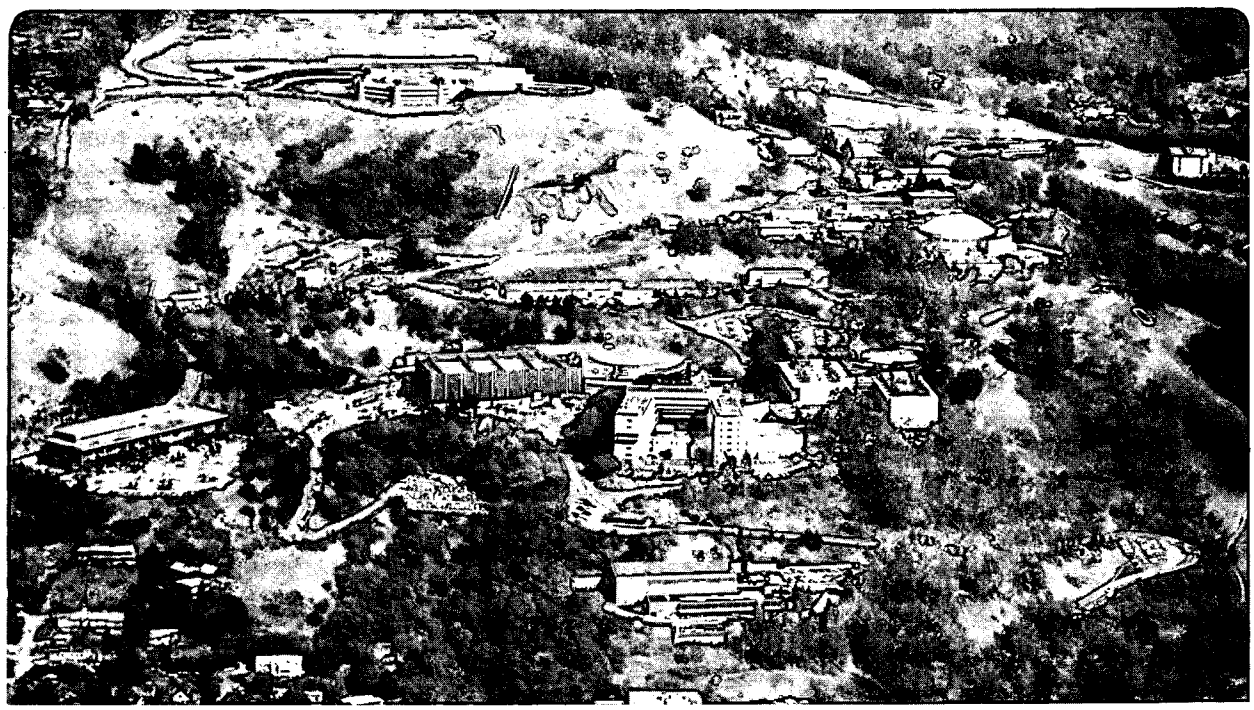
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Engineering & Technical Services Division

XRF CONTROL AND DATA ANALYSIS PROGRAM

Joseph M. Jaklevic

May 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

XRF CONTROL AND DATA ANALYSIS PROGRAM

Joseph M. Jaklevic

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

May 1980

This work was supported by the U. S. Department of Energy under Contract W-7405-ENG-48

XRF CONTROL AND DATA ANALYSIS PROGRAM

TABLE OF CONTENTS

INTRODUCTION

The assembly language program operating in the TI 960 computer was designed to facilitate the automatic elemental analysis of thin aerosol deposits on slide mounted membrane filters. As such, it is adaptable to the analysis of any specimens which can be prepared in such a way as to satisfy the 'thin' and 'uniform' criterion. The automatic sample sequencing functions and the spectral analysis program can be referenced either independently in what will be termed the 'semiautomatic' mode or as a part of a completely automated sequence in what is termed the 'automatic' mode. In addition, the sample manipulation functions and certain data acquisition procedures can be operated via front panel switches in what is called the 'manual' mode. The 'manual' or automatic modes are selected via a pushbutton switch or the x-ray tube controller.

The entire system has been designed to be as free of operator induced problems as possible. Sample manipulation Options are interlocked so that a potentially destruction function will not be allowed. The entire main frame has been interlocked to the x-ray controller to prevent the possible emission of x-rays when the doors are open. In order to operate in either the manual or automatic modes all doors must be closed and the interlock clear button on the x-ray controller must have been activated.

II. DESCRIPTION OF PROGRAMS

A) Automatic Control Program

The control program sequences the samples through an analysis cycle automatically. This sequence includes inserting the sample, selecting a secondary fluorescer, and turning the x-ray tube on and off over the interval specified by the electronic timer. This cycle is repreated for each sample specified until it is terminated either by internal information in the program or by the mechanical detection of the end of a sample tray.

A number of operations which are referenced in the automatic sequencing program can also be initiated by the keyboard when the computer is in the semiautomatic mode.

Flow diagrams for the program are given in the text. Appendix A-1 gives an explanation of the information which is entered in the heading, and A-2 is a listing of the keyboard options available in the semiautomatic mode.

B) Data Analysis Program

The data analysis program is included either as a subroutine of the automatic sample analysis program or as a separate program executed by a pushbutton option in the semiautomatic mode.

The program is a straightforward spectrum stripping routine in which the contributions due to scattered background and individual fluorescence peaks are sequentially subtracted from the spectrum to be analyzed. No complex fitting or peak shape algorithms are employed. The background spectra and fluorescence spectrum for individual elements are obtained from experimentally measured spectra of standard samples. This method obviates the necessity for complex calculations to generate a typical spectral response. It has the disadvantage that the individual samples used to generate the standard spectra must replicate the final sample form as nearly as possible. This is no problem if one is analyzing a class

of samples such as air filters in which the substrates are relatively invariant from one to the next and where there are no absorption effects in the individual elemental x-ray peaks.

