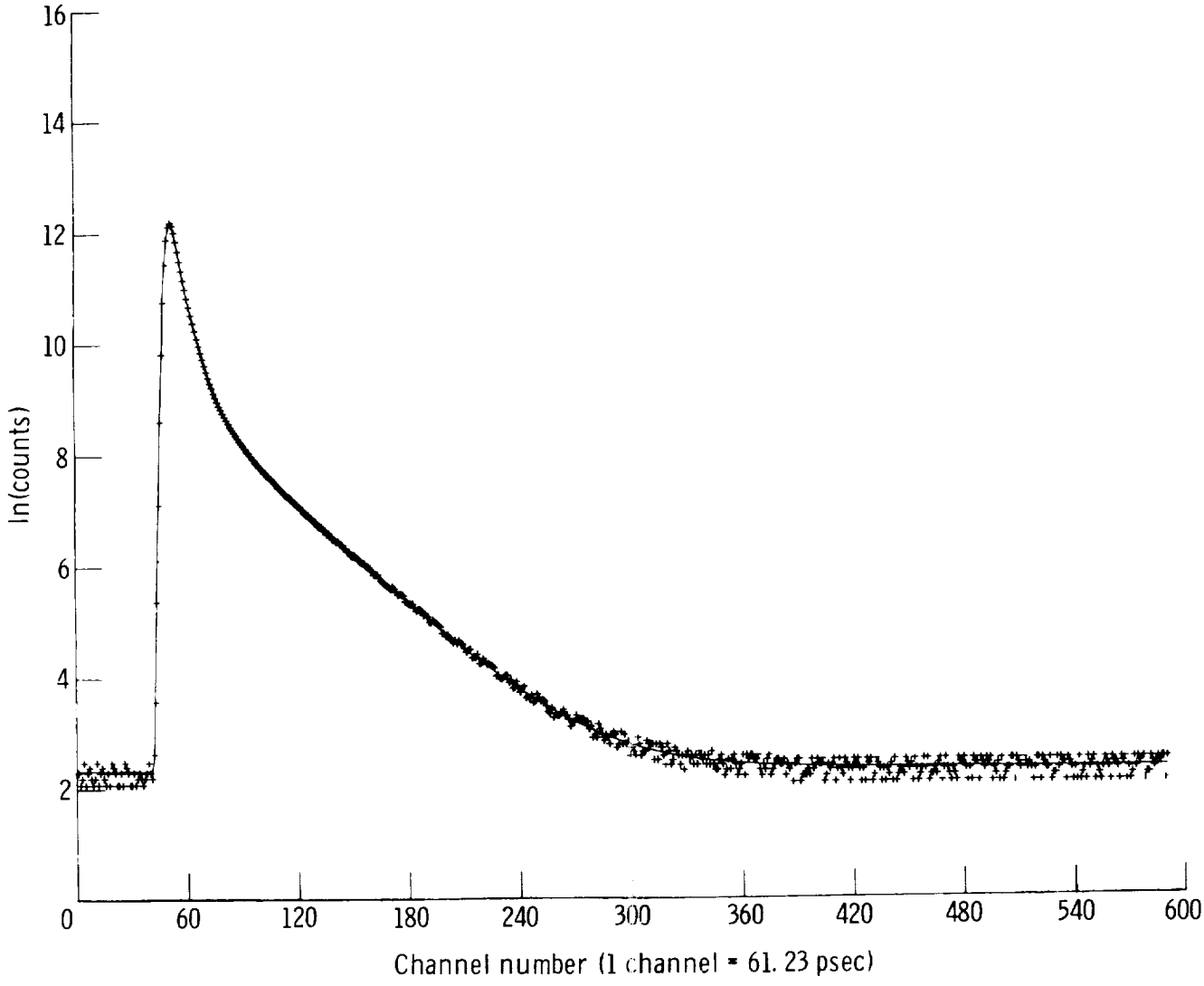
(f) Comparison of experimental and initial computed spectra.

Figure 4. Continued.



