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**TSOAK-M1: A COMPUTER CODE TO DETERMINE
TRITIUM REACTION/ADSORPTION/RELEASE PARAMETERS
FROM EXPERIMENTAL RESULTS OF
AIR-DETRITIATION TESTS**

by

R. H. Land, V. A. Maroni, and M. Minkoff

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS
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R. H. Land, V. A. Maroni, and M. Minkoff[†]

Chemical Engineering Division

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
II. DESCRIPTION OF THE PHYSICOCHEMICAL MODEL	2
A. Cleanup Operation	3
B. Reaction of T ₂ with H ₂ O	3
C. Adsorption and Release of HTO	4
D. Soak Effect	5
E. The Resulting Family of Differential Equations	5
III. DESCRIPTION OF THE MATHEMATICAL ALGORITHM	6
A. Correlation of the Algorithm with the Model	6
B. Computational Method	7
C. Optimization Process	8
D. Input Format and Output Description.	10
1. Format for Fixed Parameters	10
2. Format for Experimental Data	11
3. Description of Output	12
E. Operational Characteristics of the Code	12
F. Adaptation of TSOAK-M1 to Other Computer Facilities	13
IV. APPLICATION OF THE CODE TO EXISTING EXPERIMENTS AND PLANNED FACILITIES	13
A. Testing of TSOAK-M1 against Experimental Data	13
B. Correlation of TSOAK-M1 Findings with Other Experimental Observations	17
C. Analysis of Large-Enclosure Detritiation Using TSOAK-M1 Results	20
V. CONCLUSIONS AND RECOMMENDATIONS	21
VI. ACKNOWLEDGMENTS	23
REFERENCES	23
APPENDIX A. CALCULATION OF DERIVATIVES WITH RESPECT TO Z ₁	25
APPENDIX B. CALCULATION OF THE VARIANCE-COVARIANCE MATRIX	27

TABLE OF CONTENTS (contd)

	<u>Page</u>
APPENDIX C. DIAGNOSTIC MESSAGES WHEN IDEBUG = 1	28
APPENDIX D. TSOAK-M1 PRINTED OUTPUT DISPLAY	30

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	The Bench-Scale Air-Detrition Test Apparatus at ANL	14
2.	Reaction/Adsorption/Release and Instrument Correction Parameters Derived from Bench-Scale Air-Detrition Test Data Using TSOAK-M1	15
3.	Analysis of Test Data on Atmospheric Detrition in a Closed-Cycle Experiment	16
4.	Calculated Curves for Individual Species Concentrations Determined from the Analysis Shown in Fig. 3	17
5.	Test of HTO Formation Kinetics During Detrition Using an 0.008-m ³ Test Cubicle	18
6.	Tests of Meter Memory Effects on Observed Instrument Correction Factors	19
7.	Tests of the Effect of Processor Flow Rate on the Detrition Characteristics of the Apparatus Shown in Fig. 1	20

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Summary of Hypothetical Reactor-Building Scenarios Using TSOAK-M1-Generated Parameters from Bench-Scale Experiments . . .	22

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ABSTRACT

A computer code has been developed which permits the determination of tritium reaction (T_2 to HTO)/adsorption/release and instrument correction parameters from enclosure (building)-detritiation test data. The code is based on a simplified model which treats each parameter as a normalized time-independent constant throughout the data-unfolding steps. Because of the complicated four-dimensional mathematical surface generated by the resulting differential equation system, occasional local-minima effects are observed, but these effects can be overcome in most instances by selecting a series of trial guesses for the initial parameter values and observing the reproducibility of final parameter values for cases where the best overall fit to experimental data is achieved. The code was then used to analyze existing small-cubicle test data with good success, and the resulting normalized parameters were employed to evaluate hypothetical reactor-building detritiation scenarios. It was concluded from the latter evaluation that the complications associated with moisture formation, adsorption, and release, particularly in terms of extended cleanup times, may not be as great as was previously thought. It is recommended that the validity of the TSOAK-M1 model be tested using data from detritiation tests conducted on large experimental enclosures (5-10 m³) and, if possible, actual facility buildings.

I. INTRODUCTION

The problem of cleaning up accidental tritium releases to large enclosures has been well recognized for all types of D-T-burning fusion reactors (see, for example, Refs. 1-3), and a number of studies addressing the problem have appeared in the literature.⁴⁻⁹ Previous work at this laboratory⁴ involved the development of a computer code (TSOAK) to analyze air cleanup operations in terms of various reaction/adsorption/release-type phenomena that could occur during the time period between the initial release of tritium and the ultimate completion of a detritiation process of the type described in Refs. 1, 2, 4, 6, and 8. In connection with this code-development activity, some parallel experiments^{4,9} were performed on a small (~0.05-m³) enclosure in which detritiation runs were conducted for releases with initial tritium concentrations (as T_2) on the order of 10^3 $\mu\text{Ci}/\text{m}^3$. Qualitative comparisons of the results of experiments and corresponding computer simulations indicated that the formation of tritiated water and its subsequent adsorption on and release from enclosure surfaces had a significant

impact on the time required to complete a cleanup operation. In particular, tritiated species which were adsorbed on surfaces during the early and intermediate phases of the cleanup would later return to the enclosure atmosphere, creating a tritium source term that caused an extension of the time required to reduce the atmospheric tritium level to the breathable limit (maximum permissible concentration) of $5 \mu\text{Ci}/\text{m}^3$.

Many aspects of the qualitative observations and predictions in Refs. 4 and 9 have been shown to be consistent with the findings of more recent related studies, such as those by Sherwood⁵ and Flanagan *et al.*⁷ More of these kinds of tests are planned as an integral part of the program to be conducted at the Tritium Systems Test Assembly (TSTA).⁸ The TSTA program and other ongoing programs in this general area should result in the understanding and processing technology needed to deal effectively with tritium releases in fusion-reactor facilities.

The work presented in this report was stimulated by the recognition that both existing detritiation test programs⁵⁻⁷ and planned studies⁸ could benefit from a computational modeling algorithm that would permit the direct correlation of air-detritiation data from simulated enclosures with some type of physically and chemically reasonable model. To this end, an effort was initiated (*via* funding from EG&G Idaho, Inc.) to upgrade the computer code TSOAK to a new version (called TSOAK-M1) capable of accepting raw detritiation test data and determining from those data the corresponding parameters related to tritiated water formation, adsorption on surfaces, and subsequent release back to the enclosure. The following sections include: (1) a description of the time-dependent physicochemical model upon which the code is based, (2) a discussion of the mathematical algorithms and iteration methods used to solve the resulting differential equations, (3) examples of the application of the code to existing air-detritiation data sets, and (4) a section containing the principal conclusions drawn from this study and recommendations for future work.

II. DESCRIPTION OF THE PHYSICOCHEMICAL MODEL

The model used in constructing TSOAK-M1 is similar in many respects to the one incorporated into TSOAK as discussed in Ref. 4. However, only the three interactive mechanisms related to the formation, adsorption, and release of HTO were retained for TSOAK-M1, since the permeation mechanisms used in the earlier code-development effort were found to make only a very minor contribution to the overall tritium "soaking"* problem. A constant instrument correction factor, ICF, is incorporated in the new model; the ICF helps to compensate for the asymptotic nature of most measured detritiation curves at long times in the cleanup operation. The model, in its present form, is constructed as follows:

* In the context of this report, "soaking" is defined as the uptake of tritiated species by the surfaces in a fusion-reactor building due to adsorption-related phenomena. These phenomena are discussed in more detail in Ref. 4.

A. Cleanup Operation

The principal pathway for removal of any gaseous tritium-bearing species from the reactor-building atmosphere following an accidental tritium release should be the cleanup operation itself. Here it is assumed that the air in a room of volume V is circulated through a detritiation system at a volumetric flow rate Q and that the efficiency of the detritiation system for removal of all tritium-containing species in the circulated air (regardless of the chemical form) is ϵ . The rate of reduction in the concentration of any species, N_i , with time, t , is, therefore, given by

$$\left(\frac{\partial N_i}{\partial t} \right)_A = - \left(\frac{\epsilon Q}{V} \right) N_i = -AN_i \quad (1)$$

where

$$A = \frac{\epsilon Q}{V} \quad (2)$$

B. Reaction of T_2 with H_2O

The dominant reaction mechanism treated in the model is the formation of HTO and HT from T_2 and ambient moisture (H_2O), although it is possible that reaction of T_2 with surface-adsorbed moisture is also a major contributor to the overall buildup of tritiated water in a given enclosure. In recent years, examination of the interplay between tritiated-water formation and detritiation has shown that there are numerous ways to treat the problem and no one of them is totally adequate. For the purposes of this study an approximate treatment was arrived at based on the following considerations:

(1) Existing physicochemical data on the formation of tritiated water from reactions involving molecular tritium generally indicate that these reactions are pseudo-second order in the concentration of the molecular tritium species (primarily because of radiolytic effects associated with tritium β -decay) and for the most part pseudo-zero order with respect to the concentration of the oxygen donor (H_2O , O_2 , etc.). (See Refs. 4, 10, and 11 for discussions and analysis of existing data.)

(2) Some of these same physicochemical data also indicate⁴ that the reaction of tritium with H_2O makes at least a tenfold greater contribution to the overall HTO level than does the reaction with O_2 , wherever there is a measurable amount of moisture present.

