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SOME REMARKS ON THE EVALUATION
OF THE CONVOLUTIONALLY
DISTORTED DECAY CURVES

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DISTORTED DECAY CURVES

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ABSTRACT

A nonlinear least squares procedure based on the Meiron method is described for the evaluation of the convolutionally distorted decay curves consisting of exponentials. Most of the special procedures are well known and the selected ones proved to be the most effective. Some new procedures are introduced to facilitate the evaluation work and literature data are analysed as an example.

АННОТАЦИЯ

Описывается нелинейный метод наименьших квадратов, основывающийся на методе Мейрона, служащий для оценки кривых затухания, искаженных сверткой и определенных экспоненциальной суммой. Большинство специальных процедур, используемых в программе, выбирались из хорошо известных, наиболее эффективных. Введено несколько новых процедур, облегчающих проведение анализа и, в качестве примера, анализируется экспериментальный результат, приведенный в литературе.

KIVONAT

A Meiron módszerre alapozott nem-lineáris legkisebb négyzetek módszert ismertettünk exponenciális összeggel értelmezett, konvolúciósan torzított lecsengési görbék kiértékelésére. A programban alkalmazott speciális eljárások többségét a jól ismertek közül választottuk ki a hatékonyság alapján. Néhány új eljárást is bevezettünk a kiértékelő munka megkönnyítésére és példaként az irodalomban közölt kísérleti eredményt analizáltunk.

1. INTRODUCTION

Nowadays the parameters of convolutionally distorted multicomponent exponential decay curves can be evaluated [1] without difficulty, but even so because many laboratories are working in this field it is thought that the publication of these results might help to crystalize the best method. In this paper we summarize our own experience and offer some new ideas to facilitate the evaluation work.

The instrument independent $D(t)$ decay curve characteristic of materials is assumed to be the sum of exponentials

$$D(t) = \sum A_k \exp[-t/\tau_k] \quad (1)$$

Because all the components of the $D(t)$ decay curves are convolutionally distorted by the instrument function $K(t)$ the k th convolute

$$C^k(t) = \int_0^t K(t-t') \cdot D^k(t-t') dt' \quad (2)$$

and the experimental decay curve $F(t)$ is simulated by the sum of the convolute components $C^k(t)$:

$$F(t) \approx C(t) = \sum_{k=1}^m C^k(t) \quad (3)$$

The determination of the decay parameters A_k and τ_k is then a deconvolution procedure.

A rather large error comes from the usage of $K(t)$ in Eq.(2) if it is supposed that it does not contain any noise.

The calculations were performed on a home-made microcomputer consisting of a Z-80 microprocessor with a 16K ROM and 48K RAM memory. The software system is based on CP/M BASIC using two MOM (Hungarian Optical Works) floppy discs. We found that TRS-80 BASIC was the most effective and economic because of its integer, single and double precision representation. A DZM-180 line printer was utilized to represent the alphanumeric and HP-MOSELY Model 135 AM X-Y Recorder the graphic information.

2. THE NON-LINEAR LEAST SQUARES (NLSQ) METHOD

Of the numerous known methods [1] for evaluating Eq. (2), the most effective and fastest procedure is the non-linear least squares method. The basic equation is for the improvement of the i -th parameter in the $(j+1)$ th iteration step

$$x_i^{j+1} = x_i^j - u_i \quad (4)$$

where u_i is an element of "correction vector" \underline{U} . Using the Gauss-Newton approximation \underline{U} can be defined as a scalar product

$$\underline{U} \approx \text{restr } \underline{V} = \underline{Q}^{-1} \cdot \underline{G} \quad (5)$$

where \underline{Q}^{-1} and \underline{G} are the inverse of the covariance matrix (Hessian) and the gradient vector, respectively and "restr" means a special restriction procedure applied to \underline{V} . The quadratic Hess matrix is generated as a scalar product of the P matrix (Jacobian)

$$\underline{Q} = \underline{P}^T \cdot \underline{P} \quad (6)$$

where \underline{P} contains the first order partial derivatives of the descriptive $C(t)$ function against the parameters

$$P_{ti} = \partial C(t) / \partial x_i, \quad (7)$$

thus the size of the \underline{P} matrix is $N \times M$, where N and M are the numbers of measured data points and parameters, respectively and \underline{P}^T is the transpose of \underline{P} . The gradient vector is calculated as the scalar product of the transposed Jacobian and the residual vector \underline{R}

$$\underline{G} = \underline{P}^T \cdot \underline{R}, \quad (8)$$

where

$$\underline{R} = \underline{C} - \underline{F} \quad (9)$$

represent the difference of the calculated \underline{C} and experimental \underline{F} decay curves.

In general there is no problem in calculating the Jacobian, Hessian and gradient vectors. However, we are not able to calculate the optimum value of the "correction vector" defined by Eq. (4) because the elements of vector \underline{V} are usually greater than the required value. Therefore the direct application of Eq. (3) usually leads to a bad correction. Fortunately, numerous methods are known for the selection of a good value of the correction vector to solve the fitting problem. Pitha and Norman-Jones [2] very carefully studied the available NLSQ methods and they found the Marquardt procedure [4] to be the best.

The correction vector \underline{V} calculated by solving the linear equation system (4) is independent of the experimental noise but is influenced by the relation of the actual and fitting parameter set. The elements of vector \underline{V} may, particularly at the beginning of the fitting procedure, be greater than those of parameter set. Therefore to prevent this overshooting an appropriate restriction of the correction vector is essential.

In an unfavourable case the equation system becomes "ill-conditioned", i.e. one or more elements of \underline{V} have enormous values and the fitting problem cannot be solved because the hyperellipsoid in the m -dimensional space extremely eccentric and the gradient does not point to the centre. The ill-conditioned state can be avoided by the damping of Hessian. In the literature there are a number of methods for this restriction that are based on the increasing of the diagonal elements of the Hessian.

$$\underline{V} = [\underline{Q} + p\underline{S}]^{-1} \cdot \underline{G} \quad (10)$$

where \underline{S} is a diagonal matrix. In the Meiron [3] procedure, \underline{S} contains the diagonal elements of \underline{Q} . The scalar p is usually between 0 and 1 but may be greater than 1. If it is zero Eq. (4) is valid for \underline{V} ; if it is equal to or greater than 1 the diagonal elements of the Hessian will be dominant and the effect of the off-diagonal elements in the value of the inverse matrix is not significant. The hyperellipsoid is transformed by scalar p into an approximate hypersphere. In this case the gradient points to the quasi-centre. In the Marquardt method [4] which is an often used procedure, the diagonal elements of the Hessian are reduced to 1 by using diagonal matrix \underline{H} ($H_{ii} = 1/\sqrt{Q_{ii}}$) and the \underline{S} matrix becomes a unity matrix \underline{I} . In this case the complete equation for the parameter improvement is

$$\underline{x}^{j+1} = \underline{x}^j \underline{H}^{1/2} - (\underline{H}^{-1/2} \underline{Q} \underline{H}^{-1/2} + p\underline{I}^{-1}) \cdot \underline{G} \cdot \underline{H}^{-1/2}. \quad (11)$$

We do not use this procedure because the reduction of the Hessian into a Marquardt matrix has no advantages if the word length used in the computation is long enough to give reliable results at the end of elimination.

Another and simple way to restrict vector \underline{V} is "truncation". In this case the extreme values of vector \underline{V} are restricted to an arbitrarily chosen value which may be between zero and a definite part of the elements to be restricted. The truncation is a very effective tool in the initial part of the iterations and helps us to form a good assessment for the parameter values.

3. SPECIAL PROCEDURES

When performing the fitting procedure it is required to give as input information the \underline{x}^0 initial parameter vector. The elements of \underline{x}^0 are assessed and the actual \underline{x}^j parameter vector at the j th iteration is a better approximation of the \underline{x}^f fitting parameter set than \underline{x}^{j-1} .

There are a number of different procedures for a given task of the iterative improvement of the parameter set. Later in this paper we shall indicate the advantages of the selected procedure.

a) Convolution and Jacobian

Calculation of the convolution integral and the Jacobian is the most time consuming process in the fitting procedure. Therefore the fastest Grinwald-Steinberg formulae [5] were applied: The $(t + 1)$ th point of the convolution function for the k th component is calculated by the equation

$$C^k(t + 1) = (C^k(t) + h \cdot K(t)) \exp[-E/\tau_k] + h \cdot K \quad (12)$$

where $C_0^k = 0$; E is the dwell time of a channel and

$$h = 0.5 E A_k$$

where A_k is the amplitude of the k th component, and $C(t)$ is calculated by Eq. (3).