In order for the program to function properly the operator must enter into the memory certain information regarding the location of regions of interest in the spectra and associated identifying codes and calibration factors. This is the key portion of the operator interaction with the program and requires a thorough understanding of the program details.

The operation of the program in stripping a peak is illustrated in Fig. 1. In Step #1 the unknown spectrum is compared to a background spectrum from a blank substrate which is stored in the memory. The comparison is performed over the shaded region which had been previously specified by the operator when the background spectrum was initially stored. The comparison results in a ratio which is used to normalize the stored data to the unknown. They are then subtracted point for point over the entire spectrum. The resultant spectrum is shown in Step #2. Subsequent steps sequentially remove all of the specified elements from the spectrum. As each element is subtracted, a calibration factor is applied to the concentration to convert it to ng/cm^2.

In order to store all the necessary spectral data in the computer memory it is necessary to compress the spectra of the fluorescence x-rays using the limits on the important regions entered by the operator. The background spectra and compressed x-ray fluorescence data are organized into the computer memory according to Fig. 2. The data storage area consists of nine buffers of 1024 channels each. The first five 1024 channel buffers are reserved for the compressed XRF spectra of the individual elements together with their associated numerical calibration data. Experience has shown this storage area adequate for 40 to 50 elements. Buffers 6, 7 and 8 are reserved for the complete 1024 channel background spectra obtained on a clean substrate using secondary targets 1, 2 and 3 respectively.

Buffer 9 is the main data buffer. It has a capacity of 10^9 counts per channel as compared to only 64 K in the other buffers. All spectral analyses operations are performed on the data in Buffer 9. Buffers 1 through 8 are specially protected against inadvertant destruction by entering or acquiring data whereas direct access is always permitted to Buffer 9.

Figures 3, 4 and 5 are flow diagrams of the data analysis program. Figure 3 is the basic program with the details of the subprogram indicated in Figs. 4 and 5. In Fig. 4 we show the spectrum shifting routine which preceeds the background substraction. This compensates for long-term drifts in the amplifier baseline by comparing a peak in the most recent spectrum with the one in the original background.

Figure 5 gives the flow chart for the actual peak stripping routine. The details of the individual calculations are given in Appendix A-3. It is important that these program steps and the associated calculations be understood in detail before the program is set up to run. The rational for selecting various limit in the standard spectra is dependent on the way they are used in the calculation. The best way to acquire this understanding is to proceed through a complete calibration procedure as described in the next section. Hopefully one will then grasp the significance of the various regions used in the calculation.

III. OPERATION OF PROGRAM

In the following, the step-by-step procedure for entering the necessary spectral data and calibration information is detailed. It is assumed that the program has been loaded and is operating normally.

A) Generate Calibration Tape

Using the pushbutton options in either the 'manual' or 'semiautomatic' mode generate a magnetic tape with the following spectral information:

i) Individual spectra for each element of interest. These should be acquired using samples whose form is similar to the samples to be analyzed; the easiest approach is to use thin samples of course. Since the sensitivity of the instrument is so high, it is necessary to check to insure the ADC deadtimes are less than 20% when the spectra are being acquired.

ii) Background spectra of specimen blanks acquired using each fluorescer of interest.

It is essential that the data in any given channel not exceed 64 K in magnitude. In order to achieve this with adequate statistical accuracy in the spectrum it is recommended that the data be acquired in Buffer #4 with a large number of counts. Pushbutton option 30 XMIT can be used to reduce spectrum to appropriate limits.

B) Load Background Information

In this step the background spectra for the specimen blanks are loaded into Buffers 6, 7 and 8 depending upon the secondary fluorescer used for the measurement. It is these spectra which will be suitably normalized and subtracted from the unknown spectrum in the stripping procedure.

In order to enter data into any buffer other than number nine it is necessary that all switches in the register are UP. The sequences for reading the data into the buffers is as follows:

1 ALT 6 XMIT	(sets display to Buffer 6)
2 ALT m	(reads spectrum m into displayed buffer)
1 ALT 7 XMIT	(display Buffer 7)
2 ALT n	(reads spectrum n)
1 ALT 8 XMIT	(etc.)
2 ALT p	

The ancillary calibration data for each background can now be entered. It is important that the proper background is displayed and that all switches are UP before the calibration data can be entered or modified. The background program is called by 10 XMIT, the operator then answers the following questions:

OPTION	QUESTIONS	TELETYPE RESPONSE
	Background	Fluorescer #
0	Primary Peak	Hit Return
1	Region 2	Set marks on prominent peak used for calculating zero shift of spectrum. Return.
2	Region 3	Return.
3	Fit Region	Set marks on region you wish used to calculate area with which comparison to unknown will be made. Return.
4	Mark Peak	Return.
5	F Number	Return.
6	Group Option	9 Return.

The Option number in the left hand column is included since it is possible to reference any particular line by executing a 10 ALT n XMIT where n is the option number. This is useful when inspecting the data after it has been entered. The entry sequence must be repeated for each fluorescer. Make sure the proper background is displayed before proceeding, however. It should be pointed out that the only questions over which the operator exerts any influence are Options 2 and 3. The large number of useless options arise from the fact that this same subroutine is used to enter data for the individual elements where all the options have meaning.

