DETERMINATION OF FRACTURE APERTURE
A MULTI-TRACER APPROACH

A REPORT
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By
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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Abstract

This work shows that fracture aperture can be calculated from tracer tests involving two tracers with different affinities for adsorption onto the rock. In 1983 Jensen proved that fissure aperture can be determined when adsorptive effects are neglected. Adsorption introduces an additional unknown, the retardation factor, into the governing equations. When two tracers are injected, the number of available equations expands to match the number of unknowns.

This report also presents equations based on the matrix diffusion model which allow estimation of fracture aperture through visual examination of tracer tests. Tracer data from tests in the Wairakei geothermal field in New Zealand were analyzed by the visual method. The results were compared to computations using nonlinear regression. The two analyses differed randomly with an average variation of ± 40%.

Experiments were performed in which three tracers, sodium chloride, ethyl alcohol and isopropyl alcohol, were flowed through a fractured core. The effective diffusivity of the rock was determined by measuring the salt concentration at the inlet and at two points along the fracture. The analysis of the data made use of an analytical solution to the matrix diffusion model in which the inlet boundary condition is expressed in terms of a complementary error function. Although the effective diffusivity was estimated, the amount of adsorption which occurred during the flow tests could not be determined quantitatively. The sampling frequency was too low to provide good resolution of the breakthrough curve. Interestingly, the differences in molecular diffusion of the tracers seemed to dominate over adsorption effects.

Acknowledgements

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Chapter 1

Introduction

The disposal of produced water is an important part of geothermal development. Often the water contains pollutants which preclude dumping into the biosphere. Reinjection of waste fluids into the productive formation is normally the most economical solution. Injection programs can have positive effects such as pressure maintenance and the replacement of reservoir fluid. Conversely the introduction of cooled fluids may damage the productivity of the reservoir. Cold water could flow into production wells and decrease thermal recovery.

Geothermal fields are especially prone to breakthrough problems because the primary flow paths are through fractures. Cooled fluids can short circuit the low permeability matrix and flow quickly through the fissures from the injector to the producer. The prediction of the arrival of the cold front is therefore of considerable economic importance.

The process of heat transfer between fluids and heat sources has been extensively studied. Solutions are readily available for the flow of fluids through heat exchangers of almost any configuration. The major problem for the geothermal engineer is to define the geometry of the system since the other parameters such as heat transfer coefficients are known.

Recently the matrix diffusion model has been developed to describe the flow of tracers or contaminants through fractured porous media. The use of this model is extended in this report to cover the determination of fracture aperture from tracer tests in which adsorption is significant. Once this parameter is known the estimation of thermal breakthrough is straight forward.

Chapter 2

Literature Review

Tracer tests are used extensively to determine the behavior of fracture networks. They are utilized in preference to pressure transient analysis because well testing does not predict the existence of preferential returns (Grant, Donaldson and Bixley 1982). Horne (1982) gathered information from geothermal fields in Japan where tracer tests were able to discern short-circuiting of injection water. Qualitative descriptions of subsurface conditions have also been obtained from tracer tests for fields in New Zealand by McCabe, Barry and Manning (1983) and Fossum (1982). As of yet few quantitative descriptions of fracture systems have been acquired from tracer tests.

Accurate estimation of contaminant transport through fractures is extremely important in the nuclear waste disposal industry. **A** large amount of work is being done to predict the flow of radioactive elements through basement rock. It has been observed that the breakthrough of a species transported through a fractured porous medium is delayed. The retardation is due to the interaction of the fluids in the fracture and the matrix (Freeze and Cherry 1979, Neretnieks 1980, Grisak and Pickens 1980). Neretnieks and other researchers working with the nuclear waste problem have used the matrix diffusion model to explain these effects. The model has received wide acceptance.

The extension of the conceptual model has proceeded rapidly with mathematical developments preceding experimental and field verification. Tang, Frind and

Sudicky (1981) were the first to solve analytically the problem of flow through two parallel plates. The next year Sudicky and Frind (1982) extended the solution to a series of parallel fractures. Chen (1986) increased the scope of the model to include radial flow through a horizontal fracture. Most recently van Duijn and van der Zee (1986) have used the matrix diffusion model to solve the problem involving diffusion between two porous zones of different permeability.

Experimental and field verification have followed closely behind the mathematical developments. An experiment done on flow through fractured glacial till confirmed that diffusion is an important part of advective transport (Grisak 1980). In 1982 Neretnieks *et al.* proved that diffusive effects must be considered even with a granitic matrix of low porosity and low permeability (Neretnieks, Eriksen and Tahtinen 1982). Later Jensen (1983) showed that the matrix diffusion model explains the results of tracer tests in the Wairakei geothermal field in New Zealand. Maloszewski and Zuber (1985) were also able to match larger scale groundwater tests. Finally Johns (1987) determined experimentally that the matrix diffusion model simulates observations better than a model based on dispersion alone.

The field and experimental work all shared one drawback. The model was verified by inference only. The important parameters were not all determinable beforehand. As the simulations were run, various coefficients (diffusion and adsorption) were changed to improve the fit. In every case a good match was obtained with reasonable input values.

As the name of the model suggests, the diffusion properties of the rock are key determinants in the transport process. Good data would clearly enhance the value of a simulation. Fortunately simple, standard methods are available to measure the diffusion coefficient (Stoessell and Hannor 1975), and attempts have been made to directly quantify diffusion where rock samples have been available (Skagius and Neretnieks 1986).

Adsorption is not nearly as easy to handle as diffusion. While diffusion can normally be represented by one number, quantifying adsorption requires selection of a model. Boast (1971) summarizes ten models which could be used for forecasting transport through soils. Some researchers prefer using more complicated models

(Gupta and Greenkorn 1973); most, however, favor using the Freundlich isotherm of which linear adsorption is a subset (Greenkorn 1983, Lindstrom, Boersma and Stockard 1971, Skagius, Svedberg and Neretnieks 1982). Breitenbach (1982) found that the linear model was adequate to explain the sorption of two geothermal tracers on andesite. Published work involving the matrix diffusion model all use the linear model because additional mathematical complexity would make analytical solutions extremely formidable.

Even as adsorption is difficult to manage conceptually, it is more troublesome to measure experimentally. Skagius *et al.* (1982) outline one straightforward method to quantify this type of rock-tracer interaction. The effort is worthwhile because the effect of adsorption on advective transport is significant even for weakly sorbing tracers (Johns 1987).

Vetter and Crishlow (1979) also understood the importance of quantifying the adsorptive behavior of geothermal tracers. They suggest that the contacted surface area may be measured through chromatographic analysis. They expect one could also draw conclusions about the porosity and permeability of flow channels by comparing the breakthrough curves of two sorbing tracers.

Although the matrix diffusion model has recently received much favor as a means to describe advection through fractured rock, some investigators have suggested that it must be modified. Neretnieks *et ak.* and Abelin *et ak.* have presented evidence that fluid flow through fractured rock is through channels not parallel plates (Neretnieks 1982, Abelin, Birgersson, Gidlund, Moreno, Neretnieks and Tunbrant 1985). It is a simple matter, however, to change the mathematical construction to represent the new geometry (Tsang and Tsang 1981).

Chapter 3

Theory

As stated in the introduction, many authors have utilized the matrix diffusion model to study the flow of tracers through fractures. Contributions of this work include the definition of several dimensionless groups, the derivation of a fracture aperture equation and the coupling of the matrix diffusion model to chromatographic analysis.

3.1 Derivation of the Governing Equations

The two governing equations are expressions of material balance. Figures 1.1 and 1.2 show the control volumes used to develop the fracture flow and matrix diffusion governing equations. The fracture and adjoining matrix are assumed to be homogeneous and isotropic. Convection, diffusion and adsorption occur within the system, and while longitudinal dispersion terms are not included, Taylor Dispersion is used to describe diffusion within the fracture itself (Taylor **1953).** Taylor Dispersion holds that diffusion in the direction of flow is negligible in relation to the velocity of flow but is quick enough so that there is no concentration gradient across the small width of the fracture. While the effective diffusivity is used throughout this report, Neretnieks **(1980)** presents an excellent survey of the various diffusion constants used in other literature. Adsorption is modeled as linear, instantaneous

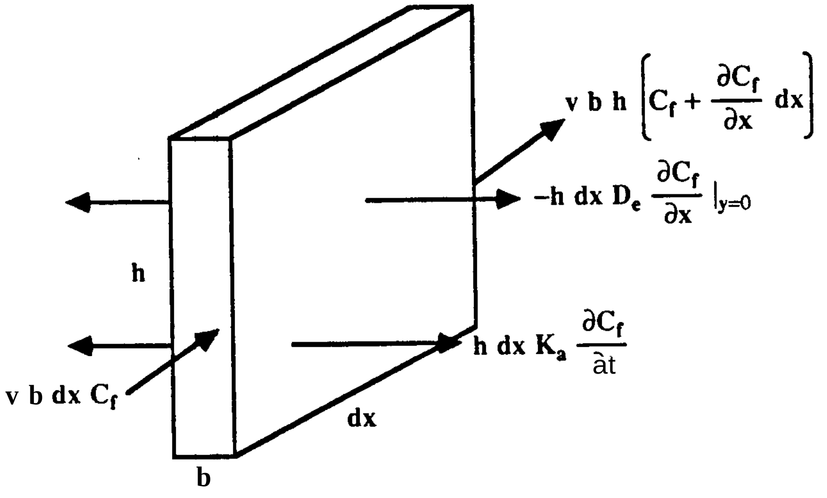

Figure 3.1: Fracture Flow

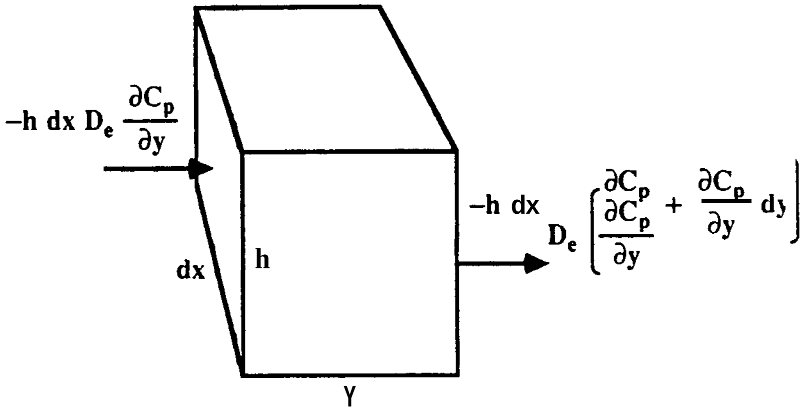

Figure 3.2: Matrix Diffusion

reaction (mass adsorbed is proportional to the concentration). Appendix A discusses adsorption further.

3.1.1 Fracture Flow Governing Equation

The fracture flow equation describes the transport of a tracer through a fissure. Figure 1.1 depicts a fracture with a width, b, a height, h, and a differential length, dx. A tracer of concentration C_f is transported through the fracture with a velocity, v. Fick's Law of diffusion describes the flux of tracer which flows through the fracture wall. Tracer is also lost from the fracture due to adsorption which is characterized as a linear function of concentration. K_a, the areal partition coefficient, models the equilibrium between the mass of tracer adsorbed onto the fracture wall and the concentration of the tracer in the fracture.

Placing the terms shown in Figure 1.1 into a mass balance equation:

$$MassEntering - MassLeaving = MassAccumulating \tag{3.1}$$

$$vbhC_f - vbh(C_f + \frac{\partial C_f}{\partial x}dx) + 2hdxD_e\frac{\partial C_f}{\partial y}|_{y=0} - 2hdxK_a\frac{\partial C_f}{\partial t} = hbdx\frac{\partial C_f}{\partial t} \tag{3.2}$$

Dividing both sides of the equation by $hbdx$ yields:

$$-v\frac{\partial C_f}{\partial x} + \frac{2}{b}D_e\frac{\partial C_f}{\partial y}|_{y=0} - \frac{2}{b}K_a\frac{\partial C_f}{\partial t} = \frac{\partial C_f}{\partial t} \tag{3.3}$$

Note that h dropped out of the equation.

Rearranging Equation 3.3:

$$(1 + \frac{2}{b}K_a)\frac{\partial C_f}{\partial t} = \frac{2}{b}D_e\frac{\partial C_f}{\partial y}|_{y=0} - v\frac{\partial C_f}{\partial x} \tag{3.4}$$

The retardation factor, R_D, is defined to be $(1+\frac{2}{b}K_a)$ (Freeze and Cherry 1979), hence:

$$R_D\frac{\partial C_f}{\partial t} = \frac{2}{b}D_e\frac{\partial C_f}{\partial y}|_{y=0} - v\frac{\partial C_f}{\partial x} \tag{3.5}$$

This report will refer to both Equations **3.4** and **3.5** as the fracture flow governing equation.

3.1.2 Matrix Diffusion Governing Equation

The matrix diffusion equation describes the transport of tracer through the porous matrix. Figure 1.2 depicts an elemental volume representing the matrix. Fick's Second Law of Diffusion models the diffusion of tracer through the rock where C_p denotes the concentration in the pores of the matrix (mass per volume of liquid). Mass accumulates in the volume due to adsorption onto the rock grains.

Placing the terms shown in Figure 1.2 into a mass balance equation:

$$MassEntering - MassLeaving = MassAccumulating \tag{3.6}$$

$$-(hdx)D_e\frac{\partial C_p}{\partial y} - [-(hdx)D_e(\frac{\partial C_p}{\partial y} + \frac{\partial^2 C_p}{\partial y^2}dy)] = (hdxdy)\frac{\partial C_m}{\partial t} \tag{3.7}$$

C_m is the concentration within a given volume of rock (mass per volume of liquid and solid).

Dividing both sides of the equation by $(hdx)dy$ yields:

$$D_e\frac{\partial^2 C_p}{\partial y^2} = \frac{\partial C_m}{\partial t} \tag{3.8}$$

Again h divides out of the equation. h does not appear in either governing equation. The solution will not depend on the fracture height.

The mass in the matrix, C_m (mass per bulk volume), is comprised of free solute in the pores, C_p (mass per **pore** volume), and adsorbed mass on the grains S (mass per bulk volume).

$$C_m = \phi C_p + S \tag{3.9}$$

For small concentrations a linear isotherm may be used to model the partitioning between the rock and fluid. K_v (pore volume per bulk volume) is the volumetric partition coefficient. K_v is related to K_d by the surface area to volume ratio of the rock.

$$S = K_v C_p \tag{3.10}$$

Substituting Equation **3.10** into Equation **3.9**

$$C_m = (\phi + K_v) C_p \tag{3.11}$$

Equations **3.8** and 3.11 may be combined:

$$(\phi + K_v)\frac{\partial C_p}{\partial t} = D_e \frac{\partial^2 C_p}{\partial y^2} \tag{3.12}$$

Some authors define $(\phi + K,)$ as the volumetric equilibrium constant, $K_d \rho_p$ and utilize the apparent diffusivity, D_a where $D_a = D_e / K_d \rho_p$ (Neretnieks 1980). Equation **3.13** is the matrix diffusion governing equation.

$$\frac{\partial C_p}{\partial t} = \frac{D_e}{\phi + K_v} \frac{\partial^2 C_p}{\partial y^2} \tag{3.13}$$

3.2 Solution

The governing equations may be solved for a step change at the inlet (Figure **3.3)** where there is no tracer present prior to injection (Carslaw and Jaegar 1959). The details of this operation are given in Appendix B. The major difference between this approach and published works is the use of dimensionless groups.

The equations were nondimensionalized by using six dimensionless groups. Concentration was nondimensionalized by dividing by the injection or reference concentration ($C_D = C/C_0$). The lengths were divided by the distance between the inlet and outlet ($x_D = x/L$ etc.). The retardation factor, R_D, is the same as previously defined. K_D is the dimensionless partition coefficient where $K_D = \phi + K_v$.

Two groups were defined using an unknown time, t^*. t^* defines the length of the fracture divided by the velocity of flow (L/v). This is the time for a tracer to travel from an injector to a producer where there is no adsorption or diffusion.

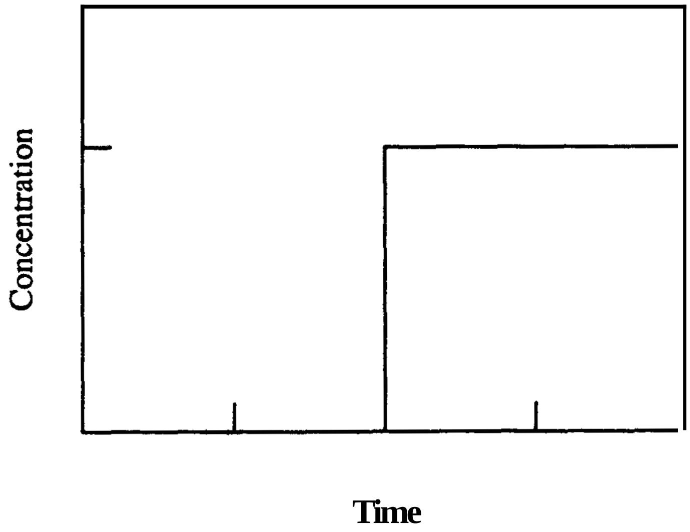

Figure 3.3: Inlet Condition - Step Change

It is the breakthrough time for a nonsorbing tracer. The dimensionless time and dimensionless diffusivity are defined as follows: $t_D = t/t^*$; $D_D = D_e t^*/L^2$.

The solution to the step input is given in Equation 3.14 (and Appendix B). Notice that the retardation factor is buried with the dimensionless time inside a square root. The retardation factor does not affect the shape of the response. It simply translates the profile forward or backward in time. Also at the outlet or producing well, $x = L$ or $x_D = 1$; therefore, the solution does not depend of the fracture length. Figure 3.4 shows the response to a step input.

$$C_{fD} = erfc\left[\frac{x_D(D_D K_D)^{1/2}}{b_D(t_D - x_D R_D)^{1/2}}\right];\ for\ t_D > x_D R_D \tag{3.14}$$

$$C_{fD} = 0;\ for\ t_D \le x_D R_D \tag{3.15}$$

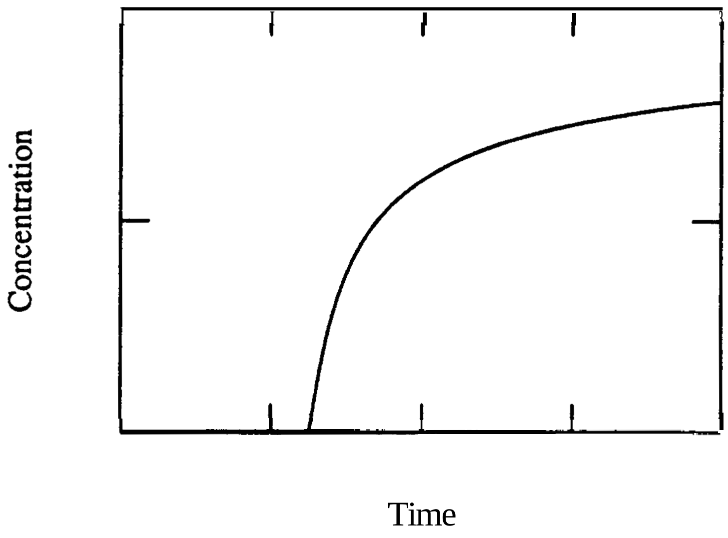

Figure 3.4: Outlet Response to Step Change

3.3 Fracture Aperture Equation

Most field tests do not usually involve simple step changes at the inlet. Instead, tracers are more commonly injected over a short period of time. When a tracer is injected into an injection well for a time, *At* (Figure 3.5), the response will be as shown in Figure 3.6. This boundary condition can be handled by superposition of the step change solution (Equation 3.14). Equation 3.16 is the derivative of the solution to this input Condition (see Appendix C).

$$C'_{fD} = A_D \left\{ \frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2 (t_D - R_D)}\right]}{(t_D - x_D R_D)^{3/2}} - \frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2 (t_D - \Delta t_D - R_D)}\right]}{(t_D - \Delta t_D - x_D R_D)^{3/2}} \right\} \qquad (3.16)$$

$$for\ t_D - \Delta t > x_D R_D$$

$$where\ A_D = \frac{x_D (D_D K_D)^{1/2}}{\sqrt{\pi}\, b_D (t_D - x_D R_D)^{3/2}}$$

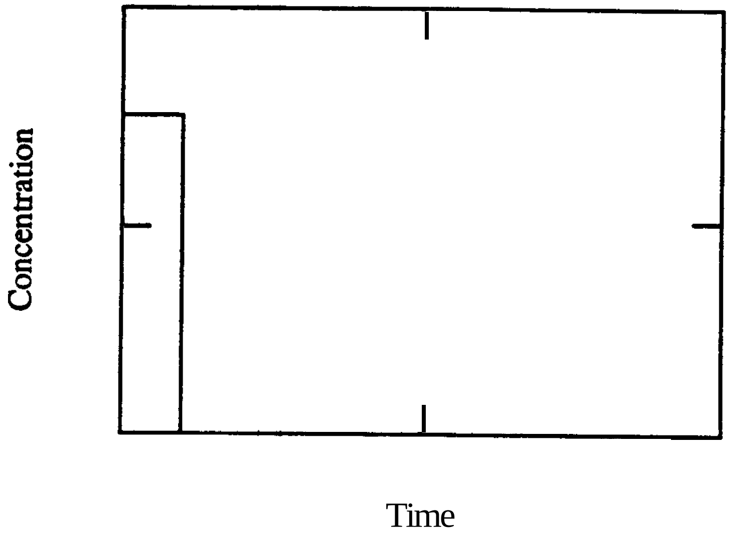

Figure 3.5: Inlet Condition - Pulsed Injection

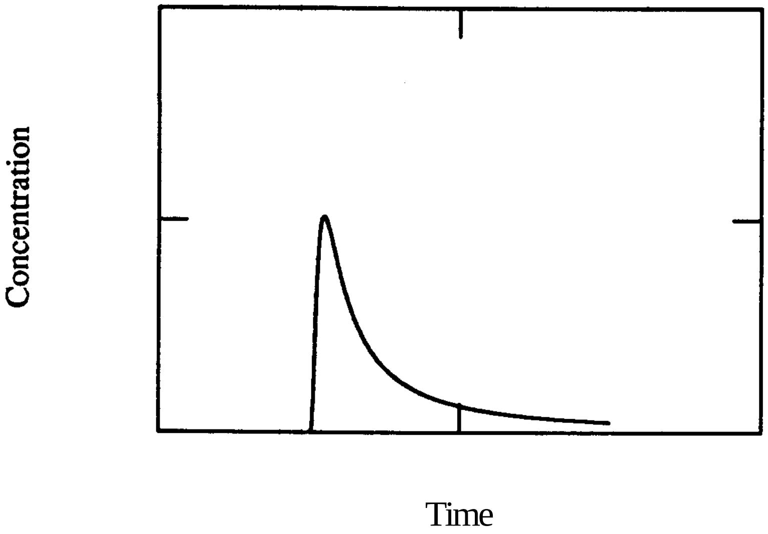

Figure 3.6: Outlet Response to Pulsed Injection

At the peak of the tracer recovery curve, the derivative of the concentration with respect to time is zero. By setting Equation **3.16** to zero and rearranging the result in dimensional form, one can derive the fracture aperture equation (Equation **3.17).** Equation **3.17** relates the fracture aperture to t^* and several other parameters. The other parameters can be determined through logs or laboratory tests on cores. The fracture aperture appears on both sides of the equation and an iterative solution is required.

Fracture Aperture Equation

$$b^2 = \frac{D_e(\phi + K_v)t^{*2}\Delta t}{(t_p - R_D t^*)(t_p - At - R_D t^*)\ln\left[1 - \frac{At}{t_p - R_D t^*}\right]^{-3/2}} \qquad \textbf{(3.17)}$$

$$\textit{where } R_D = 1 + \frac{2}{b}K_a$$

For no adsorption $(K, = K_v = 0)$:

$$b^2 = \frac{D_e\phi t^{*2}\Delta t}{(t_p - t^*)(t_p - At - t^*)\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}} \qquad \textbf{(3.18)}$$

For an instantaneous or spike injection, At approaches zero. This is the normal boundary condition for injection of a radioactive tracer. Equation **3.19** is the fracture aperture equation for instantaneous injection. This expression provides a noniterative solution.

Fracture Aperture Equation - Instantaneous Injection

$$b = \frac{K_a t^* + \sqrt{K_a^2 t^{*2} + 6D_e(\phi + K_v)(t_p - t^*)t^{*2}}}{3(t_p - t*)} \qquad \textbf{(3.19)}$$

For no adsorption $(K, = K_v = 0)$:

$$b = t^*\sqrt{\frac{2D_e\phi}{3(t_p - t^*)}} \qquad \textbf{(3.20)}$$

Inferring values of b from the fracture aperture equation requires the injection of either one nonsorbing or two dissimilar adsorbing tracers. Either method will allow estimation of t^*. This parameter appears in every form of the aperture equation and must be determined before the fracture width can be estimated. When a nonsorbing tracer is injected, the breakthrough time corresponds to t^*, and the aperture can be calculated in a straightforward manner. t^* cannot be determined directly when dealing with a sorbing tracer because adsorption causes a retardation of the tracer movement. When one sorbing tracer is utilized, two unknowns, b and t^*,appear in the one equation. If two tracers with different affinities for adsorption are injected, one can write the fracture aperture equation twice – once for each tracer. With two equations, the two unknowns can both be calculated. Although the evaluation is simpler when using a nonsorbing tracer, it is important to note that truly nonsorbing tracers are uncommon. Skagius ***et al.*** *(1982)* have noted the adsorption of radioactive elements on minerals.

In many cases adsorption is the major cause for delaying the peak returns from t^*. Adsorption will dominate the slower diffusion process. Remember that surface adsorption will translate the entire profile while diffusion will simply separate the breakthrough and peak times. Figure **3.7** illustrates this point. Tracer **1** is a nonsorbing tracer; therefore, the breakthrough time and t^* are identical. Diffusion causes the small difference between t^* and t,. Tracer **2** is an adsorbing tracer in which adsorptive effects cause a translation. This translation is the major reason that t^* and the peak time are different. Notice the relatively small diffusional effects. For the case where adsorptive effects dominate:

$$t_p - At - R_D t^* \; x \; 0 \tag{3.21}$$

Substituting for R_D and solving for b yields the:

Approximate Fracture Aperture Equation

$$b \approx \frac{2K_a t^*}{t_p - At - t^*} \tag{3.22}$$

Note the great dependence on K,. This is unfortunate because K_a is the most difficult parameter to measure (Appendix A).

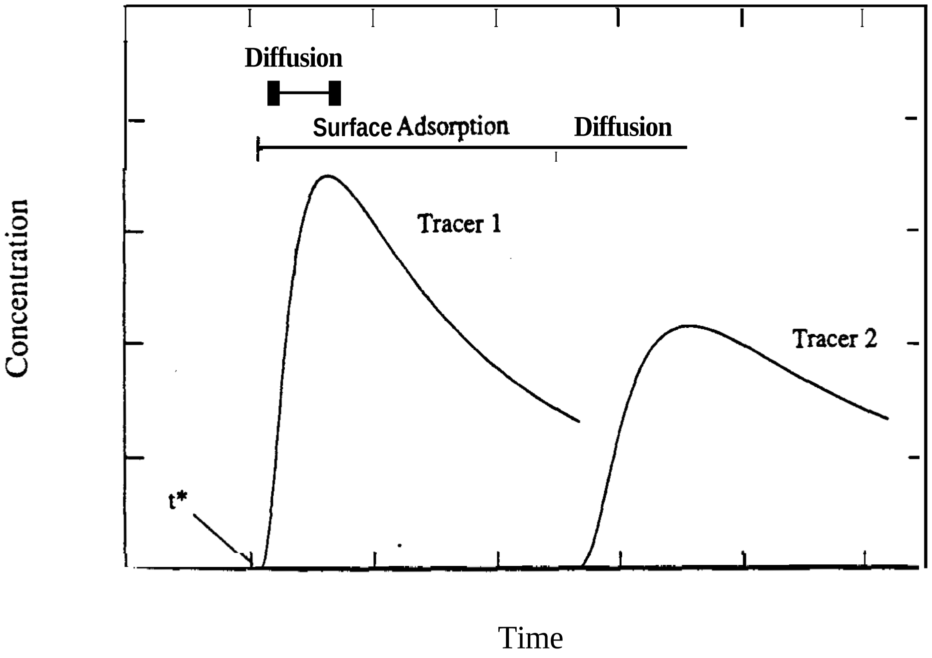

Figure **3.7:** Chromatographic Effects of Diffusion and Adsorption

3.4 Analysis of Synthetic Tracer Tests

Synthetic tracer tests were generated using the matrix diffusion model. They are analyzed in this section to illustrate the utility of the fracture aperture equation.

Figure **3.8** shows breakthrough tracer returns for three tracers. The flow is through a fracture of 0.004 inches in width. Tracer 1 is nonsorbing. Tracer 2 has an areal partition coefficient of twice the aperture. Tracer **3's** areal partition coefficient is five times the width. The input data are summarized in Tables **3.1** and **3.2.**

It is a simple matter to analyze the nonsorbing tracer test. The breakthrough and peak times are determined from the graph. Along with these parameters, the diffusivity, porosity and injection time are plugged into Equation 3.18. Note that the breakthrough time for the nonsorbing tracer is equal to t^* (5 hr $=$ 1000 ft/200 ft/hr).

When analyzing adsorbing tracers, two tracers are necessary. Figure **3.9** presents a cross plot of t^* vs. fracture aperture for tracers **2** and **3.** The approximate equation **(3.22)** was used to generate these curves. There is little separation between the two

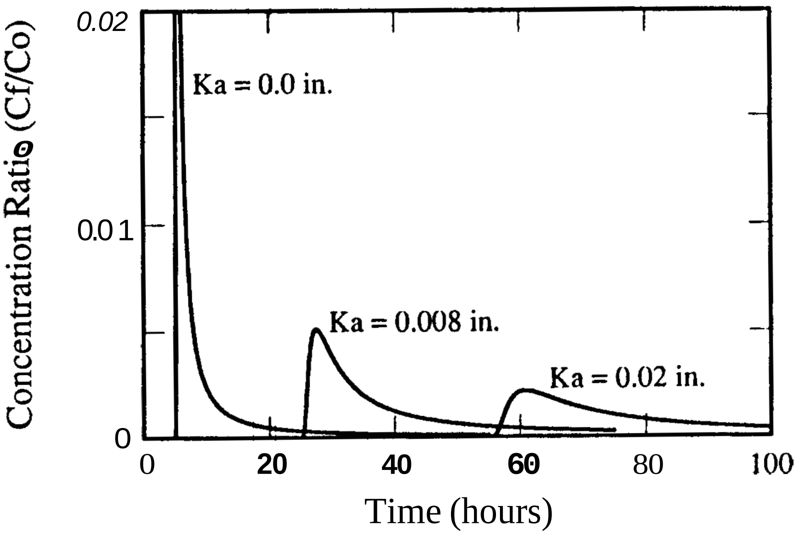

Figure 3.8: Synthetic Tracer Breakthrough Curves

	Fracture Data	
b	0.004	*in.*
x	1000	ft
h	100	ft
v	200	ft/hr
	Matrix Data	
ϕ	2	%
D_e	$1.86 \cdot 10^{-6}$	ft^2/hr

Table 3.1: Synthetic Tracer Test – Formation Data

Tracer Data					
Tracer 1		Tracer 2		Tracer **3**	
K,	0.000	*K,*	*0.500*	*K,*	1.000
K_a	*0.000 in*	*K,*	*0.008 in.*	*K,*	*0.020 in.*
Injection Interval					
At			**5** *min*		

Table **3.2:** Synthetic Tracer Test – Injection Data

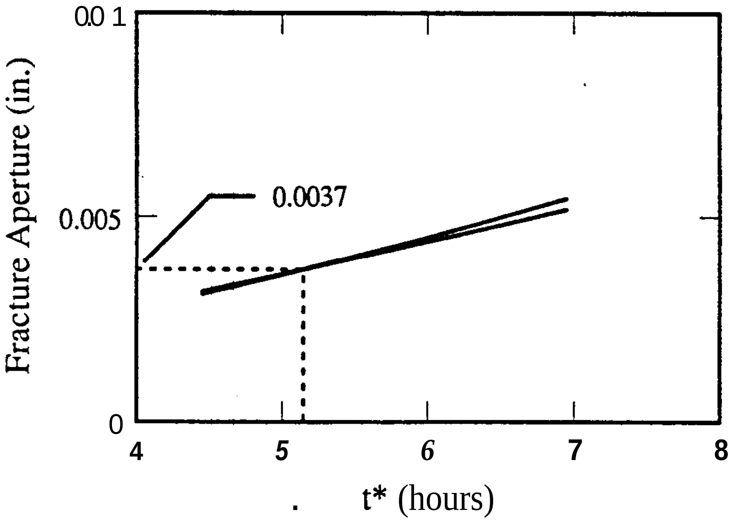

Figure **3.9:** Fracture Aperture Cross Plot - Approximate Equation

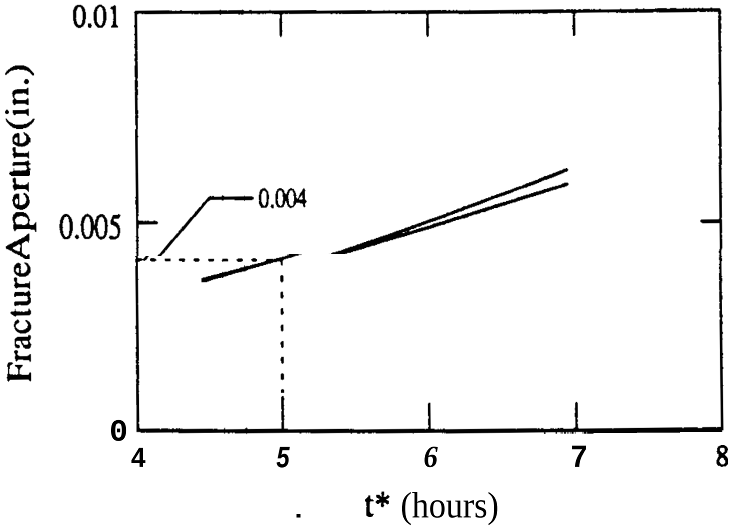

Figure **3.10:** Fracture Aperture Cross Plot - Iterative Solution

curves; highlighting the sensitivity of the solution to K_a. The lines cross at 5.15 hrs and 0.0037 in. while the input parameters were **5** hours and 0.004 in. If the iterative equation were used (Figure 3.10), the solution would be exact (excluding round off error). Figure 3.11 compares the two solutions.

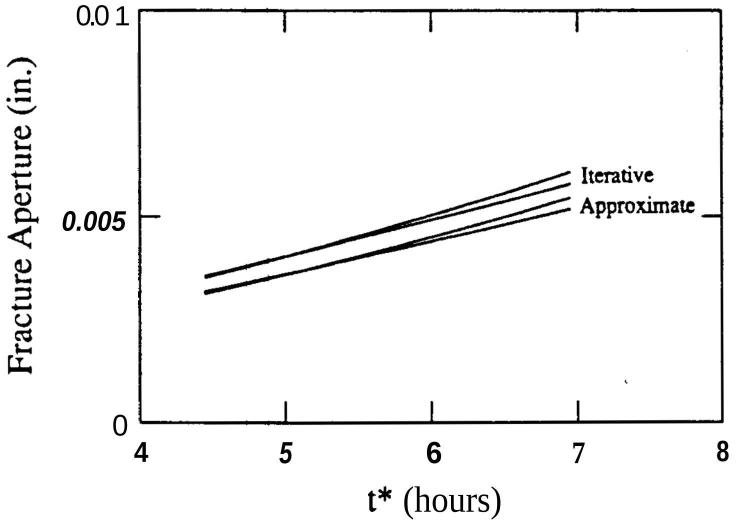

Figure 3.11: Approximate vs. Iterative Solution

Chapter 4

Analysis of Wairakei Field Data

This chapter describes the analysis of tracer tests from the Wairakei Geothermal Field in New Zealand. The results compare favorably to those of an investigation by Jensen **(1983).** While he also used the matrix diffusion model, his analysis was done using a nonlinear regression program.

4.1 Geology

Wairakei is one of New Zealand's larger geothermal resources. The field lies in a large thermal area, 200 miles north of Wellington on the North Island (Figure **4.1).** The primary production comes from the interface between the Waiora and Wairakei formations (Figure 4.2), and the primarily flow paths are through fissures. The major faults, the Kaiapo, Wairakei and Waiora, all strike northeast to southwest and are intersected by minor faults inside the productive area (Figure **4.3).** Jensen **(1983)** provides a fairly complete synopsis of the geology. For a more complete description see Grindley **(1965).**

4.2 Tracer Tests

Two tracer injection tests are analyzed in this report. They were performed by the Institute of Nuclear Sciences, Department of Scientific and Industrial Research,

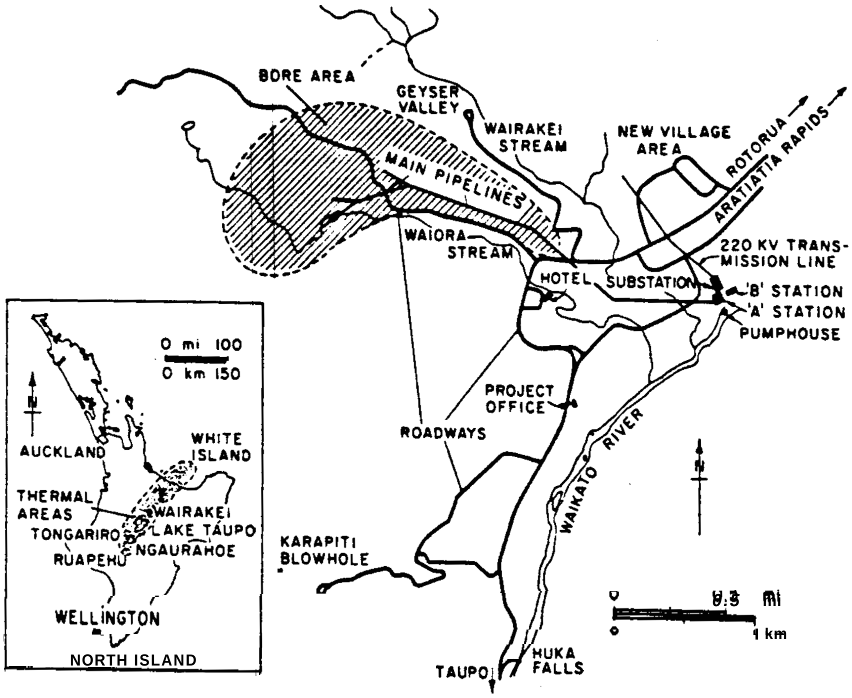

Figure **4.1:** Location of Wairakei Field (from DiPippo 1980)

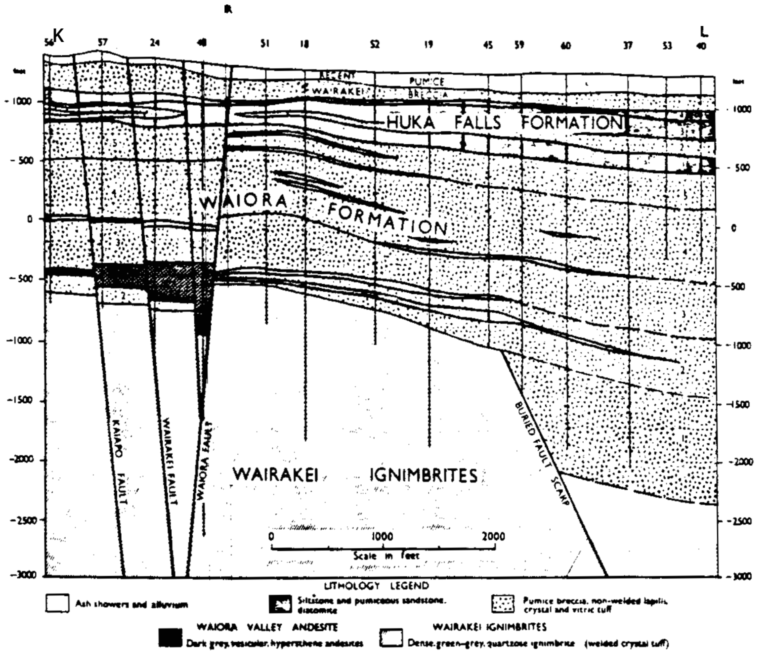

Figure 4.2: Geology of Wairakei Field (from Grindley 1965)

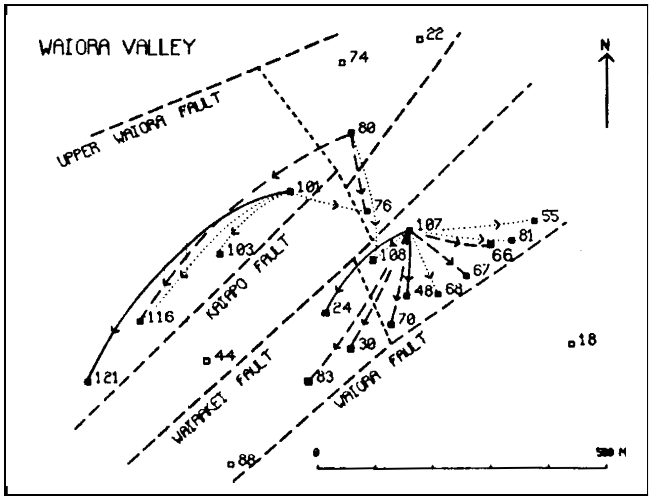

Figure 4.3: Well Locations in Wairakei Field (from McCabe *et al.* 1983)

New Zealand. In March 1979, 155 GBq of iodine-131 were injected into well WK107 at 1096 feet (Figure 4.3). A vial containing the tracer was shattered inside a surface by-pass connection thus producing an instantaneous injection (McCabe, Barry and Manning 1983). Radioactivity was subsequently seen in ten wells. Later in June, 165 GBq were injected into well WK101 at 1312 feet, and sensors detected the iodide in twelve wells. Some wells did not show significant response and were not analyzed by Jensen (1983).