The partial derivatives can be calculated by the following equations using the same quantities given in convolution expression (12). The partial derivation with respect to τ_k :

$$\frac{\partial C^k(t+1)}{\partial \tau_k} = \left\{ \frac{\partial C^k(t)}{\partial \tau_k} + \frac{E}{\tau_k} (C^k(t) + h \cdot K(t)) \right\} \exp[-\frac{E}{\tau_k}] \quad (13)$$

and with respect to A_k :

$$\frac{\partial C^k(t)}{\partial A_k} = \frac{C^k(t)}{A_k} \quad (14)$$

b) The "step-length"

The relative values of the \underline{V} vector elements defined by

$$B = V_i/x_i \quad (15)$$

are very important because they determine the changing rate of vector \underline{X} . Our experience can be summarized as follows:

- If the relative values are too small the convergence is also too small and a number of iteration are required to solve the problem.
- If the relative values are higher than 0.5 the parameter values show big oscillations during the iteration. In such cases the equation system is predisposed to become ill-conditioned.
- In especially bad conditions V_i may be greater than X_i and as a consequence X_{i+1} becomes negative and the result is unreal.

We have found that the optimum convergence can be achieved if the relative value of the maximum \underline{V} elements are not greater than 0.4. Thus value is termed "step-length" in the further discussion. In each iteration cycle, only vector \underline{V} is accepted as correction vector \underline{U} if the maximum relative value is less than the step-length

$$B_{\max} \leq 0.4 \quad (16)$$

c) Improvement index

From the NLSQ procedure, better agreement is required between the experimental and calculated decay curves in each iteration cycle than in the previous iteration. The most appropriate index (number) is the root mean square (RMS), which can be calculated from the residual vector (see Eq.(9))

$$RMS = \left[\left(\sum_{t=1}^n R_t^2 \right) / n \right]^{1/2} \quad (17)$$

d) Damping parameter, p

The initial value of damping parameter p (denoted by p₀) was arbitrarily chosen as 0.001 (e.g. in [1] on p.88). It was found better to use the suggestions of Brown and Dennis [6] who calculated p₀ in each iteration step from the gradient length (GL) and the length of the diagonal vector of the Hessian (QL)

$$p_0 = GL/QL \quad (18)$$

where

$$GL = \left(\left(\sum_{i=1}^m G_i^2 \right) / m \right)^{1/2} \quad (19)$$

and

$$QL = \left(\left(\sum_{i=1}^m Q_{ii}^2 \right) / m \right)^{1/2} \quad (20)$$

In the NLSQ procedure the residual vector element R_i is calculated by Eq.(19) and as a consequence the GL value is usually decreased in each iteration step. Because QL is nearly constant the damping factor is also decreased with the iteration and its value at the end of the fitting procedure approaches zero ($\leq 10^{-8}$). In an advantageous case the Hessian becomes practically undamped.

The elements of vector V can be changed significantly during the fitting procedure and they can oscillate, too. The values of the vector V_i elements have powerfully decreased by the end of the iteration. In a favourable case they may be less than 10⁻⁴ - 10⁻⁶ and they cause no significant changes in the parameters.

If vector V cannot be accepted as the U vector because of the unfilled relation (16) we can use either the TRUNC or the procedure to improve the RMS depending on the difference of the RMS values of the two last iterations, viz. whether they were greater (TRUNC) or less (REFINE) than 0.1. The REFINE procedure is used in such cases, too when the TRUNC procedure gives no improvement. The following logical condition is applied:

$$\begin{array}{ccc}
 0.1 < & \left[\begin{array}{c} (RMS)_{j-1} - (RMS)_j \\ \text{and} \\ B_{\max} > SL \end{array} \right] & < 0.1 \\
 \downarrow & & \downarrow \\
 \boxed{\text{TRUNC}} & & \boxed{\text{REFINE}} \\
 \downarrow & & \uparrow \\
 (RMS)_{j-1} < (RMS)_j & &
 \end{array} \quad (21)$$

e) Truncation

At the beginning of the fitting procedure we are usually very far from the fitted state. Some of the parameters are bad and therefore some of the vector elements V_i and the RMS values are too big. In such cases the RMS value decreases if we use only the small calculated vector elements V_i and big values are zeros in the \underline{U} vector:

$$\begin{array}{ccc} V_i < & B < & V_i \\ \downarrow & & \downarrow \\ U_i = & V_i & U_i = 0 \end{array} \quad (22)$$

The TRUNC procedure is a very effective tool for decreasing the RMS value and usually gives a refined parameter set.

f) REFINE procedure

When the rough procedure of the parameter restriction (TRUNC) is not successful or the RMS change is less than 0.1 a finer method is necessary to improve vector \underline{U} . One way to achieve this is by using the REFINE procedure to select a p value giving a smaller RMS value. Starting from the initial p calculated by Eq.(18) a new p' is generated by

$$p' = 10 \cdot p \quad (23)$$

following the proposal of Bevington (cited in [1] p.90). After that the Hessian is reconstructed and the diagonal elements are multiplied by $(1 + p')$. The new vector \underline{V} is calculated by elimination and is investigated to see if it satisfies relation (16). With the increasing of p the elements of \underline{V} are continuously decreased* (some elements can change their sign, too) and the slope of change is different for each element (see Fig. 1a). This is the reason why we can find a good p to decrease the RMS. The increasing of p by Eq.(23) is repeated until relation (16) is fulfilled. After that the convolution integral is calculated and the RMS is evaluated. If the RMS is greater than the best value obtained in the previous iteration the whole procedure is repeated from the step of increasing p . The maximum permitted value of p is 1. If the REFINE procedure cannot improve the RMS value the fitting procedure is terminated.

On approaching the fitted state the absolute value of the modifying vector elements is decreased thus the resolution of p calculated by Eq.(23) is good enough to reach the fitted state (at the optimum direction of the gradient vector is practically zero) with the required precision.

The REFINE procedure is suitable for searching the best value of p in each iteration. However, the extreme refinement of p is not required because this can lead to a local minimum. Therefore we accept the 1st p value which

*Sometimes, mainly at the beginning of the fitting procedure the elements of \underline{V} can show a maximum curve with increasing of p (see Fig. 1).

diminishes the previous RMS and the iteration step is finished. This method has proved to be the most economic.

g) Initial parameters and number of components

The non-linear least squares method requires a knowledge of the assessed initial parameter set symbolized by \underline{X}^O and the fitting procedure may be unsuccessful if the elements of \underline{X}^O are "very poor" (e.g. very far from the fitting values). For the analysis of the decay curves it was found to be useful to take into consideration the following statements:

- (i) At first, all the curves are fitted for a single component;
- (ii) The number of components is increased one by one;
- (iii) The parameter set in the previous approximation is adopted with little or no modification;
- (iv) The value of the new parameters is assessed with the aid of some rationalistic consideration.

Fitting for a single component. The procedure consists of two steps. Firstly the parameters are calculated by the moment method and these are the initial parameters for the NLSQ procedure

The moment method gives the τ value by the Bay formula* [7]

$$\tau = \frac{M_F^1}{M_F^0} - \frac{M_K^1}{M_K^0} \quad (24)$$

where M means the moment of the function given in the subscript and the order of the moment is indicated by a superscript.

The amplitude parameter can be calculated by using the Isenberg-Dyson formula [8]

$$A = M_F^0 / \tau M_K^0. \quad (25)$$

τ and A are usually rough parameters because the functions - mainly the F(t) - are truncated. In principle this can be improved by iterative "cutoff" correction [8] but the procedure is faster if we use the rough parameters directly.

The complete fit can be achieved by the NLSQ method in one or two iterations.

Increasing the number of components. At the higher component approximation an assessment would be performed by using the appropriate component version of the moment method but this procedure is too complicated. The parameters can be obtained by the application of the following rules and they are as good as the moment parameters.

*The equivalent formula $\tau = (M_F^2/M_F^1) - (M_K^2/M_K^1)$ can also be used where M_F^2 and M_K^1 are the second moments of the appropriate functions.

(i) For the amplitudes the general rule can be used

$$S_a = \sum_{i=1}^m A_i \sim \text{const}$$

and from this

$$A_i = S_a/m \quad (26)$$

where m is the number of components.

(ii) At the two component fit τ_1 is less and τ_2 is greater than the τ in the single component fit. For example the assessed τ -s are

$$\begin{aligned} \tau_1 &\approx \tau/2 \\ \tau_2 &\approx 1.5 * \tau \end{aligned} \quad (27)$$

(iii) For higher components all the τ -s obtained in the previous fit are accepted and only the new τ is to be assessed. A practical formula for the assessment of the nth τ is

$$\tau_n = (1 + 1/n)\tau_{n-1} \quad (28)$$

In particular cases there may also be better formulae for the assessment (e.g. in the presence of a long time component).

h) Integrated intensity

The parameters of the exponentials are usually not sufficiently expressive (descriptive or representative) because they do not demonstrated the weight of the individual components in the formation of the decay phenomenon. For example: A decay component characterized by $\tau = 1$ and $A = 0.1$ is only 1/3 of a component with parameters $\tau = 6$ and $A = 0.05$. It is therefore very practical to supply the I integrated intensity of the decay curve components

$$I_k = \int_0^{\infty} A_k \cdot \exp[-t/\tau_k] = A_k \cdot \tau_k \quad (29)$$

If we calculate this value in each iteration step we can see that the integral comes nearer and nearer to a limiting value. In many cases the integrated intensity is a more sensitive parameter of the fitting process than the RMS.

i) The expected RMS

It is known that the experimental decay curve F contains the information defined by C in Eq.(3) with superimposed noise r on it. For all the elements it is valid that

$$F(t) = C(t) + r(t) \quad (30)$$

As the theory of photon counting has it, $r(t)$ noise in the t -th channel is proportional to the square root of the $F(t)$ channel constant

$$r(t) = \sqrt{F(t)} \quad (31)$$

For the fitted curve, the total noise N is the sum of the channel noise

$$N = \sum_{t=1}^n r(t) \quad (32)$$

The calculated decay curve C runs partly above partly below the experimental decay curve F . For the assessment of the averaged experimental noise the following empirical formula has successfully been applied in the case of component

$$N_m = \frac{N}{(2.74 + \log m)n} \quad (33)$$

The calculated RMS is in good agreement with this assessed noise.

