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USE OF A DEDICATED COMPUTER FOR REAL-TIME CONTROL OF
GAS CHROMATOGRAPHIC MEASUREMENTS

by

Richard Gary Thurman

A Dissertation Submitted to the Faculty of the

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For the Degree of

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In the Graduate College

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Richard Gary Thurman
entitled Use of a Dedicated Computer for Real-Time Control
of Gas Chromatographic Measurements
be accepted as fulfilling the dissertation requirement of the
degree of Doctor of Philosophy

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December 16, 1970
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Richard Gary Thurman

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ABSTRACT

A small dedicated computer has been employed with a gas chromatograph in a "closed-loop" mode to provide optimized experimental conditions and measurements. The computer interacts with the experiment in real-time to control the sampling system, and to measure and control the carrier gas flow rate and the column oven temperature. Both the hardware system and the related software which were developed for this work are described and evaluated. Simple solid state logic control systems are used to control a pneumatically driven sampling system as well as motors which are used to position a proportional temperature controller and a differential flow controller. The real-time interaction of the software allows the optimization of the carrier gas flow rate and the column oven temperature. Experiments are described such as automatic "van Deemter" experiments as a function of temperature and the determination of thermodynamic parameters at optimum flow rates.

Application of this instrumental system to the study of the separation processes on certain adsorbents in gas-solid chromatography is reported. Peak position and peak broadening experiments were done on selected adsorbents to characterize the type of interactions

present. The type of interactions are studied by the evaluation of the variation of the peak position as a function of temperature to determine certain thermodynamic parameters. The study of peak broadening as a function of flow rate and temperature allows investigation of the effect of the pores through "van Deemter" studies. The adsorbents were porous polymer, porous glass, and porous zeolite beads. They represent potential interactions including adsorption, partitioning, and sieving. The adsorption characteristics also include those capable of nonspecific and specific interactions. The adsorbates were selected to provide a range of nonspecific and specific interactions to adsorption and also to provide a size factor for looking at the pore effects. There is the possibility of partitioning in the porous polymer beads as the adsorbate may dissolve in the bead.

Porasil C was shown to be an adsorbent of type II according to Kiselev's classification. The enthalpies and entropies of adsorption determined here are similar to those of silica gel. The peak broadening experiments indicate that no pore or kinetic effects are present.

Durapak (n-octane on Porasil C) was also shown to be an adsorbent of type II. It has part of its surface deactivated by the bonded n-octane. There is the possibility of interaction with both the remaining specific interacting OH groups and the bonded n-octanes. There is

also a possible pore or kinetic effect or partitioning with this "quasi-liquid" phase. The enthalpies of adsorption for all the adsorbates are lower than on Porasil C. For the adsorbates showing only nonspecific interactions the HETP values increased with increasing temperature in the peak broadening experiments. This is a reversal of behavior for HETP with temperature for adsorption and partitioning. This behavior can be explained if there has been a pore or kinetic effect produced by the bonded phase.

Porapak Q was shown to be a nonspecific adsorbent of type I. The enthalpies and entropies of adsorption determined for the various adsorbates are very similar to those reported for graphitized carbon black which is a very homogeneous adsorbent. This similarity would also indicate that partitioning is not occurring. The peak broadening experiments show some intermediate behavior indicating that there may be a pore or kinetic effect.

Molecular Sieve 5A in addition to its known sieving capability is also a strong adsorbent of type II. The large values of the enthalpies and entropies of adsorption bear this out. The peak broadening experiments indicate that there may be a pore or kinetic effect present for benzene, but not for the other adsorbates.

CHAPTER I

INTRODUCTION

In the past several years there has been a rapid increase in the number of chemists using digital data acquisition systems with chemical instrumentation (1-10). The reasons for this are manifold: improved precision of data taking, easier and quicker data processing in that tedious and time-consuming calculations are done automatically, and removal of human error at certain points in the operation thereby increasing system reliability. A second step toward automation is the use of the computer to control the experiment in such a fashion as to enable the course of the experiment to be altered in real-time based on the data being taken. Such an approach is generally referred to as "closing the loop." It is in this mode that the small computer offers the greatest possibility of enhancing chemical research. The computer is capable of being interfaced for optimizing the operating parameters for each sample and providing data which would not otherwise be available to the researcher. Because of the speed of the digital computer, the large increase in time resolution of the digital computer over analog systems enables the researcher to look at fast systems or events that may

not be resolved even on an oscilloscope. This represents a major step forward not only in the amount of data which can be handled but also in the precision of the data which can be obtained from the experiment.

The use of a dedicated computer in "closed-loop" configuration with an instrumental system has been reported for electrochemical systems (2, 4), and spectrophotometric systems (11, 12). Much development and use have gone into systems for control of process instrumentation (7, 8); however, these cases generally do not allow the flexibility which is necessary for use with a piece of research equipment. There have been a few reported time-shared systems for instrumental control and data acquisition, such as, spectroscopy (5), gas chromatographs (13), and mixed instrumentation (10, 14). If there are a number of relatively routine functions to be performed on several instruments, then time sharing of a computer is especially ideal. In this mode the instruments share a computer and each "gets" the computer to itself for a specified time period. Each instrument is serviced in a set pattern, such as, a sequential pattern. This is a fine method for data acquisition particularly when systems are used that acquire data at the same rate. Addition of control functions complicates the situation by creating timing problems in servicing the instruments. These timing problems are especially acute if one of the instruments is considerably

faster than another. Since the faster one must be serviced more often, data can be easily lost. This is why the systems mentioned above are essentially data acquisition systems.

The field of gas chromatography (GC) is quite adaptable to this computer data acquisition methodology. This is due to GC's inherent speed and the wide linear range of the very sensitive detectors. Several systems have been reported which involve the use of dedicated computers and sharing of a large computer for data acquisition from a large number of chromatographs (7-10, 13).

There is a strong need for an instrument in gas chromatography that would allow precise determination and control of experimental parameters that govern the chromatographic behavior of a wide range of samples. This type of parameter-controlled instrument could provide the necessary control and measurements for basic studies of separation processes as well as for standard analytical work. It is proposed here to build and evaluate a computer-controlled gas chromatograph that will have the following variables under computer control: the sampling system, column temperature, and carrier gas flow rate. Real-time measurements of these will be used to determine the retention behavior and to make decisions to change the experimental parameters as needed. This instrument should provide optimization of experimental parameters and provide

sufficiently precise data so that basic separation processes may be studied on certain adsorbents for gas-solid chromatography.

Prior to the discussion of the usefulness of this instrument, it will be necessary to describe the basic chromatographic processes and the mathematical relationships used to obtain the thermodynamic and kinetic quantities which describe the above processes. Chromatography is a separation process applicable to molecular mixtures as well as to ions. It relies on distribution of the mixture between an essentially two dimensional or thin phase and one or more bulk phases which are brought into contact in differential countercurrent manner (15). The driving force to move the sample in the column or on the paper is the mobile phase, the bulk phase in the above definition. The mixture components can be thought of being separated by some retardation factor or factors as the result of some interaction with the stationary phase in which the sample components have different strengths of retardation. Some of these retardation factors are adsorption, partitioning between two phases or extraction, ion-exchange, and molecular exclusion (sieving). These four retardation factors provide the basis for the classification of chromatographic methods. Chromatographic methods have become the principal method for separation of chemical mixtures. They are inherently faster and the

resolution is often much better. A general description of these methods with extensive references can be found in reference (16). The following discussion is not meant to be complete or totally comprehensive. The reader who is interested in a more detailed coverage is directed to the extensive literature on the subject. Some good sources for gas chromatography are in references (17-20). A good review series may be found in reference (21).

Of the various chromatographic methods gas chromatography has become the most important. It has two major advantages over other separation techniques. These are the speed of analysis possible and the sensitivity of the detectors which are available.

In gas chromatography, the bulk or mobile phase is a gas, such as, helium or nitrogen, and the thin or stationary phase is a solid or a liquid coated on a solid support. There are essentially three kinds of retarding factors in gas chromatography. The first is partitioning, that is, the distribution of mixture's components between the moving gas phase and the stationary liquid phase. This type is known as gas-liquid chromatography (GLC). The retention of the species on the stationary phase depends on K , the partition coefficient, defined as the ratio of the concentration of the solute in the liquid phase to the concentration in the mobile phase. How long the sample is

retarded then depends on the fraction of time the sample stays in the liquid phase.

Gas-liquid chromatography is the most widely used form of gas chromatography. This advantage is in part due to its wide applicability to many kinds of solutes because there are a multitude of liquid phases available. There is no sample size dependence on the retention of the solute on the column. The useful range of the liquid phase is limited by the volatility of the liquid phase at the operating temperature. If the temperature is too high, the liquid phase will bleed off the column. The maximum temperature of a given liquid phase may cause a separation problem for high boiling mixtures in that the separations will be poor and take a long time if the temperature is too low. There is also some limitation in the difficult separation of closely related compounds, such as, isomeric compounds, arising from the lack of selectivity resulting generally from the nonspecific interaction of partitioning.

The second retardation factor is adsorption of the sample species onto the surface of a solid adsorbent. This form is known as gas-solid chromatography (GSC). The length of time the sample is retained depends on the fraction of time it is in the adsorbed phase. Its advantages over GLC are selectivity and speed. Specific interaction of the two-dimensional adsorption sites makes gas-solid chromatography quite useful for separating

closely related compounds, such as geometric isomers. Since there is no liquid phase, the lack of the contributions to the band broadening resulting from the slow kinetics of the liquid phase mass transport gives a significant advantage. This is the result of liquid diffusion being 10^5 times slower than gaseous diffusion. Also as a result of no liquid phase being present, there is a large useful temperature range which can enhance the speed.

The chief disadvantage is the sample size dependence of the retention behavior. Small samples have to be used to combat this. A second disadvantage has been a lack of reproducibility of the surface characteristics of given adsorbents. The chromatographic behavior of an adsorbent is very dependent on its surface area and pore structure. Recent advances in technology have provided a wide variety of adsorbents which are much more reproducible.

The third retardation factor is sieving, that is, molecular exclusion based on the size of the species. The volume of mobile phase necessary to elute the species is inversely proportional to the size of the molecule being chromatographed. This method can be classified actually as gas-solid chromatography. If sieving is the only mechanism operating, its speed is determined by the free volume of the column, that is, the longest retained component cannot be held up longer than the time it takes

to elute the volume of the column. However, in gas chromatography it is seldom that only a single retarding factor is in operation. A short description of how to determine the effects due to two mechanisms will be described below. The major disadvantages to sieving adsorbents are adsorption and a narrow range of selectivity due to the fixed size of the pores due to adverse competition between the two processes.

There are two approaches to studying the separation processes using gas chromatography as a physico-chemical technique, that is, thermodynamic measurements and the dynamic approach. The thermodynamic approach uses retention behavior as a function of temperature. The dynamic approach uses peak shape as a function of gas velocity. An excellent review of the use of gas-liquid chromatography to determine thermodynamic values is given by Young (22). The following is a short summary of the more basic ideas.

The parameter that describes the behavior of a solute in a given chromatographic system is the retention volume, V_R . This is the volume of gas necessary to elute one-half of the solute from the column (23). It is necessary to correct the retention volumes described here for the pressure drop across the column. The relationship between V_R and a thermodynamic equilibrium constant (K) is shown by the following equations:

$$V_R = V_M + K_1 V_s \quad (\text{partitioning}) \quad (\text{I-1})$$

$$V_R = V_M + K_2 A_s \quad (\text{adsorption}) \quad (\text{I-2})$$

$$V_R = V_0 + K_3 V_I \quad (\text{sieving}) \quad (\text{I-3})$$

V_M is the volume of the mobile phase or the "dead volume" of the column, V_s is the volume of stationary liquid phase, K_1 is the partition coefficient, K_2 is the adsorption coefficient, A_s is the surface area, K_3 is the sieving coefficient, V_I is the volume of the inner volume of the inner volume of the cavities or protected pores, and V_0 is the outer volume of the column excluding the volume of the cavities. For adsorption and partitioning the K 's are defined as the ratio of the concentration of the sample component in the stationary phase to the concentration in the mobile phase. The sieving K is the concentration fraction in the inner volume over the concentration in the outer volume. Dilute solutions are assumed here so that activities may be approximated by concentrations and to give K 's thermodynamics significance. Due to the speed of the diffusion processes between phases relative to the rate of migration through the column, the chromatographic process can be accurately approximated by the assumption that it involves an equilibrium process. Therefore the adsorption and partitioning K 's can be considered to be true thermodynamic equilibrium constants.

Using the adsorption case for example, one can solve for K obtaining the following expression

$$K = \frac{V_R - V_M}{A_s} = \frac{V_N}{A_s} = V_s^T \quad (I-4)$$

where V_N is the net corrected retention volume and V_s^T is the specific retention volume. V_N is equal to

$$V_N = V_R - V_M \quad (I-5)$$

K is equal to V_s^T in the linear portion of the adsorption isotherm (24). The free energy of adsorption for the adsorbate going from the gas phase to the adsorbed phase may be obtained from

$$\Delta G_o = -RT \ln K \quad (I-6)$$

where R is the gas constant and T the Kelvin temperature.

The variation in the retention volume and thereby K with temperature can be described by the Clausius-Clapeyron equation as

$$\ln K = \ln \frac{V_N}{A_s} = - \left(\frac{\Delta H_o}{R} \right) \left(\frac{1}{T} \right) + \text{constant} \quad (I-7)$$

where ΔH_o is the standard heat of adsorption per mole of adsorbate at low surface coverage. By plotting $\ln K$ vs. $1/T$, ΔH_o can be determined from the slope of the line obtained. Nonlinearity is a possible indication that a

second retarding process may be entering in, such as, partitioning or sieving.

The entropy of adsorption may then be calculated from

$$\Delta S_o = \frac{\Delta H_o - \Delta G_o}{T} \quad (I-8)$$

The enthalpy data gives information about the strength of adsorption. These may be either specific or nonspecific interactions. This will be discussed in Chapter IV. The entropy data can give much information on the molecular structure or orientation contributions to adsorption. How the molecule sits on the surface will affect the retention behavior. If only part of the molecule is flat on the surface, the strength of adsorption may be affected in comparison to one which is entirely flat on the surface. Remembering that the entropy change is the change in going from the gas phase to the two-dimensional adsorbed phase, this change requires an orientation of the molecules. This orientation effect can also significantly alter the retention behavior. The more the orientation obtained the longer the molecule is retained.

At this point it can be shown how to get the K's if two mechanisms are operating at once. If adsorption and partitioning are operating, using the equations for V_R above, the following combination is obtained

$$V_{\text{NET}} = K_1 V_s + K_2 A_s \quad (\text{I-9})$$

where V_{NET} is defined in equation (I-5). Rearranging the equation, a straight type of the form $y = mx + b$ is obtained

$$\frac{V_{\text{NET}}}{A_s} = \frac{K_1 V_s}{A_s} + K_2 \quad (\text{I-10})$$

By plotting V_{NET}/A_s vs. V_s/A_s , the intercept is the adsorption coefficient and the slope is the partitioning coefficient. Similarly for adsorption and sieving, one obtains

$$\frac{V_{\text{NET}}}{A_s} = K_3 \frac{V_o}{V_s} + K_2 \quad (\text{I-11})$$

Again the intercept is the adsorption coefficient and the slope is the sieving coefficient. Both of these necessitate a series of adsorbents of the same type but with differing surface areas.

Further information on the chromatographic processes may be obtained from the peak shape. The peak shape is a function of the effect of column gas velocities. The narrow band of sample injected into the column is broadened by numerous non-equilibrium processes, such as, surface area, pore size, particle size, multiple paths, diffusion in the gas phase, kinetics of

adsorption-desorption, and mass transportation effects. This band broadening was related to the height of a theoretical plate (HETP or H), that is, the distance in the column equivalent to one step of "equilibration" between the two phases as in distillation. A number of empirical equations have been developed relating the various effects mentioned above. These generally take into account the non-equilibrium processes that are occurring. The equations also have in general been based on a statistical approach. Van Deemter, Zuiderweg, and Klinkenberg (25) in their original formulation of the rate equation assumed that the various contributions to column inefficiencies are independent of each other and that the variances contributing to H are additive.

The coupled form of the van Deemter equation is given as

$$H = 1/[(1/2\lambda d_p) + (D_g/u d_p^2)] + 2\gamma D_g/u + q \left(1 - \frac{V_M}{V_M + KV_L} \right) \frac{V_M}{V_M + KV_L} d^2 u / D_L \quad (I-12)$$

where

λ = tortuosity factor

d_p = average particle diameter

D_g = diffusion coefficient of the solute in the gas phase

- u = average linear gas velocity in the column
 γ = obstruction factor
 ω = a transchannel flow velocity coefficient
 q = liquid configuration term
 d = average liquid film thickness of the stationary phase
 D_ℓ = solute diffusion coefficient in the liquid phase
 K = thermodynamic partition coefficient
 V_L = volume of the liquid phase
 V_M = volume of the gas phase.

Equation (I-12) may be written as

$$H = \frac{1}{1/A + 1/C_g u} + \frac{B}{u} + C_\ell u \quad (\text{I-13})$$

where

- $A = 2\lambda d_p$ (classical eddy diffusion term)
 $B = 2\gamma D_g$ (molecular diffusion term)
 $C_g = \omega d_p^2 / D_g$ (gas phase mass transfer term)
 $C_\ell = q \left(1 - \frac{V_M}{V_M + K V_L} \right) \frac{V_M}{V_M + K V_L} d^2 / D_\ell$ (liquid phase mass transfer term)

The band broadening of the eddy diffusion term is due to the multiple paths available to the molecule as it travels through the column. It is a random process. It is dependent on the particle size and randomness of packing and the distribution of channels available.

The B term is the molecular diffusion term and is dependent on the gas phase diffusion coefficient. It has the most effect at low gas velocities. The gas phase mass transfer term, as shown here in the coupled equation also has its greatest effect at low gas velocities. It is a result of a distribution of gas velocities across a channel.

Resistance to mass transfer in the liquid phase contributes to band broadening as the molecule must decide which phase it wants to stay in longer and it may travel through the liquid to get out. C_ℓ is dependent then on K, the liquid phase diffusion coefficient and the thickness of the liquid film. This term is absent in gas-solid chromatography.

There is a similar term that replaces the C_ℓ . It (C_k) is related to the kinetics of the adsorption-desorption process which is dependent on the adsorption coefficient. The size of this term is much smaller than C_ℓ as there is no slow diffusion in the liquid phase. The van Deemter equation for adsorption is then

$$H = \frac{1}{1/A + 1/C_g u} + \frac{B}{u} + C_k u \quad (\text{I-14})$$

where

$$C_k = 2 \frac{V_M}{V_M + K A_s} \left(1 - \frac{V_M}{V_M + K A_s} \right) \bar{t}_d \quad (\text{I-15})$$

and

A_s = surface area of the adsorbent

$\bar{t}_d$ = mean desorption time.

The van Deemter equation can be simplified for adsorption to

$$H = A + B/u + Cu \quad (I-16)$$

where C is the coefficient due to resistance to mass transfer in the gas phase and from the kinetics of the adsorption-desorption processes. It should be noted that at low gas velocities the A term is not independent of the gas phase mass transfer effects. For a more complete discussion of the various forms of the equation see Giddings (26) and dal Nogare and Juvet (17). The variation of HETP with flow rate and temperature gives insight into the effects of pores in the support, the kinetics of adsorption-desorption, and diffusion coefficients.

The development of the newer models such as Giddings' random walk (26) and Grubner's statistical moments theory (27) has led to another way of describing a chromatographic peak by its shape. The normal curve is characterized by statistical moments. These moments are related to various parameters such as HETP, peak tailing, and departure from Gaussian behavior which can lead to information on various column processes.

The individual moments describe a peak in the following manner. The zeroth moment of the peak (not normalized) is its area calculated from

$$A = \sum_{i=P_1}^{i=P_2} Y_i \quad (\text{I-17})$$

where A is the area, Y_i is the i -th ordinate, and P_1 and P_2 are the data points at the start and end of the peak. A uniform time interval is assumed between each point. The first is the coordinate of the center of gravity of the peak and thus is equal to the retention time.

$$\mu_1 = \frac{\sum_{i=P_1}^{i=P_2} Y_i t_i}{A} \quad (\text{I-18})$$

All higher moments are taken around μ_1 , the center of gravity. The second moment then is a measure of the peak's width. The third moment shows the magnitude as well as the direction of the peak's asymmetry (skew). The fourth moment is a measure of peak flattening (excess) as well as peak width

$$\mu_K = \frac{\sum_{i=P_1}^{i=P_2} Y_i (t - \mu_1)^K}{A} \quad (\text{I-19})$$

where $K = 2, 3, 4$. μ_3 and μ_4 are converted coefficients to measure directly the departure from Gaussian.

$$c_3 = \frac{\mu_3}{\mu_2^{3/2}} \quad (\text{I-20})$$

$$c_4 = \frac{\mu_4}{\mu_2^2} - 3 \quad (\text{I-21})$$

The second moment is a source of information on gaseous diffusion coefficients, adsorption-desorption kinetics, and other mass-transport properties. The importance of the precision of the measurement of retention time is seen in the higher moments as they are very sensitive to experimental error.

There is a lack of data, particularly good data, that could be used to test the newer models for the separation processes. Also there are the newer, more reproducible supports for gas-solid chromatography such as the Porasils, Porapaks, and Durapaks which have not been characterized. In order to study the separation processes on the solid supports, good retention volume measurements are needed as a function of temperature to get enthalpies of adsorption and to determine the other thermodynamic parameters. This would be best at the optimum conditions. The effect of the pores can be determined from the variation in retention behavior and column efficiency with flow rate and temperature. Good

area measurements and precise timing for the data points are needed for determination of the statistical moments.

To get all this--good data, precise knowledge of retention time, good temperature control, good flow rate control--an instrument that provides these is needed. Its capability would be enhanced if some of the experimental decisions can be taken away from a human and placed under a digital computer where there is less chance for accidental error. The digital system would make the data easier to work with, as again humans are removed from part of the chain, thereby improving the decision. The data taking would also be much easier and less time-consuming under computer control.

CHAPTER II

STATEMENT OF THE PROBLEM

The purpose of this work is the development and evaluation of a computer-controlled gas chromatograph.

In addition, the software for running this instrument must be developed and evaluated.

Finally, the instrument will be used to obtain thermodynamic and rate data to be used in the study of the separation processes on and characterization of certain adsorbents in gas-solid chromatography.

CHAPTER III

INSTRUMENT DEVELOPMENT AND EVALUATION

Automation of gas chromatographs has followed three general courses. The first approach was a data acquisition system. The data were acquired through a digitizer and punched on tape or cards. It was then sent to a computer for processing. Examples are in references (28) and (29). The second step was to use the computer for data acquisition and process the data acquired on-line. This approach has been widely used in both industrial and research application (9, 10, 13, 30, 31). This method allowed the experiments to immediately evaluate the results. Necessary adjustments or decisions could be made without having to wait for a long period of time.

The next step is the control of the instrument. One approach has been to add digital control to the data acquisition system (6, 32). The computer which is used in the data acquisition system has a feedback capability to the digital control system. The control unit then continues according to the preset conditions given it initially by the experimenter. In this approach, the computer does not have the capability of changing the course of the experiment based on the information it has

taken. The second approach then is that the computer is in complete control. It not only has feedback capability but also can modify the experiment basing its decision on information it has taken from the instrument. There are industrial applications of the first approach of digital control with the time-shared systems (10). There are numerous applications of computer control of process systems (7, 8). However, these systems are not flexible being set for one application. They are not very useful for research applications.

A computer controlled gas chromatograph and the associated data acquisition system is greatly needed for research applications. Areas where it could be used were noted in Chapter I. Development of this type of instrumental system will also require the designing of interfacing logic for the control feedback functions. These interfaces and the associated electronics are not available commercially. The software needed for the controlling programs will have to be developed. It is proposed here to develop and build such a system.

The instrument described here was developed in two phases. In the first phase the chromatograph was developed and the sampling system placed under computer control. The initial software was developed and the system was evaluated. In the second phase, the control of the column oven temperature and the carrier gas flow rate

was added. In addition, the software was made more sophisticated and the complete control algorithm was developed. A system block diagram of the total experimental apparatus is shown in Figure 1. The instrument will be discussed using a modular approach.

Chromatograph

A schematic of the chromatograph designed for the study of adsorption characteristics of various porous solids and under "closed-loop" control of the computer is shown in Figure 2.

Oven

The oven used is a Becker Model 1452D (Becker, Delft, Holland). With a slight modification of the control unit--better transformer and silicon controlled rectifiers --and the use of a constant voltage transformer, the oven was found to provide a constant temperature of better than $\pm 0.02^{\circ}\text{C}$ over the depth of the oven occupied by the columns used in this study. Mapping of the temperature profile of this oven showed that modification of the flow pattern would be necessary if one were to attempt to use the entire oven with this sort of temperature control. The oven was used in an isothermal mode only. In the second phase the column oven temperature was placed under computer control. A Clifton MSA-15-AS-1 stepper motor (Clifton Co., Clifton Heights, Pennsylvania) was attached to the ten-turn

Figure 2. Gas chromatograph block diagram.