C) Load Elemental X-ray Response Information

In this step the relevant information concerning the regions of interest of the individual element is entered along with other data concerning calibration factors. The procedure is to read the spectrum of interest from the calibration tape into the data Buffer (#9). Make sure the maximum counts have been reduced below 64 K by using the 30 XMIT option and that all switches are UP to allow the data to be written into the protected buffers. The program for entering informations is then called by 11 XMIT. The questions and responses are as follows:

OPTION	QUESTIONS	TELETYPE RESPONSE
	Element	Number or symbol of element
0	Primary Peak	Principal peak in spectrum. The intensity of the element is based on this area.*
1	Region 2	A second portion of the standard spectrum to be removed equally as the primary peak.*

* Examples of these regions are shown in Fig. 6 for a typical case of Kα, Kβ x-rays.

OPTION	QUESTIONS	TELETYPE RESPONSE
2	Region 3	A third portion to be taken out.*
3	Fit Region	Area of peak which is used for comparison with unknown.*
4	Mark Peak, Hit Car. Ref.	Indicate peak channel. This is used to identify this element.
5	F =	Enter relative efficiency factor. Type comma to retain existing nymber, otherwise type new number followed by RETURN.
6	Group (0 - 9)	Enter analysis group, see Fig. 7.

D) Inspecting Data

The data which has been previously entered can be inspected at any time by calling the programs 10 or 11 or using the 10, n or 11, n specific options. To inspect data and leave unchanged, type a comma instead of a RETURN. To change a portion of the data, type RETURN. This will replace the data in the stage buffers with the appropriate data in the main buffer provided that all the switches are in the UP position.

E) Enter Normalizing Factor

The normalizing factor is a constant entered for each fluorescer and which take into account the variation in running times, tube current, etc. which change the total yields for a given secondary fluorescer but do not affect the relative yields between the element. To initialize these correctly proceed as follows:

---

* Examples of these regions are shown in Fig. 6 for a typical case of Kα, Kβ x-rays.

1) Enter a factor of 1.000 for each element.

F1 15 ALT 1 ALT 1 ALT 1 XMIT

F2 15 ALT 2 ALT 1 ALT 1 XMIT

15 ALT 3 ALT 1 ALT 1 XMIT

2) Analyze one or more calibration standards for each fluorescer.

3) Calculate ratio of standard concentration to that calculated by the program. Express this ratio as a fraction m/n.

4) Enter for each fluorescer: 15 ALT 1 ALT m ALT n XMIT, etc.

5) If the analysis time is increased (decreased) by a certain factor, decrease (increase) the normalizer by the same amount. This is done by replacing with a new m/n.

APPENDIX A-1

ENTERING DATA FOR AUTOMATIC OPERATION

When the "GO" button is pushed the computer is prepared to automatically cycle the samples provided that appropriate information has been applied. After checking to insure that the x-ray tube controller is in the "AUTO" position and that the appropriate time interval has been set in the timer, a RETURN pressed on the teletype will cause the first line of the heading to be typed. The teletype then returns and awaits an answer for each subject in the heading. Numerical data are entered by pressing the appropriate entries followed by a comma at the end of the complete number. Answers requiring YES (NO) answers are satisfied by 1 (0). The end of a line is signified by a carriage return. The COMMENT can contain any set of alpha numeric characters. The following is an example of a typical heading.

```
*1*  STATION    TRAY  SIZE    1ST SLIDE    2ND SLIDE    LAST SLIDE    NO OF SLIDES
     124,       11011,1,      57375,       57702,       57736,        36,,
*2*  COLLECTION?  DATA  START TIME  HRS?MIN   PERIOD   HRS?MIN   YEAR
                  241,              12, 00,             6,  00,,
*3*  ANALYSIS?  DATE  START TIME  HRS?MIN
                 357,             1,  00,,
*4*  HELIUM?   F1?   F2?   F3?
     1,         1,    1,    1,,
*5*  COMMENT   (UP TO 240 CHARACTERS.  TERMINATE WITH EOT)

CALIBRATION CHANGE?     1,,
*6*  CALIBRATION   DATE       TIME,   TIME MULT
                   356,
*7*  F1  KV   MA            F2  KV    MA            F3  KV   MA
         55,  5,   1000,        60,   5,   1000,        80,  5,    1000,

SECOND BLOCK?       0,
INFORMATION BLOCK COMPLETE.  IF SATISFIED, TYPE COMMA.  OTHERWISE TYPE G OR P ,
UNABLE TO READ BAR CODE.  ASSIGNED VALUE...  57375
```

APPENDIX A-2

PUSHBUTTON OPTIONS

In the following table the notation of (,) = ALT is employed. The XMIT instruction required to execute the option is implied at the end of that instruction. Instructions can be cleared without execution by using CTRL-BEL on the teletype.

DATA ACCUMMULATION

7	ADC OFF
8	ERASE BUFFER, START ADC
9	START ADC
39	COUNT FOR ONE PERIOD (for Las Vegas System, count for 1 clock period)

DATA HANDLING/DISPLAY

1,n	BUFFER n TO DISPLAY
4	DATA BUFFER (BUFFER #9) TO DISPLAY
22	DISPLAY BASELINE NORMAL
21	DISPLAY CENTERED (USE FOR OBSERVING NEGATIVE NUMBERS)

DATA HANDLING/TELETYPE

25	SUPPRESS ALL TYPEOUT (types slide number only)
26	ENABLE TYPEOUT
29	TYPE DATA BETWEEN MARKERS
31	TYPE CENTROID OF DATA BETWEEN MARKERS (result expressed as 1/64 ths of channels referred to left marker)
32	TYPE INTEGRAL BETWEEN MARKERS