(3) Computer comparisons⁴ (using TSOAK) of various mechanistic formalisms for treating the rate of formation of tritiated water (including the one advanced by Galloway¹¹) showed that there were no significant differences in the final result obtained for any of the pseudo-second-order formulations used.^{4,9}

In view of these considerations, the T_2 reaction was treated as a very simple pseudo-second-order process (see Ref. 4) where the rate of formation of tritiated water (represented in subscript form as T_0) *via* the reaction

is given by

$$\left(\frac{\partial N_{\text{TO}}}{\partial t} \right)_C = \left(\frac{\partial N_{\text{HT}}}{\partial t} \right)_C = C N_{\text{T}_2} \bar{N} \quad (3)$$

where C is the reaction rate constant, $\bar{N}$ is the total tritium concentration in the enclosure atmosphere, and N_{T_2} is the concentration of T_2 in the enclosure (all concentrations in $\mu\text{Ci}/\text{m}^3$). This formalism is computationally simple, reasonably representative of existing experimental observations, and generally consistent with the concept that both the T_2 level and the total radiolytic activity in the enclosure are important in determining the rate of formation of tritiated water.

(4) Results of air-detrification tests conducted on a room-type enclosure at the Mound Facility⁷ strongly suggest that even on the time scale of only an hour or so, detectable quantities of the released molecular tritium are converted to tritiated water in large, heterogeneous enclosures.

C. Adsorption and Release of HTO

The adsorption on enclosure surfaces and subsequent back-release of HTO were modeled in much the same way as described in Ref. 4. However, considering the convincing discussion of Sherwood,⁵ regarding surface area-to-volume effects in enclosures of different sizes, the adsorption and release coefficients were normalized for such effects by including the ratio of surface area, $\bar{SA}$, to volume, V , in the terms corresponding to these phenomena. The HTO-adsorption rate term was related to the concentration of HTO, N_{TO} , as follows:

$$\left(\frac{\partial N_{\text{TO}}}{\partial t} \right)_E = -E N_{\text{TO}} \left(\frac{\bar{SA}}{V} \right) \quad (4)$$

The release term was then expressed as

$$\left(\frac{\partial N_{\text{TO}}}{\partial t} \right)_F = F S_{\text{TO}} \left(\frac{\bar{SA}}{V} \right) \quad (5)$$

where

$$\frac{dS_{\text{TO}}}{dt} = \left[E N_{\text{TO}} \left(\frac{\bar{SA}}{V} \right) - F S_{\text{TO}} \left(\frac{\bar{SA}}{V} \right) \right] \quad (6)$$

In these expressions, $\bar{SA}$ and V are in m^2 and m^3 , respectively; E and F (the volume-averaged adsorption and release coefficients, respectively) are both

in m/s; and S_{TO} is the amount of adsorbed tritium (as HTO) in μCi adsorbed/ m^3 of room volume. The value of S_{TO} is of course obtained from the time-averaged integration of Eq. 6. The total amount of soaked tritium, $\bar{S}_{TOT}$, at any time is then given by

$$\bar{S}_{TOT} = S_{TO} \cdot V \quad (7)$$

D. Soak Effect

The "soak effect," Δ , remains as defined in Ref. 4, that is,

$$\Delta = (\bar{N}_0 - \bar{N})V \quad (8)$$

where

$$\bar{N}_0 = T_0 \exp(-At) \quad (9)$$

In Eqs. 8 and 9, $\bar{N}_0$ is the ideal calculated total tritium concentration (obtained by integration of Eq. 1), T_0 is the initial tritium concentration (at $t = 0$), and $\bar{N}$ is the TSOAK-M1 calculated value of the total tritium concentration. The soak effect is in essence a measure of the absolute differences between ideal and HTO-affected tritium levels in the enclosure at any time during the cleanup operation.

E. The Resulting Family of Differential Equations

From the partial differential equations developed above, one can assemble the family of interdependent ordinary differential equations which form the basis for TSOAK-M1.

$$\bar{N} = N_{T2} + N_{TO} + N_{HT} \quad (10)$$

$$\frac{d\bar{N}}{dt} = \frac{dN_{T2}}{dt} + \frac{dN_{TO}}{dt} + \frac{dN_{HT}}{dt} \quad (11)$$

$$\frac{dN_{T2}}{dt} = -AN_{T2} - 2CN_{T2}\bar{N} \quad (12)$$

$$\frac{dN_{TO}}{dt} = -AN_{TO} - EN_{TO}\left(\frac{\bar{SA}}{V}\right) + FS_{TO}\left(\frac{\bar{SA}}{V}\right) + CN_{T2}\bar{N} \quad (13)$$

$$\frac{dN_{HT}}{dt} = -AN_{HT} + CN_{T2}\bar{N} \quad (14)$$

$$\frac{dS_{TO}}{dt} = EN_{TO}\left(\frac{\bar{SA}}{V}\right) - FS_{TO}\left(\frac{\bar{SA}}{V}\right) \quad (15)$$

$$\bar{N}_{(\text{expt})} = \bar{N} + \text{ICF} \quad (16)$$

These equations have been programmed into the TSOAK-M1 driver package together with differential equation and matrix inversion solution packages which employ measured values of ϵ , Q , V , T , T_Q , and measured $\bar{N}$ -versus- t data sets to compute time-dependent values for $\bar{N}$, N_{T2} , N_{HT} , N_{TO} , Δ , and $\bar{S}_{TOT}$, as well as refined values for C , E , F , and ICF which give the best fit between observed ($\bar{N}_{\text{expt}}$, t) data points and the TSOAK-M1 model described above. Details of the code-development strategy are given in Section III and in Appendices A, B, and C.

III. DESCRIPTION OF THE MATHEMATICAL ALGORITHM

A. Correlation of the Algorithm with the Model

Before describing the mathematical algorithm and associated calculational techniques, it is necessary to introduce the notation which is used hereafter in Section III to correlate the algorithm with the model. The quantities N_i are expressed by the variables Y_i as follows:

$$\bar{N} = Y_5$$

$$N_{T2} = Y_1$$

$$N_{TO} = Y_2$$

$$N_{HT} = Y_3$$

$$S_{TO} = Y_4$$

The corresponding derivatives, $(\partial N_i / \partial t)$, are given by $\dot{Y}_i$, and the four adjustable parameters are expressed as Z_i 's with

$$C = Z_1$$

$$E\left(\frac{\bar{S}A}{V}\right) = Z_2$$

$$F\left(\frac{\bar{S}A}{V}\right) = Z_3$$

$$ICF = Z_4$$

The notation N_{EXP} is used as an integer to indicate the number of experimental points ($\bar{N}_{\text{expt}}$, t). Using these relationships, the set of differential equations given in Section II can now be expressed in terms of the dependent variables Y_i and the parameters to be optimally determined, Z_i , as will be shown in Section III-B.

B. Computational Method

In order to fit the observed data to the model, some measure of the "goodness" of a particular fit was needed. The following weighted sum-of-squares measure was used:

$$f(Z_1, Z_2, Z_3, Z_4) = \sum_{i=1}^{NEXP} W_i \left[\frac{Y_{1i} + Y_{2i} + Y_{3i} + Z_4 - X_i}{X_i} \right]^2 \quad (17)$$

where the W_i are weighting factors (normally set equal to one) and X_i are the observed values of $\bar{N}_i$ at t_i . Note that when $W_i = 1$, the error being measured is the relative error in the fit at t_i , since the error is divided by X_i . Given a vector of parameters $Z = (Z_1, Z_2, Z_3, Z_4)$ the values of Y_{1i} , Y_{2i} , and Y_{3i} are determined by solving the following system of ordinary differential equations (ODEs):

$$\left. \begin{aligned} \dot{Y}_1 &= -AY_1 - 2Z_1Y_SY_1 \\ \dot{Y}_2 &= -AY_2 - (Z_2Y_2 - Z_3Y_4) + Z_1Y_1Y_S \\ \dot{Y}_3 &= -AY_3 + Z_1Y_1Y_S \\ \dot{Y}_4 &= Z_2Y_2 - Z_3Y_4 \\ Y_1(0) &= X_1 - Z_4 \\ Y_j(0) &= 0, \quad j = 2, 3, 4 \end{aligned} \right\} \quad (18)$$

where

$$Y_S = Y_1 + Y_2 + Y_3$$

In summary, given a vector Z it is possible to solve the system of Eq. 18 and evaluate the fitting function (Eq. 17).

The numerical solution of Eq. 18 at the time t_i was obtained by use of A. C. Hindmarsh's GEAR code.¹² The following features of this package were of importance:

- (1) The GEAR code can be used to integrate to specific time values. Thus, the values Y_{1i} , Y_{2i} , and Y_{3i} were obtained directly by the code.
- (2) A user-specified error tolerance can be provided. Thus by providing a value of δ , the solution values Y_{1i} , Y_{2i} , and Y_{3i} were assured to be accurate to this value.
- (3) The GEAR code can be used as a stiff or non-stiff ODE solver. By using it as a non-stiff solver, it is not necessary to provide the derivatives of the right hand side of the ODEs with respect to Y_i , $i = 1, 2, 3, 4$.

C. Optimization Process

While the above procedure can be used to evaluate the fit for a specified Z , there remains the question of selecting Z . Although it is possible for the experimentalist to select reasonable values of Z to examine, this responsibility can be assumed by a digital computer routine designed to minimize the measure of error in the fit as given by Eq. 17. The independent variables for the optimization are the Z_i , which appear nonlinearly in Eq. 17 and are solved *via* the ODE system in Eq. 18. It is therefore appropriate to consider the problem of minimizing Eq. 17 as a nonlinear least-squares problem. Such problems can be solved by the Levenberg-Marquardt method¹³ and two routines based on this method were tried--LMDIF and LMDER.¹⁴

As in many optimization algorithms, derivatives of the function being minimized are required by the Levenberg-Marquardt method. The derivatives required are $\partial f / \partial Z_i$, $i = 1, 2, 3, 4$, and are obtained by solving an additional 12 ODEs. The derivation of these equations is given in Appendix A. It should be noted that the computational cost of evaluating these additional 12 equations is actually less than using a numerical differencing technique to evaluate $\partial f / \partial X_j$ (which would require the four ODEs in Eq. 18 to be evaluated four additional times). The LMDER routine is a Levenberg-Marquardt method which requires derivatives while LMDIF is a derivative-free version of the method (it uses numerical differentiation when necessary).

