COMPUTER PROGRAMS IN BASIC LANGUAGE FOR GRAPHITE FURNACE ATOMIC ABSORPTION USING THE METHOD OF ADDITIONS Part 2—Documentation

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MASTER

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FOREWORD

This report covers work performed by the Lawrence Livermore Laboratory for the United States Environmental Protection Agency under Interagency Agreement 78-D-X0085.

Part 1, "Operating Instructions," of this report contains the operating instructions for the programs described in more detail here in Part 2, as well as instructions for loading and running the programs.

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COMPUTER PROGRAMS IN BASIC LANGUAGE FOR GRAPHITE FURNACE
ATOMIC ABSORPTION USING THE METHODS OF ADDITIONS
PART 2--DOCUMENTATION

ABSTRACT

There are four computer programs, written in the BASIC language, used for taking and processing data from an atomic absorption spectrophotometer using the graphite furnace and the method of additions for calibration. The programs chain to each other and are divided into logical sections that have been flow-charted. The chaining sequences, general features, structure, order of subroutines and functions, and the storage of data are discussed. In addition, variables are listed and defined, and a complete listing of each program with a symbol occurrence table is provided.

INTRODUCTION

METHODOLOGY

In the graphite furnace method of atomic absorption (GFAA),¹ atomic vapor is produced by heating a sample contained in a graphite tube to very high temperatures (2000-2700°C), usually under flowing argon. The analytical signal is produced by measuring the light absorbed by the analyte atoms. The light source is a hollow cathode made from the element of interest. The rise and fall of the atomic vapor as it is formed in and swept from the graphite tube is indicated by a corresponding rise and fall of the absorption of the light from the hollow cathode source, and thus the signal takes the form of a rising and falling curve with a maximum. It has been shown that concentration can be considered proportional to the peak optical absorbance or the integrated optical absorbance.²

The solution to be measured is injected into the graphite tube through a small entry hole by means of a micropipet. The injection can be done manually or with a commercially available automatic sampler.³ The volume of solution injected is about 5 to 100 microliters, and the concentration of the analyte is about 0.05 to 0.5 micrograms per milliliter. The technique is used primarily for trace metal determinations. The actual parameters used for each determination are very dependent on the matrix of the sample and the element of interest.⁴

The method of additions or standard additions technique⁵ is used to develop a calibration curve when there is a reason to suspect that the physical and chemical properties of the sample matrix itself might cause significant interference of the signal attributable to the analyte, i.e., the substance being measured. The method consists of adding known amounts of a standard solution of the analyte to aliquots of the sample solution. The usual practice is to do this in such a way that each sample solution plus added standard solution is diluted to a constant volume. The known amounts of standard solution added to the sample solutions are called spikes.

The idea of the method is that the unknown solutions spiked with standards will be affected by the sample matrix in the same way as the unspiked sample. If this is so and if the response is linear, a plot of signal vs concentration may be extrapolated to give the analyte concentration in the sample solution.

Since GFAA is known to have a high probability of matrix interference, the method of additions is often used here (see Fig. 1).

FIG. 1. Methods of additions.

HISTORY

The original programs⁶ written in BASIC for GFAA depended mainly upon standard calibration curves for the calculation of unknown concentrations. These programs were originally based on a program written for the determination of total organic carbon using an infrared analyzer for CO₂ measurement.⁷ This program was expanded and adopted for GFAA by W. G. Boyle of LLL and modified somewhat by C. Brodbeck and J. Teuschler of the Environmental Monitoring Support Laboratory (EMSL), Environmental Protection Agency (EPA), Cincinnati, Ohio.

Although a method of additions option was available, it could be used only on one sample for each complete program cycle. Furthermore, this option did not allow for statistical inference or automatic sampling. The new programs are specifically written for the method of additions technique and calculate the statistics of the calibration curve, allow for multiple entry of samples, and can be used with an automatic sampler.

Since the calibration technique of the method of additions is so different from the standard calibration curve used previously, the programming had to be revised extensively. The programs have been written for a double-beam instrument with options to use a variable as a flag to convert to single-beam routines. It should be noted that an automatic sampler is not available at LLL; therefore, this section of the program and the single-beam option could be tested only by simulation.

GENERAL DESCRIPTION OF PROGRAMS

Program names begin with the prefix MAD (Method of Additions) and are terminated with the dot prefix .GF (Graphite Furnace). File names also start with the prefix MAD and are terminated with the dot prefix .DF (Data File).

The main program called MADSTART.GF chains to three subprograms. One of the subprograms is MADDAT.GF, which reads the data and plots them if desired and calculates the peak height or integral under the curve. This program is an extensive revision of the older version of the data processing routine.⁶ The new subprogram (MADDAT.GF) has been shortened and simplified so that it runs more efficiently; it was adopted from Dennis Ryan's programs for an ultraviolet visible spectrophotometer.⁸

The names assigned to these graphite furnace method of additions (GFMA) BASIC language programs are as follows:

1. MADSTART.GF for the main program
2. MADDAT.GF for data accumulations and interpretation
3. MADFIT.GF for linear regression and statistics
4. MADREP.GF for report generation.

The main program MADSTART.GF does the initialization, allows the operator to investigate the timing of his data logging, sets parameters for data logging, logs in samples in either an automatic or a manual mode of operation, and interprets commands to the program with the command string interpreter (CSI). The main program also contains sections that allow some editing of the data files.

The data-taking program (MADDAT.GF) takes the raw data, converts them to optical absorbance, and calculates a smoothed peak height and an integral. A plot of the data can be produced on the line printer or terminal.

The calculational program MADFIT.GF does the first-degree linear fit and calculates the concentration of the unknown by mathematically extrapolating the equation for this fit. This computation is somewhat different from the regression routines used in the previous calibration programs in that the computation uses each individual reading of the spiked sample rather than an average to develop the necessary mathematical matrices. In this way the statistical standard deviation for the extrapolation routine may be determined more conveniently. The standard deviation of the extrapolation is valid only if equal numbers of replicates (if any) are run on each spiked sample.

Finally, the report program MADREP.GF reports results during the analysis and formulates a final report when the analysis is over. Figure 2 shows the general chaining sequence.

MADSTART.GF

GENERAL FEATURES

This program is the main program for running GFMA. It sets the timing for acquiring data, sets up files, stores spike and sample information, allows manual or automatic modes of operation, prints out a loading pattern for an

FIG. 2. Main function and chaining of programs for GEMA.

automatic sampler, and interprets command strings. The program also executes some of the commands given to the CSI such as erase, delete, and display data files. Other CSI commands are carried out by chaining to one of the subprograms.

One should remember while reading these program descriptions that standards and samples are mixed. That is, standards (spikes) are added to samples to form a series of solutions (up to six), and these solutions are injected into the graphite furnace one at a time. The data obtained from these solutions are then used to calculate the concentration of the analyte in the original sample. The measurement on each spike may be repeated up to a maximum of six times.

Figure 3 shows the general program flow for the manual mode of operation, and Fig. 4 shows the general program flow for the automatic mode of operation. Upon completing the samples in the automatic mode, the program reverts to the manual mode.

FILES

There are three main data files used in the program. They are all opened in random mode. File 7, named MADHOLD.DF and opened at line number 170, contains most of the miscellaneous variables required to chain from one program to another. File 5, named MADID.DF, and opened at line number 1535 for the automatic mode and line number 2505 for the manual mode contains the sample names, the number of spikes, the number of times the sample will be run if done automatically, the concentration of each spike in ascending order, and the dilution factor. File 1, named MADGFC.DF and opened at line number 860 contains the data obtained on spiked samples and on completed samples.

Opening the files in random access mode means that the data in these files may be located by means of record numbers. Records are lines of information numbered starting from 0. Each variable in a given record occupies a position.

The data on completed samples are kept in two records for each sample starting at record number 7. Thus, data on sample number 1 are kept in records 7 and 8, sample number 2 in record number 9 and 10. Each sample can be repeated a maximum of six times. A complete set of spikes is run for each repetition. Records numbered 1 to 6 are used to store data on spiked samples

FIG. 3. MADSTART.GF main program manual mode.

FIG. 4. MADSTART.GF main program automatic sampler mode.

for the current sample being run. These records are cleared whenever a new sample is started. Figure 5 shows the structure of the data files for spiked samples, and Fig. 6 for completed samples. Figure 7 shows the structure of the sample identification file. A "run" is defined as being one complete set of data on a set of spiked samples resulting in an answer for an unknown sample. A set of spiked samples includes the unspiked sample.

<u>Positions</u>	First spiked sample in record #1	Second spiked sample in record #2	
↓	Av signal	Av signal	
	Spike conc	Spike conc	
	Number of reps	Number of reps	
	--	--	
	Signal, 1st rep	Signal, 1st rep	
	2nd	2nd	
	3rd	3rd	
	4th	4th	
	5th	5th	
	6th	6th	

Up to
six spiked
samples →

(Records 1 to 6 cleared for each new sample)

FIG. 5. Data file for spiked samples.

Positions	Unknown #1		Unknown #2		Futher samples
	Record #7	Record #8	Record #9	Record #10	
↓	Ave conc	Ave variance within sample	Ave conc	Ave variance within sample	
	Dilution factor	Variance among samples	Dilution factor	Variance among samples	
	No. of reps	No. of reps	etc.	etc.	
	No. of spikes	— —			
	Conc 1st run	Var. 1st sample			
	2nd	2nd			
	3rd	3rd			
	4th	4th			
	5th	5th			
	6th	6th			
	Slope 1st run	1st coeff. of det			
	2nd	2nd			
	3rd	3rd			
	4th	4th			
	5th	5th			
	6th	6th			

FIG. 6. Data file for completed samples.

FIG. 7. Sample identification file.

TIMING

After a sample has been injected into the graphite furnace, a temperature control that is part of the instrumental system and separate from the computer, cycles the furnace through three preset temperatures for three preset times. First there is a drying time (typically 110°C for 30 seconds), then a charring time to burn off organic matter (say 600°C for 30 seconds) and finally an ignition time to atomize the sample (2300°C for 20 seconds, for example). The actual setting of these times and temperatures on the furnace controller depends on the nature of the sample and analyte. Therefore, the program must be told when to start taking data so that the peak and baselines during the atomization cycle are well defined. This is done by using a signal that the instrument generates during the charring cycle. This signal is used to turn on a strip chart recorder; it is also used here to send a signal to the computer to enable the data-taking assembly language call.⁹

Data are collected by means of a call to an assembly language routine.¹⁰ This call is written CALL 7, A, B, C, D, E; A is a number that selects the proper data channels for the A/D converter, B is a delay time in 1/60 second intervals, C is the interval in 1/60 second units between pairs of points, D is the number of points and is set at the maximum number of 300, and E is an array that holds the 300 points starting with the reference beam and alternating between the reference and sample beams. These 300 points are converted to 150 ratios of reference-to-sample beams and converted to optical absorbances. This array of 150 optical absorbances makes up the points used for plotting, finding the peak height, or integration under the curve. On a single-beam instrument, only 150 points are taken because there is no reference beam. A different call is used for single-beam instruments.^{10,11}

Refer to Fig. 8 for the explanation of the following timing procedure.

The timing algorithm uses the knowledge that a full 150 points are always taken to define the curve and that the time between when the graphite furnace call is enabled by the autoswitch and the ignition cycle of the furnace begins is a constant. This constant is called the hardware delay. If we decide on a constant number of points to define the leading baseline (20

FIG. 8. Timing for data collection.

points are used here) and the trailing baseline (40 points), then 90 points are left to define the curve. All that need be entered is the time required to define the peak, and the timing algorithm will calculate everything that is necessary for the BASIC call to take data.

The following algorithm is implemented in lines 500 to 700 of MADSTART.GF.

1. Determine the numbers of points needed in each section of the curve: the leading baseline, the peak, and the trailing baseline. We have found that 20, 90, and 40 points respectively are reasonable values. Also determine the hardware delay for the instrument.

2. Determine the time for defining the peak by preliminary runs and prior information. The peak define time is the time between when the signal first begins to rise above the baseline and the time when it first returns to the baseline. This time is highly dependent on the element of interest and its matrix.

3. Determine the total time for the run by calculating the rate needed to define the peak (seconds/point) and multiplying by the total number of points (150).

4. Determine the time for the leading baseline by taking proportional parts of the total time. For example, if the total time to define the curve is 15 seconds, the leading baseline would take $20/150$ times 15 seconds or 2 seconds.

5. Subtract the result in step 4 from the experimentally determined hardware delay. This gives you the delay time, that is the time between when the call is enabled and the call actually begins taking data.

Values for the graphite furnace call must be integers. Times are recalculated as the number of $1/60$ th of a second intervals, and these are rounded to integer values. If the interval is less than $1/60$ th of a second, an error message is generated and the user is directed to try a new value.

A more formal representation of timing and the calculation of total time is given in Appendix A. Figure 9 shows the program flow for the timing of data acquisition.

SAMPLE WHEEL PATTERN GENERATION

When using the automatic sampler, it is convenient to have a map of how the sample wheel should be loaded. The computer program allows the options of no map or printing out a map on the terminal, the line printer, or both. The program reads the sample identification file (No. 5, MADID.DF) and from the information in this file prints out the sample wheel position number, an identifier similar to what would be typed to the CSI, the word BLANK or the name of the sample, and the spike concentration for samples. It is mandatory in this scheme that a blank be read before each new set of spiked samples. This is a reasonable action and is built into the automatic mode.

If replicate measurements are to be made on each solution, a mechanical counter is set to the proper value on the sample wheel. Thus, blanks are read for the same number of replicates as samples. The blank values are averaged in this case. (They are not averaged in the manual mode.) Figure 10 shows an example of a sample wheel pattern.

FIG. 9. Timing data collection.

***** SAMPLE WHEEL PATTERN *****

POSITION		I.D.	SPIKE
1	B	BLANK	
2	S 1 /1	FIRST #1	0
3	S 2 /1	FIRST #1	50
4	S 3 /1	FIRST #1	100
5	B	BLANK	
6	S 1 /1	FIRST #1	0
7	S 2 /1	FIRST #1	50
8	S 3 /1	FIRST #1	100
9	B	BLANK	
10	S 1 /1	SECOND #2	0
11	S 2 /1	SECOND #2	25
12	B	BLANK	
13	S 1 /1	SECOND #2	0
14	S 2 /1	SECOND #2	25
15	B	BLANK	
16	S 1 /1	RETHIRD	0
17	S 2 /1	RETHIRD	10
18	B	BLANK	
19	S 1 /1	RETHIRD	0
20	S 2 /1	RETHIRD	10
21	B	BLANK	
22	S 1 /1	FOUR #4	0
23	S 2 /1	FOUR #4	1
24	S 3 /1	FOUR #4	2
25	S 4 /1	FOUR #4	3
26	B	BLANK	
27	S 1 /1	FOUR #4	0
28	S 2 /1	FOUR #4	1
29	S 3 /1	FOUR #4	2
30	S 4 /1	FOUR #4	3

FIG. 10. Sample wheel pattern.

AUTOMATIC MODE

The MADSTART.GF program is directed by keyboard commands. When running in the automatic mode, these commands are generated by reading the sample I.D. file and concatenating string variables to form a proper command. This string is stored in the variable for the CSI, and the CSI routine is entered at a point just beyond manual input for the CSI. A string variable flag is used to indicate an automatic run, so when the program arrives at the end of the CSI routine it returns to the CSI generator automatically.

Figure 11 shows the general flow of the automatic mode of operation.

FIG. 11. Automatic mode of operation.

COMMAND STRING ENTRIES

Command string entries control the functions of MADSTART.GF. These commands and their functions are listed in Table 1. Any other input gives a syntax error message and returns the user to the double asterisk command input prompt. If a number representing a spiked sample beyond those listed in the sample identification file or a number representing a sample not listed is entered, a similar syntax error action is initiated. Figure 12 shows what each command does. The CSI looks at the command and if it is not a B, R, C, or MS assigns numerical values to the variables M0, M1 and M2. M0 is assigned a 1 or 2 depending on whether the first letter of the command is a S (for spike) or U (for unknown). M1 is for the spike number of unknown number and M2 is the replicate number. File positions are calculated on the values of M2 and are assigned to the variable A4. File records are calculated on the values for M1 and are assigned to the variable A5.

TABLE 1. Responses to CSI double asterisk prompt.

Response	Function
SX/Y	Get data for spiked sample X, replicate Y.
UX/Y	Display average concentration for unknown X and concentration for replicate Y.
B	Get data for blank solution.
R	Print interim report. If no more samples, print final report.
C	Calculate first-degree linear regression curve and print curve parameters, unknown concentration, and statistics.
MS	Perform another complete run on the same sample or begin run on a new sample.
UX/P	Display raw data files for unknown X, and concentration and statistics.
SX/P	Display raw data file for spiked standard X.
SX/E or UX/E	Erase results (zero raw data files) for spiked sample X or final results on unknown X.
SX/YD or UX/YD	Delete results on spiked sample X, replicate Y, or current run Y on unknown X file. Unknown file deletions are not allowed following MS.

FIG. 12. Command string entries.

Figure 13 shows what the program does in response to the CSI command B or MS. When the response is B, the program executes a short routine that checks the value of the sample and reference beams with no sample present, as mentioned previously. This is for double-beam instruments only. The difference in the two beams is calculated and used as a correction factor for absorbance calculations. This feature is optional, because the correction is used mainly to adjust the optical absorbances produced by the program to correspond to any instrumental optical absorbance that may be displayed. The relative optical absorbance is what is used in the calculation of concentration.

When in the automatic mode, the blank is necessarily read the same number of times as the spiked samples and therefore this blank is averaged. Blanks are not averaged in the manual mode.

Since samples are entered before beginning a manual run, the CSI command MS is used only in the manual mode. MS results in a computer prompt that determines whether the next sample run (the set of spiked samples) is a repeat of the current sample or is going to be a new sample. In any case, a warning flag (G1) is cleared upon typing MS. This warning flag is used to prohibit a C response to the CSI after deleting a sample run. If a C response were accepted at this point, the next sample would be recalculated using the wrong spike concentrations. The rest of the MS routine follows the flow chart shown in the second half of Fig. 13, starting at point B.

The functions of the P, D, and E commands are shown in Fig. 14. The P command (peek) writes out the values contained in the appropriate file on the console. Since finished sample data are stored in two records, more information is read out for the UX/P command than for the SX/P command.

When deleting a replicate run in the completed sample file, the replicate must be the current sample being run; otherwise an error message is given. Also, when a sample run has been deleted, the positions in the file containing sample data are closed up so that the next sample data go into the proper position. Of course, corrected statistics must be calculated and this makes up most of the routine. The erase routine E is fairly straightforward, because in this case an entire file is zeroed. The G1 flag is set here for sample erasures (see MS response).

The general command to read an injected sample is SX/Y, where X is the number of the spiked sample and Y is the replicate number. This routine goes

FIG. 13. Blank and sample entry routines.

FIG. 14. Flowchart for the P, D, and E commands.

to a subroutine that chains to MADDAT.GF and routines with either a peak height value or an integral. These values are stored in the spiked sample file and when all the spikes have been read a concentration may be determined by typing C. Because sample and standards are combined in the method of additions, typing the analogy of SX/Y for an unknown, say UX/Y, is not used for acquiring data. In these programs, such a command results in the display of the average concentration for sample No. X and the concentration for run Y, if any. If there are no values for a run, a zero will be typed (see Fig. 15).

The general operation of the command string interpreter is shown in Fig. 16. The command is first divided into parts--the part before the slash (/) is stored in K1\$ (S or U), and the part after the slash is stored in T1\$ and K2\$. These last two literals are eventually converted to numbers by the BASIC VAL function and used to determine the program location that accomplishes the appropriate action. There are a number of checks throughout the routine for invalid commands. The values determined from the command are also used to calculate the proper file, record, and position as explained above.