DATA HANDLING/TAPE

2	READ NEXT SPECTRUM FROM TAPE
2,n	READ SPECTRUM #n FROM TAPE
20	WRITE EOF
12	REWIND
19,n	WRITE BUFFER ON TAPE, SPECTRUM #n
16	WRITE CALIBRATION DATA ON TAPE (BUFFERS 1-8)
17	READ CALIBRATION DATA FROM TAPE (BUFFERS 1-8)

SYSTEM CONTROL

40	WITHDRAW SAMPLE
41	LOWER SAMPLE CARTRIDGE
42	INSERT SAMPLE
45	SELECT FLUORESCER #1
46	SELECT FLUORESCER #2
47	SELECT FLUORESCER #3
48	TURN ON X-RAYS
49	TURN OFF X-RAYS
50	RAISE SAMPLE CARTRIDGE
51	RETURN TO LOAD POSITION
52	He PURSE (on helium trickle after purge time out)
53	He OFF

DATA HANDLING/DIGITAL

14,m	DO MANUAL DATA ANALYSIS, FLUORESCER #m
27,m	SHIFT SPECTRUM ACCORDING TO BACKGROUND #m
30	SUBTRACT BACKGROUND #m
31	DIVIDE SPECTRUM ÷ 2
15,p,m,n	SET NORMALIZING MULTIPLIER TO m/p FOR FLUORESCER p

MARKER MANIPULATION

3	SET MARKER TO DISPLAY ORIGIN
5,n	MOVE MARKER LEFT n CHANNELS
5	MOVE MARKER LEFT ONE CHANNEL
6,n	MOVE MARKER RIGHT n CHANNELS
6	MOVE MARKER RIGHT ONE CHANNEL
24	SWITCH MARKERS

CALIBRATION INFORMATION ENTRY

10	ENTER BACKGROUND INFORMATION
10,n	ENTER BACKGROUND INFORMATION, OPTION n
11	ENTER CALIBRATION INFORMATION FOR ELEMENTS
11,n	ENTER CALIBRATION INFORMATION FOR ELEMENTS, OPTION n

INTERRUPTS

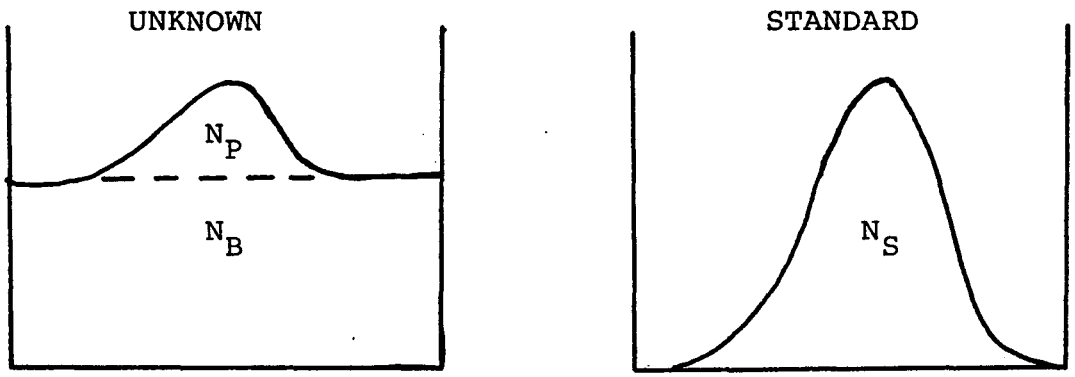
CTRL-BELL	ON TELETYPE RESTARTS PROGRAM
STOP	ON CONTROL PANEL RESTARTS PROGRAM IF IN GO CONDITION
38	STOPS SYSTEM AFTER THIS SAMPLE

LOADING OF PROGRAM

1	HALT
2	RESET
3	01C0 → STATUS REGISTER
4	HANG TAPE (REMOTE)
5	RUN
6	START
7	HALT
8	RESET
9	096C → PROGRAM COUNTER
10	RUN
11	START

APPENDIX A-3

SUMMARY OF PROGRAM CALCULATIONS



N_P is raw spectrum of unknown

$( )^f \Rightarrow$ fit region

$( )^p \Rightarrow$ primary region

---

1) $$\text{AREA} = \frac{N_P^f}{N_S^f} \; N_S^p \quad *$$

2) $$\Delta\text{AREA} = \text{AREA} \sqrt{\left(\frac{\Delta N_P^f}{N_P^f}\right)^2 + \left(\frac{\Delta N_S^f}{N_S^f}\right)^2 + \left(\frac{\Delta N_S^p}{N_S^p}\right)^2}$$

$$\left(\frac{\Delta N_P^f}{N_P^f}\right)^2 = \frac{2\,N_R^f - N_P^f}{(N_P^f)^2} \quad **$$

$$\left(\frac{\Delta N_S^f}{N_S^f}\right)^2 = \frac{1}{N_S^f}$$

$$\left(\frac{\Delta N_S^p}{N_S^p}\right)^2 = \frac{1}{N_S^p}$$

* If $N_P \leq 0$

$$\text{AREA} \leq 3\sqrt{N_S{}^f}$$

If $\left(\frac{\Delta N_P{}^f}{N_P{}^f}\right)^2 \geq 1$

$$\Delta\text{AREA} \leq 3\sqrt{N_S{}^f}$$

$$\text{CONCENTRATION } (\text{ngm/cm}^2) = \frac{(\text{NORM. FACTOR})\ (\text{AREA})}{(\text{F FACTOR})}$$

$$\Delta\text{CONCENTRATION } (\text{ngm/cm}^2) = \frac{(\text{NORM. FACTOR})\ (\Delta\text{AREA})}{(\text{F FACTOR})}$$