Appendix D presents plots of the data. The concentrations have been scaled to units of injected amount divided by 10^{12} liters and corrected for decay and background emissions. Additionally, negative values have also been omitted. The raw data and the nonlinear regression fit is also presented in Jensen's 1983 report.

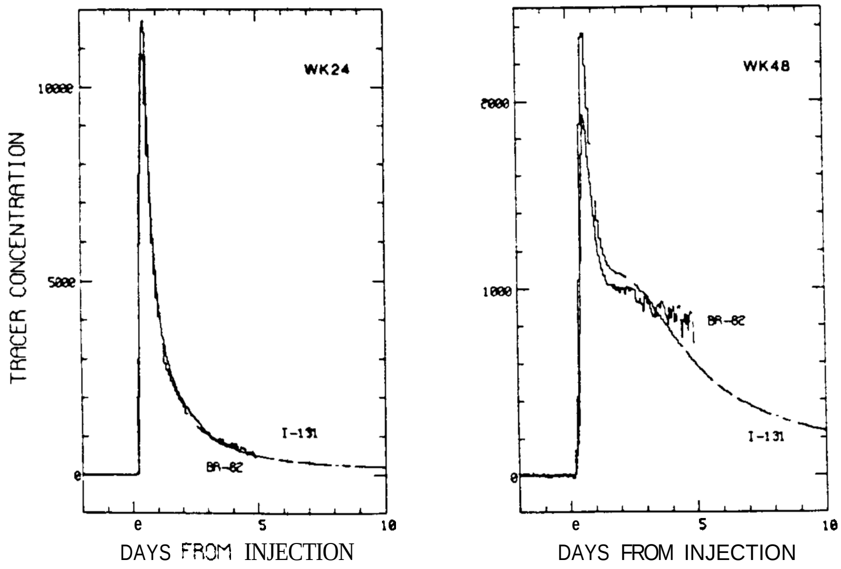

Figure **4.4:** Chromatographic Movement of Iodide and Bromide - Wairakei (from McCabe et al. 1983)

4.3 Analysis and Comparison

The data could only be analyzed if an adsorption isotherm were assumed. **A** literature survey produced no publications regarding the sorption of iodide on the minerals found in the Wairakei field although the chromatographic performance of iodide vs. bromide was tested in Wairakei (Figure **4.4**). There was no difference in the arrival times or shapes of the breakthrough curves (McCabe *et al.* 1983). The responses may have been alike either because neither tracer adsorbed, or both adsorbed similarly. The similarity is probable since both iodide and bromide are halogens. **A** factor which tended to reduce the affinity of iodide for the rock was its electrical potential. Anions have little attraction for identically charged formations: however, they are known to adsorb onto the crystal edges of otherwise negatively charged clays (Gray and Darley 1980). In the absence of better information the best assumption was that iodide does not adsorb.

Equation 3.12, valid for a nonsorbing tracer, was used to analyze the data. Only four parameters were needed: porosity, diffusivity, breakthrough time and time to peak concentration. The two times were found by inspecting the concentration vs. time plots, and the porosity was estimated by logs and core analysis. The diffusivity could have been inferred from the porosity (Perkins and Johnston 1963) or measured directly. To facilitate comparison with Jensen's calculations, this analysis assumed a porosity of 1%and a diffusivity of $4.32 \cdot 10^{-6}\ ft^2/day$ $(5 \cdot 10^{-7}\ cm^2/s)$.

Equation 3.12 repeated:

$$b = t^* \sqrt{\frac{2D_e\phi}{3(t_p - t^*)}}$$

From Perkins and Johnston (1963):

$$D_e = \frac{D_0}{F\phi} \tag{4.1}$$

For a carbonate or consolidated formation:

$$F = \frac{1}{\phi^2} \tag{4.2}$$

For a sandstone:

$$F = \frac{0.62}{42.15} \tag{4.3}$$

The analysis of WK68 was typical and proceeded as follows. A plot similar to Figure 4.5 was inspected. The breakthrough and peak times were determined visually, in this case 2.3 and 11.09 days. The fracture aperture of 0.0043 in. was then calculated using Equation 3.12.

Jensen used a nonlinear regression technique. Three parameters were needed to fit the data. α determined the shape of the curve. $1/\beta$ was equal to the breakthrough time, and the third factor was a simple scaling coefficient. The time to peak concentration was not determined explicitly but could be found by manipulating Jensen's equations (Appendix E). For the WK68 Jensen computed a breakthrough time of 2.92 days and a peak time of 11.09 days. The resulting fracture aperture was 0.0068 in., approximately 50 % greater than the width estimated visually. Since

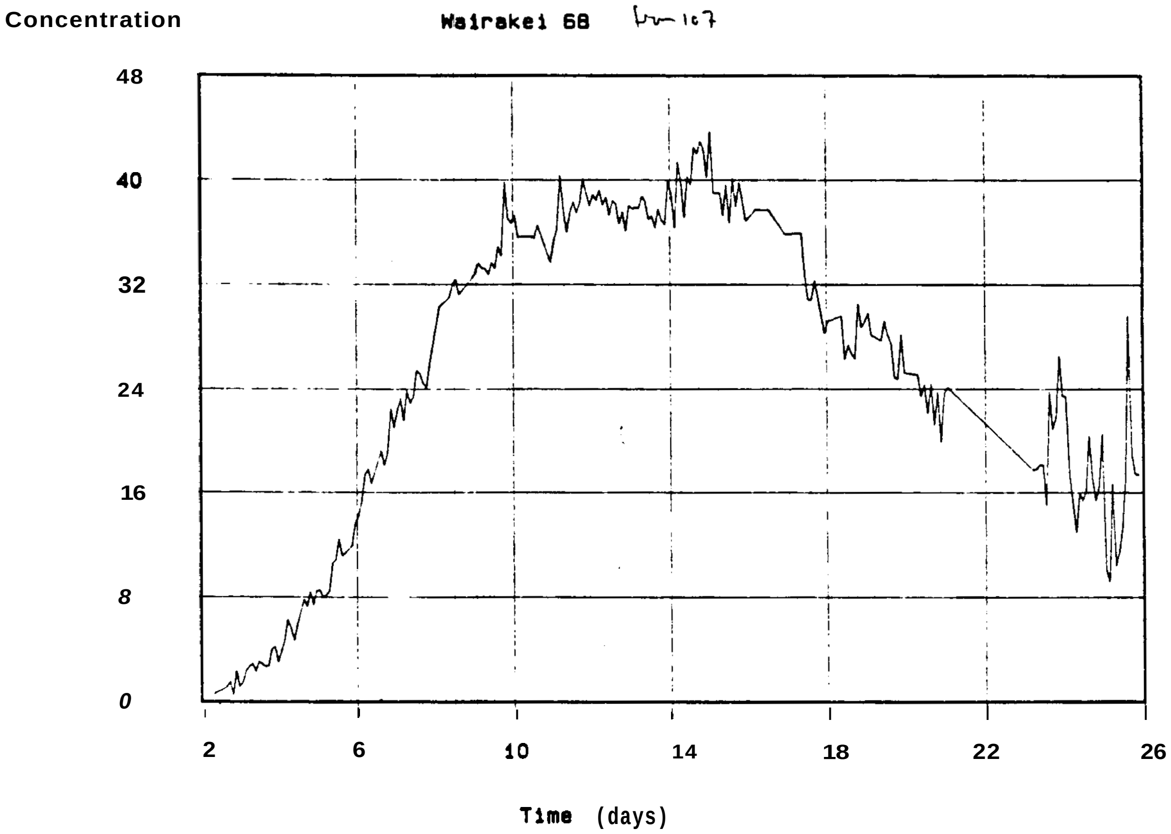

Figure 4.5: WK68 **Tracer Breakthrough Curve** - from WK107

Inj. Well	Prod. Well	Regression				Visual			
		α	$1/\beta$ days	t_p days	b in.	t^* days	t_p days	b in.	A b %
CWK107	WK24	1.25	0.23	0.47	0.0031	0.22	0.51	0.0027	-14
	WK30	1.37	4.37	9.83	0.013	3.7	9.3	0.010	-16
		1.27	3.22	6.67	0.012				- 7
	WK48	1.39	0.29	0.67	0.0032	0.26	0.70	0.0026	-17
		1.67	1.04	2.97	0.0050				-48
	WK55	2.50	2.67	14.51	0.0052	3.3	15.7	0.0063	-23
	WK67	2.74	1.65	9.89	0.0038	0.46	15.3	0.0008	-80
	WK68	2.05	2.92	11.09	0.0068	2.3	14.8	0.0043	-35
	WK70	2.48	2.03	10.39	0.0047	2.8	9.9	0.0070	+50
	WK81	1.54	3.66	9.41	0.010	4.0	8.4	0.013	+23
	WK83	2.17	2.55	10.53	0.0060	3.7	9.7	0.010	+73
	WK108	1.69	6.78	19.62	0.013	10.7	25.6	0.019	+47
CWK101	WK103	3.44	0.62	5.49	0.0019	0.54	5.1	0.0017	-10
	WK116	3.84	0.63	6.79	0.0017	2.4	7.0	0.0075	+342
		0.92	4.79	7.35	0.019				-61
	WK121	0.92	1.45	2.26	0.011	1.1	2.5	0.0062	-41

Table **4.1:** Estimation of Fracture Aperture - Regression and Visual Methods

both methods were based on the matrix diffusion model, identical picks for the times yielded identical aperture estimates.

Table 4.1 presents the results of the visual and regression methods. In three cases Jensen found a better match using a double fracture model. Visual analysis of this kind was impossible. When only the ten single fracture fit curves were compared, the estimates of fracture aperture agreed fairly well. Figure 4.6 shows a plot of width found from the regression and visual procedures. The divergence between the two methods lie within the definitions of accuracy and precision. The average absolute value of the difference between the procedures was 40% (low precision). If the differences are summed while maintaining the positive and negative signs, the average of the discrepancies is only 0.9% (high accuracy).

Figures 4.7 and 4.8 attempt to discern the reasons for the discrepancies. The regression method computed both longer breakthrough and peak times. Since the difference between the two times is important, the relative overestimation was not

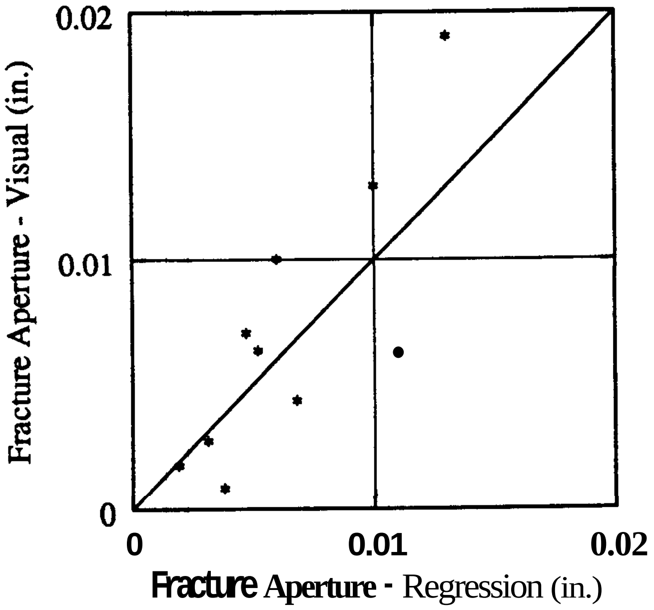

Figure **4.6:** Fracture Aperture - Visual **vs.** Regression Method

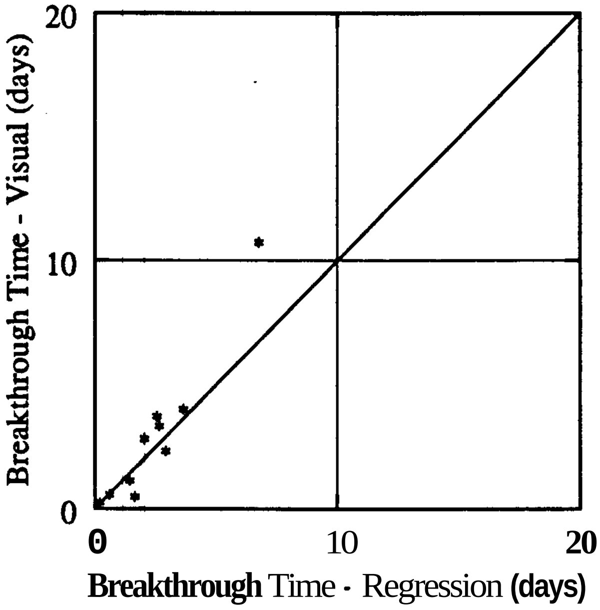

Figure **4.7:** Breakthrough Time - Visual **vs.** Regression Method

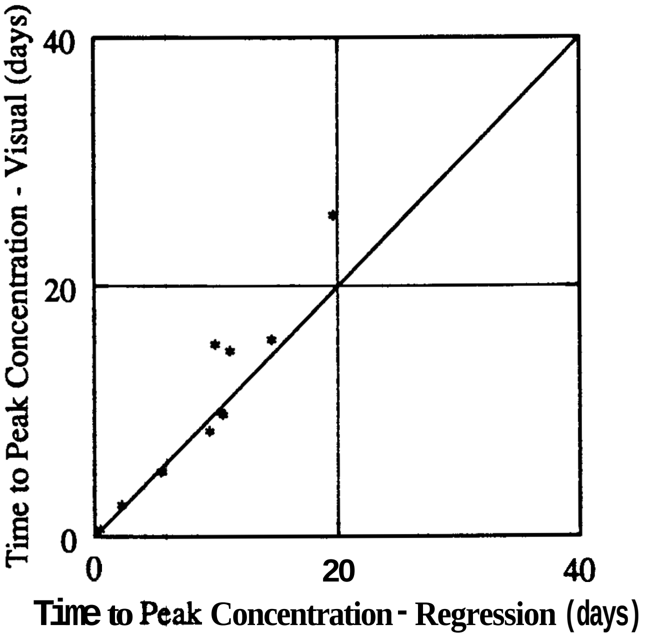

Figure 4.8: Peak Concentration Time - Visual vs. Regression Method

the cause of the divergence. The difference was simply a random variation. Perhaps with practice, an engineer could fine tune his judgement.

The visual estimation was probably more accurate in at least one case. In his analysis of the WK116 well **(Figure 4.9)**, Jensen incorporated data from 0 to **2.4** days. These points include random background radiation. Their inclusion may be the origin of the double fracture fit.

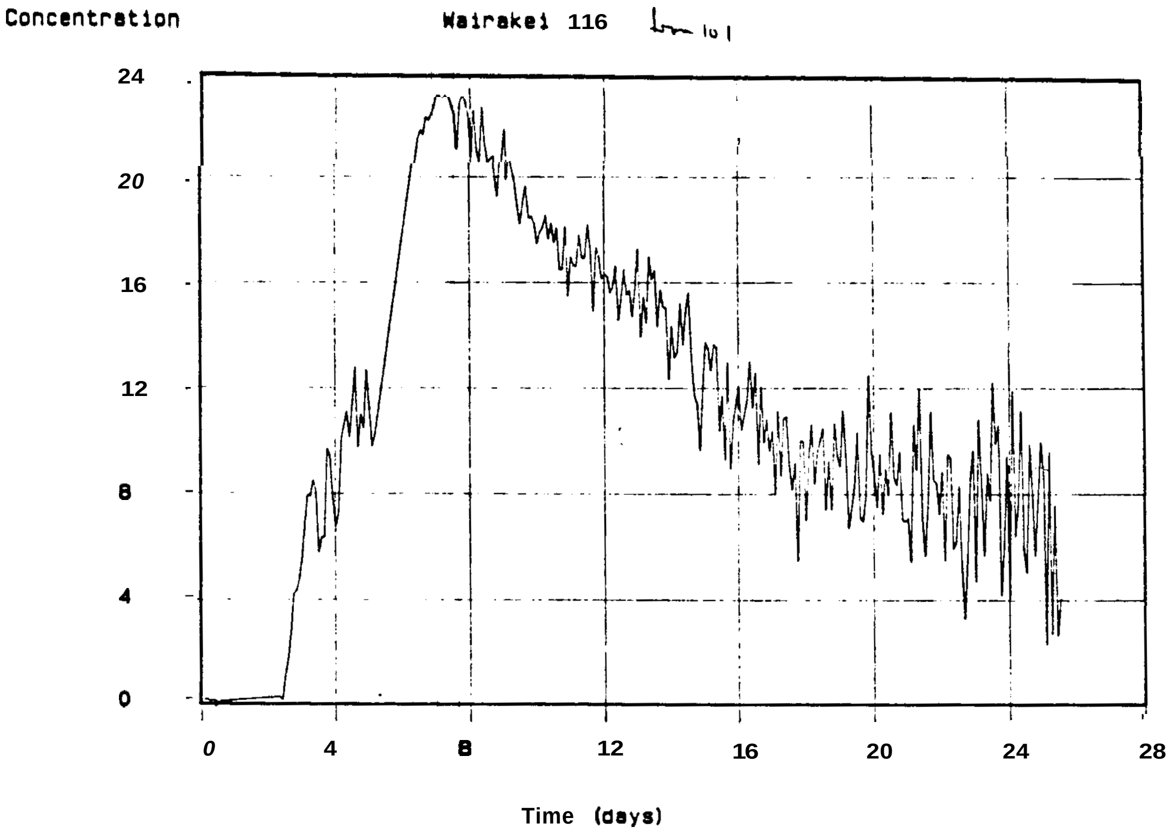

Figure 4.9: WK116 Tracer Breakthrough Curve - from WK101

Chapter 5

Experimental Objectives

The experiment had four major objectives:

- Determine the significance of adsorption in tracer tests
- Determine the effective diffusivity of a fractured **rock** through flow tests
- Measure the volumetric partition coefficient of several tracers by static adsorption tests
- Relate the volumetric and areal partition coefficients by performing fracture flow tests in which K_a the only unknown parameter

Chapter 6

Experimental Apparatus

In this experiment an aqueous solution containing tracers was flowed through a fracture. The equipment was built to allow concentration measurements to be made at the inlet, at the outlet, along the fracture and within the rock matrix.

6.1 Flow System

The flow apparatus is illustrated in Figure 6.1. **A** 6.00 in. long, 2.83 in. diameter, Berea sandstone core formed the matrix, The fracture was created by slicing the core lengthwise. Two 0.010 in. shims, sandwiched between the two halves, propped open the fracture (Figures 6.2 and **6.3).** The two halves were held together by clamps, and the outer surface was coated with epoxy to prevent leakage. Because the ends were sealed, fluid could enter or leave the core only through the fracture. The inlet, machined from plexiglass, was affixed to one end of the core with RTV silicone adhesive (Figure 6.4). The outlet was formed by cementing three hypodermic needles onto the fracture outlet with RTV. The dead volume within each needle was 0.032 ml. Leaks were plugged with either epoxy or RTV, and the core was inclined to prevent drainage.

Fluid flowed into the core from one of two constant pressure reservoirs (Figure 6.5) (Gilardi 1984). Air suction ports located below the water surface held the pressure constant. The flow rate was controlled by the difference between the elevation

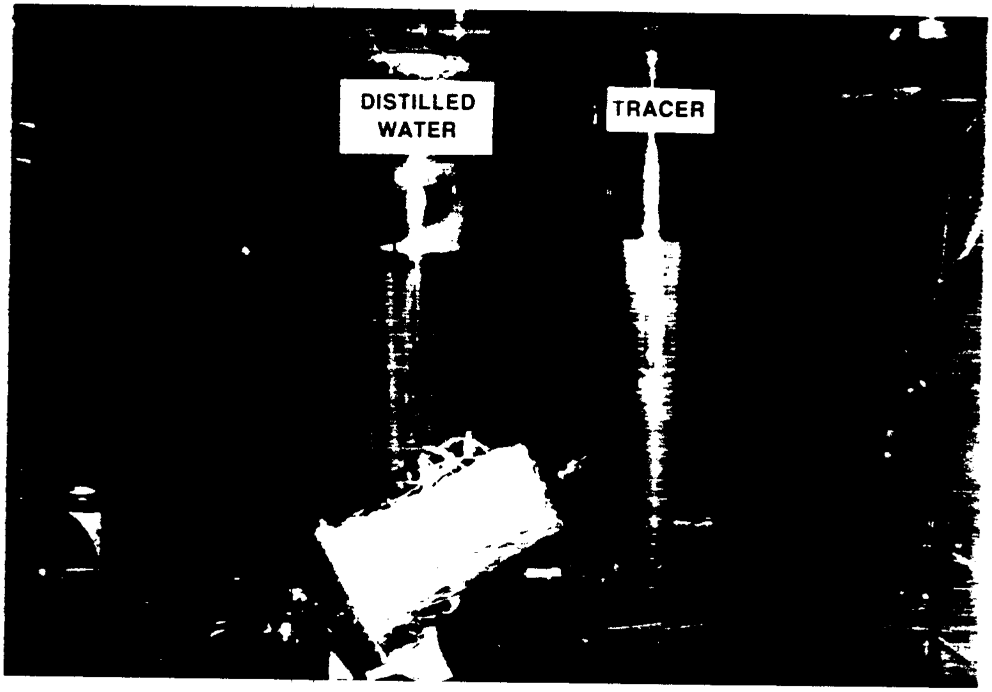

Figure 6.1: Photograph of the Flow System

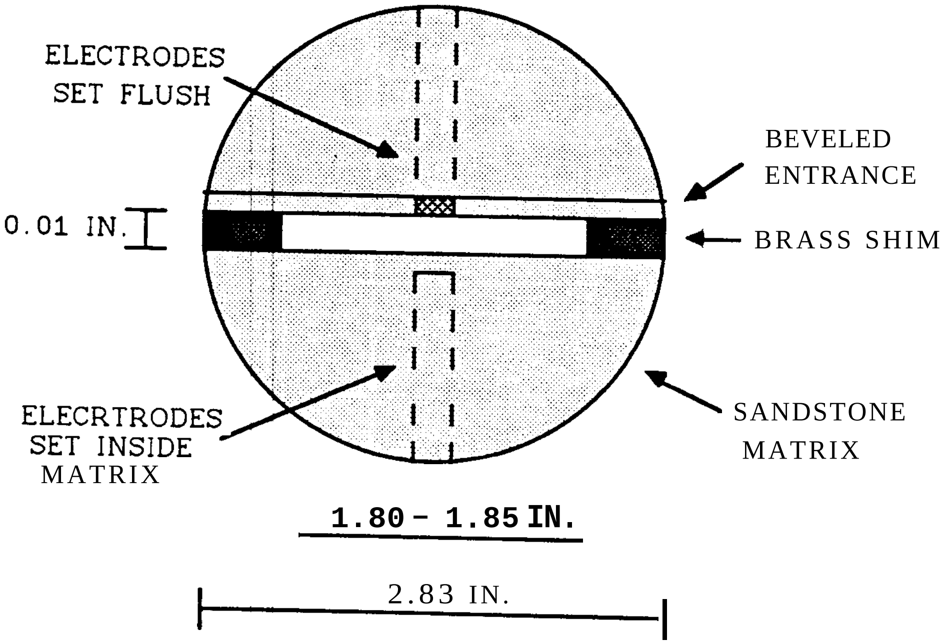

Figure 6.2: End View of the Fracture Entrance

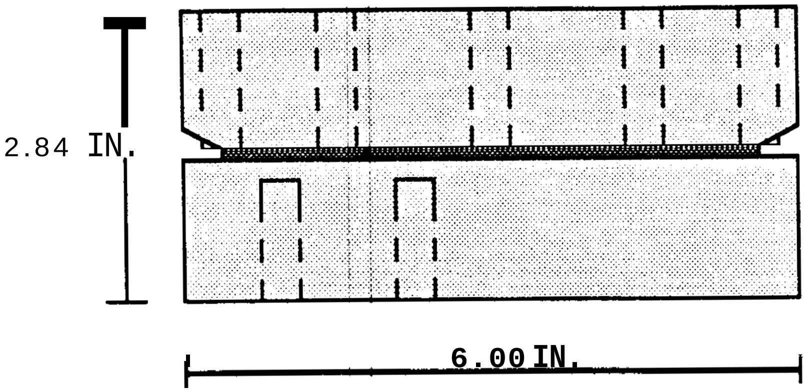

Figure 6.3: Side View of the Core

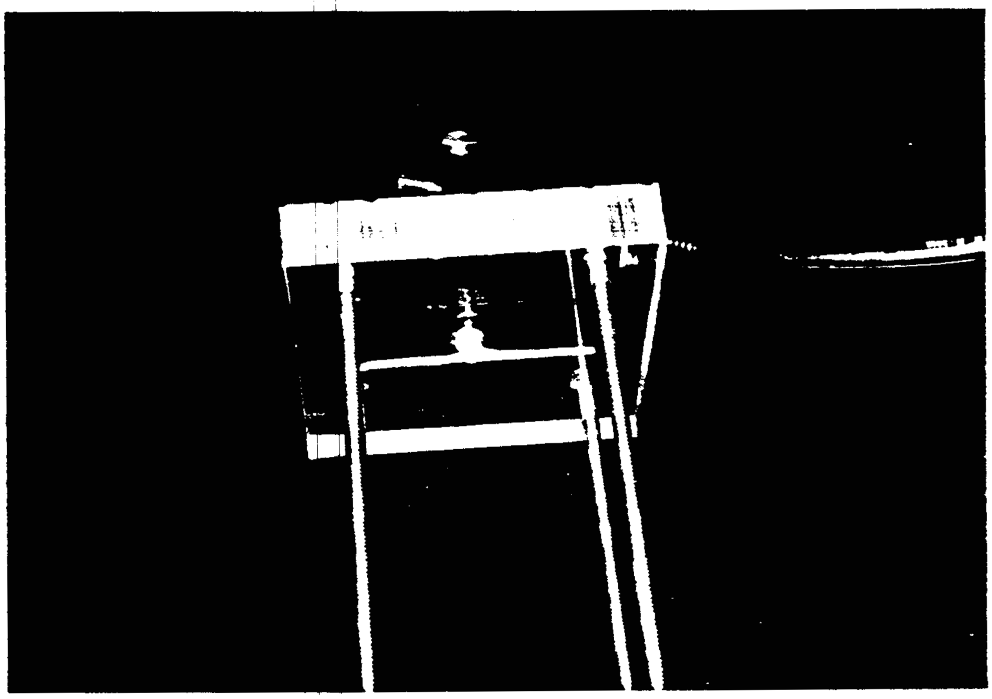

Figure 6.4: Photograph of the Inlet Plate

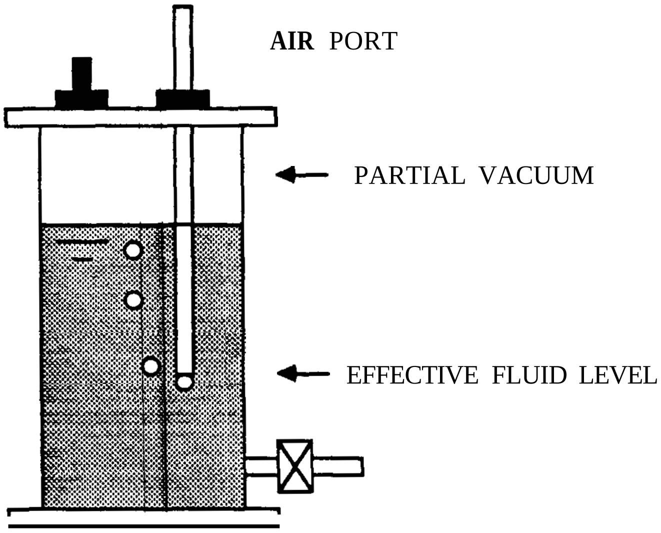

Figure 6.5: Constant Pressure Vessel

of the port and the tips of the needles. **A** valve switched flow between one vessel containing distilled water and the other containing tracer fluid. After the solution exited the outlet, samples were captured in 2 ml bottles for later analysis.

6.2 Tracer Detection System

Two detection systems were used. The first utilized electrodes to measure sodium chloride concentration in situ. The second determined alcohol concentration through gas chromatography of effluent samples collected in bottles.

6.2.1 Conductivity Measurement System

Salt concentration was measured by seven gold plated, ring disk electrodes positioned within the core (Gilardi 1984). The five electrodes recording concentration in the fracture were set flush with the wall (Figures 6.6 and 6.7). The two others were set within the other core half **0.3** in. from the fracture (Figure 6.8). **A** current

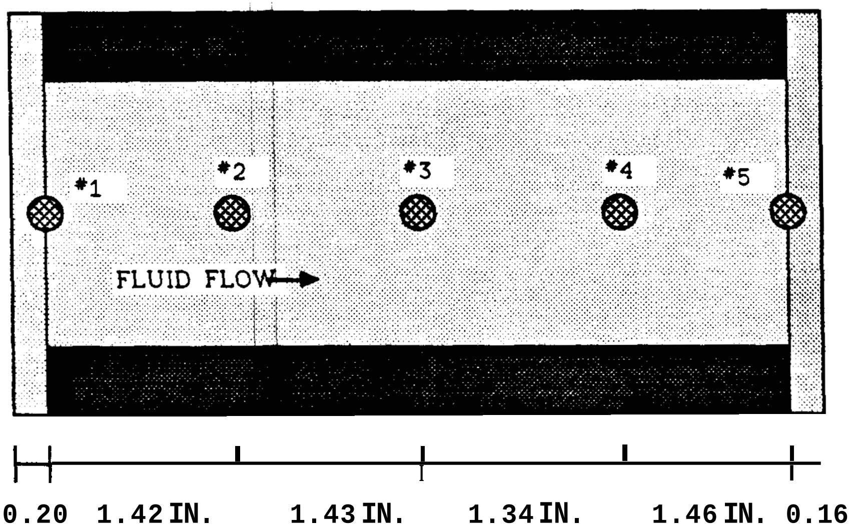

Figure 6.6: Location of Electrodes - Fracture Wall View, Top Slice

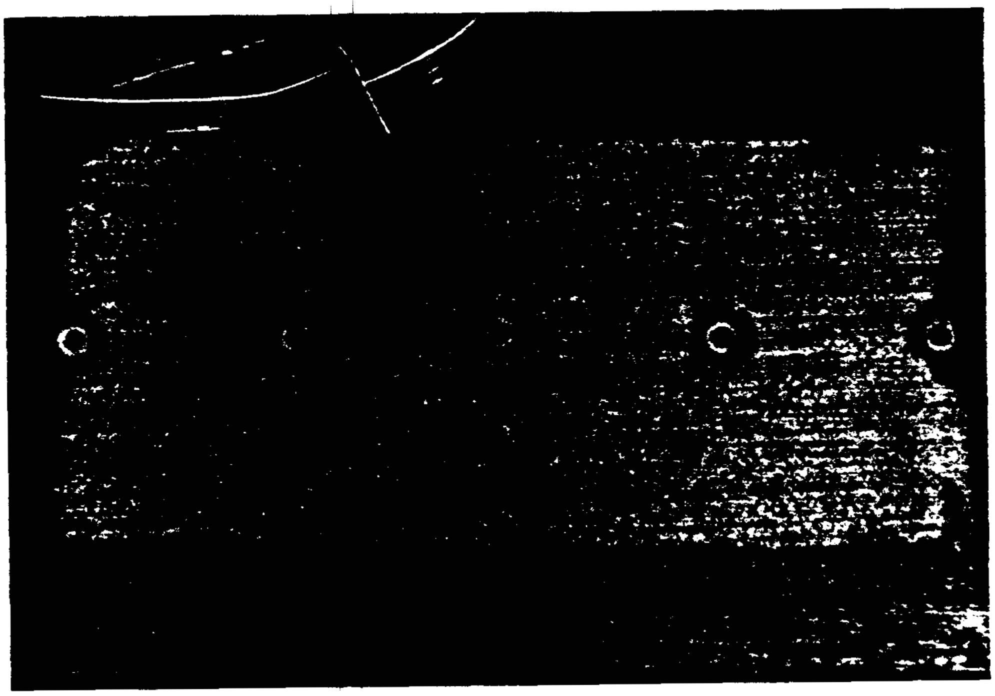

Figure **6.7:** Photograph of the Fracture Wall

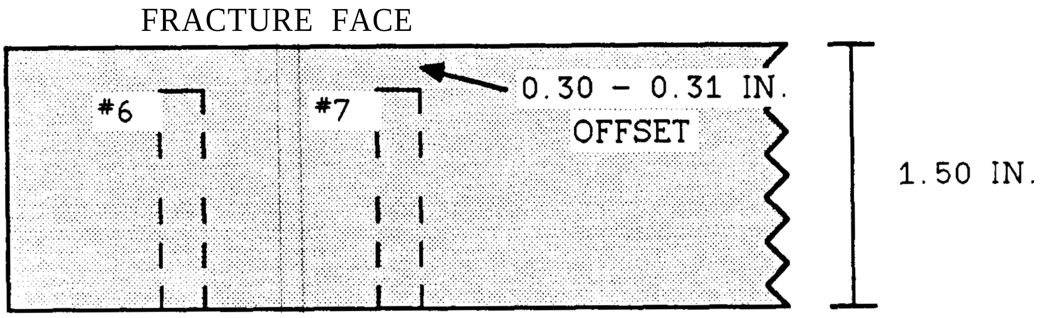

Figure 6.8: Location of Electrodes - Side View, Bottom Slice

was pulsed through each electrode and across the gap between the central charged pole and the grounded outer ring. The voltage drop across the gap was related to the concentration of salt in solution. Installation of sensors at various locations within the core enabled tracking of the tracer front.

The data collection and storage was handled by a digital-analog converter and a personal computer. A KEITHLEY/das Series 500 Measurement and Control System pulsed current to the electrodes and measured the voltage drop. The KEITHLEY received instructions from a COMPAQ personal computer. and converted the data into digital form for storage on a floppy disk. A similar system was used by Johns (1987).

The data acquisition proceeded as follows:

- A positive five volt current was output across the reference resistors and the electrodes.
- The elapsed time was determined and the voltage drop was measured.
- The time and voltages were recorded.

  - Zero voltage was output to the electrodes.
  - A negative five volt signal was output for approximately the same duration as the positive signal. The reversal of polarity prevented a charge from accumulating around the electrode.
  - Zero voltage was output to the electrode.
- The entire process was immediately repeated.

The data acquisition software can be found in Appendix F.

6.2.2 Alcohol Detection System

Alcohol content was measured by a Hewlett Packard 5880 Series Gas Chromatograph (Appendix G). The effluent drained into small 2 ml hand held sample bottles. Each time a new sample bottle was positioned, the time was recorded by toggling a control which connected the KEITHLEY to either a 1.6 volt or a 6.3 volt source (Appendix F).

6.3 Berea Sandstone

The finely grained uniform sandstone was quarried in Lorain County, Ohio. The porosity of 17.7 % and grain density of 2.65 g/cc were measured by the resaturation method. The supplier estimated that the longitudinal and transverse permeabilities were 550 md and 100 md respectively.

6.4 Tracer

The tracer solution contained 2081 ppm NaCl, 180,300 pprn ethanol and 217,500 ppm isopropyl alcohol.

Chapter 7

Experimental Procedure

Five primary tasks were required in conducting this experiment, (1) measurement of the porosity and grain density of the sandstone, (2) calibration of the chromatograph (3) measurement of the volumetric partition coefficient (K_v) and (4) performance of the flow tests.

7.1 Porosity Measurement

The porosity and grain density were measured using the resaturation method. A 65 g. sample, previously joined to the core, was heated to 120°C for approximately three hours. The dry sample was then weighed. Next the rock was saturated with water under vacuum conditions. Both the wet weight and the buoyant weight were then measured.

7.2 Chromatograph Calibration

The chromatograph was calibrated by analyzing a known solution to determine response factors for the components of the mixture. A 205,200 ppm ethanol solution and a 246,500 ppm isopropanol standard were prepared and analyzed by the gas chromatograph. Multipliers were then calculated which converted the raw data into mass and weight percentages (Table 7.1). The accuracy of the equipment is ±0.1

GC Units	Response Factors		
	Water	Ethanol	Propanol
$1\cdot 10^6$	0.1950 mg	0.2218 mg	0.2231 mg

Table 7.1: Gas Chromatograph Response Factors

weight percent.

7.3 Measurement of K_v

The volumetric partition coefficient was measured in 15 minute and 24 hour static adsorption tests. 5.0 g of crushed Berea sandstone were placed in a dry 20 ml sample bottles. 1.373 g of standard solution were then added to the bottle which was the capped to prevent evaporation. At this solid-liquid ratio the fluid completely wet the rock with no excess. Later approximately one-half ml of fluid was withdrawn from the 20 ml bottle and prepared for injection into the gas chromatograph. The sample was analyzed ten times to estimate precision. These analyses were compared to ten runs done on the unexposed solution. The difference in concentration was attributed to adsorption (Appendix I).

7.4 Flow System Operation

Conducting the flow test required four simple operations, (1) flushing the core, (2) measuring the flow rate, (3) switching flow to the tracer vessel and (4) capturing the effluent for chromatographic analysis. Prior to the injection of the tracer solution, distilled water was flowed through the fracture. This flushing action was needed to stabilize the ion concentration at the outlet. Ions dissolved into solution due to a non-equilibrium reaction between the distilled water and the rock. During this time the flow rate was measured by capturing fluid at the outlet in a graduated cylinder. After the voltages at the inlet and outlet (Electrodes #1 and #5) had stabilized for at least 5 minutes, the majority of the data acquisition began. Approximately five samples were caught at the outlet before the valve was switched from the distilled water to the tracer solution. The effluent was gathered for analysis at a rate of one sample every 15 – 20 seconds for the remainder of the test. The run was halted after the voltage at outlet had stabilized for several minutes.

Chapter 8

Experimental Results

The experiments were conducted in three major areas: (1) measurements of the Berea sandstone characteristics, (2) determination of the capacity of the rock to adsorb the alcohol tracers and (3) tracking of the tracer fronts during flow tests.

8.1 Sandstone Measurements

The porosity and grain density were measured by the resaturation method. Table 8.1 presents the data which were analyzed using following standard formulas:

$$Total\ Sample\ Vol. = (Dry\ Weight - Buoy.\ Weight)\ x\ Water\ Density \tag{8.1}$$

$$Vol.of\ Water\ Absorbed = (Dry\ Weight - Sat.\ Weight)\ x\ Water\ Density \tag{8.2}$$

$$Porosity = \frac{Vol.of\ Water\ Absorbed}{Total\ Sample\ Volume} \tag{8.3}$$

$$Grain\ Density = \frac{Dry\ Weight}{Total\ Sample\ Vol.\ x\ (1 - Porosity)} \tag{8.4}$$

Dry Weight	65.2610	g
Saturated Weight	70.5536	g
Buoyant Weight	40.587	g
Water Density	1.0	g/cc

Table 8.1: Experimental Data – Sandstone Porosity and Grain Density

Calculations yield estimates of 17.7 % porosity and 2.65 g/cc grain density. Since the expected density for a sandstone is 2.65 g/cc, the experimental values are considered reliable.

8.2 Static Adsorption Tests

The volumetric partition coefficients were measured in two static adsorption tests. The equilibrium concentrations of the tracer fluids which had been in contact with the rock for 15 minutes and for **24** hours were compared to the concentrations prior to exposure. The difference was assumed to be caused by adsorption. In the 15 minute test the concentrations of ethanol and isopropanol dropped from 20.86% to 20.26% and from 20.30% to **19.53%** respectively. Table 8.2 presents the summary of the chromatograph analysis for the **24** hour test while the complete chromatograph output (including the 15 minute test) is given in Appendix H.

The partition coefficients were estimated using the concentration data, the supplemental data presented in Table 7.3 and Equations 7.5 – 7.8. Because in situ estimates of K_v were desired, the porosity of the undamaged core and not that of the crushed sample was used in Equation 7.8. The results of these calculations are presented in Table 7.4. The effect of time was significant; K_v more than doubled over a 24 hour period.

From Equation 3.10:

$$K_v = \frac{S}{C_p} \tag{8.5}$$

where:

Run	Unexposed Tracer Ethanol Wt. %	 IPA Wt. %	24 Hr Exposure Ethanol Wt. %	 IPA Wt. %
1	20.36	19.83	18.89	18.14
2	20.14	19.62	18.84	18.08
3	20.29	19.78	18.91	18.11
4	20.21	19.65	18.71	17.89
5	20.32	19.81	18.88	18.11
6	20.34	19.76	18.80	17.99
7	20.41	19.81	18.80	18.00
8	20.31	19.74	18.80	18.00
9	20.30	19.70	18.85	18.01
10	20.37	19.80	18.85	18.02
Ave.	20.30	19.75	18.83	18.04

Table 8.2: Determination of K_v - Summary of Chromatograph Results

	15 min Test	24 hr Test
Rock Mass	4.997 g.	4.994 g.
Mass of Solution	1.328 g.	1.373 g.
Solution Density	0.894 g/cc.	0.894 g/cc

Table 8.3: Determination of K_v - Supplemental Data

Component	15 min. Test	24 hr. Test
Ethyl Alcohol	0.0178	0.0468
Isopropyl Alcohol	0.0236	0.0568

Table 8.4: Estimates of K_v

$$S = \frac{mass\ of\ tracer\ adsorbed\ on\ rock}{bulk\ volume\ of\ rock} \tag{8.6}$$

$$C_p = tracer\ concentration\ at\ equilibrium \tag{8.7}$$

and

$$Bulk\ Volume\ of\ Rock = \frac{Mass\ of\ Rock}{Rock\ Density \times (1 - Porosity)} \tag{8.8}$$

8.3 Flow Tests

Although seven complete flow tests were conducted, only one provided enough good data to model. The major problem was electrode malfunctions, most likely caused by the attachment of air bubbles to the electrodes. Gilardi (1984) witnessed this phenomenon when he performed experiments with his Hele-Shaw cell. Additional difficulties were encountered due to cross-talk between input channels on the KEITHLEY AMM1 board.

