COSMIC PROGRAM # DOD-00065

NRLXRF, A FORTRAN PROGRAM FOR X-RAY FLUORESCENCE ANALYSIS:

Users' Reference Manual and General Documentation

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Washington, D.C.

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SUPPLEMENTAL DOCUMENTATION

DISTRIBUTION FORMAT

The standard distribution format for this program is as an unlabeled 9 track magnetic tape recorded at 800 BPI and containing four physical files. Each file contains unblocked 80 EBCDIC character card image records.

FILE	CONTENTS
1	NRLXRF Program Source Code
2	Sample Physical-Parameters File XRDATP
3	Sample Spectrum File XRDATS
4	Sample Compounds-Definition File XRDATC

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ABSTRACT

This is a versatile, user-oriented program for chemical analysis by x-ray fluorescence. It is suitable for use by technicians performing routine analysis, by analytical chemists solving complicated problems, or by researchers designing better instrumentation and analysis strategies. The program presumes that the problems are simple ones; the user automatically invokes more elaborate treatments just by providing additional information (as for fluxes, internal standards, particle sizes, etc.).

Three general kinds of samples may be treated, according to physical characteristics: (1) homogeneous (any thickness), (2) particulate (bulk, any thickness), and (3) separate particles that do not shadow each other. The automatic calculation method for analysis is a continuous blend of empirical regression techniques and physical theory. In effect, theory provides the shape of the calibration relationships, which are then scaled to agree with the measured standard reference materials most like the unknown sample. When very few standards are available, or when the standards are quite different from the unknown, then the burden is on theory to have the correct shape over a range of compositions. On the other hand, when there is even one standard similar to the unknown, then it matters very little what errors might exist in the theory or in the fundamental parameters (absorption coefficients, spectra from isotopes, fluorescers, or x-ray tubes, etc.).

Theoretical intensity calculations use the formulas of Gillam and Heal for primary and secondary contributions in homogeneous samples, plus a thickness correction from Compton. Particulate samples are simulated with the same formulas, but with the substitution of effective absorption coefficients to account for the overall effects of heterogeneity on x-ray transport, plus other formulas of Criss for the fluorescence production rates in individual particles. The incident radiation spectrum is treated by numerical integration (a composite of trapezoid and Simpson rules). The program can calculate very useful approximations to x-ray tube spectra, using modifications of formulas due to Kramers, Green and Cosslett, Philibert, and Heinrich. Fluorescence yields (including effects of Auger and Coster-Kronig transitions) are calculated using formulas and data in Bambynek et al. Data files provided with the program include line and edge wavelengths of Bearden and Burr, parametric representations of absorption coefficients from McMaster et al., and tabulated x-ray tube spectra from the measurements and calculations of Gilfrich et al. and Brown

et al. A generalization of the regression model of Lachance is used for efficient iteration and to facilitate the calculation of precision in composition (as affected by precision in measured intensities).

The program runs in less than 60K bytes on a Digital Equipment Corporation PDP-10 computer, in either interactive or batch mode. The source language is a fairly standard FORTRAN IV, to facilitate conversion to other computers. This document contains user instructions, implementation instructions, and suggestions for reducing core requirements.

A magnetic tape containing the source program and three data files may be purchased from the Computer Software Management and Information Center (COSMIC), Suite 112, Barrow Hall, Athens, Georgia, 30602, (404) 542-3265. The COSMIC program number is DOD-00065

FOREWORD

This reference manual is designed mainly for the user, rather than the programmer, and so it describes the input and output features of the program, rather than its internal workings, except for brief explanations to help analysts use the program efficiently. Programmer-oriented documentation is deferred to the Appendices.

If the reader has never used a program directly, any user of the appropriate computer can provide the basic concepts for starting a run and inputting data. This program can be run either as a batch job or interactively; the form of input is the same for both modes.

Both the program and this manual were designed to help the user get started with a minimum of instruction. It takes just five pages (Sections 1-3) to describe, with an example, how to analyze thick, homogeneous samples. It is hoped that the rest of the manual would need to be consulted only as more versatility is desired. Note that there is an Index.

An annotated bibliography is included for those interested in further details of experimental method and theoretical technique. However, many of the theoretical treatments and statistical methods used in the program are based on unpublished research by the author.

Appendix A is designed as a quick reference for the user who has already run problems successfully, but needs to look up some of the features used less frequently. Appendix B lists the program-imposed limits on the "size" of problem that can be run. Appendix C sketches the calculation method used to combine physical theory and standards for analysis.

Appendices D, E, and F would be needed only if the analyst wanted to verify, add, or change data in one of the fundamental-parameters data files.

Appendix G contains a brief general documentation, including implementation instructions for a Digital Equipment Corp. PDP-10 computer. Appendices H and I might be useful to a programmer who needed to reduce the core requirements.

Frequently, a data-analysis program is limited mainly to the approach used in the originating laboratory. Much of the versatility represented by this program can be credited to the questions and suggestions of many researchers and analysts, too numerous to name, from a great variety of laboratories.

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JULY 1978 UPDATE TO NRLXRF, COSMIC PROGRAM DOD-00065

The following groups of modifications are given as lines to be changed or added to the July 1977 version. The first 5 digits shown refer to the card-sequence numbers, originally appearing in columns 73-77.

The following changes should be made at all installations, to correct known errors, and to avoid possible execution errors on some systems.

```
11483        1 / 2X, 24H UPDATE NRL JWC  JULY 78,
15189        DATA HTEST/ 3HRES/
18101C:XXX
20491  182   FORMAT( A3)
28998        KCONT= 0
29003        IF ( SP1( IW).EQ. 0.) KCONT= 1
29005        CON= EXP2F( -23., - TFN* CMACF( HFILT, W1( IW), 1, KMAC))
29007        IF ( KCONT.NE. 0) SP1( IW)= SP1( IW)* CON
29009        IF ( KCONT.NE. 0) GO TO 10
29011        IF ( CON.NE. 0.) SP1( IW)= SP1( IW)* CON
29013        IF ( CON.EQ. 0.) SP1( IW)= - SP1( IW)
29021  10    CONTINUE
48153        IF ( NW2.LT. 1) GO TO 10
48203     10 CONTINUE
56055        CALL SORT( WEDG, NEDG+ 0, NEDG, 1)
56057        CALL SORT( WLIN, NLIN+ 0, NLIN, 1)
56156        IF ( SP1( IW).LT. 0.) GO TO 1
 8313        DO 16 ISP= 1, NSP
58315     16 JSP2( ISP)=( ISP- 1)* NW2
58401C:XXX
58476        IF ( SP1( IW).LT. 0.) GO TO 1
58551  14    IF ( NEDG.LE. 1) GO TO 15
59233        DO 62 IX= 1, NX
59235        DX( IX)= 0.
59237     62 BX( IX)= 0.
68693        IF ( ABS( VC( IC)- VS( IC)).LE. 0.0001* VS( IC)) GO TO 4
69081        IF ( KPREP.EQ. 0) GO TO 7
69121  7     IF ( KIND.LT. 3) GO TO 8
70181        ROC( IY)= 0.
70203        IF ( JWL( IL).LT. 1) GO TO 12
74143        IF ( JWL( IL).LE. 0) GO TO 12
74591  12    IF ( PURE( IY).LE. 0.) PURE( IY)= 1.E-34
76183        IF ( JWL( IL).LT. 1) GO TO 12
77123        IF ( JWL( IL).LT. 1) GO TO 15
77251  15    IF ( ROMZ( IY).LE. 0.) ROMZ( IY)= 1.E-34
78536        IF ( JWL( IL).LT. 1) GO TO 12
80721  703   FORMAT( A1, 15X, E16.0)
86463        IF ( WAVE.LE. 0.) GO TO 19
88963        SPL= CON1* SPL* FCHIF( VOLT, NZI, WLL, RAD1, RAD2)
88965        SPL= SPL* EXP2F( -23., - EMACF( 4, WLL, 1, KMAC)* BET)
88967        IF ( SPL.LE. 0.) GO TO 4
88991C:XXX
 9001        SP1( NW1)= SPL
 9141        DO 8 IWC= 2, NWC2
91621  9007  IF ( KR.NE. KUF( 5)) I1= 7
93121        NR= -1
93171        NR= -1
98199        REWIND NUNIT
```

In addition to the necessary changes, the following modifications should be made for (and only for) batch-processing operation.

```
11345C:BAT FOR BATCH PROCESSING, ADD LINES 11346, 18036, AND 18116
  346        CALL IN( 999, -4, 2, KEND, HIN)
18036        GO TO 99
18116 99     CONTINUE
```

The following modifications should be made for compilers that require a BLOCK DATA subprogram for initializing variables in COMMON. The "C:XXX" means delete the original card.

```
10401C:XXX
10411C:XXX
10821C:I/O  STATEMENT IN THE BLOCK DATA SUBPROGRAM.
10866C:DELETE LINES 10401, 10411, 10871--10941, AND 10961--10981.
10871C:XXX
10881C:XXX
10891C:XXX
10901C:XXX
10911C:XXX
10921C:XXX
10931C:XXX
10941C:XXX
10961C:XXX
10971C:XXX
10981C:XXX
12001C:****BEGIN   BLOCK DATA
 2011        BLOCK DATA
  021        COMMON/KIO/ KR, KS, KW, KEND, IH, HIN( 200), KOUT
12031        COMMON/MXS/ MNW, MNIN, MNX, MNY, MNEL, MNOL, MNS
12041        COMMON/HFS/ HFE( 3), HFA( 2)
12051        COMMON/KUS/ KU( 10)
12061        DATA MNX/ 20/, MNY/ 30/, MNEL/ 20/, MNW/ 300/
12071        DATA MNIN/ 80/, MNOL/ 50/, MNS/ 51/
12081        DATA KR/ 5/, KS/ 2/, KW/ 6/, KOUT/ 1/
12091        DATA KU/ 1, 2, 3, 4, 5, 6, 7, 8, 9, 10/
12101        DATA HFE/ 3H( E, 3H16., 2H0)/, HFA/ 3H( A, 2H4)/
12111        END
12121C:****END     BLOCK DATA
```

The following modifications should be made for compilers that do not allow ENCODE/DECODE, and for which the "C:SCR" statements are used.

```
23139C:SCR      READ( KS, HFA) HTST
23233C:SCR      READ( KS, HFA) HTST
32731C:XXX
46301C:XXX
46326C:SCR      READ( KS, HFE) (W1( IW), SP1( IW), IW= IW1, IW2)
```

The following changes are necessary when NRLXRF is to be implemented as two separate programs, NRLSIM and NRLEMP.

```
4134C:XXX
34216C:MOD  BEGIN                                      OMIT FROM NRLEMP
34436C:XXX
34486C:MOD  BEGIN                                      OMIT FROM NRLEMP
```

The following changes are optional. They permit the incident spectrum to be treated in more detail than the original NRLXRF. Such detail is sometimes needed, as when very few lines are excited, or when the highest-energy line is far removed from the spectrum cutoff (see page 37 of the Reference Manual). A new keyword, RMESH, is allowed; it is used, if desired, in the form "RMESH 1.2". The value of RMESH (1.2 by default) is the minimum ratio of successive wavelengths sampled from the incident spectrum. The smallest value allowed is 1.01; for such small values, there can occasionally be cases for which the number of wavelength samples would be too large for some of the array sizes, and error messages would be output.

```
10451         COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
13042         COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
13271         RMESH= 1.2
15043C:MOD     BEGIN                                      OMIT FROM NRLEMP
15045         COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
15047C:MOD     END                                        OMIT FROM NRLEMP
15111        1 HRME/ 3HRME/, HHEL/ 3HHEL/, HCON/ 3HCON/, HPAR/ 3HPAR/,
15409        1 / 2X, 52H RMESH          QUIT
15411        1 / 2X, 52H FATAL          PCT            LONG          REMARKS
15421        1 / 2X, 52H PARROT
15834         IF ( HTEST.EQ. HRME) NQ= 9
15839         IF ( HTEST.EQ. HRME) KPREP= 1
16941C:SCR          READ( KS, 183) HX, XXX
16951         DECODE( 16, 183, HIN( IH)) HX, XXX
16963         IF ( HTEST.EQ. HRME) RMESH= AMAX1( 1.01, XXX)
16965         IF ( HTEST.EQ. HRME) GO TO 2
16967         XUS= XXX
47061         COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
58041         COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
58071C:XXX
58091C:XXX
58161         K= K+ 1
58163         W2( K)= WEDG( 1)
58165         WT( K)= 0.
58167         NW2T= NLIN+ NEDG+ NEDG- 2
58168         NWERR= 0
58169         WLAST= WEDG( 1)
58171         DO 5 IEDG= 2, NEDG
58173         WTEST= WEDG( IEDG)- 0.0001
58175      17 IF ( NW2T.GT. MNIN- 2) NWERR= NWERR+ 2
58176         IF ( NW2T.GT. MNIN- 2) GO TO 18
58177         IF ( WTEST.LE. RMESH* WLAST) GO TO 18
58179         KSKP= 0
58181         DELW= RMESH* WLAST- WLAST
58183         IF (( WLAST+ 2.0* DELW).GT. WTEST) KSKP= 1
58185         IF ( KSKP.NE. 0) DELW= 0.5*( WTEST- WLAST)
58187         WTK= DELW/ 3.
58189         WT( K)= WT( K)+ WTK
58191         K= K+ 1
58193         NW2T= NW2T+ 1
58195         W2( K)= W2( K- 1)+ DELW
58197         WT( K)= 4.* WTK
58199         K= K+ 1
```

```
58201       W2( K)= W2( K- 1)+ DELW
58203       WT( K)= WTK
58205       WLAST= W2( K)
 3207       IF ( KSKP.NE. 0) GO TO 22
 8209       NW2T= NW2T+ 1
58211       GO TO 17
58213    18 CONTINUE
58215       WTK=( WTEST- WLAST)/ 2.
58217       WT( K)= WT( K)+ WTK
58221       K= K+ 1
58231       W2( K)= WTEST
58241       WT( K)= WTK
58251    22 IF ( IEDG.GE. NEDG) GO TO 5
58261       K= K+ 1
58271       W2( K)= WEDG( IEDG)+ 0.0001
58281       WT( K)= 2.0* 0.0001
58291       WLAST= W2( K)
58293 5      CONTINUE
58294       NWERR= K+ NWERR
58295       IF ( K.NE. NWERR) WRITE( KW, 601) K, NWERR
58301   601 FORMAT( 2X,11HWARN: USING, I3,3H OF, I4,20H PTS IN LAMBDA GRID.)
70021       COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
74021       COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
76021       COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
77021       COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
78021       COMMON/SPEC2/ NW2, W2( 80), SP2( 300), JSP2( 30), RMESH
```

