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ANALYSIS OF CHROMATOGRAPH SYSTEMS  
USING ORTHOGONAL COLLOCATION

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Analysis and Design of a Capsule Landing System  
and Surface Vehicle Control System for  
Mars Exploration

Rensselaer Polytechnic Institute  
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## ABSTRACT

Current research at Rensselaer is generating fundamental engineering design techniques and concepts for the chromatographic separator of a chemical analysis system for an unmanned, martian roving vehicle. Previously developed mathematical models of the gas chromatograph were inadequate for predicting peak height and spreading for some experimental conditions and chemical systems. Consequently, a new chromatograph model is developed which incorporates previously neglected transport mechanisms. A closed-form analytical solution to the model is not available so the numerical technique of Orthogonal Collocation is studied. To establish the utility of the method, three models of increasing complexity are considered, the latter two being limiting cases of the derived model: 1) a simple, diffusion-convection model; 2) a rate of adsorption limited, inter-intraparticle model; and 3) an inter-intraparticle model with negligible mass transfer resistance. The first model involves one dependent variable and one spatial dimension; the second, two dependent variables and one spatial dimension; and the third, three dependent variables and two spatial dimensions. The orthogonal collocation treatment reduces the models to sets of ordinary differential equations which are integrated using the Bulirsch-Stoer extrapolation technique.

Simulations with the first model using actual chro-

matographic input pulse data show the collocation procedure to accurately represent system behavior. Large Peclet numbers usually observed in practical chromatographic columns require a higher degree of approximation than low values. In general, 15 collocation points suffice. Similar results are obtained from a study of the second model which involves two coupled partial differential equations. The model is successfully solved numerically, although computation time becomes excessive. The investigation is concluded with a preliminary study of the third model which involves three coupled partial differential equations. Estimated computational times based upon partial simulations of this model show complete numerical solution within available computer capabilities and financial constraints to be unfeasible. It is therefore concluded that if orthogonal collocation is to be applied successfully to pulsed, distributed systems of the chromatograph within computer constraints, further research on the different characteristics of the orthogonal functions and the formulation of the trial function must be undertaken.

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## PART 1

### INTRODUCTION AND SUMMARY

The synthesis and analysis of mathematical models of the gas chromatograph is one subtask of a group effort designed to define fundamental design criteria for an optimal design of a combination gas chromatograph - mass spectrometer system which is to be part of an unmanned mission to Mars. The task which must be performed by this part of a Martian Roving Vehicle is the analysis of samples to determine the existence of organic matter and living organisms on the Martian surface. The analysis will involve the subjection of gaseous, liquid and solid samples to biological and chemical reactions, with subsequent product separation and identification using the gas chromatograph - mass spectrometer system.

The chromatograph may be looked upon as a separating device where the phenomenon of adsorption-desorption is utilized. Owing to the different characteristics of various chemicals, each species will adsorb and desorb at different rates when exposed to a packed bed of granular particles with or without a liquid substrate. Because of the unique behavior of each chemical, a multicomponent sample may be injected into a chromatograph and elute as separate waves of specific chemical species.

Prior to this investigation, chromatograph models have been formulated based on interparticle transport mechan-

isms with simple adsorbed phase behavior assumed. These previous model formulations, which have all had closed-form, analytic, time-domain solutions, have proven incapable of adequately predicting component behavior in all cases. Consequently, a new model has been derived which includes both interparticle and intraparticle transport mechanisms. The complexity of this new model precludes direct analytical solution, and hence application of an appropriate numerical technique is necessary to effect time-domain solution. Prior to any time-domain analysis, the model is analysed in the Laplace transform domain using the method of moments. The first three moments of the impulse response of the model are derived. Using actual input data, predictions for the first three moments of the output data are made and are compared with actual chromatographic data and predictions of a simpler, interparticle model. The results indicate that the new model is more capable of predicting the moments of the actual data.

Because the mathematical complexity of the new model prohibits a direct, closed-form analytic expression for a response, appropriate numerical techniques applicable to the equations of the new model (and future models which may involve nonlinear terms) must be used to allow direct comparisons between prediction and experiment. For the systems of equations encountered in chromatograph modeling, numerical techniques require a finite terminal boundary condition as opposed to an infinite column boundary condition usually used in deriving

analytical solutions to simpler chromatograph models. As a prelude to numerical technique considerations, a simple, transient, diffusion-convection, mass transfer equation is analysed and criteria are developed wherein a finite terminal boundary condition can be applied to yield infinite column behavior at the bed outlet.

Subsequent to the development of a complex chromatograph model and the realization that model simulation and verification require a numerical technique, attention is directed to the study of Orthogonal Collocation as a technique suitable for routine analysis of complex chromatograph models. The motivation for conducting this investigation is several-fold: computational limitations of the widely used Finite Difference method, successful use of orthogonal collocation to solve certain chemical reaction engineering problems, and the lack of documentation for the application of orthogonal collocation to pulsed, distributed systems such as the chromatograph system. The general theory and computational aspects of orthogonal collocation are reviewed and discussed. One of the steps in the application of orthogonal collocation involves the inversion of a matrix. Previously documented developments have given formulations where the matrix to be inverted becomes increasingly ill-conditioned with increasing size and may, due to computer precision limitations, prove non-invertable. Heretofore, this has not been documented. An alternative development, theoretically equivalent, is presented which is shown

to successfully eliminate this problem to a high degree.

In order to establish whether orthogonal collocation is a technique worthy of exploitation in the analysis of chromatographic systems, three models of increasing complexity are solved using the method:

1. A simple, transient, diffusion-convection mass transfer problem.
2. A rate-of-adsorption-limited, inter-intraparticle problem - a limiting case of the derived model.
3. An inter-intraparticle adsorption problem with negligible mass transfer resistance between the interparticle and intraparticle regions - another limiting case of the derived model.

For each model, the orthogonal collocation treatment reduces the partial differential equation(s) to a set of ordinary differential equations.

The first model is studied because it possesses response characteristics found in more complex models, possesses an analytic solution for direct comparisons with numerical results, and establishes guidelines for more complex models to be considered. Prior to solution of the resultant set of ordinary differential equations, an eigenanalysis is made of the differential equation set. This set or the resultant discretization of the distributed system is stable for axial Peclet numbers from 1 to 10000 and approximation orders of 3 to 21. This model is solved for cases of rectangular and actual system

input data pulses. The effects of high (10000) and low (32) values of axial Peclet number are studied to determine the degree of approximation required for good representation of the exact system response. The high Peclet number (10000), characteristic of the magnitudes encountered in actual chromatographic system data, requires a higher degree of approximation than the low value. The sharpness of the forcing function also affects the numerical results; i.e., a higher order of approximation is required for very sharp input pulses. For the smoother actual input data and the high Peclet number, a fifteenth order approximation is adequate. The set of ordinary differential equations is integrated using the Bulirsch and Stoer extrapolation technique. For this type of problem, this method is more efficient (for equivalent error tolerance) than the more well-known Euler, fourth order Runge-Kutta and Hamming Predictor-Corrector techniques. Consequently, the extrapolation treatment is used exclusively for integration of the sets of ordinary differential equations that result from the application of orthogonal collocation to the problems considered in this investigation.

Following a study of the simple model, orthogonal collocation is applied to solve the second model given above. This problem possesses an analytical solution which is used for comparison with the different degrees of approximation considered. The system parameters which appear in this model correspond to parameters encountered in actual chromatographic

system experimental work. This is important because the parameter choice; e.g., Peclet number, is dictated by actual experiment rather than convenience. This problem is more complex than the simple problem in that two coupled partial differential equations are treated using the orthogonal collocation method. As a consequence, a higher degree of approximation is necessary and the constraints of excessive computer time and suitable computer hardware availability come to the forefront of the investigation.

The investigation is terminated with the application of orthogonal collocation to the third model listed above. This model has no direct, analytic solution available. Hence, the strategy is to successively apply orthogonal collocation with increasing orders of approximation until a convergent response is realized. Unlike the previous two problems where only one spatial domain is discretized, the interparticle, this problem requires orthogonal collocation discretizations for both the interparticle and intraparticle regions. The problem involves the solution of three coupled partial differential equations. Again, actual chromatographic system parameter values are used. To effect the above strategy of successive simulations with increasing order of approximation, several cases are studied for short computer run times. These times are extrapolated to give estimates of computer requirements necessary to complete the analysis. These extrapolations indicate that within available computer hardware capabilities



and financial constraints, thorough analysis of this problem is not feasible using orthogonal collocation. This does not rule out the utility of the theory of orthogonal collocation as a technique but points out a problem where innovation and further study may be necessary for the realization of a practical solution.

## PART 2

### CHROMATOGRAPH SYSTEM MODELING

#### A. Chromatograph Modeling Background

One area of the overall gas chromatograph systems study has been the mathematical modeling of the chromatograph system. Work in the area has been carried out by several investigators (Sliva, 1968; Voytus, 1969; Taylor, 1970; Keba and Woodrow, 1972). A course has been pursued wherein successively more complex models have been considered. These models have all yielded analytical expressions from which a simulated chromatogram could be computed directly. Comparison of predicted system behavior with actual system data has directed modeling efforts to consider more adequate and hence more complicated models.

Prior to this investigation, the most complex model proposed for the chromatograph system was based on an interparticle phase mass balance and an adsorbed phase mass balance. Several transport mechanisms were included: axial diffusion, convection, and mass transfer between the interparticle and adsorbed phases. A linear isotherm was used to describe the adsorption kinetics. This model has been studied and compared (Keba and Woodrow, 1972) for the cases of finite rates of mass transfer to the adsorbed phase (nonequilibrium adsorption) and infinitely high rates of mass transfer to the adsorbed phase (equilibrium adsorption). In both cases, simulations using the models failed to predict the degree of dispersion

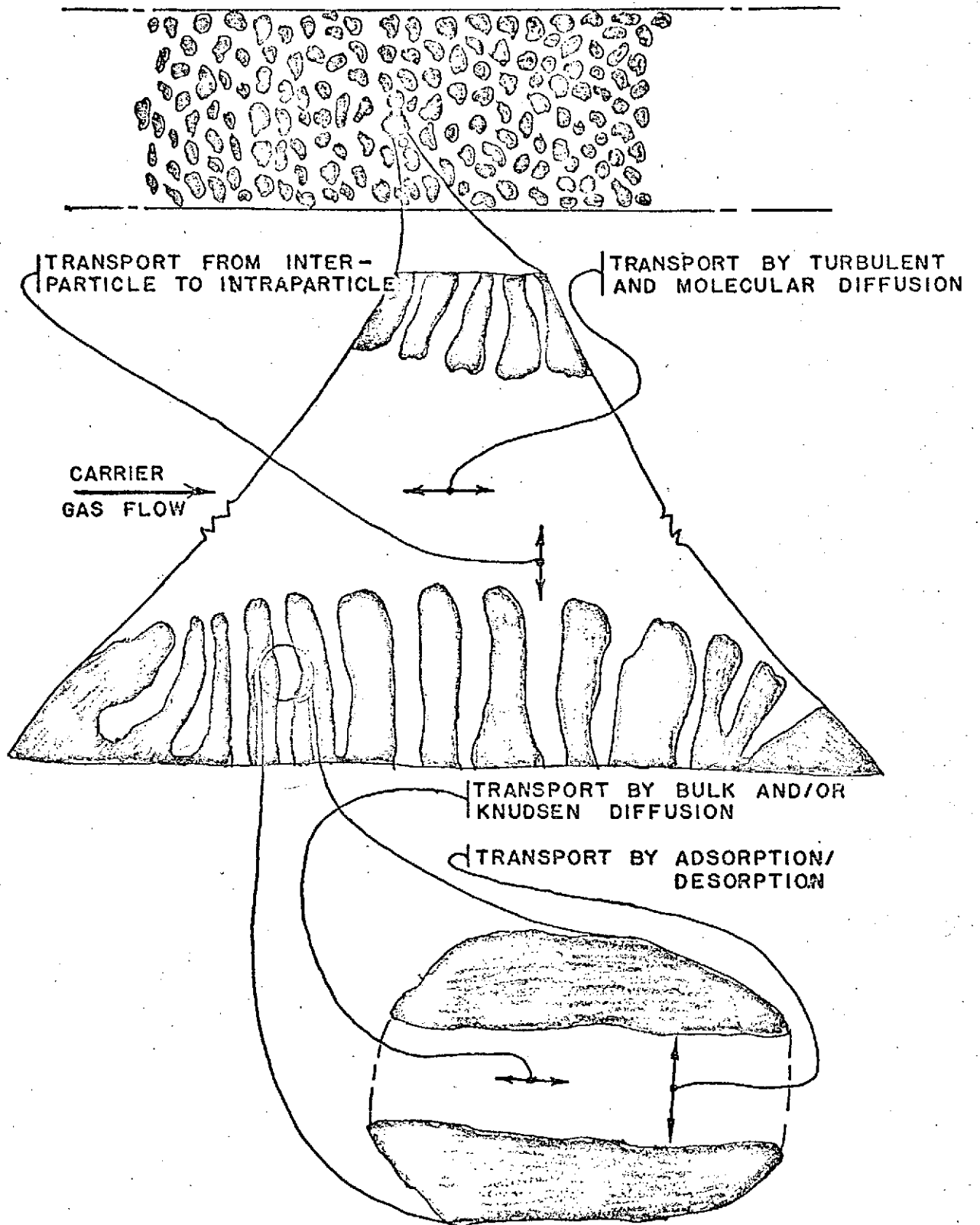
exhibited by many of the experimental data. It was concluded that additional transport mechanisms, e.g., intraparticle diffusion, may be contributing appreciably to the overall adsorption-desorption process. Hence, further model development and analysis was indicated.

B. Development of the Inter-Intraparticle Adsorption Model

Previously, the intraparticle region of the chromatograph packing material has been modeled as being nonexistent or as a region where the transport processes occur at such a rapid so as not to significantly affect the dynamic behavior of the system. It is the purpose of this section to reformulate the chromatograph system model by including the transport process which are presumed most likely to affect the dynamics of the adsorption-desorption process within the chromatograph packing material.

Figure 1 presents graphically the transport processes to be modeled. The sample to be separated is injected into a relatively inert carrier gas, e.g., helium. As this slug of sample is transported down the chromatograph by the carrier gas, the various species diffuse, adsorb, and desorb. Diffusion of the chemicals in the direction of the carrier gas flow in the interparticle region is represented by the dimensionless parameter,  $Pe_E$ , which is determined by the system fluid mechanics. Mass transport from the interparticle region to the intraparticle region is represented by a

CHROMATOGRAPHIC COLUMN INTER-INTRAPARTICLE MODEL CONCEPTS



dimensionless parameter,  $N_{tOG}$ , which is essentially determined by the system fluid mechanics. Diffusion in the intraparticle region is represented by a dimensionless parameter,  $Pe_A$ , which is in part determined by the properties of the particle packing. The rate of adsorption within the particle is characterized by the dimensionless parameter,  $N_{RU}$ . Adsorption-desorption within the particle is represented by  $mR_I$ , a thermodynamic parameter peculiar to each species. This parameter contains an equilibrium constant,  $m$ , and the quantity  $R_I$ .  $R_I$  is the ratio of moles of fluid within the particle to the moles of adsorptive sites within the particle. The quantity  $R_I$  is directly related to the quantity  $R_0$  where  $R_0$  is the ratio of moles of fluid within the total bed to the moles of adsorptive sites within the bed. The relationship between these quantities is:

$$R_I = \frac{\epsilon}{(1-\epsilon)\beta} R_0 \quad (1)^*$$

The reason for noting this relationship is that the parameter,  $mR_0$  has been noted in previous models and the above relationship serves as a unifying concept for the new model formulation which follows.

With the above concepts in mind, the following set of dimensionless equations has been derived\*\* based on the assumptions which follow:

\* See Part 12, Nomenclature, for definition of terms.

\*\* See Appendix A for derivation.

An interparticle phase mass balance:

$$\left[ \frac{1}{Pe_E} \right] \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - N_{tOG}(y-y_1)_{\alpha=1} = \frac{\partial y}{\partial \theta} \quad (2)$$

An intraparticle phase mass balance:

$$\left[ \frac{1}{Pe_A} \right] \left( \frac{L}{R} \right)^2 \left[ \frac{\partial^2 y_1}{\partial r^2} + \frac{2}{r} \frac{\partial y_1}{\partial r} \right] - N_{RU}(y_1 - y_1^*) = \frac{\partial y_1}{\partial \theta} \quad (3)$$

An adsorbed phase mass balance:

$$\left[ \frac{1}{R_I} \right] \frac{\partial x_a}{\partial \theta} = N_{RU}(y_1 - y_1^*) \quad (4)$$

A thermodynamic relationship between the intraparticle and adsorbed phases:

$$y_1^* = m x_a \quad (5)$$

The above equations are valid under the following assumptions:

1. The column is isothermal.
2. The carrier gas velocity profile is flat.
3. The axial diffusion coefficient is a composite factor which may or may not have a turbulent component.
4. The gas composition is approximately constant in the radial direction at a given axial position. The concentration gradient occurs in a thin boundary layer at the inter-intraparticle interface.
5. The gas composition within the particle is approximately constant in the angular direction

at a given radial position; the concentration gradient occurs only in a thin boundary layer near the adsorbent surface.

6. The adsorbent layer is so thin that there is no diffusional resistance within the layer in the direction normal to the surface.
7. The diffusivity in the adsorbent layer is so small that there is no diffusion in the direction parallel to the surface in the intraparticle radial direction.
8. The net rate of adsorption for the carrier gas is negligible.
9. Only one component is adsorbed and its gas phase composition as a mole fraction is small compared to unity.
10. The carrier gas behaves as an ideal gas.

An applicable set of boundary and initial conditions are as follows:

Initial Conditions:

$$y(z, 0) = 0 \quad (6)$$

$$y_1(z, \tau, 0) = 0 \quad (7)$$

$$x_a(z, \tau, 0) = 0 \quad (8)$$

Boundary Conditions:

$$y(0, \theta) = A_f \quad (9)$$

$$\left[ (\beta/\epsilon) a_p L(L/R)/Pe_A \right] \partial y_1 / \partial \tau = N_{TOG} (y - y_1); \text{ when } \tau = 1 \quad (10)$$

$$\partial y_1 / \partial z = 0 ; z = 0 \quad (11)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite} \quad (12)$$

These conditions reflect a sample-free column at zero time, a sample injected as an impulse, mass transfer between the interparticle and intraparticle regions, no concentration gradient at the center of the column packing, and no end effects at the column exit.

For the systems under consideration it has been shown by Keba and Woodrow (1972) that inclusion of the parameter  $N_{tOG}$  is of minor importance. If one were to consider the case of infinite rates of mass transfer, i.e.,  $N_{tOG} \rightarrow \infty$ , the coupling condition given by equation (10) would be replaced by

$$y_1(z, 1, \theta) = y(z, \theta) \quad (13)$$

Thus, a model in the form of a set of coupled, partial differential equations is proposed. Prior to consideration of the time domain solution of the equations, a moment analysis can be made to ascertain the predictive capabilities of the proposed model. This analysis is the subject of the next part of this investigation.



## PART 3

### MOMENT ANALYSIS OF THE INTER-INTRAPARTICLE ADSORPTION MODEL

#### A. Theory and Background

An analysis of a proposed model can be made prior to determination of the model's time-domain solution to yield the gross characteristics of the impulse response of the model. In addition, because of the poor predictions of previous models (Keba and Woodrow, 1972) with respect to chromatogram spreading, it is desirable to know the nature of the response of the proposed model for the pulse-type functions which are the sample injections seen in experimental work. The nature of the response can be characterized by statistical quantities known as moments which may be obtained without knowledge of the time-domain model solution. The moments may be derived directly from the Laplace domain solution of the model. The following development will indicate how the moments of a model are obtained and how the analysis can be extended to give the moments of systems forced by general pulse-type inputs.

The impulse response of the chromatogram may be viewed as the residence time frequency distribution (Douglas, 1972). This quantity resembles the probability distribution function which appears in statistical analysis. The moments of the distribution function about the time origin are defined by the following:

$$\mu_n = \int_0^{\infty} \theta^n f(\theta) d\theta / \int_0^{\infty} f(\theta) d\theta \quad (14)$$

where

$f(\theta)$  = the distribution function being analysed.

The denominator of equation (14) is the area under the function.

The relationship of the moments about the origin to the

Laplace transform is developed in Appendix B. The result is:

$$\mu_n = (-1)^n \lim_{s \rightarrow 0} \left\{ \frac{\partial^n}{\partial s^n} [\tilde{f}(s)] \right\} / \lim_{s \rightarrow 0} \tilde{f}(s) \quad (15)$$

where

$$\tilde{f}(s) = \mathcal{L}[f(\theta)] \triangleq \int_0^{\infty} e^{-s\theta} f(\theta) d\theta \quad (16)$$

Interest also centers on the moments about the first absolute moment or mean,  $\mu_1$ . Mathematically these are defined by:

$$\bar{\mu}_n = \int_0^{\infty} (\theta - \mu_1)^n f(\theta) d\theta / \int_0^{\infty} f(\theta) d\theta ; n \geq 2 \quad (17)$$

These moments about the mean  $\mu_1$ , are directly related to the moments about the origin. The relationships are obtained by formal expansion of equation (17). Appendix B gives the relationship for  $n=2$  and  $n=3$ . For  $n=2$ , the moment about the mean is exactly the variance of the response. For  $n=3$ , the moment about the mean is related to the skew of the response.

One can use the preceding to develop equations relating the moments of system responses for arbitrary pulse-type forcing functions (see Appendix B for details). That is, given the system input data (the moments of which can be

computed from equations (14) and (17)) and the system transfer function (the Laplace transform of the impulse response), the moments of the system response may be determined and compared with the moments of the actual output data. Referring to the block diagram in Figure 2, the results are:

$$A_Y = A_X \cdot A_G \quad (18)$$

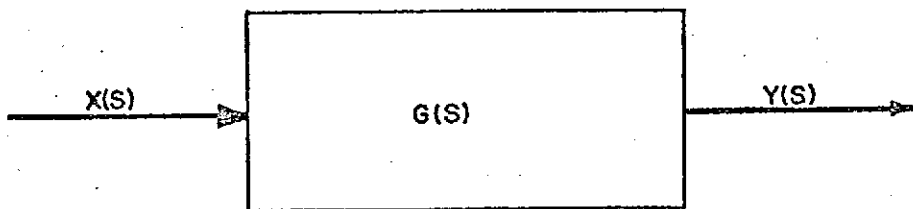
$$\mu_{1Y} = \mu_{1X} + \mu_{1G} \quad (19)$$

$$\bar{\mu}_{2Y} = \bar{\mu}_{2X} + \bar{\mu}_{2G} \quad (20)$$

$$\bar{\mu}_{3Y} = \bar{\mu}_{3X} + \bar{\mu}_{3G} \quad (21)$$

Equation (18) states that the area under the output curve is the product of the area under the input curve and the impulse response curve. Equation (19) states that the mean of the output occurs at the sum of the mean of the input function and impulse response. Equation (20) states that the variance of the output is the sum of the variance of the input function and the variance of the impulse response. Equation (21) states that the third moment about the mean of the output is the sum of the third moments about the means of the input function and impulse response, respectively.

This technique can also be used for estimating system parameters. Douglas (1972) uses an equation similar to equation (20) to estimate an axial Peclet number for a packed bed. Schneider and Smith (1968) apply moment analysis to estimate adsorption equilibrium constants, rate constants, and intraparticle diffusivities for a chromatographic system mod-



$X(S) = \mathcal{L}[x(\theta)]$  ;  $x(\theta)$  IS THE FORCING FUNCTION

$Y(S) = \mathcal{L}[y(\theta)]$  ;  $y(\theta)$  IS THE SYSTEM RESPONSE

$G(S) =$  SYSTEM TRANSFER FUNCTION

FIGURE 2 TYPICAL SYSTEM BLOCK DIAGRAM

eled similarly to that of Part 2. However, accurate parameter estimation using this method is limited by the accuracy of the data used for analysis.

B. Application of Moment Analysis to the Inter-Intraparticle Adsorption Model

The previous section outlined a method which can be used to analyse pulsed systems to determine the gross characteristics of the system response. This section will document an application of the concepts of moment analysis to the proposed model of Part 2.

Consider the set of partial differential equations, boundary conditions, and initial conditions, equations (2) through (12). A Laplace transform domain solution for the impulse response or transfer function was derived and appears in Figure 3; details appear in Appendix C.

Applying the definition given by equation (15) and using equation (17), the moments  $\mu_1$ ,  $\bar{\mu}_2$ , and  $\bar{\mu}_3$  are derived for the impulse of the Inter-Intraparticle Adsorption Model. The results are presented in Figure 4; details of the manipulations appear in Appendix D.

The parameters  $Pe_E$ ,  $N_{TOG}$ , and  $Pe_A$  can be estimated a priori. The parameters  $mR_0$  and  $N_{RU}$  are not predictable a priori. Previous modeling analysis has estimated  $mR_0$  by a curve fitting process (Benoit, 1971). The estimation of  $N_{RU}$  will most likely involve curve fitting also.