In using these optimization routines, difficulty in achieving accuracy arose due to errors which occurred in solving the ODEs. This difficulty was corrected by noting that the ODE solution was accurate only to δ (the accuracy specified for the solution) and not to the full computer accuracy. Thus the function in the optimization routine appeared to have "noise" beyond δ . By modifying the optimization routine's threshold for numerical accuracy to δ , this problem was corrected. However, even with this correction, failures often occurred when the optimization routine selected an unrealistic vector Z for which the ODEs could not be solved. The problem was resolved to some extent by examining the sensitivity of the model to each Z_i . This led to solving two least-squares problems: first minimizing with respect to only Z_1 , Z_2 , and Z_3 , then minimizing with respect to Z_1 , Z_2 , Z_3 , and Z_4 . Also, the routines LMDER and LMDIF allow the user to specify an initial step length limit, which could be used to define the initial search region. Nevertheless, to develop an automatic procedure, it is preferable to explicitly define the region of search. In particular, the model is expected to have a minimum error when

$$\left. \begin{aligned} c_1(Z) &\equiv Z_1 \geq 0 \\ c_2(Z) &\equiv Z_2 \geq 0 \\ c_3(Z) &\equiv Z_3 \geq 0 \\ c_4(Z) &\equiv Z_4 \geq 0 \\ c_5(Z) &\equiv -Z_4 \geq -X_{NEXP} \end{aligned} \right\} \quad (19)$$

These five inequalities provide constraints for the least-squares fit. There are two basic approaches to dealing with Eq. 19: (1) use transformations to generate a new unconstrained nonlinear least-squares problem or (2) use a constrained optimization method. In dealing with transformations, the following example illustrates the approach: Use Eqs. 20 and 21

$$Z_i = v_i^2, i = 1, 2, 3 \quad (20)$$

$$Z_4 = X_{NEXP} e^{-v_4} \quad (21)$$

and minimize f with respect to v_1, v_2, v_3, v_4 . While this approach was explored, it was found that the transformation contributed to the numerical sensitivity of the optimization problem.

In dealing with the constraints directly, it is important to note that the bounds of Eq. 18 are linear constraints. There are, in fact, Levenberg-Marquardt algorithms which handle linear constraints.¹⁵ For our purposes, a particular general constrained optimization algorithm was used. This computer routine, VMCON, is based on the use of recursive quadratic programming, *i.e.*, it solves sequences of subproblems which involve the minimization of a quadratic function subject to linear constraints. While a description of the method is given elsewhere,¹⁶ there are certain features of importance in the current application:

(1) When VMCON is used with linear constraints and the algorithm starts at a feasible point (a point satisfying Eq. 19), only feasible points are evaluated. Thus the ODE system is evaluated only at feasible points with respect to Z .

(2) The approach used in VMCON requires a small number of function evaluations when compared with other methods. This is significant because a function evaluation involves the solution of the ODE system.

(3) VMCON provides the Lagrange multipliers at the solution. If the solution occurs with one of the constraints active (satisfied as an equality), it is useful to know the sensitivity of the solution with respect to a change in the constraint. These sensitivities are the Lagrange multipliers:

$$\lambda_i = \left. \frac{\partial f}{\partial c_i} \right|_{Z=Z^*} \quad (22)$$

where λ_i is the multiplier, c_i is the i^{th} constraint, and Z^* is the solution. Notice that if c_i is not satisfied as an equality, perturbing c_i will not change the solution; thus $\lambda_i = 0$ in this case.

(4) VMCON can deal with a general nonlinear function subject to linear and nonlinear constraints. Therefore, in further work, the weighting function, Eq. 17, and the constraints, Eq. 19, could be extended while using the current optimization technique.

(5) VMCON uses a positive, definite, symmetric matrix, B , which approximates the second derivatives of the Lagrangian function¹⁶

$$f(Z) + \sum_{i=1}^M \lambda_i c_i(Z) \quad (23)$$

at the solution where there are M constraints in the problem. In the current application, $c_i(Z)$ is linear and B just approximates the second derivative of f . While B is normally set to the unit matrix, it is helpful to provide an estimate. This was done as follows:

(1) By using $N + 1$ function evaluations and numerical differencing of derivatives, an initial estimate of the second derivatives was obtained.

(2) By averaging off-diagonal terms in the matrix, a symmetric but not necessarily positive definite matrix $\hat{B}$ was determined.

(3) By using routines TRED1 and TQLRAT from EISPACK,¹⁷ the minimum eigenvalue of $\hat{B}$ was determined. If the eigenvalue was positive, $\hat{B}$ was used as a starting estimate for B . If not, then the quantity

$$[(\text{minimum eigenvalue} + 0.3) I + \hat{B}]$$

provided a starting estimate for B . Finally, after determining a data fit, it proved useful to consider statistical properties of the solution. For this purpose, the variance-covariance matrix was calculated (see Appendix B and Section III-D).

D. Input Format and Output Description

This subsection contains descriptions of the format for reading fixed parameters and experimental data into TSOAK-M1, and a general description of the output.

1. Format for Fixed Parameters

Fixed input parameters are read from unit 5 on three data cards. The variable names called for in the program are provided below, followed in parentheses by the corresponding variable name used in this report, together with a brief description of the variable.

CARD 1

(Format 4F10.2)

VTOT, (V)	--- Room volume in m^3 .
TI,	--- Total tritium release in grams.
EFF, (ϵ)	--- Process efficiency (fractional).
Q, (Q)	--- Volumetric flow rate in m^3/s .

CARD 2

(Format 4F10.2)

SR, (SA)	--- Surface area of the room in m^2 .
Z(1), (Z_1 , C)	--- Initial* reaction-rate parameter $m^3/s \cdot \mu Ci$.
Z(2), (Z_2 , E)	--- Initial* HTO adsorption parameter in m/s .
Z(3), (Z_3 , F)	--- Initial* HTO release parameter in m/s .

* Initial test value prior to refinement or final value to be used when no data set is included.

CARD 3

(Format F10.2, 4I5)

Z(4), (Z₄, ICF) --- Initial* instrument asymptote in $\mu\text{Ci}/\text{m}^3$.

[The following four variables on CARD 3 serve the function of option flags in the program. If these flags are equal to one, the option is utilized and if they are zero the option is turned off. The four options will be discussed in detail below.]

INTERP --- Option for interpolation of noisy data.

NOFIT --- Option to bypass the reading of experimental data.

IDEBUG --- Option to print additional diagnostic information for cases where the code incurs difficulties in obtaining a solution to the problem.

NOEXP --- Option to suppress the plotting of experimental data points in the graphical output.

2. Format for Experimental Data

The experimental data sets are read from unit 11. Each card image has a 3F10.1 format and represents one experimental observation. The first card of a set contains only two variables, the time (in seconds) of the initially observed tritium concentration, $\bar{N}$, and the initially measured value of $\bar{N} \approx N_{T2}$. This first observation is used to determine N_{T2} at $t = 0$. The remaining cards contain the time and experimental concentration values for the second through NEXP data points along with a weighting factor in the third field of each card. The format is, therefore, as follows:

CARD 1

(Format 3F10.1)

TT(1), (t₁) --- Time of initial experimental observation in seconds.ENEXP(1), ($\bar{N}_1$) --- Initial total tritium concentration (experimental) in $\mu\text{Ci}/\text{m}^3$.CARD 2 through NEXP

(Format 3F10.1)

TT(I), (t_i) --- Time of data point I (I = 2, NEXP) in seconds.ENEXP(I), ($\bar{N}_i$) --- Total measured tritium concentration at TT(I) in $\mu\text{Ci}/\text{m}^3$.

WT(I), (W_i) --- Weighting factor given to the Ith observation. If WT(I) = 0, the code equally weighs all experimental points. In all cases, the weights are normalized so that $\sum WT(I) = 1$.

The option flags in CARD 3 read from unit 5 provide several alternative modes of operation:

• The INTERP option is used when the experimental data are noisy at times near $t = 0$. This option inserts nine extra points, equally spaced in time, between the first two experimental data points. The logarithm of $\bar{N}$ is

* Initial test value prior to refinement or final value to be used when no data set is included.

then linearly interpolated over this time interval. One should note that this option automatically gives extra weight to experimental points at times near $t = 0$.

- The NOFIT option is used to bypass experimental data. The initial parameter values are used in the final calculation.

- The IDEBUG option is used to provide additional printed diagnostic output when the code encounters difficulties in finding a solution. Difficulties may arise due to a failure in the solution of the ODE system or in an abnormal conclusion of the optimization process. The additional output produced is described in Appendix C.

- The NOEXT option is used to prevent the plotting of experimental points in the graphical output when these points obscure the difference between the ideal curve and the theoretically calculated curve.

3. Description of Output

The printed output is produced on unit 6. Examples of the printed and graphical output are given in the following section and in Appendix D. Most of the output is self-explanatory, however, the following points may be helpful:

- If a particular Lagrange multiplier is non-zero, then the solution has encountered the corresponding constraint.

- The final objective function, *i.e.*, Eq. 17, is evaluated for the final set of Z_i 's. This value can be used to compare the "goodness" of fit of various solutions.

- The dependence of the final value of the objective function on the parameter Z_i is exhibited through the i^{th} diagonal element of the variance-covariance matrix. Specifically, if the i^{th} diagonal element is small in magnitude, then the objective function is strongly dependent on Z_i . Thus by observing the diagonal elements of the variance-covariance matrix, the relative importance of the various Z_i 's is immediately apparent.