Five successive runs were conducted without success. Runs 1 and 2 could not be interpreted due to anomalous voltage responses later attributed to air bubbles. Runs 3, 4, and 5 were performed while attempts were made to modify the equipment to correct the problem. The results of these tests are not considered reliable.

Although Run 6 furnished good data, it also provided an example of an electrode malfunction. Figures 8.1 – 8.5 show voltage vs. time plots for each sensor. Electrode #2 does not exhibit the relatively sharp profile that is seen in the sensors positioned upstream and downstream (#1 and #3) while Electrode #4 hardly responds to the passing front.

Cross-talk can be seen by comparing the voltage records of Electrodes #3 and #5 (Figure 8.6). The voltage drop across Electrode #5 tracked that of #3 before the outlet sensor responded to its own signal. In an attempt to investigate this phenomenon, the KEITHLEY was disconnected from the core. A 1.6 voltage drop was then placed across each input channel of the AMMl board. All the channels

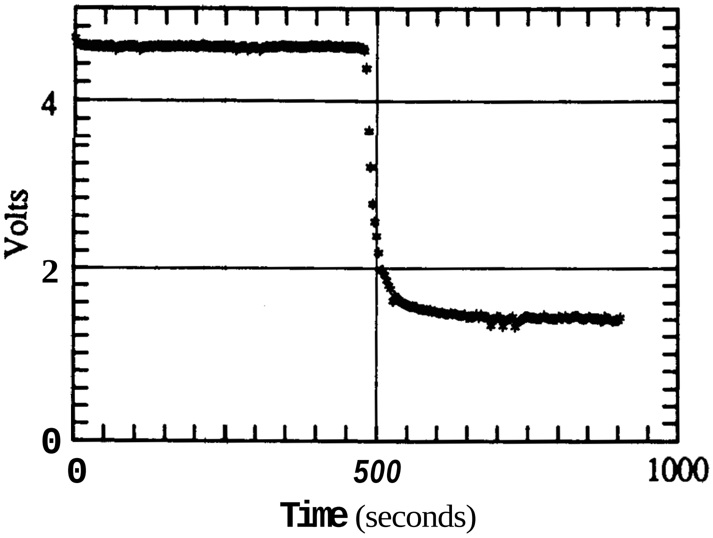

Figure 8.1: Run 6 – Electrode #1 (Inlet)

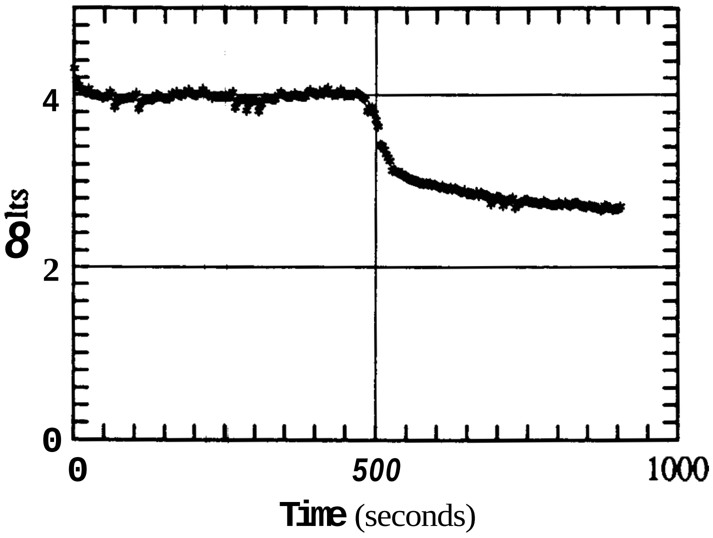

Figure 8.2: Run 6 – Electrode #2 (L/4)

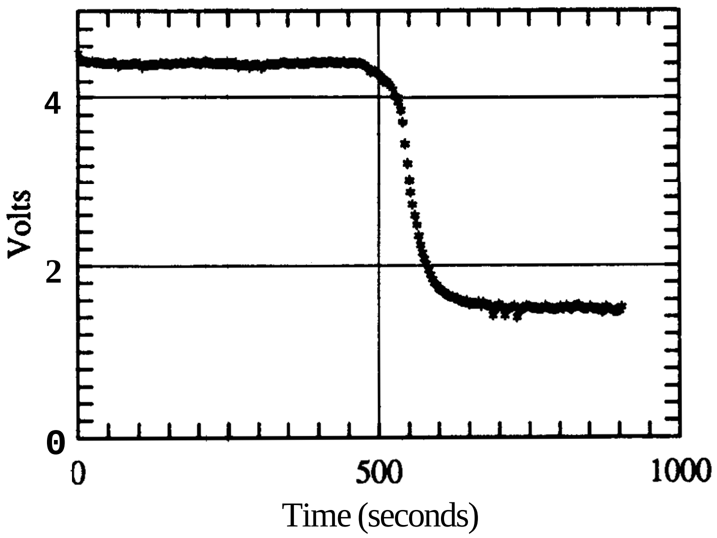

Figure **8.3:** Run 6 – Electrode #3 (Midpoint)

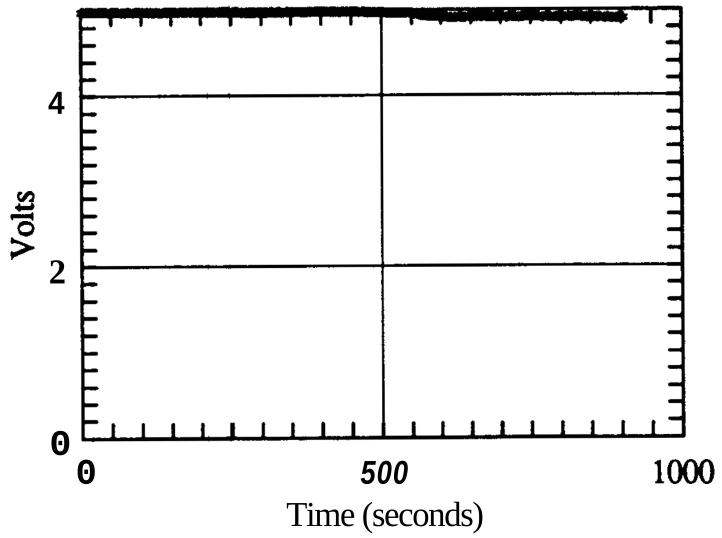

Figure **8.4:** Run 6 – Electrode #4 (3L/4)

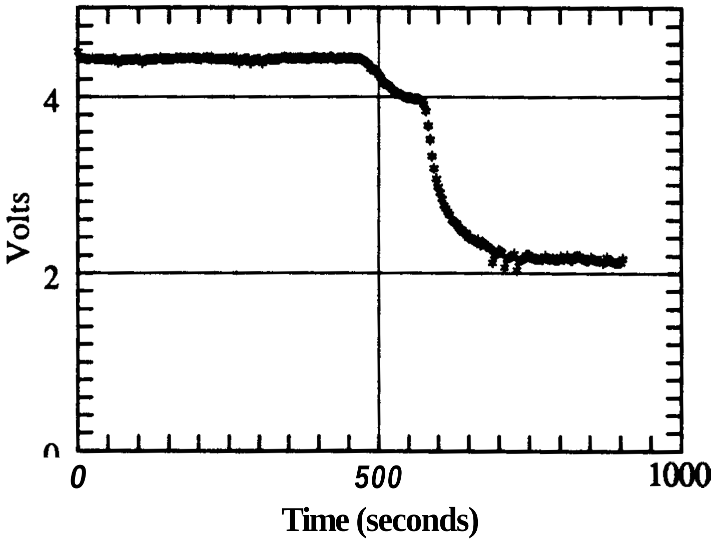

Figure *8.5:* Run 6 – Electrode #5 (Outlet)

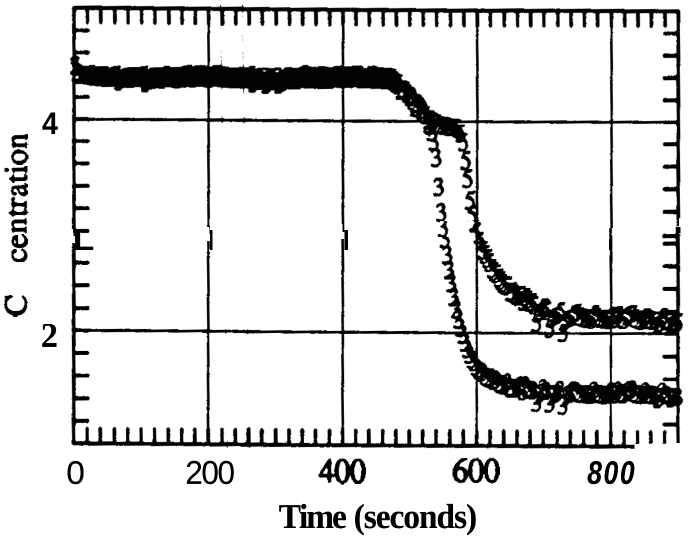

Figure 8.6:. Comparison of Voltage Response - Run 6, Electrodes #3 and #5

were seen to respond in varying degrees to inputs in the other channels. Following this observation, Electrodes #6 and #7 were disconnected and then Runs 6 and 7 were conducted.

8.3.1 Conversion of Voltages to Salt Concentration

The voltages were converted to concentrations by assuming that the voltage drop and the concentration are related by a straight line function on a semilog plot of voltage vs. concentration (Gilardi 1984). The following formula was used:

$$Concentration\ (ppm.) = C_2(C_1 - \log V) \tag{8.9}$$

where

$$C_1 = \log V_0 \tag{8.10}$$

$$C_2 = \frac{Tracer\ Conc.}{(\log V_0 - \log V_{tracer})} \tag{8.11}$$

Use of Equation 8.9 requires calibration of the electrodes to distilled water (0 ppm) and the concentration of the tracer solution (2081 pprn.) The voltage drop registered for V_0 was considered to be the average of the voltages from 250 – 450 s. During this period the response had stabilized prior to the injection of the tracer. Although some background concentration was undoubtably present due to dissolution of the rock, the amount of dissolved matter in solution was probably less than 10 ppm (Johns 1987). The voltage drop for 2081 ppm, V_{tracer} was estimated as the average of the voltages from 850 – 900 s. By this time it was assumed that the concentration at the outlet had asymptotically approached the injection value. V_0, V_{tracer} and the resultant constants used in the conversion formula are given in Table 8.5. Figures 8.7 – 8.9 show plots of dimensionless concentration (Conc./2081 ppm.) vs. time.

Electrode	V_0	V_{tracer}	C_1	C_2
#1	4.577	1.403	0.6606	4052
#3	4.394	1.480	0.6429	4403
#5	4.423	2.134	0.6457	6575

Table 8.5: Voltage Conversion Coefficients

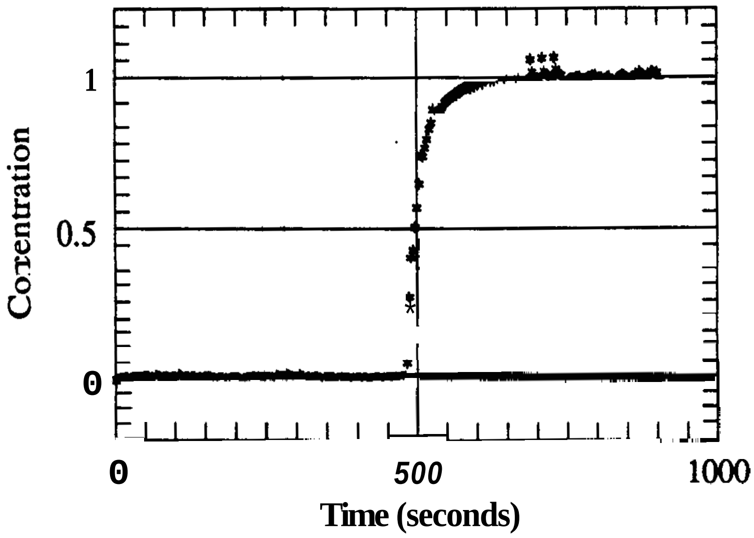

Figure 8.7: Dimensionless Salt Concentration at Electrode #1 (Inlet)

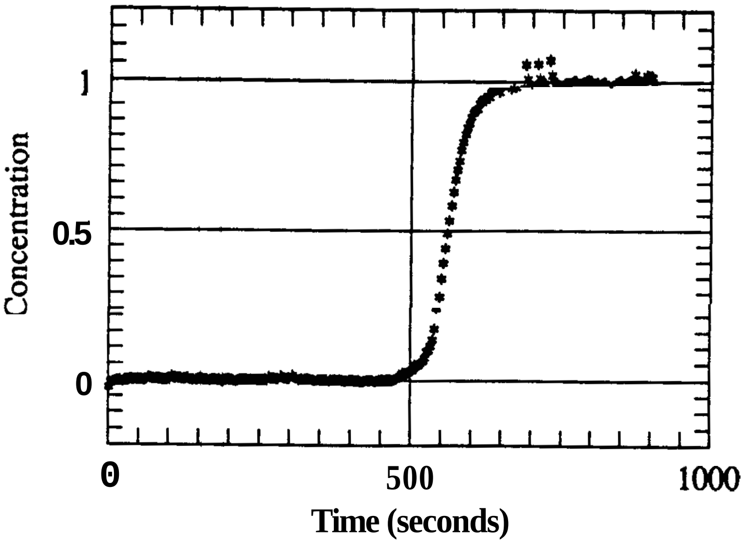

Figure 8.8: Dimensionless Salt Concentration at Electrode #3 (Midpoint)

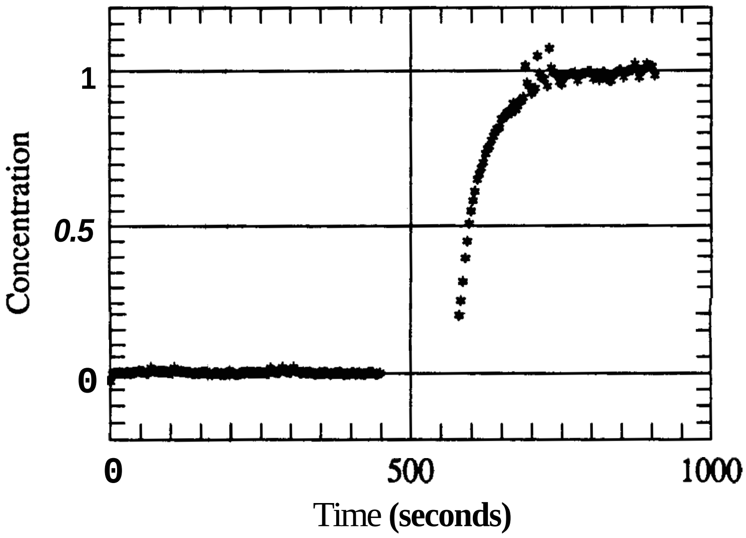

Figure 8.9: Dimensionless Salt Concentration at Electrode #5 (Outlet)

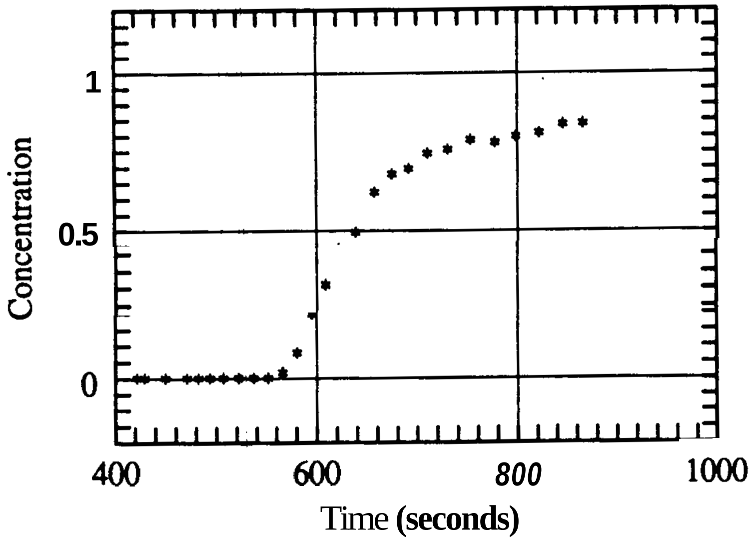

Figure 8.10: Dimensionless Alcohol Concentration vs. Time

8.3.2 Alcohol Concentrations

The effluent was captured in sample bottles and then analyzed by a gas chromatograph. The results of this analysis are presented in Table 8.6. Figure 8.10 plots the sample concentrations vs. the midpoint of the time interval over which they were collected. The raw data are presented in Appendices H and I.

	Weight %		C/C_0		Time	Average
Sample	Ethanol	Propanol	Ethanol	Propanol	Interval (s)	Time (s)
53					419.2 - 424.2	421.7
54					425.4 - 433.5	429.5
55					434.2 - 465.2	449.8
56					466.0 - 476.7	471.4
57					477.8 - 487.7	482.8
58					488.4 - 499.6	494.0
59					501.5 - 512.7	507.1
60					513.4 - 530.1	521.8
61					531.3 - 543.1	537.2
62					544.2 - 558.6	551.5
63	0.28	0.39	1.55	1.79	559.2 - 572.5	565.9
64	1.40	1.94	7.76	8.92	573.7 - 587.4	580.6
65	3.55	4.68	19.69	21.52	588.1 - 602.4	595.3
66	5.56	7.02	30.84	32.28	603.5 - 613.5	608.6
67	7.97	10.05	44.20	46.21	614.2 - 629.4	621.8
68	8.89	10.56	49.31	48.55	630.6 - 646.8	638.7
69	11.22	13.72	62.23	63.08	648.1 - 666.7	657.4
70	12.22	14.86	67.78	68.28	668.1 - 682.5	675.3
71	12.53	15.21	69.50	69.93	683.6 - 699.2	691.4
72	13.40	16.19	74.32	74.44	700.4 - 720.3	710.4
73	13.65	16.48	75.71	75.77	720.9 - 740.2	730.6
74	14.21	17.26	78.81	79.36	740.8 - 765.0	752.9
75	14.04	16.99	77.87	78.11	766.1 - 788.9	777.5
76	14.39	17.40	79.81	80.00	790.0 - 808.0	799.0
77	14.55	17.59	80.70	80.87	809.9 - 833.7	821.8
78	15.06	18.27	83.53	84.00	834.3 - 857.5	845.9
79	15.09	18.28	83.69	84.05	858.0 - 874.0	866.0

Table 8.6: Results of Chromatograph Runs vs. Time

Chapter 9

Modeling of the Experimental Data

The data were analyzed in three steps (1) selection of a model to specify the inlet condition (2) analysis of the salt concentration data (3) analysis of the alcohol data.

9.1 Inlet Condition

Solution of the matrix diffusion model requires the specification of an inlet boundary condition. The solutions presented in Chapter 3 are for step and pulse injections. Inspection of data recorded by the inlet sensor reveals that this system did not have a simple change in inlet concentration. Johns (1987) showed that the concentration at the inlet must be closely matched for the matrix diffusion model to yield useful results. He used a complementary error function to specify the boundary condition. This analysis also used a complementary error function but one of a slightly different nature:

$$C_{fD} = \xi erfc_i \left[\frac{\sigma_i}{\sqrt{t - \theta_i}} \right] \tag{9.1}$$

where ξ, σ_i and θ_i are determined by performing nonlinear regression on the inlet concentration data. θ_i is defined as the time at which the tracer enters the core. σ_i is the inlet dispersion term, and ξ_i is a scaling factor. The inlet condition specifies the constant A_2 in Equation B.42. Equation 9.2 is Equation B.42 in dimensional form.

$$\overline{C}_{fD} = A_2 \exp\left[-\frac{x}{L}R_D t^*\right] \exp\left[-\frac{2x\sqrt{D_e K_D}t^*}{bL}\sqrt{s}\right] \tag{9.2}$$

When x $= 0$, A_2 is equal to the Laplace transform of the inlet condition:

$$A_2 = \frac{\xi_i}{s}\exp\left[-\theta_i s\right]\exp\left[-\sigma_i\sqrt{s}\right] \tag{9.3}$$

Substituting Equation 9.3 into Equation 9.2:

$$\overline{C}_{fD} = \frac{\xi}{s}\exp\left[-\left(\frac{x}{L}R_D t^* + \theta_i\right)s\right]\exp\left[-2\left(\frac{\sqrt{D_e K_D}t^*}{b} + \sigma_i\right)\sqrt{s}\right] \tag{9.4}$$

Let

$$\sigma_f = \frac{\sqrt{D_e K_D}t^*}{b} \tag{9.5}$$

$$\theta_f = \frac{x}{L}R_D t^* \tag{9.6}$$

$$\sigma_{total} = \sigma_i + \sigma_f \tag{9.7}$$

$$\theta_{total} = \theta_i + \theta_f \tag{9.8}$$

and

$$\xi_{total} = \xi_i \xi_f \tag{9.9}$$

then inversion of Equation 9.4 yields:

$$C_{fD} = \xi_{total} erfc\left[\frac{\sigma_{total}}{\sqrt{t - \theta_{total}}}\right] \tag{9.10}$$

Equation 9.10 is of the same form as the inlet condition. This allows use of the same nonlinear regression program to calculate both the inlet and total regression parameters. Once these are known, σ_f, the fracture dispersion parameter, and θ_f, the breakthrough time, can be determined.

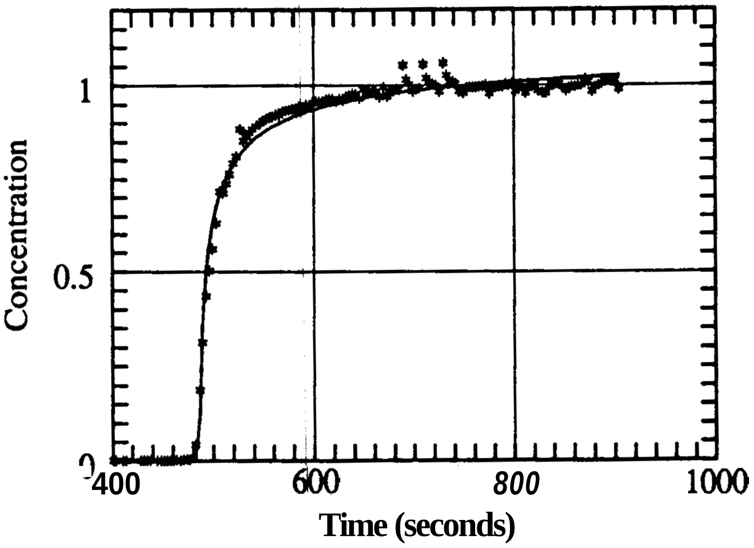

Figure 9.1: Model Match – Dimensionless Salt Concentration at the Inlet

9.2 Modeling of the Salt Tracer

The data matched the theory well. Using the complementary error function as the inlet condition, the matrix diffusion model matched the progress of the salt tracer through the fracture. The effective diffusivity, estimated with the model, was on the same order of magnitude as that computed with Equation 4.1.

9.2.1 Nonlinear Regression Fit

The data were fit to Equation 9.10 using a least squares nonlinear regression program. The regression subroutine, VARPRO, and the front end driving program are given in Appendices J and K. Figures 9.1 – 9.3 illustrate the match, while the regression parameters are listed in Table 9.1. The inlet function condition closely matched the fairly sharp front recorded by the inlet sensor. The fit at the midpoint electrode (Figure 8.2) was not quite as good because the leading edge of the front was diffuse. This dispersion could be the result of channeling or cross-talk between

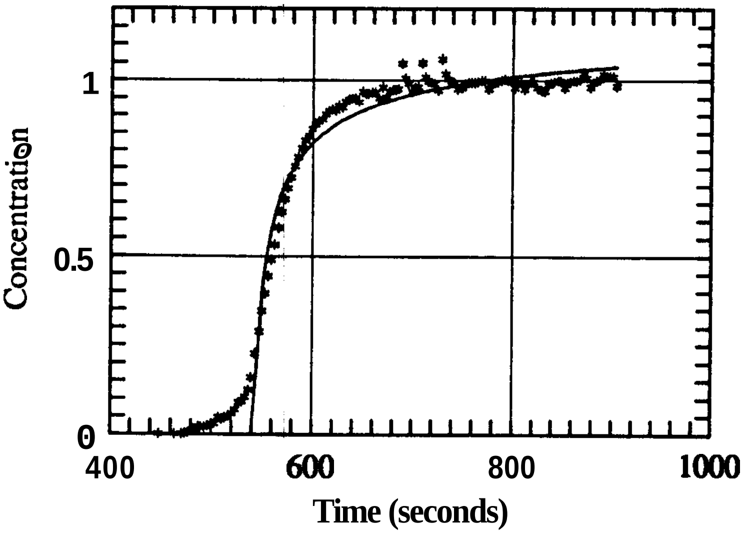

Figure 9.2: Model Match – Dimensionless Salt Concentration at the Midpoint

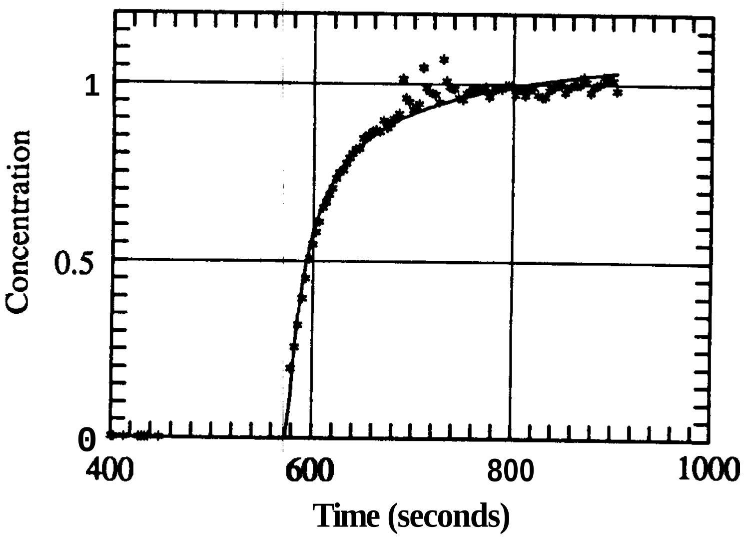

Figure 9.3: Model Match – Dimensionless Salt Concentration at the Outlet

	Location		
	Inlet	Midpoint	Outlet
ξ_{total}	1.125	1.195	1.230
σ_{total}	1.612	2.217	2.591
θ_{total}	484.5	539.5	573.8
ξ_f		1.062	1.093
σ_f		0.605	0.979
θ_f		55.0	89.3

Table 9.1: Results of 'NonlinearRegression - Salt Concentration

channels on the AMM1. Interestingly exclusion of the leading edge data from 475 – 539 s did not change the regression parameters to the fourth significant figure. The data between 450 and 576 s were not included in the regression analysis of the outlet sensor (see Chapter 8.3), and Equation 9.10 fit the remaining data well (Figure 9.3).

Inspection of the numerical parameters reveals that the results did not agree completely with theory. As time approached infinity, the concentration should have approached 1.0; however, the laast squares fit for the downstream data sets gave ξ_f values between 1.05 and 1.10. If more data had been collected, regression analysis would have yielded lower final concentrations. Additional data was not necessarily desirable, though, because the effect of honoring the late time response would have been to place less emphasis on the more important early time breakthrough.

The experimental relationship between θ_f at the midpoint and the exit also diverged from expectations. θ_f for the midpoint sensor should have been one-half ($x/L = 0.5044$) of the outlet value. The actual ratio, 0.616, was 22 % higher than expected and indicated possible channeling.

9.2.2 Estimation of the Effective Diffusivity

The effective diffusivity was estimated using the regression parameters. If the rock properties were isotropic, the ratio of σ_f/θ_f measured at all points within the fissure should have been constant:

	Midpoint	Outlet
σ_f	0.605	0.979
θ_f	55.0	89.3
σ_f/θ_f	0.0110	0.0110
$D_e(cm^2/s)$	$4.41 \cdot 10^{-7}$	$4.38 \cdot 10^{-7}$

Table 9.2: Estimation of D_e Using Nonlinear Parameters

$$\frac{\sigma_f}{\theta_f} = \frac{\sqrt{D_e K_D}}{b R_D} \tag{9.11}$$

Assuming no adsorption, K_D was equal to the porosity, and R_D equaled 1.0. These values were used to construct Table 9.2 in which the two estimates of effective diffusivity differ by less than 1%.The confidence in the data was greatly enhanced by the close agreement.

The effective diffusivity was also estimated using Equation **4.1** presented by Perkins and Johnston in 1963. Equation **4.1** repeated:

$$D_e = \frac{D_0}{F\phi}$$

where for a sandstone (Equation **4.3** repeated):

$$F = \frac{0.62}{\phi^{2.15}}$$

Using $1.3 \cdot 10^{-5} cm^2/s$ as the molecular diffusivity of sodium chloride in water (Jost 1960), an effective diffusivity of $2.86 \cdot 10^{-6} cm^2/s$ was calculated. The diffusivity estimated with the nonlinear parameters was 15% of this value. One explanation is that the fracture face was modified during construction of the fissure. The pores in the fracture walls did appear'to be plugged with dust after they had been sanded flat. Because the two estimatas utilizing the nonlinear parameters agreed so well and these measurements were made in situ following the alteration, $4.40 \cdot 10^{-7} cm^2/s$ was considered the better estimate.

In addition to D_e, the flow rate was also estimated. θ_f at the outlet was assumed to be the breakthrough time for a nonsorbing tracer, t^*. Given the 5.65 inches

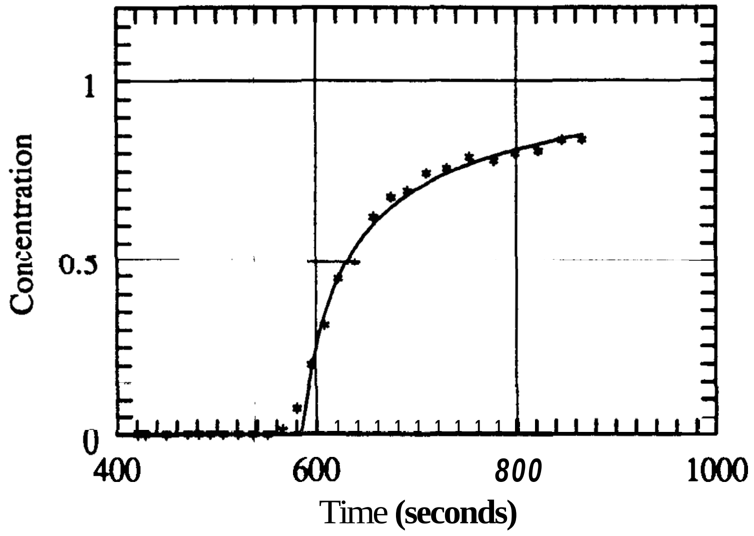

Figure 9.4: Model Match – Dimensionless Ethanol Concentration at the Effluent

distance between Electrodes #1 and #5 a 0.316 ft/min flow velocity and a 1.13 ml/min flow rate were calculated.

9.3 Modeling the Alcohol Tracers

The alcohol breakthrough curves were also fit using the programs given in Appendices J and K. Even though isopropyl alcohol adsorbed more than ethanol, the dimensionless concentration of isopropanol exceeded that of ethanol throughout the test. This phenomenon was due to ethyl alcohol's higher molecular diffusivity.

9.4 Nonlinear Regression Fit

As with the salt concentration, Equation 9.10 fit the alcohol data well (Figures 9.4 and 9.5). Again the mechanism causing the additional dispersion at the front was not matched by the model. Table 9.3 lists the regression parameters for the three

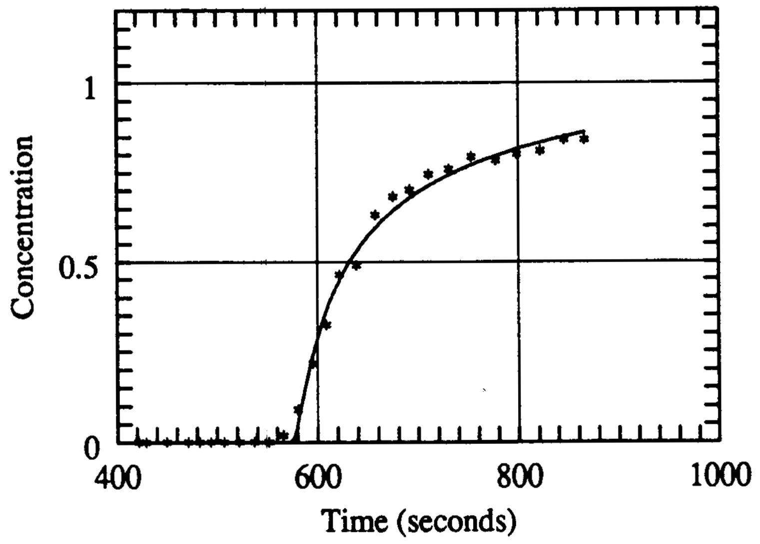

Figure 9.5: Model Match – Dimensionless Isopropanol Concentration at the Effluent

solutes measured at the outlet. Calculations of the fracture parameters assumed that the inlet conditions for the salt and alcohol were identical. Comparison of the σ_f values reveals that the alcohols are much more dispersed than the salt. The increased dispersion was due to both increased adsorption and end effects. The salt concentration was measured with an electrode positioned within the core while the chromatograph samples were captured after the fluid had flowed past the sensor

	Salt	Ethanol	Propanol
ξ_{total}	1.230	1.151	1.220
σ_{total}	2.591	3.981	4.578
θ_{total}	573.8	579.7	570.5
ξ_f	1.093	1.023	1.085
σ_f	0.979	2.369	2.966
θ_f	89.3	95.2	86.0

Table 9.3: Results of Nonlinear Regression – Outlet

Chapter 10

Conclusions

1) Adsorption is a significant factor in the flow of tracers through through fractured rock, Adsorption can occur in two places, on the fissure wall and in the matrix. The effect of areal adsorption is to translate the entire breakthrough curve in time. Adsorption within the rock pores tends to increase dispersion. In the case of a pulsed injection, volumetric adsorption increases the time between breakthrough and the peak concentration. Estimating fracture aperture from tracer tests requires an accurate estimation of the partition coefficients.

2) The fracture aperture may be determined by visually examining tracer breakthrough curves. Accurate estimation of fissure width requires good appraisals of the times to breakthrough and peak concentration. Choosing the correct values of $R_D t^*$ and t_p is not always easy especially when analyzing radioactive tracer data.

3) An analytical solution is available to the matrix diffusion model for any inlet boundary condition which can be expressed in terms of a complementary error function.

4) The effective diffusivity can be determined from flow tests through a fractured core. Accurate estimates rely an adequate sampling frequency.

5) The measurements involving salt concentration are considered accurate because the ratio of σ_f/θ_f was constant along the fracture. Since the data are good, the ratio of θ_f at the midpoint to θ_f at the exit is an indication of channeling within the fracture.

Chapter 11

Recommendations

1) An similar experiment should be repeated with two changes. a) The sampling frequency should exceed $25/t^*$. (The salt concentration was measured at a rate of $30/t^*$.) b) The concentrations should all be measured at the same points to allow comparison of the tracers.

2) The adsorptive behavior of field tracers is not known. Adsorption tests should be performed with tracers and **rocks** found in geothermal fields.

Chapter 12

Nomenclature

A_1, A_2, A_3, A_4	constants of integration
A_D	dimensionless coefficient
b	fracture aperture, $[L]$
b_D	dimensionless fracture aperture
C	concentration (mass/volume), $[m/L^3]$
C_D	dimensionless concentration (C/C_0)
C_f	concentration in fracture (mass/liquid volume), $[m/L^3]$
C_{fD}	dimensionless concentration in fracture (C_f/C_0)
C_m	concentration in matrix (mass/volume of rock), $[m/L^3]$
C_p	concentration in pores (mass/liquid volume), $[m/L^3]$
C_{pD}	dimensionless concentration in pores (C_p/C_0)
C_0	injection or reference concentration, $[m/L^3]$
C_{fD}	dimensionless fracture concentration (C_f/C_0)
C_1, C_2	constants in conversion of voltage to concentration
D_a	apparent diffusivity $(D_e/(\phi + K_v))$, $[L^2/t]$
D_D	dimensionless diffusivity $(D_e t^*/L^2)$
D_e	effective diffusivity, $[L^2/t]$
D_0	molecular diffusivity in water, $[L^2/t]$
F	formation factor
h	fracture height, $[L]$

k	coefficients in adsorption isotherms
K_a	areal partition coefficient, $[L]$
K_v	volumetric partition coefficient, $[porevol./bulkvol.]$
$K_d\rho_p$	volumetric equilibrium constant $(\phi + K_v)$
K_D	dimensionless partition coefficient $(\phi +$ K,)
L	fracture length, $[L]$
M	mass of injected tracer, $[m]$
Q	total volume **flow** rate, $[L^3/t]$
R	retardation factor, $[dimensionless]$
R_D	retardation factor $(1 + \frac{2}{b}K_a)$
s	the Laplace variable
S	concentration of mass adsorbed on rock (mass/rock volume), $[m/L^3]$
$Smax$	maximum concentration of tracer adsorbed on rock
t	time, $[t]$
t_D	dimensionless time (t/t^*)
t_p	time from injectian to peak concentration, $[t]$
t_{pD}	dimensionless peak time (t_p/t^*)
t^*	t-star (L/v), $[t]$
Δt	injection time, $[t]$
Δt_D	dimensionless injection time $(\Delta t/t^*)$
v	velocity of flow in fracture, $[L/t]$
V_0	voltage drop across an electrode exposed to distilled water
V_{tracer}	voltage drop across an electrode exposed to a tracer solution
x	length along fracture axis, $[L]$
x_D	dimensionless fracture length
y	distance normal to fracture axis into matrix, $[L]$
y_D	dimensionless distance into the matrix
α	regression shape parameter, $[dimensionless]$
β	regression breakthrough parameter, $[1/t]$
θ	regression breakthrough time, $[t]$

ξ	regression scaling factor, *[dimensionless]*
σ	regression dispersion factor, $[\sqrt{t}]$
ϕ	porosity
ω_D	dimensionless variable

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Appendix A

Adsorption

The purpose of this appendix is to suggest several considerations for choosing a geothermal tracer and a corresponding adsorption model. These considerations may include:

Does the tracer chemically react with the rock?
What is the extent of surface coverage?
How quickly does the process reach equilibrium?
Is the reaction reversible?
What type of isotherm should be chosen?
Are temperature effects significant?

Adsorption may be divided into chemical and physical processes. Physical adsorption involves van der Waals interactions between the adsorbent and adsorbate. In the process of accommodation a molecule loses its kinetic energy and adheres to the surface. The molecule vibrates in a shallow potential energy well, and sometimes the atoms shake themselves from the surface. Since the attractive forces are relatively weak, a physically adsorbed molecule normally retains its integrity. Chemical adsorption is the result of chemical bonding. This process is normally much stronger than physical adsorption. In fact the adsorbed molecule may be torn apart (Atkins 1982). Of the two processes physical adsorption is more likely to be reversible.

Tracers may also be categorized into two groups, electrolytes and nonelectrolytes. Electrolytes are adsorbed through electromagnetic forces. Ions of opposite sign are attracted to a charged surface. Those of the same sign are repelled (Jaycock 1981). Specific chemical reactions may also occur at the interface (Adamson 1982). In addition to simple attraction-repulsion, ion exchange is possible. An example is the interaction of a KC1 mud with sodium-montmorillonite clay. The potassium replaces the sodium in the crystal lattice and liberates the second element in the process.

Nonelectrolytes also adsorb. Adamson (1982) describes their general behavior: "a polar (nonpolar) adsorbent will preferentially adsorb the more polar (nonpolar) part of a nonpolar (polar) solution". Polarity refers to ability to engage in hydrogen bonding or dipole interactions. The adsorption coefficient is larger where there are specific opportunities for hydrogen bonding. Another general principle, the Lundelius Rule, states that the less soluble the solute the more likely it is to adsorb. This rule of thumb also applies to electrolytes.

