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To the Graduate Council:

I am submitting herewith a thesis written by Edwin Ray Shelton entitled "Digital Data Acquisition and Numerical Computations in Electrochemistry: Cyclic Voltammetry." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

James Q. Chambers

James Q. Chambers, Major Professor

We have read this thesis
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DIGITAL DATA ACQUISITION AND NUMERICAL COMPUTATIONS IN ELECTROCHEMISTRY: CYCLIC VOLTAMMETRY

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

Edwin Ray Shelton

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ABSTRACT

An introduction to the evolution of the use of computers in the field of electrochemistry from data processing to on-line real-time applications has been presented. In addition, a discussion is given of the calculations of the parameters necessary to evaluate cyclic voltammograms and the problems inherent in these calculations.

A software package is presented which will acquire and analyze cyclic voltammetric data. Features of the program include the following.

1. On-line data acquisition over a time scale of 4 sec to 27 μsec per data point is available to the user.
2. Subtraction of background currents may be carried out by either of two methods. Backgrounds previously recorded and stored on LINCtapes or linear background defined by cursors presented on an oscilloscopic display may be subtracted from the data.
3. Background corrected data are stored on LINCtape and may be saved for later evaluation or evaluated immediately.
4. Determination of the peak potentials and peak currents is done by numerical analysis after an initial guess of the peak maxima is entered to the program via a cursor display.
5. Correction of the data for $1/t^{1/2}$ current decays is also made via a cursor display which is used to define a region of the post peak wave to which an equation with $1/t^{1/2}$ dependence is fitted. Using this equation, the contribution of $1/t^{1/2}$ decay at each remaining data point in the cyclic voltammogram is subtracted, and the corrected data are displayed on the oscilloscope for user inspection.

6. A printout of the calculated parameters — peak potential, half-peak potential, peak width, peak current, and current function — is given in tabular form.
7. Previously evaluated data from LINCtape for reevaluation or teletypewriter copies of the experimental and calculated parameters may be printed out.

Preliminary investigations on the model system 3,3'-dimethoxybenzidine dihydrochloride at the carbon paste electrode demonstrated that the program possessed the desired accuracy in recording and evaluating data.

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CHAPTER I

INTRODUCTION

The advent of minicomputers in the last ten to fifteen years has relieved the modern scientist of much of the drudgery formerly required for acquisition and analysis of data. Most manufacturers of minicomputers supply generalized software packages for data acquisition. However, due to the generalized nature of these systems, such programs are not always well suited to the specific needs of an individual user. For this reason, it is necessary for many users to develop their own software for specific applications.

A variety of programming languages and computer configurations are available to the software developer. The hardest approach to programming is to use machine language. Machine language requires coding the entire program in binary, i.e., using only ones and zeros. Assembly languages are quicker to program since the code is developed using symbolic names for many of the standard computer operations such as addition and storage of variables. Much less time consuming is programming in an interpretive language. Essentially this type of program has a routine which decodes the program at run time and then calls subroutines to execute a statement. A high level language such as Fortran is decoded by a compiler. In addition to decoding the user's program, the compiler calls standard library routines to perform the mathematical operations for the program and links the user program with the subroutines and loads the combination into core.

Of great importance to the software developer is the configuration in which the computer will be used. In an off-line configuration the computer is used strictly for purposes of calculations. When used in an on-line configuration the computer has active control of the data acquisition instrumentation. In real-time applications, the computer monitors the data acquisition and as a result of computations made during the acquisition process, is used in guiding either the physical process occurring or the rate of data acquisition. A program which stops at certain points and waits for the user to make a decision about what computations will then be made on the data is a user-interactive configuration.

The purpose of this work was to develop an assembly language program to obtain data from cyclic voltammetric experiments and analyze it in an on-line, user-interactive configuration. The advantages of such a program may best be appreciated after a brief survey of some of the techniques used in the field of electrochemistry and a description of what would be required of such a program for cyclic voltammetric data analysis.

A. Digital Methods of Acquisition and Processing of Electrochemical Data

1. Off-line Methods

A laborious technique that has been practiced from the earliest use of computers, and is still used today, is the reduction of analog data to digital form by hand. An example of this method is the recording of electrochemical data by an X-Y recorder, then reading the values

from the plot. The data would then be punched onto cards or paper tape for submission to a computer. After a period of several hours or perhaps even days, the evaluated data would be returned to the user for further consideration.

Herman and Bard[1] improved on this method by using a digital recorder for chronopotentiometry. The output of the digital recorder was connected to a digital printer. Thus, the data were available for immediate inspection, but it was still necessary to punch the data onto data cards to read them into a computer.

Further improvement was reported by Breiter[2] for acquisition of cyclic voltammetric data at slow sweep rates (less than 100 mv sec^{-1}). The data were recorded by a multichannel analyzer. The analyzer was in turn connected to a paper tape punch. The paper tape could then be read directly into a computer. Lauer and Osteryoung[3] reported a similar system for the study of chronocoulometry. Brown, et al.[4] used a digital voltmeter connected to a card punch for recording a.c. and d.c. polarography over long periods of time. The minimum time for recording a data point was one minute.

The above methods illustrate means of converting data to digital form with less time and effort than had been previously used. However, there was not shown any way of decreasing the computational time, since the data still had to be read into a large computer and the experimenter had to wait as long as before to obtain the results of the calculations.

2. On-line Methods

a. Non-user interactive systems. Anson, et al.[5] were apparently the first to report a generalized system for computer control of

acquisition and analysis of electrochemical data. Their system consisted of a small computer (4K core), an analog to digital converter (ADC) and an external real-time clock. Once the necessary parameters for a run were given to the computer, it controlled the initiation and rate of data acquisition. Upon completion of data acquisition, the data were analyzed by a program written in assembly language. The system was initially designed for double step chronocoulometry, but the authors state that only minor modifications in the interfacing and program are necessary to run other experiments such as potential sweep chronoamperometry or chronopotentiometry.

Lauer and Osteryoung[6] first reported the use of a computer to completely control electrochemical experiments. The parameters necessary to run the experiment are input to the computer. The computer then calculates the potentials which should be applied to the cell. Once the experiment is started by pushing a button on the computer, the potential is generated by means of a digital to analog converter under computer control. The digital to analog converter works by reading a number placed in the accumulator and converting it into a voltage. The computer also measures the output of the cell and terminates the experiment. Although the configuration reported was used for analysis of chronocoulometry, the approach is general enough to be applied to other electrochemical methods.

Perone, Jones and Gertknecht[7] also reported the use of a digital to analog converter to supply the applied potential to stationary electrode experiments. The major difference from the configuration reported by Lauer and Osteryoung is that the computer was used in a real-time

mode. The computer monitored the output of the cell, and whenever a reduction peak was encountered, the computer discontinued the potential sweep and maintained a constant potential. This was done to minimize the currents produced by easily reduced species near the electrode. After a delay period, calculated by the computer, the potential sweep was reinitiated by the computer and the experiment continued until the end of the specified voltage range was reached. The use of this technique allows any reducible species to dissipate from the diffusion layer, thus causing less interference for any following waves.

Other programs reported by Perone, et al.[8,9] were used for deconvolution of cyclic voltammetric peaks.

An application, of great chemical significance, of an on-line configuration was reported by Mohilner.[10] A minicomputer was used to control all the apparatus of a capillary electrometer based on the bubble pressure principle. The computer monitored and varied the pressure applied to the mercury drop, in additon to supplying the potential to the electrode via a digital to analog converter. Since the entire system was controlled by the computer during the entire acquisition period, typically three hours, a great savings in the time of the experimenter was achieved. The computer control of the pressure and potential achieved results comparable to capacitance bridge measurements in simple salt solution, but superior results for solutions of neutral organic compounds.

b. User interactive system. Many types of electrochemical data, such as chronoamperometry, need only to be corrected for contributions from background currents. In such a situation the data may be acquired,

a stored background subtracted, and numerical analysis performed. In other methods such as cyclic voltammetry other contributions to the measured current are present. For example, current contributions from previous peaks must be taken into account for cyclic voltammetry. For nonideal decays of previous peaks, user interaction with the computer to decide the region of best fit for decay curves is often the best approach due to the complexity of the experimental data.

Perone, et al.[11] have reported the use of such a system. The data are acquired in a real-time configuration and the data stored on a disk. A second program is called into core for analysis of the data. The second program is written in Focal (Digital Equipment Corporation). Focal, a high level, interpretive language, facilitates easier programming at the expense of core space. This factor is offset by the use of a 32K disk, from which data may be rapidly read into core as needed. The user decides what regions may be best fit by linear baselines and $1/t^{1/2}$ decay curves. These regions are specified through the use of potentiometer controls or "joysticks" which control the x-y coordinates of cursors on the oscilloscope display of the data. Once the regions to be fitted are decided upon, the calculated curves are subtracted from that peak and following peaks. This process gives corrected values of currents for the succeeding peaks and removes the current contribution due to the present peak from the following peaks.

Moses[12] has described the use of an assembly language program to obtain cyclic voltammetric data and to perform some analyses of the data. This program utilizes cursors whose position may be read in terms of millivolts and microamperes. One of the cursors is placed at

the maximum of a peak and the peak height and the potential are read from a digital display on the oscilloscope. Half-peak potentials may be determined by placing the cursor such that one half of the peak current is read and moving the cursor to lie on the displayed curve. Current functions are also calculated after a peak height is registered by striking a key on the teletype keyboard. This program has been used successfully to evaluate peak potentials of a large set of linear sweep voltammograms at various sweep rates and concentrations.[13]

B. Cyclic Voltammetry

1. The Method

Cyclic voltammetry is an electrochemical technique which can give much qualitative and quantitative information about electrode processes. The topic has been discussed in considerable detail by Adams.[14] The method, apparently first practiced by Sevcik,[15] is a variation of linear sweep voltammetry. In cyclic voltammetry a triangle-wave potential ramp is applied between the working electrode and the reference electrode. For a three electrode system consisting of a working electrode, a counter electrode and a reference electrode, the current passing between the working and counter electrodes is monitored. There are two equivalent methods of recording cyclic voltammograms which differ only in the manner of presentation. The first is current-time recording. The second is current-potential recording. A typical voltammogram, recorded by the current-potential method, for a reversible couple is illustrated in Figure 1.

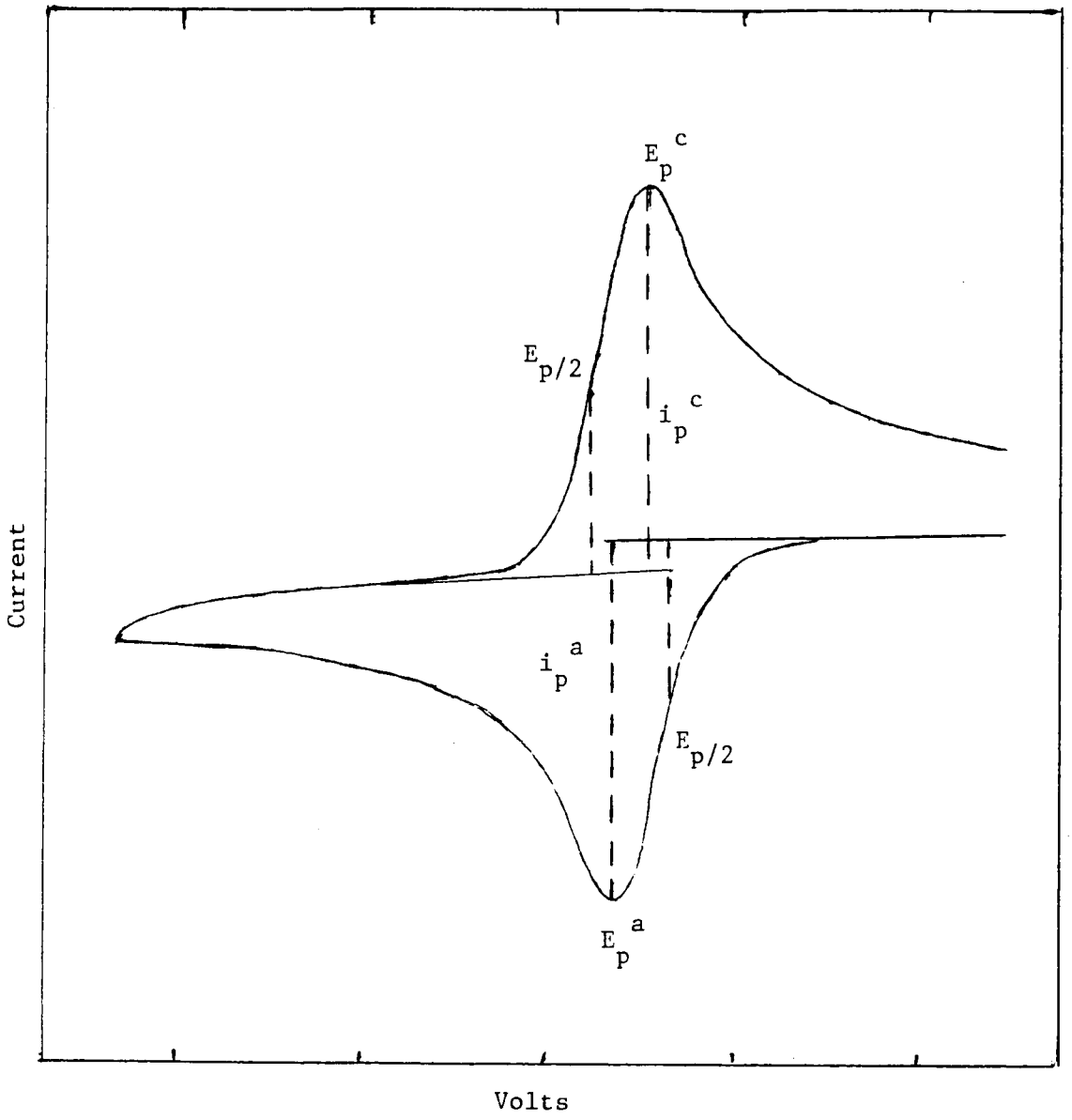


Figure 1. Parameters of cyclic voltammetry.

2. Measured Parameters

The measurements taken from a cyclic voltammogram used for diagnostic criteria are shown in Figure 1. The peak potentials E_p^c and E_p^a are measured at the points where the current has a maximum on the cathodic and anodic scans respectively. The currents measured at E_p^c and E_p^a are i_p^c and i_p^a respectively. For any peak $E_{p/2}$ is the potential prior to the current maximum which corresponds to a value of $i_{p/2}$.

The value of the current maximum for any peak in a cyclic voltammogram is given by the Randles-Sevcik equation:

$$i_p = kn^{3/2}AD^{1/2}C^bV^{1/2}$$

where i_p is the current in amperes, A is the area of the electrode in cm^2, D is the diffusion coefficient of the reacting species in cm^2/sec, C^b is the bulk concentration of the reacting species in moles/liter, V is the rate of potential change in volts/sec, n is the number of electrons involved in the overall electrode reaction, and k is a constant known as the Randles-Sevcik constant, whose value depends on the type of process occurring at the electrode.

Technically, the evaluation of peak currents is not easy. As noted from Figure 1, the current decays slowly past E_p^a. For diffusion limited processes the current in this potential region is given by the Cottrell equation:

$$i = \frac{nFAC^bD^{1/2}}{\pi^{1/2}t^{1/2}} \qquad (1)$$

where t is time in sec, F is the Faraday, and all other variables are as previously defined. It is evident from the Cottrell equation that as time increases the current decrease is proportional with $1/t^{1/2}$.

Therefore, when a second peak is encountered, there is a contribution to the measured current from the previous peak. In order to evaluate the second or later peak currents in a cyclic voltammogram, the value of the current contribution from a previous peak must be calculated and subtracted from the peak of interest in order to obtain a base line. Adams[14] presents various techniques for manual correction of the $1/t^{1/2}$ decay.

Another problem in evaluating peak currents is the correction for background currents. The somewhat nebulous term background current is used to describe all processes taking place at the electrode that are not due to the reaction of interest. These may include non-faradaic processes such as charging the double layer, reaction of impurities in the electrolyte, or reaction of the electrolyte or solvent.

One method of subtraction of background current is to run the solvent and supporting electrolyte at the same conditions the compound to be studied is run, and subtract the contribution from the cyclic voltammograms of the compound. This method suffers the disadvantage that it assumes the double layer capacity, and hence the charging current does not change in the presence of the compound of interest. Another method is to assume that the background current varies linearly with the applied potential and to draw a straight line through the linear portion of the cyclic voltammograms preceding the first peak and subtract this value from the peak current on the forward scan. This assumes that the double layer capacity remains constant in the potential region of the peak. On the reverse sweep the background current is assumed to be

of the same magnitude but of opposite sign as that for the forward sweep.

The program described in this thesis has the capability of both of these methods of background subtraction.

3. Diagnostic Criteria

Among the criteria used for analyzing cyclic voltammograms are the peak width, the ratio of anodic to cathodic peak currents and the current function.

The separation of E_p and $E_{p/2}$ (peak width) is related to the number of electrons transferred. For a reversible couple, Matsuda and Ayabe[16] determined that E_p and $E_{p/2}$ are related to the polarographic $E_{1/2}$, and therefore to each other by the following equations:

$$E_p = E_{1/2} - \frac{0.029}{n} \text{ volts} \tag{2}$$

$$E_{p/2} = E_{1/2} + \frac{0.028}{n} \text{ volts} \tag{3}$$

$$|E_p - E_{p/2}| = \frac{0.057}{n} \text{ volts} \tag{4}$$

For a reversible couple, which has a one to one stoichiometric ratio, the ratio of the anodic to cathodic peak currents should be equal to one. The ratio is taken such that the peak current on the forward sweep is the denominator.

The current function (CF) at the peak maximum may be calculated as follows:

$$CF = \frac{i_p}{AC\sqrt{V}} \tag{5}$$

Substitution of the value of i_p from the Randles-Sevcik equation reveals that for a particular electrode process, the current function is dependent on the number of electrons transferred and the diffusion coefficient of the electroactive species.

The examples given above apply only to simple charge transfer, reversible couples. Many other cases have been studied by various workers. For a review of the work done for other cases, the reader is referred to Adams[14] and Brown.[17]

CHAPTER II

INSTRUMENTATION

A. PDP-12A

A PDP-12A computer manufactured by Digital Equipment Corporation (DEC) was used for this work. The PDP-12A is a versatile, dual mode computer. It has the combined characteristics and working capabilities of the PDP8/I and the LINC computers also manufactured by DEC. This model uses a basic word length of 12 bits and has a central processor cycle time of 1.6 microseconds. Most instructions require two or three cycles for execution.

The computer used in this work has two sections of core, each consisting of 4096_{10} 12 bit words. Each of these sections is subdivided into four fields of 1024_{10} words if working in LINC mode or 32_{10} pages of 128_{10} words if working in 8-mode.

Some of the features of the PDP-12A are:

1. A VR12 display cathode ray tube (CRT). The display on the CRT is controlled by the VC12 display control. The CRT may be programmed to display either points or characters. The face of the CRT is divided into a 512_{10} by 512_{10} grid for purposes of specifying the location of any point to be displayed on the screen. A schematic representation of the grid is shown in Figure 2. The grid coordinates are given in octal notation.
2. An AD12 Analog to Digital Converter and Multiplexer system consisting of 16 input channels, a Sample and Hold amplifier, a Multiplexer, and a 10 bit ADC. Eight of the channels are for

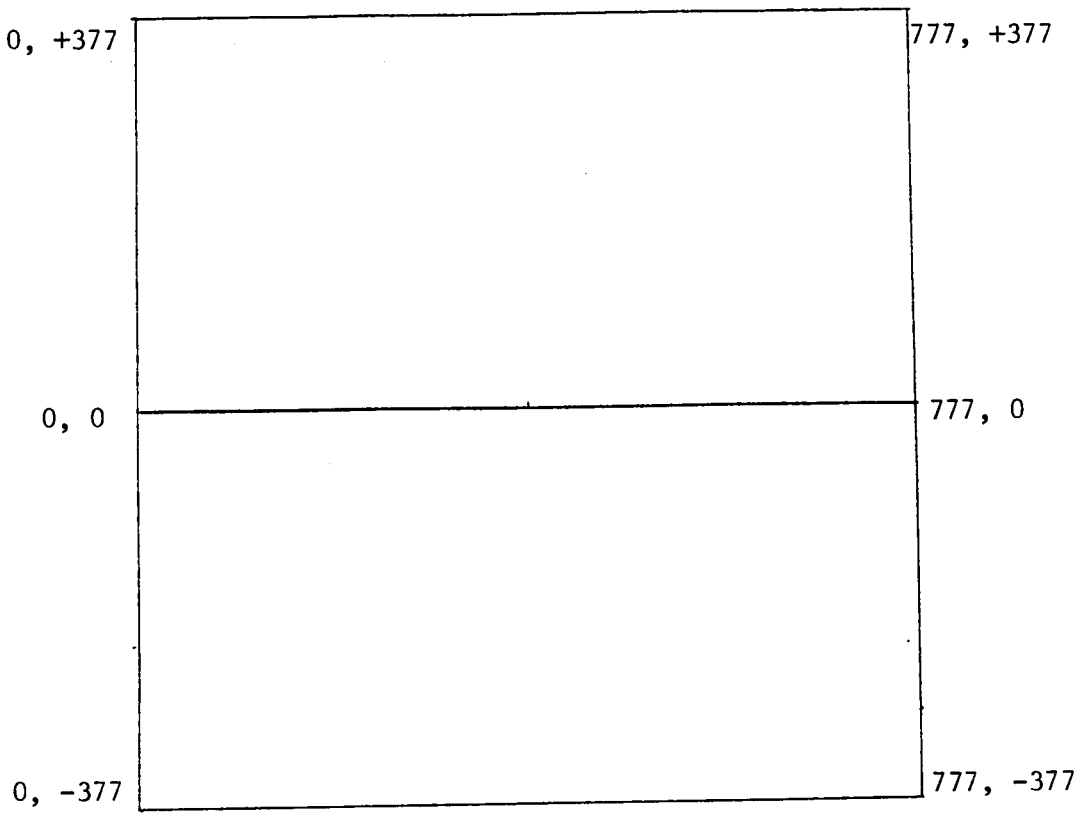


Figure 2. Schematic representation of grid coordinates of the VR12 display scope.

external inputs. The voltage range of these inputs is + 1 volt to - 1 volt with a sensitivity of approximately 2 mv per count. The other eight channels are controlled by continuously variable knobs located on the front of the computer. The range of these channels is $+777_8$ to -777_8. Any of these channels may be sampled by issuing a LINC mode command and the channel number.

3. Two TU55 LINCtape transports. Each tape may contain either 1000_8 or 1600_8 addressable blocks consisting of 256_{10} words. Transfers between tape and core are made in units of 256 words.
4. A KW12-A Real Time Clock. The KW-12A may be programmed to synchronize the central processor to external events at time intervals from 2.5 μsec to over 40 seconds. The clock may be set ticking at any of the five different rates of 400, 100, 10, 1, or .1KHz. The clock also employs Schmidt triggers for each of the three clock input channels, which provide a selection of any threshold between $\pm$ 6V with either positive or negative-going slope for synchronization of the computer with real-time events.
5. Six programmable relays. These relays may be used to trigger external equipment connected to the computer.

   A block diagram of the PDP-12A is shown in Figure 3.
6. An ASR-33 teletype. Input and output to the computer is made through an ASR-33 teletype.