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MARCH 1979 UPDATE TO NRLXRF, COSMIC PROGRAM DOD-00065

The following modifications are recommended for all installations, and should be made to the July 1978 updated version of NRLXRF (including the optional changes). The changes below with "C:SCR" should be implemented on systems not permitting ENCODE/DECODE; those containing "C:BAT" should be implemented on batch systems.

```
11485        1 / 2X, 24H UPDATE NRL JWC MARCH 79,
11503         KA= 0
13047         COMMON/YNORC/ YNOR( 51, 30)
13523         DO 11 IY= 1, MNY
13524         DO 11 IS= 1, MNS
13525     11  YNOR( IS, IY)= 0.
19437         IF ( RAD2.GT. 3.14159/ 4.) RAD1= RAD2
24226         IF ( NQ.EQ. 33) Y1( JSR, IY)= -1.
24671C:SCR        READ( KS, HFE) ( YPAR( IY, 7), IY= 1, KEND)
32411C:XXX
46783         IF ( RAD2.GT. 3.14159/ 4.) RAD1= RAD2
47535         IF ( WL.GE. 999.) GO TO 5
47743         GO TO 5
47793         CALL ERROR( 0)
47795         NL= NL- 1
47797         GO TO 6
47801C:XXX
50271         IF ( NZ.GE. NZLAST) GO TO 4
56223         NEDGC= 0
56231         GO TO 13
69143         IF ( TBAR( IX).EQ. 0.) GO TO 19
69145         IF ( XU( IX).EQ. 0.) GO TO 19
80611 701     FORMAT(/ E16.0/ A1/ E16.0)
91043         DATA NIU/ 5* -99/
92713C:BAT        GO TO 63
92883C:BAT        GO TO 63
```

The most serious error discovered since July 1978 (at card 80611) would affect only those who were using the scratch input file, instead of ENCODE/DECODE, and who were also reading definitions of multi-element components from the data file XRDATC. The program would always assume weight proportions — never atomic proportions.

The changes at 19437 and 46783 permit calculation of spectra from end-window x-ray tubes. Transmission-target tubes are not treated.

The other changes are for initializing variables, avoiding minor errors and unnecessary error messages, and parroting batch data.

The data file XRDATP should be changed, to correct a reversal of the M IV and M V edge wavelengths for barium. The appropriate card is

```
15646  .116900E+02 .155600E+02 .158900E+02          0          0
```

In general, NRLXRF can treat wavelengths longer than 12.4 Angstroms only if all necessary parameters are added to XRDATP. See Appendix F (p 46).

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AUGUST 1979 UPDATE TO NRLXRF, COSMIC PROGRAM DOD-00065

The following modifications are recommended for all installations, and **should be made** after the July 1978 and March 1979 updates.

```
  11487       1 / 2X, 25H UPDATE NRL JWC AUGUST 79,
  25681        IF ( Y1( IS, IY).GE. 0.) KNZ= 1
  25682    23 CONTINUE
  47261        IF ( HLY( IY).EQ. HLINE( IND)) GO TO 21
  47263    15 CONTINUE
* 50223       NZLAST= 111
* 56223C:XXX
* 56231       GO TO 4
* 58043       COMMON/MXS/ MNW, MNINT, MNX, MNY, MNEL, MNOL, MNS
* 58413       IF ( IIIL.GT. MNW) GO TO 9902
* 58703       IF ( IWK.GT. MNW) GO TO 9902
* 58852 9902 CONTINUE
* 58853       WRITE( KW, 9903) MNW
* 58854 9903 FORMAT(20H ERROR: NO MORE THAN, I4,21H INCIDENT INTENSITIES,
* 58855     1  16H MAY BE TREATED./37H   USE 'CONDITIONS' AND THEN 'LINES'.)
* 58856       CALL ERROR( 0)
* 58857       GO TO 15
  59401       IF ( XG( N).GE. 0.) NXIND= NXIND- 1
  59403    81 CONTINUE
  59449       IF ( YU( IY).GE. 0.) NFREE= NFREE+ 1
  59451    90 CONTINUE
  59541       IF ( ROOT( IX).EQ. 0.) ROOT( IX)= 1.E-30
  59543    72 CONTINUE
* 74141       IF ( IL.LE. 0) GO TO 11
* 74143       IF ( JWL( IL).LE. 0) GO TO 11
* 74591 11    IF ( PURE( IY).LE. 0.) PURE( IY)= 1.E-34
* 74593 12    CONTINUE
  77121       IF ( IL.LE. 0) GO TO 16
  77123       IF ( JWL( IL).LT. 1) GO TO 16
  77251 16    IF ( ROMZ( IY).LE. 0.) ROMZ( IY)= 1.E-34
  77253 15    CONTINUE
* 88681C:XXX
  92441       IF ( HTEST.EQ. HDIG( J)) GO TO 44
  92443    43 CONTINUE
  95091       IF ( TMX.GT. XMX) XMX= TMX
  95093     1 CONTINUE
  95121       IF ( TMX.GT. XMX) XMX= TMX
  95123     2 CONTINUE
```

Most of these changes are to avoid ending a DO loop on an IF statement. It has been found that some compilers would translate such code incorrectly, without even giving any diagnostic messages.

Users are reminded that suggestions should be directed to COSMIC, since the X-Ray Optics Branch of the Naval Research Laboratory has not been engaged in the development or support of x-ray fluorescence analysis programs for the past two years. Updates issued by N.R.L. (such as this one) reflect mainly the suggestions received (via COSMIC) from users.

* Represent changes that are not just avoiding the ending of a DO loop on an IF.

CONTENTS

RUNNING COMMON PROBLEMS

ADDITIONAL FEATURES

NON-IDEAL SAMPLES

APPENDICES

NRLXRF, A FORTRAN PROGRAM FOR X-RAY FLUORESCENCE ANALYSIS:

Users' Reference Manual

INTRODUCTION

The Naval Research Laboratory (NRL) x-ray analysis program has evolved during a decade of great change in automated data interpretation. The present program takes advantage of the fact that computers now can handle large quantities of data, in a very complex fashion, at a cost that is no more than what the primitive approaches required just a few years ago. It is now economically appropriate to include the more detailed physical theories, more extensive data for the fundamental parameters, and more sophisticated error analysis. The automation of these treatments has been so successful that the program can be run by a technician with no training in x-ray physics or computer programming. Although this program was developed on large computers, very similar versions probably could be implemented on many existing minicomputers equipped with disk storage (see Appendix I).

The design of the program was guided by considerations of user convenience, computational power, versatility, and efficiency. The input style is quite user-oriented.

The analyst inputs only the data that distinguish the problem at hand from other possible problems. A data file provided with the program automatically supplies fundamental physical parameters (absorption coefficients etc.) as required. Ordinary problems can be run simply, without any knowledge of how to run more complicated problems. The program presumes that the problems are simple, until the user indicates otherwise.

Besides the traditional "influence-coefficients" and "fundamental-parameters" equations, the program incorporates physical theory and numerical methods developed at NRL for treating three general types of samples: (1) homogeneous (including secondary fluorescence and a correction for sample thickness), (2) particulate (same effects as for homogeneous, plus effects of particle sizes, voids size, and voids fraction), and (3) separate particles that do not shadow each other, as for many environmental samples.

The physical theories and associated "fundamental parameters" that the program uses will not be detailed in this reference manual, since those things are taken care of automatically. It is sufficient for the user to know which experimental conditions and sample characteristics to supply.

Unlike most previous calculation methods, this program does not require the analyst to make an absolute choice between strictly "influence-coefficients" and strictly "fundamental-parameters" treatments. Instead, the program automatically uses a new combined approach (see Appendix C) that includes whatever reference standards the user provides, together with the physical theory found to be best for fast, accurate analysis. Theoretical calculations are automatically adjusted to make them conform to measured intensities from standards. Still, the analyst has the option of using an empirical regression method alone.

Whatever scheme is used, the analyst can obtain useful estimates of precision in calculated concentrations, plus estimates of consistency among measured (and calculated) intensities. The program can treat data from many different kinds of samples, measured under a great variety of experimental conditions, and thus can be useful not only for performing chemical analysis, but also for improving analysis strategies and experimental techniques.

RUNNING COMMON PROBLEMS

1. Input Style

A simple command may be issued by inputting a keyword. During interactive runs, the program will print the prompting-character "*" when it is ready for input. Two examples of simple commands are

```
* HELP        (causes the program to list all keywords)

* QUIT        (causes the program to terminate)
```

Data are input by groups. Each group is introduced by a keyword, such as COMPOSITION, that announces to the program what sort of information follows. For example, to input the composition of a standard reference material with the arbitrary name SRM1102, one might use the data group

```
* COMPOSITION SRM1102
* CU 72.9
* ZN 27.1
*
```

The separate data items are input in a specific format for each keyword, as described throughout this manual, and summarized in Appendix A.

The important characteristics of the input formats include (1) what data follow the keyword on the same card (or card-image, as for a line of input at an interactive terminal), (2) what data appear on subsequent "cards" in the same group, (3) the order of data on each card, (4) how the group is terminated (usually with blank input), and (5) what data may be omitted, so that the program will use default values -- either initial values in the program, or previously-input data of the same nature.

Only the first three letters of a keyword are required -- e.g., one may use "COM" or "COMP" instead of "COMPOSITION". There are very few restrictions on the spacing of data (i.e., card-column positions). It is sufficient to separate data by one or more blanks and/or commas. This free-field style of input is built into the program, and so does not depend on what compiler or computer is used.

The data groups may be input in practically any order, just so the necessary information has been input before one calls for calculations. Data may be changed by repeating a group.

2. Simple Analysis Problems

The following simple example is for analysis of a brass, using just one standard reference material. Only four different keywords are required: LINES, COMPOSITION, INTENSITIES, and ANALYZE. Following the complete example run, the input formats are explained (also see Appendix A).

User-supplied information is indicated by stars (printed by the program in interactive runs; normally absent in batch runs). The other indented material is output by the program.

```
* LINES
* 1 CU KA 57 40 W 50
* 2 ZN KA
*

* COMPOSITION SRM1102
* CU 72.9
* ZN 27.1
*

* INTENSITIES SRM1102
* 1 23957
* 2 31826
*

* INTENSITIES BRASS
* 1 22873
* 2 35249
*

* ANALYZE BRASS

 COMPONENT    AMOUNT

 CU           69.57
 ZN           30.15
 (TOTAL)      99.71
```

LINES introduces the list of measured lines and their measurement conditions. The lines are numbered, in any order, using the numbers 1, 2,..., n, where n is the number of lines; the list is ended with blank input. The lines are designated by element and one of the six abbreviations KA, KB, LA1, LB1, LB2, MA1. After each line abbreviation, the user may put the x-ray incidence and take-off angles (in degrees, with respect to the sample surface). Following the angles, the user may specify the incident radiation -- by x-ray tube target and kV, as above, or by other means, described in Section 3 (page 6). If angles etc. are omitted for some lines (as for ZN KA above), the program will use the last set of values input (e.g., those for CU KA). If angles etc. are not input for any lines, the program will use default analysis conditions (they may be inappropriate in a strict sense, but still can permit accurate analysis if some of the measured standards are similar to the unknown). One can add or change the data for selected lines by inputting another LINES group with data for those lines.

