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COLORIMETRIC ANALYSIS PROGRAMS FOR THE PDP-10 TIME SHARING SYSTEM

D. FRASER AND R. F. PILGRIM

EXTRACTION METALLURGY DIVISION

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COLORIMETRIC ANALYSIS PROGRAMS FOR THE PDP-10 TIME SHARING SYSTEM

by

D. Fraser* and R. F. Pilgrim**

ABSTRACT

Three computer programs have been developed for a PDP-10 time sharing system to process the output data obtained at regular time intervals from a continuous colorimetric analyzer. The programs maintain a library of calibration curves, compute the concentrations of reacting species and, by means of selected plots and regressions, yield chemical rate constants. A unique feature of the programs permits the use of unformatted data input.

The report is produced in two parts:

Part 1 - User's manual - This describes the purpose of the three programs and the entry of data.

Part 2 - Programmer's manual - This describes the structure of the programs and the related files. A tested method for loading, compiling and executing the programs is given.

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LES PROGRAMMES d'ANALYSE COLORIMÉTRIQUE POUR LE SYSTÈME de "TIME SHARING" de L'ORDINATEUR PDP-10

par

D. Fraser* et R. F. Pilgrim**

RÉSUMÉ

On a développé trois programmes pour le système de l'ordinateur PDP-10 pour traiter l'information obtenue à intervalles de temps régulier d'un analyseur colorimétrique en continu. Les programmes maintiennent une bibliothéque des courbes d'étalonnage, calculent les concentrations des espèces réactives et par moyen des tracés et des rebroussements choisis produisent les taux de constantes chimiques. Une unique particularité des programmes permet l'utilisation de l'information non-éditée.

Le rapport se devise en deux parties:

1ère Partie - Manuel de l'usager - Description du but des trois programmes et l'introduction des données.

2ième Partie - Manuel du programmeur - Description de la structure des programmes et des fichiers relatifs. On présente une méthode vérifiée pour le chargement, la compilation et l'exécution des programmes.

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PART TWO

Programmer's Manual

GENERAL INTRODUCTION

Continuous colorimetric analysis has become a valuable research tool for the study of chemical reactions, both qualitatively and quantitatively. Since this procedure has the capability of analyzing a large number of samples, taken at equal time intervals, the determination of reaction rates and kinetic rate constants is considerably more accurate than when done by individual manual analysis. However, the amount of calculation required to obtain these constants is increased proportionally. The three computer programs described in this Technical Bulletin were written to perform all the calculations required to reduce continuous colorimetric data.

The first program sets up and maintains a library of colorimeter calibration curves. This is done by fitting parabolic equations to calibration data and storing the calibration coefficients obtained. The second program computes the total weight of metal in solution at each time interval. This involves corrections to the calibration due to machine drift, corrections for the dissolved metal removed in the regular samples and in random samples taken for extra analyses, and corrections for evaporation losses. This program also permits the weight-time curve to be plotted to determine the order of the reaction being studied and the ffective time interval. The final program

performs selected regressions on these data to obtain the rate constants.

The programs have been written and are being used primarily in the chemical field related to metallurgy. In this Division they have been applied to studies of metal sulphide leaching. The fields of application are, however, not restrictive. The programs could be used in any system where rate data are being generated by a continuous colorimetric analyzer.

PART ONE

User's Manual

1. INTRODUCTION

The following sections give the documentation necessary for understanding and using the colorimetric analysis programs. The three programs, as written, will operate only on a Digital Equipment Corporation PDP-10 Time Sharing System. It is not necessary that the reader be familiar with computer programming in order to use the programs. Most time sharing companies will load and compile the programs. The second part of this report (Programmer's Manual) was written specifically to assist PDP-10 programmers with the initial loading of the programs.

There are three linked programs in the colorimetric analysis series: CALIB, CONCAL and REGRES. The first program, CALIB, maintains a permanent library of the user's colorimetric calibration curves. The program CONCAL accepts experimental colorimetric data and calculates the cumulative weight of the analyzed element at each sample time. The output from this program is a complete table of results together with selected graphs of these results on the line printer. The third program, REGRES, fits selected rate equations to the tabulated results.

2. DATA INPUT

The three colorimetric analysis programs accept data

in the form of a simple "language". Each program has its own elementary language consisting of words, abbreviations (mnemonics) and numbers. The data may be prepared on paper tape or data cards. The programs process full 80-character records (punched cards) even though the standard teletype terminal allows only 72 characters per line. All data sets are read into a disk file prior to program execution so that the physical origin of the data, either tape or cards, does not matter.

An important feature of these programs is the "free format" used for data input. In free format, data items may be punched in any column with any number of data elements on each line (card). The items must be separated by at least one blank or comma but can otherwise be arranged as desired. Examples of complete data sets are found in the sections which deal individually with each of the three programs.

In the following sections, some rules applying to the usage of numbers and mnemonics are given. In addition, a simple method for correcting errors or for inserting comments is presented.

1) Numbers

Numbers may be expressed in any of the usual computer forms - integer, decimal or scientific notation (E-format). For example, the following line of numbers would be valid:

36 , +29 -127 +.12 , -49.3 , 1.2E-7 12E2 2.E+02

Note the use of commas and blanks to separate the numbers. Since the blank is a delimiter, it is clear that a number expression cannot have spaces within it. For example, the number 1.2 E-3 would be marked as an error. Similarly, it is not valid to continue a number from the end of one line (card) to the beginning of the next.

2) Mnemonics

A word or abbreviation must be spelled as shown, and must not be split between lines. As mentioned previously, any number of blanks and/or commas may be used to improve the appearance and readability of the data set.

Example: The program CALIB accepts the word RENAME or its abbreviation REN. In use, both of these commands would be followed by one or more pairs of letters. Thus, the next three commands are equivalent and all are correct.

```
     RENAME,  A , B T, Z
or   REN A B T Z
or   REN A
     B,T,Z
```

The following would be incorrect:

```
RE                        (The word RENAME is split
NAME A, B, T, Z            between lines)

RENAM  A, B T Z           (RENAM is not a valid
                           abbreviation)
```

3) Correcting Errors and Placing Comments in the Data

Whenever a question mark (?) is typed in a line of

data, everything from the left hand margin to the question mark is ignored. This provides a method for correcting typing errors or for placing short comments in the data.

Example: RENAM A B ? RENAME A B

or
```
RENAM A B ?
RENAME   A,B
```

```
SHORT COMMENT ? RENAME A,B
```

or
```
SHORT COMMENT ?
RENAME A,B
```

4) Error Messages

Input data errors can be divided into two groups - "spelling" and "logical". For example, the number 1.2E3. is spelled incorrectly (1.2E3), whereas the command RENAME A B C 1.2E3 represents an illogical operation to the program CALIB.

The spelling-type error messages are the same for all three programs and are listed in Appendix A. Each message will be followed by a type-out of the line (card) which is in error. In most cases, an arrow will point to the invalid character, but for words and mnemonics the arrow may be either at the first character or a few characters beyond the actual error.

The logical error messages differ for each program and have been listed in separate appendices: those for the program CALIB in Appendix B, for CONCAL in Appendix C and for REGRES in Appendix D. These error messages are not followed by a printout of the incorrect data line (card). Instead, most

of the messages will include an ITEM number and a CODE number. For example, if the following set of instructions were given to the program CALIB:

RENAME A B C DELETE F G

the following error message would be returned:

RENAME COMMAND - A LETTER-NAME WAS EXPECTED: ITEM 5, CODE 54

Since the message is not listed in Appendix A, the problem is not the result of a spelling error. However, the message does occur in Appendix B, indicating a logical problem in the command string. The ITEM number after the error message is the data element at which the program detected this logical error. Counting every word, mnenonic and number as a separate item, it can be seen that ITEM 5 is the word DELETE. Also, the CODE number can be searched in Appendix E; code 54 indicates DELETE or its abbreviation DEL. In other words, the CODE number is a short way of indicating the ITEM. Thus, the error message given in the above example indicates that there is something missing in the RENAME command and that the omission was detected at the word DELETE. At this point, a program user would review the RENAME command rules to detect the exact problem. (RENAME commands must occur in pairs).