1. Exponential dilution flask
2. Saturator for liquid samples
3. Gas sampling valve
4. Oven and column
5. Flame ionization detector
6. Electrometer
7. Recorder
8. Flow controller
9. Flow sensor

Figure 2. Gas chromatograph block diagram.

potentiometer which determines the set point of the proportional temperature controller. The stepping angle of the motor is $90^\circ \pm 3^\circ$ and has a holding torque of 3.2 oz.-in. per phase.

In setting the temperature of the column oven, the precision is limited at this point only by the degree of resolution possible from the potentiometer used in the control loop of the proportional controller and stepping angle of the control motor. In our case, this is a ten-turn 200 ohm potentiometer to control from 0 to 400°C with a stepping angle of 90° . Assuming that the temperature is linear with respect to the potentiometer, each step results in 10°C increments. The actual step is $12\text{-}13^\circ\text{C}$. However, this variation does not affect the experiments done here.

This arrangement of the temperature step is not optimum, but serves the purpose for the studies being done now. Greater resolution can be obtained by either using a smaller potentiometer or decreasing the stepping angle.

Column Temperature Measurement

The column oven temperature is monitored by means of a Burr-Brown Model 8109 temperature read-out module (Burr-Brown, Tucson, Arizona). This system utilizes the temperature coefficient of the zener potential of a diode which is in the feedback loop of an operational amplifier to sense the temperature. The output signal of the

temperature module is introduced into the computer through the multiplexed digital voltmeter described below.

The Burr-Brown temperature module has a linear 0 to 10 volt output which can be calibrated for whatever range desired. If a one hundred degree range is set, then the output is 100 mv/degree. The module is calibrated using a water-ice bath for the low set point and boiling H₂O for the high set point. Temperature resolution using the Hewlett-Packard 2401C integrating digital voltmeter, the A-to-D converter used here, in its autoranging mode is $\pm 0.001^{\circ}\text{C}$. The short term stability (10-15 minutes) of the column oven over the length of a given set of samples is better than $\pm 0.02^{\circ}\text{C}$.

Detector

The detector used in the studies was a flame ionization system from the Varian-Aerograph 1200 Series chromatograph (Varian-Aerograph, Walnut Creek, California). The carrier gas input of the detector was reduced with 1/16 in. stainless steel tubing and mounted directly on top of the column oven to minimize the "dead volume" from the end of the column. The detector was thermally isolated from the top of the oven by an asbestos top. The detector was heated with a separate cartridge heater and maintained above 100°C to avoid water condensation from the flame.

Electrometers

Two different electrometers were used with the detector described above. A Varian-Aerograph 550 electrometer was used in the early studies; however, the sensitivity of 3×10^{-12} amp per millivolt output (50 millivolt maximum output) was found to be a limiting factor. A Keithley Model 610C with a 10^{-14} amp to 0.3 amp input for a full scale 10 volt output was also used. This provided a larger signal and thereby a greater dynamic range. A Leeds and Northrup Model H potentiometer recorder was used to monitor the detector output in parallel with the digital voltmeter.

Flow Control

The carrier gas as well as the gases used in the sampling systems were controlled using Brooks Model 8744 flow controllers (Brooks Instrument Division, Emerson Electric Co., Hatfield, Pa.). The flow rates were found to be controlled to better than 0.4% over a range of 5 to 100 cm³/min. For computer control of the carrier gas flow rate in the second phase, a continuous drive synchronous motor (Hurst Manufacturing Corp., Princeton, Ind., 10 RPM) was attached to the shaft of the needle of the flow controller. The motor was connected to an electrical controlling circuit (33) which provided a predetermined power which determined the on time of the motor. The

continuous drive motor was used as it provided sufficient torque to turn the flow controller shaft. A stepper motor with greater torque could be expected to give a more reproducible step. However, considering the nonlinearity of the flow controller step, the more reproducible motor step would not result in an equal step each time in flow rate.

The size of the steps on the control motor on the carrier gas flow controller are set by switching different capacitors into the one shot in control interface board described later. The two positions most commonly used here are positions 2 and 4 which result in steps of about one-eighth and one-quarter turn of the needle valve stem, respectively. This corresponds to a flow rate change of $0.4\text{--}0.5\text{ cm}^3/\text{min.}$ and $1.0\text{--}1.5\text{ cm}^3/\text{min.}$, respectively. The variance is due to the inertia of the flow controller shaft and the torque available from the motor.

Flow Measurement

Classically the soap bubble flowmeter has been used the most due to its simplicity and accuracy. It was used here where possible. Since a destructive type detector was used to measure the flow rate of the carrier gas without dismantling the system, it was necessary to build an in-line flow sensor.

Of the common methods of in-line systems, rotameters do not have sufficient resolution for most work and have the distinct disadvantage of depending on the pressure drop across the system. Turbine flowmeters are accurate. But, for the most part, they are inconvenient for use with the small tubing employed in gas chromatography and are of limited value for measuring low flow rates.

It was decided to build one of the thermal mass flowmeters. The thermal mass flowmeters use a temperature measurement for determining the flow rate. These flowmeters operate on the principle that the mass flow is proportional to a heat transfer process. Specifically, the principle used is heat capacity, that is, the amount of heat needed to raise the temperature of a given mass one Celsius degree. If a constant heat input is applied, then the mass flow rate of a gas passing by the heat source is proportional to the heat input divided by the heat capacity and the temperature change of the gas. It has been shown (34) that the heat capacity of gases show very small changes over wide ranges of temperature and pressure. Therefore, under the conditions used in gas chromatography, the change in temperature of the gas is proportional only to the flow rate as the heat capacity of the gas is essentially constant.

Various approaches have been taken for designing systems where the temperature differential between two

sensors can be related to the mass flow of a gas stream. Several kinds have been developed or described (35, 36). The electrical output of the temperature sensors is easily amplified and displayed and is especially useful in systems involving automated control. Since the flow rate is measured directly in the tubing it is possible to use such a system with ionization type detectors.

The flow detector designed for and used in this work involves the use of a differential thermometer in which Microtab transistors are used for the sensors. The difference signal from a bridge in which the transistors and incorporated is amplified by means of an instrumentation amplifier. The system depends on the heat capacity and flow rate of the carrier gas and is reasonably sensitive for gases such as hydrogen and helium even though their heat capacities are quite low.

The temperature distribution across the tube varies as a function of the flow rate of the gas through the tube. This causes the temperature difference between the two sensors to vary as a function of the gas flow. This difference is then related to the mass flow by a calibration curve.

The flow sensor is shown in Figure 3. A 3.8 cm section of 1.19 mm i.d. stainless steel tubing brazed to two 1 in. x 1 in. x 1/2 in. brass blocks is used as the measuring tube. This system is heated to approximately

Figure 3. Flow sensor diagram.

100°C by direct passage of current. A step-down transformer, 17 volts, Triad Model F-48U (Triad, Huntington, Ind.), along with a variable transformer is used to provide constant electrical power input. The sensor is placed in the chromatographic stream by means of Swagelock fittings (Crawford Fitting Co., Solon, Ohio) which are brazed to the brass blocks. The sensor unit is located in the carrier stream between the flow controller and the gas sampling valve. Polyethylene tubing is used to isolate the chromatograph from the heated tube. A heat sink of aluminum is used to cause a temperature distribution across the stainless steel tube. The heat sink is electrically isolated from the brass blocks by thin mica disks. The sensors (transistors) are mounted 0.75 inch from the center of the tube with an electrically non-conducting epoxy resin. The top half of the unit is mounted in an insulated box to keep temperature fluctuations down around the tube and temperature sensors, but the bottom is open so that the aluminum heat sink can more rapidly equilibrate with ambient temperature.

The temperature sensing elements are GE microtab D26G-1 transistors utilized as diodes (base-emitter). The temperature coefficient of the Zener potential of the base-emitter diode is used to track the temperature changes. As shown in Figure 4, the diodes are used as two arms of a bridge which is in the feedback loop of an

Figure 4. Schematic diagram for flow sensor.

All resistor values are in ohms, 5%.

A	Operational amplifier, Burr-Brown 3062
IA	Instrumentation amplifier, Burr-Brown 3264
T1, T2	Transistors, Microtab D26-G1, General Electric
VM	Voltmeter
R1	10K, 10-turn potentiometer

Figure 4. Schematic diagram for flow sensor.

operational amplifier. A Burr-Brown Model 3062 operational amplifier (Burr-Brown, Inc., Tucson, Arizona) was used in the system. A constant current of 1 milliamperes is kept in each arm of the bridge. A voltage difference is developed across the bridge as a function of the temperature change in the tube and this differential is amplified by means of a Burr-Brown Model 3264 instrumentation amplifier.

The temperature sensors are mounted on the outside of the small diameter flow tube and are placed so that under conditions of no flow there is a symmetrical distribution of heat and no temperature difference. The flowing gas causes some of the heat to be transferred to the gas and then back to the tube further down the sensor. This causes a temperature differential between the two sensors. Since only temperature differences are being measured from the bridge network and not absolute temperatures, the flow sensor is relatively insensitive to changes in ambient temperature. The box mounted around the top of the sensor minimized convection currents around the tube as the flow sensor as used here in this laboratory is mounted in a large thermostated box where a small fan keeps the air moving. The transistors used as temperature sensors have very rapid response to temperature changes and can easily resolve 0.001°C when used in a Zener diode mode. The fact that they are faster and more sensitive makes them more

useful than thermocouples. Their response is also more linear and sensitive than that of thermistors. Their response time is about the same as thermistors.

The bridge output is amplified and conditioned through the instrumentation amplifier described above. This was used instead of an ordinary differential operational amplifier to solve the grounding problems that occurred. The operational amplifiers give us a signal that is more easily digitized for use in an automated system.

The output voltage is related to the mass flow rate by using a calibration curve. Typical curves are shown in Figure 5 for N_2 and He. The X-axis values were measured by a bubble meter. As it may be seen the flow sensor is linear up to a flow rate of about $30 \text{ cm}^3/\text{min}$. This linear range makes the setup here quite useful for the flow rates normally used for 1/8 in. columns. The sensor could be used linearly down to about $3 \text{ cm}^3/\text{min}$. The flow controller used here could not control effectively below this. The linear range could be expanded by changing the flow tube size and length and the heat input. The sensitivity for N_2 in the linear region is $11.5 \text{ mv/cm}^3/\text{min}$. The sensitivity for He is $8.27 \text{ mv/cm}^3/\text{min}$. The long term stability of the sensor of a period of one hour is quite good. The range on the one hour test at a flow rate of $11 \text{ cm}^3/\text{min}$. was $\pm 1.5 \text{ mv}$ with a standard deviation of $\pm 0.77 \text{ mv}$ and a relative standard deviation of 0.25%.

Figure 5. Typical calibration curves for N_2 and He.

This standard deviation is 6.7% of the 11.5 mv sensitivity, but when the signal is time-averaged, the uncertainty reduces to 1% or less. Over 15 hours, there was no significant increase in the standard deviation. Time averaging of a specified number of samples of the output is the method used in this system for sampling the sensor. The short term stability over this sampling period of three to six seconds which is set by the operator as one of the initial parameters in the control program for the computer-controlled chromatograph has a range of ± 0.30 mv and a standard deviation of ± 0.13 mv. The relative standard deviation is 0.04%. The standard deviation is 1% or less of the 11.5 mv sensitivity. The accuracy of the flow sensor is about 1% using the bubble meter as a standard.

Sampling System

The sampling system was a Carle micro gas sampling valve No. 2014 with automatic actuator (Carle Instrument Inc., Fullerton, California). The valve was equipped with an unmatched pair of 50 microliter loops. The valve was operated by a solenoid-actuated pneumatic piston. The solenoids could be fired either manually or by computer command. Three methods of sampling were used in these studies: (1) direct sampling of a gas stream diluted with nitrogen, (2) sampling of the output of an exponential dilution flask (Varian-Aerograph, Walnut Creek, Calif.),

(3) sampling of a stream of nitrogen which has been saturated with the vapor of an organic sample by being passed through a series of bubblers and then diluted with another nitrogen stream. All tubing between the sampling valve and the column and all other system tubing was 1/16 inch stainless steel to minimize the dead volume. The dead volume of the system was 0.75 cm^3 .

Columns

The chromatographic columns used were 1/8 inch o.d. stainless steel with lengths varying from 3 cm to 183 cm. Care was taken to minimize dead volume in the columns. The packings used will be discussed later.

Digital Hardware

Computer Hardware

A Hewlett-Packard Model 2115A computer was used to for control of the experiment, data acquisition, and processing of the chromatographic data. The computer was equipped with an 8192 word core memory, a high-speed paper tape reader (HP Model 2737A, 300 characters per second), a high-speed paper tape punch (HP Model 2753, 110 characters per second), and a teleprinter Model ASR-33 (Teletype Corp., Skokie, Illinois). All of the control logic used in this system was interfaced to the computer through a Hewlett-Packard 16-bit duplex register board (GPR) (HP

interface kit 12554A). The high level logic (10 volt) of the GPR card and the interfacing control logic boards were used to provide greater noise immunity for control of the high current motors and solenoids.

Analog-to-Digital Conversion

The analog-to-digital (A-to-D) conversion was done with a Hewlett-Packard Model 2401C Digital Voltmeter (DVM). The relatively slow speed of this A-to-D converter is adequate as it is fast enough for the slower chromatographic processes. It was chosen also because it is an integrating type voltmeter which gives excellent signal noise rejection. The overall effective common mode rejection is 140 db at all frequencies and 160 db at dc. The common mode rejection to superimposed noise is 120 db at 60HZ and 160 db at dc. The digital voltmeter interface to the computer is commercially available as interface kit number HP 12604A. The DVM was modified (per instruction from Hewlett-Packard) to eliminate the built-in time delays which allow the use of the Nixie tube visual readout. With this modification the maximum rate of data taking was 16.54 milliseconds (about 60 points per second). Rates of one and ten data points per second were also available.

I/O Interface

The system block diagram of the system is shown in Figure 1. The experiment is initiated by a command from the computer through the GPR card to the multiplexer for analog signals or to the interface logic boards of the control devices. Control of the devices are accomplished by setting a predetermined 16-bit "word" for each external function.

Multiplexer

In Figure 6 is shown the logic for the multiplexer including that of the control devices and that of the analog signals to the DVM.

Digital. In Figure 6, computer bits 6-15 (bits on output register) are for device control and are not used by the analog part of the multiplexer. At the present time only three of the ten channels are being used for device control. The flag inputs from the devices and the multiplexer are gated together to provide a single flag to the computer. This is a "wired OR" using NAND gates with passive pullup. Under the present system, this single flag is used for indicating the completion of the desired control or analog function. This could be easily expanded so that, in addition to the system flag, a flag pulse from each device would go back as a particular bit which would

Figure 6. Multiplexer schematic diagram.

F1, F2, F3, F4 RS Flipflop
 MS Monostable multivibrator, flag
 pulse
 R1, R2, R3, R4 Relay, Magnecraft, W101MX2
 ST Schmitt trigger

allow software routines to verify which device had been activated.

Analog. The analog multiplexer for the digital voltmeter utilizes the same type of encodes as the control devices (a single bit in the output register as set by the predetermined word). This multiplexer allows the digital voltmeter to sample the electrometer, the flow sensor, or the column temperature. The encode pulse sets the corresponding R-S flipflop and, at the same time, the rest of the flipflops are reset by the system of gates so that only one channel is "on" at a time. The $\bar{Q}$ output of the flipflops each connect to an inverting power amplifier which drives the relay. The settling time of the relays is less than 0.5 milliseconds which sets the limit on how fast one can sample. This is not a limitation in this system, since it is not proposed to sample the temperature or flow rate during the run. Also, the data rate is not normally this fast as most chromatographic peaks are wide enough that very fast data rates, such as 100 points or more per second, result in more points than the number needed to adequately define the peaks.

Sampling Valve Interface

The sampling valve control logic is shown in Figure 7. The encode pulse from the computer set by the

Figure 7. Schematic diagram for sampling interface logic.

B1	Bridge Rectifier Motorola MDA 962-3
D1, D2	Diode 1N547
FF	JK Flipflop
MS1, MS2	Monostable multivibrator, SCR pulse former
MS3	Monostable multivibrator, flag pulse
PA1, PA2	Pulse amplifier
ST	Schmitt Trigger
SCR1, SCR2	Silicon-controlled rectifier 2N685
Z1, Z2	Zener Diode 3V 1N4372

software provides the gating pulse for the SCR switches. These switches control the solenoids which fire the pneumatic piston of the sampling valve. The JK flipflop is needed to direct the pulse to the right solenoid as there are two sample loops. The flag back to the computer is initiated by the encode pulse on the logic board as seen in Figure 7. The sampling takes about 120 milliseconds for the gating and firing of the solenoids.

Carrier Gas Stepper Interface

The control logic board used for controlling the carrier gas flow rate is described in detail elsewhere (33).

Column Oven Temperature Interface

The control logic board for the stepper motor which positions the set point potentiometer of the temperature controller is described elsewhere (33).

It should be noted that the flags are not necessary under the present system of operation in the non-interrupt mode. The necessary resetting of the interface boards can be taken care of by changes in the software. However, the interfaces and control logic were designed so that operation in the interrupt mode which requires a flag can be done in the future, such as, the addition of an external clock.

Software

The software developed for this work has been written in Assembler (mnemonic machine) language. This approach has distinct advantages in efficiency and flexibility for purposes of data acquisition and control of peripheral equipment. The programs were developed in two phases: the first for the initial instrument to include data acquisition and sampling valve control, and the second for the additional control parameters and sophistication of the data processing.

The software was developed to include the capabilities listed in Table 1. It should be noted that the operating parameters can be varied by means of the teletype. The parameters which can be varied externally include the number of samples to be taken, the baseline and noise rejection thresholds, the number of temperature or flow increments to be taken, the estimated total retention time, as well as the options on the data output.

The punched paper tape capability is important in that we are able to use the small computer for data acquisition and control and the large computer for the statistical analysis and curve-fitting routines. The curve smoothing and peak-finding routines as described by Savitzky and Golay (37) are used to find a more precisely located peak maximum. The curve-fitting allows the interpolation

Table 1. Capabilities of Software

-
1. Communication with the experimenter through the teletype for setting the initial parameters.
 2. Taking and storing of the data at a rate set by the DVM with the capability of a software averaging routine to modify the rate set by the DVM.
 3. Choice of computer or manual control of the sampling system, the temperature controller, or the carrier flow system.
 4. Rejection of baseline data and determination of the start and end of a peak.
 5. Noise spike rejection on both the increasing and decreasing sides of the peak.
 6. Location of the peak maximum.
 7. Determination of the retention time and peak width at half-height.
 8. Integration of the area under the peak.
 9. Simple curve smoothing on the slopes of the peaks.
 10. Control of the sample injection based on either the number of peaks sensed or on a preset time.
 11. Optimization of carrier gas flow rate.
 12. Printout on the teletype of the areas, retention time, etc.
 13. Option of dumping data, either raw or calculated, onto punched paper tape for processing on an offline computer.
-

between two data points to find the exact peak maximum and location.

First Phase Software

For the initial instrument where only the sampling system was under control, Figure 8 shows the simplified flowchart of the computer-controlled experiment for the controlling program CART. The large block in the lower right of the flowchart is the processing routine RTIM. These will be discussed below.

Figure 9 shows a typical sequence of input/output statements and the computer print-out of the calculated information. The run identification number, sample code, and the electrometer settings are for the operator's convenience and are also stored for possible readout on the punched tape if further calculations are to be carried out on the data. The sampling rate is stored for use in converting the peak areas from millivolts to the more precise form of millivolt-seconds. The thresholds are for rejection of the baseline data and refer to millivolts or microvolts depending on the electrometer settings. The number of points to start integration refer to the number of consecutive data points which have to be above the established threshold before a peak is defined as having started. The reason for a second number for cutting off the integration is because of the tailing which is found with many chromatographic peaks. The number of peaks per

Figure 8. Flowchart for controlling program--CART.

```

BE WISE DIGITIZE !!!
RUN IDENTIFICATION NUMBER      57
CODE OF COMPOUND IN SAMPLE     1
VOLTAGE RANGE                   3
SAMPLING RATE                   10
ELECTROMETER RANGE              -10
ELECTROMETER ATTENUATION        1
INITIAL THRESHOLD               15
CUT OFF THRESHOLD               15
# PTS TO START INTEGRATION      3
# PTS TO STOP INTEGRATION       3
NUMBER OF SAMPLES TO BE INJECTED 20
# OF PEAKS PER SAMPLE           1
SET BUFFER LENGTHS(TOTAL PEAKS) 20
TOTAL RETENTION TIME. 4 OF PTS. 1000
TYPE IN # DATA PTS. 1240
SWITCH 0 UP FOR COMPUTER SAMPLING.
SWITCH 15 UP TO TAKE DATA.
PEAK AREAS
+0000104204
+00000005699
...
...
PEAK HEIGHTS
+04237
+03532
...
...
PEAK LOCATIONS
+0000000405
+0000000068
...
...
NUMBER OF POINTS IN PEAK
+00089
+00083
...
...
SAMPLE INJECTION TIME(PTS)
+0000000000
+0000000466
...
...
SWITCH 2 UP TO SUPPRESS DUMP, SWITCH 1 UP TO RESTART

+00016 +00025 +00036 +00053 +00077 +00111 +00155 +00213
+00296 +00336 +00504 +00640 +00817 +01015 +01240 +01491
+01763 +02052 +02352 +02655 +02954 +03224 +03590 +03731
+03985 +04076 +04172 +04233 +04287 +04194 +04106 +03979
.....
SWITCH 4 UP TO PUNCH BINARY TAPE, SWITCH 3 UP TO CONT.

```

Figure 9. Typical computer Input/Output--CART.

sample and also the total number of samples which can be handled in a single run is determined by the total number of data points per peak and the total amount of memory core available for storage. It would be possible to dump the data using a high-speed punch after a given number of runs at a cost of only a few seconds, which for most chromatographic experiments would not be an excessive price.

Capabilities of the Processing Software-RTIM.

Development of the software for determining the various quantities of interest in chromatography requires recognition of noise and time problems inherent to the system versus those sources of error which can be minimized by careful selection of the experimental conditions. In this study we chose to evaluate our software under as nearly ideal experimental conditions as possible. This was both possible and practical due to the systems that we are planning to study. The use of the digital voltmeter, an integrating type of analog-to-digital converter, provided protection from any high-frequency and 60 Hz noise in the system. For this system algorithms had to be developed for sensing the peaks, determining the peak maximum and the peak area, noise rejection, and retention time determination.

The onset of a peak was sensed by a variable counter which required that a given number of consecutive

data points be over the established threshold. The required number can be varied by the operator depending on the noise level of the baseline. The baseline normally was zero or within a few microvolts of zero. In the experiments done in this study, three points above the baseline were sufficient to accurately determine the start of a peak. The return of the signal to the baseline was determined in a similar fashion. The effect of the magnitude of the chosen threshold was studied. In a typical run with methane, an increase in the threshold value from 8 to 15 millivolts resulted in a 20% reduction in the number of points in the peak (a measure of the peak width) and only a 4.5% reduction in the area of 10,000 millivolts-sec. There is, of course, no effect on the measured peak height. In another run using a benzene-saturated nitrogen stream an increase in the threshold from 15 to 25 millivolts resulted in a 20% reduction in the peak width at the base and only a 2% reduction in the peak area of 22,500 millivolts-sec. As can be seen, the choice of the threshold would be determined only by the total signal available. There are two means of combating this apparent loss of area due to the threshold. The first approach is to improve the hardware by including autoranging of the analog-to-digital converter. This would provide significantly better resolution for integration. The second approach would be to improve the software by having the program include in the area the points used in

determining break-through of the threshold. It should be noted that the main purpose of the software in this study was to provide a means of evaluating the closed-loop system and is not meant to provide the ultimate in area determinations.

The routine used for determination of the peak maximum works on the basis of a change in slope from positive to negative. A counter which can be set from the teleprinter is used to decide the number of decreasing data points necessary to define that the maximum has been found. Under the conditions used in this work, it was found that two decreasing points past the maximum was sufficient to accurately find the maximum. The precision in the location of the peak maximum is ± 1 data point (± 100 msec at 10 points per second). This is the best that can be accomplished without resorting to the more sophisticated smoothing techniques such as those used by Savitzky and Golay (37). This routine also senses noise spikes using the same type of consecutive point algorithm as at the start of a peak along with the changing slope algorithm. Slightly different logic is necessary on the increasing and decreasing slopes. This is because on the increasing slope all of the points to be used in the noise detection are already taken by the time the noise spike is detected. On the decreasing slope, the possible noise spike is detected before enough points for comparison are taken.