CONDITIONS is a keyword (not illustrated above) that can be used to specify measurement conditions that apply to all lines. For example, instead of including the angles etc. under LINES above, one could have used the separate input

```
* CONDITIONS 57 40 W 50
```

COMPOSITION introduces the composition of a sample with some arbitrary name (e.g., SRM1102). The name should consist of only letters and digits, with no imbedded blanks; only the first 8 characters are used. The data group includes the name and weight per cent of each component. In the example, the components are elements, but if compounds are to be treated as the separate constituents, they may be listed as well (see the DEFINE keyword, discussed in Section 6, page 12). Each use of a COMPOSITION group redefines the entire composition of the named sample.

INTENSITIES is followed by an arbitrary sample name (such as SRM1102 or BRASS). This keyword introduces the measured intensities, which may be in the form of net counting rate: the number of counts per second, after corrections for counting times, dead time, and background. The program can make these corrections if the appropriate information is input (see Section 5 on Measured Intensities, page 10).

A single group of INTENSITIES data may contain intensities for all measured lines, as illustrated, or it may contain intensities for only some of the lines — subsequent INTENSITIES groups may be used to add or change intensity values. Note that each intensity must be labeled with a line number that was defined by LINES.

ANALYZE causes the program to calculate and output the composition of the sample named. The example above shows answers output in the short form, which is the default situation. The number of digits printed is no indication of accuracy. Estimates of consistency and precision are produced if the user has already issued the simple command LONG, which is discussed in Section 7 (page 15).

For brevity, the above example showed only one standard, but it is recommended that the user input compositions and measured intensities for all available reference materials that are well characterized and reasonably like the unknown.

To predict relative intensities, one would use a LINES group, a COMPOSITION group, and the command PREDICT (which has the same form as ANALYZE -- see page 13 for an example).

RESET is an optional command that is useful if different kinds of problems are to be run. Although one can change data by repeating groups, it is usually best to start a new kind of problem (e.g., steel, rather than brass) as though no previous data had been input. The simple command RESET accomplishes this by returning the program to the same condition it was in when the run began, except that most input/output options (pages 18-20) are not affected.

The material presented up to this point covers the essentials of data input for simple problems. The next section describes alternative ways to specify the incident radiation. When that information has been consulted as necessary, the user will be ready to run the kinds of problems that account for the majority encountered in practice. The new user should try running such problems, to test the program and its applicability. Then, the rest of this manual can be used, as desired, for greater versatility.

3. Incident Radiation

There are several ways to specify the incident radiation, using data following the incidence and take-off angles input after CONDITIONS (or under LINES). For monochromatic radiation there are three forms: by photon energy in keV,

```
* CONDITIONS 45 45  22.1 KEV
```

by photon wavelength in angstroms,

```
* CONDITIONS 45 45  .561 A
```

and by element and characteristic line,

```
* CONDITIONS 45 45  AG KA
```

as from a fluorescer or K-capture isotope (the line designation may be KA, KB, LA1, LB1, LB2, or MA1).

X-ray tube radiation may be specified by providing as many of the following four data as are available (and in the the order indicated): (1) anode element, (2) operating voltage (kV), (3) x-ray take-off angle from the tube (in degrees, with respect to the anode surface), and (4) the thickness of the beryllium window (mm). If not all of these are input, the remainder will automatically be set equal to the values most recently input for the missing data. When the program is started (and after a RESET) it assumes (by default) that data were input for a tungsten-target tube, at 50 kV, with a 30-degree take-off angle, and a 1-mm beryllium window; for example,

```
* CONDITIONS 45 45  W 50 30 1
```

If there is a filter or other absorber (such as an air path) between the tube window and the analysis sample, its name and mass-thickness (g/ sq cm) may be input following the complete specification of the tube; for example

```
* CONDITIONS 45 45  W 50 30 1  AL .07
```

If the filter is not an element, then it must be a mixture of elements (e.g., AIR) defined in the data file XRDATC.

Another way to specify an incident spectrum, whether monochromatic, polychromatic, continuous, or a combination of lines and continuum, is simply to name a spectrum that is tabulated in the data file XRDATS. The detailed format for such a spectrum is described in Appendix D. For example,

```
* CONDITIONS 45 45  W45C
```

The filter for a tabulated spectrum is specified as shown:

```
* CONDITIONS 45 45  W45C  AL .07
```

If the user inputs the word TEMP in the place of a tabulated spectrum (e.g., in place of W45C), the program will not look in the data file XRDATS, but will expect the spectrum to be input on one card (or line from a terminal) immediately following the word TEMP (see Appendix D for the required format). This facility might be useful in calculating the effects of various simple polychromatic spectra (as from isotopes that were not tabulated in XRDATS). For example, to input a spectrum consisting of 3 lines with wavelengths 0.2, 0.5, and 0.7 (angstroms) and with relative intensities 6, 4, and 1, one might use

```
* CONDITIONS 45 45  TEMP
* 3  0.2 6  0.5 4  0.7 1
```

4. Samples and Compositions

The simple analysis example given earlier (page 4) used only one standard reference material. In general, however, one should input data for as many standards as are well-known and similar to the unknown in composition.

Each line defined under LINES must be measured from at least one standard -- a pure element may be used if good multi-component standards are not available. Beyond this minimum requirement, the more standards used, the more accurate the analysis in general. The program automatically considers all standards, making its calculations agree best with the standards that are most like the unknown (see Appendix C).

The standards may be quite different from the unknown, as is sometimes necessary. For example, suppose one wished to analyze a phosphorus-containing steel, and did not have a standard alloy that contained phosphorus. In such a case, the analyst could simply use any convenient compound of phosphorus (e.g., a glassy sample of ammonium dihydrogen phosphate, "ADP"), and define its composition accordingly (by weight per cent):

```
* COMPOSITION ADP
* P 26.93
* N 12.18
* H 5.25
* O 55.64
*
```

The analyst could then input an INTENSITIES ADP group that contained only the measured intensity for P KA. The program would automatically take account of all elements in this standard. It would not matter that no x-ray lines of nitrogen, hydrogen, or oxygen were measured, and that these elements are absent from the unknown sample to be analyzed. However, the analyst would need to specify just which elements are to be considered in the unknown, e.g.

```
* COMPOSITION STEEL
* SI ?
* P ?
* S ?
* CR ?
* MN ?
* FE ?
* NI ?
*
```

This composition group was necessary because ordinarily the program will consider all components that have been named for any samples (including standards). The earlier example for brass (page 4) showed no explicit COMPOSITION group for BRASS, since no extra components had been named. However, it would be good practice to always input such a COMPOSITION group for the unknown.

For a standard (e.g., ADP) the weight per cent of every component is input. For an unknown sample (e.g., STEEL) any unknown amount is indicated by a question mark. If any amount in an unknown sample is known, its value may be input, whether or not any line from that component was measured. This feature is useful when the analyst has added a flux, binder, diluent, or internal standard, or when the amount of some component is fixed by assumption or is known from an independent analysis method. For example,

```
* COMPOSITION STEEL
* CR ?
* MN .6
* FE ?
* NI ?
*
```

In contrast to INTENSITIES, each use of a COMPOSITION group re-defines the entire composition of the sample (see page 5).

Usually, there will be no problem with the criterion that relates the number of measured lines and the number of unknown amounts in a sample: there must be a non-negative "number of degrees of freedom" for analysis to be possible. This number usually equals the number of measured lines minus the number of components with unknown amounts; however, if the SUM of the component amounts is fixed (see page 13), then the "number of degrees of freedom" is increased by one.

The program will remember the input composition and measured x-ray intensities for any named sample, until the information is changed by new input for that sample, or until the user issues a RESET command. For this reason, one should RESET the program before changing to problems that involve different sample components and measured LINES. Otherwise, inappropriate standards and incorrect intensities might be used by the program in analyzing the new unknowns.

To list the values of concentrations and intensities that the program has on hand for a particular sample, one may issue the command "LIST xxx", where xxx is the sample name (see page 20 for an example). To list the data on hand for all samples that are standards, one may issue the simple command DUMP (see page 20).

5. X-ray Intensities

Previous examples showed the line intensities input as net counts per second, after correction for dead time, background, and counting times. However, the program can make these corrections if input is in the general form

```
* INTENSITIES TEST1
* 1 265900 20 340 20 2.2
* 2 146271 100 28 10 2.2
* 3 124266 20 281 20 2.2
*
```

After the line-number, one puts the total number of counts (signal+ background), then the corresponding counting time (in seconds), then the total counts for background, then its counting time, and finally the detection-system dead-time (in microseconds). The data for background might be obtained by spectrum analysis, by measurement of a "blank" sample with similar scattering properties, or by other means. If the corrections for background etc. lead to negative net counts per second, the value will be set to zero.

It is not necessary to input intensity data for every line in a sample, although one usually does so for unknowns. For standards, one could input data just for the lines that were measured, or the lines that are to be considered.

It is not even necessary to input all six data for each line treated, since the program can use previously input data as defaults. For each line-number, the program will use as default values the last values input for total-counts time, counts for background, etc. (i.e., there is no default for total counts). Once data have been input for a particular line, then subsequent entries for that line do not need to include data beyond the last item that changes. For example, the above INTENSITIES group could be followed by the group

```
* INTENSITIES TEST2
* 1 457632 10
* 2 87492
* 3 105738 20 263
*
```

which would be the same as the complete input

```
* INTENSITIES TEST2
* 1 457632 10 340 20 2.2
* 2 87492 100 28 10 2.2
* 3 105738 20 263 20 2.2
*
```

At the beginning of a run, and after a RESET, the default values of counting-time for signal plus background, counts for background, time for background, and dead-time are 1, 0, 1, and 0. Then, if one inputs only one datum after each line-number (as in the example on page 4), that datum will be interpreted as net counts per second.

The user is cautioned that the program makes only the simplest kinds of dead-time and background corrections, so for complex situations (e.g., when the dead-time is large, or when energy-dispersive techniques are used) it might be best to make more specialized dead-time and background corrections before inputting data to this program.

If a line-number is the only datum input, the program will assume that the line was not measured for that sample.

A value of zero for total-counts time causes the program to assume that the "total counts" is actually in units of "relative x-ray intensity" (RXI, the same units output by the PREDICT command — see page 13).

Ordinarily, the user will want the program to consider all standards when calculating the composition of an unknown. Then, theoretical calculations will automatically be adjusted to match the standards most similar to the unknown (see Appendix C). However, it is sometimes desirable to observe the results of using selected standards.

NORMALIZE is an optional keyword that lets the user name a specific standard to be used as the only reference for some line, rather than having the program use all standards that have been input. One standard is named for each line:

```
* NORMALIZE
* 1 CRSTD
* 2 FESTD
* 3 NISTD
*
```

If a single multicomponent standard is the "normalizing" standard for all lines, then that standard would be named for each of the lines under NORMALIZE.

If, for any line, all standards are to be used for normalization, then the word ALL would be input in place of the name of a specific standard. If all standards are to be used for all lines (the default treatment) then a special one-card command may be used:

```
* NORMALIZE ALL
```

6. Other Features Often Useful

DEFINE is used to define sample components that are not separate elements (e.g., oxides and fluxes). Once such a component is defined, it may be used in any subsequent COMPOSITION group of data; however, definitions created by DEFINE are deleted by RESET, and must be repeated if needed later. For example, lithium tetraborate could be defined by

```
* DEFINE BORATE 1.4 AT
* LI 2
* B 4
* O 7
*
```

and used along with other defined components in

```
* COMPOSITION GLASS
* BORATE 85
* CAO ?
* SILICA ?
* PBO ?
*
```

The component name is arbitrary -- instead of BORATE, one could have used LI2B4O7, or FLUX, etc., subject to the same rules as sample names (page 5). After the name comes the density (which the program uses only for particle effects -- see pages 24-27). The "AT" tells the program that the composition will be given in atomic proportions. Instead of the "AT", one may use "WT", indicating weight proportions. In either case, the program will automatically scale the given proportions to 100 per cent. The DEFINE command does not need to be used if the definition has been placed in the permanent data file XRDATC, as explained in Appendix F. Note that DEFINE defines a component, not a sample.

A special one-line form of DEFINE provides a convenient way to define a synonym for an element, or for another component that is defined (either by DEFINE or the file XRDATC); e.g.,

```
* DEFINE IRON EQUALS FE
```

Synonyms are useful for internal standards and when there are several particle sizes for a single component (repeated use of the same name under "COMPOSITION" will change the data for that name). "EQUALS" may be abbreviated to "EQ".