- In the event of a return from VMCON under abnormal conditions, the message ... INFO FROM VMCON = (number) ... is printed. The meaning of this value of INFO can be obtained from the program listing.

- Some diagnostic messages may occur from the GEAR package during the ODE solution process (see Appendix C).

E. Operational Characteristics of the Code

Besides occasional difficulties in the ODE and optimization process that can lead to an abnormal termination, it is possible to obtain a solution from the code which may not be satisfactory to the user. There can be several reasons for this:

- (1) The data-fitting problem being solved is nonlinear and, as is often the case in dealing with such problems, the computational methods used can

cause the solution to become trapped at a local minimum rather than proceeding to find a global minimum. This difficulty can often be overcome by selecting alternative initial sets of Z_i 's and by following the progress of the code in reducing the objective function.

(2) The solution obtained may rest against one or more of the constraints even though such a result is not physically meaningful. This difficulty may also be caused by the solution being trapped at a local minimum and can often be dealt with as in item (1) above.

(3) The experimental data may not fit the model. In this case no appreciable progress is made in decreasing the sum of squares in Eq. 17 and an abnormal termination may occur in VMCON. (The resulting sum of squares does not seem to be affected significantly by changing the initial set of Z_i values. The problem more than likely rests with an inconsistent data set, particularly at times near $t = 0$.)

F. Adaptation of TSOAK-M1 to Other Computer Facilities

The source code of TSOAK-M1 is written in IBM Fortran IV. All of the floating-point calculations are done in double precision arithmetic (approximately 17 decimal digits). The program should be easily convertible, especially for use on other large-scale computers. As is, it should run on IBM 360, 370, or 303X series computers. Some of the non-portable features used in the code are: (1) the use of IMPLICIT REAL*8 statements; (2) the use of double precision library functions, numerical constants and formats; and (3) the use of the IBM double precision value for UROUND. UROUND is the unit roundoff of the computer, i.e., the smallest positive δ such that $1 + \delta \neq 1$. The value of UROUND is defined in SUBROUTINE DRIVE just above statement number 10.

The program is completely self-contained, except for graphic subroutines called from the main program. These subroutines are proprietary software in the DISSPLA graphics package produced by Integrated Software Systems Corporation.¹⁸

If the DISSPLA package is not available, one must modify the main program following the format statement number 2600, using another graphics package or eliminate this part of the program. In the latter case, one will not obtain graphical output.

IV. APPLICATION OF THE CODE TO EXISTING EXPERIMENTS AND PLANNED FACILITIES

A. Testing of TSOAK-M1 against Experimental Data

The testing of TSOAK-M1 was carried out using experimental air-detrition data sets measured during the course of prior work done on the 0.05-m^3 test cubicle described in Refs. 4 and 9 and shown in its final configuration in Fig. 1. The methods used to carry out these tests have already been described^{4,9} and will not be discussed at length in this report. In all, eight data sets were fed into TSOAK-M1. In six cases convergence to a reasonable solution was achieved, and in two cases, where the data appeared to

Fig. 1. The Bench-Scale Air-Detritionation Test Apparatus at ANL

be suspect, the code failed to converge to any solution. The parameter values obtained for four of the six cases that converged are plotted in Fig. 2. Illustrations of the TSOAK-M1-plotted concentration and soaking profiles are shown in Figs. 3 and 4. Note especially in Fig. 3 the excellent coincidence between the observed data points and the TSOAK-M1-calculated cleanup curve. Appendix D shows the correlation between observed and calculated points and the detritionation analysis for the same calculation that is illustrated in Figs. 3 and 4. The results in Appendix D and in Figs. 3 and 4 are typical of the output obtained for each of the six converged data sets.

Interpretation of the information in Figs. 2-4 requires that some background be given concerning the respective experiments. The four experiments represent duplicate pairs of tests under two different sets of detritionation conditions. The differences between the two sets of conditions were that for one set, room air ($\sim 50\%$ relative humidity) was pulled through the cubicle and exhausted in a "once-through-flushing" manner. For the other set, closed-cycle detritionation was carried out wherein the atmosphere in the cubicle (originally room air at $\sim 50\%$ relative humidity) was circulated through an oxidation catalyst bed (to convert all molecular tritium to tritiated water) and a molecular sieve bed to remove the tritiated water from the return stream. Otherwise, all other experimental conditions were the same, *e.g.*, a flow rate of $\sim 1.7 \times 10^{-5} \text{ m}^3/\text{s}$ and a starting tritium concentration of $\sim 10^3 \text{ } \mu\text{Ci}/\text{m}^3$.

The results of these analyses have been interpreted in the following way. Within the scatter of a given duplicate pair, the reaction rate ($\text{H}_2\text{O} + \text{T}_2 \rightarrow \text{HTO} + \text{HT}$) for the once-through-flushing set is $\sim 10^2$ greater than that for the closed-cycle set. This effect is attributed to the fact that the average moisture level during the cleanup is much higher in the former

Fig. 2. Reaction/Adsorption/Release and Instrument Correction Parameters Derived from Bench-Scale Air-Detritiation Test Data Using TSOAK-M1

test than in the latter. Whereas about 50% relative humidity is maintained throughout the once-through-flushing test, the scrubbing system acts to dry out the cubicle atmosphere during the closed-cycle tests. This finding is consistent with previous observations by other workers^{4,10,11} that conversion of molecular tritium to tritiated water occurs much more rapidly in moist air than in dry air.

Similarly, it is possible to reconcile the higher adsorption and release rate parameters observed for the closed-cycle tests, in that the reduced humidity (due to the drying effect of closed-cycle operation) increases the tendency for surface-held moisture to desorb and at the same time creates more surface adsorption sites to which gaseous molecules of HTO can attach. The difference in the ranges of the instrument correction factors for the two sets of experiments is not easily interpreted, but this factor makes a significant contribution to the result only near the tail end of the cleanup operation where uncertainties are greatest. It too may be related to increased adsorption of HTO in the Kanné chambers of the counting instrument due to the dehydrating nature of the closed-cycle cleanup operation.

Fig. 3. Analysis of Test Data on Atmospheric Detritiation in a Closed-Cycle Experiment. Curves for ideal and calculated total residual tritium and amount of soaked tritium are shown.

In general, the range of observed pseudo-second-order reaction rate parameters, 10^{-4} to 10^{-8} $\text{m}^3/\mu\text{Ci}\cdot\text{s}$, is four to ten orders of magnitude greater than the range observed in static glass bulb experiments^{4,10,11} (normally 10^{-12} to 10^{-14} $\text{m}^3/\mu\text{Ci}\cdot\text{s}$). Because of the heterogeneous nature of the cubicle used in the tests analyzed above, there is little basis for correlating the adsorption and release rate parameters with related types of experimental data in the literature.

The instrument correction factor (ICF) is, as expected, on the order of 1 to 10 $\mu\text{Ci}/\text{m}^3$. Even in the absence of tritium, the background obtained with both of the meters used (Johnston Laboratories, Inc., Model 955B; and Overhoff and Assoc., Inc., Model SR-206) is normally in the 2- to 4- $\mu\text{Ci}/\text{m}^3$ range. The need for an ICF was highlighted in previous work,⁹ where an instrument effect was observed that was small in magnitude (around 5 $\mu\text{Ci}/\text{m}^3$) but became significant towards the end of a detritiation operation. The inclusion of an ICF in subsequent utilizations of TSOAK-M1 is likely to be important if commercially available tritium monitors are employed for concentration measurements. Its use has been essential in achieving a good fit at long times in the analyses of detritiation data.

Fig. 4. Calculated Curves for Individual Species Concentrations Determined from the Analysis Shown in Fig. 3.

B. Correlation of TSOAK-M1 Findings with Other Experimental Observations

Before extending the findings presented in Section IV-A above to fusion-reactor-sized facilities, there are a number of aspects of these findings that can be further substantiated by correlation with other types of experimental observations derived from previous bench-scale tests at ANL.^{4,9} For instance, the calculated results in Fig. 4, which are unfolded from the TSOAK-M1 data-fitting exercise in Fig. 3, imply that tritiated water forms very rapidly in the test cubicle, and on the time scale of tens of seconds is approximately equal in concentration to the amount of residual T_2 in the cubicle. Although no definitive experiments were ever done on this time scale with the ANL test cubicle, tests were done to confirm (1) that the initial charge of tritium to the cubicle is indeed in the molecular form (T_2), and (2) that on a time scale of tens of minutes virtually all of the tritium left in the cubicle atmosphere is in the tritiated water form. An example of the latter test is shown in Fig. 5 for a detritiation experiment wherein flow through the oxidizer bed and water-adsorbing trap was stopped for ~20 minutes, after which flow was reinitiated through the water-adsorbing trap only. The rise in tritium concentration following complete processor flow stoppage (trap and bed off) is generally considered to be indicative of the effects of

Fig. 5. Test of HTO Formation Kinetics During Detritiation Using an 0.008-m^3 Test Cubicle

desorption of HTO which had been adsorbed during the initial phases of the cleanup. The dramatic continuation of detritiation (to the instrument baseline) after the reestablishment of flow through the water-sorbing trap shows quite conclusively that virtually all of the residual tritium in the enclosure after 40 minutes (2400 seconds) is in the water form already and need not be oxidized to effect trapping. Although the condition of $N_{T0} \gg (N_{T2} + N_{HT})$ is not achieved until $>2 \times 10^4$ seconds for the experiment in Fig. 3, the differences between this time span for $N_{T0} \gg (N_{T2} + N_{HT})$ and the span indicated by Fig. 5 can be reconciled from considerations of differences in starting T_2 concentration (~ 5 times greater for Fig. 5 than for Figs. 3 and 4) and test-cubicle surface area-to-volume ratio (also ~ 5 times greater for Fig. 5 than for Figs. 3 and 4).