The routine must wait for an additional point before deciding. It should be noted that the noise smoothing routines are closely tied together with the peak maximum algorithm and must depend on each other for information. Single point noise spikes are smoothed by simply averaging the two adjacent data points as a three point moving average. Testing of these routines required use of synthetic data, input from a standard voltage source, since the experimental noise level was extremely low.

Integration of the area under the peak was accomplished by simple addition of the data points above the established threshold (Simpson's rule). The validity of such an approach is contingent upon the rate of data acquisition versus the rate at which the signal varies. It has been found to be as accurate and precise as other area determination methods (38). In this work a rate of about 10 data points per second was found to be most useful. All calculations were done with integers for convenience. The size of the area totals was large enough to require the use of double precision arithmetic (i.e., a 32-bit word). It should be noted that since much of the work was done at a single data rate (10 per second) the areas are reported as millivolts rather than as millivolt-seconds. Tests of the system under the chosen chromatographic conditions at the three rates of 60, 10, and 1 point per second showed that there was no rate

dependence on the area between the 60 and 10 points per second, but that there was definite loss in area and peak definition at the rate of one point per second for sharp, narrow peaks.

The retention time was calculated by means of a software counter which gives the number of data points taken from injection until the peak maximum. In replicate measurements the retention time precision for the experiments reported here was ± 1 data point. The precision of this measurement is therefore limited by the rate of data acquisition since no hardware variation was found. An experimental precision of ± 1 data point corresponds to ± 16.54 milliseconds at our fastest data rate. The use of an external clock with faster data rates and data curve fitting routines could be used to improve this precision.

Control Sampling Software-CART. A control algorithm was developed for the sampling system. As it may be seen from the flowchart in Figure 8, the computer decides when to inject a new sample. Its decision is based on an estimate of the number of samples desired as set by the operator and its decision of when a sample is completely eluted. When the computer decides that a new sample is to be injected, a predetermined word is output through the GPR card to the sampling interface system to inject a new

sample. The algorithm for the computer's decision that a sample has been completely eluted will be discussed below.

In order to check the sampling algorithm a series of chromatographic experiments were carried out. These experiments will also provide a critical test of the whole system as well as checking out some of the processing software.

Precision studies involving the total system were done by repetitive sampling of a stream of methane gas diluted with nitrogen and streams of nitrogen saturated with benzene and/or cyclohexane. The dilution of the methane with the nitrogen was necessary in order to obtain a sufficiently small sample. All experiments were carried out with an isothermal column oven temperature at 100°C and a carrier gas (helium) flow rate of 25.0 cm³/min. The columns used were both 1/8 in. o.d. stainless steel. The Porapak Q column was 6 feet in length, and the Durapak (n-octane on Porasil C) column was 50 cm in length. Both columns provided baseline separation of the mixture and the second column was used only to test the variation in the peak width. Table 2 shows the type of precision which was obtained in the hardware evaluation. The data shown in this table for the benzene and cyclohexane have not been corrected for change in sample size due to slight temperature variations in the saturator. The retention time measurements obtained in these experiments are given

Table 2. Precision Studies of P

	Number Samples	Forward Loop Average mv	Standard Deviation mv	Rel. Stan Dev. (%)
Methane*				
Area	15	99506	± 1651.33	1.66
Peak Height	15	4067	± 68.48	1.68
Benzene ⁺				
Area	5	256575	± 328.18	0.13
Peak Height	5	4761	± 4.98	0.10
Cyclohexane ⁺				
Area	10	265123	± 856.17	0.32
Peak Height	10	8428	± 20.88	0.25
Mixture ⁺ 50% v/v Benzene-Cyclohexane				
First Peak (Cyclohexane)				
Area	10	144561	± 720.36	0.50
Peak Height	10	4688	± 12.86	0.27
Second Peak (Benzene)				
Area	10	163637	± 1452.45	0.89
Peak Height	10	3062	± 10.71	0.35

*Varian electrometer used. The Keithley electrometer
others.

⁺No correction for change in sample size due to temper

Precision Studies of Peak Areas and Height

Standard Deviation mv	Rel. Stan. Dev. (%)	Number Samples	Back Loop Average mv	Standard Deviation mv	Rel. Stan. Dev. (%)
1651.33	1.66	15	103248	± 1795.61	1.74
68.48	1.68	15	4285	± 77.61	1.81
328.18	0.13	5	217142	± 789.52	0.36
4.98	0.10	5	4329	± 9.92	0.23
856.17	0.32	10	220838	± 500.69	0.23
20.88	0.25	10	7651	± 20.72	0.27
720.36	0.50	11	122710	± 811.54	0.66
12.86	0.27	11	4251	± 14.03	0.33
1452.45	0.89	11	139528	± 785.11	0.56
10.71	0.35	11	2785	± 8.27	0.30

Keithley electrometer with higher output voltage was used on all

the size due to temperature change in saturator was made.

in Table 3. The precision in every case was ± 1 data point, which at the sampling rate used, would correspond to ± 100 milliseconds.

Table 3. Retention Time Precision

	Retention Time Data Points	Time (sec)
Methane*	399 ± 1	42.5
Ethane*	995 ± 1	106.0
Propane*	2957 ± 1	315.0
Benzene ⁺	579 ± 1	61.7
Cyclohexane ⁺	317 ± 1	33.8
Cyclohexene ⁺	442 ± 1	47.1

*Porapak Q column.

⁺Durapak (n-octane on Porasil C) column.

The exponential dilution flask was used for another series of experiments designed to evaluate the detector and electrometers as well as to test portions of the software. A plot of the log of the measured peak areas and heights versus the time of injection, of which the sample concentration is a function, is shown in Figure 10. These curves represent a 100-fold change in concentration with the

Figure 10. Typical detector response curve obtained with closed-loop configuration.

Exponential dilution flask was used for sampling; upper trace in each set is the back loop on gas sampling valve; lower trace in each set is the forward loop on gas sampling valve; time scale for plotted points corresponds to an absolute concentration of 1.29×10^{-7} g to 5.25×10^{-9} g.

Figure 10. Typical detector response curve obtained with closed-loop configuration.

smallest concentration being approximately 1 nanogram. At the lower concentration the area determination is seen to be affected by the noise rejection threshold since the threshold is a significant portion of the total signal. The peak height of course is not affected by this arbitrary threshold. It should be remembered that the lower limit for a given system is a function of the chromatographic signal rather than any limitation on the part of the computer system. The use of signal autoranging on the analog-to-digital converter would provide a greater sample concentration range. The dual curves shown in Figure 10 for both the area and the peak heights are due to the fact that the loops on the sampling valve are not perfectly matched. There is approximately 3.5% difference in the two loops.

An experiment using ethane contaminated with about 0.5% of propane proved useful in testing the sample injection decision software routines. The ethane sample is injected into the dilution flask and the large difference in the relative concentrations of the ethane and propane causes the propane peak to fall below the established threshold while the ethane peak is still quite large. This causes a situation where the first samples to be taken from the effluent of the flask contain two peaks and later samples contain only a single peak. If the computer is making the decision on when to inject a new sample on the

basis of having seen two peaks, the system would be placed in an essentially endless loop. In this case, we found it necessary to provide the computer with a second choice on which to base its decision. This is accomplished by having the operator type in an estimate not only of the number of peaks per sample but also of the total retention time of all peaks in the sample expressed in data points. The computer then continues to wait for the second (or nth) peak only for a certain length of time based on the number of points taken and then proceeds to inject the next sample. This is just one example of the type of decision that the computer is capable of making when it is being operated in real time with respect to the experiment.

Second Phase Software

A simplified flowchart of the completely computer-controlled experiment for the control program CART2 is shown in Figure 11. The large block in the lower right of the flowchart is the processing routine RTIM2. These will be discussed below. A listing of CART2, RTIM2, and a brief description of the other routines used are shown in Appendices A, B, and C.

Figure 12 shows a typical sequence of input/output statements from CART2 and the computer printout of the calculated information. Many of the initial parameters and options were described earlier in the initial system.

Figure 11. Flowchart for real-time computer-controlled gas chromatograph for program CART2.

```

EXPT #? DURHEN 3
CMPD CODE? 6
VOLTAGE RANGE? AUTO
SAMPLING RATE? 10
RANGE? 9
ATTENUATION? 1
# PTS. TO BE AVERAGED(1&F)? 30
TEMPERATURE WINDOW? 50
FLOW SENSOR WINDOW? 200
INITIAL THRESHOLD? 8000
CUT OFF THRESHOLD? 8000
# PTS START INTEG? 3
# PTS STOP INTEG? 3
# TIMES TEMPERATURE TO BE INCREMENTED? 0
# SAMPLES AT EACH TEMP? 2
PEAKS/SAMPLE? 1
TOTAL PKSCBUFFER? 2
TOTAL RET TIME? 3600
101. TIME MULTIPLIED? 1
# DATA PTS AVERAGED? 1
# SAMPLES AFTER VD MIN? 3
SUPPRESS DATA DUMP(1=YES,0=NO)? 1
PUNCH BINARY TAPE(1=YES,0=NO)? 0
# DATA PTS? 1100
SWITCH 13 UP FOR VAN DEEMTER
SWITCH 14 UP TO SUPPRESS FLOW RATE CHANGE.
SWITCH 0 UP FOR CPU CONTROL.
SWITCH 15 UP TO TAKE DATA.

```

```

PEAK AREAS
+.767498E+08 +.834381E+08
PEAK HEIGHTS
+.454000E+06 +.477800E+06
RETENTION TIMES
+0000002032 +0000002033
NUMBER OF POINTS IN PEAK
+000450
+00523
SAMPLE INJECTION TIME(PTS)
+0000000063 +0000002389
PEAK START TIME
+0000001939 +0000004273
PEAK WIDTH AT 1/2 HT(150 TD)
+00154
+00156
TEMPERATURE BEFORE SAMPLE IS +.860883E+07
FLOW RATE BEFORE SAMPLE IS +.327763E+06
TEMPERATURE AFTER SAMPLE IS +.860807E+07
FLOW RATE AFTER SAMPLE IS +.327770E+06
AVERAGE RET(150 TD) +.522105E+06

```

Figure 12. Typical computer Input/Output--CART2.

The T and F points means the number of times the temperature and flow sensors are to be sampled and then averaged. The windows refer to the holding routines in CART2 so that the flow rate or temperature is stable before continuing after incrementing. All numbers which are taken from the DVM or calculated are normalized to microvolts. The number of data points to be averaged provides a software averaging routine to vary the data rates set by the DVM. So that the sample size will not be limited by the switch to the multiplexed DVM which in integer arithmetic is limited to a single voltage range, a change from integer to floating point arithmetic was necessary to utilize the full autoranging capability of the DVM. Due to limited memory and the use of floating point arithmetic (this requires two words per data point), the number of peaks and data points that can be stored is limited. This makes the capability of punching out the raw data points and calculated values on paper tape on the high speed punch a very valuable aid. Any further processing was then done at the University Computer Center.

Capabilities of the Processing Software--RTIM2.

As a reminder, development of the software for determining the various quantities of interest in chromatography requires recognition of noise problems inherent in the system versus those sources of error which can be minimized

by careful selection of the experimental conditions. It was shown before that the magnitude of the thresholds made little difference in peak areas so long as the threshold magnitude was not a significant portion of the peak height. Integration of the area under the peak was accomplished by simple addition of the data points above the established threshold. As shown before, an increase in the threshold from 15 to 25 millivolts in a benzene sample resulted in a 20% reduction in the peak area. The choice of threshold is determined by the total signal available. To combat this apparent loss of area, auto-ranging, which is now done, provides a significantly better resolution for integration. Along with this, the complete conversion to floating point arithmetic was done to take full advantage of the autoranged signal. This allowed the use of small samples without the loss of precision or peak definition. The algorithms for peak maximum sensing, peak sensing, noise rejection, and retention time used in RTIM are also used in RTIM2. Since the column oven temperature and carrier gas flow rate are being controlled in this phase, an algorithm had to be developed for determining the values of the height equivalent of the theoretical plate (HETP). This was needed so that optimized flow rates could be found or automatic van Deemter experiments could be done. To do this (variation of HETP with flow rate), the peak width at the half-height

routine searches on both sides of the peak maximum for the point nearest the half-height of the peak. Upon finding these points, it then determines the number of points between them. This is the peak width. HETP is then calculated from

$$\text{HETP} = \frac{L}{5.545 \left(\frac{X}{Y} \right)^2} \quad (\text{III-1})$$

where L is the column length, X is the retention time at the peak maximum, and Y is the peak width at the half-height.

Control Software--CART2. A new algorithm had to be developed to incorporate the control oven temperature and the carrier gas flow rate into the control algorithm described earlier for the sampling system. Column temperature and carrier gas flow rate are measured before and after a set of samples which are done at a given temperature and flow rate. Based on previously set information by the operator and on the computed values of HETP, the computer will decide whether to inject a new sample, change the flow rate, or increment the temperature.

The same decision-making routines for deciding when to inject a new sample as described earlier are used here. Upon completion of a set of samples at a given temperature and flow rate, the computer decides the next

step. Looking at the flowchart in Figure 11, it may be seen that there is a multi-faceted algorithm. The temperature may be held constant. Or, the flow rate of the carrier gas may be held constant and the temperature incremented. Or, both flow rate and column temperature may be incremented. The algorithm is set up such that after a set of samples is completed at a given temperature and flow rate, the flow rate will be incremented providing it was not to be held constant and the average HETP was smaller than the HETP on the previous set. Then a new set of samples at the same temperature will be done. This is continued until the average HETP is larger than the last set. The flow rate is then optimized, that is, the minimum is found in the van Deemter curve. At this point the computer makes another decision. If the experiment being performed is a van Deemter experiment, then the computer will continue to increment the flow rate the number of times desired after the minimum. If not, then the temperature can be incremented. The algorithm also provides the option at the end of a van Deemter experiment at a given temperature to back up the flow controller and increment the temperature and then start over at the new temperature. Proof that algorithm works can be seen as all the experiments performed in the evaluation of the adsorbents in a later chapter were done automatically using this system.

It should be noted that there are holding routines after incrementing the flow rate or the temperature to allow time for the system to stabilize. The algorithm for this uses a comparison of the average of 10 points with the last point taken. The experiment will continue when the average comes within the specified window, such as, 1% of the last point.

One of the primary purposes of the software is to provide the experimenter with capability of optimizing the flow rate of the carrier and the temperature for each chromatographic experiment. When the minimum in the HETP curve is found as described above, the flow rate is considered optimized. At this point, the temperature effects on retention volume may be done to get enthalpies of adsorption. If the van Deemter option was chosen by the operator, then the computer will continue to increment the flow rate the desired number of times after the minimum. This gives the capability of doing automatic van Deemter plots. The minimum for benzene on a 50 cm, 2 mm i.d. stainless steel Durapak (n-octane on Porasil C) column at 86°C was 7.59 ml/min. Van Deemter studies as a function of temperature will give the contributions of pore size and pore depth of the adsorbent to the diffusivity and the mass transfer term in the van Deemter equation. Enthalpies of adsorption--variation of

retention volume as a function of temperature--can be done at optimized flow rates automatically.

The temperature can be optimized by comparing the difference in retention time in a mixture until there is a significant overlap in the adjacent peaks as indicated by a change in the peak areas. This would have to be done in coordination with the flow rate. This capability would be very useful for the chemist who has many samples of the same type to do. Optimization would cut down analysis time significantly.

CHAPTER IV

CHROMATOGRAPHIC ADSORBENT EXPERIMENTS

There are two approaches to studying the separation processes using gas chromatography as a physico-chemical technique. These are a study of peak position and peak broadening. The peak position approach uses retention behavior as a function of temperature. Thermodynamic measurements can be made. Enthalpies and entropies of adsorption can be determined from the peak position. The peak broadening approach uses a dynamic approach, that is, peak shape as a function of gas velocity.

Peak Position Approach

The parameter that describes the behavior of a solute in a given chromatographic system is the retention volume (V_R). For the adsorption case, the retention volume is related to the adsorption coefficient (K) by equation (I-2). The dead volume of the system described here is 0.75 cm^3 . This does not include the column dead volume. The column dead volume (V_{CM}) is calculated from the following equation since methane, the normal air peak for flame ionization detectors, is too strongly adsorbed.

$$V_{CM} = \epsilon \pi R^2 L \quad (\text{IV-1})$$

L is the column length in centimeters, R is the internal radius of the column in centimeters, and ϵ is the interstitial porosity equal here to 0.4 (18). The total dead volume (V_M) is the sum of the two dead volumes.

K, therefore, has the units of cm^3/m^2 which corresponds to the units of the specific retention volume (V_s^T) at the column temperature. At low sample sizes and in the linear portion of the isotherm K is equal to V_s^T (24). Since a comparison of relative rather than absolute values is to be done primarily in this work, idealized standard states were chosen. The gas phase standard state of the adsorbate is defined as a partial pressure of 1 atmosphere with the adsorbate vapor behaving as an ideal gas. The adsorbed standard state is the two-dimensional perfect gas at one atmosphere as described in references (39) and (40). Therefore, the mean distance between adsorbed molecules is defined to be the same as in the three-dimensional gas phase standard state. This leads to a standard state surface concentration of $4.1 \times 10^{-9}/T$ moles/ cm^2 at the column temperature (40). This is in the region of the linear isotherm.

The enthalpy and entropy of adsorption can be considered combinations of nonspecific and specific interaction contributions (41) between the adsorbate molecules and the surface of the adsorbent. A system of classification of solid adsorbents and adsorbates is discussed by

Kiselev (42). The nonspecific interactions are due to dispersion forces. Adsorbates possessing either sigma bonds (no locally concentrated electron density on the molecular peripheries such as hydrocarbons) or spherically symmetrical electron shells (such as the noble gases) interact with the adsorbent by this process. Specific interaction requires molecules having isolated sites, individual bonds, or a system of bonds of high electron density. Molecules with π -electron systems, lone electron pairs, and related functional groups interact specifically in addition to nonspecific interactions. A summary of the classification of Kiselev is given in Table 4 (42).

The porous adsorbent can be considered to be a grain that is criss-crossed with pores. The grain may be assumed to be spherical for simplicity. A simplified schematic of part of a surface may be seen in Figure 13. Most of the surface available to adsorbates is found in the pores. For adsorption to occur the molecule must diffuse out of the mainstream and into the pores. Specific interaction sites of adsorbents such as silica with its acidic OH groups are represented by the raised lines on the surface in Figure 13. An adsorbate may interact nonspecifically with the surface by dispersion interaction forces. This interaction may be at any place along the surface. If the adsorbate has the functional groups present that can adsorb specifically, then the molecule

Table 4. Classification of Adsorbents and Adsorbates According to Their Interactions

Adsorbent type	Adsorbate Group			
	A. Spherically symmetric shells or σ bonds	B. Electron density locally concentrated on the peripheries of bonds or links: π bonds and lone pair electrons	C. Positive charges locally concentrated on the peripheries of links (some organometallic compounds)	D. Functional groups having both electron density and a positive charge concentrated on the peripheries of adjacent links (OH and NH)
I. No ions or active groups on the surface	Nonspecific interactions due mainly to dispersion forces			
II. Locally concentrated positive charges (acid hydroxyl small-radius cations)	Nonspecific interactions	Nonspecific plus specific interactions		

Table 4.--Continued

III. Locally concentrated negative charges (ether, nitrite, other group B, small- radius ex- change anions)			Nonspecific interactions	Nonspecific plus specific interactions
--	--	--	-----------------------------	--

Taken from Kiselev (42, p. 122).

Figure 13. Simplified schematic of the surface of an adsorbent.

may be selectively adsorbed at one of the specific sites. If a molecule is adsorbed specifically at the entrance of a pore, the pore is essentially blocked and no other adsorbates can get past as long as the molecule is there. The size of the pore opening may also result in exclusion of adsorbates. The opening may be large enough to let in a small molecule such as N_2 but a larger one such as benzene may be excluded. This is the sieving mechanism. The inkbottle pores are unavailable to many adsorbates. Pore size and depth, surface area available, type of interaction, the kinetics of adsorption-desorption are all important parameters when studying the mechanisms at the surface.

Trends and contributions from the two types of interactions can be evaluated from the enthalpies and entropies of adsorption. The enthalpy of adsorption can be determined from equation (I-7) which is the variation of retention volume (peak position) with temperature. The free energy change (ΔG_o) can be determined from equation (I-6). The entropy of adsorption (ΔS_o) can be calculated then from equation (I-8).

Peak Broadening Approach

The narrow band of sample injected into the column is broadened by numerous effects. Some of these are surface area, pore size, particle size, multiple paths,

diffusion in the gas phase, kinetics of adsorption-desorption, and mass transportation effects. All of these column inefficiencies have been related to a term called HETP as discussed in Chapter I. The value of HETP is calculated from equation (III-1). HETP was related by van Deemter et al. (25) to the rate equation described earlier in equation (I-16).

The variation in retention behavior and HETP with flow rate of the carrier gas and with temperature will give an insight to the contribution of the pores to either exclusion from or increased diffusion into the pores. Changes in HETP are a complicated function of temperature since the many factors that influence plate height change differently with temperature (43). Normally, on adsorption columns HETP decreases as temperature is increased. The van Deemter curve becomes flatter, and its minimum shifts to a higher flow rate (42-44). These are due to the lessening of K at higher temperatures and an increase in the rate of desorption in the adsorption-desorption kinetics. This makes the C term of the van Deemter equation (equation I-16) smaller.

Kiselev (42) has shown that the HETP increased as pore radius was decreased as constant radius pores were made deeper in silica gels. Altenau and Rogers (45) observed increases in HETP in the mass-transfer-limited region using inorganic salts as adsorbants when the

temperature was increased. They suggested that the anomalous behavior might in part be due to an increased rate of diffusion of the molecules at the higher temperatures into finer pores, which contained higher energy adsorption sites. More surface and adsorption sites are available and the increased diffusion and kinetics would tend to broaden the band and decrease efficiency. Keibal et al. (46) obtained similar results on zeolites. Oberholtzer and Rogers (47) also observed increases in HETP with temperature on zeolites for certain compounds. They showed that this can be attributed to a kinetic effect due to either slow kinetics of adsorption or slow intraparticle diffusion into the small opening pores of the sieve.

The peak broadening can also be approached through Grubner's theory (27). As described in Chapter I, the peak shape can be described by the statistical moments. These moments can be related to the column effects enumerated above. A term similar to HETP is related to μ_2 and μ_1 by

$$\text{HETP} = \frac{L}{\left(\frac{\mu_1^2}{\mu_2} \right)} \quad (\text{IV-2})$$

The same studies as described above can be done using this theory.

Chemicals

To get a varying degree of strength of adsorption and molecular size and configuration, the following compounds will be used: benzene, cyclohexene, cyclohexane, n-hexane. Benzene and cyclohexene are type B adsorbates having π bonds. They can show nonspecific interactions. They will interact specifically with a specific adsorbent since they have high electron density on the peripheries of the π bonds. Cyclohexane and n-hexane are type A adsorbates. They can show only nonspecific interactions. N-hexane will apparently have the smallest cross-sectional area. However, cyclohexane may be equally small due to its chair and boat conformations. Size will play an important part for looking at the effect of pore size in the peak broadening effects. Methylcyclohexane will also be used if the results on a given adsorbent warrant it. The size effect is important here as the methyl group will make it somewhat larger than cyclohexane.

Column Adsorbents

The adsorbents to be characterized are Porasil C, Durapak (n-octane on Porasil C), Porapak Q, and Molecular Sieve 5A. All columns used were 1/8 inch o.d. stainless steel ranging in length from 3 cm to 50 cm. All were carefully packed to minimize column dead volume.

Porasil C

Porasil C (Waters Associates, Inc., Framingham, Mass.) is a porous glass bead adsorbent that is quite uniform. It has a N_2 surface area of $50 \text{ m}^2/\text{g}$ (48) and a mean pore size of $200\text{-}400 \text{ \AA}$ (48). The particle size used here was 80-100 mesh.

Durapak (n-Octane on Porasil C)

Durapak (n-octane on Porasil C) (Waters) is a porous glass bead (Porasil C) on which n-octane has been bonded onto the surface of the glass. This results in a deactivation of some of the strongly adsorbing surface OH groups, thereby cutting down on the tailing of the sample peaks. The surface area is about $50 \text{ m}^2/\text{g}$. Particle size is 120-150 mesh.

Porapak Q

Porapak Q (Waters) is a porous polymer bead composed of polystyrene cross-linked with divinyl benzene. It has a very high N_2 surface area of $660 \text{ m}^2/\text{g}$ (49). Particle size used here was 100-120 mesh.

Molecular Sieve 5A

Molecular Sieve 5A (Linde, Union Carbide, New York) is a synthetic calcium zeolite having $5 \text{ \AA}$ pore openings into the inner cage surfaces. This inner and outer surface gives it sieving capability based on molecular size. The

surface area is $10 \text{ m}^2/\text{g}$ (47). Particle size used here was 30-60 mesh.