If a great number of points is used in the evaluation the sum of R elements is near to zero.

$$\sum_{t=1}^n R(t) \approx 0 \quad (34)$$

j) The end of fitting

In general the "end-conditions" of the fitting procedure are determined at the beginning of the iterations. These conditions may be the convergence rate, the limiting value of the improvement index etc. We found that the convergence tests are too arbitrary and they do not help us to indicate the true end of the fitting procedure. Near to a local minimum, convergence may be very slow (see *Fig. 2*) the parameters and the improvement index perhaps hardly changing. Since this behaviour often leads to the conclusion that the fitting is complete, we do not use this type of convergence tests in our program. The procedure will be continued until there is no further improvement.

The only "end-condition" we apply is if all the U_i/X_i relative values are less than 1.10^{-5} because in this case U_i cannot modify the value of the parameters nor the RMS.

k) Assessment of the parameter error

Parameter errors can correctly be determined only if we have numerous parallel measurements and fitting parameter sets, and the standard deviation (SD) of the parameters is calculated. In general we have only a single pair of the exciting and decay curve (or only one exciting curve for a number of different decay curves) therefore we are able to give a rough assessment of the calculated error of the parameters.

The idea of the "calculated parameter error" is based on the parabolic behaviour of the RMS if we change in a stepwise manner a single parameter in a discrete range using the fixed space of all the other parameters. In

the true and in the local minimum the parabola is symmetric with the nominal value of the parameter. The asymmetry will be the larger the further we are from the (true or local) minimum. For illustration, *Fig. 3* shows the error parabola for the same parameter in the first and last iteration. The width of the parabola is also not characteristic of the fitted state. In the case of τ_1 the error parabola is narrower in the first iteration than in the last one. The opposite behaviour was found at τ_2 .

The error matrix. In general the diagonal elements of the inverse Hessian are used [10] to define the standard deviation* σ_i of the i -th parameter. The incrementation of the parameters by $\pm \sigma_i$ increases the RMS by 1. This elegant method gives adequate results only if the unmodified Hessian is used (p damping factor is zero). In the unweighted case for τ_i

$$\sigma_i = [(n - m - 1)Q_{ii}^{-1}]^{1/2} \quad (35)$$

is valid ([9] pp.142).

In practice, because p is significant the error matrix does not give reliable results so we do not use it. A better assessment of the calculated parameter errors can be achieved by using the actual Hessian or by the computation of some discrete points of the error parabola.

The actual Hessian. In each iteration numerous Hess matrices are generated. We use for the evaluation of parameter errors only the inverse of the last Hessian giving an improvement in the RMS. A disadvantage of both types of Hessian is that the "error set" is not descriptive enough.

Discrete points of the "error parabola". The calculation of the error parabola is time consuming but the results are more informative than with the inverse Hessian method. For the evaluation of the error parabola at least 3 points are necessary: the RMS is known at the nominal value of the parameters from the least squares iteration; for the selection of two other points, it is practical to use the central differences $\pm \Delta_i$. The suggested value for Δ_i is $X_i/1000$.

The first item of information coming from the calculation is the A asymmetry. This is defined by the quotient of the RMS belonging to $(X_i + \Delta_i)$ and $(X_i - \Delta_i)$:

$$A = \frac{\text{RMS}(X_i + \Delta_i)}{\text{RMS}(X_i - \Delta_i)} \quad (36)$$

A is equal to 1 if the parabola is completely symmetric (with the given precision of the computation). The parabola is accepted as symmetric if the relation

$$0.999 < A < 1.001$$

is fulfilled.

*In the literature this easily understood designation is used which is more appropriate for the evaluation of the parallel experimental data.

The second item of information is similar to the "standard deviation" used for the error matrix. With this method the parameter difference is assessed which causes a required increment δ in the RMS (δ is input information for the program usually $X_i/10000$). This latter quantity is designated by ρ_i and calculated by linear interpolation with the formula

$$\rho_i = \frac{\Delta_i(y_0 + \delta)}{(y_i^\oplus + y_i^\ominus)/2 - y_0} \quad (37)$$

where y_i^\oplus , y_i^\ominus and y_0 are the RMS values calculated by the increments $+\Delta_i$, $-\Delta_i$ and 0 respectively. Because of the linear approximation the errors are somewhat smaller than the calculated values.

l) Input data

For the NLSQ evaluation it is sufficient if the number of measured points is between 50 and 100. In the case of both the boxcar averager and TCSPC (time correlated single photon counting) methods are able to measure only the optimum number of data. If the number of data points is too big (256-1024 according to the field size of the multichannel analyser applied) it is practical to reduce it to an optimum. This can be achieved by the application of a "smoothing" procedure as follows:

(i) We define the reduction factor K_r

$$K_r = \frac{\text{No of points containing information}}{\text{No of required points}} \quad (38)$$

For the calculation of the numerator it is necessary to consider both the decay and excitation curves, too. For example if the number of measured points is 1K and we want to use 50 points for the evaluation and no information above 700 and below 60 points then $K_r = (1024 - 60 - 324)/50 = 640/50 \sim 13$.

(ii) The window length is the nearest higher odd integer of K_r ; in this case: 13.

(iii) The degree D of the orthogonal polynomial is

$$D = \text{INT}(K_r/3) \quad (39)$$

For the data reduction the SELECT procedure is used which is based on our orthogonal polynomial routine [10].

4. REPRESENTATION OF THE RESULTS

The representation of the results is very important in the evaluation work because the decision of the continuing or finishing of the fitting is based on it. In general the fitting procedure can be represented by

- numerical values of the parameters;
- tabulation
- graphical representation of the experimental and calculated data.

Numerical parameters. At the end of each iteration the pairs of decay parameters, the RMS value, the integrated intensities of the components and the sum of these are obtained and pointed by line printer.

Tabulation of the results. At the end of fitting the input and calculated data can be tabulated. A practical table can be built from the sequential number of the data points, excitation \underline{K} and decay \underline{F} curves as input arrays, the calculated decay curve \underline{C} , the residual vector \underline{R} and the relative deviation vector \underline{Z} where the elements are

$$Z(t) = R(t)/[C(t)]^{1/2} . \quad (40)$$

Graphical representation. This is the most impressive method for the representation. A useful way is to make 3 plots:

- (i) Input (excitation and decay) and calculated decay curves; (see *Fig. 4*)
- (ii) Residual vectors in the different approximations of increasing number of components;
- (iii) Autocorrelation function introduced by Grinwald and Steinberg [5] using the formula:

$$A(t') = \frac{1}{m} \sum_{t=1}^{n/2} R(t) * R(T) . \quad (41)$$

where t' runs from 1 to $n/2$ and $T = t + t'$.

Curves given by (i) can be plotted by the fitting program. For plots (ii) and (iii), a separated PLOTTING program was written. Another plotting program is also used for the presentation of better resolved calculated curves using an X-Y recorder as a peripheral.

5. INVESTIGATION OF EXPERIMENTAL DATA

We shall demonstrate our NLSQ program on the only published analysis of the experimental data of Demas and Crosby [11]. Since the publication of the latter paper, measurement techniques and their evaluation have developed considerably, but even so, it was the paper of Demas and Crosby that directed our attention to the investigation of the time jitter and the accuracy of the measurements which are so important nowadays, too. The decay times are in our example in the μs region although it is known that the most interesting problems are in the ns and the sub-ns region. For the present work, it was not the time range but rather the distortion caused by convolution that was considered important.

a) Fitting

The noise is assessed by Eq.(32). $N_a = 10$.

