NOTE

A METHOD FOR ANALYZING EXPONENTIAL DECAYS*

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Abstract—The non-linear least-squares routine KPS1 is presented for the analysis of data from counting experiments which follow single exponential decays. It gives appropriate weighting to individual points, is compact (52 statements) and converges more rapidly than the widely used CURFIT program of Bevington. The routine quantifies the goodness of fit and the uncertainty in the decay coefficient. KPS1 is particularly useful for microcomputer analysis when interfaced directly to laboratory equipment. A FORTRAN listing is included which may easily be adapted for BASIC.

INTRODUCTION

Many "real time" experiments rely on detection of signals which fall exponentially with time. Examples include kinetic studies in which resonance fluorescence, laser-induced fluorescence or chemiluminescence is used as the diagnostic of reactant concentration, measurements of excited-state lifetimes and studies involving radio-isotopes. If the signals are weak single pulse counting methods can be employed, with the counts accumulated in a multichannel scaler, often linked to a microcomputer for storage and display of the data. After capture the data may be transferred to a larger computer for analysis, but clearly it would be convenient to interpret decays in the course of the experiments. A short program KPS1, which uses little memory and therefore is particularly suited to small and inexpensive microcomputers, is described for the analysis of a signal y , which decays as a function of time t . y_i is fitted to the form $f(t)$ where

$$f(t) = A \exp(-kt) + B \quad (1)$$

where k is the pseudo first-order decay coefficient and A and B are constants.

A number of ways of extracting k , especially where the background B is zero, have been discussed elsewhere (Wentworth, 1965; Swain *et al.*, 1980; Demas, 1983; Hovanec & Ward, 1984). Here it is simply noted that subtracting a measurement made after a "long" time (y_∞) to eliminate the B term requires certainty that the first term has completely decayed, gives excessive weight to y_∞ and may introduce errors if there is a second slow process, on a much longer timescale than $1/k$, which affects y . Non-linear least-squares programs have been published which fit data

to the form of equation (1) such as LSG and LSKIN1 (DeTar, 1968) and CURFIT (Bevington, 1969), which are relatively lengthy and do not always converge for poor data (Swain *et al.*, 1980). KORE (Swain *et al.*, 1980) is conveniently short, yields the uncertainty in k and quantifies the goodness of fit. The routine KPS1 given here is a modification of KORE which takes proper weighting of multichannel scaler data into account and uses an alternative statistical analysis to derive the goodness of fit and the SD of k , whilst retaining KORE's compactness. KPS1 is a subroutine able to be included in a data collection program interfaced to experimental apparatus.

PRINCIPLES

The method of least-squares aims to minimize

$$\chi^2 = \sum_{i=1}^n [y_i - f(t)]^2 w_i \quad (2)$$

with respect to the parameters of $f(t)$, where w_i represents a statistical weighting factor equal to the reciprocal of the variance of y_i (Bevington, 1969). The importance of correct weighting, particularly for poor data, has been emphasized previously (Demas, 1983). For pulse counting experiments Poisson statistics apply so that $w_i = 1/y_i$. Minimizing equation (2) for A and B and solving the simultaneous equations in terms of k yields optimized values of A and B for any particular k :

$$A = \left\{ \sum y_i^{-1} \sum \exp(-kt) - n \sum \exp(-kt) y_i^{-1} \right\} / \left\{ \sum y_i^{-1} \sum \exp(-2kt) y_i^{-1} - \left[\sum \exp(-kt) y_i^{-1} \right]^2 / n \right\} \quad (3)$$