ELEMENTS is useful if there are any multi-element components in a sample. The simple command ELEMENTS causes the program to output the elemental composition of a sample just ANALYZEd (or PREDICTed or SIMULATEd -- see next page).

SUM is used when the analyst wants calculated compositions to have a specified sum (e.g., in weight per cent). Input any time prior to an ANALYZE command, SUM has the form

```
* SUM 100
```

A question mark or a negative value (the initial default) causes the total to be unconstrained. When the sum is fixed, it does not simply cause the calculated amounts to be rescaled, but is used as additional information (a "side condition") in the calculation procedure; usually, minor concentrations are affected much less than major amounts. The output from an ANALYZE command indicates when the SUM (or the amount of any component — see page 9) is fixed:

```
COMPONENT   AMOUNT

CR          17.76
MN           0.6000 (FIXED)
FE          69.44
NI          12.20
(TOTAL)    100.0000 (FIXED)
```

PREDICT causes the program to calculate the theoretical relative x-ray intensities (RXI's) for any sample whose complete COMPOSITION has been defined. For each line, RXI is the ratio of x-ray intensity from the sample, divided by the intensity from a thick, homogeneous, pure-element standard under the same experimental conditions. RXI is simply a unit of measure; its use does not necessarily imply that the pure element is measured. An example of PREDICT is

```
* PREDICT SAMP1

  LINE      RXI

1 CR KA   0.172238
2 FE KA   0.480056
3 NI KA   0.037609
```

SIMULATE is identical to PREDICT in the form of the command and in the output. The difference is that under SIMULATE the program will also calculate intensities in absolute units (counts per second), on the basis of measured intensities that have been input so far for standards. Then, these calculated intensities will be saved, to be used later just as if they had been measured and input. The adjusted intensities may be observed in the output from LIST (see page 20). SIMULATE is useful if the analyst wants to use the cheaper EMPIRICAL option (see next page) for routine analysis, but wants to consider a few hypothetical standards in addition to the real standards.

Choice of calculation method for analysis

There are three basic approaches available for analysis. The selection is made by issuing one of the three simple commands EMPIRICAL, THEORETICAL, or FULL. Whenever ANALYZE is issued, calculations will depend on the current setting of this option. A RESET command will re-establish the default option, FULL.

FULL analysis calculations use all standards to adjust the theoretical intensities (see Appendix C). It is advisable, but not required, that some of the standards be similar to the unknown not only in composition, but also with regard to sample thickness and homogeneity. When standards differ in these physical characteristics, the appropriate parameters need to be input (see pages 23-27).

EMPIRICAL analyses ignore physical theory, and use a regression method that considers all standards, emphasizing those standards most like the unknown (see Appendix C). All intensities must be in the same units (i.e., all RXI's or all raw intensities). Since the regression method does not include parameters for sample thickness, particle sizes, etc., these properties should be the same for all samples. It is not necessary to include the line abbreviation, angles, etc. after the element under LINES, since those parameters would not be used by the program (likewise, CONDITIONS is not needed). If not enough different standards have been input, then the program will output warning messages and automatically simplify the regression model. For the full regression, each line must have been measured in at least as many standards as there are components in the unknown; also, for each combination of component and measured line, there must be at least one standard for which both the component concentration and measured intensity are nonzero. When only these minimum criteria are met, the standards might still be insufficient (e.g., if two of the standards have almost the same composition, but random errors prevent good correlation with intensities); under such circumstances, numerical errors can result. In general, the more standards, the better, except for computing costs. EMPIRICAL runs cost only about half as much as those using the FULL option.

THEORETICAL analyses use predictions from physical theory (made automatically), but ignore all standards except those named under NORMALIZE (which command must have been used, but without the word ALL). Thus, for each line, only one reference material is used to adjust the physical theory. Under this option, the program will run somewhat faster than when FULL calculations are made, and the statistical estimates (see pages 15-17) are more approximate.

7. Consistency and Precision

Almost as important as calculated composition are estimates of accuracy. Unfortunately, accuracy can be checked only for a material whose composition is well known from other techniques (e.g., wet chemistry). Since such a comparison is impossible for most analysis problems, one usually must be satisfied with estimates of consistency and precision: consistency of the results with whatever standards and theories are available, and precision in the sense of variations in results caused by variations in data. This section describes the estimates of consistency and precision that are produced under the LONG output option.

LONG is a simple command that sets an output option to include various statistics along with analysis results -- unlike the short form illustrated earlier. The user may revert to the short form with the two-word command NO LONG.

Under the LONG option, the ANALYZE command causes the program to output a comparison between the x-ray intensities measured and the x-ray intensities calculated by regression (see Appendix C for a description of the analysis method). The first part of the output has the form

```
   LINE        XI MEAS.   XI CALC.  PCT DIFF   ASSUMED
 1 CR KA     .7587E+04 .7643E+04    -0.7     +/-  1.0
 2 MN KA     .6000E+03 .6002E+03    -0.0     +/-  1.0
 3 FE KA     .1294E+05 .1308E+05    -1.1     +/-  1.0
 4 NI KA     .8941E+03 .8950E+03    -0.1     +/-  1.0
```

The columns, in order, are line designation, measured and calculated x-ray intensities (ordinarily in counts/second), the per cent difference between these two, and the assumed random disagreement (see below). The values in the last two columns are used to produce other statistics to be described.

ERRORS is a keyword used to input estimated random errors in the measured intensities. The assumed per cent errors may be input for any or all lines:

```
* ERRORS TEST1
* 2 3.
* 4 2.
*
```

The assumed random error in measured intensities is set to 1 per cent relative by default, as illustrated above (under ASSUMED). For each line, the value input under ERRORS will become the new default value (until a RESET).

The program computes a "normalized chi-square" value that can be used to assess the overall consistency of measured (and calculated) intensities. "Chi", the square root of this value, is perhaps easier to interpret. It is output in the form

```
CHI= 1.35 (EST. RMS RATIO OF OBSERVED TO ASSUMED PCT DIFF)
FOR  1 DEGREE OF FREEDOM.
```

This output indicates that chi is an estimate of the root-mean-square ratio of observed per cent difference to assumed average disagreement. This estimate is more dependable as the number of degrees of freedom is greater. In the example, that number equals 1 -- i.e., 4 independent intensity measurements, minus 4 components to be found, plus one constraint (SUM 100). Without this constraint, there would have been 0 degrees of freedom, and the value of chi would have been undefined — that is, there would have been no basis for assessing the consistency among measured and calculated intensities: one would expect exact agreement for each line, in spite of possible experimental and theoretical errors.

If chi is on the order of 1 (as in the example), then there is general consistency among the statistical assumptions and the observed results; if chi is much different from 1, then there is general inconsistency, and the analyst should try to discover why. Chi is really an estimate of what one might expect in the analysis of many samples having approximately the same composition, rather than a precise measure of errors for the particular sample just run. A single value of chi is useful mainly as a warning of extreme errors. It is better to view chi on the average, for several samples.

A rough interpretation of chi values is as follows. If the program is using assumed errors of 1 per cent, and if the average chi is about 3, then there is reason to suspect that the random errors in intensities (or disagreements with calculated intensities) are more like 3 per cent, on the average. Similarly, if the user has input specific estimates of intensity errors, and if chi is generally on the order of 0.5, then perhaps the user has overestimated the errors by a factor of two, on the average. One should be aware that chi is based on theories of random effects, so it might not be an accurate measure of systematic differences. Moreover, the program does not consider any errors in the compositions of standards or in the amounts of fixed components, for the calculation of either chi or imprecision in composition (see below).

The next section of output under the LONG option has the form

```
ESTIMATE  3: COMPOSITION CONVERGED.

COMPONENT   AMOUNT       IMPREC.     BIAS       ADJUSTED

FE          69.3952 +/- 0.21       - 0.71        68.7
NI           6.9721 +/- 0.067      - 0.0099       6.96
CR          21.5110 +/- 0.21       - 0.088       21.4
MN           2.1217 +/- 0.021      - 0.0009       2.12
(TOTAL)    100.0000 (FIXED)        - 0.81        99.2

IMPREC IS IMPRECISION (STD DEV) DUE TO ASSUMED RANDOM ERRORS.
BIAS IS A LINEAR ADJUSTMENT, IGNORING THE OTHER COMPONENTS.
```

The estimate number and convergence criteria are described under STEP on page 21. As indicated above, the program estimates propagated error and expresses it as standard deviation in calculated amount. These estimates are based on the assumed random errors in relative intensities (input under ERRORS, or set by default to 1 per cent relative).

The program estimates "bias" values, which are measures of inconsistency in composition — in contrast to the numbers under PCT DIFF, which apply to intensities. Each "bias" is a first-order adjustment made to each component separately, in an attempt to remove the disagreement observed between measured and calculated intensities. Note that this bias is useful mainly in identifying components for which the inconsistency is greatest. The amounts listed under "AMOUNT" are the program's best estimates for the situation at hand, considering all components and their mutual effects, plus any constraints on the amounts of individual components, or on the total amount. If the value under BIAS is greater than the value under IMPRECision (as for FE in the example), then the bias value should be considered in assessing errors in composition. The amounts listed under ADJUSTED have been adjusted for the bias; however, they would normally not be better than those under AMOUNT, unless the analyst wished to relax some constraints (in which case the problem should be re-run without the constraints).

The values under IMPREC and BIAS are given to two "significant digits" (to a maximum of four digits after the decimal point), but perhaps only the first nonzero digit is dependable. The values under ADJUSTED are given to the number of digits that includes the first nonzero digit of the value under IMPREC.

8. Input/Output Options

FATAL is a simple command that causes the program to terminate whenever it detects an input error or a calculation error that would be likely to affect subsequent calculations in a very serious manner — especially, if an error in input data would make subsequent data in the group unintelligible. This option is recommended for batch runs.

NO FATAL is a default option, opposite to FATAL: whenever possible, the program will print error messages and skip the calculations, so that the user can input more or different data. Only some kinds of errors are treatable by the FATAL and NO FATAL options -- for some kinds of input and computational errors, the computer system itself will cause the job to terminate. For some errors, the program will merely output warnings and then proceed with the run, regardless of the FATAL option setting.

PCT is a simple command that is equivalent to the default condition for input and output of composition. All amounts input under COMPOSITION will be divided by 100 before being used in the program (e.g., as weight fraction); all amounts will be multiplied by 100 before being output (e.g., as weight per cent). This option is automatically reset to NO PCT (see below) for SEPARATE particles (see page 27).

NO PCT inhibits the division and multiplication by 100 that was described above for PCT. This option is useful when the analyst wants to input amounts as weight fraction, rather than as weight per cent. NO PCT is also useful in EMPIRICAL analyses, for which the amounts may be in any uniform units (e.g., mass or mass per unit area).

LONG sets the long form of output, described on pages 15 to 17 for analysis output. The LONG form of output from PREDICT includes the calculated ratio of RXI to weight fraction of the fluorescing element, plus other values described in Sections 10-12 (pages 23-27).

NO LONG is a default option; it reverses the preceding to the short form of output.

OUTPUT n causes the program to output to either the terminal or the file XROUT, according to whether n is 1 or 2.

INPUT n causes the program to seek input data from one of four sources: terminal, file XRDAT2, file XRDAT3, or file XRDAT4 -- according to the value of n: 1, 2, 3, or 4.

The auxiliary input files (XRDAT2, XRDAT3, and XRDAT4) may be used to provide problem set-up data or any other information that the user wishes to acquire from a permanent file — e.g., the compositions and intensities of standards, data for test runs, and data for example runs.

The form of data in an auxiliary file is the same as described in this manual for interactive terminal input or regular batch input, except that every card image is preceded by a 6-column field that the program ignores. This initial field may be used for sequence numbers, which are useful on systems that have editing features for line-numbered files. The program will automatically add sequence numbers to the output generated by the commands LIST and DUMP (described on page 20).

Whenever an "INPUT n" command is processed, the program will automatically seek the next input from the appropriate file (either terminal or an auxiliary file), and will read the next card image following the last card-image read from that file (since the run was begun). Thus, data files may be exited and re-entered repeatedly.

PARROT causes the program to output each line of data as received. In batch mode, this causes the input data to appear in the appropriate points in the output. For interactive mode, this option permits the user to see data as they are supplied by an auxiliary file.

NO PARROT is the reverse of the preceding: data appear meshed with the output only when they are input from an interactive terminal. This is the default option.

REMARKS permits the program to parrot "remarks" that are encountered in a data file (under the PARROT option). A remark is any portion of a card image that begins with the character "#". Remarks are convenient for adding descriptive material to data, as in example problems.

NO REMARKS is nearly the opposite of the above. A "remark" will not be printed unless the "#" is the first character read on a card. Whether or not PARROT and REMARKS are set, the interactive user may add commentary to the run by typing remarks anytime the program prints a "*".