Single component fit. The results of the moment method without refinement are: $\tau = 4.285$; $A = 0.2779$; $RMS = 34.1019$. The elements of the calculated decay curve are given in the 4th column of Table 1. The residual vector and the correlation function are in *Fig. 5* and *Fig. 6*, respectively. After 3 iterations the NLSQ fitting parameters are:

Parameter	Values	Error ⁺	Asymmetry	Int.int
τ	5.073	$2.45 \cdot 10^{-5}$.9999	1.222
A	.2408 ₇	$9.75 \cdot 10^{-7}$	1	
RMS	7.5749 ₉			

Two-component fit. The initial parameters were determined by Eq.(27). The values are: $\tau_1 = 2.5 \mu s$; $\tau_2 = 7.5 \mu s$; $A_1 = A_2 = 0.12$. This means that the participation is 25 and 75 per cent in the total integrated intensity for the 1st and 2nd components, respectively. The program could solve the task in 26 iterations giving the following results:

Parameter	Values	Error ⁺	Asymmetry	Int.int (in %)
τ_1	1.026	$3.37 \cdot 10^{-3}$.9999	3.32
A_1	$3.964 \cdot 10^{-2}$	$8.96 \cdot 10^{-5}$	1	
τ_2	5.269	$2.47 \cdot 10^{-5}$.9999	96.68
A_2	.2246	$8.76 \cdot 10^{-7}$.9999	
RMS	6.74055 ₅			

The values of the calculated decay curve are in the 5th column of Table 1; the residual vector and the autocorrelation function are plotted in *Figs. 5a* and *Fig. 6a*, respectively. The variation of all the parameters during the fitting procedure can be seen in *Fig. 2*.

The calculated decay curves and their components are shown in *Fig. 7* as an X-Y plot.

Three-component fit. The input τ_1 and τ_2 were practically the same as the best values in the two-component analysis. Equation (28) was used to assess τ_3 . The initial values of the amplitudes were taken as 0.1, assessed by Eq.(26).

⁺The "error" means an average RMS-difference belonging to the ± 0.0001 increment of each parameter value.

After 11 iterations the results of the fitting were:

Parameter	Values	Errors	Asymmetry	Int.int (in %)
τ_1	1.020	$3.15 \cdot 10^{-3}$	1	
A_1	$3.967 \cdot 10^{-2}$	$9.45 \cdot 10^{-5}$	1	3.30
τ_2	5.269 ₉	$9.15 \cdot 10^{-5}$.9999	
A_2	.1166 ₂	$1.68 \cdot 10^{-6}$.9999	49.60
τ_3	5.266 ₆	$1.66 \cdot 10^{-4}$.9999	
A_3	.1080 ₉	$1.82 \cdot 10^{-6}$.9999	47.10
RMS	6.74055 ₈			

The values of the calculated decay curve are practically the same as the elements of column 5 in Table 1.

The results of the complete fitting can be summarized as follows:

- (i) The 2-component fit is better than the single component one;
- (ii) The 3-component fit is really the same as the 2-component fit because the parameters of component 1 are equal in both fittings. In practice, τ_2 and τ_3 and $A_2 + A_3$ and $I_2 + I_3$ are equal to τ_2 , A_2 and I_2 in the 2-component fit.
- (iii) The experimental decay curve consists of two components.
- (iv) From Figs 5 and 6, it can be stated that the elements of vector \underline{R} are not random numbers, thus the measured curves must contain systematic errors, too.
- (v) It can also be supposed that the curve shape changes during the measurements.

b) The time shift

In the case of the two-component fit we saw that the participation of the 1st component in the total integrated intensity is rather low. On the basis of molecular theory we could expect that the decay curve consists of only a single component because all the molecules are the same in the system and the molecules have in general a single delocalized electronic system. It is possible therefore assume that the low intensity 1st component can be assigned to the measurement error. An error of this kind may come from the time shift because the decay and excitation curves are measured separately in time.

If it is supposed that the form of the curves is not distorted we are able to search for the optimum in the relative position of the curve pair by shifting one of them (e.g. the excitation curve), where the RMS gives a minimum for the single component fit.

We investigated the Demas-Crosby's curves for time shift and, as can be seen in *Fig. 8*, at a shift of -139 ns a minimum RMS was found for the single component fit. The parameter values are near to the results of the two-component fit:

Parameter	Values	Errors	Asymmetry	Int.int (in%)
τ	5.2434	$2.2487 \cdot 10^{-4}$	1	
A	0.2340	$8.0858 \cdot 10^{-6}$	1	100
RMS = 6.748548				

The good agreement suggests that the small component in the two-component fit probably comes from a time shift of the measuring instrument. The fact that the unshifted two-component fit is slightly better refer to the instability of the shape of curves under the measurements.

For checking purposes, the shifted curve pair was fitted for two components, as well. The results are:

Parameters	Values	Int.int (in %)
τ_1	5.24487	
A_1	0.10762	46.0
τ_2	5.24217	
A_2	0.12641	54.0
RMS = 6.748548		

These parameters are in good agreement with the single component fit.

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Table 1.
RESULTS OF DECAY CURVE FITTING

I	X(I)	D(I)	C(I)[1]	C(I)[2]	C(I)[3]
1	0	0	0	0	0
2	15	0	1.8065	1.98215	1.98249
3	41	4	7.90437	8.42942	8.4301
4	128	24	25.96	27.5359	27.5379
5	281	65	67.8148	71.3022	71.3059
6	393	138	130.8	135.632	135.634
7	595	222	217.919	224.498	224.501
8	691	322	320.988	327.927	327.927
9	835	438	432.454	439.461	439.46
10	890	549	544.84	550.818	550.815
11	954	665	650.267	654.94	654.937
12	999	760	748.579	751.937	751.935
13	992	840	832.91	834.577	834.575
14	990	911	901.22	901.429	901.429
15	964	955	953.98	952.927	952.929
16	913	980	988.588	986.352	986.355
17	873	998	1007.14	1004.2	1004.21
18	812	1000	1011.08	1007.65	1007.65
19	744	981	1000.09	996.355	996.36
20	672	963	975.665	971.848	971.853
21	606	929	940.545	936.942	936.948
22	533	892	896.39	893.126	893.131
23	472	849	845.57	842.869	842.873
24	412	793	790.583	788.555	788.559
25	362	745	733.48	732.234	732.237
26	319	682	676.469	676.061	676.063
27	270	628	619.505	619.778	619.779
28	236	574	563.792	564.762	564.762
29	206	521	511.072	512.705	512.704
30	172	464	460.722	462.836	462.834
31	143	415	412.526	415.008	415.005
32	122	367	367.555	370.387	370.383
33	103	330	326.265	329.38	329.376
34	88	292	288.677	292.01	292.005
35	73	257	254.524	257.974	257.969
36	64	223	223.914	227.448	227.442
37	54	196	196.686	200.225	200.22
38	47	168	172.498	175.995	175.989
39	39	145	150.981	154.37	154.364
40	34	121	131.921	135.181	135.176

Symbols: I = Number of experimental and calculated points. X(I) = Instrument function; D(I) = Experimental decay curve; C(I)[X] = Calculated experimental curve. Numbers in [] mean the component number used to the fitting.