Adsorbent Interactions

All of these packings have adsorption as the primary retarding factor. Porasil C, Durapak, and Molecular Sieve 5A are all adsorbents of type II. They can interact specifically with adsorbates of the B and D groups. Porapak Q should be a type I adsorbent. Porasil C should show adsorption primarily with the possibility of sieving occurring if there is some diffusion into the finer pores. Molecular Sieve 5A also will show sieving besides the known adsorption if the compounds studied are small enough to go through the holes. Possibly there may be other effects on the Durapak and Porapak Q. The Durapak adsorbent provides for a possible interesting effect. The n-octane has been bonded to some of the surface OH groups on silica Porasil C. Ether linkages are formed. These octanes on the surface could lead to one or more possible effects. At certain temperatures the octane on the Durapak surface may act as a bonded liquid phase. If so, this added possibility of partitioning should modify the basic adsorption characteristics to act more like gas-liquid chromatography. Halasz and Sebastian (50) describe this adsorbent as a "brush" adsorbent. They indicate that the bonded liquid stands up like a bristle on a brush. This possibly can

affect the strength of adsorption by holding the adsorbate further from the surface. These brushes may exclude the adsorbate from some of the narrower pores which are blocked by the brushes. The brushes may also retard the diffusion of the adsorbate molecules in the pores. Porapak Q with its uniform pore distribution and few high energy adsorption sites offers an excellent situation for looking possibly at all three retardation mechanisms. In addition to adsorption, sieving might occur since the pore sizes are smaller than many other adsorbents. Possibly partitioning might occur as some adsorbates may dissolve in the bead or at higher temperatures the surface of the bead may soften. There is some evidence from some surface area studies with benzene (51) that partitioning does occur.

Experiments

Using each of the above compounds the following set of experiments for characterization will be performed on each support. Retention data will be obtained both as a function of the temperature of the column oven and as a function of the flow rate of the carrier gas. The variation in retention as a function of temperature will be used to calculate the thermodynamic quantities (change in free energy, enthalpy, and entropy) which describe the process (or processes) occurring in the column. The retention data obtained as a function of the carrier gas flow rate will

not only provide the optimum flow rate for the studies to be carried out, but will also provide a good handle for interpreting the role played by exclusion from the pores. The computer-controlled system allows these van Deemter plots to be done automatically and as a function also of temperature. This temperature effect will give the effect of the pores on the column efficiency (HETP).

CHAPTER V

CHROMATOGRAPHIC ADSORBENT CHARACTERIZATION

The experimental results for the adsorbent characterization and relating of the variations of peak position and peak broadening to the separation processes will be discussed. Each adsorbent will be discussed separately.

Porasil C

Porasil C is a porous silica adsorbent. Its retarding factors should show adsorption and possibly sieving. The adsorption interactions should show the general nonspecific dispersion interactions plus specific interactions of the SiOH with molecules of class B and D. In Figure 14, it may be seen that the retention variations with temperature are linear. There appear to be no apparent dual mechanism trends here. Table 5 summarizes the differential thermodynamic parameters for the four test compounds. The temperature range for which they are determined is also given. The differential functions are relative to n-hexane. Table 6 gives the free energy relationships at two temperatures. Cyclohexane and n-hexane are subject to nonspecific interactions. Cyclohexene and benzene can interact specifically since they have π -bonds. Therefore they will be "adsorbed" more strongly since

Figure 14. Plot of $\ln K$ vs. $1/T$ for the test adsorbates on Porasil C.

Table 5. Differential Enthalpies and Entropies of Adsorption on Porasil C

$\Delta\Delta$ functions are relative to n-hexane					
Compound	ΔH_o (Kcal/mole)	$\Delta\Delta H_o$	ΔS_o (e.u.)	$\Delta\Delta S_o$	Temperature range (°C)
n-hexane	-6.24	0	-20.7	0	59-58
Cyclohexane	-6.04	+0.20	-18.2	+2.5	58-97
Cyclohexene	-7.71	-1.47	-22.6	-1.9	70-111
Benzene	-8.69	-2.45	-23.6	-2.9	70-111

Table 6. Differential Free Energies of Adsorption and Adsorption Coefficients on Porasil C

Compound	ΔG_o (Kcal/mole)	$\Delta\Delta G_o$	K (cm ³ /m ²)
<u>70.7°C</u>			
n-hexane	0.92	0	0.267
Cyclohexane	0.20	-0.72	0.759
Cyclohexene	0.064	-0.856	0.886
Benzene	-0.56	-1.48	2.260
<u>97.5°C</u>			
n-hexane	1.46	0	0.136
Cyclohexane	0.68	-0.78	0.390
Cyclohexene	0.66	-0.80	0.410
Benzene	0.092	-1.368	0.876

Porasil C has many high energy surface adsorption sites (SiOH). Therefore, for a normal adsorption column, the $\Delta\Delta H$ and $\Delta\Delta S$ values should be larger for benzene and cyclohexene than for cyclohexane and n-hexane. They are more strongly adsorbed due to the specific interactions. This is the situation with Porasil C. Benzene and cyclohexene do have a greater enthalpy of adsorption and have a greater loss of entropy than cyclohexane and n-hexane. The order of cyclohexane and n-hexane in ΔH can be explained by considering that cyclohexane is not planar and can bring only 4 carbons to the same closeness of surface while n-hexane can bring all six (41). The fact that cyclohexane is retained longer than n-hexane is not indicated by the enthalpies even though the enthalpy data are often interpreted in terms of adsorption strength. The factor producing the greatest difference in the adsorption free energy, and thus the strength of adsorption, is the entropy term. According to Brookman and Sawyer (52) this is because the normal alkane undergoes a larger entropy change upon adsorption. The linear alkanes have greater vapor phase entropies than the cyclic alkanes and thereby lose more entropy on going to essentially equivalent adsorbed states. The resulting K for the cyclic alkane is larger and it is retained longer.

The van Deemter plots for the four test compounds are shown in Figures 15 through 18. Included are both the

Figure 15. Effect of temperature and flow rate on column efficiency for benzene on Porasil C.

Figure 16. Effect of temperature and flow rate on column efficiency for cyclohexene on Porasil C.

Figure 17. Effect of temperature and flow rate on column efficiency for cyclohexane on Porasil C.

Figure 18. Effect of temperature and flow rate on column efficiency for n-hexane on Porasil C.

variation of retention with flow rate and column efficiency with temperature. The curves in general are quite flat, that is, small B and C coefficients in the van Deemter equation. The C coefficients are small as expected since Porasil C has no liquid phase mass transportation problem. The HETP minimum gets lower with increasing temperature. This is expected for adsorption as the K becomes smaller at higher temperatures. Since K enters into the C term of the van Deemter equation, then as K gets smaller, the minimum gets lower and the curve broadens. The B term is smaller since the carrier gas is N_2 and diffusion in a higher molecular weight gas is smaller. In general, Porasil C may be described as a normal adsorption support with little evidence for other mechanisms.

Durapak (n-Octane on Porasil C)

Durapak (n-octane) is Porasil C on which n-octane has been bonded to some of the surface OH groups. This reduces some of the surface specific activity. This should also produce a partial covering on the surface making the adsorbent more like a type III classification where a dense monolayer is deposited on the surface. The enthalpy of adsorption should be lowered. This quasi-liquid phase possibly may cause other effects such as sieving or partitioning.

In Figure 19 it may be seen that the retention variations with temperature are linear. This suggests the absence of a dual mechanism. Table 7 summarizes the differential thermodynamic parameters for the four test compounds. A fifth test compound, methylcyclohexane, was added specifically for checking the results described below for the peak broadening. The differential functions are relative to n-hexane. The temperature range for which they are determined is also given. Table 8 gives the free energy relationships at two temperatures. The $\Delta\Delta H$ and $\Delta\Delta S$ trends are similar to that of Porasil C but the changes have been reduced in magnitude. This is because reducing of the surface activity by the reaction with octane to form ether linkages with SiOH has lowered the specific interactions. There has been an increase in the nonspecific interactions shown by the ΔH of n-hexane and cyclohexane. This increase in nonspecific interactions has resulted in larger entropy terms but lessened the differences in entropy relative to hexane. The reduction in entropy difference between hexane and cyclohexane is sufficient to change the retention behavior observed on Porasil C. Hexane is now eluted before cyclohexane. Methylcyclohexane is intermediate in behavior between cyclohexane and cyclohexene even though its boiling point is considerably higher. Evidently the entropy loss for methylcyclohexane is not as large as the others. The enthalpy increase is

Figure 19. Plot of $\ln K$ vs. $1/T$ for the test adsorbates on Durapak (n-octane on Porasil C).

Table 7. Differential Enthalpies and Entropies of Adsorption on Durapak (n-Octane)

$\Delta\Delta$ functions are relative to n-hexane

Compound	ΔH_o (Kcal/mole)	$\Delta\Delta H_o$	ΔS_o (e.u.)	$\Delta\Delta S_o$	Temperature range (°C)
n-hexane	-6.35	0	-21.1	0	72-127
Cyclohexene	-5.86	+0.49	-19.5	+1.6	70-111
Methyl- cyclohexane	-7.21	-0.86	-22.3	-1.2	57-111
Cyclohexene	-7.64	-1.29	-23.4	-2.3	58-98
Benzene	-8.04	-1.69	-23.8	-2.7	69-124

Table 8. Differential Free Energies of Adsorption and Adsorption Coefficients on Durapak (n-Octane)

Compound	ΔG_o (Kcal/mole)	$\Delta\Delta G_o$	K (cm ³ /m ²)
<u>71°C</u>			
n-hexane	0.90	0	0.256
Cyclohexane	0.80	-0.10	0.311
Methyl- cyclohexane	0.44	-0.46	0.522
Cyclohexene	0.42	-0.48	0.548
Benzene	0.21	-0.69	0.740
<u>98°C</u>			
n-hexane	1.47	0	0.138
Cyclohexane	1.34	-0.13	0.159
Methyl- cyclohexane	1.08	-0.39	0.224
Cyclohexene	1.04	-0.43	0.244
Benzene	0.86	-0.61	0.294

is due to more carbon and more CH bonds. Combining the enthalpy and entropy changes makes methylcyclohexane's retention behavior almost the same as cyclohexene's.

The van Deemter plots and the variation of HETP with temperature for the test compounds are shown in Figures 20 to 23. Methylcyclohexane was added to the test compounds for checking the results obtained for cyclohexane and n-hexane. Benzene was not plotted as its curves were very flat and close together. No definite trends can be seen for benzene's behavior except that it is similar to that on Porasil C. The interactions with benzene and cyclohexene are still specific enough so that the normal adsorption behavior is predominate. Cyclohexene also acted similar to that on Porasil C. HETP decreased with increasing temperature as the K's decreased making the C term smaller. The minimums on Durapak for all tend to be lower than on Porasil C since the K's are smaller on Durapak than on Porasil C. The retention volume for benzene did not change with flow rate. There is a slight increase in retention volume with increasing flow rate for all others except the first two temperatures for cyclohexene. The only explanation that might be possible is that with increasing flow rate there is diffusion further into the pores and more surface area is seen by the molecules. This is born out by the effect of temperature on HETP with cyclohexane, methylcyclohexane, and n-hexane, the compounds

Figure 20. Effect of temperature and flow rate on column efficiency for cyclohexene on Durapak (n-octane on Porasil C).

Figure 21. Effect of temperature and flow rate on column efficiency for methylcyclohexane on Durapak (n-octane on Porasil C).

Figure 22. Effect of temperature and flow rate on column efficiency for cyclohexane on Durapak (n-octane on Porasil C).

Figure 23. Effect of temperature and flow rate on column efficiency for n-hexane on Durapak (n-octane on Porasil C).

with nonspecific interactions. HETP increased with increasing temperature. This can be attributed to a pore or kinetic (slow diffusion) effect (47). At the lower temperature, the brushes (the octane molecules) may be lying down more and acting as a quasi-liquid phase. This is evidenced by the sharpening of the curves as observed in Figures 22 and 23 for cyclohexane and n-hexane. At the higher temperatures the brushes may stand up more and the support acts more as an adsorption support with reduced activity (less closeness of approach). The lessening of the mass transfer term (linear portion) may be observed in Figures 22 and 23 at the higher temperatures. The same type of reasoning may be used to explain the sharpening of the curves for cyclohexene. In Figure 20 at the lower temperatures the curves have the appearance of ordinary adsorption behavior as the cyclohexene can get close enough to the surface for the specific interactions to be effective. At the higher temperatures there appears to be an increase in the diffusion and mass transfer terms. The B and C terms are larger. Possibly as the brushes stand up the cyclohexene cannot come as close to the surface for the specific interactions, but the increased interactions with the brushes (nonspecific) gives it an intermediate character but not sufficient to reverse the HETP trend as with cyclohexane. This interaction with the brushes may slow down the adsorption-desorption kinetics increasing the C

term. The slight increase in retention volume with flow rate at the higher temperatures would tend to support this.

The Durapak column support is still an adsorption support, but with reduced activity. The thermodynamic parameters do not indicate that there are two mechanisms acting such as partitioning in addition to adsorption. However, the HETP effects show that with molecules exhibiting nonspecific interactions only there is a pore or slow diffusion effect that reverses the normal trend of HETP with increasing temperature.

Porapak Q

Porapak Q is a porous polymer adsorbent which presents a very homogeneous surface to the adsorbates. If there are no specific interaction sites present, then the homogeneous adsorbent should show nonspecific adsorption properties. The enthalpy of adsorption should be higher. The adsorption is not restricted to specific sites. This allows the adsorbate molecules to approach each other more closely so that adsorbate-adsorbate interactions also may occur. Therefore, the enthalpy will increase over that of specific site adsorbents. There may be sieving due to its great surface area and uniform, but relatively small pore size. Also, there could be partitioning as the adsorbate may dissolve in the bead.

In Figure 24 it may be seen that the retention variations with temperature are linear. There appears to be no apparent dual mechanism trends observable from the enthalpy data. Table 9 summarizes the differential thermodynamic parameters for the four test compounds. The differential functions are relative to n-hexane. The temperature range for which they are determined is also given. Table 10 gives the free energy relationships at two temperatures. The lack of differentiation between the four compounds was unpredicted. Looking at the $\Delta\Delta G$'s the relative differences are about 25% of the absolute value. The column length here was 3 cm. Therefore, this means that the free energy and entropy differences are quite large relatively and using a longer column would make the compounds easily distinguishable.

Waters Associates, the manufacturers of Porapak Q, claim that the Porapaks have no OH adsorption sites and that the pore size is very uniform (53). If this is so, then Porapak Q is a nonspecific adsorbent like graphitized carbon. This would account for cyclohexene and benzene not having larger enthalpies than cyclohexane and n-hexane since there are no specific interactions and there are fewer C-H bonds for nonspecific interactions. According to Kiselev (42) the enthalpies and entropies determined for graphitized carbon black which is a nonspecific adsorbent are in the same range as those determined here for Porapak

Figure 24. Plot of $\ln K$ vs. $1/T$ for the test adsorbates on Porapak Q.

Table 9. Differential Enthalpies and Entropies of Adsorption on Porapak Q

$\Delta\Delta$ functions are relative to n-hexane					
Compound	ΔH_o (Kcal/mole)	$\Delta\Delta H_o$	ΔS_o (e.u.)	$\Delta\Delta S_o$	Temperature range (°C)
n-hexane	-12.06	0	-31.8	0	97-135
Cyclohexane	-12.14	-0.08	-31.7	+0.1	97-136
Cyclohexene	-11.68	+0.38	-30.4	+1.4	98-138
Benzene	-11.94	+0.12	-31.6	+0.2	98-136

Table 10. Differential Free Energies of Adsorption and Adsorption Coefficients on Porapak Q

Compound	ΔG_o (Kcal/mole)	$\Delta\Delta G_o$	K (cm ³ /m ²)
<u>98°C</u>			
n-hexane	-0.28	0	1.489
Cyclohexane	-0.38	-0.10	1.650
Cyclohexene	-0.38	-0.10	1.666
Benzene	-0.21	+0.07	1.378
<u>136.5°C</u>			
n-hexane	0.93	0	0.319
Cyclohexane	0.85	-0.08	0.348
Cyclohexene	0.83	-0.10	0.363
Benzene	0.99	+0.06	0.303

Q. This similarity would also indicate that partitioning is not occurring.

The van Deemter plots and the variation of HETP with temperature for the test compounds are shown in Figures 25 to 28. The general trend is that Porapak Q is a normal adsorption support. The HETP's at the minimum get smaller with high temperature which is the normal adsorption effect. However, the curves do not get as broadened as would be expected for an adsorbent. The mass transfer term tends to be larger than normal for an adsorbent. The K's for the test compounds are considerably higher on Porapak Q than on Porasil C. This should increase the C term making the van Deemter curves sharper as seen in Figures 25 to 28. There is considerable intermediate behavior (the crossing of the curves) as described by Oberholtzer and Rogers (47) indicating that a pore or kinetic effect is operating in some regions. The evidence indicates that Porapak Q is a nonspecific adsorbent. The peak position data indicate that no other mechanism is in effect. However, it appears from the band broadening data that there may be some sort of pore effect or slow kinetic effect in operation part of the time.

Molecular Sieve 5A

Molecular Sieve 5A is a synthetic zeolite in which the exchange cation is calcium. The pore openings are

Figure 25. Effect of temperature and flow rate on column efficiency for benzene on Porapak Q.

Figure 26. Effect of temperature and flow rate on column efficiency for cyclohexene on Porapak Q.

Figure 27. Effect of temperature and flow rate on column efficiency for cyclohexane on Porapak Q.

Figure 28. Effect of temperature and flow rate on column efficiency for n-hexane on Porapak Q.

about 5 Å. Molecular Sieve 5A should show both adsorption and sieving. With the test compounds used here all should be excluded except n-hexane. The adsorption is of type II where there should be specific interactions possible. The strength of adsorption should be larger than Porasil C as the concentration of oxygens on the surface is quite high. Table 11 summarizes the differential thermodynamic parameters for three of the test compounds. N-hexane is not shown as it is not excluded from the pores and has an excessive retention time even at temperatures above 200°C which is beyond the measuring limits of the temperature module used here. The differential functions are relative to cyclohexane. The temperature range for which they are determined is also given. The free energy relationships are given in Table 12. No comparisons for $\Delta\Delta G$ can be made as there is no temperature common to all three compounds. It should be noted that the K's are much larger here than on the other adsorbents. In Figure 29, it may be seen that the retention variations with temperature are of questionable linearity. Even with the uncertainty of only three temperatures for benzene, the retention data would support a dual mechanism as the retention times and peak widths remain static or increase at the higher flow rates. All three molecules should be excluded from the molecular sieve's inner volume as their cross-sectional areas are all larger than 5 Å. It appears, however, that at least with

Table 11. Differential Enthalpies and Entropies of Adsorption on Molecular Sieve 5A

$\Delta\Delta$ functions are relative to cyclohexane					
Compound	ΔH_o (Kcal/mole)	$\Delta\Delta H_o$	ΔS_o (e.u.)	$\Delta\Delta S_o$	Temperature range (°C)
Cyclohexane	-11.10	0	-29.5	0	70-111
Cyclohexene	-16.54	-5.44	-38.8	-9.3	111-152
Benzene	-29.06	-17.96	-61.4	-31.9	167-194

Table 12. Differential Free Energies of Adsorption and Adsorption Coefficients on Molecular Sieve 5A

Compound	ΔG_o (Kcal/mole)	K (cm ³ /m ²)	Temperature (°C)
Cyclohexane	-0.995	4.306	70.0
Cyclohexene	-1.740	9.794	110.7
Benzene	-1.834	8.109	167.8
Cyclohexane	0.189	0.780	110.7
Cyclohexene	-0.131	1.168	151.8
Benzene	-0.252	1.311	194.3

Figure 29. Plot of $\ln K$ vs. $1/T$ for the test adsorbates on Molecular Sieve 5A.

benzene that it gains sufficient energy for further penetration into the pores which would account for the "change" in slope. Molecular Sieve 5A as an adsorption support shows very strong specific interactions as evidenced the enthalpies and entropies.

The van Deemter plots and the variation of HETP with temperature are shown in Figures 30 to 32. The curves are normal in appearance for an adsorption support, that is, HETP decreases with increasing temperature except for benzene. The mass transfer coefficient is quite large. This could be expected from the large K values obtained. There appears to be a pore or kinetic effect with benzene.

Molecular Sieve 5A is very definitely an adsorption packing along with its known sieving capability. The peak broadening results do not clarify the already confused situation on the van Deemter behavior of solutes on Molecular Sieve 5A (47).

Statistical Moments

The statistical moments were determined for all of the compounds on each of the column supports. HETP values were calculated from the moments by equation (IV-2). The peak mean generally occurred after the peak maximum since the peaks usually had tails. The minima in the van Deemter curves generally were at a much slower flow rate than those determined from the peak width method using the peak height

Figure 30. Effect of temperature and flow rate on column efficiency for benzene on Molecular Sieve 5A.

Figure 31. Effect of temperature and flow rate on column efficiency for cyclohexene on Molecular Sieve 5A.

Figure 32. Effect of temperature and flow rate on column efficiency for cyclohexane on Molecular Sieve 5A.

maximum retention time. Except for the quite symmetrical peaks on Porapak Q, the HETP values determined by the statistical moments were considerably larger than the half-height method. This is probably due to the tailing on the peaks as most of the peaks were skewed. The statistical moment method weights heavily the contributions from the peak tail. The Martin and Synge approach (23) for calculation of HETP could be used without concern about the tailing. The reason is that the HETP is calculated using the peak width at the half-height where the tail is of no concern. The meaning of the differences in the HETP curve shapes is not clear. This approach appears to be good only for symmetrical peaks. Only then could the data be used to evaluate some of the column inefficiency effects.

CHAPTER VI

CONCLUSIONS

From the adsorbent studies it may be seen that Porasil C is a normal adsorption support of Type II according to Kiselev's classification (42). This type is one that is a specific interaction adsorbent carrying concentrated positive charges on its surfaces, such as, OH. The enthalpies and entropies of adsorption determined here are similar to the values for silica gel (54). The modification of the surface of Porasil C with n-octane (the Durapak support) to deactivate some of the surface OH's results in a support with some rather different characteristics. It is still an adsorption support of type II. The enthalpies indicate this. Also the smallness of the enthalpies difference from Porasil C also indicate that the surface is not fully deactivated. The reversal of the behavior of HETP with temperature for some of the compounds indicate that the "quasi-liquid" phase (the brushes) are either producing a pore or kinetic effect by restricting the pores a little or by changing the adsorption characteristics by restricting the closeness of approach to the surface as the brushes stand up or lie down.

Porapak Q can be classified as a nonspecific support of type I. According to Kiselev's classification (42) this makes it like graphitized carbon black. The enthalpies and entropies determined are quite similar to those of graphitized carbon black (42). The considerably larger enthalpies on Porapak Q over those on Porasil C and Durapak can be explained by an argument similar to that of graphitized carbon black. On the silica adsorbent the interactions are specific at individual sites. There are generally few adsorbate-adsorbate interactions. On the nonspecific support there is high surface homogeneity allowing adsorbate-adsorbate interactions to come into play during adsorption on the surface. This results in an increase in the enthalpy of adsorption as the surface film of adsorbate increases.

The Molecular Sieve 5A is an adsorbent of type II. It differs from the silica supports in that it is ionic in which the exchange cations are near the surface and the negative charge is spread out over a complex anion on the inner surface. It has very strong adsorbing sites. The large values of the enthalpy and entropy bear this out.

It is quite evident that the results and comparisons presented here would have been difficult to obtain without the good chromatographic system developed during this project. The digital control in real time by the computer significantly enhanced the precision of the data

taking and the sampling for better retention measurements. Furthermore, the computer-controlled chromatograph provided an excellent method for optimizing conditions, such as, flow rates, for determining the thermodynamic parameters.

Suggestions for Further Work

Additional work needs to be done on determining the effects of the quasi-liquid phase bonded to the surface of the Durapak adsorbents. Perhaps a series of increasing carbon chain lengths could be bonded to Porasil C. Then the effect of the brushes could be studied as a function of the size and coverage of the brush and also the amount of surface deactivation.

Dual mechanism studies could be done on the Porapaks. There are a whole series of them having different surface areas and interaction modifications. This could be done by the method indicated in Chapter I.

A complete characterization of the family of Porasils could be done. This would help to clarify the effect of pore size and surface area on peak position and peak broadening.