B. Potentiostats

The program presented in this thesis provides the software interface for two potentiostats which have somewhat different designs

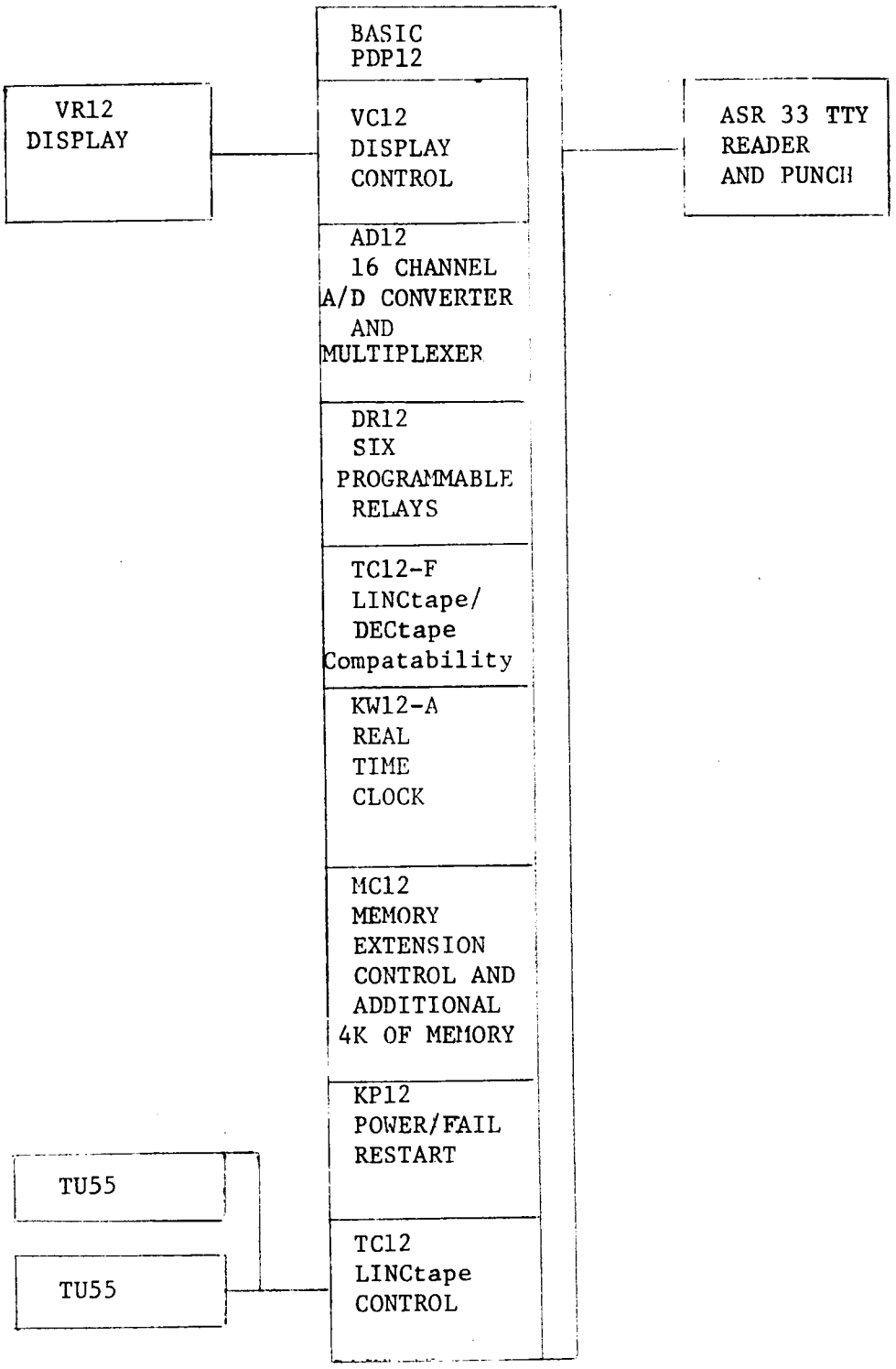


Figure 3. Block diagram of PDP12-A.

and operating characteristics. One potentiostat is designed for cyclic voltammetric measurements on long time scales (> 10 sec), or slow sweep rates. The other potentiostat is designed for short time scales (< 10 sec) or fast sweep rates.

The slow sweep instrument, designed and constructed by P. R. Moses (University of Tennessee), incorporates features convenient for computer control. The circuitry has been described in detail by Moses.[12]

An instrument after Brown,[18] et al., is used for fast sweep rates. This instrument consists of a Hewlett-Packard 3300A function generator equipped with a 3302A phase lock trigger plug-in. The potential from the function generator is fed to a three electrode potentiostat utilizing transitorized operational amplifiers. The potentiostat is also equipped with circuitry for compensating for the iR drop between the tip of the reference electrode and the working electrode. A small interface board used to scale the output of this instrument to voltage compatible with the PDP-12 ADCs has been described by Moses.[12]

CHAPTER III

THIS PROGRAM

A. Commercial Software Utilized

1. LAP6-DIAL

LAP6-DIAL is a standard package provided by Digital Equipment Corporation for use with the PDP-12 computer for editing and assembling 8-mode and LINC mode assembly language programs. The package also contains routines for saving and retrieving named files on or from magnetic tape (LINCtape). The specific version of LAP6-DIAL used at this location is DIAL-MS. DIAL-MS is designed for the user with 8K of core and will support three different types of disks in addition to LINCtape. The basic version of DIAL-MS received with the computer was designed for LINCtapes with 1000_8 blocks per tape. A modification of DIAL-MS was purchased from Digital Equipment Computer Users Society (DECUS) which operates on LINCtapes with a format of 1600_8 blocks per tape (256_{10} 12 bit words per block). This results in a 75% increase of usable space per tape.

One very noticeable problem encountered when using DIAL-MS for assembling programs containing both 8-mode and LINC mode instructions was the large amount of time the program spent going to tape blocks 341 and 342 on LINCtape 0. This problem was caused by the transfer of the appropriate symbol table for either 8-mode or LINC mode into core whenever instructions for the particular mode were encountered in the program being assembled. A solution to this problem was reported by Rapoport.[19] He presented an easily implemented modification to DIAL-MS

which permits both symbol tables to remain in core in exchange for a decrease of 64 symbols in the user symbol table. Since there are 895_{10} spaces normally allocated for user symbols, this is only a 7.2% decrease in user symbol space. Using the modified version of DIAL-MS, assembly time for this program was reduced from twenty minutes to ten and one-half minutes.

2. Twenty Seven Bit Floating Point Package

The 27 bit Floating Point Package (FPP: DEC number DEC-08-NFPEA-A) provides the user with the capability of performing addition, subtraction, multiplication and division with the retention of approximately eight significant decimal digits. The range of the Floating Point Package is 10^{+38} to 10^{-38}. The Package contains commands which will convert normal 12 bit binary integers to 27 bit binary floating point numbers with an 8 bit binary exponent and vice-versa. The package also has input and output routines. Integers, decimal numbers and floating point numbers are accepted by the package via the teletype keyboard and these numbers must be terminated by either a space or any alphabetical character except the letter E. Output from the package may be E14.7 or Fxx.y, where xx can be any number less than 72_{10} (and y should not exceed 7.0). If y is zero then no decimal point is printed. The Package rounds decimals greater than .5 to the next highest number rather than truncating them.

3. DIAL I/O Routines

DIAL-MS has a set of ready to use read, write, or move input/output routines to perform block transfer on LINCtape. The routines are stored

on blocks 322 and 323 of LINCtape 0 of a DIAL-MS system. These routines were saved as a named file and assembled with the rest of the program. The I/O routines are used extensively in the transfer of data from tape to core and moving data to various places in core.

4. Teletype Message Output Routine

A modified version of the standard DEC teletype output routine (DEC number DEC-08-FIKA-PA) is used to print stored messages. The modifications include the ability to call the subroutine from any location in the same 4K field as the output routine, the use of "!" to indicate the printing of a carriage return-line feed, and the use of a "$" to indicate the end of the message.

B. Major Program Options

1. Mode Options

a. Mode 1. When the program is in mode 1, data from background solutions may be acquired and averaged or normal cyclic voltammetric data may be acquired. Once a normal cyclic voltammogram has been acquired, the background current may be subtracted by using a background stored on LINCtape or by using cursors displayed on the VR12 CRT. Once the background has been subtracted from a cyclic voltammogram, the data are stored on LINCtape for later evaluation and the program restarts at the beginning.

b. Mode 2. Mode 2 is the numerical evaluation portion of the program. When stored data are recalled from LINCtape, this part of the program allows the user to select the peaks of interest for calculation

of the peak potential, half-peak potential, peak width, peak current, and current function for a cyclic voltammogram. When the calculations are completed, the above values are printed on the teletype in tabular form. Mode 2 may also be used to print out these values from previously evaluated data stored on tape.

c. Mode 3. Mode 3 is used to link Modes 1 and 2 together. The program will start and proceed in the same manner as Mode 1 until after the data are stored on LINCtape. At this point, control of the program is transferred to Mode 2 for immediate evaluation of the data.

2. Sense Switch Options

a. Modes 1 and 3. Six sense switches are used to determine the flow of the program in Modes 1 and 3. The effect of each switch setting is shown in Figure 4. It may be seen from the flowchart of the main program in Appendix A, that all of these settings are not independent of other switch settings. For example, the settings of SNS's 1 and 3 apply only when SNS 0 = 1. Similarly SNS 2 only changes the flow when SNS 0 = 0. These logic operations are illustrated in Figure 4.

b. Mode 2. In Mode 2 there is only one sense switch option. SNS 4 is used to determine whether new data are being input for calculations or previously calculated parameters are to be printed out. The settings are shown in Figure 4.

3. Other Options

Other options are presented to the user throughout the program in the various subroutines. These options will be explained in the discussion of the individual subroutines.

SNS 0 = 0	SINGLE SCAN RECORDING
SNS 0 = 1	DOUBLE SCAN RECORDING
SNS 1 = 0	GET NEW FREQUENCY
SNS 1 = 1	USE OLD FREQUENCY
SNS 2 = 0	GET NEW SWEEP RATE
SNS 2 = 1	USE OLD SWEEP RATE
SNS 3 = 0	PARTIAL SCAN NOT AVAILABLE
SNS 3 = 1	PARTIAL SCAN AVAILABLE
SNS 4 = 0	SAVE DATA AS NORMAL CYCLIC
SNS 4 = 1	SAVE DATA AS BACKGROUND CYCLIC
SNS 5 = 0	USE STORED DATA FOR BACKGROUND SUBTRACTION
SNS 5 = 1	USE CURSORS FOR BACKGROUND SUBTRACTION

Mode 1

SNS 4 = 0	CALCULATE DIAGNOSTIC PARAMETERS
SNS 4 = 1	PRINT OUT PREVIOUSLY CALCULATED PARAMETERS

Mode 2

Figure 4. Sense switch options for Mode 1 and Mode 2.

C. Discussion of Subroutines

Prior to the discussion of the individual subroutines a brief introduction to the user response to messages and displays is presented. There are four basic types of messages printed by the program. The first type is for informational purposes only, such as printing the standard deviation of a calculation. The second type tells the user to do something, such as setting the sense switches. The third and fourth type ask the user to give the program some information. Any message terminated by a colon requires the user to type in a number. This number may be an integer, decimal or floating point number. The input is terminated by entering any letter of the alphabet except an E or hitting the space bar of the teletype. When the program asks for a tape file number, only decimal numbers between 0 and 98 may be used. Messages which are terminated with a question mark require a reply of Y for Yes and any other key on the teletype for No. When the user has taken sufficient time to view a display and wishes to continue with the program, the display may be exited by striking any key on the teletype.

1. Determination of Number of Clock Ticks/Data Point

a. Double scan recording. Subroutine R1 is used to determine the frequency of the clock and calculate the number of clock ticks at that frequency between the acquisition of data points. The routine asks for the frequency and total voltage range. The number of seconds between data points is calculated from the formula:

$$\frac{\text{seconds}}{\text{point}} = \frac{1}{\text{frequency(cycles/sec)}*1000\text{(data points/cycle)}} \qquad (6)$$

Once the number of seconds/point has been determined, the routine selects the optimum clock frequency to obtain as high a precision of timing as possible. The number of ticks/point for a frequency may not exceed 2000_{10} which is the maximum value which can be converted into an integer by the FPP. This corresponds to a minimum frequency of 0.005 Hz. The flowchart for the routine is shown in the Appendix, p 60. It may be noted from the Appendix that the smallest number of ticks/point at 400 KHz.is eleven. This corresponds to a time of 27.5 μsecs between data points. This is the fastest rate allowed since the actual time to acquire a data point and to store it requires 25.0 μsecs. This corresponds to a maximum frequency of 36.3 Hz.

When SNS 3 is set equal to one, it is possible to scan only part of the total voltage range without changing any of the settings on the potentiostat or reentering the frequency and total voltage range. The new value of seconds/data point is determined by taking a fractional part of the seconds/data point calculated by R1. This calculation is made by subroutine R2 (see Appendix, p 60) from the following equation:

$$\frac{\text{new seconds}}{\text{data point}} = \frac{\text{old value of seconds}}{\text{data point}} * \frac{\text{partial scan range}}{\text{total scan range}} \quad (7)$$

Once this value has been calculated, subroutine R1 calculates the new value of ticks/data point as described above. The maximum frequency that may be used for partial scans is determined from the following inequality:

$$\text{Freq} \frac{\text{total scan range}}{\text{partial scan range}} \leq 36.3 \text{ Hz} \quad (8)$$

If too large or too small a frequency is entered, the routine is exited and an error message is printed.

b. Single scan recording. Subroutine R3 (see Appendix, p 61) is used to determine the frequency of the clock and calculate the number of clock ticks, at the chosen clock frequency, between the acquisition of the first point of a pair of data points. The number of seconds between the acquisition of the initial data point of a pair of data points is calculated from the following equation:

$$\frac{\text{seconds}}{\text{point}} = \frac{\text{total voltage scan range (mv/cycle)}}{\text{sweep rate (mv/sec)*(1000 points/cycle)}} \qquad (9)$$

The optimum clock frequency is chosen in a manner similar to that described for the double scan recording routine. The decision process is shown in the Appendix, p 61.

The maximum and minimum sweep rates that may be used with this routine are determined by the total scan range chosen. The maximum and minimum sweep rates may be calculated by dividing the total scan range by 0.250 and 4000 respectively. If the operator chooses a sweep rate which does not lie within these limits, an error message is printed.

2. Data Acquisition Routines

a. Double scan recording. The double scan recording routine, R-4 (see Appendix, p 63) is designed primarily for the fast sweep instrument; therefore when the routine is entered, the operator sees a display of the output potential from the current measuring circuit of the potentiostat as a function of time. Once the operator has adjusted the iR compensation for a run, he may hit any teletype key to move to the acquisition part of the routine.

The first scan is initiated by striking any key on the teletype in response to the message "RDY1/2". On the first scan, data are taken

only from the current axis of the potentiostat. Once this scan has been completed, the data from the potential axis are taken. The second scan is initiated in response to the message "RDY2/2" by striking a key on the teletype. When both scans are completed, a display of the data is shown on the CRT. The operator then may decide to keep the data or reject it.

b. Single scan mode. The one scan recording routine, R5 (see Appendix, p 64) is designed primarily for the slow sweep instrument. Therefore there is sufficient time between clock overflows to acquire both data points from a pair. When the program is ready to take data the message "RDY 1/1" is printed. Striking any key on the teletype initiates data acquisition. The y-axis is sampled first and stored. Immediately following storage of that point, the x-axis is sampled and stored and the routine waits for another clock overflow. When all data points are taken, they are displayed on the CRT and the operator has the option of keeping or rejecting the data.

3. Display Routines

The basic display routine, R6, is used immediately after the data are taken. The basic display consists of the data appropriately scaled for the CRT and a cross. The vertical bar of the cross corresponds to the location of the initial data point on the x-axis. The horizontal bar corresponds to y=0. The data are displayed in normal electrochemical format, i.e., positive potentials to the left and positive currents are to the top. This is the form in which the data are obtained from the potentiostats. This should be noted, since when the actual potentials

of peaks are calculated the sign of the potentials are the reverse of that applied to the working electrode.

b. Display corrected for current offset. Except for the initial display given immediately after the data are acquired, the horizontal bar of the cross is displaced by an amount equivalent to the offset current in ADC units. The displacement shows the true location of zero current from the potentiostat.

c. Display with cursors. At various points in the program one or three cursors are displayed for the user to determine core locations on which he wishes to have calculations performed. In addition to the cursors the LINC instruction field location of each cursor is displayed in the upper left portion of the screen.

4. Experimental Parameters Input Routine

The experimental parameters input routine, R7 (Appendix, p 66), obtains all of the experimental parameters not previously obtained. The routine prints a coded message to which the user should reply with the appropriate number. Figure 5 (p 28) shows the messages printed by the routine and the parameters that each message asks for.

5. Background Averaging Routine

Since background solutions have a tendency to be noisy, a provision has been made to average a maximum of four backgrounds to be stored on LINCtape. The routine stores all the data from the first background, including a message typed in by the user for identification purposes, on LINCtape. If more backgrounds are desired, the program

E A (CM↑2)	ELECTRODE AREA
P O (MV)	POTENTIAL OFFSET
V S F	VOLTAGE SCALING FACTOR
I P (MV)	INITIAL INSTRUMENT POTENTIAL PRIOR TO APPLYING OFFSET POTENTIAL
C F (UA/V)	CURRENT SCALING FACTOR
C O (MV)	CURRENT OFFSET
CONC (MM)	CONCENTRATION

Figure 5. Experimental parameters message codes.

returns directly to the data acquisition routine used for the first background using the same clock rate and time per data point as before. Once these data are taken, the first 512 data points from the first background are recalled from tape and stored in a buffer in Field 0. Corresponding data points are then summed until 512_{10} have been summed. These sums are then stored on tape and the next 488_{10} points are called into core and the sums are found. These sums are also stored on tape. If the user wishes to take more backgrounds, the process is repeated until a maximum of four backgrounds are taken. When either four backgrounds are taken, or the user decides he has taken enough backgrounds, the sums are recalled into the buffer and the averages are determined and stored back on tape.

6. Background Subtraction Routines

a. Subtraction using stored backgrounds. This subroutine, R9, subtracts background currents by converting into microamps both the data stored on tape and the latest data taken and doing a location by location subtraction of the current stored on tape from the last data taken.

The data stored on tape and in core are in terms of ADC units. Before the currents may be added or subtracted, they must be converted into microamps. This is necessary because the two sets of data will probably be recorded with different scaling factors and offsets. The offset current may be determined for the background from the following equation:

$$\text{CSHIFTB} = \text{IOFFSB}*\text{IFACTB} \qquad (10)$$

Where CSHIFTB is the offset current in μa, IOFFSB is the offset potential

applied to the current measuring output in mv, and IFACTB is the current scaling factor in μA/mv.

The offset current for the data from which the background is to be subtracted can be obtained in a similar fashion from the equation

$$CSHIFT = IOFFST * IFACT \tag{11}$$

where CSHIFT is the offset current in μA, IOFFST is the offset potential applied to the current measuring output in mv and IFACT is the current factor in μA/mv.

The true current due to the background may be calculated from the formula:

$$TEMP1 = \frac{Y(COUNT2) * IFACTB}{ADCRG} - CSHFTB \tag{12}$$

where TEMP1 = the true current from the background, Y(COUNT2) is the contents of location COUNT2 in ADC units, COUNT2 is a location in the background buffer, and ADCRG is the number of ADC units per mv.

The true current for the cyclic voltammogram may be found by using the above equation with the appropriate substitutions of the corresponding terms of IFACT for IFACTB, CSHIFT for CSHFTB, and Y(CORCUR) for Y(COUNT2) where CORCUR is a location in the cyclic voltammogram buffer. Once both true currents are determined, the background current is subtracted from the current of the cyclic voltammogram.

In order to have the corrected data scaled for display and for storage, the data must be reconverted to 12 bit integers. This is accomplished by the following equation:

$$\text{Corrected data} = \frac{[C(FLAC) + CSHIFT]}{IFACT} * ADCRG \tag{13}$$

where C(FLAC) is the content of the floating accumulator which contains

the result of the previous current subtraction. This process is followed until all 1000_{10} points have been corrected. The corrected data are then displayed on the VR12 CRT.

b. Subtraction of backgrounds using cursors. For situations that warrant the assumption that the background current is linear, a subroutine is supplied that will subtract a linear background current. When the routine is entered, three cursors are displayed on the screen along with the data. The position of the cursors are controlled by analog channels 0, 4, and 7. The location to which each cursor corresponds within a LINC instruction field is shown on the screen with channel 0 being the leftmost position and channel 7 the rightmost position. Cursors 0 and 4 are placed along the linear portion of the cyclic voltammogram preceding the first peak, with the magnitude of cursor 4 always being greater than cursor 0. Cursor 7 is placed at the position where the direction of the potential sweep is reversed. Once the cursors are positioned, striking any key on the teletype will cause the program to proceed to a routine that will fit the region enclosed by cursors 0 and 4 with a linear least squares line. Once the coefficients of the least squares fit line are determined a new current value is calculated for each potential in the cyclic voltammogram using the equation

$$YCALC = M*X + B \qquad (14)$$

where YCALC is the calculated background current, X is the potential in ADC units, M and B are the slope and intercept of the least squares fitted line.

This value is then subtracted from the previous value of the current. In order to preserve any offset current used in recording

the data the term IOFFST*ADCRG must be added to the correct value of the current, for display purposes. This process is continued until the switching potential is reached, at which time the sign of the slope is negated and the calculations continued until all data points are corrected. The corrected data are then displayed on the CRT. This routine may be used only for data with one switching potential point during the scan.

7. Determination of Approximate Peak Locations Routine

The approximate location of the peaks in a cyclic voltammogram are determined by the user with this routine. The data are displayed on the VR12 CRT along with cursor 0 and the numerical position in a LINC instruction field that cursor 0 corresponds to. The user then adjusts cursor 0 until it falls on the maximum of the first peak. Once the operator is satisfied that the cursor is correctly placed the letter S is struck on the teletype. When the letter is struck, the core location corresponding to cursor 0 is stored in a buffer for holding peak locations. This process is continued until the operator has located all the peaks in the cyclic voltammogram, being certain that each new peak location has a higher numerical value for the cursor reading than the last peak. When the peak location process is finished, the operator strikes the letter T (for terminate routine) on the teletype. This causes minus one to be stored in the peak location buffer. The minus one is used at a later point in the program to signify that all of the peaks located for the particular cyclic voltammogram have been operated on. The peak buffer will hold a maximum of seven peak locations.

If more than seven peak locations are entered the program will not operate properly.

8. Cubic Fit of a Peak

It has been previously shown by Whitson, et al.[20] that the region near the maximum of a cyclic voltammogram peak may be described in terms of a cubic equation. This program uses a nonlinear least squares fit of ten data pairs on either side of the potential selected by the user as the peak maximum. The actual mathematics involved in finding the coefficients are discussed in Appendix C. The final result of the routine given by an equation of the form

$$A3*X^3 + A2*X^2 + A1*X + A0 = f(x) \qquad (15)$$

9. Solution of Roots of the Cubic

The roots of the cubic are found by first reducing the cubic to a quadratic, and then solving by the quadratic equation if applicable. The quadratic equation is formed by taking the first derivative of the cubic to give an equation of the form

$$QCA*X^2 + QCB*X + QCC = 0 \qquad (16)$$

where QCA=3*A3, QCB=2*A2, and QCC=A1.

From this notation the roots of the equation from the quadratic formula are:

$$ROOT1 = \frac{-QCB - \sqrt{QCB^2 - 4*QCA*QCC}}{2*QCA} \qquad (17)$$

$$ROOT2 = \frac{-QCB + \sqrt{QCB^2 - 4*QCA*QCC}}{2*QCA} \qquad (18)$$

To avoid imaginary roots, the terms inside the radical are evaluated

to make certain the quantity is positive. If it is not then the subroutine is left by an error exit.

If the quantity 4*ACA*QCB is less than 5% of QCB the quadratic equation may be approximated by the equation[21]

$$QCB*X + QCC = 0 \tag{19}$$

and the root of the equation is given by

$$\text{Root} = \frac{-QCC}{QCB} \quad . \tag{20}$$

This subroutine checks for this last possibility and if found to exist the routine does not try to solve the quadratic but uses the approximation.

Whether the roots are solved by means of the quadratic equation or the approximation, the routine checks to see if the roots found are within ten ADC units of the original, guessed location of the peak. If none of the roots found fall within this limit, an error exit is taken from the routine.

10. Calculation of Some Parameters Used for Diagnostic Criteria

a. Determination of E_p. Once the root of the cubic is solved, the peak potential (E_p) in mv may be determined from the equation

$$E_p = \frac{(VSCLF*FXMAX)}{ADCRG} - VOFFST \tag{21}$$

where VOFFST in mv is the offset potential applied to the output of the potentiostat, FXMAX is the potential at which a peak has a maximum (in ADC Units), ADCRG is as previously defined, and VSCLF is an adimensional number corresponding to the scaling factor to account for the attentuation or amplification of the potential applied to the electrochemical cell.

b. Determination of the peak current. The peak current is found by first calculating a value in ADC units from the coefficients of the cubic equation fitted around the peak and the value of FXMAX from the following equation

$$YCALC2 = ((A3*FXMAX + A2)FXMAX + A1)*FXMAX + A0 \quad (22)$$

where YCALC2 is the peak current in ADC units, and all other terms are as previously defined.