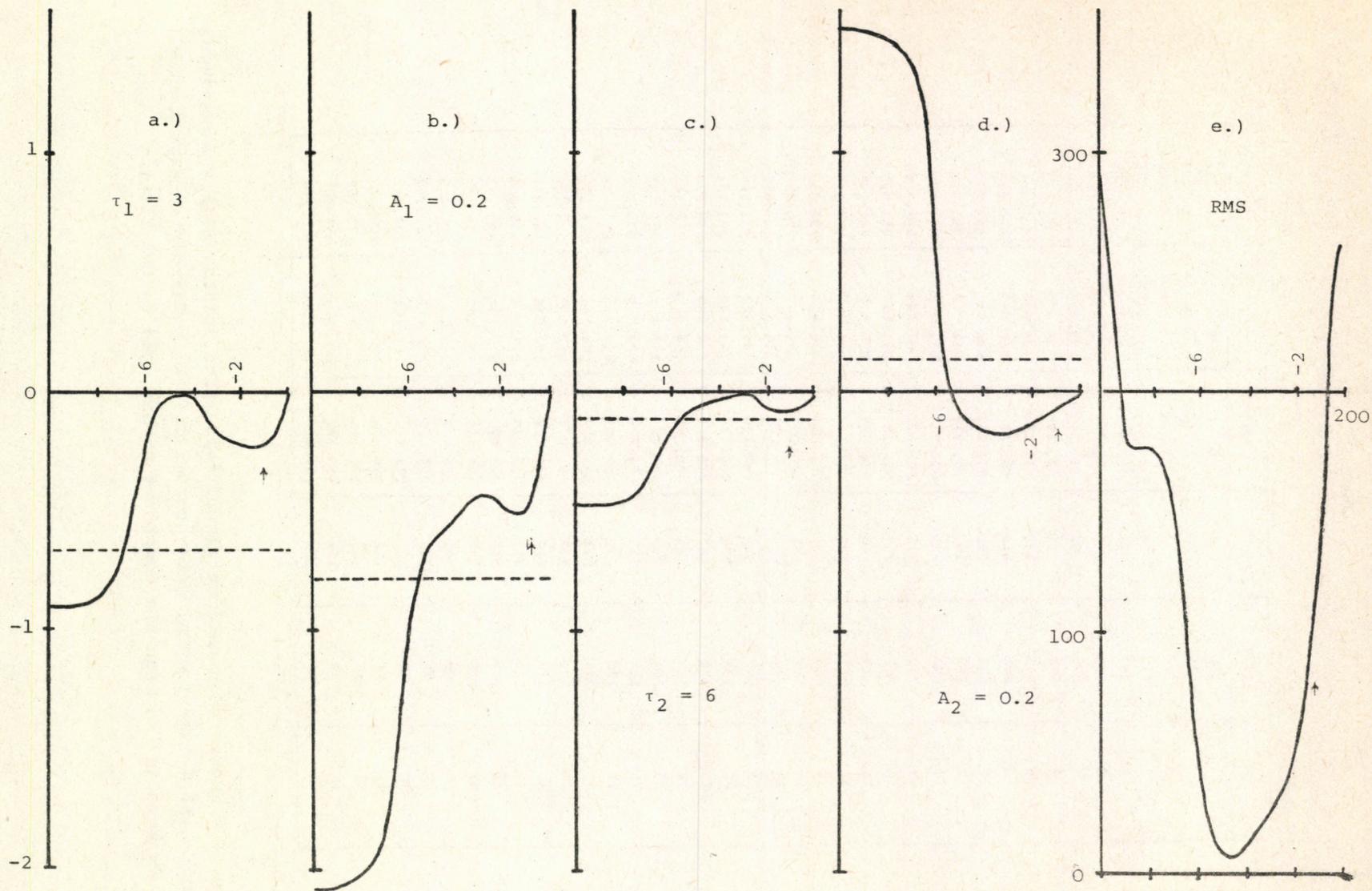


Fig.1. Change of the vector elements V_i versus damping parameter p . Abscissa scale is in $\log p$. Dashed horizontal lines mean the fitting values. The ordinates are in relative values defined by Eq. (15). Arrows show the selected p value using Eq. (18).

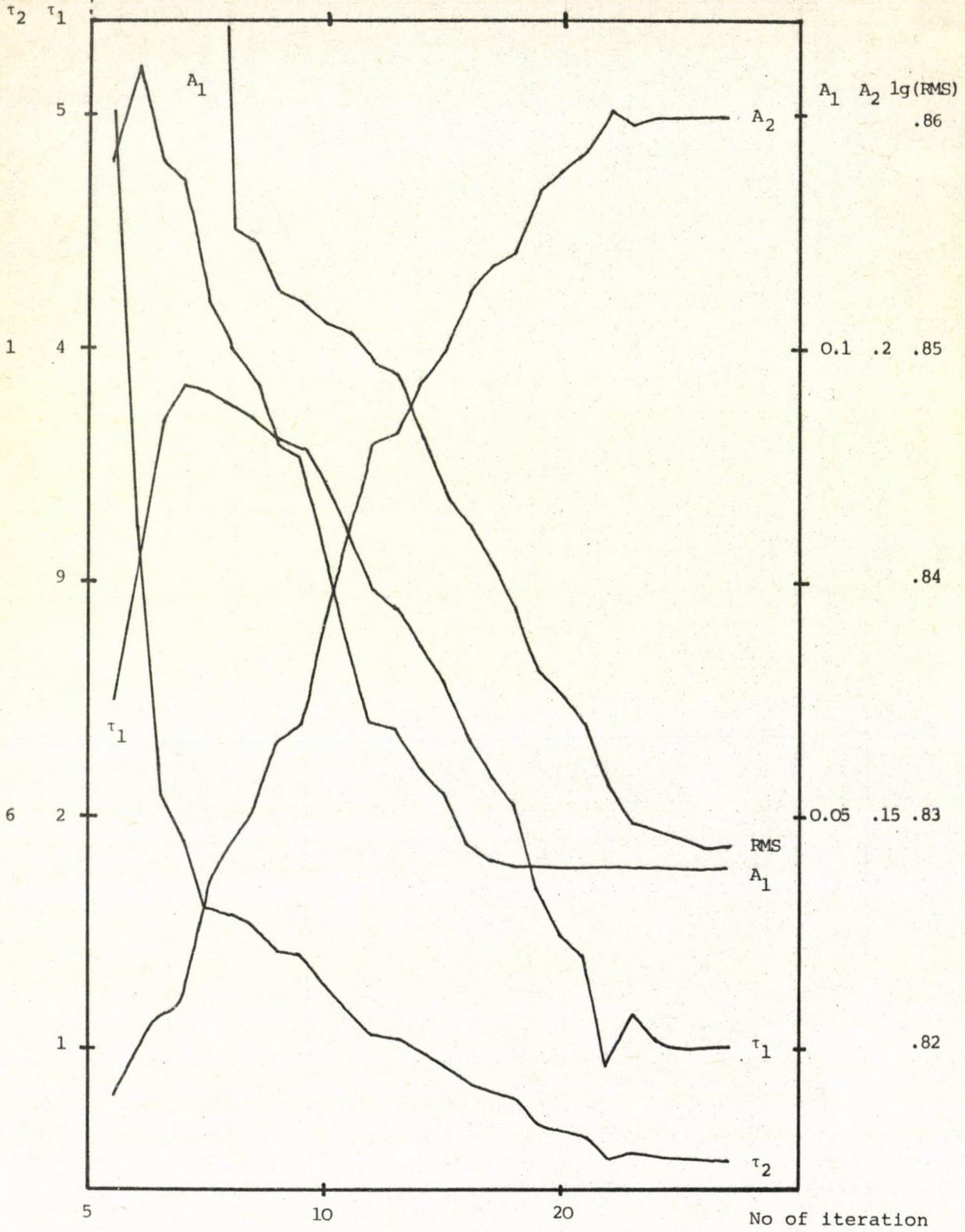


Fig. 2. Change of parameters versus the iteration steps for a two-component fit

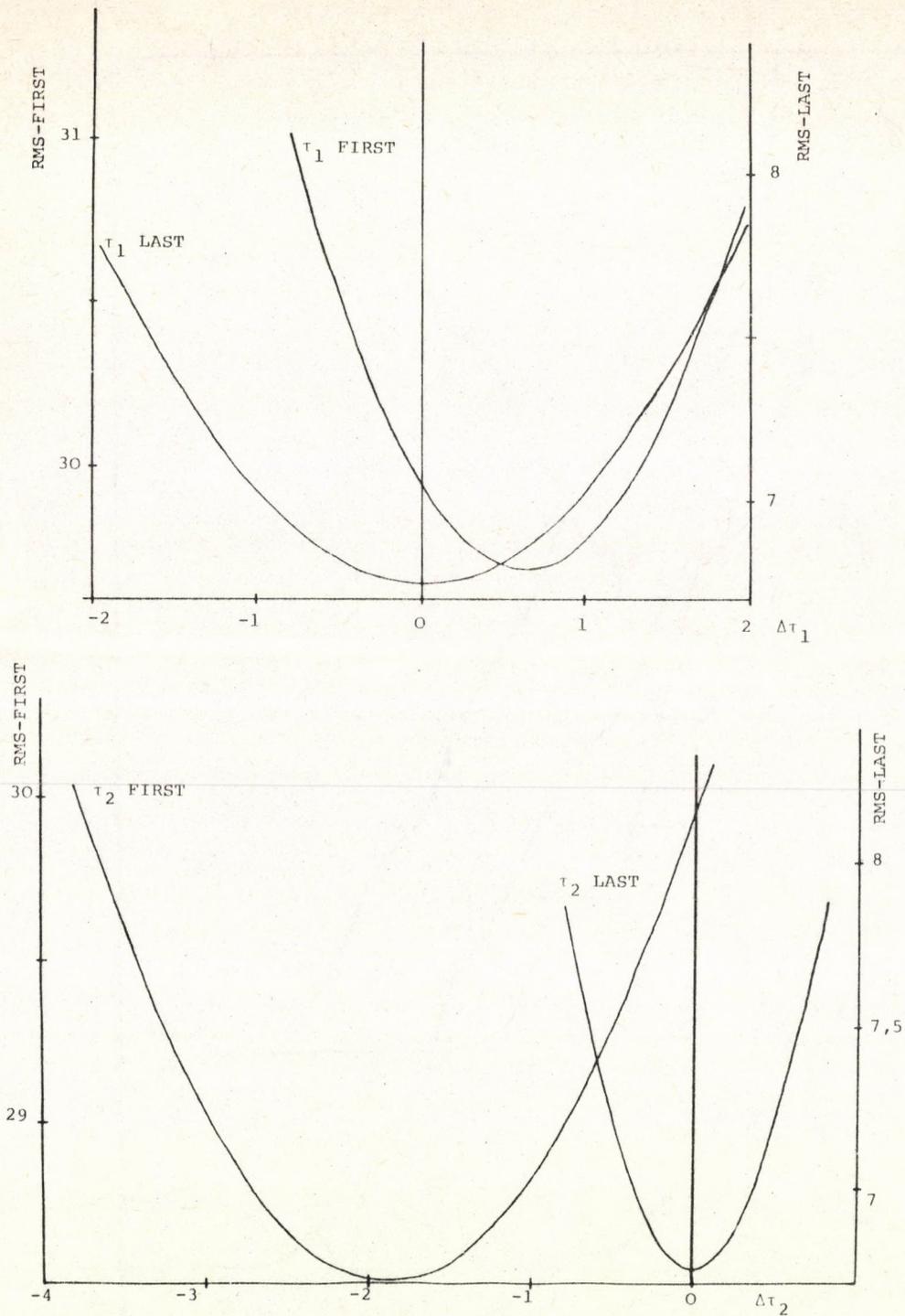


Fig. 3. Error parabolas in the two-component fit at the first and last iteration. a/ for τ_1 and b/ for τ_2 . Δ means the difference of the parameter value from the nominal value in the given iteration