RESET (see page 6) does not affect any of the above input or output options, except that the PCT option is established.

LIST causes the program to list the data it has for a sample, in the form necessary for input from an auxiliary file (including sequence numbers). Some of the parameters output are used only for samples that are not homogeneous and thick (see Sections 10-12: pages 23-27). Example output for LIST SAMP1 is

```
1020  COMPOSITION SAMP1     HOMOG   100.0000 0.0000 0.00 1.0000
1030   CR           12.0000  0
1040   FE           72.0000  0
1050   NI           16.0000  0
1060
1070  INTENSITIES SAMP1     HOMOG   100.0000 0.0000 0.00 1.0000
1080   1    0.17000E+00   0
1090   2    0.48000E+00   0
1100   3    0.38000E-01   0
1110
```

An unknown amount of a component is listed as -1. The digit after an intensity is 0 if RXI's are output; otherwise, it is 1, indicating net intensity in counts per second. Under the LONG option, an ERRORS group (page 15) is also output.

DUMP is a simple command that is useful for saving information necessary to set up NRLXRF (or another program) for EMPIRICAL analysis. By using OUTPUT 2 and DUMP, the analyst can create a data file that is readable by NRLXRF. The output will identify the LINES by element, and will specify whether the PCT or NO PCT option is used:

```
2020  EMPIRICAL
2030
2040  LINES
2050   1 CR
2060   2 FE
2070   3 NI
2080
2090  PCT
```

Next, the program will automatically LIST all samples that are standards — a sample is a standard if its complete composition has been specified. The output will include intensities for all standards that were input and all that were SIMULATEd (page 13), since the last RESET. For each standard, the output has the same form as LIST, except that no information follows the sample name on the COMPOSITION or INTENSITIES line, and particle sizes are not included after the amounts. The LONG option will cause ERRORS groups to be output. If any multielement components are not defined in the file XRDATC, the analyst will need to add the necessary DEFINE groups (page 12) before making later runs based on the output from DUMP.

9. Further Versatility

STEP is used in the same way as ANALYZE, but it causes only one step of the iteration to be calculated. With STEP, the analyst can observe successive estimates of composition, and verify the convergence. In normal analysis, the iteration will stop, and answers will be output, if any one of three convergence criteria is satisfied: (1) the relative change in amount, for every component, is less than 0.0005, (2) the number of degrees of freedom (page 16) is positive, and the relative change in calculated intensity, for every line, is less than 0.2 times the assumed relative error, or (3) the number of estimates (iterations) is 12. The number of estimates and the criterion satisfied are shown in LONG output by one of the forms

```
ESTIMATE  3: COMPOSITION CONVERGED.
ESTIMATE  4: INTENSITIES CONVERGED.
ESTIMATE 12: ITERATION LIMIT.
```

MULTIPLIERS introduces a list of one or more multipliers, which can be used to compensate for equipment drift, changes in detector response, etc. between the measurements of various samples. If one multiplier is input, for example

```
* MULTIPLIERS 1.02
```

then all subsequent intensities input under any INTENSITIES groups will be multiplied by the multiplier (e.g., 1.02), after correction for dead-time. If there are different multipliers for the different lines, they are input in the order of the line-numbers; for example,

```
* MULTIPLIERS 1.02 1.04 1.03
```

MAC causes the program to output the x-ray photoelectric mass absorption coefficient of a named material, for x-rays with an energy (or wavelength) specified by two data, as under LINES (but no polychromatic radiation). For example,

```
* MAC NI 22.1 KEV
   23.7680
```

TUBE causes the program to calculate and output the spectrum from an x-ray tube with specified anode, kV, take-off angle, and window thickness (as under CONDITIONS page 7); e.g.,

```
* TUBE  W 50 30 1
```

will produce output with the format described in Appendix D.

COEFFICIENTS is a simple command that causes the program to output the current values of the parameters used in the regression model (discussed in Appendix C). These values pertain to a limited composition range in the vicinity of the last sample analyzed, and might be useful in some other program that uses a more traditional empirical approach. The table of parameters is output in the form

```
 FOR EACH LINE, THE EMPIRICAL EXPRESSION,
 AS AN EQUATION LINEAR IN THE AMOUNTS (W'S), IS

  (G1-B1*XI)*W1 +(G2-B2*XI)*W2 +... = BO*XI

                      COMPONENTS:
                      FECL3          FE2O3          NACL

 CL KA
 G'S:                 0.65567E+00   0.00000E+00   0.60653E+00
 B'S:                 0.00000E+00  -0.12678E+00   0.66474E+00
 BO=    0.14983E+01

 FE KA
 G'S:                 0.34433E+00   0.69945E+00   0.00000E+00
 B'S:                 0.12138E+01   0.00000E+00   0.10373E+01
 BO=    0.77612E+00
```

BFIXED is the default option affecting the form of the regression model (see Appendix C and the example under COEFFICIENTS above). For each line, the "B" parameter is set to zero for the component with the largest "G" value. In some cases the model has a form comparable to that used by Lachance and others — e.g., when all components are elements and the intensities are RXI's.

BFREE permits all "B" parameters in the regression model to be free, thus allowing more flexibility in fitting standards. One should not use BFREE when the sum of amounts is essentially the same for all standards (or for THEORETICAL), or else numerical (roundoff) errors might result.

NON-IDEAL SAMPLES

10. Finite Thickness

At any place where one may input the name of a sample, the sample name may be followed by one of three words used to define the sample kind: HOMOGENEOUS, PARTICULATE, or SEPARATE. Each of these words may be abbreviated by as few as the first three letters: HOM, PAR, or SEP. The examples in this section will be for homogeneous samples; the other two kinds are discussed in Sections 11 and 12.

Following the sample kind, the user may specify the mass-thickness of the sample, in grams per square centimeter. For example,

```
   * PREDICT SAMP1 HOMOG .02
```

The sample characteristics HOMOG .02 will be saved in the program, and thus will be available later whenever SAMP1 is used, unless the user inputs different data after the name SAMP1. The initial default data (e.g., after a RESET) are HOMOG 100. The default values (initial or current) will be used automatically for all samples not yet named. Under the LONG option, the output resulting from the above command might look like

```
   LINE      RXI        RXI/C      XI/XIO     PH/SR/SR    PH/SR/SR/G

1 CR KA   0.168442   1.403682   0.476909   0.2880E-03  0.1200E+00
2 FE KA   0.472483   0.656227   0.255043   0.1475E-02  0.1025E+00
3 NI KA   0.037608   0.235049   0.099583   0.1913E-03  0.5979E-01
```

RXI is the relative x-ray intensity (relative to a pure-element standard of effectively infinite thickness).

RXI/C is RXI, divided by the weight fraction of the fluorescing element in the sample.

XI/XIO is the fluorescence intensity, relative to that from a sample with the same total mass, but in the form of an ultra-thin foil. Thus XI/XIO expresses the departure from an ideally thin sample. If the mass-thickness of SAMP1 had been 0.0001, then the values under XI/XIO would have been very close to unity. For very thick samples (the initial default assumption), the values under XI/XIO would have been zeros.

PH/SR/SR gives the fluorescence intensity in more nearly absolute units — photons per steradian per steradian. These units are appropriate if the sample intercepts one steradian of the incident radiation, and if the incident line intensities are given in units of photons per steradian emitted from the source, and if incident continuum radiation is given in units of photons per steradian per angstrom (see Appendix D). If the incident radiation is expressed in other units acceptable to the program, the values under PH/SR/SR are strictly proportional to the absolute units, with the same factor applying to all fluorescence lines. The program does not treat collimator or slit sizes, crystal diffraction efficiency, detector efficiency, or any air-path absorption etc. between the sample and the detection system.

PH/SR/SR/G values equal the PH/SR/SR values, divided by the mass per unit area of the fluorescing element. For very thick samples, the values under PH/SR/SR/G will be zeros.

Analysis of finite-thickness samples should not be attempted under the EMPIRICAL method unless all samples (unknown and standards) have the same thickness. A sample is treated as a standard if the relevant intensity has been input and the complete composition has been given. Under EMPIRICAL, the program does not check that the sample thickness and other physical characteristics are the same as for the unknown sample, so there is a posibility of inappropriate samples being used as standards. The FULL and THEORETICAL methods avoid this problem by automatically taking account of all sample characteristics during analysis.

11. Bulk Particulate Samples

After the name of a sample, wherever it is input, the user may input the sample-kind PARTICULATE, or an abbreviation with the same first three letters, PAR. Then, theoretical calculations using that sample will treat it as a bulk, particulate sample (for loose powders, pressed powders, sintered materials, slurries, environmental particles evenly distributed randomly in a filter, etc.). Several sample characteristics may be input after the sample name.

As illustrated next, these include the sample kind, its mass-thickness (grams per square centimeter), the volume fraction occupied by voids, and the effective size of individual voids (as diameter, in micrometers):

```
* COMPOSITION RAWMIX PARTIC 100 .2 10
```

A large value of mass-thickness (e.g., 100) may be used for samples that have effectively infinite thickness. Another datum that may be input at the end of such a list (for any sample kind) is the area of the sample (in square cm) that is both irradiated by the incident x-rays and viewed by the detection system. The initial default values for all data after a sample name are HOMOG 100 0 0 1. Once input for a specific sample name, they do need to be repeated with subsequent uses of that name. Moreover, the current values of these data will be the new default values, to be used for any sample name not yet mentioned (until the next RESET).

A complete description of the physical characteristics of a bulk particulate sample requires the information described above, plus the names and particle sizes of all the different materials in the sample. For each component listed under COMPOSITION, one may input the particle size (as effective diameter, in micrometers), following the weight per cent, as illustrated by the data group

```
* COMPOSITION RAWMIX PARTICULATE 100 .2 10
* CACO3 80 30
* SIO2 16 40
* FE2O3 4 25
*
```

The component names should be already defined, either by the DEFINE command (see page 12) or in the data file XRDATC (Appendix D). The initial default values for particle sizes are zeros. Once a value is input for a component, it will become the new default value for that component in future COMPOSITION groups (until the next RESET). If the percentages of the components are unknown, those numbers can be replaced by question marks. If one wants to predict the intensities from a sample with several sizes for one component, the components can be repeated under COMPOSITION, with the appropriate weight per cent and particle size used each time; however, one must use synonyms, because a second entry for the same name will replace the data for that name. Synonyms can be defined by one-line commands:
"DEFINE SILICA EQUALS SIO2", "DEFINE PLATINUM EQ PT", etc.

If the voids volume, voids size, and particle sizes have been input for a sample, as illustrated above, then predicted intensities will be output when one issues the command PREDICT RAWMIX (the sample kind has already been set to PARTICULATE under COMPOSITION). The output for a PREDICT command has the form described earlier (pages 23-24). The effects of heterogeneity will be ignored by the program if one issues the command PREDICT RAWMIX HOMOG, but none of the data will be lost — another command PREDICT RAWMIX PARTIC will give the same results as before.

In a practical sense, the treatment of particulate samples is useful mainly in predicting the effects of sizes etc. on measured intensities, which might be either greater or less than for the homogeneous case. The program can also calculate composition from measured intensities, provided the user inputs the particle sizes etc. — information that usually is not known very well for samples being analyzed. The preferred method for analysis of particulate samples is FULL or THEORETICAL, rather than EMPIRICAL (see page 24).

The accuracy of calculations for particulate samples suffers from two problems: practical uncertainty in voids volume, voids size, and particle sizes; and lack of theory to treat the details of particle shapes, orientations, and size distributions, even if they could be known. If the program predicts an effect greater than about 10 per cent, compared to a homogeneous sample, then there probably are large uncertainties in calculated values.

12. Non-Interfering Particles

Many environmental samples consist of separate particles on the surface of some substrate, such as a collection filter. Unless the particles shadow each other or penetrate deep into a filter that tends to shield them, analysis will be simple. Specifically, for particles with given compositions and sizes (under COMPOSITION — see page 25), the emitted fluorescence intensity (above background) will be strictly proportional to the amount of the emitting element. The problem for which this program is useful is determining the proportionality constant (or, more properly, the dependence of this constant on particle compositions and sizes). The sample kind is specified by the word SEPARATE following the sample name, as illustrated in the following complete run:

```
  * RESET

  * LINES
  * 1 S KA 57 40 CR45C
  *

  * DEFINE N2H8SO4 1.8 AT
  * N 2
  * H 8
  * S 1
  * O 4
  *

  * COMPOSITION SULFATE SEPARATE
  * N2H8SO4 1.E-6 10
  *

  * LONG

  * PREDICT SULFATE

  LINE      RXI      RXI/C      XI/XIO     PH/SR/SR     PH/SR/SR/G

1 S  KA                         0.782433   0.1966E-09   0.8105E-03
```

The program does not use the angles for SEPARATE particles — the 57 and 40 merely occupy data positions so that the x-ray tube (CR45C) may be specified. In the COMPOSITION group, the sample thickness, voids volume, and voids size do not apply, and are omitted from the example. Particle sizes are input as described on pages 25-26, but the amount of material is input as grams per square centimeter (the example is for 1 microgram/ sq cm), rather than as mass per cent, which is used for other sample kinds. The output format has been described on pages 23-24 for non-thick samples. RXI and RXI/C are zero for SEPARATE; the number under XI/XIO in this example means that the emission of S K radiation from particles of the specified composition and size is only 78 per cent as great as from the same total mass of sulfur present as infinitesimal particles.