The peak potential corrected for current offset is found from the following equation

$$I_p = \left(\frac{YCALC2}{ADCRG} - IOFFST\right) * IFACT \quad (23)$$

where all terms are as previously defined.

c. Determination of $I_{p/2}$. $I_{p/2}$ in microamps may be found by simply dividing the value of I_p by two. However, in order to locate the half peak potential, the half peak current must be converted back into ADC units. This is accomplished through the use of the following formula,

$$I_{p/2}\ (\text{ADC units}) = \left[\frac{I_{p/2}\ (\mu A)}{IFACT\ \frac{\mu A}{mv}} + IOFFST\ (mv)\right] *ADCRG\ \left(\frac{\text{ADC units}}{mv}\right) \quad (24)$$

11. Determination of the Half-Peak Potential

The first approximation to the half-peak potential is found by starting at the location where the first approximation for the peak potential was determined and decrementing the core location and testing the value of the current in each location until the value found in core is less than the half-peak current found in the previous routine. Once this location has been found, five data pairs on either side of the

location are fitted with a least squares line after each potential and current have been converted to mv and μA respectively. The equation fit to the data is of the form

$$I = mE + B \tag{25}$$

where I is the current in microamps, E is the potential in mv, m is the slope in μA/mv and b is the intercept in μA. Rearranging the equation and solving for E gives the following result,

$$E = (I - b)/m \tag{26}$$

The half-peak potential may then be found by substituting the value of $I_{p/2}$ into the above equation with the result that

$$E_{p/2} = (I_{p/2} - b)/m \tag{27}$$

if no offset potential was applied to the output for the potentiostat. If an offset potential was applied, then the half-peak potential is given by the equation

$$E_{p/2} = \frac{(I_{p/2} - b)}{m} - \text{VOFFST} \tag{28}$$

12. Calculation and Subtraction of $it^{-1/2}$ Decay

It has been previously shown that the current more than 60/n mv past the peak maximum decays as a function of $i/t^{1/2}$.[20] The current contribution of a peak to a following peak may be found from the equation

$$i = \frac{A}{(t - B)^{1/2}} \tag{29}$$

where t is the time elapsed since the beginning of the experiment. This equation may be rearranged to the form

$$i^2 t = A^2 + Bi^2. \tag{30}$$

Thus if the current and time are known and i^2 is considered to be the independent variable and i^2t is the dependent variable, the data may be fitted with a linear least squares line with slope of B and intercept of A^2. When this routine is entered, a display of the data along with three cursors may be seen on the VR12 CRT. A printed message asks the user if he wants to fit a $i/t^{1/2}$ decay curve to the last peak for which diagnostic parameters were calculated. If the answer is no, the program goes to the next peak for further calculations. For an answer of yes the routine waits for the user to place cursors 0 and 4 at the ends of the region of the peak to be fitted. Once the operator has done this, making certain that the displayed location of cursor 4 is greater than that for cursor 0, he may strike any key on the teletype to have the data in the delimited region fitted with a least squares line as described in Equation 33.

Using the values of A and B determined by the least squares fit, the contribution of current left by a previous peak is calculated and subtracted from each current value left in that particular scan. It may be seen that A must have the same sign as the sign of the current of the peak which was previously evaluated. Therefore, for cathodic peaks, whose current is positive by convention, the contribution of that peak for the rest of the currents in the cyclic voltammogram is subtracted, and for an anodic peak the current will be added, since the subtraction of a negative number amounts to the addition of a positive number.

13. Output of Calculated Parameters

Once all the peaks in a cyclic voltammogram have been numerically evaluated, the calculated parameters are printed on the teletype. In

order to achieve the desired output format, the calculated parameters are recalled from their storage locations and placed in a special print out buffer. Prior to the printing of these parameters, the peak width ($E_p - E_{p/2}$) is calculated and placed in the print out buffer.

The calculated parameters are printed in the order of peak potential, half-peak potential, peak width, peak current (all in F8.1) and the current function (in F11.4 format). All potentials are in mv and the peak current is in microamps.

14. Data Smoothing

The data may be smoothed prior to numerical evaluation. This smoothing is accomplished by applying a moving five point cubic fit to the data over the entire range of the data.[22]

15. Least Squares Routine

The linear least squares routine used in this program is of standard form. The routine also has capabilities of performing some function on the x and y data prior to fitting the data.

The equations used for calculating the slope, intercept, and the standard deviation of each of former variables is given below.

$$m = \text{slope} = \frac{\Sigma x * \Sigma y - N * \Sigma xy}{(\Sigma x)^2 - N * \Sigma x^2} \tag{31}$$

$$\text{Standard deviation} = \sqrt{\frac{N * \Sigma (m*x + b - y)^2}{(N-2) * \left| (\Sigma x)^2 - N * \Sigma x^2 \right|}} \tag{32}$$

$$b = \text{Intercept} \quad \frac{\Sigma x * y - \Sigma x^2 * \Sigma y}{(\Sigma x)^2 - N * \Sigma x^2} \tag{33}$$

$$\text{Standard deviation} = \sqrt{\frac{(\Sigma x)^2 * \Sigma (m*x + b - y)^2}{(N-2) * 1 \left| (\Sigma x)^2 - N * \Sigma x^2 \right|}} \tag{34}$$

where x is the independent variable, y is the dependent variable and N is the number of data pairs used.

16. Error Messages

The FPP will detect certain error conditions which may arise during the course of calculations. When these conditions occur the FPP exits to specific core locations, where the programmer may determine through the use of error routines which error occurred. The error messages from the floating point package are of the form

xxxx?@.cccc

where xxxx indicates the type of error that occurred and cccc indicates the location of the error within the 8-mode data field on which the FPP was operating. In order to determine in which data field the error occurred, the user must be aware of what part of the program was operating at the time of the error and consult a listing of the program.

Other error conditions which result as a failure of calculated values to meet programmed test criteria may also be printed. These error messages are of the form

?@ccccc

where ccccc is the absolute core location where the error occurred.

A list of the FPP error codes and programmer determined error conditions are shown in Table 1.

After an error occurs the FPP's temporary storage locations are cleared and the program restarts with the "which mode" message.

TABLE I

SPECIFIC ERROR CODES PRINTED BY PROGRAM

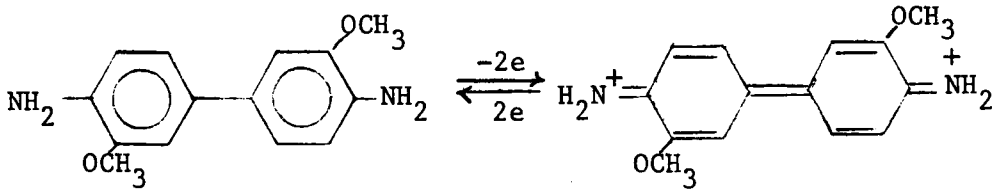
Error Codes	Meaning
4117?@•	Integer > 2047>
4120?@•	Division by Zero
4121?@•	Illegal function arguments
4122?@•	Exponent overflow
4123?@•	Exponent underflow
?@01305	Invalid cubic fit
?@01505	Cannot find $E_{p/2}$ for a peak
?@10436	Frequency too slow
?@10456	Frequency too fast
?@10634	Sweep rate too slow
?@10657	Sweep rate too fast

CHAPTER IV

AN EXPERIMENTAL APPLICATION

A well behaved model system was chosen to evaluate the program under practical operating conditions. In the process of debugging CV-ERS, real cyclic voltammograms which had been recorded previously and stored on magnetic tape were used extensively. However it was felt that the total software package should be exercised on a "real time" basis.

The potential scan resolution and peak fitting ability of the program may be tested adequately using a sharp reversible electrochemical system. The compound 3,3'-dimethoxybenzidine dihydrochloride exhibits a reversible two electron couple at the carbon paste electrode (14-pp 280-283) as shown in Equation 35.



(35)

A. Experimental

A 1.5 mM solution of reagent grade 3,3'-dimethoxybenzidine dihydrochloride (Eastman) in twice distilled water was prepared with 0.05 M sulfuric acid as the supporting electrolyte. Saturated calomel electrodes were used for both the reference and counter electrodes. A carbon paste electrode, with a surface area of 0.775 cm^2 (diameter measured with calipers), was the working electrode.

A fresh surface for the carbon paste electrode (C.P.E.) was prepared and three cyclic voltammograms were recorded using the software package. A new surface was prepared and one cyclic voltammogram was recorded using a storage oscilloscope.[13] The above procedure was repeated until a total of twelve voltammograms were recorded. The sweep rate used for all the voltammograms was 325 mv/sec.

The cyclic voltammograms recorded on the oscilloscope were manually evaluated using the method described by Adams.[14] Backgrounds were subtracted assuming a linear base line. Corrections for $1/t^{1/2}$ decay of previous currents were made by using a straight line drawn through the region just preceding the cathodic peak as a base line for measuring the cathodic peak current.

The data acquired under computer control were corrected for background current in the manner described previously (p 31). Figure 6 shows an example of the placement of the cursors just prior to subtracting the background current. The $1/t^{1/2}$ current decay for the cathodic peak was corrected in the manner described in Chapter III (p 36). Figures 7 and 8 show the placement of the cursors prior to correction and after correction.

B. Results and Discussion

Table II shows the experimental results. The linearity of the base line for the peak after correction may be used as one criteria for the quality of the $1/t^{1/2}$ fit. Figure 9 shows typical user-computer interaction for the data acquisition. User responses are underlined for clarity. The frequency and the total voltage range have been entered previously in trial runs. It may be seen that the peak

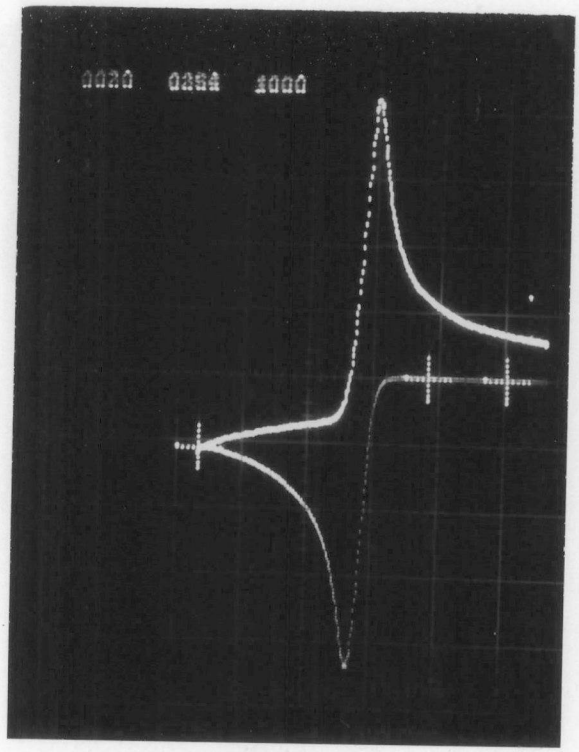


Figure 6. Display of cursors prior to background subtraction.

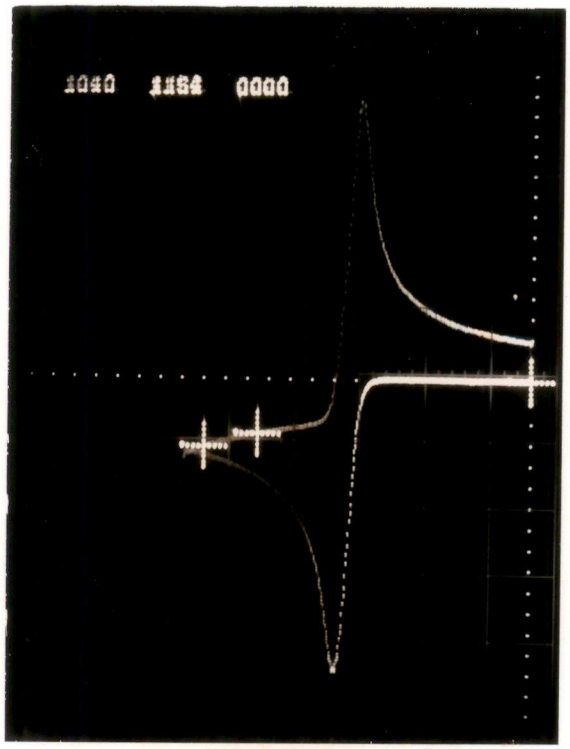


Figure 7. Display of the placement of cursors prior to $1/t^{1/2}$ decay subtraction.

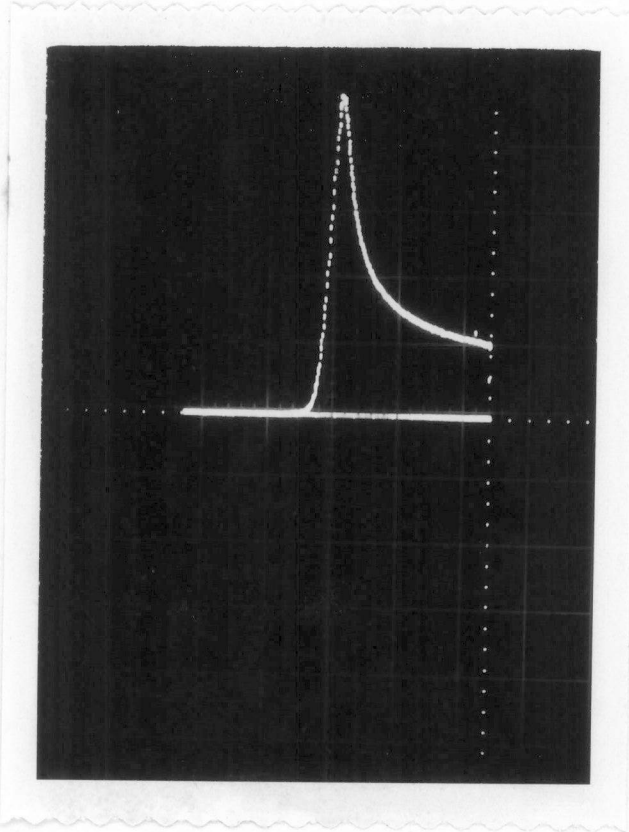


Figure 8. Display of data shown in Figure 7 after correction for $1/t^{1/2}$ decay.

TABLE II

CYCLIC VOLTAMMETRIC DATA FOR 1.5 mM 3,3'-DIMETHOXYBENZIDENE DIHYDROCHLORIDE IN 0.05 M H_2SO_4, CARBON PASTE ELECTRODE

C.P.E.	Run	E_p (mv)	$E_{p/2}$ (mv)	ΔE_p (mv)	I_p (μa)	C.F.[a]	E_p (mv)	$E_{p/2}$ (mv)	ΔE_p (mv)	I_p (μa)	C.F.[a]
1[b]	1	557	521	36	-887	-1.36	495	525	-30	991	1.52
1	2	557	520	37	-850	-1.30	495	526	-31	975	1.49
1	3	559	522	37	-804	-1.23	495	524	-29	960	1.47
2[c]	1	533	480	47	-771	-1.18	437	489	-52	885	1.36
3[b]	1	558	522	36	-871	-1.33	497	529	-32	973	1.49
3	2	557	521	36	-875	-1.34	498	529	-31	961	1.47
3	3	559	522	37	-836	-1.28	497	528	-31	952	1.46
4[c]	1	537	495	41	-941	-1.44	465	506	-41	971	1.49
5[b]	1	556	520	36	-907	-1.39	496	527	-31	1014	1.55
5	2	557	523	34	-895	-1.37	495	526	-31	1004	1.54
5	3	558	521	37	-868	-1.33	495	526	-31	994	1.52
6[c]	1	539	488	51	-903	-1.38	465	500	-35	968	1.48

[a] Units: $\mu A\ cm^{-2}\ (mv/sec)^{-1/2}\ mM^{-1}$.

[b] Computer evaluted using CV-ERS.

[c] Manually evaluated from oscilloscope tracings.

```
MODE (1-ACQ,2-PROCESS,3-BOTH):1

SET SNS SWITCHES
RDY1/2 SPACE
RDY2/2 SPACE
KEEP DATA?N


SET SNS SWITCHES SPACE
RDY1/2 SPACE
RDY2/2 SPACE
KEEP DATA?Y
EXP PARAMETERS SAME?N
E A (CM↑2)  :.775
P O (MV)    :506
V S F       :1
I P (MV)    :-497
C F (UA/V)  :1000
C O (MV)    :10
CONC (MM)   :1.5

BASE LINE FIT

SLOPE     = +0.3886088E-01
STD DEV   = +0.1057689E-02
INTERCEPT = -0.9559970E+01
STD DEV   = +0.1570548E+00
 +169 POINTS WERE USED

ENTER YOUR MSG
RUN #1 ON CPE 1-1.5MM 0-DIA/.05MH2SO4 27 JUN 74$

SAVING CYCLIC
FILE NO.:70
```

Figure 9. Print out obtained in the data acquisition mode.

potentials and half-peak potentials determined with the software packages are much more consistent with each other than those determined by manual evaluation. For example the range of the anodic peak potentials determined by manual evaluation is 6 mv for three cyclic voltammograms as opposed to a range of 4 mv for 9 evaluations performed with the program. A range of 15 mv for the determination of the anodic half-peak potentials by manual evaluation is much larger than the range of 4 mv found by the program.

The difference between the potentials determined by the manual evaluation and software evaluation may in part be accounted for by the lack of resolution of the oscilloscope. The width of the oscilloscope trace in this experiment was on the order of 20 mv. Therefore great care must be taken in locating the point the scan was initiated. Any small error in judgement will cause a significant error in the determination of the peak potentials. For the software evaluation the experimenter may place a cursor exactly on the point where the peak height is a maximum. If the peak is very flat, placement of the cursor slightly to either side of the maximum is not critical since a cubic equation is fitted to 10 points on either side of the initial guess for the determination of the peak potential.

The determination of the half-peak potentials by manual methods is very susceptible to error since the experimenter must judge the location by sliding a ruler or dividers along the cyclic voltammogram until the difference between the trace of the voltammogram peak and the drawn base line equals half the peak potential. Also the experimenter generally draws a linear base line as opposed to the true $1/t^{1/2}$ curve found by the program.

Figure 10 shows the user-computer interaction for evaluation of the data previously stored on LINCtape. Figure 11 shows the results of recalling a cyclic voltammogram which has been previously evaluated.

The above results indicate that the program has the desired accuracy in recording and evaluating the data. Furthermore, the user-interactive characteristics of the program make evaluation more rapid and convenient than manual evaluation. However, thorough evaluation of this program should be subsequently performed by users of this program in order to find any presently unseen limitations. In addition restrictions should be found to reject "unreasonable" evaluations.

```
MODE (1-ACQ,2-PROCESS,3-BOTH):2
RECALLING CYCLIC
FILE NO.:70
RUN #1 ON CPE 1-1.5MM 0-DIA/.05MH2SO4 27JUN74
WANT REST?N
O.K. TO USE?Y
SMOOTH?N
SST

EP/2 FIT


SLOPE       = +0.1220406E+02
STD DEV     = +0.9770033E+00
INTERCEPT   = -0.2606079E+03
STD DEV     = +0.6018552E+01
  + 11 POINTS WERE USED

DECAY?Y

IT↑1/2 FIT

SLOPE       = +0.2751365E+01
STD DEV     = +0.4336865E-01
INTERCEPT   = +0.8711807E+04
STD DEV     = +0.3928932E+03
  + 58 POINTS WERE USED
  + 58 POINTS WERE USED

EP/2 FIT

SLOPE       = +0.1051948E+02
STD DEV     = +0.4548578E+00
INTERCEPT   = +0.6913916E+03
STD DEV     = +0.2024663E+02
  + 11 POINTS WERE USED

    EP     EP/2    EP-EP/2       IP      C FUN

+556.7   +521.0    +35.8    -887.1    -1.3592
+495.3   +524.6    -29.3    +990.7    +1.5180
```

Figure 10. Print out obtained in the evaluation mode.

```
MODE (1-ACQ,2-PROCESS,3-BOTH):2
RECALLING CYCLIC
FILE NO.:70
RUN #1 ON CPE 1-1.5MM 0-DIA/.05MH2SO4 27JUN74
WANT REST?Y
FREQ (HZ)      :    +0.1600
T V R (MV)     : +1970.0000
E A (CM↑2)          +0.7750
P O (MV)          +506.0000
V S F               +1.0000
I P (MV)          -497.0000
C F (UA/MV)         +1.0000
C O (MV)            +0.0000
CONC (MM)           +1.5000
O.K. TO USE?Y
SMOOTH?N
```

EP	EP/2	EP-EP/2	IP	C FUN
+556.7	+521.0	+35.8	-887.1	-1.3592
+495.3	+524.6	-29.3	+990.7	+1.5180

Figure 11. Print out obtained in Mode 2—calculated parameters recall option.

LIST OF REFERENCES

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1. H. B. Herman and H. J. Bard, Anal. Chem., 36, 510 (1964).

2. M. W. Breiter, J. Electrochem. Soc., 112, 845 (1965).

3. G. Lauer and R. A. Osteryoung, Anal. Chem., 38, 1137 (1966).

4. E. R. Brown, D. E. Smith, and D. D. DeFord, Ibid., 38, 1130 (1966).

5. G. Lauer, R. Abel, and F. C. Anson, Ibid., 39, 765 (1967).

6. G. Lauer and R. A. Osteryoung, Ibid., 40 (10), 30A (1968).

7. S. P. Perone, D. O. Jones, and W. F. Gutknecht, Ibid., 41, 1154 (1969).

8. W. T. Gutknecht and S. P. Perone, Ibid., 42, 906 (1970).

9. L. B. Sybrandt and S. P. Perone, Ibid., 43, 382 (1971).

10. J. Lawrence and D. M. Mohilner, J. Electrochem. Soc., 118, 1596 (1971).

11. S. P. Perone, J. W. Frazer, and A. Kray, Anal. Chem., 43, 1485 (1971).

12. P. R. Moses, Doctoral Dissertation, University of Tennessee, 1974.

13. P. R. Moses and J. Q. Chambers, J. Electroanal. Chem., 49, 105 (1974).

14. R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, Inc., New York, New York, 1969.

15. A. Sevcik, Coll. Czech. Chem. Comm., 13, 349 (1948).

16. H. Matsuda and Y. Ayabe, Z. Elektrochem., 59, 494 (1955).

17. E. R. Brown and R. F. Large, in "Techniques of Chemistry, Physical Methods," Vol. 1, Part IIa, A. Weissberger and W. B. Rossiter, eds., Wiley-Interscience, New York, New York (1971).

18. E. R. Brown, T. G. McCord, D. E. Smith, and D. D. DeFord, Anal. Chem., 38, 1119 (1966).

19. E. Rapoport, Decuscope, 12, 18 (1973).

20. P. E. Whitson, H. N. Vandenborn, and D. H. Evans, Anal. Chem., 45, 1298 (1973).

21. J. N. Butler, "Ionic Equilibrium: A Mathematical Approach," Addison-Wesley, Reading, Massachusetts, 1964, p 76.

22. A. Savitzky and M. J. E. Golay, Anal. Chem., 36, 1627 (1964).

23. R. Pennington, "Introductory Computer Methods and Numerical Analysis," Macmillan Co., New York, New York, 1965, pp 361-373.

24. Ibid., p 291.

25. S. P. Conte, "Elementary Numerical Analysis," McGraw-Hill, New York, New York, 1965, p 159.

APPENDIXES

APPENDIX A

INSTRUCTIONS FOR LOADING AND RESTARTING THE PROGRAM

A. Loading the Program

1. Mount data tape on Unit 1.
2. Mount system tape on Unit 0.
3. LSW = 0701.
4. RSW = 7300
5. Mode key = LINC
6. Press I/O preset; Do; Start 20.
7. Type: (L.F.) LO CV-ERS, 0(C.R.)

B. General Restart

1. Press STOP.
2. Instruction Field Register = 001.
3. Mode key = LINC.
4. LSW = 0200.
5. Press I/O preset; Start LS.

C. Restarting from Experimental Parameters Input Routine

1. Press STOP.
2. Instruction Field Register = 001.
3. LSW = 0260.
4. Press Start LS.

APPENDIX B

FLOWCHARTS

Flowcharts for the program described in this thesis are diagrammed in Figures B-1 through B-28. The main program is shown in Figure B-1 and subroutines in the remaining figures.