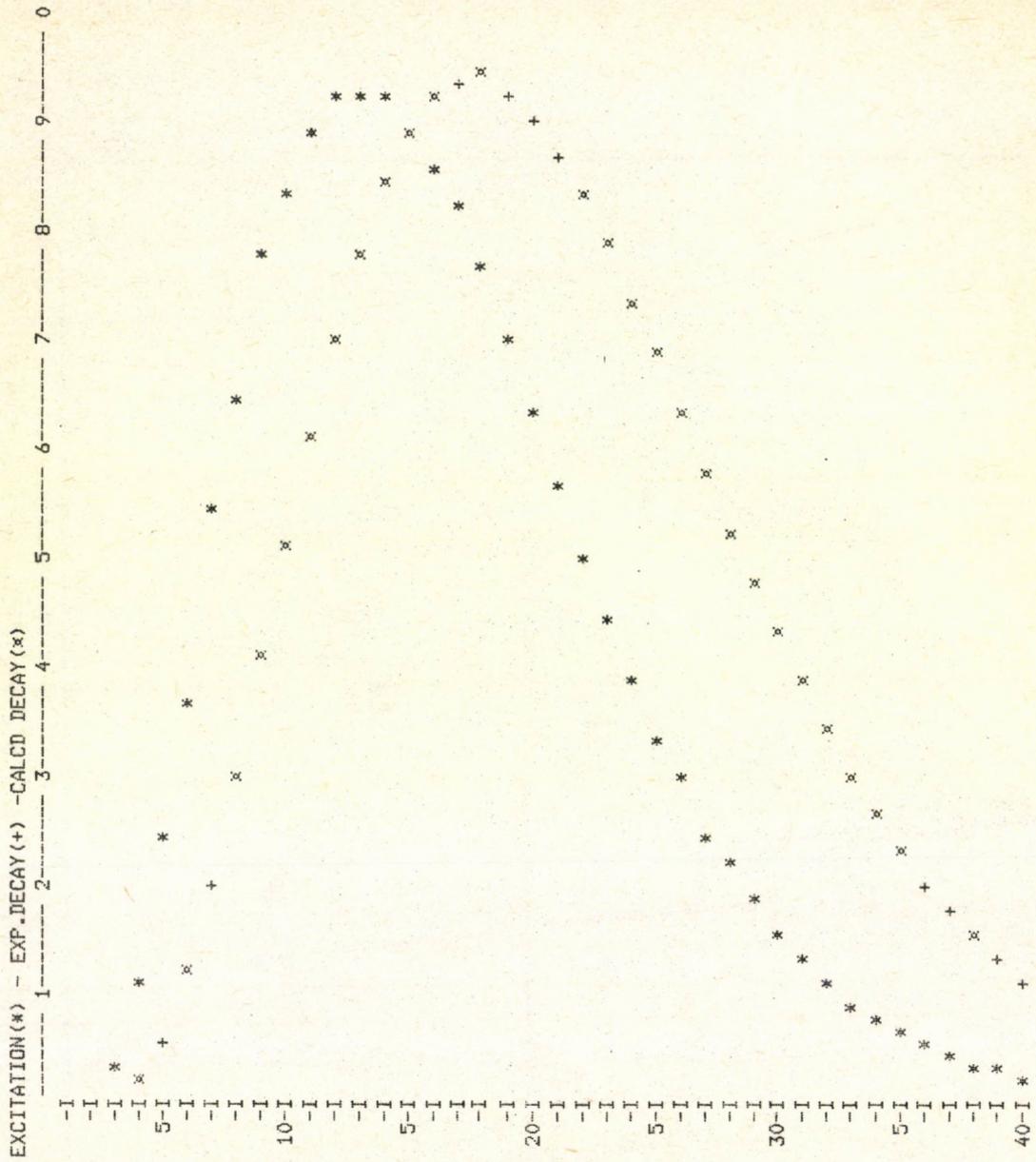


Fig. 4. Result of the two-component fit in line printer representation. Symbols: * excitation function; x calculated decay curve; + experimental decay curve.