MADFIT.GF PROGRAM TO CALCULATE VALUES FOR UNKNOWN BY METHOD OF ADDITIONS

The program MADFIT.GF is called by MADSTART.GF when a set of spiked unknowns has been completed. This is done automatically when using the automatic sampler and is done manually by typing C in response to the CSI command. Upon first entering the program, a routine counts the number of spiked samples that have been measured and compares this number with the number of spiked samples originally entered. If the two numbers are not equal, the program prints a warning message and chains back to the MADSTART program at the CSI.

If all of the spikes have been measured, several of matrices are constructed according to the following algorithm^{*} in which the spike concentrations are the dependent variables and the signals are the independent variables.

^{*} Acknowledgments to John Magistad of JCM Associates, statistical consultant to LLL for his contribution to this section.

FIG. 15. Routine to take a reading and calculate new averages.

FIG. 16. Command string interpreter.

First, a matrix labeled H in the program is set up containing the spike concentrations. Say the spikes were 0, 50, and 100 ppm and each was measured (injected into the furnace) twice. Then the H matrix would be:

$$\underline{H} = \begin{Bmatrix} 0 \\ 0 \\ 50 \\ 50 \\ 100 \\ 100 \end{Bmatrix}$$

Next, a matrix of values obtained for these spikes is constructed called the F matrix. For example:

$$\underline{F} = \begin{Bmatrix} 1 & .1 \\ 1 & .11 \\ 1 & .2 \\ 1 & .21 \\ 1 & .3 \\ 1 & .31 \end{Bmatrix}$$

The transpose of $\underline{F}$ is called R.

$$\text{MAT R} = \text{TRN(F)} \quad \text{or} \quad \text{R} = \text{F}'$$

then a matrix called B is calculated

$$\text{MAT B} = \text{R} * \text{F} \quad \text{or} \quad \text{F}' * \text{F}$$

then a matrix called L is calculated

$$\text{MAT L} = \text{R} * \text{H} \quad \text{or} \quad \text{F}' * \text{H}$$

The least squares solution for the X axis intercept of the linear equation $\underline{H} = \underline{F} * \underline{W}$ is

$$\underline{W} = \text{F}' * \text{F}^{-1} \text{F}' * \text{H} \quad \text{or} \quad \underline{W} = \text{BL}$$

which will yield in this example (called MAT W in the program)

$$\underline{W} = \begin{bmatrix} -52.11706110 \\ 498.1320050 \end{bmatrix}$$

where $W(1,1)$ is the intercept, and the concentration of the unknown is equal to $-W(1,1)$. $W(1,2)$ is the slope of the equation.

The overall variance of the spike measurements can also be calculated from these matrices and the differences between the observed and calculated spike concentration. ϵ_i is the difference between the observed and calculated spike concentrations using the equation developed from $\underline{W}$. That is, in the example concentration of the spike C is calculated using the signal S from the equation

$$C = 498.1320050 \cdot S - 52.11706110$$

Table 2 shows some differences calculated from the values in this example. The variance can be calculated from the differences. First calculate

$$S^2 = \frac{\sum_{i=1}^6 \epsilon_i^2}{n - 2} = \frac{37.35990}{4}$$

where there are two degrees of freedom. Multiplying S^2 by $B(1,1)$ gives the variance (Matrix B is $(F'F)^{-1}$). The square root of the variance gives the standard deviation of the spike measurements. Actually, the program calculates a running variance equivalent to the above. That is, it uses the formula

$$S_k^2 = \frac{k-3}{k-2} S_{k-1}^2 + \epsilon_k^2 / k - 2; \quad k \geq 4$$

TABLE 2. Calculated vs observed spike concentrations.

Observed C	Calculated C	Difference ϵ_2
0	-2.30386	+2.30386
0	+2.67746	-2.67746
50	47.50934	+2.49066
50	52.49066	-2.49066
100	97.32254	+2.67746
100	102.30386	-2.30386

It can be seen that at least three measurements must be taken before a value for the spike standard deviation can be calculated.

The final statistical value to be calculated is the regression coefficient or coefficient of determination.

The coefficient of determination, labeled C9 in the program, is calculated from the relation

$$C9 = 1 - \sum \epsilon_i^2 / \sum Y_i^2$$

where the $\sum \epsilon_i^2$ is the same as above and

$$\sum Y_i^2 = \sum (Y_i - \bar{Y})^2$$

where Y_i is the i th spike concentration and $\bar{Y}$ is the average of the spike concentrations. (The H matrix contains the spike concentrations.) See Appendix B for a formal derivation of these equations.

When samples are run more than once--that is, when a set of spiked samples is run again as a separate entity--a sample variance may be calculated. Also, in this case a new spiked sample variance can be calculated. This may be made clearer by noting that to do this automatically, a new loading of the sample wheel with the same spiked unknowns would be necessary (see Fig. 10). The sample variance and the variance within each sample run are kept in the data file for completed samples (see Fig. 6). The sample average and the sample variance are calculated from formulas for the running average and running variance developed for other programs.¹¹ The running variance is more easily calculated as the variance for $N1$ degrees of freedom where $N1$ is the number of samples and this is the value that is stored in position 2 of the 2nd record of each sample file. This is converted to the usual $N1 - 1$ degrees of freedom when printed in various reports. The conversion is done by multiplying the running variance by $N1$ and dividing by $N1 - 1$. The standard deviation is the square root of the new variance.

After all the values have been written into the proper files, the program chains back to MADSTART.GF. Figure 17 shows the flow of MADFIT.GF.

FIG. 17. Flowchart for MADFIT.GF.

MADDAT.GF PROGRAM TO TAKE DATA AND RETURN PEAKS OR INTEGRALS

INTRODUCTION

MADDAT.GF is called by MADSTART.GF whenever the CSI in MADSTART issues a command requiring the injection of a sample into the furnace. MADDAT uses the assembly language Call 7 mentioned previously and timing parameters determined in MADSTART to measure the rise and fall of the optical absorbance as the sample is atomized in the graphite furnace. The signal is taken as a voltage from the photomultiplier tube so that the values returned to the array in Call 7 are a set of numbers, each of which represents a number proportional to the absorption of light from a hollow cathode source by the atomized sample.

When using the automatic sampler, another assembly language call is used--Call 257 as well as Call 7. This call sets up the logic for the sampler. For more details, see Ref. 9.

REAL-TIME DATA ACQUISITION

The program first checks the run status to determine if the current injection is the first in the run sequence. If it is, system CALLs are made to reset switches in the digital equipment, and the analyst is alerted to start the sample changer. The program will be held in a wait-state until it receives a signal from the instrument. This signal is usually emitted during the second period of the three preset temperatures (see page 12). It prepares the computer to receive data. The computer waits a defined amount of time and then takes a defined number of readings at defined time intervals. These data will be stored in an array for further processing (see section on timing starting on page 12). The resulting signal array (V) will be composed of either 300 relative transmittance values from a single-beam instrument or 150 pairs of relative transmittance values for a double-beam instrument. In the case of the double-beam instrument, the difference between the reference and sample beam, determined on an empty cell before each blank is read, may be subtracted from the reference beam before conversion to absorbance.

TRANSMITTANCE TO ABSORBANCE CONVERSION

The V array acquired in the CALL must be converted to a relative absorbance array. A conversion loop is used to step through the array and perform the log ratio on each element. The resulting array consists of a

relative absorbance signal representing atomization. Note that the single-beam signal will have 300 points in the converted V array, while the double-beam signal will be compressed to 150 points. See Appendix C for a formal description of this measurement.

ARRAY LIMITS

Once the relative absorbance array has been computed, the highest and lowest points are determined. The magnitude and array location are stored for both the highest and lowest points in the array. The lowest point in the array is adjusted to zero and the rest of the points are made relative to this level. The values will be used to develop scaling factors in the peak plotting routines.

BASELINE

The leading and trailing points in the array are then used to determine the baseline. The first ten points are averaged and the last ten points are averaged. An equation is then developed relating the baseline value to the array position. If the analyst chooses to use only the leading baseline, the slope term of the equation is set to zero. See Appendix C for these equations.

PEAK HEIGHT DETERMINATION

The next step in the program is the evaluation of peak height. This is done by fitting the five peak points to a second degree equation, computing the exact array location where the slope equals zero, and then using the exact array location in the second degree equation to evaluate the peak absorbance. The baseline computed at the peak array location is then subtracted from the peak height to produce the relative peak absorbance. See Appendix C for a description of the peak fitting routine.

PEAK INTEGRAL

The peak integral is then determined by summing the V array over the integration interval and simultaneously correcting for the baseline. The interval is determined through a comparison of the peak array V and the baseline.

Both the peak height and the peak integral are computed for each signal array even though only one mode may be used during an analysis sequence. See Appendix C.

BLANK SUBTRACTION

After the relative absorbance has been computed, the last instrument-blank absorbance is subtracted and the value is displayed on the user terminal. All of the pertinent information on the peak array is written to a file for further reference such as using the data for plotting routines when available.

PLOTTING OF THE ABSORBANCE ARRAY

If the analyst chooses to generate a plot of the absorbance array in order to verify timing, a routine is available for generating the plot on the line printer or terminal. This routine outputs each point to the line printer (or terminal) using the TAB function. The entire array need not be output and so the frequency may be adjusted. For example, the 150 points collected from the double-beam instrument may be plotted with only 75 points. In this case, only every other point is plotted. This presents a plot with sufficient resolution to determine whether the timing is adequate. This type of plotting is not done on a regular basis, because it takes too much time in the analysis sequence and requires an abnormal amount of system resources. Extensive previewing of the processed peaks will still be available after the analysis through the flameless atomic absorption (AA) peak plot program that is available at EPA.

ENDING THE ROUTINE

When all computations have been made, and a single relative absorbance measurement has been evaluated, the program stores the measurement and chains to the main program MADSTART.GF for further measurements and/or concentration calculations. See Fig. 18 for the general flow of MADDAT.GF.

FIG. 18. MADDAT.GF. take data and return a value.

MADREP.GF REPORT PROGRAM

This program, which writes reports using the sample data files and the sample I.D. files, can be used in three different ways. First, it is used to write interim reports to the analyst when he finishes an automatic run or when he responds with an "R" to the CSI. Second, it will write a final report if requested when the analyst responds with "N" to the MORE MEASUREMENTS prompt. Finally, it may be called up as an independent program. In this case, the sample data and sample I.D. files and a third file called a header file have been saved on the disk under names different from the programs use. This feature is useful for writing new reports on old samples.

When the program is called by MADSTART, it begins at a point that sets a flag to "N" (for new). If the program is called up directly, it starts at the beginning, the flag is set to "U," and the program jumps around the routine that sets the flag to "N." Thus, this flag (Z2\$) can be used to distinguish the various sections of the program for old and new reports.

There is a subroutine to set a flag (Z5\$) to "Y" or "N" that determines whether the individual statistics are set forth in the report. There is also a subroutine to find a reagent blank, if any, and query the operator about subtracting its value from the data. Reagent blanks are identified by the letters RB in the sample I.D. code. Only the first RB found in the sample I.D. file is determined to be the reagent blank.

The reports, final or interim, new or old, may be printed on the terminal or on the line printer or both. As many final reports as desired may be printed.

In the final report section for new final reports, there is a routine that allows dilution factors to be entered and written into the sample I.D. file. The dilution factors are then used to recalculate the concentrations of the samples. The dilution factor is read as a 1 if no dilution factors have been entered. Also in this section is an opportunity to enter miscellaneous information about the analysis. This information includes the date, operator's name, instrument conditions, source of the standards, element of interest (analyte), whether the run was made using an automatic sampler or manually or both, comments, and units of concentration.

This information is placed at the beginning of the report as a heading and is also written into a file called "HEADER.GF."

The value for the number of samples (N1) is normally found in file 7 (MADHOLD.DF) in the last position of record 1. It is also placed in position 4 of record 1 of file 1 (MADGFC.DF): the spiked standards section of that file, so that file 7 need not be used in the report section. Figure 19 shows the general flow of the report program.

FIG. 19. MADREP.GF report program.

APPENDIX A
FLAMELESS ATOMIC ABSORPTION PEAK DATA ACQUISITION
AND REDUCTION ROUTINE

TIMING FOR PEAK DATA ACQUISITION

Figure A1 shows the five timing parameters necessary to acquire an atomization signal from the flameless atomic absorption spectrophotometer. Essentially, a window must be opened just prior to atomization. The signal will then be collected until after the atomization has been completed. The window must be long enough to include the leading and trailing edges of the signal so that baseline values can be established.

The two important timing parameters are T_1 which represents the actual atomization time, and T_4 which represents the computer data acquisition time. The step function shown in Fig. A2 shows the relationship of these two parameters for atomization times from 0 to 15 seconds.

The ratio of T_1 to T_4 is about 60%. In the example case where 150 points are collected over time T_4 , the 60% ratio implies that about 90 points will contain the actual atomization signal. The leading 20 points will contain the leading baseline, and the trailing 40 points will contain the trailing baseline. The Δ and f values shown on Fig. A2 are based on a maximum sampling rate (F) of 60 hertz. Δ represents the time interval between each point (in 1/60 second increments), and f represents the actual acquisition frequency in hertz.

PARAMETERS

The necessary parameters required to collect atomization data normally include the number of points to be collected (N) and the interval between each point (Δ). If n is 150 points and T_1 is known, then Δ can be computed with the following equation:

$$\Delta = \text{INT} \left[\frac{T_1 * F}{P_3} + 0.5 \right] \quad (\text{highest integer function})$$

Where: T_0 — Instrument constant delay time
 T_1 — Time setting for atomization cycle
 T_2 — Delay time before data acquisition
 T_3 — Time to acquire leading base line
 T_4 — Total data acquisition time

FIG. A1. Major timing parameters for flameless AA peak data acquisition.

FIG. A2. Data acquisition time T_4 as a function of atomization time T_1 .

where

T_1 is the atomization time,

$F = 60$ hertz (maximum sampling rate),

$P_3 = 90$ points (span of atomization),

T_4 may then be computed with the equation:

$$T_4 = \frac{\Delta * P_0}{F} \quad (\text{data acquisition time in seconds})$$

where

$P_0 = 150$ points (span of data acquisition).

The time delay before atomization (T_0) is an instrument parameter that is available on instruments that trigger a strip-chart start mechanism prior to atomization. In cases where this signal is available, the actual delay before data acquisition can be computed through the equation:

$$T_3 = \frac{\Delta * B_2}{F} \quad (\text{time for leading baseline in seconds})$$
$$T_2 = T_0 - T_3 \quad (\text{delay time})$$

where

$B_2 = 120$ points (leading baseline).

In cases where the instrument does not produce a signal prior to atomization, data acquisition must begin at the moment of atomization. In such cases, the timing algorithm must be slightly modified.

APPENDIX B^{*}

ESTIMATION OF UNKNOWN CONCENTRATION BY THE METHOD OF ADDITIONS

INTRODUCTION

This appendix compares two methods of estimating the unknown concentration, the ratio estimator and the direct estimator, when using the method of additions. Equations are derived that show that the two methods are analytically equivalent, and considerations are presented to show that the direct method should be used.

FUNDAMENTALS

The fundamental relation assumed with the "Method of Additions" is

$$\eta = \alpha + \beta\xi \quad (B1)$$

where

η = actual level of absorbance

ξ = concentration of added spike

α = intercept parameter denoting the value of η when $\xi = 0$

β = slope parameter denoting the incremental change in η for a given change in ξ .

The objective is to estimate the concentration level, ξ_0 , when the absorbance is zero (i.e., $\eta = 0$). Thus, there is an estimate based on the ratio

$$\hat{\xi}_0 = -\frac{\hat{\alpha}}{\hat{\beta}} \quad (B2)$$

where the estimates $\hat{\alpha}$ and $\hat{\beta}$ represent least squares estimates of the linear relation[†]

^{*} Author: John Magistad, JGM Associates, Inc.

[†] Memorandum from John Magistad. Estimation of unknown concentrations by Method of Additions, 31 January 1978.

$$y_i = \alpha + \beta x + \epsilon_i \quad i = 1, 2, \dots, n \quad (B3)$$

which assumes

$$\begin{aligned} y_i &= \eta(\xi) + \epsilon_i & i &= 1, 2, \dots, n \\ x &= \xi & \xi &= 0, k, 2k \end{aligned} \quad (B4)$$

indicating that ξ is known without error (i.e., $x = \xi$) and that the observed values y_i of $\eta(\xi)$ contain the measurement errors ϵ_i . It is further assumed that the measurement errors are homogenous over the experimental range of ξ , such that

$$E(x_i) = 0 \text{ all } i, \quad E(\epsilon_i^2) = \sigma^2 \text{ all } i,$$

$$E(\epsilon_i \epsilon_j) = 0, \text{ and } E(\epsilon_i y_i) = 0 \text{ all } i \quad i \neq j.$$

There is also an alternative relation

$$\xi = \frac{\eta - \alpha}{\beta} \quad (B5)$$

which is merely an algebraic identity with equation (B1). Equation (B5) may be simplified to give

$$\xi = -\frac{\alpha}{\beta} + \frac{1}{\beta} \eta. \quad (B6)$$

Note that when $\eta = 0$ then $\xi_0 = -\frac{\alpha}{\beta}$ as shown in Eq. (B2).

Equation (B6) is then reparameterized to give the simple linear form

$$\xi = a + b\eta. \quad (B7)$$

In terms of the observed values this becomes

$$\begin{aligned} x_i &= a + b(y_i - \epsilon_i) & i = 1, 2, \dots, n \\ &= a + by_i - b\epsilon_i \end{aligned} \quad (B8)$$

It is important to note that the error term, $b\epsilon_i$, involves the parameter b , which is to be estimated. However, in this situation, b is a constant such that minimizing the sum, $\sum b\epsilon_i$, is equivalent to the usual least squares criteria of minimizing $\sum \epsilon_i$. This implies that a least squares solution of Eq. (B8) will provide a direct estimate of the parameters a and b . Thus, ξ_0 can be estimated directly by the relation

$$\hat{\xi}_0 = \hat{a} \quad (B9)$$

which is derived from Eq. (B7) when $\eta = 0$.

At this point there are two alternative estimates of ξ_0 . One is a ratio estimation

$$\hat{\xi}_0 = -\frac{\hat{\alpha}}{\hat{\beta}} \quad (B10)$$

The other is a direct estimator

$$\hat{\xi}_0 = \hat{a} \quad (B11)$$

which is described in greater detail later.

The objective of this appendix is to compare the two estimators (B10) and (B11) with respect to bias and precision.

ESTIMATES OF THE UNKNOWN CONCENTRATION ξ ,
 VARIANCE OF ESTIMATE $V(\xi_0)$, AND THE
 COEFFICIENT OF DETERMINATION, R^2

The least squares solution for the estimate of a and b of Eq. (B8) is described below:

$$\text{Model } x_i = a + by_i + e_i \quad i = 1, 2, \dots, n \quad (\text{B12})$$

where

$$e_i = b\epsilon_i$$

In matrix notation this is written as

$$\underline{x} = \underline{y} \underline{b} + \underline{e} \quad (\text{B13})$$

where

$$\underline{x} = \begin{Bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{Bmatrix} \quad \underline{y} = \begin{Bmatrix} 1 & y_1 \\ 1 & y_2 \\ 1 & y_3 \\ \vdots & \vdots \\ 1 & y_n \end{Bmatrix} \quad \underline{b} = \begin{Bmatrix} a \\ b \end{Bmatrix} \quad \underline{e} = \begin{Bmatrix} e_1 \\ e_2 \\ \vdots \\ e_n \end{Bmatrix} \quad .$$

Then the least squares solution for $\underline{b}$ is

$$\hat{\underline{b}} = [\underline{y}'\underline{y}]^{-1} [\underline{y}'\underline{x}] \quad (\text{B14})$$

which will be unbiased. The variance matrix of the estimate is

$$V(\hat{\underline{b}}) = [\underline{y}'\underline{y}]^{-1} \sigma^2 \quad (\text{B15})$$

The estimate of σ^2 is obtained by the relation

$$s^2 = \frac{e'e}{n-2} ; \quad (n-2)df \quad (B16)$$

where

$$e = [X - Yb]$$

The coefficient of determination, R^2 , is estimated by the relation

$$R^2 = 1 - \frac{e'e}{X'X}^{-1}$$

where

$$X = [X - \bar{X} \ 1]$$

$$\bar{X} = X' 1/n$$

$$1' = [1, 1, \dots, 1]$$

MEAN VALUES VS INDIVIDUAL VALUES

When the dependent and independent variables are interchanged, as with the current method of estimation, it is important that all measured values ($i = 1, 2, \dots, n$) are listed in the matrix. A substitution of mean values, x and y , at each separate level of concentration will lead to incorrect results. This phenomenon does not occur when using ordinary least squares.