3. THE PROGRAM 'CALIB'

The program CALIB maintains a permanent library of the user's colorimeter calibration curves. This means that the

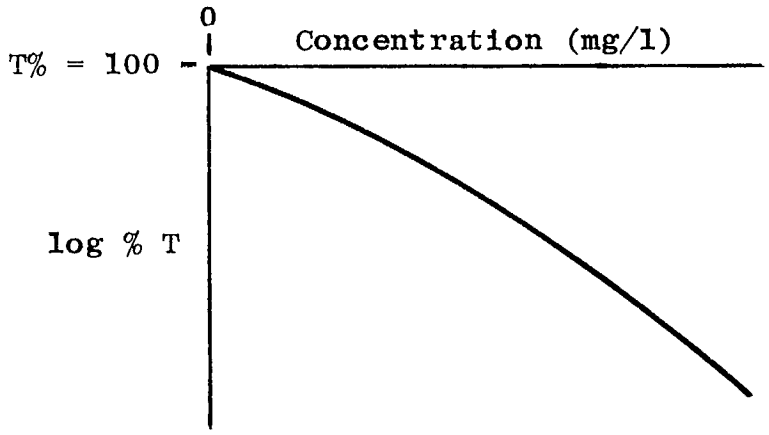
calibration data for a given curve are entered only once, no matter how many times they may be required. As many as 26 different curves (each identified by a letter of the alphabet) may be stored simultaneously. This provides considerable flexibility since it is possible to use the program CONCAL to process colorimetric data from several different machines having separate calibration curves.

The experimental calibration data are entered with the STORE command. The user may delete curves from the library (DELETE command), change their letter-names (RENAME command), or list the entire contents (LIST). Curves which have been deleted from the library can be restored without re-entering the original experimental data (INSERT command). The library contents may be erased with the NEWLIB instruction.

The mathematical method used by CALIB to store calibration curves is given in Appendix F.

1) Entering Calibration Curve Data

Colorimeter calibration curves are obtained by recording the percent transmission of several standard samples. These curves are generally plotted as (log %T) against concentration, as follows:



The program CALIB calculates and stores a mathematical representation of each calibration curve. The only information required by the program is the known concentration and the percent transmission of each of the standard samples. The user, however, should note the following conditions:

(a) Concentrations must be expressed in milligrams per litre.

(b) The calibration curve need not be linear. The programs do not assume that Beer's Law is obeyed.

(c) The calibration curve data must show approximately 100% transmission at zero concentration, otherwise, the programs will not give correct results.

The following table presents typical calibration data obtained for various copper solutions.

% Transmission	Mg/l Copper
96.2	10
90.5	20
85.4	30
79.4	40
74.9	50
69.0	60
64.0	70
58.3	80
46.7	100

These experimental data are entered with the STORE command which has the general form:

STORE [letter-name] [% transmission, concentration (mg/l)]

The letter-name is chosen from the alphabet, A through Z. The letter will become the name by which the calibration curve is recognized in the colorimeter programs. For this example, the calibration curve has been designated as "D". After the letter-name, the transmission-concentration readings are listed in pairs.

```
STORE  D  96.2  10  90.5  20  85.4  30  79.4  40  74.9  50
69.0  60  64.0  70  58.3  80  46.7  100
```

In this example, the transmission-concentration readings were listed in order of decreasing percentage transmission. Actually, the paired readings can be taken in any order as long as the percent transmission precedes the concentration. As many as 100 transmission-concentration pairs may be entered for each calibration curve. The program will not accept fewer than three pairs of readings.

Several calibration curves can be entered at one time with the same STORE command. After one set of calibration data has been entered, the next letter-name and data set can follow. For example:

STORE D [data #1] F [data #2]

is the same as the separate commands

STORE D [data #1] STORE F [data #2]

The terminal printout from a STORE command lists the original experimental data points and the mathematically predicted values of the concentration (CONC-PRED) at each measured transmission. The difference between the experimental and calculated concentrations is shown in a fourth column. It is suggested that both the experimental and calculated values be plotted on the same graph so that the accuracy of the mathematical representation of the calibration curve can be verified. The two constants, called C1 and C2, listed above the table are the two least-squares constants which are used in the mathematical approximation, and it is these numbers that are actually stored in the library.

2) Other Commands for Curve Library Operations

In addition to the STORE command, the following commands are available to perform various clerical library operations as required. Some of these commands have abbreviations which may be used.

NEWLIB This command has two uses:

1) When the program CALIB is initially compiled, NEWLIB must be the first command given to the program. The message

CALIBRATION CURVE LIBRARY STARTED ON [date]

must be obtained before the program will work properly. Failure to enter this command will result in system error messages.

2) If this command is given when a curve-library has been established, the entire library will be erased so that a new one may begin.

INSERT

This command is a fast way of entering calibration curves that have been removed from the library. The C_1 and C_2 coefficients for each curve that is to be re-entered must be obtained from the print-out of a previous LIST command or the original STORE commands.

General Form:

INSERT [letter-name] C_1 C_2 [letter-name] C_1 C_2 etc.

Example:

INSERT D 27.4 -1.7E-1 L 3.2 -1.2

is the same as the separate commands

INSERT D 27.4 -1.7E-1 INSERT L 3.2 -1.2

DELETE or DEL

This command is followed by one or more letter-names. The curves will be deleted from the library.

Example:

DELETE F - delete curve F

DEL F, M, B - delete curves F, M and B

RENAME or REN

Curves in the library may have their letter-names changed. This is useful when curves are rearranged to make room for new calibration curves.

General Form:

RENAME [present name] [new name] ... etc.

Examples:

RENAME D Z - change the name of curve D to curve Z

REN D Z C, Y - change the name of curve D to Z, and of C to Y

LIST

This command produces a listing of the library contents. The table will list all letter-names, the date the curve was established, and the C_1 and C_2 coefficients.

END — Optional command. It has no significance except that it may be used to indicate the end of the data. Do not use this word in the middle of the data or the program will stop at that point. CALIB works equally well if this word is omitted.

3) Demonstration Data Set

The set of data given in Figure 1 of this report will provide a demonstration of the use of the program CALIB. Note that the data (reproduced directly from the teletype sheet) are in free format, with items separated by blanks and/or commas. The question mark has been used to place some comments in the data.

The command NEWLIB at the beginning is required since it is assumed that the program has never been used before. Three calibration curves, representing different ranges of the same instrument, are then stored with letter-names U, V and W. The LIST command which follows would then produce a summary of the library contents and show three curves present. Next, the INSERT command is used to add some additional curves to the library. Again, the LIST command would show that the library now contains seven curves - B, F, G, M, U, V and W. Finally some of the curves are renamed and two are deleted. The net result leaves four curves in the library - A, B, C and D. The library thus established will be required to run the next demonstration data set for the program CONCAL.

Provided the programs have been loaded as described

in the Programmer's Manual, the demonstration data set may be executed as follows:

a) Put a copy of the data into a disk file called "DATA"

b) Execute the program CALIB with the monitor command .EX @ CALIB

4. THE PROGRAM CONCAL

The progress of many chemical reactions, both homogeneous and heterogeneous, can often be followed colorimetrically by noting, as a function of time, the changes in the degree of transmission of light of suitable wavelength through the reacting solution. The measurements may be continuous or intermitant depending on the speed of reaction. The normal method of correlating the optical transmission values thus obtained to actual concentrations is by means of one or more calibration curves. The program CONCAL treats the data obtained from a reacting system whose course was followed by a systematic sampling procedure. The program functions only if the sampling is done at regular intervals. From the inputted percentage optical transmissions, this program uses a stored calibration curve to determine the concentration of the samples at the appropriate times. It then computes the cumulative weight of the analyzed element from a knowledge of the initial volume together with the determined weight of the element removed in all the samples. The program assumes that the sample volume is replaced by blank solution at the time of the sampling. The actual volume is continuously corrected for

the average evaporation loss (if any) as determined by the difference of the initial and final volumes. The results calculated by CONCAL are presented in tabular form; in addition, various graphical outputs of the cumulative element reacted versus time are available.