Values of XI/XIO may be calculated for various compositions and sizes of separate particles, and for any thin-film standards (see page 23) that might be used to calibrate the equipment. For more information on uncertainties, and on the use of XI/XIO in a convenient empirical correction for analysis, consult the annotated bibliography [Criss, Anal. Chem., 1976].

ANNOTATED BIBLIOGRAPHY

Many of the formulas, calculation methods, and data employed in NRLXRF may be found in the following sources, listed chronologically:

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"On the Theory of X-Ray Absorption and of the Continuous X-Ray Spectrum"
Phil. Mag., 46, pp 836-871 (1923)
(formula for bremsstrahlung spectrum, as generated)

R. Glocker and H. Schreiber,
"Quantitative Rontgenspektralanalyse mit Kalterregung des Spektrums"
Annalen der Physik, 85, p 1089 (1928)
(primary contribution from homogeneous, thick samples)

A.H. Compton,
"The Efficiency of Production of Fluorescent X-rays"
Philosophical Magazine, 8, p 961 (1929)
(primary contribution from homogeneous samples, and the correction factor for thin samples)

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E. Gillam and H.T. Heal,
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British Journal of Applied Physics, 3, p 353 (1952)
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Proc. Phys. Soc. 78, pp 1206-1214 (1961)
(intensities of electron-excited K lines, as generated)

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Academic Press, New York, pp 379-392 (1963)
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G. R. Lachance,
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Geological Survey of Canada paper 64-50 (1964)
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J.A. Bearden,
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(wavelengths of absorption edges and emission lines)

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Wiley, New York, pp 284-295 (1966)
(formula for "Lenard coefficient" in Philibert's equation)

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"X-ray Wavelengths"
Reviews of Modern Physics, 39, p 78 (1967)
(wavelengths of absorption edges and emission lines)

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"Reevaluation of X-ray Atomic Energy Levels"
Reviews of Modern Physics, 39, p 125 (1967)
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(republication of the two preceding articles)
NSRDS-NBS 14 (1967)

J.V. Gilfrich and L.S. Birks,
"Spectral Distributions of X-Ray Tubes for Quantitative X-Ray Fluorescence Analysis"
Analytical Chemistry, 40, p 1077 (1968)
(measurement of x-ray-tube spectra)

J.W. Criss and L.S. Birks,
"Calculation Methods for Fluorescent X-ray Spectrometry — Empirical Coefficients vs. Fundamental Parameters"
Analytical Chemistry, 40, p 1080 (1968)
(primary and secondary contributions from thick, homogeneous samples, and the use of tabulated x-ray-tube spectra) Note: in NRLXRF, integration over the incident spectrum uses a composite of trapezoidal and Simpsons rules, rather than a histogram treatment; the "iteration method" described in the 1968 paper is not used in the current program (see Appendix C of this manual).

L.S. Birks,
X-Ray Spectrochemical Analysis
Interscience, New York (1969)
(tabulated spectra for copper and molybdenum x-ray tubes)

W.H.McMaster, N.K. del Grande, J.H. Mallet, J.H. Hubbell,
"Compilation of X-ray Cross Sections"
Lawrence Radiation Laboratory rept UCRL-50174 sec II rev
(x-ray cross sections, from tabulated parameters)

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Plenum Press, New York (1970); or 2nd Edition (1975)
(general text for physical theory and experimental method)

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Electron Probe Microanalysis
Nat. Bur. Stand. (U.S.) Tech. Note 521 (1970)
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J.W. Criss,
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Analytical Chemistry, 48, p 179 (1976)
(primary contribution from isolated particles, empirical correction for analysis)

D.B. Brown, J.W. Criss, and L.S. Birks,
"The Sensitivity of X-ray Films: Part I — A Model for Sensitivity in the 1-100 keV Region"
Journal of Applied Physics, 47, p 3722 (1976)
(effective absorption coefficients for particulate bulk samples) Note: NRLXRF treats a more general case.

APPENDIX A. Summary of Input Formats

Data on a single card-image must be separated by one or more blanks and/or commas. The data groups may be input in any order (unless default data are to be changed), just so the necessary information has been input before calculations are made. Data may be changed by repeating a group. The symbolism is described at the end of this outline.

```
HELP

RESET

QUIT

CONDITIONS [<ang1> <ang2> <sp1> <sp2> <sp3> <sp4> <sp5> <sp6>

CONDITIONS [<ang1> <ang2> <energy> KEV

CONDITIONS [<ang1> <ang2> <wavelength> A

CONDITIONS [<ang1> <ang2> <el> <line>

CONDITIONS [<ang1> <ang2> <el> <kV> <deg> <mm> <filt> <g/sqcm>

CONDITIONS [<ang1> <ang2> <spectrum> <filt> <g/sqcm>

CONDITIONS [<ang1> <ang2> TEMP <filt> <g/sqcm>

LINES
<line num> <element> [<line> <ang1> <ang2> <sp1> <sp2> ...
<etc>

DEFINE <component> <density> [<AT or WT>
<element> <proportion>
<etc>

DEFINE <component 2> EQUALS <component 1>

COMPOSITION [<sample> <kind> <g/sqcm> <vvoid> <tvoid> <area>
<component> <amount> [<part. size>
<etc>

INTENSITIES [<sample> ...
<line num> <n(sig+bkg)> [<t(sig+bkg)> <n(bkg)> <t(bkg)> <d-t>
<etc>

ANALYZE [<sample> ...

PREDICT [<sample> ...

SIMULATE [<sample> ...
```

```
SUM <sum>

ERRORS [<sample> ...
<line num> <relerr>
<etc>

EMPIRICAL

THEORETICAL

FULL

STEP [<sample> ...

NORMALIZE [ALL
<line num> [<sample> ...
<line num> [ALL
<etc>

MULTIPLIERS <mult1> [<mult2> ...

INPUT <in-file>

OUTPUT <out-file>

LIST [<sample> ...

DUMP

BFIXED

BFREE

ELEMENTS

MAC <material> [<el> <line>

MAC <material> [<energy> KEV

MAC <material> [<wavelength> A

TUBE [<el> <kV> <deg> <mm>

(NO) LONG

(NO) PARROT

(NO) REMARKS

(NO) PCT

(NO) FATAL
```

In the outline above, a phrase enclosed by "< >" denotes a datum that is input (either a number or a word). To input data, provide all words not enclosed by "< >", and provide the data in the appropriate places (but without the "< >"). A keyword may be abbreviated to its first three letters.

The symbolism "<etc>" means that additional lines of data may be input in the same format as the line above, and that the entire group of data is terminated by a blank line.

The symbolism "<sample> ..." means that wherever <sample> may be input, it may be followed, on the same line, by the additional data for <sample>, as shown for COMPOSITION.

Under LINES, "<sp1> <sp2> ..." represents data sp1 thru sp6.

A word in parentheses — e.g., "(NO)"— is optional. Data following a "[" are optional, if default values have been established by the program or by earlier entries. An additional feature of the input style is that a semicolon (;) may be used instead of an end-of-line. Thus, one card (or card-image) can contain data that would otherwise require separate cards — e.g., "LONG; NO FATAL; ANALYZE".

Next are definitions for the data items referred to above.

ang1 ang2	X-ray incidence angle and take-off angle, in degrees with respect to the sample surface.
sp1 sp2 ...	Data that specify the incident radiation. There are 6 ways to do this, as described in Section 3 (pages 6-7):

sp1	sp2	sp3	sp4	sp5	sp6
energy	"KEV"				
wavelength	"A"				
element	line				
anode	kV	deg	mm	filt	g/sqcm
spectrum	filt	g/sqcm			
"TEMP"	filt	g/sqcm			

energy	The photon energy, in keV.
wavelength	The photon wavelength, in angstroms.
element	Element symbol.
line	One of the following six abbreviations for lines: KA KB LA1 LB1 LB2 MA1

anode	Element symbol of x-ray tube anode.
kV	X-ray tube operating potential, in kilovolts.
deg	X-ray take-off angle from tube, in degrees with respect to the anode surface.
mm	Thickness of beryllium x-ray-tube-window, in mm.
filt	The name of the material used to filter the incident spectrum; it may be either an element symbol or the name of a material defined in the data file XRDATC.
g/sqcm	Mass-thickness of filter or sample, in grams per square centimeter.
spectrum	Name of a spectrum tabulated in the file XRDATS.
el	Element symbol, as for a K-capture isotope, a fluorescer, or the anode of an x-ray tube.
line num	A number (e.g., 1, 2,...) that is used to label the characteristic emission line of interest.
component	The name of a component of the samples: either an element symbol or an arbitrary name (only the first 8 characters will be used by the program.
density	The density, in grams per cubic centimeter.
AT or WT	Either "AT" (for atomic proportions) or "WT" (for weight proportions).
proportion	Either the atomic proportion or the weight proportion of the element in the component, according to whether "AT" or "WT" was used.
sample	An arbitrary name used to identify a sample. Only the first 8 characters of the name will be used by the program.
kind	One of the words HOMOGENEOUS, PARTICULATE, or SEPARATE. (Each may be abbreviated to as few as the first 3 letters)
vvoid	The volume fraction occupied by voids.
tvoid	The average void size, as diameter in micrometers.
area	The sample area, in square centimeters.

amount	Weight per cent of a component (exception: it is the mass per square centimeter, for sample kind SEPARATE). A "?" means the amount is unknown.
part. size	The particle size, as diameter in micrometers.
n(sig+bkg)	The number of counts for both signal and background.
t(sig+bkg)	The counting time, in seconds, for n(sig+bkg). If zero, then n(sig+bkg) is assumed to be RXI.
n(bkg)	The number of counts for the background.
t(bkg)	The counting time, in seconds, for n(bkg).
d-t	The detection-system dead time, in microseconds.
sum	The fixed total amount for all components (use a question mark or negative amount if sum is free)
relerr	The assumed relative error in RXI, in per cent.
mult1,...	Multipliers for the measured intensities, in order of the line numbers.
in-file	Either the number 1 (for terminal input) or one of the numbers 2, 3, or 4 (for input from file XRDAT2, XRDAT3, or XRDAT4).
out-file	Either the number 1 (for output to the terminal) or the number 2 (for output to file XROUT).
material	Either an element symbol or the name of a material defined in the file XRDATC.

APPENDIX C. Calculation Methods Used for Analysis

In both the general approach and in computational details, this program includes several methods that have not been used before in x-ray fluorescence analysis. However, this manual is intended for analysts, rather than mathematicians or other theorists, so the outline below describes the general approach in terms of basic data-analysis concepts, merely mentioning the calculation techniques, and not dwelling on the novelties. Following sections discuss the regression methods and the physical theory.

General Approach

The program calculates composition in a way that is quite analogous to the familiar method of establishing and using a calibration curve for a binary sample. There are four basic parts to the problem: (1) what known points — i.e., what standards — are to be used, (2) what shape of curve should fit them -- straight line, etc., (3) how is the particular curve established — i.e., how does one fit the data best with the shape chosen, and (4) what composition corresponds to the measured intensities, according to the calibration curve. For binaries, one can do the calibration, analysis, and assessment of results in a straightforward and natural way — by "eyeball".

Fundamentally, the program automates this familiar analysis concept. The difference between the graphical approach and the computer program is not so much a matter of concept as a matter of complexity and detail. In general, a sample has more than two components, each affecting every measured intensity, so the mental picture of a two-dimensional graph no longer works. Moreover, a digital computer operates at a very primitive level (arithmetic) and so it must be programmed in agonizing detail. There is no single best way to program a computer for the analysis problem, any more than there is a best "eyeball" method. The numerical methods were devised to satisfy, as well as possible, the competing goals of accuracy, flexibility, speed, and interpretability (in terms of common statistical concepts).

There is one additional concept used that is not part of the traditional approach. In most previous graphical and numerical techniques, there were two separate stages: first, the calibration curve was determined, and second, it was used to find compositions of unknowns. This program goes through both stages automatically for each unknown sample, rather than using the same calibration for all samples of the same general type. The advantage here is that the calibration process itself is influenced by the observed intensities from each unknown: the curve is fit to the standards in a "local" sense (i.e., it is required to agree with those standards most similar to the unknown in intensities), rather than in a "global" sense (a compromise fit to all standards).