The reason for this discrepancy is as follows:

The $[Y'Y]$ matrix is

$$[Y'Y] = \begin{pmatrix} n & \sum_{i=1}^n y_i \\ \sum_{i=1}^n y_i & \sum_{i=1}^n y_i^2 \end{pmatrix} .$$

If a mean, $\bar{y}$, of k values y_i is used with respect to a common set of x levels, then the resultant $[Y'Y]_k$ matrix associated with this cell is

$$[Y'Y]_k = \begin{pmatrix} n & \sum_1^k y_i \\ \sum_1^k y_i & \frac{1}{k^2} \sum_1^k y_i^2 + \sum_{i \neq j}^k y_i y_j \end{pmatrix}.$$

In this case

$$\bar{y}_k = \frac{(y_1 + y_2 + \dots + y_n)}{k}$$

and

$$\bar{y}_k^2 = \left\{ \sum_1^k y_i^2 + \sum_{i=j}^k y_i y_j / k^2 \right\}$$

instead of

$$\sum_1^k y_i^2.$$

This phenomenon does not occur when using ordinary least squares since the x values are all equal, by definition, at a given cell. Thus

$$\bar{x}_k = \frac{(x_1 + x_2 + \dots + x_k)}{k} = x_1,$$

say, since $x_i = x_1$ for all $i = 1, 2, \dots, k$.

Consequently

$$kx_k^2 = kx_1^2 = \sum_1^k x_i^2$$

The point is, the x 's are all constant in ordinary least squares but in the modified least squares where y is used instead of x , the y 's are not all constant. This will have an impact on the matrix, and resultant solutions.

ILLUSTRATIVE EXAMPLES

Example 1

This first example illustrates that the two methods of estimation are analytically equivalent.

There are three paired data values listed as follows:

i	y_i	x_i
1	0.053321	0
2	0.088250	19.09
3	0.162425	50.90

Method of Ratio Estimate

$$\xi = - \frac{\hat{\alpha}}{\hat{\beta}},$$

$$Y = \begin{Bmatrix} 0.053321 \\ 0.088250 \\ 0.162425 \end{Bmatrix} \quad \underline{x} = \begin{Bmatrix} 1 & 0 \\ 1 & 19.09 \\ 1 & 50.90 \end{Bmatrix}.$$

Then

$$[x'x] = \begin{Bmatrix} 3 & 69.99 \\ 69.99 & 2955.238124 \end{Bmatrix},$$

$$[x'y] = \begin{Bmatrix} 0.30399600 \\ 9.95212500 \end{Bmatrix},$$

and

$$\hat{\underline{\beta}} = \begin{Bmatrix} \hat{\alpha} \\ \hat{\beta} \end{Bmatrix} = [x'x]^{-1} [x'y]$$

$$= \begin{Bmatrix} 0.05087611 \\ 0.00216270 \end{Bmatrix}.$$

Thus

$$\hat{\xi}_0 = \frac{\hat{\alpha}}{\hat{\beta}} = -23.5243.$$

Because this is a ratio estimator, a correction should be made for the bias,

$$\begin{aligned} \text{Bias} &= \hat{\xi}_0 \left\{ \frac{\sigma_{\beta}^2}{\beta^2} + \frac{\hat{\sigma}_{\alpha\beta}^2}{\alpha\beta} \right\} \sigma^2 \\ &= 0.1776 \end{aligned}$$

so that the corrected value is

$$\hat{\xi}_c = -23.3467$$

and

$$v(\hat{\xi}_c) = 9.9881$$

$$SE(\hat{\xi}_c) = 3.1604$$

where

$$v(\hat{\xi}_0) = \xi^2 \left\{ \frac{v(\alpha)}{\alpha^2} + \frac{v(\beta)}{\beta^2} + \frac{2v(\alpha, \beta)}{\alpha\beta} \right\} \sigma^2.$$

Direct Estimate, $\hat{\xi}_0 = \hat{a}$

In this case

$$\underline{x} = \begin{Bmatrix} 0 \\ 19.09 \\ 50.90 \end{Bmatrix} \quad \text{and} \quad \underline{y} = \begin{Bmatrix} 1 & 0.053321 \\ 1 & 0.088250 \\ 1 & 0.162425 \end{Bmatrix}.$$

Then

$$\underline{b} = \begin{Bmatrix} a \\ b \end{Bmatrix} = [y'y]^{-1}[y'x]$$

$$= \begin{Bmatrix} -23.3474 \\ 460.6387 \end{Bmatrix}.$$

The estimate of ξ_0 is

$$\hat{\xi}_0 = \hat{a}$$

$$= -23.74.$$

In this case there is no bias to be estimated and the variance of ξ is

$$v(\hat{\xi}_0) = v(\hat{a})$$

$$= 9.9787$$

$$SE(\hat{\xi}_0) = 3.1589.$$

A comparison of the two results is tabulated below.

From the tabulated results, it is observed that the two methods give close to identical results. The discrepancies are believed to be those caused by the round-off errors of computation.

TABLE B1. Numerical comparison of two estimators.

Estimator	$\hat{\xi}_0 = -\hat{\alpha}/\hat{\beta}$	$\hat{\xi}_0 = \hat{a}$
Estimate $\hat{\xi}_0$	-23.5243	-23.3474
Estimated bias	0.1776	0
Corrected estimate ($\hat{\xi}_c$)	-23.3467	-23.3474
SE($\hat{\xi}_0$)	3.1604	3.1589

It is noted that in this case the bias correction for the ratio estimator was appreciable. Furthermore, the equations for calculating the variance of this estimator are more complex. Because of the numerical simplicity associated with the method of modified least squares, it is suggested that this method be used.

Example 2

This example is presented to illustrate the biasing impact that results when using means instead of individual observations--even when the number of observations at each condition is equal.

Method of Individual Observations

Consider the following data:

i	x_i	y_i
1	0	0.1
2	0	0.11
3	50	0.2
4	50	0.21
5	100	0.3
6	100	0.31

Using individual values

$$\underline{x} = \begin{Bmatrix} 0 \\ 0 \\ 50 \\ 50 \\ 100 \\ 100 \end{Bmatrix} \quad \underline{y} = \begin{Bmatrix} 1 & 0.1 \\ 1 & 0.11 \\ 1 & 0.2 \\ 1 & 0.21 \\ 1 & 0.3 \\ 1 & 0.31 \end{Bmatrix}$$

$$[y'y] = \begin{Bmatrix} 6 & 1.23 \\ 1.23 & 0.2923 \end{Bmatrix} \quad [y'x] = \begin{Bmatrix} 300 \\ 81.5 \end{Bmatrix}$$

then

$$\hat{\underline{b}} = \begin{Bmatrix} \hat{a} \\ \hat{b} \end{Bmatrix} = \begin{Bmatrix} -52.1171 \\ 498.1320 \end{Bmatrix}.$$

Method of Mean Observations

Consider next the analysis based on mean values:

$$\underline{x} = \begin{Bmatrix} 0 \\ 50 \\ 100 \end{Bmatrix} \quad y = \begin{Bmatrix} 1 & 0.105 \\ 1 & 0.205 \\ 1 & 0.302 \end{Bmatrix}$$

$$[y'y] = \begin{Bmatrix} 3 & 0.615000 \\ 0.615000 & 0.146075 \end{Bmatrix} \quad [y'x] = \begin{Bmatrix} 150.0 \\ 40.7500 \end{Bmatrix}$$

$$\hat{\underline{b}} = \begin{Bmatrix} \hat{a} \\ \hat{b} \end{Bmatrix} = \begin{Bmatrix} -52.5000 \\ 500.0000 \end{Bmatrix}.$$

The parameter of interest is $\xi_0 = \alpha$ so that a comparison of both results is shown below.

Comparison	
<u>Method</u>	<u>Estimate of $\hat{\alpha}$</u>
Individual	-52.1171
Means	<u>-52.5000</u>
Difference	0.3829

This discrepancy cannot be attributed to round-off error. It will be noticed that the elements of the $y'y$ matrix associated with the method of means is one half of the corresponding elements in the other $y'y$ matrix. The factor of one half is because the means are based on samples of two. There is one exception, however, and that is with respect to the lower right hand element. In this case, the value expected is $1/2 \cdot 0.2933 = 0.146150$; however, the observed result is 0.146075. This difference appears minimal but it has a significant impact when inverting the matrix.

SUMMARY AND CONCLUSIONS

It was observed that the results obtained by the ratio estimator $\hat{\xi}_0 = -\hat{\alpha}/\hat{\beta}$ are equivalent to those derived by the direct estimator $\hat{\xi}_0 = \hat{a}$. The latter method is easier to apply, because special routines are not needed to correct for biases and to estimate the variance of estimation. Furthermore, the direct method easily provides a capability and flexibility for analyzing "messy data" situations where spike concentrations are not evenly spaced, sample sizes at each spike are different, and where measurement errors are not homogeneous.

Consequently, it is recommended that the direct method of estimation, $\hat{\xi}_0 = \hat{a}$, be adopted and that the program process all observations rather than mean results.

APPENDIX C

TRANSMITTANCE TO ABSORBANCE TRANSFORMATION

As a sample is atomized in the furnace chamber, it absorbs some of the light passing through the chamber. This change is registered at the photo-detector in the form of lower voltage readings. The detector voltage is sampled at a constant rate and the voltages are converted to digital signals through a system CALL. The resulting array represents the decrease in transmitted light caused by the atomizing sample. Once this array is collected over the atomization cycle, it must be converted to an equivalent relative absorbance signal array. Since absorbance is related to transmittance through the equation:

$$A = \log_{10} \frac{T_{\text{reference}}}{T_{\text{sample}}}$$

it is a simple matter to convert each point in the array to a relative absorbance value. Two different forms of this equation are used to translate the transmittance signal to a relative absorbance signal.

The single-beam conversion equation is similar to the general equation shown above with one exception. An arbitrary constant is included so that the relative absorbance values that are computed will be roughly equivalent to the absorbance output of the internal instrument signal processor. The single-beam transformation equation is shown below:

$$V'_i = \log_{10} \frac{C}{V_i}$$

where

C is the arbitrary constant ($C > 0$),

V_i is an element of the raw transmittance data array,

V'_i is an element of the relative absorbance data array.

Each point in the array is processed with this equation such that the transmittance array V is converted to the relative absorbance array V'.

The double-beam signal contains two distinct arrays: one that represents the reference signal and one that represents the sample signal. The reference signal may be caused by a split hollow cathode beam or by a deuterium lamp correction beam. The split beam is shunted around the sample and serves as a stable reference during atomization. The deuterium correction beam, on the other hand, is shown directly through the sample and serves as an indicator of the non-atomic absorption reference. The sample signal is always processed relative to the reference signal using the following equation:

$$V'_i = \log_{10} \frac{R_i}{S_i}$$

where

R_i is an element of the reference data array,

S_i is an element of the sample transmittance array,

V_i is an element of the relative absorbance data array.

The three types of transmittance data are shown in Fig. C1, along with each corresponding absorbance signal. Once the relative absorbance signal has been obtained, the signal may be reduced to a single relative absorbance value using the peak height or peak integration algorithm.

It should be noted that the relative nature of the processed signal indicates its usefulness only in the context of a series of consistent measurements within the course of an analysis sequence. In other words, the value of the signal is lost if conditions change relative to the standard measurements and the stable instrument conditions. With this in mind, the reduction of the relative absorbance array will now be described.

BASELINE COMPUTATION

The first step in evaluating a relative absorbance signal (RAS) is to establish a baseline. The particular baseline option must be established before real samples are processed, and the baseline mode will remain invariant throughout the run.

When only the leading baseline is used (Fig. C2-a and C2-c), the average value of the first ten points of the signal array will be computed. When the

FIG. C1. Three types of data conversion for flameless atomic absorption peak atomization array.

FIG. C2. Four methods for evaluating relative absorbance measurements based on peak array data obtained from flameless atomic absorption spectrometer.

combined baseline option is selected, the first and last ten points of the data array will be used to develop a straight line that will connect the end points of the signal array (Figs. C2-b and C2-d).

Once the baseline has been established, the peak height or peak integral will be adjusted relative to the baseline. The equations used to establish the combined leading/trailing baseline are shown below:

$$A_1 = \left(\sum_{i=1}^{10} v_i \right) / 10$$

$$A_2 = \left(\sum_{i=n-9}^n v_i \right) / 10$$

$$C_i = A_1 + \left(\frac{A_2 - A_1}{n - 10} \right) * i$$

where

A_1 is the average of the leading points,

A_2 is the average of the trailing points,

C_i is the combined baseline correction,

n is the number of points in the data array.

When only the leading baseline is used, the correction equation reduces to the following form:

$$C_i = A_1.$$

Once the baseline has been determined, it is used to adjust the peak height or peak integral value.

PEAK HEIGHT MEASUREMENT

The peak height will be computed through the use of a simplified least squares procedure. The technique fits the top-most five points of the peak data array to a quadratic equation. The algorithm will also establish the location and magnitude of the peak value. The following equations constitute the peak height algorithm^{12,13}:

$$B_1 = -3(V_{k-2} + V_{k+2}) + 12(V_{k-1} + V_{k+1}) + 17(V_k) / 35$$

$$B_2 = 2(V_{k+2} - V_{k-2}) + V_{k+1} - V_{k-1} / 10$$

$$B_3 = 2(V_{k+2} + V_{k-2}) - V_{k+1} - V_{k-1} - 2(V_k) / 14$$

$$P = B_1 + k'B_2 + B_3(k')^2 \quad \text{where} \quad -2 < k' < 2$$

$$k'_{\max} = -B_2 / (2B_3) \quad \text{at} \quad P_{\max}$$

where

k is the time position of the maximum absorbance point in the array,

B_1, B_2, B_3 are polynomial coefficients,

k' is the peak locator relative to k ,

$P_{\max}$ is the computed peak height at position $k + k'$.

Figure C3 shows an example of the peak height determination. Once the peak height has been computed, the appropriate baseline value is subtracted. In the case where the combined baseline is used, the peak height calculation will be made with the following equation:

$$RAS_P = P - \left[A_1 + \frac{A_2 - A_1}{n - 10} (k + k') \right] = P - C_{k+k'}$$

where

Where: $V_{k-2} = 0.228$, $V_{k-1} = 0.240$, $V_k = 0.241$, $V_{k+1} = 0.228$, and $V_{k+2} = 0.205$

$$B_1 = [-3(V_{k-2} + V_{k+2}) + 12(V_{k-1} + V_{k+1}) + 17(V_k)]/35 = 0.2404$$

$$B_2 = [2(V_{k+2} - V_{k-2}) + V_{k+1} - V_{k-1}] = -0.0058$$

$$B_3 = [2(V_{k+2} + V_{k-2}) - V_{k+1} - 2(V_k)] = -0.0060$$

$P = B_1 + B_2 k' + B_3 (k')^2$ least squares quadratic fit of peak points

$$k' = -B_2/(2B_3) \text{ at maximum } P = -0.4833$$

$$P_{\max} = B_1 + (-B_2^2/2B_3) + B_2^2/(4B_3) = 0.2418$$

FIG. C3. Simplified least squares procedure to fit five-point peak flameless AA data.

RAS_p is the relative absorbance signal using peak height.

When only the leading baseline equation is used, the equation reduces to the following form:

$$RAS_p = P - A_1 .$$

PEAK INTEGRATION MEASUREMENT

The peak integral will be computed by summing the array points over the "active region" of the curve. This active region is defined by the intersection of the peak array data with the appropriate baseline. Figure C2-c and C2-d illustrate the two forms of integration. The active region starts at I_0 and ends at I_1 . The following equation represents the RAS for peak integration:

$$RAS_I = \sum_{i=I_0}^{I_1} (V_i - C_i)$$

where

C_i has been defined above as the baseline correction.

APPENDIX D DEFINITION OF VARIABLES

APPENDIX D1: PROGRAM MADSTART.GF

<u>Variable</u>	<u>Definition</u>
A1	Store sum of reference beam readings
A2	Store sum of sample beam readings
A4	Position in the record of the data file
A5	Record of the data file
A6	Counter used for closing up sample files
A[I]	Array to hold data from CALL 7 for beam correction
B2	Number of points for leading baseline
B3	Store sum of blanks for averaging
C\$	Variable which holds input to CSI
CL	Beam correction. Difference between reference beam and sample beam during "empty" run
CL\$	Temporary storage for generating CSI command
C2\$	Temporary storage for generating CSI command
C3\$	Temporary storage for generating CSI command
C9	Coefficient of determination
C[I]	Array to hold spike concentrations
D	Matrix for D array which holds spike and unknown values
D[I]	D array D(1) + D(16) position labels for records which hold spike and unknown values. (see files write up)
D1	Dummy variable for reading file 5 prior to writing in position 3 the number of sample runs
D2	Dummy variable, same as D1
F1	Constant equal to 1 for preliminary dilution factor
F1\$	Holds name of program "MADSTART.GF"
G1	Warning flag to prevent standardization after erasing a data set or running spikes
I	General counter
I2	Counter for number of samples in automatic mode
J	General counter

<u>Variable</u>	<u>Definition</u>
J1	Contains number converted from string by VAL function
J2	Counter for number of spikes in automatic mode
K	Number of spike for spike input correction. Replicate counter for CSI in automatic mode
K1\$	Holds first part of CSI string
K2\$	Flag for P, D, and E functions
K3\$	Not used
K[I]	General purpose array as follows:
K(3)	Constant for 3/60 second. Value for fast CALL 7 to get beam corrections
K(9)	Extra constant or flag set equal to 1
K(10)	Constant for 10 points for fast CALL 7 to get beam correction
K(35)	Time to furnace ignition (16.8 seconds)
K(40)	Holds coefficient of determination for special fit. Not used here
K(41)	Holds coefficient of determination
K(49)	Value for blank
K(51)	Flag to determine if this is the first run
K(52)	Graphite furnace number for CALL 7. Selects proper A/D channels
K(53)	Delay time 1/60 sec units in CALL 7
K(54)	Time to define peak. 1/60 sec units in CALL 7
K(55)	Number of points to read (300 for double beam)
L	Position counter
L\$	Variable to hold "S" or "D" for single or double beam
L2	Number of times sample is to be run
M0	Spiked standard M0 = 1; completed unknown M0 = 2; S or U
M1	Number of the spiked unknown (standard) or completed sample $S5/1$ or $U3/2$
M2	Number of the repeated measurements--replicate number $S5/1$ or $U3/2$
M3	Same as M2 used to chain to data taking routine
N0	Number of spiked unknowns used for standardization
N1	Number of samples

<u>Variable</u>	<u>Definition</u>
P3	Number of points to define peak (usually 90 for double-beam instruments)
R1	Run number
R2	Number of times measurement is repeated
R5\$	Parameter for peak height "P" or integral "RI"
S	Position number of auto-sampler
S\$	Repeat present sample flag
S1	Counter for number of times sample is run
S5	Holds average value for recalculation
S6	Holds single value for deletion
T	Terminal or line printer output flag
T\$	Timing run and time OK flag. Set or change parameter flag. More than one reading flag. Regular or irregular run flag. Spike OK flag. Sample I.D. OK flag. Print out flag. General input variable.
T1\$	Sample identification (sample name)
T3	Total time of data taking in seconds
U\$	Manual or automatic flag
U1	Number of spike corrections. Number of I.D. corrections
V1	Signal from processed data. Measurement
X\$	Input to sample I.D. OK flag
Y\$	Leading or combined baseline flag
Z\$	Flag for plotting of data