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SUBROUTINE KPS1(NPTS,K,A,B,Y,TBASE,SDK,RCS)
DIMENSION Y(256),E(0:256)
REAL K,M
DATA E(0),F,DELTA2,S2,RCS,A12,A13/1.,4.,0.,0.,0.,0.,0./
DO 102 I=1,NPTS
102 S2=S2+1./Y(I)
103 S1=0.
S3=0.
S4=0.
X=EXP(K)
DO 104 I=1,NPTS
E(I)=E(I-1)/X
S1=S1+E(I)/Y(I)
S3=S3+E(I)*E(I)/Y(I)
104 S4=S4+E(I)
A=(S4-S1*NPTS/S2)/(S3-S1*S1/S2)
B=(NPTS-A*S1)/S2
T1=0.
T2=0.
DO 105 I=1,NPTS
U=I*E(I)/Y(I)
T1=T1+(Y(I)-A*E(I)-B)*U
105 T2=T2+(2*A*E(I)-Y(I)+B)*I*U
IF (F.EQ.0) GOTO 106
DELTA=T1/T2
K=K-(1.+F)*DELTA
M=1.
T=DELTA2/DELTA
IF (T.LE.0.7) THEN
M=0.5
ELSE IF (T.LT.4) THEN
M=2.
END IF
IF (F*M.GT.0.5) THEN
F=F*M
ELSE
F=0.5
END IF
DELTA2=DELTA
IF (ABS(DELTA/K).LT.1E-5) F=0.
GOTO 103
106 DO 107 I=1,NPTS
T=Y(I)-A*E(I)-B
RCS=RCS+T*T/Y(I)
U=I*E(I)/Y(I)
A12=A12+(T-A*E(I))*U
107 A13=A13-A*U
RCS=RCS/(NPTS-4)
DET=A*T2*(S3*S2-S1*S1)-A12*(A12*S2-S1*A13)+A13*(A12*S1-
+ S1*A13)
SDK=SQRT((S3*S2-S1*S1)/DET)/TBASE
K=K/TBASE
END

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Fig. 1. FORTRAN-77 Listing of KPS1.

$$B = \left(n - A \sum \exp(-kt) y_i^{-1} \right) / \sum y_i^{-1} \quad (4)$$

where Σ means summation of the n data points over t . k is sought such that $g(k) = \partial \chi^2 / \partial k$ is zero. An iterative technique is applied so that

$$k_{i+1} = k_i - (1 + F)g(k)[\partial g(k)/\partial k]^{-1} \quad (5)$$

gives an improved estimate k_{i+1} from an earlier estimate k_i . The condition $F = 0$ corresponds to the traditional Newton-Raphson method but Swain *et al.* showed that provided F is adjusted suitably, a dramatically faster convergence can be obtained using $F > 0$, which forms their over-relaxation technique (Swain *et al.*, 1980). Iteration is repeated with updated values of A and B until changes in k are sufficiently small.

Swain *et al.* used a correlation coefficient to quantify the goodness of fit, but a more convenient quantity which is widely tabulated is the reduced chi

square χ_r^2 . The number of degrees of freedom ν is $n - 4$ (Demas, 1983) and χ_r^2 is easily calculated via equation (2) since $\chi_r^2 = \chi^2/(n - 4)$: it should be approximately unity if equation (1) is indeed a fair fit to the observed data. Distributions of χ_r^2 give bounds at various confidence levels and degrees of freedom. To obtain the uncertainty in k the error matrix ϵ is employed (Bevington, 1969). With parameters α_1 , α_2 and α_3 the elements α_{lm} of the curvature matrix α are defined by $\alpha_{lm} = 0.5 \partial^2 \chi^2 / \partial \alpha_l \partial \alpha_m$. The error matrix is

Table 1. Comparison of KPS1 and CURFIT with "perfect" data (entries rounded to 4 decimal places)

Initial k	Final k , KPS1	Final k , CURFIT
0.02	0.2000	0.0644
0.15	0.2000	0.1954
0.21	0.2000	0.1999
0.25	0.2000	0.1951
0.30	0.2000	0.1772
0.40	0.2000	0.1796

Table 2. Comparison of KPS1 and CURFIT with scattered data* (entries rounded to 4 significant figures)