The method of automating these concepts is essentially a multivariate nonlinear inverse regression. The "model" (i.e., the mathematical function for the calibration curve) is a slight generalization of that used by Lachance (1964); its parameters ("influence coefficients") are determined by a weighted least-squares procedure with local emphasis. The composition of the unknown is obtained by solving the model equations for the amounts of the components, taking account of any fixed amounts and fixed total amount.

For EMPIRICAL analysis, the standards used in the regression are all the standards defined by the user. For the FULL analysis option (which includes physical theory), the same regression method is used, but standards are used in an indirect fashion. In particular, the regression is not done on the user-defined standards, but on "simulated" standards. Simulated standards consist of hypothetical compositions and corresponding theoretical intensities generated automatically by the program. The user-defined standards are used to adjust the theoretical calculations, to make them agree with the real standards that are most similar to the unknown.

When the FULL option is used (the default situation), there is also an automatic iteration of a simulation-regression cycle. For each successive estimate of sample composition, the program scales the amounts to 100 per cent, simulates a standard with the resulting composition, adds it to the existing list of simulated standards, and repeats the regression to obtain the next estimate of sample composition. The simulation-regression cycle is repeated until one of the three convergence criteria is satisfied (see STEP, page 21). When the iteration is finished, the program outputs the final estimate of composition.

Output of various statistics is optional (see Section 7, pages 15-17). Propagated errors (imprecision in calculated amounts, due to imprecision in measured intensities for the unknown) are obtained by a common statistical approximation that uses the sensitivities of each amount to each intensity; values of these sensitivities (partial derivatives) are obtained by solving differentiated forms of the model equations.

Regression Methods

This outline of the regression methods parallels the outline given earlier for the usual graphical procedure.

First, one has standards — i.e., given compositions and corresponding intensities. For EMPIRICAL analysis, these are the user-defined standards; for the FULL option, they are simulated standards whose intensities are forced to be consistent with the real standards most like the unknown.

Second, one has a regression model -- i.e., a mathematical expression used to approximate the known data, especially in the composition range of interest. The model used in this program was devised for its mathematical properties; in many cases, it is very similar to the expression used by Lachance (1964) and others. The model expresses intensity as a nonlinear function of weight fractions and other parameters. One way of expressing the model is given in Section 9 (page 22), under COEFFICIENTS.

Third, one has a method for fitting the model to the available data, in order to calculate values for the parameters (e.g., the "influence coefficients"). In this program, there can more information available than the minimum necessary (the problem would be overdetermined), so the fitting would not be exact for all data. The program takes advantage of excess information by using a weighted least-squares criterion that places emphasis on those standards with the smallest assumed errors in intensities, and on those standards whose intensities are closest to the intensities measured from the unknown. The nonlinear "normal equations" are solved by the standard Newton method.

Fourth, one has a method for finding the composition at which intensities calculated from the regression model agree with the intensities measured. In the general case, excess information can be handled to advantage. This program calculates the composition that minimizes the root-mean-square value of weighted disagreement in intensities: the difference between measured and calculated intensities is divided by the assumed random difference. When the amount of a component is fixed, the corresponding normal equation is replaced by that constraint; when the total amount is fixed, the method of Lagrange is used; solution of the nonlinear equations is by Newton's method. The statistic chi equals the minimum r.m.s. value mentioned above, multiplied by the square root of the number of lines, and divided by the number of degrees of freedom. The number of degrees of freedom equals the number of lines, minus the number of components, plus the number of constraints (total amount fixed, amount of a component fixed, etc.).

Physical Theories and Fundamental Parameters

Theoretical predictions of intensities use formulas that have appeared many times in the literature since the 1920's (see the annotated bibliography, page 28), plus unpublished modifications by this author.

Homogeneous samples are treated using the formulas of Gillam and Heal (1952) for the primary and secondary contributions to intensity.

The incident radiation spectrum is treated by numerical integration (a composite of trapezoid and Simpson's rules).

Wavelengths of absorption edges and emission lines are from the tabulations of Bearden and Burr (1964-1967).

Photoelectric mass absorption coefficients are calculated from the parametric representations of McMaster et al.

Fluorescence yields (considering the effects of Auger and Coster-Kronig transitions) are calculated from the equations and data in Bambynek et al. (1972).

Sample-thickness corrections use Compton's (1929) formula.

Separate particles that do not shadow each other are handled by the formulas of Criss (1976).

Bulk particulate samples are treated using formulas like those for the homogeneous case, except that "effective" absorption coefficients account for overall effects of heterogeneity on x-ray transport, as in Brown, Criss, and Birks (1976), and adjustments are made for fluorescence emission from individual particles, as in Criss (1976).

Program-calculated x-ray tube spectra use the Kramers law (1923) for the generated continuum, and modifications of the expressions of Green and Cosslett (1961) for the generated line intensities (including an approximate treatment of fluorescence by the continuum). The spectrum as generated is adjusted for absorption in the anode using the expression of Philibert (1963), as modified by Duncumb and Shields (1966) and Heinrich (1970). In addition, the spectrum is adjusted to account for absorption in the x-ray tube window (and in any filter or air-path from the tube to the sample). These calculations agree surprisingly well with measurements, especially for the purpose of x-ray fluorescence analysis.

Tabulated x-ray tube spectra are from Gilfrich et al. and Brown et al. (1971-1975).

Use of Standards to Adjust Theoretical Intensities

The physical theories used here express characteristic line intensities in terms of sample composition and other parameters (absorption coefficients, particle sizes, etc.). The intensity units used are RXI — the ratio of intensity from the sample, divided by the intensity of the same line from a thick, homogeneous sample of the pure element. The use of these units does not imply that such a pure-element standard is necessarily measured. Rather, RXI is used so that a number of experimental parameters will cancel out, and thus be eliminated from consideration (for example, x-ray tube current, detector efficiency, and various solid angles).

For each standard that is input, the program calculates the theoretical RXI's. Each measured count rate is divided by the appropriate RXI to produce an "effective pure-element intensity". Since theories (and measurements) are not perfectly accurate, the "effective pure-element intensity" for a given line will vary from standard to standard.

For an unknown, the "effective pure-element intensity" to be used in relating theory and measurement is a weighted average of the values obtained from the various standards. The "weights" in this weighted average are designed to favor the values from standards whose intensities are most like the intensities from the unknown, and the standards for which the assumed errors in intensities are the smallest. These two weighting criteria are balanced in such a way that if an unknown happened to be the same as one of the standards already measured, then the caclulated composition would be the same as the composition of that standard, with an uncertainty corresponding to the uncertainty in intensities.

The treatment just described is the essence of how this program represents a continuous blend of regression and theoretical approaches. In effect, physical theory provides the "shape" of the calibration relations, and standards are used to scale the theory to match the experimental reality. When very few standards are available, or when they are very different from the unknown, then the burden is on theory to have the correct "shape". On the other hand, when even one standard is avaliable that is reasonably similar to the unknown, then it matters very little what errors might exist in the theory or in the "fundamental parameters" (such as x-ray tube output, absorption coefficients, and fluorescence yields).

APPENDIX D. Format for the Spectrum-File XRDATS

The data file XRDATS contains tabulated incident spectra that are read automatically by the program whenever they are referenced by name in a group of LINES data.

Each spectrum is labeled by a name that begins with a letter and consists of not more than 8 letters and digits. The spectrum name must be left-justified in the first 10 character-positions of a line (not counting a 5-digit sequence number and a blank).

For each spectrum, all data besides the name are in free-field format. That is, data may occur anywhere in a line (except following a "#"), and are separated from each other by one or more blanks or commas.

The first datum following the spectrum name is the number of tabulated points. Each tabulated point consists of a pair of data: a wavelength (in angstroms) and an "intensity" (as described next).

After the number of points (which includes both lines and points on a continuum), one puts first the lines, arranged by increasing wavelength. The "intensity" of a line is the total intensity emitted from the source, in units of photons per steradian. The intensity units may also include "per second", "per milliamp", "per millicurie", or other units that do not involve wavelength or photons.

After the lines (if any), come the points from the continuum (if any), arranged by increasing wavelength. The first point must have an intensity equal to zero, to signal the program that subsequent points are from a continuum. The "intensity" of each subsequent point must be in units of photons per steradian per angstrom (plus any optional units used for the lines). The spacing of these points need not be equal by wavelength, but should be close enough to permit acceptable linear interpolation on a graph of log intensity vs wavelength. Discontinuities (edges) in a continuum are represented by having two successive points with exactly the same wavelength; the two intensities are for the short-wavelength and long-wavelength sides of the edge.

After all data for a spectrum, the next spectrum is formatted as described above. The word "END" in place of a spectrum name signals the end of the spectrum file.

Remarks may occur anywhere; a remark consists of the character "#" plus the remainder of the line.

Following is an example file XRDATS, not including the 5-digit card-number and blank that preceed each card-image. Notice the free use of remarks in the file.

```
 # THIS EXAMPLE FILE CONTAINS CD109, CR45C, W45C
 #--------------------------------------------------------------
CD109       # CADMIUM 109 ISOTOPE SOURCE
1           # NUMBER OF POINTS (CONSIDERING ONLY SILVER KA)
 .559 1     # THE WAVELENGTH AND INTENSITY (PHOTONS/STERADIAN)
 #--------------------------------------------------------------
CR45C       # PHILIPS  CR-TARGET  FAQ 60/1  AT 45 KV (CP)
            # BASED ON MEASUREMENT AND CALCULATION:
            # D.B. BROWN, J.V. GILFRICH, AND M.C. PECKERAR,
            # JOURNAL OF APPLIED PHYSICS 46, P 4537 (1975)
            #
22          # NUMBER OF TABULATED POINTS
            # 2 K LINES; UNITS: PHOTONS/STERADIAN/ELECTRON
2.0849 8.59E-5  2.2910 51.4E-5
            # NOTE: K BETA INTENSITY REVISED BY J.V. GILFRICH
0.27 0.0    # BEGINNING OF CONTINUUM
            # UNITS: PHOTONS/STERADIAN/ANGSTROM/ELECTRON
0.32  8.0E-5   0.36 11.2E-5   0.40 13.3E-5   0.45 14.8E-5
0.50 15.4E-5   0.60 15.2E-5   0.80 13.6E-5   1.00 11.8E-5
1.50  7.1E-5   2.00  4.1E-5   2.07  3.8E-5   2.07  7.6E-5
2.50  5.3E-5   3.00  3.3E-5   3.50  1.9E-5   4.00 0.98E-5
4.50 0.46E-5   5.00 0.19E-5   5.50 0.069E-5  # END OF CONT.
 #--------------------------------------------------------------
W45C        # PHILIPS   W-TARGET  FAAQ 60/3.5  AT 45 KV (CP)
            # BASED ON MEASUREMENT AND CALCULATION:
            # D.B. BROWN, J.V. GILFRICH, AND M.C. PECKERAR,
            # JOURNAL OF APPLIED PHYSICS 46, P 4537 (1975)
            #
28          # NUMBER OF TABULATED POINTS
            # 9 L LINES;  UNITS: PHOTONS/STERADIAN/ELECTRON
1.0620 0.139E-5 1.06861 0.185E-5 1.0986 1.22E-5
1.2454  3.06E-5 1.2627    1.00E-5 1.2818 6.63E-5
1.3016  1.00E-5 1.4776   10.7E-5 1.6782 0.364E-5
0.27 0.0    # BEGINNING OF CONTINUUM
            # UNITS: PHOTONS/STERADIAN/ANGSTROM/ELECTRON
0.32 17.5E-5 0.36 31.0E-5 0.40 37.0E-5 0.45 39.3E-5
0.50 38.5E-5 0.60 34.3E-5 0.70 30.0E-5 0.90 22.3E-5
1.02 18.7E-5 1.02 19.8E-5 1.07 18.4E-5 1.07 20.2E-5
1.15 18.0E-5 1.22 16.4E-5 1.22 22.3E-5 1.50 14.9E-5
2.00  6.8E-5 2.50  2.6E-5  # END OF CONTINUUM
 #--------------------------------------------------------------
END         # MARKS THE END OF THE SPECTRUM FILE
```

APPENDIX E. Format for Compounds-Definition File XRDATC

The data file XRDATC contains definitions of multielement materials, for automatic access by the program NRLXRF.

The name of a compound (or other fixed combination of elements) consists of a word beginning with a letter, and containing not more than 8 letters and numerals. The name is left-justified in the first 11 character-positions of a card-image (not counting a 5-digit card-number and a blank). The remaining data for each compound may occupy any character-positions after the first 11, and are in free-form format. That is, data may occur anywhere in a line (except following a "#"), and are separated from each other by one or more blanks or commas.