APPENDIX D2: PROGRAM MADFIT.GF

<u>Variable</u>	<u>Definition</u>
A	Variable to count number of spiked standards
A6	Average concentration or spike variance
B and B I	Matrix $B = R * F$
C0	Concentration of unknown
C9	Coefficient of determination
C[I]	Array for spike concentrations
D and D[I]	Array to hold spike and unknown values

<u>Variable</u>	<u>Definition</u>
D1	Difference between observed and calculated spike concentrations
E1	Same as above but used for variance calculations
F and F[I]	Matrix containing a column of 1's and signals obtained from spikes
F1	File number
F1\$	File name
H and H[I]	Matrix containing spike concentrations
I	General counter
I1	Counts number of values to dimension matrices
J	General counter
J1	Counter to define matrices
K[I]	K array carried over from MADSTART.GF
L and L[I]	Matrix $L \approx R * H$
L\$	Single or double beam (not used here)
M9	Counter for spikes, concentrations, and variance
N0	Number of spiked samples
N1	Number of the sample of interest, found in position 4 of first spiked sample record
R and R[I]	Matrix $R \approx$ transpose of matrix F
R1	Run number
S1	Number of times sample is run
S5	Variance of spike measurements
S6	Average value of spike concentrations
S7	Average sample variance
T1\$	Sample name (not used here)
W and W[I]	Matrix $W = B * L$
Y0	Concentration or intercept from fitted equation
Y1	Slope of fitted equation

APPENDIX D3: PROGRAM MADDAT.GF

B0	Average of leading 10 points for baseline
B1	Average of trailing 10 points for baseline
C\$	Last input to CSI

<u>Variable</u>	<u>Definition</u>
C1	Beam correction
F1\$	Name of program chained from "MADSTART.GF"
H0	Highest value of data array
H2	Line limit for plotting routine on line printer
H3	Line limit for plotting routine on console
H8	Holds highest value of data array
I	General counter
I0	Location of minimum (see L0)
I1	Peak location after smoothing relative to I2
I2	Peak location before smoothing (see H0)
I3	Peak location after smoothing
I6	Left intercept for integration
I8	Right intercept for integration
J	Counter for calculating absorbances
K1\$	Holds CSI input
K3	Tab value for plotting on line printer
K4	Tab value for printing on console
K [I]	K array carried over from MADSTART.GF
K [44]	Baseline intercept
K [45]	Baseline slope
K [46]	Values for Savitsky Golay fit
K [47]	Values for Savitsky Golay fit
K [48]	Values for Savitsky Golay fit
L\$	Single- or double-beam flag ("S" or "D")
L0	Lowest value of data array
N2	Number of data points after absorbance conversion (double beam)
R5\$	Peak height or integral flag
S1	Number of points plotted
S2	Scaling factor for plotting on line printer
S3	Scaling factor for plotting on console
U\$	Auto or manual sampling flag
V and V [I]	Array to hold data points
V1	Processed final signal
V2	Processed data values

<u>Variable</u>	<u>Definition</u>
V3	Baseline data value
V4	Final processed peak height
V5	Final processed integral
Y\$	Flag for combined or leading baseline
Z\$	Flag for plot or no plot
Z0	NOVA/HGA reset (CALL 257) *
Z2	Single-beam constant *
Z3	NOVA-SENSE reset *
Z6	NOVA-READY set *
Z7	Dummy accumulator *

APPENDIX D4: PROGRAM MADREP.GF

<u>Variable</u>	<u>Definition</u>
A1	Original volume for calculating dilution factor
A2	Final volume for calculating dilution factor
B1\$	Flag for reagent blank subtraction
C [I]	Spike concentrations
D and D [I]	Array to hold spike and unknown values
D1\$	Header information: analysis date
D2	Dummy variable to read file
D5	Value of reagent blank
E1\$	Header information: element
F1	Dilution factor
F2	Dilution factor for reagent blank
H1	File number for H1\$
H1\$	File name for sample data file saved previously
H3	File number for H3\$
H3\$	File name for header file saved previously
H4\$	Temporary storage when renaming files
H5	File number for H5\$
H5\$	File name for sample identification file saved previously
I	General counter

* See Ref. 9.

<u>Variable</u>	<u>Definition</u>
I1\$	Header information: instrument conditions
I2	Sample number of reagent blank
J	Counter for number of repetitions
L2	Number of repetitions
M1\$	Header information: method
M2\$	Header information: comments
M3\$	Header information: units
N0	Number of spiked samples
N1	Total number of samples
N7	Number of diluted samples
01\$	Header information: operator
R\$	General variable for reply to queries
S, S I	Matrix containing sample statistics
S1\$	Header information: standards source
T	Flag for output medium
V1, V2, V3	Constants to adjust tabulations
Z2\$	Flag which determines if report is new or old
Z3\$	Response to final report query
Z4\$	Response to more measurements query
Z5\$	Individual statistics flag

APPENDIX E
LISTINGS AND SYMBOL TABLES

APPENDIX E1: MADSTART.GF

LISTING OF FILE MADSTARTGF.AS *
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```