Another set of experiments, done with the test configuration and cubicle (0.05 m^3) shown in Fig. 1, was conducted to measure the approximate magnitude of the shift in instrument correction factor associated with tritium soaking effects in the counting chambers of the tritium monitors used. Air containing $\sim 40\text{ }\mu\text{Ci}/\text{m}^3$ of tritium was left in the instrument chambers for about 3 days

then flushed out. As is shown in Fig. 6, recalibration of the instruments following flushing indicated 3- to 8- $\mu\text{Ci}/\text{m}^3$ higher backgrounds than were obtained prior to the 3-day soak. This range of values for instrument soak effects is close to the range implied by the TSOAK-M1 calculated instrument correction factors in Fig. 2. The value of the tritium concentration used in the meter soaking test, $\sim 40 \mu\text{Ci}/\text{m}^3$, is close to the time-average value of $\bar{N}$ for most of the detritiation tests done using the apparatus in Fig. 1.^{4,9}

Fig. 6. Tests of Meter Memory Effects on Observed Instrument Correction Factors. Meter A is the Overhoff Model SR-206 and meter B is the Johnston Laboratories Model 955-B.

Another important consideration in evaluating the test data developed with the ANL 0.05- m^3 cubicle relates to the effect of flow rate on observed detritiation behavior. It is important to show that the processor flow rate used for the TSOAK-M1-analyzed tests is in a range that allows the model described in Section II to be applicable. It was found in early cubicle tests that flow rates of $\leq 0.1 \text{ L/min}$ ($1.7 \times 10^{-6} \text{ m}^3/\text{s}$) caused distortion of the test data associated with what appeared to be numerous second-order effects resulting from the long required cleanup times (several days). On the other hand, tests run with processor flow rates in excess of 2.0 L/min ($3.3 \times 10^{-5} \text{ m}^3/\text{s}$) tended to lead to flooding of the processor section and, in addition, represented fractional processing rates that would

be considerably greater than those that could be achieved in a large-scale facility ($>10^5 \text{ m}^3$). Based on the flooding-threshold tests shown in Fig. 7 and on considerations related to achievable fractional processing rates (*i.e.*, $\sim 1\%$ of building volume per minute⁹), a value of $\sim 1.0 \text{ L/min}$ ($1.7 \times 10^{-5} \text{ m}^3/\text{s}$) was selected for all the tests analyzed in Fig. 2. This corresponds to an upper limit processing rate for large enclosures of $\sim 2\%$ of the building volume per minute, and clearly, from Fig. 7, is in the range of unflooded values (*i.e.*, 0.5 to 2.0 L/min or 8.3×10^{-6} to $3.3 \times 10^{-5} \text{ m}^3/\text{s}$). The results presented in Section IV-A above are, therefore, representative of small-scale experiments conducted for a range of parameters that come as close as possible to the range of applicability of the model described in Section II.

Fig. 7. Tests of the Effect of Processor Flow Rate on the Detritiation Characteristics of the Apparatus Shown in Fig. 1.

C. Analysis of Large-Enclosure Detritiation Using TSOAK-M1 Results

Following the successful testing of TSOAK-M1 with the small-cubicle data developed previously at ANL, the iteratively determined reaction/adsorption/release and ICF parameters were employed to evaluate hypothetical detritiation operations on reactor-size enclosures ($\sim 10^5 \text{ m}^3$). These evaluations were conducted for two plausible tritium-release sizes that bracket the range of credible "significant releases" (*i.e.*, 1 g and 100 g as T_2 which correspond

to initial $\bar{N}$ s of ~ 0.1 to ~ 10 Ci/m³), using processor flow rates of 10 and 100 m³/s (0.6 to 6% of the building volume per minute).^{4,9} Results of these analyses are presented in Table 1 for a selected set of reaction, adsorption, and release-rate parameters. Because the range of the ICF parameter was relatively small in the cubicle analyses (see Fig. 2), a mean value of 3 μ Ci/m³ was used throughout the calculations. The amount of soaked tritium (HTO) at the point in time where the total concentration of tritium, $\bar{N}$, reaches 5 μ Ci/m³ is included in Table 1, together with the time it takes for the concentration of HTO to build to a level equal to the residual T₂ level, *i.e.*, $N_{T0} = N_{T2}$.

The results in Table 1 indicate that the cleanup time is most sensitive to processor flow rate, PFR, and that indeed it is desirable to have PFRs >1% of the building volume per minute. Note in particular for cases 6 and 12 (where PFR = 10 m³/s was used) how large the amount of soaked tritium is relative to other cases involving equivalent release sizes. On the other hand, the cleanup time was relatively insensitive to the reaction/adsorption/release parameters over the ranges of these parameters that were studied. The amount of soaked tritium at the end of the cleanup operation was generally proportional to the release size for fixed PFR and adsorption rate, but did show a tendency to increase in proportion to the adsorption rate parameter. The time required for $N_{T0} = N_{T2}$ was quite sensitive to both release size and reaction-rate parameter as expected. In all cases, the cleanup time was very close to the ideal value that would be calculated by integration of Eq. 1 in Section II.

One disconcerting feature of the calculations in Table 2 is the observation that for reaction rates $\geq 10^{-7}$ m³/ μ Ci·s, the time for $N_{T0} = N_{T2}$ is on the order of a second or less. This is probably somewhat artificial and reflects the difficulty associated with extrapolating the bench-scale experiments to much larger enclosures. In that light, therefore, the results in Table 1 should be taken to be worst-case estimates of conditions during and at the end of a detritiation operation on a large building. Of course, much larger-scale tests than the ones performed at ANL^{4,9} must be conducted and analyzed to verify this conclusion.

V. CONCLUSIONS AND RECOMMENDATIONS

The principal conclusions and recommendations derived from this study may be summarized as follows: (1) The simplified reaction/adsorption/release model employed in TSOAK-M1 appears to be capable of predicting the observations of experimental detritiation tests, but should be subjected to further examination using results from large enclosures and, if possible, from actual facility buildings. Only through extended utilization for a wide range of test conditions will it be possible to validate the credibility of the model. (2) Pseudo-second-order reaction rate parameters (for $T_2 + H_2O \rightleftharpoons HTO + HT$) derived from previous small-cubicle detritiation experiments conducted at ANL are 10^4 - to 10^8 -times greater than comparable parameters derived from iso-static kinetics studies done in well characterized glass bulbs. This is believed to be related, more than anything else, to the heterogeneity of surface conditions in typical enclosures and the convective environments that result from recycling of the enclosure atmosphere. (3) The projected consequences of the effects incorporated in the TSOAK-M1 model, when extrapolated

Table 1. Summary of Hypothetical Reactor-Building Cleanup Scenarios Using TSOAK-M1-Generated Parameters from Bench-Scale Experiments

Fixed Parameters: Room Volume = 10^5 m^3 Process Efficiency = 100%
Room Surface Area = $2 \times 10^4 \text{ m}^2$ Instrument Correction = $3 \text{ } \mu\text{Ci}/\text{m}^3$

Test Case Number	Weight of Tritium Released, g	Processor Flow Rate, m^3/s	Reaction Rate, m/s	Adsorption Rate, m/s	Release Rate, m/s	Cleanup Time, ^a s	Amount Soaked, ^b Ci	Time ^c for $N_{T0} = N_{T2}$, s
1	100	100	10^{-5}	10^{-6}	10^{-5}	$<2 \text{ E} + 04$	~ 100	$<<1$
2	100	100	10^{-5}	10^{-6}	10^{-7}	$<2 \text{ E} + 04$	~ 100	$<<1$
3	100	100	10^{-7}	10^{-6}	10^{-5}	$<2 \text{ E} + 04$	~ 100	~ 1
4	100	100	10^{-7}	10^{-6}	10^{-7}	$<2 \text{ E} + 04$	~ 100	~ 1
5	100	100	10^{-8}	10^{-5}	10^{-7}	$<2 \text{ E} + 04$	$\sim 1 \text{ E} + 03$	~ 6
6	100	10	10^{-8}	10^{-5}	10^{-7}	$>4 \text{ E} + 05$	$\sim 1 \text{ E} + 04$	~ 6
7	1	100	10^{-5}	10^{-6}	10^{-5}	$\sim 1 \text{ E} + 04$	~ 1	~ 1
8	1	100	10^{-5}	10^{-6}	10^{-7}	$\sim 1 \text{ E} + 04$	~ 1	~ 1
9	1	100	10^{-7}	10^{-6}	10^{-5}	$\sim 1 \text{ E} + 04$	~ 1	~ 55
10	1	100	10^{-7}	10^{-6}	10^{-7}	$\sim 1 \text{ E} + 04$	~ 1	~ 55
11	1	100	10^{-8}	10^{-5}	10^{-7}	$\sim 1 \text{ E} + 04$	~ 6	~ 800
12	1	10	10^{-8}	10^{-5}	10^{-7}	$\sim 1 \text{ E} + 05$	~ 100	~ 600

^aTime required for the total tritium level, $\bar{N}$, to reach $5 \text{ } \mu\text{Ci}/\text{m}^3$.

^bAmount of HTO adsorbed on building surfaces at the time indicated in the column to the left.

^cThe time during the cleanup operation (following the release) at which the HTO level in the building equals the residual T_2 level.

to anticipated fusion-reactor facilities, seem to be less serious than was previously suggested, at least to the extent that parameter values from the ANL cubicle experiments are close to being representative of conditions in such facilities.