** $\left(\Delta N_P{}^f\right)^2 = N_R + N_B = N_R + N_R - N_P = 2\,N_R - N_P$

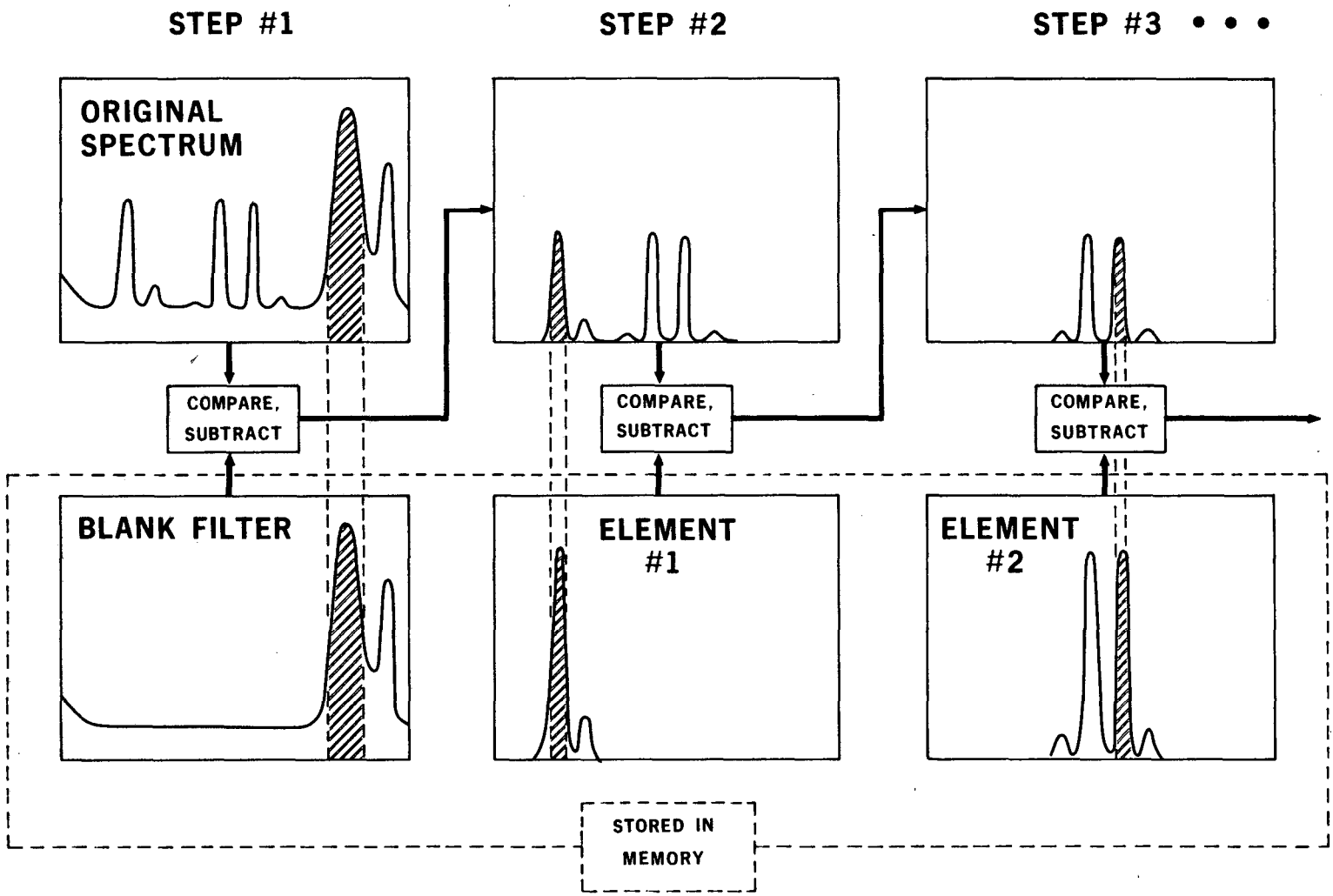


FIGURE 1.

SCHEMATIC ILLUSTRATION OF PEAK STRIPPING PROCEDURE.