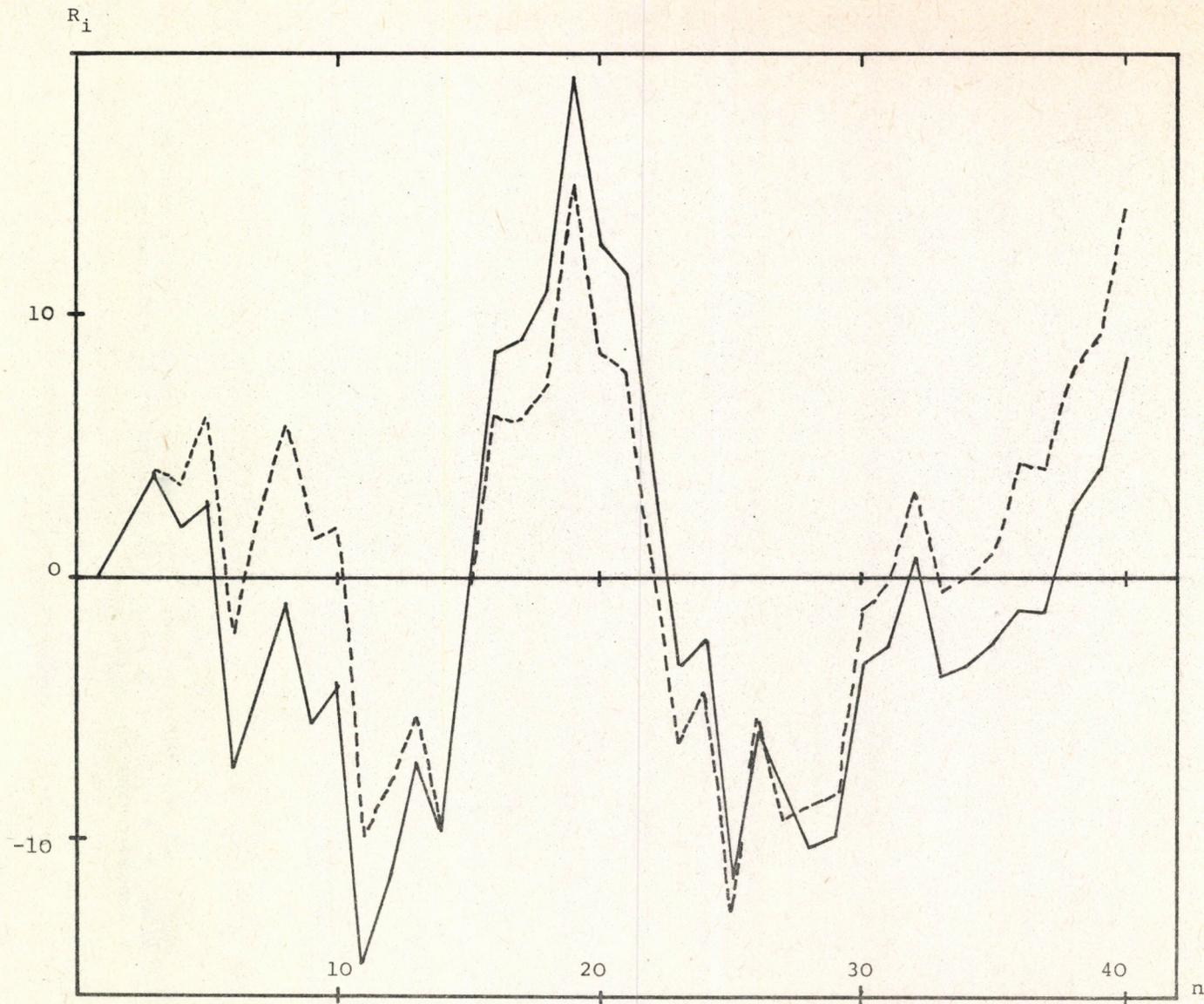


Fig. 5. Residual vector for the single /—/ and the two-/-/-/ component fits

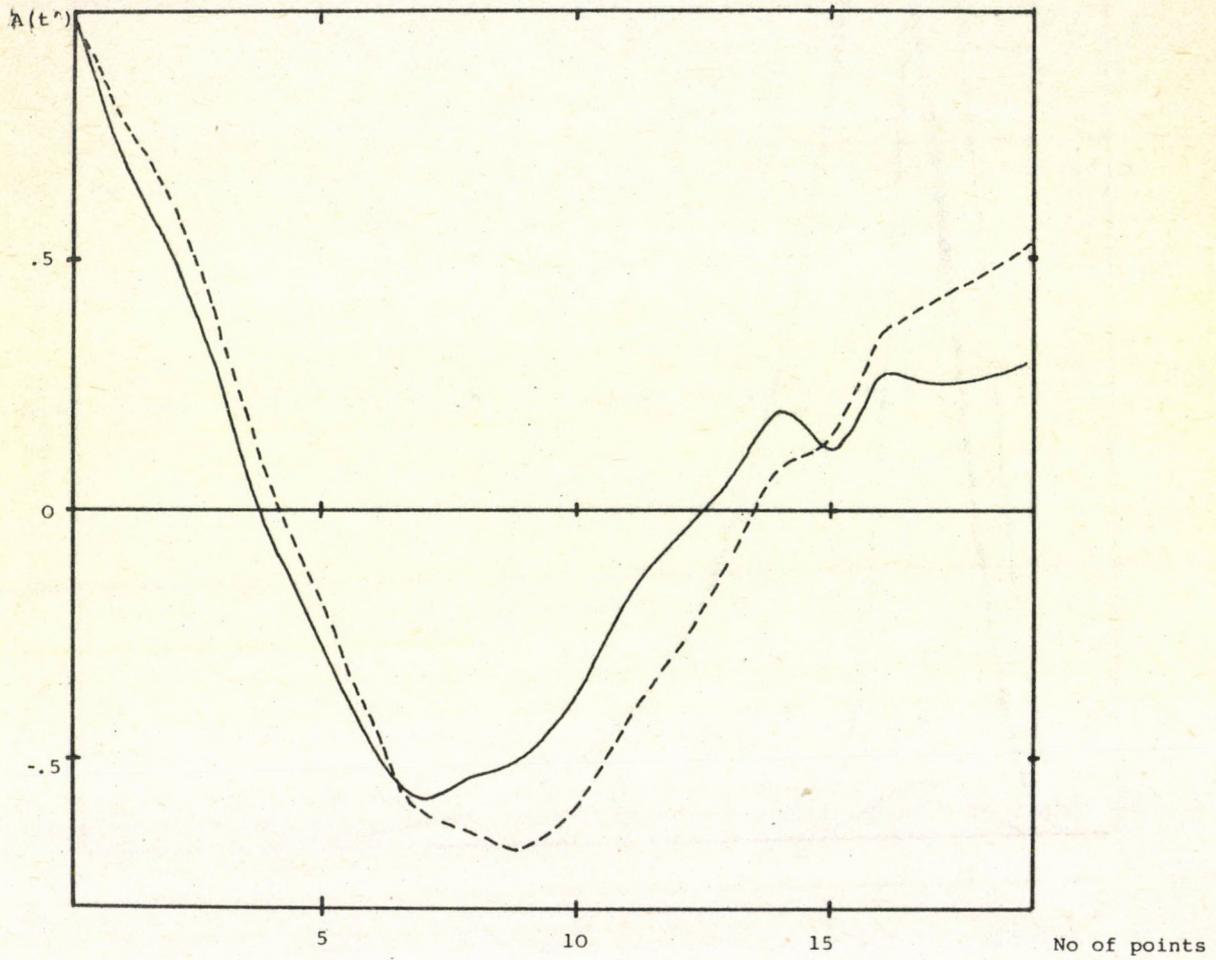


Fig.6. The autocorrelation functions for the single (----) and the two- (—) component fits.

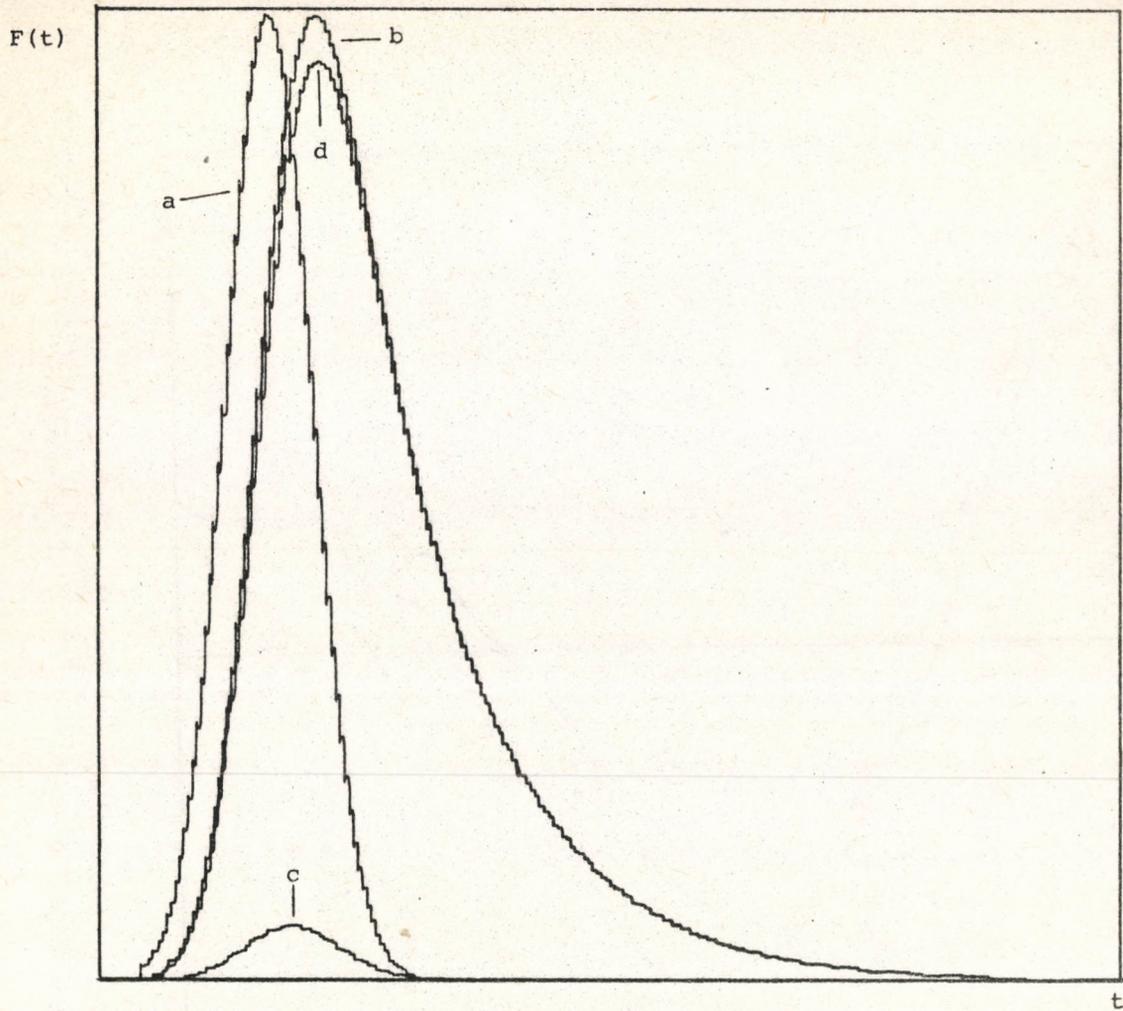


Fig. 7. X-Y plot of the convoluted two components and the calculated decay curve

- a*: experimental excitation function
- b*: calculated decay curve at the two component fit
- c*: first component of the calculated decay curve
- d*: second component of the calculated decay curve