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APPENDIX A

CALCULATION OF DERIVATIVES WITH RESPECT TO Z_i

In the formulation of the mathematical algorithm, it is necessary to solve a constrained optimization problem. This problem involves the selection of the adjustable parameters Z_k , $k = 1, 2, 3, 4$ defined in Section III-A so as to minimize f in Eq. 17 of Section III-B subject to the constraints in Eq. 19 of that subsection. This constrained optimization problem is solved by use of the algorithm VMCON¹⁶ which requires the partial derivatives of f with respect to Z_k . These derivatives involve Y_{ji} , $j = 1, 2, 3, 4$, $i = 1, \dots, \text{NEXP}$ and their derivatives with respect to the Z_k . By direct calculation one obtains

$$\frac{\partial f}{\partial Z_j} = 2 \sum_{i=1}^{\text{NEXP}} w_i \left(\frac{Y_{1i} + Y_{2i} + Y_{3i} + Z_4 - X_i}{X_i^2} \right) \left(\frac{\partial Y_{1i}}{\partial Z_j} + \frac{\partial Y_{2i}}{\partial Z_j} + \frac{\partial Y_{3i}}{\partial Z_j} \right) \quad j = 1, 2, 3$$

$$\frac{\partial f}{\partial Z_4} = 2 \sum_{i=1}^{\text{NEXP}} w_i \left(\frac{Y_{1i} + Y_{2i} + Y_{3i} + Z_4 - X_i}{X_i^2} \right)$$

It is therefore necessary to determine

$$\frac{\partial Y_{1i}}{\partial Z_j}, \frac{\partial Y_{2i}}{\partial Z_j}, \text{ and } \frac{\partial Y_{3i}}{\partial Z_j}$$

for $j = 1, 2, 3$. To accomplish this, define:

$$\begin{aligned} Y_5 &= \frac{\partial Y_1}{\partial Z_1} & Y_9 &= \frac{\partial Y_1}{\partial Z_2} & Y_{13} &= \frac{\partial Y_1}{\partial Z_3} \\ Y_6 &= \frac{\partial Y_2}{\partial Z_1} & Y_{10} &= \frac{\partial Y_2}{\partial Z_2} & Y_{14} &= \frac{\partial Y_2}{\partial Z_3} \\ Y_7 &= \frac{\partial Y_3}{\partial Z_1} & Y_{11} &= \frac{\partial Y_3}{\partial Z_2} & Y_{15} &= \frac{\partial Y_3}{\partial Z_3} \\ Y_8 &= \frac{\partial Y_4}{\partial Z_1} & Y_{12} &= \frac{\partial Y_4}{\partial Z_2} & Y_{16} &= \frac{\partial Y_4}{\partial Z_3} \\ Y_s &= Y_1 + Y_2 + Y_3 \end{aligned}$$

By differentiation of the ODE system, Eq. 18 in Section III-B, the differential equations for $Y_5, \dots, Y_{16}$ are:

$$\dot{Y}_5 = -AY_5 - 2Y_1Y_S - 2Z_1Y_5Y_S - 2Z_1Y_1(Y_5 + Y_6 + Y_7)$$

$$\dot{Y}_6 = -AY_6 - (Z_2Y_6 - Z_3Y_8) + Y_1Y_S + Z_1Y_5Y_S + Z_1Y_1(Y_5 + Y_6 + Y_7)$$

$$\dot{Y}_7 = -AY_7 + Y_1Y_S + Z_1Y_5Y_S + Z_1Y_1(Y_5 + Y_6 + Y_7)$$

$$\dot{Y}_8 = (Z_2Y_6 - Z_3Y_8)$$

$$\dot{Y}_9 = -AY_9 - 2Z_1Y_9Y_S - 2Z_1Y_1(Y_9 + Y_{10} + Y_{11})$$

$$\dot{Y}_{10} = -AY_{10} - (Y_2 + Z_2Y_{10} - Z_3Y_{12}) + Z_1Y_9Y_S + Z_1Y_1(Y_9 + Y_{10} + Y_{11})$$

$$\dot{Y}_{11} = -AY_{11} + Z_1Y_9Y_S + Z_1Y_1(Y_9 + Y_{10} + Y_{11})$$

$$\dot{Y}_{12} = (Y_2 + Z_2Y_{10} - Z_3Y_{12})$$

$$\dot{Y}_{13} = -AY_{13} - 2Z_1Y_{13}Y_S - 2Z_1Y_1(Y_{13} + Y_{14} + Y_{15})$$

$$\dot{Y}_{14} = -AY_{14} - (Z_2Y_{14} - Y_4 - Z_3Y_{16}) + Z_1Y_{13}Y_S + Z_1Y_1(Y_{13} + Y_{14} + Y_{15})$$

$$\dot{Y}_{15} = -AY_{15} + Z_1Y_{13}Y_S + Z_1Y_1(Y_{13} + Y_{14} + Y_{15})$$

$$\dot{Y}_{16} = (Z_2Y_{14} - Y_4 - Z_3Y_{16})$$

$$Y_j(0) = 0 \quad j = 5, \dots, 16$$

APPENDIX B

CALCULATION OF THE VARIANCE-COVARIANCE MATRIX

In the mathematical algorithm described in Section III, the adjustable parameters Z_k , $k = 1, 2, 3, 4$ defined in Section III-A are chosen to minimize the sum-of-squares error function given by Eq. 17 in Section III-B. This function measures the error between the mathematical model and the observed data points. Once the Z_k values are selected, it is useful to have information concerning the sensitivity of the Z_k to the error function Eq. 17.

Most of the statistical measures concerning the accuracy of models deal with linear models. Results for nonlinear models, such as the one used in Eq. 17, are often based on local linearization as is done for the calculation of the variance-covariance matrix.¹⁹ The use of the variance-covariance matrix is illustrated by the observation in Section III-C that if the k^{th} diagonal element of this matrix is small, then the function in Eq. 17 is strongly dependent on Z_k . The variance-covariance matrix for the model in this report is

$$\frac{1}{\text{NEXP} - N} (J^T J)^{-1}$$

where J is the Jacobian of the functions:

$$W_i^{1/2} \left(\frac{Y_{1i} + Y_{2i} + Y_{3i} + Z_4 - X_i}{X_i} \right) \quad (24)$$

treated as functions of Z_1, Z_2, Z_3 , and Z_4 . That is, the (i, j) element of J is the partial derivative of (Eq. 24) with respect to Z_j . Notice that the information required to calculate J has already been provided in the calculation of the derivatives of f (see Appendix A). While it is possible to directly calculate $(J^T J)^{-1}$ this is known to be a numerically unstable approach.²⁰ Instead, a QR decomposition is used. In this approach matrices Q and R are determined such that $J = QR$ where R is an upper triangular matrix and Q is an orthogonal matrix, *i.e.*, $Q^T Q = I$. The calculation of $(J^T J)^{-1}$ then becomes:

$$(J^T J)^{-1} = (R^T Q^T Q R)^{-1} = (R^T R)^{-1} = R^{-1} R^{-T}$$

The QR decomposition is done numerically by routine DQRDC in LINPACK²¹ and the inversion of R is done numerically by routine DTRDI in LINPACK.²¹

The calculation of the variance-covariance matrix given here is based on no constraints being active at the solution (which is the expected situation). The extension to active constraints and other means of examining the model reliability²² could be of use in the further upgrading of TSOAK-M1.

APPENDIX C

DIAGNOSTIC MESSAGES WHEN IDEBUG = 1

Among the input parameters for TSOAK-M1 described in Section III-D, there is a flag IDEBUG used to generate additional printed output. Normally TSOAK-M1 should be run with this flag off (IDEBUG = 0). However, if difficulties occur in a computation, the case should be rerun with the flag on (IDEBUG = 1). The additional printout caused by the use of this flag is useful in understanding the computations of the mathematical algorithm (Section III). The format of this additional printout is discussed below.

1. At each optimization iteration printout occurs as follows:

```
ITER = (iteration number)
Z = (Z values)
OBJECTIVE FUNCTION = (least-squares function value).
```

2. During optimization iterations it is possible to encounter difficulties in solving the ordinary differential equations. In this case printout may occur from the GEAR package. The most common such message is:

```
KFLAG = -1 FROM INTEGRATOR AT T = (time)
ERROR TEST FAILED WITH DABS (H) = HMIN
H HAS BEEN REDUCED TO (step size) AND STEP WILL BE RETRIED
```

and can only occur if IDEBUG = 1. Other error messages from the GEAR package may occur regardless of the setting of IDEBUG. The GEAR user's guide¹² should be consulted for the interpretation of these messages. Note: The above message and many of the other GEAR messages are not fatal--they merely provide information about the ODE solution process.

3. Before beginning the optimization process, it is necessary to determine scale factors for the objective function, Eq. 17 in Section III-B, and to determine the initial B matrix (see Section III-B). The scale factors determine variables $Z'_i = (\text{factor})_i Z_i$, $i = 1, 2, 3, 4$ which are actually used in the optimization routine VMCON. The use of these scale factors improves the reliability of the mathematical algorithm. The scale factors are determined by doing an initial function evaluation (calculating Eq. 17) and using

$\frac{\partial f}{\partial Z_i}$ to cause $\left| \frac{\partial f}{\partial Z_i} \right|$ to be one. The scale factors are then printed

```
SCALE FACTORS FOR OPTIMIZATION
(factor1) (factor2) (factor3) (factor4)
```

After forming the $\hat{B}$ matrix (see Section III-C), eigenvalues of the matrix are calculated to check the positive definiteness of the matrix. If all of the eigenvalues are positive, $\hat{B}$ can be used as the initial B matrix. If not, B is set to (minimum eigenvalue + 0.3)I + $\hat{B}$. The calculated eigenvalues of $\hat{B}$ are printed as

```
EIGENVALUES FOR DETERMINING INITIAL B MATRIX
(value1) (value2) (value3) (value4)
```

The initial B matrix is then printed

```
INITIAL B MATRIX  
(matrix elements)
```

The B matrix is used in VMCON and modified as the calculation proceeds.