APPENDIX A

LISTING OF CONTROLLING PROGRAM CART2

```

0001          ASMR,R,R,L
0003 00000    NAM CART2
0004          EXT OUTPT,WRITE,..AD2R,AD2FN
0005          EXT KYRDR,..RTIM,..F2DC,..VMFL,..FCM
0006          EXT RDAV,FLOAT,ETIME,RTIM,..PACK
0007          EXT VLTRD,EDUMP,WDPLN,WRDP
0008*VERSION: 30 AUGUST 1970
0009*
0010*****
0011*PROGRAM PARAMETERS *
0012*****
0013 00000 000000 START NOP
0014 00001 016002X OUCH JSB WRITE EXPT IDENT. NO.
0015 00002 002341R DEF STMT4
0016 00003 000005 DEC 5
0017 00004 016005X JSB KYRDR
0018 00005 002141R DEF TDATA
0019 00006 000005 DEC 5
0020 00007 016002X JSB WRITE COMPOUND CODE NO.
0021 00010 002346R DEF STMT5
0022 00011 000006 DEC 6
0023 00012 016005X JSB KYRDR
0024 00013 002141R DEF TDATA
0025 00014 000005 DEC 5
0026 00015 016002X JSB WRITE DVM VOLTAGE RANGE
0027 00016 002354R DEF STMT6
0028 00017 000010 DEC 8
0029 00020 016005X JSB KYRDR
0030 00021 002141R DEF TDATA
0031 00022 000005 DEC 5
0032 00023 016002X JSB WRITE SAMPLING RATE
0033 00024 002364R DEF STMT7
0034 00025 000010 DEC 8
0035 00026 016005X JSB KYRDR
0036 00027 002141R DEF TDATA
0037 00030 000005 DEC 5
0038 00031 016002X JSB WRITE ELECTROMETER RANGE
0039 00032 002374R DEF STMT8
0040 00033 000004 DEC 4
0041 00034 016005X JSB KYRDR
0042 00035 002141R DEF TDATA
0043 00036 000005 DEC 5
0044 00037 016002X JSB WRITE ELECTROMETER ATTENUATION
0045 00040 002400R DEF STMT9
0046 00041 000007 DEC 7
0047 00042 016005X JSB KYRDR
0048 00043 002141R DEF TDATA
0049 00044 000005 DEC 5
0050 00045 016003X JSB .AD2R
0051 00046 002141R DEF TDATA
0052 00047 016002X JSB WRITE COLUMN LENGTH
0053 00050 003331P DEF STMT38
0054 00051 000007 DEC 7
0055 00052 016005X JSB KYRDR
0056 00053 002141R DEF TDATA
0057 00054 000005 DEC 5
0058 00055 016004X JSB AD2FN
0059 00056 002141R DEF TDATA

```

0060	00057	000001R	DEF OUCH	
0061	00060	000001R	DEF OUCH	
0062	00061	060001	LDA 1	
0063	00062	016013X	JSB FLOAT	
0064	00063	072560C	STA LNG	
0065	00064	076561C	STB LNG+1	
0066	00065	016002X	JSB WRITE	# PTS TO AVERAGE(T&F)
0067	00066	002577R	DEF STM20	
0068	00067	000017	DEC 15	
0069	00070	016005X	JSB KYRDR	
0070	00071	002141R	DEF TDATA	
0071	00072	000005	DEC 5	
0072	00073	016004X	JSB AD2FN	
0073	00074	002141R	DEF TDATA	
0074	00075	000001R	DEF OUCH	
0075	00076	000001R	DEF OUCH	
0076	00077	076205R	STB PAVER	
0077	00100	016002X	JSB WRITE	TEMPERATURE WINDOW
0078	00101	003152R	DEF STM29	
0079	00102	000013	DEC 11	
0080	00103	016005X	JSB KYRDR	
0081	00104	002141R	DEF TDATA	
0082	00105	000005	DEC 5	
0083	00106	016004X	JSB AD2FN	
0084	00107	002141R	DEF TDATA	
0085	00110	000001R	DEF OUCH	
0086	00111	000001R	DEF OUCH	
0087	00112	060001	LDA 1	
0088	00113	016013X	JSB FLOAT	
0089	00114	016023X	FDV FACT	
	00115	002265R		
0090	00116	072263R	STA WIN	
0091	00117	076264R	STB WIN+1	
0092	00120	016002X	JSB WRITE	FLOW SENSOR WINDOW
0093	00121	003165R	DEF STM30	
0094	00122	000013	DEC 11	
0095	00123	016005X	JSB KYRDR	
0096	00124	002141R	DEF TDATA	
0097	00125	000005	DEC 5	
0098	00126	016004X	JSB AD2FN	
0099	00127	002141R	DEF TDATA	
0100	00130	000001R	DEF OUCH	
0101	00131	000001R	DEF OUCH	
0102	00132	060001	LDA 1	
0103	00133	016013X	JSB FLOAT	
0104	00134	016023X	FDV FACT	
	00135	002265R		
0105	00136	072261R	STA .01	
0106	00137	076262R	STB .01+1	
0107	00140	016002X	JSB WRITE	INITIAL THRESHOLD
0108	00141	002407R	DEF STM10	
0109	00142	000012	DEC 10	
0110	00143	016005X	JSB KYRDR	
0111	00144	002141R	DEF TDATA	
0112	00145	000005	DEC 5	
0113	00146	016004X	JSB AD2FN	
0114	00147	002141R	DEF TDATA	
0115	00150	000001R	DEF OUCH	

0116	00151	000001R	DEF OUCH	
0117	00152	007004	CMB, INR	
0118	00153	000001	LDA 1	
0119	00154	016013X	JSR FLOAT	
0120	00155	072146R	STA THR1	
0121	00156	076147R	STR THR1+1	
0122	00157	016002X	JSR WRITE	CUT OFF THRESHOLD
0123	00160	002421R	DEF STM11	
0124	00161	000012	DEC 10	
0125	00162	016005X	JSR KYRDR	
0126	00163	002141R	DEF TDATA	
0127	00164	000005	DEC 5	
0128	00165	016004X	JSR AD2EN	
0129	00166	002141R	DEF TDATA	
0130	00167	000001R	DEF OUCH	
0131	00170	000001R	DEF OUCH	
0132	00171	007004	CMB, INR	
0133	00172	000001	LDA 1	
0134	00173	016013X	JSR FLOAT	
0135	00174	072150R	STA THR2	
0136	00175	076151R	STR THR2+1	
0137	00176	016002X	JSR WRITE	# PTS TO START INTEGRATION
0138	00177	002433R	DEF STM12	
0139	00200	000013	DEC 11	
0140	00201	016005X	JSR KYRDR	
0141	00202	002141R	DEF TDATA	
0142	00203	000005	DEC 5	
0143	00204	016004X	JSR AD2EN	
0144	00205	002141R	DEF TDATA	
0145	00206	000001R	DEF OUCH	
0146	00207	000001R	DEF OUCH	
0147	00210	007004	CMB, INR	
0148	00211	076322C	STR TARST	
0149	00212	016002X	JSR WRITE	# PTS TO STOP INTEGRATION
0150	00213	002446R	DEF STM13	
0151	00214	000012	DEC 10	
0152	00215	016005X	JSR KYRDR	
0153	00216	002141R	DEF TDATA	
0154	00217	000005	DEC 5	
0155	00220	016004X	JSR AD2EN	
0156	00221	002141R	DEF TDATA	
0157	00222	000001R	DEF OUCH	
0158	00223	000001R	DEF OUCH	
0159	00224	007004	CMB, INR	
0160	00225	076154R	STR LESST	
0161	00226	076153R	STR LESS	
0162	00227	016002X	JSR WRITE	# TIMES TEMP. TO BE INCREMENTED
0163	00230	002616R	DEF STM21	
0164	00231	000024	DEC 20	
0165	00232	016005X	JSR KYRDR	
0166	00233	002141R	DEF TDATA	
0167	00234	000005	DEC 5	
0168	00235	016004X	JSR AD2EN	
0169	00236	002141R	DEF TDATA	
0170	00237	000001R	DEF OUCH	
0171	00240	000001R	DEF OUCH	
0172	00241	007004	CMB, INR	
0173	00242	076206R	STR TINCR	

0174	00243	016002X	JSB WRITE	# SAMPLES AT EACH TEMP.
0175	00244	002642R	DEF STM22	
0176	00245	000015	DEC 13	
0177	00246	016005X	JSB KYRDR	
0178	00247	002141R	DEF TDATA	
0179	00250	000005	DEC 5	
0180	00251	016004X	JSB AD2EN	
0181	00252	002141R	DEF TDATA	
0182	00253	000001R	DEF OUCH	
0183	00254	000001R	DEF OUCH	
0184	00255	076252R	STB WD	
0185	00256	007004	CMB, INB	
0186	00257	076204R	STB KPTS	
0187	00260	076223R	STB KPTS.	
0188	00261	062252R	LDA WD	
0189	00262	016013X	JSB FLOAT	
0190	00263	072252R	STA WD	
0191	00264	076253R	STB WD+1	
0192	00265	016002X	JSB WRITE	# PEAKS PER SAMPLE
0193	00266	002525R	DEF STM17	
0194	00267	000010	DEC 8	
0195	00270	016005X	JSB KYRDR	
0196	00271	002141R	DEF TDATA	
0197	00272	000005	DEC 5	
0198	00273	016004X	JSB AD2EN	
0199	00274	002141R	DEF TDATA	
0200	00275	000001R	DEF OUCH	
0201	00276	000001R	DEF OUCH	
0202	00277	076224R	STB PPC	
0203	00300	007004	CMB, INB	
0204	00301	076176R	STB PCS	
0205	00302	076177R	STB PC	
0206	00303	016002X	JSB WRITE	SET BUFFER LENGTHS(TOTAL PEAKS)
0207	00304	002460R	DEF STM15	
0208	00305	000012	DEC 10	
0209	00306	016005X	JSB KYRDR	
0210	00307	002141R	DEF TDATA	
0211	00310	000005	DEC 5	
0212	00311	016004X	JSB AD2EN	
0213	00312	002141R	DEF TDATA	
0214	00313	000001R	DEF OUCH	
0215	00314	000001R	DEF OUCH	
0216	00315	076323C	STB CTR	
0217	00316	007004	CMB, INB	
0218	00317	076255R	STB CNTST	
0219	00320	016002X	JSB WRITE	TOTAL RET. TIME--# OF PTS.
0220	00321	002535R	DEF STM18	
0221	00322	000011	DEC 9	
0222	00323	016005X	JSB KYRDR	
0223	00324	002141R	DEF TDATA	
0224	00325	000005	DEC 5	
0225	00326	016004X	JSB AD2EN	
0226	00327	002141R	DEF TDATA	
0227	00330	000001R	DEF OUCH	
0228	00331	000001R	DEF OUCH	
0229	00332	076200R	STB TIM	
0230	00333	016002X	JSB WRITE	TOT RET TIME MULTIPLIER
0231	00334	003315R	DEF STM37	FOR NUMBER > SINGLE PREC.

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0232 00335 000014      DEC 12
0233 00336 016005X     JSR KYRDR
0234 00337 002141R     DEF TDATA
0235 00340 000005      DEC 5
0236 00341 016004X     JSB AD2EN
0237 00342 002141R     DEF TDATA
0238 00343 000001R     DEF OUCH
0239 00344 000001R     DEF OUCH
0240 00345 076202R     STB MUL
0241 00346 062200R     LDA TIM
0242 00347 016024X     MPY MUL
      00350 062202R
0243 00351 072200R     STA TIM
0244 00352 076201R     STB TIM+1
0245 00353 016002X     JSB WRITE #DATA PTS TO BE AVERAGED
0246 00354 003200R     DEF STM31
0247 00355 000013      DEC 11
0248 00356 016005X     JSR KYRDR
0249 00357 002141R     DEF TDATA
0250 00360 000005      DEC 5
0251 00361 016004X     JSB AD2EN
0252 00362 002141R     DEF TDATA
0253 00363 000001R     DEF OUCH
0254 00364 000001R     DEF OUCH
0255 00365 076562C     STB DAV
0256 00366 076355C     STB DAVS
0257 00367 007004      CMB, INB
0258 00370 076267R     STR NDAV
0259 00371 076270R     STB NDAVS
0260 00372 066562C     LDB DAV      SET UP CORRECTION FOR
0261 00373 056273R     CPB .3      PEAK LOCATION NECESSARY
0262 00374 026413R     JMP THREE      SINCE POINT AVERAGING USED.
0263 00375 056274R     CPB ..4      IF 1 OR 2 PTS, NO CORRECTION;
0264 00376 026422R     JMP FOUR      3, SUBTRACT 1; 4, SUBTRACT 2;
0265 00377 056275R     CPB .5      5, SUBTR. 3.
0266 00400 026432R     JMP FIVE
0267 00401 002400      CLA
0268 00402 072352C     STA RUP
0269 00403 072353C     STA RUP+1
0270 00404 056236R     CPB PLUS1      CORRECTION
0271 00405 026411R     JMP ++4      ROUTINE
0272 00406 066235R     LDB MIN1      FOR NOISE
0273 00407 076354C     STB CUP      CHECK IN
0274 00410 026441R     JMP AFT      RTIME2
0275 00411 072354C     STA CUP
0276 00412 026441R     JMP AFT
0277 00413 007400      THPEE CCP
0278 00414 076352C     STB RUP
0279 00415 076353C     STR RUP+1
0280 00416 006404      CLR, INB
0281 00417 007000      CMB      GIVES -2
0282 00420 076354C     STB CUP
0283 00421 026441R     JMP AFT
0284 00422 007400      FOUR CCP
0285 00423 076352C     STB RUP
0286 00424 046235R     ADB MIN1
0287 00425 076353C     STB RUP+1
0288 00426 066273R     LDB .3

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0289	00427	007004	CMB, INB	
0290	00430	076354C	STR CUP	
0291	00431	026441R	JMP AFT	
0292	00432	066234R	LDR MIN4	
0293	00433	006004	INP	
0294	00434	076353C	STR RUP+1	
0295	00435	007400	CCR	
0296	00436	076352C	STR FUP	
0297	00437	066234R	LDR MIN4	
0298	00440	076354C	STR CUP	
0299	00441	062562C	LDA DAV	
0300	00442	016013X	JSB FLOAT	
0301	00443	072562C	STA DAV	
0302	00444	076563C	STP DAV+1	
0303	00445	016002X	JSB WRITE	#SAMPLES AFTER MINIMUM
0304	00446	003213R	DEF STM32	IN VD CURVE
0305	00447	000015	DEC 13	
0306	00450	016005X	JSB KYRDR	
0307	00451	002141R	DEF TDATA	
0308	00452	000005	DEC 5	
0309	00453	016004X	JSB AD2FN	
0310	00454	002141R	DEF TDATA	
0311	00455	000001R	DEF OUCH	
0312	00456	000001R	DEF OUCH	
0313	00457	007004	CMB, INB	
0314	00460	076271R	STR AVD	
0315	00461	076272R	STR AVDS	
0316	00462	016002X	JSB WRITE	DATA DUMP SUPPRESS FLAG
0317	00463	002722R	DEF STM24	
0318	00464	000021	DEC 17	
0319	00465	016005X	JSB KYRDR	
0320	00466	002141R	DEF TDATA	
0321	00467	000005	DEC 5	
0322	00470	016004X	JSB AD2FN	
0323	00471	002141R	DEF TDATA	
0324	00472	000001R	DEF OUCH	
0325	00473	000001R	DEF OUCH	
0326	00474	076243R	STR DSFL	
0327	00475	016002X	JSB WRITE	PUNCH RIN TAPE FLAG
0328	00476	002743R	DEF STM25	
0329	00477	000020	DEC 16	
0330	00500	016005X	JSB KYRDR	
0331	00501	002141R	DEF TDATA	
0332	00502	000005	DEC 5	
0333	00503	016004X	JSB AD2FN	
0334	00504	002141R	DEF TDATA	
0335	00505	000001R	DEF OUCH	
0336	00506	000001R	DEF OUCH	
0337	00507	076244R	STR PMSFL	
0338	00510	016002X	JSB WRITE	# DATA PTS.
0339	00511	002332R	DEF STM13	
0340	00512	000007	DEC 7	
0341	00513	016005X	JSB KYRDR	
0342	00514	002141R	DEF TDATA	
0343	00515	000005	DEC 5	
0344	00516	016004X	JSB AD2FN	
0345	00517	002141R	DEF TDATA	
0346	00520	000001R	DEF OUCH	

0347	00521	001610R	DEF FINAL
0348	00522	076140R	STR NPTS.
0349	00523	007004	CMR, INF
0350	00524	076155R	STR NPTS
0351	00525	076251R	STR .NPTS
0352	00526	016002X	JSR WRITE
0353	00527	003230R	DEF STM33
0354	00530	000016	DEC 14
0355	00531	016002X	JSR WRITE
0356	00532	002657R	DEF STM23
0357	00533	000025	DEC 21
0358	00534	016002X	JSR WRITE
0359	00535	002472R	DEF STM16
0360	00536	000016	DEC 14
0361	00537	016002X	JSR WRITE
0362	00540	002510R	DEF STM19
0363	00541	000015	DEC 13

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0365*****
0366*INITIALIZATION *
0367*****
0368 00542 062227R L8 LDA APWD PUT LARGE VALUE IN LAST
0369 00543 066230R LDB APWD+1 AVERAGE HETP
0370 00544 072231R STA LHETP
0371 00545 076232R STB LHETP+1
0372 00546 062174R L6 LDA AS1 SET VARIOUS CNTRS OR
0373 00547 072272C STA LCTR1 ADDRESSES TO INITIAL VALUES
0374 00550 062175R LDA AS2 & CLEAR FLAGS
0375 00551 072273C STA LCTR2
0376 00552 062251R LDA .NPTS
0377 00553 072155R STA NPTS
0378 00554 002400 CLA
0379 00555 072156R STA FLAG1
0380 00556 072270C STA NFLAG
0381 00557 072271C STA LOCFL
0382 00560 072245R STA TEMPO
0383 00561 072246R STA TEMPO+1
0384 00562 062157R LDA PDA.
0385 00563 072064C STA BDAT
0386 00564 072065C STA BDT.
0387 00565 062161R LDA PL1..
0388 00566 072241C STA PKL1.
0389 00567 072240C STA .PKL1
0390 00570 062162R LDA PL2..
0391 00571 072267C STA PKL2.
0392 00572 072266C STA .PKL2
0393 00573 062163R LDA PKH.
0394 00574 072137C STA PKHT.
0395 00575 072136C STA .PKHT
0396 00576 062164R LDA PKW..
0397 00577 072351C STA PKWD.
0398 00600 072350C STA .PKWD
0399 00601 062165R LDA PKP..
0400 00602 072274C STA PKPT.
0401 00603 072275C STA .PKPT
0402 00604 062160R LDA AR..
0403 00605 072211C STA AREA.
0404 00606 072210C STA .AREA
0405 00607 062166R LDA SN1..
0406 00610 072457C STA SIN1.
0407 00611 072456C STA .SIN1
0408 00612 062167R LDA SN2..
0409 00613 072505C STA SIN2.
0410 00614 072504C STA .SIN2
0411 00615 062304R LDA PS1..
0412 00616 072403C STA PST1.
0413 00617 062305R LDA PS2..
0414 00620 072431C STA PST2.
0415 00621 062170R LDA HTP
0416 00622 072556C STA .HETP
0417 00623 072557C STA HETP.
0418 00624 062255R LDA CNTST
0419 00625 072203R STA C
0420 00626 006400 CLF
0421 00627 062456C LDA .SIN1
0422 00630 174000 STB 0,I

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0423	00631	034000	ISZ 0
0424	00632	036203R	ISZ C
0425	00633	026630R	JMP *-3
0426	00634	062255R	LDA CNTS1
0427	00635	072203R	STA C
0428	00636	062504C	LDA •SIN2
0429	00637	174000	STR 0,I
0430	00640	034000	ISZ 0
0431	00641	036203R	ISZ C
0432	00642	026637R	JMP *-3

0434*****

0435* MAIN CONTROL SECTION *

0436*****

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0437 00643 062211R LDA AELC SET MULTIPLEXER TO ELECTROMETER
0438 00644 016001X JSR OUTPT
0439 00645 103100 L5 CLF 0 RELEASE DVM TO ZERO ELECTR.
0440 00646 103716 STC 16R,C WAIT LOOP
0441 00647 102316 SFS 16R
0442 00650 026647R JMP *-1
0443 00651 106716 CLC 16R
0444 00652 103716 STC 16R,C
0445 00653 102501 LIA 1
0446 00654 002021 SSA,RSS READY TO START?
0447 00655 026645R JMP L5 NO.
0448 00656 001222 RAL,RAL YES,CHK BIT 13
0449 00657 002021 SSA,RSS VAN DEEMTER EXPERIMENT?
0450 00660 026665R JMP **5 NO,GO ON.
0451 00661 001300 RAR YES, SET FLAG & ROTATE TO BIT 14.
0452 00662 007400 CCB
0453 00663 076276R STB VD
0454 00664 026670R JMP **4
0455 00665 001300 RAR INSURE VD FLAG IS CLEAR & ROTATE BACK
0456 00666 006400 CLB TO BIT 14.
0457 00667 076276R STB VD
0458 00670 002021 SSA,RSS IS FLOW RATE SUPPRESS SET?
0459 00671 026676R JMP **5 NO, GO ON.
0460 00672 001300 RAR YES, SET FLAG & ROTATE BACK.
0461 00673 007400 CCR
0462 00674 076254R STB FRFSL
0463 00675 026701R JMP **4
0464 00676 001300 RAR INSURE FLAG IS CLEAR & ROTATE BACK
0465 00677 006400 CLB
0466 00700 076254R STB FRFSL
0467 00701 002011 SLA,RSS COMPUTER OR MANUAL CONTROL?
0468 00702 027111R JMP MAN MANUAL
0469 00703 017356R JSB RFLOW DETERMINE FLOW RATE BEFORE SAMPLES
0470 00704 072216R STA BFLR STORE BUFFER ADDRESS
0471 00705 016025X DLD BFLR,1 PUT FLOW RATE
00706 102216R
0472 00707 016026X DST BFFL IN RIGHT BUFFER
00710 002217R
0473 00711 017366R JSB RTEM DETERMINE COL. TEMP
0474 00712 072216R STA BFLR
0475 00713 016025X DLD BFLR,1
00714 102216R
0476 00715 016026X DST BITEM
00716 002221P
0477 00717 062211R LDA AELC SET MULTIPLEXER TO ELECTROMETER
0478 00720 016001X JSR OUTPT
0479 00721 016017X JSB VLTD TAKE DUMMY PT.
0480 00722 026730R JMP SAMO GO TO SAMPLING LOOP
0481 00723 036204R L3 ISZ KPTS INCREMENT # SAMPLE COUNTER
0482 00724 026726R JMP **2 INJECT NEW SAMPLE
0483 00725 027102R JMP OUT MAKE A DECISION, ALL SAMPLES TAKEN
0484 00726 036456C ISZ .SIN1 INCREMENT SAMPLE
0485 00727 036504C ISZ .SIN2 INJECTION TIME ADDRESS
0486 00730 062212R SAMO LDA DESAM INJECT SAMPLE
0487 00731 016001X JSR OUTPT

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0488	00732	000040	CLE	
0489	00733	062273C	LDA LCTR2	DETERMINE INJECTION
0490	00734	066272C	LDB LCTR1	TIME
0491	00735	042173R	ADA A2	
0492	00736	002140	SEZ,CLE	
0493	00737	006004	INB	
0494	00740	046172R	ADB A1	
0495	00741	172504C	STA .SIN2,I	
0496	00742	176456C	STH .SIN1,I	
0497	00743	000040	CLE	
0498	00744	062156R	LDA FLAG1	1ST DATA POINT?
0499	00745	002021	SSA,RSS	
0500	00746	026766R	JMP L1	YES,SKIP
0501	00747	103501	LIA 1,C	NO,MAKE SURE SWITCH15 IS UP
0502	00750	002021	SSA,RSS	
0503	00751	026747R	JMP *-2	IT'S NOT,SO HOLD.
0504	00752	002011	SLA,RSS	SEE IF CHANGE IN MAN OR CPU CONTROL
0505	00753	027111R	JMP MAN	
0506	00754	000040	CLE	
0507	00755	062273C	LDA LCTR2	INCREMENT TIMER
0508	00756	066272C	LDB LCTR1	
0509	00757	002004	INA	
0510	00760	002140	SEZ,CLE	
0511	00761	006004	INB	
0512	00762	076272C	STF LCTR1	
0513	00763	072273C	STA LCTR2	
0514	00764	006021	SSE,RSS	CHECK FOR TIMER OVERFLOW
0515	00765	102017	HLT 17R	
0516	00766	000040	CLE	CHECK
0517	00767	062273C	LDA LCTR2	
0518	00770	066272C	LDB LCTR1	RETENTION
0519	00771	042173R	ADA A2	
0520	00772	002140	SEZ,CLE	TIME(TIMER)
0521	00773	006004	INB	
0522	00774	046172R	ADB A1	OF SAMPLE
0523	00775	007100	CMB,CLE	
0524	00776	003024	CMA,INA	AGAINST
0525	00777	002040	SEZ	
0526	01000	006004	INB	EXPECTED
0527	01001	000040	CLE	
0528	01002	142504C	ADA .SIN2,I	TOTAL
0529	01003	002040	SEZ	
0530	01004	006004	INB	RETENTION
0531	01005	146456C	ADB .SIN1,I	
0532	01006	000040	CLE	TIME.
0533	01007	042200R	ADA TIM	
0534	01010	002040	SEZ	IF EXCEEDED,
0535	01011	006004	INB	
0536	01012	046201R	ADB TIM+1	
0537	01013	006020	SSE	INJECT
0538	01014	027016R	JMP *-2	NEW SAMPLE.
0539	01015	027044R	JMP L4	NOT EXCEEDED,GO ON.
0540	01016	036136C	ISZ .PKHT	INCREMENT ADDRESSES
0541	01017	036136C	ISZ .PKHT	OF UNUSED PEAK IN
0542	01020	036275C	ISZ .PKPT	SAMPLE
0543	01021	036210C	ISZ .AREA	
0544	01022	036210C	ISZ .AREA	
0545	01023	036266C	ISZ .PKL2	

