TFMFIT: A PROGRAM TO FIT A GENERALIZED CONVECTION-DISPERSION MODEL TO EXPERIMENTAL DATA

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The task of obtaining estimates of model parameters (the "inverse problem") is encountered frequently in practice. The transfer function model is a general formulation describing solute transport from an "entrance surface" to an "exit surface" of a porous domain. The probability that solute will arrive at an exit surface is given by its travel time probability density function (pdf). A very general pdf based on the convection-dispersion equation is presented. The pdf incorporates many solute transport mechanisms, including sorption, volatilization and biodegradation. This document describes the pdf as well as the structure and usage of a versatile computer code. The code uses nonlinear least-squares fitting to find optimal parameter values by matching transfer function model predictions with measured experimental data. The program makes use of some standard computational algorithms in the widely-available IMSL package. Use of the program is demonstrated with synthetic data as well as data from a comprehensive field experiment. Breakthrough curves can be plotted using an additional code.

ANNOUNCEMENT

Persons wishing to obtain machine-readable copies of the codes listed here should contact D. A. Barry at the given departmental address or via electronic mail at BARRYD@UCRVMS.BITNET.
BIBLIOGRAPHY

Key:  CDE - Convection-Dispersion Equation
      CF - Curve Fitting
      TFM - Transfer Function Model


Parker, J. C., and M. Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bulletin 84-3, Virginia Agricultural Experiment Station, Blacksburg. (CF, CDE)


THE TRANSFER FUNCTION MODEL

Fundamental Concepts

Central to the theory of subsurface solute transport is the prediction of concentrations and mass fluxes as functions of space and time, given prior information on the manner in which solute has entered the subsurface zone. Typically, the prior information required specifies fluxes and concentrations during the time period in which solute passed through an interface separating the zone of transport from the solute source. Transport into a vadose zone, for example, can involve the movement of deposited solute downward across the land surface or through the interface between a disposal site (landfill) and the underlying vadose zone. Transport into a groundwater zone can involve solute movement across a phreatic surface, or through an aquitard, or through the perforated casing of an injection well. More subtle modes of entry of solute into the subsurface zone are possible. Solutes can enter subsurface waters by traversing solid/liquid interfaces (desorption and dissolution processes) or by crossing air/liquid interfaces (absorption processes). Solutes can simply appear in subsurface water as a result of biological or chemical transformations of other solutes. In these cases, the "entrance surface" through which solute passes to begin a subsurface transport process takes on a highly convoluted, evanescent shape that defies smooth mathematical description at the local scale. This same difficulty may also attend the specification of an "exit surface", through which solute moves out of a monitored subsurface zone.
The very complicated nature of the initial conditions of solute movement in natural porous media apply equally to the subsurface transport process itself. Heterogeneity in the solid matrix and void spaces of the vadose and groundwater zones contributes to pronounced variability in the mechanisms by which solutes are moved and transformed. Identification of the broad classes of these mechanisms is reasonably complete, but quantitative details of their modes of operation at field and regional scales are mostly lacking.

These uncertainties and the goal of developing a predictive theory of subsurface solute transport that is not overly specialized lead one to a consideration of the problem based on probability and only fundamental physical notions. Under the broadest possible circumstances, let \( t' \) be the time at which a solute molecule first appears in the transporting portion of the void space of a vadose or groundwater zone, and let \( \tau \) denote the time interval during which it exists in a monitored subsurface zone. The variable \( t' \) is the solute input time and \( \tau \) will be termed the solute lifetime. Now define \( g(\tau|t') \, d\tau \) as the conditional probability that the solute lifetime lies in the interval \( \tau \) to \( \tau + d\tau \), given that the input time was \( t' \). The function \( g(\tau|t') \) is the solute lifetime probability density function. Thus \( g(\tau|t') \, d\tau \) is the probability that a monitored solute molecule which entered the transporting portion of a subsurface zone at time \( t' \) has disappeared from the subsurface zone at a later time \( t' + \tau \). The geometric complexity associated with the modes of solute entrance or disappearance, noted above, and the mechanisms by which transport and transformation are realized in the subsurface zone are contained implicitly in \( g(\tau|t') \).
Physical Significance of $g(\tau | t')$

The lifetime probability density function (pdf) contains all of the information necessary to construct a solute transport theory with predictive capability. If $Q_{in}(t')$ is the rate of solute mass input divided by the total mass input, and $Q_{out}(t)$ is the rate of solute mass output similarly normalized, then the identity

$$Q_{out}(t) = \int_{0}^{t} g(t - t' | t') Q_{in}(t') \, dt'$$  \hspace{1cm} (1)

relates the input rate over the time interval $(0,t)$ to the output rate observed at time $t$. Equation 1 is a result derived from probability theory applied to $g(\tau | t')$ (Jury et al., 1986). Under conditions wherein it is meaningful to relate $Q_{out}$ and $Q_{in}$ directly to solute concentrations (e.g., steady water flow), eq. 1 can be reformulated in terms of those concentrations instead of mass transfer rates.

If solute input occurs after "time zero" over an interval that is very small compared to the time period over which output monitoring occurs, then $Q_{out}$ is simply proportional to the conditional lifetime pdf $g(t | 0)$. This lifetime pdf can be measured by observing the response of a subsurface zone to a narrow-pulse input of solute, and the measured $g(t | 0)$ will represent the net effect of convection, dispersion, sorption, interphase transfer, biochemical transformation, etc., on the lifetime of a solute in the monitored region. Since eq. 1 is essentially a probabilistic statement of mass balance, no particular mechanistic
cause of solute transport is implied by it. Any subsurface process or combination of processes consistent with mass balance is representable by a lifetime pdf, so long as the strong law of large numbers can be applied to interpret eq. 1 physically (cf. Barry and Sposito, 1988).

Since \( g(\tau | t') \) is a pdf, it can be normalized and used to calculate (conditional) moments in the usual way (cf. Valocchi, 1986):

\[
\int_{0}^{\infty} g(\tau | t') \, d\tau = 1 \quad (2)
\]

\[
\int_{0}^{\infty} \tau^n g(\tau | t') \, d\tau = E(\tau^n | t') \quad (3)
\]

where \( E(\cdot) \) is the mathematical expectation operator. Of interest also is the median lifetime, \( t_m \), which is the solution of the integral equation:

\[
\int_{0}^{t_m} g(\tau | t') \, d\tau = \frac{1}{2} \quad (4)
\]

under the condition that eq. 2 holds. Note that \( t_m \) is conditional on the input time \( t' \). For a conservative solute whose loss from a subsurface zone is monitored at a well-defined exit surface (e.g., a perforated well casing), the parameter \( t_m \) can serve to establish the time-of-arrival of the solute at this surface. If the volumetric water flux density is known and steady throughout the zone of transport, it can be multiplied by \( t_m \) and divided by a nominal distance of transport to estimate the void space fraction that is effective as the transporting portion.
If enough physical information about a subsurface transport process is available to permit a parametric model of the lifetime pdf (e.g., a lognormal function or an inverse Gaussian function), this model can be introduced into eqs. 1 to 4 to provide explicit mathematical representations of $Q_{\text{out}}$ and the time-moments for use in model validation studies of field-scale solute transport.

**Travel Time pdfs and the CDE**

Analytical models of the travel time pdf for reactive solutes can be constructed from solutions of the convection-dispersion equation (CDE). The mathematical basis for this possibility is the Duhamel theorem (Carslaw and Jaeger, 1959) which states, in the present context, that solutions of linear CDEs always can be written in the form of eq. 1, with effluent and input flux concentrations replacing $Q_{\text{out}}$ and $Q_{\text{in}}$, respectively, and with the travel time pdf explicitly independent of the input time. For solute transport under steady water flow conditions, the Duhamel theorem leads to the linear convolution expression:

$$c_{\text{ex}}(t) = \int_{0}^{t} g(t - t') c_{\text{ent}}(t') \, dt'$$  \hspace{1cm} (5)$$

where $c_{\text{ex}}$ and $c_{\text{ent}}$ are flux concentrations at the exit and entrance surfaces, respectively. The pdf $g(t)$ is identified with the time-derivative of a flux concentration solution of a linear CDE subject to a constant flux at the entrance surface. It follows from eq. 5
that travel time pdfs can be calculated as time derivatives of solutions of the CDE subject to a constant flux concentration boundary condition (Sposito et al., 1986). These model pdfs are independent of the input time \( t' \) and contain physical parameters — like dispersion coefficients, convection velocities, and sorption distribution coefficients — that model the solute transport and transformation mechanisms assumed in the underlying CDE. The model pdfs thus are useful for comparative studies of transport phenomena in different vadose or groundwater zone situations and for studies of the influences of different transport mechanisms on the lineshapes of travel time spectra.

The general relationship between the travel time pdf in eq. 5 and a steady-flow, linear CDE can be epitomized in the following algorithm:

1. A steady-water-flow CDE is established on the basis of hypotheses about the mechanisms of solute transport in a vadose or groundwater zone (convection, dispersion, sorption, biodegradation, etc.).

2. The linear partial differential equation developed in step (1) is solved subject to a step-input boundary condition on the entrance surface.

3. The travel time pdf is calculated as the time-derivative of the solution developed in step (2) on the exit surface. This pdf can be introduced into eq. 5 to predict exit-surface concentrations for arbitrary entrance-surface concentrations.
A GENERAL CONVECTION-DISPERSION EQUATION

A CDE can be developed to describe mathematically the following mechanistic picture of solute transport in groundwater:

(1) Solute moves in three spatial dimensions through an aquifer of uniform porosity in which the groundwater flow velocity \( v \) is steady and uniform, with the \( x_3 \)-axis chosen to point along the direction of flow.

(2) Solute dispersion is anisotropic and is represented by the three constant dispersion coefficients, \( D_1, D_2, \) and \( D_3 \).

(3) The solute can be partitioned among the gas phase, the mobile and immobile portions of the liquid phase, and the solid phase. Biodegradation is possible in all phases.

The convection-dispersion equation that results from the mechanistic picture above can be expressed in the dimensionless form:

\[
\frac{\partial c_m}{\partial T} + (1 - B) R \frac{\partial c_{im}}{\partial T} = \sum_{i=1}^{3} \frac{1}{P_i} \frac{\partial^2 c_m}{\partial x_i^2} - \frac{\partial c_m}{\partial x_3} - BC c_m - (1 - B) D c_{im}
\]

(6)

\[
(1 - B) R \frac{\partial c_{im}}{\partial T} + (1 - B) D c_{im} = W(c_m - c_{im})
\]

(7)

where: 

- \( c_m \) = solute concentration [ML^{-3}] in the mobile portion of the liquid phase
- \( c_{im} \) = solute concentration [ML^{-3}] in the immobile portion of the liquid phase
- \( T = a_m v t / (a L) \) = dimensionless time coordinate
- \( X_i = x_i / L \) = dimensionless space coordinate (\( i = 1, 2, 3 \))
Dimensionless Model Parameters

\[ B = \left( \theta_m + f \rho_b K_d + \theta_{gm} K_H^{-1} \right) / \left( \theta + \rho_b K_d + \theta_g K_H^{-1} \right) \]  

where:

\[ \theta \text{(im)} = \text{(im)mobile liquid content} [L^3L^{-3}] \]

\[ \theta_g \text{(im)} = \text{air content in contact with (im)mobile liquid} [L^3L^{-3}] \]

\[ \theta = \text{liquid content} [L^3L^{-3}] = \theta_{im} + \theta_m \]

\[ \theta_g = \text{air content} [L^3L^{-3}] = \theta_{gim} + \theta_{gm} \]

\[ f = \text{fraction of adsorbing solid phase in contact with mobile liquid} \]

\[ \rho_b = \text{dry bulk density} [ML^{-3}] \]

\[ K_d = \text{distribution coefficient for adsorption} [L^3M^{-1}] \]

\[ K_H = \text{Henry's Law constant for solute partitioning between liquid and air} (c_{\text{liquid}} = K_H c_{\text{gas}}) \]

\[ R = 1 + \left( \rho_b K_d + \theta_g K_H^{-1} \right) / \theta \]  

\[ P_i = vL/D_i \quad (i=1,2,3) \]

where:

\[ v = \text{velocity of mobile liquid phase} [LT^{-1}], \text{taken along } x_3 \]

\[ L = \text{distance from solute input point to monitoring point} [L], \]

\[ \text{taken along } x_3 \]

\[ D_i = \text{solute dispersion coefficient} [L^2T^{-1}] \text{ in the } x_i \text{ direction} \]

\[ (i=1,2,3) = D_i + \left( \theta_{gm} K_H^{-1} D_i^g / \theta_m \right) \]

\[ C = \left( \theta_m \beta_m^{-1} + fK_d \beta_m^s + \theta_{gm} K_H^{-1} \beta_{im}^g \right) L / \left[ \theta_m v(1 - B) \right] \]
where: $\beta_j^i$ = first-order solute decay constant [T$^{-1}$] for $i^{th}$ component (gas, liquid, or solid) in or contacting the $j^{th}$ portion of the liquid phase (mobile or immobile)

$D_{ij}^j$ = solute dispersion coefficient [L$^{2}$T$^{-1}$] in the $X_i$ direction in the $j^{th}$ (gas, liquid) phase.

$$D = \left[ \theta_{im} \beta_{im}^l + (1 - f) K_d \beta_{im}^s + \theta_{im} + \theta_{gim} K_H^{\text{im}} \right] L$$

$$/[\theta_{im} v(1 - B)]$$

$$W = (\alpha^1 + \alpha^g K_H^{\text{im}}) L/(\theta_{im} v)$$

where: $\alpha_j^i = \text{linear solute transfer coefficient [T}^{-1}]$ for $i^{th}$ component into the immobile portion of the liquid phase, $j = 1$ (liquid) or $g$ (gas).

The initial and boundary conditions imposed on eqs. 6 and 7 are:

$$c_m^+(X,0) = c_{im}^+(X,0) = 0$$

$$c_m^+(X_{\text{entr}},T) = 1, \lim_{X_i \to \infty} c_m^+(X,T) = 0$$

where $X_{\text{entr}}$ refers to any point on the entrance surface. Specific, uniform initial values of $c_m$ and $c_{im}$ in the aquifer and of $c_m$ on the entrance surface have been assumed to be removed explicitly by subtraction and scaling operations.

An area-averaged, dimensionless travel time pdf corresponding to the boundary-value problem expressed in eqs. 6 and 14 is calculated according to the equation:

$$g(T) = \int_{X_3}^{Y_0} \frac{ac_m}{aT} Y \, dY$$

(15)
where \( X_3 \) and \( Y_0 \) are the chosen spatial limits on the exit surface and \( Y \) is a dimensionless polar coordinate:

\[
Y^2 = \left( \frac{P_1}{P_3} \right) X_1^2 + \left( \frac{P_2}{P_3} \right) X_2^2 + X_3^2
\]  

(16)

Equation 15 represents an effective travel time pdf averaged over the directions transverse to the direction of groundwater flow. The averaging process in eq. 15 has the effect of creating a one-dimensional travel time pdf.

SOLUTIONS FOR THE TRAVEL TIME PDF

Laplace Domain Solution

Equations 6, 7, and 14 can be solved by Laplace transformation.