Many isotherms are available to model adsorption. Although one may predict which model will be suitable in advance, experimental confirmation is required. In his **1973** paper, Boast summarizes ten adsorption models used in groundwater studies. They are presented **below:**

Equilibrium Models

Linear:

$$S = k_1C + k_2 \tag{A.1}$$

Freundlich:

$$S = k_3C^{k_4} \tag{A.2}$$

Competition between ions a and *b:*

$$S_a = S_b(k_5C_a/C_b) \tag{A.3}$$

Modified Kjelland:

$$S = S_{max} \frac{C/C_0}{\frac{C}{C_0} + \left(1 - \frac{C}{C_0}\right)} \exp[\ln k_5 + k_7(1 - 2C/C_0)] \tag{A.4}$$

Nonequilibrium Models

Linear:

$$\partial S/\partial t = kg(k_1 C + k_2 - S) \tag{A.5}$$

Freundlich:

$$\partial S/\partial t = k_9(k_3 C^{k_4} - S) \tag{A.6}$$

Competition between ions a and *b:*

$$\partial S_a/\partial t = k_{10} \left(C_a S_b - \frac{1}{k_5} S_a C_b\right) \tag{A.7}$$

Lindstrom and Boersma (1970):

$$\partial S/\partial t = k_{11}(S_{max} - k_3 C) \sinh \left[k_{12} \left(1 - \frac{k_3 C}{S_{max}}\right)\right] \tag{A.8}$$

Lindstrom, Boersma and Stockard (1971):

$$\partial S/\partial t = k_{13} e^{k_{14} S} \left(k_{15} C e^{-2k_{14} S} - S\right) \tag{A.9}$$

Appendix B

Solution of the Matrix Diffusion Model

B.1 Governing Equations

$$(1+\frac{2}{b}K_a)\frac{\partial C_f}{\partial t}=\frac{2}{b}D_e\frac{\partial C_f}{\partial y}\mid_{y=0}-v\frac{\partial C_f}{\partial x} \tag{B.1}$$

$$\frac{\partial C_p}{\partial t}=\frac{D_e}{\phi+K_v}\frac{\partial^2 C_p}{\partial y^2} \tag{B.2}$$

B.2 Boundary Conditions

$$C_f\mid_{y=0}=C_p\mid_{y=0} \tag{B.3}$$

$$C_f=C_0;\ for\ x=0 \tag{B.4}$$

$$\lim_{x\to\infty}C_f=0 \tag{B.5}$$

$$\lim_{x\to\infty}C_p=0 \tag{B.6}$$

B.3 Initial Conditions

$$C_f = 0;\ for\ t \leq 0 \tag{B.7}$$

$$C_p = 0;\ for\ t \leq 0 \tag{B.8}$$

B.4 Dimensionless Groups

The following dimensionless groups are defined:

$$C_D = \frac{C}{C_0} \tag{B.9}$$

$$x_D = \frac{x}{L} \tag{B.10}$$

$$y_D = \frac{y}{L} \tag{B.11}$$

$$b_D = \frac{b}{L} \tag{B.12}$$

$$R_D = 1 + \frac{2}{b} K_a \tag{B.13}$$

$$K_D = \phi + K_v \tag{B.14}$$

$$t_D = \frac{t}{t^*} \tag{B.15}$$

$$D_D = \frac{D_e t^*}{L^2} \tag{B.16}$$

B.5 Governing Equations in Dimensionless Form

$$R_D\frac{\partial C_{fD}}{\partial t_D} = 2\frac{D_D}{b_D}\frac{\partial C_{fD}}{\partial y_D}\Big|_{y_D=0} - \frac{\partial C_{fD}}{\partial x_D} \tag{B.17}$$

$$\frac{\partial C_{pD}}{\partial t_D} = \frac{D_D}{K_D}\frac{\partial^2 C_{pD}}{\partial y_D^2} \tag{B.18}$$

B.6 Boundary Conditions in Dimensionless Form

$$C_{fD}\Big|_{y_D=0} = C_{pD}\Big|_{y_D=0} \tag{B.19}$$

$$C_{fD} = 1;\ for\ x_D = 0 \tag{B.20}$$

$$\lim_{x_D\to\infty} C_{fD} = 0 \tag{B.21}$$

$$\lim_{x_D\to\infty} C_{pD} = 0 \tag{B.22}$$

B.7 Initial Conditions in Dimensionless Form

$$C_{fD} = 0;\ for\ t_D \le 0 \tag{B.23}$$

$$C_{pD} = 0;\ for\ t_D \le 0 \tag{B.24}$$

B.8 Laplace Transform of Governing Equations

$$R_D(s\overline{C}_{fD} - \overline{C}_{fD}\Big|_{t_D=0}) = 2\frac{D_D}{b_D}\frac{d\overline{C}_{fD}}{dy_D}\Big|_{y_D=0} - \frac{d\overline{C}_{fD}}{dx_D} \tag{B.25}$$

$$s\overline{C}_{pD} - \overline{C}_{pD}\mid_{t_D=0} = \frac{D_D}{K_D}\frac{d^2\overline{C}_{pD}}{dy_D^2} \tag{B.26}$$

B.9 Laplace Transform of Boundary Conditions

$$\overline{C}_{fD}\mid_{y_D=0} = \overline{C}_{pD}\mid_{y_D=0} \tag{B.27}$$

$$\overline{C}_{fD} = \frac{1}{s}\ for\ x_D = 0 \tag{B.28}$$

$$\lim_{x_D\to\infty}\overline{C}_{fD} = 0 \tag{B.29}$$

$$\lim_{x_D\to\infty}\overline{C}_{pD} = 0 \tag{B.30}$$

B.10 Laplace Transform of Initial Conditions

$$\overline{C}_{fD} = 0;\ for\ t_D \leq 0 \tag{B.31}$$

$$\overline{C}_{pD} = 0;\ for\ t_D \leq 0 \tag{B.32}$$

B.11 Manipulation of Transformed Equations

Rearranging Equation B.26 and utilizing Equation B.32:

$$\frac{D_D}{sK_D}\frac{d^2\overline{C}_{pD}}{dy_D^2} - \overline{C}_D = 0 \tag{B.33}$$

The solution to this ordinary differential equation is:

$$\overline{C}_{pD} = A_1\ \exp\left[-y_D\sqrt{\frac{sK_D}{D_D}}\right] + A_2\ \exp\left[+y_D\sqrt{\frac{sK_D}{D_D}}\right] \tag{B.34}$$

From Equation B.30, $\overline{C}_{pD}$ is bounded; therefore, A2 must equal zero:

$$\overline{C}_{pD} = A_1 \ \exp\left[-y_D\sqrt{\frac{sK_D}{D_D}}\right] \tag{B.35}$$

At $y_D = 0$:

$$\overline{C}_{pD} = \overline{C}_{fD} = A_1 \tag{B.36}$$

Substituting into Equation B.35:

$$\overline{C}_{pD} = \overline{C}_{fD} \ \exp\left[-y_D\sqrt{\frac{sK_D}{D_D}}\right] \tag{B.37}$$

Taking the derivative:

$$\overline{C}'_{pD} = -\overline{C}_{fD}\sqrt{\frac{sK_D}{D_D}} \ \exp\left|-y_D\sqrt{\frac{sK_D}{D_D}}\right| \tag{B.38}$$

At $y_D = 0$:

$$\overline{C}'_{pD} \mid_{y_D=0} = -\overline{C}_{fD}\sqrt{\frac{sK_D}{D_D}} \tag{B.39}$$

Rearranging Equation B.25 and utilizing Equations B.31 and B.39:

$$\frac{d\overline{C}_{fD}}{dx_D} + \left(sR_D + 2\frac{D_D}{b_D}\sqrt{\frac{sK_D}{D_D}}\right)\overline{C}_{fD} = 0 \tag{B.40}$$

The solution to this ordinary differential equation is:

$$\overline{C}_{fD} = A_3 \ \exp\left[-\left(sR_D + 2\frac{D_D}{b_D}\sqrt{\frac{sK_D}{D_D}}\right)x_D\right] + A_4 \ \exp\left[\left(sR_D + 2\frac{D_D}{b_D}\sqrt{\frac{sK_D}{D_D}}\right)x_D\right] \tag{B.41}$$

From Equation B.29, $\overline{C}_{fD}$ is bounded; therefore A_4 must equal zero:

$$\overline{C}_{fD} = A_2 \ \exp\left[-\left(sR_D + 2\frac{D_D}{b_D}\sqrt{\frac{sK_D}{D_D}}\right)x_D\right] \tag{B.42}$$

At $x_D = 0$:

$$\overline{C}_{fD} = \frac{1}{s} = A_2 \tag{B43}$$

Substituting Equation B.42 into Equation B.43:

$$\overline{C}_{fD} = \frac{1}{s}\ \exp\left[-x_D R_D s\right]\ \exp\left[-2\frac{D_D x_D}{b_D}\sqrt{\frac{K_D}{D_D}}\sqrt{s}\right] \tag{B44}$$

B.12 Solution

Equation B.44 may be inverted using Equations 29.2.15 and 29.3.83 from *Handbook of Mathematical Functions* (Abramowitz and Stegun 1972):

$$C_{fD} = erfc\left[\frac{x_D(D_D K_D)^{1/2}}{b_D(t_D - x_D R_D)^{1/2}}\right];\ for\ t_D > R_D \tag{B.45}$$

$$C_{fD} = 0;for\ t_D \leq x_D R_D \tag{B.46}$$

Appendix C

Fracture Aperture Equation Derivation

C.1 Solution of the Matrix Diffusion Model

Equations **B.45** and **B.46** repeated:

$$C_{fD} = erfc\left[\frac{x_D(D_DK_D)^{1/2}}{b_D(t_D - x_DR_D)^{\frac{1}{2}}}\right];\ for\ t_D > x_DR_D$$

$$C_{fD} = 0; \qquad for\ t_D \leq x_DR_D$$

C.2 Laplace Transform of Solution

Equation **B.44** repeated:

$$\overline{C}_{fD} = \frac{1}{s}\exp\left[-x_DR_Ds\right]\exp\left[-2\frac{D_Dx_D}{b_D}\sqrt{\frac{K_D}{D_D}}\sqrt{s}\right]$$

C.3 Derivative

The derivative of a function mag be found by multiplying its Laplace Transform by s and then taking the inverse.

$$\overline{C}'_{fD} = \exp\left[-x_D R_D s\right] \exp\left[-2\frac{D_D x_D}{b_D}\sqrt{\frac{K_D}{D_D}}\sqrt{s}\right] \tag{C.1}$$

Equation C.1 may be inverted using Equations 29.2.15 and 29.3.82 from *Handbook of Mathematical Functions* (Abramowitz 1972):

$$C'_{fD} = \frac{x_D(D_D K_D)^{1/2}}{\sqrt{\pi}\, b_D(t_D - x_D R_D)^{3/2}} \exp\left[\frac{-D_D K_D x_D^2}{b_D^2(t_D - x_D R_D)}\right];\, for\ t_D > x_D R_D \tag{C.2}$$

$$C'_{fD} = 0;\, for\ t_D \leq R_D \tag{C.3}$$

C.4 Superposition

At this point superposition will be used to provide a solution to an inlet condition where a given concentration of tracer is injected for time, *At.* Previously the inlet condition was constant injection for $0 \geq t \leq \infty$.

From Equation B:45:

$$C_{fD} = erfc\left[\frac{x_D(D_D K_D)^{1/2}}{b_D(t_D - x_D R_D)^{1/2}}\right] - erfc\left[\frac{x_D(D_D K_D)^{1/2}}{b_D(t_D - \Delta t_D - x_D R_D)^{1/2}}\right] \tag{C.4}$$

$$for\ t_D - At > x_D R_D$$

From Equation C.2:

$$C'_{fD} = A_D \left\{ \frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2(t_D - x_D R_D)}\right]}{(t_D - x_D R_D)^{3/2}} - \frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2(t_D - \Delta t_D - x_D R_D)}\right]}{(t_D - \Delta t_D - x_D R_D)^{3/2}} \right\} \tag{C.5}$$

$$for\ t_D - At > x_D R_D$$

$$where\ A_D = \frac{x_D (D_D K_D)^{1/2}}{\sqrt{\pi}\, b_D (t_D - x_D R_D)^{3/2}}$$

C.5 Manipulation of the Superposed Derivative Equation

At the peak concentration the derivative of the concentration function is equal to zero. Equation **C.5** can only equal zero when the two term inside the braces are equal. Thus:

$$\frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2(t_{pD} - x_D R_D)}\right]}{(t_{pD} - x_D R_D)^{3/2}} = \frac{\exp\left[\frac{-D_D K_D x_D^2}{b_D^2(t_{pD} - \Delta t_D - x_D R_D)}\right]}{(t_{pD} - \Delta t_D - x_D R_D)^{3/2}} \tag{C.6}$$

Let $\omega_D = (D_D K_D x_D^2)/b_D^2$.
Then:

$$\frac{\exp\left[\frac{-\omega_D}{(t_{pD} - x_D R_D)}\right]}{(t_{pD} - x_D R_D)^{3/2}} = \frac{\exp\left[\frac{-\omega_D}{(t_{pD} - \Delta t_D - x_D R_D)}\right]}{(t_{pD} - \Delta t_D - x_D R_D)^{3/2}} \tag{C.7}$$

Gathering the exponential terms on one side:

$$\frac{(t_{pD} - \Delta t_D - x_D R_D)^{3/2}}{(t_{pD} - x_D R_D)^{3/2}} = \frac{\exp\left[\frac{\omega_D}{(t_{pD} - x_D R_D)}\right]}{\exp\left[\frac{\omega_D}{(t_{pD} - \Delta t_D - x_D R_D)}\right]} \tag{C.8}$$

$$\left(1 - \frac{\Delta t_D}{t_{pD} - x_D R_D}\right)^{3/2} = \exp\left[\frac{\omega_D}{t_{pD} - x_D R_D} - \frac{\omega_D}{t_{pD} - \Delta t_D - x_D R_D}\right] \tag{C.9}$$

$$\left(1-\frac{\Delta t_D}{t_{pD}-x_D R_D}\right)^{3/2}=\exp\left[\frac{-\omega_D \Delta t_D}{(t_{pD}-x_D R_D)(t_{pD}-\Delta t_D-x_d R_D)}\right] \tag{C.10}$$

Taking the natural log of both sides:

$$\ln\left(1-\frac{\Delta t_D}{t_{pD}-x_D R_D}\right)^{3/2}=\frac{-\omega_D \Delta t_D}{(t_{pD}-x_D R_D)(t_{pD}-\Delta t_D-x_D R_D)} \tag{C.11}$$

Solving for ω_D:

$$\omega_D=\frac{-(t_{pD}-x_D R_D)(t_{pD}-\Delta t_D-x_D R_D)}{\Delta t_D}\ln\left(1-\frac{\Delta t_D}{t_{pD}-x_D R_D}\right)^{3/2} \tag{C.12}$$

Substituting for ω_D:

$$\frac{D_D K_D x_D^2}{b_D^2}=\frac{-(t_{pD}-x_D R_D)(t_{pD}-\Delta t_D-x_D R_D)}{\Delta t_D}\ln\left(1-\frac{\Delta t_D}{t_{pD}-x_D R_D}\right)^{3/2} \tag{C.13}$$

Solving for b_D:

$$b_D^2=\frac{D_D K_D x_D^2 \Delta t_D}{(t_{pD}-x_D R_D)(t_{pD}-\Delta t_D-x_D R_D)\ln\left[1-\frac{\Delta t_D}{t_{pD}-x_D R_D}\right]^{-3/2}} \tag{C.14}$$

Substituting for the dimensionless variables and letting $x_D=1$:

$$\frac{b^2}{L^2}=\frac{\left(\frac{D_e t^*}{L^2}\right)(1)\,(\phi+K_v)\,(\Delta t/t^*)}{(t_p/t^*-R_D)\,(t_p/t^*-\Delta t/t^*-R_D)\ln\left[1-\frac{\Delta t/t^*}{t_p/t^*-R_D}\right]^{-3/2}} \tag{C.15}$$

$$\textit{where } R_D=1+\frac{2}{b}K_a$$

C.6 Fracture Aperture Equation

$$b^2 = \frac{D_e(\phi + K_v)t^{*2}\Delta t}{(t_p - R_D t^*)(t_p - \Delta t - R_D t^*)\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}} \qquad \text{(C.16)}$$

$$where\ R_D = 1 + \frac{2}{b}K_a$$

For no adsorption ($K_a = K_v = 0$):

$$b^2 = \frac{D_e\phi t^{*2}\Delta t}{(t_p - t^*)(t, -At - t^*)\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}} \qquad \text{(C.17)}$$

C.7 Fracture Aperture Equation - Instantaneous Injection

For an instantaneous injection of tracer, At approaches zero. From Equation C.16:

$$b2 = \lim_{\Delta t \to 0} \frac{D_e(\phi + K_v)t^{*2}\Delta t}{(t_p - R_D t^*)(t_p - At - R_D t^*)\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}} \qquad \text{(C.18)}$$

In order to solve Equation C.18, the following limit will be evaluated using L'Hopital's Rule:

$$\lim_{\Delta t \to 0} \frac{\Delta t}{\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}} = \lim_{\Delta t \to 0} \frac{\frac{d}{d\Delta t}(\Delta t)}{\frac{d}{d\Delta t}\left\{\ln\left[1 - \frac{\Delta t}{t_p - R_D t^*}\right]^{-3/2}\right\}}$$

$$= \lim_{\Delta t \to 0} \frac{2}{3}(t_p - t^*)\left(1 - \frac{\Delta t}{t_p - R_D t^*}\right)$$

$$= \frac{2}{3}(t_p - R_D t^*)$$

Substituting into Equation C.18:

$$b^2 = \frac{2D_e(\phi + K_v)t^{*2}}{3(t_p - R_D t^*)} \tag{C.19}$$

Substituting for R_D and solving the resulting quadratic:

$$b = \frac{K_a t^* + \sqrt{K_a^2 t^{*2}} + 6D_e(\phi + K_v)(t_p - t^*)t^{*2}}{3(t_p - t^*)} \tag{C.20}$$

For no adsorption (K, $= K_v = 0$):

$$b = t^* \sqrt{\frac{2D_e\phi}{3(t_p - t^*)}} \tag{C.21}$$

Appendix D

Wairakei Tracer Tests

This appendix presents plots of the Wairakei tracer tests. The concentrations have been scaled to units of injected amount divided by 10^{12} liters and corrected for decay and background radiation. Negative values have also been omitted.

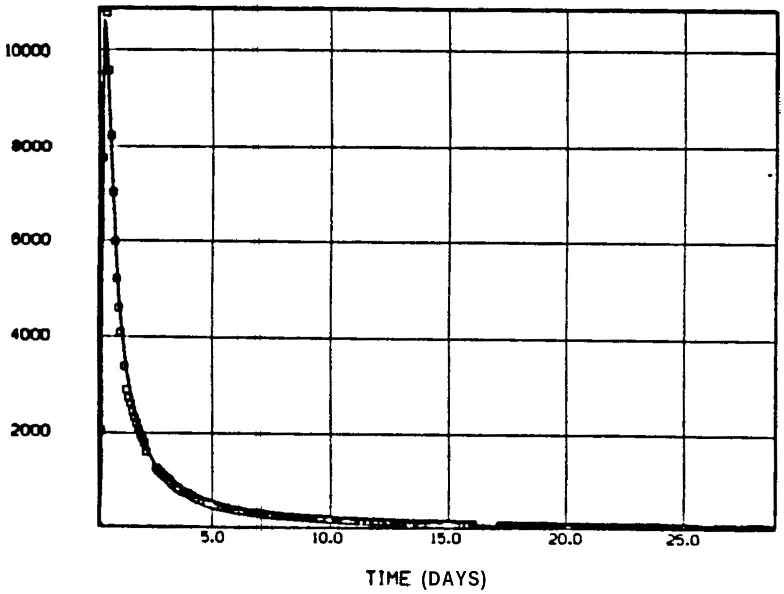


Figure D.l: Regression Fit, **CWK** 107 – **WK24** (from Jensen **1983)**

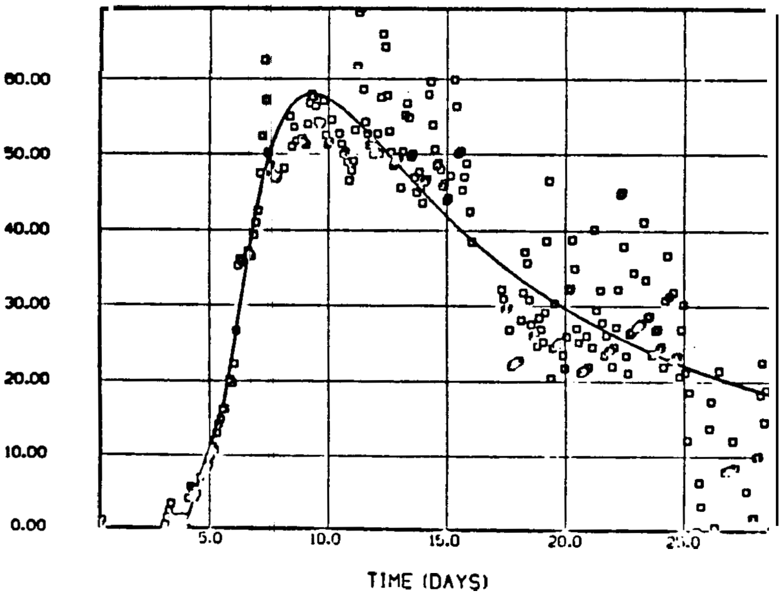


Figure D.2: Regression Fit, **CWK107** – **WK30** (from Jensen **1983)**

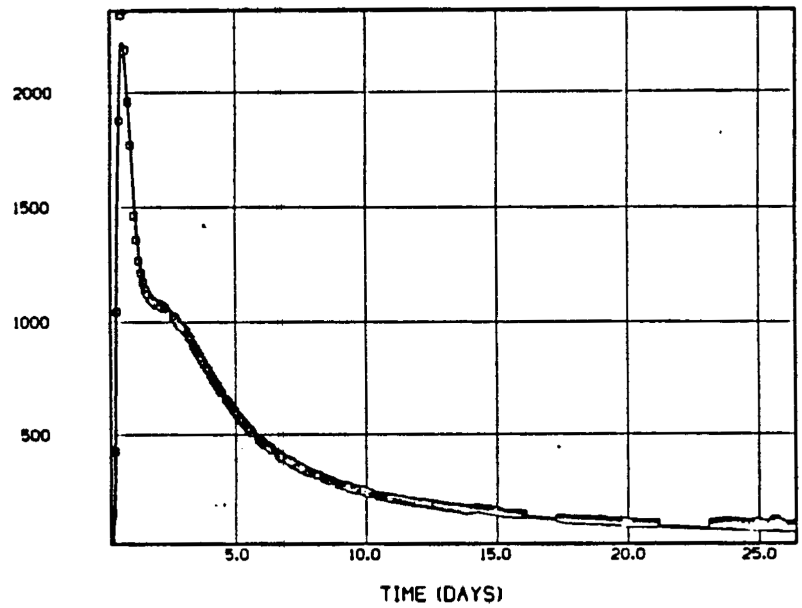


Figure **D.3:** Regression Fit, CWK107 – WK48 (from Jensen 1983)

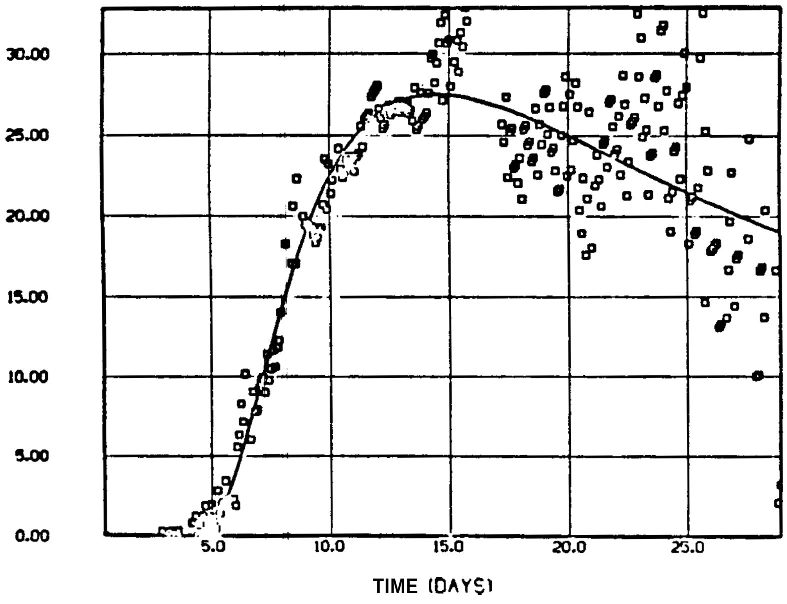


Figure D.4: Regression Fit, CWK107 – WK55 (from Jensen 1983)

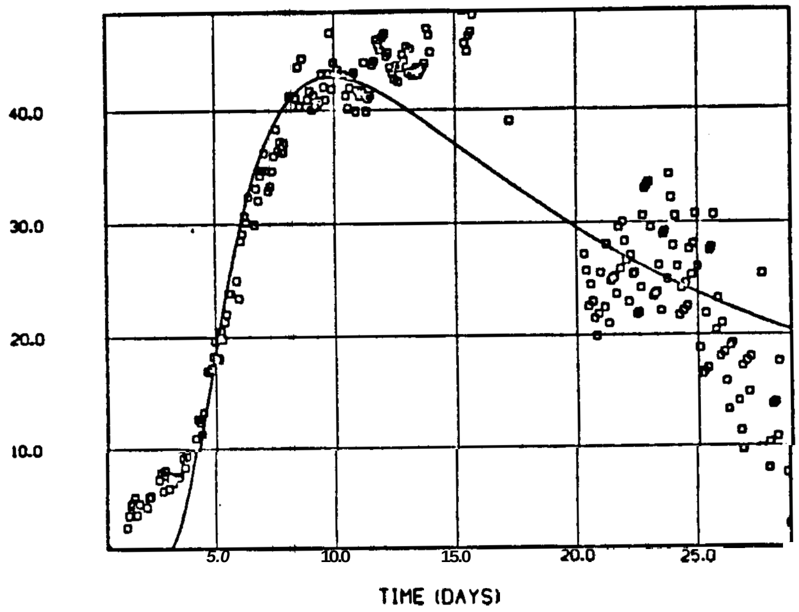


Figure **D.5:** Regression Fit, CWK107 – WK67 (from Jensen 1983)

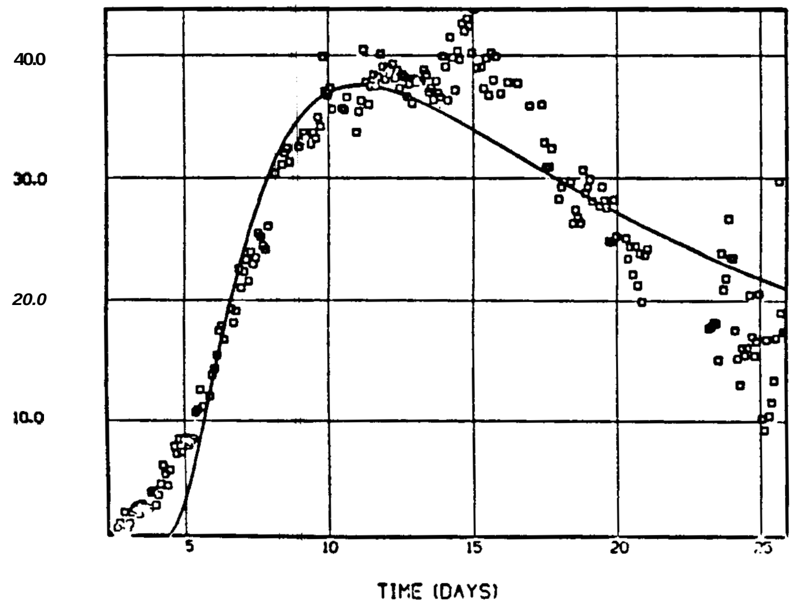


Figure D.6: Regression Fit, CWK107 – WK68 (from Jensen 1983)

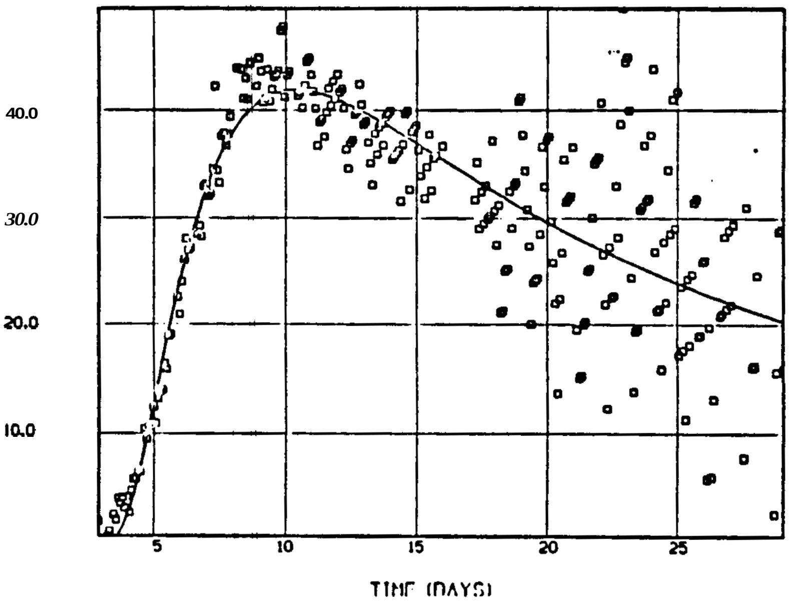


Figure D.7: Regression Fit, CWK107 – WK70 (from Jensen 1983)

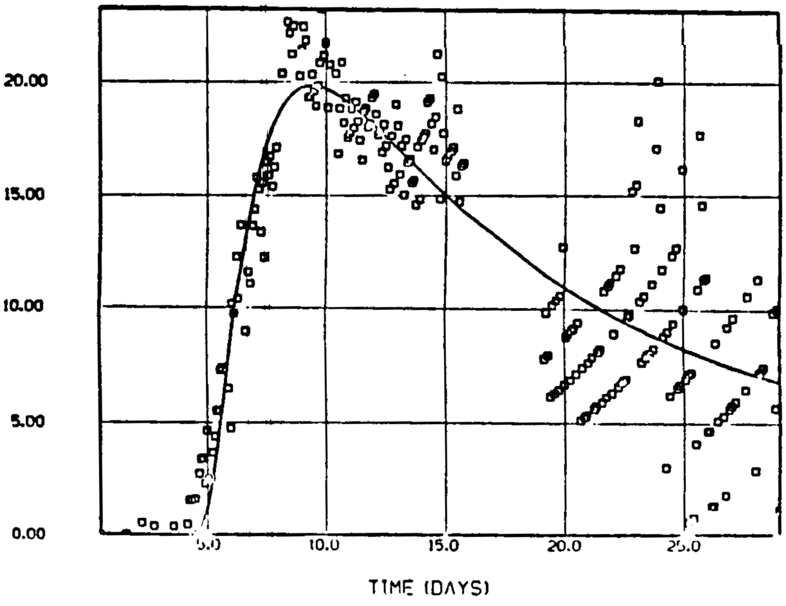


Figure D.8: Regression Fit, CWK107 – WK81 (from Jensen 1983)

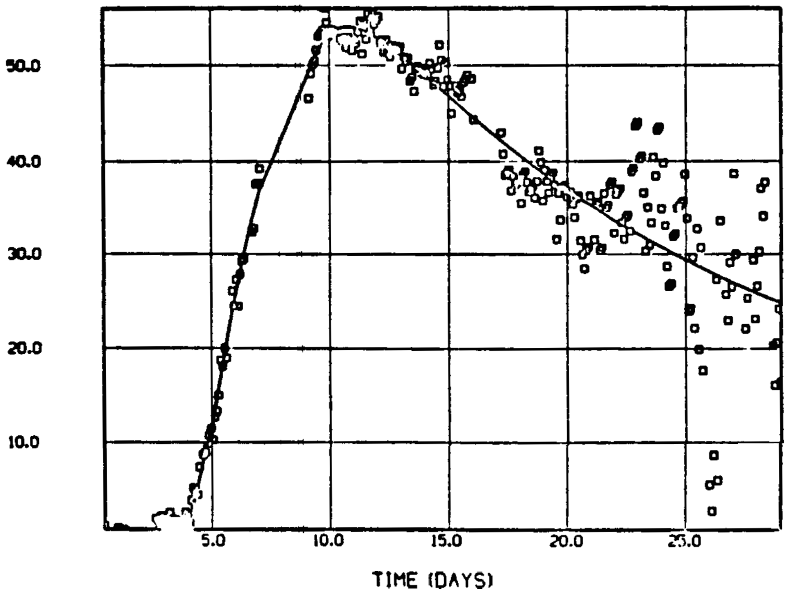


Figure D.9: Regression Fit, CWK107 – WK83 (from Jensen 1983)

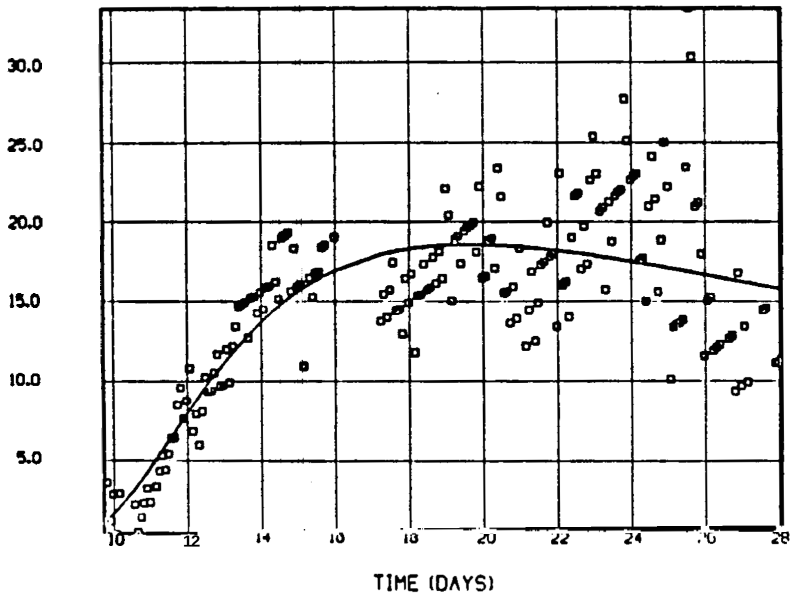


Figure D.lO: Regression Fit, CWK107 – WK108 (from Jensen 1983)

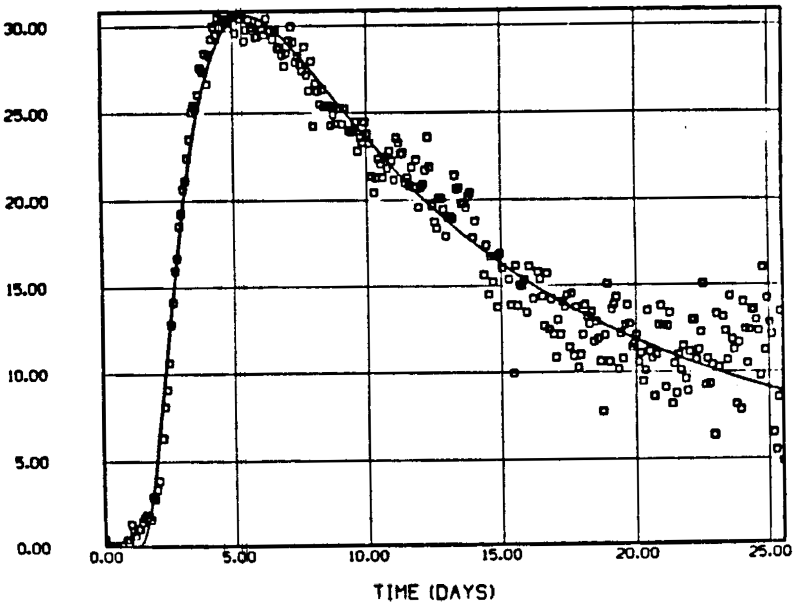


Figure D.11: Regression Fit, CWK101 – WK103 (from Jensen 1983)

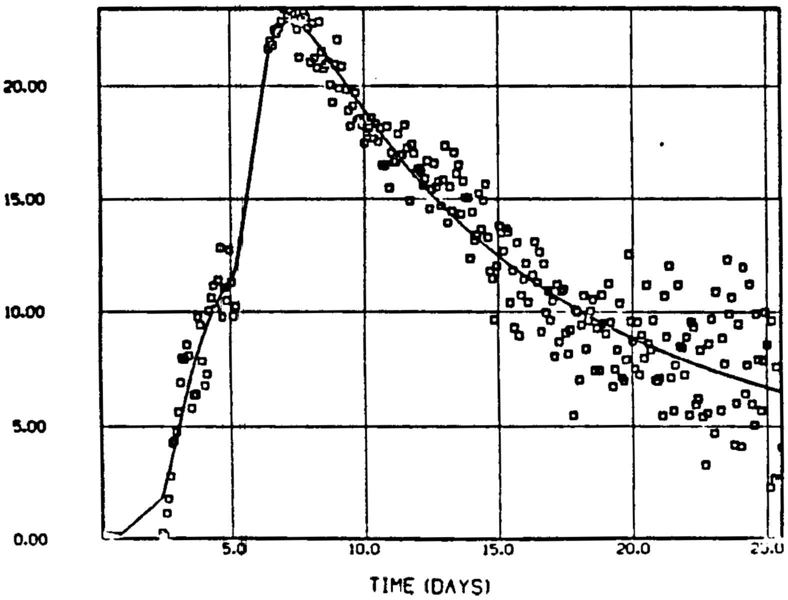


Figure D.12: Regression Fit, CWK101 – WK116 (from Jensen 1983)

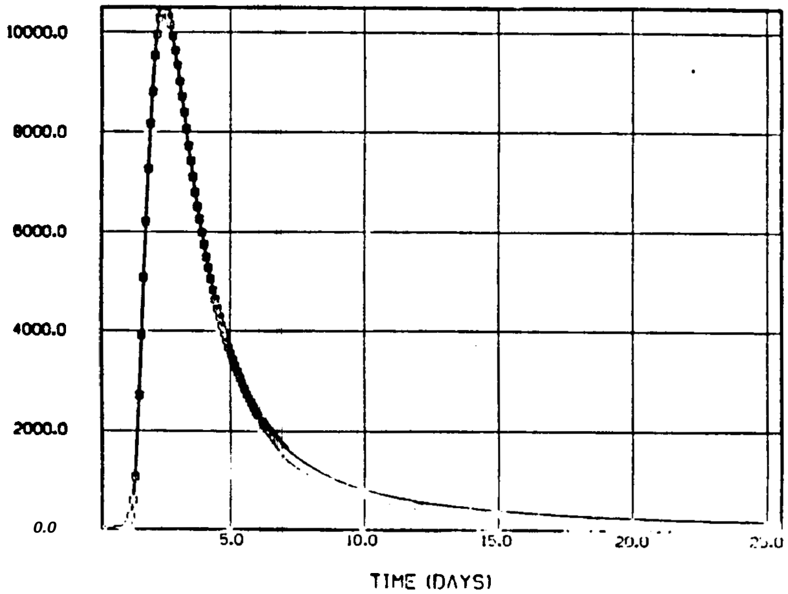


Figure **D.13:** Regression Fit, CWK101 – WK121 (from Jensen 1983)

Appendix E

Regression Equations

The equations presented in Jensen's report (1983) are similar to those given in this work. His Equation **3.12** is closely related to Equation C.8 in this report. Equation 3.12 holds for an instantaneous injection. It is repeated here in the nomenclature of this report:

$$C_f = \frac{M}{Q}\left\{\frac{D_e t^*}{b\sqrt{\pi}D_a^{1/2}(t^*R)^{3/2}\left(\frac{t}{t^*R}-1\right)^{3/2}}\exp\left[\frac{-\frac{D_e^2 t^{*2}}{D_a(t^*R)b^2}}{\frac{t}{t^*R}-1}\right]\right\} \tag{E.1}$$

R is defined as the retardation factor. The breakthrough time is equal to (t^*R). Jensen defines two nonlinear parameters, a and β:

$$a = \frac{D_e t^*}{b\sqrt{D_a(t^*R)}} \tag{E.2}$$

For no adsorption $(R = 1)$:

$$a = \frac{\sqrt{D_e \phi t^*}}{b} \tag{E.3}$$

$$\beta = \frac{1}{t^*R} \tag{E.4}$$

Using the newly defined parameters, Jensen reduces Equation E.1 to:

$$C_f = \frac{M}{Q}\left\{\frac{\alpha\beta}{\sqrt{\pi}(\beta t-1)^{3/2}}\exp\left[-\frac{\alpha^2}{\beta t-1}\right]\right\} \tag{E.5}$$

A form of this expression is used to fit the Wairakei field data.

Although $1/\beta$ equals the breakthrough time, Jensen never explicitly found the time to peak concentration. t_p may be expressed in term of α and β by setting the derivative of Equation E.5 equal to zero.. This allows better comparison between the visual and regression methods.

$$t_p = \frac{\frac{2}{3}\alpha^2 + 1}{\beta} \tag{E.6}$$

Appendix F

Computer Data Acquisition System

This appendix presents a brief explanation of the computer data acquisition system (hardware and software) and provides a listing of the program code. The equipment was used for the collection of sodium chloride concentration data. The instruments also recorded the positioning of a new sample bottle under the effluent.

F.1 Hardware

The hardware consisted of a KEITHLEY system baseboard, two circuit board modules, an interface card and a CQMPAQ computer. Figure F.1 illustrates the circuit diagram. The Analog Output Module 1 (AOM1) was placed in slot 2 of the baseboard. This module controlled the voltage output. While the AOMl had two output channels, only AOMl Channel 1 was used in this experiment. The Analog Measurement Module 1 (AMM1), located in slot 1 of the base board, measured the voltage drop across the electrodes. AMM1 Channels 1 - 7 were connected to Electrodes #1 - #7. Each channel measured the voltage at a single sensor. AMMl Channel 0 was connected through a switch to either of two voltage sources. The switch was toggled manually each time a new sample was collected at the outlet. The AMM1, AOMl and each electrode were connected to a common ground buried

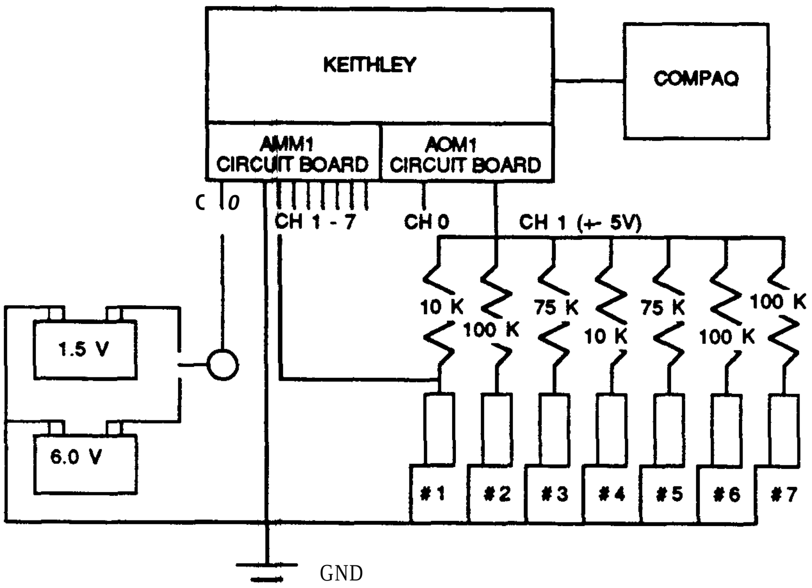


Figure F.1: Circuit Diagram - Computer Data Acquisition System

in the earth outside the laboratory. **A** clock was contained in the interface card located inside the COMPAQ.