0002 PRINT
0003 PRINT
0005 REM*****MADSTART.GF*****4/25/79*****WALTER BOYLE/DENNIS
      RYAN
0010 REM*****COMBINED MANUAL AND AUTO METHOD OF ADDITIONS
      FOR THE GF
0015 REM*****BASED ON GF.11 AND GFMERL
0020 REM **RUN AUTOMATICALLY OR MANUALLY FOR DOUBLE BEAM**
0030 REM**SINGLE BEAM NOT IMPLEMENTED**USE L$ TO IMPLEMENT
0045 REM***FOR HAND ENTRY OF DATA CHANGE 3022 AND 6006
0050 REM**MADSTART.GF CHAINS TO MADDAT.GF FOR EACH INJECTION
      MANUAL OR AUTO
0055 REM**CHAINS TO MADFIT.GF FOR CALCULATIONS
0060 PRINT
0065 PRINT "***** MADSTART.GF *****"
0070 PRINT TAB(20);SYS(3);"/";SYS(2);"/";SYS(1)
0075 PRINT TAB(23);INT(SYS(0)/3600);": ";
0080 PRINT INT((SYS(0)-(INT(SYS(0)/3600)*3600))/60)
0085 REM
0100 DIM T$(3),U$(5),X$(5),Y$(5),Z$(5),L$(5),C$(8)
0105 DIM A(20),C(10),D(17),K(70)
0110 DIM K1$(5),K2$(5),T1$(25),F1$(15),R5$(5)
0115 DIM S$(5),C1$(2),C2$(2),C3$(2)
0120 CLOSE
0125 LET S$=""
0130 LET S1=1
0135 LET I3=0
0140 LET N1=0
0145 LET L$="D"
0150 REM      ASSIGN L$ TO EITHER "S" OR "D"
0155 LET F1$="MADSTART.GF"
0160 REM      ASSIGN F1$ TO NAME OF PROGRAM
0165 LET K(51)=0
0170 OPEN FILE(7,0),"MADHOLD.DF"
0175 WRITE FILE(7,0),L$,F1$,K(40),K(41)
0180 IF K(51)>0 THEN GOTO 0190
0195 LET G1=0
0200 LET V1=0
0202 LET B3=0
0205 IF L$="D" THEN LET C1=2500

```

*Programs are slightly renamed in order to produce these special listings.

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0210 LET F1=1
0220 REM****SET DEFAULT PARAMETERS TO PEAK HEIGHT WITH LEADING BASELINE
0230 REM****AND NO PLOT
0240 LET Y$="L"
0250 LET R5$="P"
0270 LET K(9)=1
0280 LET Z$="N"
0500 REM*****SET PARAMETERS FOR TIMING FURNACE
0505 REM**MEASURE TIME FOR FURNACE TO GO TO IGNITION
0510 REM**AFTER SIGNAL FROM STRIP CHART RECORDER IS RECEIVED
0515 REM**USE 300 POINTS FOR DOUBLE BEAM; 150 PAIRS, REF AND SAMPLE
0525 LET K(55)=300
0530 REM: TIME TO FURNACE ON IS 16.8 SECONDS
0535 LET K(35)=16.8
0540 REM: ASSIGN 20 POINTS FOR LEADING BASELINE
0545 LET B2=20
0550 REM: ASSIGN 90 POINTS FOR DEFINING PEAK
0555 REM: THIS LEAVES 40 POINTS FOR TRAILING BASELINE
0560 LET P3=90
0565 REM: MEASURE TIME REQUIRED FOR DEFINING PEAK
0570 INPUT "TIME TO DEFINE PEAK IN SECONDS ? ",K(54)
0575 REM: CALCULATE K(54) AS TOTAL TIME IN SECONDS
0580 LET K(54)=(K(54)*K(55))/(2*P3)
0585 LET T3=K(54)
0590 REM: CALCULATE NO. OF 1/60 SEC "TICKS" BETWEEN PAIRS OF POINTS
0595 LET K(54)=K(54)*60*2/K(55)
0600 LET K(54)=INT(K(54)+.5)
0605 PRINT "TIME BETWEEN POINTS IS ";K(54);"/60 SECONDS"
0610 IF K(54)<1 THEN PRINT "INTERVAL TOO SHORT"
0615 IF K(54)<1 THEN GOTO 0570
0620 PRINT "TOTAL TIME IS ";K(54)*150/60;" SECONDS"
0625 REM****CALCULATE DELAY TIME; SHOULD BE LESS THAN K(35) (16.8
      SECONDS)
0630 LET K(53)=K(35)-(B2*2*T3)/K(55)
0635 LET K(53)=K(53)*60
0640 LET K(53)=INT(K(53)+.5)
0645 PRINT "DELAY TIME IS ";K(53)/60;"SECONDS"
0650 IF (K(53))<(1/60) THEN GOTO 0660
0655 GOTO 0670
0660 PRINT "DELAY TIME TOO SHORT"
0665 GOTO 0535

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LISTING OF FILE MADSTARTGF.AS

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0670 WRITE FILE(7,1),K(53),K(54),K(55)
0675 PRINT "INJECT SAMPLE BY HAND FOR TIMING ? "
0680 INPUT T$
0685 IF T$(1,1)="N" THEN GOTO 0795
0690 IF T$(1,1)<>"Y" THEN GOTO 0675
0695 REM**SET CONTROL PARAMETERS FOR PRELIMINARY RUN
0700 REM**SET Z$=Y FOR PLOT
0705 LET Z$="Y"
0710 INPUT "BASELINE: LEADING OR COMBINED (L/C) ? ",Y$
0715 IF Y$(1,1)="C" THEN GOTO 0725
0720 IF Y$(1,1)<>"L" THEN GOTO 0710
0725 INPUT "PK. HEIGHT, OR REG. INTEGRAL (P/RI) ? ",R$
0730 IF R$(1,1)="P" THEN GOTO 0765
0735 IF R$(1,2)<>"RI" THEN GOTO 0725
0765 LET K(9)=1
0767 LET U$="MMA"
0770 IF T$="PC" THEN GOTO 0835
0775 WRITE FILE(7,2),R$,K(9),Y$,Z$
0780 WRITE FILE(7,3),V1,K(49),C$,C1,K(1$,U$
0785 SAVE "MADSTART.GF"
0790 GOSUB 6000
0795 INPUT "TIMING O.K. ? ",T$
0800 IF T$(1,1)="Y" THEN GOTO 0820
0805 IF T$(1,1)<>"N" THEN GOTO 0795
0810 GOTO 0570
0815 REM**CHANGE CONTROL PARAMETERS IF NECESSARY
0820 PRINT "REQUIRE PLOT ?; Y/N; IF Y THEN A PLOT IS MADE FOR
      EVERY INJECTION ";
0822 INPUT Z$
0825 IF Z$(1,1)="Y" THEN GOTO 0835
0830 IF Z$<>"N" THEN GOTO 0820
0835 INPUT "SET OR CHANGE PARAMETERS Y/N ? ",T$
0840 IF T$(1,1)="N" THEN GOTO 0860
0845 IF T$(1,1)="Y" THEN LET T$="PC"
0850 IF T$="PC" THEN GOTO 0710
0855 GOTO 0835
0860 OPEN FILE(1,0),"MADGFC.DF"
0863 INPUT "AUTOMATIC OR MANUAL A/M ? ",U$
0865 IF U$(1,1)="A" THEN LET U$="AMA"
0867 IF U$="AMA" THEN GOTO 0875

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LISTING OF FILE MADSTARTGF.AS

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0870 IF US[1,1]<>"M" THEN GOTO 0863
0873 LET US="MMA"
0875 WRITE FILE[7,2],R5$,K[9],Y$,Z$
0880 WRITE FILE[7,3],V1,K[49],C$,C1,K1$,US
0885 IF US[1,1]="M" THEN GOTO 2500
1500 REM*****ENTER SAMPLE I.D.'S AND SPIKES FOR AUTOMATIC RUN
1505 INPUT "NO. OF SAMPLES ? ",N1
1510 INPUT "GOING TO TAKE MORE THAN ONE READING PER SPIKED SAMPLE
      Y/N ? ",T$
1515 IF T$[1,1]="N" THEN LET R2=1
1520 IF T$[1,1]="N" THEN GOTO 1535
1525 IF T$[1,1]<>"Y" THEN GOTO 1510
1530 INPUT "HOW MANY FOR EACH SPIKED SAMPLE ? ",R2
1535 OPEN FILE[5,0],"MADID.DF"
1540 INPUT "REGULAR OR IRREGULAR RUN R/I ? ",T$
1545 REM**IRREGULAR MEANS DIFFERENT NO. AND CONC OF SPIKES FOR EACH UNK
1550 REM**REGULAR MEANS SAME NO. AND CONC OF SPIKES FOR EACH UNKNOWN
1555 IF T$[1,1]="R" THEN GOTO 1650
1560 IF T$[1,1]<>"I" THEN GOTO 1540
1570 FOR I=1 TO N1
1575   PRINT "SAMPLE NO. ";I;
1580   INPUT "SAMPLE I.D. ? ",T1$
1585   INPUT "SAMPLE TO BE RUN HOW MANY TIMES ? ",L2
1590   INPUT "NO. OF SPIKES ? ",N0
1593   PRINT "INCLUDE ZERO IN CONCENTRATION OF SPIKES "
1595   FOR J=1 TO N0
1600     PRINT "CONC OF SPIKE ";J;
1605     INPUT C[J]
1610   NEXT J
1615   INPUT "SPIKES O.K. Y/N ? ",T$
1620   IF T$[1,1]="Y" THEN GOTO 1635
1625   IF T$[1,1]<>"N" THEN GOTO 1615
1630   GOSUB 2025
1635   WRITE FILE[5,1],T1$,N0,L2,C[1],C[2],C[3],C[4],C[5],C[6],F1
1640 NEXT I
1645 GOTO 1730
1650 INPUT "NO. OF SPIKES ? ",N0
1655 PRINT "INCLUDE ZERO IN CONCENTRATION OF SPIKES"
1660 FOR I=1 TO N0
1665   PRINT "CONC. OF SPIKE ";I;

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1670 INPUT C[1]
1675 NEXT I
1680 INPUT "SPIKES O.K. Y/N ? ",T$
1685 IF T$[1,1]="Y" THEN GOTO 1700
1690 IF T$[1,1]<>"N" THEN GOTO 1680
1695 GOSUB 2025
1700 FOR I=1 TO N1
1705 PRINT "SAMPLE NO. ";I;
1710 INPUT "SAMPLE I.D. ? ".T1$
1715 INPUT "SAMPLE TO BE RUN HOW MANY TIMES ? ",L2
1720 WRITE FILE[5,1],T1$,N0,L2,C[1],C[2],C[3],C[4],C[5],C[6],F1
1725 NEXT I
1730 INPUT "SAMPLE I.D.'S O.K. Y/N ? ",T$
1735 IF T$[1,1]="Y" THEN GOTO 1760
1740 IF T$[1,1]<>"N" THEN GOTO 1730
1745 GOSUB 2060
1755 REM
1760 REM ***** WHEEL PATTERN FOR AUTOMATIC RUN *****
      *****
1765 REM
1770 INPUT "DO YOU WANT SAMPLE WHEEL PATTERN PRINTED OUT (Y/N) ? ",T$
1775 IF T$[1,1]="N" THEN GOTO 2200
1780 IF T$<>"Y" THEN GOTO 1760
1785 INPUT "WHERE ? TYPE 0 FOR LINE PRINTER, 1 FOR TERMINAL, 2
      FOR BOTH ",T
1790 IF T=0 THEN GOTO 1890
1795 PRINT
1800 PRINT "***** SAMPLE WHEEL PATTERN *****
      **"
1805 PRINT
1810 PRINT "POSITION"; TAB(30);"I.D."; TAB(55);"SPIKE"
1815 PRINT "-----"
      ----"
1820 PRINT
1825 LET S=1
1830 FOR I=1 TO N1
1835 READ FILE[5,1],T1$,N0,L2,C[1],C[2],C[3],C[4],C[5],C[6]
1840 FOR S1=1 TO L2
1845 PRINT TAB(1);S; TAB(10);"B"; TAB(30);"BLANK"
1850 FOR J=1 TO N0
1855 PRINT TAB(1);S+J; TAB(10);"S";J;"/";"I"; TAB(30);T1$;
      TAB(56);C[J]

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1860     NEXT J
1865     LET S=S+N0+1
1870     NEXT S1
1875     NEXT I
1880     PRINT
1885     IF T=1 THEN GOTO 2200
1890     OPEN FILE(0,1),"$LPT"
1895     PAGE =120
1900     PRINT FILE(0)
1905     PRINT FILE(0), TAB(40);"***** SAMPLE WHEEL PATIERN
          *****"
1910     PRINT FILE(0)
1915     PRINT FILE(0)
1920     PRINT FILE(0), TAB(10);"GRAPHITE FURNACE"; TAB(30);SYS(3);
          "/";SYS(2);"/";SYS(1)
1925     PRINT FILE(0)
1930     PRINT FILE(0)
1935     PRINT FILE(0), TAB(40);"POSITION"; TAB(60);"I.D."; TAB(77);"SPIKE"
1940     PRINT FILE(0), TAB(30);"*****"
          *****"
1945     PRINT FILE(0)
1950     LET S=1
1955     FOR I=1 TO N1
1960         READ FILE(5,1),T1$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
1965         FOR S1=1 TO L2
1970             PRINT FILE(0), TAB(41);S; TAB(47);"B"; TAB(60);"BLANK"
1975             FOR J=1 TO N0
1980                 PRINT FILE(0), TAB(41);S+J; TAB(47);"S";J;"/";"1";
                    TAB(60);T1$; T. B(7B);C(J)
1985             NEXT J
1990             LET S=S+N0+1
1995         NEXT S1
2000     NEXT I
2005     CLOSE FILE(0)
2010     PAGE =72
2015     GOTO 2200
2020     REM *****CORRECTIONS TO SPIKE CONCENTRATIONS
2025     INPUT "HOW MANY SPIKE CORRECTIONS ? ",U1
2030     FOR J=1 TO U1
2035         PRINT "NUMBER AND CONC. ";

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2040 INPUT K,C(K)
2045 NEXT J
2050 RETURN
2055 REM*****CORRECT SAMPLE I.D.'S
2060 INPUT "HOW MANY I.D. CORRECTIONS ? ",U1
2065 FOR J=1 TO U1
2070 INPUT "SAMPLE NO. ? ",I
2075 READ FILE(5,I),T1$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
2080 INPUT "CORRECT I.D. ? ",T1$
2085 WRITE FILE(5,I),T1$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
2090 NEXT J
2095 RETURN
2200 REM*****START AUTOMATIC RUN***
2202 INPUT "TYPE CARRIAGE RETURN WHEN READY TO BEGIN ? ",T$
2205 LET S=1
2210 FOR I2=1 TO N1
2215 READ FILE(5,I2),T1$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
2220 FOR L=1 TO I6
2225 LET D(L)=0
2230 NEXT L
2235 MAT WRITE FILE(1,2*I2+5),D
2237 MAT WRITE FILE(1,2*I2+6),D
2240 FOR S1=1 TO L2
2245 FOR L=1 TO I6
2250 LET D(L)=0
2255 NEXT L
2260 FOR L=1 TO 6
2262 LET D(2)=C(L)
2265 MAT WRITE FILE(1,L),D
2270 NEXT L
2275 PRINT TAB(1);S; TAB(10);"B"; TAB(30);"BLANK"
2280 FOR K=1 TO R2
2285 LET C$="8"
2287 PRINT C$
2290 GOSUB 2390
2295 NEXT K
2300 FOR J2=1 TO N0
2302 READ FILE(5,I2),T1$
2305 PRINT TAB(1);S+J2; TAB(10);"S";J2; TAB(20);T1$; TAB(56);
C(J2)
2310 FOR K=1 TO R2

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2315      LET C$="S"
2320      LET C1$=STR$(J2)
2325      LET C2$="/"
2330      LET C3$=STR$(K)
2335      LET C$=C$,C1$,C2$,C3$
2340      PRINT C$
2345      GOSUB 2390
2350      NEXT K
2355      NEXT J2
2360      LET C$="C"
2362      LET N1=12
2363      READ FILE(5,N1),T1$,NO,D1,C(1),C(2),C(3),C(4),C(5),C(6),F1
2364      WRITE FILE(5,N1),T1$,NO,S1,C(1),C(2),C(3),C(4),C(5),C(6),F1
2365      GOSUB 2390
2367      LET I2=N1
2370      LET S=S+NO+1
2375      NEXT S1
2380      NEXT I2
2385      GOTO 3000
2390      GOTO 3010
2395      RETURN
2500 REM*****INITIALIZE FOR MANUAL SAMPLING****
2505 OPEN FILE(5,0),"MADID.DF"
2510 LET C9=0
2515 FOR I=1 TO 16
2520   LET D(I)=0
2525 NEXT I
2530 IF S$(1,1)="-Y" THEN GOTO 2630
2535 LET D(2)=1
2540 LET I=N1+1
2545 PRINT "SAMPLE NO. ":I;" ";
2550 INPUT "SAMPLE I.D. ? ",T1$
2555 INPUT "OK? Y/N ",X$
2560 IF X$(1,1)="-N" THEN GOTO 2545
2565 LET N1=N1+1
2570 INPUT "NO. OF SPIKES ?",NO
2573 PRINT "INCLUDE ZERO IN CONCENTRATION OF SPIKES"
2575 FOR I=1 TO NO
2580   PRINT "CONC OF SPIKE ":I;
2585   INPUT C(I)

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2590 NEXT I
2595 INPUT "NO. OF CORRECTIONS ? ",U1
2600 IF U1=0 THEN GOTO 2625
2605 FOR J=1 TO U1
2610 PRINT "NO. AND CONC. ";
2615 INPUT I,C[1]
2620 NEXT J
2625 WRITE FILE(5,N11,T1$,N0,S1,C[1],C[2],C[3],C[4],C[5],C[6],F1
2630 FOR I=1 TO N0
2650 LET D[21]=C[1]
2660 MAT WRITE FILE[1,1],D
2665 NEXT I
2670 IF S$(1,1)="Y" THEN GOTO 3000
2675 FOR I=1 TO 16
2680 LET D[I]=0
2685 NEXT I
2690 MAT WRITE FILE[1,2*N1+5],D
2695 MAT WRITE FILE[1,2*N1+6],D
3000 INPUT " * * * ",C$
3005 LET U$="MMA"
3010 WRITE FILE[7,3],V1,K[49],C$,C1,K1$,U$
3015 REM:***TEST FOR BLANK, STD CALIB, OR REPORT HERE
3020 IF C$<>"B" THEN GOTO 3110
3022 REM***FOR HAND ENTRY OF DATA GOTO 3085
3025 IF L$="S" THEN GOTO 3090
3030 LET K[52]=1
3031 LET K[3]=3
3033 LET K[10]=10
3035 LET C1=0
3040 CALL 7,K[52],K[3],K[3],K[10],A[1]
3050 LET A1=0
3055 LET A2=0
3060 FOR I=1 TO 9 STEP 2
3065 LET A1=A1+A[I]
3070 LET A2=A2+A[I+1]
3075 NEXT I
3080 LET C1=(A1-A2)/5
3082 PRINT "BEAM DIFF= ";A1/5;" - ";A2/5;"="";C1
3083 REM*****PLACE GOTO 3030 HERE TO LOOP FOR BEAM READINGS
3085 WRITE FILE[7,3],V1,K[49],C$,C1,K1$,U$

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3090 GOSUB 6000
3092 REM****TAKE DATA
3095 IF U$(1,1)="A" THEN GOSUB 3900
3097 IF U$="AMA" THEN GOTO 2395
3100 GOTO 3000
3110 IF C$<>"MS" THEN GOTO 3155
3115 LET G1=0
3120 REM*****SUBROUTINE TO RUN MORE SAMPLES OR REPEAT A SAMPLE (MS)
3125 INPUT "REPEAT THIS SAMPLE? ",S$
3130 IF S$(1,1)="Y" THEN LET S1=S1+1
3131 IF S$(1,1)="Y" THEN READ FILE(5,N1),T1$,NO,D1,C(1),C(2),C(3),
      C(4),C(5),C(6),F1
3132 IF S$(1,1)="Y" THEN WRITE FILE(5,N1),T1$,NO,S1,C(1),C(2),
      C(3),C(4),C(5),C(6),F1
3135 IF S$(1,1)="Y" THEN GOTO 2510
3137 REM**C9=0 ON MANSAMP
3140 IF S$(1,1)="N" THEN LET S1=1
3145 IF S$(1,1)="N" THEN GOTO 2510
3150 GOTO 3125
3155 IF C$<>"C" THEN GOTO 3190
3160 IF G1=1 THEN PRINT "LAST SAMPLE RUN HAS BEEN DELETED"
3165 IF G1=1 THEN PRINT "DO AN MS BEFORE A C"
3170 IF G1=1 THEN GOTO 3220
3175 GOSUB 4000
3177 REM***REGRESSION
3190 IF U$="AMA" THEN GOTO 2395
3182 REM**RETURN ON AUTOCL1
3185 GOTO 3000
3190 IF C$="R" THEN GOTO 7000
3200 REM*****INTERPRET COMMAND STRING
3205 GOSUB 3300
3210 IF M1<>0 THEN GOTO 3230
3215 REM INVALID COMMAND
3220 PRINT " SYNTAX ERROR"
3225 GOTO 3000
3230 LET A4=M2+4
3235 ON M0 THEN GOTO 3240, 3250
3240 LET A5=M1
3245 GOTO 3265
3260 LET A5=2*M1+5

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3265 IF K2$(">"X" THEN GOTO 3275
3270 ON M0 THEN GOTO 5000, 5000
3272 REM*****TAKE DATA AND STORE, MADGFC.DF
3275 REM: SPEC FUNCTION P.D,OR E
3280 GOSUB 5500
3282 REM***DELETE, ERASE.AS
3285 GOTO 3000
3290 REM
3295 REM ***** SUBROUTINE TO INTERPRET COMMAND STRING
      *****
3300 REM
3305 LET M0=0
3310 LET M1=1
3315 LET M2=1
3345 LET K1$=C$(1,1)
3350 IF K1$="U" THEN LET M0=2
3355 IF K1$="S" THEN LET M0=1
3360 IF G1=1 THEN PRINT "LAST SAMPLE RUN HAS BEEN DELETED"
3365 IF G1=1 THEN PRINT "DO AN MS BEFORE RUNNING MORE SPIKES"
3370 IF G1=1 THEN GOTO 3385
3375 ON M0 THEN GOTO 3395, 3395
3380 REM * * * UNRECOGNIZED COMMAND
3385 LET M1=0
3390 RETURN
3395 LET C$=C$(2)
3410 REM * * * FIND THE
3415 FOR I=1 TO LEN(C$)
3420 IF C$(I,1)="/" THEN GOTO 3435
3425 NEXT I
3430 GOTO 3380
3435 LET T1$=C$(1,1-1)
3436 ON ERR THEN GOTO 3380
3440 LET C$=C$(1+1)
3443 ON ERR THEN STOP
3445 REM * * * GET M1
3450 GOSUB 3800
3452 IF J1=0 THEN GOTO 3380
3454 ON ERR THEN STOP
3455 LET M1=J1
3460 IF LEN(C$)<=1 THEN GOTO 3495

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3465 IF LEN(C$)>2 THEN GOTO 3380
3470 IF C$(2,2)<>"D" THEN GOTO 3380
3475 LET T1$=C$(1,1)
3480 LET K2$=C$(2,2)
3485 GOTO 3505
3490 REM GET REMAINDER OF CMD STRING
3495 LET K2$=C$(1,1)
3500 LET T1$=C$
3505 IF K2$="P" THEN GOTO 3730
3507 REM***TEST VALIDITY
3510 IF K2$="E" THEN GOTO 3730
3512 REM***TEST VALIDITY
3515 IF K2$<>"D" THEN GOTO 3535
3520 GOSUB 3800
3522 REM***GET VAL
3525 LET M2=J1
3530 GOTO 3700
3532 REM***TEST VALIDITY
3535 LET T1$=C$(1,1)
3540 GOSUB 3800
3545 LET K2$="X"
3550 LET M2=J1
3700 REM*****ERROR CHECKING ROUTINE
3705 FOR I=1 TO 6
3710   IF M2=I THEN GOTO 3735
3715 NEXT I
3720 GOTO 3380
3725 REM*****TEST VALIDITY
3730 LET K3$=K2$
3735 ON M0 THEN GOTO 3740, 3760
3740 FOR I=1 TO N0
3745   IF M1=I THEN RETURN
3750 NEXT I
3755 GOTO 3380
3760 FOR I=1 TO N1
3765   IF M1=I THEN RETURN
3770 NEXT I
3775 GOTO 3380
3800 REM ***** CALCULATE VALUE OF T1$ AND RETURN IT AS J1
3810 ON ERR THEN LET J1=0

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3820 LET J1=VAL(T1$)
3830 RETURN
3890 REM****AVERAGE BLANKS IN AUTOMATIC RUN
3900 LET B3=K(49)+B3
3910 IF K=R2 THEN LET K(49)=B3/R2
3920 IF K=R2 THEN LET B3=0
3930 IF K=R2 THEN PRINT "NEW AVERAGED BLANK= ";K(49)
3940 IF K=R2 THEN WRITE FILE(7,3),V1,K(49),C$,C1,K1$,U$
3950 RETURN
4000 REM****CHAIN TO MADFIT.GF FOR CALCULATIONS
4010 MAT READ FILE(1,1),D
4015 LET D(4)=N1
4020 MAT WRITE FILE(1,1),D
4030 SAVE "MADSTART.GF"
4040 CHAIN "MADFIT.GF"
4050 RETURN
5000 REM****ROUTINE TO TAKE A READING STORE ACCORDING TO M0,M1,AND
      M2***
5005 REM
5010 REM DATA READ AS V1 AND V2
5015 IF M0=2 THEN GOTO 5025
5020 GOSUB 6000
5025 MAT READ FILE(1,A5),D
5030 IF M0=2 THEN GOTO 5065
5035 IF D(A4)<>0 THEN GOTO 5055
5040 LET D(3)=D(3)+1
5045 LET D(1)=(D(1)*(D(3)-1)+V1)/D(3)
5050 GOTO 5060
5055 LET D(1)=(D(1)*D(3)+V1-D(A4))/D(3)
5060 LET D(A4)=V1
5065 MAT WRITE FILE(1,A5),D
5080 IF M0=1 THEN GOTO 5120
5081 PRINT
5082 PRINT "U";M1;"/";M2; TAB(15);"CONC= ";D(A4)
5083 PRINT "AVE"; TAB(15);D(1)
5085 PRINT
5115 GOTO 5130
5120 PRINT "S";M1;"/";M2; TAB(15);"SIG.=";V1; TAB(40);"AVE.SIG.=";D(1)
5125 PRINT
5130 IF U$="AMA" THEN GOTO 2395

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5135 GOTO 3000
5500 REM
5505 REM ***** SUBROUTINE TO DELETE A REPLICATE OR ALL
      OF A SET *****
5510 REM
5515 REM****AVERAGE CONC. REPORTED BY P
5520 MAT READ FILE(1,A5),D
5525 IF K2$="D" THEN GOTO 5640
5530 IF K2$="E" THEN GOTO 5585
5533 IF M0=1 THEN GOTO 5582
5535 PRINT
5540 PRINT "AVE CONC= ";D(1)
5545 PRINT
5550 PRINT D(1);D(2);D(3);D(4);D(5);D(6);D(7);D(8);D(9);D(10);
      D(11);D(12);D(13);D(14);D(15);D(16)
5555 MAT READ FILE(1,A5+1),D
5560 PRINT
5565 IF D(3)<=1 THEN GOTO 5575
5570 PRINT "SAMPLE STD DEV= ";SQR(D(2)*D(3)/(D(3)-1))
5575 PRINT "AVERAGE SPIKE STD DEV= ";SQR(D(1))
5576 PRINT
5577 PRINT D(1);D(2);D(3);D(4);D(5);D(6);D(7);D(8);D(9);D(10);
      D(11);D(12);D(13);D(14);D(15);D(16)
5578 PRINT
5580 RETURN
5582 PRINT D(1);D(2);D(3);D(4);D(5);D(6);D(7);D(8);D(9);D(10)
5583 RETURN
5585 REM * * * ERASE ONE M1 SET
5590 MAT READ FILE(1,A5),D
5595 LET D(1)=0
5600 LET D(3)=0
5603 IF M1=N1 THEN GOTO 5605
5604 GOTO 5607
5605 IF M0=2 THEN LET S1=0
5607 IF M0=2 THEN LET G1=1
5610 FOR I=5 TO 16
5615   LET D(I)=0
5616 NEXT I
5618 GOSUB 5625
5619 IF M0=1 THEN RETURN

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5621 LET D(2)=0
5622 LET A5=A5+1
5623 GOSUB 5625
5624 RETURN
5625 MAT WRITE FILE(1,A5),D
5630 PRINT K1$;M1;" ERASED"
5635 RETURN
5640 REM * * * DELETE ONE REPLICATE AND CORRECT FILES
5645 IF M0<>2 THEN GOTO 5665
5650 IF N1<>M1 THEN PRINT "CANNOT DELETE PREVIOUS SAMPLES"
5655 IF N1<>M1 THEN PRINT "CAN ERASE ALL AND REPEAT SAMPLE"
5660 IF N1<>M1 THEN RETURN
5665 MAT READ FILE(1,A5),D
5670 IF D(A4)=0 THEN PRINT " SYNTAX ERROR
5675 IF D(A4)=0 THEN RETURN
5677 LET S5=D(1)
5678 LET S6=D(A4)
5680 IF D(3)>1 THEN GOTO 5705
5685 LET D(1)=0
5690 IF M0=2 THEN LET S1=S1-1
5695 LET D(3)=0
5700 GOTO 5720
5705 LET D(1)=(D(1)*D(3)-D(A4))/(D(3)-1)
5710 LET D(3)=D(3)-1
5715 IF M0=2 THEN LET S1=S1-1
5720 LET D(A4)=0
5723 LET D(A4+6)=0
5725 IF M0=1 THEN GOSUB 5855
5726 IF M0=1 THEN GOTO 5780
5727 GOSUB 5810
5730 REM***ADJUST STATISTICS FILE FOR UNKNOWN SAMPLE
5731 REM***FIRST GET NEW AVERAGE FOR SPIKE VARIANCE
5732 MAT READ FILE(1,A5+1),D
5733 IF D(3)>1 THEN GOTO 5736
5734 LET D(1)=0
5735 GOTO 5738
5736 LET D(1)=(D(1)*D(3)-D(A4))/(D(3)-1)
5738 LET D(A4)=0
5739 LET D(A4+6)=0
5740 REM***NEXT CALCULATE NEW SAMPLE VARIANCE

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5745 IF (D(3)-1)=0 THEN LET D(2)=0
5750 IF (D(3)-1)=0 THEN GOTO 5760
5755 LET D(2)=D(2)*D(3)/(D(3)-1)-(55-S6)/(D(3)-1)+2*D(3)
5760 LET D(3)=D(3)-1
5762 LET A5=A5+1
5765 GOSUB 5810
5780 PRINT K1$,M1;" / ";M2;" DELETED"
5785 IF M0=1 THEN RETURN
5790 IF M0=2 THEN PRINT "UNKNOWN FILES ADJUSTED "
5795 IF S1+1=M2 THEN LET G1=1
5800 RETURN
5805 REM***CLOSE-UP UNKNOWN FILES
5810 LET A6=4
5812 FOR I=5 TO 16
5815 IF D(I)=0 THEN GOTO 5850
5820 IF D(I)<>0 THEN LET A6=A6+1
5825 IF A6=1 THEN GOTO 5850
5830 LET D(A6)=D(I)
5835 LET D(I)=0
5840 LET D(A6+6)=D(I+6)
5845 LET D(I+6)=0
5850 NEXT I
5855 MAT WRITE FILE(1,A5),D
5860 RETURN
5877 PRINT D(1);D(2);D(3);D(4);D(5);D(6);D(7);D(8);D(9);D(10);
      D(11);D(12);D(13);D(14);D(15);D(16)
6000 REM*****SUBROUTINE TO TAKE DATA*****
6002 LET M3=M2
6004 READ FILE(7,1),K(53),K(54),K(55)
6005 WRITE FILE(7,1),K(53),K(54),K(55),NO,N1,M3
6006 REM***FOR HAND ENTRY OF DATA GOTO 6050
6007 SAVE "MADSTART.GF"
6008 CHAIN "MADDAT.GF"
6010 READ FILE(7,3),V1,K(49),C$,C1,K1$,U$
6030 READ FILE(7,0),L$,F1$,K(40),K(41)
6035 READ FILE(7,1),K(53),K(54),K(55),NO,N1,M3
6040 RETURN
6050 INPUT "PEAK HEIGHT? ",V1
6060 IF C$="B" THEN LET K(49)=V1
6070 WRITE FILE(7,3),V1,K(49),C$,C1,K1$,U$

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6080 GOTO 6010
7000 MAT READ FILE(1,1),D
7005 REM*****PICKUP N1 IN STD FILE*****
7006 LET D(4)=N1
7010 MAT WRITE FILE(1,1),D
7020 SAVE "MADSTART.GF"
7030 CHAIN "MADREP.GF" THEN GOTO 0140

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0140 IS REFERENCED ON LINES:
7030

0190 IS REFERENCED ON LINES:
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0535 IS REFERENCED ON LINES:
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0570 IS REFERENCED ON LINES:
0615 0810

0660 IS REFERENCED ON LINES:
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0670 IS REFERENCED ON LINES:
0655

0675 IS REFERENCED ON LINES:
0690

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0720 0850

0725 IS REFERENCED ON LINES:
0715 0735

0765 IS REFERENCED ON LINES:
0730

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0800 0830

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1650 IS REFERENCED ON LINES:
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1735 1780

1890 IS REFERENCED ON LINES:
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1630 1695

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1775 1885 2015

2390 IS REFERENCED ON LINES:
2290 2345 2365

2395 IS REFERENCED ON LINES:
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2500 IS REFERENCED ON LINES:
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2510 IS REFERENCED ON LINES:
3135 3145

2545 IS REFERENCED ON LINES:
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2625 IS REFERENCED ON LINES:
2600

2630 IS REFERENCED ON LINES:
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3000 IS REFERENCED ON LINES:
2385 2670 3100 3185 3225
3285 5135

3010 IS REFERENCED ON LINES:
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3090 IS REFERENCED ON LINES:
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3110 IS REFERENCED ON LINES:
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3125 IS REFERENCED ON LINES:
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3155 IS REFERENCED ON LINES:
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3190 IS REFERENCED ON LINES:
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3230 IS REFERENCED ON LINES:
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3265 IS REFERENCED ON LINES:
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3380 IS REFERENCED ON LINES:
3430 3436 3452 3465 3470
3720 3755 3775

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3385 IS REFERENCED ON LINES:
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3395 IS REFERENCED ON LINES:
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3435 IS REFERENCED ON LINES:
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3495 IS REFERENCED ON LINES:
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3535 IS REFERENCED ON LINES:
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3700 IS REFERENCED ON LINES:
3530

3730 IS REFERENCED ON LINES:
3505 3510

3735 IS REFERENCED ON LINES:
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3740 IS REFERENCED ON LINES:
3735

3760 IS REFERENCED ON LINES:
3735

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3800 IS REFERENCED ON LINES:
3450 3520 3540

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5025 IS REFERENCED ON LINES:
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5065 IS REFERENCED ON LINES:
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5120 IS REFERENCED ON LINES:
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5130 IS REFERENCED ON LINES:
5115

5500 IS REFERENCED ON LINES:
3280

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5575 IS REFERENCED ON LINES:
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5582 IS REFERENCED ON LINES:
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5585 IS REFERENCED ON LINES:
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5605 IS REFERENCED ON LINES:
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5607 IS REFERENCED ON LINES:
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5640 IS REFERENCED ON LINES:
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5665 IS REFERENCED ON LINES:
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5705 IS REFERENCED ON LINES:
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5720 IS REFERENCED ON LINES:
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5736 IS REFERENCED ON LINES:
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5738 IS REFERENCED ON LINES:
5735

5760 IS REFERENCED ON LINES:
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5780 IS REFERENCED ON LINES:
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5810 IS REFERENCED ON LINES:
5727 5765

5850 IS REFERENCED ON LINES:
5815 5825

5855 IS REFERENCED ON LINES:
5725

6000 IS REFERENCED ON LINES:
0790 3090 5020

6010 IS REFERENCED ON LINES:
6080

7000 IS REFERENCED ON LINES:
3190

A1 OCCURS ON LINES:
3050 3065 3080 3082

A2 OCCURS ON LINES:
3055 3070 3080 3082

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A4 OCCURS ON LINES:
 3230 5035 5055 5060 5082
 5670 5675 5678 5705 5720
 5723 5736 5738 5739

A5 OCCURS ON LINES:
 3240 3260 5025 5065 5520
 5555 5580 5622 5625 5665
 5732 5762 5855

A6 OCCURS ON LINES:
 5810 5820 5825 5830 5840

A1 OCCURS ON LINES:
 0105 3040 3065 3070

B2 OCCURS ON LINES:
 0545 0630

B3 OCCURS ON LINES:
 0202 3900 3910 3920

C\$ OCCURS ON LINES:
 0100 0780 0880 2285 2287
 2315 2335 2340 2360 3000
 3010 3020 3085 3110 3155
 3190 3345 3395 3415 3420
 3435 3440 3460 3465 3470
 3475 3480 3495 3500 3535
 3940 6010 6060 6070

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C1 OCCURS ON LINES:
0205 0780 0880 3010 3035
3080 3082 3085 3940 6010
6070

C1\$ OCCURS ON LINES:
0115 2320 2335

C2\$ OCCURS ON LINES:
0115 2325 2335

C3\$ OCCURS ON LINES:
0115 2330 2335

C9 OCCURS ON LINES:
2510

CI OCCURS ON LINES:
0105 1605 1635 1670 1720
1835 1855 1960 1980 2040
2075 2085 2215 2262 2305
2363 2364 2585 2615 2625
2650 3131 3132

O OCCURS ON LINES:
2235 2237 2265 2660 2690
2695 4010 4020 5025 5065
5520 5555 5590 5625 5665
5732 5855 7000 7010

D1 OCCURS ON LINES:
2363 3131

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DI OCCURS ON LINES:

0105	2225	2250	2262	2520
2535	2650	2680	4015	5035
5040	5045	5055	5060	5082
5083	5120	5540	5550	5565
5570	5575	5577	5582	5595
5600	5615	5621	5670	5675
5677	5678	5680	5685	5695
5705	5710	5720	5723	5733
5734	5736	5738	5739	5745
5750	5755	5760	5815	5820
5830	5835	5840	5845	5877
7006				

F1 OCCURS ON LINES:

0210	1635	1720	2363	2364
2625	3131	3132		

F1\$ OCCURS ON LINES:

0110	0155	0175	6030	
------	------	------	------	--

G1 OCCURS ON LINES:

0195	3115	3160	3165	3170
3360	3365	3370	5607	5795

I OCCURS ON LINES:

1570	1575	1635	1640	1660
1665	1670	1675	1700	1705
1720	1725	1830	1835	1875
1955	1960	2000	2070	2075
2085	2515	2520	2525	2540
2545	2575	2580	2585	2590
2615	2630	2650	2660	2665
2675	2680	2685	3060	3065
3070	3075	3415	3420	3425
3435	3440	3705	3710	3715
3740	3745	3750	3760	3765
3770	5610	5615	5616	5812
5815	5820	5825	5830	5835
5840	5845	5850		

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I2 OCCURS ON LINES:
 2210 2215 2235 2237 2302
 2362 2367 2380

J OCCURS ON LINES:
 1595 1600 1605 1610 1850
 1855 1860 1975 1980 1985
 2030 2045 2065 2090 2605
 2620

J1 OCCURS ON LINES:
 3452 3455 3525 3550 3810
 3820

J2 OCCURS ON LINES:
 2300 2305 2320 2355

K OCCURS ON LINES:
 2040 2280 2295 2310 2330
 2350 3910 3920 3930 3940

K1\$ OCCURS ON LINES:
 0110 0780 0880 3010 3085
 3345 3350 3355 3940 5630
 5780 6010 6070

K2\$ OCCURS ON LINES:
 0110 3265 3480 3495 3505
 3510 3515 3545 3730 5525
 5530

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K3\$ OCCURS ON LINES:
 3730

KI OCCURS ON LINES:
 0105 0165 0175 0180 0270
 0525 0535 0570 0580 0585
 0595 0600 0605 0610 0615
 0620 0630 0635 0640 0645
 0650 0670 0765 0775 0780
 0875 0880 3010 3030 3031
 3033 3040 3085 3900 3910
 3930 3940 6004 6005 6010
 6030 6035 6060 6070

L OCCURS ON LINES:
 2220 2225 2230 2245 2250
 2255 2260 2262 2265 2270

L\$ OCCURS ON LINES:
 0100 0145 0175 0205 3025
 6030

L2 OCCURS ON LINES:
 1585 1635 1715 1720 1835
 1840 1960 1965 2075 2085
 2215 2240

M0 OCCURS ON LINES:
 3235 3270 3305 3350 3355
 3375 3735 5015 5030 5080
 5533 5605 5607 5619 5645
 5690 5715 5725 5726 5785
 5790

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M1 OCCURS ON LINES:
 3210 3240 3260 3310 3385
 3455 3745 3765 5082 5120
 5603 5630 5650 5655 5660
 5780

M2 OCCURS ON LINES:
 3230 3315 3525 3550 3710
 5082 5120 5780 5795 6002

M3 OCCURS ON LINES:
 0135 6002 6005 6035

N0 OCCURS ON LINES:
 1590 1595 1635 1650 1660
 1720 1835 1850 1865 1960
 1975 1990 2075 2085 2215
 2300 2363 2364 2370 2570
 2575 2625 2630 3131 3132
 3740 6005 6035

N1 OCCURS ON LINES:
 0140 1505 1570 1700 1830
 1955 2210 2362 2363 2364
 2367 2540 2565 2625 2690
 2695 3131 3132 3760 4015
 5603 5650 5655 5660 6005
 6035 7006

P3 OCCURS ON LINES:
 0560 0580

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R2 OCCURS ON LINES:
1515 1530 2280 2310 3910
3920 3930 3940

R5\$ OCCURS ON LINES:
0110 0250 0725 0730 0735
0775 0875

S OCCURS ON LINES:
1825 1845 1855 1865 1950
1970 1980 1990 2205 2275
2305 2370

S\$ OCCURS ON LINES:
0115 0125 2530 2670 3125
3130 3131 3132 3135 3140
3145

S1 OCCURS ON LINES:
0130 1840 1870 1965 1995
2240 2364 2375 2625 3130
3132 3140 5605 5690 5715
5795

S5 OCCURS ON LINES:
5677 5755

S6 OCCURS ON LINES:
5678 5755

T OCCURS ON LINES:
1785 1790 1885

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T\$ OCCURS ON LINES:

0100	0680	0685	0690	0770
0795	0800	0805	0835	0840
0845	0850	1510	1515	1520
1525	1540	1555	1560	1615
1620	1625	1680	1685	1690
1730	1735	1740	1770	1775
1780	2202			

T1\$ OCCURS ON LINES:

0110	1580	1635	1710	1720
1835	1855	1960	1980	2075
2080	2085	2215	2302	2305
2363	2364	2550	2625	3131
3132	3435	3475	3500	3535
3820				

T3 OCCURS ON LINES:

0585	0630
------	------

U\$ OCCURS ON LINES:

0100	0767	0780	0863	0865
0867	0870	0873	0890	0885
3005	3010	3085	3095	3097
3180	3940	5130	6010	6070

U1 OCCURS ON LINES:

2025	2030	2060	2065	2595
2600	2605			

V1 OCCURS ON LINES:

0200	0780	0880	3010	3085
3940	5045	5055	5060	5120
6010	6050	6060	6070	

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X\$ OCCURS ON LINES:
0100 2555 2560

Y\$ OCCURS ON LINES:
0100 0240 0710 0715 0720
0775 0875

Z\$ OCCURS ON LINES:
0100 0280 0705 0775 0822
0825 0830 0875

APPENDIX E2: MADFIT.GF

LISTING OF FILE MADFITGF.AS
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```

0100 REM*****MADFIT.GF*****4/23/79*****WALTER BOYLE
0150 REM*****FORMERLY LSGADD.GF*****4/4/78*****WALTER BOYLE
0200 REM*****CHAINED TO FROM COMMA.GF FOR CALCULATIONS*****
0300 REM*****FOR METHOD OF ADDITIONS*****
3000 DIM B(2,2),F(36,2),H(36,1)
3010 DIM L(2,1),R(2,36),W(2,1)
3020 DIM D(17),K(70),C(10)
3030 DIM F$(15),L$(15)
3040 DIM T$(25)
3500 READ FILE(1,1),D(1),D(2),D(3),N1
3510 READ FILE(5,N1),T$,NO,S1,C(1),C(2),C(3),C(4),C(5),C(6),F1
3520 READ FILE(7,4),K(51),R1
3530 READ FILE(7,0),L$,F$,K(40),K(41)
4000 REM*****SUBROUTINE FOR 1ST DEG. LEAST SQUARES FIT*****
4005 REM
4010 REM***M9=NO. OF STDS IN CALIB SET C(1), SIG IN FILE 1
4015 REM COUNT THE NO. OF STDS RUN
4020 LET M9=0
4025 LET K(41)=0
4030 FOR J=1 TO NO
4035   READ FILE(1,J),A
4040   IF A<=0 THEN GOTO 4050
4045   LET M9=M9+1
4050 NEXT J
4055 PRINT M9;"   STDS IN CALIB SET"
4060 IF M9<>NO THEN PRINT " NOT ENOUGH STANDARDS "
4065 IF M9<>NO THEN GOTO 4640
4067 PRINT
4070 LET K(51)=M9
4075 WRITE FILE(7,4),K(51),R1
4110 LET M9=0
4111 REM***GET DIM OF SPIKE CONC MATRIX H AND ABS MATRIX F AND
      R THE TRNP OF F
4115 LET I1=0
4120 FOR I=1 TO NO
4125   READ FILE(1,1),D(1),D(2),D(3)
4130   LET I1=D(3)+I1
4135 NEXT I
4140 MAT H=ZER(11,1)
4148 MAT F=ZER(11,2)
4149 MAT R=ZER(2,11)