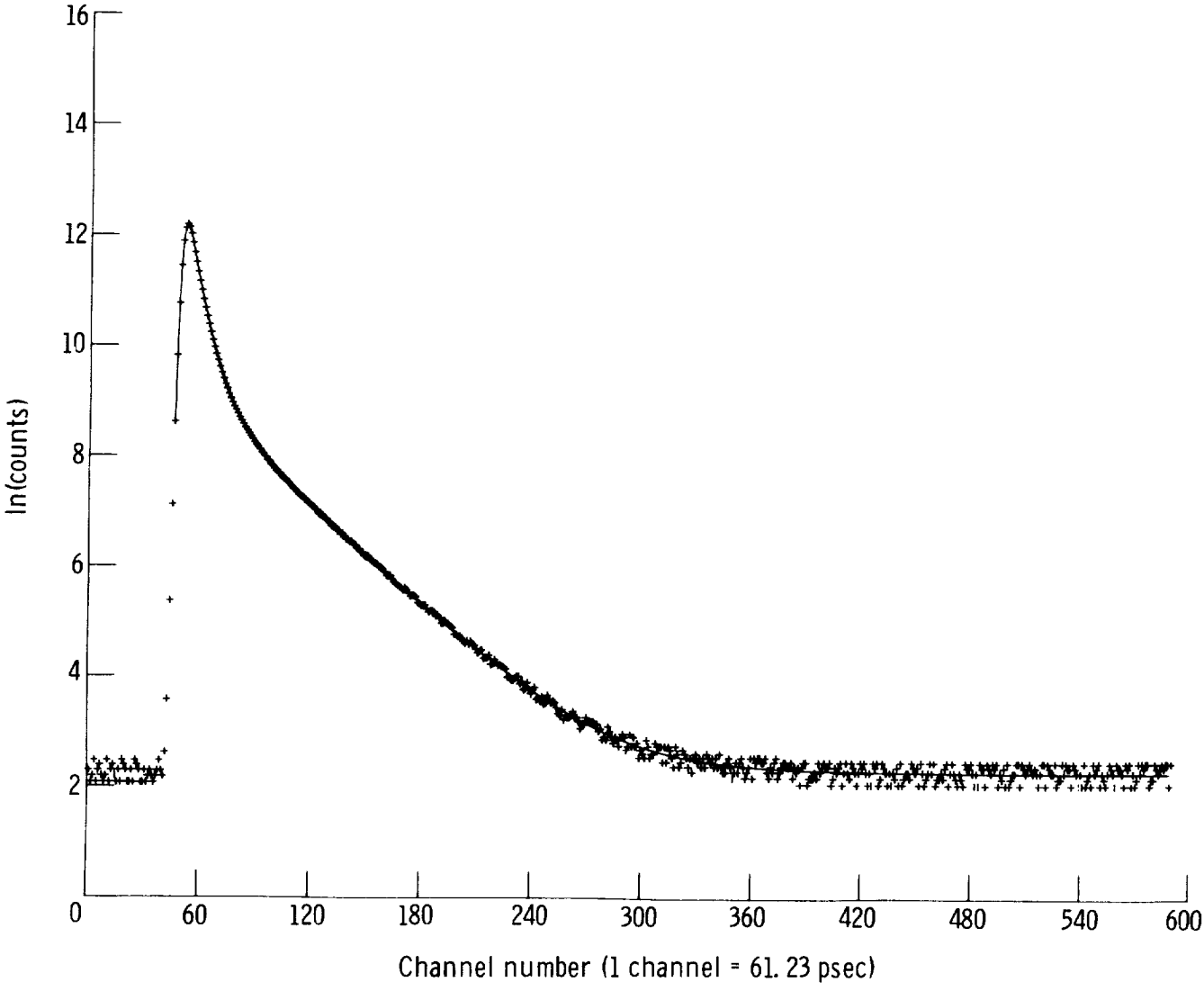
(g) Comparison of experimental and final computed spectra.

Figure 4. Concluded.



(a) PAPLS.

Figure 5. Comparison of PAPLS and POSITRONFIT programs for case 1.



(b) POSITRONFIT.

Figure 5. Concluded.

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16. Abstract

A new procedure for analyzing multicomponent positron lifetime spectra in polymers has been developed. It requires initial estimates of the lifetimes and intensities of various components, which are readily obtainable by a standard spectrum stripping process. These initial estimates, after convolution with the timing-system-resolution function, are then used as the inputs for a nonlinear least-squares analysis to compute the estimates that conform to a global-error minimization criterion. The convolution integral uses the full experimental resolution function, in contrast to the previous studies in which analytical approximations of it were utilized. These concepts have been incorporated into a generalized computer program for analyzing positron lifetime spectra (PAPLS) in polymers. The validity of this program has been tested by using several artificially generated data sets. These data sets were also analyzed with the widely used POSITRONFIT program. In almost all cases, the PAPLS program gives closer fit to the input values. The new procedure has been applied to the analysis of several lifetime spectra measured in metal-ion containing Epon 828 samples. The results are described in this report.

17. Key Words (Suggested by Authors(s))	18. Distribution Statement
Positron lifetime spectrum Sum of exponentials Multicomponent deconvolution Experimental resolution function Nonlinear least-squares method Metal-ion containing epoxies	Unclassified—Unlimited Subject Category 61

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