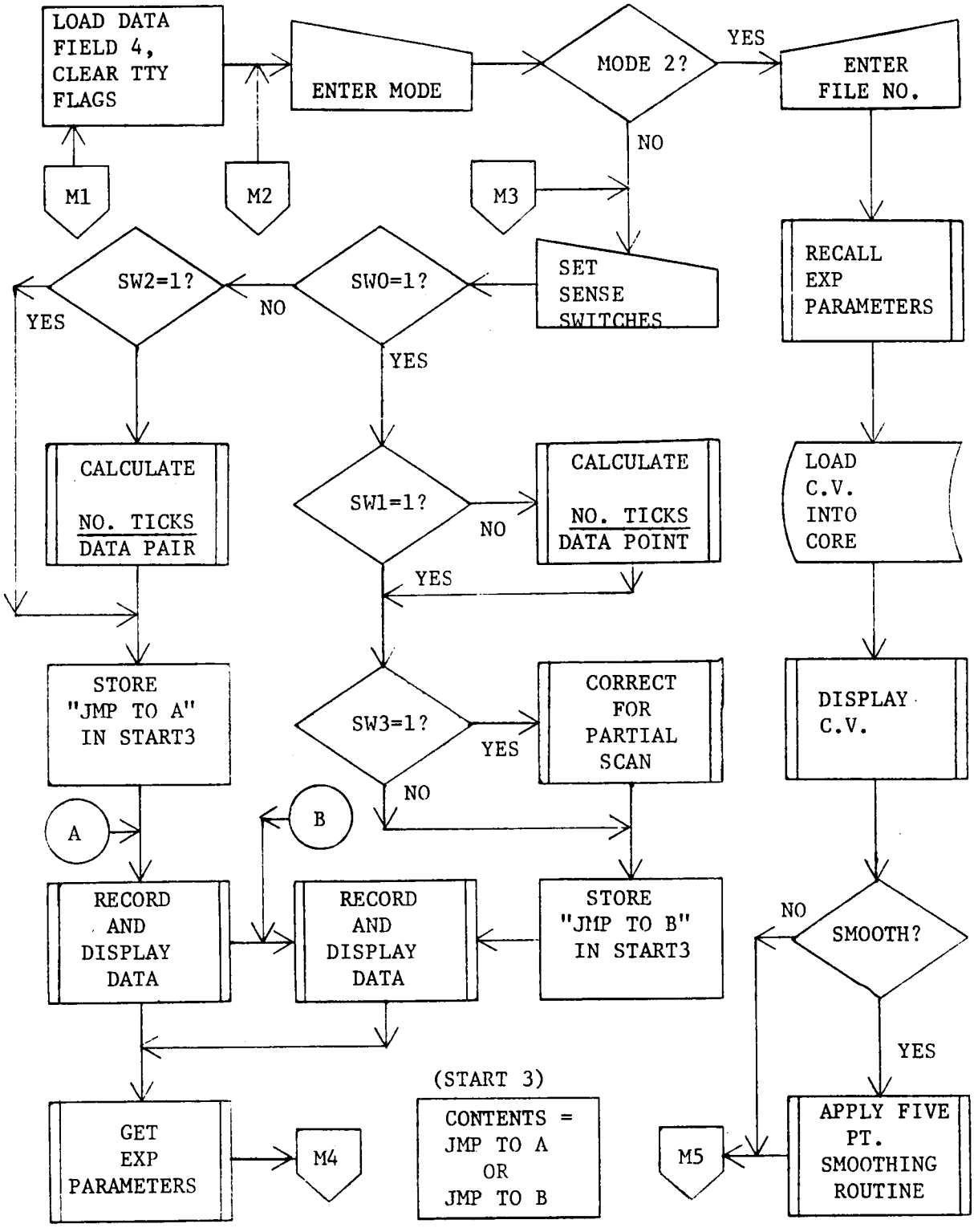


Figure B-1. Main program.

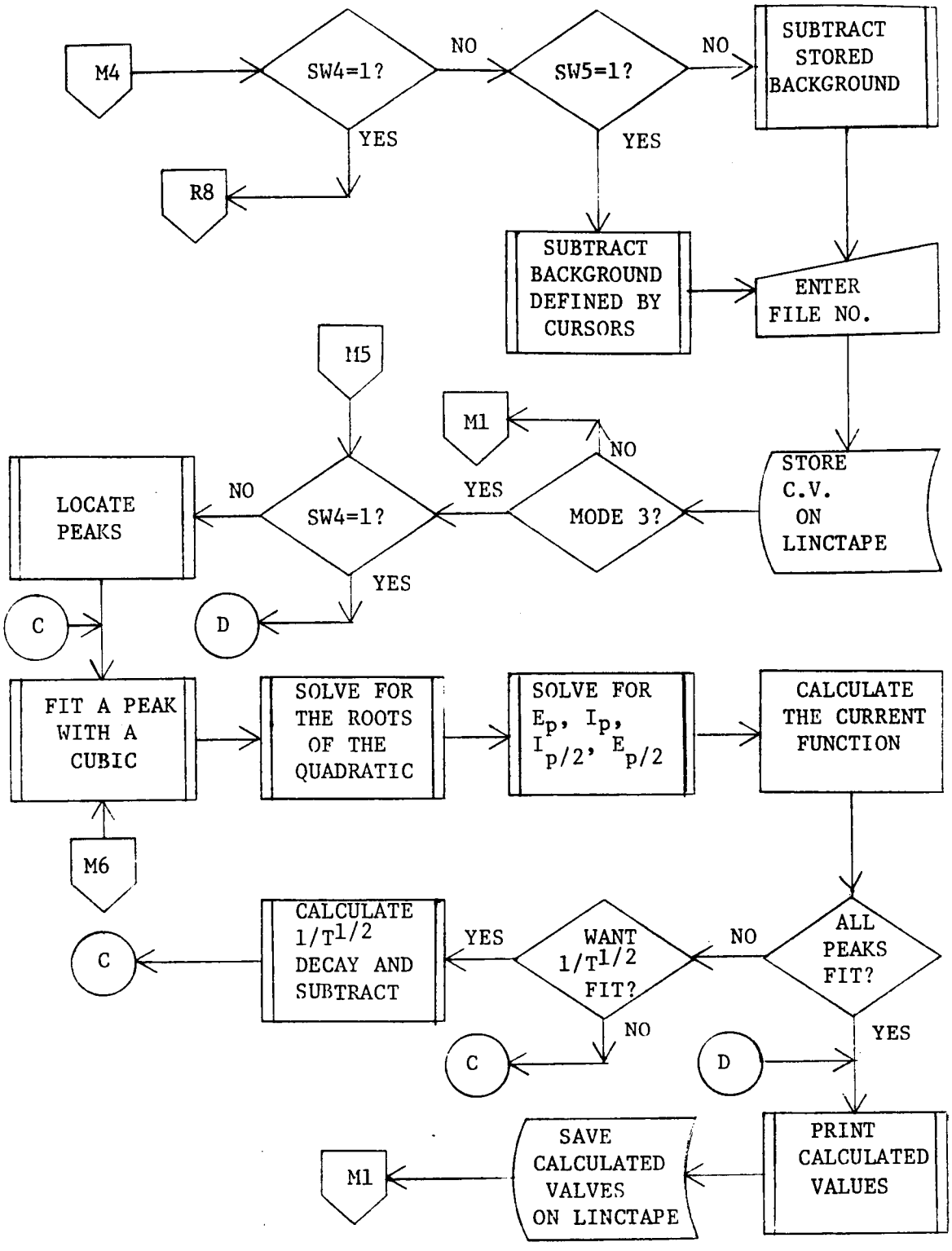


Figure B-1. (Continued).

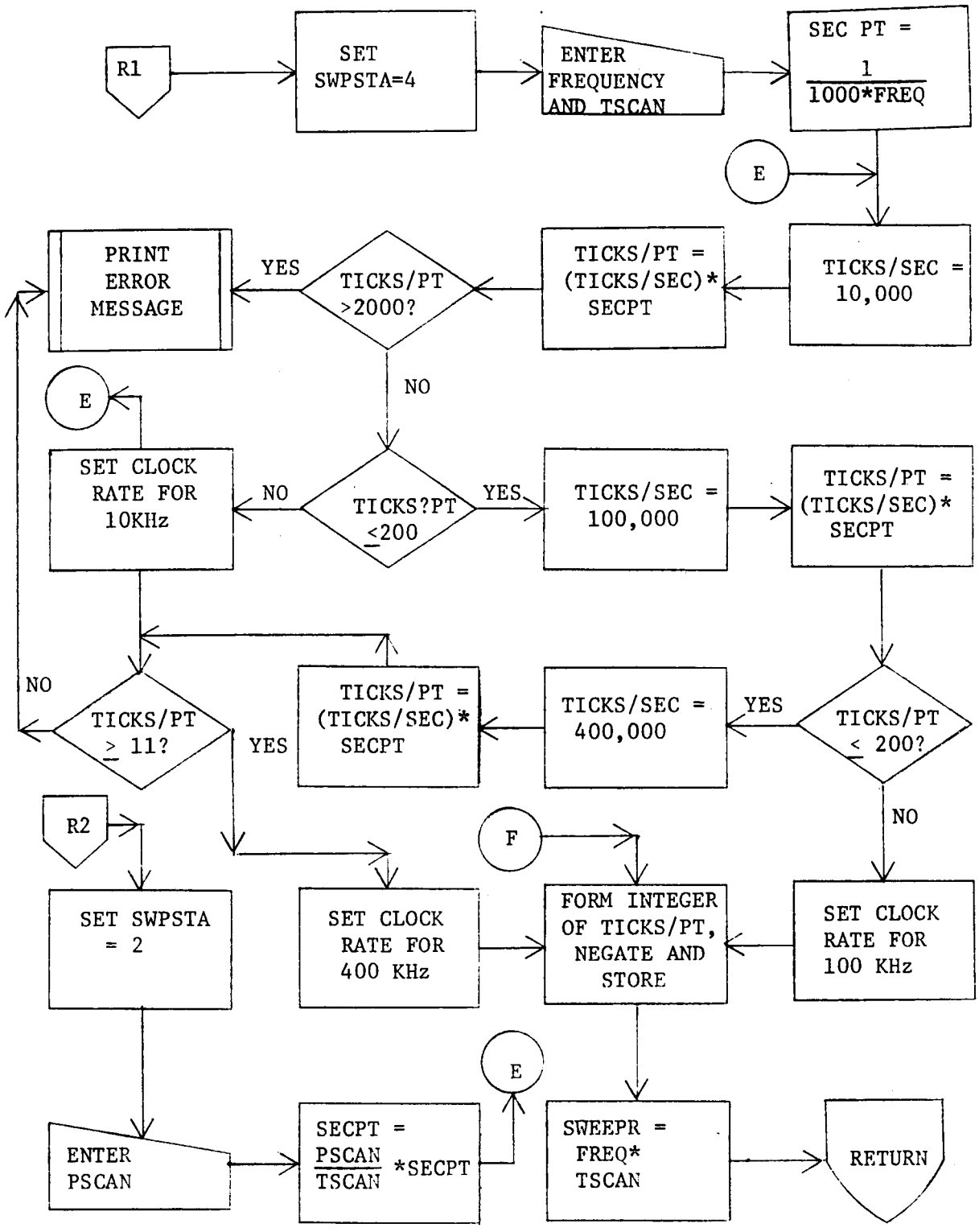


Figure B-2. Calculation of TICKS/PT for double scan recording.

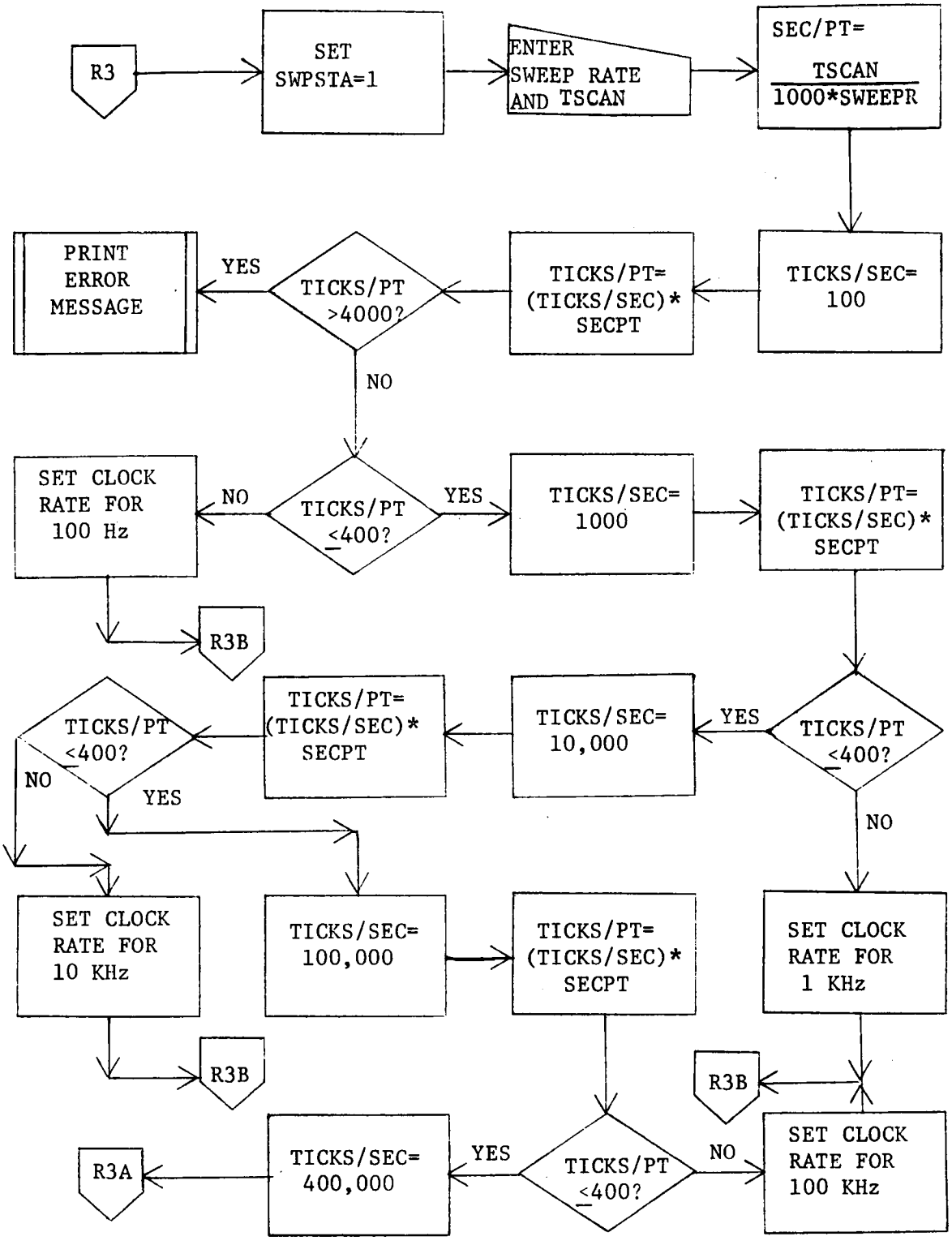


Figure B-3. Calculation of TICKS/PT for single scan recording.

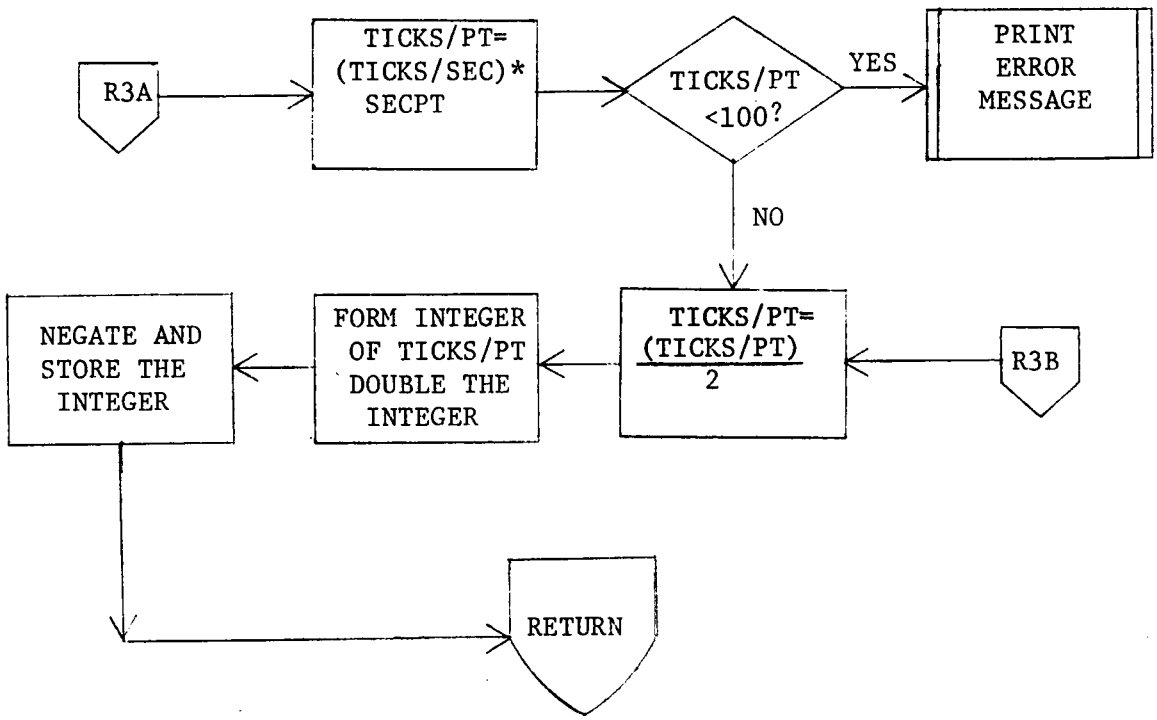


Figure B-3. (Continued).

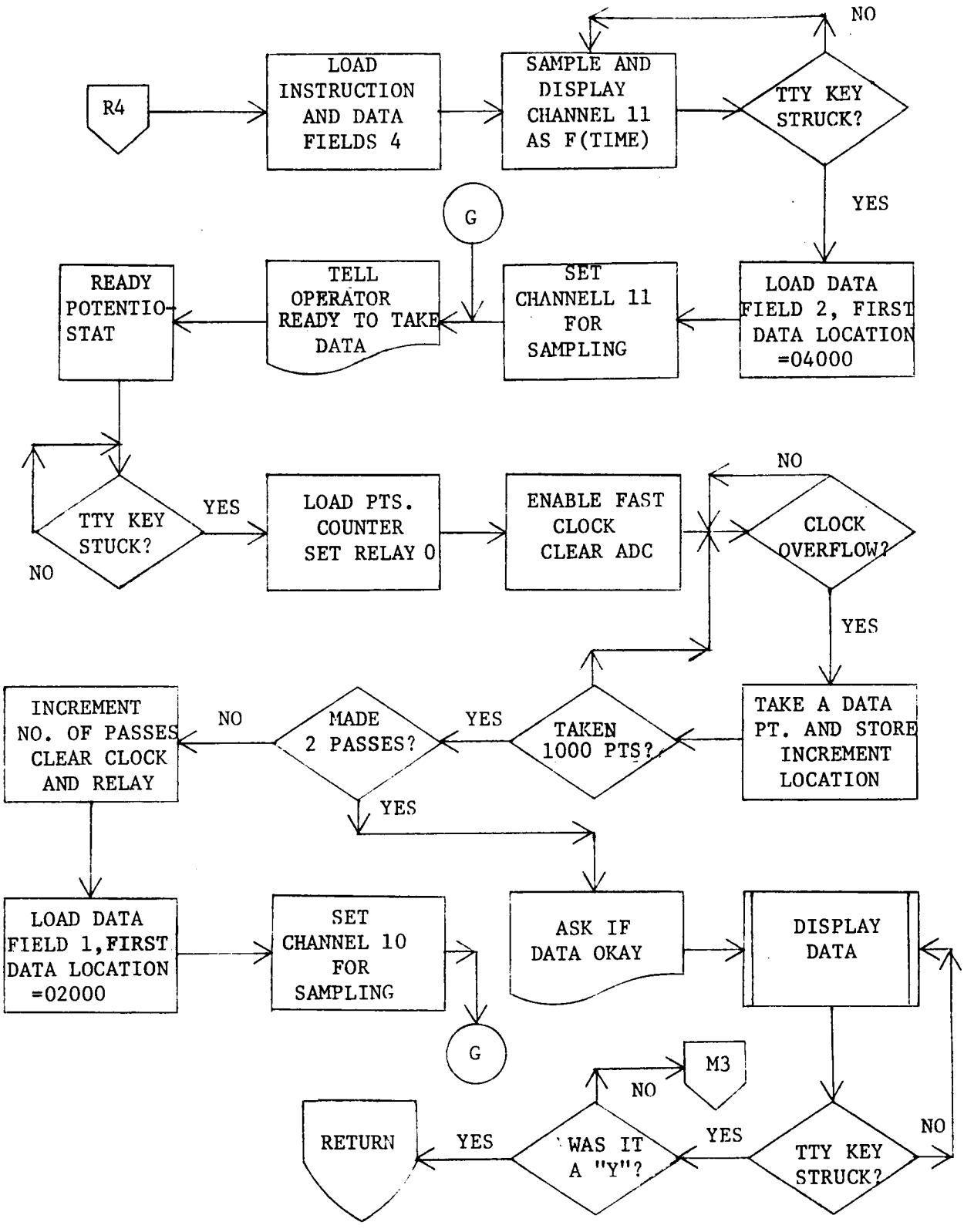


Figure B-4. Double scan recording routine.

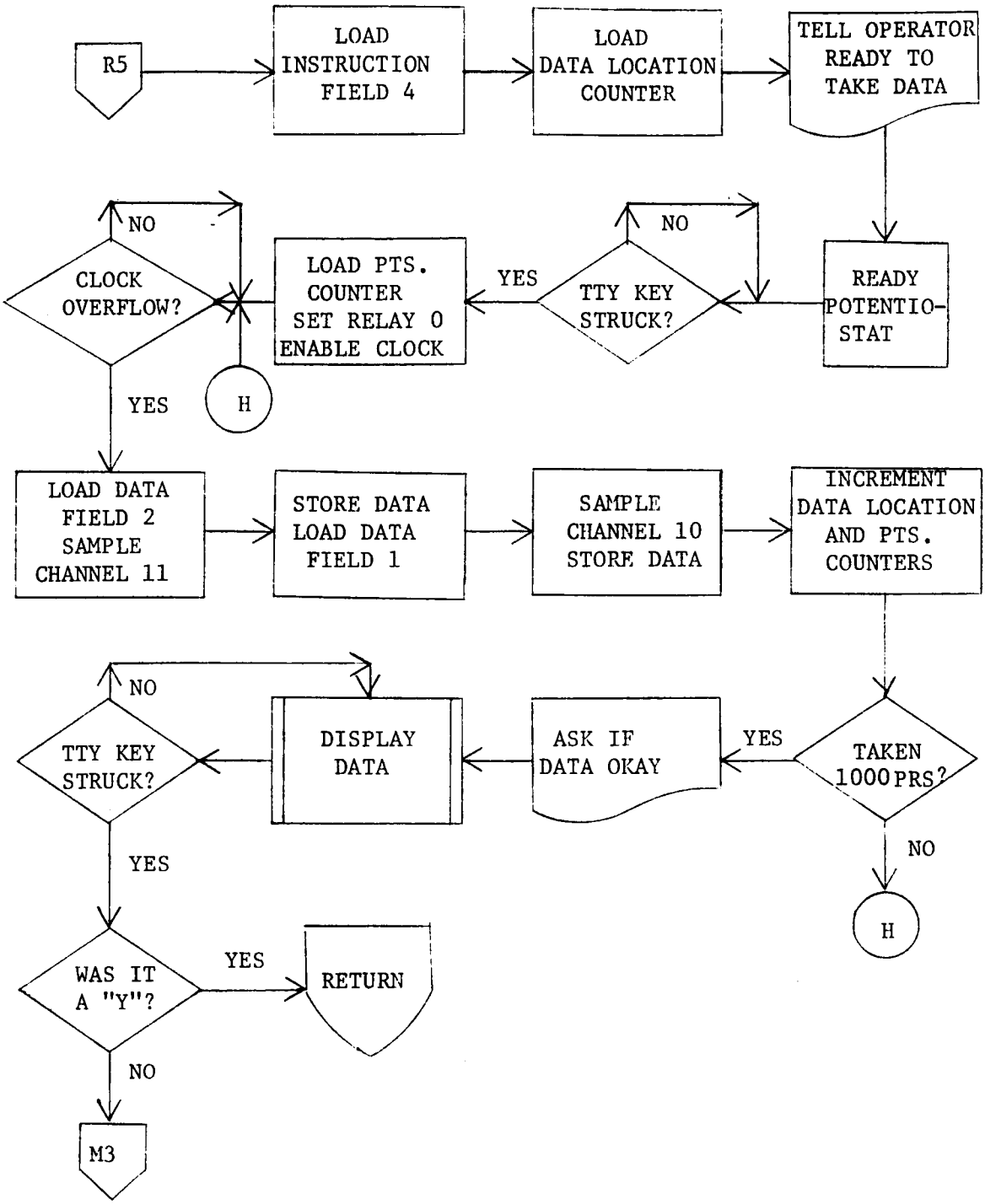


Figure B-5. Single scan recording routine.