0546	01024	036240C	ISZ	.PKL1	
0547	01025	036350C	ISZ	.PKWD	
0548	01026	036402C	ISZ	.PST1	
0549	01027	036430C	ISZ	.PST2	
0550	01030	036556C	ISZ	.HETP	
0551	01031	036556C	ISZ	.HETP	
0552	01032	036177R	ISZ	PC	
0553	01033	027016R	JMP	L7	
0554	01034	062176R	LDA	PCS	RESET PEAK COUNTER
0555	01035	072177R	STA	PC	AND INJECT NEW
0556	01036	062270R	LDA	NDAVS	SAMPLE; RESET COUNTERS
0557	01037	072267R	STA	NDAV	
0558	01040	062400	CLA		
0559	01041	072245R	STA	TEMPO	
0560	01042	072246R	STA	TEMPO+1	
0561	01043	026723R	JMP	L3	
0562	01044	016017X L4	JSB	VLTRD	GET DATA PT FROM DVM
0563	01045	016010X	JSE	.VMFL	CONVERT TO FLOATING PT
0564	01046	016027X	FAD	TEMPO	DATA PT. AVERAGING
	01047	002245R			
0565	01050	072245R	STA	TEMPO	ROUTINE.
0566	01051	076246R	STB	TEMPO+1	
0567	01052	036267R	ISZ	NDAV	
0568	01053	026747R	JMP	L2	
0569	01054	016023X	FDV	DAV	
	01055	004562C			
0570	01056	072212C	STA	TEMP	STORE IN TEMPORARY
0571	01057	076213C	STR	TEMP+1	LOCATION
0572	01060	002400	CLA		CLEAR SUMMING BUFFER.
0573	01061	072245R	STA	TEMPO	
0574	01062	072246R	STA	TEMPO+1	
0575	01063	062270R	LDA	NDAVS	RESET COUNTER
0576	01064	072267R	STA	NDAV	
0577	01065	062212C	LDA	TEMP	
0578	01066	016027X	FAD	THR1	CHECK IF OVER INITIAL
	01067	002146R			
0579	01070	002020	SSA		THRESHOLD
0580	01071	027151R	JMP	NFLCK	NO, GO CHECK OTHER PARAMETERS
0581	01072	062156R	LDA	FLAG1	IS THIS 1ST PT OVER THRD?
0582	01073	002020	SSA		
0583	01074	027124R	JMP	TOIN	NO
0584	01075	003400	CCA		YES, SET FLAG.
0585	01076	072156R	STA	FLAG1	AND GO TO 1ST POINT
0586	01077	036155R	ISZ	NPTS	
0587	01100	016014X	JSP	RTIME	INITIALIZATION
0588	01101	026747R	JMP	L2	GET ANOTHER PT.
0589	01102	062206R OUT	LDA	TINCR	ALL SAMPLES TAKEN AT 1 TEMP.
0590	01103	002002	SZA		IS TEMPERATURE TO BE INCREMENTED
0591	01104	027177R	JMP	DETPW	YES, DETERMINE PEAK WIDTH
0592	01105	062254R	LDA	FRSFL	NO, CHECK FLOW RATE
0593	01106	002020	SSA		CHANGE FLAG.
0594	01107	027337R	JMP	AFINL	SUPPRESS. GO TO PRINT OUT.
0595	01110	027177R	JMP	DETPW	NO, DETERMINE PEAK WIDTH
0596	01111	003040 MAN	CLE		MANUAL CONTROL
0597	01112	062273C	LDA	LCTR2	INCREMENT TIMER
0598	01113	066272C	LDR	LCTR1	
0599	01114	002004	INA		
0600	01115	022140	SEZ, CLE		

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0601 01116 0060004      INB
0602 01117 076272C      STB LCTR1
0603 01120 072273C      STA LCTR2
0604 01121 0060021      SSE,RSS
0605 01122 102013      HLT 13B
0606 01123 027044R      JMP L4      GET A DATA PT.
0607 01124 036155R TOIN  ISZ NPTS      INCREMENT POINT COUNTER
0608 01125 027127R      JMP **2      OK.
0609 01126 027144R      JMP POUT      OVERFLOWED # DATA PTS.
0610 01127 062271C      LDA LOCFL      HAS PEAK MAX. BEEN FOUND
0611 01130 0020021      SSA,RSS
0612 01131 027140R      JMP INTO      NO
0613 01132 062212C      LDA TEMP      YES, CHECK IF PT OVER
0614 01133 066213C      LDB TEMP+1    THRESHOLD 2(CUTOFF)
0615 01134 016027X      FAD THR2
      01135 002150R
0616 01136 0020020      SSA
0617 01137 027151R      JMP NFLCK      NO, CHECK COUNTERS
0618 01140 016006X INTO  JSB .RTIM      GO TO MAIN INTEGRATION, ETC. ROUTIN
0619 01141 026747R      JMP L2      GET ANOTHER PT.
0620 01142 036155R BYPAS  ISZ NPTS      INCREMENT DATA COUNTER
0621 01143 027140R      JMP INTO      ALL PTS NOT TAKEN
0622 01144 016002X POUT  JSB WRITE      OUT OF POINTS. REJECT
0623 01145 003117R      DEF STM28      REVISE ESTIMATES & START
0624 01146 000033      DEC 27      OVER.
0625 01147 102044      HLT 44B
0626 01150 026000R      JMP START
0627 01151 062270C NFLCK  LDA NFLAG      PT NOT OVER THRESHOLD
0628 01152 0020021      SSA,RSS      IS INTEGRATION FLAG SET?
0629 01153 026747R      JMP L2      NO, REJECT BASELINE
0630 01154 036153R      ISZ LESS      INCREMENT INTEG. CUTOFF COUNTER
0631 01155 027142R      JMP BYPAS      NOT YET
0632 01156 006400      CLB      CUTOFF, CLEAR INTEGRATE
0633 01157 076270C      STB NFLAG      FLAG
0634 01160 062154R      LDA LESST      RESET CUTOFF COUNTER
0635 01161 072153R      STA LESS
0636 01162 062155R      LDA NPTS      CORRECT DATA PT COUNTER
0637 01163 042322C      ADA TABST      FOR TOO MANY INCREMENTS
0638 01164 042236R      ADA PLUS1      (WHEN STARTING INTEGR.)
0639 01165 072155R      STA NPTS
0640 01166 016015X      JSB RTIM.      END OF PEAK PROCESSING
0641 01167 103501      LIA 1,C      CPU OR MAN?
0642 01170 0020011      SLA,RSS
0643 01171 027111R      JMP MAN
0644 01172 036177R      ISZ PC      ANY MORE PEAKS IN SAMPLE
0645 01173 026747R      JMP L2      YES.
0646 01174 062176R      LDA PCS      NO, RESET COUNTER
0647 01175 072177R      STA PC
0648 01176 026723R      JMP L3      NEW SAMPLE CHECK.
0649 01177 062223R DETPW  LDA KPTS.      RESET SAMPLE COUNTER TO DETER.
0650 01200 072204R      STA KPTS      AVERAGE HETP
0651 01201 002400      CLA      SUM HETP'S
0652 01202 066557C      LDB HETP.
0653 01203 076556C      STP .HETP
0654 01204 006400      CLB
0655 01205 016027X WLOOP  FAD .HETP,1
      01206 104556C
0656 01207 072245R      STA TEMPO

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0657	01210	062556C	LDA .HETP	
0658	01211	042224R	ADA PPC	1ST PEAK IN SAMPLE USED.
0659	01212	042224R	ADA PPC	
0660	01213	072556C	STA .HETP	
0661	01214	062245R	LDA TEMPO	
0662	01215	036204R	ISZ KPTS	
0663	01216	027205R	JMP WLOOP	
0664	01217	016023X	FDV WD	AVERAGE
	01220	002252R		
0665	01221	072225R	STA AHETP	
0666	01222	076226R	STR AHETP+1	
0667	01223	062254R	LDA FRFSL	IS FLOW RATE CHANGE
0668	01224	002020	SSA	SUPPRESSED?
0669	01225	027376R	JMP EQUAL	YES, CHECK TEMP.
0670	01226	062225R	LDA AHETP	NO, COMPARE WITH LAST
0671	01227	066226R	LDB AHETP+1	HETP TO SEE IF
0672	01230	016030X	FSB LHETP	SMALLER OR EQUAL
	01231	002231R		
0673	01232	006003	SZB, RSS	EQUAL?
0674	01233	002002	SZA	
0675	01234	027236R	JMP *+2	NO
0676	01235	027376R	JMP EQUAL	YES, CHECK TEMP.
0677	01236	002021	SSA, RSS	
0678	01237	027376R	JMP EQUAL	NOT SMALLER, CHECK TEMP.
0679	01240	017356R	JSB RFLOW	PKWD SMALLER, CHANGE FLOW RATE.
0680	01241	072216R	STA BFLR	FLOW RATE AFTER SAMPLE
0681	01242	016025X	DLD BFLR, I	
	01243	102216R		
0682	01244	016026X	DST AFFL	
	01245	002241R		
0683	01246	017366R	JSB RTEM	TEMPERATURE AFTER SAMPLE
0684	01247	072216R	STA BFLR	
0685	01250	016025X	DLD BFLR, I	
	01251	102216R		
0686	01252	016026X	DST AFTEM	
	01253	002237R		
0687	01254	062213R	LDA DEFLO	INCREMENT FLOW
0688	01255	016001X	JSB OUTPT	
0689	01256	017610R	JSB FINAL	PRINT THIS SEGMENT'S RESULTS
0690	01257	002400	CLA	FOLLOWING IS A WAIT LOOP
0691	01260	072245R	STA TEMPO	FOR NEW FLOW RATE TO STABILIZE
0692	01261	072246R	STA TEMPO+1	
0693	01262	062247R	LDA .CNT4	
0694	01263	072250R	STA CNT4	
0695	01264	017356R	JSB RFLOW	
0696	01265	072216R	STA BFLR	
0697	01266	016025X	DLD BFLR, I	
	01267	102216R		
0698	01270	016026X	DST BFFL	
	01271	002217R		
0699	01272	016027X	FAD TEMPO	
	01273	002245R		
0700	01274	016026X	DST TEMPO	
	01275	002245R		
0701	01276	036250R	ISZ CNT4	
0702	01277	027264R	JMP L10	
0703	01300	016023X	FDV .10	
	01301	002257R		

0704	01302	016030X	FSB	FFFL	
	01303	002217R			
0705	01304	072245R	STA	TEMPO	
0706	01305	076246R	STB	TEMPO+1	
0707	01306	0022021	SSA, RSS		IF DIFFERENCE IS NEG.,
0708	01307	027313R	JMP	**4	
0709	01310	016011X	JSP	..FCM	COMPLEMENT 1T.
0710	01311	072245R	STA	TEMPO	
0711	01312	076246R	STB	TEMPO+1	
0712	01313	062261R	LDA	.01	
0713	01314	066262R	LDE	.01+1	
0714	01315	016031X	FMP	FFFL	
	01316	002217R			
0715	01317	016030X	FSB	TEMPO	
	01320	002245R			
0716	01321	0022021	SSA, RSS		< WINDOW?
0717	01322	027257R	JMP	L11	
0718	01323	062223R	LDA	KPTS.	RESET SAMPLE COUNTER
0719	01324	072204R	STA	KPTS	
0720	01325	002400	CLA		
0721	01326	072245R	STA	TEMPO	
0722	01327	072246R	STA	TEMPO+1	
0723	01330	062270R	LDA	NDAVS	
0724	01331	072267R	STA	NDAV	
0725	01332	062225R	LDA	AHETP	
0726	01333	072231R	STA	LHETP	
0727	01334	062226R	LDA	AHETP+1	
0728	01335	072232R	STA	LHETP+1	
0729	01336	026546R	JMP	L6	REPEAT SET AT SAME TEMP.

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0001 01337 017356R AFINL JSB RFLOW MEASURE FLOW RATE AFTER SAMPLE
0002 01340 072216R STA BFLR
0003 01341 016025X DLD BFLR,I
      01342 102216R
0004 01343 016026X DST AFFL
      01344 002241R
0005 01345 017366R JSB RTEM MEASURE TEMP. AFTER SAMPLE
0006 01346 072216R STA BFLR
0007 01347 016025X DLD BFLR,I
      01350 102216R
0008 01351 016026X DST AFTEM
      01352 002237R
0009 01353 017610R JSB FINAL PRINT RESULTS
0010 01354 102077 HLT 77R
0011 01355 026000R JMP START GO BACK TO START NEW EXPT.
0012 01356 000000 RFLOW NOP MEASURE FLOW RATE ROUTINE
0013 01357 062207R LDA AFLO SET MULTIPLEXER TO FLOW DET.
0014 01360 016001X JSB OUTPT
0015 01361 016017X JSB VLTRD
0016 01362 016012X JSB RDAV TAKE SPECIFIED # PTS AND AVERAGE
0017 01363 002207R DEF AFLO
0018 01364 002205R DEF PAVER
0019 01365 127356R JMP RFLOW,I RETURN
0020 01366 000000 RTEM NOP TEMPERATURE MEASURING ROUTINE
0021 01367 062210R LDA ATEM MULTIPLEXER TO TEMP. DET.
0022 01370 016001X JSB OUTPT
0023 01371 016017X JSB VLTRD
0024 01372 016012X JSB RDAV
0025 01373 002210R DEF ATEM
0026 01374 002205R DEF PAVER
0027 01375 127366R JMP RTEM,I RETURN
0028 01376 062276R EQUAL LDA VD VAN DEEMTER EXPERIMENT?
0029 01377 002020 SSA
0030 01400 027533R JMP YVD YES.
0031 01401 062206R TIVD LDA TIVCR IS TEMPERATURE TO BE
0032 01402 002003 SZA,RSS INCREMENTED?(OPTIMUM FF. FOUND)
0033 01403 027337R JMP AFINL NO, PRINT OUT RESULTS
0034 01404 017356R JSB RFLOW YES, MEASURE FLOW RATE
0035 01405 072216R STA BFLR
0036 01406 016025X DLD BFLR,I
      01407 102216R
0037 01410 016026X DST AFFL
      01411 002241R
0038 01412 017366R JSB RTEM MEASURE TEMPERATURE
0039 01413 072216R STA BFLR
0040 01414 016025X DLD BFLR,I
      01415 102216R
0041 01416 016026X DST AFTEM
      01417 002237R
0042 01420 062215R LDA DETEM INCREMENT TEMPERATURE
0043 01421 016001X JSB OUTPT
0044 01422 017610R JSB FINAL PRINT OUT RESULTS
0045 01423 062276R LDA VD VAN DEEMTER?
0046 01424 002020 SSA
0047 01425 027544R JMP RINCRK YES, REVERSE FLOW RATE.
0048 01426 016002X JSB WRITE STMT-OPT. FLOW RATE FOUND
0049 01427 003052R DEF STM26
0050 01430 000015 DEC 13

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0051	01431	016002X	JSR WRITE	TYPE IN 0 IF SUPPRESSION
0052	01432	003067R	DEF STM27	OF FLOW RATE CHANGE WANTED
0053	01433	000030	DEC 24	REMOVED
0054	01434	016005X	JSR KYFDR	
0055	01435	002141R	DEF TDATA	
0056	01436	000005	DEC 5	
0057	01437	016004X	JSR AD2FN	
0058	01440	002141R	DEF TDATA	
0059	01441	000001R	DEF OUCH	
0060	01442	000001R	DEF OUCH	
0061	01443	006002	SZR	
0062	01444	027450R	JMP **4	DON'T REMOVE SUPPRESSOR
0063	01445	006400	CLR	REMOVE SUPPRESS
0064	01446	076254R	STB FRSFL	
0065	01447	027452R	JMP L13	
0066	01450	007400	CCB	
0067	01451	076254R	STB FRSFL	
0068	01452	002400 L13	CLA	WAIT LOOP FOR TEMP TO
0069	01453	072245R	STA TEMPO	STABILIZE
0070	01454	072246R	STA TEMPO+1	
0071	01455	062247R	LDA .CNT4	
0072	01456	072250R	STA CNT4	
0073	01457	017366R L12	JSR RTEM	
0074	01460	072216R	STA BFLR	
0075	01461	016025X	DLD BFLR,I	
	01462	102216R		
0076	01463	002021	SSA,RSS	IF NEG, COMPLEMENT
0077	01464	027466R	JMP **2	
0078	01465	016011X	JSR ..FCM	
0079	01466	016026X	DST BFTEM	
	01467	002221R		
0080	01470	016027X	FAD TEMPO	
	01471	002245R		
0081	01472	016026X	DST TEMPO	
	01473	002245R		
0082	01474	036250R	ISZ CNT4	
0083	01475	027457R	JMP L12	
0084	01476	016023X	FDV .10	
	01477	002257R		
0085	01500	016030X	FSB BFTEM	
	01501	002221R		
0086	01502	072245R	STA TEMPO	
0087	01503	076246R	STB TEMPO+1	
0088	01504	002021	SSA,RSS	IF DIFFERENCE IS NEG.,
0089	01505	027511R	JMP **4	
0090	01506	016011X	JSR ..FCM	COMPLEMENT IT.
0091	01507	072245R	STA TEMPO	
0092	01510	076246R	STB TEMPO+1	
0093	01511	062263R	LDA WIN	
0094	01512	066264R	LDR WIN+1	
0095	01513	016031X	FMP BFTEM	
	01514	002221R		
0096	01515	016030X	FSB TEMPO	
	01516	002245R		
0097	01517	002020	SSA	< WINDOW
0098	01520	027452R	JMP L13	
0099	01521	062223R	LDA KPTS.	RESET SAMPLE COUNTER
0100	01522	072204R	STA KPTS	

0101	01523	002400	CLA	
0102	01524	072245R	STA TEMP0	
0103	01525	072246R	STA TEMP0+1	
0104	01526	062270R	LDA NDAVS	
0105	01527	072267F	STA NDAV	
0106	01530	036206R	ISZ TINCR	INCREMENT TEMPERATURE COUNTER
0107	01531	000000	NOP	
0108	01532	026542R	JMP L8	START NEW CYCLE.
0109	01533	062271R	LDA AVD	CHECK TO SEE IF PAST MIN.
0110	01534	002003	SZA, FSS	IN VD CURVE DESIRED # OF TIMES.
0111	01535	027541R	JMP **4	YES, CHECK TEMP INCREMENT.
0112	01536	036271R	ISZ AVD	NO, INCREMENT COUNTER
0113	01537	000000	NOP	
0114	01540	027240R	JMP VEGO	DO SETS AFTER MINIMUM
0115	01541	062272R	LDA AVDS	RESET AFTER MINIMUM
0116	01542	072271R	STA AVD	COUNTER
0117	01543	027401R	JMP TIVD	
0118	01544	016002X	JSP WRITE	HOW MANY BACK INCREMENTS
0119	01545	003246R	DEF STM34	(FLOW RATE) ARE TO BE DONE?
0120	01546	000023	DEC 19	
0121	01547	016005X	JSR KYEDR	
0122	01550	002141R	DEF TDATA	
0123	01551	000005	DEC 5	
0124	01552	016004X	JSB AD2EN	
0125	01553	002141R	DEF TDATA	
0126	01554	000001R	DEF OUCH	
0127	01555	000001R	DEF OUCH	
0128	01556	007004	CME, INB	
0129	01557	076277R	STB BAK	PACKUP COUNTER
0130	01560	062211R	LDA AELC	BACK
0131	01561	016001X	JSR OUTPT	UP
0132	01562	062214R	LDA BEFLO	FLOW
0133	01563	016001X	JSB OUTPT	FLOW
0134	01564	036277R	ISZ BAK	
0135	01565	027567R	JMP L21	DELAY
0136	01566	027600R	JMP HOLD	
0137	01567	062300R	LDA CNT11	SET UP 2 SECOND DELAY
0138	01570	072301R	STA .CT11	LOOP BETWEEN STEPS
0139	01571	062302R	LDA SEC.	
0140	01572	072303R	STA .SEC	
0141	01573	036303R	ISZ .SEC	
0142	01574	027573R	JMP *-1	
0143	01575	036301R	ISZ .CT11	
0144	01576	027571R	JMP L22	
0145	01577	027560R	JMP L23	
0146	01600	016002X	JSP WRITE	WAIT FOR FLOW RATE TO STABILIZE
0147	01601	003271R	DEF STM35	
0148	01602	000014	DEC 12	
0149	01603	103501	LIA 1,C	LOAD SWITCH 7 AND CHECK
0150	01604	001727	ALF, ALF	ROTATE TO BIT 15
0151	01605	002021	SSA, FSS	
0152	01606	027603R	JMP *-3	7 NOT UP, HOLD
0153	01607	027452R	JMP L13	START NEW SET AT NEXT TEMP.