The resulting Laplace transform of \( g(T) \) defined by eq. 15 is then:

\[
\overline{g}(s) = \frac{P_3 \exp(P_3 X_3/2) \left[ \exp[-X_3 F(s)/2] - \exp[-Y_0 F(s)/2] \right]}{F(s) \left[ 1 - \exp[P_3 (X_3 - Y_0)/2] \right]}
\]  

(17)

where:

\( s \) is the Laplace transform parameter

\( \overline{g}(s) \) is the Laplace transform of \( g(T) \), and

\[
F(s) = \left\{ P_3^2 + 4BRP_3 s \left[ 1 + \frac{(1 - B) W/B}{(1 - B) Rs + W + D(1 - B)} \right] \right. \\
\left. + 4BP_3 C + \frac{4(1 - B) P_3 WD}{(1 - B) Rs + W + D(1 - B)} \right\}^{1/2}
\]  

(18)

The value of \( X_3 \) is either 0 (for volatilization at the surface) or 1 (for transport within the porous domain), whereas \( X_1 \) and \( X_2 \) can have
any non-negative value. The pdf is area-averaged, so, from eq. 15, \( X_2 \) and \( X_3 \) define the region averaged over. If \( x_3 \) is the distance along the vertical axis, \( X_3 = 0 \) is the soil surface and \( X_3 = 1 \) is the monitoring depth \( L \).

The model pdf describes the travel times of a solute which can move by convection and dispersion in the mobile liquid and air phases, can be volatilized, can adsorb, and can decay by first-order kinetics. Adsorption, decay, and volatilization are permitted in both the mobile and immobile phases. The volatilization pdf is found by setting \( X_3 = 0 \).

**Inversion of the Laplace-Transformed pdf**

Two choices are available to compute numerical values of \( g(t) \). The Laplace transform of \( g(t) \), i.e., \( \bar{g}(s) \), can be inverted numerically using standard inversion routines (e.g. Talbot, 1979) or \( g(t) \) itself can be derived and computed directly. TFMMFIT uses both approaches and, therefore, the analytical inversion of \( \bar{g}(s) \), as given by eq. 17, is now presented.

Equation 17 is rewritten as:

\[
\bar{g}(s) = A[\bar{g}_1(s) - \bar{g}_2(s)]
\]

(19)

where

\[
A = P_3 \exp(P_3 X_3/2)/(1 - a)
\]

\[
\bar{g}_1(s) = \exp[-X_3 F(s)/2]/[\sqrt{4BP_3 R} F_1(s)]
\]

\[
\bar{g}_2(s) = \exp[-Y_0 F(s)/2]/[\sqrt{4BP_3 R} F_1(s)]
\]

with

\[
a = \exp[P_3 (X_3 - Y_0)/2]
\]

and

\[
F_1(s) = \left[ s + \frac{C}{R} \right] \left[ \frac{P_3}{4BR} + \frac{W}{BR} \right] + \frac{P_3 W}{4R^2B(1-B)} \right]^{1/2}
\]

\[
s + \frac{D}{R} + \frac{W}{R(1-B)}
\]
Observe that
\[
\bar{g}_1(s) = \int_{-\infty}^{-X_3 \sqrt{BP_3 R}} \frac{\exp[F_1(s)X]}{2 \sqrt{BP_3 R}} \, dX
\]  \hspace{1cm} (20)

the function \( \bar{g}_2(s) \) can be similarly defined by replacing the upper limit of integration in eq. 20 by \(-Y_0 \sqrt{BP_3 R} \). Thus, the problem of inverting eq. 17 has been reduced to finding the inverse of \( \exp[F_1(s)X] \).

A convenient method of achieving this goal is the iterated Laplace Transform inversion procedure (Sneddon, 1972) as illustrated by De Smedt and Wierenga (1979). Briefly, the basic steps involved in this procedure are: (i) to denote the Laplace transform parameter \( s \) as two (or more) new parameters \( s_1 \) and \( s_2 \), with \( s_1 \) and \( s_2 \) chosen such that inversion with respect to these variables is straightforward, (ii) to invert with respect to \( s_1 \) and \( s_2 \) so that the final result is given as a convolution over the expression obtained. Carrying out (i) first, one writes \( F_1(s) \) as \( F_1(s_1, s_2) \) where

\[
F_1(s_1, s_2) = \left[ s_1 + \frac{C}{R} + \frac{(s_2 + \frac{D}{R})(\frac{P_3}{4BR} + \frac{W}{BR}) + \frac{P_3 W}{4R^2B(1-B)}}{s_2 + \frac{D}{R} + \frac{W}{R(1-B)}} \right]^{1/2}
\]  \hspace{1cm} (21)

The operation of inverting eq. 21 with respect to \( s_1 \), treating \( s_2 \) as a constant (the Laplace Transform operator is denoted by \( \mathcal{L} \)) gives

\[
\mathcal{L}^{-1} \{ \exp[XF_1(s_1, s_2)] \} =
\]

\[
-X^2 \exp\left[ -\frac{X^2}{4T_1} \right] \frac{CT_1}{R} \frac{[(s_2 + \frac{D}{R})(\frac{P_3}{4BR} + \frac{W}{BR}) + \frac{P_3 W}{4R^2B(1-B)}]}{s_2 + \frac{D}{R} + \frac{W}{R(1-B)}} \] \hspace{1cm} (22)
Next, the right-hand side of eq. 22 is inverted with respect to $s_2$ using the result of Appendix 2,

$$
\mathcal{L}_2^{-1}\left\{\exp[XF_1(s_1,s_2)]\right\} = -X \exp\left[\frac{-X^2}{4T_1} - \frac{CT_1}{R} - \frac{DT_2}{R} - T_1 \left(\frac{P_3}{4BR} + \frac{W}{BR}\right)\right]
$$

$$
\left\{\delta(T_2) + \frac{W}{R} \sqrt{\frac{T_1}{T_2B(1-B)}} \exp\left[-\frac{WT_2}{R(1-B)}\right] I_1\left[\frac{2W}{R} \frac{T_1T_2}{B(1-B)}\right] \right\} / \sqrt{4\pi T_1}^{3/2}
$$

(23)

where $I_n(\ )$ is the modified Bessel function of order $n$ and $\delta(\ )$ represents the Dirac delta function. Finally, after performing the integrations defined by eq. 20 and carrying out some algebra, step (ii) is performed and $g(T)$ is given as

$$
g(T) = \sqrt{\frac{P_3}{4\pi RB}} \frac{\frac{h_1(-T)}{(1-a)}} {\left\{ \frac{h_2(X_3,T) - ah_2(Y_0,T)}{\sqrt{T}} \right\} +
$$

$$
\frac{W}{R^{1/2}(1-B)} \int_0^T \frac{2W}{R} \frac{\frac{\tau(T-\tau)}{\sqrt{B(1-B)}}}{\sqrt{\tau}} \frac{h_1(\tau)}{\sqrt{\tau}} \exp\left[-\tau(D + \frac{W}{1-B})/R\right]
$$

$$
\left[h_2(X_3,T-\tau) - ah_2(Y_0,T-\tau)\right] d\tau
$$

(24)

where

$$
h_1(T) = \exp[T(C + W/B)/R]
$$

$$
h_2(X,T) = \exp\left[-\frac{T(BR)^{-1}(X - \frac{T}{BR})^2}{4T}\right]
$$
The Case $B = 1$

This case arises typically when the porous medium is completely saturated, there is no immobile water within the system, and the solute under consideration acts as an ideal tracer ($C=0$), or is subject to first-order production or decay ($C \neq 0$). Letting $B=1$ in eq. 24 presents obvious computational difficulties and so an explicit $g(t)$ for $B=1$ is necessary. Finding $g(t)$ under this restriction is straightforward. The result is:

$$g(T) = \frac{\sqrt{\frac{P_3}{4\pi RT}} \exp[-(T/R)(C + P_3/4) + P_3X_3/2]}{1-a}$$

$$\{ \exp[-X_3^2P_3R/(4T)] - \exp[-Y_0^2P_3R/(4T)] \}$$

(25)

DESCRIPTION OF THE CODE

A FORTRAN program to accomplish the nonlinear least-squares fitting of the model to experimental data has been implemented on a CRAY X-MP/48 using single precision CRAY FORTRAN (CFT) and operating under the CRAY Time Sharing System (CTSS). An analogous version operates on a VAX 8000 series system using double precision VAX FORTRAN. CRAY single precision storage is as precise as VAX double precision storage, so both codes yield virtually identical results. The code, which is named TFMFIT, is based on the maximum neighborhood method of Marquardt (1963) as implemented by van Genuchten (1980, 1981) and Parker and van Genuchten (1984) (cf. Meeter, 1964; Daniel and Wood, 1973). The CRAY and VAX versions of the
source code are given in Appendix 1a and 1b, respectively. The algorithm attempts to find the combination of parameter values that will minimize the sum of the residuals squared between the experimental data and model predictions.

There are many existing parameter estimation procedures (Beck and Arnold, 1977), of which the Marquardt (1963) algorithm is but one. Hendrickson et al. (1988) have shown that, in the particular case of rainfall-runoff models, there is no single "best" algorithm that is optimally efficient, or even convergent to prior known parameter values. This conclusion likely applies to the estimation of transport parameters as well. It is suggested, therefore, that all parameter estimates provided by TFMFIT be subjected to critical scrutiny in the light of the model used and the experiment being modeled.

The code consists of the main program (named TFMFIT), the subroutines MATINV, MODEL, ZRES, FLINV, DCADRE, and REALTIME, and the functions ROOT, F, F1, MMBSI1, and FGRAND. The main program handles the input and output of data, checks that parameters are within allowable ranges, and implements the fitting algorithm. MATINV performs matrix inversion as required by the fitting algorithm. MODEL organizes data for evaluating the TFM. ZRES converts parameters from real to complex values, then calls FLINV, the IMSL (International Mathematical Subroutine Library, 1982) subroutine for the numerical inversion of Laplace transforms, which inverts eq. 17 to give solute concentrations in "real" time. FLINV requires an estimate of the maximum of the real part of the singularities of the function to be inverted. This estimate is calculated by ZRES using the function ROOT. The actual evaluation of
eq. 17 occurs in the functions F and F1. REALTIME computes the analytical solution for the TFM as given by eqs. 24 or 25. The integration in eq. 24 is calculated numerically with the IMSL subroutine DCADRE. FGRAND calculates the integrand in eq. 24 for use in DCADRE, while MMBSI1 (IMSL, 1982) evaluates the Bessel function as required by FGRAND. The fact that the code calls IMSL routines does not limit its usefulness, since the IMSL package is very widely available.

As was noted above, model predictions can be obtained either through numerical inversion of eq. 17, or via numerical integration of eq. 24. Both methods require roughly the same amount of CPU time except for the case B=1 (eq. 25), when the analytical solution is much more efficient. The numerical inversion is more sensitive to numerical instabilities, particularly for large values of \( P_3 \) (e.g., \( P_3 > 90 \)). However, the properties of the Laplace transform facilitate the incorporation of arbitrary boundary conditions into the solution. This version of TFMFIT includes the Laplace transform inversion primarily to allow users a straightforward way of incorporating complex time variations in the boundary conditions into their analyses with very few modifications of the code.

The code has been optimized to take advantage of the vector processing available on the CRAY computer. Compared with a scalar machine (e.g., the VAX computer), the relative speed of the vectorized code increases with the number of experimental data points. However, it should be pointed out that the main computational chore is the many numerical transform inversions of eq. 17, or numerical evaluation of eq. 24, required to achieve an optimal fit of the model with the
experimental data. The IMSL library has not been vectorized to date, although a CRAY-vectorized IMSL is to appear sometime in the future. In the following, a number of fitting examples are given. It was found that TFMFIT ran roughly 10 times faster on the San Diego Supercomputer Center CRAY X-MP/48, as compared with the VAX 8700 at the University of California, Riverside. This increase in speed will almost certainly jump by at least another factor of 10 when the vectorized IMSL object code becomes available.

Table 1. Parameter file required by TFMFIT. This particular file is used in Example 1c.

| P3 .... X3 .... Y0 .... B .... R .... W .... D .... |
| 5 .... 1 .... 1.5 .... .8 .... 1.1 .... 15 .... 4 |
| 1 .... 0 .... 1 .... 1 .... 1 .... 0 .... 0 |
| 1 .... 0 .... 1.0001 .... 1 .... 1 .... 1 .... 1 |
| 1000. .... 1 .... 1000. .... 1 .... 1000. .... 1000. .... 1000. |
| C .... .3 |
| .0 |
| .1 |
| 1000. |

Operation

On execution, TFMFIT accepts an input file, a file containing the experimental data, and prompts for a "results" file name. A plot file can also be created if desired. Table 1 contains an example input parameter file. The line-by-line organization of this file is documented in Table 2. Table 3 contains an example experimental data file.
<table>
<thead>
<tr>
<th>Line</th>
<th>Columns</th>
<th>Format</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-10</td>
<td>I10</td>
<td>Maximum number of interactions allowed in the least-squares fitting. If set to 0, the program simply calculates concentrations at specified times using the initial parameter values.</td>
</tr>
<tr>
<td></td>
<td>11-20</td>
<td>I10</td>
<td>Number of trial solutions allowed at each iteration.</td>
</tr>
<tr>
<td></td>
<td>21-30</td>
<td>I10</td>
<td>Plot code 1(0) - do (not) create plot file.</td>
</tr>
<tr>
<td></td>
<td>31-40</td>
<td>I10</td>
<td>0 Use numerical Laplace transform always. 1 Use numerical Laplace transform until numerical problems occur, then use analytical solution. 2 Use analytical solution always.</td>
</tr>
<tr>
<td>2-3</td>
<td>1-80</td>
<td>A80</td>
<td>Descriptive labels.</td>
</tr>
<tr>
<td>4,9</td>
<td></td>
<td></td>
<td>Parameter names ((P_3, X_3, \text{etc.}))</td>
</tr>
<tr>
<td>5,10</td>
<td>1-10,11-20,etc.</td>
<td>F10.5</td>
<td>Initial guesses for parameters</td>
</tr>
<tr>
<td>6,11</td>
<td></td>
<td>I10</td>
<td>Fitting code: (0)1 - (don't) fit this parameter.</td>
</tr>
<tr>
<td>7,12</td>
<td></td>
<td>F10.5</td>
<td>Lower limit allowed for parameter.</td>
</tr>
<tr>
<td>8,13</td>
<td></td>
<td></td>
<td>Upper limit allowed for parameter.</td>
</tr>
</tbody>
</table>