Run	Parameter values at beginning of run							
	KPS1				CURFIT			
	A	B	k	T†	A	B	k	T†
1	36.00	24.00	0.1100	60	36.00	24.00	0.1100	30
2	40.62	23.06	0.1340	10	40.24	23.02	0.1322	30
3	40.62	23.06	0.1340	10	40.63	23.03	0.1336	30
4	40.62	23.06	0.1340	10	40.62	23.05	0.1339	30
5	40.62	23.06	0.1340	10	40.62	23.06	0.1339	30

* 16 points: 60, 58, 42, 55, 44, 36, 44, 34, 32, 40, 30, 36, 38, 24, 33, 24.

† Execution time (s).

given by $\epsilon = \alpha^{-1}$. The variances of the parameters then lie on the leading diagonal of ϵ , thus $\sigma_{\epsilon_i}^2 = \epsilon_{ii}$.

ALGORITHM

Figure 1 is a listing of the KPS1 routine as used with a Digital Research FORTRAN-77 compiler for an IBM PC. On entry the datapoints are in the array Y, NPTS being the number of points and TBASE the time per channel. K should contain an initial estimate of the decay coefficient (see later) and a rough value can be obtained from the expression

$$K = (3./NPTS) * \text{LOG}((Y(1) - Y(NPTS)) / (Y(NPTS/3) - Y(NPTS))). \quad (6)$$

Operation is with single precision arithmetic and iteration stops when K changes by <1 part in 10^5 . This may be unnecessarily precise for most kinetic data but serves for demonstration. In the program the array of consecutive exponentials E is generated without repeated calls to the EXP function, which can save significant time for large numbers of points (Demas, 1983). The accumulated error after 256 points using this procedure is about 1 part in 10^5 (or <2 parts in 10^6 with IBM interpreted Advanced BASIC, BASICA). The variables S1-S4 accumulate the summations of equations (3) and (4), F is the over-relaxation factor (Swain *et al.*, 1980) and lines from 106 onwards evaluate the curvature matrix and calculate σ_k . Values returned are the decay coefficient K, its standard deviation SDK, the other fitted parameters A and B, and χ^2 as RCS. The array Y is unaltered.

The routine will fail if the initial value of K is so large that the Newton-Raphson correction overshoots and makes K negative. Like any comparable program KPS1 will also fail if any of the data are zero since no meaningful weight can be attached for a Poisson distribution.

RESULTS

In Table 1 KPS1 is compared to CURFIT, one of the more commonly referenced general least-squares

programs (Bevington, 1969), using synthetic input data where $A = 50$, $B = 20$ and $k = 0.2$ for 16 points (TBASE = 1, $t = 1-16$). KPS1 has only 52 statements whereas CURFIT and its subroutines occupy 157. KPS1 needs only an initial estimate of k while CURFIT requires estimates of all three parameters: here A and B were set to their "true" values to begin with. Table 1 illustrates the results. Clearly CURFIT is much more sensitive than KPS1 to the starting value of k. The crude estimate equation (6) is therefore suitable for KPS1 which converges to the same answer irrespective of the starting value. Equation (6) could be added to the start of the subroutine.

Table 2 is a comparison of the two routines with a scattered dataset of 16 numbers. The first and last were used as initial estimates of $A + B$ and B (not required for KPS1). Although CURFIT executes faster (30 s vs 60 s for KPS1) several consecutive runs, using the previous output as initial estimates, are needed to ensure convergence. KPS1 converges in a single run and so has the shorter overall time.

The KPS1 program is easily translated into other popular microcomputer languages such as BASIC. In fact it executes some three times more rapidly under BASICA on an IBM PC and for large numbers of points (more typical of an experimental dataset) the execution time is <1 s per point, the exact time depending on their scatter. The algorithm presented here is therefore a useful addition to a computerized data acquisition system because of its small size, few input parameters and rapid convergence.

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