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0155*****
0156* PRINT AND PUNCH SECTION *
0157*****
0158 01610 000000 FINAL NOP
0159 01611 016002X JSB WRITE PEAK AREAS
0160 01612 002306R DEF ASTMT
0161 01613 000006 DEC 6
0162 01614 062211C LDA AREA.
0163 01615 072210C STA .AREA
0164 01616 016020X JSB EDUMP
0165 01617 004140C DEF AREA
0166 01620 004323C DEF CTR
0167 01621 016002X JSB WRITE PEAK HEIGHTS
0168 01622 002314R DEF PSTMT
0169 01623 000006 DEC 6
0170 01624 062137C LDA PKHT.
0171 01625 072136C STA .PKHT
0172 01626 016020X JSB EDUMP
0173 01627 004066C DEF PKHT
0174 01630 004323C DEF CTR
0175 01631 016002X JSB WRITE RETENTION TIME IN TIMER PTS.
0176 01632 002322R DEF LSTMT
0177 01633 000010 DEC 8
0178 01634 062241C LDA PKL1.
0179 01635 072240C STA .PKL1
0180 01636 062267C LDA PKL2.
0181 01637 072266C STA .PKL2
0182 01640 062255R LDA CNTST
0183 01641 073645R STA .AS
0184 01642 016022X JSB WRDP
0185 01643 004214C DEF PKL1
0186 01644 004242C DEF PKL2
0187 01645 000000 .AS DEC 0
0188 01646 016002X JSB WRITE # PTS IN PEAK
0189 01647 002563R DEF TSTMT
0190 01650 000014 DEC 12
0191 01651 062255R LDA CNTST
0192 01652 072171R STA ACNTR
0193 01653 062274C LDA PKPT.
0194 01654 072275C STA .PKPT
0195 01655 162275C TWRT LDA .PKPT,I
0196 01656 016007X JSB P2DC
0197 01657 073661R STA .TSRF
0198 01660 016002X JSB WRITE
0199 01661 000000 .TSRF DEF 0
0200 01662 000003 DEC 3
0201 01663 036275C ISZ .PKPT
0202 01664 036171R ISZ ACNTR
0203 01665 027655R JMP TWRT
0204 01666 016002X JSB WRITE SAMPLE INJECTION TIME
0205 01667 002546R DEF 1STMT IN TIMER PTS.
0206 01670 000015 DEC 13
0207 01671 062457C LDA SIN1.
0208 01672 072456C STA .SIN1
0209 01673 062505C LDA SIN2.
0210 01674 072504C STA .SIN2
0211 01675 062255R LDA CNTST
0212 01676 073702R STA .DS

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0213	01677	016022X	JSB WRDP	
0214	01700	004432C	DEF SIN1	
0215	01701	004460C	DEF SIN2	
0216	01702	000000	.DS DEC 0	
0217	01703	016002X	JSB WRITE	PEAK START TIME
0218	01704	003305R	DEF STM36	
0219	01705	000010	DEC 3	
0220	01706	062403C	LDA PST1.	
0221	01707	072432C	STA .PST1	
0222	01710	062431C	LDA PST2.	
0223	01711	072430C	STA .PST2	
0224	01712	062255R	LDA CNTST	
0225	01713	073717R	STA .GS	
0226	01714	016022X	JSB WRDP	
0227	01715	004356C	DEF PKST1	
0228	01716	004404C	DEF PKST2	
0229	01717	000000	.GS DEC 0	
0230	01720	016002X	JSB WRITE	PEAK WIDTH AT 1/2 HT. AS
0231	01721	002704R	DEF WSTMT	# PTS AT ISO. TEMP.
0232	01722	000016	DEC 14	
0233	01723	062255R	LDA CNTST	
0234	01724	072171R	STA ACNTR	
0235	01725	062351C	LDA PKWD.	
0236	01726	072350C	STA .PKWD	
0237	01727	162350C	WWRIT LDA .PKWD,I	
0238	01730	016007X	JSB .B2DC	
0239	01731	073733R	STA .WSBF	
0240	01732	016002X	JSB WRITE	
0241	01733	000000	.WSBF DEF 0	
0242	01734	000003	DEC 3	
0243	01735	036350C	ISZ .PKWD	
0244	01736	036171R	ISZ ACNTR	
0245	01737	027727R	JMP WWRIT	
0246	01740	016002X	JSB WRITE	TEMP. BEFORE SAMPLES
0247	01741	002763R	DEF RSTMT	
0248	01742	000015	DEC 13	
0249	01743	016020X	JSB EDUMP	
0250	01744	002221R	DEF BFTM	
0251	01745	002236R	DEF PLUS1	
0252	01746	016002X	JSB WRITE	FLOW RATE BEFORE SAMPLES
0253	01747	003000R	DEF CSTMT	
0254	01750	000014	DEC 12	
0255	01751	016020X	JSB EDUMP	
0256	01752	002217R	DEF RFFL	
0257	01753	002236R	DEF PLUS1	
0258	01754	016002X	JSB WRITE	TEMP. AFTER SAMPLES
0259	01755	003014R	DEF DSTMT	
0260	01756	000014	DEC 12	
0261	01757	016020X	JSB EDUMP	
0262	01760	002237R	DEF AFTEM	
0263	01761	002236R	DEF PLUS1	
0264	01762	016002X	JSB WRITE	FLOW RATE AFTER SAMPLES
0265	01763	003030R	DEF ESTMT	
0266	01764	000013	DEC 11	
0267	01765	016020X	JSB EDUMP	
0268	01766	002241R	DEF AFFL	
0269	01767	002236R	DEF PLUS1	
0270	01770	016002X	JSB WRITE	

0271	01771	003043R	DEF FSMT	
0272	01772	000007	DEC 7	
0273	01773	016020X	JSR EDUMP	
0274	01774	002225R	DEF AHETP	
0275	01775	002236R	DEF PLUS1	
0276	01776	062140R	LDA NPTS.	
0277	01777	042155R	ADA NPTS	
0278	02000	072152R	STA NOPT	
0279	02001	062243R	LDA DSFL	ARE DATA PTS TO BE
0280	02002	000010	SLA	PRINTED?
0281	02003	026011R	JMP PUN	NO
0282	02004	062065C	LDA RDT.	YES
0283	02005	072064C	STA PDAT	
0284	02006	016020X	JSR EDUMP	
0285	02007	000000C	DEF DATA	
0286	02010	002152R	DEF NOPT	
0287	02011	062244R	LDA PMSFL	PUNCH A PINARY TAPE OF ALL
0288	02012	002011	SLA, RSS	INFORMATION?
0289	02013	026137R	JMP GOEAK	NO, RETURN
0290	02014	062021R	LDA LEEDS	PUNCH 1'S FILL LEADER
0291	02015	072256R	STA LEED	
0292	02016	003400	CCA	
0293	02017	007400	CCB	
0294	02020	016021X	JSR WDPUN	
0295	02021	177740	LEEDS OCT -40	128 FRAMES OF 377B
0296	02022	036256R	ISZ LEED	
0297	02023	026016R	JMP L20	
0298	02024	062255R	LDA CNTST	
0299	02025	072171R	STA ACNTR	
0300	02026	062351C	LDA PKWD.	
0301	02027	072350C	STA .PKWD	
0302	02030	162350C	DLOOP LDA .PKWD, I	
0303	02031	016013X	JSR FLOAT	
0304	02032	016021X	JSR WDPUN	
0305	02033	000000	NOP	
0306	02034	036350C	ISZ .PKWD	
0307	02035	036171R	ISZ ACNTR	
0308	02036	026030R	JMP DLOOP	
0309	02037	062255R	LDA CNTST	
0310	02040	072171R	STA ACNTR	
0311	02041	062457C	LDA SIN1.	
0312	02042	072456C	STA .SIN1	
0313	02043	062505C	LDA SIN2.	
0314	02044	072504C	STA .SIN2	
0315	02045	162456C	ILOOP LDA .SIN1, I	
0316	02046	166504C	LDR .SIN2, I	
0317	02047	016016X	JSR .PACK	
0318	02050	000037	DEC 31	
0319	02051	016021X	JSR WDPUN	
0320	02052	000000	NOP	
0321	02053	036456C	ISZ .SIN1	
0322	02054	036504C	ISZ .SIN2	
0323	02055	036171R	ISZ ACNTR	
0324	02056	026045R	JMP ILOOP	
0325	02057	062255R	LDA CNTST	
0326	02060	072171R	STA ACNTR	
0327	02061	062274C	LDA PKPT.	
0328	02062	072275C	STA .PKPT	

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0329 02063 162275C PLOOP LDA .PKPT,I
0330 02064 016013X JSR FLOAT
0331 02065 016021X JSR WDPUN
0332 02066 000000 NOP
0333 02067 036275C ISZ .PKPT
0334 02070 036171R ISZ ACNTR
0335 02071 026063R JMP PLOOP
0336 02072 062255R LDA CNTST
0337 02073 072171R STA ACNTR
0338 02074 062403C LDA PST1.
0339 02075 072402C STA .PST1
0340 02076 062431C LDA PST2.
0341 02077 072430C STA .PST2
0342 02100 162402C SLOOP LDA .PST1,I
0343 02101 166430C LDE .PST2,I
0344 02102 016016X JSR .PACK
0345 02103 000037 DEC 31
0346 02104 016021X JSR WDPUN
0347 02105 000000 NOP
0348 02106 036402C ISZ .PST1
0349 02107 036430C ISZ .PST2
0350 02110 036171R ISZ ACNTR
0351 02111 026100R JMP SLOOP
0352 02112 062152R LDA NOPT
0353 02113 003004 CMA,INA
0354 02114 072134R STA NOD
0355 02115 062065C LDA EDT.
0356 02116 072064C STA EDAT
0357 02117 016025X LOPD DLD EDAT,I
      02120 104064C
0358 02121 016021X JSR WDPUN
0359 02122 000000 NOP
0360 02123 036064C ISZ EDAT
0361 02124 036064C ISZ EDAT
0362 02125 036134R ISZ NOD
0363 02126 026117R JMP LOPD
0364 02127 062021R LDA LEEDS 1'S FILL LEADER
0365 02130 072256R STA LEED
0366 02131 003400 LOP CCA
0367 02132 007400 CCE
0368 02133 016021X JSR WDPUN
0369 02134 000000 NOD DEC 0
0370 02135 036256R ISZ LEED
0371 02136 026131R JMP LOP
0372 02137 127610R GORAK JMP FINAL,I

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0374*****
0375* CONSTANT SECTION *
0376*****
0377 02140 000000 NPTS. DEC 0 TOTAL # PTS TO BE TAKEN
0378 02141 000000 TDATA BSS 5 TTY INPUT BUFFER
0379 02146 000000 THR1 BSS 2 INITIAL THRESHOLD
0380 02150 000000 THR2 BSS 2 CUTOFF THRESHOLD
0381 02152 000000 NPT1 DEC 0 ACTUAL # PTS TAKEN
0382 02153 000000 LESS DEC 0 # PTS TO STOP INTEGRATION
0383 02154 000000 LESST DEC 0
0384 02155 000000 NPTS DEC 0 TOTAL # PTS COUNTER
0385 02156 000000 FLAG1 OCT 0 1ST PT FLAG
0386 02157 000000C PDA. DEF DATA DEFINE STARTING ADDRESS OF BUFFER
0387 02160 004140C AR.. DEF AREA
0388 02161 004214C PL1.. DEF PKL1
0389 02162 004242C PL2.. DEF PKL2
0390 02163 004066C PKH. DEF PKHT
0391 02164 004324C PKW.. DEF PKWD
0392 02165 004276C PKP.. DEF PKP1S
0393 02166 004432C SN1.. DEF SIN1
0394 02167 004460C SN2.. DEF SIN2
0395 02170 004506C HTP DEF HETP
0396 02171 000000 ACNTR DEC 0
0397 02172 073465 A1 OCT 73465 TIMER(POS.)
0398 02173 112000 A2 OCT 112000
0399 02174 104312 AS1 OCT 104312 TIMER RESET
0400 02175 066000 AS2 OCT 066000
0401 02176 000000 PCS DEC 0 PEAK COUNTER SET
0402 02177 000000 PC DEC 0 PEAK COUNTER
0403 02200 000000 TIM BSS 2 ESTIMATED TOTAL RET. TIME
0404 02202 000000 MUL DEC 0 MULTIPLIER FOR TIM FOR DOUB. PREC.
0405 02203 000000 C DEC 0 CLEARING COUNTER
0406 02204 000000 KPTS DEC 0 SAMPLE COUNTER
0407 02205 000000 PAVER DEC 0 # PTS TO BE AVERAGED
0408 02206 000000 TINCRC DEC 0 TEMP. INCREMENT COUNTER AND FLAG
0409 02207 000020 AFLO OCT 20 SWITCH MULTIPLEXER TO FLOW DET.
0410 02210 000010 ATEM OCT 10 SWITCH MULTIPLEXER TO TEMP DET.
0411 02211 000004 AFLC OCT 4 SWITCH MULTIPLEXER TO ELECTROMETER
0412 02212 100004 DESAM OCT 100004 SAMPLING VALVE COMMAND
0413 02213 050004 DEFLO OCT 50004 FLOW RATE CHANGE COMMAND
0414 02214 040004 REFLO OCT 40004 BACK UP FLOW COMMAND
0415 02215 020004 DETEM OCT 20004 TEMP. CHANGE COMMAND
0416 02216 000000 BFLR OCT 0 TEMPORARY STORAGE
0417 02217 000000 RFFL BSS 2 FLOW RATE BEFORE SAMPLES
0418 02221 000000 RFTM BSS 2 TEMP. BEFORE SAMPLES
0419 02223 000000 KPTS. DEC 0 # SAMPLES COUNTER RESET
0420 02224 000000 PPC DEC 0 NUMBER PEAKS PER SAMPLE
0421 02225 000000 AHETP BSS 2 AVERAGE HETP
0422 02227 076400 APWD DEC 1000.
02230 000024
0423 02231 000000 LHETP BSS 2 LAST AVERAGE HETP
0424 02233 177776 MIN2 OCT -2
0425 02234 177774 MIN4 OCT -4
0426 02235 177777 MIN1 OCT -1
0427 02236 000001 PLUS1 OCT 1
0428 02237 000000 AFTEM BSS 2 TEMPERATURE AFTER SAMPLES
0429 02241 000000 AFFL BSS 2 FLOW RATE AFTER SAMPLES
0430 02243 000000 DSFL OCT 0 DATA DUMP SUPPRESS FLAG

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0431 02244 000000 PNSFL OCT 0 PUNCH SUPPRESS FLAG
0432 02245 000000 TEMPO BSS 2 TEMPORARY STORAGE
0433 02247 177766 .CNT4 DEC -10
0434 02250 000000 CNT4 DEC 0
0435 02251 000000 .NPTS DEC 0 DATA POINT COUNTER
0436 02252 000000 WD BSS 2 # SAMPLES AT ONE TEMPERATURE
0437 02254 000000 FRSFL OCT 0 FLOW RATE SUPPRESS FLAG
0438 02255 000000 CNTST DEC 0 TOTAL PEAK COUNTER
0439 02256 000000 LEED DEC 0 1'S FILL LEADER COUNTER
0440 02257 050000 .10 DEC 10.
02260 000010
0441 02261 000000 .01 BSS 2 FLOW SENSOR WINDOW
0442 02263 000000 WIN BSS 2 TEMPERATURE WINDOW
0443 02265 047040 FACT DEC 10000. CORRECTION FACTOR
02266 000034
0444 02267 000000 NDAV DEC 0 COUNTER FOR AVER. DATA PTS
0445 02270 000000 NDAVS DEC 0 NDAV RESET
0446 02271 000000 AVD DEC 0 # SAMPLES AFTER MIN. IN VD
0447 02272 000000 AVDS DEC 0 AVD RESET
0448 02273 000003 .3 OCT 3
0449 02274 000004 .4 OCT 4
0450 02275 000005 .5 OCT 5
0451 02276 000000 VD OCT 0 VAN DEEMTER EXPERIMENT FLAG.
0452 02277 000000 FAK OCT 0 BACK UP COUNTER FOR FLOW RATE.
0453 02300 177765 CNT11 DEC -11 PART OF 2 SECOND DELAY COUNTER
0454 02301 000000 .CT11 DEC 0
0455 02302 100001 SEC. DEC -32767 REST OF 2 SECOND DELAY COUNTER
0456 02303 000000 .SEC DEC 0
0457 02304 004356C PS1.. DEF PKST1
0458 02305 004404C PS2.. DEF PKST2
0459 SUP
0460 02306 005012 ASTMT OCT 5012 LF LF
0461 02307 050105 ASC 5, PEAK AREAS
0462 02314 050105 PSTMT ASC 6, PEAK HEIGHTS
0463 02322 051105 LSTMT ASC 8, RETENTION TIMES
0464 02332 021440 STMT3 ASC 7, # DATA PTS? -
0465 02341 042530 STMT4 ASC 5, EXPT #? -
0466 02346 041515 STMT5 ASC 6, CMPD CODE? -
0467 02354 053117 STMT6 ASC 8, VOLTAGE RANGE? -
0468 02364 051501 STMT7 ASC 8, SAMPLING RATE? -
0469 02374 051101 STMT8 ASC 4, RANGE? -
0470 02400 040524 STMT9 ASC 7, ATTENUATION? -
0471 02407 044516 STM10 ASC 10, INITIAL THRESHOLD? -
0472 02421 041525 STM11 ASC 10, CUT OFF THRESHOLD? -
0473 02433 021440 STM12 ASC 11, # PTS START INTEGR? -
0474 02446 021440 STM13 ASC 10, # PTS STOP INTEGR? -
0475 02460 052117 STM15 ASC 10, TOTAL PKS(BUFFER)? -
0476 02472 051527 STM16 ASC 14, SWITCH 0 UP FOR CPU CONTROL.
0477 02510 051527 STM19 ASC 13, SWITCH 15 UP TO TAKE DATA.
0478 02525 050105 STM17 ASC 8, PEAKS/SAMPLE? -
0479 02535 052117 STM18 ASC 9, TOTAL PET TIME? -
0480 02546 051501 ISTMT ASC 13, SAMPLE INJECTION TIME(PTS)
0481 02563 047125 TSTMT ASC 12, NUMBER OF POINTS IN PEAK
0482 02577 021440 STM20 ASC 15, # PTS. TO BE AVERAGED(T&F)? -
0483 02616 021440 STM21 ASC 20, # TIMES TEMPERATURE TO BE INCREMENTED?
0484 02642 021440 STM22 ASC 13, # SAMPLES AT EACH TEMP? -
0485 02657 051527 STM23 / SC 21, SWITCH 14 UP TO SUPPRESS FLOW RATE CHAN
0486 02704 050105 WSTMT ASC 14, PEAK WIDTH AT 1/2 HT(150 T)

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0487 02722 051525 STM24 ASC 17,SUPPRESS DATA DUMP(1=YES,0=NO)? -
0488 02743 050125 STM25 ASC 16,PUNCH BINARY TAPE(1=YES,0=NO)? -
0489 02763 052105 BSTMT ASC 13,TEMPERATURE BEFORE WAS -
0490 03000 043114 CSTMT ASC 12,FLOW RATE BEFORE WAS -
0491 03014 052105 DSTMT ASC 12,TEMPERATURE AFTER WAS -
0492 03030 043114 ESTMT ASC 11,FLOW RATE AFTER WAS -
0493 03043 040526 FSTMT ASC 7,AVERAGE HETP -
0494 03052 047520 STM26 ASC 12,OPTIMUM FLOW RATE FOUND:
0495 03066 000007 OCT 7
0496 03067 052131 STM27 ASC 24,TYPE IN 0 IF REMOVAL OF FR SUPPR WANTED
0497 03117 047525 STM28 ASC 27,OUT OF DATA PTS. REVISE ESTIMATES. PUSH
0498 03152 052105 STM29 ASC 11,TEMPERATURE WINDOW? -
0499 03165 043114 STM30 ASC 11,FLOW SENSOR WINDOW? -
0500 03200 021440 STM31 ASC 11,# DATA PTS AVERAGED? -
0501 03213 021440 STM32 ASC 13,# SAMPLES AFTER VD MIN? -
0502 03230 051527 STM33 ASC 14,SWITCH 13 UP FOR VAN DEEMTER
0503 03246 003407 STM34 OCT 3407
0504 03247 003407 OCT 3407
0505 03250 041510 ASC 17,CHANGE SWITCH. # PACK INCREMENTS -
0506 03271 051527 STM35 ASC 12,SWITCH 7 UP WHEN STABLE.
0507 03305 050105 STM36 ASC 8,PEAK START TIME
0508 03315 052117 STM37 ASC 12,TOT. TIME MULTIPLIER? -
0509 03331 041517 STM38 ASC 7,COL. LENGTH? -
0510 UNS
0511 COM DATA(2100),RDAT,EDT.,PKHT(40),.PKHT,PKHT.
0512 COM AREA(40),.AREA,AREA.,TEMP(2),PKL1(20),.PKL
0513 COM PKL1.,PKL2(20),.PKL2,PKL2.,NFLAG,LOCFL
0514 COM LCTR1,LCTR2,PKPT.,.PKPT,PKPTS(20),TARST,CT
0515 COM PKWD(20),.PKWD,PKWD.,FUP(2),CUP,DAVS
0516 COM PKST1(20),.PST1,PST1.,PKST2(20),.PST2,PST2
0517 COM SIN1(20),.SIN1,SIN1.,SIN2(20),.SIN2,SIN2.
0518 COM HETP(40),.HETP,HETP.,LNG(2),DAV(2)
0519 END START
** NO ERRORS*

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APPENDIX B

LISTING OF PROCESSING PROGRAM RT1M2

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0001          ASMB,R,B,L
0003 00000      NAM RTIME2
0004          EXT .ZFRO,...DLC,...FCM,FLOAT,.PACK
0005          ENT RTIME
0006          ENT .RTIM
0007          ENT RTIM.
0008*SUBROUTINE TO INTEGRATE THE AREA UNDER ONE OR MORE GC PEAKS IN REAL
0009*TIME, FIND THE PEAK MAXIMUM AND STORE THE PEAK MAX, LOCATION,
0010*AND AREA IN SPECIFIC LOCATIONS. CORRECTIONS FOR POINT
0011*AVERAGING IN PEAK LOCATION AND NOISE ROUTINES ARE ADDED IN
0012*RTIME2
0013*VERSION: 30 AUGUST 1970
0014*
0015*CALLING SEQUENCE: JSB RTIME /THIS IS 1ST PT OVER
0016*                  THEDI-INITIALIZATION
0017*
0018*                  JSB .RTIM /NORMAL AFTER 1ST PT
0019*
0020*                  JSB RTIM. /ENTRY AFTER INTEGRATION
0021*                  STOPS ON A PEAK
0022*CONTROL IS RETURNED TO NEXT STMT IN MAIN PROGRAM FROM ALL
0023*3 ENTRIES.
0024*
0025*****
0026* 1ST POINT INITIALIZATION *
0027*****
0028 00000 000000 RTIME NOP
0029 00001 002400 CLA
0030 00002 072726R STA .LAS1 ZERO VARIOUS
0031 00003 072727R STA .LAS2
0032 00004 062211C LDA AREA.
0033 00005 072210C STA .AREA BUFFERS AND
0034 00006 062137C LDA PKHT.
0035 00007 072136C STA .PKHT
0036 00010 062351C LDA PKWD. INITIALIZE
0037 00011 072350C STA .PKWD
0038 00012 062241C LDA PKL1.
0039 00013 072240C STA .PKL1 BUFFER ADDRESSES.
0040 00014 062267C LDA PKL2.
0041 00015 072266C STA .PKL2
0042 00016 062274C LDA PKPT.
0043 00017 072275C STA .PKPT
0044 00020 062403C LDA PST1.
0045 00021 072402C STA .PST1
0046 00022 062431C LDA PST2.
0047 00023 072430C STA .PST2
0048 00024 062557C LDA HETP.
0049 00025 072556C STA .HETP
0050 00026 062323C LDA CTRIT
0051 00027 001000 ALS
0052 00030 072750R STA CTRT
0053 00031 016001X JSB .ZERO
0054 00032 004140C DEF APEA
0055 00033 000750P DEF CTRT
0056 00034 016001X JSB .ZERO
0057 00035 004066C DEF PKHT
0058 00036 000750P DEF CTRT
0059 00037 016001X JSB .ZERO

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0060	00040	004356C	DEF PKST1
0061	00041	004323C	DEF CTR1T
0062	00042	016001X	JSR .ZERO
0063	00043	004404C	DEF PKST2
0064	00044	004323C	DEF CTR1T
0065	00045	016001X	JSR .ZERO
0066	00046	004214C	DEF PKL1
0067	00047	004323C	DEF CTR1T
0068	00050	016001X	JSR .ZERO
0069	00051	004242C	DEF PKL2
0070	00052	004323C	DEF CTR1T
0071	00053	016001X	JSR .ZERO
0072	00054	004276C	DEF PKPTS
0073	00055	004323C	DEF CTR1T
0074	00056	016001X	JSR .ZERO
0075	00057	004324C	DEF PKWD
0076	00060	004323C	DEF CTR1T
0077	00061	016001X	JSR .ZERO
0078	00062	004506C	DEF HETP
0079	00063	000750R	DEF CTRT
0080	00064	002400	CLA
0081	00065	072722R	STA IFLAG
0082	00066	072723R	STA DFLAG
0083	00067	072720C	STA NFLAG
0084	00070	072730R	STA TLOC1
0085	00071	072731R	STA TLOC1+1
0086	00072	072732R	STA TLOC2
0087	00073	072733R	STA TLOC2+1
0088	00074	072734R	STA TLOC3
0089	00075	072735R	STA TLOC3+1
0090	00076	072724R	STA SUM
0091	00077	072725R	STA SUM+1
0092	00100	072271C	STA LOCFL
0093	00101	072736R	STA REJFL
0094	00102	062065C	LDA BDT.
0095	00103	072064C	STA EDAT
0096	00104	062322C	LDA TABST
0097	00105	072721R	STA TAB
0098	00106	036721R	ISZ TAB
0099	00107	000000	INC INCREMENT START INTEGRATE COUNTER
0100	00110	062273C	LDA LCTR2
0101	00111	072727R	STA .LAS2
0102	00112	066272C	LDB LCTR1
0103	00113	076726R	STR .LAS1
0104	00114	062355C	LDA DAVS
0105	00115	003004	CMA, INA
0106	00116	072757R	STA NDAVS
0107	00117	126000R	JMP RTIME, I

STORE TIMER IN .LAS(LAST PT.)
TO USE FOR NOISE CHECKS.