Each line in this file contains, in order, observed concentration and normalized time, formatted as 2F10.5. Table 4c contains the output file for the example contained in Table 1. The information contained in this file is self-explanatory for the most part. In order, the file gives:
Table 3. File of observed experimental concentration data and corresponding normalized time (used in Example 1a and b).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time (normalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>0.025</td>
</tr>
<tr>
<td>0.289</td>
<td>0.05</td>
</tr>
<tr>
<td>0.787</td>
<td>0.075</td>
</tr>
<tr>
<td>1.134</td>
<td>0.1</td>
</tr>
<tr>
<td>1.300</td>
<td>0.125</td>
</tr>
<tr>
<td>1.346</td>
<td>0.15</td>
</tr>
<tr>
<td>1.326</td>
<td>0.175</td>
</tr>
<tr>
<td>1.271</td>
<td>0.2</td>
</tr>
<tr>
<td>1.202</td>
<td>0.225</td>
</tr>
<tr>
<td>1.128</td>
<td>0.25</td>
</tr>
<tr>
<td>1.055</td>
<td>0.275</td>
</tr>
<tr>
<td>0.985</td>
<td>0.3</td>
</tr>
<tr>
<td>0.919</td>
<td>0.325</td>
</tr>
<tr>
<td>0.858</td>
<td>0.35</td>
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<tr>
<td>0.802</td>
<td>0.375</td>
</tr>
<tr>
<td>0.751</td>
<td>0.4</td>
</tr>
<tr>
<td>0.703</td>
<td>0.425</td>
</tr>
<tr>
<td>0.660</td>
<td>0.45</td>
</tr>
<tr>
<td>0.620</td>
<td>0.475</td>
</tr>
<tr>
<td>0.584</td>
<td>0.5</td>
</tr>
<tr>
<td>0.550</td>
<td>0.525</td>
</tr>
<tr>
<td>0.519</td>
<td>0.55</td>
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<tr>
<td>0.491</td>
<td>0.575</td>
</tr>
<tr>
<td>0.464</td>
<td>0.6</td>
</tr>
<tr>
<td>0.417</td>
<td>0.65</td>
</tr>
<tr>
<td>0.375</td>
<td>0.7</td>
</tr>
<tr>
<td>0.339</td>
<td>0.75</td>
</tr>
<tr>
<td>0.308</td>
<td>0.8</td>
</tr>
<tr>
<td>0.280</td>
<td>0.85</td>
</tr>
<tr>
<td>0.256</td>
<td>0.9</td>
</tr>
<tr>
<td>0.234</td>
<td>0.95</td>
</tr>
<tr>
<td>0.214</td>
<td>1.</td>
</tr>
<tr>
<td>0.197</td>
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<tr>
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<tr>
<td>0.167</td>
<td>1.15</td>
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<td>0.154</td>
<td>1.2</td>
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<td>0.142</td>
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<tr>
<td>0.132</td>
<td>1.3</td>
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<tr>
<td>0.122</td>
<td>1.35</td>
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<tr>
<td>0.113</td>
<td>1.4</td>
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<tr>
<td>0.105</td>
<td>1.45</td>
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<tr>
<td>0.098</td>
<td>1.5</td>
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<tr>
<td>0.091</td>
<td>1.55</td>
</tr>
<tr>
<td>0.085</td>
<td>1.6</td>
</tr>
<tr>
<td>0.080</td>
<td>1.65</td>
</tr>
<tr>
<td>0.075</td>
<td>1.7</td>
</tr>
<tr>
<td>0.070</td>
<td>1.75</td>
</tr>
<tr>
<td>0.065</td>
<td>1.8</td>
</tr>
<tr>
<td>0.061</td>
<td>1.85</td>
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<tr>
<td>0.057</td>
<td>1.9</td>
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<tr>
<td>0.054</td>
<td>1.95</td>
</tr>
<tr>
<td>0.051</td>
<td>2.</td>
</tr>
<tr>
<td>0.048</td>
<td>2.05</td>
</tr>
<tr>
<td>0.045</td>
<td>2.1</td>
</tr>
<tr>
<td>0.042</td>
<td>2.15</td>
</tr>
<tr>
<td>0.040</td>
<td>2.2</td>
</tr>
<tr>
<td>0.038</td>
<td>2.25</td>
</tr>
<tr>
<td>0.035</td>
<td>2.3</td>
</tr>
<tr>
<td>0.033</td>
<td>2.35</td>
</tr>
<tr>
<td>0.032</td>
<td>2.4</td>
</tr>
<tr>
<td>0.030</td>
<td>2.45</td>
</tr>
<tr>
<td>0.028</td>
<td>2.5</td>
</tr>
</tbody>
</table>
(i) descriptive title,
(ii) names and initial values of the TFM parameters,
(iii) iteration number and sum-of-squares for the given parameter values,
(iv) correlation matrix of the varied parameters,
(v) the \( R^2 \) value for the regression,
(vi) optimized parameter values and their 95% confidence limit bounds,
(vii) fitted and observed data as ordered by the input file,
(viii) fitted and observed data as ordered by the residual magnitude.

Finally, Table 7 contains the plot file for Example 1a. The file contains the experimental data, followed by the fitting results. Each line in the file contains

(i) concentration (observed or fitted)
(ii) measurement time
(iii) number of observation (corresponds to experimental-data file).

Data in the plot file can be accessed using the format: 2(1PE15.4),I3.

EXAMPLE APPLICATIONS

Three examples of the use of TFMFIT are given in the following.
The first example is based on a synthetic data set, while the second and third fit actual field breakthrough data.

The first example is designed to demonstrate (i) the importance of choosing an accurate set of initial estimates of the model parameters; and (ii) the effect of random noise in the data on the parameter estimates given by TFMFIT.
## Table 4a. TFMTFIT results for Example la.

### Nonlinear Least-Squares Analysis.

**Example la. Synthetic data.**  
Run on the University of California, Riverside VAX 8700.

#### Initial values of coefficients

<table>
<thead>
<tr>
<th>Name</th>
<th>Initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3</td>
<td>1.0000D+01</td>
</tr>
<tr>
<td>X3</td>
<td>1.0000D+00</td>
</tr>
<tr>
<td>Yo</td>
<td>2.0000D+00</td>
</tr>
<tr>
<td>B</td>
<td>7.0000D-01</td>
</tr>
<tr>
<td>R</td>
<td>1.5000D+00</td>
</tr>
<tr>
<td>W</td>
<td>5.0000D-01</td>
</tr>
<tr>
<td>D</td>
<td>4.0000D-01</td>
</tr>
<tr>
<td>C</td>
<td>3.0000D-01</td>
</tr>
</tbody>
</table>

### Iteration Summary

<table>
<thead>
<tr>
<th>Iteration</th>
<th>SSQ</th>
<th>P3</th>
<th>Yo</th>
<th>B</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8529D+01</td>
<td>1.0000D+01</td>
<td>2.0000D+00</td>
<td>7.0000D-01</td>
<td>1.5000D+00</td>
</tr>
<tr>
<td>1</td>
<td>6.8219D+00</td>
<td>1.0000D+00</td>
<td>4.3867D+00</td>
<td>6.4063D-01</td>
<td>1.4218D+00</td>
</tr>
<tr>
<td>2</td>
<td>4.7969D+00</td>
<td>1.0737D-01</td>
<td>1.9842D+00</td>
<td>1.0000D+00</td>
<td>2.2021D+00</td>
</tr>
<tr>
<td>3</td>
<td>4.3949D+00</td>
<td>2.9970D+00</td>
<td>2.3464D+00</td>
<td>1.0000D+00</td>
<td>1.0635D+00</td>
</tr>
<tr>
<td>4</td>
<td>3.5267D+00</td>
<td>3.8783D+00</td>
<td>2.5608D+00</td>
<td>1.0000D+00</td>
<td>5.8744D-01</td>
</tr>
<tr>
<td>5</td>
<td>5.2240D-01</td>
<td>6.1306D+00</td>
<td>2.5398D+00</td>
<td>1.0000D+00</td>
<td>5.7978D-01</td>
</tr>
<tr>
<td>6</td>
<td>1.2371D-01</td>
<td>8.0911D+00</td>
<td>1.7804D+00</td>
<td>1.0000D+00</td>
<td>6.6648D-01</td>
</tr>
<tr>
<td>7</td>
<td>2.1128D-02</td>
<td>8.4716D+00</td>
<td>1.6386D+00</td>
<td>1.0000D+00</td>
<td>7.3615D+01</td>
</tr>
<tr>
<td>8</td>
<td>1.3683D-02</td>
<td>8.3317D-01</td>
<td>1.5404D+00</td>
<td>1.0000D+00</td>
<td>7.8885D-01</td>
</tr>
<tr>
<td>9</td>
<td>9.5114D-03</td>
<td>8.1665D-01</td>
<td>1.4746D+00</td>
<td>1.0000D+00</td>
<td>8.3373D-01</td>
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<tr>
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<td>8.0340D-01</td>
<td>1.4239D+00</td>
<td>1.0000D+00</td>
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<tr>
<td>11</td>
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<td>1.0000D+00</td>
<td>9.0297D-01</td>
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<td>9.3020D-01</td>
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<tr>
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<td>7.8031D-01</td>
<td>1.3208D+00</td>
<td>1.0000D+00</td>
<td>9.5357D-01</td>
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<td>7.5984D+00</td>
<td>1.2022D+00</td>
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<td>1.0501D+00</td>
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<tr>
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<td>1.1090D+00</td>
<td>1.0000D+00</td>
<td>1.1398D+00</td>
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<tr>
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<td>7.8661D+00</td>
<td>1.0936D+00</td>
<td>1.0000D+00</td>
<td>1.1468D+00</td>
</tr>
<tr>
<td>17</td>
<td>9.7076D-04</td>
<td>7.6625D+00</td>
<td>1.0969D+00</td>
<td>1.0000D+00</td>
<td>1.1441D+00</td>
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<tr>
<td>18</td>
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<td>1.0959D+00</td>
<td>1.0000D+00</td>
<td>1.1450D+00</td>
</tr>
<tr>
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<td>1.1447D+00</td>
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</tbody>
</table>

### Correlation Matrix

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
</tr>
<tr>
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<td>-0.4948</td>
<td>1.0000</td>
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</tr>
<tr>
<td>3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
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<td>-0.9667</td>
<td>0.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Rsquare for regression = 0.999964965D+00.

### Nonlinear Least-Squares Analysis, Final Results.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Name</th>
<th>Value</th>
<th>S.E.Coeff.</th>
<th>T-Value</th>
<th>95% Confidence Limits</th>
</tr>
</thead>
<tbody>
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<td>Yo</td>
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<td>2.4983D-02</td>
<td>4.3880D+01</td>
<td>1.0461D+00</td>
</tr>
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<td>3</td>
<td>B</td>
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<tr>
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<tr>
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<td>Conc Obs</td>
<td>Conc Fit</td>
<td>Residual</td>
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<td>----------</td>
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<td>3.7780-02</td>
<td>-4.7830-03</td>
<td></td>
</tr>
<tr>
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<td>3.9780-02</td>
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<tr>
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<td>4.6740-03</td>
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<td>4.2000-02</td>
<td>4.6600-02</td>
<td>-4.6000-03</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.9000+00</td>
<td>5.7000-02</td>
<td>6.1530-02</td>
<td>-4.5340-03</td>
<td></td>
</tr>
<tr>
<td>62</td>
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Ordered by residual
Example 1a

Fig. 1a. Model fit for Example 1a.
A data set was created using TFMFIT (with MIT = 0 in the input data file) with the following parameters:

\[
\begin{align*}
\text{P}_3 &= 1 \\
\text{X}_3 &= 1 \\
\text{Y}_0 &= 1.1 \\
\text{B} &= 0.9 \\
\text{R} &= 1 \\
\text{W} &= 0.5 \\
\text{D} &= 0.4 \\
\text{C} &= 0.3
\end{align*}
\]

The results produced by the model were stored for the range \(0.025 \leq T \leq 2.5\), with an increment of 0.025 or 0.05, giving a total of 62 \((T, C)\) data pairs. These data were rounded to three decimal places (Table 3) and then used as the experimental data set. In Example 1a (cf. Table 1), the initial parameter estimates were assumed to be

\[
\begin{align*}
\text{P}_3 &= 10 \\
\text{Y}_0 &= 2 \\
\text{B} &= 0.7 \\
\text{R} &= 1.5
\end{align*}
\]

with the other parameters assumed known and set to their exact values. The results of this exercise are given in Table 4a, where the fitted values are found to be

\[
\begin{align*}
\text{P}_3 &= 0.766 \\
\text{Y}_0 &= 1.096 \\
\text{B} &= 1 \\
\text{R} &= 1.145
\end{align*}
\]

The model prediction using these parameters is compared with the input data in Fig. 1a. Although the fit is excellent, the fitting algorithm has converged to incorrect parameter values.

In the next case, Example 1b, the initial parameter guesses were altered to
\[ P_3 = 5 \quad \text{and} \quad B = 0.8 \]
\[ \gamma_0 = 1.5 \quad \text{and} \quad R = 1.1 \]

with results in Table 4b. With more accurate initial guesses, the results indicate a rapid convergence to the known parameter values. It is clear that the most sound procedure is to estimate as precisely as possible the allowable parameter ranges prior to, and independently of, fitting the data.

The effect of random noise in the data is illustrated in Example 1c. A pseudo-random error term was added to each of the synthetic concentration data used previously. The error terms were drawn from a Gaussian distribution with a mean and standard deviation of 0 and 0.05, respectively (IMSL routine G05DDF). Noisy data less than zero were reset to zero. Utilizing the same input parameters as Example 1b, the fitting algorithm gives the output shown in Table 4c. Figure 1b displays the best-fit curve compared with the noisy data. The disparity between the best-fit curve and the source data is apparent in the 95% confidence limits of the parameters given in Table 4c. Although it is true that the range of each parameter encompasses the known value, it is also clear that the random noise in the initial data set decreases the reliability of parameter estimates. The true values lie close to the center of the given ranges because of the simple structure of the random errors. We observe that random noise with a non-zero drift component, or noise that is multiplicative, will produce correspondingly different behavior in the parameter estimates and ranges. The major point is that the nature of random noise has a direct effect on the best-fit parameters obtained.
Table 4b. TFMTF results for Example 1b.

Nonlinear Least-Squares Analysis.

Example 1b. Synthetic data.
Run on the San Diego Supercomputer Center's CRAY X-MP/48.

Initial values of coefficients

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Nonlinear Least Squares Analysis, Final Results.

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Table 4c. TFMFIT results for Example lc.

Nonlinear Least-Squares Analysis.

Example lc. Synthetic data with some random noise.
Run on the San Diego Supercomputer Center’s CRAY X-MP/48.

**Initial values of coefficients**

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<thead>
<tr>
<th>Name</th>
<th>Initial value</th>
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<td>P3</td>
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<tr>
<td>X3</td>
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<tr>
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**Correlation Matrix**

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R-squared for regression = 0.9904731890e+00.

Nonlinear Least Squares Analysis, Final Results.

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<tr>
<th>Variable</th>
<th>Name</th>
<th>Value</th>
<th>S.E.Coeff.</th>
<th>T-Value</th>
<th>95% Confidence Limits</th>
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Ordered by computer input

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<th>Residual</th>
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Ordered by residual.
Example 1c

\[ g(t) \]

\[ \text{Time} \]

Fig. 1b. TFMFIT results for the noisy synthetic data.

The second and third examples are based on data obtained from a large-scale solute transport experiment at the Borden site, Ontario, Canada (Roberts and Mackay, 1986). The details of the experiment are readily available (e.g., Freyberg, 1986; Goltz and Roberts, 1986; Mackay et al., 1986; Sudicky, 1986), and will not be repeated here except in the context of using TFMFIT. In the following the measured breakthrough curves of two solutes—carbon tetrachloride and tetrachloroethylene—are considered.