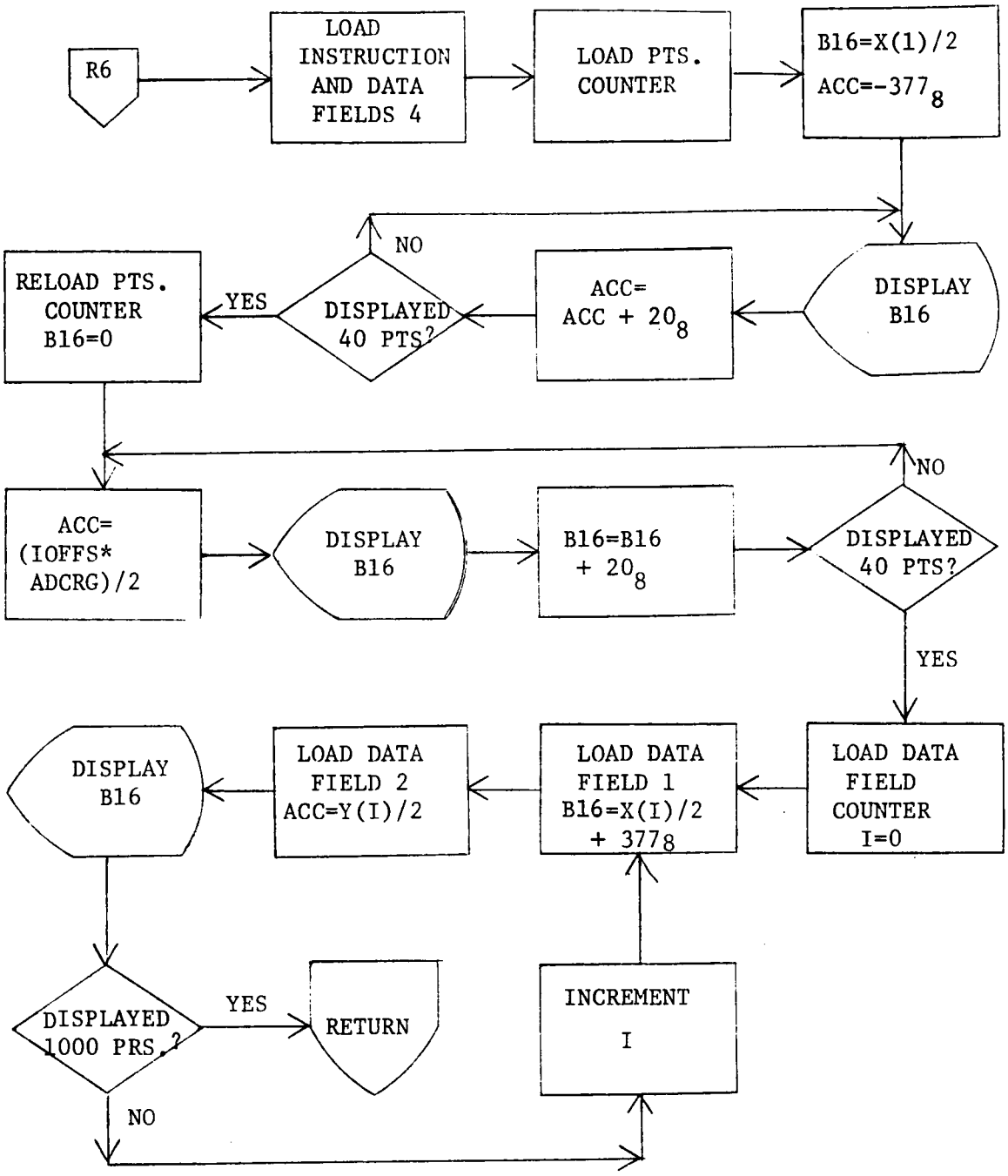


Figure B-6. Basic display routine.

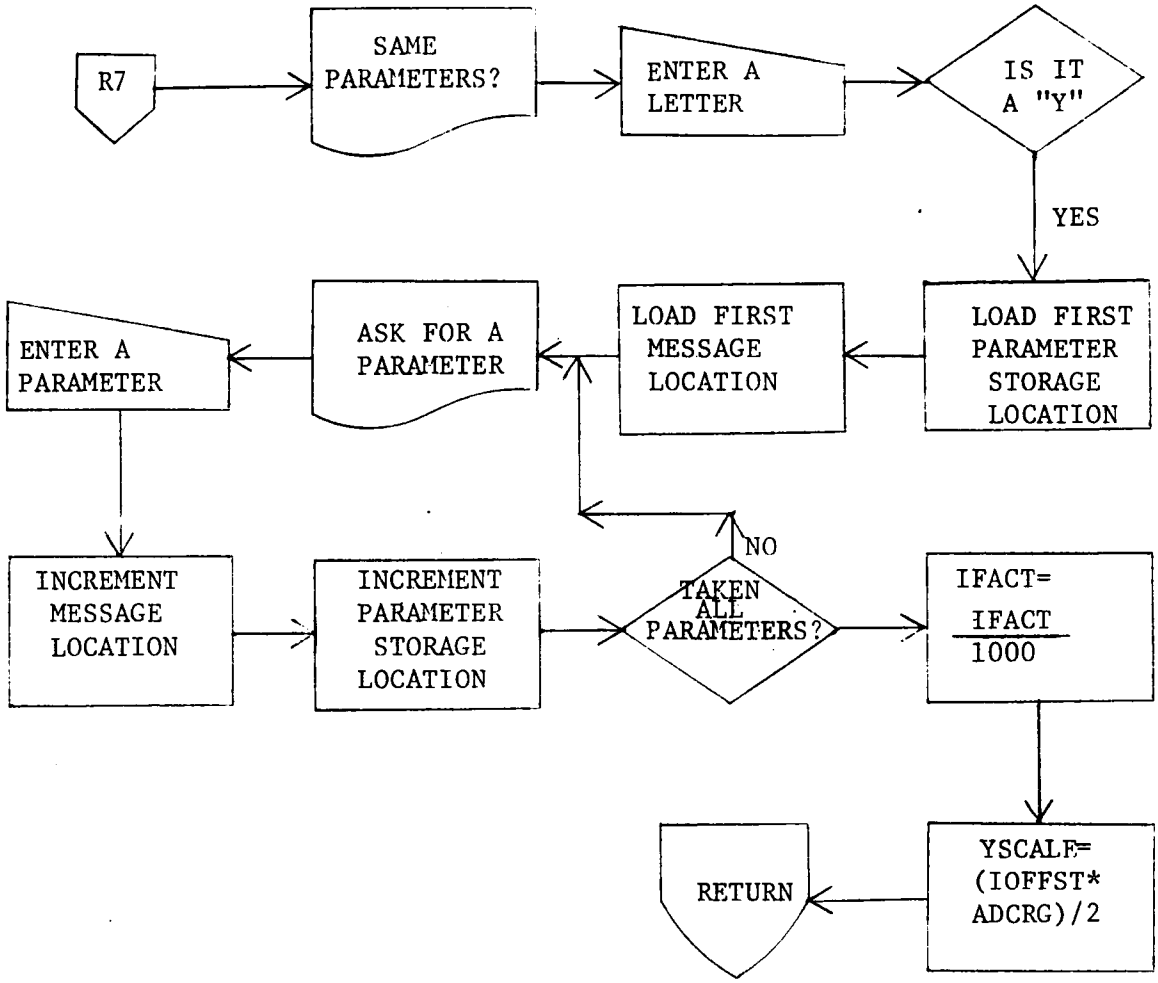


Figure B-7. Storage of experimental parameters.

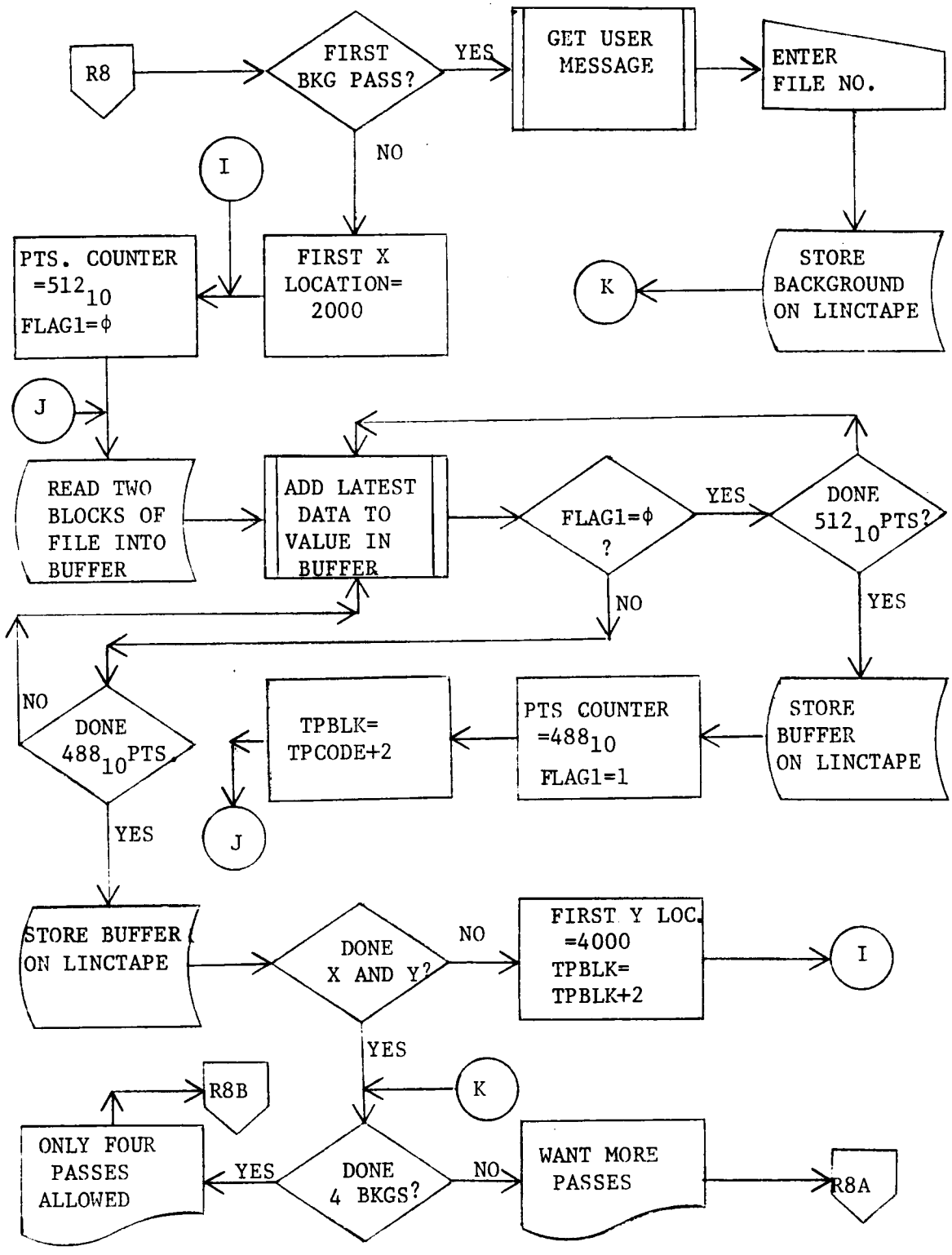


Figure B-8. Averaging and storage of backgrounds.

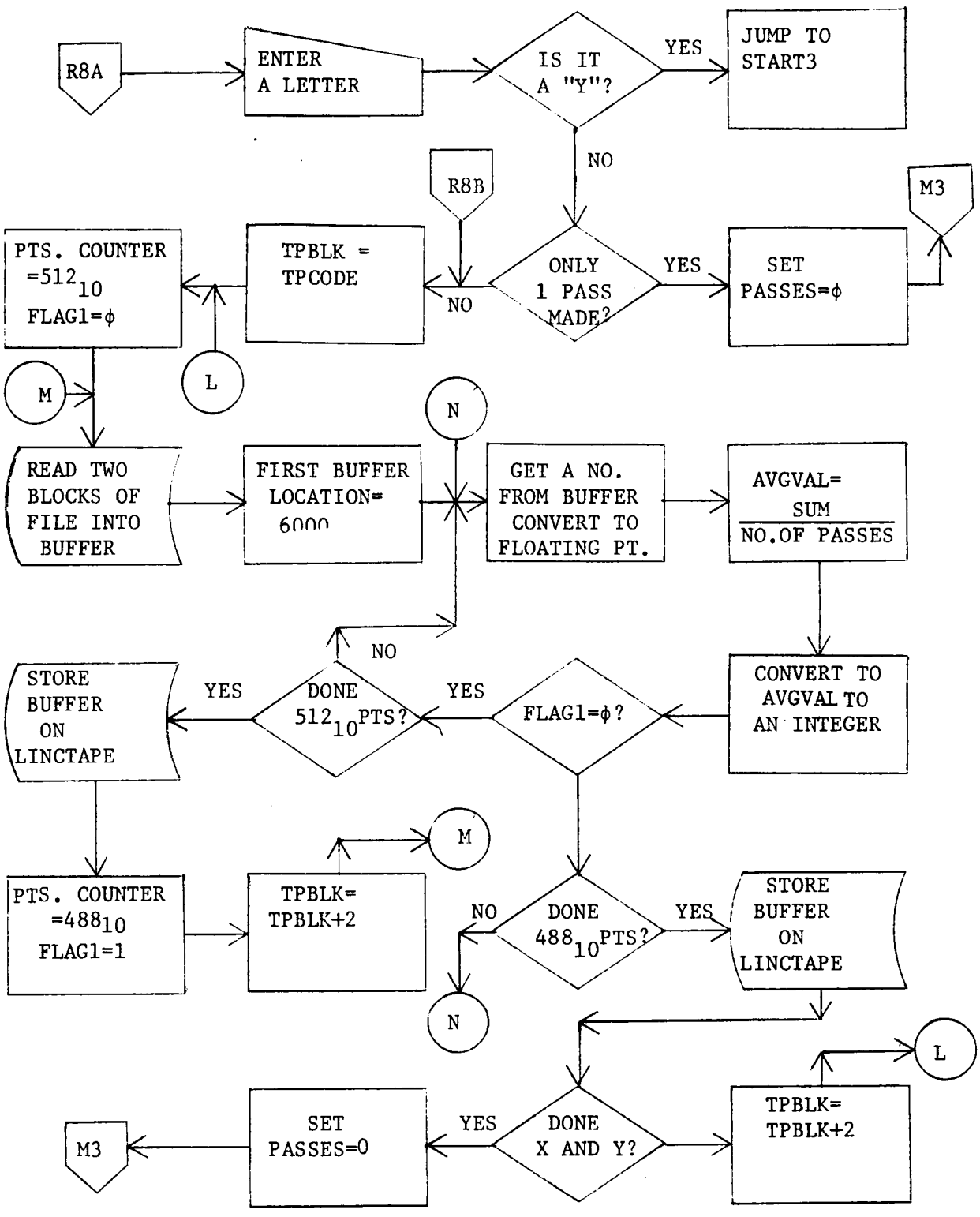


Figure B-8. (Continued)

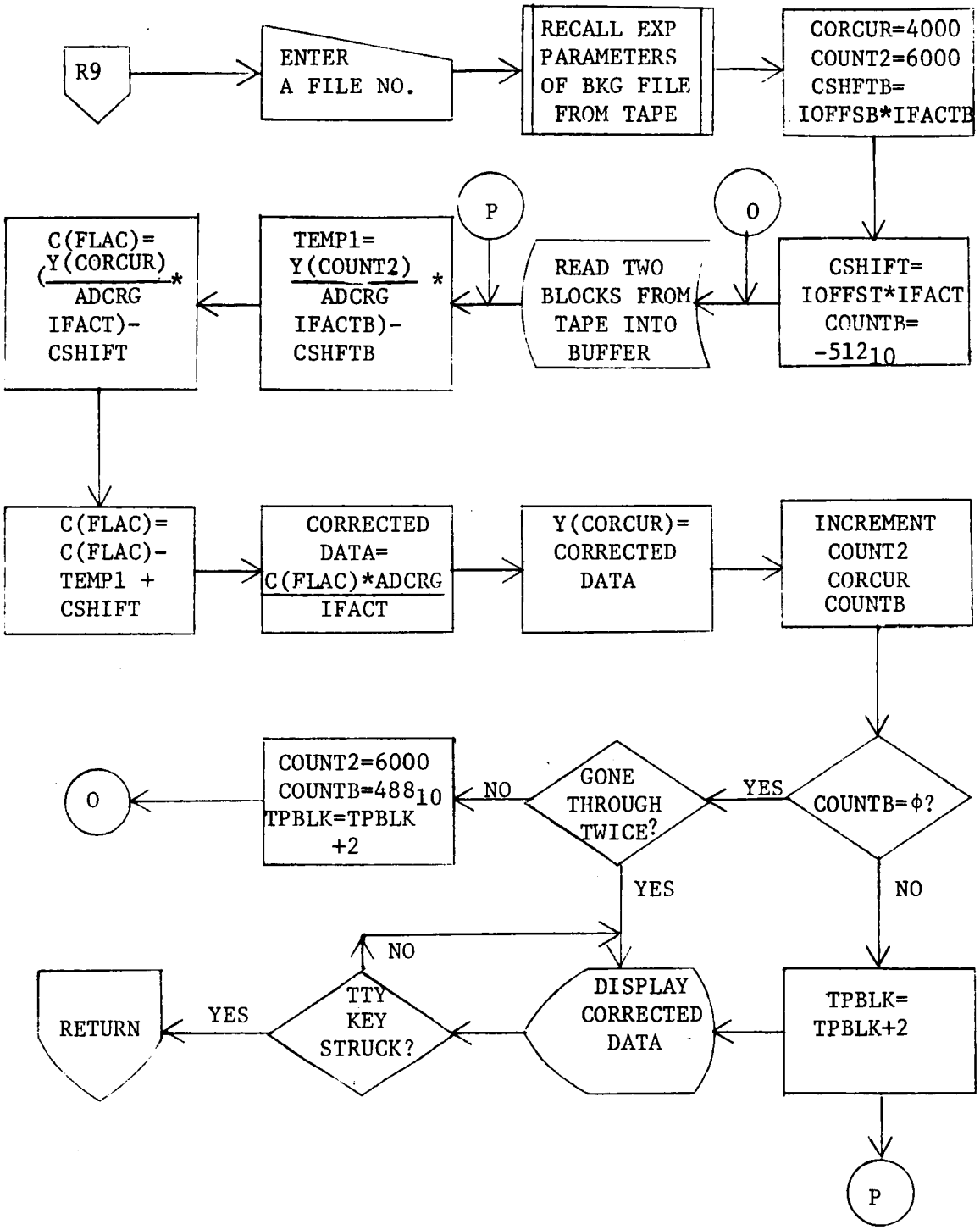


Figure B-9. Subtraction of background stored on LINCtape.

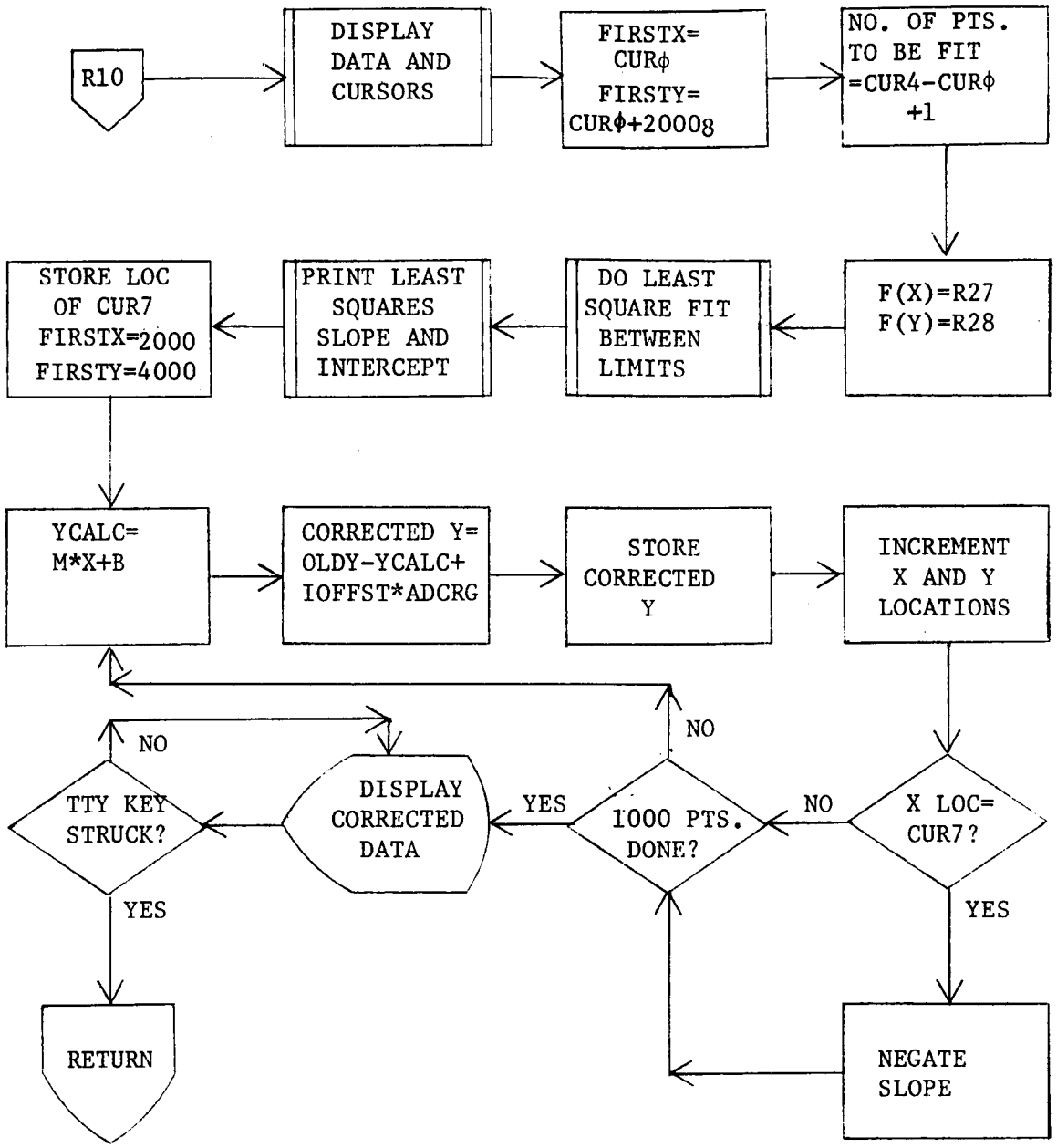


Figure B-10. Subtraction of linear background.

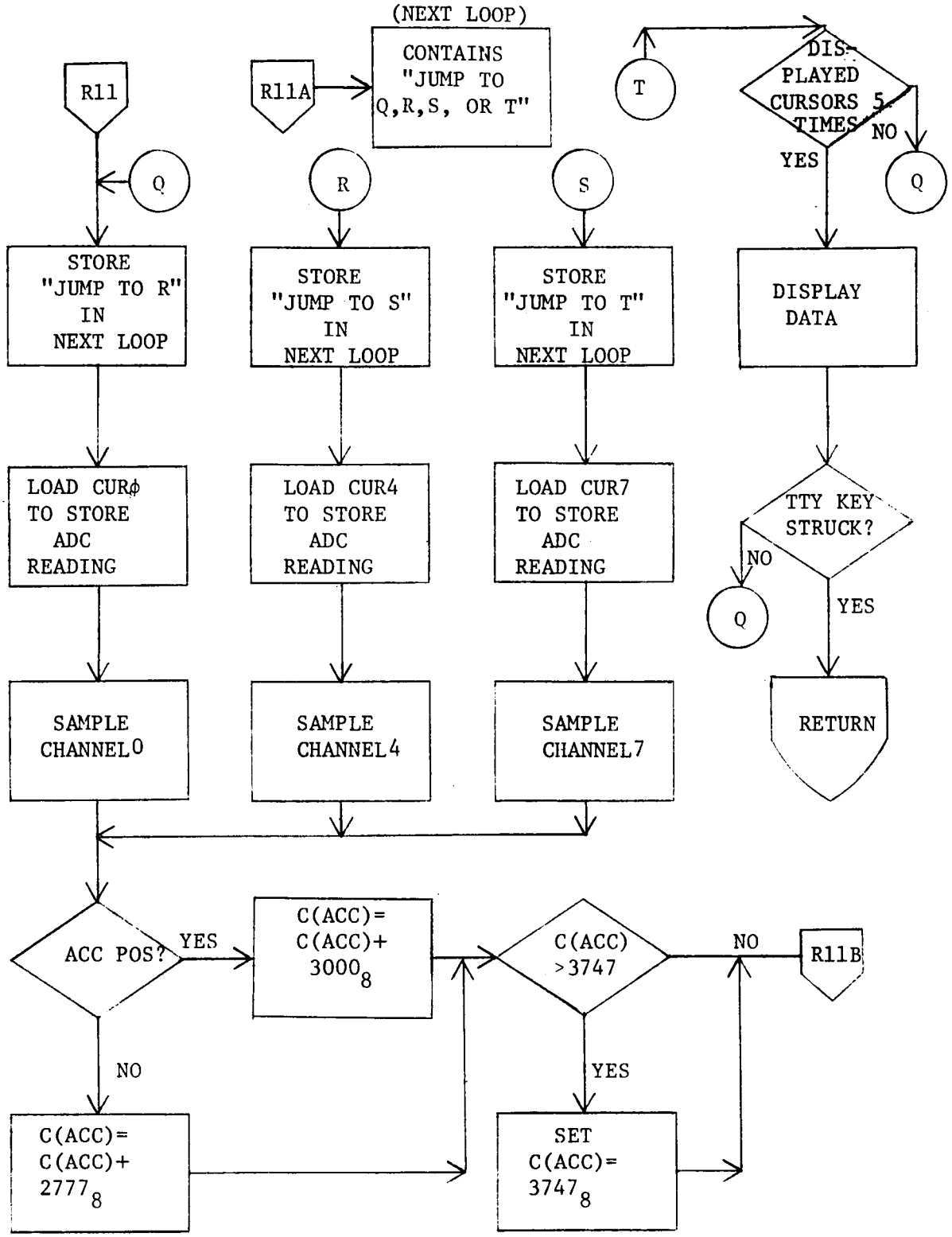


Figure B-11. Cursor display with core location.