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0109*****
0110* MAIN PEAK PROCESSING ROUTINE *
0111*****
0112*
0113*THIS SECTION DOES THE MAIN PROCESSING ON THE PEAK.
0114*NOISE ON THE BASELINE IS CHECKED FOR AND REJECTED.
0115*AFTER INTEGRATION STARTS,NOISE ON THE PEAK SLOPES
0116*IS CONTINUOUSLY LOOKED FOR USING A 3 POINT MOVING
0117*AVERAGE. RUDIMENTARY AVERAGING OF THIS NOISE IS
0118*DONE. ROUTINE HAS TO CHECK WHERE ON THE PEAK THE
0119*DATA POINT IS(FRONT OR BACKSIDE) WHEN CHECKING FOR
0120*NOISE WHILE ALSO LOOKING FOR THE PEAK MAXIMUM.
0121* THIS ACCOUNTS FOR SOME OF THE APPARENT DUPLICATION
0122*IN SOME PARTS OF THIS ROUTINE.
0123*
0124 00120 000000 .RTIM NOP
0125 00121 062727P LDA .LAS2 CHECK FOR NOISE ON
0126 00122 003004 CMA,INA BASELINE(USES TIMER).
0127 00123 042273C ADA LCTR2
0128 00124 042354C ADA CUP
0129 00125 002011 SLA,RSS
0130 00126 026155R JMP NOISE
0131 00127 001110 ARS,SLA
0132 00130 026155R JMP NOISE
0133 00131 001110 ARS,SLA
0134 00132 026155R JMP NOISE
0135 00133 062270C LDA NFLAG INTEGRATE FLAG SET?(SUFFICIENT
0136 00134 002020 SSA POINTS OVER THRESHOLD?)
0137 00135 026150R JMP GRATE YES
0138 00136 036721R ISZ TAB NO, INCREMENT COUNTER.
0139 00137 026143R JMP RET NOT ENOUGH OVER THPRD YET. GO BACK.
0140 00140 062322C LDA TABST ENOUGH PTS OVER. RESET COUNTER.
0141 00141 072721R STA TAB
0142 00142 026150R JMP GRATE GO ON TO SLOPE CHECK ROUTINES.
0143 00143 062273C RET LDA LCTR2 STORE TIMER IN LAST PT.
0144 00144 072727R STA .LAS2
0145 00145 066272C LDB LCTR1
0146 00146 076726R STB .LAS1
0147 00147 126120R JMP .RTIM,I GO GET ANOTHER PT.
0148 00150 062273C GRATE LDA LCTR2 PUT TIMER IN LAST PT.
0149 00151 072727R STA .LAS2
0150 00152 066272C LDR LCTR1
0151 00153 076726P STB .LAS1
0152 00154 026160R JMP NGRAT
0153 00155 062322C NOISE LDA TABST REJECT NOISE ON BASELINE.
0154 00156 072721R STA TAB RESET START INTEGRATE COUNTER.
0155 00157 026143R JMP RET GO BACK.
0156 00160 062212C NGRAT LDA TEMP STORE PRESENT POINT.
0157 00161 066213C LDB TEMP+1
0158 00162 016006X DST PDAT,I
0163 104064C
0159 00164 062736P LDA REJFL IS REJECT FLAG SET?(BACKSIDE
0160 00165 002020 SSA OF PEAK SMOOTHING)
0161 00166 026476R JMP OREJT YES
0162 00167 062270C HORN LDA NFLAG IS INTEGRATE FLAG SET?
0163 00170 002020 SSA
0164 00171 026202R JMP MAX YES.
0165 00172 007400 CCP NO. SET INTEGRATE FLAG.

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0166	00173	076270C	STF NFLAG	
0167	00174	062273C	LDA LCIR2	STORE TIMER AT PEAK START.
0168	00175	072736R	STA RGPKE2	
0169	00176	062272C	LDA LCIP1	
0170	00177	072737R	STA RGPKE1	
0171	00200	062064C	LDA PDAT	DATA ADDR AT PK START
0172	00201	072746R	STA DAPK	
0173	00202	016002X MAX	JSR ..DLC	LOAD AND COMPLEMENT
0174	00203	000732R	DEF TLOC2	COMPARE LAST POINT
0175	00204	016007X	FAD TEMP	WITH THE PRESENT POINT.
	00205	004212C		
0176	00206	006003	SZR, RSS	EQUAL?
0177	00207	002002	SZA	
0178	00210	026212R	JMP **2	NO.
0179	00211	026240R	JMP GOON	YES. CHECK OTHER PARAMETERS.
0180	00212	002021	SSA, RSS	PRESENT>LAST PT.?
0181	00213	026372R	JMP REJT	YES. CHECK OTHER PARAMETERS.
0182	00214	062723R	LDA DFLAG	NO. IS DECREASING SLOPE
0183	00215	002021	SSA, RSS	FLAG SET?
0184	00216	026264R	JMP MVAL	NO. GO TO PEAK MAX ROUTINE.
0185	00217	062271C	LDA LOCFL	YES. IS PEAK MAX FLAG SET?
0186	00220	002002	SZA	
0187	00221	026247R	JMP UNEQ	YES. GO ON.
0188	00222	003400	CCA	SET PEAK MAX FLAG AS IT HAS
0189	00223	072271C	STA LOCFL	BEEN FOUND(DEC. SLOPE SET)
0190	00224	026247R	JMP UNEQ	GO ON.
0191	00225	062734R CON	LDA TLOC3	PUT THE PT IN TLOC3
0192	00226	066735R	LDR TLOC3+1	INTO TLOC1 FOR REJECTION
0193	00227	072730R	STA TLOC1	CONSIDERATIONS.
0194	00230	076731R	STR TLOC1+1	
0195	00231	062212C	LDA TEMP	PUT PRESENT PT IN
0196	00232	066213C	LDR TEMP+1	THE OTHER MOVING
0197	00233	072732R	STA TLOC2	AVERAGE LOCATIONS.
0198	00234	076733R	STR TLOC2+1	
0199	00235	072734R	STA TLOC3	
0200	00236	076735R	STR TLOC3+1	
0201	00237	026361R	JMP AED	INTEGRATE.
0202	00240	062271C GOON	LDA LOCFL	LAST 2 PTS =. HAS PEAK
0203	00241	002020	SSA	MAX BEEN FOUND?
0204	00242	026225R	JMP CON	YES. GO ON.
0205	00243	062723R	LDA DFLAG	IS DECREASING SLOPE FLAG
0206	00244	002021	SSA, RSS	SET?
0207	00245	026225R	JMP CON	NO. GO ON.
0208	00246	026361R	JMP ADD	YES. DON'T CHANGE MOVING AVER.
0209	00247	062734R UNEQ	LDA TLOC3	NORMAL DOWNSWING.
0210	00250	066735R	LDR TLOC3+1	ADVANCE THE MOVING
0211	00251	072730R	STA TLOC1	AVERAGE ONE POINT.
0212	00252	076731R	STR TLOC1+1	
0213	00253	062732R	LDA TLOC2	
0214	00254	066733R	LDR TLOC2+1	
0215	00255	072734R	STA TLOC3	
0216	00256	076735R	STR TLOC3+1	
0217	00257	062212C	LDA TEMP	
0218	00260	066213C	LDR TEMP+1	
0219	00261	072732R	STA TLOC2	
0220	00262	076735R	STR TLOC2+1	
0221	00263	026361R	JMP ADD	INTEGRATE
0222*PEAK MAXIMUM LOCATING ROUTINE.				

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0223 00264 016002X MVAL JSR ..DLC      IS PRESENT PT =
0224 00265 104136C      DEF .PKHT,I  TO PT STORED AS PK MAX?
0225 00266 016007X      FAD TLOC2
      00267 000732R
0226 00270 006003      SZR,RSS
0227 00271 002002      SZA
0228 00272 026274R      JMP **2
0229 00273 026247R      JMP UNEQ      =,CONTINUE NORMALLY.
0230 00274 002020      SSA      PRESENT PT > PT IN PKHT?
0231 00275 026247R      JMP UNEQ      NO, CONTINUE NORMALLY.
0232 00276 062734R      LDA TLOC3      ADVANCE THE MOVING
0233 00277 066735R      LDR TLOC3+1    AVERAGE AND STORE SECOND
0234 00300 072730R      STA TLOC1      PT BACK IN PEAK HEIGHT.
0235 00301 076731R      STB TLOC1+1
0236 00302 062732R      LDA TLOC2
0237 00303 066733R      LDB TLOC2+1
0238 00304 072734R      STA TLOC3
0239 00305 076735R      STB TLOC3+1
0240 00306 016006X      DST .PKHT,I
      00307 104136C
0241 00310 016010X      FDV .2          DETERMINE HALF-HEIGHT
      00311 000751R
0242 00312 016006X      DST HHT
      00313 000743R
0243 00314 000040      CLE          DETERMINE PEAK LOCATION
0244 00315 062273C      LDA LCTR2      (TIMER PTS)
0245 00316 066272C      LDB LCTR1
0246 00317 042742R      ADA A2
0247 00320 002140      SEZ,CLE
0248 00321 006004      INB
0249 00322 046741R      ADB A1
0250 00323 000040      CLE
0251 00324 172266C      STA .PKL2,I
0252 00325 176240C      STR .PKL1,I
0253 00326 007500      CCB,CLE
0254 00327 062757R      LDA NDAVS
0255 00330 142266C      ADA .PKL2,I
0256 00331 002040      SEZ
0257 00332 006004      INB
0258 00333 146240C      ADB .PKL1,I
0259 00334 172266C      STA .PKL2,I
0260 00335 176240C      STB .PKL1,I
0261 00336 000040      CLE          CORRECT FOR POINT AVERAGING
0262 00337 066352C      LDR RUP
0263 00340 042353C      ADA RUP+1
0264 00341 002040      SEZ
0265 00342 006004      INB
0266 00343 146240C      ADB .PKL1,I
0267 00344 172266C      STA .PKL2,I
0268 00345 176240C      STR .PKL1,I
0269 00346 062212C      LDA TEMP
0270 00347 066213C      LDB TEMP+1
0271 00350 072732R      STA TLOC2
0272 00351 076733R      STR TLOC2+1
0273 00352 062064C      LDA EDAT      DETERMINE DATA ADDRESS
0274 00353 042756R      ADA MIN2      AT PK MAX( FOR PK WIDTH
0275 00354 072747R      STA MXD      DETERMINATION)
0276 00355 006400      CLR          CLEAR INCREASING SLOPE FLAG

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0277	00356	076722R	STB IFLAG	
0278	00357	007000	CMR	SET DECREASING SLOPE FLAG
0279	00360	076723R	STB DFLAG	
0280	00361	062724R	LDA SUM	INTEGRATING SECTION
0281	00362	066725R	LDB SUM+1	
0282	00363	016007X	FAD TEMP	
	00364	004212C		
0283	00365	072724R	STA SUM	
0284	00366	076725R	STB SUM+1	
0285	00367	036064C	ISZ EDAT	INCREMENT DATA ADDRESS
0286	00370	036064C	ISZ EDAT	
0287	00371	126120R	JMP .RTIM,1	
0288	00372	066723R	LDB DFLAG	REJECTION ROUTINES
0289	00373	006020	SSR	DECREASING SLOPE FLAG SET?
0290	00374	026415R	JMP PREJT	YES. REJECT PT.
0291	00375	066722R	LDB IFLAG	INCREASING SLOPE FLAG SET?
0292	00376	006020	SSR	
0293	00377	026404R	JMP DETUR	YES. GO ON.
0294	00400	006400	CLB	SET INCREASING SLOPE FLAG.
0295	00401	076723R	STB DFLAG	
0296	00402	007000	CMR	
0297	00403	076722R	STB IFLAG	
0298	00404	062732R	LDA TLOC2	NORMAL ROUTE FO FRONT
0299	00405	066733R	LDB TLOC2+1	HALF OF PEAK. ADVANCE
0300	00406	072734R	STA TLOC3	THE 3 PT MOVING AVERAGE.
0301	00407	076735R	STB TLOC3+1	
0302	00410	062212C	LDA TEMP	
0303	00411	066213C	LDB TEMP+1	
0304	00412	072732R	STA TLOC2	
0305	00413	076733R	STB TLOC2+1	
0306	00414	026361R	JMP ADD	INTEGRATE
0307	00415	066271C	LDB LOCFL	FRONT OR BACKSIDE OF PK?
0308	00416	006020	SSR	
0309	00417	026461R	JMP DREJT	BACKSIDE. ROUTINE DIFFERENT.
0310	00420	062732R	LDA TLOC2	REJECT 2ND PT BACK BY AVERAGING
0311	00421	066733R	LDB TLOC2+1	THE LAST PT & 3RD PT
0312	00422	016007X	FAD TLOC1	BACK & STORE IT. SUBTRACT
	00423	000730R		
0313	00424	016010X	FDV .2	AVERAGE FROM RAD PT. &
	00425	000751R		
0314	00426	072730R	STA TLOC1	THEN SUBTRACT FROM AREA
0315	00427	076731R	STB TLOC1+1	SUM.
0316	00430	016003X	JSB ..FCM	
0317	00431	016007X	FAD TLOC3	
	00432	000734R		
0318	00433	016003X	JSB ..FCM	
0319	00434	016007X	FAD SUM	
	00435	000724R		
0320	00436	016007X	FAD TEMP	ADD PRESENT PT TO AREA
	00437	004212C		
0321	00440	072724R	STA SUM	
0322	00441	076725R	STB SUM+1	
0323	00442	062732R	LDA TLOC2	ADVANCE MOVING AVERAGE.
0324	00443	066733R	LDB TLOC2+1	
0325	00444	072734R	STA TLOC3	
0326	00445	076735R	STB TLOC3+1	
0327	00446	062212C	LDA TEMP	
0328	00447	066213C	LDB TEMP+1	

0329	00450	072732R	STA TLOC2	
0330	00451	076733R	STB TLOC2+1	
0331	00452	007400	CCB	RESET INCREASING SLOPE FLAG.
0332	00453	076722R	STB IFLAG	
0333	00454	006400	CLR	
0334	00455	076723R	STB DFLAG	
0335	00456	036064C	ISZ BDAT	
0336	00457	036064C	ISZ EDAT	
0337	00460	126120R	JMP .RTIN,I	RETURN.
0338	00461	062734R	DREJT LDA TLOC3	BACKSIDE REJECTION. MOVE
0339	00462	066735R	LDE TLOC3+1	PTS. HAVE TO GET NEXT PT FOR
0340	00463	072730R	STA TLOC1	AVERAGING. PRESENT PT
0341	00464	076731R	STB TLOC1+1	IS TO BE REJECTED NEXT
0342	00465	062732R	LDA TLOC2	TIME. NEXT PT AND TLOC3
0343	00466	066733R	LDE TLOC2+1	WILL BE AVERAGED.
0344	00467	072734R	STA TLOC3	
0345	00470	076735R	STB TLOC3+1	
0346	00471	007400	CCB	SET REJECT FLAG (CHECKED
0347	00472	076736R	STB REJFL	EARLIER IN SUBROUTINE)
0348	00473	036064C	ISZ EDAT	
0349	00474	036064C	ISZ EDAT	
0350	00475	126120R	JMP .RTIN,I	RETURN.
0351	00476	062212C	OREJT LDA TEMP	BACKSIDE REJECTION ROUTINE.
0352	00477	066213C	LDB TEMP+1	
0353	00500	016007X	FAD TLOC3	
	00501	000734R		
0354	00502	016010X	FDV .2	
	00503	000751R		
0355	00504	072732R	STA TLOC2	STORE AVERAGE IN LAST PT.
0356	00505	076733R	STB TLOC2+1	AND ADD TO AREA SUM.
0357	00506	016007X	FAD SUM	
	00507	000724R		
0358	00510	072724R	STA SUM	
0359	00511	076725R	STB SUM+1	
0360	00512	002400	CLA	CLEAR REJECT FLAG
0361	00513	072736R	STA REJFL	
0362	00514	026167R	JMP HORN	CONTINUE NORMALLY ON PRES. PT.

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0364*****
0365* PEAK COMPLETION ROUTINE *
0366*****
0367 00515 000000 RTIM. NOP
0368 00516 062724R LDA SUM STORE SUM IN PEAK AREA.
0369 00517 066725R LDR SUM+1
0370 00520 016006X DST .AREA,I
00521 104210C
0371 00522 162504C LDA .SIN2,I DET. RETENTION TIME
0372 00523 166456C LDR .SIN1,I
0373 00524 007100 CML,CLE
0374 00525 003004 CMA,INA
0375 00526 002040 SEZ
0376 00527 006004 INB
0377 00530 000040 CLE
0378 00531 142266C ADA .PKL2,I
0379 00532 002040 SEZ
0380 00533 006004 INB
0381 00534 146240C ADR .PKL1,I
0382 00535 172266C STA .PKL2,I
0383 00536 176240C STR .PKL1,I
0384 00537 036210C ISZ .AREA INCREMENT PARAMETER ADDRESSES.
0385 00540 036210C ISZ .AFEA
0386 00541 036136C ISZ .PKHT
0387 00542 036136C ISZ .PKHT
0388 00543 002400 CLA CLEAR ALL FLAGS AND
0389 00544 072722R STA IFLAG TEMPORARY LOCATIONS.
0390 00545 072723R STA DFLAG
0391 00546 072726C STA NFLAG
0392 00547 072730R STA TLOC1
0393 00550 072731R STA TLOC1+1
0394 00551 072732R STA TLOC2
0395 00552 072733R STA TLOC2+1
0396 00553 072734R STA TLOC3
0397 00554 072735R STA TLOC3+1
0398 00555 072271C STA LOCFL
0399 00556 062322C LDA TAEST RESET START INTEGRATE COUNTER.
0400 00557 072721R STA TAB
0401 00560 000040 CLE DETERMINE THE NUMBER OF
0402 00561 062740R LDA BGPK2 POINTS IN THE PEAK
0403 00562 066737R LDR BGPK1
0404 00563 007000 CMB
0405 00564 003004 CMA,INA
0406 00565 002040 SEZ
0407 00566 006004 INB
0408 00567 000040 CLE
0409 00570 042273C ADA LCTR2
0410 00571 002040 SEZ
0411 00572 006004 INB
0412 00573 046272C ADR LCTR1
0413 00574 016011X DIV DAVS
00575 004355C
0414 00576 172275C STA .PKPT,I
0415 00577 036275C ISZ .PKPT
0416 00600 000040 CLE DETERMINE TIME OF START OF PEAK
0417 00601 062740R LDA BGPK2
0418 00602 066737R LDR BGPK1
0419 00603 042742R ADA A2

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0420	00604	002040	SEZ	
0421	00605	006004	INB	
0422	00606	046741R	ADB A1	
0423	00607	176402C	STB .PST1,I	
0424	00610	172430C	STA .PST2,I	
0425	00611	036402C	ISZ .PST1	
0426	00612	036430C	ISZ .PST2	
0427	00613	016012X PW	DLD DAPK,I	ROUTINE FOR DETERMINING
	00614	100746R		
0428	00615	016013X	FSB HHT	PK WIDTH AT 1/2 HEIGHT.
	00616	000743R		
0429	00617	006003	SZB,RSS	
0430	00620	002002	SZA	
0431	00621	026623R	JMP **2	
0432	00622	026630R	JMP PM	
0433	00623	002021	SSA,RSS	
0434	00624	026630R	JMP PM	FRONT SIDE PT FOUND.
0435	00625	036746R	ISZ DAPK	
0436	00626	036746R	ISZ DAPK	
0437	00627	026613R	JMP PW	
0438	00630	016012X PM	DLD MXD,I	
	00631	100747R		
0439	00632	016013X	FSB HHT	
	00633	000743R		
0440	00634	006003	SZB,RSS	
0441	00635	002002	SZA	
0442	00636	026640R	JMP **2	
0443	00637	026650R	JMP HH	BACKSIDE PT FOUND.
0444	00640	002020	SSA	
0445	00641	026645R	JMP **4	
0446	00642	036747R	ISZ MXD	
0447	00643	036747R	ISZ MXD	
0448	00644	026630R	JMP PM	
0449	00645	062747R	LDA MXD	
0450	00646	042756R	ADA MIN2	
0451	00647	072747R	STA MXD	
0452	00650	062746R HH	LDA DAPK	CALCULATE NUMBER OF PTS.
0453	00651	003004	CMA,INA	
0454	00652	042747R	ADA MXD	
0455	00653	001100	ARS	DIVIDE BY 2(DOUBLE PRECISION)
0456	00654	042755R	ADA PLUS1	
0457	00655	172350C	STA .PKWD,I	
0458	00656	162350C	LDA .PKWD,I	CALC. HETP
0459	00657	016004X	JSB FLOAT	
0460	00660	072724R	STA SUM	
0461	00661	076725R	STR SUM+1	
0462	00662	162240C	LDA .PKL1,I	
0463	00663	166266C	LDB .PKL2,I	
0464	00664	016005X	JSB .PACK	
0465	00665	000037	DEC 31	
0466	00666	016010X	FDV SUM	
	00667	000724R		
0467	00670	016010X	FDV DAV	
	00671	004562C		
0468	00672	072724R	STA SUM	
0469	00673	076725R	STR SUM+1	
0470	00674	016014X	FMP SUM	
	00675	000724R		

0471	00676	016014X	FMP CONST	
	00677	000753R		
0472	00720	016006X	DST .HETP,I	
	00701	104556C		
0473	00702	062560C	LDA LNG	
0474	00703	066561C	LDB LNG+1	
0475	00704	016010X	FDV .HETP,1	
	00705	104556C		
0476	00706	016006X	DST .HETP,I	
	00707	104556C		
0477	00710	036556C	ISZ .HETP	
0478	00711	036556C	ISZ .HETP	
0479	00712	036240C	ISZ .PKL1	
0480	00713	036266C	ISZ .PKL2	
0481	00714	036350C	ISZ .PKWD	
0482	00715	002400	CLA	
0483	00716	072724R	STA SUM	
0484	00717	072725R	STA SUM+1	
0485	00720	126515R	JMP RTIM.,1	RETUFW.

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0487*****
0488* CONSTANT SECTION *
0489*****
0490 00721 000000 TAF DEC 0 COUNTER FOR INTEGRATE START
0491 00722 000000 IFLAG OCT 0 INCREASING SLOPE FLAG
0492 00723 000000 DFLAG OCT 0 DECREASING SLOPE FLAG
0493 00724 000000 SUM FSS 2 AREA SUM
0494 00726 000000 .LAS1 OCT 0 NOISE CHECK PT ON BASELINE
0495 00727 000000 .LAS2 OCT 0
0496 00730 000000 TLOC1 FSS 2 3RD PT BACK
0497 00732 000000 TLOC2 FSS 2 LAST POINT
0498 00734 000000 TLOC3 FSS 2 END PT BACK
0499 00736 000000 REJFL OCT 0 REJECT FLAG ON DOWNSLOPE
0500 00737 000000 RGPK1 OCT 0 LOCATION OF START OF PEAK
0501 00740 000000 RGPK2 OCT 0
0502 00741 073465 A1 OCT 73465 TIMER (POSITIVE RESET)
0503 00742 112000 A2 OCT 112000
0504 00743 000000 HHT FSS 2 HALF-HEIGHT OF PEAK
0505 00745 177777 MIN1 OCT -1
0506 00746 000000 DAPK OCT 0 DATA ADDRESS AT PEAK BEGINNING
0507 00747 000000 MXD OCT 0 DATA ADDRESS AT PEAK MAX.
0508 00750 000000 CTRT DEC 0
0509 00751 040000 .2 DEC 2.
00752 000004
0510 00753 054270 CONST DEC 5.545
00754 051006
0511 00755 000001 PLUS1 OCT 1
0512 00756 177776 MIN2 OCT -2
0513 00757 000000 NDAVS OCT 0 PEAK LOCATION CORRECTION
0514 COM DATA(2100),EDAT,EDT.,PKHT(40),.PKHT,PKHT.
0515 COM AREAC(40),.AREA,AREA.,TEMP(2),PKL1(20),.PKL
0516 COM PKL1,.PKL2(20),.PKL2,PKL2,.NFLAG,LOCFL
0517 COM LCTR1,LCTR2,PKPT.,.PKPT,PKPTS(20),TARST,CT
0518 COM PKWD(20),.PKWD,PKWD.,RUP(2),CUP,DAVS
0519 COM PKST1(20),.PST1,PST1,.PKST2(20),.PST2,PST2
0520 COM SIN1(20),.SIN1,SIN1,.SIN2(20),.SIN2,SIN2.
0521 COM HETP(40),.HETP,HETP.,LNG(2),DAV(2)
0522 END
** NO ERRORS*

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APPENDIX C

LISTING OF OTHER SOFTWARE ROUTINES

OUTPT	A routine to output signals through the 16-bit duplex register board (GPR card).
VLTRD	A routine to read the BCD input from the digital voltmeter.
RDAV	A routine to set the multiplexer to a given device and then read and average a specified number of points from that device.
KYRDR	A routine to read an ASCII statement from the teleprinter keyboard.
WRITE	A routine to write an ASCII buffer on the teleprinter.
EDUMP	A routine to print an array of real numbers in an E12.6 format on the teleprinter.
WDPUN	A routine to punch one binary number on the high speed punch (non-.IOC. control).
.VMFL	A routine to convert a BCD number to a binary floating point number.
.AD2B	A routine to clear a five word ASCII input buffer.
AD2BN	A routine to convert an ASCII decimal number to a binary single precision integer.
.B2DC	A routine to convert a single precision binary number to an ASCII decimal number.
WRDP	A routine to convert to ASCII decimal and print on the teleprinter an array of binary double precision integer numbers.
.ZERO	A general purpose routine to clear a variable length buffer.
FLOAT	A routine to float an integer.

.PACK A routine to pack in the exponent of a floating point number and normalize the number.

..DLC A routine to load into the registers a floating point number and make the two's complement of it.

..FCM A routine to make the two's complement of a floating point number.

DLD Load a floating point number into the registers.

DST Store a floating point number.

.FAD Floating point addition.

.FSB Floating point subtraction.

.FMP Floating point multiplication.

.FDV Floating point division.

.MPY Integer multiplication.

.DIV Integer division.

.FLUN Unpack a normalized floating point number.

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