As shown by eq. 15, the pdf \( g(T) \) is averaged over \( Y \) from \( Y = X_3 \) to \( Y = Y_0 \), where \( X_3 \leq Y_0 \). From eq. 16 it can be seen that \( Y = X_3 \) implies \( X_1 = X_2 = 0 \). Thus, the pdf is averaged from a specified position on
the $X_3$ axis ($X_3 = 0$ or $1$) to $Y_0$. In principle, the limits of eq. 15 can be specified according to the location of the data, given that data are often collected away from the $X_3$ axis. This would require, however, a priori knowledge of $P_i$, $i=1,2,3$, in eq. 16. Because this information is unavailable, it is recommended that data be fitted using $X_3 = 0$ or $1$. TFMFIT has been restricted to these possibilities.

In Example 2, we consider first the measured breakthrough of carbon tetrachloride at a sampling location in the Borden aquifer (see Roberts et al., 1986, for details). The physical characteristics of this chemical, as well as tetrachloroethylene (considered in Example 3), with respect to the Borden site have been documented by Curtis et al. (1986),

**Example 2**

![Graph](image)

**Fig. 2.** TFMFIT results for the carbon tetrachloride data from the Borden transport experiment.
Goltz and Roberts (1986), Mackay et al. (1986) and Roberts et al. (1986). As a first approximation, we assume that carbon tetrachloride moves in a fully saturated medium in which the mobile liquid content is the entire water content \( B = 1 \) and that it does not undergo first-order decay \( C = 0 \). The required solution is then given by eq. 25 with \( C = 0 \).

The model is given in dimensionless form. The data, therefore, must be given in dimensionless form also, so that the physical meaning of the parameters may be determined. For the time variable, the following operation is performed: \( T = vt/L \). This definition of dimensionless time is a specialization of that given below eq. 7 for the case \( \theta_m = \theta \). This condition seems to be a reasonable assumption for the Borden aquifer. For porous media not satisfying this condition, \( \theta_m \) must be estimated a priori, but it can be seen from eqs. 6 and 7 that \( T \) and \( R \) are inversely proportional, so that any error in defining \( T \) will adjust \( R \) proportionally (cf. Barry, 1988). Secondly, the model assumes a Dirac pulse of solute as the initial condition. Although the exact form of the initial condition becomes less important with increasing time as the solute pulse loses its "memory" of its initial shape, normalization of the concentration data is still required. The concentration data were normalized to a dimensionless variable according to

\[
C_{\text{norm}} = \frac{C_{\text{meas}}}{vA_r} \tag{26}
\]

where \( C_{\text{norm}} = \) normalized concentration, \( C_{\text{meas}} = \) measured concentration, and \( A_r \) is given by

\[
A_r = \int_0^\infty C_{\text{meas}}(L,t)dt \tag{27}
\]

The results of the fitting for this case are given in Fig. 2 and Table 5. Figure 2 indicates that a good fit of the data has been
obtained. This is confirmed by the data presented in Table 5. An interesting result in this table is contained in the correlation matrix, where it is shown that the correlation of $Y_0$ with itself is 0. This result implies that varying $Y_0$ has no effect on the quality of the model fit to the data. Of course, this result is theoretically invalid. However, it holds in that there is no difference numerically. The reason for insensitivity becomes clear on examination of eq. 25. When $P_3$ is large then the terms containing $Y_0$ become relatively small, and their effect on the solution becomes negligible. In such cases, the fitted value of the parameter has little significance.

The final example (Example 3) uses breakthrough curve data for tetrachloroethylene, also from the Borden experiment. The assumptions

Example 3

![Graph](image)

Fig. 3. TFMFIT results for the tetrachloroethylene data from the Borden experiment.
Table 5. TF MFIT results for Example 2.

Nonlinear Least-Squares Analysis.

Example 2. Borden Experiment Data. Carbon Tetrachloride
Run on the San Diego Supercomputer Center's CRAY X-MP/48.

Initial values of coefficients

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<tr>
<td>X3</td>
<td>1.0000e+00</td>
</tr>
<tr>
<td>Yo</td>
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<tr>
<td>B</td>
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<tr>
<td>R</td>
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<tr>
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<td>0.0000e+00</td>
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<tr>
<td>D</td>
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<tr>
<td>C</td>
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</table>

Iteration | SSQ  | P3     | Yo     | R     |
----------|------|--------|--------|-------|
   0      | 6.7241e+00 | 4.0000e+01 | 1.4000e+00 | 2.0000e+00 |
   1      | 4.6922e+00 | 4.0967e+01 | 4.6245e+01 | 1.5904e+00 |
   2      | 6.9345e-01 | 4.5320e+01 | 4.6245e+01 | 1.7561e+00 |
   3      | 4.3173e-01 | 5.5005e+01 | 4.6245e+01 | 1.7429e+00 |
   4      | 4.2567e-01 | 5.6833e+01 | 4.6245e+01 | 1.7426e+00 |
   5      | 4.2564e-01 | 5.6937e+01 | 4.6245e+01 | 1.7424e+00 |
   6      | 4.2564e-01 | 5.6942e+01 | 4.6245e+01 | 1.7423e+00 |

Correlation Matrix

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R squared for regression = 0.97427779735e+00.

Nonlinear Least Squares Analysis, Final Results.

<table>
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<tr>
<th>Variable</th>
<th>Name</th>
<th>Value</th>
<th>S.E.Coeff.</th>
<th>T-Value</th>
<th>95% Confidence Limits</th>
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made regarding the model parameters for carbon tetrachloride apply to
tetachloroethylene except that, in this case, some kinetically-controlled
partitioning of the solute between the liquid and solid phases is
expected ($f < 1$ in eq. 8; i.e., $B < 1$). The parameters $D$ and $C$ (eqs.
11 and 12) were assigned values of zero based on the physical behavior of
the chemical. The other parameters were fitted with the results given
in Table 6 and Fig. 3. Again, the optimal model fit is quite good and
the model is insensitive to $Y_0$, as shown by the correlation matrix in
Table 6.

Plotting the TFMFIT Results

The data provided in the main TFMFIT output file (Tables 4-6) are
essential for the purpose of model fitting. Often, however, a plot of
the experimental data and model fit is required. The figures in this
document were produced using the TFMPLT code contained in Appendix 3.
TFMFIT produces, if requested, a plot file. A particular case is given
in Table 7, which is based on Example 1a (Fig. 1a). TFMPLT reads the
plot file data, as well as a parameter file, to produce a device-
compatible file. In creating TFMPLT, we have used the DISSPLA software
package (Integrated Software Systems Corporation, 1985). Therefore,
those wishing to use TFMPLT will have to have access to the DISSPLA
library on their system. The output devices supported by this soft-
ware are IMAGEN and Tektronics terminals.
Table 6. TFMFIT results for Example 3.

Nonlinear Least-Squares Analysis.

Example 3. Borden Experiment Data, Tetrachloroethylene
Run on the San Diego Supercomputer Center's CRAY X-MP/48.

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No further decrease in SSQ obtained after 30 trials.

Correlation Matrix

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Rsquare for regression = 0.8841283406e+00.

Nonlinear Least Squares Analysis, Final Results.

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<tr>
<td>7.0000e-02</td>
<td>1.7500e+00</td>
<td>47</td>
</tr>
<tr>
<td>6.5000e-02</td>
<td>1.8000e+00</td>
<td>48</td>
</tr>
<tr>
<td>6.1000e-02</td>
<td>1.8500e+00</td>
<td>49</td>
</tr>
<tr>
<td>5.7000e-02</td>
<td>1.9000e+00</td>
<td>50</td>
</tr>
<tr>
<td>5.4000e-02</td>
<td>1.9500e+00</td>
<td>51</td>
</tr>
<tr>
<td>5.1000e-02</td>
<td>2.0000e+00</td>
<td>52</td>
</tr>
<tr>
<td>4.8000e-02</td>
<td>2.0500e+00</td>
<td>53</td>
</tr>
<tr>
<td>4.5000e-02</td>
<td>2.1000e+00</td>
<td>54</td>
</tr>
<tr>
<td>4.2000e-02</td>
<td>2.1500e+00</td>
<td>55</td>
</tr>
<tr>
<td>4.0000e-02</td>
<td>2.2000e+00</td>
<td>56</td>
</tr>
<tr>
<td>3.8000e-02</td>
<td>2.2500e+00</td>
<td>57</td>
</tr>
<tr>
<td>3.5000e-02</td>
<td>2.3000e+00</td>
<td>58</td>
</tr>
<tr>
<td>3.3000e-02</td>
<td>2.3500e+00</td>
<td>59</td>
</tr>
<tr>
<td>3.2000e-02</td>
<td>2.4000e+00</td>
<td>60</td>
</tr>
</tbody>
</table>
An example parameter file required by TFMPLLOT is given in Table 8. This file was used to create Fig. 2. The structure of the file is as follows: line 1 controls the total size of the plot; line 2 controls the position of the axes relative to the assumed physical edges of the plot (these first two lines normally will be unchanged); lines 3 and 4 give the limits and tick increments on the x and y axes, respectively; and lines 4-7 contain descriptive labels.