F.2 Software

The software was written in BASIC. The program accomplished five operations:

- Initializing the clock
- Pulsing voltage
- Reading the time
- Reading the voltage
- Recording time **and** voltage data

Many of the instructions required specific knowledge of hardware memory locations referenced in the KEITHLEY manual. **A** synopsis of the program follows.

Lines 1000 – 1001

Lines 1000 – 1001 define the starting memory location.

Lines 1010 – 1013

This section opens the data files. The voltage readings marking the introduction of new sample bottles are stored in the file VOLT0.DAT. The data collected from Electrode #1 is stored in VOLT1.DAT. The readings from the remaining six electrodes are placed VOLT27.DAT.

Lines 1020 – 1198

This section initializes the interval timer. The timer consists of three counters which are analogous to the hour, minute and second hands of a clock. Counter 2 moves the fastest. It counts down from its initial value at the rate of one count every 1.046 μs. If Counter 2 and Counter 1 are linked, Counter 1 counts down once each time Counter 2 reaches zero. Counters 1 and 0 may be similarly joined. The counters are initialized by placing starting values into memory locations. Each value must be broken into two octadecimal bytes before it is poked into memory. Line 1198 provides a delay. The program will not always run properly without it.

Lines 1200 – 1212

These lines set PT and OLDTIME equal to zero. PT increments each time the program finishes an iteration.

Lines 1220 – 1222

These lines determine the REMAINDER when PT is divided by 4. The value of REMAINDER determines the voltage level which is output from the AOM1.

Lines 1225 – 1252

This section determines the output level of AOMl Channel 0. AOMl CH 0 was not used in these experiments. See the next section for additional details.

Lines 1260 – 1292

This section determines the output level of AOMl Channel 1. The AOMl was configured to send voltages in the ± 5 volt range. When REMAINDER = 0, a positive **5** volts is pulsed across the electrodes. When REMAINDER = 2, a negative 5 volts is output. Zero voltage is sent from AOMl CH 1 when REMAINDER is odd.

The output range is divided into 4096 possible voltage levels. Possible input values are 0 – 4095. When 0 is placed into memory, the lowest value is output. When 4095 is sent to memory the highest voltage is pulsed. The inputs must be in octadecimal form. HB1 and LB1 represent the high and low bytes sent to the memory locations controlling the voltage.

Lines 1295 – 1300

Disables AOMl Channel 0 output.

Lines 1301 – 1630

This section accomplishes the main goals of the program. The following operations are performed:

- *o* Voltage output from AOMl CH 1
- *o* Time measurement
- *o* Voltages measurement from AMM1 CH 0 – 7
- *o* Recording the data in output files
- *o* Printing to the screen voltages from Electrodes #1 and #5 and the time

Because electrode data are only recorded for positive current, the positive voltage is pulsed for a slightly longer duration than the negative current.

Lines 1700 – 1711

This code provides a solution to a hardware malfunction. The equipment will not allow input into the Counter 0 memory location, &HC0. Each time the COMPAQ is booted up, a new random number is placed into &HC0. If the number is different than that chosen on line **1033,** the program will not normally work.

The solution chosen is to query the memory for the random number and then manually change the input to match it. CCZ, which is printed to the screen, is the random number. It must be entered in place of the value found on line 1033. When the program fails, the operator should:

type CONTROL-BREAK
type LIST 1033
change CZ on line **1033** to CCZ

Lines 1800 – 2000

This section increments PT, sets OLDTIME equal to the last measured time and returns the program to line 1221. The operator should type CONTROL-BREAK, to end the program.

Subroutines

Lines 4000 – 4199: Reads the counters and computes the elapsed time.
Lines 5000 – 5099: Pulses voltage from Channel 0.
Lines 5500 – 5599: Pulses voltage to electrodes from Channel 1.
Lines 6000 – 6199: Reads voltage across Channel 0.
Lines 6200 – 6399: Reads voltage across Channel 1.
Lines 6500 – 6999: Reads voltage across Channels 2 – 7.

Each line of these subroutines is commented. For additional information see the KEITHLEY reference manual (Lessons 1 – 5, Reference Sections AOMl and AMM1).

F.3 Software Listing

F.3.1 Main Program

```
1000   REM this program controls the data acquisition system
1001   DEF SEG=&HAFF0:            REM defines starting memory location

1010   REM the following section opens the output files
1011   OPEN "B:VOLT0.DAT"FOR OUTPUT AS #1
1012   OPEN "B:VOLT1.DAT"FOR OUTPUT AS #2
1013   OPEN "B:VOLT27.DAT"FOR OUTPUT AS #3

1020   REM the following section initializes the interval timer
1031   CT=65000!:                 REM initialize interval counter 2
1032   CO=65000!:                 REM initialize interval counter 1
1033   CZ=51134!:                 REM initialize interval counter 0
1041   HT=INT(CT/256):            REM high byte counter 2
1042   LT=CT-(256*HT):            REM low byte counter 2
1045   HO=INT(CO/256):            REM high byte counter 1
1046   LO=CO-(256*HO):            REM low  byte counter 1
1048   HZ=INT(CZ/256):            REM high byte counter 0
1049   LZ=CZ-(256*HZ):            REM low  byte counter 0
1150   POKE &HE0,3:               REM set timer global, carry 2-1-0
1161   POKE &HC3,180:             REM counter 2 set for carry mode
1162   POKE &HC2,LT:              REM low byte for counter 2
1163   POKE &HC2,HT:              REM high byte for counter 2
1171   POKE &HC3,116:             REM counter 1 set for carry mode
1172   POKE &HC1,LO:              REM low  byte for counter 1
1173   POKE &HC1,HO:              REM high byte for counter 1
1181   POKE &HC3,54:              REM counter 0 set as timer
1182   POKE &HC0,LZ:              REM low  byte for counter 0
1183   POKE &HC0,HZ:              REM high byte for counter 0
1198   FOR I=1 TO 500:  NEXT I

1200   REM the following section pulses the voltage and records the data
1201   PT=0:                      REM set pointer to 0
1212   OLDTIME-O

1220   REM lines 1221 - 1252 determine how to pulse the voltage
1221   WHOLE=INT(PT/4)
1222   REMAINDER-PT-(WHOLE*4)

1225   REM this subsection determines how to pulse channel 0 voltage
1230   REM when remainder = 0, pulse positive voltage
1231   IF REMAINDER=0 THEN HB=15
1232   IF REMAINDER=0 THEN LB=255
1240   REM when remainder = 1 or 3, pulse zero voltage
1241   IF REMAINDER=1 OR REMAINDER=3 THEN HB=8
1242   IF REMAINDER-1 OR REMAINDER=3 THEN LB=0
1250   REM when remainder = 2, pulse negative voltage
1251   IF REMAINDER=2 'THENHB=0
1252   IF REMAINDER4 THEN LB-6
```

```
1260   REM this subsection Uetermines how to pulse channel 1 voltage
1270   REM when remainder = 0 or 2, pulse zero voltage
1271   IF REMAINDER=0 OR REMAINDER=2 THEN HB1=8
1272   IF REMAINDER-0 OR REMAINDER=2 THEN LB1=0
1280   REM when remainder = 1, pulse positive voltage
1281   IF REMAINDER-1 THEN HB1=15
1282   IF REMAINDER-1 THEN LB1=255
1290   REM when remainder = 3, pulse negative voltage
1291   IF REMAINDER=3 THEN HB1=0
1292   IF REMAINDER=3 THEN LB1=6

1295   GOTO 1301:  REM do not pulse channel 0 voltage
1300   GOSUB 5000:                REM pulse the voltage (channel 0)

1301   GOSUB 5500:                REM pulse the voltage (channel 1)
1400   GOSUB 4000:                REM read time
1500   GOSUB 6000:                          REM read voltage (channel 0)
1510   IF REMAINDER=1 THEN GOSUB 6200:  REM read voltage (channel 1)

1520   IF REMAINDER=1 THEN GOSUB 6500:  REM read voltage (channels 2-7)
1600   REM print to output files and screen
1610   PRINT #1, USING "#####.#### ###.####"; TIME, VOLT0
1620   IF REMAINDER=1 THEN PRINT #2, USING "#####.#### ###.####"; TIME, VOLT1
1621   IF REMAINDER=1 THEN PRINT #3, USING "#####.#### ###.#### ###.####
###.#### ###.#### ###.#### ###.####"; TIME, VOLT2, VOLT3, VOLT4, VOLT5,
VOLT6, VOLT7
1630   IF REMAINDER-1 THEN PRINT TIME, VOLTO, VOLT1, VOLT5

1700   REM set time interval for data recovery
1701   GOSUB 4000:                REM read time
1702   ELAPSE=TIME-OLDTIME:       REM calculate elapsed time
1703   IF (ELAPSE>.1) THEN GOTO 1800
1704   PRINT" LINE 1704:  YOU ARE  IN TROUBLE"
1705   PRINT "LINE 1705:  TYPE - CONTROL-BREAK"
1706   PRINT "LINE 1706:  TYPE - LIST 1033"
1707   PRINT "LINE 1707:  CHANGE CZ TO THE NUMBER GIVEN BELOW (CCZ)"
1708   PRINT "LINE 1705:  CCZ"  CCZ
1710   FOR I=1 TO 10: NEXT I:  REM time delay
1711   GOTO 1701

1800   PT=PT+1
1801   OLDTIME=TIME
1900   GOTO 1221
1999   CLOSE
2000   END
```

F.3.2 Subroutines

```
4000   REM subroutine: time
4001   DEF SEG=&HAFF0:           REM defines starting memory location
4111   POKE &HC3,0:              REM counter 0 used in latching mode
4112   LOWZ=PEEK(&HC0):          REM recover low byte
4113   HIZ=PEEK(&HC0):           REM recover high byte
4114   CCZ=LOWZ+(HIZ*256):       REM combine high and low bytes
4121   POKE &HC3,64:             REM counter 1 used in latching mode
4122   LOWO-PEEK(&HC1):          REM recover low byte
4123   HIO=PEEK(&HC1):           REM recover high byte
4124   CCO=LOWO+(HIO*256):       REM combine high and low bytes
4131   POKE &HC3,128:            REM counter 2 used in latching mode
4132   LOW=PEEK(&HC2):           REM recover low byte
4133   HIT=PEEK(&HC2):           REM recover high byte
4134   CCT=LOWT+(HIT*256):       REM combine high and low bytes
4140   REM calculate the number of current pulses received from the PC
4141   PULSENO=((CZ-CCZ)*(CT*CO))+((CO-CCO)*CT)+(CT-CCT)
4150   REM convert pulses to seconds (1 pulse = 1.046 micro sec.)
4151   TIME=PULSENO*1.046E-06
4199   RETURN


5000   REM subroutine: pulse current to sensors (from channel 0)
5001   DEF SEG=&HAFF0:           REM defines starting memory location
5010   POKE &H9A,0:              REM set global gain to 1
5020   POKE &H9D,64:             REM enable strobe
5030   REM select slot 2, channel 0 for digital-analog control - low byte
5031   POKE &H82,0
5035   REM place low byte data into memory for slot 2 channel 0
5036   POKE &H83,LB
5040   REM select slot 2, channel 0 for digital-analog control - high byte
5041   POKE &H82,1
5045   REM place high byte data into memory for slot 2 channel 0
5046   POKE &H83,HB
5050   POKE &H9D,1:              REM issue data (send voltage)
5060   FOR I =1 TO 200: NEXT I:  REM time delay to stabilize voltage
5099   RETURN


5500   REM subroutine: pulse current to sensors (from channel 1)
5501   DEF SEG=&HAFF0:           REM defines starting memory location
5510   POKE &H9A,0:              REM set global gain to 1
5520   POKE &H9D,64:             REM enable strobe
5530   REM select slot 2, channel 1 for digital-analog control - low byte
5531   POKE &H82,2
5535   REM place low byte data into memory for slot 2, channel 1
5536   POKE &H83,LB1
5540   REM select slot 2, channel 1 for digital-analog control - high byte
5541   POKE &H82,3
5545   REM place high byte data into memory for slot 2, channel 1
5546   POKE &H83,HB1
5550   POKE &H9D,1:              REM issue data (send voltage)
5560   FOR I=1 TO 200: NEXT I:   REM time delay to stabilize voltage
5599   RETURN
```

```
6000   REM subroutine:  read voltage channel 0
6001   DEF SEG=&HAFF0:           REM defines starting memory location
6010   POKE &H9A,0:              REM select a gain of 1
6100   REM this section reads the voltage drop across channel 0, slot 1
6111   POKE &H80,0:              REM select channel 0
6112   POKE &H81,1:              REM select slot 1
6120   POKE &H9B,255:            REM starts analog-digital conversion
6131   DLOW=PEEK(&H80) :         REM read low byte
6132   DHI=PEEK(&H81) :          REM read high byte
6133   REM combine high and low bytes
6134   COUNTS=DLOW+(DHI-240)*256
6135   REM calc value of voltage for input range = +-10 v and gain = 1
6136   VOLT0=(COUNTS*(20/4095)-10)
6199   RETURN


6200   REM subroutine:  read voltage channel 1
6201   DEF SEG=&HAFF0:           REM defines starting memory location
6210   POKE &H9A,0:              REM select a gain of 1
6300   REM this section reads the voltage drop across channel 1, slot 1
6311   POKE &H80,1:              REM select channel 1
6312   POKE &H81,1:              REM select slot 1
6320   POKE &H9B,255:            REM starts analog-digital conversion
6331   DLOW=PEEK(&H80) :         REM read low byte
6332   DHI=PEEK(&H81) :          REM read high byte
6333   REM combine high and low bytes
6334   COUNTS=DLOW+ (DHI-240)*256
6335   REM calc value of voltage for input range = +-10 v and gain = 1
6336   VOLT1=(COUNTS*(20/4095)-10)
6399   RETURN


6500   REM subroutine: read voltage channels 2-7
6501   DEF SEG=&HAFF0:           REM defines starting memory location
6502   POKE &H9A,0:              REM select a gain of 1


6510   REM this section reads the voltage of channel 2, slot 1
6511   POKE &H80,2:              REM select channel 2
6512   POKE &H81,1:              REM select slot 1
6520   POKE &H9B,255:            REM starts analog-digital conversion
6531   DLOW=PEEK(&H80) :         REM read low byte
6532   DHI=PEEK(&H81) :          REM read high byte
6533   REM combine high and low bytes
6534   COUNTS=DLOW+(DHI-240)*256
6535   REM calc value of voltage for input range = +-10 v and gain = 1
6536   VOLT2=(COUNTS*(20/4095)-10)

6610   REM this section reads the voltage of channel 3, slot 1
6611   POKE CH80,3:              REM select channel 3
6612   POKE &H81,1:              REM select slot 1
6620   POKE &H9B,255:            REM starts analog-digital conversion
6631   DLOW-PEEK(&H80) :         REM read low byte
6632   DHI=PEEK(&H81) :          REM read high byte
6633   REM combine high and low bytes
6634   COUNTS=DLOW+(DHI-240)*256
6635   REM calc value of voltage for input range = +-10 v and gain = 1
6636   VOLT3= (COUNTS*(20/4095)-10)
```

```
6710  REM this section reads the voltage of channel 4, slot 1
6711  POKE &H80,4:              REM select channel 4
6712  POKE &H81,1:              REM select slot 1
6720  POKE &H9B,255:            REM starts analog-digital conversion
6731  DLOW=PEEK(&H80):          REM read low byte
6732  DHI=PEEK(&H81):           REM read high byte
6733  REM combine high and low bytes
6734  COUNTS=DLOW+(DHI-240)*256
6735  REM calc value of voltage for input range = +-10 v and gain = 1
6736  VOLT4=(COUNTS*(20/4095)-10)

6810  REM this section reads the voltage of channel 5, slot 1
6811  POKE &H80,5:              REM select channel 5
6812  POKE &H81,1:              REM select slot 1
6820  POKE &H9B,255:            REM starts analog-digital conversion
6831  DLOW=PEEK(&H80):          REM read low byte
6832  DHI=PEEK(&H81):           REM read high byte
6833  REM combine high and low bytes
6834  COUNTS=DLOW+(DHI-240)*256
6835  REM calc value of voltage for input range = +-10 v and gain = 1
6836  VOLT5=(COUNTS*(20/4095)-10)

6910  REM this section reads the voltage of channel 6, slot 1
6911  POKE &H80,6:              REM select channel 6
6912  POKE &H81,1:              REM select slot 1
6920  POKE &H9B,255:            REM starts analog-digital conversion
6931  DLOW=PEEK(&H80):          REM read low byte
6932  DHI=PEEK(&H81):           REM read high byte
6933  REM combine high and low bytes
6934  COUNTS=DLOW+(DHI-240)*256
6935  REM calc value of voltage for input range = +-10 v and gain = 1
6936  VOLT6=(COUNTS*(20/4095)-10)

6960  REM this section reads the voltage of channel 7, slot 1
6961  POKE &H80,7:              REM select channel 6
6962  POKE &H81,1:              REM select slot 1
6970  POKE &H9B,255:            REM starts analog-digital conversion
6981  DLOW=PEEK(&H80):          REM read low byte
6982  DHI=PEEK(&H81):           REM read high byte
6983  REM combine high and low bytes
6984  COUNTS=DLOW+(DHI-240)*256
6985  REM calc value of voltage for input range = +-10 v and gain = 1
6986  VOLT7=(COUNTS*(20/4095)-10)
6999  RETURN
```

Appendix G

Chromatograph Specifications/Settings

G.1 Equipment

- Hewlett Packard 5880 Series Gas Chromatograph
- Hewlett Packard 7673A Controller
- Hewlett Packard Automatic Sampler
- Hewlett Packard Column (Separation) - Porapak QS, 6 ft, 1/8 in. I.D., mesh range 80/100
- Hewlett Packard Column (Reference) - 2 % OV-101, 20 in., 100-120 WHP

G.2 Instrument Settings

G.2.1 Detector/Oven/Presentation Settings

- INJ 2 TEMP 200 [°C]
- DET 2 TEMP 200 [°C]
- DETECTOR D ON
- SIGNAL D

- OVEN TEMP INITIAL VALUE 180 [“C]
- OVEN TEMP FINAL VALUE 240 [“C]
- OVEN TEMP PGRM RATE 20 [$°C/min$]
- OVEN TEMP INITIAL TIME 0 [min]
- OVEN TEMP FINAL TIME **2** [min]
- ATTN 2↑14

G.2.2 Injection Settings

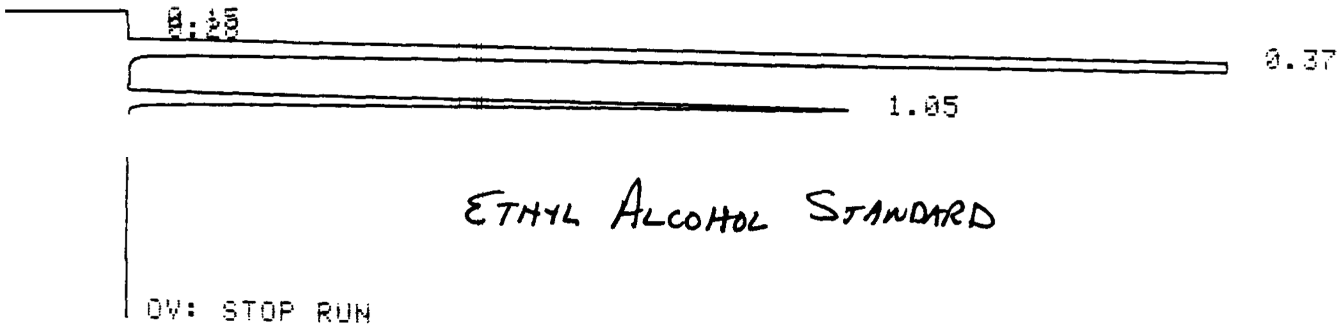
AUTO SEQ 2
INJECTOR 2:

0. MODE = 0 [*normal*]
1. PRE-INJECTION SAMPLE WASHES = 0
2. VISCOSITY = 1 *[wait* **1** *second at the top of each pump]*
3. SAMPLE PUMPS = 6
4. SAMPLE VOLUME = 1 [μl]
5. POST-INJECTION SOLVENT A WASHES = 0
6. POST-INJECTION SOLVENT B WASHES = 0
7. INJECTIONS PER BOTTLE = 1
8. FIRST BOTTLE = 1
9. LAST BOTTLE = *varies*

Appendix H

Chromatograph Runs

H.1 Calibration Runs



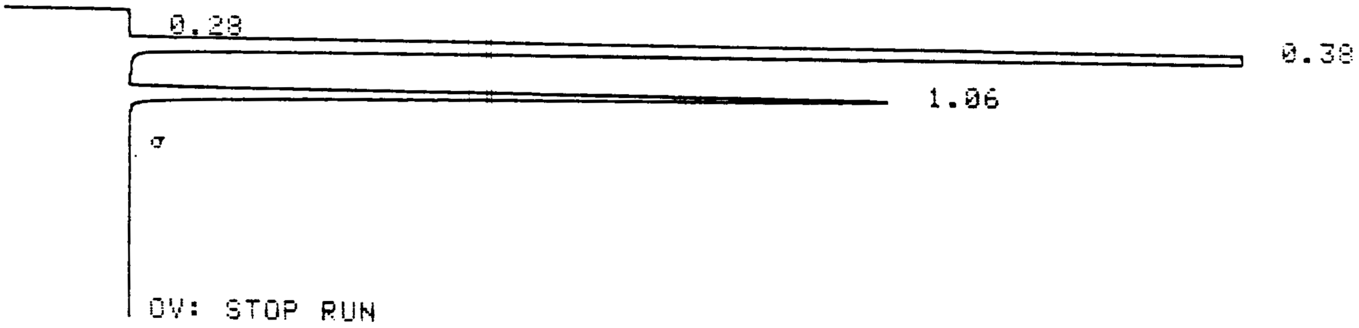
ETHYL ALCOHOL STANDARD

```
[hP] 5880A   SAMPLER INJECTION @ 21:58  MAY 26, 1988
  SAMPLE # :   ID CODE    :
         99
AREA %

   RT              AREA  TYPE     AREA %

  0.15           210.23   BV       0.004
  0.28           284.36   VV       0.006
  0.37       3863840.00   VV      81.636
  1.05        868675.00   VB      18.354

TOTAL AREA = 4733010.00
MULTIPLIER = 1
```



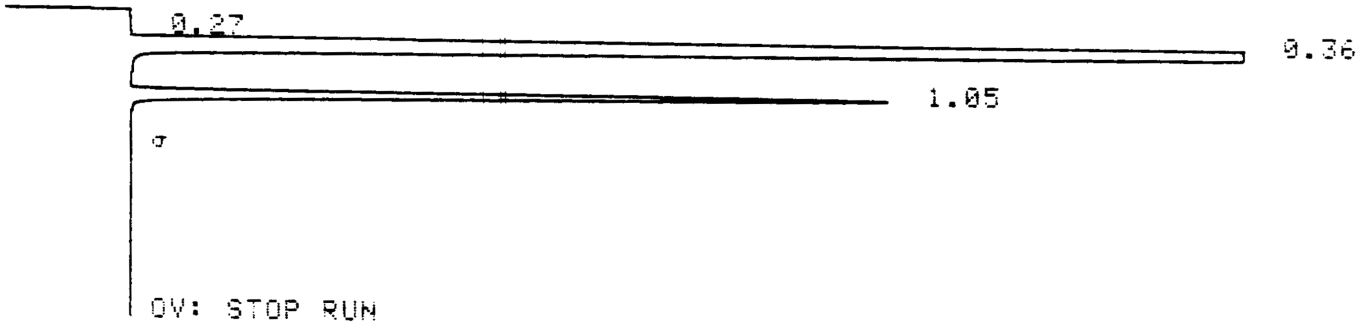
```
【hp】 5880A  SAMPLER INJECTION @ 22:07  MAY 26, 1988
  SAMPLE # :  ID CODE   :
         99
AREA %

   RT              AREA  TYPE    AREA %

  0.28            95.71   BH      0.002
  0.38       3967810.00   HH     81.722
  1.06        887333.00   HH     18.276

TOTAL AREA = 4855240.00
MULTIPLIER = 1
```

ETHYL ALCOHOL STANDARD



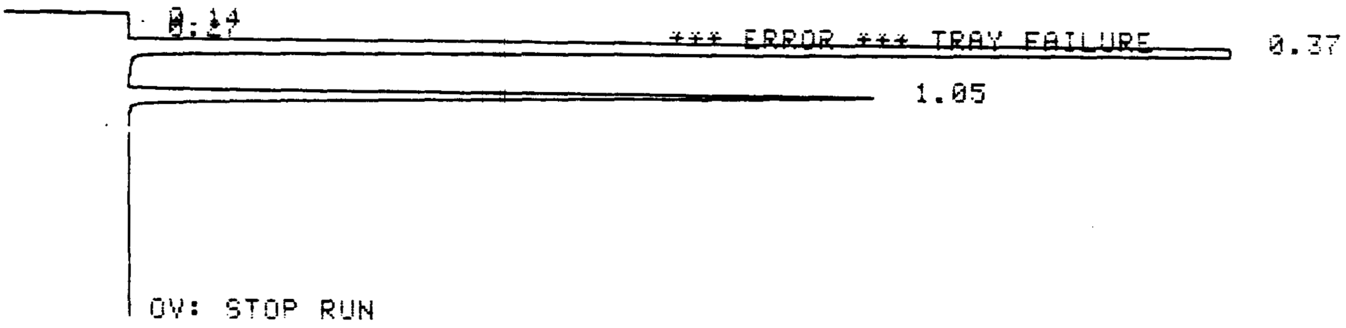
```
【hp】 5880A  SAMPLER INJECTION @ 22:17  MAY 26, 1988
  SAMPLE # :  ID CODE   :
         99
AREA %

   RT              AREA  TYPE    AREA %

  0.27            90.17   BH      0.002
  0.36       3902320.00   HH     81.641
  1.05        877450.00   HH     18.357

TOTAL AREA = 4779850.00
MULTIPLIER = 1
```

ETHYL ALCOHOL STANDARD



```
[hp] 5880A  SAMPLER INJECTION @ 22:26  MAY 26, 1988
  SAMPLE # :  ID CODE    :
         99
AREA %

   RT               AREA  TYPE    AREA %

  0.14             34.61   BB      0.001
  0.27             89.71   BP      0.002
  0.37        3938090.00   PV     81.792
  1.05         876547.00   VB     18.205

TOTAL AREA = 4814760.00
MULTIPLIER = 1

STOP AUTO SEQ

EDIT 2 AUTO SEQ 8, 99

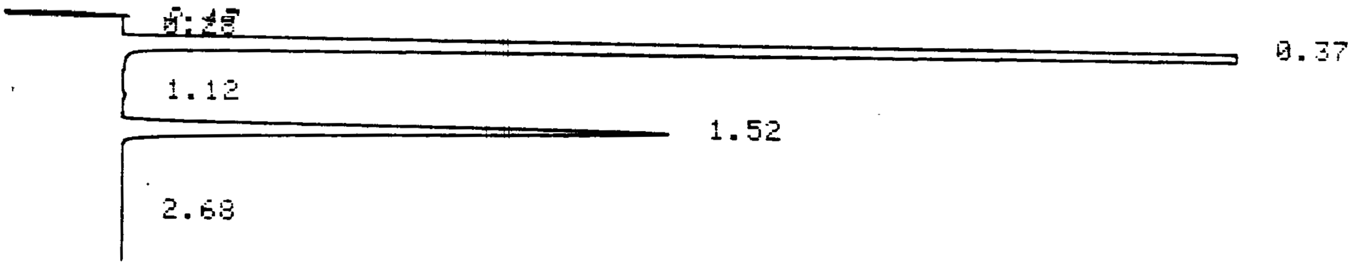
START 2 AUTO SEQ

*** ERROR *** TRAY MISSING BOTTLE 99

STOP AUTO SEQ

EDIT 2 AUTO SEQ 8, 100
```

ETHYL
ALCOHOL
STANDARD



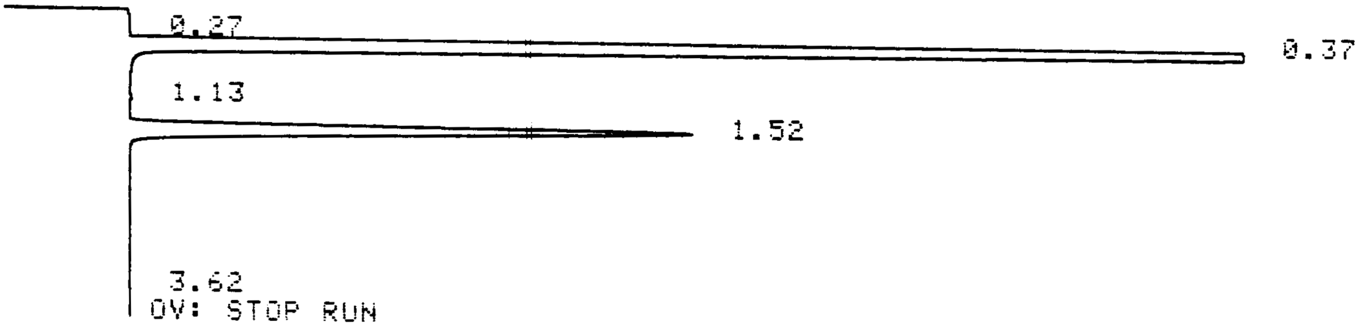
```
【hP】 5880A   SAMPLER INJECTION @ 23:41   MAY 26, 1988
  SAMPLE # :   ID CODE    :
        100
AREA %

   RT                 AREA  TYPE     AREA %

  0.13               39.46   BB       0.001
  0.28               71.39   BP       0.002
  0.37          3821120.00   PV      82.417
  1.12             3036.85   VP       0.066
  1.52           811947.00   PB      17.513
  2.68               95.57   BH       0.002

TOTAL AREA = 4636310.00
MULTIPLIER = 1
```

ISO PROPYL
ALCOHOL
STANDARD



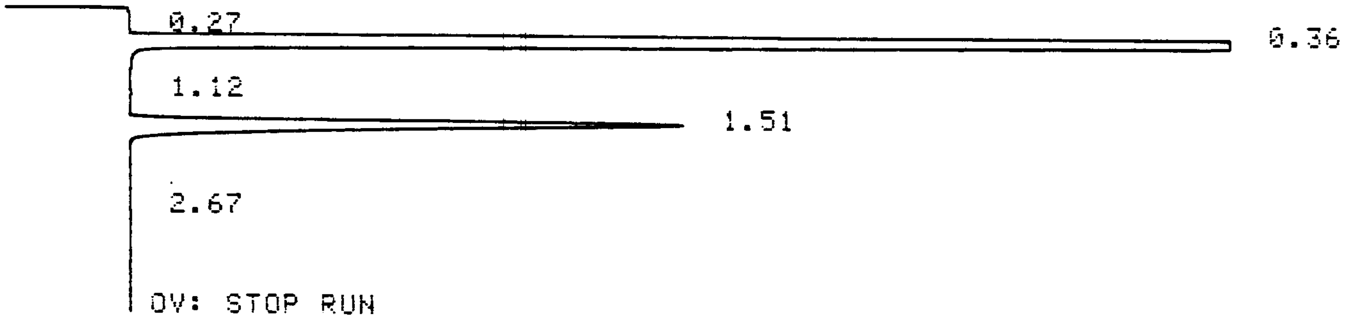
```
【hP】 5880A   SAMPLER INJECTION @ 23:49   MAY 26, 1988
  SAMPLE # :   ID CODE    :
        100
AREA %

   RT                 AREA  TYPE     AREA %

  0.27               73.41   BP       0.002
  0.37          3840910.00   PV      82.115
  1.13             1829.41   VP       0.039
  1.52           834642.00   PB      17.844
  3.62               18.01   BH       0.000

TOTAL AREA = 4677470.00
MULTIPLIER = 1
```

ISO PROPYL
ALCOHOL
STANDARD



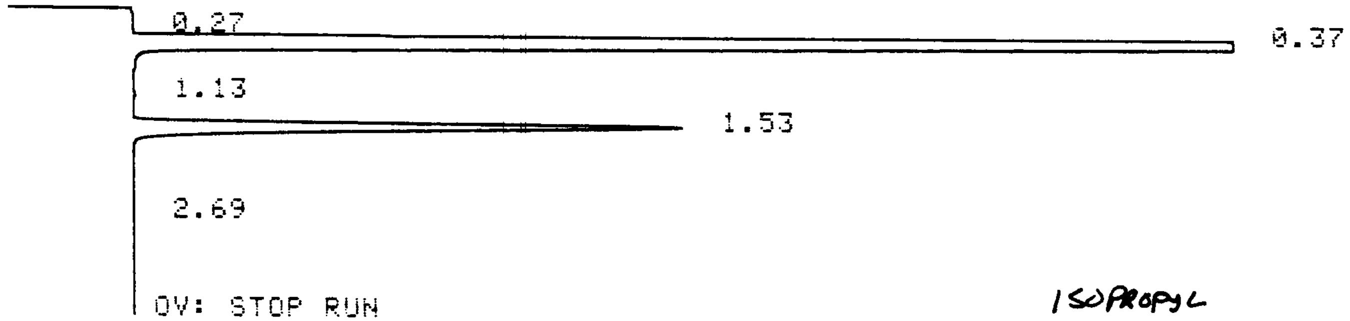
```
【hp】 5880A   SAMPLER INJECTION @ 00:09   MAY 27, 1988
  SAMPLE # :   ID CODE    :
        100
AREA %

   RT                  AREA  TYPE    AREA %

  0.27                72.82   BP      0.002
  0.36           3829250.00   PV     82.098
  1.12              1818.13   VP      0.039
  1.51            833058.00   PB     17.861
  2.67                29.13   BB      0.001

TOTAL AREA = 4664230.00
MULTIPLIER = 1
```

ISO PROPYL
ALCOHOL
STANDARD



ISOPROPYL
ALCOHOL
STANDARD

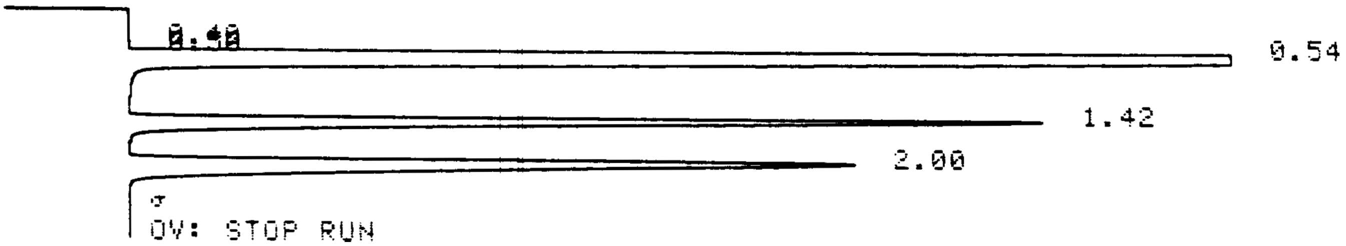
```
【hp】 5880A   SAMPLER INJECTION @ 00:18   MAY 27, 1988
  SAMPLE # :   ID CODE    :
        100
AREA %

   RT                  AREA  TYPE    AREA %

  0.27                70.76   BP      0.002
  0.37           3839770.00   PV     82.246
  1.13              1828.07   VP      0.039
  1.53            826938.00   PB     17.713
  2.69                 9.48   BB      0.000

TOTAL AREA = 4668620.00
MULTIPLIER = 1
```

H.2 15 minute Adsorption Test



```
[hp] 5880A  SAMPLER INJECTION @ 02:32  MAY 26, 1988
  SAMPLE # :  ID CODE    :
       81
AREA %

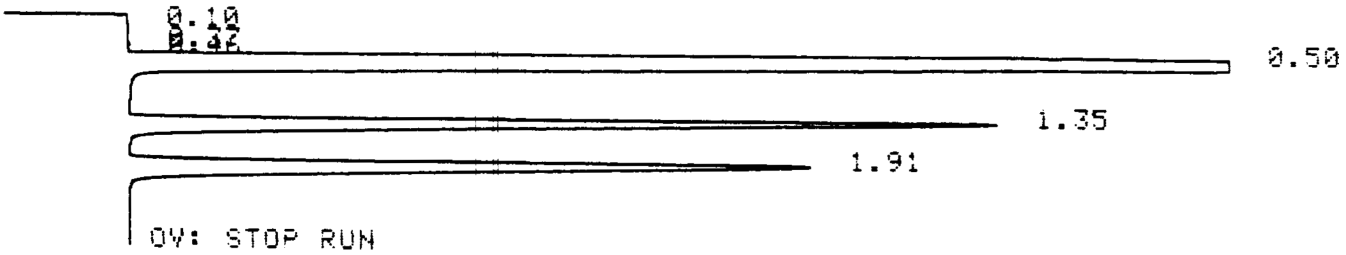
   RT              AREA  TYPE    AREA %

  0.40          1667.38   BH      0.024
  0.50           481.38   HH      0.007
  0.54       4377220.00   HH     62.000
  1.42       1363730.00   HH     19.316
  2.00       1316940.00   HH     18.653

TOTAL AREA = 7060030.00
MULTIPLIER = 1
```

~~STD SOLN~~

Tracer Solution used in 15 minute Static Adsorption Test



```
[hp] 5880A  SAMPLER INJECTION @ 02:41  MAY 26, 1988
  SAMPLE # :  ID CODE    :
        82
AREA %
```

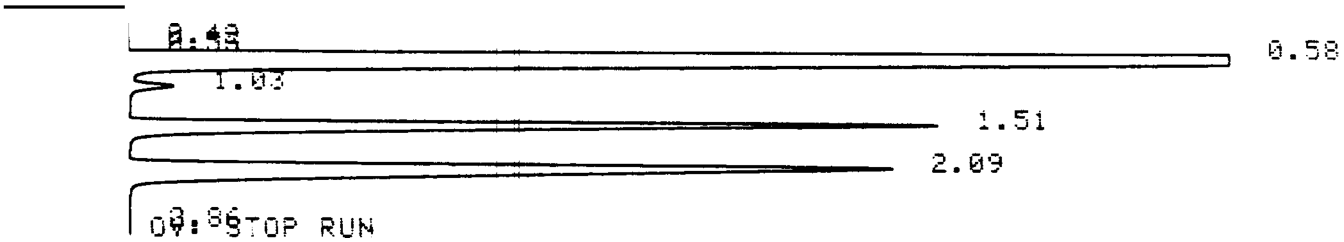
15 minute Static Adsorption Test

```
   RT               AREA  TYPE    AREA %

  0.10            141.99   BV      0.002
  0.37            177.68   BP      0.003
  0.46             87.84   PV      0.001
  0.50        4142700.00   VV     63.271
  1.35        1229250.00   VP     18.774
  1.91        1175150.00   PB     17.948

TOTAL AREA = 6547510.00
MULTIPLIER = 1
```

H.3 Run 6



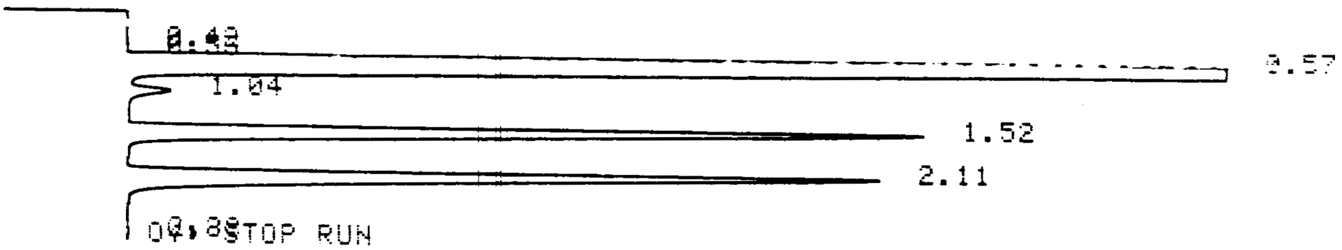
```
[hp] 5880A  SAMPLER INJECTION @ 04:23  MAY 26, 1988
  SAMPLE # :  ID CODE    :
        83
AREA %

   RT              AREA  TYPE    AREA %

  0.42           198.15   BB      0.003
  0.53           119.54   BH      0.002
  0.58       4549180.00   HH     62.568
  1.03         64487.90   HH      0.887
  1.51       1205670.00   HH     16.582
  2.09       1447140.00   HH     19.904
  2.86          3937.04 A HH      0.054

TOTAL AREA = 7270730.00
MULTIPLIER = 1
```

Tracer Solution from Inlet line



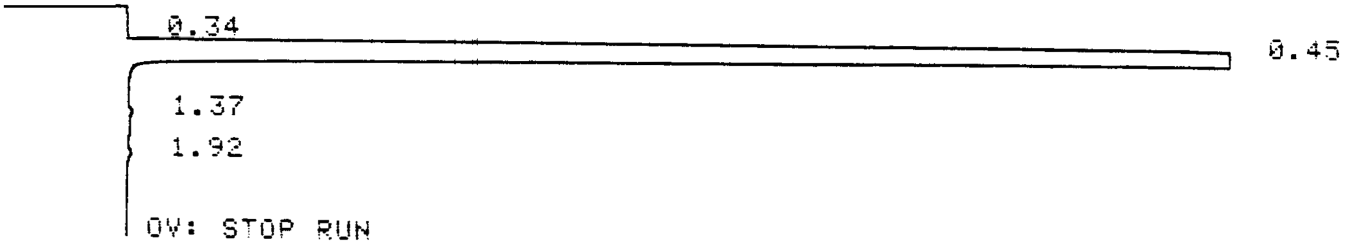
```
[hP] 5880A  SAMPLER INJECTION @ 04:02  MAY 26, 1988
  SAMPLE # :  ID CODE    :
         83
AREA %
```