4. At the conclusion of the optimization process the INFO flag from VMCON indicates the nature of normal or abnormal exits from the optimization. (INFO = 1 indicates a normal termination. Other values of INFO are described in the program listing of VMCON.) INFO is printed as

```
INFO FROM VMCON = (number)
```

5. The final B matrix is the matrix after VMCON has modified it. This matrix is printed as

```
FINAL B MATRIX  
(matrix elements)
```

The user can compare the initial and final B matrix to check how accurate the initial estimate was.

APPENDIX D

TSOAK-M1 PRINTED OUTPUT DISPLAY

This appendix contains a sample of TSOAK-M1 printed output for the test case shown in Figs. 3 and 4 in Section IV of the report. Appearing in order are the initial input parameters, a listing of experimental time and concentration data used as input, the final adjusted parameters, a comparative listing of observed and calculated data (including the status of Lagrangian multipliers, the final objective function, and the variance-covariance matrix), and an output summary table.

ROOM VOLUME IN CU M = 4.6000000D-02

TOTAL TRITIUM RELEASE IN GRAMS = 5.0600000D-09

PROCESS EFFICIENCY = 9.8100000D-01

VOLUMETRIC FLOW RATE IN CU M/SEC = 1.6670000D-05

SURFACE AREA OF ROOM IN SQ M = 7.7000000D-01

INITIAL REACTION RATE IN CU M/SEC-MICRO CI = 1.0000000D-06

INITIAL HTO ADSORPTION PARAMETER IN M/SEC = 1.0000000D-07

INITIAL HTO RELEASE PARAMETER IN M/SEC = 1.0000000D-08

INITIAL INSTRUMENT ASYMPTOTE IN MICRO CI/CU M = 3.0000000D 00

EXPERIMENTAL DATA

TIME SECONDS	N EXPERIMENTAL	MICRO CI/M**3
0.0	03	1.100000000
3.000000	01	1.050000000
6.000000	01	1.000000000
9.000000	01	9.900000000
1.200000	02	9.810000000
1.500000	02	9.750000000
1.800000	02	9.650000000
2.100000	02	9.500000000
2.400000	02	9.400000000
2.700000	02	9.300000000
3.000000	02	9.200000000
3.300000	02	9.100000000
3.600000	02	9.000000000
3.900000	02	8.900000000
4.200000	02	8.800000000
4.500000	02	8.720000000
4.800000	02	8.610000000
5.100000	02	8.500000000
5.400000	02	8.410000000
5.700000	02	8.350000000
6.000000	02	8.250000000
6.300000	02	8.190000000
6.600000	02	8.110000000
6.900000	02	8.000000000
7.200000	02	7.910000000
7.500000	02	7.850000000
7.800000	02	7.750000000
8.100000	02	7.650000000
8.400000	02	7.550000000
8.700000	02	7.490000000
9.000000	02	7.360000000
9.300000	02	7.290000000
9.600000	02	7.210000000
9.900000	02	7.110000000
1.020000	03	7.030000000
1.250000	03	6.450000000
1.500000	03	5.850000000
1.750000	03	5.280000000
2.000000	03	4.800000000

EXPERIMENTAL DATA

TIME SECONDS	N EXPERIMENTAL	MICRO CI/M**3
2.250000	03	4.380000000
2.500000	03	4.000000000
2.750000	03	3.650000000
3.000000	03	3.300000000
3.250000	03	3.000000000
3.500000	03	2.750000000
3.750000	03	2.500000000
4.000000	03	2.290000000
4.250000	03	2.090000000
4.500000	03	1.900000000
4.750000	03	1.700000000
5.000000	03	1.550000000
5.250000	03	1.450000000
5.500000	03	1.300000000
5.750000	03	1.200000000
6.000000	03	1.100000000
6.250000	03	1.000000000
6.500000	03	9.200000000
6.750000	03	8.300000000
7.000000	03	7.550000000
7.250000	03	7.000000000
7.500000	03	6.400000000
7.750000	03	5.900000000
8.000000	03	5.350000000
8.250000	03	4.950000000
8.500000	03	4.550000000
8.750000	03	4.150000000
9.000000	03	3.800000000
9.250000	03	3.550000000
9.500000	03	3.250000000
9.750000	03	3.000000000
1.000000	04	2.820000000
1.250000	04	1.290000000
1.500000	04	7.500000000
1.750000	04	5.500000000
2.000000	04	4.500000000
2.250000	04	3.800000000

***** ADJUSTED PARAMETERS *****

FINAL REACTION RATE IN CU M/SEC-MICRO CI = 7.4834031D-05

FINAL HTO ADSORPTION PARAMETER IN M/SEC = 4.8240067D-06

FINAL HTO RELEASE PARAMETER IN M/SEC = 7.5438545D-07

FINAL INSTRUMENT ASYMPOTTE IN MICRO CI/CU M = 1.4765012D 00

***** COMPARISON OF EXPERIMENTAL AND CALCULATED DATA POINTS *****

TIME SECONDS	N CALCULATED MICRO CI/M**3	N EXPERIMENTAL MICRO CI/M**3	RELATIVE DIFF (UNITLESS)
3.000000 01	1.0872966D 03	1.0500000D 03	3.5520566D-02
6.000000 01	1.0744319D 03	1.0000000D 03	7.4481865D-02
9.000000 01	1.0618185D 03	9.9000000D 02	7.2543933D-02
1.200000 02	1.0493066D 03	9.8100000D 02	6.9629550D-02
1.500000 02	1.0369443D 03	9.7500000D 02	6.3532649D-02
1.800000 02	1.0247299D 03	9.6500000D 02	6.1896283D-02
2.100000 02	1.0126616D 03	9.5000000D 02	6.5959534D-02
2.400000 02	1.0007375D 03	9.4000000D 02	6.4614347D-02
2.700000 02	9.8895596D 02	9.3000000D 02	6.3393507D-02
3.000000 02	9.7731526D 02	9.2000000D 02	6.2299196D-02
3.300000 02	9.6581368D 02	9.1000000D 02	6.1333716D-02
3.600000 02	9.5444955D 02	9.0000000D 02	6.0499495D-02
3.900000 02	9.4322119D 02	8.9000000D 02	5.9799092D-02
4.200000 02	9.3212698D 02	8.8000000D 02	5.9235205D-02
4.500000 02	9.2116529D 02	8.7200000D 02	5.6382216D-02
4.800000 02	9.1033453D 02	8.6100000D 02	5.7299103D-02
5.100000 02	8.9963311D 02	8.5000000D 02	5.8391890D-02
5.400000 02	8.8905947D 02	8.4100000D 02	5.7145620D-02
5.700000 02	8.7861207D 02	8.3500000D 02	5.2230019D-02
6.000000 02	8.6828938D 02	8.2500000D 02	5.2471979D-02
6.300000 02	8.5808991D 02	8.1900000D 02	4.7728829D-02
6.600000 02	8.4801216D 02	8.1100000D 02	4.5637687D-02
6.900000 02	8.3805468D 02	8.0000000D 02	4.7568344D-02
7.200000 02	8.2821599D 02	7.9100000D 02	4.7049296D-02
7.500000 02	8.1849468D 02	7.8500000D 02	4.2668388D-02
7.800000 02	8.0883934D 02	7.7500000D 02	4.3728175D-02
8.100000 02	7.9939855D 02	7.6500000D 02	4.4965421D-02
8.400000 02	7.9002094D 02	7.5500000D 02	4.6385349D-02
8.700000 02	7.8075515D 02	7.4900000D 02	4.2396723D-02
9.000000 02	7.7159982D 02	7.3600000D 02	4.8369321D-02
9.300000 02	7.6255363D 02	7.2900000D 02	4.6026931D-02
9.600000 02	7.5361527D 02	7.2100000D 02	4.5236154D-02
9.900000 02	7.4478342D 02	7.1100000D 02	4.7515365D-02
1.020000 03	7.3605682D 02	7.0300000D 02	4.7022506D-02
1.250000 03	6.7251620D 02	6.4500000D 02	4.2660776D-02
1.500000 03	6.0975513D 02	5.8500000D 02	4.2316460D-02
1.750000 03	5.5294810D 02	5.2800000D 02	4.7250196D-02