Copies of the colorimetric calibration curves required to analyze a particular data set are taken by CONCAL from the curve library established by the program CALIB. Since the library is permanent, it is clear that CONCAL can process data sets using any combination of calibration curves. Each curve will be recognized in CONCAL by the same letter-name given it in CALIB.

When colorimetric data are obtained, it is usual to record the percent transmission readings for both the unknown solution and a standard solution. The percent transmissions of the standard then indicate the amount of instrument drift over a period of hours or days. The program CONCAL automatically compensates for calibration curve drift by internally performing a polar coordinate rotation of the original calibration curve. The mathematical theory for this, as well as for other calculations performed by CONCAL, is given in Appendix G.

A compact "language" is used to enter curve standardization readings, percent transmission data of the experimental solution, and the volume of individual "random" samples removed from the reaction vessel for other experimental purposes. This

language is introduced in Section 1. Users who do not record a standard sample along with the unknown should also read section 3. In section 4, the four line-printer plots that CONCAL will draw are discussed. Finally, in section 5, the preceding information is integrated to show the complete structure of a data set.

1) The Language for Entering Colorimeter Data

The percentage transmission data for both the unknown and standard solutions relative to a common baseline are determined from the colorimeter output. Before CONCAL can process such data, the calibration curve or curves required must have been placed in the curve library maintained by CALIB. The command which causes a particular calibration curve to be standardized against a known concentration and percent transmission reading has the general form:

Sx [% transmission] [concentration, mg/l]

where x is the letter-name of the library curve. This command instructs CONCAL to perform a polar coordinate rotation on curve "x" so that the data set following the "Sx" mnemonic are on the curve; for example:

SB 72.4 200	Standardize curve B so that 200 mg/l of the unknown correspond to a transmission reading of 72.4%.
SS 89.9 40	Standardize curve S to 89.0% transmission for 40 mg/l of the unknown.

Note that the mnemonic consists of the letter "S" prefixing the letter-name of the curve to be standardized, and that the percent

transmission precedes the concentration.

In the following four examples an abbreviated language is developed for making the necessary data entries to the program CONCAL.

Example 1. The short table of colorimetric data which follows will be used to illustrate how the S-type command is used. It is assumed that the calibration curve "A" was previously placed in the curve library.

Standard Sample		Unknown
% Trans	mg/l	% Trans
72.4	200	69
72.4	200	67
72.4	200	65
72.4	200	63

Since curve A must be standardized to (72.4%, 200 mg/l), the S-type command must be used before entering the transmission readings of the unknown. For example, we could enter

SA 72.4 200 69, SA 72.4 200 67, SA 72.4 200 65,

SA 72.4 200 63

Here the SA command has been entered before each percent transmission reading for the unknown.

However, it is not necessary to standardize repeatedly curve A to the same reading, since CONCAL will use the standardized curve until a different standardization is encountered.

The first SA command is sufficient and will hold for all successive transmission readings of the unknown. It is necessary to enter only the following:

SA 72.4 200 69 67 65 63

It must be emphasized that the language structure of CONCAL is not rigid. While the above is the shortest entry, the following is equally correct:

SA 72.4 200 69 67 SA 72.4 200 65 SA 72.4 200 63

The computed results would be the same for all three entries.

Example 2. In this example it is supposed that curves A and B, representing different ranges, have been placed in the library. In this particular data set, it was necessary to switch from curve A (low range) to curve B (high range).

Curve	Standard Sample		Unknown
	% Trans.	mg/l	% Trans.
A	33.3	50	31
	33.3	50	27
	33.3	50	23
B	66.6	200	78
	66.6	200	76
	66.6	200	74

The easiest way to enter the data is with two S-type commands, as follows:

SA 33.3 50 31 27 23 SB 66.6 200 78 76 74

Generally, the colorimeter standard sample readings change slightly over a period of time. There is a second command, related to the S-type command, that provides a rapid way of entering such changes. First, it is necessary to define the "letter" command:

(letter-name) (% transmission)

This command causes the curve specified by the letter-name to be standardized against the percent transmission reading given

and the concentration used in the last S-type command having the same letter-name. Some examples will clarify this:

SG 76.1 300 ..... G 76.3 .....

will cause G 76.3 to standardize curve G to (76.3%, 300 mg/l). The concentration value was taken from the preceding SG command. Similarly, if we have

SL 84.1 100 ..... SB 84.2 200 ..... L 84.2 .....

the command L 84.2 standardizes curve L to (84.2%, 100 mg/l). The concentration reading was taken from the previous SL command, not from the SB command.

Example 3. In this example, all the unknown readings fall in the range of calibration curve A. However, the percent transmission readings for the standard sample varied slightly owing to experimental limitations.

Standard Sample		Unknown
% Trans.	Mg/l	% Trans.
67.7	200	78
"	200	77
67.5	200	76
67.4	200	75
"	200	74
"	200	73
67.6	200	72

This data could be entered using only SA commands at appropriate places:

SA 67.7 200 78 77 SA 67.5 200 76 SA 67.4 200 75 74 73 SA 67.6 200 72

It is much simpler, however to use the "letter" command:

SA 67.7 200 78 77 A 67.5 76 A 67.4 75 74 73 A 67.6 72

In each case, the A command replaces the SA command of the longer method. It should be noted that the program automatically supplies the concentration value of 200 mg/L at each occurrence of the A command.

The program obtains concentration values for letter commands from an internal table which contains the concentration readings found in previous S-type commands. It does not matter where letter commands occur in the data, as long as the corresponding S-type command has been given previously. If the S-type command has not been given, an error message is printed.

Example 4. In this final example, both the S-type commands and letter commands will be used to enter a set of data requiring three different calibration curves (B, C and D), each of which is drifting excessively.

Curve	Standard Sample		Unknown
	% Trans.	Mg/l	% Trans.
B	96.3	100	100
	96.4	100	88
	96.4	100	74
	95.5	100	65
C	87.4	100	76
	87.3	100	71
	87.2	100	67
D	69.4	300	74
	69.4	300	72
	69.4	300	70
	69.2	300	68

This set of data may be entered most efficiently with the following string of commands:

```
SB 96.3 100 100 B 96.4 88 74 B 95.5 65 SC 87.4 100 76
C 87.3 71 C 87.2 67 SD 69.4 300 74 72 70 D 69.2 68
```

Several data sets may be processed by CONCAL in the same computer run. The concentration values occurring in the S-type commands are carried through successive data sets. For example, suppose curve A is used in the first data set with the command SA 86.3 200, but the next use of curve A is in data set four. Then the command A 85.6 would cause the program to use the concentration value of 200 mg/l, held over from the SA command in the first data set. Similarly, if a data set (other than the first) does not begin with an S-type command, the program continues with the curve that was in use for the previous data set. The first data set of a group must, however, begin with an S-type command.

2) The RANDOM Command

When a random sample is taken from the reaction solution for independent analysis, the RANDOM command (abbreviation RAN) must be used to correct for both the resulting volume change and the weight of element removed in the sample. The form of the command is:

RANDOM (solution volume removed, in litres)

Examples:	RANDOM .025	A sample of 25 ml. was taken
	RAN 0.01	The solution volume removed was 10 ml.

This command corrects the solution volume before calculations are performed on the next unknown percent transmission reading that occurs in the data. The program uses the concentration

obtained immediately before sampling to compute the weight of element removed in the sample.

Example: RAN .01 SA 68.7 200 83.6 82.1 ...

or SA 68.7 200 RANDOM 0.01 83.6 82.1 ...

will decrease the solution volume by 10 ml. before the next percent transmission reading of the unknown (83.6) is employed. CONCAL assumes that the last of a series of consecutive RANDOM commands is to be used. This provides a method of correcting errors. Each command must be in the proper form, however.