An analysis was made using existing single component

$$Y(1,s) = \exp \left\{ \frac{Pe_E}{2} - \sqrt{\frac{Pe_E^2}{4} + \gamma(s) Pe_E} \right\}$$

where:

$$\gamma(s) = N_{tOG}(1 - \lambda(s)) + s$$

$$\lambda(s) = \frac{b \sinh(\sqrt{a_1})}{[(b-1)\sinh(\sqrt{a_1}) + \sqrt{a_1} \cosh(\sqrt{a_1})]}$$

$$a_1(s) = \left\{ \left[ \frac{-N_{RU}^2 mR_I}{(s + N_{RU} mR_I)} + N_{RU} + s \right] \left( \frac{R}{L} \right)^2 Pe_A \right\}$$

$$b = \frac{N_{tOG}}{\frac{3(1-\epsilon)\beta}{\epsilon} \left( \frac{L}{R} \right)^2 \frac{1}{Pe_A}}$$

$$\beta = \text{Particle porosity}$$

$$\epsilon = \text{Bed void fraction}$$

Figure 3 Transfer Function for the Inter-Intraparticle Adsorption Model

$$\mu_1 = 1 + 1/mR_0 + (1-\epsilon)\beta/\epsilon$$

$$\begin{aligned} \bar{\mu}_2 = & 2(\mu_1)^2/Pe_E + 2 \cdot [(1-\epsilon)\beta/\epsilon] \\ & \cdot \left\{ (1 + 1/mR_I)^2 \left[ (R/L)^2 Pe_A/15 + (1-\epsilon)\beta/\epsilon N_{tOG} \right] \right. \\ & \left. + 1/N_{RU}(mR_I)^2 \right\} \end{aligned}$$

$$\begin{aligned} \bar{\mu}_3 = & 6\mu_1\bar{\mu}_2 / Pe_E + 6 [(1-\epsilon)\beta/\epsilon] \left\{ 2 \left[ (1+1/mR_I)/N_{RU}(mR_I)^2 \right] \right. \\ & \left[ (R/L)^2 Pe_A/15 + (1-\epsilon)\beta/\epsilon N_{tOG} \right] + (1+1/mR_I)^3 \\ & \left[ ((1-\epsilon)\beta/\epsilon N_{tOG})^2 + 2(1-\epsilon)\beta(R/L)^2 Pe_A/15 \epsilon N_{tOG} \right. \\ & \left. - 23 (R/L)^4 Pe_A^2/315 \right] + 1/N_{RU}^2 (mR_I)^3 \left. \right\} \end{aligned}$$

Figure 4 Moments of the Impulse Response of the Inter-Intraparticle Adsorption Model

data. The parameters  $Pe_E$ ,  $Pe_A$ , and  $N_{tOG}$  were estimated using existing correlations. The values of  $mR_0$  which were estimated by Keba and Woodrow (1972) using simpler models were used and the  $N_{RU}$  was varied. Tables 1 and 2 give results of this analysis for acetone at 100 C and ethylene at 50 C. Both experiments used Chromasorb 102 column packing, a porous material. In each case, the moments for the impulse response of the model were computed using the equations given in Figure 4. Use of system input data and equations (19) through (21) give predictions as a function of  $N_{RU}$  for the output moments. These predicted values are compared with actual moments of the output data and with the predictions of the simpler, interparticle equilibrium adsorption model. Expressions for the moments of the simpler model were initially developed by Voytus (1969).

The results indicate that the proposed model can more closely predict the characteristics of the output data than the simpler, interparticle model. The results indicate that a value of  $N_{RU}$  on the order of several hundred will give a predicted second moment very close to the second moment of the output data. This magnitude of  $N_{RU}$  is consistent with the values of  $N_{RU}$  which can be deduced from the independent research of Schneider and Smith (1968). Tables 1 and 2 further indicate that matching of the third moments would give different values of  $N_{RU}$ . However, the use of third moments is not as reliable because data inaccuracies are further magnified in the analysis.

It should be noted that if one accepts the value of



TABLE 1

MOMENT ANALYSIS AND PARAMETRIC  
STUDY - ACETONE 100 °C.

$mR_0$	$\mu_{1, \text{observed}}$	$\mu_{1, \text{predicted}}^{(1)}$	$\mu_{1, \text{predicted}}^{(2)}$
0.029	173.29	158.69	156.49

$N_{RU}$	$\bar{\mu}_{2, \text{observed}}$	$\bar{\mu}_{2, \text{predicted}}$	$\bar{\mu}_{2, \text{predicted}}$
100	815.67	977.55	437.28
200	↓	723.41	↓
400		686.34	
800		517.80	
1600		483.53	
3200		466.40	
6400		457.83	
12800		453.55	
25600		451.41	

$N_{RU}$	$\bar{\mu}_{3, \text{observed}}$	$\bar{\mu}_{3, \text{predicted}}$	$\bar{\mu}_{3, \text{predicted}}$
100	25404.0	23192.0	19499.0
200	↓	20454.8	↓
400		19745.3	
800		19555.4	
1600		19501.7	
3200		19485.1	
6400		19480.4	
12800		19477.2	
25600		19476.2	

$$Pe_E = 8689.$$

$$N_{tOG} = 88960.$$

$$(L/R)^2 / Pe_A = 328.2$$

(1) Inter-Intraparticle Adsorption Model

(2) Interparticle Equilibrium Adsorption Model

TABLE 2

MOMENT ANALYSIS AND PARAMETRIC  
STUDY - ETHYLENE 50 C.

$mR_0$	$\mu_{1, \text{observed}}$	$\mu_{1, \text{predicted}}^{(1)}$	$\mu_{1, \text{predicted}}^{(2)}$
<u>0.194</u>	<u>26.475</u>	<u>25.986</u>	<u>23.719</u>

$N_{RU}$	$\bar{\mu}_{2, \text{observed}}$	$\bar{\mu}_{2, \text{predicted}}^{(1)}$	$\bar{\mu}_{2, \text{predicted}}^{(2)}$	
100	7.024	13.283	0.388	
200		6.973		
400		3.817		
800		2.240		
1600		1.451		
3200		1.056		
6400		0.859		
12800		0.760		
25600		0.711		

$N_{RU}$	$\bar{\mu}_{3, \text{observed}}$	$\bar{\mu}_{3, \text{predicted}}^{(1)}$	$\bar{\mu}_{3, \text{predicted}}^{(2)}$	
100	19.623	13.049	0.191	
200		3.519		
400		1.058		
800		0.403		
1600		0.219		
3200		0.163		
6400		0.144		
12800		0.137		
25600		0.134		

---


$$Pe_E = 9744.$$

$$N_{TOG} = 79750.$$

$$(L/R)^2 / Pe_A = 436.2$$

(1) Inter-Intraparticle Adsorption Model

(2) Interparticle Equilibrium Adsorption Model

$N_{RU}$  as being on the order of several hundred for each case, all other parameters, excluding  $mR_0$ , are of the same magnitude. The key to the difference in the two component behaviors is the parameter  $mR_0$ .

## PART 4

### TERMINAL BOUNDARY CONDITION ANALYSIS

Mathematical modeling of chromatographic systems commonly require solutions to equations of the form:

$$(1/Pe)(\partial^2 y / \partial z^2) - \partial y / \partial z - R_A = \partial y / \partial \theta \quad (22)$$

Application of analytical techniques to the above equation, when possible, commonly utilize the terminal boundary condition:

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite}; \theta > 0 \quad (23)$$

Use of the above boundary condition in analytical work yields a great deal of mathematical simplification. In addition, the use of this boundary condition is consistent with the theory which has been developed for prediction of the dispersion in packed beds; see, for example, Gunn (1969).

However, when numerical techniques must be applied to solve equation (22) or any other model which defies analytical solution, the terminal boundary condition given by equation (23) must be replaced by a terminal boundary condition which is both computationally expedient and physically meaningful. A finite boundary condition which has found general usage in chemical reaction engineering problems (Danckwerts, 1953) and (Wehner and Wilhelm, 1956) is:

$$\partial y(1, \theta) / \partial z = 0; \theta > 0 \quad (24)$$

Bastian and Lapidus (1956) considered the case where  $R$  in equation (22) was an adsorption term. A linear relationship was assumed to describe the adsorption kinetics. For a step-input and the conditions chosen, Bastian and Lapidus showed that finite column calculations, using equation (24) as a terminal boundary condition, closely approximated infinite column calculations, using equation (23) as a terminal boundary condition.

The analysis of chromatograph systems for pulse-type forcing functions has prompted consideration of the two terminal boundary conditions. The question arises as to how the use of a finite terminal boundary condition affects output prediction as compared to the infinite column case when the system is forced by pulse-type functions. It is desirable for the two predictions of column outlet behavior ( $z=1$ ) to be similar so that the use of a priori estimates of  $Pe$  are valid in complicated models having the form of equation (22).

In order to answer the above question and to establish the conditions under which a finite terminal boundary can be used to yield infinite column behavior at the column outlet ( $z=1$ ), two relatively simple problems can be considered:

Case I:

$$(1/Pe)(\partial^2 y / \partial z^2) - \partial y / \partial z - R_A = \partial y / \partial \theta \quad (25)$$

$$y(z, 0) = 0; \quad z > 0 \quad (26)$$

$$y(0, \theta) = \delta(\theta); \quad \theta \geq 0 \quad (27)$$

$$\lim_{z \rightarrow \infty} y(z, \theta) = \text{finite}; \quad \theta > 0 \quad (28)$$

$$R_A = 0 \quad (29)$$

and

Case II:

$$(1/Pe)(\partial^2 y / \partial z^2) - \partial y / \partial z - R_A = \partial y / \partial \theta \quad (30)$$

$$y(z, 0) = 0; z > 0 \quad (31)$$

$$y(0, \theta) = \delta(\theta); \theta \geq 0 \quad (32)$$

$$\partial y(z_0, \theta) / \partial z = 0; \theta > 0, z_0 \geq 1 \text{ and arbitrary} \quad (33)$$

$$R_A = 0 \quad (34)$$

Case I considers the impulse response of the simple, one-dimensional, axial dispersion-convection model in an infinite column. Case II considers the unit impulse response of the simple, one-dimensional, axial dispersion-convection model with the finite boundary condition. It is desirable to determine the conditions under which the two responses are equivalent. These conditions can be determined without resorting to the comparisons of the analytical solutions for each case, through use of the method of moments.

At a dimensionless length of unity, the column outlet, the Laplace transforms of the two solutions are\*:

Case I:

$$y(1, s) = \exp[(Pe/2) - (arg)] \quad (35)$$

Case II:

$$y(1, s) = \exp(Pe/2) \left\{ \frac{\left[ (Pe/2) + (arg) \right] \exp[-(1-z_0)(arg)] - \left[ (Pe/2) - (arg) \right] \exp[(1-z_0)(arg)]}{\left[ (Pe/2) + (arg) \right] \exp(z_0(arg)) - \left[ (Pe/2) - (arg) \right] \exp(-z_0(arg))} \right\} \quad (36)$$

\* see Appendix E for details.

where

$$\arg = \sqrt{(Pe/2)^2 + Pe s} \quad (37)$$

Each respective output curve can be characterized by its moments. Two moments are considered here - the first moment about the origin and the second moment about the mean. The first moment about the origin gives the time of appearance of the mean of the output curve. The second moment about the mean gives the variance of the output curve. These moments, as has been previously noted in Part 3, are directly obtainable from the Laplace transform domain solution. The general relationships were given in equations (14) through (17). Using these relationships, the Case I and Case II transfer functions were analysed to yield:

$$\mu_{1I} = 1 \quad (38)$$

$$\bar{\mu}_{2I} = 2/Pe \quad (39)$$

and

$$\mu_{1II} = 1 + [\exp(-Pe z_0) - \exp(Pe - Pe z_0)] / Pe \quad (40)$$

$$\begin{aligned} \bar{\mu}_{2II} = 2/Pe + \exp(Pe - Pe z_0) [4/Pe - 4z_0/Pe \\ - 4/Pe^2] + \exp(-2 z_0 Pe)/Pe^2 \\ - \exp(2 Pe - 2 z_0 Pe)/Pe^2 \end{aligned} \quad (41)$$

If one considers the limit of the Case II moments as  $z_0$  becomes very large, the two results are equivalent, or:

$$\lim_{z_0 \rightarrow \infty} \mu_{1II} = \mu_{1I} = 1$$

and

$$\lim_{z_0 \rightarrow \infty} \bar{\mu}_{2II} = \bar{\mu}_{2I} = 2/Pe$$

Table 3 summarizes the results of parametric studies of the two moments considered for each case. The errors in Case II versus Case I moments for  $z_0=1$  are significant for low Peclet number. The error diminishes with increasing Peclet number. This confirms the qualitative conclusions of Friedly (1972) for high values of Pe. Table 3 also gives the value of  $z_0$  which, when used in Case II, will yield output characteristics the same as Case I output characteristics. This means that for a given Peclet number, application of equation (33) at the noted  $z_0$ , will yield output characteristics at  $z=1$  that are, for all intents and purposes, the same as those predicted by Case I.

Table 4 presents some typical values of the Peclet parameter for several systems. For chromatographic systems, the range of the Peclet number is on the order of 5,000 to 10,000. Thus in this research, it appears that use of the zero-derivative condition (equation (33)) at the column exit will not cause serious problems.

In conclusion, the comparison of the mean and variance for impulse responses at  $z=1$  for the two different boundary conditions has yielded guidelines which are useful when approximating infinite column behavior using a finite terminal boundary condition. The use of the criteria for general pulse-type forcing functions would yield results wherein the absolute errors between the two cases would be the same but the relative errors between cases would decrease. The guide-



TABLE 3

## Case I and Case II Comparison Results

Errors at  $z_0 = 1.0$ 

Pe	Absolute Error $\mu_{1I} - \mu_{1II}$	Relative Error, % $((\mu_{1I} - \mu_{1II}) / \mu_{1I}) \times 100$	Absolute Error $\bar{\mu}_{2I} - \bar{\mu}_{2II}$	Relative Error, % $((\bar{\mu}_{2I} - \bar{\mu}_{2II}) / \bar{\mu}_{2I}) \times 100$
2	0.4323	43.23	1.245	124.5
4	0.2454	24.54	0.3125	62.9
8	0.1250	12.50	0.07813	31.2
16	0.06250	6.250	0.01953	15.6
32	0.03125	3.125	0.004883	7.91
64	0.01563	1.563	0.001221	3.91
128	0.00781	0.781	0.0003052	1.99
256	0.00391	0.391	0.0000763	0.976
512	0.00195	0.195	0.0000191	0.489
1024	0.00098	0.098	0.0000047	0.241
2048	0.00049	0.049	0.0000012	0.123
4096	0.00024	0.024	0.0000003	0.0615
8192	0.00012	0.012	0.0000000	0.0

Case I characteristics  $\cong$  Case II characteristics

Pe	Safe $z_0$ $(\mu_{1I} = \mu_{1II})^*$	Safe $z_0$ $(\bar{\mu}_{2I} = \bar{\mu}_{2II})^{**}$
2	9.791	11.768
4	5.254	6.021
8	3.043	3.328
16	1.978	2.073
32	1.467	1.490
64	1.223	1.222
128	1.106	1.044
256	1.050	1.002
512	1.024	1.0005
1024	1.011	1.0001
2048	1.005	1.00002
4096	1.002	1.000005
8192	1.001	1.000001

\*  $(\mu_{1I} - \mu_{1II}) \leq 10^{-8}$ \*\*  $(\bar{\mu}_{2I} - \bar{\mu}_{2II}) \leq 10^{-8}$

TABLE 4

## Peclet Numbers for Four Typical Systems

<u>System</u>	<u>Pe</u>	<u>Reference</u>
Micro Gas Chromatograph Column (Water in Helium)	233	(Wilhite, 1966)
Typical Gas Chromatograph Column (Water in Helium)	5622	(Keba and Woodrow, 1972)
Typical Gas Dehydrator (Water in Helium)	1777	(Lashmet, 1973)
Small Experimental Reactor (SO <sub>2</sub> in Air)	155	(Smith, 1970)

lines developed here should also prove useful for models including other transport mechanisms ( $R_A \neq 0$ ). When applicable to more complicated models, the method of analysis used here will give more definite guidelines for each specific situation.

## PART 5

### ORTHOGONAL COLLOCATION AS A NUMERICAL TECHNIQUE

#### A. Motivation for Study of Orthogonal Collocation

The complexity of the model formulation in Part 2 necessitates the application of numerical approximation techniques to effect solution of the system of partial differential equations. A preliminary study of the widely prevalent technique known as Finite Differences has been made to ascertain whether or not this computational technique would prove suitable and effective for solution of the type of equations encountered in chromatograph system modeling.

Finite difference approximations have predominantly been used in the analysis of partial differential equations. To obtain numerical solutions to partial differential equations, one replaces the continuous variables with discrete variables. The relations between these discrete variables in the method of finite differences are called finite difference equations. The relationships are based on Taylor series representations of the dependent variable. The domains of the independent variables that are discretized form a system of grid points. Figure 5 shows a grid representation for the transient analysis of a system with one spatial independent variable. The spatial dimension,  $z$ , is shown as being bounded and the time variable,  $\theta$ , is shown with no particular bound. The grid is a fixed grid; i.e., spatial discretizations and time discretizations are uniform for each domain. Note that

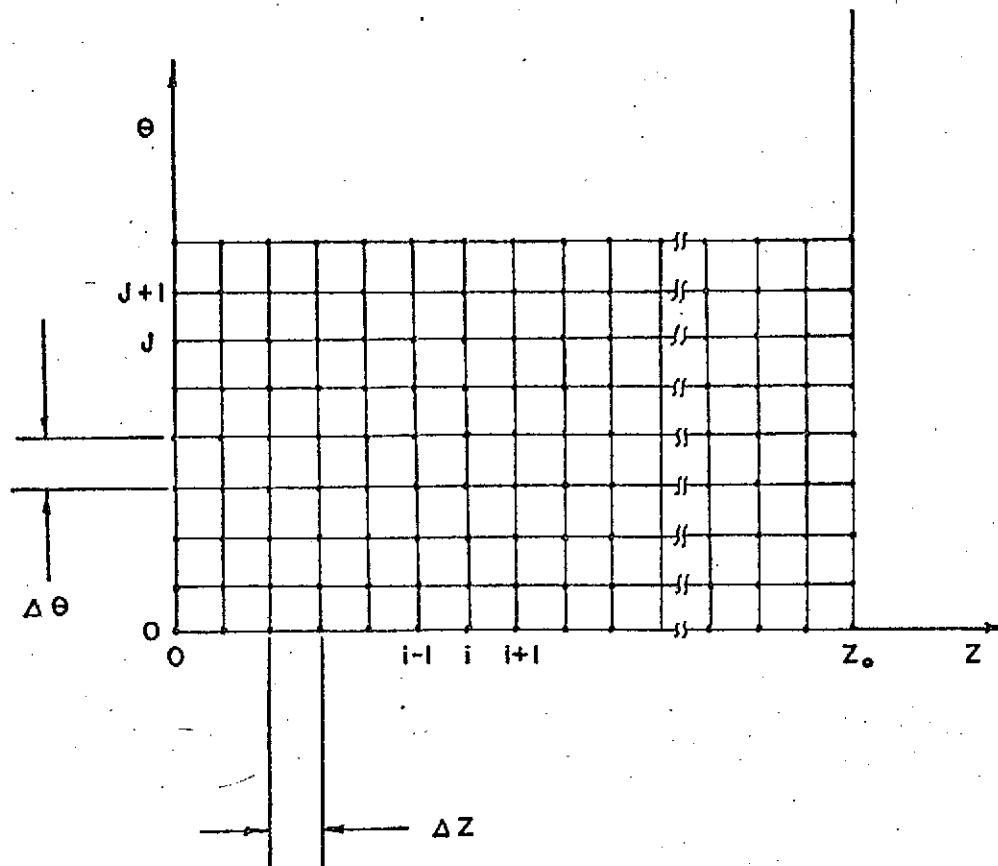


FIGURE 5 GRID REPRESENTATION FOR FINITE DIFFERENCE METHOD

the value of  $z$ , the continuous space dimension is given by:

$$z = i \cdot (\Delta z)$$

where  $i$  refers to a particular spatial grid point and  $\Delta z$  is the spacing between spatial grid points. Similarly, the value of  $\theta$ , the continuous time variable is given by:

$$\theta = j \cdot (\Delta \theta)$$

where  $j$  refers to a particular time grid point and  $\Delta \theta$  is the interval between time grid points.

For parabolic problems (as is the case for the second-order chromatograph system models), the two-level implicit method known as the Crank-Nicolson method is probably most popular and is well documented (Lapidus, 1962). In this method, the following approximations are made for the first and second spatial derivatives and the first time derivative:

$$(\partial y / \partial z)_{1j} \approx \frac{1}{2} \left\{ \frac{y_{i+1,j} - y_{i-1,j}}{2(\Delta z)} + \frac{y_{i+1,j+1} - y_{i-1,j+1}}{2(\Delta z)} \right\}$$

$$(\partial^2 y / \partial z^2)_{1j} \approx \frac{1}{2} \left\{ \frac{y_{i+1,j} - 2y_{i,j} + y_{i-1,j}}{(\Delta z)^2} + \frac{y_{i+1,j+1} - 2y_{i,j+1} + y_{i-1,j+1}}{(\Delta z)^2} \right\}$$

$$(\partial y / \partial \theta)_{1j} \approx (y_{1,j+1} - y_{1j}) / (\Delta \theta)$$

where the  $i$  subscript denotes a coordinate in the spatial domain and the  $j$  subscript denotes a coordinate in the time domain.

Preliminary studies have been made applying the Crank-Nicolson method to the problem:

$$(1/Pe) (\partial^2 y / \partial z^2) - \partial y / \partial z = \partial y / \partial \theta$$

$$y(z, 0) = 0; z \geq 0$$

$$y(0, \theta) = \phi(\theta); \theta > 0$$

$$\partial y(z_0, \theta) / \partial \theta = 0; \theta > 0$$

Simulations were made with following conditions:

1.  $\phi(\theta)$  was a triangular-type pulse of duration 0.01 and with unit area. This is quite a sharp pulse as far as typical chromatograph input pulses are concerned, but it was used mainly in the interest of saving computer time.
2. The Peclet was fixed at 8,000.
3. The time increment,  $\Delta\theta$ , was held at 0.0004
4. The response was studied at  $z=0.05$ . This is a drastic reduction in the normal spatial coordinate studied, but, again, this was in the interest of conserving computer time.
5. The terminal boundary condition was applied at  $z_0 = 0.20$ .
6. The spatial increment,  $\Delta z$ , was varied in the following sequence:

0.0002, 0.0004, 0.0010, 0.0025

For spatial increment values of 0.0010 and less, the simulations were stable. However, when  $\Delta z$  was increased to 0.0025, instability in the form of oscillation in the response was exhibited. The very small  $\Delta z$  required is directly attributable to the Pe value used. This instable  $\Delta z$  value is not quite as

small as the value that is predicted by the stability of Price, et. al. (1966)

The simulations for spatial increments of 0.0002, 0.0004, 0.0010 gave reasonable results when compared to results convolving  $\phi(\theta)$  with the analytical impulse response. The discrepancy between the analytic and numerical computations appeared in the magnitudes of each response point - the numerical results were on the order of 20% too low. This in turn affected the areas beneath the response curve for the numerical results - all areas were on the order of 0.80 as compared with the correct area of 1.0. The area under the analytical response curve was 0.96 which is tolerable considering the sharp input. This discrepancy in response area can be resolved by adding additional parameters to the difference equations to yield an exact conservative relationship (Rogers, 1973):

$$\left[ \begin{array}{l} \text{System Input - System Output over} \\ \text{the interval } j \text{ to } j+1 \end{array} \right] \\ = \sum_{i=1}^N y_{1,j+1} - \sum_{i=1}^N y_{1,j}$$

where N is the total number of spatial points. This analysis was not performed because it was felt that the method already suffered from a more alarming feature - the high degree of spatial discretization which is necessary for the large Pe values encountered in chromatographic systems analysis. Extrapolation of the computing time required for the simulations performed yields an estimate of one to two hours of computer time (IBM 360/50, FORTRAN G) required for complete simulations



over the space interval  $(0, 1.0^+)$ . The time would naturally increase when broader input pulses are used. Similar conclusions on the use of finite difference schemes were reported earlier (Pfeiffer, 1972).

Because of the high degree of spatial discretization required by the finite difference method and the subsequent high cost of computer simulations, it was felt that further pursuit of finite difference formulations for problems similar to the above was not warranted in this investigation and that other techniques should be studied to determine if they would be computationally more expedient and desirable.

#### B. Theory and Background of Orthogonal Collocation

A recent text (Finlayson, 1972) has dealt with several approximation techniques for the solution of the differential equations which arise in the analysis of transport phenomena. A group of approximation techniques has been designated the Method of Weighted Residuals (MWR). A subclass of MWR is the Method of Orthogonal Collocation. This method has been successfully applied to several problems in the realm of chemical reaction engineering. Investigators in this area include Ferguson and Finlayson (1970), Finlayson (1971), Villadsen and Stewart (1967), Villadsen and Sorensen (1969), and Villadsen (1970). The purpose of this section is to present a summary of the theory behind the method. Discussion of investigations that concern general computational aspects will follow in the following section.

The Method of Weighted Residuals approach to the solution of partial differential equations starts with a representation of the dependent variable,  $y$ , by a finite sum of trial functions  $P_1$ . An example might be:

$$y(z, \theta) \cong \phi_0(z, \theta) + \sum_{i=1}^N a_i(\theta) P_{i-1}(z) \quad (42)$$

where  $\phi_0(z, \theta)$  is a function which may be chosen to satisfy one or more boundary conditions. The functions  $P_1(z)$  are normally specified and the time-varying coefficients,  $a_1(\theta)$ , are determined in a manner to give the "best" solution of the differential equation.