LBID-198

ORGANIZATION OF MEMORY

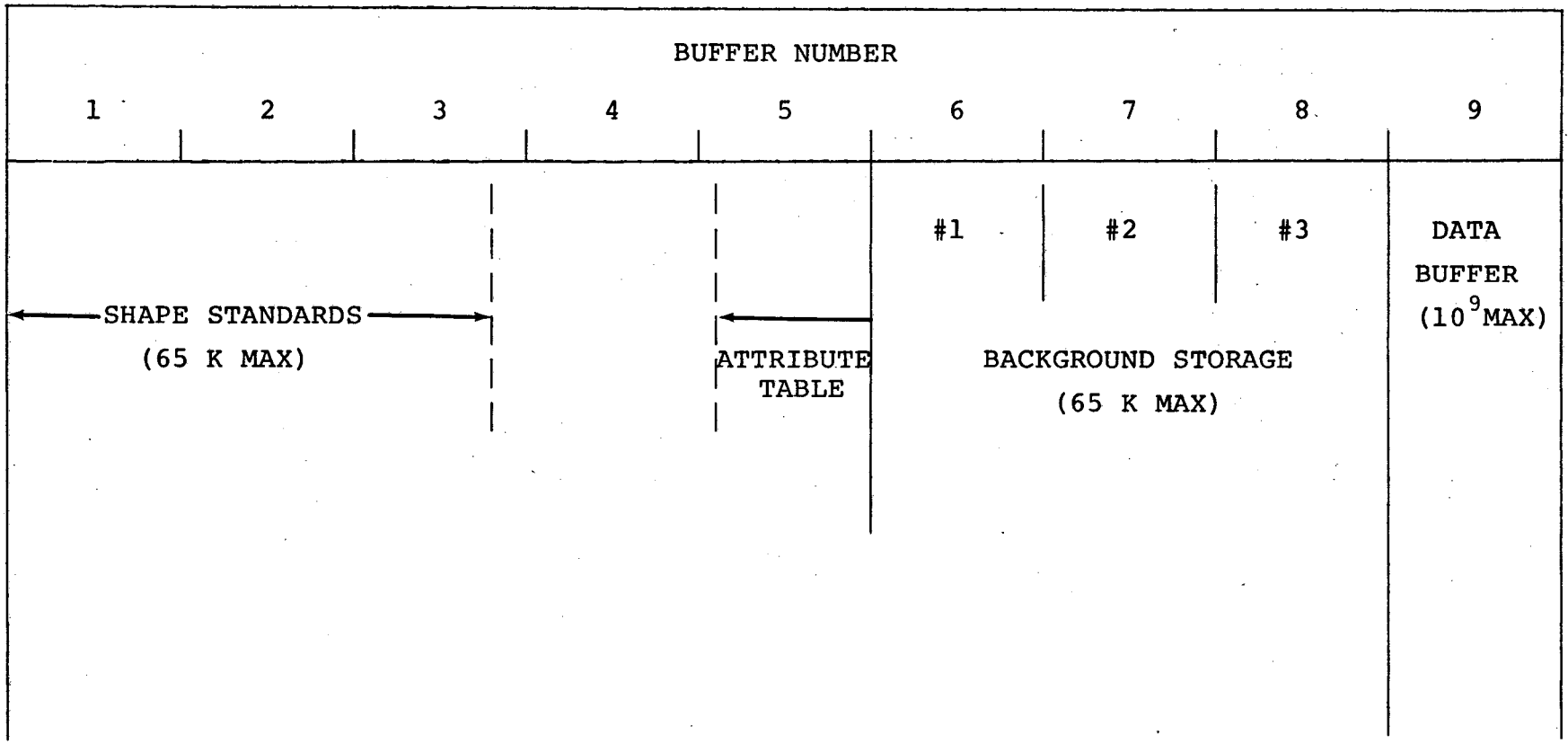


FIGURE 2.

MEMORY MAP OF THE NINE STORAGE BUFFERS.