Table 8. Parameter file for TFMPLLOT. An explanation of the file is given in the text.

```
xlong,ylong  * 9   * 5.5  ********
xphy yphy    * 1.5 * .5  ********
xorig ste max* 0   * 1.   * 3.5 *
yorig ste max* 0   * .5  * 1.5 *
title        *Example 2 *
x label      * Time *
y label      * g(T)  *
REFERENCES


APPENDIX 1a. FORTRAN SOURCE CODE FOR TFMFIT
(SINGLE PRECISION CRAY VERSION)

Copyright, the Regents of the University of California.
Nonlinear least squares fitting for the TFM model. The fitting portion
of the code is derived from the CXTFIT program in: Parker, J. C., and
M. Th. van Genuchten. 1984. Determining transport parameters from
laboratory and field tracer experiments. Bulletin 84-3, Virginia
Agricultural Experiment Station, Blacksburg. The program is intended to
run on CRAY machines using CRAY FORTRAN.

program tfmfit
dimension (300), f(300), r(300), delz(300,8), th(16), b(16), e(8), p(8)

z, phi(8), q(8), isort(300), tb(16), a(8,8), d(8,8), x(300),

z, bmax(8), bmin(8), bi(16), sumtot(300), ssqtot(300),

z, sumt(300), sum1t(8), sum2t(8), sum3t(8), sec(8),

z, tvalue(8), index(8), tpcos(8), tmcos(8), temp1(300),

z, yyi(300), th(8), tsec(8)

common/modat1/x, index, nob, nvar, nu1, nu2, iopt
character*80, b#4, tit1#4, tit2#4, f#8
parameter (stopcr=1.e-4, p3low=1.e-6, blow=1.e-6)
datanvar, nu1, nu2/8, 9, 16/

The following two subroutine calls are for CRAY machines running
CTSS (Cray Time Sharing System). This call is to allow bidirectional
memory on the CRAY.

call q8ebm

Send IMSL error and warning messages to the file named imslerr; the
terminal is unit 6.

call ugetoi(3, nin, 5)
call link(3, nin, 5)
call ugetio(3, nin, 5)
call link('unit5=(imslerr,create,text),unit6=tty//')
go to 2
1 write(6, 1000)
go to 2
2 write(6, 2000)
read(6, 2001) fname
if (fname.eq. ' ') fname = 'tmfdat'
open(2, file=fname, status='old', err=1)
go to 4
3 write(6, 1000)
go to 4
4 write(6, 2002)
read(6, 2001) fname
if (fname.eq. ' ') fname = 'tfmout'
open(1, file=fname, status='new', err=3)

There are ncase fittings to do.

do 150 ncase=1, 20

Read input parameters.

read(2, 1006, end=999) mit, maxty, iplot, iopt

nvar = number of coefficients (8, see parameter statement above).
nob = number of observations (300 maximum, see experimental data
every at label 10 below; can be increased if necessary).
mit = maximum number of iterations (mit=0 solves the direct problem
only).
maxtry = maximum number of trial solutions at iteration before quitting. It is suggested that maxtry be in the range 10 to 50; smaller values reduce the run time but you may miss a convergent solution.

iplot = code for plot file output:
0 = no plot file; 1 = plot file is output.

iopt = solution procedure option;
0 - use numerical Laplace transform inversion always;
1 - use numerical Laplace transform inversion until numerical problems occur then use analytical solution;
2 - use analytical solution always.

if (mit.ne.0) then
  For mit = 0, do not produce a plot file.
    if (iplot.eq.1.and.iplot1.ne.1) then
      goto6
      write(6,1000)
      write(6,2003)
      read(6,2001)fname
      if (fname.eq.' ')fname='tfmplt'
      open(3, file=fname,status='new',err=5)
      iplot1=1
    endif
  else
    iplot=0
  endif
  if (maxtry.eq.0) maxtry=5
  if (mit.ne.0) write(1,1035)
  write(1,1002)
  do7i=1,2
    read(2,1001)title
    write(1,1001)title
  enddo

Input the model parameters.

do8n=1,2
  n14=n*n+14
  n7=n*n7
  nvar7=nvar+n7

Read the coefficient names.

n1=n14-13
n2=min0 (n14,nu2)
read (2,1004) (bi(i),i=n1,n2)

Read the initial parameter estimates.

n1=nvar7-6
n2=min0 (nvar7,nu2)
read (2,1005) (b(i),i=n1,n2)

Read the parameter indices.

n1=n7-6
n2=min0 (n7,nvar)
read (2,1006) (index(i),i=n1,n2)
Read in the constraints on parameter values. bmin and bmax are the arrays containing the minimum and maximum constraints. bmin(i) = bmax(i) will omit constraint on parameter i.

read(2,1005) (bmin(i),i=n1,n2)
read(2,1005) (bmax(i),i=n1,n2)

Check that the X3 index is set to 0 (i.e., X3 cannot be fitted).

if(index(2).ne.0) then
  write(6,2015)
  index(2)=0
endif

Check that the constraints on initial parameter values are allowable.

if(b(9).le.0.) then
  b(9)=p3low
  write(6,2006)
endif
if(b(10).ne.0..and.b(10).ne.1.) then
  write(6,2007)
  stop
endif
if(b(10).eq.0.) then
  if(b(11).le.b(10)) then
    write(6,2008)
    stop
  endif
else
  if(b(11).le.b(10)) then
    write(6,2009)
    stop
  endif
endif
if(b(12).le.0..or.b(12).gt.1.) then
  write(6,2010)
  stop
endif
if(b(13).lt.0.) then
  b(13)=0.
  write(6,2011)
endif
if(b(14).lt.0.) then
  b(14)=0.
  write(6,2012)
endif
if(b(15).lt.0.) then
  b(15)=0.
  write(6,2013)
endif
if(b(16).lt.0.) then
  b(16)=0.
  write(6,2014)
endif

Check that the parameter ranges are correct.

if(bmin(1).ne.bmax(1).and.index(1).eq.1) then
  if(bmin(1).le.0.) then

write(6,2016)
  bmin(1)=p3low
endif
endif
if (bmin(3).ne.bmax(3).and.index(3).eq.1) then
  if (b(10).eq.0.) then
    if (bmin(3).le.b(10)) then
      write(6,2017)
      stop
    endif
  endif
  if (b(10).eq.1.) then
    if (bmin(3).le.b(10)) then
      write(6,2018)
      stop
    endif
  endif
endif
endif
if (bmin(4).ne.bmax(4).and.index(4).eq.1) then
  if (bmin(4).le.0.) then
    write(6,2019)
    bmin(4)=b3low
  endif
  if (bmax(4).gt.1.) then
    write(6,2020)
    bmax(4)=1.
  endif
endif
endif
if (bmin(5).ne.bmax(5).and.index(5).eq.1) then
  if (bmin(5).lt.0.) then
    write(6,2021)
    bmin(5)=0.
  endif
endif
endif
if (bmin(6).ne.bmax(6).and.index(6).eq.1) then
  if (bmin(6).lt.0.) then
    write(6,2022)
    bmin(6)=0.
  endif
endif
endif
if (bmin(7).ne.bmax(7).and.index(7).eq.1) then
  if (bmin(7).lt.0.) then
    write(6,2023)
    bmin(7)=0.
  endif
endif
endif
if (bmin(8).ne.bmax(8).and.index(8).eq.1) then
  if (bmin(5).lt.0.) then
    write(6,2024)
    bmin(5)=0.
  endif
endif
endif
write(1,1007)
do9i=1,nvar
  j=2*i-1
  write(1,1008)bi(j),bi(j+1),b(i+nvar)
go to 11
Read in the experimental data.
go to 11
write(6,1000)
write(6,2004)
read(6,2001)fname
if(fname.eq.'')fname='exptdata'
open(4,filen=fname,status='old',err=10)
d012i=1,300
read(4,1005,end=13)y(i),x(i)
nob=i-1
write(6,2005)nob
nob1=i
close(4)

Check that t > 0 for each datum.

d014i=1,nob
if(x(i).le.0.)then
  write(6,2026)
  stop
endif
continue

Check that the data outnumber the number of variables to be fitted.

ncnvar=0
do15i=1,nvar
  if(index(i).eq.1)ncnvar=ncnvar+1
continue
if(ncnvar.ge.nob)then
  write(6,2025)
  stop
endif

Rearrange the variable arrays.

np=0
do19i=nul1,nul2
  tb(i)=b(i)
d020i=nul1,nul2
  invar=i-nvar
  if(index(invar).eq.0)goto20
  np=np+1
  k=2*np-1
  j=2*invar-1
  tit11=bj(j)
  tit12=bj(j+1)
  b(k)=tit11
  b(k+1)=tit12
  b(np)=b(i)
  tb(np)=b(i)
  th(np)=b(np)
  bmin(np)=bmin(invar)
  bmax(np)=bmax(invar)
  th(i)=b(i)

Evaluate the initial residual vector.

ga=.02
nit=0
np2=2*np
callmodel(th,f)
if (mit.eq.0) goto 140
ssq = 0
do 31 i = 1, nob
   r(i) = y(i) - f(i)
31
ssqtot(i) = r(i) * r(i)
do 32 i = 1, nob
ssq = ssq + ssqtot(i)
write (1, 1011) (bi(j), bi(j+1), j = 1, np2, 2)
write (1, 1012) nit, ssq, (b(i), i = 1, np)
c
Iterate to find the optimal model fit.
c
nit = nit + 1
ntrial = 0
ga = .1 * ga
do 34 j = 1, np
temp1(j) = th(j)
if (nit.eq.1) then
do 35 j = 1, np
e(j) = 1.
endif
do 38 j = 1, np
   th(j) = 1.01 * th(j)
   if (th(j).eq.0.) th(j) = .01
   q(j) = 0.
call model (th, delz(1, j))
do 36 i = 1, nob
   delz(i, j) = delz(i, j) - f(i)
   q(j) = q(j) + delz(i, j) * r(i)
   q(j) = 100. * q(j) / th(j)
38
th(j) = temp1(j)
c
q = xt * r (steepest descent).
c
do 44 i = 1, np
do 42 j = 1, i
   sum = 0.
do 40 k = 1, nob
   sumtot(k) = delz(k, i) * delz(k, j)
do 41 k = 1, nob
   sum = sum + sumtot(k)
if (sum.ne.0.) then
d(i, j) = 10000. * sum / th(i) / th(j)
else
d(i, j) = 0.
endif
do 42
   d(j, i) = d(i, j)
   e(i) = sqrt(d(i, i))
44
if (e(i).eq.0.) e(i) = 1.e-30
50
do 52 i = 1, np
do 52 j = 1, np
   a(i, j) = d(i, j) / e(i) / e(j)
c
a is the scaled moment matrix.
c
do 54 i = 1, np
   p(i) = q(i) / e(i)
54
   phi(i) = p(i)
   a(i, i) = a(i, i) + ga
call matinv (a, np, p)
p/e is the correction vector.

step=1.
do56i=1,np
  tb(i)=p(i)*step/e(i)+th(i)
do58i=1,np
  if (bmin(i).eq.bmax(i)) goto58
  if (tb(i).gt.bmax(i)) tb(i)=bmax(i)
  if (tb(i).lt.bmin(i)) tb(i)=bmin(i)
  p(i)=(tb(i)-th(i))*e(i)/step
continue
do59i=1,np
thh(i)=th(i)+tb(i)
do62i=1,np
  if (thh(i)) 66,66,62
continue
sumb=0.
call model(tb,f)
do64i=1,nob
  r(i)=y(i)-f(i)
do65i=1,nob
sumt(i)=r(i)*r(i)
do65i=1,nob
sumb=sumt(i)+sumb
sum1=0.
sum2=0.
sum3=0.
do68i=1,np
  sum1t(i)=p(i)*phi(i)
  sum2t(i)=p(i)*p(i)
  sum3t(i)=phi(i)*phi(i)
do69i=1,np
  sum1=sum1+sum1t(i)
  sum2=sum2+sum2t(i)
  sum3=sum3+sum3t(i)
arg=0.
sum=2*sum3
if (sum.gt.0.) arg=1/sqrt(sum)
arg=0.
if (np.gt.1) arg=1-sqrt(1.-arg*arg)
if (arg.eq.0. .and. arg1.eq.0.) arg=1.
angle=57.29579*atan2(arg1,arg)
do72i=1,np
  if (thh(i)) 74,74,72
continue
ntrial=ntrial+1
if (ntrial.gt.nmaxtry) goto95
if (sumb/ssq-1.) 80,80,74
if (angle-30.) 76,76,78
step=-.5*step
goto55

Print the coefficients after each iteration.

c
continue
do82i=1,np
  th(i)=tb(i)
write(1,1012) nit,sumb,(th(i),i=1,np)
do86i=1,np
    if(abs(p(i)*step/e(i))/(1.e-20+abs(th(i)))-
       stopcr) 86, 86, 94
 86 continue
 goto96
 ssq=sumb
 if(nit.lt.mit)goto33
 if(nit.eq.mit)write(1,1034)mit
 goto96
 write(1,1038)maxtry

 End of the iteration loop.

 callmatinv(d,np,p)

 Write the correlation matrix.

do98i=1,np
 e(i)=sqrt(abs(d(i,i)))
do99i=1,np
 if(e(i).eq.0.)e(i)=1.e-30
 if(np.eq.1)goto104
 write(1,1013)(i,i=1,np)
do102i=1,np
   do100j=1,i
    a(j,i)=d(j,i)/e(i)/e(j)
   write(1,1014)i,(a(j,i),j=1,i)

 Calculate the regression coefficient.

 sumc=0.
 sumc2=0.
do105i=1,nob
 yyi(i)=y(i)*y(i)
do106i=1,nob
   sumc=sumc+yy(i)
 sumc2=sumc2+yy(i)
 vinny=nob
 rsq=1.-sumb/(sumc2-sumc*sumc/vinny)
 write(1,1041)rsq

 Calculate the 95% confidence interval.

 qx=nob-np
 z=1./qx
 sdev=sqrt(z*sumb)
tvar=1.96+z*(2.3779+z*(2.7135+z*(3.187936+2.466666*z*z)))
 if(np.eq.1)write(1,1042)
 if(np.gt.1)write(1,1015)
do107i=1,np
    secof(i)=e(i)*sdev
 tvalue(i)=th(i)/secof(i)
do108i=1,np
 tsec(i)=tvar*secof(i)
do109i=1,np
   tmcoe(i)=th(i)-tsec(i)
do110i=1,np
    tpmoe(i)=th(i)+tsec(i)
 if(np.eq.1)then
   do110i=1,np
    j=2*i-1
else
    do111i=1,np
    j=2*i-1
    write(1,1016)i,bi(j),bi(j+1),th(i),secgf(i),
    tvalue(i),tmcof(i),tpcof(i)
endif

Prepare the final output.

lslrt(1)=1
do112j=2,nob
    temp1(j)=abs(r(j))
    do117j=2,nob
        k=j-1
        do113l=1,k
            if(temp1(j)-abs(r(lslrt(1))))114,114,113
        continue
        lslrt(j)=j
        goto117
    enddo
    k=k-1
    lslrt(kk+1)=lslrt(kk)
    if(kk-1)116,116,115
    lslrt(1)=j
continue
write(1,1017)
do118i=1,nob
    write(1,1018)i,x(i),y(i),f(i),r(i)
    if(iplot.ne.0)then
        do119i=1,nob
            write(3,1047)y(i),x(i),i
        enddo
        do120i=1,nob
            write(3,1047)f(i),x(i),i
        enddo
    endif
write(1,1019)
do121i=1,nob
    j=lslrt(nob1-i)
write(1,1018)j,x(j),y(j),f(j),r(j)
goto150
write(1,1030)(j,j=1,nx)
do145i=1,nob
write(1,1033)i,x(i),f(i)

End of this job.

continue
stop
format('Choose another file name.')(a80)
format(/)
format(7(2x,2a4))
format(7f10.5)
format(7i10)
format(/x,'Initial values of coefficients'/x,30(1h=)/3x,
    'Name',4x,'Initial value')
format(x,2a4,4(1h.),1pe12.4)
format(/x,'Iteration',6x,'SSQ',4x,8(5x,2a4))
format(x,i5,3x,1pe13.4,2x,8(1pe13.4))
format (/3x,'Correlation Matrix',/3x,18(1h=)/4x,10(4x,i2,5x))
format (x,3,i3,10(2x,f7.4,2x))
format (/,'Nonlinear Least Squares Analysis, Final Results.'
z,/,48(1h=)/57x,'95% Confidence Limits'/x,'Variable',3x,'Name'
z,7x,'Value',7x,'S.E.Coeff.',2x,'T-Value',4x,'Lower',9x,'Upper')
format (4x,i2,3x,2a4,1pe13.4,2x,1pe13.4,4,1e10.3,1pe12.4,
x,1pe12.4)
format (/,29x,'Ordered by computer input',/2x,'No.',4x,' T ',
z,8x,'Conc Obs',6x,'Conc Fit',6x,'Residual')
format (x,i3,x,1pe12.3,3(2x,1pe12.3))
format (/,29x,'Ordered by residual',/2x,'No.',4x,' T ',
z,8x,'Conc Obs',6x,'Conc Fit',6x,'Residual')
format (/,'Results for initial coefficient values',/x,'No.',
z,8x,' T ',7x,' Conc ')
format (x,i2.2(3x,1pe12.4))
format (/,'Convergence criteria not met in',i3,' iterations.'
format (5x,/, 'Nonlinear Least-Squares Analysis.')
format (/,'No further decrease in SSQ obtained after ',i2,
z,' trials.')
format (/,'Rsquare for regression =',e20.10,')')
format (x,,'Nonlinear Least Squares Analysis, Final Results.'
z,49(1h=)/57x,'95% Confidence Limits'/x,'Variable',3x,'Name'
z,8x,'Value',8x,'S.E.Coeff.',6x,'Lower',10x,'Upper')
format (x,i2,6x,2a4,x,1pe13.4,3x,1pe13.4,x,1pe13.4,2x,
z,1pe13.4)
format (2(1pe15.4),i3)
format ('Enter the name of the input data file',
' (default = tfmdat).')
format (a8)
format ('Enter the name of the primary output file',
' (default = tfmout).')
format ('Enter the name of the plot output file',
' (default = tmplt).')
format ('Enter the name of the file containing the ',
' experimental data (default = exptdata).')
format ('There were ',i3,' experimental data read.')
format ('P3 must not be less than zero, it has been reset',
' to zero.')
format ('Set X3 as zero or one in the data file and rerun',
' the program.')
format ('Y must be greater than X3 (zero). Reset Y in the',
' data file and rerun the program.')</format('Y must be greater than X3 (one). Reset Y in the',
' data file and rerun the program.')</format('B must not be less than or equal to zero or greater',
' than one.','Reset B in the data file and rerun the program.')
format ('R must not be less than zero, it has been reset ',
' to zero.')
format ('W must not be less than zero, it has been reset ',
' to zero.')
format ('D must not be less than zero, it has been reset ',
' to zero.')
format ('C must not be less than zero, it has been reset ',
' to zero.')
format ('X3 cannot be fitted. INDEX(2) is reset to 0.')
format ('The minimum value of P3 cannot be less than or equal',