RANDOM 1.0 RAN 0.01	Both commands are valid RANDOM instructions. The last one will be used. The sample volume is taken as 0.01 litres.

3) The Special Case where there is no Standard Sample

If the sample transmissions are recorded without accompanying readings for a standard solution, it is necessary to "dummy" one standard reading in entering data into CONCAL. The reason for this is that CONCAL cannot use a curve from the library unless the letter-name of the curve is introduced in an S-type command. (See examples 1 and 2 of Section 1). However, a valid percent transmission reading and concentration value for the S-command is available from the program CALIB. Refer to the print-out obtained when the curve was place in the library with the STORE command. Choose a percent transmission reading of 20% to 50%, and then obtain the corresponding concentration value from the column marked "CONC-PRED". Use this

pair of numbers in the appropriate S-command whenever the curve is required in CONCAL. Since the "dummy" standardization values are already on the curve, CONCAL obtains the curve and rotates it through zero radians (i.e. does not change the curve). Of course, "letter" commands do not apply when no standard samples are taken.

4) Line Printer Plots

Four different line printer plots are available from CONCAL. Graphs are obtained by giving the command PLOT or PLOTS followed by a list of the desired plots. In the table of available plots given below, W is the cumulative weight of the element and t is the elapsed reaction time.

Mnemonic	Form of Plot
LIN (L)	W vs. t
SQR (S)	W^2 vs. t
CUBE (C)	W^3 vs. t
LOG	log(W) vs. log(t)

Examples: PLOT LIN LOG

PLOT S

PLOTS, LOG, S, C, L

The graphs are made by interpolating 36 points from the printer column marked "TOT-MET". Each interpolated point, represented on the graph by an asterisk, has beside it the number ("NO" column of the printer output) of the nearest point in

the data. The plots are adequate for examining the general trend of the data. No axis information is printed because it is unnecessary to calculate by hand the slope of any section of a graph. The program REGRES will do this automatically for the user.

The Programmer's Manual contains a section which will be of assistance should the user wish to interface the program CONCAL with an external plotting program.

5) Structure of a Complete Data Set

Each set of data, representing one colorimetric analysis experiment, must have a definite order. The data set begins with a title which is then followed by six constants. The colorimetric data is next. The final item of data is always the word "END".

Any number of data sets may be processed during a program execution. The individual sets of data are simply placed one after another.

(a) Title

The title must be on a separate line and should begin in the first 10 columns. The program uses only the first 60 characters from the beginning of the line. Extra characters are ignored. Note that a blank line will not work and that other data items may not appear on the same line as the title.

(b) Data Constants

After the title line, the program requires six constants which must be in order:

INITIAL TIME	Time of the first reading, in hours. This value is commonly zero.
SAMPLE TIME	Time interval between colorimetric samples, in hours. The sampling must be done at regular intervals.
INITIAL VOLUME	Volume of the solution at the time of the first sample, in litres.
EVAPORATION LOSS	Average loss (a positive number) from evaporation, in litres per cycle. A gain (a negative number) is also acceptable to the program.
SAMPLE VOLUME	The volume of solution removed for each colorimetric sample, in litres per sample.
AREA	For heterogeneous reactions, this is the measured solid area, in cm^2. If the surface area is not measured, or if the reaction is homogeneous, this constant must be set equal to one, otherwise the graphs and regression equations will be meaningless.

(c) Colorimetric Data

Figure 2 illustrates the method by which complete sets of data are entered into the program CONCAL. Two complete sets of data are given (Test No. 5-11-67 and EN-77 IMP). The data for the first of these tests are given below. A comparison of the data in this table with Figure 2 will illustrate the manner by which the data are entered.

Experiment Title:	TEST NO. 5-11-67 CU2S
Initial Time	0.0 hrs.
Sample Time	0.5 hrs.
Initial volume	2.7 litres
Evaporation loss	0.000235 litres per sample cycle
Sample volume	0.00170 litres per sample cycle
Area	5.11 cm^2

Random Sample	Curve Name	Standard Sample		Unknown
		% Trans	Mg/l	% Trans
	C	78.9	100	100
	"	"	"	98.2
	"	"	"	96.3
	"	"	"	94.0
	"	"	"	90.8
	C	79.2	100	85.8
	B	52.0	500	87.0
5 ml.	"	"	"	77.6
	B	51.8	500	70.1
	B	51.5	500	63.6
	"	"	"	58.2
	A	58.5	1000	77.7
	"	"	"	75.6
	"	"	"	73.7
10 ml.	A	58.3	1000	72.0
	"	"	"	70.4
	A	58.2	1000	69.0
	A	58.0	1000	67.5
				66.2

(d) "END" mnemonic

Each individual data set must have "END" as the final word. If printer plots are required, put the PLOT(S) command between the last item of colorimetric data and the word END

Examples:

..... 82.4 81.1 END

..... 82.4 81.1 PLOT L, LOG END

6) Demonstration Data Set

The data given in Figure 2 may be used to demonstrate the program CONCAL. To run the data set, proceed as follows:

a) Place the data in a disk file called "DATA"

b) Execute the program CONCAL with the monitor command

.EX @ CONCAL

c) Obtain a line printer listing of the disk file named PRINT.DAT which will be produced by the program. Then delete this file to release the disk space.

Note that this demonstration data set cannot be run unless the demonstration data set for the program CALIB has been run previously.

5. THE PROGRAM REGRES

REGRES, the final program in the colorimetric analysis group, allows the choice of several least-squares regression equations to be fitted to various ranges of points from the data sets processed by CONCAL. The regression equations available are:

$$W = A + Bt$$

$$W^2 = A + Bt$$

$$W^3 = A + Bt$$

$$\log W = A + B(\log t)$$

$$W^X = A + Bt$$

$$W = A + Bt + Ct^2$$

where A, B and C are constants
X is a real number
W is the cumulative weight of the element
t is elapsed reaction time.

The information required by REGRES to fit the regression equations is obtained from a binary file previously written by the program CONCAL. The values used are those in the three right-most columns of the line printer output. The W values are taken from the column marked "TOT-MET"; the t values are the corresponding times from the "TIME" column. The column marked "NO" provides numbering information for the points so that a user may select a range or ranges over which a regression equation is to be fitted.

1) Commands

The program REGRES uses several commands which are explained below. Note that most commands have single letter abbreviations, given in parentheses.

FIND (F) — When data sets are processed by CONCAL, each data set is automatically given a "Regression Access Number". This number is printed after the data title on both the calculations and graphs. The access number is required by REGRES to locate a particular data set. For example, if the Regression Access Number is 6, the command that will make REGRES locate the appropriate data is:

FIND 6 or, more simply, F 6

NEXT (N) — The command NEXT causes the program REGRES to locate the next data set in sequence. For example, after performing regressions on the data set with Access Number 6, it is desired to do regressions on the next data set (Access Number 7). This can be done by giving the instruction NEXT.

Example:

FIND 6 (other instructions) NEXT

will locate the data set with the Regression Access Number of 7

LIN (L) This command causes a linear regression of the form

$$W = A + Bt$$

to be fitted over the range of points indicated by the user. The general form of the command is:

LIN [first limit] [second limit]

The first and second limits are taken from the "NO" column of the CONCAL printer results. For example, in a data set that has points numbered from 1 to 57, it is desired to fit a linear regression to the points from number 27 to number 42, inclusive. The command to do this is:

LIN 27 42 or LIN 42 27

Note that the order of the limits does not matter. More than one linear regression can be performed by including additional lower and upper limits.

Example:

LIN 27 42 1 27

is the same as the separate commands

LIN 27 42 LIN 1 27

If the lower and upper limits are omitted from the LIN command, REGRES assumes that all points are to be used in the linear regression.

Example:

FIND 6 LIN Find data set 6 and fit a linear regression over the entire range of points.