The next step in the MWR is to manipulate the differential equation such that one side, say the right hand side, of the equation is zero. Then, the trial function expansion is substituted into the left hand side. This substitution of the trial function expansion into the manipulated differential equation forms what is termed the residual, Res. If the trial function were exact, the residual would be zero. In MWR, the coefficients,  $a_1(\theta)$ , are determined by specifying weighted integrals of the residual to be zero; i.e.,

$$\int_V W_j (\text{Res}) dV = 0; \quad j=1, 2, \dots, N \quad (43)$$

The choice of weighting functions,  $W_j$ , determines what class of MWR is to be applied. For the general collocation method, the weighting functions are chosen as displaced Dirac delta functions:

$$W_j = \delta(z - z_j); \quad j=1, 2, \dots, N \quad (44)$$

Substitution of equation (44) into equation (43) gives the result of forcing the residual to be zero at  $N$  specified collocation points. As the degree of approximation is increased, the residual will be forced to be zero at an increasing number of points in the spatial domain and the trial function should converge to the true solution within a given accuracy.

Within the class of collocation methods is the subclass of orthogonal collocation. The distinguishing feature of this method is that the trial functions,  $P_i(z)$ , are chosen as orthogonal polynomials defined by the following relationship:

$$\int_a^b w(z) P_i(z) P_j(z) dz = C_i \delta_{ij} \quad (45)$$

where  $[a, b]$  is the interval of orthogonality,  $w(z)$  is a positive weighting function on  $[a, b]$ ,  $C_i$  is a scale factor, and  $\delta_{ij}$  is the Kronecker delta. The group of polynomials defined by equation (44) is said to be orthogonal on the interval  $[a, b]$  with respect to the weighting function  $w(z)$ .

The  $N$  collocation points are chosen as roots to  $P_N(z)$ , which is the polynomial of the next highest order in the trial function expansion, the highest being  $P_{N-1}$  in equation (42). The basis for choosing the roots of the polynomial as the collocation points instead of equidistant points in the interval of interest can be found in the theory of polynomial interpolation. Several results, as documented by Lanczos (1956) are summarized here:

1. Polynomial expansions are justified due to the

fundamental theorem proved by Weierstrass in 1885 which establishes that any continuous function in a finite interval can always be approximated to any degree of accuracy by finite power series.

2. The Weierstrass theorem does not imply that an approximating polynomial can be obtained by using equidistant points. This behavior was studied by Runge in 1901 who showed that equidistant interpolation of some very simple analytical functions could in certain regions yield very erroneous results which did not disappear with increased points. This behavior is termed the "Runge phenomenon."
3. The difficulties which occur with equidistant interpolation disappear when the zeros of the first neglected polynomial in the polynomial approximation are used as the interpolation points. However, this introduces the need to know the roots of the particular polynomial.

### C. General Computational Aspects of Orthogonal Collocation

The solution of parabolic partial differential equations using orthogonal collocation requires several steps which are independent of the particular equation under consideration. This section presents two formulations which are theoretically equivalent but which differ in computational

and coding advantages. The first formulation, although somewhat more complex from a coding point of view, will be shown to be superior for computations.

A trial function has been proposed, Finlayson (1972, p. 105), for second order systems on the spatial interval  $[0,1]$ . For transient analysis, the trial function is of the form:

$$y(z, \theta) = f(\theta) + g(\theta)z + z(1-z) \sum_{i=1}^N a_i(\theta) P_{i-1}(z) \quad (46)$$

The above equation has  $N+2$  unknowns: The functions  $f(\theta)$ ,  $g(\theta)$ , and  $a_i(\theta)$ ,  $i=1, N$ . These are determined by the boundary conditions at  $z=0$  and  $z=1$  and by performing collocation at the  $N$  roots of  $P_N(z)$ . Thus one has a set of  $N+2$  points:

$$\begin{aligned} z_1 &= 0 \\ z_{N+2} &= 1 \\ \text{and } \{z_j\}; & j=2, N+1; \text{ the roots of } P_N \end{aligned}$$

Now, if one were to construct the approximate solution at these  $N+2$  points, a matrix equation would result:

$$\begin{bmatrix} y(z_1, \theta) \\ y(z_2, \theta) \\ \vdots \\ y(z_{N+1}, \theta) \\ y(z_{N+2}, \theta) \end{bmatrix} = \begin{bmatrix} 1 & z_1 & z_1(1-z_1)P_0(z_1) & \dots & z_1(1-z_1)P_{N-1}(z_1) \\ 1 & z_2 & z_2(1-z_2)P_0(z_2) & \dots & z_2(1-z_2)P_{N-1}(z_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & z_{N+1} & z_{N+1}(1-z_{N+1})P_0(z_{N+1}) & \dots & z_{N+1}(1-z_{N+1})P_{N-1}(z_{N+1}) \\ 1 & z_{N+2} & z_{N+2}(1-z_{N+2})P_0(z_{N+2}) & \dots & z_{N+2}(1-z_{N+2})P_{N-1}(z_{N+2}) \end{bmatrix} \begin{bmatrix} f(\theta) \\ g(\theta) \\ a_1(\theta) \\ \vdots \\ a_N(\theta) \end{bmatrix} \quad (47)$$

Now define the following quantities:

$$\underline{y} \triangleq \begin{bmatrix} y(z_1, \theta) \\ y(z_2, \theta) \\ \vdots \\ y(z_{N+1}, \theta) \\ y(z_{N+2}, \theta) \end{bmatrix} \quad (48)$$

$$\underline{R} \triangleq \begin{bmatrix} 1 & z_1 & z_1(1-z_1)P_0(z_1) & \dots & z_1(1-z_1)P_{N-1}(z_1) \\ 1 & z_2 & z_2(1-z_2)P_0(z_2) & \dots & z_2(1-z_2)P_{N-1}(z_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & z_{N+1} & z_{N+1}(1-z_{N+1})P_0(z_{N+1}) & \dots & z_{N+1}(1-z_{N+1})P_{N-1}(z_{N+1}) \\ 1 & z_{N+2} & z_{N+2}(1-z_{N+2})P_0(z_{N+2}) & \dots & z_{N+2}(1-z_{N+2})P_{N-1}(z_{N+2}) \end{bmatrix} \quad (49)$$

$$\underline{f} \triangleq \begin{bmatrix} f(\theta) \\ g(\theta) \\ a_1(\theta) \\ \vdots \\ a_N(\theta) \end{bmatrix} \quad (50)$$

Use of equations (48), (49) and (50) reduces equation (47) to the more compact form:

$$\underline{y} = \underline{R} \underline{f} \quad (51)$$

The spatial derivatives may be expressed in a similar form:

$$\partial \underline{y} / \partial z = \underline{R1} \underline{f} \quad (52)$$

$$\partial^2 \underline{y} / \partial z^2 = \underline{R2} \underline{f} \quad (53)$$

where

$$\partial \underline{y} / \partial z = \begin{bmatrix} \partial y(z_1, \theta) / \partial z \\ \partial y(z_2, \theta) / \partial z \\ \vdots \\ \partial y(z_{N+1}, \theta) / \partial z \\ \partial y(z_{N+2}, \theta) / \partial z \end{bmatrix} \quad (54)$$

$$\underline{\delta^2 y} / \delta z^2 = \begin{bmatrix} \delta^2 y(z_1, \theta) / \delta z^2 \\ \delta^2 y(z_2, \theta) / \delta z^2 \\ \vdots \\ \delta^2 y(z_{N+1}, \theta) / \delta z^2 \\ \delta^2 y(z_{N+2}, \theta) / \delta z^2 \end{bmatrix} \quad (55)$$

$$\begin{aligned} [R1]_{j,1} &= 0; \quad j=1, N+2 \\ [R1]_{j,2} &= 1; \quad j=1, N+2 \\ [R1]_{j,1} &= z_j(1-z_j) \frac{dP_{1-3}(z_j)}{dz} \\ &\quad + (1-2z_j) P_{1-3}(z_j); \quad \begin{matrix} j=1, N+2 \\ i=3, N+2 \end{matrix} \end{aligned} \quad (56)$$

and

$$\begin{aligned} [R2]_{j,1} &= [R2]_{j,2} = 0; \quad j=1, N+2 \\ [R2]_{j,1} &= z_j(1-z_j) \frac{d^2 P_{1-3}(z_j)}{dz^2} \\ &\quad + 2(1-2z_j) \frac{dP_{1-3}(z_j)}{dz} \\ &\quad - 2P_{1-3}(z_j); \quad \begin{matrix} j=1, N+2 \\ i=3, N+2 \end{matrix} \end{aligned} \quad (57)$$

The time-varying vector  $\underline{f}$  may be eliminated from equations (52) and (53) by premultiplying equation (51) by the inverse of  $\underline{R}$ ,  $\underline{R}^{-1}$ , or:

$$\underline{f} = \underline{R}^{-1} \underline{y}$$

and

$$\underline{\delta y} / \delta z = \underline{R1} \underline{R}^{-1} \underline{y} \quad (58)$$

$$\underline{\delta^2 y} / \delta z^2 = \underline{R2} \underline{R}^{-1} \underline{y} \quad (59)$$

Equations (58) and (59) thus yield expressions for the first

and second spatial derivatives at the  $N+2$  points in terms of the solution at the  $N+2$  points.

Alternative to the formulation of above is a formulation which is presented by Finlayson (1972, pp. 105-106). Expansion of equation (46) yields an  $(N+1)$  order polynomial:

$$y(z, \theta) = f(\theta) + \sum_{i=1}^{N+1} d_i(\theta) z^i \quad (60)$$

Writing the approximate solution at the  $N+2$  points yields a matrix equation similar to equation (51):

$$\underline{y} = \underline{Q} \underline{d} \quad (61)$$

where:

$$\underline{Q} \triangleq \begin{bmatrix} 1 & z_1 & z_1^2 & \dots & z_1^{N+1} \\ 1 & z_2 & z_2^2 & \dots & z_2^{N+1} \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \\ 1 & z_{N+1} & z_{N+1}^2 & \dots & z_{N+1}^{N+1} \\ 1 & z_{N+2} & z_{N+2}^2 & \dots & z_{N+2}^{N+1} \end{bmatrix} \quad (62)$$

$$\underline{d} \triangleq \begin{bmatrix} f(\theta) \\ d_1(\theta) \\ d_2(\theta) \\ \cdot \\ \cdot \\ d_{N+1}(\theta) \end{bmatrix} \quad (63)$$

The first and second spatial derivative vectors can be written as:



$$\partial \underline{y} / \partial z = \underline{Q1} \underline{d} \quad (64)$$

$$\partial^2 \underline{y} / \partial z^2 = \underline{Q2} \underline{d} \quad (65)$$

where:

$$[\underline{Q1}]_{j1} = (i-1) z_j^{1-2}; \quad \begin{matrix} j=1, N+2 \\ i=1, N+2 \end{matrix} \quad (66)$$

$$[\underline{Q2}]_{j1} = (i-1)(i-2) z_j^{1-3}; \quad \begin{matrix} j=1, N+2 \\ i=1, N+2 \end{matrix} \quad (67)$$

As in the first formulation, the time-varying vector,  $\underline{d}$ , may be eliminated from equations (64) and (65) by pre-multiplying equation (61) by the inverse of  $\underline{Q}$ ,  $\underline{Q}^{-1}$ , or:

$$\underline{d} = \underline{Q}^{-1} \underline{y}$$

and

$$\partial \underline{y} / \partial z = \underline{Q1} \underline{Q}^{-1} \underline{y} \quad (68)$$

$$\partial^2 \underline{y} / \partial z^2 = \underline{Q2} \underline{Q}^{-1} \underline{y} \quad (69)$$

Thus, equations (68) and (69) give expressions which are identical to equations (58) and (59). The matrix product  $\underline{R1} \underline{R}^{-1}$  is equivalent to  $\underline{Q1} \underline{Q}^{-1}$  and  $\underline{R2} \underline{R}^{-1}$  is equivalent to  $\underline{Q2} \underline{Q}^{-1}$ . Since the computations of  $\underline{Q}$ ,  $\underline{Q1}$ , and  $\underline{Q2}$  only require knowledge of the collocation points and not knowledge of the particular polynomial coefficients being considered, one might conceivably prefer the second formulation. Both formulations require the computation of the inverse of an (N+2) square matrix.

Computationally, it is desirable for the matrix being inverted to be well-conditioned with respect to inversion. An analysis was made comparing the inversion qualities of the matrices  $\underline{R}$  and  $\underline{Q}$ . The ease of inversion is measured by the condition number of  $\underline{R}$  and  $\underline{Q}$  respectively and with the number of decimal digits which are left unchanged following iterative improvement of the initial Gauss-Jordan reduction of each matrix. Stewart (1973) discusses the problem of ill-conditioning and the use of iterative improvement in matrix inversion. Table 5 compares the inversion characteristics of  $\underline{R}$  and  $\underline{Q}$  for increasing  $N$ . The condition numbers cited are lower bounds on the true condition numbers relative to the  $L_1$  norm\*. Appendix F shows how the lower bound and upper bound on the condition number is computed. Except in the analysis of  $\underline{Q}$  for  $(N+2) \geq 22$ , there were no practical differences in the lower and upper bounds.

Table 5 indicates that the matrix  $\underline{R}$  is well-conditioned with respect to inversion using the double precision word length available on the IBM 360/50 computer. In all cases, the computation of the product  $\underline{R} \underline{R}^{-1}$  yielded a matrix whose off-diagonal elements were less than or equal to  $10^{-16}$ . The table also shows the progressively poorer conditioning of  $\underline{Q}$  with respect to inversion. The (26 x 26) case is so ill-

\* the  $L_1$  norm of an  $(n \times n)$  matrix  $A$  is defined as:

$$L_1 \text{ norm}(A) = \max_j \left\{ \sum_{i=1}^n |A_{ij}| \right\} ; j=1, 2, \dots, n$$

TABLE 5

Comparison of Conditioning of  $\underline{R}$  and  $\underline{Q}$   
Matrices with Respect to Inversion

Matrix Size	Lower Bound on Condition of $\underline{R}$	IDGT* $\underline{R}$	Lower Bound on Condition of $\underline{Q}$	IDGT* $\underline{Q}$
( 3 x 3 )	0.120 x 10 <sup>0</sup>	15	0.240 x 10 <sup>0</sup>	15
( 4 x 4 )	0.328 x 10 <sup>2</sup>	15	0.149 x 10 <sup>3</sup>	15
( 5 x 5 )	0.739 x 10 <sup>2</sup>	15	0.944 x 10 <sup>3</sup>	15
( 6 x 6 )	0.142 x 10 <sup>3</sup>	15	0.591 x 10 <sup>4</sup>	14
( 7 x 7 )	0.243 x 10 <sup>3</sup>	15	0.366 x 10 <sup>5</sup>	14
( 8 x 8 )	0.384 x 10 <sup>3</sup>	15	0.225 x 10 <sup>6</sup>	13
( 9 x 9 )	0.571 x 10 <sup>3</sup>	15	0.138 x 10 <sup>7</sup>	13
(10 x 10)	0.812 x 10 <sup>3</sup>	15	0.840 x 10 <sup>7</sup>	11
(11 x 11)	0.111 x 10 <sup>4</sup>	15	0.510 x 10 <sup>8</sup>	11
(12 x 12)	0.148 x 10 <sup>4</sup>	15	0.309 x 10 <sup>9</sup>	11
(14 x 14)	0.244 x 10 <sup>4</sup>	15	0.112 x 10 <sup>11</sup>	9
(18 x 18)	0.545 x 10 <sup>4</sup>	15	0.145 x 10 <sup>14</sup>	6
(22 x 22)	0.103 x 10 <sup>5</sup>	15	0.177 x 10 <sup>17</sup>	2
(26 x 26)	0.179 x 10 <sup>5</sup>	15	0.907 x 10 <sup>18</sup>	0**

\* IDGT is the approximate number of digits in the inverse which were left unchanged after iterative improvement

\*\* There was no convergence in the iterative improvement. The upper bound on the condition of  $\underline{Q}$  was  $0.202 \times 10^{39}$  based on the "best"  $\underline{Q}^{-1}$ .

Note: Subscripts R and Q on IDGT refer to inversion of  $\underline{R}$  and  $\underline{Q}$  respectively.

conditioned that inversion using the available computer is computationally impossible. Based on condition numbers and accuracy, either formulation is acceptable for  $(N+2) \leq 5$ ; while for  $(N+2) > 6$ , the first formulation is preferable.

It should be noted that Finlayson(1972, p.35) alludes to this problem but the comment is quite qualitative and somewhat obscure:

"The orthogonality of the polynomials gives computational advantages, although the same approximation can be expressed in terms of powers of  $x$ , if the computations can be done accurately enough".

The preceding analysis used the roots of the so-called shifted Legendre polynomials. These are defined by equation (45) if one lets  $a=0$ ,  $b=1$ , and  $w(z)=1$ . The polynomial coefficients were computed using the relationships of Villadsen (1970). Figure 6 shows the behavior of the first four of these polynomials. The roots were computed by shifting the abscissas from Gaussian quadrature formulae, available in Abramowitz and Segun (1965), Love (1966), and Stroud and Secrest (1966).

Although most of the problems solved by others using orthogonal collocation have not required over 12 collocation points, the results of this section point out a computation disadvantage of the second formulation which appears at a fairly small degree of discretization and gets progressively worse. The first formulation requires some additional information but successfully circumvents the problems inherent in

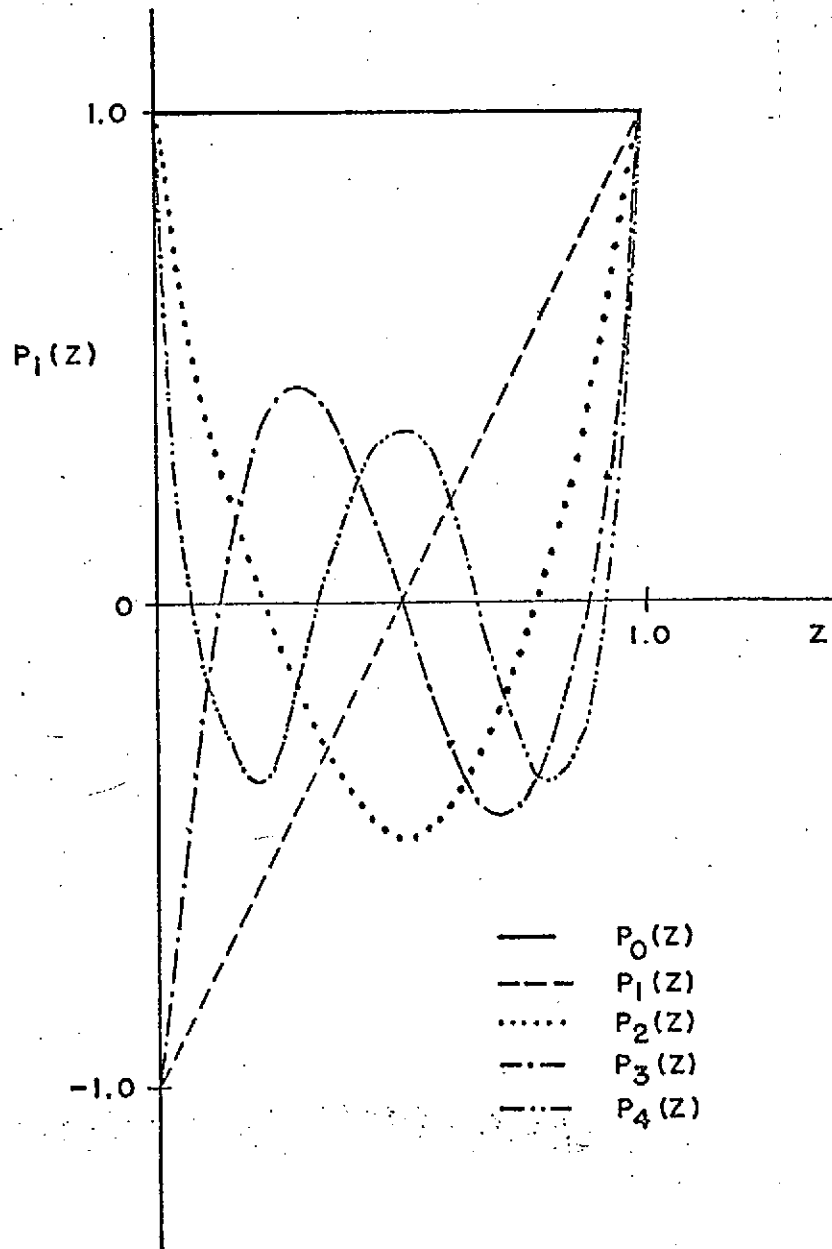


FIGURE 6 SHIFTED LEGENDRE POLYNOMIALS OF ORDER ZERO TO FOUR

the second formulation. Of course, the precision capabilities of the computer used for computations must be taken into account also.

In addition, these remarks carry over into problems where it is chosen to use polynomials in the squared spatial dimension. For example, a trial function which has been proposed for solution of a catalyst modeling problem is:

$$y(\lambda, \theta) = h(\theta) + (1-\lambda^2) \sum_{i=1}^N a_i(\theta) P_{i-1}(\lambda^2) \quad (70)$$

where  $h(\theta)$  is determined by the boundary condition at  $\lambda=1$  and the boundary condition  $\partial y(0, \theta) / \partial \lambda = 0$  is satisfied by the trial function. Subsequent expansion and formulation at the respective collocation points yields a matrix to be inverted and the procedure of retaining polynomials within a coefficient matrix similar to R is favored over a formulation yielding a matrix similar to Q for the reasons previously listed.

## PART 6

### APPLICATION OF ORTHOGONAL COLLOCATION TO A TRANSIENT, DIFFUSION-CONVECTION MASS TRANSFER PROBLEM

The use of orthogonal collocation as a technique for solution of pulsed, distributed systems, the chromatograph system being only one such system, is an area which has not been documented in current literature. Because of this lack of contribution in this area, guidelines for effective use of this method must be established and documented.

In this section the general aspects of orthogonal collocation enumerated upon in the previous section will be applied to solve a simple, transient diffusion-convection mass transfer problem:

$$(1/Pe)(\partial^2 y / \partial z^2) - \partial y / \partial z = \partial y / \partial \theta \quad (71)$$

$$y(z, 0) = 0; \quad z > 0 \quad (72)$$

$$y(0, \theta) = \phi(\theta); \quad \theta \geq 0 \quad (73)$$

$$\partial y(z_0, \theta) / \partial z = 0; \quad \theta > 0 \quad (74)$$

Motivation for the study of this problem is several fold. First of all, the problem has a direct analytic solution, therefore giving a result useful for comparison. Secondly, the problem possesses characteristics of more complex models. Thirdly, successful application of orthogonal collocation should give guidelines for subsequent applications.

The preceding analysis has been conducted based on a spatial interval of  $[0,1]$  as the interval of orthogonality for the orthogonal polynomials in the trial function expansion. However, as was shown in Part 4, application of boundary condition (74) should be made at some point  $z_0$  which should be different than unity depending on the value of the Peclet number. To avoid derivation of additional polynomials orthogonal on the interval  $[0, z_0]$  and the determination of the required roots, the above problem may be rescaled in the spatial domain by the following change in variable:

$$z_{NEW} = (1/z_0) z$$

Therefore

$$(1/\partial z) = (1/z_0) (1/\partial z_{NEW}) \quad (75)$$

$$(1/\partial z)^2 = (1/z_0)^2 (1/\partial z_{NEW})^2 \quad (76)$$

Use of equations (75) and (76) and deletion of the subscript "NEW" yields the rescaled problem:

$$(1/Pe)(1/z_0)^2 (\partial^2 y / \partial z^2) - (1/z_0) \partial y / \partial z = \partial y / \partial \theta \quad (77)$$

$$y(z, 0) = 0; \quad z > 0 \quad (78)$$

$$y(0, \theta) = \phi(\theta); \quad \theta \geq 0 \quad (79)$$

$$\partial y(1, \theta) / \partial z = 0; \quad \theta > 0 \quad (80)$$

Where one was concerned with the dimensionless length of unity in the old coordinate system, one is now concerned with



the dimensionless length of  $(1/z_0)$  which now corresponds to the outlet of the bed.

As a variant of the favored formulation of Part 5, one may represent the solution at the  $N$  collocation points,  $[z_2, z_{N+1}]$ , as:

$$\begin{bmatrix} y(z_2, \theta) \\ \vdots \\ y(z_{N+1}, \theta) \end{bmatrix} = \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} f(\theta) + \begin{bmatrix} z_2 \\ \vdots \\ z_{N+1} \end{bmatrix} g(\theta) + \begin{bmatrix} z_2(1-z_2)P_0(z_2) & \dots & z_2(1-z_2)P_{N-1}(z_2) \\ \vdots & \dots & \vdots \\ z_{N+1}(1-z_{N+1})P_0(z_{N+1}) & \dots & z_{N+1}(1-z_{N+1})P_{N-1}(z_{N+1}) \end{bmatrix} \begin{bmatrix} a_1(\theta) \\ \vdots \\ a_N(\theta) \end{bmatrix} \quad (81)$$

Formulation of the problem in this manner reduces the size of the matrix which must be inverted from  $(N+2) \times (N+2)$  to  $N \times N$ , although increasing the coding effort. Application of equation (81) to the above problem reduces the distributed system to a set of  $N$  ordinary differential equations represented by:

$$\dot{\underline{y}} = \underline{W} (\underline{y} - \underline{1} \phi(\theta)); \quad \underline{y}(0) = \underline{0} \quad (82)$$

Manipulative details and full matrix definitions for this problem are provided in Appendices G and H. It should be noted that the function,  $w(z)$ , which appears outside the summation sign in the general trial function (Appendix G) has been taken as  $w(z) = z(1-z)$  as previously seen in equation (46). This specific form is used exclusively in this investigation for

all of the interparticle approximations. However, one might possibly specify the form of  $w(z)$  relative to the types of polynomials used. That is, for a given function  $w(z)$ , one might specify the polynomials such that the columns of the  $N \times N$  coefficient matrix in equation (81) become orthogonal. Thus, one would be taking advantage of the orthogonality properties of the specific polynomials rather than using an arbitrary polynomial set. For example, if one used  $w(z) = z(1-z)$  in the trial function (as is shown in equation (81)), the columns of the  $N \times N$  matrix could be made orthogonal by defining the polynomial set by:

$$\int_0^1 z^2(1-z)^2 P_i(z) P_j(z) dz = C_i \delta_{ij}$$

The inner products of the matrix columns would represent the discrete form of this integral.