```

LISTING OF FILE MADFITGF.AS
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```

4150 REM***GET VALUES FOR SPIKE CONC MATRIX H AND ABS CONC MATRIX F
4157 LET J1=0
4160 FOR I=1 TO NO
4165   MAT READ FILE[I,1],D
4167   LET I1=0
4170   FOR J=1 TO D[3]
4175     LET I1=I1+1
4177     IF D[I1+4]=0 THEN GOTO 4175
4178     LET J1=J1+1
4179     LET H[J1,I1]=D[2]
4181     LET F[J1,I1]=I
4183     LET F[J1,2]=D[I1+4]
4185   NEXT J
4190 NEXT I
4210 MAT R=TRN(F)
4217 MAT B=ZER(2,2)
4220 MAT B=R*F
4227 MAT L=ZER(2,1)
4230 MAT L=R*H
4240 MAT B=INV(B)
4250 MAT W=ZER(2,1)
4255 MAT W=B*L
4261 REM*****CALCULATE VARIANCE OF MEASUREMENTS*****
4262 REM*****COUNT NO. OF MEASUREMENTS
4265 LET I1=0
4270 FOR I=1 TO NO
4275   READ FILE[I,1],D[1],D[2],D[3]
4280   LET I1=I1+D[3]
4285 NEXT I
4287 REM***VARIANCE CALCULATION--NEEDS THREE MEASUREMENTS
4288 REM***CALCULATES A RUNNING VARIANCE AFTER THREE MEASUREMENTS
4290 LET S5=0
4292 LET S6=0
4295 FOR I=1 TO I1
4297   LET S6=(S6*(I-1)+H[I,1])/I
4300   LET E1=H[I,1]-(W[I,1]+W[2,1]*F[I,2])
4305   IF I<=3 THEN GOTO 4320
4310   LET S5=S5*(I-3)/(I-2)+E1*E1/(I-2)
4315 NEXT I
4317 GOTO 4330

```

LISTING OF FILE MADFITGF.AS
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```

4320 LET S5=E1*E1+S5
4325 NEXT I
4330 IF I<3 THEN LET S5=0
4335 IF I<3 THEN PRINT "VARIANCE INDETERMINATE"
4340 PRINT
4345 LET S5=S5*B(1,1)
4350 PRINT "STANDARD DEV OF SPIKE MEASUREMENTS= ";SQR(S5)
4355 PRINT
4360 LET S7=0
4365 FOR I=1 TO 11
4370   LET S7=S7+(H(1,1)-S5)^2
4375 NEXT I
4380 LET C9=1-(S5*(11-2)/B(1,1))/S7
4385 PRINT "COEFF OF DETERM= ";C9
4387 PRINT
4400 LET Y0=W(1,1)
4405 LET Y1=W(2,1)
4415 PRINT " CONC= ";Y0;"+";Y1;"*ABS"
4420 PRINT
4425 FOR I=1 TO N0
4427   READ FILE(1,1),D(1)
4430   LET D1=(Y0+Y1*D(1))-C(1)
4435   PRINT I;"DIFF : ";C(1)+D1;" - ";C(1);" = ";D1
4450 NEXT I
4455 LET K(41)=C9
4460 WRITE FILE(7,0),L$,F1$,K(40),K(41)
4465 PRINT
4480 WRITE FILE(7,4),K(51),R1
4490 REM***CALCULATE BY METHOD OF ADDITIONS AND STANDARDIZE
4495 LET C0=-Y0
4500 LET Y0=0
4505 REM***TRANSFER STDS DATA ON TO SAMPLE FILE
4510 LET I=2*N1+5
4520 MAT READ FILE(1,1),D
4525 LET D(3)=S1
4527 LET D(4)=N0
4530 LET D(S1+4)=C0
4535 LET D(2)=1
4540 LET D(S1+10)=Y1
4543 LET S7=0

```

LISTING OF FILE MADFITGF.AS
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```
4545 LET A6=0
4547 LET M9=0
4548 REM***CALCULATE AVERAGE CONC AND SAMPLE VARIANCE
4550 FOR J=5 TO 10
4555 IF D(J)<>0 THEN LET M9=M9+1
4556 IF D(J)<>0 THEN LET A6=(A6*(M9-1)+D(J))/M9
4557 IF D(J)=0 THEN GOTO 4560
4558 IF M9>1 THEN LET S7=S7*(M9-1)/M9+(A6-D(J))2/(M9-1)
4560 NEXT J
4562 REM**S7 IS STORED AT 4625
4565 LET D(1)=A6
4570 MAT WRITE FILE(1,1),D
4575 PRINT "CONC= ";D(S1+4);"   AVG CONC= ";D(1)
4580 LET I=2*N1+6
4585 MAT READ FILE(1,1),D
4587 LET D(3)=S1
4590 LET D(S1+4)=S5
4595 LET D(S1+10)=C9
4600 REM***CALCULATE THE AVERAGE OF THE SPIKE MEASUREMENT VARIANCE
4605 LET A6=0
4608 LET M9=0
4610 FOR J=5 TO 10
4612 IF D(J)<>0 THEN LET M9=M9+1
4615 IF D(J)<>0 THEN LET A6=(A6*(M9-1)+D(J))/M9
4617 NEXT J
4620 LET D(1)=A6
4625 LET D(2)=S7
4635 MAT WRITE FILE(1,1),D
4640 CHAIN "MADSTART.GF" THEN GOTO 4050
```

REFERENCES AND SYMBOLS IN MADFITGF.AS
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4050 IS REFERENCED ON LINES:
4040 4640

4175 IS REFERENCED ON LINES:
4177

4320 IS REFERENCED ON LINES:
4305

4330 IS REFERENCED ON LINES:
4317

4560 IS REFERENCED ON LINES:
4557

4640 IS REFERENCED ON LINES:
4065

A OCCURS ON LINES:
4035 4040

A6 OCCURS ON LINES:
4545 4556 4558 4565 4605
4615 4620

B OCCURS ON LINES:
4217 4220 4240 4255

B1 OCCURS ON LINES:
3000 4345 4380

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C0 OCCURS ON LINES:

4495 4530

C9 OCCURS ON LINES:

4380 4385 4455 4595

C1 OCCURS ON LINES:

3020 3510 4430 4435

D OCCURS ON LINES:

4165 4520 4570 4585 4635

D1 OCCURS ON LINES:

4430 4435

D1 OCCURS ON LINES:

3020 3500 4125 4130 4170
4177 4179 4183 4275 4280
4427 4430 4525 4527 4530
4535 4540 4555 4556 4557
4558 4565 4575 4587 4590
4595 4612 4615 4620 4625

E1 OCCURS ON LINES:

4300 4310 4320

F OCCURS ON LINES:

4148 4210 4220

F1 OCCURS ON LINES:

3510

REFERENCES AND SYMBOLS IN MADFITG.F.AS
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F15 OCCURS ON LINES:
3030 3530 4460

F1 OCCURS ON LINES:
3000 4181 4183 4300

H OCCURS ON LINES:
4140 4230

H1 OCCURS ON LINES:
3000 4179 4297 4300 4370

I OCCURS ON LINES:
4120 4125 4135 4160 4165
4190 4270 4275 4285 4295
4297 4300 4305 4310 4315
4325 4330 4335 4365 4370
4375 4425 4427 4430 4435
4450 4510 4520 4570 4580
4585 4635

I1 OCCURS ON LINES:
4115 4130 4140 4148 4149
4167 4175 4177 4183 4265
4280 4295 4365 4380

J OCCURS ON LINES:
4030 4035 4050 4170 4185
4550 4555 4556 4557 4558
4560 4610 4612 4615 4617

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J1 OCCURS ON LINES:
4157 4178 4179 4181 4183

K1 OCCURS ON LINES:
3020 3520 3530 4025 4070
4075 4455 4460 4480

L OCCURS ON LINES:
4227 4230 4255

LS OCCURS ON LINES:
3030 3530 4460

LI OCCURS ON LINES:
3010

M9 OCCURS ON LINES:
4020 4045 4055 4060 4065
4070 4110 4547 4555 4556
4558 4608 4612 4615

NO OCCURS ON LINES:
3510 4030 4060 4065 4120
4160 4270 4425 4527

N1 OCCURS ON LINES:
3500 3510 4510 4580

R OCCURS ON LINES:
4149 4210 4220 4230

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RI OCCURS ON LINES:
3520 4075 4480

RI OCCURS ON LINES:
3010 ,

SI OCCURS ON LINES:
3510 4525 4530 4540 4575
4587 4590 4595

S5 OCCURS ON LINES:
4290 4310 4320 4330 4345
4350 4380 4590

S6 OCCURS ON LINES:
4292 4297 4370

S7 OCCURS ON LINES:
4360 4370 4380 4543 4558
4625

TIS OCCURS ON LINES:
3040 3510

W OCCURS ON LINES:
4250 4255

WI OCCURS ON LINES:
3010 4300 4400 4405

Y0 OCCURS ON LINES:
4400 4415 4430 4495 4500

REFERENCES AND SYMBOLS IN MADFITGF.AS
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Y1 OCCURS ON LINES:
4405 4415 4430 4540

APPENDIX E3: MADDAT.GF

LISTING OF FILE MADDATGF.AS

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```

0010 REM****MADDAT.GF***DATA TAKER AND FITTER FOR METHOD OF ADDITIONS
0015 REM*****DENNIS RYAN***WALT BOYLE***4/25/79
0020 DIM K(56),V(300)
0030 DIM CS(6),LS(1),US(5),YS(2),ZS(2)
0040 DIM R5(3),K1S(2),FIS(15)
0050 LET Z0=24753
0060 LET Z6=24689
0065 LET Z7=0
0070 LET Z3=25393
0075 REM***GRAPHITE FURNACE NUMBER SETS CHANNELS
0080 LET K(52)=1
0090 LET Z2=1200
0100 READ FILE(7,0),LS,FIS
0120 READ FILE(7,1),K(53),K(54),K(55)
0130 READ FILE(7,2),R5S,K(9),YS,ZS
0140 READ FILE(7,3),V1,K(49),CS,C1,K1S,US
0150 REM***IF V1=0 THEN IF K(49)=0 THEN 180 FOR EPA
0160 REM***IF US(1,1)="A" THEN 250****FOR EPA
0170 REM***GOTO 260 FOR EPA
0175 PRINT "ENTERING DATA TAKING CALL 7"
0176 PRINT
0177 GOTO 0260
0180 CALL 257,Z0,Z7
0190 CALL 257,Z3,Z7
0200 PRINT "**** START SAMPLER NOW ****"
0243 REM***CAN GOTO 268 AND READ A SET OF VALUES FROM THE FILE
0250 CALL 257,Z6,Z7
0260 CALL 7,K(52),K(53),K(54),K(55),V(1)
0261 REM***OPEN FILE(4,2),"RYANPEAKS.DF" FOR EPA
0262 OPEN FILE(4,1),"GFPOINTS.DF"
0264 MAT WRITE FILE(4),V
0266 CLOSE FILE(4)
0267 GOTO 0279
0268 OPEN FILE(4,3),"GFPOINTS.DF"
0270 MAT READ FILE(4),V
0272 CLOSE FILE(4)
0273 MAT PRINT V
0274 INPUT "C1= ",C1
0276 PRINT "YS= ";YS
0279 LET J=1