The following extended example shows how the first three commands might be used:

```
FIND  4  LIN  2  16  NEXT  LIN  27  42  1  27  LIN
```

Find data set 4 and perform a linear regression from point number 2 to point number 16. Locate the next data set (NEXT) and perform two regressions: the first from points 27 to 42, and the second on points 1 to 27. Finally, do a linear regression on all data points of the latter data set.

If abbreviations were used, this command would become:

```
F  4  L  2  16  N  L  27  42  1  27  L
```

SQR (S) This command fits a regression equation of the form

$$W^2 = A + Bt$$

over a selected range of points. Its usage is the same as the LIN command, discussed previously.

Examples:

SQR 17 49	perform the "square" regression on points numbered 17 to 49
S 17 49 49 71	Do two regressions; the first on points 17 to 49 and the second on points 49 to 71
N S	Locate the next data set (N) and do a "square" regression on all points (S).

CUBE (C) Performs a regression fit of the form

$$W^3 = A + Bt$$

Its usage is similar to the LIN and SQR commands.

Examples:

CUBE 17 49	Do a "cube" regression over the range of points from number 17 to 49
NEXT C	Locate the next data set in sequence. Perform the cubic regression with all points.

PAR (P) This command fits an equation of the form

$$W = A + Bt + Ct^2$$

Examples:

PAR 1 18	Fit a parabola over the points from number 1 to 18.
F 3 PAR P 7 38	Find the data for Access Number 3. Perform a parabolic regression (PAR) with all points, and another with points 7 to 38.

LOG The equation fitted by this command is of particular interest since the constant B indicates the "order" of the reaction.

$$\log W = A + B(\log t)$$

This command is used in an analogous manner to the preceding ones.

Examples:

LOG 1 18	Perform a log-log regression from point number 1 to number 18
F 2 LOG	Find the data for Access Number 2 and perform a log-log regression with all the data points

EXP (E) This command fits an equation of the form

$$W^x = A + Bt$$

It differs from the proceding commands in that

three numbers are required for the general form of this command:

EXP [x value] [first limit] [second limit]

The value of x may be an integer or decimal number, but never zero. For example, if x is 2.5, the fitted equation would be:

$$W^{2.5} = A + Bt$$

Like the other commands, the lower and upper limits may be omitted and all the points in the data will be used.

Examples:

EXP 0.5 1 27	Fit the exponential regression from points 1 to 27, using an exponent of 0.5
EXP .66667	Use an exponent of .66667 for a regression fit to all the data points.
EXP 1.5 18 36 EXP 2.5 20 50	Perform two exponential regressions, first with an exponent of 1.5 on points 18 to 36, and secondly with an exponent of 2.5 on points 20 to 50.

The following will not work because the EXP command does not follow the same structure as the previous commands.

EXP .667 1 20 13 67	Wrong. This will not fit two regressions with exponent .667 to the ranges 1-20 and 13-67
EXP .667 1.5	Wrong. This will not fit two equations over the complete range with the exponents .667 and 1.5

2) Demonstration Data Set

The data given in Figure 3 may be used to demonstrate the program REGRES. Note that the preceding demonstration data sets for the programs CALIB and CONCAL must have been run first. The procedure is:

a) Put the data into a disk file called "DATA"

b) Execute the program with the monitor command

.EX @ REGRES

c) When the demonstration is finished, delete the binary disk file BIFIL.DAT. This is the standard procedure after one has finished with the program REGRES. This file is in binary and transmits intermediate results from the program CONCAL. When regressions are being performed on real data, the user may wish to run REGRES several times before finally deleting the intermediate file.

PART TWO

Programmer's Manual

1. INTRODUCTION

The programmer's manual includes the information required to put the colorimetric analysis program package in operation. It is important for the programmer to observe the structure of the package. Details of this structure are given in Section 3. This package has been arranged to provide simple loading, compiling and executing of the three programs in the group, as described in Section 4. The relationship between the disk files and the programs is discussed in Section 5. A method is also suggested in the final section for interfacing the program CONCAL to an external plotter program, or alternative regression program.

2. GENERAL SYSTEM INFORMATION

The three main programs for analyzing colorimetric data are CALIB, CONCAL and REGRES. These were developed on a Digital Equipment Corporation Time Sharing PDP-10/50 which, at the time of program development, was running under Monitor Level C, version 4S72. Access to the computer was from a model 35 teletype.

The programs are written in DEC Fortran IV, with two routines in Macro-10 Assembler. The Fortran programming and

and system functions (IFILE, OFILE and DATE) conform to the requirements of the 1970 PDP-10 Time Sharing Handbook, Book 5. The programs have been compiled with a modified Fortran compiler, version DEC 21B. Disk files are used by the programs for data input and intermediate results (binary files). Output is to the user's console, or to a disk file for subsequent line printer listing.

Advantage has been taken of the time sharing environment by having the programs return all error messages directly to the console. Two of the three programs also use the console for output of results, since the volume is small. The programs are not conversational and will probably run on a batch PDP-10. In such cases, the console output would be directed to the line printer.

The input/output logical numbers used in these programs are from the standard Device Table (1970 PDP-10 Timesharing Handbook, 5-129). The numbers presently assigned are:

READ/WRITE variable	Number	Device
KTTY	5	user's console
KDATA	21	disk file (ASC II)
LIB	22	disk file (binary)
LP	23	disk file (ASC II)
KBIF	24	disk file (binary)

If a change in device number is required, it can be made by altering the single Fortran DATA statement near the beginning of each main program in BLOCKA, BLOCKB and BLOCKC.

3. STRUCTURE OF PROGRAM PACKAGE

The colorimetric package consists of five files of source language coding, as follows:

File Name	Size*	Contents of File	
BLOCKA	16	CALIB	Fortran Main program
		ZERFIT	subroutine
BLOCKB	27	CONCAL	Fortran Main program
		PLOT	subroutine
		CURVE	subroutine
BLOCKC	13	REGRES	Fortran Main program
		LINFIT	subroutine
		PARFIT	subroutine
BLOCKD	16	FREFOR	subroutine
		LETTER	function
BLOCKE.MAC	6	UNPACK.MAC	Macro-10 routine
		PACK.MAC	Macro-10 routine

*in disk blocks of 128 words.

It will be noted that the main programs are in BLOCKA, BLOCKB and BLOCKC, respectively. BLOCKD and BLOCKE.MAC contain subroutines common to all three main programs. Thus, the complete source coding for the program CONCAL, for example, consists of BLOCKB plus BLOCKD and BLOCKE.MAC. A procedure for running each program from these five files is given in the next section.

4. LOADING AND COMPILING

The programs can be loaded and compiled from disk or DECtape as source, relocatable or absolute coding. However, the following method has been tested and is suggested as a good initial procedure. Once the programmer is familiar with the approach, he can modify the procedure to suit the system and the user's requirements.

In this method all programs are kept in relocatable form in five disk files. The source language files are stored on DECtape so that the disk files can be quickly restored in the event of loss.

The steps in this procedure are as follows:

(1) Load the source files (as described in Section 3) on disk.

(2) Compile in turn, using the Fortran compiler

BLOCKA to obtain BLOCKA.REL
BLOCKB to obtain BLOCKB.REL
BLOCKC to obtain BLOCKC.REL
BLOCKD to obtain BLOCKD.REL

(3) Use the Assembler to obtain BLOCKE.REL from BLOCKE.MAC

(4) To enable the user to execute each program with the simple commands:

```
.EX @ CALIB
.EX @ CONCAL
.EX @ REGRES
```

(See 1970 PDP-10 Reference Handbook, page 326) set up three one block disk files, each of which holds the names of the relocatable files, as follows:

File Name	Contents of File (ASCII)
CALIB	BLOCKA.REL, BLOCKD.REL, BLOCKE.REL
CONCAL	BLOCKB.REL, BLOCKD.REL, BLOCKE.REL
REGRES	BLOCKC.REL, BLOCKD.REL, BLOCKE.REL

(5) Transfer to DECtape the five source files BLOCKA, BLOCKB, BLOCKC, BLOCKD and BLOCKE.MAC. Then delete these files from the disk.