' to 0. It ', 'has been reset to P3low.')
format ('The minimum value of Yo must be greater than 0 (x3)',
' to 0. It ', 'Reset the lower limit on Yo and rerun.')
format ('The minimum value of Yo must be greater than 1 (x3).')
format('The minimum value of B cannot be less than or equal to 0.',/
   'It has been reset to Blow.')
format('The maximum value of B cannot be greater than 1.',/
   'It has been reset to one.')
format('The minimum value of R cannot be less than 0.',/
   'It has been reset to zero.')
format('The minimum value of W cannot be less than 0.',/
   'It has been reset to zero.')
format('The minimum value of D cannot be less than 0.',/
   'It has been reset to zero.')
format('The minimum value of C cannot be less than 0.',/
   'It has been reset to zero.')
format('The experimental data must outnumber the number of parameters being fitted.')
format('At least one time in the data file is less than or equal to zero. Check and rerun.')
end
subroutinematinv(a,np,b)

Purpose: perform matrix inversion for parameter estimation.
dimensionpp(8), a(8,8), b(16), index(8,2)
do2j=1,8
index(j,1)=0
i=0
amax=-1.
do10j=1,np
   if(index(j,1))10,6,10
do9k=1,np
   if(index(k,1))9,8,9
p=abs(a(j,k))
   if(p.le.amax)goto9
   ic=k
   amax=p
9 continue
10 continue
   if(amax)30,30,14
index(ic,1)=ir
   if(ir.eq.ic)goto18
do15i=1,np
pp(i)=a(ir,i)
do16i=1,np
   a(ir,i)=a(ic,1)
a(ic,1)=pp(i)
p=b(ir)
b(ir)=b(ic)
b(ic)=p
i=i+1
index(i,2)=ic
p=1./a(ic,ic)
a(ic,ic)=1.
do20i=1,np
   a(ic,1)=a(ic,1)*p
   b(ic)=b(ic)*p
do24k=1,np
   if(k.eq.ic)goto24
   p=a(k,ic)
a(k,ic)=0.
do221=1,np
a(k,1)=a(k,1)-a(ic,1)*p
b(k)=b(k)-b(ic)*p
continue
goto4
ic=index(i,2)
ir=index(ic,1)
d027k=1,np
pp(k)=a(k,ir)
d028k=1,np
a(k,ir)=a(k,ic)
a(k,ic)=pp(k)
i=i-1
continue
if(i)26,32,26
return
end
subroutinemodel(bn,ycalc)
dimensionycalc(300),bn(16),c(8),index(8),x(300)
parameter(p3low=1.e-6,blow=1.e-6)
common/modat1/x,index,nob,nvar,nu1,nu2,iopt

Update the coefficient array.

k=0
d02i=nu1,nu2
if(index(i-nvar).eq.0)goto2
k=k+1
bn(i)=bn(k)
continue
do5i=1,nvar
c(i)=bn(nvar+i)

Check the parameter ranges.

if(index(1).eq.1)then
  if(c(1).le.0.)c(1)=p3low
endif
if(index(3).eq.1)then
  if(c(3).le.c(2))c(3)=c(2)+1.e-10
endif
if(index(4).eq.1)then
  if(c(4).gt.1.)c(4)=1.
  if(c(4).le.0.)c(4)=blow
endif
if(index(5).eq.1)then
  if(c(5).lt.0.)c(5)=0.
endif
if(index(6).eq.1)then
  if(c(6).lt.0.)c(6)=0.
endif
if(index(7).eq.1)then
  if(c(7).lt.0.)c(7)=0.
endif
if(index(8).eq.1)then
  if(c(8).lt.0.)c(8)=0.
endif

Call the TFM model function.
callzres(ycalc,x,c,nob)
return
end
subroutine zres(zfinv,zt,zc,n)
implicit complex(a-h,o-y)
external
dimension zt(n), zfinv(n), zc(8), zx(300), index(8)
common/modat1/zx,index,nob,nvar,nub,nu1,nu2,i,opt/rw/p3,x3,y,b,
     r,w,d,c
datanotice/1/

The following parameters are for the IMSL Laplace inversion routine. The
inversion is accurate to nsig significant figures. The maximum
number of iterations for each inversion is kmax. See the IMSL manual
for details.

parameter (nsig=4,kmax=499)
if (iopt.eq.2) then
   call realtime (zc,zt,zfinv,n)
   return
end if
icount=0
p3=cmplx(zc(1),0.)
x3=cmplx(zc(2),0.)
y=cmplx(zc(3),0.)
b=cmplx(zc(4),0.)
r=cmplx(zc(5),0.)
w=cmplx(zc(6),0.)
d=cmplx(zc(7),0.)
c=cmplx(zc(8),0.)

The function root calculates a number greater than or equal to the
real part of the maximum of the singularities of the function to be
inverted. The argument is a dummy parameter.

alpha=root(op)
zzz=f1(alpha)
if (zzz.lt.0.) then
   zalpha=alpha
   alpha=alpha-cmplx(1.e-6*zalpha,0.)
   zzz=f1(alpha)
endif
icount=icount+1
if (icount.le.10.and.zzz.lt.0.) goto 1
if (icount.gt.10) write (6,4)
zalpha=alpha

The estimate has been found; proceed to the inversion using the IMSL
numerical Laplace transform inverter.

call flinv(f,n,zt,zalpha,nsig,kmax,zfinv,ier)
do2i=1,n
   if (zfinv(i).lt.0.) zfinv(i)=0.
   if (ier.eq.0) return
2
Stop printing error messages for more than 10 errors.

ierc=ierc+1
if (ierc.eq.11) write(6,9)
if (ierc.gt.10) goto 3
write (5, 6) ier, (zc (i), i=1, 8)
if (ier.eq.129) then
  write (6, 6)
  goto 3
endif
if (ier.eq.130) then
  write (6, 7)
  goto 3
endif
write (6, 8)
if (iopt.eq.1) then
  call realtime (zc, zt, zfinv, n)
  if (notice.eq.1) then
    notice=0
    write (6, 11)
  endif
endif
return
format ('Problem in the required estimate for the maximum of the'
  'singularities in the Laplace transform of the TFM.', '/,
  'Check the result subroutine (zres).')
format ('Error in IMSL numerical Laplace transform inversion'
  'The parameter values used are: '
  'p3 = ', e16.8,' , x3 = ', e16.8,' , '
  'y = ', e16.8,' , b = ',
  'e16.8,' , r = ', e16.8,' , '
  'w = ', e16.8,' , d = ', e16.8,
  ' and c = ', e16.8,' .'
  'This error is due to the ',
  'following:')
format ('The inversion algorithm was not able to achieve the'
  'accuracy requested within the kmax function'
  'evaluations for some times.')
format ('An overflow would have occurred for a particular time.')
format ('The inversion algorithm increased the integration'
  'limit', '/,' eight times without obtaining the requested '
  'accuracy.')
format ('Further error descriptions will not be printed.')
format ('Analytical solution being utilized.')
end
complexfunction root (op)

The estimate of the maximum of the real part of the singularities of
the TFM is obtained here.

implicit complex (a-h, o-y)
parameter (yzero = (0., 0.), four = (4., 0.), two = (2., 0.), one = (1., 0.))
common/rw/p3, x3, y, b, r, w, d, c
if (b.eq.yzero) then
  w1=four*xw
  root=-(p3*(w+d) + w1*d) / (p3+w1) / r
  return
endif
a=p3*p3 + four*b*p3*c
e=four*b*r*p3
if (b.eq.one) then
  root=-a/e
  return
endif
if (w.eq.yzero) then
  bb=four*b
  root=-(p3+bb*c) / bb / r
  return
endif
f=four*r*p3*w
g=four*p3*w*d
h=d+w/(one-b)
esr=e*r
bi=(h*e+f+a*r)/esr
bj=(a*h+g)/esr
root=csqrt(bi*b1-four*bj)
r2=(root+bi)/two
root=(root-bi)/two
zr1=root
zr2=r2
if(zr2.gt.zr1) root=r2
return
end
complexfunctionf(s)

The Laplace-transformed TFM is calculated here.

implicitcomplex(a-h,o-y)
common/rw/p3,x3,y,b,r,w,d,c
parameter(yzero=(0.,0.),one=(1.,0.),two=(2.,0.))
if(s.eq.yzero) then
  f=yzero
  return
endif
f11=f1(s)
x32=x3/two
f=p3*(cexp(x32*p3-f11))-cexp(x32*p3-y/two*f11)) / f11/(one-
  -cexp(p3/two*(x3-y)))
return
end
complexfunctionf1(s)

Function to calculate the f(s) portion of the TFM.

implicitcomplex(a-h,o-y)
common/rw/p3,x3,y,b,r,w,d,c
parameter(yzero=(0.,0.),one=(1.,0.),four=(4.,0.))
if(b.eq.one) then
  f1=csqrt(p3*(p3+four*(r*s+c)))
  return
endif
if(b.eq.yzero) then
  r1=r*s+d
  f1=csqrt(p3*p3+four*p3*w*r1/(r1+w))
  return
endif
b1=one-b
b22=four*p3
b2=b22*b
r1=r*s
r2=b1*r1+w+d*b1
f1=p3*p3+b2*r1*(one+b1*w/b/r2)+b2*c+b22*b1*w*d/r2
zff1=f1
if(zff1.gt.0.) f1=csqrt(f1)
return
end

c

CRAY function to evaluate the TFM analytically.
c

subroutinerealtime(cc,tt,res,n)
dimensioncc(n),tt(n),res(n)
externalgrand
common/param/d,p,b,r,w,c,t/tit1/os,p4p,rb,w1,tt,x,c1,b1,y
parameter(zero=0.,pi=3.141592653589793238462643,rerr=1.e-5)
x=cc(2)
y=cc(3)
p=cc(1)
b=cc(4)
r=cc(5)
c=cc(8)
d=cc(7)
w=cc(6)
pl=p/2.
if (b.eq.1.) then
  pip=p4p/pi/r
  x2=x*x
  y2=y*y
  pl1=pl*x
  cz=c+p4p
  oz=1.-exp((x-y)*pl)
doi=1,n
  tr=tt(i)/r
  pq=p4p/tr
  res(i)=sqrt(pip/tt(i))*exp(pl1-tr*cz)/oz*(exp(x2*pq)-
  exp(y2*pq))
else
  os=pl*(x-y)
c1=c+w/b
rb=r*b
  pt1=sqrt(p4p/pi/rb)/(1.-exp(os))
doi=1,n
  pt=pt1*exp(-tt(i)/r*c1)
ty=tt(i)/rb
tr=-p4p/ty
tv=exp(tr*(x-ty)**2)-exp(tr*(y-ty)**2+os)
st=sqrt(tt(i))
res(i)=tv/st
b1=1.-b
w1=w/r/sqrt(b*b1)
if (w.eq.zero) then
  res(i)=res(i)*pt
else
  t=tt(i)
  res(i)=pt*(res(i)+d cadre(fgrand,zero,t(i),zero,rerr,0.
    err,ier)*)w1)
  if (icount.gt.10) goto4
  if (ier.eq.131.or.ier.eq.132.or.ier.eq.133) then
    icount=icount+1
    write(6,6)
  endif
endif
continue
endif
return
format('Problem in the IML subroutine d cadre. Treat results',
  'with caution.')
Calculating the integrand in the analytical real time solution.

function fgrand(tau)
realmmbsi1
common/param/d,p,b,r,w,c,t/tit1/os,p4p,rb,w1,tv,st,x,c1,b1,y
parameter (zero=0.)
if (t.eq.tau) then
  fgrand=zero
  return
endif
if (tau.eq.zero) then
  fgrand=w1*st*tv
  return
endif
o=t-tau
ff=-p4p*rb/o
dd=o/rb
fgrand=mmbsi1(1,2.*w1*sqrt(tau*o),ier)*exp(tau/r*(c1-d-w/
b1))*(exp(ff*(x-dd)**2)-exp(ff*(y-dd)**2+os))/sqrt(tau)
if (ic.gt.10) goto1
if (ier.eq.129.or.ier.eq.130) then
  ic=ic+1
  write(6,2)
endif
return
format('Problem in the IMSL subroutine mmbsi1. Check'
,/'the function fgrand.')
end

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Copyright, the Regents of the University of California.
Nonlinear least squares fitting for the TFM model. The fitting portion
of the code is derived from the CXTFIT program in: Parker, J. C., and M.
Th. van Genuchten. 1984. Determining transport parameters from
laboratory and field tracer experiments. Bulletin 84-3, Virginia
Agricultural Experiment Station, Blacksburg. The program is intended
to run on VAX machines using VAX FORTRAN.

program tfmfifit
implicit double precision(a-h,o-z)
dimension y(300),f(300),r(300),delz(300,8),th(16),b(16),e(8)
 z  p(8), phi(8), q(8), lsort(300), tb(16), a(8,8), d(8,8),
 z  x(300), bmax(8), bmin(8), bi(16), sumtot(300),
 z  ssqtot(300), sumbt(300), sum1t(8), sum2t(8), sum3t(8),
 z  secoef(8), tvalue(8), index(8), tpcoe(8), tmcoe(8),
 z  temp1(300), yyi(300), thh(8), tsec(8)
common/modat1/x,index,nob,nvar,nu1,nu2,iopt
character*80,bi*4,tit11*4,tit12*4,fname*16
parameter(stopcr=1.d-4,p10lw=1.d-6,blow=1.d-6)
datanvar,nu1,nu2/8,9,16/

Send IMSL error and warning messages to imslerr.dat; the terminal is
unit 6.

call ugetio(3,nin,5)
open(5,file='imslerr.dat',status='new')
write(6,2000)
read(6,2001)fname
if(fname.eq.' ')fname='tfm.dat'
open(2,file=fname,status='old')
goto2
write(6,1000)
write(6,2002)
read(6,2001)fname
if(fname.eq.' ')fname='tfm.out'
open(1,file=fname,status='new',err=1)

There are ncase fittings to do.
do150ncase=1,20

Read input parameters.
read(2,1006,end=999)mit, maxtry, iplot, iopt

nvar = number of coefficients (8, see parameter statement above).
nob = number of observations (300 maximum, see experimental data
entry below).
mit = maximum number of iterations (mit=0 solves the direct problem
only).
maxtry = maximum number of trial solutions at iteration before
quitting. It is suggested that this parameter be in the
range 10 to 50; smaller values reduce the run
time but you may miss a convergent solution.
iplot = code for plot file output:
  0 - no plot file;
  1 - plot file is output.
iopt = solution procedure option;
  0 - use numerical Laplace transform inversion always;
  1 - use numerical Laplace transform inversion until numerical
      problems occur then use analytical solution;
  2 - use analytical solution always.

if (mit.ne.0) then
  For mit = 0 do not produce a plot file.
    if (iplot.eq.1.and.iplot1.ne.1) then
      write (6, 2003)
      read (6, 2001) fname
      if (fname.eq.' ') fname='tfm.plt'
      open (3, file=fname, status='new')
      iplot1=1
    endif
  else
    iplot=0
  endif
  if (maxtry.eq.0) maxtry=5
  if (mit.ne.0) write (1, 1035)
  do4i=1,2
    read (2, 1001) title
  write (1, 1001) title

Input the model parameters.

do5n=1,2
  n14=n*n14
  n7=n*n7
  nvar7=nvar+n7

Read the coefficient names.

n1=n14-13
n2=jmin0 (n14, nu2)
read (2, 1004) (b1(i), i=n1,n2)

Read the initial estimates.

n1=nvar7-6
n2=jmin0 (nvar7, nu2)
read (2, 1005) (b(i), i=n1,n2)

Read in the indices.

n1=n7-6
n2=jmin0 (n7, nvar)
read (2, 1006) (index(i), i=n1,n2)

Read in the constraints on the parameter values. bmin and bmax
are the arrays containing the minimum and maximum constraints.
bmin(i) = bmax(i) will omit constraint on parameter i.

read (2, 1005) (bmin(i), i=n1,n2)
read (2, 1005) (bmax(i), i=n1,n2)

Check that the x3 index is set to 0 (i.e., x3 cannot be fitted).
if (index(2).ne.0) then
  write(6,2015)
  index(2)=0
endif

Check the constraints on initial parameter values.

if (b(9).le.0.d0) then
  b(9)=p3low
  write(6,2006)
endif
if (b(10).ne.0.d0.and.b(10).ne.1.d0) then
  write(6,2007)
  stop
endif
if (b(10).eq.0.d0) then
  if (b(11).le.b(10)) then
    write(6,2008)
    stop
  endif
else
  if (b(11).le.b(10)) then
    write(6,2009)
    stop
  endif
endif
if (b(12).le.0.d0.or.b(12).gt.1.d0) then
  write(6,2010)
  stop
endif
if (b(13).lt.0.d0) then
  b(13)=0.d0
  write(6,2011)
endif
if (b(14).lt.0.d0) then
  b(14)=0.d0
  write(6,2012)
endif
if (b(15).lt.0.d0) then
  b(15)=0.d0
  write(6,2013)
endif
if (b(16).lt.0.d0) then
  b(16)=0.d0
  write(6,2014)
endif

Check that the parameter ranges are correct.

if (bmin(1).ne.bmax(1).and.index(1).eq.1) then
  if (bmin(1).le.0.d0) then
    write(6,2016)
    bmin(1)=p3low
  endif
endif
if (bmin(3).ne.bmax(3).and.index(3).eq.1) then
  if (b(10).eq.0.d0) then
    if (bmin(3).le.b(10)) then
      write(6,2017)
      stop
    endif
  endif
endif
endif
if (b(10).eq.1.d0) then
  if (bmin(3).le.b(10)) then
    write (6,2018)
    stop
  endif
endif
if (bmin(4).ne.bmax(4).and.index(4).eq.1) then
  if (bmin(4).le.0.d0) then
    write (6,2019)
    bmin(4)=blow
  endif
  if (bmax(4).gt.1.d0) then
    write (6,2020)
    bmax(4)=1.d0
  endif
if (bmin(5).ne.bmax(5).and.index(5).eq.1) then
  if (bmin(5).lt.0.d0) then
    write (6,2021)
    bmin(5)=0.d0
  endif
if (bmin(6).ne.bmax(6).and.index(6).eq.1) then
  if (bmin(6).lt.0.d0) then
    write (6,2022)
    bmin(6)=0.d0
  endif
if (bmin(7).ne.bmax(7).and.index(7).eq.1) then
  if (bmin(7).lt.0.d0) then
    write (6,2023)
    bmin(7)=0.d0
  endif
if (bmin(8).ne.bmax(8).and.index(8).eq.1) then
  if (bmin(5).lt.0.d0) then
    write (6,2024)
    bmin(5)=0.d0
  endif
write (1,1007)
doi=1,nvar
  j=2*i-1
write (1,1008) bi(j),bi(j+1),b(i+nvar)

Read in the experimental data.
write (6,2004)
read (6,2001) fname
if (fname.eq.' ')fname='expt.dat'
open (4,file=fname,status='old')
do10:i=1,300
read (4,1005,end=11)y(i),x(i)
10
nob=i-1
write (6,2005) nob
nob1=i
close (4)
Check that $t > 0$ for each datum.