```

LISTING OF FILE MADDATGF.AS
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```

0280 IF L$="D" THEN GOTO 0340
0290 FOR I=1 TO K(55)
0300   LET V(I)=LOG((Z2-C1)/(V(I)-C1))/LOG(10)
0310   LET J=J+1
0320 NEXT I
0330 GOTO 0420
0340 FOR I=1 TO K(55) STEP 2
0345   LET V(I)=V(I)-C1
0355   IF V(I)/V(I+1)<=0 THEN STOP
0360   LET V(J)=V(I)/V(I+1)
0370   LET V(J)=LOG(V(J))/LOG(10)
0380   LET J=J+1
0400 NEXT I
0410 LET N2=K(55)/2
0420 LET L0=V(I)
0430 LET H0=V(I)
0440 FOR I=1 TO N2
0450   IF L0<V(I) THEN GOTO 0480
0460   LET L0=V(I)
0470   LET I0=I
0480   IF H0>V(I) THEN GOTO 0510
0490   LET H0=V(I)
0500   LET I2=I
0510 NEXT I
0511 REM***ADJUST POINTS SO THAT L0 IS ZERO AND NO NEGATIVES OCCUR
0512 FOR I=1 TO N2
0513   LET V(I)=V(I)-L0
0515 NEXT I
0516 REM***REDEFINE L0 AND H0
0517 LET L0=V(I0)
0518 LET H0=V(I2)
0520 LET H0=H0
0530 LET B0=0
0540 FOR I=1 TO I0
0550   LET B0=B0+V(I)
0560 NEXT I
0570 LET B0=B0/I0
0580 LET B1=0
0590 FOR I=N2-9 TO N2
0600   LET B1=B1+V(I)

```

LISTING OF FILE MADDATGF.AS
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```

0610 NEXT I
0620 LET B1=B1/10
0625 REM***SLOPE OF BASELINE FOR COMBINED MODE
0630 LET K[45]=(B1-80)/(N2-10)
0635 REM***INTERCEPT FOR COMBINED MODE
0640 LET K[44]=80
0650 IF Y$="C" THEN GOTO 0670
0660 LET K[45]=0
0670 IF I2>=5 THEN IF I2<=N2-5 THEN GOTO 0700
0680 LET V4=V[I2]-K[44]-K[45]*I2
0690 GOTO 0780
0700 LET K[46]=(-3*(V[I2-2]+V[I2+2])+12*(V[I2-1]+V[I2+1])+17*V[I2])/35
0710 LET K[47]=(2*(V[I2+2]-V[I2-2])+V[I2+1]-V[I2-1])/10
0720 LET K[48]=(2*(V[I2+2]+V[I2-2])-(V[I2+1]+V[I2-1])-2*V[I2])/14
0730 LET I1=K[47]/(-2*K[48])
0740 LET V2=K[46]+I1*K[47]+K[48]*I1*I1
0750 LET I3=I2+I1
0760 LET V3=K[44]+K[45]*I3
0770 LET V4=V2-V3
0775 REM***BEGIN INTEGRATION--FIND LEFT INTERCEPT
0780 LET I=I2
0790 LET K[2]=K[44]+K[45]*I
0800 IF K[2]>=V[I] THEN GOTO 0850
0810 LET I=I-1
0820 IF I<=1 THEN LET I=1
0830 IF I=1 THEN GOTO 0850
0840 GOTO 0790
0850 LET I6=I
0855 REM***FIND RIGHT INTERCEPT
0860 LET I=I2
0870 LET K[1]=K[44]+K[45]*I
0880 IF K[1]>=V[I] THEN GOTO 0930
0890 LET I=I+1
0900 IF I>=N2 THEN LET I=N2
0910 IF I=N2 THEN GOTO 0930
0920 GOTO 0870
0930 LET I8=I
0935 REM***INTEGRATE
0940 LET V5=0
0950 FOR I=I6 TO I8

```


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```

0960 LET V5=V5+V[I]-K[44]-K[45]*I
0970 NEXT I
0980 IF R5$="P" THEN LET V1=V4
0990 IF R5$="I" THEN LET V1=V5
1000 IF U$="A" THEN LET C$=K1$
1010 IF C$[1,1]<>"B" THEN GOTO 1035
1020 LET K[49]=V1
1025 PRINT "BLANK SIG= ";V1
1030 GOTO 1045
1035 LET V1=V1-K[49]
1040 PRINT "SIG=";V1
1045 GOTO 1120
1047 REM***REMOVE 1045 FOR EPA**CHANGE LINE 1030 ALSO
1050 OPEN FILE[6,21,"GFPEAKS.DF"
1060 WRITE FILE[6],SYS(2),SYS(1),SYS(3),SYS(11),SYS(12),SYS(13)
1070 WRITE FILE[6],L$,F1$,R5$,Y$,Z$,C$,K1$,U$
1080 WRITE FILE[6],K[52],K[53],K[54],K[55],K[44],K[45],K[49],C1
1090 WRITE FILE[6],I1,I2,I3,V2,V3,V4,I6,I8,V5,N2,H9,L0,B0,B1
1100 MAT WRITE FILE[6],V
1110 CLOSE FILE[6]
1120 IF Z$="N" THEN GOTO 1360
1130 PAGE =120
1140 LET H2=110
1150 LET H3=70
1160 REM PLOT FREQUENCY=S1
1170 LET S1=2
1180 LET S2=H2/H8
1190 LET S3=H3/H8
1200 GOTO 1240
1210 PRINT "X";
1220 IF ABS(SYS(7))<>48 THEN S10P
1230 DELAY =2
1240 ON ERR THEN GOTO 1210
1250 OPEN FILE[0,1],"$LPT"
1260 ON ERR THEN STOP
1270 PRINT
1280 FOR I=1 TO N2 STEP S1
1290 LET K3=INT(S2*V[I]+.5)
1300 LET K4=INT(S3*V[I]+.5)
1310 PRINT FILE[0], TAB(K3+1);" ";V[I]

```

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```
1320 REM**PRINT TAB(K4+1);"";V(I)
1330 NEXT I
1340 CLOSE FILE10)
1350 PAGE =72
1360 WRITE FILE(7,3),V!,K(49),CS,C1,K1$,US
1365 REM***STOP HERE WHEN READING DATA FROM FILE
1370 CHAIN F1$ THEN GOTO 6010
1380 END
```

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0260 IS REFERENCED ON LINES:
0177

0279 IS REFERENCED ON LINES:
0267

0340 IS REFERENCED ON LINES:
0280

0420 IS REFERENCED ON LINES:
0330

0480 IS REFERENCED ON LINES:
0450

0510 IS REFERENCED ON LINES:
0480

0670 IS REFERENCED ON LINES:
0650

0700 IS REFERENCED ON LINES:
0670

0780 IS REFERENCED ON LINES:
0690

0790 IS REFERENCED ON LINES:
0840

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0850 IS REFERENCED ON LINES:
0800 0830

0870 IS REFERENCED ON LINES:
0920

0930 IS REFERENCED ON LINES:
0880 0910

1035 IS REFERENCED ON LINES:
1010

1045 IS REFERENCED ON LINES:
1030

1120 IS REFERENCED ON LINES:
1045

1210 IS REFERENCED ON LINES:
1240

1240 IS REFERENCED ON LINES:
1200

1360 IS REFERENCED ON LINES:
1120

6010 IS REFERENCED ON LINES:
1370

B0 OCCURS ON LINES:
0530 0550 0570 0630 0640
1090

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B1 OCCURS ON LINES:
0580 0600 0620 0630 1090

C\$ OCCURS ON LINES:
0030 0140 1000 1010 1070
1360

C1 OCCURS ON LINES:
0140 0274 0300 0345 1080
1360

F1\$ OCCURS ON LINES:
0040 0100 1070 1370

H0 OCCURS ON LINES:
0430 0480 0490 0518 0520

H2 OCCURS ON LINES:
1140 1180

H3 OCCURS ON LINES:
1150 1190

H8 OCCURS ON LINES:
0520 1090 1180 1190

I OCCURS ON LINES:
0290 0300 0320 0340 0345
0355 0360 0400 0440 0450
0460 0470 0480 0490 0500
0510 0512 0513 0515 0540
0550 0560 0590 0600 0610
0780 0790 0800 0810 0820
0830 0850 0860 0870 0880
0890 0900 0910 0930 0950
0960 0970 1280 1290 1300
1310 1330

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I0 OCCURS ON LINES:
0470 0517

I1 OCCURS ON LINES:
0730 0740 0750 1090

I2 OCCURS ON LINES:
0500 0518 0670 0680 0700
0710 0720 0750 0780 0860
1090

I3 OCCURS ON LINES:
0750 0760 1090

I6 OCCURS ON LINES:
0850 0950 1090

I8 OCCURS ON LINES:
0930 0950 1090

J OCCURS ON LINES:
0279 0310 0360 0370 0380

K1\$ OCCURS ON LINES:
0040 0140 1000 1070 1360

K3 OCCURS ON LINES:
1290 1310

K4 OCCURS ON LINES:
1300

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K1 OCCURS ON LINES:

0020	0080	0120	0130	0140
0260	0290	0340	0410	0630
0640	0660	0690	0700	0710
0720	0730	0740	0760	0790
0800	0870	0880	0960	1020
1035	1080	1360		

L\$ OCCURS ON LINES:

0030	0100	0280	1070	
------	------	------	------	--

L0 OCCURS ON LINES:

0420	0450	0460	0513	0517
1090				

N2 OCCURS ON LINES:

0410	0440	0512	0590	0630
0670	0900	0910	1090	1280

R5\$ OCCURS ON LINES:

0040	0130	0980	0990	1070
------	------	------	------	------

S1 OCCURS ON LINES:

1170	1280			
------	------	--	--	--

S2 OCCURS ON LINES:

1180	1290			
------	------	--	--	--

S3 OCCURS ON LINES:

1190	1300			
------	------	--	--	--

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US OCCURS ON LINES:
 0030 0140 1000 1070 1360

V OCCURS ON LINES:
 0264 0270 0273 1100

V1 OCCURS ON LINES:
 0140 0980 0990 1020 1025
 1035 1040 1360

V2 OCCURS ON LINES:
 0740 0770 1090

V3 OCCURS ON LINES:
 0760 0770 1090

V4 OCCURS ON LINES:
 0680 0770 0980 1090

V5 OCCURS ON LINES:
 0940 0960 0990 1090

V6 OCCURS ON LINES:
 0020 0260 0300 0345 0355
 0360 0370 0420 0430 0450
 0460 0480 0490 0513 0517
 0518 0550 0600 0680 0700
 0710 0720 0800 0880 0960
 1290 1300 1310

YS OCCURS ON LINES:
 0030 0130 0276 0650 1070

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Z5 OCCURS ON LINES:
0030 0130 1070 1120

Z0 OCCURS ON LINES:
0050 0180

Z2 OCCURS ON LINES:
0090 0300

Z3 OCCURS ON LINES:
0070 0190

Z6 OCCURS ON LINES:
0060 0250

Z7 OCCURS ON LINES:
0065 0180 0190 0250

APPENDIX E4: MADREP.GF

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0030 REM***** "MADREP.GF" *****
0040 REM*****GRAPHITE FURNACE METHOD OF ADDITIONS REPORT*****
      *
0050 REM*****WALTER BOYLE*****4/16/79*****
0060 REM**REPORTS SAMPLE RESULTS ON LINE PRINTER OR TERMINAL*****
0070 REM*****ALLOWS CHAINING TO MADSTART.GF FOR MORE SAMPLES*****
0080 REM***ALLOWS FOR DILUTION FACTORS AND REAGENT BLANKS***
0090 REM***CAN BE CALLED DIRECTLY FOR REPORT FROM DATA FILES***
0092 REM***ALLOWS FOR FILE NAME CHANGES FOR DIRECT CALLS
0095 DIM Z$(1)
0110 LET Z$="O"
0120 GOTO 0200
0130 REM*****MADSTART.GF CHAINS TO 140*****
0140 DIM Z$(1)
0150 LET Z$="N"
0200 DIM D1$(20),O1$(25),I1$(72),S1$(72)
0210 DIM E1$(20),M1$(72),M2$(72),M3$(25)
0220 DIM Z3$(5),Z4$(5),Z5$(5)
0230 DIM H1$(10),H3$(10),H4$(10),H5$(10)
0240 DIM C1(6),S1(6),D1(6)
0300 LET H1=1
0310 LET H5=5
0320 LET H3=3
0330 LET F1=1
0340 LET F2=1
0350 LET I2=0
0400 LET B1$=""
0500 IF Z$="N" THEN GOTO 1000
0540 INPUT "FILE NAME FOR HEADER FILE ? ",H3$
0550 INPUT "FILE NAME FOR SAMPLE 1 D FILE ? ",H5$
0560 INPUT "FILE NAME FOR SAMPLE DATA FILE ? ",H1$
0570 OPEN FILE(H1,O1,H1$
0580 OPEN FILE(H5,O1,H5$
0590 OPEN FILE(H3,O),H3$
0600 READ FILE(1,1),D2,D2,D2,N1
0610 GOSUB 4000
0620 REM*****REAGENT BLANKS*****
0630 GOSUB 4500
0640 REM*****SET INDIVIDUAL STATISTICS FLAG*****
0650 GOSUB 2000

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LISTING OF FILE MADREPGF.AS

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0670 REM*****REPORT WRITER*****
0680 INPUT "ANOTHER REPORT Y/N ? ",R$
0690 IF R$(1,1)="N" THEN GOTO 6000
0700 IF R$(1,1)<>"Y" THEN GOTO 0680
0710 GOTO 0650
1000 REM*****FOR NEW REPORTS FROM ACTIVE CHAINING START HERE***
1010 READ FILE(1,11,D2,D2,D2,N1
1020 GOSUB 4500
1030 REM***SET INDIVIDUAL STATISTIC FLAG***
1040 GOSUB 2000
1050 REM*****REPORT WRITER
1060 INPUT "MORE MEASUREMENTS Y/N ? ",Z4$
1070 IF Z4$(1,1)="N" THEN GOTO 1092
1080 IF Z4$(1,1)<>"Y" THEN GOTO 1060
1090 CHAIN "MADSTART.GF" THEN GOTO 3000
1092 INPUT "DO YOU WANT A FINAL REPORT Y/N ? ",Z3$
1094 IF Z3$(1,1)="N" THEN GOTO 6000
1096 IF Z3$(1,1)<>"Y" THEN GOTO 1092
1100 INPUT "NO. OF DILUTIONS ? ",N7
1110 IF N7<=0 THEN GOTO 1210
1120 FOR I=1 TO N7
1130 PRINT "SAMPLE NUMBER, VOL 1,(DILUTED TO) VOL 2";
1140 INPUT J,A1,A2
1150 LET F1=A2/A1
1160 READ FILE(H5,J),M3$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
1170 WRITE FILE(H5,J),M3$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6),F1
1180 NEXT I
1190 INPUT "CORRECTIONS Y/N ? ",R$
1200 IF R$(1,1)="Y" THEN GOTO 1100
1210 GOSUB 4000
1220 REM***REAGENT BLANKS
1230 GOSUB 4500
1240 REM*****SET INDIVIDUAL STATISTIC FLAG*****
1250 LET H3$="HEADER.GF"
1260 OPEN FILE(H3,0),H3$
1310 INPUT "DATE OF ANALYSIS ? ",D1$
1320 INPUT "OPERATOR ? ",O1$
1330 INPUT "INSTRUMENT CONDITIONS ? ",I1$
1340 INPUT "STANDARDS SOURCE ? ",S1$
1350 INPUT "ELEMENT ",E1$

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LISTING OF FILE MADREPGF.AS
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1360 INPUT "METHOD (AUTOSAMPLER, MANUAL, OR BOTH) ? ",M1$
1370 INPUT "COMMENTS ? ",M2$
1380 INPUT "UNITS ? ",M3$
1390 WRITE FILE(H3,1),D1$,O1$
1392 WRITE FILE(H3,2),I1$,S1$
1394 WRITE FILE(H3,3),E1$,M1$
1396 WRITE FILE(H3,4),M2$,M3$
1400 LET Z2$="0"
1405 REM***CHANGE Z2$ TO PRINT HEADER***
1410 GOSUB 2000
1420 INPUT "ANOTHER REPORT Y/N ? ",R$
1430 IF R$(1,1)="N" THEN GOTO 1450
1435 IF R$(1,1)="Y" THEN GOTO 1410
1440 IF R$(1,1)<>"Y" THEN GOTO 1420
1450 INPUT "CHANGE FILE NAMES (Y/N) ? ",R$
1460 IF R$(1,1)="N" THEN GOTO 6000
1470 IF R$(1,1)<>"Y" THEN GOTO 1450
1500 INPUT "NEW FILE NAME FOR HEADER FILE ? ",H4$
1510 CLOSE FILE(H3)
1520 RENAME H3$,H4$
1530 INPUT "NEW FILE NAME FOR SAMPLE 1 D FILE ? ",H4$
1540 LET H5$="MAD1D.DF"
1545 CLOSE FILE(H5)
1550 RENAME H5$,H4$
1560 INPUT "NEW FILE NAME FOR SAMPLE DATA FILE ? ",H4$
1570 LET H1$="MADGFC.DF"
1575 CLOSE FILE(H1)
1580 RENAME H1$,H4$
1590 PRINT "RECORD NEW FILE NAMES"
1600 GOTO 6000
2000 PRINT "TYPE 0 FOR REPORT ON LINE PRINTER, 1 FOR TERMINAL,
      2 FOR BOTH"
2010 INPUT T
2020 IF T=0 THEN GOTO 2760
2030 REM*****PRINTS REPORT ON TERMINAL
2040 LET V1=1
2050 TAB =1
2060 PAGE =73
2070 IF Z2$(1,1)="N" THEN GOTO 2120
2080 READ FILE(H3,1),D1$,O1$
2090 READ FILE(H3,2),I1$,S1$