The merits of utilizing the orthogonality properties of the specified function set has not been established. As will be pointed out in Part 9, Discussion, the undertaking of such a study requires computing capabilities (precision) to determine roots of polynomials which may be "uncommon" and not tabulated to a large number of significant figures. For these reasons, the choice of polynomials in this investigation was dictated by the availability of the high precision roots.

An eigenanalysis\* of the matrix  $W$  in equation (82)

\*A computer program listing is given as part of Appendix H. This program performed all the manipulations and computations documented in Appendices G and H as well as the eigenanalysis.

was made for Peclet numbers of 1, 10, 100, 1000, and 10000. The number of collocation points,  $N$ , was varied in the sequence 3, 4, 7, 15, and 21. The shifted Legendre polynomials and roots were used in the analysis. The value of  $z_0$  was held at 2.0 for all cases.

For all cases, the eigenanalysis yielded eigenvalues with negative real parts indicating a stable set of ordinary differential equations. This result contradicts the results obtained earlier (Woodrow, 1973) for  $Pe=1$ . The difference between the analysis lies in the sequence of manipulations and computations made in arriving at the matrix, in this paper  $\underline{W}$ , to be analysed. Although the approaches are equivalent theoretically, the computations produced different. The approach detailed in Appendix G is therefore favored.

While stability is indicated by the negative real parts of the eigenvalues, an oscillatory behavior was indicated by the presence of imaginary parts for a majority of the eigenvalues in each case. The magnitudes of the imaginary parts increased with increasing  $Pe$ . Therefore, it was reasonable to expect that simulations using the orthogonal collocation technique would exhibit some degree of oscillation depending on how the modes of the matrix,  $\underline{W}$ , were coupled.

Various simulations have been performed for this problem. Table 6 summarizes the different cases considered in this investigation. The method by which the set of differential

TABLE 6

Summary of Orthogonal Collocation Simulations  
for the Transient, Diffusion-Convection Problem

$\phi(\theta) = \{ \text{Unit rectangular pulse of five times duration} \}$			
<u>Pe</u>	<u>N</u>	<u>Figure Reference</u>	<u>Execution time*</u> (sec.)
32.0	3	Figure 8	23.55
32.0	7	Figure 9	102.05
32.0	15	Figure 10	1164.32
10000.0	15	Figure 12	301.62
10000.0	21	Figure 13	891.10
$\phi(\theta) = \{ \text{Actual input data, Figure 14} \}$			
<u>Pe</u>	<u>N</u>	<u>Figure Reference</u>	<u>Execution time**</u> (sec.)
10000.0	3	Figure 16	23.90
10000.0	7	Figure 17	57.10
10000.0	15	Figure 18	419.25

\* Double precision computations using FORTRAN G on IBM 360/50; integrations terminated at ten time units.

\*\*Double precision computations using FORTRAN G on IBM 360/50; integrations terminated at twenty time units.

Note: For all cases  $z_0 = 2.0$ ; responses for all collocation points outputted at each time increment.

equations was solved is based on an extrapolation treatment (Bulirsch and Stoer, 1966). This algorithm appears in a subroutine (DREBS) which is part of the IMSL scientific subroutine library (IMSL, 1973, p. DREBS) currently available on Rensselaer's IBM 360/50 computing facility. The computations were made entirely in double precision using the FORTRAN G compiler. Table 6 shows how execution time for the simulations was affected by  $N$ , the number of collocation points.

The method used to integrate the equations is not too well known. In their paper, Bulirsch and Stoer showed the superiority of the extrapolation treatment over a Runge-Kutta and Adams-Moulton-Bashforth methods. A comparison was made between the subroutine DREBS, the IBM SSP (IBM, 1968) subroutines for a fourth order Runge-Kutta and Hamming Predictor-Corrector method, and a simple Euler Method. The comparison was based on the  $N=3$  simulation for this system. For the same error criteria, it was found that the Euler method was significantly slower than the extrapolation treatment and while the Runge-Kutta and Predictor-Corrector methods used a larger step size than the Euler step size, the step was still much smaller than the extrapolation treatment and hence was computationally slower. This result agrees with Bulirsch and Stoer for the problems that they considered.

Although the eigenanalysis indicated that the system of ordinary differential equations was stable, a closer examination (made near the conclusion of this investigation) of the

computed eigenvalues indicated that the system became increasingly "stiff" with increasing approximation order. Table 7 shows this behavior and the behavior as affected by Peclet number. The parenthesised ratios are the absolute value of the largest eigenvalue real part to the absolute value of the smallest eigenvalue real part. The result of the indicated division is shown beneath each ratio. Using these ratios as measures of stiffness; one can see that the equation set is "stiffer" for low values of Peclet number and hence a smaller integration step is required when the large eigenvalue response mode contributes to the solution. This would have the effect of increasing computation time with low Peclet number for a given order of discretization. This deduction is consistent with the increased computation times for the low Peclet number versus the high Peclet number simulations for the unit rectangular forcing pulse (see Table 6). Although the Bulirsch and Stoer extrapolation technique may not be particularly well suited for the "stiff" system, it was used as the method of integration. In retrospect, another algorithm might have been better - perhaps a variable order Adams method (Hull et.al., 1972). Within the IMSL library, the subroutine DVGØER (IMSL, 1973, p.DVGØER) using Gear's implementation (Gear, 1971a,1971b) would be a likely candidate for use. This situation could form an additional area of analysis - whether orthogonal collocation approximations produce, in general, stiff ordinary differential equation sets and what integration algorithm can

TABLE 7

Largest to Smallest Eigenvalue Ratios for  
the Orthogonal Collocation Discretization  
of the Simple, Diffusion-Convection Problem

N	Pe				
	1	10	100	1000	10000
3	$\left(\frac{22.26}{1.28}\right)$ = 17.4	$\left(\frac{3.48}{1.19}\right)$ = 2.92	$\left(\frac{1.57}{0.96}\right)$ = 1.63	$\left(\frac{1.46}{0.90}\right)$ = 1.63	$\left(\frac{1.45}{0.89}\right)$ = 1.63
7	$\left(\frac{351.0}{1.28}\right)$ = 274.	$\left(\frac{44.1}{2.52}\right)$ = 17.6	$\left(\frac{10.49}{0.95}\right)$ = 11.1	$\left(\frac{2.57}{0.57}\right)$ = 4.53	$\left(\frac{3.30}{0.53}\right)$ = 6.2
15	$\left(\frac{5974.0}{1.27}\right)$ = 4700.0	$\left(\frac{639.8}{2.70}\right)$ = 236.0	$\left(\frac{99.43}{2.72}\right)$ = 36.5	$\left(\frac{33.05}{0.82}\right)$ = 40.3	$\left(\frac{18.07}{0.14}\right)$ = 127.1
21	$\left(\frac{21892.0}{1.28}\right)$ = 17100.0	$\left(\frac{2272.0}{2.70}\right)$ = 840.0	$\left(\frac{301.2}{3.67}\right)$ = 82.0	$\left(\frac{81.5}{1.00}\right)$ = 81.5	$\left(\frac{40.94}{0.30}\right)$ = 136.0

Ratios are  $(\max |\lambda_{\text{real}}| / \min |\lambda_{\text{real}}|)$   
where  $\lambda$ 's are the eigenvalues of  $\underline{W}$  in

$$\dot{\underline{y}} = \underline{W} (\underline{y} - \underline{1} \phi(\theta))$$

be used most effectively for simulation purposes.

Returning to Table 6, the first set of cases involves the use of a unit rectangular pulse of five time units duration as the forcing function,  $\phi(\theta)$ . Within this first set of cases, the Peclet number was set at 32. The exact response, computed by convolution of the impulse response with the input is given in Figure 7. Figures 8, 9, and 10 show the orthogonal collocation approximations to the response for 3, 7, and 15 collocation points respectively. Note that all responses are for  $z=0.5$  and  $z_0=2.0$ . Hence, the responses correspond to the behavior at the bed outlet. This is a convenient scaling of the problem because for the odd order approximations used and the shifted Legendre polynomials, the point  $z=0.5$  is always a root and hence collocation point. The response for 3 collocation points shows several objectionable oscillations compared to the exact solution, although qualitative characteristics are well approximated. The response for seven collocation points exhibits several oscillations of much smaller amplitude and duration and the exact response is increasingly well approximated. The response for fifteen collocation points is very close to the exact response and, within the accuracy of the plot, is virtually identical. However, the digital response did show small oscillations when the response "should have been" zero.

Subsequent to the studies for  $Pe=32$ , it was decided to use a Peclet number more representative of the magnitude



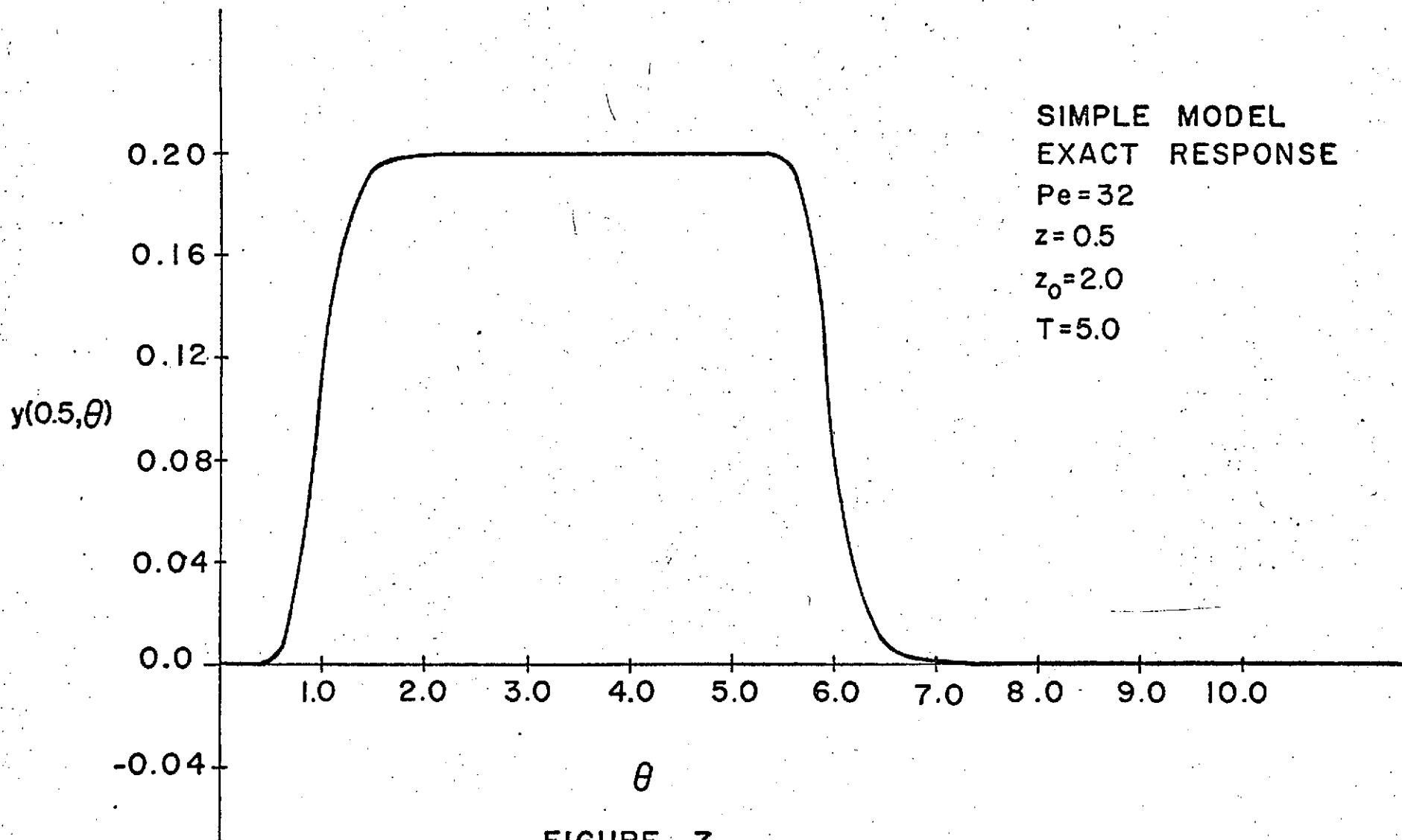


FIGURE 7

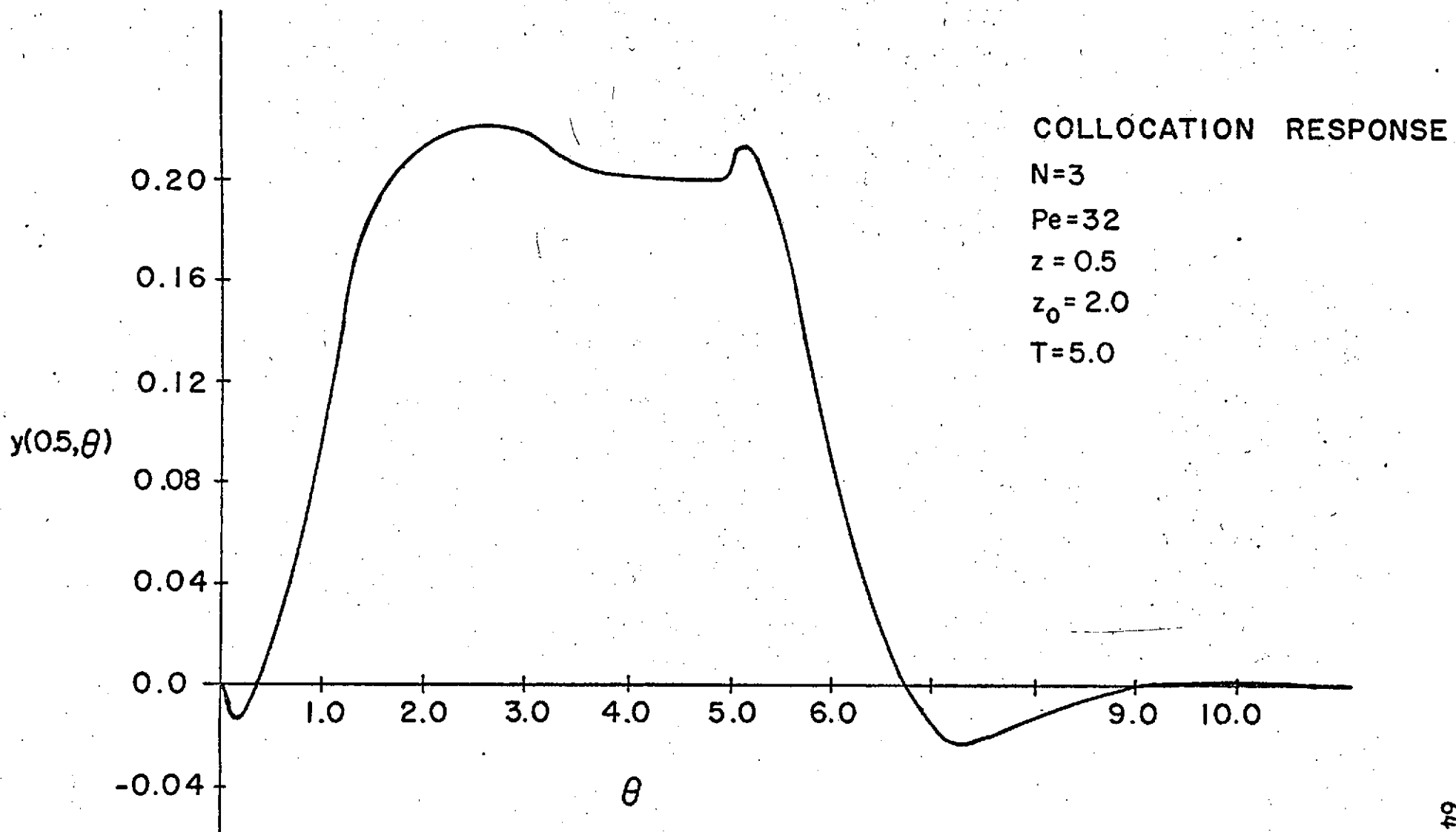


FIGURE 8

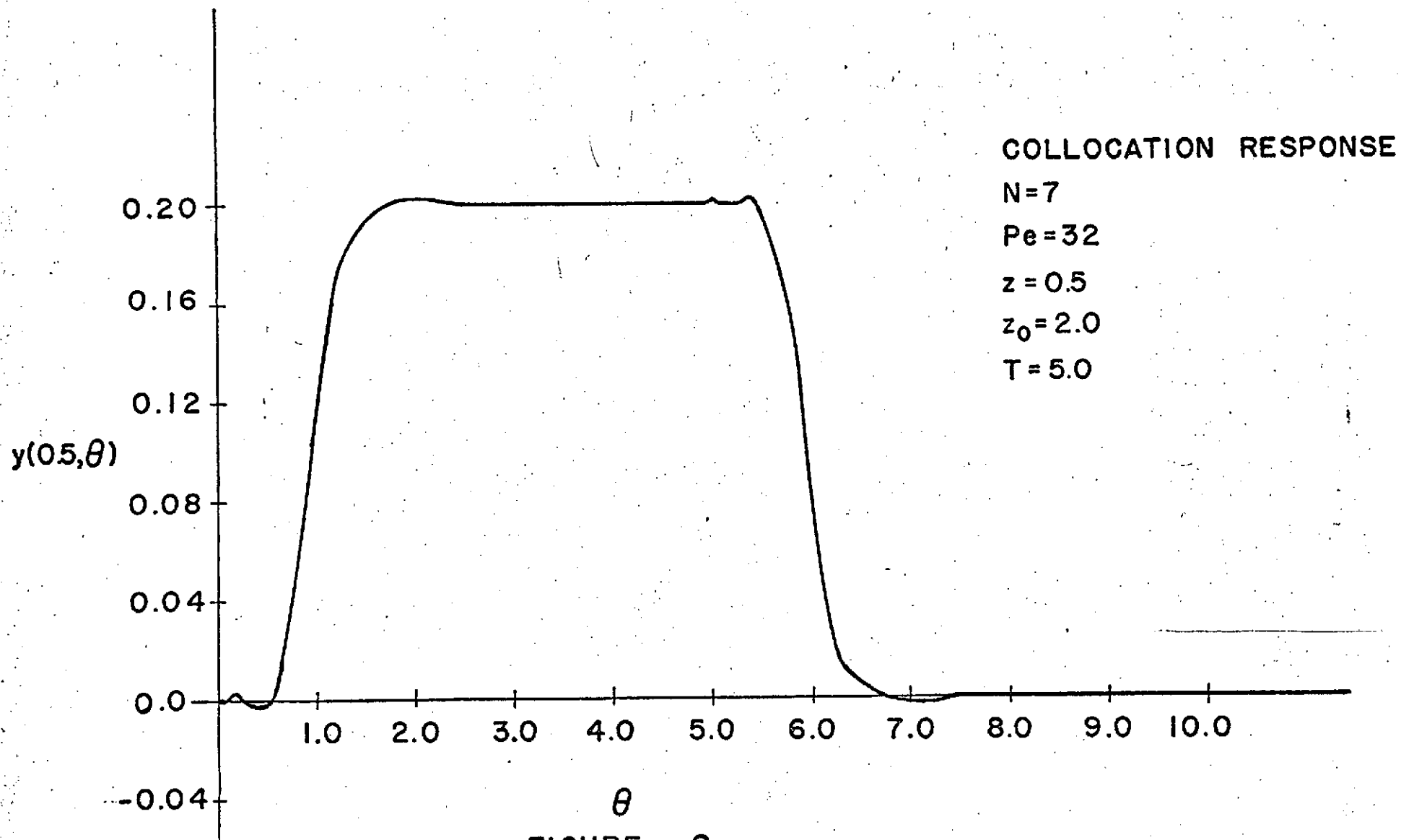


FIGURE 9

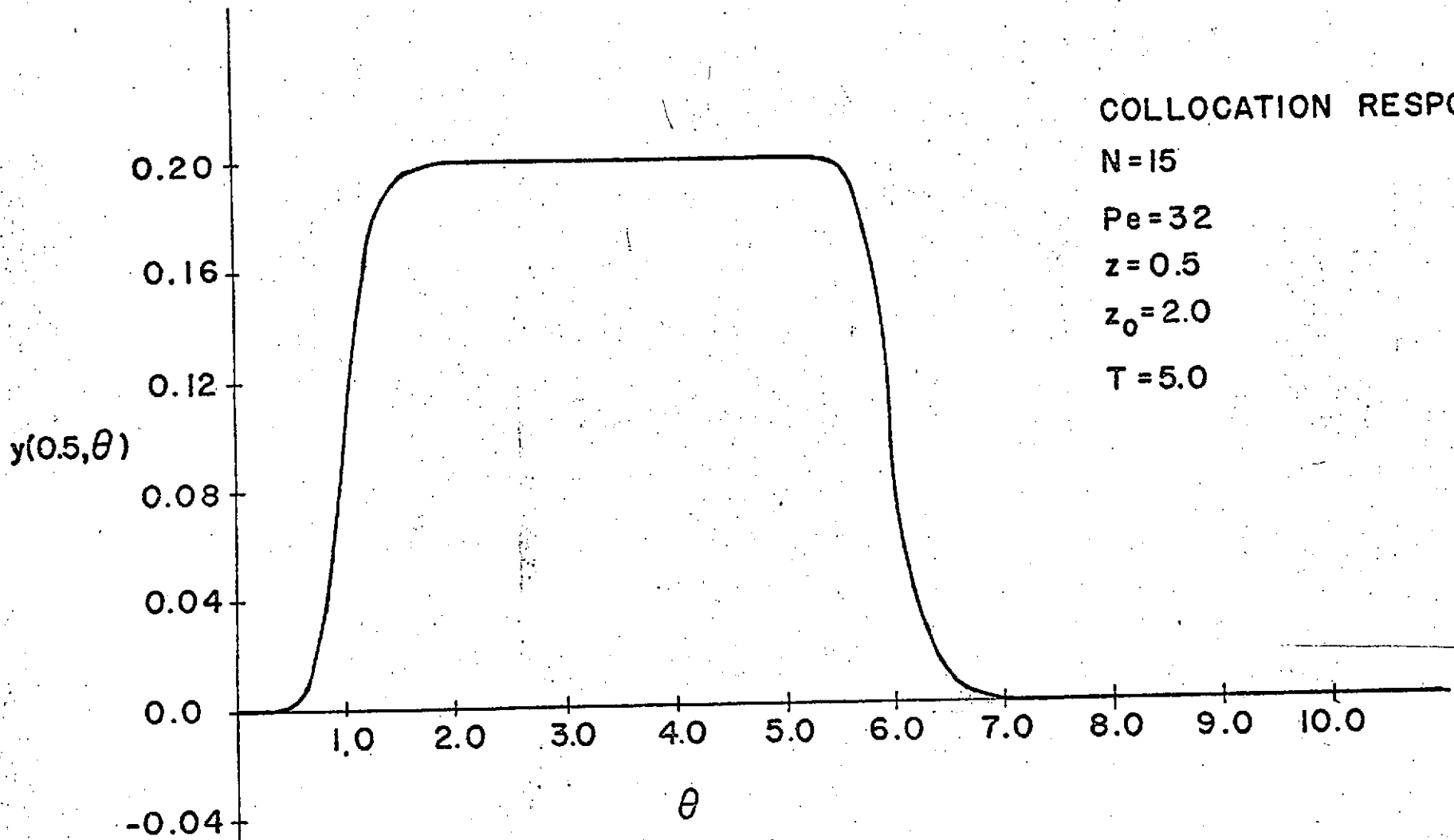


FIGURE 10

encountered in the chromatographic system, namely  $Pe = 10000$ . Figure 11 shows the exact response. With the large value of  $Pe$ , the character of the parabolic partial differential equation becomes increasingly hyperbolic. The exact response is effectively the translated input pulse with the corners slightly rounded and dispersed. The orthogonal collocation approximations to the exact response are given in Figures 12 and 13 for  $N=15$  and  $N=21$  respectively. Both approximations exhibit numerous moderate amplitude oscillations. This shows the difficulty that the orthogonal collocation technique has in approximating functions with sharp, almost discontinuous behavior. For this situation, a high degree of discretization would be desirable. An attempt to generate collocation matrices for a thirty-first order simulation was made. This attempt was not successful because the matrix  $\underline{W}$  showed instability in the form of positive eigenvalues. This result, which would completely reverse the trend of convergence to the solution with increasing  $N$ , was attributed to accumulated round-off errors in evaluation of the coefficient matrix because the required precision to carry the higher order polynomial coefficients becomes greater than the precision capability of the computer being used (IBM 360/50).