Tracer Soln from Inlet Line

```
   RT              AREA  TYPE     AREA %

  0.42           737.84   BB       0.010
  0.53           141.06   BH       0.002
  0.57       4531810.00   HH      62.916
  1.04         63279.40   HH       0.879
  1.52       1184440.00   HH      16.444
  2.11       1418970.00   HH      19.700
  2.88         3576.75 A HH        0.050

TOTAL AREA = 7202950.00
MULTIPLIER = 1
```



```
[hp] 5880A  SAMPLER INJECTION @ 20:11  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         53
AREA %

   RT                 AREA  TYPE     AREA %

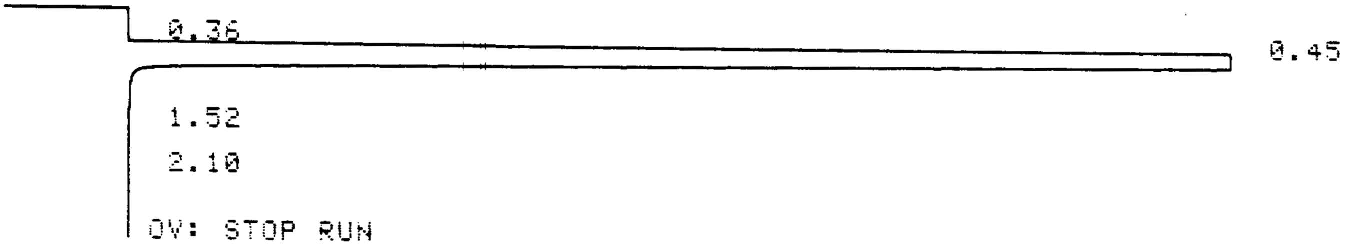
  0.34              410.15   BV       0.006
  0.45          6904300.00   VV      99.549
  1.37            21973.50   VV       0.317
  1.92             8901.59   VB       0.128

TOTAL AREA = 6935590.00
MULTIPLIER = 1
```

Bottle #53

0 %

0 %



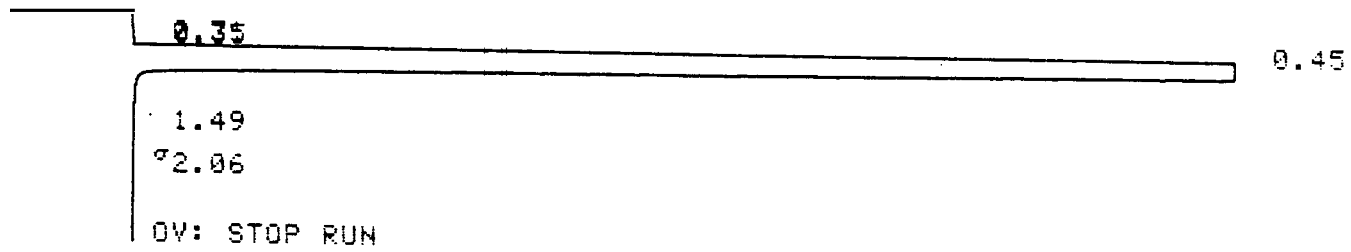
```
[hp] 5880A  SAMPLER INJECTION @ 20:19  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         54
AREA %

   RT                 AREA  TYPE     AREA %

  0.36              808.52   BV       0.011
  0.45          7450020.00   VV      99.965
  1.52             1487.70   VB       0.020
  2.10              339.64   BB       0.005

TOTAL AREA = 7452660.00
MULTIPLIER = 1
```

Bottle #54



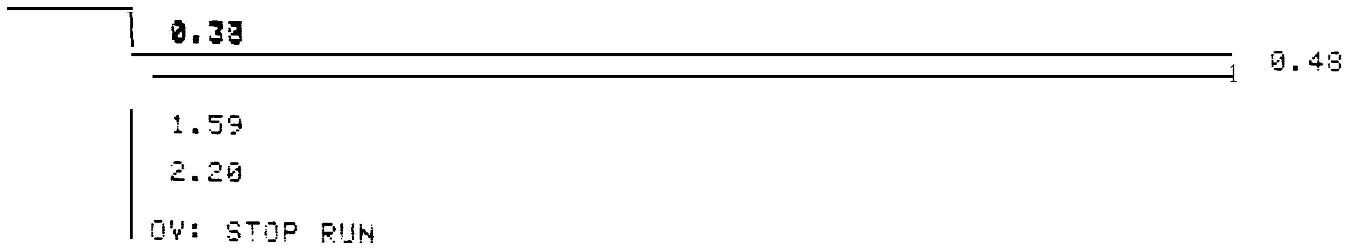
```
【hp】 5880A  SAMPLER INJECTION @ 20:28  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        55
AREA %

   RT               AREA  TYPE    AREA %

  0.31            196.91   BV       0.003
  0.35            148.61   VV       0.002
  0.45        7292100.00   VV      99.967
  1.49           1759.79   VV       0.024
  2.06            293.10   BB       0.004

TOTAL AREA = 7294500.00
MULTIPLIER = 1
```

Bottle #55



```
【hp】 5880A  SAMPLER INJECTION @ 20:36  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        56
AREA %

   RT               AREA  TYPE    AREA %

  0.33            669.16   BV       0.009
  0.38            299.24   VV       0.004
  0.48        7786460.00   VV      99.939
  1.59           3036.40   VV       0.039
  2.20            778.15   VB       0.010

TOTAL AREA = 7791240.00
MULTIPLIER = 1
```

Bottle #56

```
[hp] 5880A  SAMPLER INJECTION @ 20:45  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         57
AREA %

   RT               AREA  TYPE    AREA %

  0.37            129.30   BP      0.002
  0.49        7496590.00   PV     99.948
  1.48           2950.99   VV      0.039
  2.08            788.33   VB      0.011

TOTAL AREA = 7500450.00
MULTIPLIER = 1
```

Bottle #57

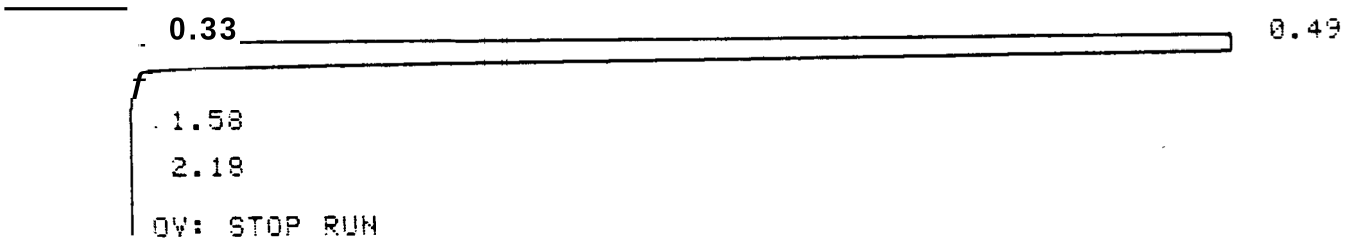
```
[hp] 5880A  SAMPLER INJECTION @ 20:53  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         58
AREA %

   RT               AREA  TYPE    AREA %

  0.38            495.74   PV      0.006
  0.50        7797380.00   VV     99.962
  1.55           2098.49   VV      0.027
  2.15            358.33   BB      0.005

TOTAL AREA = 7800330.00
MULTIPLIER = 1
```

Bottle #58



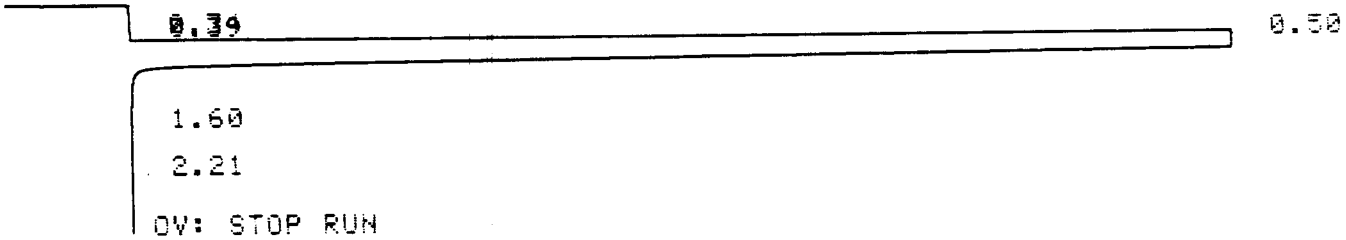
```
[hp] 5880A  SAMPLER INJECTION @ 21:02  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        59
AREA %

   RT               AREA  TYPE     AREA %

  0.33            326.25   BV       0.004
  0.38            166.72   VV       0.002
  0.49        7835320.00   VV      99.972
  1.58           1276.55   VB       0.016
  2.18            414.09   BH       0.005

TOTAL AREA = 7837510.00
MULTIPLIER = 1
```

Bottle #59



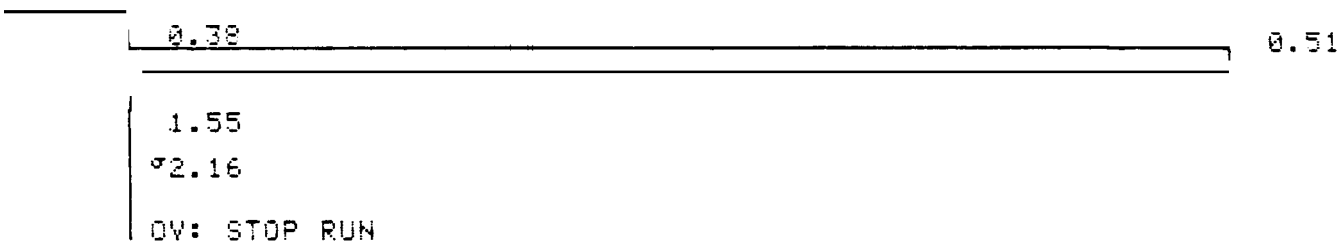
```
[hp] 5880A  SAMPLER INJECTION @ 21:10  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        60
AREA %

   RT               AREA  TYPE     AREA %

  0.34            342.95   BV       0.004
  0.39            173.90   VV       0.002
  0.50        7944220.00   VV      99.969
  1.60           1514.10   VB       0.019
  2.21            441.19   BB       0.006

TOTAL AREA = 7946690.00
MULTIPLIER = 1
```

Bottle #60



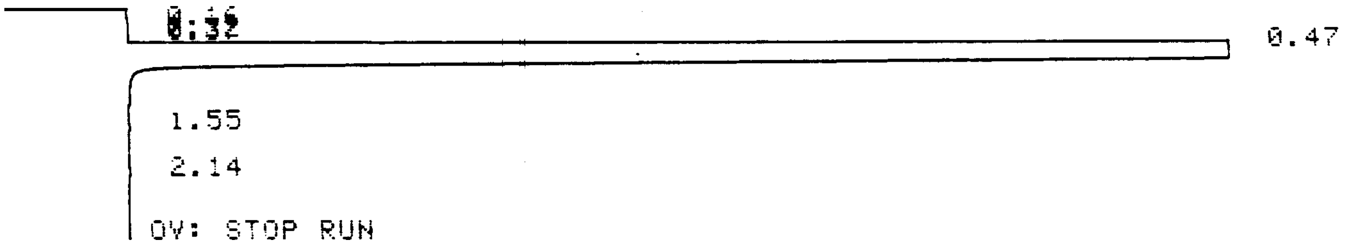
```
【hp】 5880A  SAMPLER INJECTION @ 21:19  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        61
AREA %

   RT                 AREA  TYPE     AREA %

  0.38              250.48   BP       0.003
  0.51          7885130.00   PV      99.964
  1.55             2195.96   VV       0.028
  2.16              396.56   BB       0.005

TOTAL AREA = 7887970.00
MULTIPLIER = 1
```

Bottle #61



```
【hp】 5880A  SAMPLER INJECTION @ 21:27  MAY 25, 1988
  SAMPLE # :  ID CODE    :
        62
AREA %

   RT                 AREA  TYPE     AREA %

  0.16               97.31   BV       0.001
  0.32                6.40   BP       0.000
  0.37              107.15   PP       0.001
  0.47          7573400.00   PV      99.952
  1.55             1682.99   VB       0.022
  2.14             1721.59   BH       0.023

TOTAL AREA = 7577020.00
MULTIPLIER = 1
```

Bottle #62

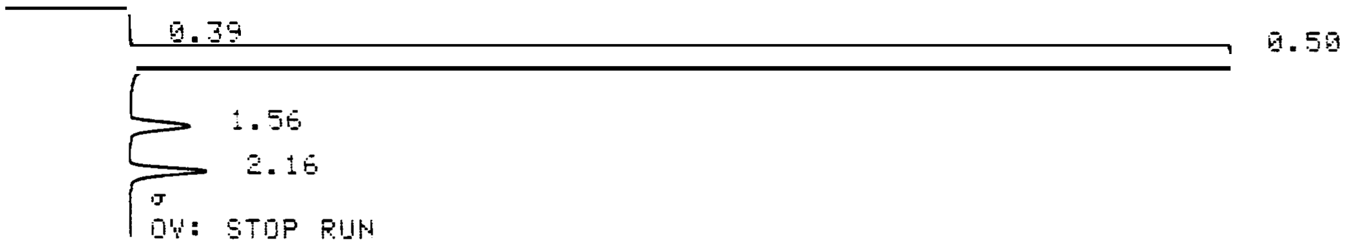
```
[hp] 5880A  SAMPLER INJECTION @ 21:35  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         63
AREA %

   RT              AREA  TYPE    AREA %

  0.37           116.42   BP      0.002
  0.48       7518890.00   PV     99.410
  1.48         18520.40   VV      0.245
  2.06         25968.80   VB      0.343

TOTAL AREA = 7563490.00
MULTIPLIER = 1
```

Bottle #63



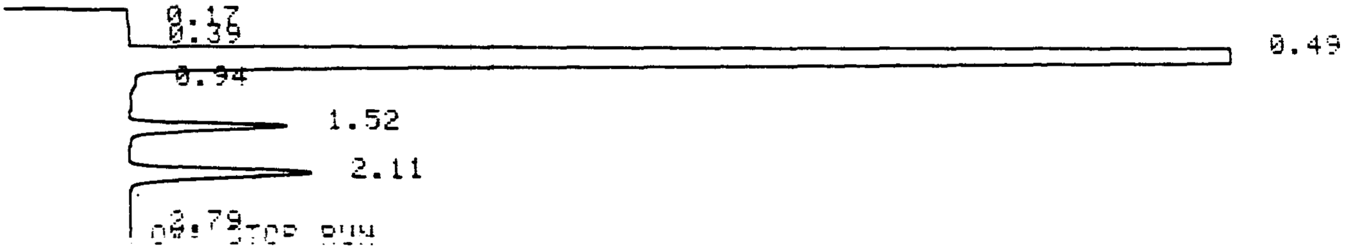
```
[hp] 5880A  SAMPLER INJECTION @ 21:44  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         64
AREA %

   RT              AREA  TYPE    AREA %

  0.39          1334.31   BH      0.017
  0.50       7599320.00   HH     97.045
  1.56         97104.80   HH      1.240
  2.16        132944.00   HH      1.698

TOTAL AREA = 7830700.00
MULTIPLIER = 1
```

Bottle #64



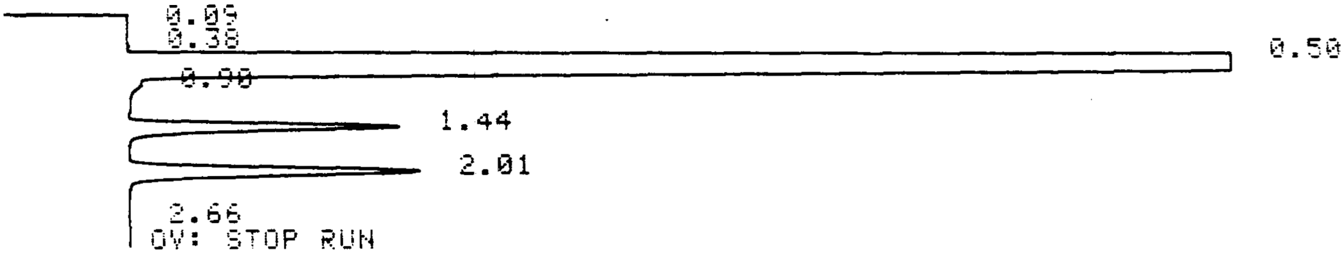
```
[hp] 5880A  SAMPLER INJECTION @ 22:47  MAY 25, 1988
  SAMPLE # :  ID CODE    :
          65
AREA %

   RT              AREA  TYPE    AREA %

  0.17            67.89   BB      0.001
  0.39           122.05   BH      0.002
  0.49       7087910.00   HH     92.760
  0.94         19840.00   HH      0.260
  1.52        229448.00   HH      3.003
  2.11        300597.00   HH      3.934
  2.79          3166.66   HH      0.041

TOTAL AREA = 7641150.00
MULTIPLIER = 1
```

Bottle #65



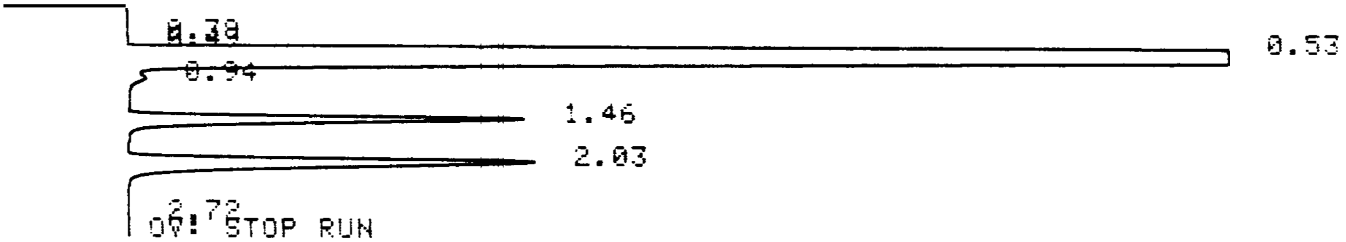
```
[hp] 5880A  SAMPLER INJECTION @ 22:56  MAY 25, 1988
  SAMPLE # :  ID CODE    :
          66
AREA %

   RT              AREA  TYPE    AREA %

  0.09            21.79   BB      0.000
  0.38           113.39   BP      0.002
  0.50       6567840.00   PV     88.502
  0.90         24912.00   VV      0.336
  1.44        366815.00   VV      4.943
  2.01        460706.00   VB      6.208
  2.66           677.48   BB      0.009

TOTAL AREA = 7421090.00
MULTIPLIER = 1
```

Bottle #66



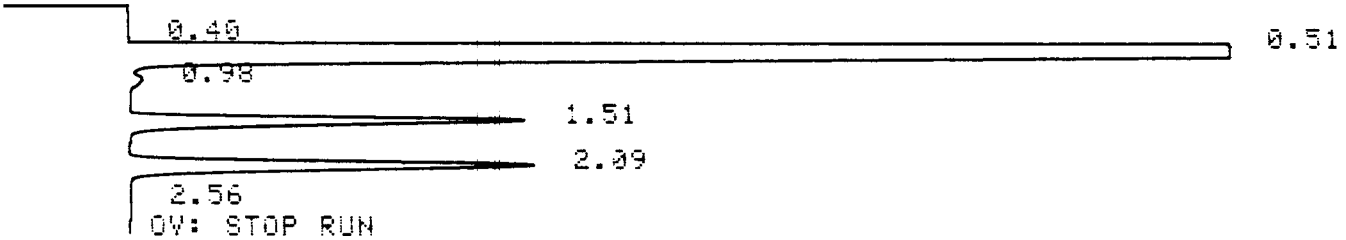
```
[hp] 5880A  SAMPLER INJECTION @ 23:47  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         67
AREA %

   RT                 AREA  TYPE    AREA %

  0.39              376.73   BP      0.005
  0.49              131.36   PV      0.002
  0.53          6206960.00   VV     83.509
  0.94            29908.70   VP      0.402
  1.46           530083.00   PB      7.132
  2.03           664958.00   BP      8.946
  2.72              280.24   PP      0.004

TOTAL AREA = 7432700.00
MULTIPLIER = 1
```

Bottle #67



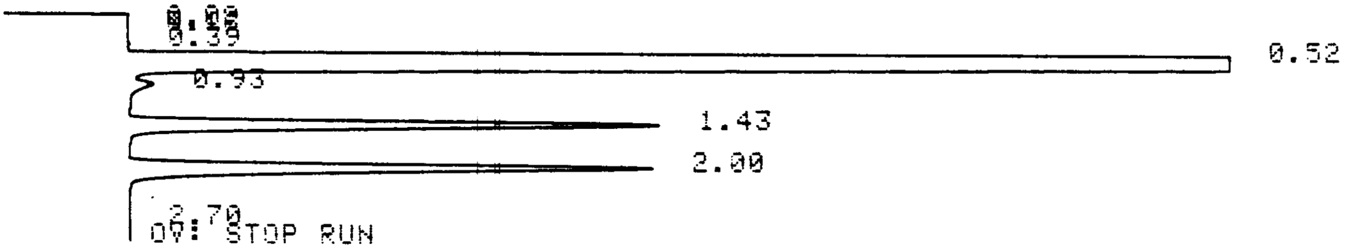
```
[hp] 5880A  SAMPLER INJECTION @ 23:55  MAY 25, 1988
  SAMPLE # :  ID CODE    :
         68
AREA %

   RT                 AREA  TYPE    AREA %

  0.40              170.47   BH      0.002
  0.51          6006090.00   HH     82.019
  0.98            35512.10   HH      0.485
  1.51           582530.00   HH      7.955
  2.09           687911.00   HH      9.394
  2.56            10584.50 A HH      0.145

TOTAL AREA = 7322800.00
MULTIPLIER = 1
```

Bottle #68



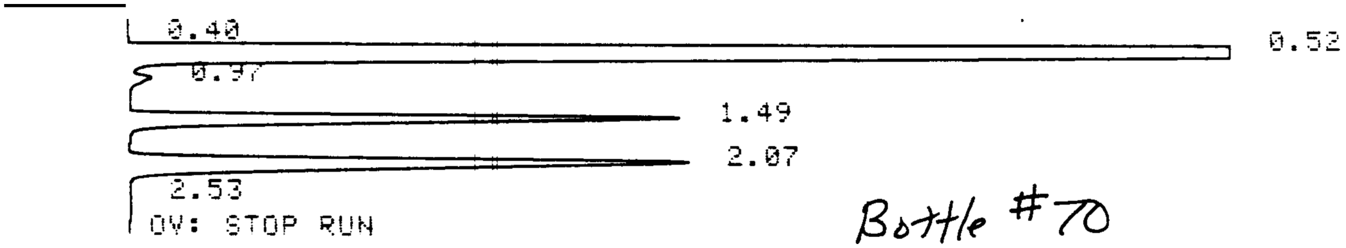
Bottle #69

```
【hp】 5880A   SAMPLER INJECTION @ 00:55  MAY 26, 1988
  SAMPLE # :  ID CODE    :
         69
AREA %

   RT               AREA  TYPE    AREA %

  0.09             29.73   BV      0.000
  0.16             77.53   VV      0.001
  0.39            128.60   BP      0.002
  0.52        5550990.00   PV     77.038
  0.93          37163.30   VP      0.516
  1.43         729475.00   PB     10.124
  2.00         887242.00   BB     12.313
  2.70            387.40   BP      0.005

TOTAL AREA = 7205490.00
MULTIPLIER = 1
```



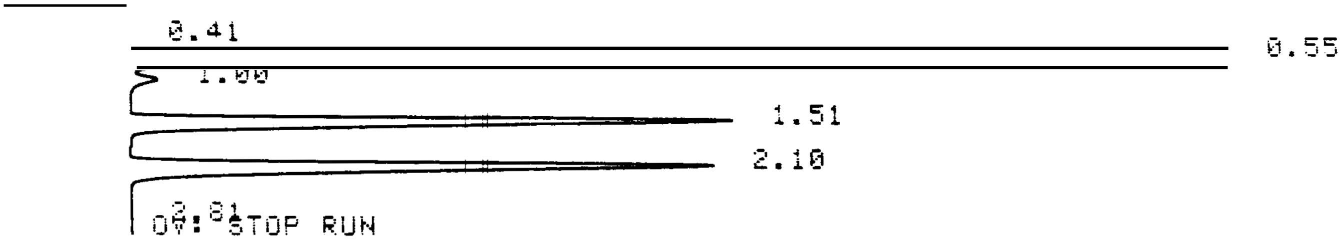
Bottle #70

```
【hp】 5880A   SAMPLER INJECTION @ 01:04  MAY 26, 1988
  SAMPLE # :  ID CODE    :
         70
AREA %

   RT               AREA  TYPE    AREA %

  0.40            515.95   BP      0.007
  0.52        5519800.00   PV     75.036
  0.97          40086.40   VV      0.545
  1.49         812712.00   VB     11.048
  2.07         981967.00   BB     13.349
  2.53          1084.55 A BP      0.015

TOTAL AREA = 7356160.00
MULTIPLIER = 1
```



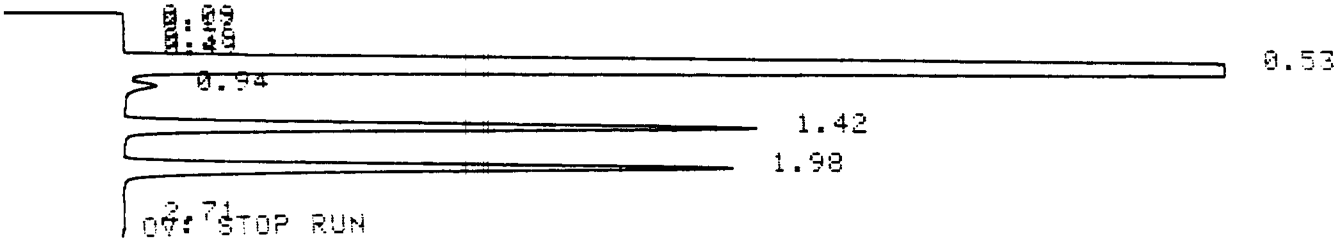
```
[hp] 5880A  SAMPLER INJECTION @ 01:12  MAY 26, 1988
  SAMPLE # :  ID CODE   :
         71
AREA %

   RT               AREA  TYPE    AREA %

  0.41            140.29   BP      0.002
  0.55        5585400.00   BV     74.374
  1.00          41431.10   VP      0.552
  1.51         851491.00   PB     11.338
  2.10        1027830.00   BB     13.686
  2.81           3621.86 A BP      0.048

TOTAL AREA = 7509910.00
MULTIPLIER = 1
```

Bottle #71



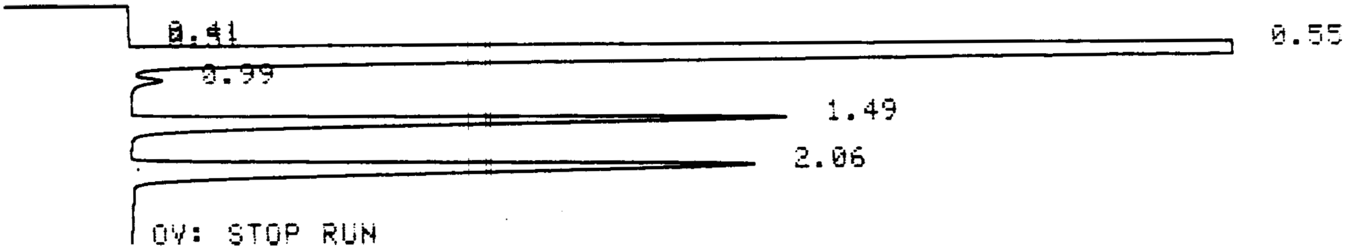
```
[hp] 5880A  SAMPLER INJECTION @ 01:21  MAY 26, 1988
  SAMPLE # :  ID CODE   :
         72
AREA %

   RT              AREA  TYPE    AREA %

  0.08            40.82   BV      0.001
  0.17            43.95   VB      0.001
  0.39           145.68   BP      0.002
  0.49           102.72   PV      0.001
  0.53       5202620.00   VV     72.572
  0.94         46374.80   VV      0.647
  1.42        870041.00   VP     12.136
  1.98       1045100.00   PB     14.578
  2.71          4408.99 A BP      0.062

TOTAL AREA = 7168880.00
MULTIPLIER = 1
```

Bottle #72



```
[hp] 5880A  SAMPLER INJECTION @ 01:29  MAY 26, 1988
  SAMPLE # :  ID CODE   :
        73
```

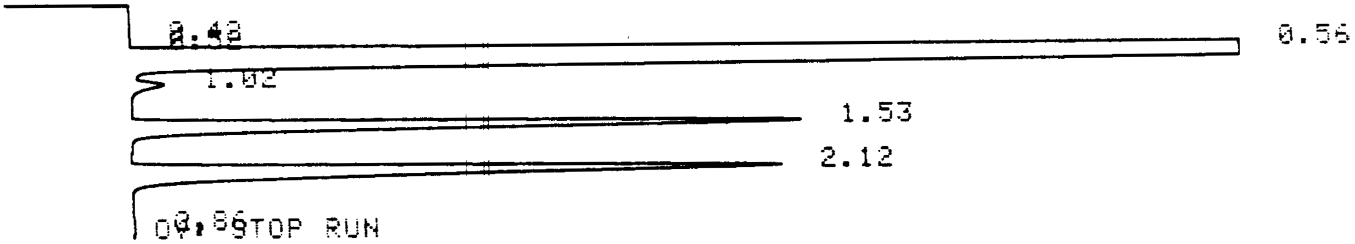
Bottle #73

```
AREA %

   RT               AREA  TYPE    AREA %

  0.41            549.70   PP      0.008
  0.51             96.36   PV      0.001
  0.55        5237450.00   VV     72.102
  0.99          47286.60   VV      0.651
  1.49         899309.00   VP     12.380
  2.06        1079270.00   PB     14.858

TOTAL AREA = 7263960.00
MULTIPLIER = 1
```



```
[hp] 5880A  SAMPLER INJECTION @ 01:38  MAY 26, 1988
  SAMPLE # :  ID CODE   :
        74
```

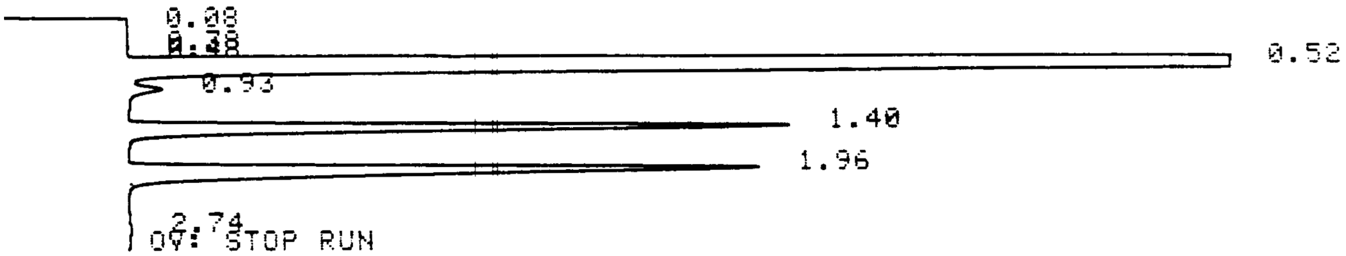
Bottle #74

```
AREA %

   RT               AREA  TYPE    AREA %

  0.42            152.34   BP      0.002
  0.52             84.79   PV      0.001
  0.56        5320290.00   VV     70.779
  1.02          50262.60   VV      0.669
  1.53         969953.00   VP     12.904
  2.12        1170560.00   PB     15.573
  2.86           5509.47 A BH      0.073

TOTAL AREA = 7516810.00
MULTIPLIER = 1
```



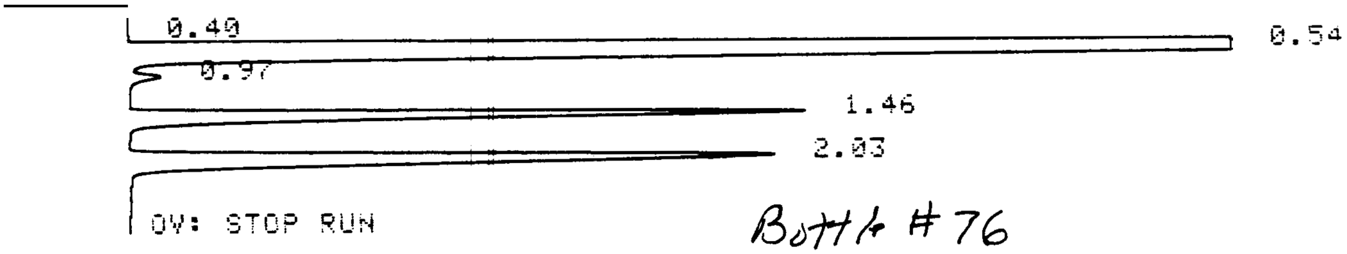
```
[hp] 5880A   SAMPLER INJECTION @ 01:46   MAY 26, 1988
  SAMPLE # :   ID CODE    :
        75
AREA %
```

Bottle #75

```
   RT                 AREA   TYPE     AREA %

  0.08               40.09    BV       0.001
  0.38              147.52    BP       0.002
  0.48               91.21    PV       0.001
  0.52          5000040.00    VV      71.168
  0.93            46262.10    VV       0.658
  1.40           894557.00    VP      12.733
  1.96          1076310.00    PB      15.320
  2.74             8212.11 A BH        0.117

TOTAL AREA = 7025660.00
MULTIPLIER = 1
```



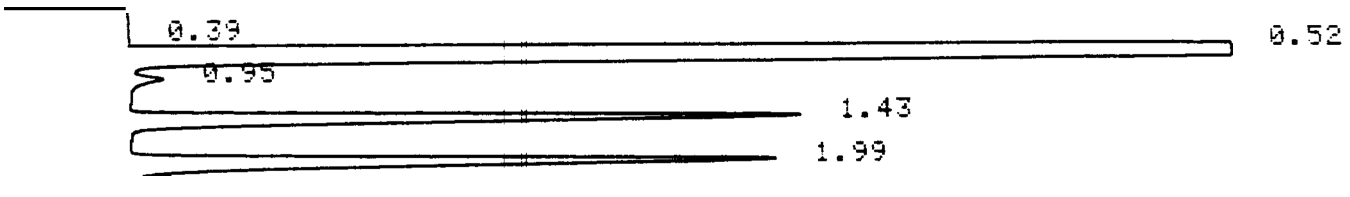
Bottle #76

```
[hp] 5880A   SAMPLER INJECTION @ 01:55   MAY 26, 1988
  SAMPLE # :   ID CODE    :
        76
AREA %

   RT                 AREA   TYPE     AREA %

  0.40              534.01    BP       0.007
  0.54          5032830.00    PV      70.518
  0.97            47427.00    VV       0.665
  1.46           933867.00    VP      13.085
  2.03          1122270.00    PB      15.725

TOTAL AREA = 7136930.00
MULTIPLIER = 1
```



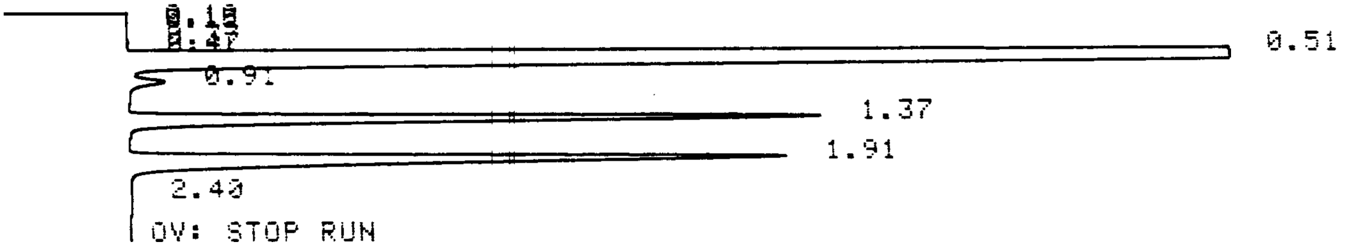
```
 OV: STOP RUN

[hp] 5880A   SAMPLER INJECTION @ 02:03   MAY 26, 1988
  SAMPLE # :   ID CODE    :             Bottle #77
        77
AREA %

   RT                  AREA   TYPE     AREA %

  0.39               153.73    BP       0.002
  0.52           4981410.00    PV      70.196
  0.95             47956.10    VV       0.676
  1.43            938836.00    VP      13.230
  1.99           1128070.00    PB      15.896

TOTAL AREA = 7096420.00
MULTIPLIER = 1
```



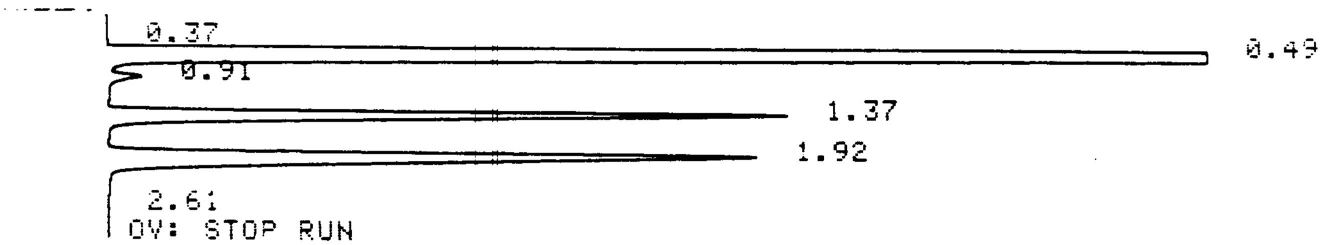
```
 OV: STOP RUN

[hp] 5880A   SAMPLER INJECTION @ 02:12   MAY 26, 1988
  SAMPLE # :   ID CODE    :
        78                                 Bottle #78
AREA %

   RT                  AREA   TYPE     AREA %

  0.10                46.62    BV       0.001
  0.15                77.97    VV       0.001
  0.37               151.89    BP       0.002
  0.47                83.10    PV       0.001
  0.51           4687630.00    VV      69.014
  0.91             48854.80    VV       0.719
  1.37            930789.00    VP      13.704
  1.91           1122790.00    PB      16.530
  2.40              1838.11    BP       0.027

TOTAL AREA = 6792270.00
MULTIPLIER = 1
```



```
[hp] 5880A  SAMPLER INJECTION @ 02:21  MAY 26, 1988
  SAMPLE # :  ID CODE   :
         79
```

Bottle #79

```
AREA %

   RT              ARE5   TYPE     AREA %

  0.37           149.61    BP       0.002
  0.49       4620970.00    BV      69.032
  0.91         44949.70    VV       0.672
  1.37        919602.00    VP      13.738
  1.92       1108190.00    PB      16.555
  2.61            51.63    BP       0.001

TOTAL AREA = 6693920.00
MULTIPLIER = 1
```

Appendix I

Voltage Data

The voltage data were stored in three output files, VOLT0.DAT VOLT1.DAT and VOLT27.DAT. The first column in each of the files is the time in seconds. The next columns are the voltages recorded from the input channels. With one exception complete data sets are given on the following pages. Data recorded in VOLT0.DAT prior to 400 s are not presented because the voltage across Channel 0 did not vary during the first 419 s.

```
OUTPUT FILE VOLT0.DAT
400.6423   1.5604
401.8013   1.5556
402.3782   1.5604
403.0913   1.5604
403.6681   1.5604
405.4798   1.5556
406.1254   1.5604
406.7702   1.5604
407.4153   1.5556
408.5781   1.5604
409.2232   1.5556
409.8721   1.5604
410.5177   1.5604
411.6714   1.5556
412.3168   1.5556
412.9621   1.5604
413.6073   1.5604
415.4427   1.5556
416.0884   1.5556
416.7334   1.5604
417.3785   1.5556
419.2180   6.2540
419.8634   6.2540
420.5144   6.2540
421.1592   6.2540
422.3132   6.2540
422.9578   6.2540
423.6026   6.2540
424.2474   6.2540
425.4059   1.5604
426.6935   1.5604
427.3385   1.5604
427.9839   1.5604
429.1392   1.5556
429.7843   1.5604
430.4297   1.5556
431.0783   1.5604
432.2403   1.5604
432.8854   1.5604
433.5302   1.5604
434.1756   6.2540
435.3311   6.2540
435.9797   6.2540
436.6243   6.2540
437.2694   6.2540
439.1841   6.2540
439.7612   6.2540
440.4743   6.2540
441.0573   6.2540
442.2176   6.2540
442.9308   6.2540
443.5073   6.2540
444.2199   6.2540
445.3813   6.2540
446.7561   6.2540
447.4007   6.2540
448.0460   6.2540
449.2011   6.2540
449.8462   6.2540
450.4913   6.2540
451.1399   6.2540
452.3005   6.2540
452.9451   6.2540
453.5897   6.2540
454.2350   6.2540
```

```
455.3890   6.2540
456.0397   6.2540
456.6843   6.2540
457.3294   6.2540
458.4922   6.2540
459.0695   6.2544)
459.7823   6.2540
460.3646   6.2540
461.5255   6.2540
462.2386   6.2540 VOLT0.DAT
462.8154   6.2540
463.5285   6.2540
465.2748   6.2540
466.0144   1.5604
466.7275   1.5556
467.3046   1.5556
468.4602   1.5556
469.1738   1.5556
469.7506   1.5604
470.4672   1.5604
471.6273   1.5556;
472.2042   1.5556;
472.9170   1.5604
473.4939   1.5604
474.6505   1.5556
475.3639   1.5604
475.9460   1.5604
476.6591   1.5604
477.8203   6.2540
478.4654   6.2540
479.1100   6.2540
479.7551   6.2540
480.9248   6.2540
481.5697   6.2540
482.2148   6.2540
482.8599   6.2540
483.9536   6.2540
484.6670   6.2540
485.8584   6.2540
486.5715   6.2540
487.7270   6.2540
488.3722   1.5556
489.0167   1.5604
489.6621   1.5556
491.4368   1.5604
492.1502   1.5556
492.7270   1.5604
493.4406   1.5604
494.5956   1.5604
495.1728   1.5604
495.8915   1.5604
496.4691   1.5604
497.6309   1.5556
498.3447   1.5556
498.9218   1.5604
499.6352   1.5604
501.4570   6.2540
502.1019   6.2540
502.7467   6.2540
503.3915   6.2540
504.5503   6.2540
505.1952   6.2540
506.5150   6.2540
507.1596   6.2540
508.3146   6.2540
508.9595   6.2540
```

```
509.6040   6.2540
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512.7056   6.2540
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514.5146   1.5604
515.0935   1.5604
515.8117   1.5604
516.3902   1.5604  VOLT0.DAT
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518.8780   1.5604
519.4567   1.5604
520.1719   1.5604
521.3428   1.5604
521.9892   1.5556
522.6357   1.5604
523.2824   1.5556
524.4505   1.5604
525.0283   1.5604
526.3502   1.5556
526.9273   1.5556
528.0903   1.5604
528.8037   1.5604
529.3811   1.5604
530.0952   1.5604
531.2521   6.2540
531.9026   6.2540
532.5482   6.2540
533.1256   6.2540
534.3570   6.2540
535.0026   6.2540
535.6482   6.2540
536.2979   6.2540
537.4558   6.2540
538.1017   6.2540
538.7468   6.2540
539.3925   6.2540
541.1779   6.2540
541.8299   6.2540
542.4751   6.2540
543.0527   6.2540
544.2778   1.5556
544.9232   1.5604
545.5686   1.5604
546.7975   1.5604
547.9608   1.5604
548.6068   1.5556
549.2524   1.5604
549.8983   1.5604
550.9923   1.5604
551.7115   1.5604
552.2889   1.5556
553.0025   1.5604
554.1672   1.5604
554.7448   1.5604
555.4585   1.5604
556.1095   1.5604
557.2709   1.5604
557.9163   1.5604
558.5622   1.5604
559.2078   6.2540
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561.0307   6.2540
561.6076   6.2540
562.3213   6.2540
```