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LISTING OF FILE MADREPGF.AS
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2100 READ FILE(H3,3),E1$,M1$
2110 READ FILE(H3,4),M2$,M3$
2120 PRINT
2130 PRINT , TAB(14+V1);"***** GRAPHITE FURNACE ANALYSIS REPORT *****"
2140 PRINT , TAB(23+V1);"** METHOD OF ADDITIONS **"
2150 PRINT
2160 PRINT
2170 IF Z2$(1,1)="N" THEN GOTO 2280
2180 PRINT , TAB(17+V1);"DATE: ";D1$
2190 PRINT , TAB(13+V1);"OPERATOR: ";O1$
2200 PRINT , TAB(V1);"INSTRUMENT CONDITIONS: ";I1$
2210 PRINT , TAB(6+V1);"STANDARD SOURCE: ";S1$
2220 PRINT , TAB(14+V1);"ELEMENT: ";E1$
2230 PRINT , TAB(15+V1);"METHOD: ";M1$
2240 PRINT , TAB(13+V1);"COMMENTS: ";M2$
2250 PRINT , TAB(16+V1);"UNITS: ";M3$
2260 PRINT
2270 PRINT
2280 PRINT , TAB(26+V1);"** SAMPLE RESULTS **"
2290 PRINT
2300 PRINT
2310 PRINT , TAB(V1);"SAMPLE"; TAB(27+V1);"NO. OF"; TAB(35+V1);"AVERAGE";
      TAB(44+V1);"STD. DEV."; TAB(58+V1);"AV. STD. DEV."
2320 PRINT , TAB(V1);" I D"; TAB(28+V1);"REPS"; TAB(36+V1);"CONC.";
      TAB(43+V1);"AMONG SAMPLES"; TAB(58+V1);"WITHIN SAMPLE"
2330 PRINT
2340 FOR I=1 TO NI
2350   READ FILE(H5,I),M3$,NO,L2,C(1),C(2),C(3),C(4),C(5),C(6),F1
2360   READ FILE(H1,2*I+5),D(1),D(2),D(3),D(4)
2370   READ FILE(H1,2*I+6),S(1),S(2),S(3),S(4)
2380   IF B1$(1,1)="Y" THEN LET D(1)=D(1)*F1-D5*F2
2390   IF B1$(1,1)="Y" THEN LET F1=1
2400   IF S(3)=1 THEN GOTO 2430
2410   PRINT , TAB(V1);M3$; TAB(28+V1);D(3); TAB(34+V1);D(1)*F1;
      TAB(45+V1);SQR(S(2)*S(3)/(S(3)-1)); TAB(60+V1);SQR(S(1))
2420   IF S(3)>1 THEN GOTO 2440
2430   PRINT , TAB(V1);M3$; TAB(28+V1);D(3); TAB(34+V1);D(1)*F1;
      TAB(45+V1);"INDET."; TAB(60+V1);SQR(S(1))
2440 NEXT I
2450 PRINT
2460 IF B1$(1,1)="Y" THEN PRINT "      REAGENT BLANK (SAMPLE NO.
      ";I2;" )= ";D5;" HAS BEEN SUBTRACTED"
2470 IF B1$(1,1)="Y" THEN PRINT

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2480 PRINT , TAB(V1);"SAMPLE I D"; TAB(30+V1);"NO. AND CONCENTRATION
      OF SPIKES"
2490 PRINT
2500 FOR I=1 TO N1
2510   READ FILE(H5,I),M3$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6)
2520   PRINT , TAB(V1);M3$; TAB(30+V1);N0;
2530   IF N0=2 THEN PRINT TAB(34+V1);C(1); TAB(44+V1);C(2)
2540   IF N0>=3 THEN PRINT TAB(34+V1);C(1); TAB(44+V1);C(2);
      TAB(54+V1);C(3)
2550   IF N0=4 THEN PRINT TAB(34+V1);C(4)
2560   IF N0=5 THEN PRINT TAB(34+V1);C(4); TAB(44+V1);C(5)
2570   IF N0=6 THEN PRINT TAB(34+V1);C(4); TAB(44+V1);C(5); TAB(54+V1);
      C(6)
2580 NEXT I
2590 IF Z5$(1,1)="N" THEN GOTO 2750
2600 PRINT
2610 PRINT
2620 PRINT , TAB(25+V1);"INDIVIDUAL STATISTICS"
2630 PRINT
2640 PRINT , TAB(44+V1);"STD. DEV. COEFF."
2650 PRINT , TAB(V1);"NO. SAMPLE I D"; TAB(35+V1);"CONC."; TAB(44+V1);"IN
      SMPL"; TAB(54+V1);"OF DTM."; TAB(64+V1);"SLOPE"
2660 PRINT
2670 FOR I=1 TO N1
2680   READ FILE(H5,I),M3$,N0,L2
2690   MAT READ FILE(H1,2*I+5),D
2700   MAT READ FILE(H1,2*I+6),S
2710   FOR J=1 TO L2
2720     PRINT , TAB(V1);I; TAB(6+V1);M3$; TAB(33+V1);D(4+J);
      TAB(43+V1);SQR(S(4+J)); TAB(53+V1);S(10+J); TAB(63+V1);D(10+J)
2730   NEXT J
2740 NEXT I
2750 IF T=1 THEN RETURN
2760 REM*****PRINTS REPORT ON LINE PRINTER
2770 LET V1=5
2780 PAGE =130
2790 IF Z2$(1,1)="N" THEN GOTO 2840
2800 READ FILE(H3,1),D1$,O1$
2810 READ FILE(H3,2),I1$,S1$
2820 READ FILE(H3,3),E1$,M1$

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2830 READ FILE(H3,4),M2$,M3$
2840 OPEN FILE(0,1),"$LPT"
2850 PRINT FILE(0), TAB(34+V1);"***** GRAPHITE FURNACE ANALYSIS
      REPORT *****"
2860 PRINT FILE(0), TAB(45+V1);"**** METHOD OF ADDITIONS ****"
2870 PRINT FILE(0)
2880 PRINT FILE(0)
2890 IF Z2$(1,1)~"N" THEN GOTO 3000
2900 PRINT FILE(0), TAB(17+V1);"DATE: ";D1$
2910 PRINT FILE(0), TAB(13+V1);"OPERATOR: ";O1$
2920 PRINT FILE(0), TAB(V1);"INSTRUMENT CONDITIONS: ";I1$
2930 PRINT FILE(0), TAB(6+V1);"STANDARD SOURCE: ";S1$
2940 PRINT FILE(0), TAB(14+V1);"ELEMENT: ";E1$
2950 PRINT FILE(0), TAB(15+V1);"METHOD: ";M1$
2960 PRINT FILE(0), TAB(13+V1);"COMMENTS: ";M2$
2970 PRINT FILE(0), TAB(16+V1);"UNITS: ";M3$
2980 PRINT FILE(0)
2990 PRINT FILE(0)
3000 PRINT FILE(0), TAB(41+V1);"***** SAMPLE RESULTS *****"
3010 PRINT FILE(0)
3020 PRINT FILE(0)
3030 LET V2=2
3040 LET V3=20
3050 PRINT FILE(0), TAB(V1);"SAMPLE"; TAB(28+V1);"NO. OF"; TAB(40+V1);"AVERAGE";
      TAB(52+V1);"STD. DEV."; TAB(66+V1);"AVE. STD. DEV."
3060 PRINT FILE(0), TAB(V1);" I D"; TAB(29+V1);"REPS"; TAB(41+V1);"CONC.";
      TAB(51+V1);"AMONG SAMPLES";
3070 PRINT FILE(0), TAB(V2);"WITHIN SAMPLE"; TAB(V3);"NO. AND
      CONCENTRATION OF SPIKES"
3080 PRINT FILE(0)
3090 LET V2=1
3100 LET V3=16
3110 FOR I=1 TO N1
3120 READ FILE(H5,1),M3$,NO,L2,C(1),C(2),C(3),C(4),C(5),C(6),F1
3130 READ FILE(H1,2*1+5),D(1),D(2),D(3),D(4)
3140 READ FILE(H1,2*1+6),S(1),S(2),S(3),S(4)
3150 IF B1$(1,1)~"Y" THEN LET D(1)=D(1)*F1-D5*F2
3160 IF B1$(1,1)~"Y" THEN LET F1=1
3170 IF S(3)=1 THEN GOTO 3200
3180 PRINT FILE(0), TAB(V1);M3$; TAB(30+V1);D(3); TAB(38+V1);D(1)*F1;
      TAB(52+V1);SQR(S(2)*S(3)/(S(3)-1)); TAB(66+V1);" ";

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3190 IF S(3)>1 THEN GOTO 3210
3200 PRINT FILE(0), TAB(V1);M3$; TAB(30+V1);D(3); TAB(38+V1);D(11)*F1;
      TAB(54+V1);"INDET. "; TAB(66+V1);" ";
3210 PRINT FILE(0), TAB(V2);SQR(S(1)); TAB(V3);N0;" ";
3220 IF N0=2 THEN PRINT FILE(0), TAB(2);C(1); TAB(14);C(2)
3230 IF N0>=3 THEN PRINT FILE(0), TAB(2);C(1); TAB(14);C(2);
      TAB(26);C(3)
3240 IF N0=4 THEN PRINT FILE(0), TAB(89+V1);C(4)
3250 IF N0=5 THEN PRINT FILE(0), TAB(89+V1);C(4); TAB(101+V1);C(5)
3260 IF N0=6 THEN PRINT FILE(0), TAB(89+V1);C(4); TAB(101+V1);C(5);
      TAB(113+V1);C(6)
3270 NEXT I
3280 IF B1$(1,1)="Y" THEN PRINT FILE(0)," REAGENT BLANK (SAMPLE
      NO. ";12;")= ";D5;" HAS BEEN SUBTRACTED"
3290 IF B1$(1,1)="Y" THEN PRINT FILE(0)
3300 IF Z5$(1,1)="N" THEN GOTO 3530
3310 PRINT FILE(0)
3320 PRINT FILE(0)
3330 PRINT FILE(0), TAB(44+V1);"**** INDIVIDUAL STATISTICS ****"
3340 PRINT FILE(0)
3350 PRINT FILE(0)
3360 PRINT FILE(0), TAB(2+V1);"SAMPLE"; TAB(59+V1);"STANDARD DEVIATION";
      TAB(81+V1);"COEFFICIENT OF"
3370 PRINT FILE(0), TAB(2+V1);"NUMBER"; TAB(12+V1);"SAMPLE I D";
      TAB(41+V1);"CONCENTRATION"; TAB(61+V1);"WITHIN SAMPLE";
3380 LET V2=7
3390 LET V3=32
3400 PRINT FILE(0), TAB(V2);"DETERMINATION"; TAB(V3);"SLOPE"
3410 PRINT FILE(0)
3420 FOR I=1 TO N1
3430 READ FILE(H5,1),M3$,N0,L2
3440 MAT READ FILE(H1,2*1+5),D
3450 MAT READ FILE(H1,2*1+6),S
3460 FOR J=1 TO L2
3470 PRINT FILE(0), TAB(4+V1);I; TAB(12+V1);M3$; TAB(44+V1);D(4+J);
      TAB(64+V1);SQR(S(4+J)); TAB(77+V1);" ";
3480 LET V2=4
3490 LET V3=26
3500 PRINT FILE(0), TAB(V2);S(10+J); TAB(V3);D(10+J)
3510 NEXT J
3520 NEXT I

```


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```
3530 CLOSE FILE(0)
3540 RETURN
4000 FOR I=1 TO N1
4010 READ FILE(H5,I),M3$,N0,L2,C(1),C(2),C(3),C(4),C(5),C(6),F1
4020 IF M3$(1,2)="R0" THEN LET I2=1
4030 IF M3$(1,2)="R0" THEN LET F2=F1
4040 IF M3$(1,2)="RB" THEN LET I=N1
4050 NEXT I
4060 IF I2=0 THEN RETURN
4070 READ FILE(H1,2*I2+5),D(1)
4080 PRINT "REAGENT BLANK (SAMPLE NO. ";I2;" )= ";D(1)
4090 LET D5=D(1)
4100 INPUT "SUBTRACT REAGENT BLANK Y/N ? ",B1$
4110 IF B1$(1,1)="Y" THEN RETURN
4120 IF B1$(1,1)="N" THEN RETURN
4130 GOTO 4100
4500 INPUT "INDIVIDUAL SAMPLE STATISTICS Y/N ? ",Z5$
4510 IF Z5$(1,1)="Y" THEN RETURN
4520 IF Z5$(1,1)="N" THEN RETURN
4530 GOTO 4500
6000 CLOSE
6010 END
```

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0200 IS REFERENCED ON LINES:
0120

0650 IS REFERENCED ON LINES:
0710

0680 IS REFERENCED ON LINES:
0700

1000 IS REFERENCED ON LINES:
0500

1060 IS REFERENCED ON LINES:
1080

1092 IS REFERENCED ON LINES:
1070 1096

1100 IS REFERENCED ON LINES:
1200

1210 IS REFERENCED ON LINES:
1110

1410 IS REFERENCED ON LINES:
1435

1420 IS REFERENCED ON LINES:
1440

REFERENCES AND SYMBOLS IN MADREPGF.AS
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1450 IS REFERENCED ON LINES:
1430 1470

2000 IS REFERENCED ON LINES:
0650 1040 1410

2120 IS REFERENCED ON LINES:
2070

2280 IS REFERENCED ON LINES:
2170

2430 IS REFERENCED ON LINES:
2400

2440 IS REFERENCED ON LINES:
2420

2750 IS REFERENCED ON LINES:
2590

2760 IS REFERENCED ON LINES:
2020

2840 IS REFERENCED ON LINES:
2790

3000 IS REFERENCED ON LINES:
1090 2890

3200 IS REFERENCED ON LINES:
3170

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3210 IS REFERENCED ON LINES:
3190

3530 IS REFERENCED ON LINES:
3300

4030 IS REFERENCED ON LINES:
0610 1210

4100 IS REFERENCED ON LINES:
4130

4500 IS REFERENCED ON LINES:
0630 1020 1230 4530

6000 IS REFERENCED ON LINES:
0690 1094 1460 1600

A1 OCCURS ON LINES:
1140 1150

A2 OCCURS ON LINES:
1140 1150

B1\$ OCCURS ON LINES:
0400 2380 2390 2460 2470
3150 3160 3280 3290 4100
4110 4120

C1 OCCURS ON LINES:
0240 1160 1170 2350 2510
2530 2540 2550 2560 2570
3120 3220 3230 3240 3250
3260 4010

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D OCCURS ON LINES:
2690 3440

D1\$ OCCURS ON LINES:
0200 1310 1390 2080 2180
2800 2900

D2 OCCURS ON LINES:
0600 1010

D5 OCCURS ON LINES:
2380 2460 3150 3280 4090

D1 OCCURS ON LINES:
0240 2360 2380 2410 2430
2720 3130 3150 3180 3200
3470 3500 4070 4080 4090

E1\$ OCCURS ON LINES:
0210 1350 1394 2100 2220
2820 2940

F1 OCCURS ON LINES:
0330 1150 1170 2350 2380
2390 2410 2430 3120 3150
3160 3180 3200 4010 4030

F2 OCCURS ON LINES:
0340 2380 3150 4030

H1 OCCURS ON LINES:
0300 0570 1575 2360 2370
2690 2700 3130 3140 3440
3450 4070

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H1\$ OCCURS ON LINES:

0230 0560 0570 1570 1580

H3 OCCURS ON LINES:

0320 0590 1260 1390 1392
1394 1396 1510 2080 2090
2100 2110 2800 2810 2820
2830

H3\$ OCCURS ON LINES:

0230 0540 0590 1250 1260
1520

H4\$ OCCURS ON LINES:

0230 1500 1520 1530 1550
1560 1580

H5 OCCURS ON LINES:

0310 0580 1160 1170 1545
2350 2510 2680 3120 3430
4010

H5\$ OCCURS ON LINES:

0230 0550 0580 1540 1550

I OCCURS ON LINES:

1120 1180 2340 2350 2360
2370 2440 2500 2510 2580
2670 2680 2690 2700 2720
2740 3110 3120 3130 3140
3270 3420 3430 3440 3450
3470 3520 4000 4010 4020
4040 4050

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I1\$ OCCURS ON LINES:

0200 1330 1392 2090 2200
2810 2920

I2 OCCURS ON LINES:

0350 2460 3280 4020 4060
4070 4080

J OCCURS ON LINES:

1140 1160 1170 2710 2720
2730 3460 3470 3500 3510

L2 OCCURS ON LINES:

1160 1170 2350 2510 2680
2710 3120 3430 3460 4010

M1\$ OCCURS ON LINES:

0210 1360 1394 2100 2230
2820 2950

M2\$ OCCURS ON LINES:

0210 1370 1396 2110 2240
2830 2960

M3\$ OCCURS ON LINES:

0210 1160 1170 1380 1396
2110 2250 2350 2410 2430
2510 2520 2680 2720 2830
2970 3120 3180 3200 3430
3470 4010 4020 4030 4040

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NO OCCURS ON LINES:
 1160 1170 2350 2510 2520
 2530 2540 2550 2560 2570
 2680 3120 3210 3220 3230
 3240 3250 3260 3430 4010

N1 OCCURS ON LINES:
 0600 1010 2340 2500 2670
 3110 3420 4000 4040

N7 OCCURS ON LINES:
 1100 1110 1120

O1\$ OCCURS ON LINES:
 0200 1320 1390 2080 2190
 2800 2910

R\$ OCCURS ON LINES:
 0680 0690 0700 1190 1200
 1420 1430 1435 1440 1450
 1460 1470

S OCCURS ON LINES:
 2700 3450

S1\$ OCCURS ON LINES:
 0200 1340 1392 2090 2210
 2810 2930

SI OCCURS ON LINES:
 0240 2370 2400 2410 2420
 2430 2720 3140 3170 3180
 3190 3210 3470 3500

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T OCCURS ON LINES:
 2010 2020 2750

V1 OCCURS ON LINES:
 2040 2130 2140 2180 2190
 2200 2210 2220 2230 2240
 2250 2280 2310 2320 2410
 2430 2480 2520 2530 2540
 2550 2560 2570 2620 2640
 2650 2720 2770 2850 2860
 2900 2910 2920 2930 2940
 2950 2960 2970 3000 3050
 3060 3180 3200 3240 3250
 3260 3330 3360 3370 3470

V2 OCCURS ON LINES:
 3030 3070 3090 3210 3380
 3400 3480 3500

V3 OCCURS ON LINES:
 3040 3070 3100 3210 3390
 3400 3490 3500

Z2\$ OCCURS ON LINES:
 0095 0110 0140 0150 0500
 1400 2070 2170 2790 2890

Z3\$ OCCURS ON LINES:
 0220 1092 1094 1096

Z4\$ OCCURS ON LINES:
 0220 1060 1070 1080

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Z5\$ OCCURS ON LINES:
0220 2590 3300 4500 4510
4520

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NMS/nll