5. PROGRAM FILE STRUCTURE

The relationship between the programs and their input/output and intermediate files is shown in Figure 1. All programs share the same input file, called DATA, although a particular data set will be processed by only one of the three programs. The binary file LIB.DAT is a permanent disk file, written and updated by the program CALIB. This file will be read by the program CONCAL every time it is executed. In turn, CONCAL writes two temporary disk files, called PRINT.DAT and BIFIL. The first file contains output for the line printer; the second is a binary file which passes intermediate results to the program REGRES. All programs use the remote console for printing error messages and other information. In the case of CALIB and REGRES,

output is also to the console since the volume is too small to warrant a line printer file.

In order to release disk space, the file PRINT.DAT should be deleted as soon as the line printer has finished. The file may be several hundred disk blocks in length. However, it will likely be necessary to retain the file BIFIL (typically 15-30 blocks) for a day or more until the printer output is received. At that time, the results can be assessed and one can then proceed with additional data calculations using the program REGRES. When these have been completed, BIFIL should also be deleted.

Finally, it is worth noting that once the file LIB.DAT has been established with the program CALIB, it may not be necessary to update it for some time. Disk space can thus be saved by moving the two files BLOCKA.REL and CALIB to dead storage, say on DECtape. However, the file LIB.DAT must remain on the disk.

6. INTERFACING THE PROGRAM CONCAL TO EXTERNAL PROGRAMS

The user may require a file of calculated results from CONCAL so that the program can interface with other existing programs; e.g., a plotting program. Although two files (PRINT.DAT and BIFIL) are written by CONCAL, neither may be satisfactory for this purpose. The best approach is to write a file that contains

the required information in the desired format. This can be done as follows:

a) Select a file name (FIL) and a logical number (LUN). In BLOCKB, near the beginning of CONCAL, insert

```
CALL OFILE (LUN,'FIL')
```

(b) About halfway through CONCAL there are descriptive comment cards. Locate these and note that they are inside a DO-loop (DO 500 I = 1,LROW) with index 1. Check in the following list to see which variables are required, and then insert coding, similar to the following, adjacent to the comment cards. Variables not needed can be omitted from the WRITE statements. The f's represent FORMAT statement numbers which may be from 540 to 580.

```
      IF (I.NE.1) GOTO 550
      WRITE (LUN,f) NAME, DAY, KSEQ
      WRITE (LUN,f) LROW, TSTART, TDEL, A, B, C, D
550 WRITE (LUN,f) RAN(I),LTR,XS(I),YS(I),X(I),SAMPLE,Z,T,W(I)
```

The variables are:

NAME	Dimensioned as NAME(12). Run name in 12A5 format
DAY	Dimensioned as DAY(2). Date in 2A5 format
KSEQ	Integer.- regression access number
LROW	Integer - number of rows of data (as on printer sheets)
TSTART thru D	Six initial data floating point constants
RAN(I)	Random sample volume
LTR	Letter-name of curve in A1 format
XS(I)	Calibration transmission
YS(I)	Calibration standard concentration (in mg/l)
X(I)	Transmission reading
SAMPLE	Concentration corresponding to X(I) reading
Z	Residual volume (litres)
T	Time
W(I)	Concentration at T, divided by constant D.

APPENDIX A - ERROR MESSAGES COMMON TO ALL PROGRAMS

```
ILLEGAL CHARACTER
 27.3  15.4  RENAME  D  $  DELETE
-------------------------↑
```

An illegal character occurs in the data

```
PREVIOUS WORD OR ABBREVIATION IS UNRECOGNIZABLE
RENAME  A,  B  RENUM  F,  G
----------------------↑
```

The character group is not a valid dictionary word or number.

```
ILLEGAL - NEXT WORD HAS MORE THAN SIX LETTERS
RENAME  A   B   DELETER  F
----------------↑
```

There are no valid words which have more than six letters.

```
WHAT?
 27.3  49.6  S3  24.7  78.3
-------------↑
```

A mnemonic could be an SA-SZ type command, but is not correct.

```
BAD NUMBER?
 29.4  18.6  57.4.  29.3
-----------------↑
```

A number contains a wrong character.

```
ERROR IN EXPONENT
  29.4  13.6  1.234E-7+  12.4
----------------------↑
```

The exponent in an E-Format number is incorrect

```
REAL NUMBERS ARE RESTRICTED TO 15 CHARACTERS OR LESS
1.23456789012345678     27.4
-------------------↑
```

A decimal or E-Format number expression cannot contain more than 15 characters.

```
INTEGERS ARE RESTRICTED TO 10 CHARACTERS OR LESS
1234567890    19.5
------------↑
```

An integer expression must not exceed 10 characters.

APPENDIX B - ERROM MESSAGES FOR THE PROGRAM CALIB

NUMBER OUT OF CONTEXT	A number does not appear to be related to a command
WORD OR ABBREVIATION OUT OF CONTEXT	A mnemonic occurs in the data and is not a valid command for CALIB
STORE COMMAND - NOT FOLLOWED BY LETTER-NAME	Letter-name is missing from a STORE command
STORE COMMAND - TOO FEW NUMBER PAIRS	At least three number pairs are required in a STORE command
STORE COMMAND - A NUMBER WAS EXPECTED	Either there is no number in the STORE command, or an unpaired number occurs
DELETE COMMAND - NOT FOLLOWED BY LETTER-NAME	
RENAME COMMAND - NOT FOLLOWED BY LETTER-NAME	
RENAME COMMAND - A LETTER-NAME WAS EXPECTED	An unpaired letter-name occurs
INSERT COMMAND - NOT FOLLOWED BY LETTER-NAME	
INSERT COMMAND - C1 COEFFICIENT MISSING	
INSERT COMMAND - C2 COEFFICIENT MISSING	
STORE COMMAND - TRANSMISSION OVER 100	A transmission reading in a STORE command is greater than 100%
STORE COMMAND - TRANSMISSION .LE. TO ZERO	A transmission reading is less than or equal (.LE.) to zero

APPENDIX C - ERROR MESSAGES FOR THE PROGRAM CONCAL

ERROR IN INITIAL CONSTANTS	The six constants required after the title line do not appear to be correct. Message is followed by the ITEM number.
DATA MUST START WITH 'SA-SZ' COMMAND	The first data set of a batch must start with an S-type command.
WORD OR ABBREVIATION OUT OF CONTEXT	A mnemonic is either not part of CONCAL's repetoire, or is out of context
% TRANSMISSION OVER 100	A transmission reading is over 100 percent.
% TRANSMISSION .LE. TO ZERO	A transmission reading is less than or equal to zero.
CURVE-x NOT PRECEDED BY Sx-COMMAND	The letter-name "x" occurs without the corresponding "Sx" command having preceded it.
A NUMBER WAS EXPECTED	A command that should be followed by one or more numbers has no numerical argument(s).
CURVE-x IS NOT IN LIBRARY	The letter-name of a curve that is not in the library occurs in the data.
UNRECOGNIZABLE ARGUMENT IN PLOT COMMAND	The PLOT or PLOTS command is followed by an invalid mnemonic.
DATA INCOMPLETE, OR 'END' MISSING	An end-of-file was encountered prematurely in the disk file DATA.

APPENDIX D - ERROR MESSAGES FOR THE PROGRAM REGRES

LETTER x NOT A VALID CODE	A letter occurs which is not one of the acceptable abbreviations for REGRES operations.
WORD OR ABBREVIATION OUT OF CONTEXT	A mnemonic is not part of the REGRES instruction group.
NUMBER OUT OF CONTEXT	A number does not appear to be related to a command.
NUMBER EXPECTED AFTER 'FIND'	Regression Access Number missing from FIND command
SECOND POINT NUMBER MISSING	The second number required to define the range for a regression is missing
AT LEAST THREE POINTS REQUIRED	All regression equations require a minimum of three points.
EXPONENT MISSING IN 'EXP'	The value of the exponent has been omitted after the EXP instruction
EXPONENT .EQ. ZERO IN 'EXP'	An exponent of zero has been specified.