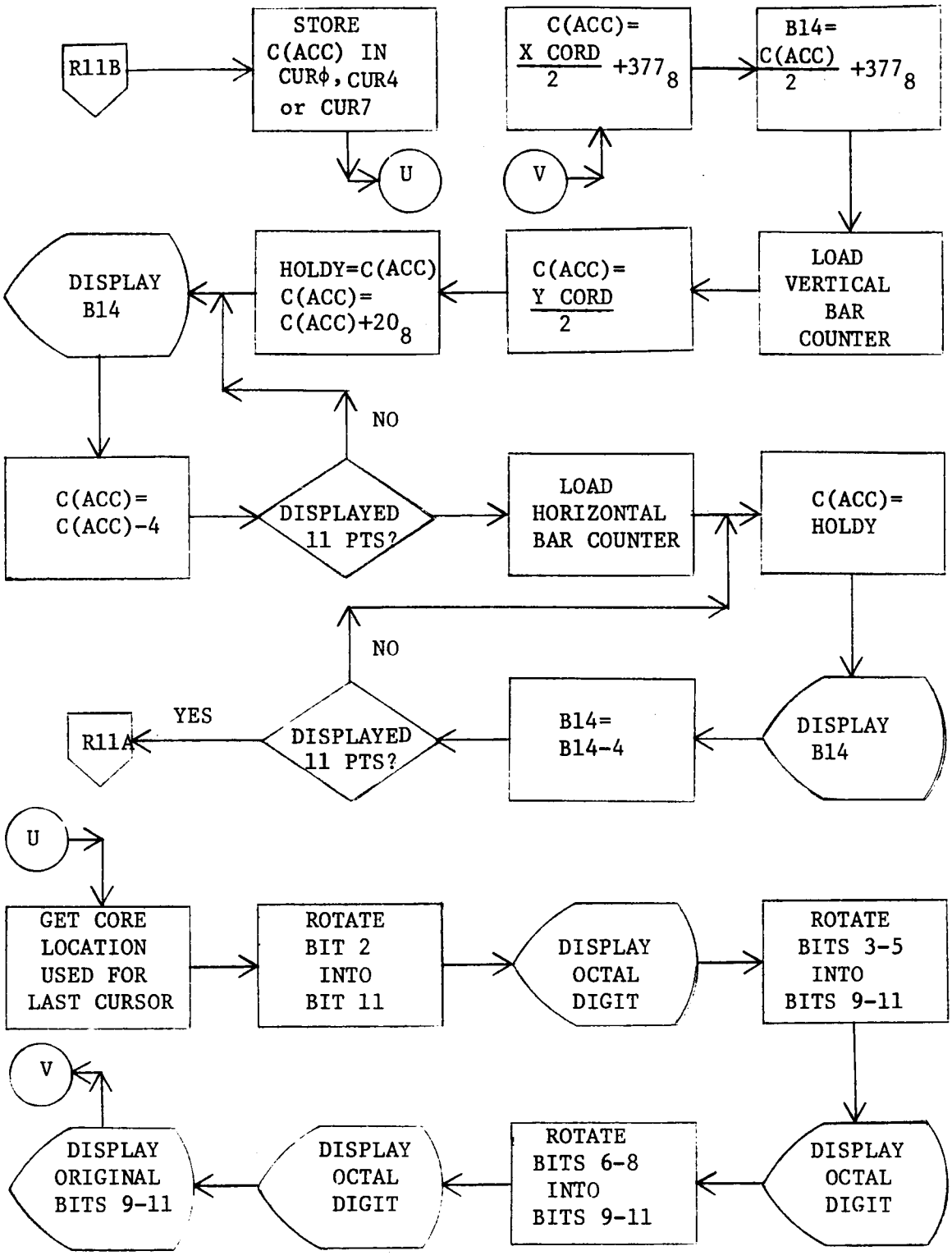


Figure B-11. (Continued).

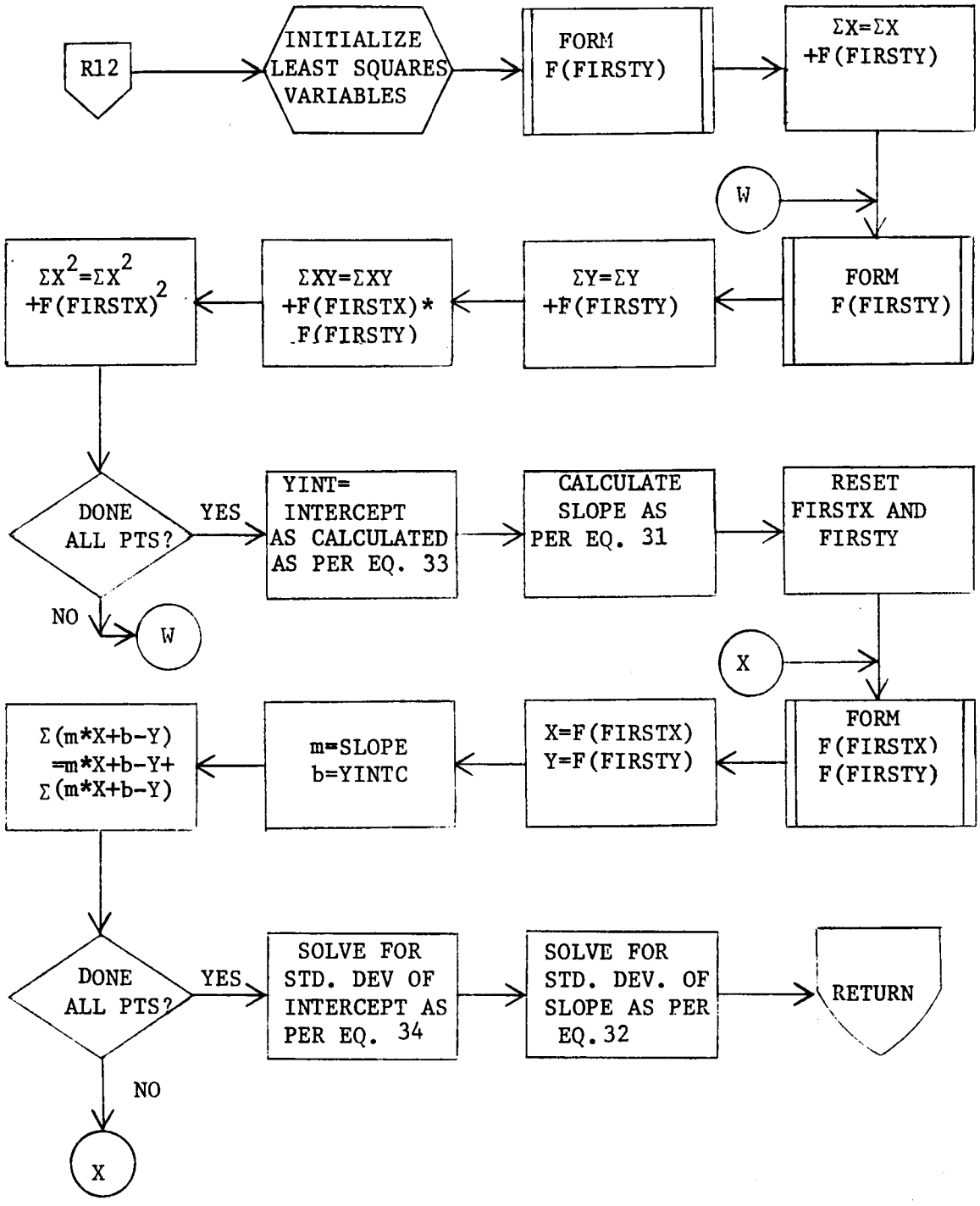


Figure B-12. Least squares fit of data.

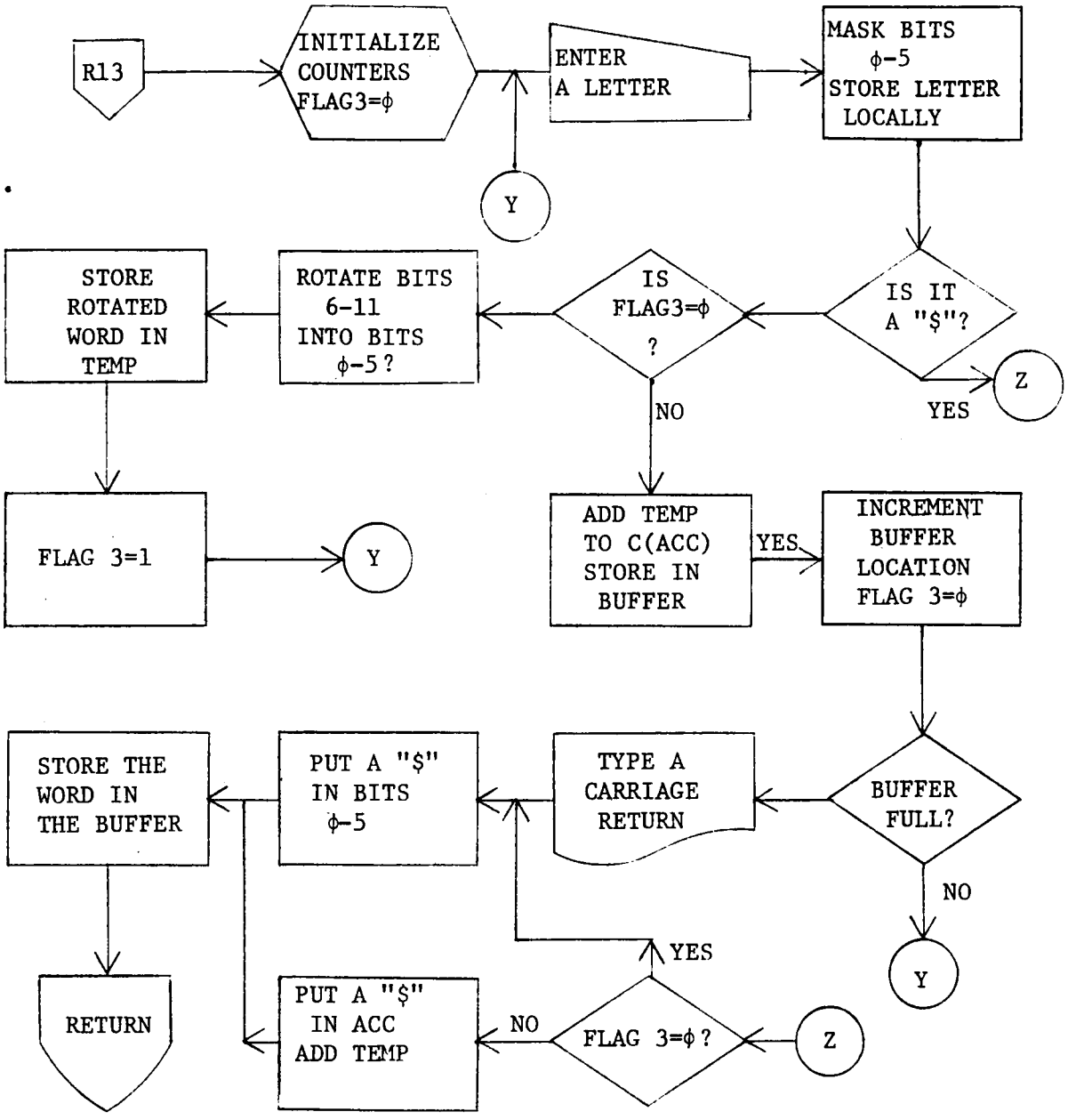


Figure B-13. Routine for storing user's message.

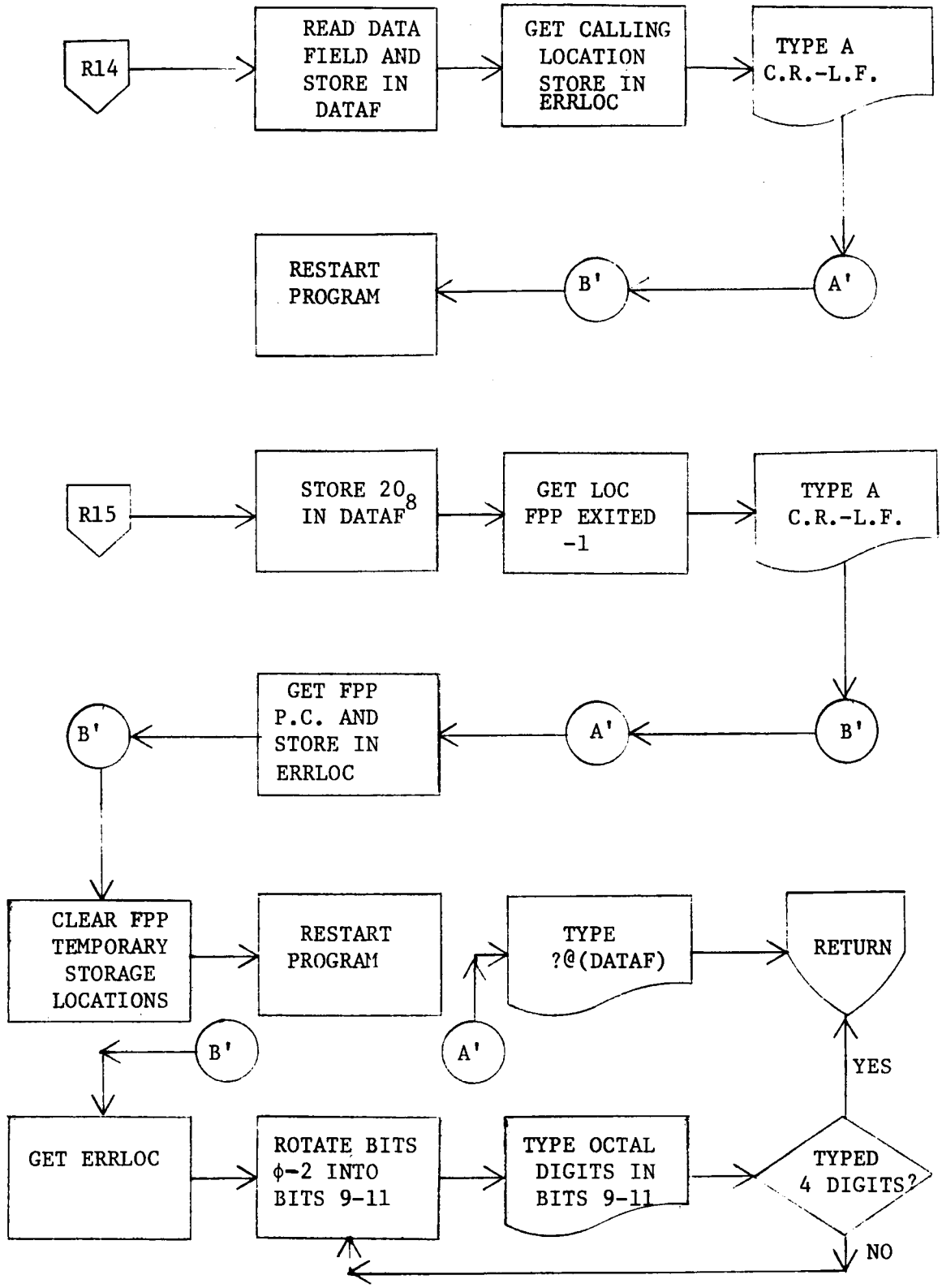


Figure B-14. Routines to print error messages.

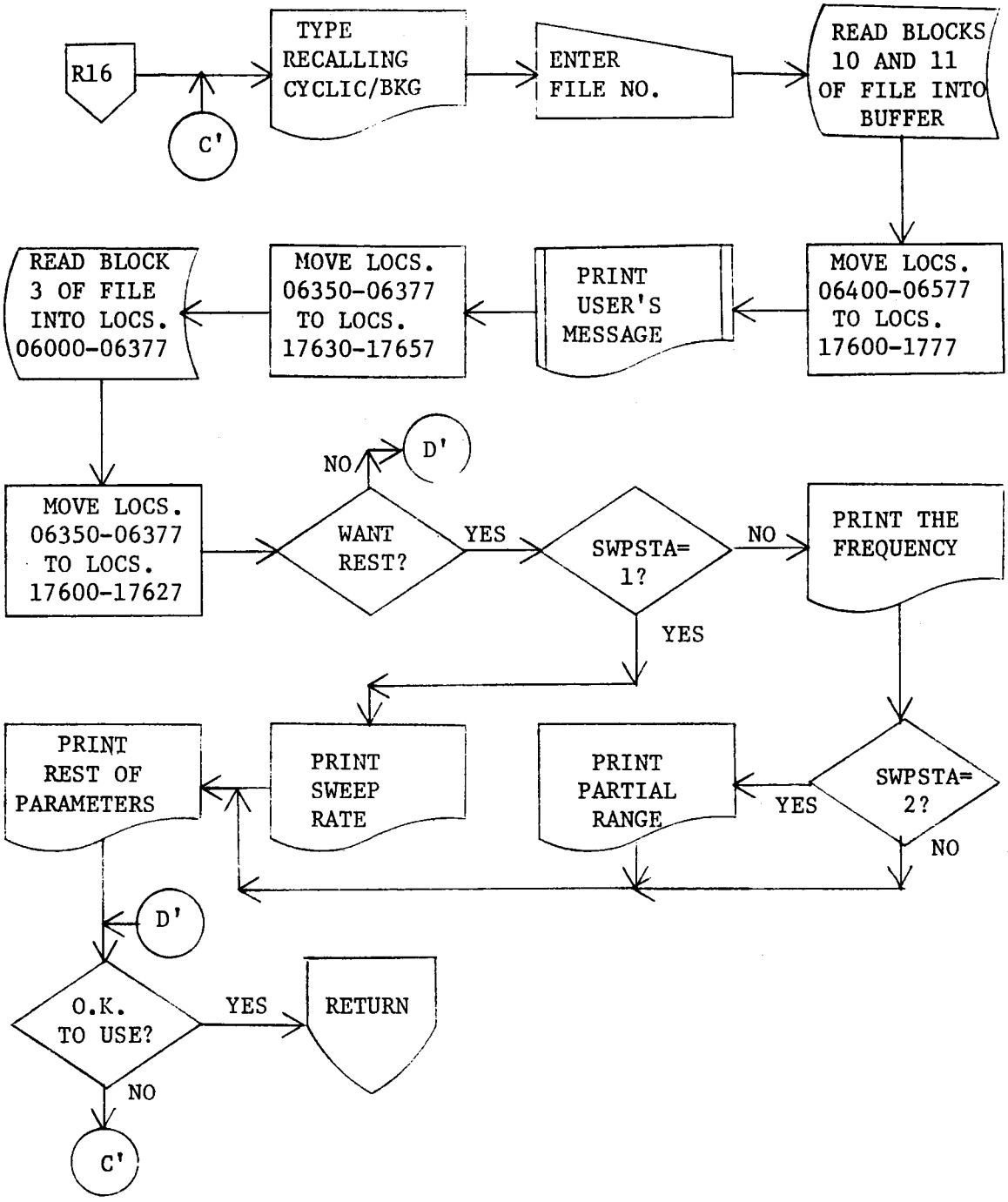


Figure B-15. Routine for recalling experimental parameters.

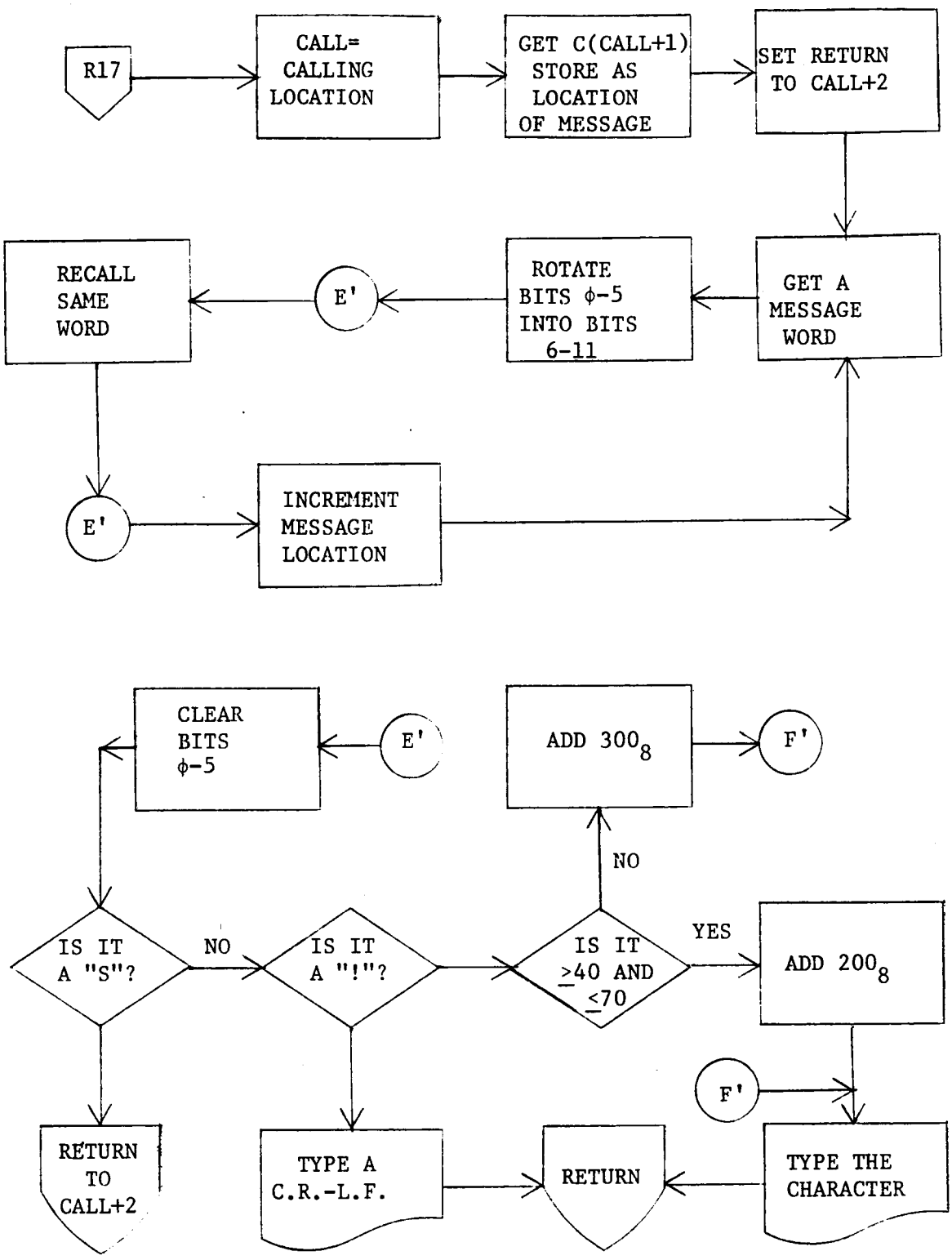


Figure B-16. Routine for printing user's message and preprogrammed messages.

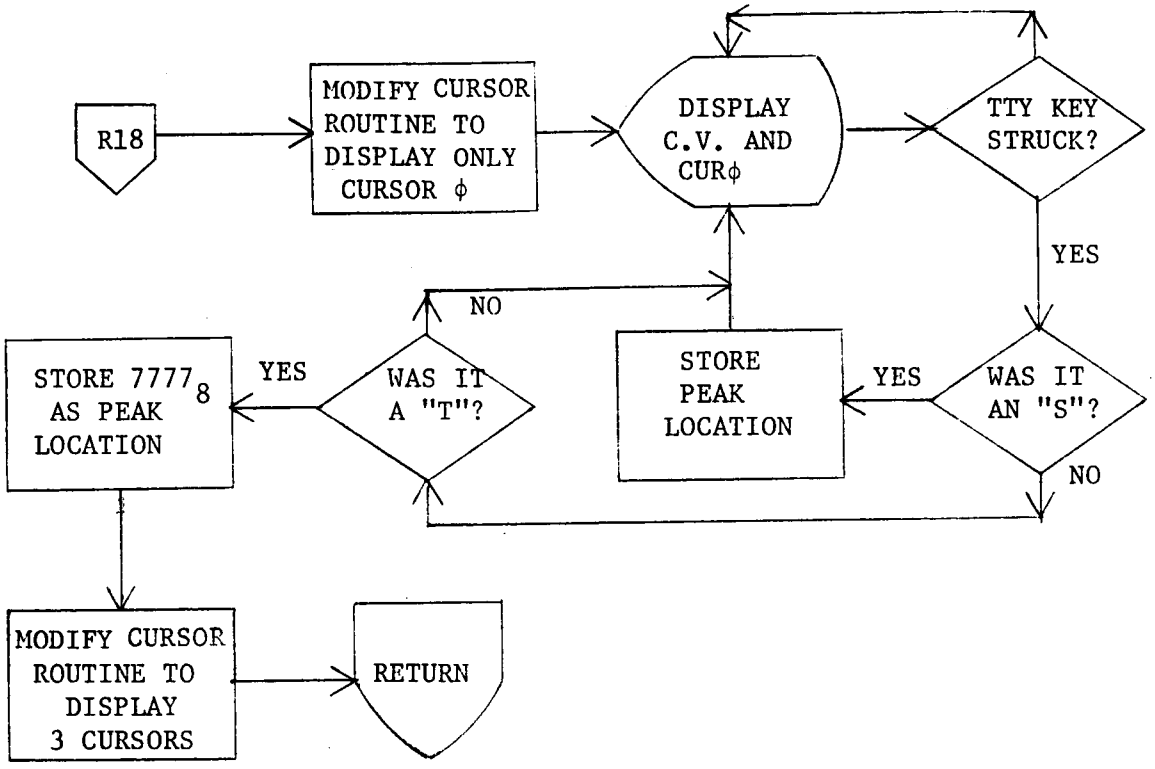


Figure B-17. Peak location routine.