AUTOMATIC SEQUENCING PROGRAM

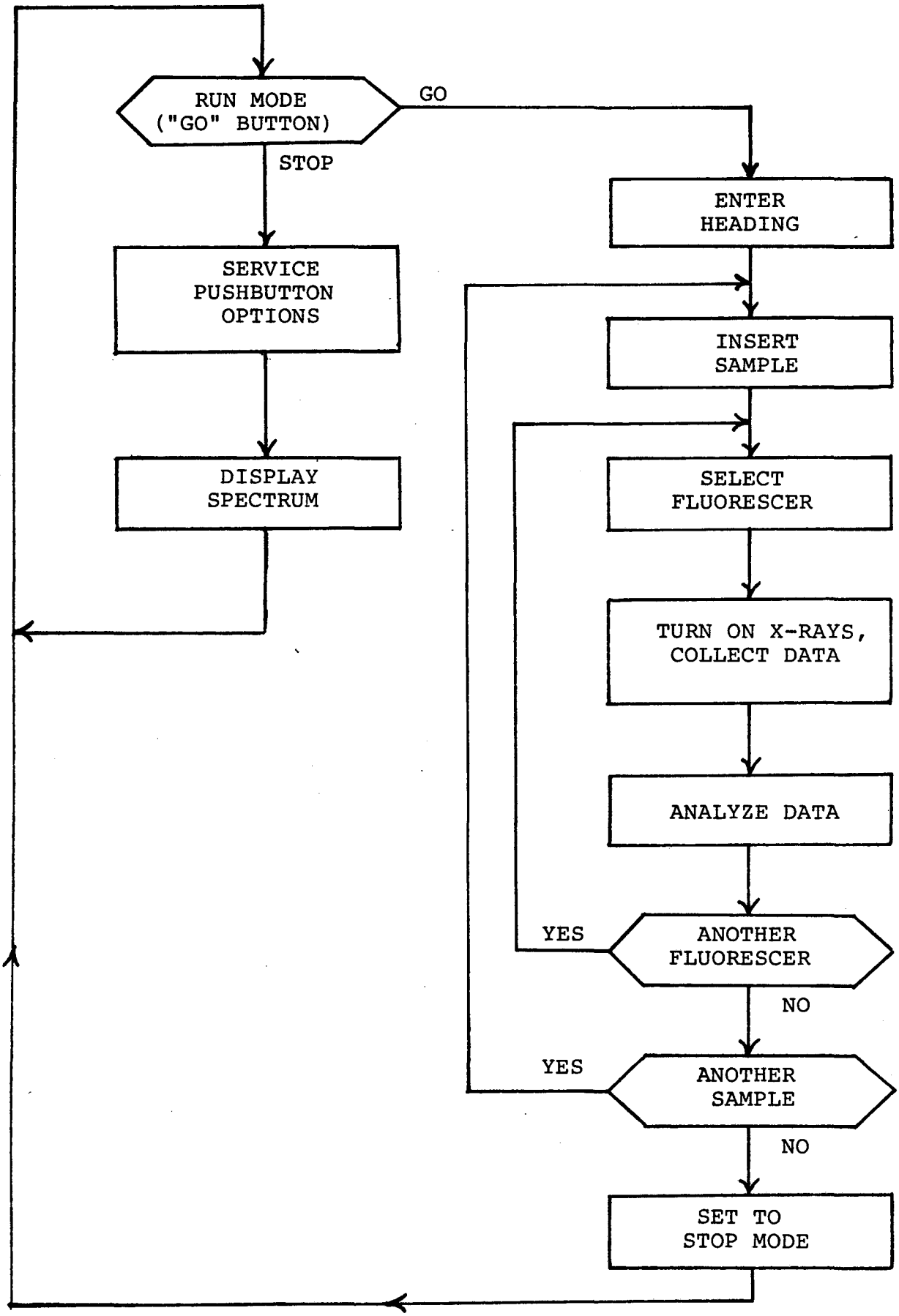


FIGURE 3.
FLOW CHART OF MAIN CONTROL PROGRAM.

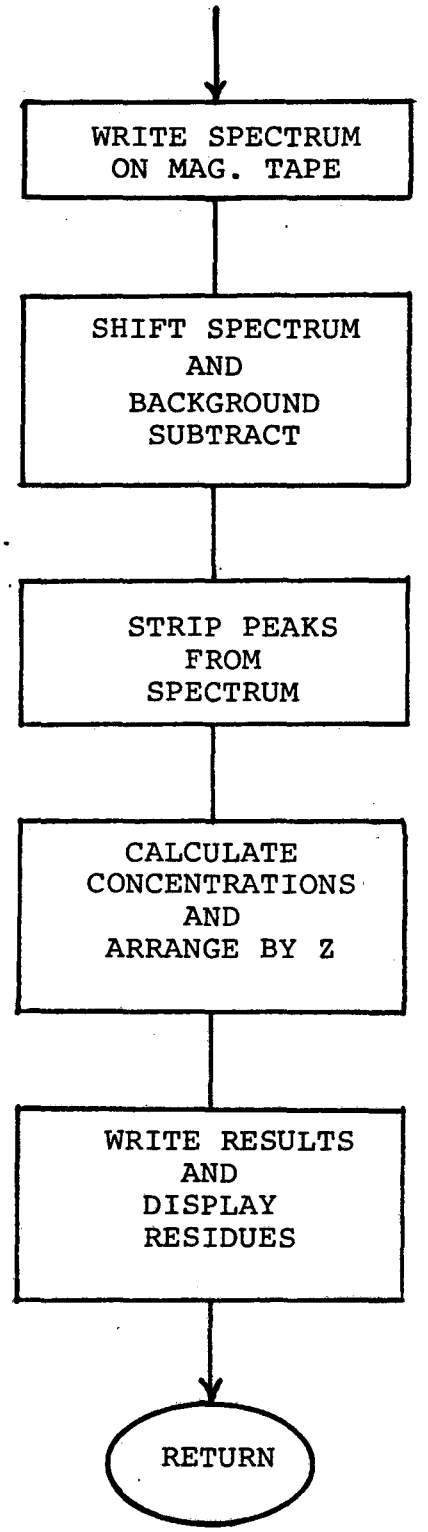


FIGURE 4. FLOW CHART FOR DATA ANALYSIS PROGRAM.