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577.9932	1.5604	
578.7068	1.5604	
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581.1185	1.5604	
581.8383	1.5556	
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597.9557	6.2540	
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666.6813	6.2540	
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733.9470   6.2540
734.5925   6.2540
735.2380   6.2540   VOLT0.DAT
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737.6315   6.2540
738.3450   6.2540
739.5133   6.2540
740.1592   6.2540
740.8040   1.5556
741.4497   1.5604
743.1901   1.5604
743.8425   1.5604
744.4881   1.5604
745.1340   1.5604
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748.0972   1.5604
749.4527   1.5604
750.5453   1.5604
751.2593   1.5604
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753.7160   1.5604
754.3670   1.5604
755.0126   1.5604
755.6582   1.5604
756.8190   1.5604
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759.8595   1.5604
760.5739   1.5604
761.1513   1.5604
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798.1713   1.5604
799.9211   1.5604
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801.8583   1.5604
803.0253   1.5604
803.6707   1.5604
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826.7718   6.2540
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831.2331   6.2540
831.8786   6.2540
832.5247   6.2540
833.6902   6.2540
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837.3702   1.5556
```

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843.6539   1.5604
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844.9514   1.5604   VOLT0.DAT
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847.4035   1.5556
847.9814   1.5604
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855.0146   1.5604
856.1801   1.5604
856.7578   1.5604
857.4711   1.5604
858.0488   6.2540
859.2774   6.2540
859.9284   6.2540
860.5738   6.2540
861.2194   6.2540
862.3843   6.2540
863.0302   6.2540
863.6754   6.2540
864.3274   6.2540
865.4929   6.2540
866.0708   6.2540
866.7842   6.2540
867.3618   6.2540
868.5971   6.2540
869.9995   6.2540
870.6451   6.2540
871.2905   6.2540
872.3823   6.2540
873.0960   6.2540
873.6728   6.2540
874.3899   6.2540
876.0664   6.2540
876.7800   6.2540
877.3574   6.2540
878.0710   6.2540
879.2317   6.2540
879.8824   6.2540
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882.9842   6.2540
883.6298   6.2540
884.2139   6.2540
885.3811   6.2540
886.0947   6.2540
886.6718   6.2540
887.3857   6.2540
888.5511   6.2540
889.8375   6.2540
890.4832   6.2540
891.1286   6.2540
```

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892.9346    6.2540
893.5800    6.2540
894.2291    6.2541)
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895.9735    6.2540
896.6871    6.2540
897.2648    6.2540
898.4258    6.2540
899.1396    6.2540   VOLT0.DAT
899.7213    6.2540
900.4352    6.2540
902.2856    6.2540
902.9312    6.2540
903.5762    6.25410
904.2218    6.2540
905.9146    6.25410
906.6279    6.2540
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OUTPUT FILE VOLT1.DAT
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   7.9297   4.5983
  11.0344   4.5884
  14.1342   4.5883
  17.2349   4.5836
  20.2752   4.5836
  24.0687   4.5883
  27.9203   4.5788
  31.0214   4.5788
  34.1224   4.5788
  37.2237   4.5788
  40.2642   4.5788
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424.2474   4.5885
427.9839   4.5788
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   11.0344     4.0611     4.4274     4.9695     4.4274     2.4151     2.5372
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  188.7539     4.0464     4.4176     4.9695     4.4371     2.4103     2.4982
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  201.2282     3.9878     4.3980     4.9695     4.4274     2.3761     2.4933
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  208.0127     4.0269     4.4078     4.9695     4.4371     2.4005     2.4933
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224.2093	3.9927	4.3980	4.9695	4.4274	2.3810	2.4933
227.9571	3.9585	4.3932	4.9695	4.4176	2.3516	2.4835
231.0592	3.9780	4.3980	4.9695	4.4225	2.3614	2.4786
234.1490	3.9731	4.3932	4.9695	4.4225	2.3614	2.4835
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262.6820	4.0220	4.4078	4,9695	4.4322	2.3956	2.4835
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295.1414	3.9194	4.3785	4.9646	4.4127	2.3272	2.4444
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321.1914	3.9487	4.3883	4.9646	4.4176	2.3419	2.4591
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334.1714	3.9438	4.3883	4.9646	4.4225	2.3419	2.4591
337.8455	3.9927	4.4029	4.9646	4.4322	2.3712	2.4689
341.6553	4.0269	4.4078	4.9695	4.4420	2.3956	2.4835
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357.7669	3.9731	84.3932	4.9695	4.4274	2.3565	2.4786
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368.3893	3.9878	4.3980	4.9646	4.4322	2.3663	2.4835
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380.7924	3.9731	(1.3932	4.9695	4.4274	2.3614	2.4786
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394.4332	4.0171	4.4078	4.9695	4.4322	2.3858	2.5031
397.5354	4.0073	4.4029	4.9695	4.4371	2.3810	2.4982
400.6423	3.9976	4.4029	4.9695	4.4274	2.3712	2.4835
403.6681	3.9927	4.4029	4.9695	4.4274	2.3663	2.4835
407.4153	4.0415	4.4127	4.9695	4.4371	2.3956	2.4884
410.5177	4.0122	4.4078	4.9695	4.4322	2.3858	2.5031
413.6073	4,0024	4.4029	4.9695	4.4274	2.3761	2.4933
417.3785	4.0513	4.4176	4.9695	4.4420	2.4054	2.4982
421.1592	4.0708	4.4225	4.9695	4.4420	2.4151	2.5031
424.2474	4.0366	4.4127	4.9695	4.4371	2.4005	2.5128
427.9839	3.9976	4.4029	4.9695	4.4225	2.3614	2.4884

431.0783	4.0024	4.4078	4.9646	4.4274	2.3663	2.4884
434.1756	4.0024	4.4029	4.9695	4.4274	2.3712	2.4835
437.2694	3.9976	4.4029	4.9695	4.4274	2.3663	2.4835
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444.2199	4.0269	4.4127	4.9695	4.4371	2.3907	2.5079
448.0460	3.9829	4.3980	4.9695	4.4274	2.3614	2.4884
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454.2350	3.9976	4.4029	4.9695	4.4322	2.3712	2.4884
457.3294	3.9927	4.4029	4.9695	4.4214	2.3663	2.4884
460.3646	3.9927	4.4029	4.9695	4.4274	2.3565	2.4786
463.5285	3.9878	4.3932	4.9646	4.4274	2.3565	2.4737
467.3046	4.0220	4.4029	4.9695	4.4274	2.3761	2.4737
470.4672	4.0073	4.3932	4.9695	4.4176	2.3565	2.4786
473.4939	3.9927	4.3883	4.9646	4.4127	2.3468	2.4689
476.6591	3.9780	4.3785	4.9646	4.3980	2.2979	2.4200
479.7551	3.9585	4.3590	4.9646	4.3785	2.2198	2.3419
482.8599	3.9438	4.3492	4.9646	4.3639	2.1514	2.2735
486.5715	3.8022	4.3004	4.9646	4.3101	2.0244	2.1514
489.6621	3.8413	4.3101	4.9646	4.3199	2.0147	2.1270
493.4406	3.8559	4.3101	4.9646	4.3004	1.9170	2.0049
496.4691	3.7827	4.2906	4.9646	4.2759	1.8144	1.9219
499.6352	3.7094	4.2711	4.9646	4.2466	1.7118	1.8144
503.3915	3.6313	4.2564	4.9646	4.2125	1.5751	1.6630
507.1596	3.4164	4.1832	4.9597	4.1441	1.4237	1.5360
510.2489	3.4115	4.1978	4.9597	4.1538	1.4237	1.5165
513.3521	3.3626	4.1880	4.9597	4.1392	1.3651	1.4579
516.3902	3.3138	4.1636	4.9597	4.1245	1.3114	1.4042
520.1719	3.2747	4.1343	4.9597	4.1001	1.2332	1.3065
523.2824	3.2357	4.0904	4.9597	4.0806	1.1941	1.2772
526.9213	3.1184	4.0024	4.9548	4.0317	1.0867	1.1893
530.0952	3.1331	3.9829	4.9597	4.0415	1.1013	1.1844
533.1256	3.1233	3.9292	4.9548	4.0317	1.0720	1.1551
536.2979	3.1038	3.8413	4.9548	4.0220	1.0476	1.1306
539.3925	3.0891	3.6996	4.9548	4.0073	1.0281	1.1111
543.0527	3.0891	3.4408	4.9548	3.9976	1.0037	1.0672
546.7975	3.0647	3.2161	4.9548	3.9878	0.9890	1.0720
549.8983	3.0501	3.0208	4.9548	3.9829	0.9792	1.0574
553.0025	3.0354	2.8596	4.9499	3.9829	0.9744	1.0525
556.10 95	3.0256	2.7131	4.9451	3.9780	0.9744	1.0525
559.2078	3.0159	2.5812	4.9402	3.9731	0.9695	1.0476
562.3213	3.0110	2.4689	4.9353	3.9731	0.9646	1.0427
566.0976	2.9963	2.3419	4.9304	3.9683	0.9548	1.0427
569.4005	2.9915	2.2344	4.9304	3.9634	0.9548	1.0281
572.5020	2.9817	2.1465	4.9255	3.9536	0.9499	1.0281
575.5413	2.9768	2.0733	4.9255	3.9145	0.9499	1.0281
518.7068	2.9719	2.0098	4.9206	3.8364	0.9499	1.0281
582.4157	2.9817	1.9365	4.9206	3.6703	0.9499	1.0037
585.5786	2.9670	1.8828	4.9158	3.5092	0.9402	1.0134
589.3692	2.9768	1.8339	4.9158	3.3187	0.9451	0.9988
592.4020	2.9573	1.7900	4.9158	3.1868	0.9353	1.0085
596.0782	2.9670	1.7656	4.9109	3.0598	0.9451	0.9988
599.2473	2.9475	1.7265	4.9109	2.9719	0.9304	1.0037
602.3615	2.9328	1.7021	4.9109	2.8987	0.9255	0.9988
605.3913	2.9280	1.6874	4.9109	2.8352	0.9255	0.9988
609.3013	2.9475	1.6777	4.9109	2.7570	0.9402	0.9841
612.4038	2.9231	1.6484	4.9060	2.7228	0.9206	0.9890
615.5060	2.9133	1.6337	4.9060	2.6838	0.9158	0.9890
618.6065	2.9084	1.6239	4.9060	2.6496	0.9158	0.9890
622.4758	2.9231	1.6288	4.9060	2.5958	0.9304	0.9744
625.5741	2.9035	1.6044	4.9060	2.5665	0.9109	0.9792
629.4258	2.9182	1.6142	4.9109	2.5519	0.9255	0.9695
632.5331	2.8987	1.5849	4.9060	2.5177	0.9011	0.9744
635.6296	2.8889	1.5751	4.9060	2.4933	0.9011	0.9695
638.7393	2.8791	1.5702	4.9060	2.4689	0.8962	0.9695
641.8438	2.8742	1.5653	4.9060	2.4493	0.8962	0.9646
645.6724	2.8938	1.5849	4.9109	2.4444	0.9158	0.9597

649.3623	2.8547	1.5360	4.9060	2.3956	0.8767	0.9499
652.4696	2.8596	1.5458	4.9060	2.3907	0.8864	0.9548
655.4986	2.8547	1.5458	4.9109	2.3761	0.8864	0.9597
658.6758	2.8498	1.5409	4.9109	2.3614	0.8913	0.9597
661.7785	2.8449	1.5409	4.9109	2.3516	0.8913	0.9597
665.5191	2.8694	1.5653	4.9109	2.3614	0.9158	0.9597
669.3441	2.8303	1.5165	4.9109	2.3077	0.8669	0.9451
673.1024	2.8645	1.5604	4.9158	2.3419	0.9109	0.9499
676.2692	2.8449	0.5360	4.9109	2.3223	0.8913	0.9548
679.3780	2.8352	1.5263	4.9109	2.2979	0.8864	0.9499
682.4806	2.8303	1.5263	4.9109	2.2930	0.8816	0.9499
685.5868	2.8205	3.5214	4.9109	2.2735	0.8816	0.9451
689.3016	2.7326	1.4090	4.9060	2.1123	0.7790	0.8571
692.4070	2.7717	1.4725	4.9109	2.2002	0.8376	0.9011
695.5096	2.7863	1.4969	4.9109	2.2149	0.8571	0.9255
699.2435	2.8205	1.5360	4.9109	2.2540	0.9011	0.9451
702.2748	2.8107	1.5165	4.9109	2.2393	0.8864	0.9499
705.4538	2.8010	1.5116	4.9109	2.2247	0.8816	0.9499
709.1531	2.7131	1.4042	4.9060	2.0635	0.7741	0.8571
712.2568	2.7473	1.4676	4.9060	2.1514	0.8327	0.8962
715.3576	2.7668	1.4872	4.9109	2.1709	0.8571	0.9206
718.3978	2.7717	1.4921	4.9109	2.1758	0.8669	0.9304
721.5634	2.7766	1.4969	4.9109	2.1807	0.8718	0.9402
725.2905	2.8010	1.5263	4.9109	2.2149	0.9011	0.9451
729.0361	2.6886	1.3895	4.9060	2.0293	0.7643	0.8474
732.1372	2.7277	1.4530	4.9060	2.1221	0.8230	0.8913
735.2380	2.7424	1.4774	4.9109	2.1465	0.8474	0.9158
738.3450	2.7521	1.4872	4.9109	2.1514	0.8571	0.9255
741.4497	2.7521	1.4921	4.9109	2.1563	0.8669	0.9353
745.1340	2.7814	1.5214	4.9109	2.1954	0.8962	0.9402
749.4527	2.7766	1.5165	4.9109	2.2051	0.8767	0.9353
752.5503	2.7619	1.4969	4.9109	2.1758	0.8669	0.9304
755.6582	2.7570	1.4921	4.9109	2.1661	0.8620	0.9304
758.7609	2.7521	1.4921	4.9109	2.1612	0.8620	0.9304
761.8651	2.7473	I.4921	4.9109	2.1563	0.8620	0.9255
764.9751	2.7473	1.4872	4.9109	2.1514	0.8620	0.9304
768.7241	2.7375	I.4823	4.9060	2.1563	0.8523	0.9255
771.8222	2.7375	1.4823	4.9060	2.1465	0.8523	0.9255
775.6966	2.7668	1.5214	4.9109	2.1905	0.8913	0.9304
778.7992	2.7473	1.4969	4.9109	2.1661	0.8669	0.9353
781.9035	2.7375	1.4921	4.9109	2.1563	0.8620	0.9304
785.0113	2.7375	1.4872	4.9060	2.1514	0.8571	0.9255
788.8607	2.7228	1.4823	4.9060	2.1563	0.8474	0.9206
791.8916	2.7179	1.4774	4.9060	2.1416	0.8474	0.9158
795.0703	2.7179	1.4823	4.9060	2.1416	0.8523	0.9158
798.1713	2.7179	1.4823	4.9060	2.1416	0.8523	0.9206
801.8583	2.7473	1.5165	4.9109	2.1807	0.8816	0.9255
804.9675	2.7277	1.4921	4.9060	2.1563	0.8620	0.9255
808.0013	2.7228	1.4872	4.9060	2.1514	0.8571	0.9206
811.9130	2.7473	1.5214	4.9109	2.1856	0.8816	0.9206
815.0196	2.7277	1.4969	4.9060	2.1612	0.8571	0.9255
818.1165	2.7179	1.4872	4.9060	2.1465	0.8523	0.9206
821.2248	2.7131	1.4872	4.9060	2.1465	0.8523	0.9158
824.9422	2.7375	1.5165	4.9109	2.1807	0.8718	0.9206
828.7767	2.7424	1.5263	4.9109	2.1905	0.8767	0.9206
832.5247	2.7424	1.5311	4.9109	2.1905	0.8767	0.9158
835.6318	2.7228	1.5018	4.9060	2.1612	0.8474	0.9109
838.6615	2.7131	1,4921	4.9060	2.1514	0.8425	0.9060
841.8366	2.7082	1.4872	4.9060	2.1465	0.8425	0.9060
844.9514	2.7033	1.4823	4.9060	2.1368	0.8376	0.9011
847.9814	2.6984	1.4823	4.9060	2.1368	0.8376	0.9011
851.9142	2.7228	1.5165	4.9060	2.1709	0.8669	0.9060
855.0146	2.7082	1.4921	4.9060	2.1514	0.8474	0.9109
858.0488	2.6984	1.4872	4.9060	2.1416	0.8376	0.9060
861.2194	2.6935	1.4823	4.9060	2.1368	0.8376	0.9011
864.3274	2.6886	1.4823	4.9060	2.1368	0.8376	0.9011

867.3618	2.6886	1.4774	4.9060	2.1368	0.8376	0.9011
871.2905	2.6593	1.4481	4.9011	2.1026	0.8083	0.8864
874.3899	2.6740	1.4676	4.9011	2.1221	0.8230	0.8913
878.0710	2.7228	1.5116	4.9060	2.1709	0.8718	0.9158
881.1736	2.7033	1.4921	4.9011	2.1465	0.8523	0.9158
884.2139	2.6886	1.4823	4.9011	2.1368	0.8425	0.9109
887.3857	2.6886	1.4774	4.9011	2.1319	0.8376	0.9109
891.1286	2.6642	1.4530	4.9011	2.1026	0.8132	0.8913
894.2291	2.6740	1.4628	4.9011	2.1123	0.8230	0.8913
897.2648	2.6740	1.4628	4.9011	2.1172	0.8278	0.8962
900.4352	2.6740	1.4628	4.9011	2.1172	0.8278	0.8962
904.2218	2.7082	1.5067	4.9011	2.1612	0.8669	0.9109