Upon discovery of this weakness of the orthogonal collocation technique and the computational constraint of the IBM 360/50, effort was directed to use of a "less" sharp forcing function in conjunction with the high  $Pe$  value. The

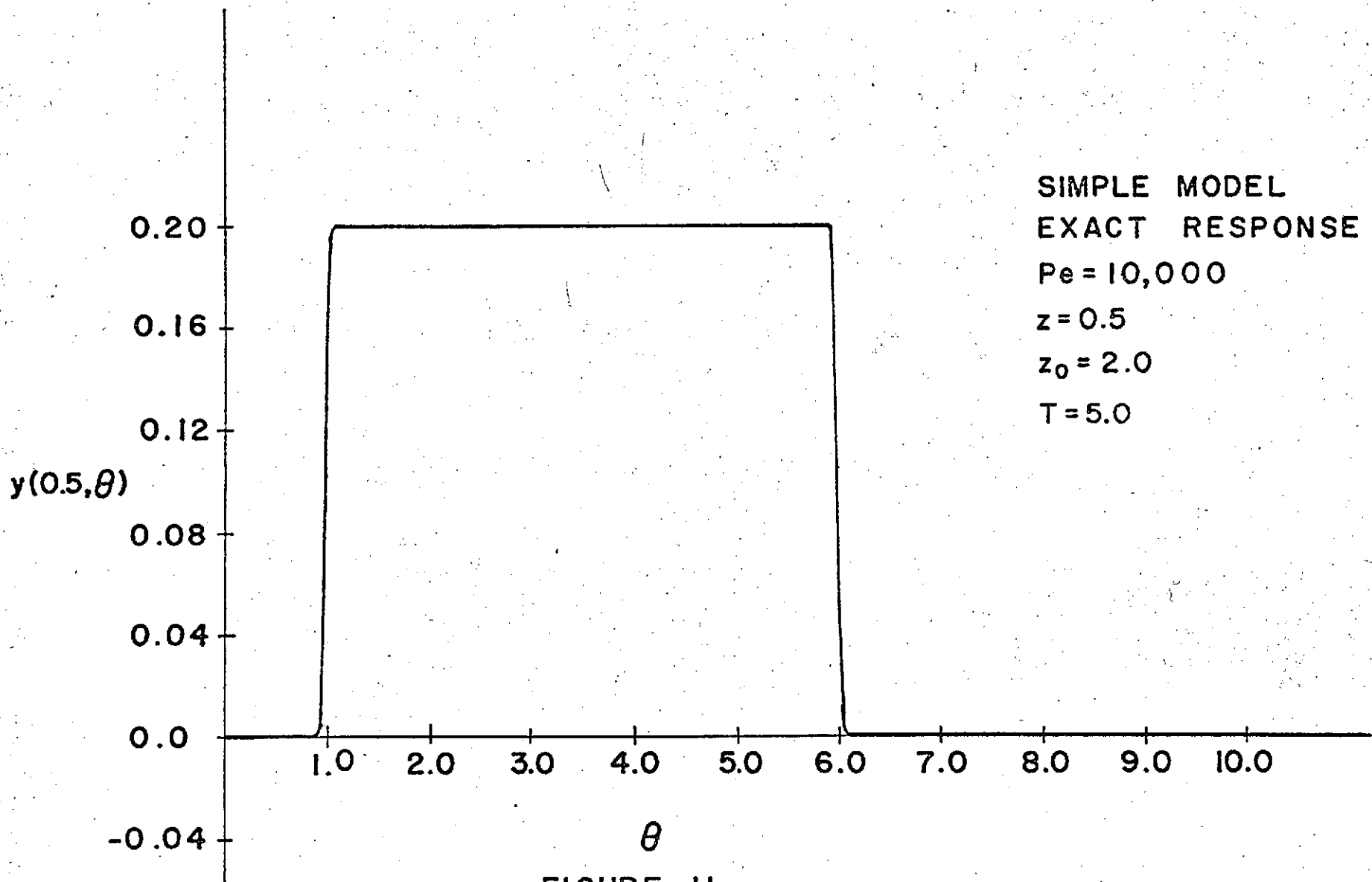


FIGURE II

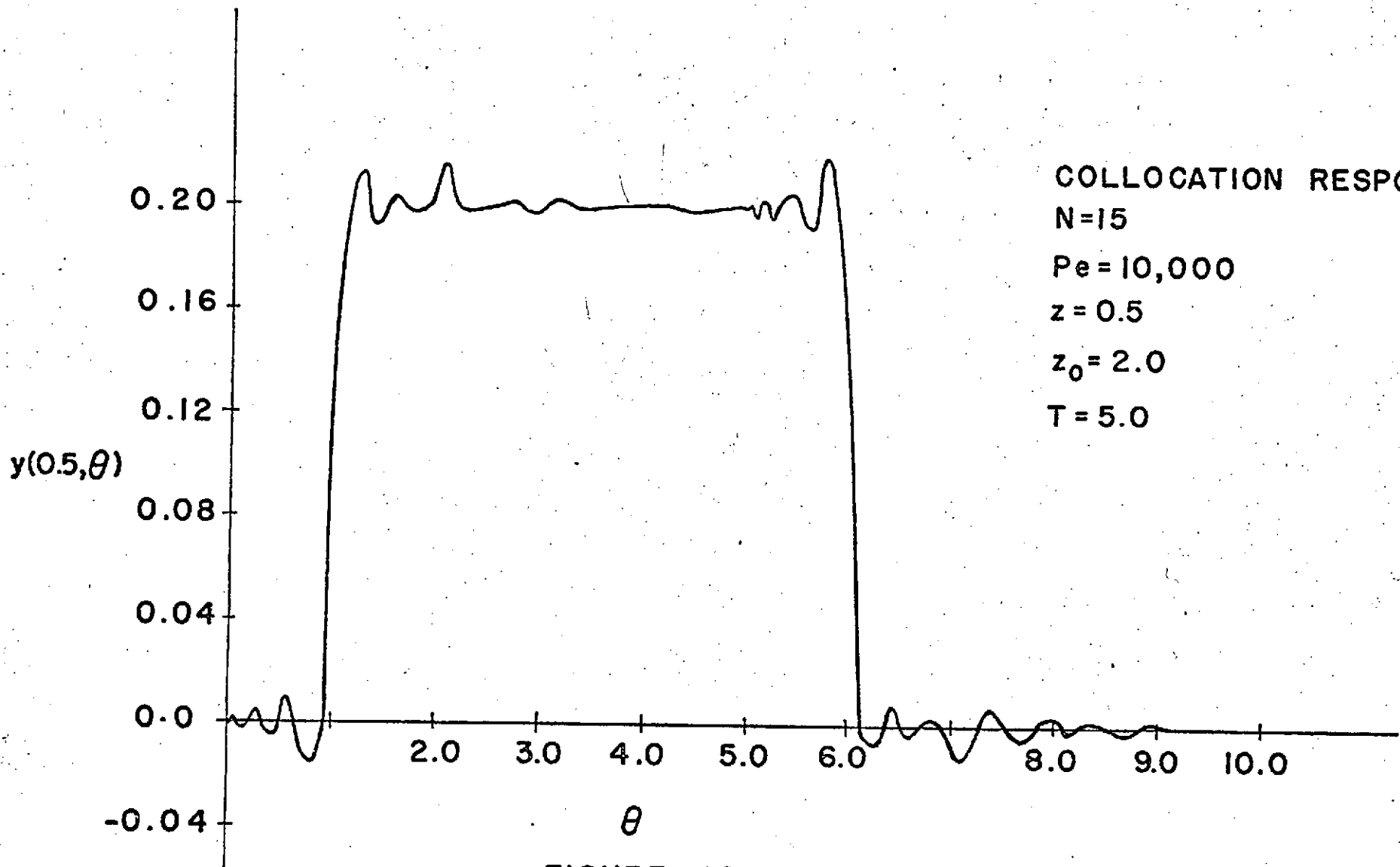


FIGURE 12

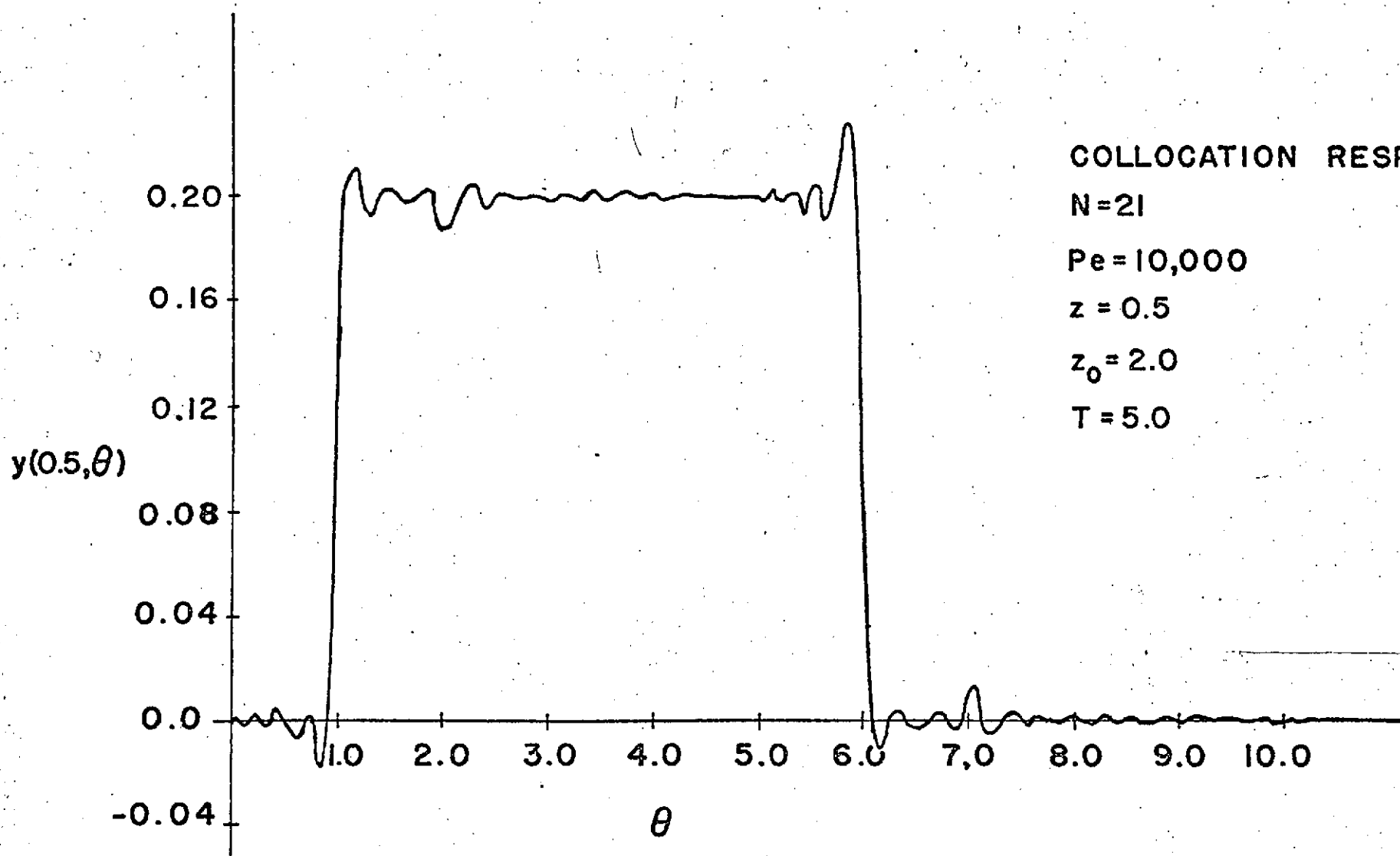


FIGURE 13



chosen forcing function was actual chromatograph input data (normalized with respect to the dimensionless time,  $\theta$ ) shown in Figure 14. This input data corresponds to an injected Pentane sample at 150 C. studied previously (Keba and Woodrow, 1972). This forcing function is used for the second set of cases listed in Table 6. The exact response, again computed by convolution of the impulse response with input is shown in Figure 15. Figures 16, 17, and 18 show the orthogonal collocation approximations to the exact response for 3, 7, and 15 collocation points respectively. For purposes of numerical integration, the input function was interpolated using cubic spline functions. Another IMSL subroutine, ICS1CE (IMSL, 1973, p. ICS1CE), was used to compute the interpolation coefficients. Again, all responses shown are for  $z=0.5$  and  $z_0=2.0$ . The result for  $N=3$ , Figure 16, exhibits an oscillatory behavior and gives a good qualitative representation of the true response. The result for  $N=7$ , Figure 17, exhibits a better approximation with reduced oscillations. The result for  $N=15$ , Figure 18, gives virtually the same result as the exact. Again, oscillations are still present in the digital results but are of very small magnitude.

The preceding results offer several conclusions as to the usefulness of orthogonal collocation for the system under consideration:

1. Orthogonal collocation greatly reduces the degree of spatial discretization required for numerical

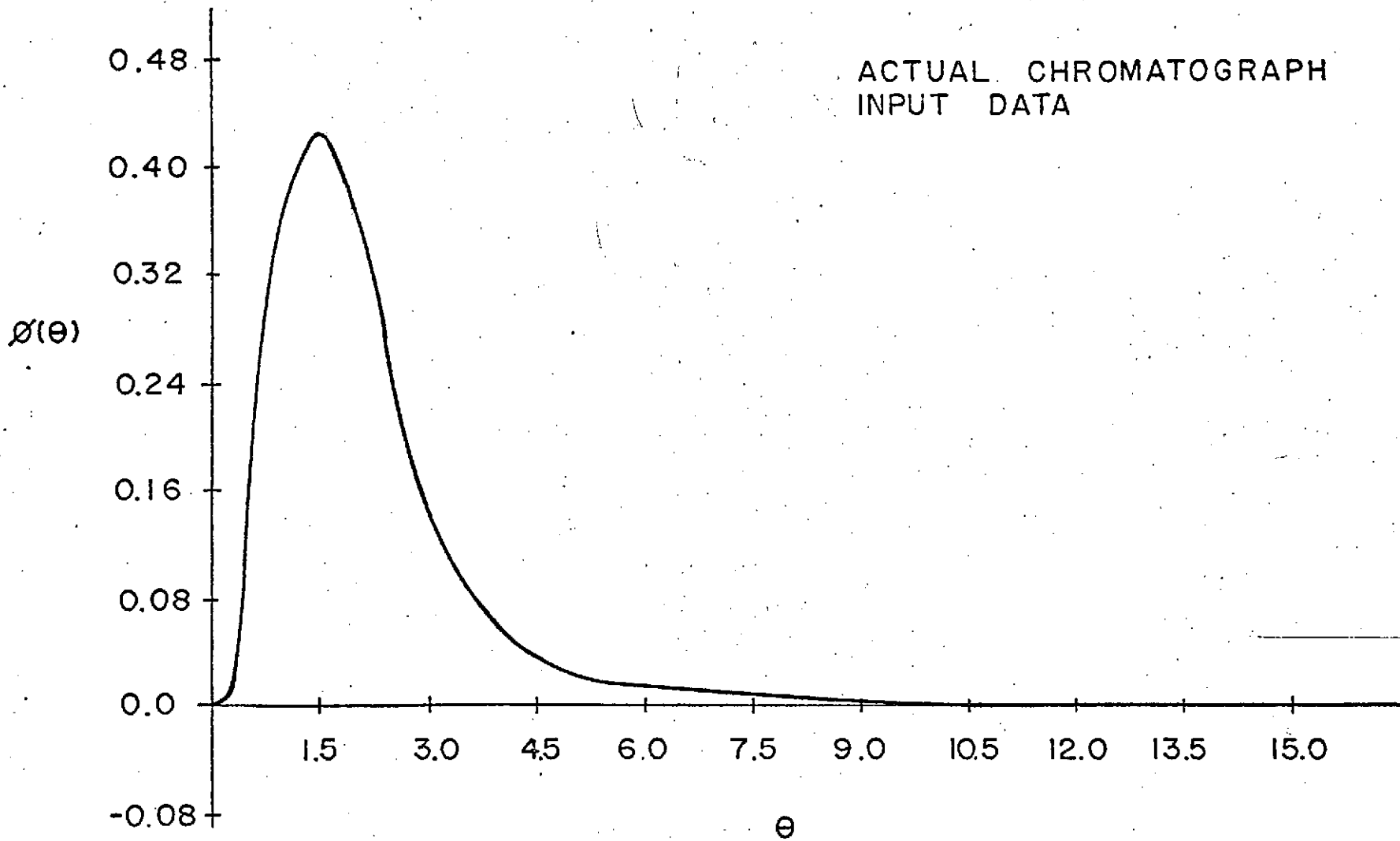


FIGURE 14

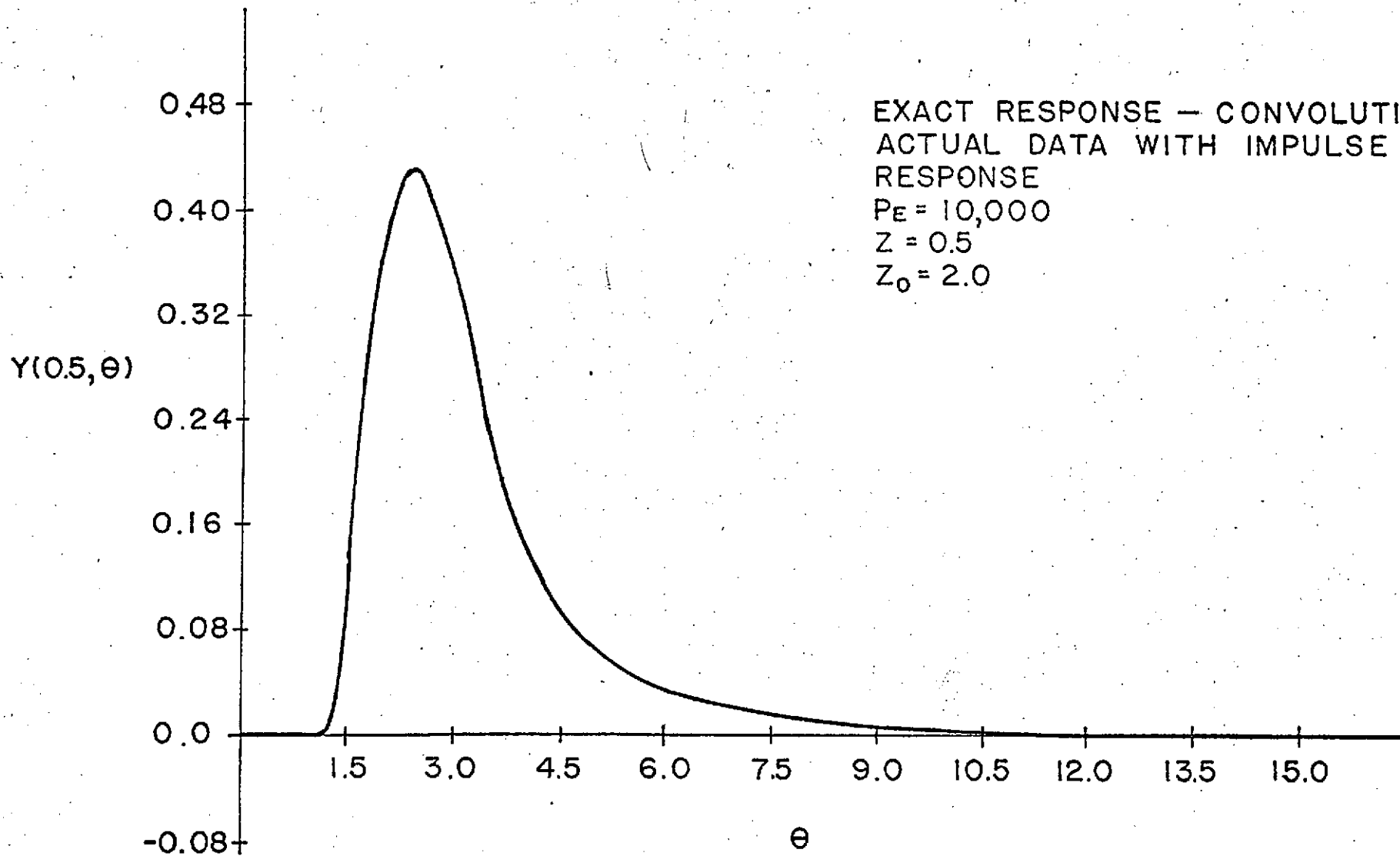


FIGURE 15

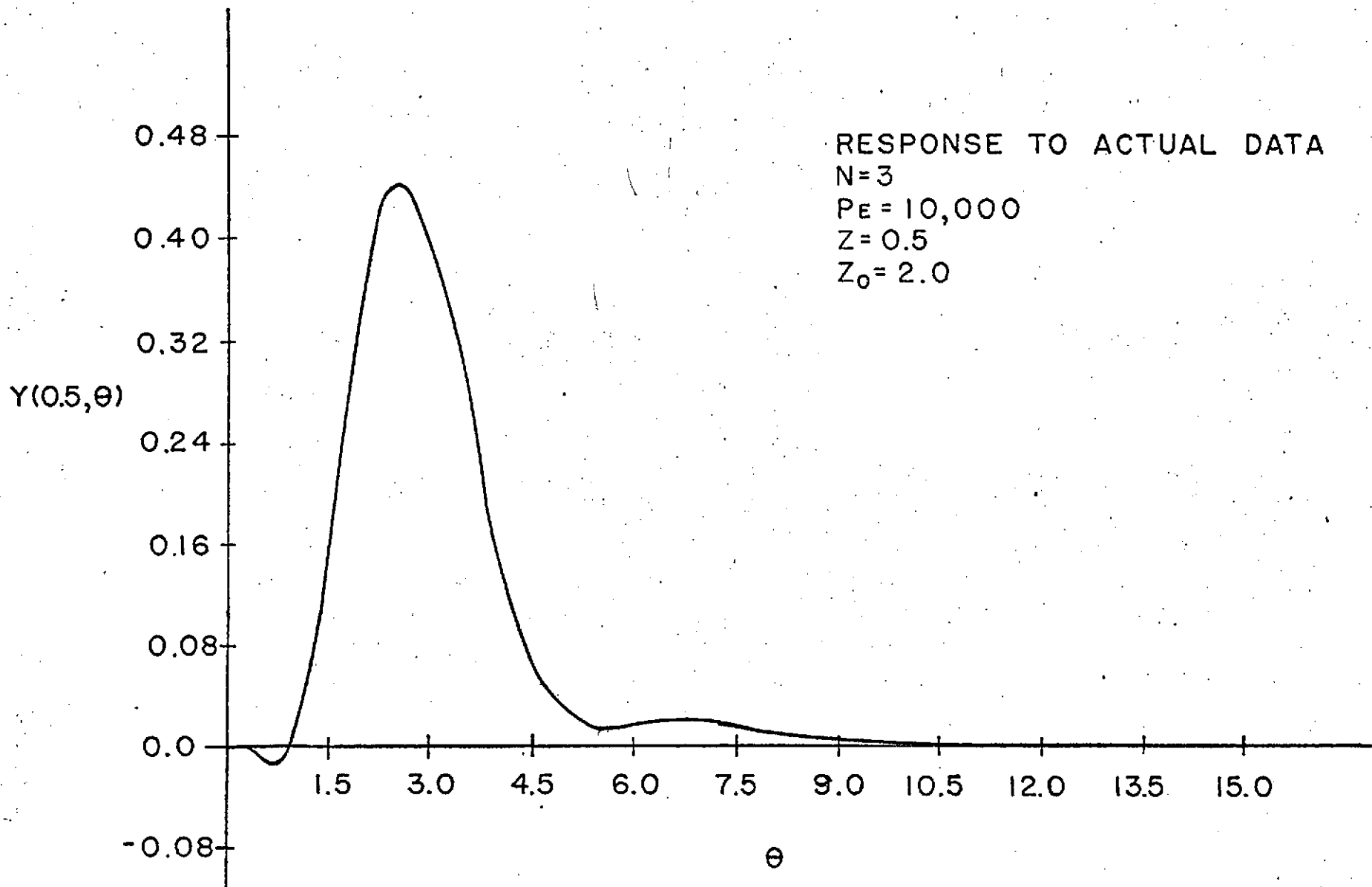


FIGURE 16

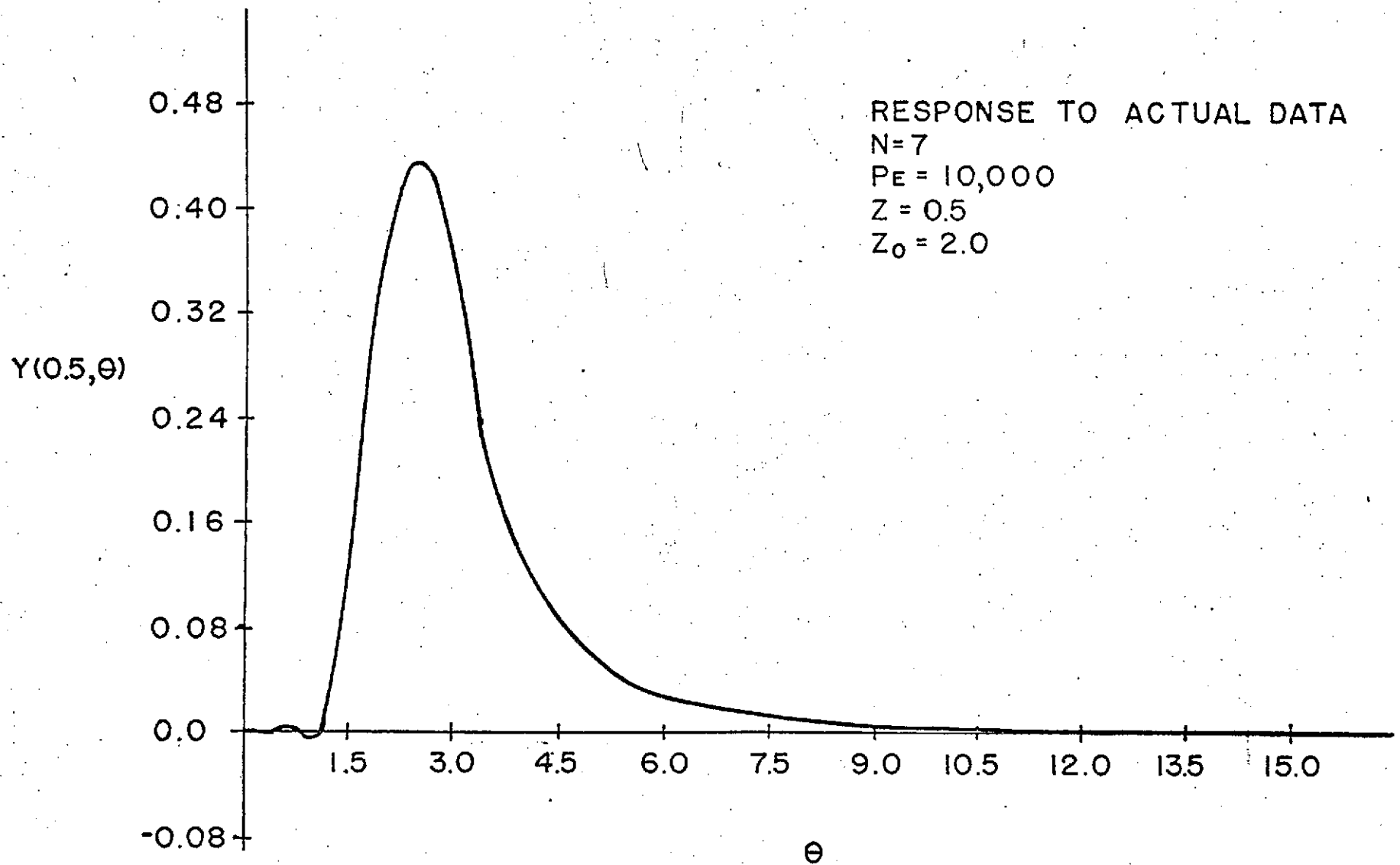


FIGURE 17

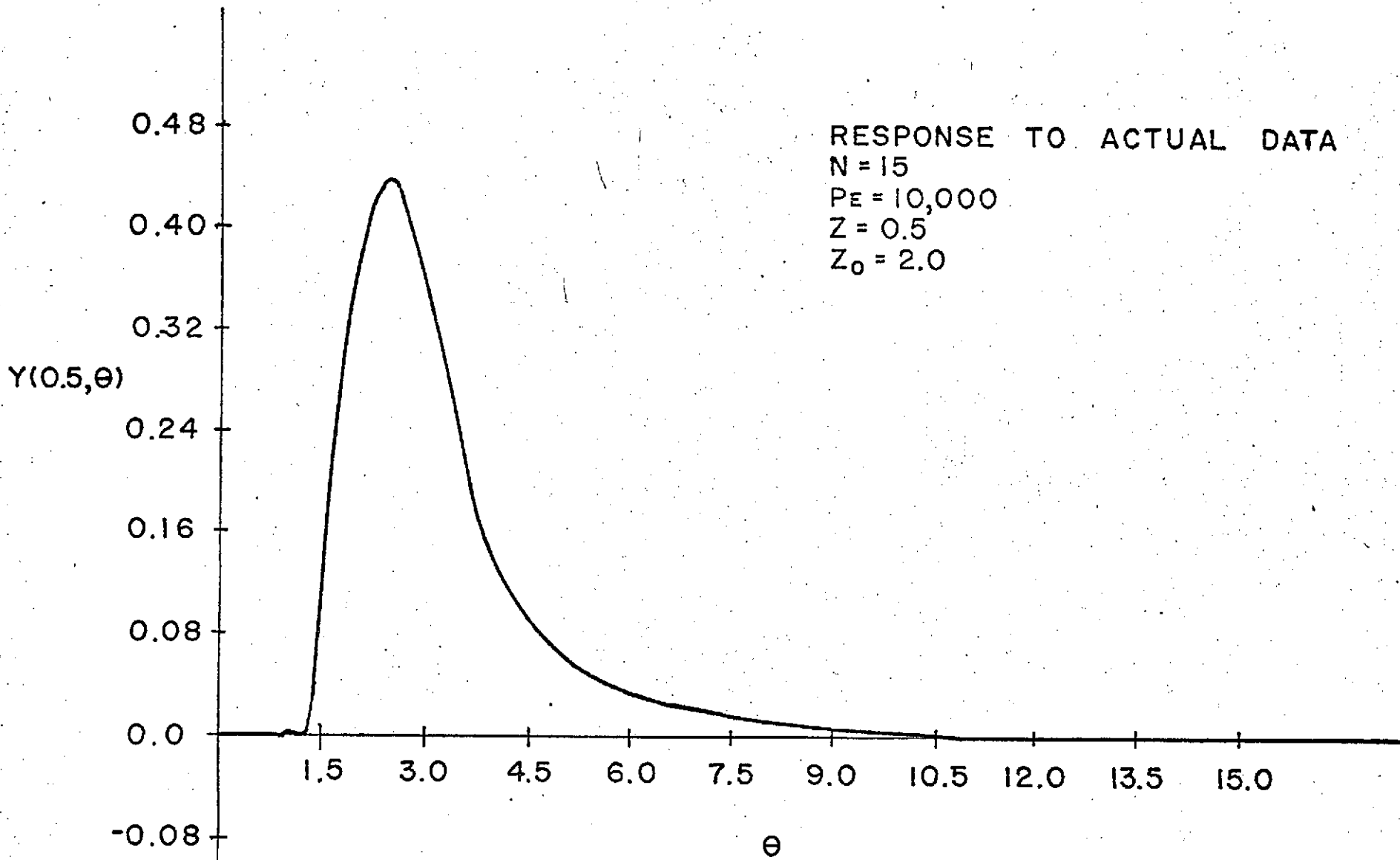


FIGURE 18

stability as compared to a finite difference discretization.

2. High values of Peclet number combined with very sharp forcing functions; i.e., rectangular pulses, require a degree of approximation which may become limited by computing capabilities.

3. The use of smoother pulses in the cases of high Peclet number allows a very good result for  $N=15$  and a very reasonable result for  $N=7$ .

## PART 7

### APPLICATION OF ORTHOGONAL COLLOCATION TO A RATE OF ADSORPTION LIMITED INTER-INTRAPARTICLE MODEL

Subsequent to the studies of the previous section, attention was directed to applying orthogonal collocation to a model which was more complex and which might be used, under certain conditions, as a viable model for a chromatographic system with porous packing material. If one considers the inter-intraparticle model represented by equations (2), (3), (4), and (5) and considers the case where  $N_{tOG} \rightarrow \infty$  and  $Pe_A \rightarrow 0$ , the following model may be deduced (see Appendix A);

$$(1/Pe_E)\partial^2 y/\partial z^2 - \partial y/\partial z - N_{RU}(y-y^*) = \partial y/\partial \theta \quad (83)$$

$$(1/R_I)\partial x_a/\partial \theta = N_{RU}(y-y^*) \quad (84)$$

$$y^* = m x_a \quad (85)$$

For analytic solutions, the applicable initial and boundary conditions are:

$$y(z,0) = 0; z > 0 \quad (86)$$

$$x_a(z,0) = 0; z > 0 \quad (87)$$

$$y(0,\theta) = c(\theta); \theta \geq 0 \quad (88)$$

$$\lim_{z \rightarrow \infty} y(z,\theta) = \text{finite}; \theta > 0 \quad (89)$$

Equations (83) through (89) form what is termed the Rate of Adsorption Limited Inter-Intraparticle Model. For purposes



of numerical solution, the terminal boundary condition, equation (89), is replaced by the finite terminal boundary condition previously applied. And the forcing function,  $\delta(\theta)$ , is replaced by a finite width pulse,  $\phi(\theta)$ .

This model is mathematically equivalent to an inter-particle with finite rates of mass transfer which was previously considered (Keba and Woodrow, 1972). By analogy, the Laplace transform of the time domain response is (column outlet):

$$y(1,s) = y(0,s) \exp \left[ (Pe_E/2) - \arg \right]$$

where

$$\arg = \frac{\sqrt{Pe_E \left[ (s + N_{RU} m_{R_I}) - N_{RU}^2 m_{R_I} / (s + N_{RU} m_{R_I}) + Pe_E/4 \right] + N_{RU} (1 - m_{R_I})}}{1}$$

From equation (88),  $y(0,s) = 1$ . Substitution and inversion gives the init impulse response for the model.

$$y(1,\theta) = c (y_1 + y_2)$$

where:

$$c = \left(\frac{1}{2}\right) \sqrt{(Pe_E/\pi)} \cdot \exp(Pe_E/2) \cdot \exp(-N_{RU} m_{R_I} \theta)$$

$$y_1 = (1/\sqrt{\theta^3}) \exp \left[ -(Pe_E/4\theta) - (Pe_E\theta/4) - N_{RU}\theta + N_{RU} m_{R_I} \right]$$

$$y_2 = 2 N_{RU}^2 m_{R_I} \int_0^\theta \frac{I_1 \left[ 2 \sqrt{N_{RU}^2 m_{R_I} (\theta-x)x} \right]}{\left[ 2 \sqrt{N_{RU}^2 m_{R_I} (\theta-x)x} \right]} \cdot \frac{1}{\sqrt{x}} \cdot \exp \left[ -\left( (Pe_E/4x) + (Pe_E x/4) + N_{RU} (1 - m_{R_I}) x \right) \right] \cdot dx$$

For inputs other than the unit impulse, numerical convolution is used to generate solutions. Using the techniques documented previously (Keba and Woodrow, 1972), a solution may be computed directly. The exact solution which is subsequently presented was computed using this previously documented technique.

This model has two parameters,  $mR_I$  and  $N_{RU}$ , which are not estimable a priori and require determination via an appropriate curve fitting technique. In the example that follows, the parameter  $mR_I$  is taken to be the same (numerically) as the  $mR_0$  value determined previously (Keba and Woodrow, 1972). The parameter,  $N_{RU}$ , is estimated by matching (graphically) the variances of the actual output data with that which is predicted by the model added to the input data variance (see equation (20)). The data set that is to be considered in this section is that for Acetone at 100 C. taken on the Chromasorb 102 column (Keba and Woodrow, 1972). The parameter  $mR_I$  is taken to be 0.029 and the parameter  $N_{RU}$  is estimated to be 87.0. Figure 19 shows how  $N_{RU}$  was determined and for comparison shows an equivalent relationship for the model developed in Part 2. The plot shows that the neglecting of the diffusion (intraparticle) and mass transfer effects requires a smaller  $N_{RU}$  to give the same predicted output variance. Hence, the diffusive and mass transfer effects (primarily diffusive due to the high  $N_{tOG}$  value) are being "lumped" into the rate of adsorption parameter,  $N_{RU}$ . Other parameter values are the same as indicated in Table 1. Figure 20 shows a plot

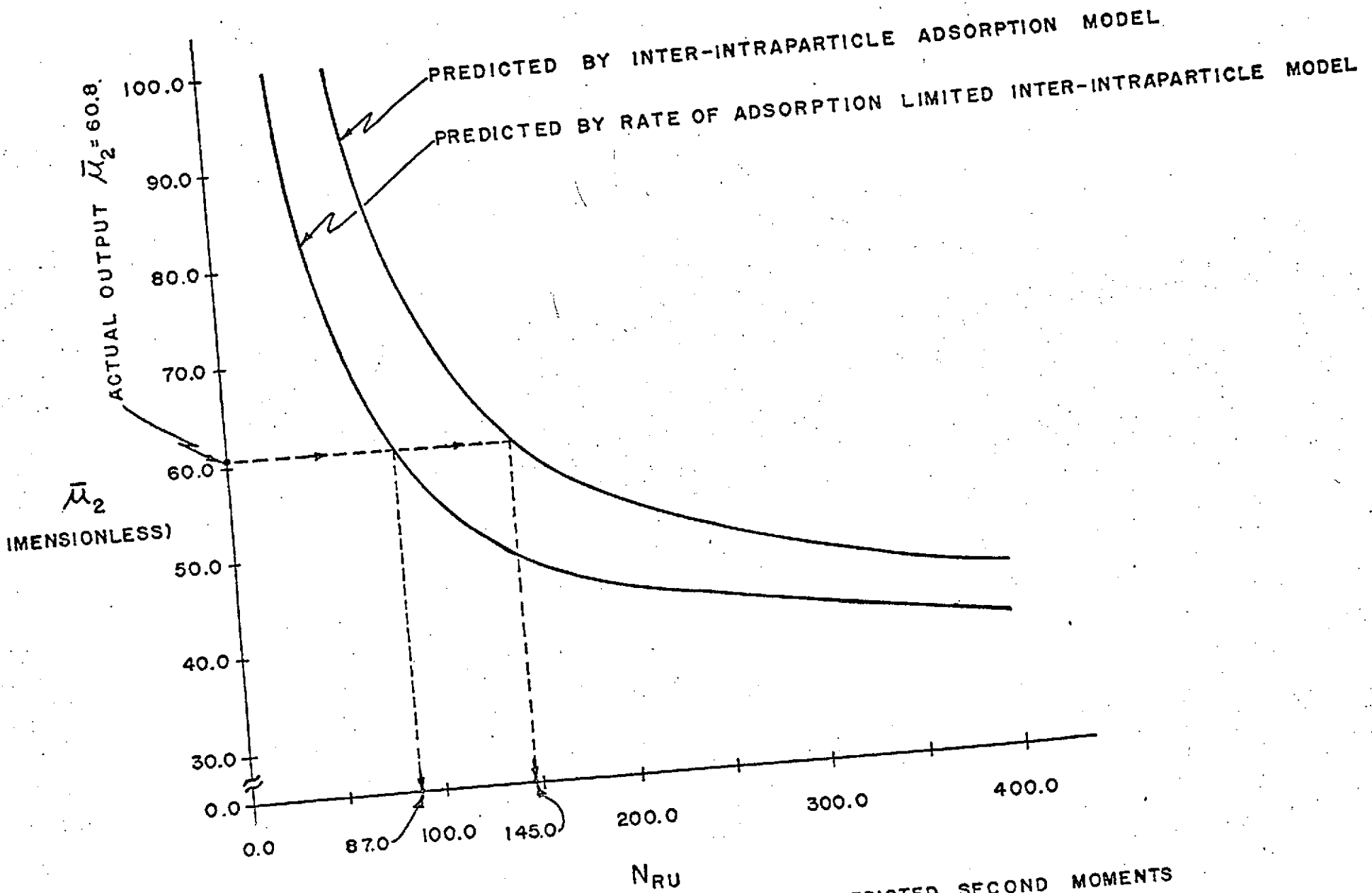


FIGURE 19 ESTIMATION OF  $N_{RU}$  USING PREDICTED SECOND MOMENTS

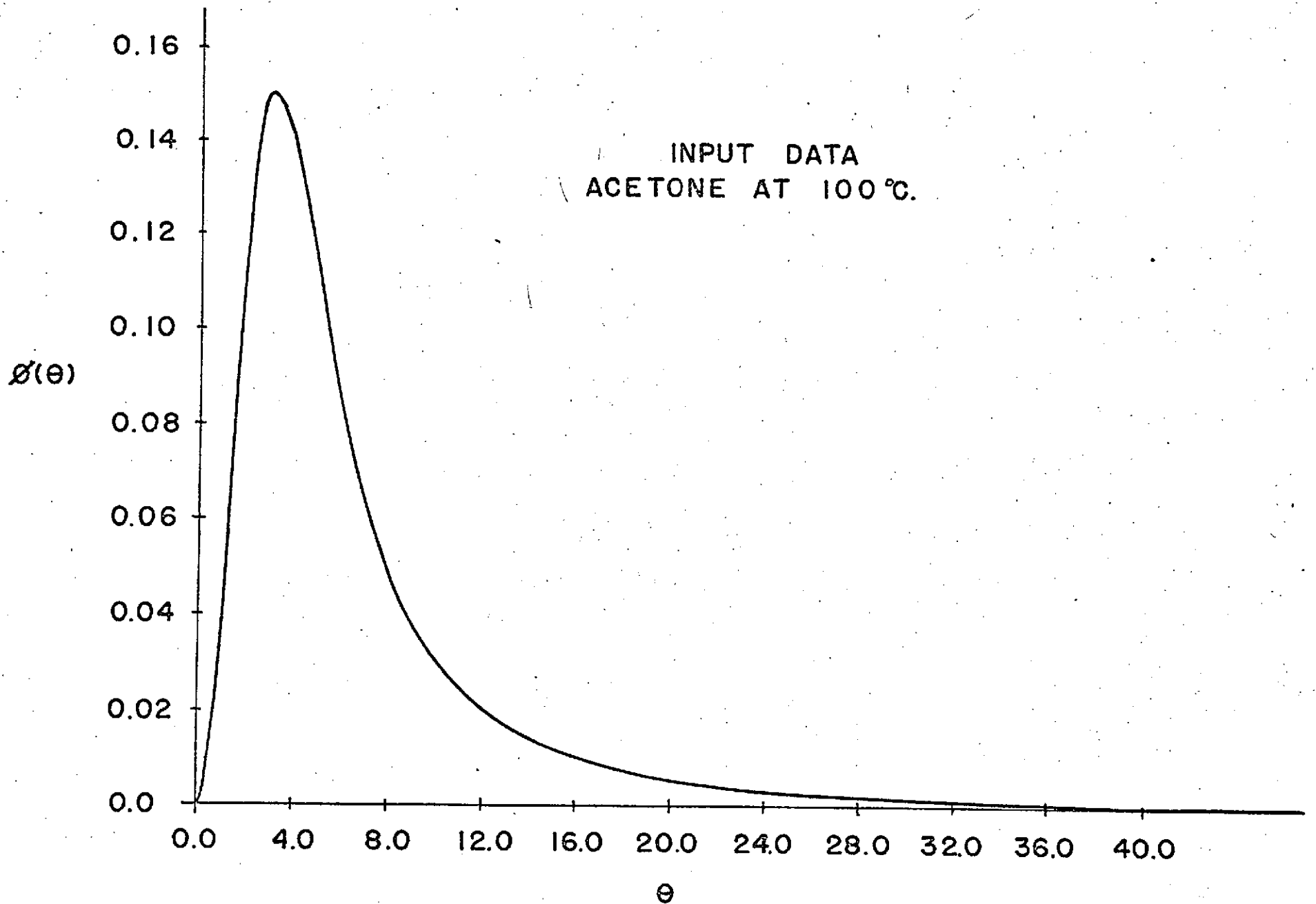


FIGURE 20

of the dimensionless time normalized input data. Figure 21 shows the exact response for this problem and the given parameters computed using the analytic impulse response and numerical convolution.

Application of orthogonal collocation to this model results in a set of  $2N$  ordinary differential equations, where  $N$  is again the number of collocation points. Appendix I gives the details of the orthogonal collocation approximation treatment of equations (83), (84), and (85). The model is reduced to the following set of  $2N$  ordinary differential equations:

$$\underline{y} = \underline{W1} \underline{y} + \underline{W2} \underline{y}^* - \underline{W1} \phi(0) ; \underline{y}(0) = \underline{0} \quad (90)$$

$$\underline{y}^* = \underline{W3} (\underline{y} - \underline{y}^*) ; \underline{y}^*(0) = \underline{0} \quad (91)$$

where  $\phi(\theta)$  is again the forcing function and  $\underline{y}$  and  $\underline{y}^*$  are the  $(N \times 1)$  vectors of the compositions and equilibrium compositions at the  $N$  collocation points, respectively. The matrices in equations (90) and (91) are fully defined in Appendix I.

Several simulations using this orthogonal collocation approximation have been made. Table 8 gives a summary of these computations. The entries in this table are not in strict chronology. The following paragraphs fully present these results and document the chronological details. In all cases, the system of ordinary differential equations was integrated by using the previously referenced IMSL library subroutine, DREBS. However, all simulations were made in single

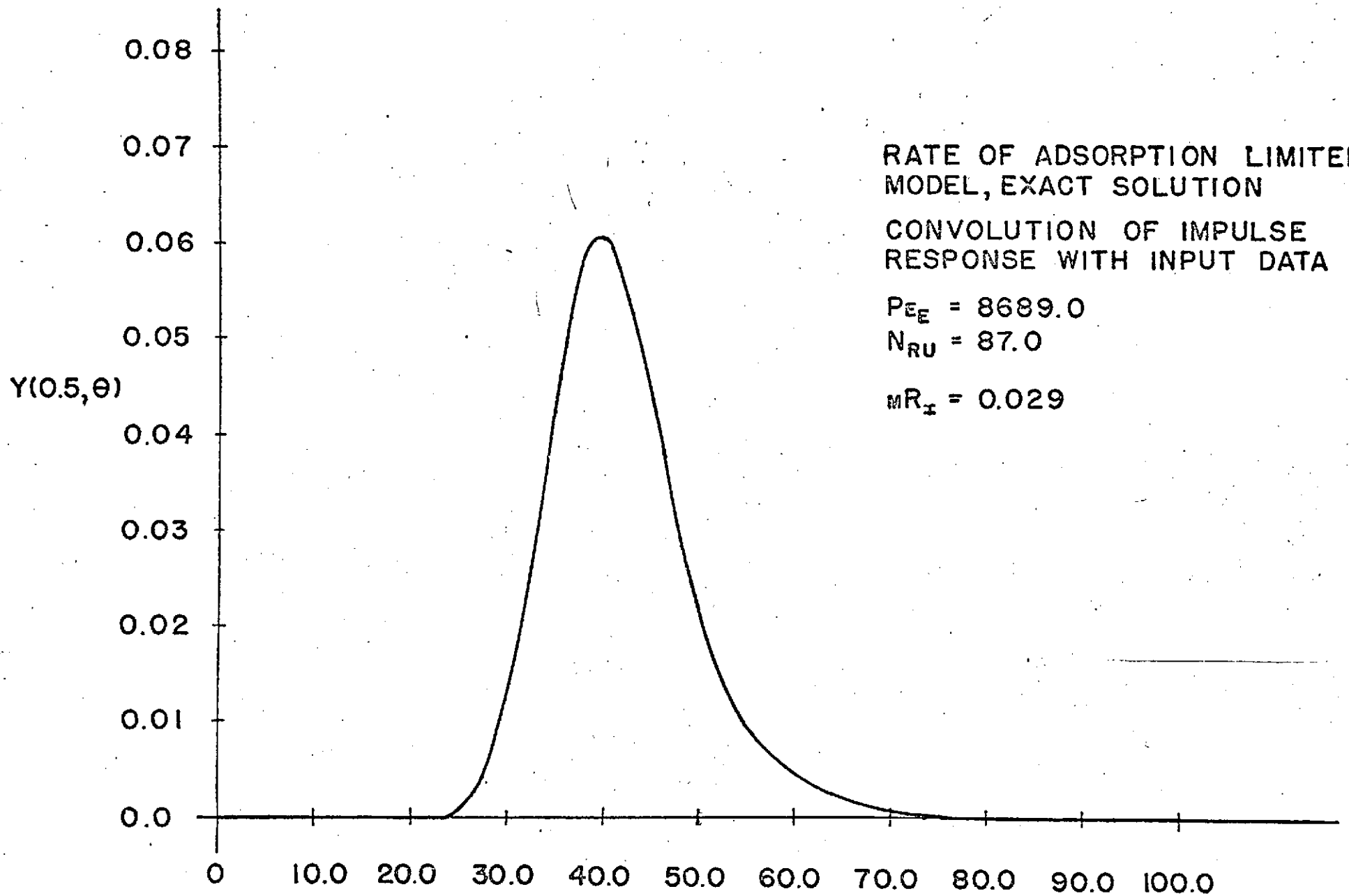


FIGURE 21

TABLE 8

Summary of Orthogonal Collocation Simulation  
Times for the Rate of Adsorption Limited,  
Inter-Intraparticle Model

<u>COMPUTER</u>	<u>N = 3</u> (Figure 22)	<u>N = 7</u> (Figure 23)	<u>N = 15</u> (Figure 24)	<u>N = 21</u> (Figure 25)
IBM 360/50 <sup>1</sup>	-----	25.05 min.	110.22 min.	390. min. (estimated)
IBM 360/50 <sup>2</sup>	6.49 min.	23.53 min.	-----	350. min. (estimated)
CDC 7600 <sup>3</sup>	-----	0.316 min.	-----	2.87 min.

All execution times are for single precision integration up to 90 units of dimensionless time.

<sup>1</sup>FØRTRAN H, output at every integration step.

<sup>2</sup>FØRTRAN H, output at approximately every 0.25 units of dimensionless time.

<sup>3</sup>Output at approximately every 0.25 units of dimensionless time.