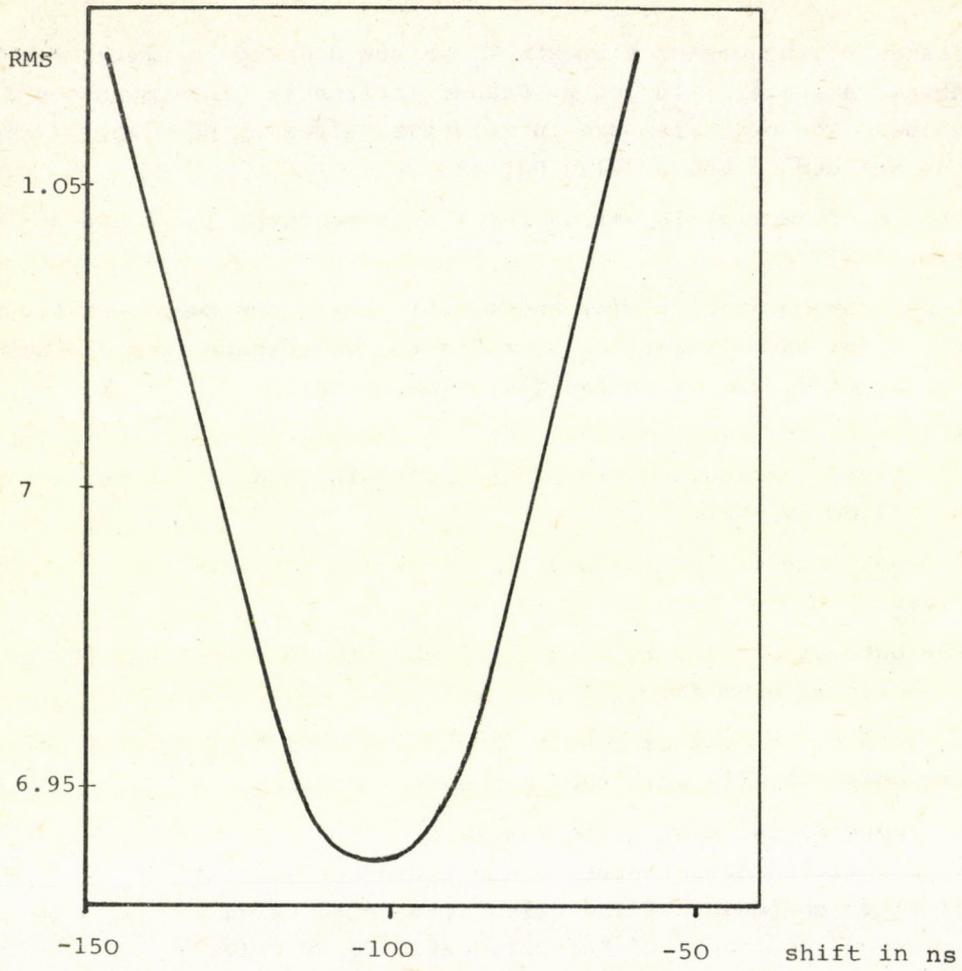
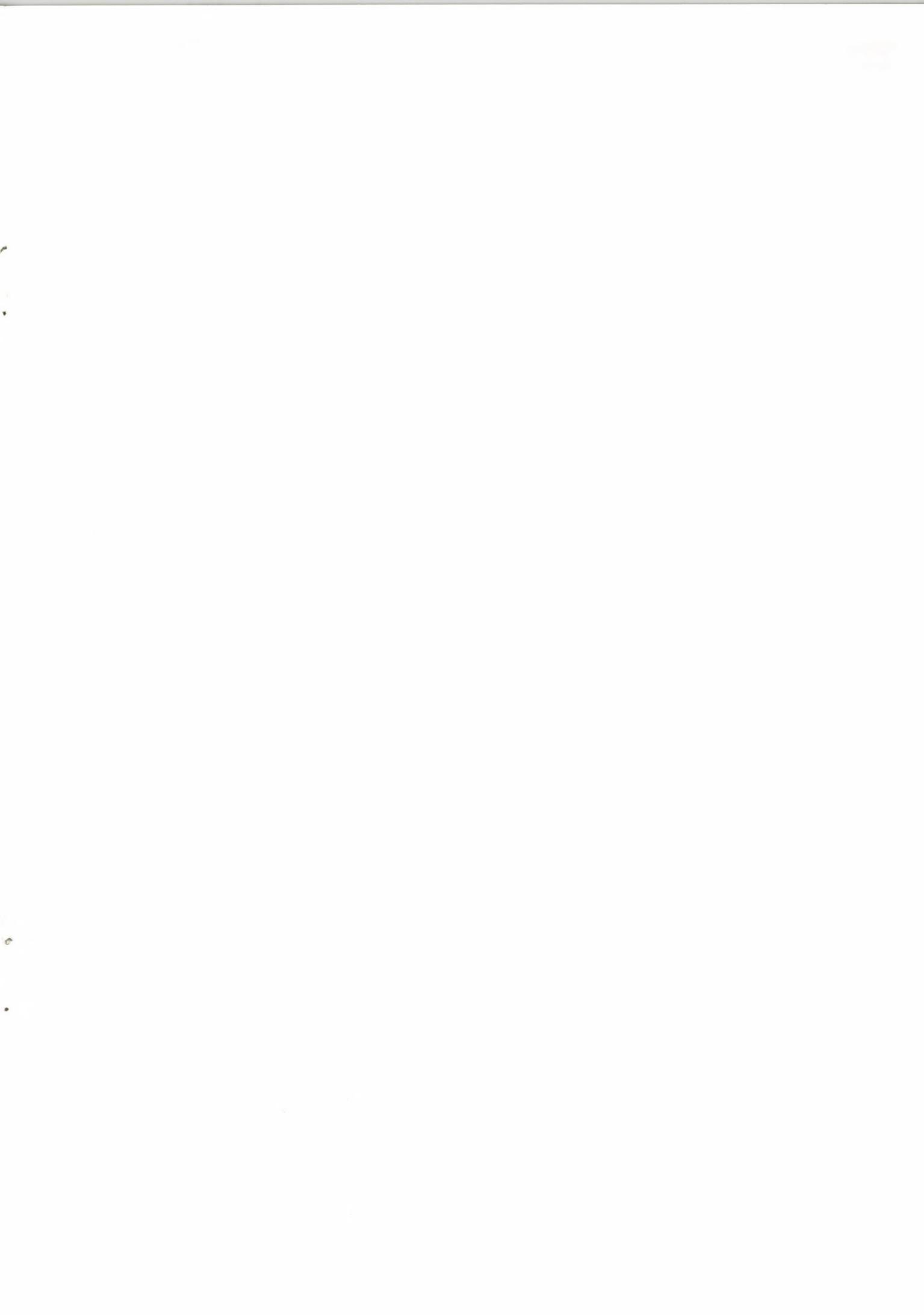


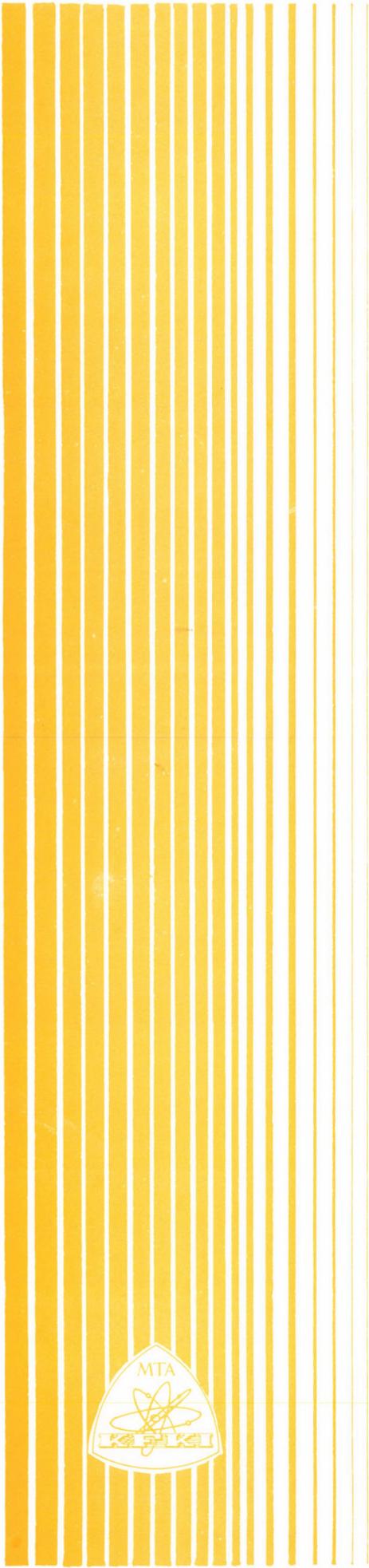
Fig.8. RMS values depending on the shift of the excitation function.

FIGURE CAPTIONS

- Fig.1. Change of the vector elements V_i versus damping parameter p . Abscissa scale is in $\log p$. Dashed horizontal lines mean the fitting values. The ordinates are in relative values by Eq. (15). Arrows show the selected p value using Eq. (18).
- Fig.2. Change of parameters versus the iteration steps for a two-component fit.
- Fig.3. Error parabolas of τ_1 (a) and τ_2 (b) in the two-component fit at the first and last iterations (Δ means the difference from the nominal values of τ_1 and τ_2 in the given iteration).
- Fig.4. Result of the two-component fit in line printer representation. Symbols: * excitation function; \otimes calculated decay curve; + experimental decay curve.
- Fig.5. Residual vector for the single (—) and the two- (----) component fits.
- Fig.6. The autocorrelation functions for the single (----) and the two- (—) component fits.
- Fig.7. X - Y plots of the excitation and calculated decay curves for the two-component fit with the component functions.
- a: experimental excitation function
 - b: calculated decay curve at the two-component fit
 - c: first component of the calculated decay curve
 - d: second component of the calculated decay curve
- Fig.8. RMS values depending on the shift of the excitation function.



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