Appendix J

VARPRO Regression Subroutine

This appendix presents the VARPRO nonlinear regression subroutine. Documentation is contained within the code. The program listing begins on the next page.

```
c
      SUBROUTINE VARPRO (L, NL, N, NMAX, LPP2, IV, T, Y, W, ADA, A,
     X IPRINT, ALF, BETA, IERR)
C
C           GIVEN A SET OF N OBSERVATIONS, CONSISTING OF VALUES Y(1),
C        Y(2), ..., Y(N) OF A DEPENDENT VARIABLE Y, WHERE Y(I)
C        CORRESPONDS TO THE IV INDEPENDENT VARIABLE(S) T(I,1), T(I,2),
C        ..., T(I,IV), VARPRO ATTEMPTS TO COMPUTE A WEIGHTED LEAST
C        SQUARES FIT TO A FUNCTION ETA (THE 'MODEL') WHICH IS A LINEAR
C        COMBINATION
C                         L
C       ETA(ALF, BETA; T) = SUM BETA  * PHI (ALF; T) + PHI    (ALF; T)
C                        J=1      J      J              Lt1
C
C        OF NONLINEAR FUNCTIONS PHI(J) (E.G., A SUM OF EXPONENTIALS AND/
C        OR GAUSSIANS). THAT IS, DETERMINE THE LINEAR PARAMETERS
C        BETA(J) AND THE VECTOR OF NONLINEAR PARAMETERS ALF BY MINIMIZ-
C        ING
C
C                      2    N                                2
C          NORM(RESIDUAL)  = SUM W  * (Y  - ETA(ALF, BETA; T )) .
C                           I=1   I     I                    I
C
C        THE (L+1)-ST TERM I6 OPTIONAL, AND IS USED WHEN IT IS DESIRED
C        TO FIX ONE OR MORE OF THE BETA'S (RATHER THAN LET THEM BE
C        DETERMINED). VARPRO REQUIRES FIRST DERIVATIVES OF THE PHI'S.
C
C                                NOTES:
C
C        A) THE ABOVE PROBLEM IS ALSO REFERRED TO AS 'MULTIPLE
C        NONLINEAR REGRESSION'. FOR USE IN STATISTICAL ESTIMATION,
C        VARPRO RETURNS THE RESIDUALS, THE COVARIANCE MATRIX OF THE
C        LINEAR AND NONLINEAR PARAMETERS, AND THE ESTIMATED VARIANCE OF
C        THE OBSERVATIONS.
C
C        B) AN ETA OF THE ABOVE FORM IS CALLED 'SEPARABLE'. THE
C        CASE OF A NONSEPARABLE ETA CAN BE HANDLED BY SETTING L = 0
C        AND USING PHI(L+1).
C
C        C) VARPRO MAY ALSO BE USED TO SOLVE LINEAR LEAST SQUARES
C        PROBLEMS (IN THAT CASE NO ITERATIONS ARE PERFORMED). SET
C        NL = 0.
C
C        D) THE MAIN ADVANTAGE OF VARPRO OVER OTHER LEAST SQUARES
C        PROGRAMS IS THAT NO INITIAL GUESSES ARE NEEDED FOR THE LINEAR
C        PARAMETERS. NOT ONLY DOES THIS MAKE IT EASIER TO USE, BUT IT
C        OFTEN LEADS TO FASTER CONVERGENCE.
C
C
C     DESCRIPTION OF PARAMETERS
C
C        L       NUMBER OF LINEAR PARAMETERS BETA (MUST BE .GE. 0).
C        NL      NUMBER OF NONLINEAR PARAMETERS ALF (MUST BE .GE. 0).
C        N       NUMBER OF OBSERVATIONS. N MUST BE GREATER THAN L + NL
C                (I.E., THE NUMBER OF OBSERVATIONS MUST EXCEED THE
C                NUMBER OF PARAMETERS).
C        IV      NUMBER OF INDEPENDENT VARIABLES T.
C        T       REAL N BY IV MATRIX OF INDEPENDENT VARIABLES. T(I, J)
C                CONTAINS THE VALUE OF THE I-TH OBSERVATION OF THE J-TH
C                INDEPENDENT VARIABLE.
C        Y       N-VECTOR OF OBSERVATIONS, ONE FOR EACH ROW OF T.
C        W       N-VECTOR OF NONNEGATIVE WEIGHTS. SHOULD BE SET TO 1'S
C                IF WEIGHTS ARE NOT DESIRED. IF VARIANCES OF THE
C                INDIVIDUAL OBSERVATIONS ARE KNOWN, W(I) SHOULD BE SET
C                TO 1./VARIANCE(I).
C        INC     NL X (L+1) INTEGER INCIDENCE MATRIX. INC(K, J) = 1 IF
```

```
C                NON-LINEAR PARAMETER ALF(K) APPEARS IN THE J-TH
C                FUNCTION PHI(J) .  (THE PROGRAM SETS ALL OTHER INC(K, J)
C                TO ZERO.)  IF PHI(L+1) IS INCLUDED IN THE MODEL,
C                THE APPROPRIATE ELEMENTS OF THE (L+1)-ST COLUMN SHOULD
C                BE SET TO 1'S.  INC IS NOT NEEDED WHEN L = 0 OR NL = 0.
C                CAUTION:  THE DECLARED ROW DIMENSION OF INC (IN ADA)
C                MUST CURRENTLY BE SET TO 12.  SEE 'RESTRICTIONS' BELOW.
C       NMAX     THE DECLARED ROW DIMENSION OF THE MATRICES A AND T.
C                IT MUST BE AT LEAST MAX(N, 2*NL+3) .
C       LPP2     L+P+2, WHERE P IS THE NUMBER OF ONES IN THE MATRIX INC.
C                THE DECLARED COLUMN DIMENSION OF A MUST BE AT LEAST
C                LPP2 .  (IF L = 0, SET LPP2 = NL+2. IF NL = 0, SET LPP2
C                L+2.)
C       A        REAL MATRIX OF SIZE MAX(N, 2*NL+3) BY L+P+2.  ON INPUT
C                IT CONTAINS THE PHI(J)'S AND THEIR DERIVATIVES (SEE
C                BELOW).  ON OUTPUT, THE FIRST L+NL ROWS AND COLUMNS OF
C                A WILL CONTAIN AN APPROXIMATION TO THE (WEIGHTED)
C                COVARIANCE MATRIX AT THE SOLUTION (THE FIRST L ROWS
C                CORRESPOND TO THE LINEAR PARAMETERS, THE LAST NL TO THE
C                NONLINEAR 'ONES), COLUMN L+NL+1 WILL CONTAIN THE
C                WEIGHTED RESIDUALS (Y - ETA) , A( 1, L+NL+2) WILL CONTAIN
C                THE (EUCLIDEAN) NORM OF THE WEIGHTED RESIDUAL, AND
C                A(2, L+NL+2) WILL CONTAIN AN ESTIMATE OF THE (WEIGHTED)
C                VARIANCE OF THE OBSERVATIONS, NORM(RESIDUAL)**2/
C                (N - L - NL) .
C       IPRINT   INPUT INTEGER CONTROLLING PRINTED OUTPUT.  IF IPRINT IS
C                POSITIVE, 'THENONLINEAR PARAMETERS, THE NORM OF THE
C                RESIDUAL, AND THE MARQUARDT PARAMETER WILL BE OUTPUT
C                EVERY IPRINT-TH ITERATION (AND INITIALLY, AND AT THE
C                FINAL ITERATION).  THE LINEAR PARAMETERS WILL BE
C                PRINTED AT THE FINAL ITERATION.  ANY ERROR MESSAGES
C                WILL ALSO BE PRINTED.  (IPRINT = 1 IS RECOMMENDED AT
C                FIRST.) IF'IPRINT = 0, ONLY THE FINAL QUANTITIES WILL
C                BE PRINTED, AS WELL AS ANY ERROR MESSAGES.  IF IPRINT =
C                -1, NO PRINTING WILL BE DONE.  THE USER IS THEN
C                RESPONSIBLE FOR CHECKING THE PARAMETER IERR FOR ERRORS.
C       ALF      NL-VECTOR OF ESTIMATES OF NONLINEAR PARAMETERS
C                (INPUT).  ON OUTPUT IT WILL CONTAIN OPTIMAL VALUES OF
C                THE NONLINEAR PARAMETERS.
C       BETA     L-VECTOR OF LINEAR PARAMETERS (OUTPUT ONLY).
C       IERR     INTEGER ERROR FLAG (OUTPUT):
C                .GT. 0 - SUCCESSFUL CONVERGENCE, IERR IS THE NUMBER OF
C                    ITERATIONS TAKEN.
C                -1  TERMINATED FOR TOO MANY ITERATIONS.
C                -2  TERMINATED FOR ILL-CONDITIONING (MARQUARDT
C                    PARAMETER TOO LARGE.)  ALSO SEE IERR = -8 BELOW.
C                -4  INPUT ERROR IN PARAMETER N, L, NL, LPP2, OR NMAX
C                -5  INC MATRIX IMPROPERLY SPECIFIED, OR P DISAGREES
C                    WITH LPP2.
C                -6  A WEIGHT WAS NEGATIVE.
C                -7  'CONSTANT' COLUMN WAS COMPUTED MORE THAN ONCE.
C                -8  CATASTROPHIC FAILURE - A COLUMN OF THE A MATRIX HAS
C                    BECOME,ZERO.  SEE 'CONVERGENCE FAILURES' BELOW.
C
C                 (IF IERR .LE. -4, THE LINEAR PARAMETERS, COVARIANCE
C                MATRIX, ETC. ARE NOT RETURNED.)
C
C     SUBROUTINES REQUIRED
C
C           NINE SUBROUTINES, DPA, ORFAC1, ORFAC2, BACSUB, POSTPR, COV,
C        XNORM, INIT, AND VARERR ARE PROVIDED.  IN ADDITION, THE USER
C        MUST PROVIDE A SUBROUTINE (CORRESPONDING TO THE ARGUMENT ADA)
C        WHICH, GIVEN ALF, WILL EVALUATE THE FUNCTIONS PHI(J) AND THEIR
C        PARTIAL DERIVATIVES D PHI(J)/D ALF(K), AT THE SAMPLE POINTS
C        T(I).  THIS ROUTINE MUST BE DECLARED 'EXTERNAL' IN THE CALLING
C        PROGRAM.  ITS CALLING SEQUENCE IS
```

```
C
C        SUBROUTINE ADA (L+1, NL, N, NMAX, LPP2, IV, A, INC, T, ALF,
C        ISEL)
C
C           THE USER SHOULD MODIFY THE EXAMPLE SUBROUTINE 'ADA'  (GIVEN
C        ELSEWHERE) FOR HIS OWN FUNCTIONS.
C
C           THE VECTOR SAMPLED FUNCTIONS PHI(J) SHOULD BE STORED IN THE
C        FIRST N ROWS AND FIRST L+1 COLUMNS OF THE MATRIX A, I.E.,
C        A(I, J) SHOULD CONTAIN PHI(J, ALF; T(I,1), T(I,2), ...,
C        T(I,IV)), I = 1, ..., N; J = 1, ..., L  (OR L+1).  THE (L+1)-ST
C        COLUMN OF A CONTAINS PHI(L+1) IF PHI(L+1) IS IN THE MODEL,
C        OTHERWISE IT IS RESERVED FOR WORKSPACE.  THE 'CONSTANT'  FUNC-
C        TIONS (THESE ARE FUNCTIONS PHI(J) WHICH DO NOT DEPEND UPON ANY
C        NONLINEAR PARAMETERS ALF, E.G., T(I)**J) (IF ANY) MUST APPEAR
C        FIRST, STARTING IN COLUMN 1.  THE COLUMN N-VECTORS OF NONZERO
C        PARTIAL DERIVATIVES D PHI(J) / D ALF(K) SHOULD BE STORED
C        SEQUENTIALLY IN THE MATRIX A IN COLUMNS L+2 THROUGH L+P+1.
C        THE ORDER IS
C
C          D PHI(1)  D PHI(2)          D PHI(L)  D PHI(L+1)  D PHI(1)
C          --------  --------, ...,   --------  ----------  --------
C          D ALF(1)  D ALF(1)          D ALF(1)   D ALF(1)   D ALF(2)
C
C          D PHI(2)       D PHI(L+1)       D PHI(1)         D PHI(L+1)
C          --------       ----------       --------         ----------,
C                  , ...,           , ...,         , ...,
C          D ALF(2)        D ALF(2)        D ALF(NL)        D ALF(NL)
C
C        OMITTING COLUMNS OF DERIVATIVES WHICH ARE ZERO, AND OMITTING
C        PHI(L+1) COLUMNS IF PHI(L+1) IS NOT IN THE MODEL.  NOTE THAT
C        THE LINEAR PARAMETERS BETA ARE NOT USED IN THE MATRIX A.
C        COLUMN L+P+2 IS RESERVED FOR WORKSPACE.
C
C        THE CODING OF ADA SHOULD BE ARRANGED SO THAT:
C
C        ISEL = 1  (WHICH OCCURS THE FIRST TIME ADA IS CALLED) MEANS:
C                  A.  FILL IN THE INCIDENCE MATRIX INC
C                  B.  STORE ANY CONSTANT PHI'S  IN A.
C                  C.  COMPUTE NONCONSTANT PHI'S  AND PARTIAL DERIVA-
C                      TIVES,
C             = 2  MEANS COMPUTE ONLY THE NONCONSTANT FUNCTIONS PHI
C             = 3  MEANS COMPUTE ONLY THE DERIVATIVES
C
C         (WHEN THE PROBLEM IS LINEAR (NL = 0) ONLY ISEL = 1 IS USED, AND
C        DERIVATIVES ARE NOT NEEDED.)
C
C     RESTRICTIONS
C
C           THE SUBROUTINES DPA, INIT (AND ADA) CONTAIN THE LOCALLY
C        DIMENSIONED MATRIX INC, WHOSE DIMENSIONS ARE CURRENTLY SET FOR
C        MAXIMA OF L+1 = 8, NL = 12.  THEY MUST BE CHANGED FOR LARGER
C        PROBLEMS.  DATA PLACED IN ARRAY A IS OVERWRITTEN ('DESTROYED').
C        DATA PLACED IN ARRAYS T, Y AND INC IS LEFT INTACT.  THE PROGRAM
C        RUNS IN WATFIV, EXCEPT WHEN L = 0 OR NL = 0.
C
C           IT IS ASSUMED THAT THE MATRIX PHI(J, ALF; T(I)) HAS FULL
C        COLUMN RANK.  THIS MEANS THAT THE FIRST L COLUMNS OF THE MATRIX
C        A MUST BE LINEARLY INDEPENDENT.
C
C           OPTIONAL NOTE:  AS WILL BE NOTED FROM THE SAMPLE SUBPROGRAM
C        ADA, THE DERIVATIVES D PHI(J)/D ALF(K) (ISEL = 3) MUST BE
C        COMPUTED INDEPENDENTLY OF THE FUNCTIONS PHI(J) (ISEL = 2),
C        SINCE THE FUNCTION VALUES ARE OVERWRITTEN AFTER ADA IS CALLED
C        WITH ISEL = 2.  THIS IS DONE TO MINIMIZE STORAGE, AT THE POS-
C        SIBLE EXPENSE OF SOME RECOMPUTATION (SINCE THE FUNCTIONS AND
C        DERIVATIVES FREQUENTLY HAVE SOME COMMON SUBEXPRESSIONS).  TO
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```
C        REDUCE THE AMOUNT OF COMPUTATION AT THE EXPENSE OF SOME
C        STORAGE, CREATE A MATRIX B OF DIMENSION NMAX BY L+1 IN ADA, AND
C        AFTER THE COMPUTATION OF THE PHI'S  (ISEL = 2), COPY THE VALUES
C        INTO B.  THESE VALUES CAN THEN BE USED TO CALCULATE THE DERIV-
C        ATIVES (ISEL = 3).  (THIS MAKES USE OF THE FACT THAT WHEN A
C        CALL TO ADA WITH ISEL = 3 FOLLOWS A CALL WITH ISEL = 2, THE
C        ALFS ARE THE SAME.)
C
C           TO CONVERT TO OTHER MACHINES, CHANGE THE OUTPUT UNIT IN THE
C        DATA STATEMENTS IN VARPRO, DPA, POSTPR, AND VARERR.  THE
C        PROGRAM HAS BEEN CHECKED FOR PORTABILITY BY THE BELL LABS PFORT
C        VERIFIER.  FOR MACHINES WITHOUT DOUBLE PRECISION HARDWARE, IT
C        MAY BE DESIRABLE TO CONVERT TO SINGLE PRECISION.  THIS CAN BE
C        DONE BY CHANGING (A) THE DECLARATIONS 'DOUBLE PRECISION' TO
C        'REAL', (B) THE PATTERN '.D' TO '.E' IN THE 'DATA' STATEMENT IN
C        VARPRO, (C) DSIGN, DSQRT AND DABS TO SIGN, SQRT AND ABS,
C        RESPECTIVELY, AND (D) DEXP TO EXP IN THE SAMPLE PROGRAMS ONLY.
C
C     NOTE ON INTERPRETATION OF COVARIANCE MATRIX
C
C           FOR USE IN STATISTICAL ESTIMATION (MULTIPLE NONLINEAR
C        REGRESSION) VARPRO RETURNS THE COVARIANCE MATRIX OF THE LINEAR
C        AND NONLINEAR PARAMETERS.  THIS MATRIX WILL BE USEFUL ONLY IF
C        THE USUAL STATISTICAL ASSUMPTIONS HOLD:  AFTER WEIGHTING, THE
C        ERRORS IN THE OBSERVATIONS ARE INDEPENDENT AND NORMALLY DISTRI-
C        BUTED, WITH MEAN ZERO AND THE SAME VARIANCE.  IF THE ERRORS DO
C        NOT HAVE MEAN ZERO (OR ARE UNKNOWN), THE PROGRAM WILL ISSUE A
C        WARNING MESSAGE (UNLESS IPRINT .LT. 0) AND THE COVARIANCE
C        MATRIX WILL NOT BE VALID.  IN THAT CASE, THE MODEL SHOULD BE
C        ALTERED TO INCLUDE A CONSTANT TERM (SET PHI(1) = 1.).
C
C           NOTE ALSO THAT, IN ORDER FOR THE USUAL ASSUMPTIONS TO HOLD,
C        THE OBSERVATIONS MUST ALL BE OF APPROXIMATELY THE SAME
C        MAGNITUDE (IN THE ABSENCE OF INFORMATION ABOUT THE ERROR OF
C        EACH OBSERVATION), OTHERWISE THE VARIANCES WILL NOT BE THE
C        SAME.  IF THE OBSERVATIONS ARE NOT THE SAME SIZE, THIS CAN BE
C        CURED BY WEIGHTING.
C
C           IF THE USUAL ASSUMPTIONS HOLD, THE SQUARE ROOTS OF THE
C        DIAGONALS OF THE COVARIANCE MATRIX A GIVE THE STANDARD ERROR
C        S(I) OF EACH PARAMETER.  DIVIDING A(I,J) BY S(I)*S(J) YIELDS
C        THE CORRELATION MATRIX OF THE PARAMETERS.  PRINCIPAL AXES AND
C        CONFIDENCE ELLIPSOIDS CAN BE OBTAINED BY PERFORMING AN EIGEN-
C        VALUE/EIGENVECTOR ANALYSIS ON A.  ONE SHOULD CALL THE EISPACK
C        PROGRAM TRED2, FOLLOWED BY TQL2 (OR USE THE EISPAC CONTROL
C        PROGRAM).
C
C     CONVERGENCE FAILURES
C
C           IF CONVERGENCE FAILURES OCCUR, FIRST CHECK FOR INCORRECT
C        CODING OF THE SUBROUTINE ADA.  CHECK ESPECIALLY THE ACTION OF
C        ISEL, AND THE COMPUTATION OF THE PARTIAL DERIVATIVES.  IF THESE
C        ARE CORRECT, TRY SEVERAL STARTING GUESSES FOR ALF.  IF ADA
C        IS CODED CORRECTLY, AND IF ERROR RETURNS IERR = -2 OR -8
C        PERSISTENTLY OCCUR, THIS IS A SIGN OF ILL-CONDITIONING, WHICH
C        MAY BE CAUSED BY SEVERAL THINGS.  ONE IS POOR SCALING OF THE
C        PARAMETERS; ANOTHER IS AN UNFORTUNATE INITIAL GUESS FOR THE
C        PARAMETERS, STILL ANOTHER IS A POOR CHOICE OF THE MODEL.
C
C     ALGORITHM
C
C           THE RESIDUAL R IS MODIFIED TO INCORPORATE, FOR ANY FIXED
C        ALF, THE OPTIMAL LINEAR PARAMETERS FOR THAT ALF.  IT IS THEN
C        POSSIBLE TO MINIMIZE ONLY ON THE NONLINEAR PARAMETERS.  AFTER
C        THE OPTIMAL VALUES OF THE NONLINEAR PARAMETERS HAVE BEEN DETER-
C        MINED, THE LINEAR PARAMETERS CAN BE RECOVERED BY LINEAR LEAST
```

```
C       SQUARES TECHNIQUES  (SEE REF. 1) .
C
C          THE MINIMIZATION IS BY A MODIFICATION OF OSBORNE'S (REF. 3)
C       MODIFICATION OF THE LEVENBERG-MARQUARDT ALGORITHM.  INSTEAD OF
C       SOLVING THE NORMAL EQUATIONS WITH MATRIX
C
C                T      2
C             (J J + NU  * D),      WHERE  J = D(ETA)/D(ALF) ,
C
C       STABLE ORTHOGONAL (HOUSEHOLDER) REFLECTIONS ARE USED ON A
C       MODIFICATION OF THE MATRIX
C                                  (----T--)
C                                  (-------) ,
C                                  ( NU*D )
C
C       WHERE D IS A DIAGONAL MATRIX CONSISTING OF THE LENGTHS OF THE
C       COLUMNS OF J.  THIS MARQUARDT STABILIZATION ALLOWS THE ROUTINE
C       TO RECOVER FROM SOME RANK DEFICIENCIES IN THE JACOBIAN.
C       OSBORNE'S EMPIRICAL STRATEGY FOR CHOOSING THE MARQUARDT PARAM-
C       ETER HAS PROVEN REASONABLY SUCCESSFUL IN PRACTICE.  (GAUSS-
C       NEWTON WITH STEP CONTROL CAN BE OBTAINED BY MAKING THE CHANGE
C       INDICATED BEFORE THE INSTRUCTION LABELED 5).  A DESCRIPTION CAN
C       BE FOUND IN REF. (3), AND A FLOW CHART IN (2), P. 22.
C
C       FOR REFERENCE, SEE
C
C       1.  GENE H. GOLUB AND V. PEREYRA, 'THE DIFFERENTIATION OF
C           PSEUDO-INVERSES AND NONLINEAR LEAST SQUARES PROBLEMS WHOSE
C           VARIABLES SEPARATE,' SIAM J. NUMER. ANAL. 10, 413-432
C           (1973).
C       2.  ------, SAME TITLE, STANFORD C.S. REPORT 72-261, FEB. 1972.
C       3.  OSBORNE, MICHAEL R., 'SOME ASPECTS OF NON-LINEAR LEAST
C           SQUARES CALCULATIONS,'  IN LOOTSMA, ED., 'NUMERICAL METHODS
C           FOR NON-LINEAR OPTIMIZATION,' ACADEMIC PRESS, LONDON, 1972.
C       4.  KROGH, FRED, 'EFFICIENT IMPLEMENTATION OF A VARIABLE PRO-
C           JECTION ALGORITHM FOR NONLINEAR LEAST SQUARES PROBLEMS,'
C           COMM. ACM 17, PP. 167-169 (MARCH, 1974).
C       5.  KAUFMAN, LINDA, 'A VARIABLE PROJECTION METHOD FOR SOLVING
C           SEPARABLE NONLINEAR LEAST SQUARES PROBLEMS',  B.I.T. 15,
C           49-57 (1975).
C       6.  DRAPER, N., AND SMITH, H., APPLIED REGRESSION ANALYSIS,
C           WILEY, N.Y.,  1966 (FOR STATISTICAL INFORMATION ONLY).
C       7.  C. LAWSON AND R. HANSON, SOLVING LEAST SQUARES PROBLEMS,
C           PRENTICE-HALL, ENGLEWOOD CLIFFS, N. J., 1974.
C
C                   JOHN BOLSTAD
C                   COMPUTER SCIENCE DEPT., SERRA HOUSE
C                   STANFORD UNIVERSITY
C                   JANUARY, 1977
C
C     ..............................................................
C
      DOUBLE PRECISION A(NMAX, LPP2), BETA(L), ALF(NL), T(NMAX, IV),
     2 W(N), Y(N), ACUM, EPS1, GNSTEP, NU, PRJRES, R, RNEW, XNORM
      INTEGER B1, OUTPUT
      LOGICAL SKIP
      EXTERNAL ADA
      DATA EPS1 /1.D-6/, ITMAX /40/, OUTPUT /6/
C
C          THE FOLLOWING TWO PARAMETERS ARE USED IN THE CONVERGENCE
C          TEST:  EPS1 IS AN ABSOLUTE AND RELATIVE TOLERANCE FOR THE
C          NORM OF THE PROJECTION OF THE RESIDUAL ONTO THE RANGE OF THE
C          JACOBIAN OF THE VARIABLE PROJECTION FUNCTIONAL.
C          ITMAX IS THE MAXIMUM NUMBER OF FUNCTION AND DERIVATIVE
C          EVALUATIONS ALLOWED.  CAUTION:  EPS1 MUST NOT BE
C          SET SMALLER THAN 10 TIMES THE UNIT ROUND-OFF OF THE MACHINE.
```

```
C
C---------------------------------------------------------------
CALL LIB MONITOR FROM VARPRO, MAINTENANCE NUMBER 509, DATE 77178
C***PLEASE DON'T REMOVE OR CHANGE THE ABOVE CALL. IT IS YOUR ONLY
C***PROTECTION AGAINST YOUR USING AN OUT-OF-DATE OR INCORRECT
C***VERSION OF THE ROUTINE. THE LIBRARY MONITOR REMOVES THIS CALL,
C***SO IT ONLY OCCURS ONCE, ON THE FIRST ENTRY TO THIS ROUTINE.
C---------------------------------------------------------------
      IERR = 1
      ITER = 0
      LP1 = L + 1
      B1 = L + 2
      LNL2 = L + NL + 2
      NLP1 = NL + 1
      SKIP = .FALSE.
      MODIT = IPRINT
      IF (IPRINT .LE. 0) MODIT = ITMAX + 2
      NU = 0.
C             IF GAUSS-NEWTON IS DESIRED REMOVE THE NEXT STATEMENT.
      NU = 1.
C
C             BEGIN OUTER ITERATION LOOP TO UPDATE ALF.
C             CALCULATE THE NORM OF THE RESIDUAL AND THE DERIVATIVE OF
C             THE MODIFIED RESIDUAL THE FIRST TIME, BUT ONLY THE
C             DERIVATIVE IN SUBSEQUENT ITERATIONS.
C
    5 CALL DPA (L, NL, N, NMAX, LPP2, IV, T, Y, W, ALF, ADA, IERR,
     X IPRINT, A, BETA, A(1, LP1), R)
      GNSTEP = 1.0
      ITERIN = 0
      IF (ITER .GT. 0) GO TO 10
         IF (NL .EQ. 0) GO TO 90
         IF (IERR .NE. 1) GO TO 99
C
         IF (IPRINT .LE. 0) GO TO 10
         WRITE (OUTPUT, 207) ITERIN, R
         WRITE (OUTPUT, 200) NU
C                                BEGIN TWO-STAGE ORTHOGONAL FACTORIZATION
   10 CALL ORFAC1(NLP1, NMAX, N, L, IPRINT, A(1, B1), PRJRES, IERR)
      IF (IERR .LT. 0) GO TO 99
      IERR = 2
      IF (NU .EQ. 0.) GO TO 30
C
C             BEGIN INNER ITERATION LOOP FOR GENERATING NEW ALF AND
C             TESTING IT FOR ACCEPTANCE.
C
   25    CALL ORFAC2(NLP1, NMAX, NU, A(1, B1))
C
C             SOLVE A NL X NL UPPER TRIANGULAR SYSTEM FOR DELTA-ALF.
C             THE TRANSFORMED RESIDUAL (IN COL. LNL2 OF A) IS OVER-
C             WRITTEN BY THE RESULT DELTA-ALF.
C
   30    CALL BACSUB (NMAX, NL, A(1, B1), A(1, LNL2))
         DO 35 K = 1, NL
   35       A(K, B1) = ALF(K) + A(K, LNL2)
C           NEW ALF(K) = ALF(K) + DELTA ALF(K)
C
C             STEP TO THE NEW POINT NEW ALF, AND COMPUTE THE NEW
C             NORM OF RESIDUAL. NEW ALF IS STORED IN COLUMN B1 OF A.
C
   40    CALL DPA (L, NL, N, NMAX, LPP2, IV, T, Y, W, A(1, B1), ADA,
     X   IERR, IPRINT, A, BETA, A(1, LP1), RNEW)
         IF (IERR .NE. 2) GO TO 99
         ITER = ITER + 1
         ITERIN = ITERIN + 1
         SKIP = MOD(ITER, MODIT) .NE. 0
```

```
      IF (SKIP) GO TO 45
         WRITE (OUTPUT, 203) ITER
         WRITE (OUTPUT, 216) (A(K, B1), K = 1, NL)
         WRITE (OUTPUT, 207) ITERIN, RNEW
C
   45 IF (ITER .LT. ITMAX) GO TO 50
         IERR = -1
         CALL VARERR (IPRINT, IERR, 1)
         GO TO 95
   50 IF (RNEW - R .LT. EPS1*(R + 1.DO)) GO TO 75
C
C           RETRACT THE STEP JUST TAKEN
C
         IF (NU .NE. 0.) GO TO 60
C                                                     GAUSS-NEWTON OPTION ONLY
         GNSTEP = 0.5*GNSTEP
         IF (GNSTEP .LT. EPS1) GO TO 95
         DO 55 K = 1, NL
   55       A(K, B1) = ALF(K) + GNSTEP*A(K, LNL2)
         GO TO 40
C                                           ENLARGE THE MARQUARDT PARAMETER
   60    NU = 1.5*NU
         IF (.NOT. SKIP) WRITE (OUTPUT, 206) NU
         IF (NU .LE. 110.) GO TO 65
            IERR = -2
            CALL VARERR (IPRINT, IERR, 1)
            GO TO 95
C                                           RETRIEVE UPPER TRIANGULAR FORM
C                                           AND RESIDUAL OF FIRST STAGE.
   65 DO 70 K = 1, NL
         KSUB = LP1 + K
         DO 70 J = K, NLP1
            JSUB = LP1 + J
            ISUB = NLP1 + J
   70       A(K, JSUB) = A(ISUB, KSUB)
      GO TO 25
C                                           END OF INNER ITERATION LOOP
C        ACCEPT THE STEP JUST TAKEN
C
   75 R = RNEW
      DO 80 K = 1, NL
   80    ALF(K) = A(K, B1)
C                                           CALC. NORM(DELTA ALF)/NORM(ALF)
      ACUM = GNSTEP*XNORM(NL, A(1, LNL2))/XNORM(NL, ALF)
C
C        IF ITERIN IS GREATER THAN 1, A STEP WAS RETRACTED DURING
C        THIS OUTER ITERATION.
C
      IF (ITERIN .EQ. 1) NU = 0.5*NU
      IF (SKIP) GO TO 85
         WRITE (OUTPUT. 200) NU
         WRITE (OUTPUT; 208) ACUM
   85 IERR = 3
      IF (PRJRES .GT. EPS1*(R + 1.D0)) GO TO 5
C        END OF OUTER ITERATION LOOP
C
C        CALCULATE FINAL QUANTITIES -- LINEAR PARAMETERS, RESIDUALS,
C        COVARIANCE MATRIX,,ETC.
C
   90 IERR = ITER
   95 IF (NL .GT. 0) CALL DPA(L, NL, N, NMAX, LPP2, IV, T, Y, W, ALF,
     X ADA, 4, IPRINT, A, BETA, A(1, LP1), R)
      CALL POSTPR(L, NL, N, NMAX, LNL2, EPS1, R, IPRINT, ALF, W, A,
     X A(1, LP1), BETA, IERR)
   99 RETURN
C
```

```
  200 FORMAT (9H     NU =, E15.7)
  203 FORMAT (12H0  ITERATION, I4, 24H    NONLINEAR PARAMETERS)
  206 FORMAT (25H     STEP RETRACTED, NU =, E15.7)
  207 FORMAT (1H0, I5, 20H  NORM OF RESIDUAL =, E15.7)
  208 FORMAT (34H     NORM(DELTA-ALF) / NORM(ALF) =, E12.3)
  216 FORMAT (1H0, 7315.7)
      END
C
      SUBROUTINE ORFAC1(NLP1, NMAX, N, L, IPRINT, B, PRJRES, IERR)
C
C             STAGE 1:  HOUSEHOLDER REDUCTION OF
C
C                      (         )     ( DR' . R3 )     NL
C                      ( DR  . R2 )  TO  (----. -- ),
C                      (         )     (  0  . R4 )  N-L-NL
C
C                        NL     1          NL    1
C
C         WHERE DR = -D(Q2)*Y IS THE DERIVATIVE OF THE MODIFIED RESIDUAL
C         PRODUCED BY DPA, R2 IS THE TRANSFORMED RESIDUAL FROM DPA, AND
C         DR' IS IN UPPER TRIANGULAR FORM (AS IN REF. (2), P. 18).
C         DR IS STORED IN ROWS L+1 TO N AND COLUMNS L+2 TO L + NL + 1 OF
C         THE MATRIX A  (I.E., COLUMNS 1 TO NL OF THE MATRIX B).  R2 IS
C         STORED IN COLUMN L + NL + 2 OF THE MATRIX A  (COLUMN NL + 1 OF
C         B).  FOR K = 1, 2, ..., NL, FIND REFLECTION I - U * U' / BETA
C         WHICH ZEROES B(I, K), I = L+K+1, ..., N.
C
C     ..............................................................
C
      DOUBLE PRECISION ACUM, ALPHA, B(NMAX, NLP1), BETA, DSIGN, PRJRES,
     X U, XNORM
C
      NL = NLP1 - 1
      NL23 = 2*NL + 3
      LP1 = L + 1
C
      DO 30 K = 1, NL
         LPK = L + K
         ALPHA = DSIGN(XNORM(N+1-LPK, B(LPK, K)), B(LPK, K))
         U = B(LPK, K) + ALPHA
         B(LPK, K) = U
         BETA = ALPHA * U
         IF (ALPHA .NE. 0.0) GO TO 13
C                                                  COLUMN WAS ZERO
         IERR = -8
         CALL VARERR (IPRINT, IERR, LP1 + K)
         GO TO 99
C                                   APPLY REFLECTIONS TO REMAINING COLUMNS
C                                   OF B AND TO RESIDUAL VECTOR.
   13    KP1 = K + 1
         DO 25 J = KP1, NLP1
            ACUM = 0.0
            DO 20 I = LPK, N
   20          ACUM = ACUM + B(I, K) * B(I, J)
            ACUM = ACUM / BETA
            DO 25 I = LPK, N
   25          B(I, J) = B(I, J) - B(I, K) * ACUM
   30    B(LPK, K) = -ALPHA
C
      PRJRES = XNORM(NL, B(LP1, NLP1))
C
C           SAVE UPPER TRIANGULAR FORM AND TRANSFORMED RESIDUAL, FOR USE
C           IN CASE A STEP IS RETRACTED. ALSO COMPUTE COLUMN LENGTHS.
C
      IF (IERR .EQ. 4) GO TO 99
      DO 50 K = 1, NL
```

```
         LPK = L + K
         DO 40 J = K, NLP1
            JSUB = NLP1 + J
            B(K, J) = B(LPK, J)
   40       B(JSUB, K) = B(LPK, J)
   50    B(NL23, K) = XNORM(K, B(LP1, K))
C
   99 RETURN
      END
C
      SUBROUTINE ORFAC2(NLP1, NMAX, NU, B)
C
C        STAGE 2:  SPECIAL HOUSEHOLDER REDUCTION OF
C
C                     NL      ( DR'  . R3 )      (DR'' . R5 )
C                             (-----. -- )      (-----. -- )
C                 N-L-NL      (  0   . R4 )  TO  (  0   . R4 )
C                             (-----. -- )      (-----. -- )
C                     NL      (NU*D  . 0  )      (  0   . R6 )
C
C                                 NL     1           NL     1
C
C        WHERE DR', R3, AND R4 ARE AS IN ORFAC1, NU IS THE MARQUARDT
C        PARAMETER, D IS A DIAGONAL MATRIX CONSISTING OF THE LENGTHS OF
C        THE COLUMNS OF DR', AND DR'' IS IN UPPER TRIANGULAR FORM.
C        DETAILS IN (1), PP. 423-424.  NOTE THAT THE (N-L-NL) BAND OF
C        ZEROES, AND R4, ARE OMITTED IN STORAGE.
C
C     ..............................................................
C
      DOUBLE PRECISION ACUM, ALPHA, B(NMAX, NLP1), BETA, DSIGN, NU, U,
     X XNORM
C
      NL = NLP1 - 1
      NL2 = 2*NL
      NL23 = NL2 + 3
      DO 30 K = 1, NL
         KP1 = K + 1
         NLPK = NL + K
         NLPKM1 = NLPK - 1
         B(NLPK, K) = NU * B(NL23, K)
         B(NL, K) = B(K, K)
         ALPHA = DSIGN(XNORM(K+1, B(NL, K)), B(K, K))
         U = B(K, K) + ALPHA
         BETA = ALPHA * U
         B(K, K) = -ALPHA
C                        THE K-TH REFLECTION MODIFIES ONLY ROWS K,
C                        NL+1, NL+2, ..., NL+K, AND COLUMNS K TO NL+1.
         DO 30 J = KP1, NLP1
            B(NLPK, J) = 0.
            ACUM = U * B(K,J)
            DO 20 I = NLP1, NLPKM1
   20          ACUM = ACUM + B(I,K) * B(I,J)
            ACUM = ACUM / BETA
            B(K,J) = B(K,J) - U * ACUM
            DO 30 I = NLP1, NLPK
   30          B(I,J) = B(I,J) - B(I,K) * ACUM
C
      RETURN
      END
C
      SUBROUTINE DPA (L, NL, N, NMAX, LPP2, IV, T, Y, W, ALF, ADA, ISEL,
     X IPRINT, A, U, R, RNORM)
C
C        COMPUTE THE NORM OF THE RESIDUAL (IF ISEL = 1 OR 2), OR THE
C        (N-L) X NL DERIVATIVE OF THE MODIFIED RESIDUAL (N-L) VECTOR
```

```
C       Q2*Y (IF ISEL = 1 OR 3).  HERE Q * PHI = S, I.E.,
C
C        L     ( Q1 ) (      .   .        )   ( S   . R1 .  F1  )
C              (----) ( PHI . Y . D(PHI) ) = (--- . -- . ---- )
C        N-L   ( Q2 ) (      .   .        )   ( 0   . R2 .  F2  )
C
C                  N       L    1      P          L     1     P
C
C       WHERE Q IS N X N ORTHOGONAL, AND S IS L X L UPPER TRIANGULAR.
C       THE NORM OF THE RESIDUAL = NORM(R2), AND THE DESIRED DERIVATIVE
C       ACCORDING TO REF. (5), IS
C                                                -1
C                     D(Q2 * Y) = -Q2 * D(PHI)* S   * Q1* Y.
C
C     ..............................................................
C
      DOUBLE PRECISION A(NMAX, LPP2), ALF(NL), T(NMAX, IV), W(N), Y(N),
     X ACUM, ALPHA, BETA, RNORM, DSIGN, DSQRT, SAVE, R(N), U(L), XNORM
      INTEGER FIRSTC, FIRSTR, INC(12, 8)
      LOGICAL NOWATE, PHILP1
      EXTERNAL ADA
C
      IF (ISEL .NE. 1) GO TO 3
         LP1 = L + 1
         LNL2 = L + 2 + NL
         LP2 = L + 2
         LPP1 = LPP2 - 1
         FIRSTC = 1
         LASTC = LPP1
         FIRSTR = LP1
         CALL INIT(L, NL, N, NMAX, LPP2, IV, T, W, ALF, ADA, ISEL,
     X   IPRINT, A, INC, NCON, NCONP1, PHILP1, NOWATE)
         IF (ISEL .NE. 1) GO TO 99
         GO TO 30
C
    3 CALL ADA (LP1, NL, N, NMAX, LPP2, IV, A, INC, T, ALF, MIN0(ISEL,
     X 3))
      IF (ISEL .EQ. 2) GO TO 6
C                                                    ISEL = 3 OR 4
      FIRSTC = LP2
      LASTC = LPP1
      FIRSTR = (4 - ISEL)*L + 1
      GO TO 50
C                                                    ISEL = 2
    6 FIRSTC = NCONP1
      LASTC = LP1
      IF (NCON .EQ. 0) GO TO 30
      IF (A(1, NCON) .EQ. SAVE) GO TO 30
         ISEL = -7
         CALL VARERR (IPRINT, ISEL, NCON)
         GO TO 99
C                                                    ISEL = 1 OR 2
   30 IF (PHILP1) GO TO 40
         DO 35 I = 1, N
   35       R(I) = Y(I)
         GO TO 50
   40    DO 45 I = 1, N
   45       R(I) = Y(I) - R(I)
C                                       WEIGHT APPROPRIATE COLUMNS
   50 IF (NOWATE) GO TO 58
      DO 55 I = 1, N
         ACUM = W(I)
         DO 55 J = FIRSTC, LASTC
   55       A(I, J) = A(I, J) * ACUM
C
C           COMPUTE ORTHOGONAL FACTORIZATIONS BY HOUSEHOLDER
```

```
C          REFLECTIONS.  IF ISEL = 1 OR 2, REDUCE PHI (STORED IN THE
C          FIRST L COLUMNS OF THE MATRIX A) TO UPPER TRIANGULAR FORM,
C          (Q*PHI = S), AND TRANSFORM Y (STORED IN COLUMN L+1), GETTING
C          Q*Y = R.  IF ISEL = 1, ALSO TRANSFORM J = D PHI (STORED IN
C          COLUMNS L+2 THROUGH L+P+1 OF THE MATRIX A), GETTING Q*J = F.
C          IF ISEL = 3 OR 4, PHI HAS ALREADY BEEN REDUCED, TRANSFORM
C          ONLY J.  S, R, AND F OVERWRITE PHI, Y, AND J, RESPECTIVELY,
C          AND A FACTORED FORM OF Q IS SAVED IN U AND THE LOWER
C          TRIANGLE OF PHI.
C
   58 IF (L .EQ. 0) GO TO 75
      DO 70 K = 1, L
         KP1 = K + 1
         IF (ISEL .GE. 3 .OR. (ISEL .EQ. 2 .AND. K .LT.NCONP1)) GO TO 66
         ALPHA = DSIGN(XNORM(N+1-K, A(K, K)), A(K, K))
         U(K) = A(K, K) + ALPHA
         A(K, K) = -ALPHA
         FIRSTC = KP1
         IF (ALPHA .NE. 0.0) GO TO 66
         ISEL = -8
         CALL VARERR (IPRINT, ISEL, K)
         GO TO 99
C                                        APPLY REFLECTIONS TO COLUMNS
C                                        FIRSTC TO LASTC.
   66    BETA = -A(K, K) * U(K)
         DO 70 J = FIRSTC, LASTC
            ACUM = U(K)*A(K, J)
            DO 68 I = KP1, N
   68          ACUM = ACUM + A(I, K)*A(I, J)
            ACUM = ACUM / BETA
            A(K,J) = A(K,J) - U(K)*ACUM
            DO 70 I = KP1, N
   70          A(I, J) = A(I, J) - A(I, K)*ACUM
C
   75 IF (ISEL .GE. 3) GO TO 85
      RNORM = XNORM(N-L, R(LP1))
      IF (ISEL .EQ. 2) GO TO 99
      IF (NCON .GT. 0) SAVE = A(1, NCON)
C
C          F2 IS NOW CONTAINED IN ROWS L+1 TO N AND COLUMNS L+2 TO
C          L+P+1 OF THE MATRIX A.  NOW SOLVE THE L X L UPPER TRIANGULAR
C          SYSTEM S*BETA = R1 FOR THE LINEAR PARAMETERS BETA.  BETA
C          OVERWRITES R1.
C
   85 IF (L .GT. 0) CALL BACSUB (NMAX, L, A, R)
C
C          MAJOR PART OF KAUFMAN'S SIMPLIFICATION OCCURS HERE.  COMPUTE
C          THE DERIVATIVE OF ETA WITH RESPECT TO THE NONLINEAR
C          PARAMETERS
C
C   T   D ETA          T    L           D PHI(J)     D PHI(L+1)
C  Q * --------   =   Q * (SUM BETA(J) --------  +  ----------I  =  F2*BETA
C       D ALF(K)            J=1         D ALF(K)      D ALF(K)
C
C          AND STORE THE RESULT IN COLUMNS L+2 TO L+NL+1.  IF ISEL NOT
C          = 4, THE FIRST L ROWS ARE OMITTED.  THIS IS -D(Q2)*Y.  IF
C          ISEL NOT = 4 THE RESIDUAL R2 = Q2*Y (IN COL. L+1) IS COPIED
C          TO COLUMN L+NL+2.  OTHERWISE ALL OF COLUMN L+1 IS COPIED.
C
      DO 95 I = FIRSTR, N
         IF (L .EQ. NCON) GO TO 95
         M = LP1
         DO 90 K = 1, NL
            ACUM = 0.
            DO 88 J = NCONP1, L
               IF (INC(K, J) .EQ. 0) GO TO 88
```

```
                M = M + 1
                ACUM = ACUM + A(I, M) * R(J)
   88           CONTINUE
             KSUB = LP1 + K
             IF (INC(K, LP1) .EQ. 0) GO TO 90
             M = M + 1
             ACUM = ACUM + A(I, M)
   90        A(I, KSUB) = ACUM
   95     A(I, LNL2) = R(I)
C
   99 RETURN
      END
C
      SUBROUTINE INIT(L, NL, N, NMAX, LPP2, IV, T, W, ALF, ADA, ISEL,
     X IPRINT, A, INC, NCON, NCONP1, PHILP1, NOWATE)
C
C        CHECK VALIDITY OF INPUT PARAMETERS, AND DETERMINE NUMBER OF
C        CONSTANT FUNCTIONS.
C
C     ..............................................................
C
      DOUBLE PRECISION A(NMAX, LPP2), ALF(NL), T(NMAX, IV), W(N),
     X DSQRT
      INTEGER OUTPUT, P, INC(12, 8)
      LOGICAL NOWATE, PHILPl
      DATA OUTPUT /6/
C
      LP1 = L + 1
      LNL2 = L + 2 + NL
C                                                 CHECK FOR VALID INPUT
      IF (L .GE. 0 .AND. NL .GE. 0 .AND. L+NL .LT. N .AND. LNL2 .LE.
     X LPP2 .AND. 2*NL t 3 .LE. NMAX AND. N .LE. NMAX AND.
     X IV .GT. 0 .AND. .NOT. (NL .EQ. 0 .AND. L .EQ. 0)) GO TO 1
         ISEL = -4
         CALL VARERR (IPRINT, ISEL, 1)
         GO TO 99
C
    1 IF (L .EQ. 0 .OR. NL .EQ. 0) GO TO 3
         DO 2 J = 1, LP1
            DO 2 K = 1, NL
    2          INC(K, J) = 0
C
    3 CALL ADA (LP1, NL, N, NMAX, LPP2, IV, A, INC, T, ALF, ISEL)
C
      NOWATE = .TRUE.
      DO 9 I - 1, N
         NOWATE = NOWATE .AND. (W(I) .EQ. 1.0)
         IF (W(I) .GE. 0.) GO TO 9
C                                                      ERROR IN WEIGHTS
         ISEL = -6
         CALL VARERR (IPRINT, ISEL, I)
         GO TO 99
    9    W(I) = DSQRT(W(I))
C
      NCON = L
      NCONPl = LP1
      PHILPl = L .EQ. 0
      IF (PHILP1 .OR. NL .EQ. 0) GO TO 99
C                                    CHECK INC MATRIX FOR VALID INPUT AND
C                                    DETERMINE NUMBER OF CONSTANT FCNS.
      P = 0
      DO 11 J = 1, LP1
         IF (P .EQ. 0) NCONPl = J
         DO 11 K = 1, NL
            INCKJ = INC(K, J)
            IF (INCKJ .NE. 0 .AND. INCKJ .NE. 1) GO TO 15
```

```
            IF (INCKJ .EQ. 1) P = P + 1
   11       CONTINUE
C
      NCON = NCONP1 - 1
      IF (IPRINT .GE. 0) WRITE (OUTPUT, 210) NCON
      IF (L+P+2 .EQ. LPP2) GO TO 20
C                                               INPUT ERROR IN INC MATRIX
   15 ISEL = -5
      CALL VARERR (IPRINT, ISEL, 1)
      GO TO 99
C                                 DETERMINE IF PHI(L+1) IS IN THE MODEL.
   20 DO 25 K = 1, NL
   25    IF (INC(K, LP1) .EQ. 1) PHILP1 = .TRUE.
C
   99 RETURN
  210 FORMAT (33H0  NUMBER OF CONSTANT FUNCTIONS =, I4 /)
      END
      SUBROUTINE BACSUB (NMAX, N, A, X)
C
C        BACKSOLVE THE N X N UPPER TRIANGULAR SYSTEM A*X = B.
C        THE SOLUTION X OVERWRITES THE RIGHT SIDE B.
C
      DOUBLE PRECISION A(NMAX, N), X(N), ACUM
C
      X(N) = X(N) / A(N, N)
      IF (N .EQ. 1) GO TO 30
      NP1 = N + 1
      DO 20 IBACK = 2, N
         I = NP1 - IBACK
C           I = N-1, N-2, ..., 2, 1
         IP1 = I + 1
         ACUM = X(I)
         DO 10 J = IP1, N
   10       ACUM = ACUM - A(I,J)*X(J)
   20    X(I) = ACUM / A(I,I)
C
   30 RETURN
      END
      SUBROUTINE POSTPR(L, NL, N, NMAX, LNL2, EPS, RNORM, IPRINT, ALF,
     X W, A, R, U, IERR)
C
C        CALCULATE RESIDUALS, SAMPLE VARIANCE, AND COVARIANCE MATRIX.
C        ON INPUT, U CONTAINS INFORMATION ABOUT HOUSEHOLDER REFLECTIONS
C        FROM DPA.  ON OUTPUT, IT CONTAINS THE LINEAR PARAMETERS.
C
      DOUBLE PRECISION A(NMAX, LNL2), ALF(NL), R(N), U(L), W(N), ACUM,
     X EPS, PRJRES, RNORM, SAVE, DABS
      INTEGER OUTPUT
      DATA OUTPUT /6/
C
      LP1 = L + 1
      LPNL = LNL2 - 2
      LNL1 = LPNL + 1
      DO 10 I = 1, N
   10    W(I) = W(I)**2
C
C              UNWIND HOUSEHOLDER TRANSFORMATIONS TO GET RESIDUALS,
C              AND MOVE THE LINEAR PARAMETERS FROM R TO U.
C
      IF (L .EQ. 0) GO TO 30
      DO 25 KBACK = 1, L
         K = LP1 - KBACK
         KP1 = K + 1
         ACUM = 0.
         DO 20 I = KP1, N
   20       ACUM = ACUM + A(I, K) * R(I)
```

```
         SAVE = R(K)
         R(K) =  ACUM / A(K, K)
         ACUM = -ACUM / (U(K) * A(K, K))
         U(K) = SAVE
         DO 25 I = KP1, N
   25       R(I) = R(I) - A(I, K)*ACUM
C                                                 COMPUTE MEAN ERROR
   30 ACUM = 0.
      DO 35 I = 1, N
   35    ACUM = ACUM + R(I)
      SAVE = ACUM / N
C
C           THE FIRST L COLUMNS OF THE MATRIX HAVE BEEN REDUCED TO
C           UPPER TRIANGULAR FORM IN DPA.  FINISH BY REDUCING ROWS
C           L+l TO N AND COLUMNS L+2 THROUGH L+NL+1 TO TRIANGULAR
C           FORM.  THEN SHIFT COLUMNS OF DERIVATIVE MATRIX OVER ONE
C           TO THE LEFT TO BE ADJACENT TO THE FIRST L COLUMNS.
C
      IF (NL .EQ. 0) GO TO 45
      CALL ORFAC1(NL+1, NMAX, N, L, IPRINT, A(1, L+2), PRJRES, 4)
      DO 40 I = 1, N
         A(I, LNL2) = R(I)
         DO 40 K = LP1, LNLl
   40       A(I, K) = A(I, K+1)
C                                                 COMPUTE COVARIANCE MATRIX
   45 A(1, LNL2) = RNORM
      ACUM = RNORM*RNORM/(N - L - NL)
      A(2, LNL2) = ACUM
      CALL COV(NMAX, LPNL, ACUM, A)
C
      IF (IPRINT .LT. 0) GO TO 99
      WRITE (OUTPUT, 209)
      IF (L .GT. 0) WRITE (OUTPUT, 210) (U(J), J = 1, L)
      IF (NL .GT. 0) WRITE (OUTPUT, 211) (ALF(K), K = 1, NL)
      WRITE (OUTPUT, 214) RNORM, SAVE, ACUM
      IF (DABS(SAVE) .GT. EPS) WRITE (OUTPUT, 215)
      WRITE (OUTPUT, 209)
   99 RETURN
C
  209 FORMAT (1H0, 50(1H'))
  210 FORMAT (20H0  LINEAR PARAMETERS // (7E15.7))
  211 FORMAT (23H0  NONLINEAR PARAMETERS // (7E15.7))
  214 FORMAT (21H0  NORM OF RESIDUAL =, E15.7, 33H EXPECTED ERROR OF OBS
     XERVATIONS =, E15.7, / 39H   ESTIMATED VARIANCE OF OBSERVATIONS =,
     X E15.7 )
  215 FORMAT (95H  WARNING -- EXPECTED ERROR OF OBSERVATIONS IS NOT ZERO
     X.  COVARIANCE MATRIX MAY BE MEANINGLESS. /)
      END
      SUBROUTINE COV(NMAX, N, SIGMA2, A)
C
C           COMPUTE THE SCALED COVARIANCE MATRIX OF THE L + NL
C        PARAMETERS.  THIS INVOLVES COMPUTING
C
C                              2      -1     -T
C                         SIGMA  *  T    *  T
C
C        WHERE THE (L+NL) X (L+NL) UPPER TRIANGULAR MATRIX T IS
C        DESCRIBED IN SUBROUTINE POSTPR.  THE RESULT OVERWRITES THE
C        FIRST L+NL ROWS AND COLUMNS OF THE MATRIX A.  THE RESULTING
C        MATRIX IS SYMMETRIC.  SEE REF. 7, PP. 67-70, 281.
C
C     ..................................................................
C
      DOUBLE PRECISION A(NMAX, N), SUM, SIGMA2
C
      DO 10 J = 1, N
```

```
   10    A(J, J) = 1./A(J, J)
C
C                 INVERT T UPON ITSELF
C
      IF (N .EQ. 1) GO TO 70
      NM1 = N - 1
      DO 60 I = 1, NM1
         IP1 = I + 1
         DO 60 J = IP1, N
            JM1 = J - 1
            SUM = 0.
            DO 50 M = I, JM1
   50          SUM = SUM + A(I, M) * A(M, J)
   60       A(I, J) = -SUM * A(J, J)
C
C                 NOW FORM THE MATRIX PRODUCT
C
   70 DO 90 I = 1, N
         DO 90 J = I, N
            SUM = 0.
            DO 80 M = J, N
   80          SUM = SUM + A(I, M) * A(J, M)
            SUM = SUM * SIGMA2
            A(I, J) = SUM
   90       A(J, I) = SUM
C
      RETURN
      END
      SUBROUTINE VARERR (IPRINT, IERR, K)
C
C        PRINT ERROR MESSAGES
C
      INTEGER ERRNO, OUTPUT
      DATA OUTPUT /6/
C
      IF (IPRINT .LT. 0) GO TO 99
      ERRNO = IABS(IERR)
      GO TO (1, 2, 99, 4, 5, 6, 7, 8), ERRNO
C
    1 WRITE (OUTPUT, 101)
      GO TO 99
    2 WRITE (OUTPUT, 102)
      GO TO 99
    4 WRITE (OUTPUT, 104)
      GO TO 99
    5 WRITE (OUTPUT, 105)
      GO TO 99
    6 WRITE (OUTPUT, 106) K
      GO TO 99
    7 WRITE (OUTPUT, 107) K
      GO TO 99
    8 WRITE (OUTPUT, 108) K
C
   99 RETURN
  101 FORMAT (46H0  PROBLEM TERMINATED FOR EXCESSIVE ITERATIONS //)
  102 FORMAT (49H0  PROBLEM TERMINATED BECAUSE OF ILL-CONDITIONING //)
  104 FORMAT (/ 50H INPUT ERROR IN PARAMETER L, NL, N, LPP2, OR NMAX /)
  105 FORMAT (68H0  ERROR -- INC MATRIX IMPROPERLY SPECIFIED, OR DISAGRE
     XES WITH LPP2. /)
  106 FORMAT (19H0  ERROR -- WEIGHT(, 14, 14H) IS NEGATIVE. /)
  107 FORMAT (28H0  ERROR -- CONSTANT COLUMN , 13, 37H MUST BE COMPUTED
     XONLY WHEN ISEL = 1.  /)
  108 FORMAT (33H0  CATASTROPHIC FAILURE -- COLUMN , 14, 28H IS ZERO, SE
     XE DOCUMENTATION. /)
      END
      DOUBLE PRECISION FUNCTION XNORM(N, X)
```

```
C
C        COMPUTE THE L2 (EUCLIDEAN) NORM OF A VECTOR, MAKING SURE TO
C        AVOID UNNECESSARY UNDERFLOWS.  NO ATTEMPT IS MADE TO SUPPRESS
C        OVERFLOWS.
C
      DOUBLE PRECISION X(N), RMAX, SUM, TERM, DABS, DSQRT
C
C           FIND LARGEST (IN ABSOLUTE VALUE) ELEMENT
      RMAX = 0.
      DO 10 I = 1, N
         IF (DABS(X(I)) .GT. RMAX) RMAX = DABS(X(I))
   10    CONTINUE
C
      SUM = 0.
      IF (RMAX .EQ. 0.) GO TO 30
      DO 20 I = 1, N
         TERM = 0.
         IF (RMAX + DABS(X(I)) .NE. RMAX) TERM = X(I)/RMAX
   20    SUM = SUM + TERM*TERM
C
   30 XNORM = RMAX*DSQRT(SUM)
   99 RETURN
      END
```

Appendix K

Main Program – Nonlinear Regression

This main program inputs the data into the nonlinear regression program, VARPRO. The data are read from the file named ppm.in, and the output is sent to the file ppm.out. Six input lines precede the data. betal, alphal and alpha2 define the inlet condition. If "total" regression parameters are desired (see Chapter 9), then betal should be set equal to 1.0 while alphal and alpha2 should be set to 0. alf(1) is equivalent to σ and alf(2) is equivalent to θ. Initial guesses of these parameters must be provided before VARPRO can process the data. The program returns values for ξ (beta), σ [alf(1)] and θ [alf(2)].

```
c
      implicit real*8 (a-b,d-h,o-z)
      dimension y(400),t(400),alf(14),beta(7),w(400),a(400,13),
     &          ctitle(20), cinit(400), ccalc(400)
      external ada
      common betal, alphal, alpha2
      nmax=400
      iprint=1

      open(unit=5, file="ppm.in")
      open(unit=6, file="ppm.out")

      read (5,1) ctitle
 1    format (20a4)
      write(6,2) ctitle
 2    format (20a4)

      read(5,*) 1
      write (6,3) 1
 3    format('number of linear parameters)'//(i1))

      read(5,*) nl
      write (6,4) nl
 4    format('number of nonlinear parameters'// (i3))

      read (5,*) betal, alpha1, alpha2
      read (5,*) alf(1), alf(2)

      lp=l+1
      lpp2=l+nl+2

      read(5,*) n
      write (6,5) n
  5   format('number of observations'// (i4))

      iv=1

      read(5,*) (t(i),y(i),i=1,n)


      wt=0.

      do 6 i=1,n
      cinit(i) = y(i)
 6    w(i)=1.

      call varpro(l,nl,n,nmax,lpp2,iv,t,y,w,ada,a
     *,iprint,alf,beta,ierr)

      write(6,7)
 7    format('ierr')
      write(6,*) ierr

      diffsum = 0
      diffno = n
      do 8 i = 1, n
         ccalc(i) = 0
         question = alpha2 + alf(2)
         if (t(i).le.question) go to 8
         ccalc(i) = beta(1) * betal *
     &                derfc( (alpha1 +  alf(1)) /
     &                ((t(i)- alpha2 - alf(2))**0.5) )
         diff = abs( ( ccalc(i) - cinit(i) )/cinit(i) )
         diff2 = diff**2
         diffsum = diffsum + diff2
         diffave = diffsum/diffno
```

```
8     continue

      write(6,9)
9     format('linear parameter - beta')
      write (6,*) beta(1)

      write(6,10)
10    format('nonlinear panameters - alf1, alf2')
      write(6,*) alf(1), alf(2)

      write(6,11)
11    format('mean of absolute value of differences')
      write(6,*) diffave

      write (6,*) n
      do 12 i = 1, n
         write(6,*) t(i) , cdnit(i)
12    continue

      write (6,*) n
      do 13, i = 1, n
         write(6,*) t(i) , ccalc(i)
13    continue


      stop
      end

      subroutine ada(lp,nl,n,nmax,lpp2,iv,a,inc,t,alf,isel)
      implicit real*8 (a-h,o-z)
      dimension alf(nl),a(nmax,lpp2),t(nmax),inc(14,8),d(400,7)
      double precision alf
      common betal, alphal, alpha2
      l=lp-1
      if(isel.eq.2) go to 90
      if(isel.eq.3) go to 165
      inc(1,1)-1.0
      inc(2,1)-1.0
90    do 81 i=1,n
      do 81 j=1,l
      k1=2*j-1
      k2=2*j
      if (t(i)/(alpha2 + alf(2)).gt.1.0) go to 82
      a(i,j)=0.0
      d(i,j)=0.
      go to 81
82    a(i,j) = betal *
     &          derfc( Kalphal +  alf(1)) /
     &          ((t(i)- alpha2 - alf(2))**0.5) )
      d(i,j)=a(i,j)
81    continue
      if(isel.eq.2) go to 200
165   do 170 i=1,n
      do 170 j=1,nl
      k1=(j+1)/2
      k2=2*k1
      k3=k2-1
      jj=l+j+1
      if (t(i)/(alpha2 + alf(2)).gt.1.0) go to 171
      a(i,jj)=0.
      go to 170
171   if(j.eq.2) go to 300
      alup = alf(1)*1.0001
      aldn = alf(1)*0. 9999
      a(i,jj) = (   betal *
```

```
     &               derfc( (alphal +  alup) /
     &               ((t(i)- alpha2 - alf(2))**0.5) ) -
     &               betal *
     &               derfc( (alphal +  aldn) /
     &               ((t(i)- alpha2 - alf(2))**0.5) ) ) /
     &               (alf(1)*0. 0002)
      go to 170
 300  a2up = alf(2)*1.0001
      a2dn = alf(2)*0. 9999
      a(i,jj) = (     betal *
     &               derfc(  (alphal +  alf(1)) /
     &               ((t(i)- alpha2 - a2up)**0.5) ) -
     &               betal *
     &               derfc(  (alphal +  alf(1)) /
     &               ((t(i)- alpha2 - a2dn)**0.5)  ) ) /
     &               (alf(2)*0. 0002)
 170  continue
 200  continue
      return
      END
```