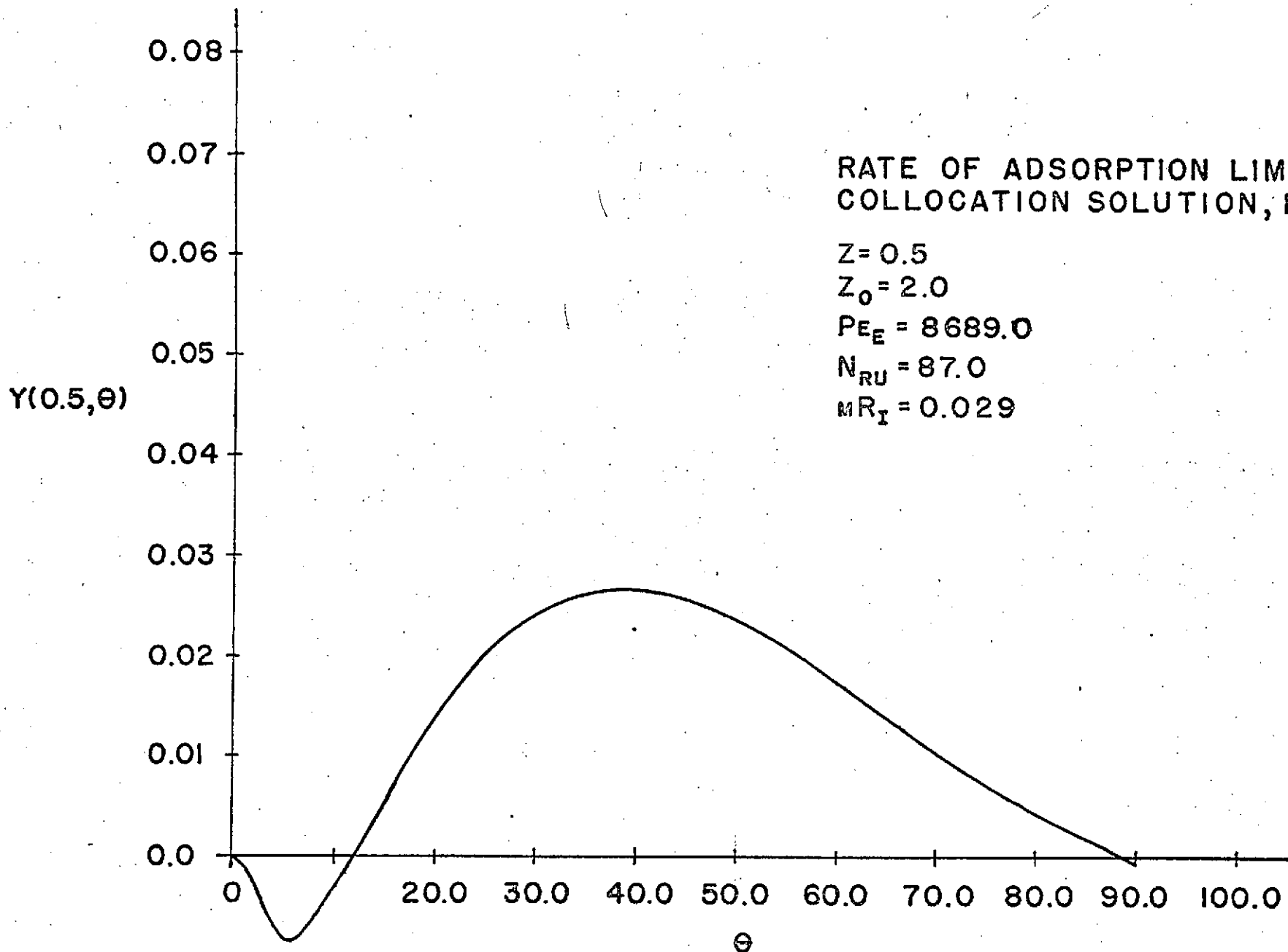
precision while some matrix addition and subtractions were made in double precision. A listing of the program used for these computations is given in Appendix I. As noted in Table 8, some responses were computed on the IBM 360/50 computing facility at RPI whereas others were made at the CDC 7600 computing facility at Combustion Engineering, Inc., Windsor, Connecticut. As in Part 6, the spatial dimension was rescaled. The plotted results are for the collocation point  $z=0.5$ , with  $z_0=2.0$ . Again this corresponds to the bed outlet.

Figure 22 shows the simulated response for  $N=3$ . This approximation is extremely qualitative as compared to the exact solution. The only correct prediction is that of the time of appearance for the peak of the response.

The result of the simulated response for  $N=7$  is given in Figure 23. The plot shows several large amplitude oscillations and a peak height which is approximately 20 percent lower than the exact response. However, as compared to the  $N=3$  case, the improvement is substantial. As far as computer time, the use of approximately 25 minutes on the IBM 360/50 was not too acceptable. This run formed a basis for a later comparative run on the CDC 7600. As table 8 shows, the gain in execution speed with the CDC machine for  $N=7$  is approximately 75 times.

The result of the simulated response for  $N=15$  is given in Figure 24. The plot shows an increasingly good





RATE OF ADSORPTION LIMITED MODEL  
COLLOCATION SOLUTION,  $N=3$

$Z = 0.5$

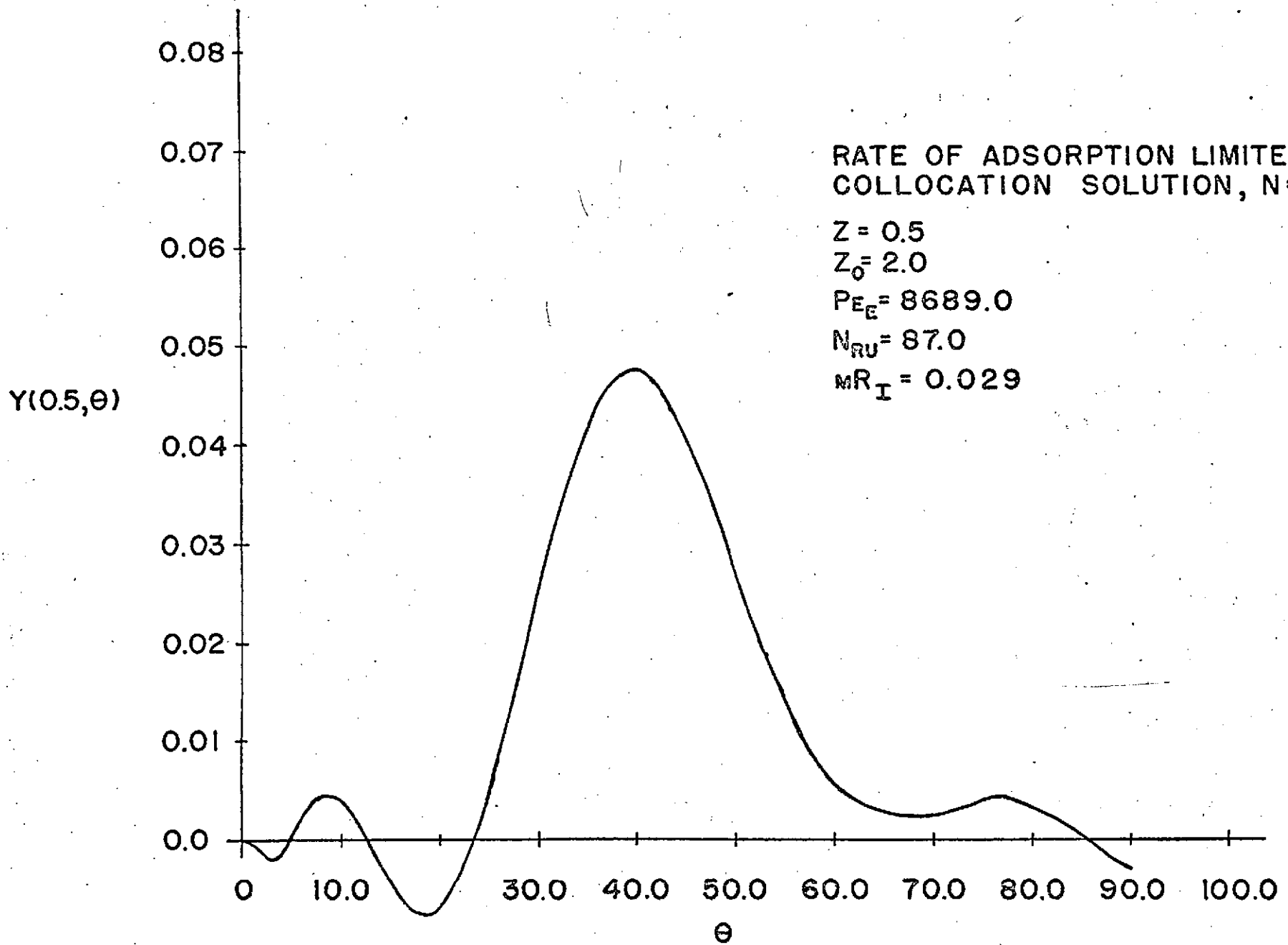
$Z_0 = 2.0$

$PE_E = 8689.0$

$N_{RU} = 87.0$

$MR_I = 0.029$

$\theta$   
FIGURE 22



RATE OF ADSORPTION LIMITED MODEL  
COLLOCATION SOLUTION, N=7

Z = 0.5

Z<sub>0</sub> = 2.0

P<sub>E<sub>E</sub></sub> = 8689.0

N<sub>RU</sub> = 87.0

mR<sub>I</sub> = 0.029

FIGURE 23

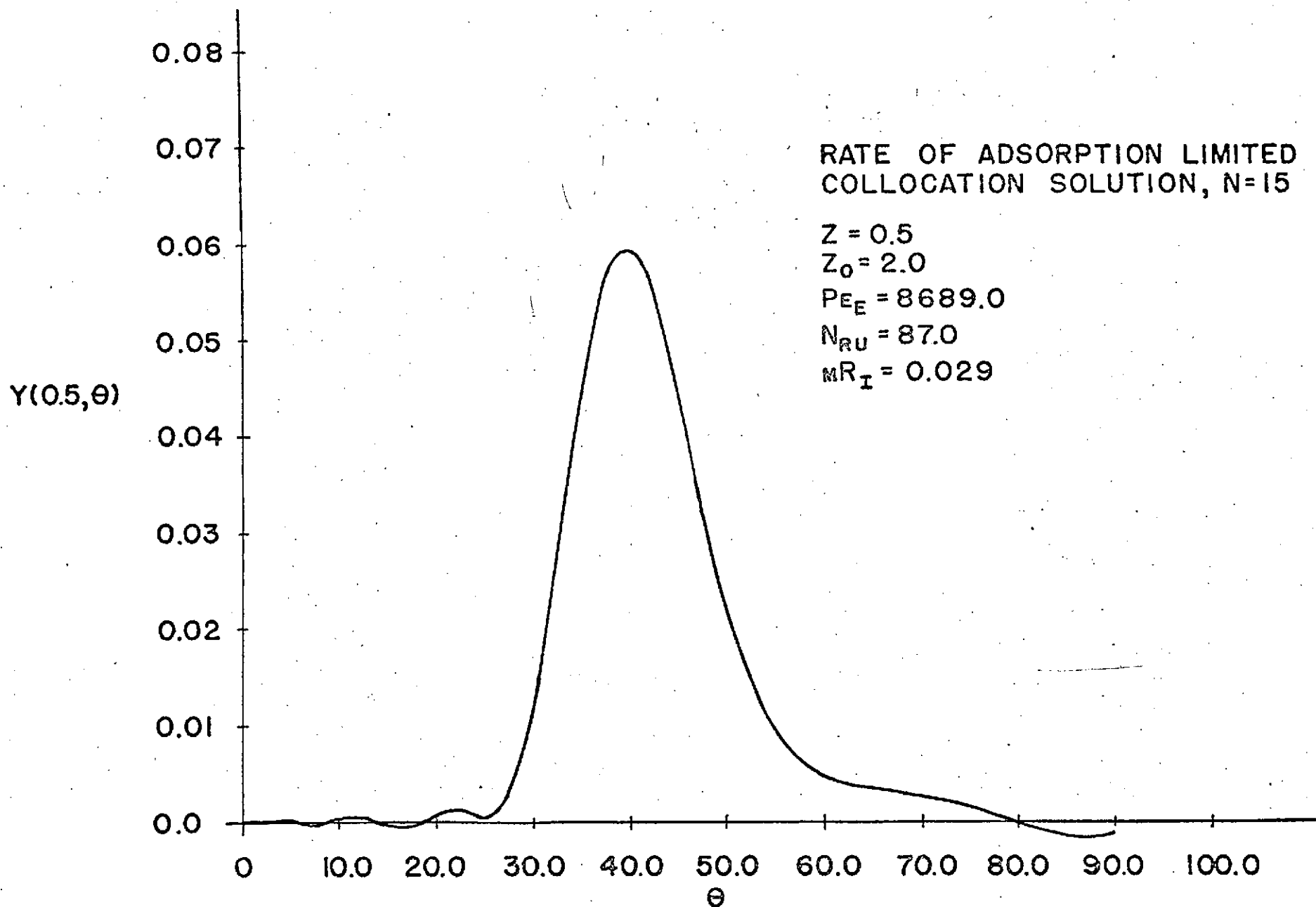


FIGURE 24

agreement with the exact response. The oscillations are still present but of much reduced amplitude. The peak height is slightly smaller than the exact height. However, the behavior of the response for  $\theta < 25$  and  $\theta > 60$  should be improved. This result indicated that a run with an additional number of collocation points was desirable. However, the large amount of computer time expended for the  $N=15$  simulation, 110 minutes, was a debit on the side of further simulation. A small time run (10 minutes of computer time) for the  $N=21$  case on the IBM 360/50 gave an extrapolated complete run time (integrating up to 90 units of dimensionless time) of approximately 390 minutes. This small time run indicated that the higher order approximation was decreasing the amplitude and frequency of initial oscillations as compared to the  $N=15$  run. However, the time required to perform the complete calculations was too long (cost and scheduling) to obtain results on the IBM 360/50.

At this point in time, effort was directed to obtaining access to a computer more suited to the type of computations being made. Arrangements were made to remotely access the CDC 7600 computer at Combustion Engineering in Windsor, Connecticut. This machine's capabilities yielded a radical improvement in expended computer time. The case of  $N=21$  was run using this machine. As Table 8 shows the run time to be approximately 122 times faster than the estimated run time for the reduced output case. Figure 25 shows the

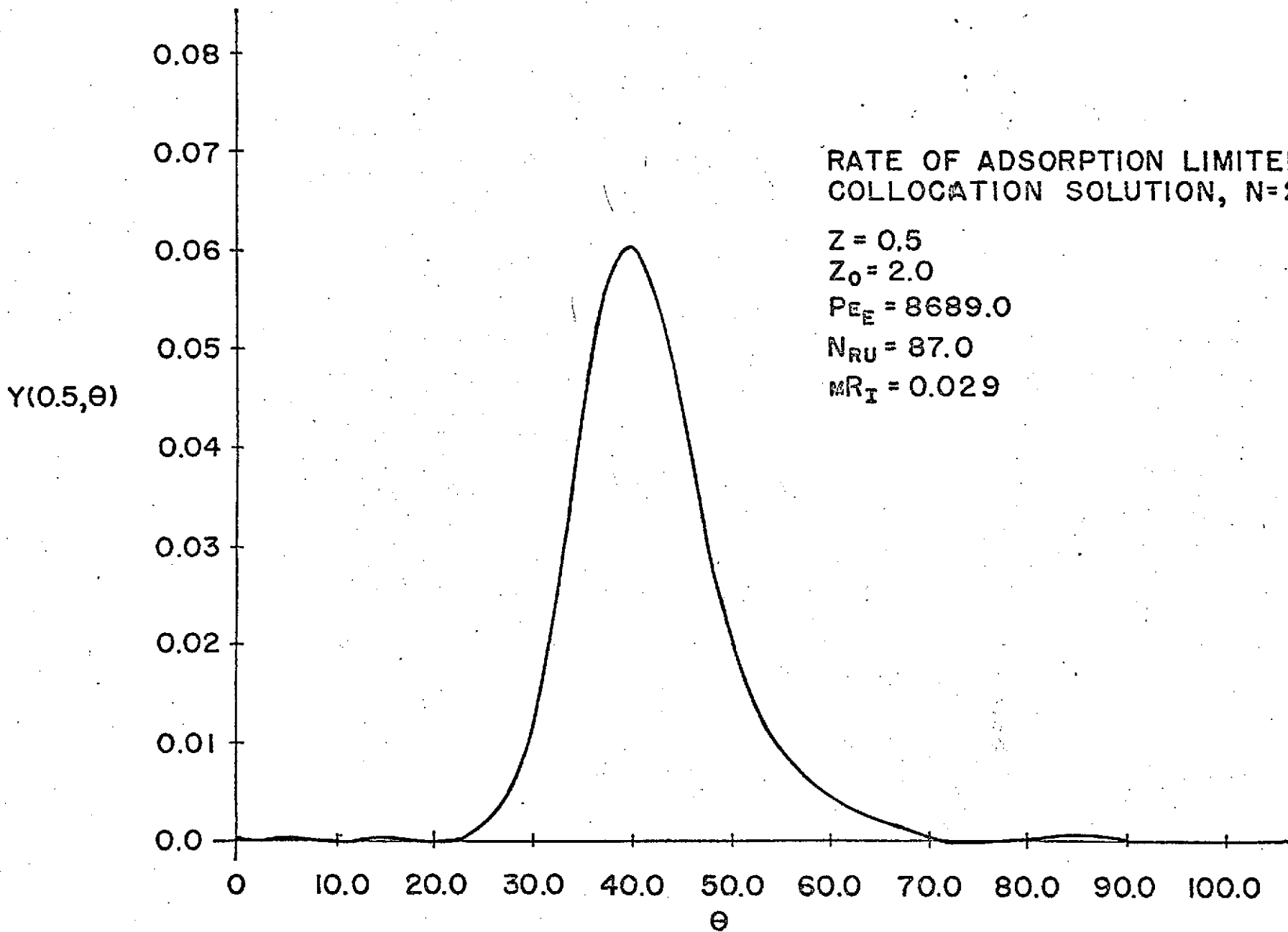


FIGURE 25

results for  $N=21$ . The results, when superimposed on the exact response, give virtual exact agreement. The only identifiable discrepancies are the oscillations for  $\theta < 20$  and  $\theta > 70$ . The largest magnitude of the noted oscillations is quite small,  $0.08 \times 10^{-2}$ .

Thus, it appears that for accurate approximation solutions for this problem, a fairly high degree of orthogonal collocation discretization in the spatial domain is required. Also, it is apparent that available computer hardware must be a very sizable consideration for extensive simulations.

As a postscript to this part, it should be noted that going from the IBM 360/50 to the CDC 7600 required some alterations in the IMSL subroutine DREBS, as the IMSL - CDC package was not available at the Combustion Engineering CDC 7600. One of the changes involved a machine-precision dependent constant. Fortunately, a CDC listing of DREBS was obtained indirectly from IMSL (Larsen, 1974).

## PART 8

### APPLICATION OF ORTHOGONAL COLLOCATION TO AN INTER-INTRAPARTICLE ADSORPTION MODEL WITH NEGLIGIBLE MASS TRANSFER RESISTANCE

Orthogonal collocation approximations for the solutions of the previous two models have used discretizations in the interparticle region or axial dimension. When the model is one where concentration gradients are assumed to exist within the intraparticle region, an approximation treatment for the intraparticle domain is necessary. If one considers the inter-intraparticle model represented by equations (2), (3), (4), and (5), and considers the case where  $N_{tOG}$  the following model may be deduced (see Appendix A):

$$(1/Pe_E)\delta^2 y/\delta z^2 - \delta y/\delta z - [(3(1-\epsilon)\beta/\epsilon)(L/R)^2/Pe_A](\delta y_1/\delta r)_{r=1} = \delta y/\delta \theta \quad (92)$$

$$(L/R)^2/Pe_A[\delta^2 y_1/\delta r^2 + (2/r)\delta y_1/\delta r] - N_{RU}(y_1 - y_1^*) = \delta y_1/\delta \theta \quad \dots(93)$$

$$(1/R_I)\delta x_a/\delta \theta = N_{RU}(y_1 - y_1^*) \quad (94)$$

$$y_1^* = m x_a \quad (95)$$

This model is one of the most complicated forms that one might encounter in isothermal, packed bed analysis. The initial and boundary conditions are the same as equations (6) through (12) with equation (13) replacing (10) as the appropriate inter-intraparticle boundary condition. This

modification in the original model gives the inter-intraparticle adsorption model negligible mass transfer resistance between the interparticle and intraparticle regions. For purposes of numerical treatment, the terminal boundary condition, equation (12), is replaced by the finite boundary condition previously applied. The forcing function,  $\delta(\theta)$ , is replaced by a finite width pulse,  $\phi(\theta)$ .

This model introduces the necessity to perform a collocation approximation in the radial (intraparticle) dimension,  $r$ , in addition to the axial (interparticle) dimension,  $z$ . For purposes of such a treatment, the trial function used by others (Finlayson, 1972, p.99) in the analysis of unsteady diffusion in a sphere, is equation (70):

$$y_1(r, \theta) = h(\theta) + (1-r^2) \sum_{i=1}^{N_A} a_i(\theta) P_{i-1}(r^2)$$

where  $N_A$  is the number of intraparticle collocation points. When used in combination with an axial treatment, the axial position,  $z$ , should be included to give:

$$y_1(z, r, \theta) = h(z, \theta) + (1-r^2) \sum_{i=1}^{N_A} a_i(z, \theta) P_{i-1}(r^2) \quad (96)$$

The polynomials in  $r^2$  in equation (96) can be defined by a condition similar to equation (45) by making the change in variable  $r^2=z$  and  $2rdr=dz$ . The result is:

$$\int_a^b w(r^2) P_i(r^2) P_j(r^2) r dr = (C_i/2) \delta_{ij} \quad (97)$$



In general,  $w(z)$  in equation (45) is of the form:

$$w(z) = z^\alpha(1-z)^\beta$$

Substituting this and the above change of variable into equation (97) gives:

$$\int_a^b r^{2\alpha+1}(1-r^2)^\beta P_i(r^2)P_j(r^2)dr = (C_1/2)\delta_{ij} \quad (98)$$

The form given by Villadsen (1970). The formulas used from that text for recursive computation of the respective polynomial coefficients defined by equation (45) may be modified, as Villadsen shows, to give formulas for recursive computation of the coefficients for the polynomials in the squared dimension defined by equation (98). In the analysis that follows, the polynomials used are those defined by equation (98) with  $a=0$ ,  $b=1$ ,  $\alpha=\frac{1}{2}$ , and  $\beta=1$ . This is the case for spherical symmetry. The coefficients are computed using the recursive formulas due to Villadsen and the roots are taken from the values reported by Finlayson (1972, p. 102).

Solution of this three, coupled partial differential equation problem requires orthogonal collocation approximations in two different spatial domains. The problem is one with three independent variables,  $z$ ,  $r$ , and  $\theta$ ; and three dependent variables  $y$ ,  $y_1$ , and  $y_1^*$  (or  $x_a$ ). A solution to this type of problem appears not to have been attempted using the orthogonal collocation technique. To aid in envisioning the two-domain discretization required in the analysis of this problem,

Figure 26 gives a representation of the orthogonal collocation "grid". Here the collocation points are denoted by  $N_E$  for the interparticle domain and  $N_A$  for the intraparticle domain, respectively.

Appendix J presents the orthogonal collocation approximation development for the intraparticle region. A computer program listing which was used to generate the first and second derivative intraparticle approximation matrices also appears in this appendix. Appendix K develops expressions for simulating transient diffusion and adsorption/desorption behavior within a single particle. Appendix L combines these results with the appropriate interparticle results to give the full representation of the orthogonal collocation approximation for the model considered in this part. The result is a system of  $(N_E + 2(N_E)(N_A))$  coupled, ordinary differential equations:

$$\begin{matrix} (N_E \times 1) \\ \text{vector} \end{matrix} \quad \dot{\underline{y}} = \underline{W} (\underline{y} - \underline{1}\phi(\theta)) - \underline{\text{COUPLE}} \quad (99)$$

and for  $j=1, \dots, N_E$

$$\begin{matrix} (N_A \times 1) \\ \text{vector} \end{matrix} \quad \dot{\underline{y}}_{1,j} = \underline{\text{INTRA}} \underline{y}_{1,j} - \underline{\text{INTRAC}} (\underline{1} y(z_j, \theta)) \\ + \underline{\text{INTRAA}} \underline{y}_{1,j}^* \quad (100)$$

$$\begin{matrix} (N_A \times 1) \\ \text{vector} \end{matrix} \quad \dot{\underline{y}}_{1,j}^* = \underline{\text{INTRAE}} (\underline{y}_{1,j} - \underline{y}_{1,j}^*) \quad (101)$$

The strategy for determining what degree of approximation is adequate for accurate model solution is different than what was previously used; i.e., comparison of approximate

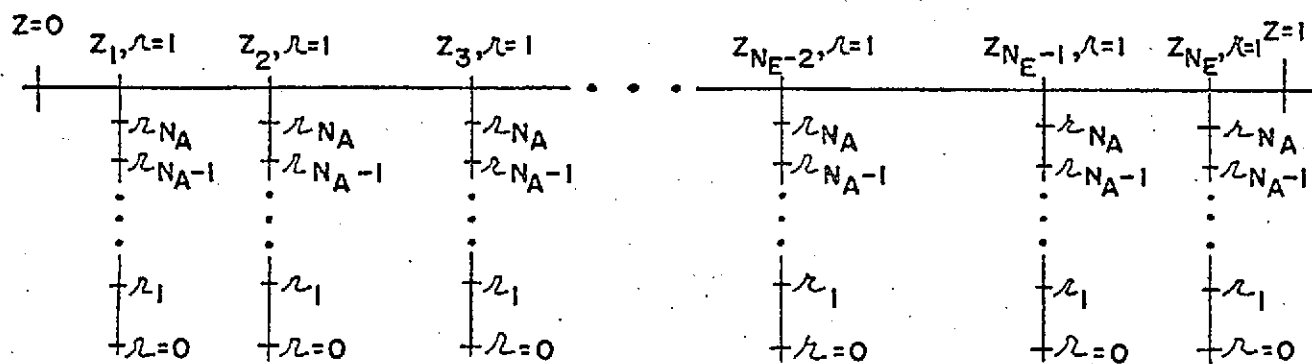


FIGURE 26 ORTHOGONAL COLLOCATION DISCRETIZATION FOR THE INTER-INTRAPARTICLE DOMAIN

solutions to the exact solution. Here, successive approximations must be compared to see if a convergent trend is noted. The appropriate order of approximation is then determined when increasing order gives no noticeable change in simulated response. This was the strategy which was to be used for analysis of this problem. However, as will be shown, completion of this strategy was not feasible.