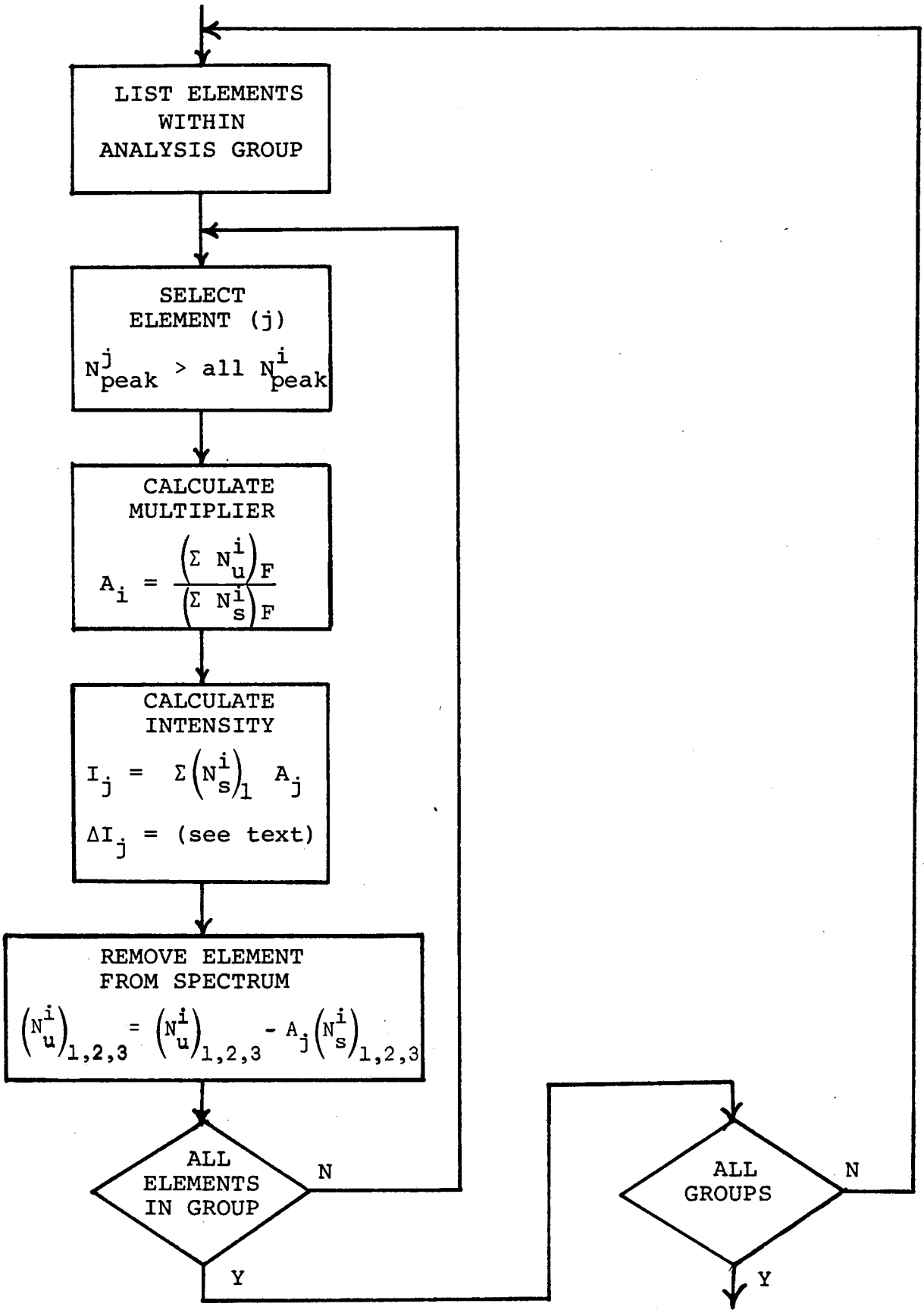


FIGURE 5. FLOW CHART FOR PEAK STRIPPING ROUTINE.

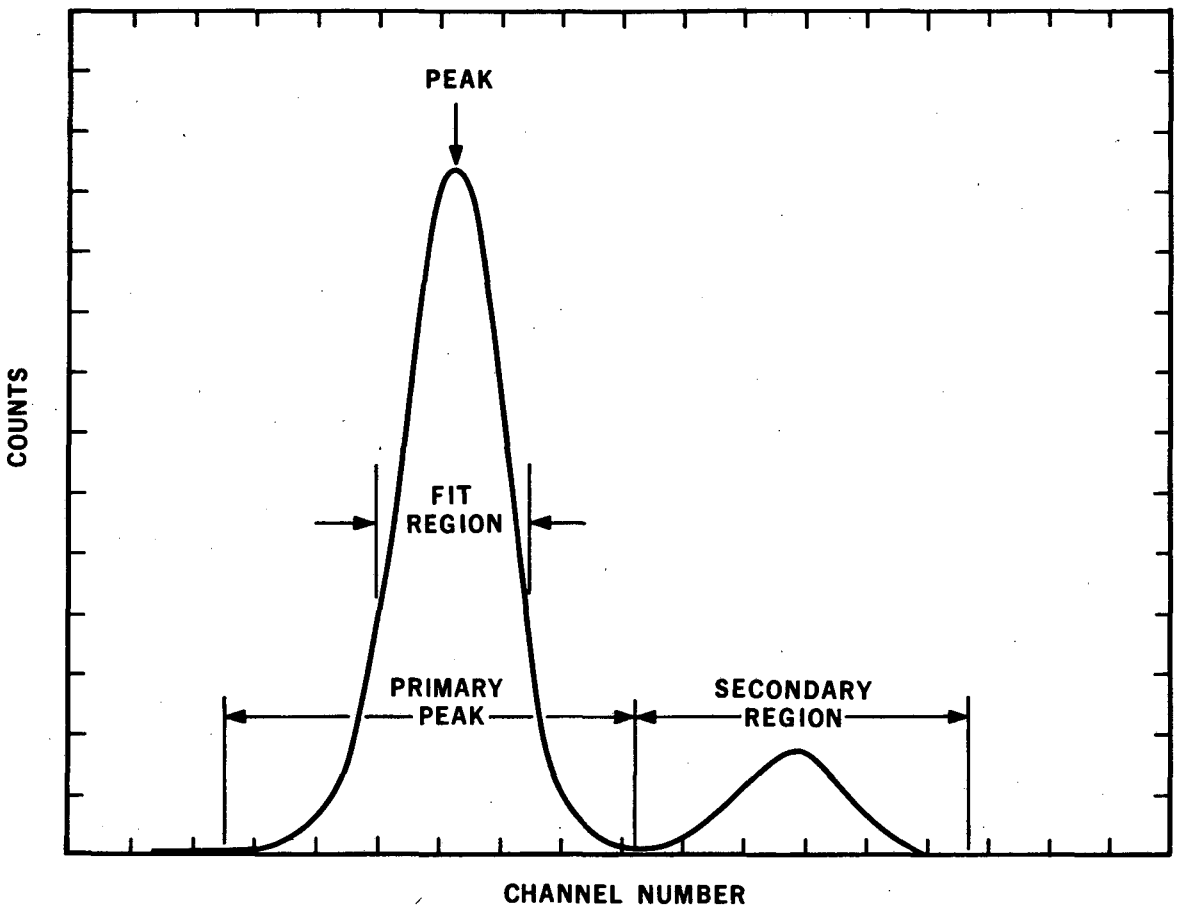


FIGURE 6.

TYPICAL REGIONS ENTERED FOR A K_α SPECTRUM.

GROUP OPTION SUMMARY

ANALYSIS GROUP NUMBER	0 1 2	3 4 5	6 7 8	9
FLUORESCER NUMBER	1	2	3	*

* Elements in this group are removed from analysis

Within a given group number, elements are subtracted out in the order of decreasing intensity in the peak channel. Groups are then treated sequentially within a given fluorescer.

FIGURE 7.

SUMMARY OF GROUP OPTION PARAMETERS.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720