***** COMPARISON OF EXPERIMENTAL AND CALCULATED DATA POINTS *****

TIME SECONDS	N CALCULATED MICRO CI/M**3	N EXPERIMENTAL MICRO CI/M**3	RELATIVE DIFF (UNITLESS)
2.000000 03	5.0152467D 02	4.8000000D 02	4.4843056D-02
2.250000 03	4.5496952D 02	4.3800000D 02	3.8743187D-02
2.500000 03	4.1281716D 02	4.0000000D 02	3.2042894D-02
2.750000 03	3.7464703D 02	3.6500000D 02	2.6430207D-02
3.000000 03	3.4007911D 02	3.3000000D 02	3.0542767D-02
3.250000 03	3.0877003D 02	3.0000000D 02	2.9233417D-02
3.500000 03	2.8040942D 02	2.7500000D 02	1.9670611D-02
3.750000 03	2.5471679D 02	2.5000000D 02	1.8867158D-02
4.000000 03	2.3143858D 02	2.2900000D 02	1.0648834D-02
4.250000 03	2.1034557D 02	2.0900000D 02	6.4381556D-03
4.500000 03	1.9123052D 02	1.9000000D 02	6.4763993D-03
4.750000 03	1.7390601D 02	1.7000000D 02	2.2976519D-02
5.000000 03	1.5820258D 02	1.5500000D 02	2.0661323D-02
5.250000 03	1.4396697D 02	1.4500000D 02	-7.1243563D-03
5.500000 03	1.3106053D 02	1.3000000D 02	8.1579236D-03
5.750000 03	1.1935786D 02	1.2000000D 02	-5.3511941D-03
6.000000 03	1.0874549D 02	1.1000000D 02	-1.1404655D-02
6.250000 03	9.9120764D 01	1.0000000D 02	-8.7923586D-03
6.500000 03	9.0390789D 01	9.2000000D 01	-1.7491429D-02
6.750000 03	8.2471490D 01	8.3000000D 01	-6.3675936D-03
7.000000 03	7.5286775D 01	7.5500000D 01	-2.8241752D-03
7.250000 03	6.8767765D 01	7.0000000D 01	-1.7603362D-02
7.500000 03	6.2852104D 01	6.4000000D 01	-1.7935872D-02
7.750000 03	5.7483337D 01	5.9000000D 01	-2.5706151D-02
8.000000 03	5.2610343D 01	5.3500000D 01	-1.6629102D-02
8.250000 03	4.8186828D 01	4.9500000D 01	-2.6528721D-02
8.500000 03	4.4170865D 01	4.5500000D 01	-2.9211753D-02
8.750000 03	4.0524477D 01	4.1500000D 01	-2.3506585D-02
9.000000 03	3.7213260D 01	3.8000000D 01	-2.0703686D-02
9.250000 03	3.4206047D 01	3.5500000D 01	-3.6449384D-02
9.500000 03	3.1474597D 01	3.2500000D 01	-3.1550865D-02
9.750000 03	2.8993319D 01	3.0000000D 01	-3.3556027D-02
1.000000 04	2.6739022D 01	2.8200000D 01	-5.1807746D-02
1.250000 04	1.2896671D 01	1.2900000D 01	-2.5808544D-04
1.500000 04	7.5153437D 00	7.5000000D 00	2.0458244D-03
1.750000 04	5.3811088D 00	5.5000000D 00	-2.1616584D-02
2.000000 04	4.5051860D 00	4.5000000D 00	1.1524465D-03
2.250000 04	4.1216137D 00	3.8000000D 00	8.4635186D-02

LAGRANGIAN MULTIPLIERS

0.0 0.0 0.0 0.0 0.0

FINAL OBJECTIVE FUNCTION 1.8293374D-03

VARIANCE-COVARIANCE MATRIX

6.2962962D-06	-5.4437914D-10	-7.5448363D-10	1.8058077D-03
-5.4437914D-10	9.8218002D-14	9.5371039D-14	-2.4973692D-07
-7.5448363D-10	9.5371039D-14	4.2850927D-13	-1.1655492D-06
1.8058077D-03	-2.4973692D-07	-1.1655492D-06	3.1947032D 00

***** TSOAK-M1 SUMMARY TABLE *****

TIME SECONDS	NT2 MICRO CI/M**3	NHTO MICRO CI/M**3	NHT MICRO CI/M**3	NT2+NHTO+NHT MICRO CI/M**3	A.NE. 0 MICRO CI/M**3	SOAK EFFECT MICRO CI	ANT SOAKED MICRO CI
1.000000 00	9.316733690 02	8.322638140 01	8.322983390 01	1.098129580 03	1.098133040 03	1.588153480-04	1.588344250-04
2.000000 00	7.902123610 02	1.537520800 02	1.537651760 02	1.097729620 03	1.097742710 03	6.024233170-04	6.025699540-04
3.000000 00	6.702705290 02	2.135130170 02	2.135410000 02	1.097324550 03	1.097352530 03	1.287245500-03	1.267721470-03
4.000000 00	5.685686410 02	2.641496090 02	2.641969210 02	1.096915170 03	1.096962480 03	2.176345240-03	2.177431310-03
5.000000 00	4.823279310 02	3.070519220 02	3.071223220 02	1.096502180 03	1.096572580 03	3.238413930-03	3.240457780-03
6.000000 00	4.091936340 02	3.433979150 02	3.434945870 02	1.096086130 03	1.096182810 03	4.446912110-03	4.450318070-03
7.000000 00	3.471702100 02	3.741858450 02	3.743114830 02	1.095667540 03	1.095793180 03	5.779341920-03	5.784562250-03
8.000000 00	2.945664740 02	4.002617220 02	4.004186050 02	1.095246800 03	1.095403580 03	7.216630530-03	7.224158090-03
9.000000 00	2.499491070 02	4.223425550 02	4.225326130 02	1.094824280 03	1.095014330 03	8.742607910-03	8.752969850-03
1.000000 01	2.121032760 02	4.410360610 02	4.412609210 02	1.094400260 03	1.094625120 03	1.034356420-02	1.035731680-02
2.000000 01	4.121279230 01	5.241418300 02	5.247638890 02	1.090118510 03	1.090740570 03	2.861468590-02	2.869683320-02
3.000000 01	8.059501010 00	5.383554390 02	5.394051530 02	1.085820090 03	1.086869810 03	4.828684170-02	4.850555640-02
4.000000 01	1.586263600 00	5.392327890 02	5.407132590 02	1.081532310 03	1.083012780 03	6.810160650-02	6.852721860-02
5.000000 01	3.142122030-01	5.375185840 02	5.394276150 02	1.077260410 03	1.079169440 03	8.781542070-02	8.851822060-02
6.000000 01	6.263874710-02	5.353041730 02	5.376385520 02	1.073005350 03	1.075339740 03	1.073814640-01	1.084312780-01
7.000000 01	1.256657750-02	5.329992020 02	5.357555340 02	1.068767300 03	1.071523630 03	1.267912970-01	1.282574060-01
8.000000 01	2.537195290-03	5.306843960 02	5.338592660 02	1.064546200 03	1.067721070 03	1.460440110-01	1.479951400-01
9.000000 01	5.155617930-04	5.283757370 02	5.319657410 02	1.060341990 03	1.063932000 03	1.651401850-01	1.676444990-01
1.000000 02	1.053364720-04	5.260763790 02	5.300781330 02	1.056154620 03	1.060156370 03	1.840806860-01	1.872057960-01
2.000000 02	5.822943440-07	5.036271020 02	5.115646350 02	1.015191740 03	1.023129260 03	3.651259350-01	3.780584380-01
3.000000 02	5.659975580-07	4.821410940 02	4.936976910 02	9.758337850 02	9.873953560 02	5.316022620-01	5.605168670-01
4.000000 02	1.151232430-09	4.615770630 02	4.764547670 02	9.380318310 02	9.529095000 02	6.843727730-01	7.349415390-01
5.000000 02	1.813146210-10	4.418954380 02	4.598140670 02	9.017095050 02	9.196280990 02	8.242553610-01	9.016774470-01
6.000000 02	2.380501820-10	4.230583530 02	4.437545610 02	8.668129140 02	8.875090880 02	9.520240200-01	1.061054770 00
7.000000 02	1.969652040-09	4.050295650 02	4.282559500 02	8.332855150 02	8.565118680 02	1.068412260 00	1.213389530 00
8.000000 02	2.045932350-08	3.877743830 02	4.132986460 02	8.010730290 02	8.265972600 02	1.174114660 00	1.358984170 00
9.000000 02	7.375818250-10	3.712596070 02	3.988637410 02	7.701233480 02	7.977274520 02	1.269788790 00	1.498128170 00
1.000000 03	7.487997350-09	3.554534620 02	3.849329910 02	7.403864530 02	7.698659540 02	1.356057020 00	1.631098560 00
2.000000 03	8.748200840-07	2.302800270 02	2.697684300 02	5.000484580 02	5.395365570 02	1.816452560 00	2.674324570 00
3.000000 03	2.533126370-06	1.495440480 02	1.890588320 02	3.386028830 02	3.781173790 02	1.817666850 00	3.330589200 00
4.000000 03	2.235429780-06	9.746627770 01	1.324959940 02	2.299622740 02	2.649917800 02	1.611357250 00	3.737467610 00
5.000000 03	5.539918320-06	6.387060170 01	9.285576970 01	1.567263770 02	1.857112290 02	1.333303200 00	3.983681670 00
6.000000 03	2.805481390-07	4.219412640 01	6.507508810 01	1.072692150 02	1.301499260 02	1.052512740 00	4.126446990 00
7.000000 03	1.908597350-07	2.820458370 01	4.560585010 01	7.381043410 01	8.121151920 01	8.004499160-01	4.202660440 00
8.000000 03	3.262157060-06	1.917251840 01	3.196144500 01	5.113396660 01	6.392275020 01	5.882840470-01	4.236115560 00
9.000000 03	4.594998240-06	1.333767690 01	2.239920110 01	3.573688250 01	4.479826710 01	4.168236900-01	4.242155380 00
1.000000 04	4.149564910-07	9.564821810 00	1.569778390 01	2.526260620 01	3.139546910 01	2.821116970-01	4.230673040 00
2.000000 04	1.045305210-06	2.580055410 00	4.486442350-01	3.028700690 00	8.972730070-01	-9.804567340-02	3.871902500 00
3.000000 04	7.000546740-10	2.253722580 00	1.282201090-02	2.266544590 00	2.564379100-02	-1.030814370-01	3.495902210 00
4.000000 04	9.959795100-09	2.033543710 00	3.665413490-04	2.033910260 00	7.328917860-04	-9.352615890-02	3.155830310 00
5.000000 04	3.426984610-08	1.835709660 00	1.058914530-05	1.835720290 00	2.094582540-05	-8.444216970-02	2.848832400 00
6.000000 04	7.238636700-11	1.657132350 00	3.005446790-07	1.657132650 00	5.986253520-07	-7.622807440-02	2.571699040 00
7.000000 04	-8.381718110-12	1.495927130 00	8.452905250-09	1.495927130 00	1.710853140-08	-6.881264740-02	2.321525110 00

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