```c
doi2i=1,nob
    if(x(i).le.0.d0) then
        write(6,2026)
        stop
    endif
    continue
endf
```

Check that the data outnumber the number of variables to be fitted.

```c
ncnvar=0
doi5i=1,nvar
    if(index(i).eq.1)ncnvar=ncnvar+1
continue
if(ncnvar.ge.nob) then
    write(6,2025)
    stop
endif
```

Rearrange the variable arrays.

```c
np=0
doi9i=nu1,nu2
    tb(i)=b(i)
doi20i=nu1,nu2
    invar=i-nvar
    if(index(invar).eq.0) goto20
    np=np+1
    k=2*np-1
    j=2*invar-1
    tit11=bi(j)
    tit12=bi(j+1)
    bi(k)=tit11
    bi(k+1)=tit12
    b(np)=b(i)
    tb(np)=b(i)
    th(np)=b(np)
    bmin(np)=bmin(invar)
    bmax(np)=bmax(invar)
```

Evaluate the initial residual vector.

```c
gam=.02d0
nit=0
np2=2*np
call model(th,f)
if(nit.eq.0) goto140
ssq=.0d0
doi3i=1,nob
    r(i)=y(i)-f(i)
ssqtot(i)=r(i)*r(i)
doi32i=1,nob
ssq=ssq+ssqtot(i)
write(1,1011) (bi(j), bi(j+1), j=1, np2, 2)
write(1,1012) nit, ssq, (b(i), i=1, np)
```
nit=nit+1
ntrial=0
ga=.1d0*ga
do34j=1,np

temp1(j)=th(j)
if(nit.eq.1) then
  do35j=1,np
e(j)=1.d0
endif
do38j=1,np
  th(j)=1.01d0*th(j)
  if(th(j).eq.0.d0) th(j)=.01d0
  q(j)=0.d0
callmodel(th,delz(1,j)).
do36i=1,nob
  delz(i,j)=delz(i,j)-f(i)
  q(j)=q(j)+delz(i,j)*r(i)
  q(j)=100.d0*q(j)/th(j)

th(j)=temp1(j)

c
q=xt*r (steepest descent).
c
do44i=1,np
do42j=1,i
  sum=0.d0
  do40k=1,nob
    sumtot(k)=delz(k,i)*delz(k,j)
  enddo
  do41k=1,nob
    sum=sum+sumtot(k)
  enddo
  if(sum.ne.0.d0) then
    d(i,j)=10000.d0*sum/th(i)/th(j)
  else
    d(i,j)=0.d0
  endif

d(j,i)=d(i,j)
e(i)=dsqrt(d(i,i))
if(e(i).eq.0.d0) e(i)=1.d-30

do52i=1,np
  do52j=1,np
    a(i,j)=d(i,j)/e(i)/e(j)

c
a is the scaled moment matrix.
c
do54i=1,np
  p(i)=q(i)/e(i)
  phi(i)=p(i)

a(i,i)=a(i,i)+ga
callmatinv(a,np,p)
c
p/e is the correction vector.
c
step=1.d0
do56i=1,np
tb(i)=p(i)*step/e(i)+th(i)
do58i=1,np
  if(bmin(i).eq.bmax(i)) goto58
  if(tb(i).gt.bmax(i)) tb(i)=bmax(i)
  if(tb(i).lt.bmin(i)) tb(i)=bmin(i)
p(i)=(tb(i)-th(i))*e(i)/step
continue
do59i=1,np
th(i)=th(i)*tb(i)
do62i=1,np
    if(th(i))66,66,62
continue
sumb=0.0d0
call model(tb,f)
d064i=1,nob
    r(i)=y(i)-f(i)
sumb(i)=r(i)*r(i)
do65i=1,nob
sumb=sumb(i)+sumb
sum1=0.0d0
sum2=0.0d0
sum3=0.0d0
do68i=1,np
    sum1t(i)=p(i)*phi(i)
    sum2t(i)=p(i)*p(i)
sum3t(i)=phi(i)*phi(i)
do69i=1,np
    sum1=sum1+sum1t(i)
    sum2=sum2+sum2t(i)
sum3=sum3+sum3t(i)
arg=0.0d0
suu=sum2*sum3
if(suu.gt.0.0d0)arg=sum1/dsqrt(suu)
arg=0.0d0
if(np.gt.1)arg1=dsqrt(1.0d0-arg*arg)
if(arg.eq.0.0d0.and.arg1.eq.0.0d0)arg=1.0d0
angle=57.295779d0*datan2(arg1,arg)
do72i=1,np
    if(th(i))74,74,72
continue
ntrial=ntrial+1
if(ntrial.gt.maxtry)goto95
if(sumb/ssq1.0d0)80,80,74
if(angle-30.0d0)76,76,78
step=.5*step
goto55
78
ga=10.0d0*ga
goto50
c
c Print out the coefficients after each iteration.
c
do82i=1,np
th(i)=tb(i)
write(1,1012)nit, Humb, (th(i),i=1,np)
do86i=1,np
    if(dabs(p(i)*step/e(i))/(1.0d-20+dabs(th(i)))-
        stopcr)86,86,94
continue
goto96
94
ssq=sumb
if(nit lt nit)goto33
if(nit eq nit)write(1,1034)nit
goto96
95
write(1,1038)maxtry
c
c This is the end of the iteration loop.
callmatinv(d,np,p)

Write out the correlation matrix.

do98i=1,np
e(i)=dsqrt(dabs(d(i,i)))
do99i=1,np
  if(e(i).eq.0.d0)e(i)=1.d-30
  if(np.eq.1)goto104
  write(1,1013)(i,i=1,np)
  do102i=1,np
    do100j=1,i
      a(j,i)=d(j,i)/e(i)/e(j)
    write(1,1014)i,(a(j,i),j=1,i)
  c
  Calculate the regression coefficient.
  c
  sumc=0.d0
  sumc2=0.d0
  do105i=1,nob
    yy(i)=y(i)*y(i)
  do106i=1,nob
    sumc=sumc+yy(i)
  sumc2=sumc2+yy(i)
  vinvynob
  rsq=1.d0-sumb/(sumc2-sumc*sumc/vinvyn)
  write(1,1041)rsq
  c
  Calculate the 95% confidence interval.
  c
  tut=nob-np
  z=1.d0/tut
  sdev=dsqrt(z*sumb)
  tvar=1.96d0+z*(2.3779d0+z*(2.7135d0+
    z*(3.187936d0+2.466666d0*z*z)))
  if(np.eq.1)write(1,1042)
  if(np.gt.1)write(1,1015)
  do107i=1,np
    secoef(i)=e(i)*sdev
    tvalue(i)=th(i)/secoef(i)
  do108i=1,np
    tsec(i)=tvar*secoef(i)
  do109i=1,np
    tmcoe(i)=th(i)-tsec(i)
  tpcoe(i)=th(i)+tsec(i)
  if(np.eq.1)
    do110i=1,np
      j=2*i-1
      write(1,1043)i,bi(j),bi(j+1),th(i),secoef(i),
        tmcoe(i),tpcoe(i)
  else
    do111i=1,np
      j=2*i-1
      write(1,1016)i,bi(j),bi(j+1),th(i),secoef(i),
        tvalue(i),tmcoe(i),tpcoe(i)
  endif

Prepare the final output.
lsort(1)=1
do112j=2,nob
112
  temp1(j)=dabs(r(j))
do117j=2,nob
  k=j-1
do113k=1,k
    if (temp1(j)-dabs(r(lsort(1)))) 114,114,113
  continue
  lsort(j)=j
  goto117
114
  kk=j
115
  lsort(kk+1)=lsort(kk)
  if (kk=1) 116,116,115
116
  lsort(1)=j
117
  continue
write(1,1017)
do118i=1,nob
118
  write(1,1018)i,x(i),y(i),f(i),r(i)
  if (iplot.ne.0) then
    do119i=1,nob
      write(3,1047)y(i),x(i),i
    do120i=1,nob
      write(3,1047)f(i),x(i),i
  endif
write(1,1019)
do121i=1,nob
  j=lsort(nob1-i)
121
  write(1,1018)j,x(j),y(j),f(j),r(j)
  goto150
140
  write(1,1030)(j,j=1,nx)
do145i=1,nob
145
  write(1,1033)i,x(i),f(i)
  continue
999
  stop
1000
  format(' Choose another file name. ')
1001
  format(a80)
1004
  format(7(2x,2a4))
1005
  format(7f10.5)
1006
  format(7f10.4)
1007
  format(/x,'Initial values of coefficients'/x,30(1h=)/3x,'Z',
    'Name',6x,'Initial value')
1008
  format(x,2a4,4(1h=),1pd12.4)
1011
  format(/x,'Iteration',6x,'SSQ',4x,8(5x,2a4))
1012
  format(x,15,3x,1pd13.4,2x,8(1pd13.4))
1013
  format(/x,'Correlation Matrix',/3x,18(1h=)/4x,10(4x,i2,5x))
1014
  format(x,13,10(2x,f7.4,2x))
1015
  format(/x,'Nonlinear Least-Squares Analysis, Final Results.'/
    z/x,48(1h=)/57x,'95% Confidence Limits'/x,'Variable',3x,'Name'
    z,7x,'Value',7x,'S.E.Coeff.',2x,'T-Value',4x,'Lower',9x,'Upper')
1016
  format(4x,i2,3x,2a4,1pd13.4,2x,1pd13.4,d10.3,1pd12.4,
    2x,1pd12.4)
1017
  format(/,29x,'Ordered by computer input',/2x,'No.',4x,'T',
    z 8x,'Conc Obs',6x,'Conc Fit',6x,'Residual')
1018
  format(x,13,x,1pd12.3,3(2x,1pd12.3))
1019
  format(/,29x,'Ordered by residual',/2x,'No.',4x,'T',
    z 8x,'Conc Obs',6x,'Conc Fit',6x,'Residual')
format(/x,'Results for initial coefficient values',/x,'No.',
  8x,'T ',7x,' Conc ') 
1033 format(x,i2,2(3x,1pd12.4)) 
1034 format(/x,'Convergence criteria not met in',i3,' iterations.') 
1035 format(5x,/, 'Nonlinear Least-Squares Analysis.') 
1038 format(/x,'No further decrease in SSQ obtained after ',i2,
  ' trials.') 
1041 format(/x,'Rsquare for regression =',d20.10,'.',/) 
1042 format(x,'Nonlinear Least-Squares Analysis, Final Results.',
  z/x,48(1h)/57x,'95% Confidence Limits'/x,'Variable',3x,'Name'
  z,8x,'Value',8x,'S.E.Coeff.',6x,'Lower',10x,'Upper') 
1043 format(x,i2,6.x,2a4,x,1pd13.4,3x,i2,10x,x,1pd13.4,2x,
  1pd13.4) 
1047 format(2(1pd15.4),i3) 
2000 format('Enter the name of the input data file',
  '(default = tfm.dat).') 
2001 format(a16) 
2002 format('Enter the name of the primary output file',
  '(default = tfm.out).') 
2003 format('Enter the name of the plot output file',
  '(default = tfm.plt).') 
2004 format('Enter the name of the file containing the ',
  'experimental data (default =',/', '/', 'expt.dat).') 
2005 format('There were ',i3,' experimental data read.') 
2006 format('P3 must not be less than zero, it has been reset ',
  'to zero.') 
2007 format('Set X3 as zero or one in the data file and rerun ',
  'the program.') 
2008 format('Yo must be greater than X3 (zero). Reset Yo in the',
  '/ ', 'data file and rerun the program.') 
2009 format('Yo must be greater than X3 (one). Reset Yo in the',
  '/ ', 'data file and rerun the program.') 
2010 format('B must not be less than or equal to zero or greater ',
  'than one.', '/', 'Reset B in the data file and rerun the ',
  'program.') 
2011 format('R must not be less than zero, it has been reset ',
  'to zero.') 
2012 format('W must not be less than zero, it has been reset ',
  'to zero.') 
2013 format('D must not be less than zero, it has been reset ',
  'to zero.') 
2014 format('C must not be less than zero, it has been reset ',
  'to zero.') 
2015 format('X3 cannot be fitted. INDEX(2) is reset to 0.') 
2016 format('The minimum value of P3 cannot be less than or equal ',
  'to 0. It ', '/', 'has been reset to P3LOW.') 
2017 format('The minimum value of Yo must be greater than 0 (X3).',
  '/ ', 'Reset the lower limit on Yo and rerun.') 
2018 format('The minimum value of Yo must be greater than 1 (X3).',
  '/ ', 'Reset the lower limit on y and rerun.') 
2019 format('The minimum value of B cannot be less than or equal to',
  '0.', '/', 'It has been reset to Blow.') 
2020 format('The maximum value of B cannot be greater than 1.', '/',
  'It has been reset to one.') 
2021 format('The minimum value of R cannot be less than 0.', '/',
  'It has been reset to zero.') 
2022 format('The minimum value of W cannot be less than 0.', '/',
  'It has been reset to zero.') 
2023 format('The minimum value of D cannot be less than 0.', '/',
  'It has been reset to zero.')
The minimum value of C cannot be less than 0.

The experimental data must outnumber the number of parameters being fitted.

At least one time in the data file is less than or equal to zero. Check and rerun.

Purpose: perform matrix inversion for parameter estimation.

implicit doubleprecision(a-h,o-z)
dimension pp(8), a(8,8), b(16), index(8,2)
do 2j=1,8
  index(j,1)=0
  i=0
  amax=-1.0d0
  do 10j=1,np
    if (index(j,1)) 10,6,10
       do 9k=1,np
           if (index(k,1)) 9,8,9
               p=dabs(a(j,k))
               if (p.le.amax) goto 9
               ic=k
               amax=p
       continue
  continue
    if (amax) 30,30,14
       index(ic,1)=ir
       if (ir.eq.ic) goto 18
       do 15l=1,np
          pp(l)=a(ir,l)
       do 16l=1,np
          a(ir,l)=a(ic,l)
       a(ic,1)=pp(1)
       p=b(ir)
       b(ir)=b(ic)
       b(ic)=p
       i=i+1
       index(i,2)=ic
    continue
  16 a(ic,1)=a(ic,1)*p
  18 b(ic)=b(ic)*p
  20 do 24k=1,np
    if (k.eq.ic) goto 24
       p=a(k,ic)
       a(k,ic)=0.0d0
       do 22l=1,np
          a(k,l)=a(k,l)-a(ic,l)*p
          b(k)=b(k)-b(ic)*p
       continue
  22 goto 4
  24 ic=index(i,2)
  26 ir=index(ic,1)
  28 do 27k=1,np
  29 pp(k)=a(k,ir)
  30 do 28k=1,np
a(k,ir)=a(k,ic)
a(k,ic)=pp(k)
i=i-1
continue
if(i)26,32,26
return
end
subroutinemodel(bn,ycalc)
implicitdoubleprecision(a-h,o-z)
dimensionycalc(300),bn(16),c(8),index(8),x(300)
parameter(p31ow=1.d-6,blow=1.d-6)
common/modat1/x,index,nob,nvar,nu1,nu2,iop
t
Update the coefficient array.
k=0
do2i=nu1,nu2
   if(index(i-nvar).eq.0)goto2
   k=k+1
   bn(i)=bn(k)
continue
do5i=1,nvar
   c(i)=bn(nvar+i)

Check the parameter ranges.
if(index(1).eq.1) then
   if(c(1).le.0.d0)c(1)=p31ow
endif
if(index(3).eq.1) then
   if(c(3).le.c(2))c(3)=c(2)+1.d-9
endif
if(index(4).eq.1) then
   if(c(4).gt.1.d0)c(4)=1.d0
   if(c(4).le.0.d0)c(4)=blow
endif
if(index(5).eq.1) then
   if(c(5).lt.0.d0)c(5)=0.d0
endif
if(index(6).eq.1) then
   if(c(6).lt.0.d0)c(6)=0.d0
endif
if(index(7).eq.1) then
   if(c(7).lt.0.d0)c(7)=0.d0
endif
if(index(8).eq.1) then
   if(c(8).lt.0.d0)c(8)=0.d0
endif

Call the TFM model function.
callzres(ycalc,x,c,nob)
return
end
subroutinerezres(zfinv,zt,zc,n)
imPLICITcomplex*16(a-h,o-y),real*8(z)
EXTERNAL
dimensionzt(n),zfinv(n),zc(8),zx(300),index(8)
common/modat1/zx,index,nob,nvar,nu1,nu2,iop/tutt/p3,x3,y,b,
   r,w,d,c
The following parameters are for the IMSL Laplace inversion routine. The inversion is accurate to nsig significant figures. The maximum number of iterations for each inversion is kmax. See the IMSL manual for details.