APPENDIX E - CODE NUMBERS

Number	Mnemonic
1	A
2	B
3	C
4	D
5	E
6	F
7	G
8	H
9	I
10	J
11	K
12	L
13	M
14	N
15	O
16	P
17	Q
18	R
19	S
20	T
21	U
22	V
23	W
24	X
25	Y
26	Z
27	SA
28	SB
29	SC
30	SD
31	SE
32	SF
33	SG
34	SH
35	SI

Number	Mnemonic
36	SJ
37	SK
38	SL
39	SM
40	SN
41	SO
42	SP
43	SQ
44	SR
45	SS
46	ST
47	SU
48	SV
49	SW
50	SX
51	SY
52	SZ
53	CUBE
54	DELETE or DEL
55	END
56	FOUR*
57	FIND
58	NEWLIB
59	LIST
60	LIN
61	LN*
62	LOG
63	NEXT
64	PAR
65	PLOT or PLOTS
66	RANDOM or RAN
67	RENAME or REN
68	STORE
69	SQR
70	INSERT
71	EXP
81, 82	number expression

* Reserved for future use

APPENDIX F - MATHEMATICAL METHOD FOR CALIB

The colorimeter method uses Beer's Law which states:

$$y = -k(\log T)$$

Where: y = concentration
k = positive constant
T = fraction of light transmitted
log = logarithm to base 10

Because of interactions in the solution, or apparatus effects, deviations from Beer's Law are frequently observed. These are reflected in non-linearity of the concentration-log T calibration curves. The calibration curves, over reasonable ranges, can be approximated to an accuracy of 1% (a normal instrumental accuracy) by including a second order term in the Beer's Law type equations.

$$y = -A(\log T) + B(\log T)^2$$

Since $T = \%T / 100$, then $\log T = \log(\%T) - 2$

where %T is the percent transmission?

Therefore Concentration $= -A(\log(\%T) - 2) + B(\log(\%T) - 2)^2$

Defining $C_1 = -A$ and $C_2 = B$, the above equation becomes

$$y = C_1(\log(\%T) - 2) + C_2(\log(\%T) - 2)^2$$

For a given calibration curve, we have available N experimentally determined pairs of y and (%T) values. A least-squares solution is used to obtain the values of C_1 and C_2. The predicted concentration value (y_p) for a given transmission (%T) is then obtained from

$$y_p = C_1(\log\%T - 2) + C_2(\log \%T - 2)^2$$

The subroutine ZERFIT in the program performs these calculations whenever the STORE command is used. The curve is retained in the library by storing the values of C_1 and C_2 in the library disk binary file LIB.DAT.

The polar coordinate rotation of the calibration curve to correct for baseline drift in the colorimeter is discussed in Appendix G.

APPENDIX G - MATHEMATICAL METHODS FOR CONCAL

a) Rotation of Calibration Curves

For various reasons, a calibration point from a standard sample might not fall exactly on the original calibration curve. To correct this problem it is assumed that the shape of the calibration curve remains unchanged as the curve is rotated about the point - zero concentration, 100% transmission. Mathematically this is equivalent to rotating the axes about the origin.

From the previous appendix the curve has the equation

$$y = C_1 x + C_2 x^2 \qquad \ldots 1$$

where $x = \log_{10}(\%\ \text{transmission}) - 2$

y = concentration

and C_1 and C_2 are constants.

If a new calibrating point (x^*, y^*) is measured which does not lie exactly on the curve (Equation 1), the axes are rotated until the new point and the curve coincide. The radius vector is defined by the equation

$$r^2 = x^{*2} + y^{*2} \qquad \ldots 2$$

This is also the radius of the corresponding point (x_e, y_e) relative to the original axes. That is

$$r^2 = x_e^2 + y_e^2 \qquad \ldots 3$$

In order to find the angle of rotation, θ, the coordinates of this point (x_e, y_e) are required. Since (x_e, y_e) lies on the calibration curve (Equation 1), substitute Equation 1 in 3 and obtain

$$r^2 = x_e^2 + (C_1 x_e + C_2 x_e^2)^2 \quad \ldots 4$$

A function is defined

$$F(x_e) = x_e^2(1 + C_1^2 + 2C_1 C_2 x_e + C_2^2 x_e^2) - r^2 \quad \ldots 5$$

where r^2 is evaluated from Equation 2, and its derivative

$$D(x_e) = 2x_e(1 + C_1^2 + 3C_1 C_2 x_e + 2C_2^2 x_e^2) \quad \ldots 6$$

A Newton-Raphson method is used to evaluate x_e, from which y_e may be calculated from Equation 3.

The angle of rotation θ is defined by the equations

$$x_e = x^* \cos\theta - y^* \sin\theta \quad \ldots 7a$$

$$y_e = x^* \sin\theta + y^* \cos\theta \quad \ldots 7b$$

If these equations are solved for $\cos\theta$ and $\sin\theta$ and we define $A = \cos\theta$ and $B = \sin\theta$

$$A = (x_e x^* + y_e y^*)/r^2 \quad \ldots 8a$$

$$B = (y_e x^* - x_e y^*)/r^2 \quad \ldots 8b$$

These equations now provide a means of calculating the y' value from the rotated curve corresponding to a measured x'. These relations are similar to Equations 7a and 7b, that is

$$x_e = Ax' - By' \quad \ldots 9a$$

$$y_e = Bx' + Ay' \quad \ldots 9b$$

Also $y_e = C_1 x_e + C_2 x_e^2$, from Equation 1.

Substituting equations 9a and 9b in 1 gives

$$Bx' + Ay' = C_1(Ax' - By') + C_2(Ax' - By')^2 \quad \ldots 10$$

The solution of this equation for y', for entered values of x', makes use of another Newton-Raphson method where

$$F(y') = C_1(Ax' - By') + C_2(Ax' - By')^2 - (Bx' + Ay')$$

and $$D(y') = - C_1 B - 2C_2 By'(Ax' - By') - A$$

These are the algorithms used in the subroutine CURVE to make the necessary corrections when there is a new calibration point which does not lie on the curve defined by the program CALIB.

b) The Equations for Calculating the Weight of Metal in Solution

The equation developed to treat the colorimetric data assumes that a solution is analyzed for some element at regular time intervals. Samples of volume V_s are withdrawn regularly but are replaced with equal volumes of blank solution. The original volume of the solution, V_o, is reduced by an evaporation loss, V_e, which is determined on a per cycle basis and by the accumulated volume of m samples of volume, V_r, withdrawn at random intervals for independent analyses.

When the kth regular sample with a measured metal concentration of x_k is taken, the accumulated weight of metal in solution, Z, is given by the equation:

$$Z = x_k\left[V_o - (k-1)V_e - \sum_1^m V_r\right] + V_s\sum_1^k x_k + \sum_1^m V_r x_r \qquad \ldots 11$$

where x_r is the measured metal concentration when the random sample is taken. The accumulated weight of metal in solution per unit area (assuming a heterogeneous reaction with a surface area, A) is

$$W = Z/A$$

On the line printer output of the program CONCAL, the column headed MET lists the computed values of Z while TOT-MET is the column of W values.