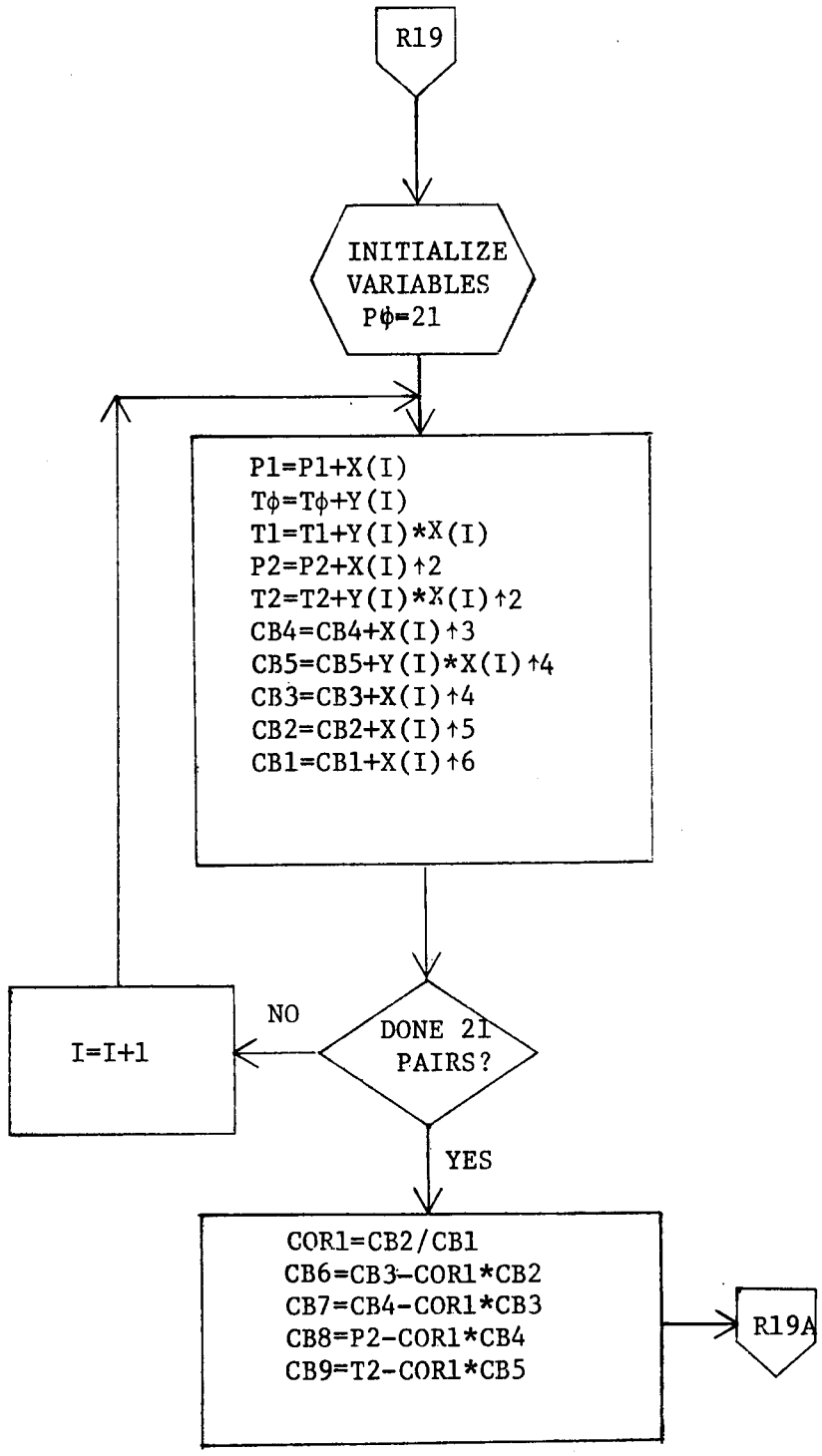


Figure B-18. Routine to fit a cubic around a cyclic voltammogram peak.

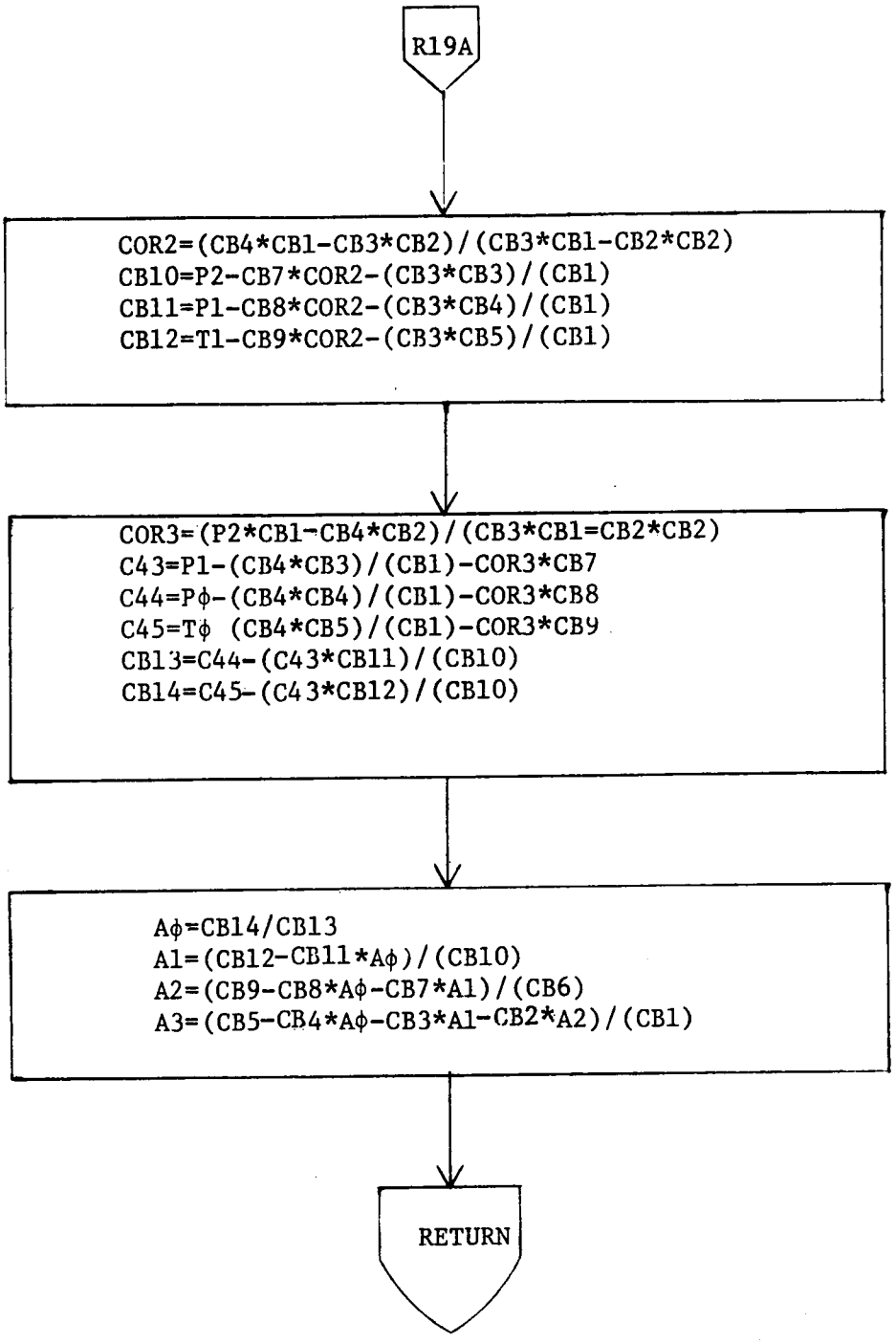


Figure B-18. (Continued).

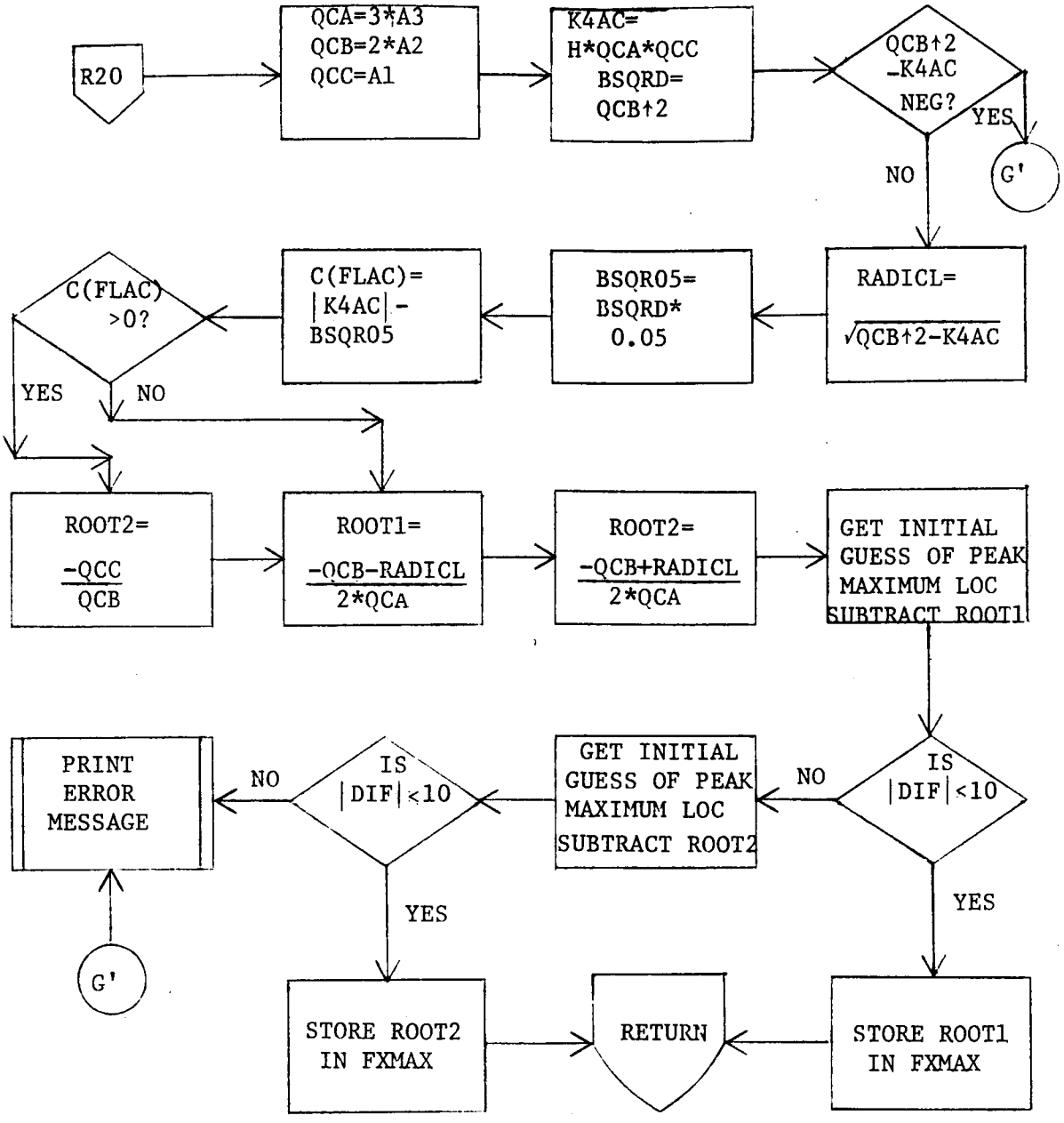


Figure B-19. Routine to solve for the roots of a quadratic equation.

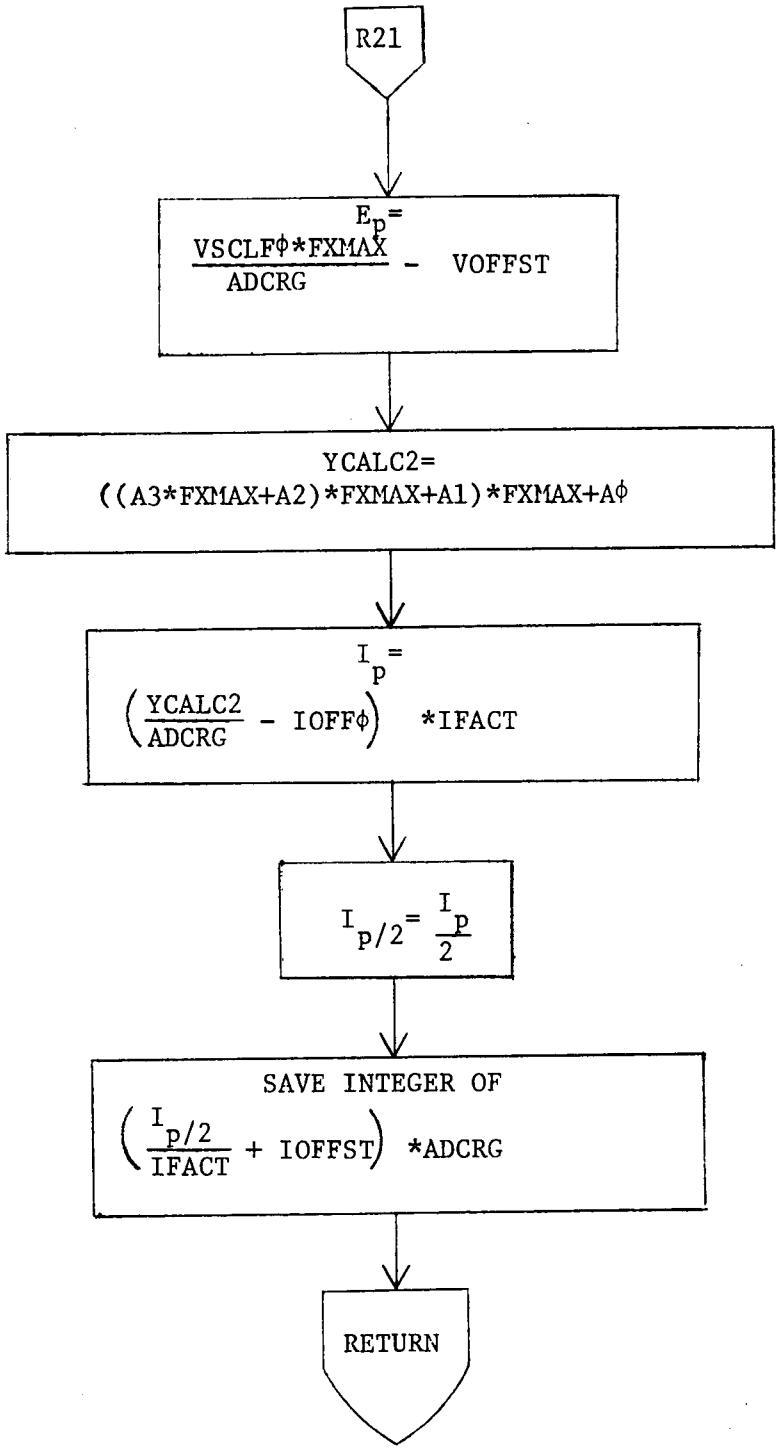


Figure B-20. Calculation of peak potential, peak height, and half peak height.

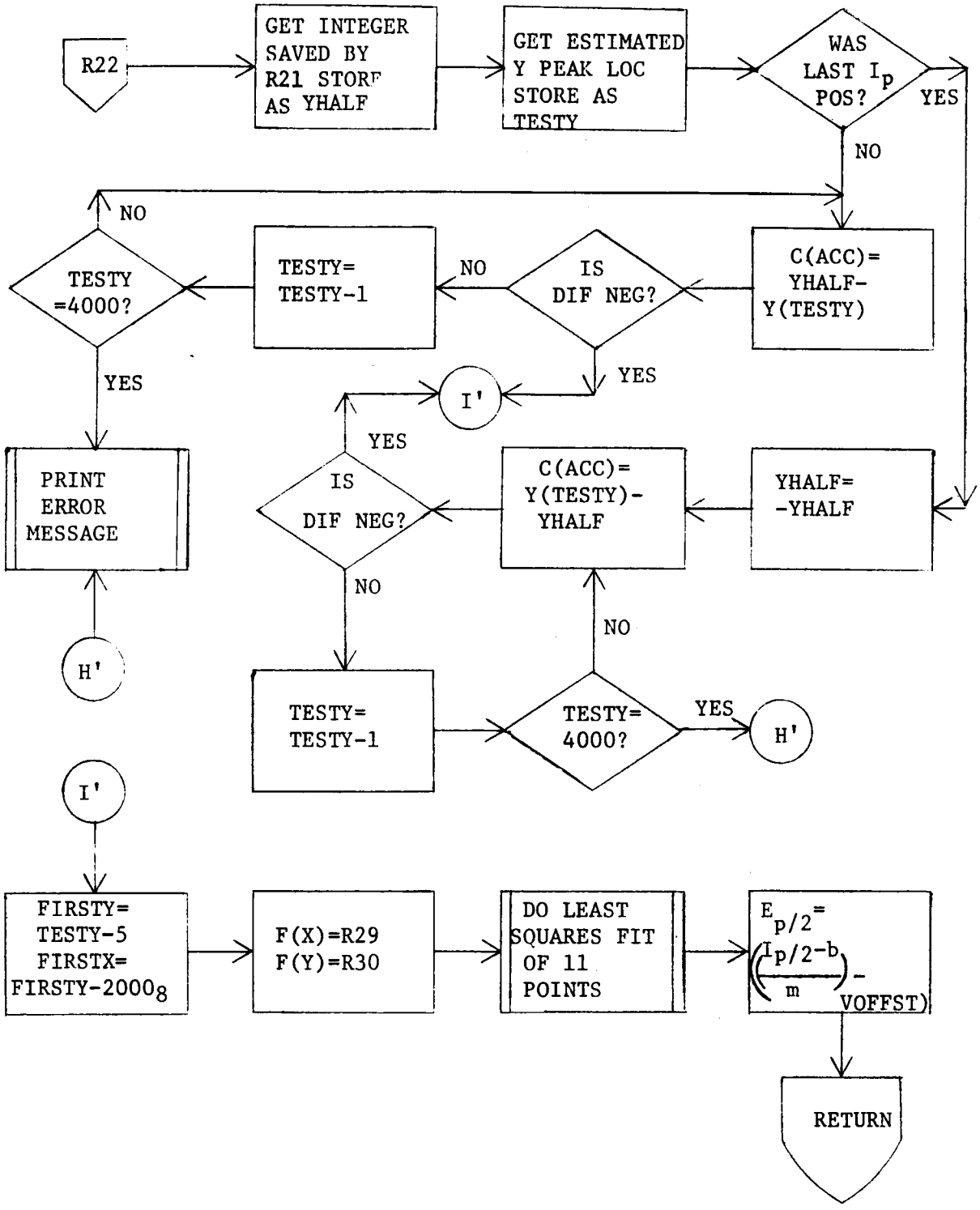


Figure B-21. Calculation of half-peak potential.

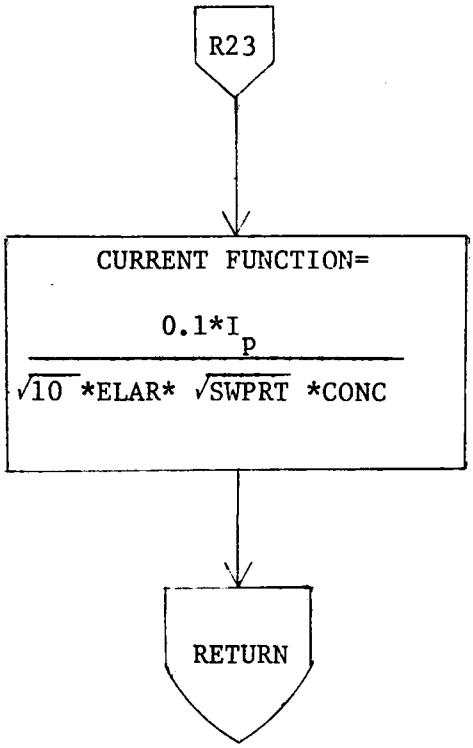


Figure B-22. Calculation of the current function.

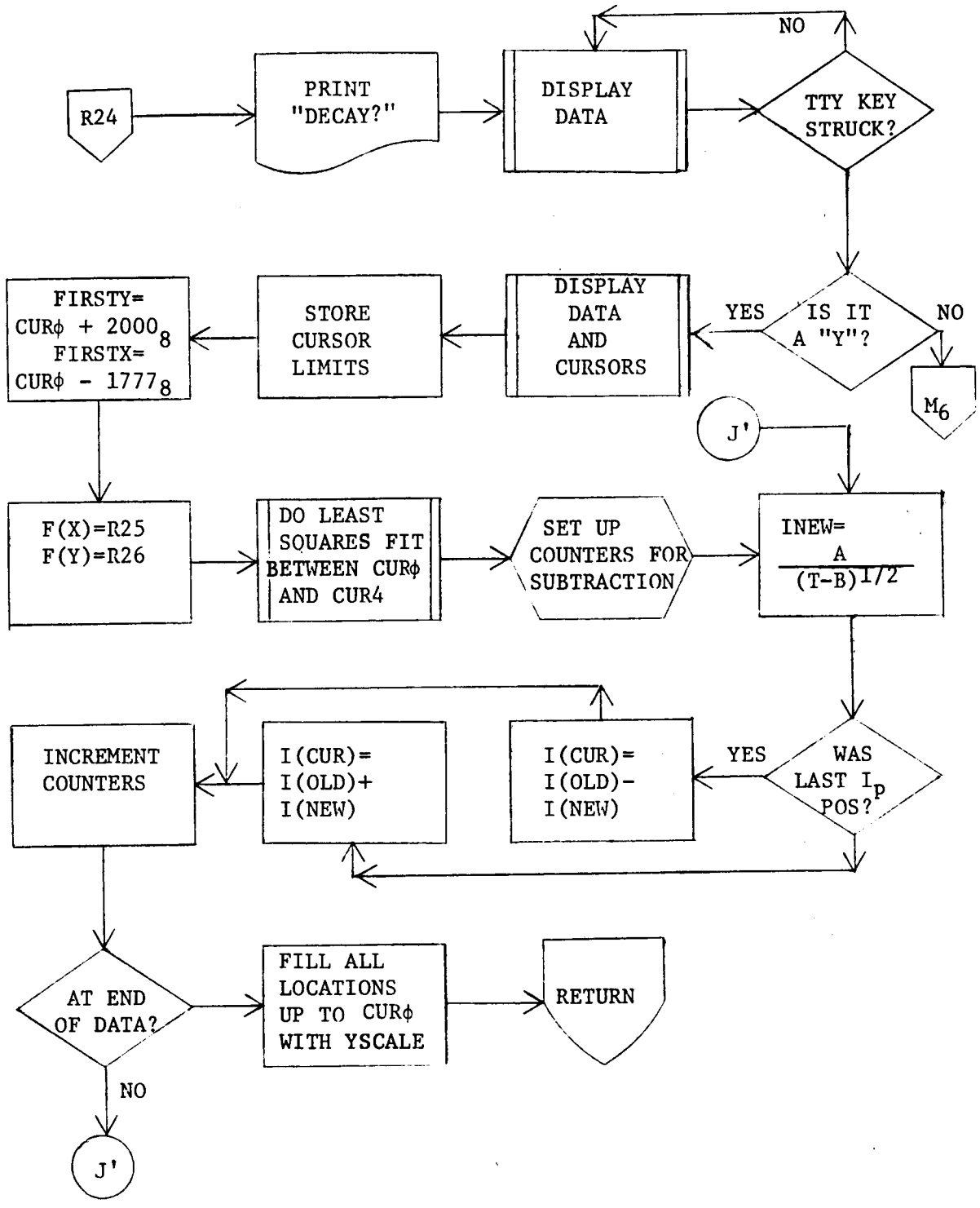


Figure B-23. Subtraction of $1/t^{1/2}$ decay.