```c
parameter (nsig=4,kmax=499)
if (iopt.eq.2) then
    call realtime(zc,zt,zfinv,n)
    return
endif
icount=0
p3=dcmplx(zc(1),0.d0)
x3=dcmplx(zc(2),0.d0)
y=dcmplx(zc(3),0.d0)
b=dcmplx(zc(4),0.d0)
r=dcmplx(zc(5),0.d0)
w=dcmplx(zc(6),0.d0)
d=dcmplx(zc(7),0.d0)
c=dcmplx(zc(8),0.d0)
```

The function root calculates a number greater than or equal to the real part of the maximum of the singularities of the function to be inverted. The argument is a dummy parameter.

```c
alpha=root(op)
zzz=f1(alpha)
if (zzz.lt.0.d0) then
    zalpha=alpha
    alpha=alpha-dcmplx(1.d-6*zalpha,0.d0)
    zzz=f1(alpha)
endif
icount=icount+1
if (icount.ge.10.and.zzz.lt.0.d0) goto 1
if (icount.gt.10) write(6,11)
    zalpha=alpha
```

The estimate has been found; proceed to the inversion using the IMSL numerical Laplace transform inverter.

```c
call flinv(f,n,zt,zalpha,nsig,kmax,zfinv,ier)
do7i=1,n
if (zfinv(i).lt.0.d0) zfinv(i)=0.d0
if (ier.eq.0) return
```

Stop printing error messages for more than 10 errors.

```c
ierc=ierc+1
if (ierc.eq.11) write(6,16)
if (ierc.gt.10) goto 10
write(6,12) ier,(zc(i),i=1,8)
if (ierc.eq.129) then
    write(6,13)
    goto 10
endif
if (ierc.eq.130) then
    write(6,14)
    goto 10
endif
```
write(6,15)  
if (iopt.eq.1) then  
call realtime(zc,zt,zfinv,n)  
if (notice.eq.1) then  
    notice=0  
    write(6,17)  
  endif  
endif  
return  
format(1 Problem with the required estimate for the maximum of  
z, the',/,' singularities in the Laplace transform of the'  
TFM',/,' Check the result subroutine (zres).'  
format(1 Error in IMSL numerical Laplace transform inversion'  
, (ier = ',i3,'),/,' the parameter values used are: ',  
P3 = ',e16.8,' , X3 = ',e16.8,' ,/,' Yo = ',e16.8,  
B = ',e16.8,' , R = ',e16.8,' ,/,' W = ',e16.8,  
D = ',e16.8,' and C = ',e16.8,' ,/,'  
/ ' This error is due to the following:)  
format(1 The inversion algorithm was not able to achieve the'  
, /,' accuracy requested within the Kmax function'  
, /,' evaluations for some times.')  
format(1 An overflow would have occurred for a particular'  
ztime.')  
format(1 The inversion algorithm increased the integration ',  
' limit',/,' eight times without obtaining the requested ',  
' accuracy.')  
format(1 Further error descriptions will not be printed.')  
format(1 Analytical solution being utilized.')  
end  
complex*16 function root(op)  
imPLICIT complex*16 (a-h, o-y), real*8(z)  
The estimate of the maximum of the real part of the singularities of  
of the TFM is obtained here.  
parameter (yzero=(0.d0,0.d0), four=(4.d0,0.d0), two=(2.d0,0.d0),  
one=(1.d0,0.d0))  
common/tutt/p3,x3,y,b,r,w,d,c  
if (b.eq.yzero) then  
w1=four*w  
root=- (p3*(w+d)+w1*d) / (p3+w1) / r  
return  
endif  
a=p3*p3+four*b*p3*c  
e=four*b*r*p3  
if (b.eq.one) then  
root=-a/e  
return  
endif  
if (w.eq.yzero) then  
  bb=four*b  
  root=- (p3+bb*c) / bb / r  
return  
endif  
f=four*r*p3*w  
g=four*p3*w*d  
h=d+w/(one-b)  
esr=e*r  
b1=(h*e+f+a*r)/esr  
bj=(a*h+g)/esr
root = cdsqrt(bi*bi-four*bj)
r2 = -(root+bi)/two
root = (root-bi)/two
zr1 = root
zr2 = r2
if (zr2.gt.zr1) root = r2
return
end
complex*16 function f(s)

The Laplace-transformed TFM is calculated here.

implicit complex*16(a-h,o-y), real*8(z)
common/tutt/p3,x3,y,b,r,w,d,c
parameter(yzero=0.d0,0.d0),one=(1.d0,0.d0),two=(2.d0,0.d0))
if (s.eq.yzero) then
  f = yzero
  return
endif
f11 = f1(s)
x32 = x3/two
f = p3*(cexp(x32*(p3-f11))-cexp(x32*p3-y/two*f11))/f11/(one
  z -cexp(p3/two*(x3-y)))
return
end
complex*16 function f1(s)

Function to calculate the f(s) portion of the TFM.

implicit complex*16(a-h,o-y), real*8(z)
common/tutt/p3,x3,y,b,r,w,d,c
parameter(yzero=0.d0,0.d0),one=(1.d0,0.d0),four=(4.d0,0.d0))
if (b.eq.one) then
  f1 = cdsqrt((p3*four*(r*s+c))
  return
endif
if (b.eq.yzero) then
  r1 = r*s+d
  f1 = cdsqrt((p3*p3+four*p3*w*r1)/(r1+w))
  return
endif
b1 = one-b
b2 = four*p3
b2 = b22*b
r1 = r*s
r2 = b1*r1+w+d*b1
f1 = p3*p3+b2*r1*(one+b1*w/b/r2)+b2*c+b22*b1*w*d/r2
zff1 = f1
if (zff1.gt.0.d0)f1 = cdsqrt(f1)
return
end

Subroutine to evaluate the TFM analytically.

subroutines real time (cc,tt, res, n)
implicit double precision (a-h,o-z)
dimension cc(n), tt(n), res(n)
external grand
common/param/d,p,b,r,w,c/tit1/0s,p4p,rb, w1, tv, st,x,c1,b1,y
parameter(zero=0.d0, pi=3.141592653589793238462643d0, rerr=1.d-5)
\begin{verbatim}
x=cc(2)
y=cc(3)
p=cc(1)
b=cc(4)
r=cc(5)
c=cc(8)
d=cc(7)
w=cc(6)
pl=p/2.d0
p4p=p/4.d0
if (b.eq.1.d0) then
    pip=p4p/pi/r
    x2=-x*x
    y2=-y*y
    pl1=pl*x
    cz=c+p4p
    oz=1.d0*dexp((x-y)*pl)
do3i=1,n
    tr=tt(i)/r
    pq=p4p/tr
    res(i)=dsqrt(pip/tt(i))*dexp(pl1-tr*cz)/oz*dexp(x2*pq)-
    dexp(y2*pq))
else
    os=pl*(x-y)
c1=c+w/b
rb=r*b
pt1=dsqrt(p4p/pi/rb)/(1.d0-dexp(os))
do4i=1,n
    pt=pt1*dexp(-tt(i)/r*c1)
ty=tt(i)/rb
    tr=-p4p/ty
    tv=dexp(tr*(x-tv)**2)-dexp(tr*(y-tv)**2+os)
st=dsqrt(tt(i))
res(i)=tv/st
b1=1.d0-b
w1=w/r/dsqrt(b*b1)
if (w.eq.zero) then
    res(i)=res(i)*pt
else
    t=tt(i)
    res(i)=pt*(res(i)+dcadre(fgrand,zero,tt(i),zero,err,
        err,ier)*w1)
    if (icount.gt.10) goto4
    if (ier.eq.131.or.ier.eq.132.or.ier.eq.133) then
        icount=icount+1
        write(6,5)
    endif
endif
continue
endif
return
end
format('Problem in the IMSL subroutine DCADRE. Treat results',
    'with caution.')
end
Calculating the integrand.
function fgrand(tau)
implicit doubleprecision(a-h,o-z)
real*8 mmbsi1
\end{verbatim}
common/param/d,p,b,r,w,c,t/tit1/os,p4p,rb,w1,tv,st,x,c1,b1,y
parameter (zero=0.d0)
if(t.eq.tau) then
  fgrand=zero
  return
endif
if(tau.eq.zero) then
  fgrand=w1*st*tv
  return
endif
o=t-tau
ff=-p4p*rb/o
dd=o/rb
fgrand=mmbsi1(1,2.*w1*dsqrt(tau*o),ier)*dexp(tau/r*(c1-d-w/
  b1))*(dexp(ff*(x-dd)**2)-dexp(ff*(y-dd)**2+os))/
  dsqrt(tau)
if(ic.gt.10)goto1
if(ier.eq.129.or.ier.eq.130) then
  ic=ic+1
  write(6,2)
endif
return
1  return
2  format(' Problem in the IMSL subroutine MMBSI1. Check '
  ,/,' the function fgrand.')
end

c
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APPENDIX 2.

A USEFUL LAPLACE TRANSFORM

To invert \( \bar{g}(s) \) as given by eq. 17, it is necessary to know the inverse transform of \( \bar{f}(s) = \exp[-(sx+a)/(s+b)] \). The procedure used to derive this transform is similar to that used by Goldstein (1953). Again, let \( \mathcal{L} \) denote the Laplace transform operator, then (Carslaw and Jaeger, 1959, pg. 495):

\[
\mathcal{L}\{I_0(2\sqrt{\chi t})\} = \frac{\exp(\chi/s)}{s} \tag{A1}
\]

Noting that the operators \( \mathcal{L} \) and \( d/dt \) are commutative, and using identities 5 and 3 of Spiegel (1965, Appendix A), one obtains from eq. A1 (cf. Walker, 1987)

\[
\mathcal{L}\{\exp(-bt)\sqrt{\frac{\chi}{t}} I_1(2\sqrt{\chi t})\} = \exp[\chi/(s+b)] - 1 \tag{A2}
\]

The next step is to replace \( \chi \) in eq. A2 by \( bx-a \). If each side of eq. A2 is multiplied by \( \exp(-x) \) and then rearranged, we arrive at the required identity

\[
\mathcal{L}\{\delta(t) \exp(-x) + \sqrt{(bx-a)/t} \exp[-(x+bt)] I_1[2\sqrt{(bx-a)t}]\} = \exp[-(sx+a)/(s+b)] \tag{A3}
\]
APPENDIX 3. TFMPLOT: A FORTRAN code utilizing the DISSPLA
(Integrated Software Systems Corp., 1985)
software package to generate plots using
the output plot files from TFMFIT.

Copyright, the Regents of the University of California.
Program to create a DISSPLA plot file for the TFM results.

program tfmplot
character xlabel*24,ylabel*24,title*24,tit*16,
datfich*8,parfich*8,plotnam*4
dimension x(300), y(300)
call link("unit6=ttv/"")
write (6,120)
read (6,122) parfich
plotnam=parfich(4:7)
call keep80(plotnam,3)
call fr80id('TFM plot',1,1,0)
call plts
call page(11,8.5)
call ucchar
call complx
call basalf('standard')
call height(.3)
call intaxs
call bsym
call sclpic(2,0)
open (2, file=parfich,status='old')
read (2,140)xlong,ylong
read (2,140)xphy,yphy
read (2,140)xorig,xstep,xmax
read (2,140)yorig,ystep,ymax
read (2,150)tit
encode (24,160,title)tit
read(2,150)tit
encode (24,160,xlabel)tit
read(2,150)tit
encode (24,160,ylabel)tit
call area2d(xlong,ylong)
call physor(xphy,yphy)
call headin(title,100,5,1)
call xname(xlabel,100)
call yname(ylabel,100)
call graf(xorig,xstep,xmax,yorig,ystep,ymax)
write(6,126)
read(6,122)datfich
open(2,file=datfich,status='old')
d0i=1,1602
read(2,170,end=2)y(i),x(i)
num=(i-1)/2
rewind2
d0i=1,2
   do3j=1,num
      read(2,170)y(j),x(j)
      if(i.eq.1)goto4
      call dash
   call curve(x,y,num,0)
call donepl
stop
format('Enter the name of the parameter file.')
format(a8)
format('Enter the name of the data file.')
format(14x,3(x,f7.0))
format(15x,a16,x)
format(a16,'$')
format(2(1pe15.4))
end

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