In the case where neither regular sample volumes, V_s, nor the evaporation loss, V_e, are replaced by blank solution, equation 11 is modified as follows:

$$Z = x_k\left[V_o - (k-1)V_e - \sum_1^m V_r - kV_s\right] + V_s\sum_1^k x_k + \sum_1^m V_r x_r \qquad .. 12$$

To alter the program to operate under these conditions requires changing only a single card. It is located in a DO-loop (DO 500 I = 1, LROW) about halfway through the program CONCAL. The sixth card beyond the DO statement is the card

```
Z = A - (I - 1)* B - RANSUM
```

This should be changed to

```
Z = A - (I - 1)* B - RANSUM - I * C
```

```
***  DEMONSTRATION DATA SET FOR PROGRAM CALIB  *** ?
    NEWLIB
    4-X RANGE ?
    STORE U 91.4 50 91.4 50 91.4 50
    83.0 100 83.0 100 83.1 100
    78.8 125 78.8 125 78.8 125
    75.0 150 75.0 150 75.0 150
    66.7 200 66.7 200 66.5 200
    51.5 300 51.5 300 51.4 300
    36.5 400 36.5 400 36.3 400
    21.8 500 21.7 500 21.5 500
    82.6 100 82.6 100 82.4 100
    2X - RANGE ?
    STORE V 91.5 100 91.5 100 91.5 100
    83.5 200 83.3 200 83.3 200 83.3 200
    75.5 300 75.5 300 75.5 300 75.4 300
    68.2 400 68.1 400 68.0 400 68.0 400
    61.2 500 61.2 500 61.1 500 60.9 500
    54.5 600 54.5 600 54.3 600 54.3 600
    47.5 700 47.6 700 47.5 700 47.5 700
    41.2 800 41.0 800 40.8 800 41.0 800
    30.0 1000 30.2 1000 29.5 1000 30.0 1000
    1X - RANGE ?
    STORE W 91.8 200 91.7 200 91.8 200
    84.5 400 84.3 400 84.5 400
    77.7 600 77.5 600 77.7 600
    71.5 800 71.4 800 71.5 800
    66.0 1000 65.8 1000 66.0 1000
    53.5 1500 53.4 1500 53.6 1500
    43.5 2000 43.5 2000 43.6 2000
    36.7 2400 36.4 2400 36.5 2400
    20.0 4000 19.8 4000 19.8 4000
    19.5 4000 19.4 4000 19.5 4000
    LIST
    INSERT F .5512764 -.00014, B 2664.2 -1532.95,
    M 1290.73 -866.453, Z 510.431 -400.781
    LIST
    RENAME L Z, REN U C, V B, W A
    LIST
    DELETE Z, DEL L,F,M
    LIST
```

Figure 1. Demonstration Data Set for CALIB

```
*** DEMONSTRATION DATA SET FOR THE PROGRAM CONCAL *** ?
    TEST NO. 5-11-67  CU2S
    0.0 .5, 2.7 0.000235 0.0017 5.11
    SC 78.9 100 100 98.2 96.3 94.0 90.8 C 79.2 85.8
    SB 52.0 500 87.0 RANDOM 0.005 77.6 B 51.8 70.1
    B 51.5 63.6 58.2 SA 58.5 1000 77.7 75.6 73.7
    RAN 0.01 A 58.3 72.0 70.4 A 58.2 69.0
    A 58.0 67.5 66.2 END
    EN-77 IMP. 80 DEG.
    0  1.0 2.7 0.0008690 0.0034 5.11
    SD 90.6 20 100 100 99.9 99.9 99.8 99.8 99.8 99.7
    99.7 D 90.9 99.6 99.5 99.5 99.4 99.3 D 90.8 99.1
    99 98.9 98.9 98.9 98.9 98.8 98.8 98.8 D 90.7 98.6
    98.6 98.3 98 98 98 98 98 97.9 97.8 97.7
    97.6 97.6 97.5 97.4 97.4 97.3 97.2 97.1 97 96.9
    96.8 96.7 96.6 96.4 96.2 96.2 96.2 96.1 96 95.8
    95.8 95.7 95.5 95.4 95.3 95.1 94.8 D 90.8 94.8
    D 90.9 94.8 D 90.8 94.6 94.6 94.6 94.6 94.6
    94.5 94.4 PLOT L,S,C  LOG END
```

Figure 2. Demonstration Data Set for CONCAL

```
***  DEMONSTRATION DATA SET FOR THE PROGRAM REGRES ***   ?
  FIND  2   LIN  2  13  SQR  LOG 8  27  LIN
  FIND  1   PAR  EXP  .5  7 19      NEXT  PAR
```

Figure 3. Demonstration Data Set for REGRES

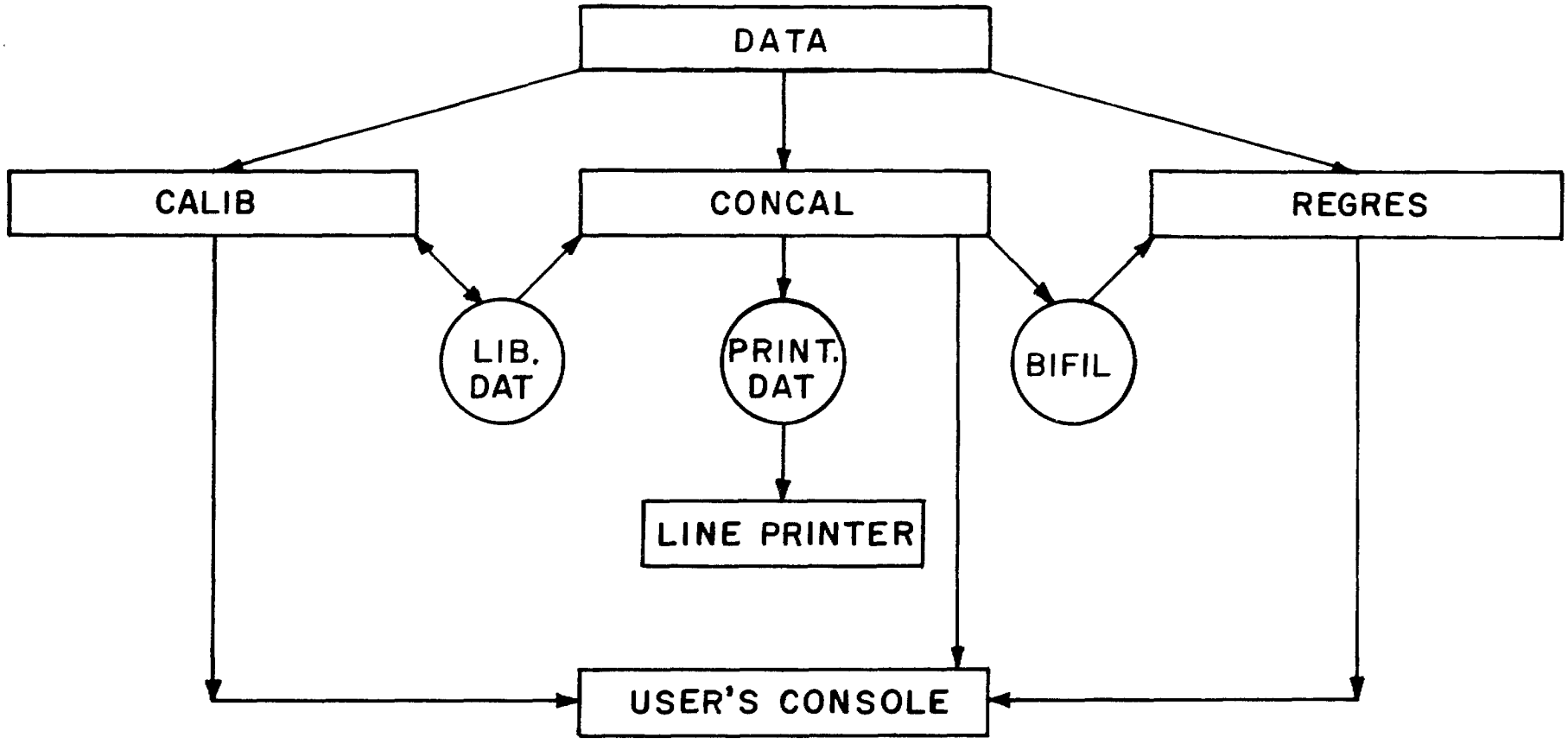


FIG.4–BLOCK DIAGRAM SHOWING THE RELATIONSHIP BETWEEN DISK FILES AND PROGRAMS

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