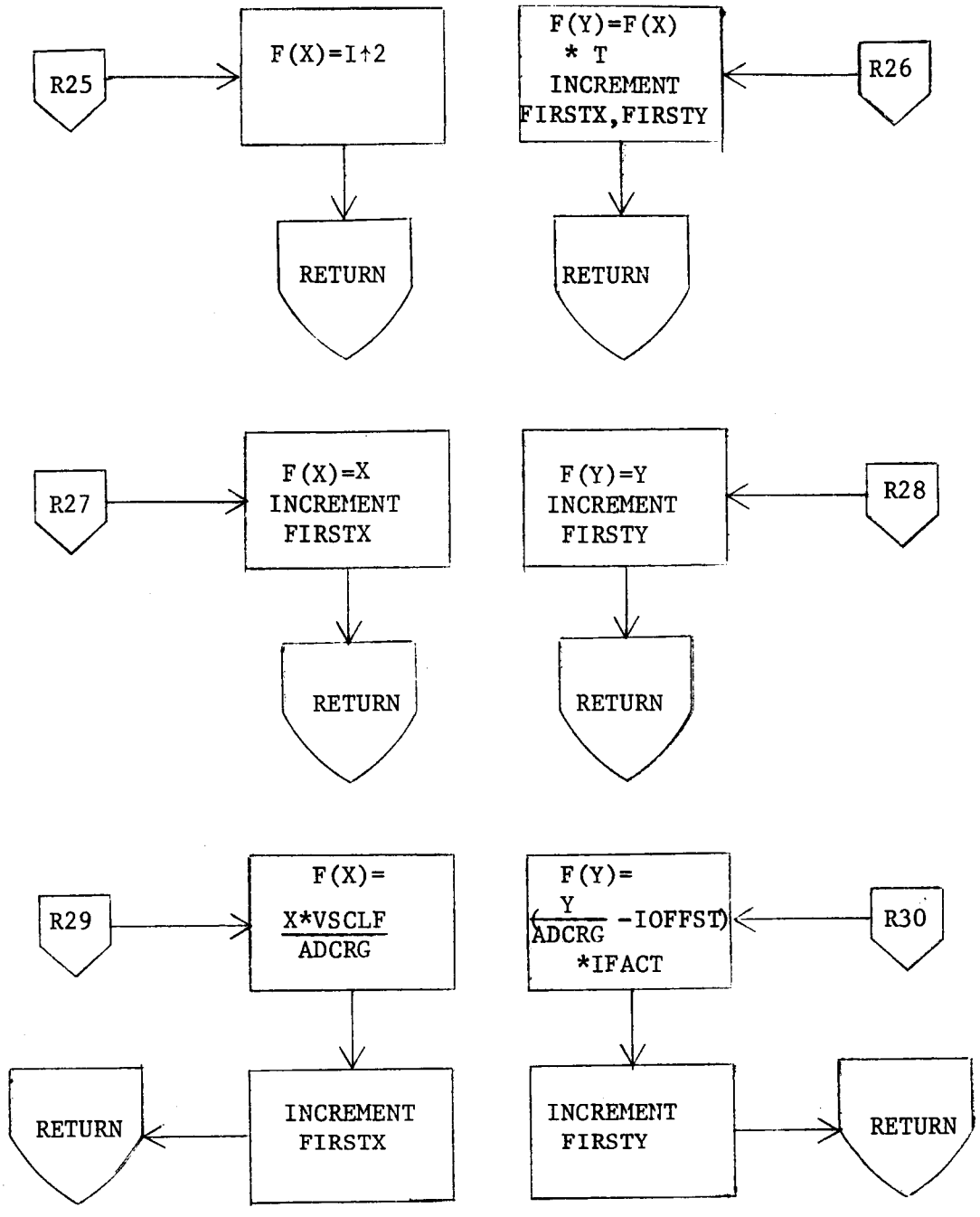


Figure B-24. Function subprograms used by least squares routine.

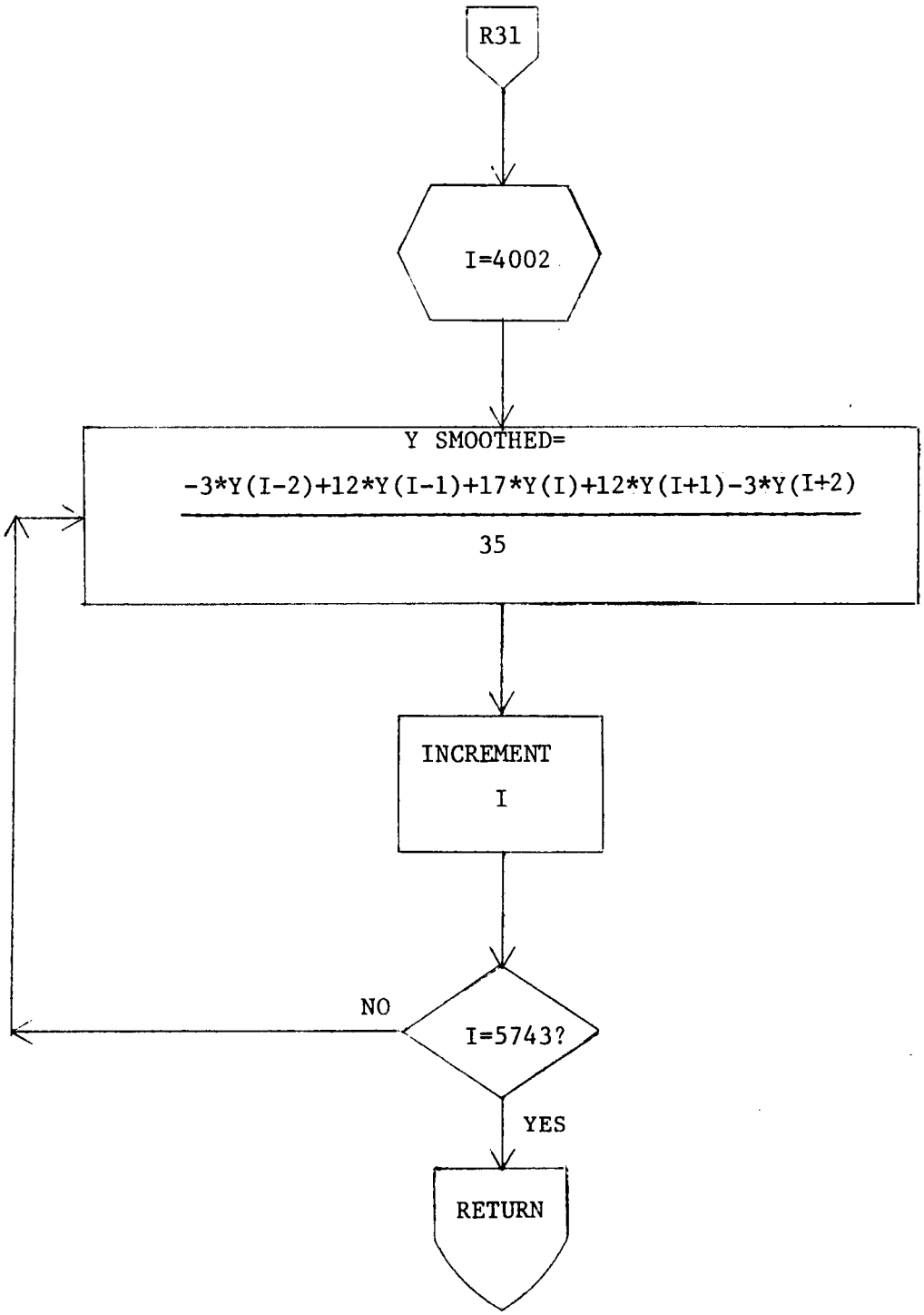


Figure B-25. Data smoothing routine.

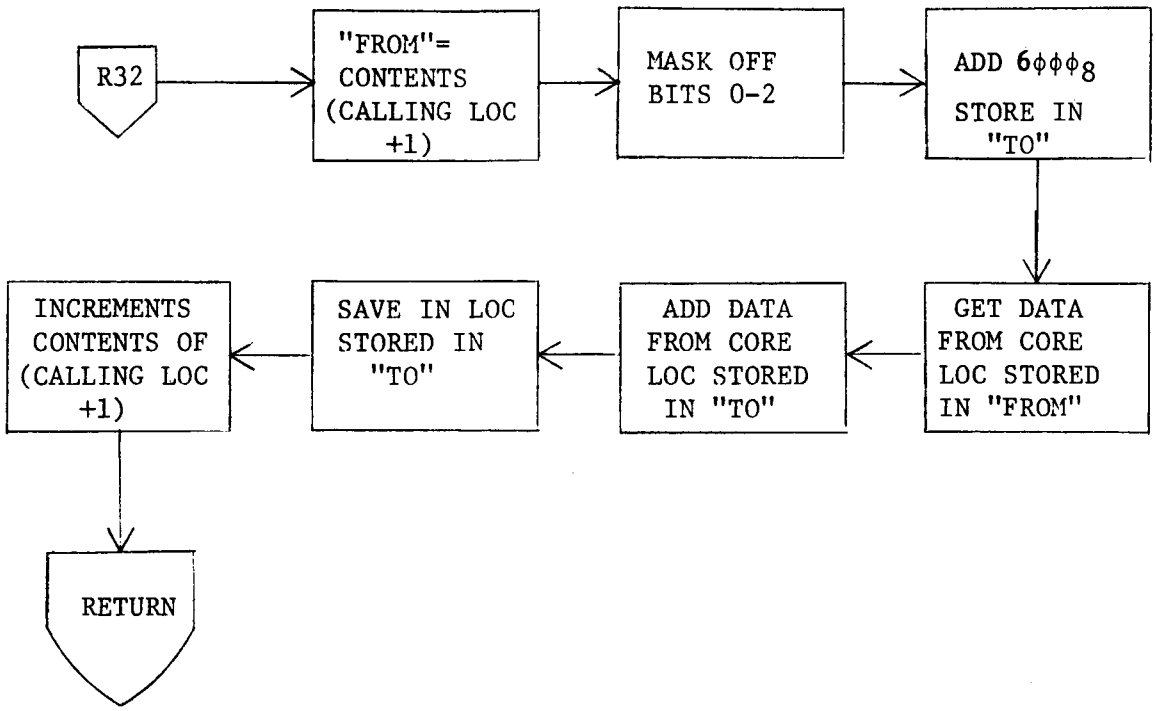


Figure B-26. Background summing routine.

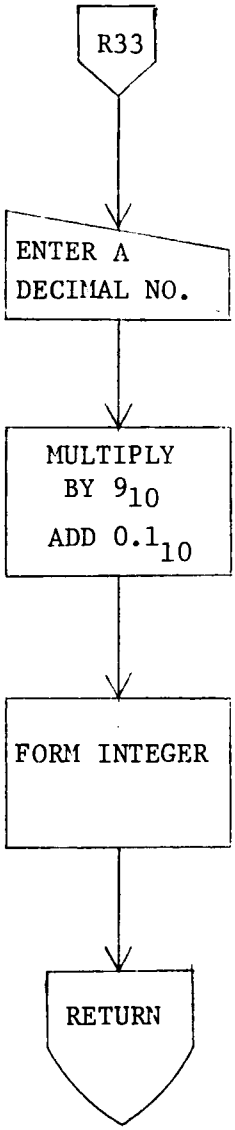


Figure B-27. Routine calculates starting block of a tape file.

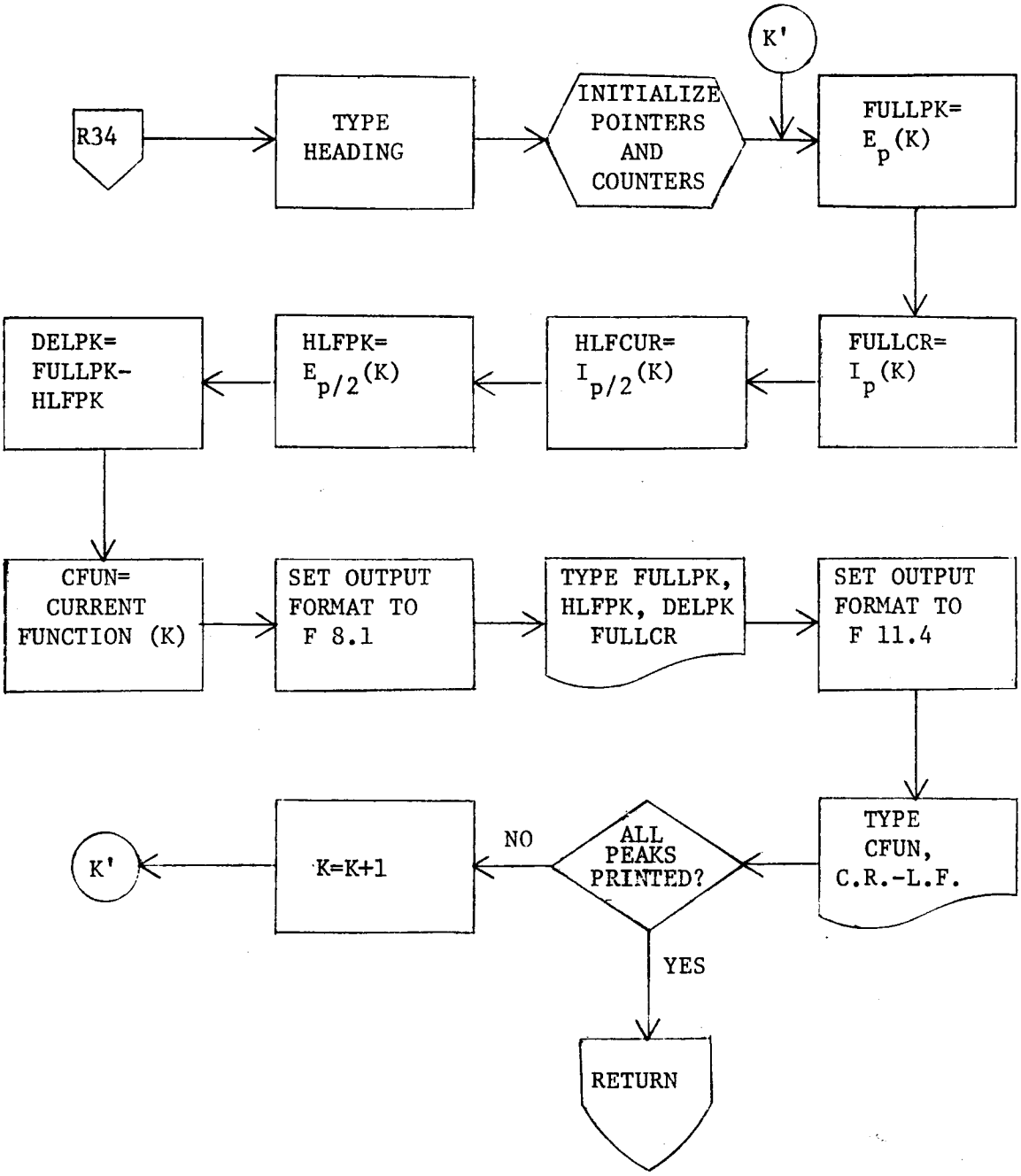


Figure B-28. Output routine for calculated parameters.

APPENDIX C

DERIVATION OF CUBIC EQUATIONS

The following derivation, for determining the coefficients of a cubic equation fitted to a set of data, was originally done by Norman Canfield (University of Tennessee). It is presented to enable the reader to follow the flowchart for the cubic fit routine since the terminology used for programming the routine is unique.

$$\sum_{i=1}^{m} y_i = \sum_{i=1}^{m} (a_0 + a_1 x_i + a_2 x_i^2 + \ldots a_n x_i^n) \qquad \text{(A 3.1)}$$

$$\sum_{i=1}^{m} y_i x_i = \sum_{i=1}^{m} (a_0 x_i + a_1 x_i^2 + a_2 x_i^3 + \ldots a_n x_i^{n+1}) \qquad \text{(A 3.2)}$$

$$\sum_{i=1}^{m} y_i x_i^2 = \sum_{i=1}^{m} (a_0 x_i^2 + a_1 x_i^3 + a_2 x_i^4 + \ldots a_n x_i^{n+2}) \qquad \text{(A 3.3)}$$

$$\vdots$$

$$\sum_{i=1}^{m} y_i x_i^n = \sum_{i=1}^{m} (a_0 x_i^x + a_1 x^{n+1} + a_2 x_i^{n+2} + \ldots a_n x_i^{2n}) \qquad \text{(A 3.4)}$$

Let $t_k = \sum_{i=1}^{m} y_i x_i^k$ and $P_k = \sum_{i=1}^{m} x_i^k$.

The system of equations may now be written as

$$t_0 = a_0 P_0 + a_1 P_1 + a_2 P_2 + \ldots + a_n P_n \qquad \text{(A 3.5)}$$

$$t_1 = a_0 P_1 + a_1 P_2 + a_2 P_3 + \ldots + a_n P_{n+1} \qquad \text{(A 3.6)}$$

$$t_2 = a_0 P_2 + a_1 P_3 + a_2 P_4 + \ldots + a_n P_{n+2} \qquad \text{(A 3.7)}$$

$$t_n = a_0 P_n + a_1 P_{n+1} + a_2 P_{n+2} + \ldots + a_n P_{2n} \qquad \text{(A 3.8)}$$

For a cubic fit n = 3, and since accuracy is improved with full pivotal searching,[24,25] the full system of equations arranged in pivotal form is

$$a_3P_6 + a_2P_5 + a_1P_4 + a_0P_3 = t_3 \qquad \text{(A 3.9)}$$

$$a_3P_5 + a_2P_4 + a_1P_3 + a_0P_2 = t_2 \qquad \text{(A 3.10)}$$

$$a_3P_4 + a_2P_3 + a_1P_2 + a_0P_1 = t_1 \qquad \text{(A 3.11)}$$

$$a_3P_3 + a_2P_2 + a_1P_1 + a_0P_0 = t_0 \qquad \text{(A 3.12)}$$

Since the P_1 values may be determined from the data to be fitted, they may be considered as the coefficients and the a_i terms considered as the unknown in these systems of equations. The a_i values may be found by the method of elimination.

The a_3 terms may be eliminated from equations A 3.10-12 by multiplying equation A 3.9 by P_5/P_6 and subtracting it from A 3.10, then multiplying A 3.9 by P_4/P_6 and subtracting it from A 3.11, and then multiplying A 3.9 by P_3/P_6 and subtracting it from A 3.12. The resulting system of equations is

$$P_6a_3 + P_5a_2 + P_4a_1 + P_3a_0 = t_3 \qquad \text{(A 3.13)}$$

$$(P_4 - \frac{P_5^2}{P_6})a_2 + (P_3 - \frac{P_4P_5}{P_6})a_1 + (P_2 - \frac{P_3P_5}{P_6})a_0 = t_2 - (\frac{P_5}{P_6} \cdot t_3) \qquad \text{(A 3.14)}$$

$$(P_3 - \frac{P_4P_5}{P_6})a_2 + (P_2 - \frac{P_4^2}{P_6})a_1 + (P_1 - \frac{P_3P_4}{P_6})a_0 = t_1 - (\frac{P_4}{P_6} \cdot t_3) \qquad \text{(A 3.15)}$$

$$(P_2 - \frac{P_3P_5}{P_6})a_2 + (P_1 - \frac{P_3P_4}{P_6})a_1 + (P_0 - \frac{P_3^2}{P_6})a_0 = t_0 - (\frac{P_3}{P_6} \cdot t_3) \; . \qquad \text{(A 3.16)}$$

The a_2 terms in Equations A 3.15 and A 3.16 may be eliminated by multiplying Equation A 3.14 by $(P_3P_6 - P_4P_5)/(P_4P_6 - P_5^2)$ and subtracting it from Equation A 3.15. Multiplying Equation A 3.14 by $(P_2P_6 - P_3P_5)/(P_4P_6 - P_5^2)$ and subtracting it from Equation A 3.16 gives

$$P_6a_3 + P_5a_2 + P_4a_1 + P_3a_0 = t_3 \qquad \text{(A 3.17)}$$

$$(P_4 - \frac{P_5^2}{P_6})a_2 + (P_3 - \frac{P_4P_5}{P_6})a_1 + (P_2 - \frac{P_3P_5}{P_6})a_0 = t_2 - (\frac{P_5}{P_6} \cdot t_3) \qquad \text{(A 3.18)}$$

$$C_{33}a_1 + C_{34}a_0 = C_{35} \qquad \text{(A 3.19)}$$

$$C_{43}a_1 + C_{44}a_0 = C_{45} \qquad \text{(A 3.20)}$$

where

$$C_{33} = (P_2 - \frac{P_4^2}{P_6}) - (\frac{P_3P_6 - P_4P_5}{P_4P_6 - P_5^2})(P_3 - \frac{P_4P_5}{P_6}) \qquad \text{(A 3.21)}$$

$$C_{34} = (P_1 - \frac{P_3P_4}{P_6}) - (\frac{P_3P_6 - P_4P_5}{P_4P_6 - P_5^2})(P_2 - \frac{P_3P_5}{P_6}) \qquad \text{(A 3.22)}$$

$$C_{35} = (t_1 - \frac{P_4}{P_6} \cdot t_3) - (\frac{P_3P_6 - P_4P_5}{P_4P_6 - P_5^2})(t_2 - \frac{P_5}{P_6} \cdot t_3) \qquad \text{(A 3.23)}$$

$$C_{43} = (P_1 - \frac{P_3P_4}{P_6}) - (\frac{P_2P_6 - P_3P_5}{P_4P_6 - P_5^2})(P_3 - \frac{P_4P_5}{P_6}) \qquad \text{(A 3.24)}$$

$$C_{44} = (P_0 - \frac{P_3^2}{P_6}) - (\frac{P_2P_6 - P_3P_5}{P_4P_6 - P_5^2})(P_2 - \frac{P_3P_5}{P_6}) \qquad \text{(A 3.25)}$$

$$C_{45} = (t_0 - \frac{P_3}{P_6} \cdot t_3) - (\frac{P_2P_6 - P_3P_5}{P_4P_6 - P_5^2})(t_2 - \frac{P_5}{P_6} \cdot t_3) \; . \qquad \text{(A 3.26)}$$

Eliminating a_1 from Equation A 3.20 by multiplying Equation A 3.19 by C_{43}/C_{33} and subtracting it from Equation A 3.20 gives the following system of equations.

$$P_6a_3 + P_5a_2 + P_4a_1 + P_3a_0 = t_3 \qquad \text{(A 3.27)}$$

$$(P_4 - \frac{P_5^2}{P_6})a_2 + (P_3 - \frac{P_4P_5}{P_6})a_1 + (P_2 - \frac{P_3P_5}{P_6})a_0 = t_2 - \frac{P_5}{P_6} \cdot t_3 \qquad \text{(A 3.28)}$$

$$C_{33}a_1 + C_{34}a_0 = C_{35} \qquad \text{(A 3.29)}$$

$$(C_{44} - \frac{C_{43}}{C_{33}} \cdot C_{34})a_0 = C_{45} - \frac{C_{43}}{C_{33}} \cdot C_{35} \qquad \text{(A 3.30)}$$

Letting the eliminated system of coefficients be designed by CB, the equations may be written as

$$CB_1a_3 + CB_2a_2 + CB_3a_1 + CB_4a_0 = CB_5 \qquad \text{(A 3.31)}$$

$$CB_6a_2 + CB_7a_1 + CB_8a_0 = CB_9 \qquad \text{(A 3.32)}$$

$$CB_{10}a_1 + CB_{11}a_0 = CB_{12} \qquad \text{(A 3.33)}$$

$$CB_{13}a_0 = CB_{14} \quad . \qquad \text{(A 3.34)}$$

Solving for the cubic coefficients from Equations A 3.31–A 3.34 gives

$$a_0 = CB_{14}/CB_{13} \qquad \text{(A 3.35)}$$

$$a_1 = (CB_{12} - CB_{11} \cdot a_0)/CB_{10} \qquad \text{(A 3.36)}$$

$$a_2 = (CB_9 - CB_8 \cdot a_0 - CB_7a_1)/CB_6 \qquad \text{(A 3.37)}$$

$$a_3 = (CB_5 - CB_4 \cdot a_0 - CB_3a_1 - CB_2a_2)/CB_1 \; . \qquad \text{(A 3.38)}$$

VITA

Edwin Ray Shelton was born on June 19, 1947, near Buffalo, Kentucky. He attended the public schools there and was graduated from LaRue County High School in 1965. The following September he enrolled at Centre College, Danville, Kentucky, where he received a B.A. degree with a major in chemistry in 1969. In September, 1969, he was made an offer he could not refuse--a McNamara fellowship for cultural exchange, which provided for four months study in the U.S. and thirteen months in Southeast Asia. On August 14, 1971, he was married to the former Ruth Nichols. In September of that year he entered the University of Tennessee for graduate study where he held a graduate assistantship until December, 1973.