The data set that is to be used in this section is the same that was used in the previous part for the rate of adsorption limited model. The differences are in the two choices of parameters  $mR_I$  and  $N_{RU}$ . The parameter  $mR_I$  was chosen to be based on an  $mR_0$  of 0.029, a bed void fraction,  $\epsilon$ , of 0.40 and a particle void fraction,  $\beta$ , of 0.40. Using equation (1), this would give the value of  $mR_I$  to be 0.0174. The value of  $N_{RU}$  was estimated from Figure 19 to be 145.0 from the model curve with a finite  $N_{tOG}$ . However, because of the high  $N_{tOG}$  in this data set, its contribution to the model variance is quite negligible and hence this value of  $N_{RU}$  is appropriate for the case of  $N_{tOG} \rightarrow \infty$ .

Table 9 presents a summary of what combination of interparticle and intraparticle approximations were slated for simulation. With access to the CDC 7600, it was decided to run small-time (10 minutes of computer time) simulations on the IBM 360/50 to gain an estimate of the computer time necessary to complete the planned analysis. A listing of the program used for this purpose is given in Appendix L. Again

TABLE 9

Inter-Intraparticle Model Orthogonal Collocation  
Approximations - Computer Time Estimates

$N_E$	$N_A$	$N$	Estimated Execution Time (min.)*
3	1	9	630.0
3	3	21	22500.0
7	1	21	1442.0
7	3	49	90000.0
15	1	45	3750.0

$$N = N_E(1 + 2N_A)$$

\* IBM 360/50, FORTRAN H, integration (single precision)  
up to 90 units of dimensionless time with output at  
approximately every 0.01 time units.

the IMSL subroutine DREBS was used to perform the integration of the system of ordinary differential equations for this problem. The time estimates in Table 9 are overwhelming even if one decreases them by the gain in speed (on the order of one hundred times) with the CDC 7600. Within the imposed financial constraints and justifications needed to motivate such an expenditure, the complete analysis of this problem was not feasible. One could have possibly improved the situation by choosing "nice" parameter values but this would have negated the objective to study a technique with real-life problem conditions.

The question arises then as to what information can be gained from this part of this investigation. First of all, it must be said that based on the computer hardware available and the technique used, the straightforward analysis of this complex problem using orthogonal collocation is not very expedient. The pulsed, distributed system with multi-coupled transport phenomena presents a complicated problem for analysis. However, one might conceivably apply successfully the two domain collocation approximation treatment for steady state or step response simulations for packed bed systems, either isothermal or non-isothermal. In addition, this analysis was based on two specific polynomial sets each orthogonal over one spatial domain interval. It could be argued that perhaps polynomials orthogonal to two domains simultaneously; i.e., a surface, would be more appropriate for this type of problem.

Although the results of this section are in the negative side, they should not be construed as a condemnation of orthogonal collocation as a technique but rather as an example where a method may not be as well suited as others and where some innovations in the theory could possibly result in a treatment that may be practical within the computational capabilities that now exist.

## PART 9

### DISCUSSION

The initial part of this investigation was motivated by previous efforts in the area of mathematical modeling of a gas chromatograph. This investigation set out to derive and study a model which incorporated more of the dynamically relevant transport phenomena thought to be occurring in the experimental systems being studied by Mars project co-workers. Hence, a model has been proposed and derived which includes both interparticle and intraparticle transport phenomena.

As with previous models, it was desirable to determine whether or not this model could be used to adequately predict chromatograph system responses. Application of Laplace transform techniques gave a transform which was not readily invertible. However, because the model was linear and transformable, the derived transform could be used to determine the predictive capabilities of the model in the time domain. Here, the techniques of moment analysis were applied and it was shown that the model possessed a high degree of flexibility in predictive capabilities using the statistical quantities known as moments which can characterize the responses of pulsed, distributed systems. This method of analysis is very useful because the effect of varying system parameters present in the model can be studied very efficiently and a great deal of insight into the model characteristics can be gained, as



was the case in this investigation. In fact, the results of the moment analysis gave sufficient motivation for the continued analysis of the complex inter-intraparticle adsorption model.

Because the derived model appeared to have no direct analytical solution, it was necessary to develop numerical capabilities in order to efficiently simulate the time domain response of the model and hence verify the model's predictive effectiveness. However, prior to the investigation of numerical techniques, some study was given to the problem of replacing the infinite column boundary condition used in analytical work with a finite column terminal boundary condition used in analysis of chemical reactor problems and which was necessary for numerical treatment of the model partial differential equations. It was desirable to apply the finite column boundary condition so that infinite column behavior would result at the bed outlet. Two simple problems were studied, one with the infinite column condition and the other with the finite column condition. Again, the technique of moment analysis proved a very effective tool in determining how infinite column response characteristics (moments) at the bed outlet might be matched by the problem with a finite terminal boundary condition. For the simple model considered, criteria were developed as a function of the Peclet number which gave guidelines for applying the finite terminal boundary. These gave reasonable assurance that column responses for both the

finite and infinite boundary conditions were essentially the same. These criteria were used, somewhat conservatively, in the numerical solutions which were later made. Although the method of developing the boundary condition criteria was applied to the simple model with one system parameter, the Peclet number, the method of analysis could be extended to more complex linear models and sets of criteria could be developed as functions of the system parameters present in each individual model.

Based on the preceding aspects of this investigation, effort was directed to the study of orthogonal collocation as a numerical approximation technique which would hopefully prove useful as an efficient tool for routine analysis of the complex chromatograph system models. These models might be linear (as was the case in this work) or non-linear partial differential equations. The study of non-linear composition effects is an area of interest for continued chromatograph modeling effort. In this investigation, orthogonal collocation was applied to approximate solutions to three linear, distributed model of increasing complexity. The first model was a simple, one equation model requiring a collocation treatment in one spatial domain, the interparticle. The second model involved solution of two coupled partial differential equations requiring a collocation treatment in the interparticle domain. The third model involved solution of three coupled partial differential equations requiring

collocation treatments in two spatial domains, the interparticle and intraparticle.

The procedure for attacking these mathematical problems is summarized in Figure 27. This schematic provides a unified framework for discussing the general aspects and specific results of this investigation into the use of orthogonal collocation.

The block denoted by STEP 1 serves as a starting point in problem analysis. This block, as indicated by the dashed lines is preliminary in nature and central to any modeling problem. For this investigation, the work of Part 2 could be lumped into this category.

The block denoted by STEP 2 corresponds to that part of an analysis where one has to make a choice of the numerical method (if required) to use in the analysis of the formulated problem(s). The choices could be a finite difference treatment, a finite element treatment, a weighted residual treatment (e.g. orthogonal collocation), or a variational treatment. This choice may be motivated by previous experience, the work of other investigators in solving similar problems, and/or the desire to establish the applicability of a certain method to a certain type of problem. In this investigation, the choice of orthogonal collocation as a method of analysis was motivated by all of the above - the inefficiency of the finite difference technique to the simple, diffusion-convection problem (previous experience), the use of orthogonal

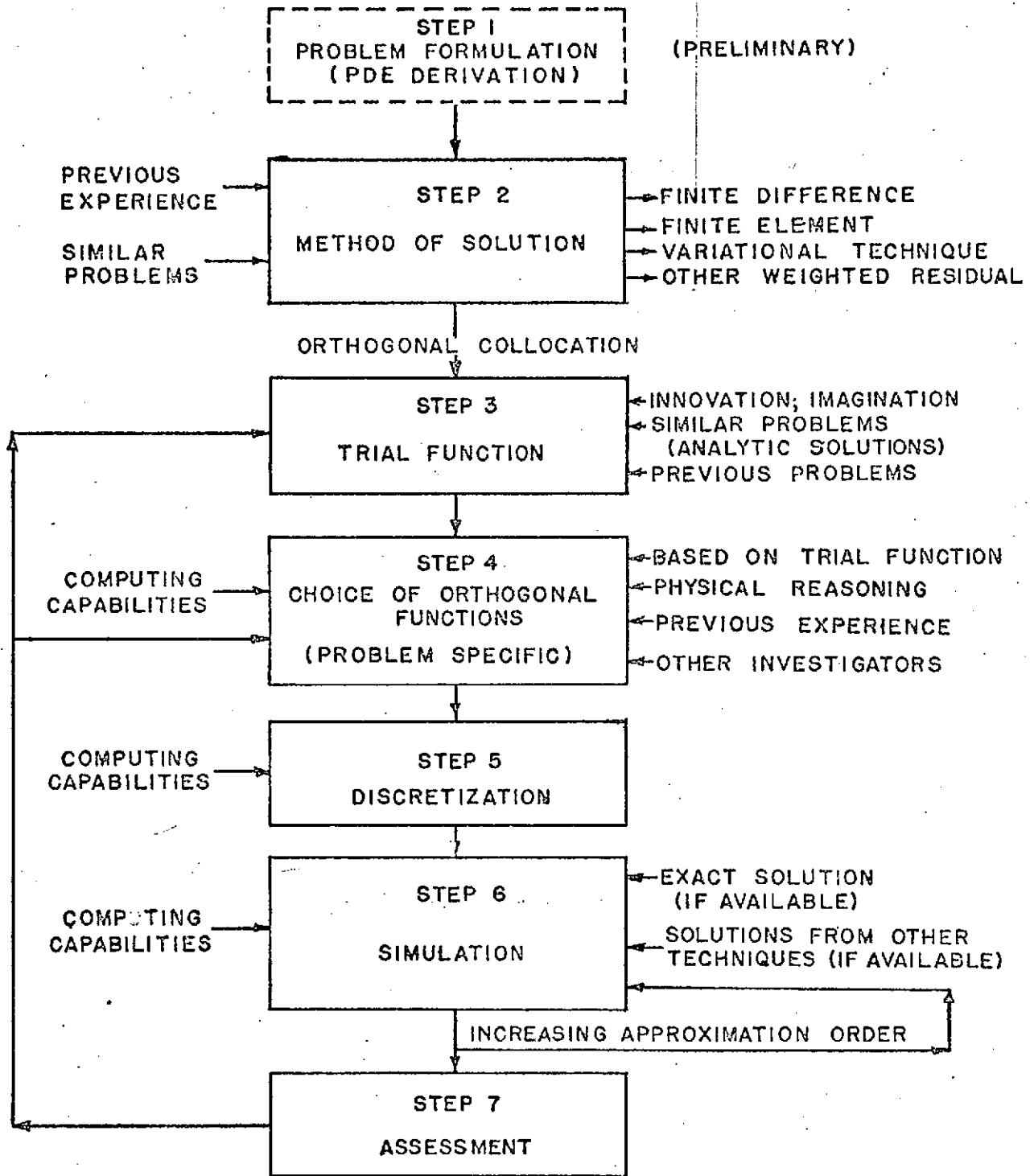


FIGURE 27 PROBLEM ANALYSIS USING ORTHOGONAL COLLOCATION

collocation by other investigators to solve certain problems in chemical reaction engineering, and the desire to ascertain the merits of orthogonal collocation as a computational tool for analysis of pulsed, distributed systems; e.g., the gas chromatograph.

Following the choice of orthogonal collocation as the method for the analysis of the formulated problems, one proceeds to STEP 3, the choice of the trial function. Inputs to this choice may be innovation or imagination, suggestions from similar problems with analytic solutions, or trial functions from previously worked examples. The trial functions used in this investigation were taken from the work of other investigators. However, the trial function for interparticle analysis was generalized to an extent (Appendix G). The generality of this trial function was not explored - thorough exploration of the effects of trial function choice in combination with orthogonal function choice (STEP 4) for even one problem would be a basis for an entire investigation at least.

This brings one to STEP 4, the choice of the orthogonal functions to be used in the trial function expansion. This block in the problem analysis can have the highest degree of variation. The choice can be dictated by the trial function itself, symmetry considerations (the polynomials in for the intraparticle region), the type of solution (perhaps suggested by physical reasoning ), previous experience

(orthogonal polynomials weighted in a certain way gave faster convergence with a previous problem), and the work of other investigators. This investigator chose very specific polynomials for use in the trial functions employed in the problems analysed. The choice was suggested by the works of other investigators and was further dictated by the availability of the required polynomial roots. Use of some less "common" polynomials require determination of roots which may not be tabulated to high accuracy. Thus, one would have to pursue root-finding computations which, based on available computer precision capabilities, may be infeasible. This type of study; i.e., different polynomial types, was a desired component of this investigation but efforts to compute new roots to sixteen figure accuracy were limited by the available IBM 360/50. Thus, this desired area of study was abandoned. In conjunction with this, one should note the added input to the STEP 4 block citing the very practical consideration of computing capabilities - in this instance, word-length capability. Recently, the notion of there being better polynomials for certain problems received attention by Ramkrishna (1973). He showed that the choice of "problem specific polynomials" to be relevant and desirable for effective use of weighted residual techniques.

The block denoted by STEP 5 is labeled DISCRETIZATION. This is descriptive of the manipulations and computations which must be made to reduce the expressions for the partial

derivatives at the collocation points to expressions in terms of the solutions at the respective collocation points. The manipulations of Appendix G and Appendix J are typical of what must be done. A key aspect of these computations is the inversion of a matrix. Part 5 showed how the conditioning of the matrix to be inverted may be enhanced by a change in formulation. One was able to retain a tolerable condition within the constraint of the available computer precision. However, as was pointed out in Part 6, attempts to generate a thirty-first order interparticle discretization were unsuccessful because the word-length of the available IBM 360/50 computer limited the accuracy of the polynomial coefficients.

Next is STEP 6, SIMULATION. This block comprises the use of the previously derived and computed discrete representations to reduce the distributed model to a set of ordinary differential equations. This set of ordinary differential equations can be integrated to yield the approximate response. As was done with the simple model (Part 6), the equations can be put in a suitable form wherein an eigenanalysis of the system can be made to determine the character of the approximation solution. This also served to expose the stiffness of the equation set. The simulated response(s) can be compared with exact solutions (if available), solutions from other techniques (if available), and with simulations using different orders of approximation. As was shown with the rate of adsorption limited inter-intraparticle model, the

available computing capabilities (execution speed) can be a factor in limiting the extent of any planned simulation program. In fact, this constraint (even with the CDC 7600) prohibited complete analysis of the inter-intraparticle adsorption model with negligible mass transfer resistance between the interparticle and intraparticle regions.

STEP 7, ASSESSMENT, serves as an area where one can assess the results and the reasons for the results. Among the questions that must be answered are:

1. Is the problem practically solvable?
2. Does the orthogonal collocation treatment, as applied, have sufficient power to be used as a routine tool in analysis of the posed problem(s)?

Regarding the first two problems solved in this investigation, the answers to the above questions would be affirmative. However, with regard to the third problem, the answers are not affirmative. The key words in the second question are "as applied" because the trial function and/or polynomial type may be unsuited to the problem at hand and may thus require some new innovations in this area. This is the reason for the "feedback" loops from STEP 7 to STEP 3 and to STEP 4.



## PART 10

### CONCLUSIONS

This investigation has been conducted in conjunction with the group effort to define fundamental system design criteria necessary for an optimal design of a combination gas chromatograph - mass spectrometer. Specifically, this investigation has dealt with the formulation of a more complex mathematical model for a gas chromatograph and subsequent efforts to ascertain the merits of the numerical technique known as orthogonal collocation as a technique worthy of routine use in the time domain simulation of complex gas chromatograph models.

Previous work dictated the formulation of a model which took into account more of the dynamically relevant transport mechanisms thought to be occurring in the chromatograph system. A model has been formulated which includes intraparticle diffusion and rates of adsorption that were heretofore neglected. The model has been analysed using the moment analysis technique. This analysis of the proposed Inter-Intraparticle Adsorption Model indicates that the gross characteristics of actual data are more adequately predicted than with previous models.

The mathematical complexity of the proposed Inter-Intraparticle Adsorption Model has prompted consideration of numerical techniques appropriate for the solution of the

partial differential equations being postulated. The use of numerical techniques for the second-order models being considered requires the use of a finite terminal boundary condition. Criteria have been developed for a simple model wherein a finite terminal boundary condition can be applied which yields system responses which are for all intents and purposes equivalent to the responses obtained using an infinite column boundary condition.

The general theory and computational aspects of the method known as orthogonal collocation have been reviewed and discussed. An alternate method of problem formulation gives a matrix (which must be inverted in either formulation) which is significantly better conditioned for inversion purposes. It is concluded that this different approach is better than previously documented approaches when computer word-length capabilities are a consideration as is the case for most practical situations.

The method of orthogonal collocation has been successfully applied to two problems of the chromatograph system type. The first problem was the simple transient diffusion-convection equation and the second was the rate of adsorption limited inter-intraparticle model. These models required orthogonal collocation treatments for one spatial domain, the interparticle. For the system parameters considered it appears that 15 collocation points are adequate for the simple model and 21 collocation points are adequate for the rate of ad-

sorption limited model. However, the latter model required the computing power of a CDC 7600.

The application of orthogonal collocation to an inter-intraparticle adsorption model with negligible mass transfer resistance between the interparticle and intraparticle regions is not, based on the two domain (interparticle and intraparticle) orthogonal collocation treatment, practically feasible even with the computing power of a CDC 7600. It is concluded that although the theory of orthogonal collocation may be viable, there could possibly be significant improvement in practical requirements if modifications in trial function and/or orthogonal function choices can successfully be effected. This conclusion applies, to a lesser degree, to the two other models considered in this investigation.

Thus, it appears that in its present state, orthogonal collocation can be a useful tool for analysis of one spatial domain, pulsed, distributed systems. Use of orthogonal collocation for two-spatial domain, pulsed, distributed systems requires the reversion back to the steps of trial function selection and orthogonal function selection in order to effect a practical approximation treatment.

Throughout this investigation certain areas of work have been mentioned as areas suitable for future research. The proceeding remarks summarize these areas.

One area is the use of specific polynomials to take

advantage of their orthogonality relative to the trial function expansion and whether specific polynomials within the trial function would produce better results from the standpoint of increased accuracy with a lower order of approximation. In addition, the form of the trial function is an area where further investigation may be made to ascertain what trial function form (in conjunction with orthogonal function choice) is best for a given problem.

The solution of the sets of ordinary differential equations produced by application of the orthogonal collocation technique is another area suitable for further research. It was shown that the equations for the orthogonal collocation approximation of the simple, diffusion-convection model possess characteristics of a stiff set. This situation raises the question as to what method of integration should be used. This could form an additional area of research - whether orthogonal collocation approximations produce, in general, stiff ordinary differential equation sets and what integration algorithm can be used most effectively for simulation purposes.

## PART 11

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## PART 12

### NOMENCLATURE

- $A_\delta$  - unit impulse, Dirac delta function.
- $A_Y, A_X, A_G$  - areas under output response curve, input response curve, and impulse curve, respectively.
- $a$  - lower bound on interval of orthogonality used in orthogonal polynomial definition, equation (45).
- $a_1(\theta)$  - time-varying coefficients in trial function expansion.
- $a_p$  - ratio of interfacial area to packed volume.
- $b$  - upper bound of interval of orthogonality used in orthogonal polynomial definition, equation (45).
- $C_1$  - scale factor used in orthogonal polynomial definition, equation (45).
- COUPLE - vector used in equation (99).
- $d_1(\theta)$  - time-varying coefficients in trial function expansion.
- $d$  - vector of time-varying coefficients defined in equation (63).
- $f(\theta)$  - time-varying function in the trial function expansion.
- $f$  - vector of time-varying coefficients defined in equation (50).

- $g(\theta)$  - time-varying function in the trial function expansion.
- $h(\theta)$  - time-varying function in equation (70). Later extended to  $h(z, \theta)$  in equation (96).
- $I_1$  - modified Bessel function of the first kind.
- INTRA - matrices used in equation (100).
- INTRAA
- INTRAC
- INTRAE - matrix used in equation (101).
- $L$  - length of chromatograph column, dimensional.
- $m$  - equilibrium constant.
- $N$  - number of collocation points except as defined differently in Part 8.
- $N_E$  - number of interparticle collocation points.
- $N_A$  - number of intraparticle collocation points.
- $NRU$  - the number of reactor units, a dimensionless measure of the rate of adsorption.
- $N_{tOG}$  - number of transfer units, dimensionless.
- $Pe$  - Peclet number, dimensionless.
- $Pe_A$  - intraparticle Peclet number, a dimensionless measure of diffusion rates within the particle.
- $Pe_G$  - interparticle Peclet number, a dimensionless measure of diffusion rates within the carrier gas.
- $P_i( )$  - group of polynomials, initially arbitrary but later constrained to be orthogonal on

- interval  $[a, b]$  by equation (45) or (98).
- $\underline{Q}$  - matrix defined by equation (62).
- $\underline{Q1}$  - matrix defined by equation (66).
- $\underline{Q2}$  - matrix defined by equation (67).
- $r$  - intraparticle space variable, dimensionless.
- $R$  - particle radius, dimensional.
- $R_A$  - rate of sample adsorption.
- $R_I$  - moles of fluid in the particle per mole of adsorption sites within the particle.
- $R_0$  - moles of fluid within the total bed per moles of adsorption sites within the bed.
- $\underline{R}$  - matrix defined by equation (49).
- $\underline{R1}$  - matrix defined by equation (56).
- $\underline{R2}$  - matrix defined by equation (57).
- Res - residual formed by trial function substitution in a differential equation.
- $s$  - Laplace transform variable.
- $w(z)$  - weighting function used in orthogonal polynomial defining equation (45).
- $W_j$  - weighting function in weighted residual integral, equation (43).
- $\underline{W}$  - matrix used initially in equation (82); then in equation (90).
- $\underline{W1}$  - matrices used in equation (90)
- $\underline{W2}$
- $\underline{W3}$  - matrix used in equation (91).



- $x_a$  - adsorbed phase concentration, dimensionless.  
 $y$  - interparticle gas phase composition, dimensionless.  
 $y_1$  - intraparticle gas phase composition, dimensionless.  
 $y_1^*$  - equilibrium intraparticle gas phase composition, dimensionless.  
 $\underline{y}$  - vector of solution values at the interparticle collocation points.  
 $\underline{y}^*$  - vector of equilibrium concentration values at the interparticle collocation points.  
 $\underline{y}_1$  - vector of intraparticle concentration values at the intraparticle collocation points.  
 $\underline{y}_1^*$  - vector of intraparticle equilibrium concentration values at the intraparticle collocation points.  
 $z$  - axial position in column, dimensionless.  
 $z_j$  - collocation point or end point, dimensionless.  
 $z_0$  - axial position where finite terminal boundary condition, equation (33), is applied.

#### GREEK LETTERS

- $\alpha$  - part of the power of  $\mathcal{N}$  in equation (98);  
 i.e.,  $\mathcal{N}^{2\alpha+1}$ .  
 $\beta$  - particle porosity or void fraction; power of

quantity  $(1-\lambda^2)$  in equation (98).

- $\Delta\theta$  - time increment in finite difference method.
- $\Delta z$  - space increment in finite difference method.
- $\delta(\ )$  - Dirac delta function.
- $\delta_{ij}$  - Kronecker delta.
- $\epsilon$  - void fraction of the bed.
- $\pi$  - 3.14159...
- $\theta$  - dimensionless time variable.
- $\mu_n$  - the  $n^{\text{th}}$  moment about the origin defined by equation (14).
- $\bar{\mu}_n$  - the  $n^{\text{th}}$  moment about  $\mu_1$ , defined by equation (17).
- $\phi_0$  - function which satisfied boundary condition in trial function expansion.
- $\phi(\theta)$  - forcing function used in analysis of chromatograph problems.

#### SUBSCRIPTS

- I - refers to Case I boundary condition analysis.
- II - refers to Case II boundary condition analysis.
- i - refers to space level in Finite Difference technique; refers to column in Orthogonal Collocation matrices.
- j - refers to time level in Finite Difference techniques; refers to row and/or collocation points in Orthogonal Collocation matrices.

MISCELLANEOUS

$[ \quad ]_{ji}$  - refers to the matrix element of the  $j^{\text{th}}$  row  
and the  $i^{\text{th}}$  column.

PART 13

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## PART 14

### APPENDICES

The appendices were not included in the report because of their length. Copies may be obtained upon request from:

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