After the name, the first datum is the density (grams per cubic centimeter); the next is either an "AT" or a "WT", according to whether the elemental proportions are to be input by number of atoms or by weight. The next datum is the number of elements in the compound. Next are the pairs of element symbols and proportions.

The data for a compound may occupy more than one line; however, lines after the first (which contains the name) should be blank in the first 10 character-positions.

The word "END", placed as though it were a compound name, signals the end of the list of compound-definitions.

Remarks may occur anywhere; a remark consists of the character "#" plus the remainder of the line.

Below is an example file XRDATC, including the arbitrary line numbers.

```
10010 EARTH      2.7 WT 8
10020            O 47 SI 28 AL 8 FE 5 MG 2 CA 3.6 NA 3 K 2.6
10030 AIR        0.0012 WT 2 N .8 O .2
10040 FIRE       0.0006 AT 4 C 3 H 4 O 8 N 28
10050 WATER      1. AT 2 H 2 O 1
10060 ETHER      2.E-29 AT 1 H 1
10080 MYLAR      1.40 AT 3 C 5 H 4 O 2
10110 CACO3      2.71 AT 3 CA 1 C 1 O 3
10150 AL2O3      3.97 AT 2 AL 2 O 3    # ALPHA ALUMINA
10160 SIO2       2.64 AT 2 SI 1 O 2    # ALPHA QUARTZ
10180 IRON       7.87 AT 1 FE 1
10200 CB         8.58 AT 1 NB 1
10210 LI2B4O7    1.4 AT 3 LI 2 B 4 O 7
12345 END        # MARKS THE END OF THE FILE XRDATC
```

APPENDIX F. Format for the Physical-Parameters File XRDATP

The data file XRDATP contains various physical parameters for the elements -- mainly line and edge wavelengths, and parameters for calculating absorption coefficients. The data are read automatically, as needed.

The first 5 columns of each card image are used for the card number, which is interpreted by the program as follows. The first 3 digits make a number that equals 100 plus the atomic number of the element to which the remaining data on the card apply. The last 2 digits of the card number make a number that is the "index" of the first of the remaining 5 data on the card, which are formatted by the Fortran FORMAT "1X,5E12.6".

The "index" can range from 1 to 55. The value of the index within the line number may be 1, 6, 11, 16, 21, 26, 31, 36, 41, 46, or 51. For each element, the physical parameters associated with the various indices are given below. Some indices are not used. The program itself contains data for fluorescence yields, Auger and Coster-Kronig transition probabilities.

1	maximum index necessary to treat wavelengths less than 12.4 A. (the program does not treat absorption edges and emission lines outside this range)
2, 3	(not used by NRLXRF)
4....7	coefficients in a third degree polynomial representation of ln(tau) vs. ln(energy), for energies (in keV) greater than the K-edge energy, where tau is the photoelectric-absorption cross section (barns per atom).
8...15	(not used by NRLXRF)
16	K-edge wavelength (angstroms)
17, 18	K alpha and K beta emission wavelengths
19, 20	(not used by NRLXRF)
21	K-edge jump

22...24	coefficients in a second degree polynomial representation of ln(tau) vs. ln(energy), for energies (in keV) less than the K-edge energy, but greater than the L-III edge energy, where tau is the photoelectric-absorption cross section (barns per atom).
25...27	wavelengths of the L-I, L-II, and L-III edges
28...30	wavelengths of the L alpha 1, L beta 1, and L beta 2 emission lines.
31...40	(not used by NRLXRF)
41	L-III edge jump
42...43	coefficients in a first degree polynomial representation of ln(tau) vs. ln(energy), for energies (in keV) less than the L-III edge energy, but greater than the M-V edge energy, where tau is the photoelectric-absorption cross section (barns per atom).
44...48	wavelengths of M-I, M-II, M-III, M-IV, M-V edges
49	wavelength of the M alpha 1 emission line
50...51	coefficients in a first degree polynomial representation of ln(tau) vs. ln(energy), for energies (in keV) less than the M-V edge energy, where tau is the photoelectric-absorption cross section (barns per atom).
52...55	(not used by NRLXRF)

Following are example data for lead (atomic number 82)

```
18201  .510000E+02            0 .113000E+02 .863374E+01 .369400E+01
18206 -.121312E+01 .774601E-01            0           0           0
18216  .140900E+00 .165376E+00 .145970E+00           0           0
18221  .478900E+01 .177963E+02-.237691E+01-.455883E-01 .781900E+00
18226  .815400E+00 .950700E+00 .117501E+01 .982910E+00 .982210E+00
18241  .246600E+01 .167131E+02-.261538E+01 .321700E+01 .349200E+01
18246  .404700E+01 .475700E+01 .495500E+01 .528600E+01 .145771E+02
18251 -.225279E+01            0           0           0           0
```

APPENDIX G. General Documentation for Implementation

Computer Configuration

The July 1977 version of the program runs on the Naval Research Laboratory DEC-10 timesharing computer. The essential hardware includes a KA10 processor, a 192K memory, RP03 disk drives, and a DC76 communications system. In addition, a TU20A 9-track tape unit is used to load the program initially. The operating system is TOPS-10, version 6.02.

Source Language

The program is written in a fairly standard Fortran IV. The specific compiler used at the Naval Research Laboratory is DEC FORTRAN 10, version 4A.

The program should be readily convertible to many other large computers whose Fortran compilers accept ANSI Fortran (American National Standards Institute X3.9-1966) and also allow the following non-ANSI features: (1) DATA statements in this program use array names, rather than listing array elements separately; (2) ENCODE and DECODE are used; however, these statements may be eliminated and the statements (now comments) beginning with "C:SCR" used instead — they use a scratch file, rather than core, for re-writing and re-reading input data; (3) this program assumes that no variable becomes undefined upon execution of a RETURN statement; (4) OPEN statements are used to set up files and establish parameters for input/output operations; analogous statements would be required for different compilers -- the program contains statements (now comments) beginning with "C:CDC" that are suggested for use on CDC 6400 timesharing.

Memory Required

The July 1977 version of the program runs in about 58K 36-bit-bytes of core on the DEC PDP-10 computer. The memory requirements can be reduced significantly by reducing the sizes of arrays, as described in comment statements in the source listing.

Further reduction in core size can be achieved by eliminating subprograms that are not essential to the kinds of problems to be run. Appendices H and I outline the program architecture and discuss specific ways to reduce core requirements.

Implementation Instructions

For the Naval Research Laboratory DEC-10 timesharing computer, implementation is straightforward. The source program is copied onto disk and given any file name desired (e.g., NRLXRF). The data files provided with this program are copied onto disk with the names XRDATP. XRDATS, and XRDATC.
Optional data files XRDAT2, XRDAT3, and XRDAT4 may be created by whatever editor is convenient (e.g., SOS). Since the magnetic tape is not in the particular format required by the PDP-10, one must copy to disk by means of a program called "CHANGE". The specific timesharing commands used to establish the disk files at NRL are illustrated below, where the magnetic-tape identification is "P540", and the tape unit assigned by the MOUNT command is "MTA001".

```
.MOUNT MTA: /REELID:P540
.REWIND MTA001
.R CHANGE
> RETAIN
> =MTA1:/BLOCK:1 /REC:80/MODE:EBCDIC/NOREWIND:ALWAYS/IND
> DSK:NRLXRF/REC:80/MODE:ASCII
> RUN
> DSK:XRDATP
> RUN
> DSK:XRDATS
> RUN
> DSK:XRDATC
> RUN


> EXIT
.REWIND MTA1:
.DISMOUNT MTA1:
```

Installers are strongly urged to retain the sequence numbers that occur in columns 73-80 of the original source file, or move them to the position of line numbers, which are handy for many timesharing systems. These numbers are particularly useful in checking the program against the listing, and in making any updates or fixes that might be announced later.

Compilation can be accomplished, once and for all, by

```
.LOAD NRLXRF
.SAVE NRLXRF.SAV
.DELETE NRLXRF.REL
```

Then, the program can be run by the command

```
.RUN NRLXRF
```

APPENDIX H. Program Architecture

List of Subprograms

The program consists of a main program plus 65 subprograms, including 48 subroutines and 17 function subprograms. Below is a list of subprogram names. Function-subprogram names end with the letter "F"; subroutine names do not.

RESET
SAMP
YNORM
LINE
SPIN
WEF
SPECW
EXP2F
COEFS
ADJB1
SIM6
EMACF
IN2
NEXTQ
DUMPS
COMP
JZYS
PREP
FLF
ITER
ADJB
DISTF
SIMP
DEFD
CMACF
SOLV
ERROR
SNORM
SPEC
QUAN
JLDF
YXF
DOTF
GAMBS
SIM
EXP1F
ATWTF
TUBE
SOLV2
KUF
MEAS
MAC
UNK
AF
POINT
NORM
XSF
YBAR
SIM4
ZABD
FCHIF
SOLV3
COND
XSAMP
DEFIN
XTOC
WLF
SORT
SETA1
SSTDS
SIM2
SIMR
FHETF
IN
FILIO

Input/Output Device Assignments

In the July 1977 version of the program (for DEC Fortran-10 timesharing), input is from the terminal and six disk files, and output is to the terminal and one disk file. The following table gives the I/O device number used in READ and WRITE statements, the kind of I/O operation, the kind of device, the file name (if disk), and the sort of information transferred. Unit 2 is not used in the original version — it does not apply unless one must modify the program to avoid ENCODE and DECODE statements, as described below.

Unit	Purpose	Device, File		Information Transferred
1	READ	disk	XRDATS.	incident spectra
#2	READ/WRITE	disk	XRSCR.	input scratch file (optional)
3	READ	disk	XRDATC.	compounds definitions
4	READ	disk	XRDATP.	elements' physical parameters
5	READ	terminal (TTY)		user-supplied input
6	WRITE	terminal (TTY)		program output
7	READ	disk	XRDAT2.	alternate user-supplied input
8	WRITE	disk	XROUT.	alternate program output
9	READ	disk	XRDAT3.	alternate user-supplied input
10	READ	disk	XRDAT4.	alternate user-supplied input

not used unless ENCODE and DECODE are disabled (see below).

The device assignments summarized above are all made in the subroutine FILIO, which would need to be modified slightly for computers other than the DEC-10. Specifically, FILIO uses the Fortran-callable system routines OPEN and CLOSE. For each file, data are accessed sequentially; all data are presumed to be ASCII (rather than binary); no file is both read and written (unless unit 2 is used — see next section); each file is automatically saved upon normal termination of the program (not all files are released explicitly with a CLOSE command). The detailed descriptions of the OPEN and CLOSE commands may be found in the appropriate DEC manuals — e.g., DECsystem-10 Fortran-10 Language Manual. Subroutine FILIO contains comments that suggest analogous commands for use on CDC Kronos timesharing. Subroutine FILIO is called from the main program, from subprogram SPIN, from subprogram AF, and from subprogram DEFD.

Free-Field Input

User-supplied input is read by subroutine IN2, which picks off the appropriate number of data from a card image of free-field input, and then ENCODEs the data in a format that is easily DECODEd. The various subprograms acquire such user-supplied data by calling subroutine IN, which calls IN2; then the data are made available by DECODE statements following the calls to IN. An alternative method is available for compilers that do not allow ENCODE and DECODE: one may disable all ENCODE and DECODE statements, and implement the statements (now comments) starting with "C:SCR"; in that way, one replaces the ENCODE/DECODE method by WRITEs and READs of the disk file XRSCR (unit 2 in the table above).

Subprograms Handling Input

The only READ statements in the program (unless DECODE statements have been disabled) occur in the subprograms SPIN, DEFD, AF, and IN2. Subroutine SPIN obtains tabulated x-ray spectra from the data file XRDATS, where only the spectrum name is formatted -- other data are in free-field form (see the Users' Reference Manual, Appendix D). Like SPIN, subroutine DEFD requires only the name of a component to be formatted (in the file XRDATC). Function subprogram AF reads the data file XRDATP, which contains only formatted data. Subroutine IN2 reads all free-field input (from the terminal, from regular batch input, or from the data files XRDATS, XRDATC, XRDAT2, XRDAT3, or XRDAT4).

All free-field input is read initially in subroutine IN2, which ENCODEs each card-image input, using formats that are easily DECODEd. Subroutine IN2 is called only from subroutine IN. MAIN calls IN only to initialize various parameters. ERROR calls IN only to reset a parameter. DEFD calls IN only to obtain the definition of a multielement component from the file XRDATC. Besides MAIN, ERROR, and DEFD, the subprograms that CALL IN and/or DECODE data are listed below, along with the routines that call them:

subprogram	called from
NEXTQ	MAIN
COND	NEXTQ (from MAIN) LINE (from MAIN)
SAMP	MAIN NEXTQ (from MAIN) SNORM (from MAIN) MEAS (from MAIN)
SNORM	MAIN
MEAS	MAIN
COMP	MAIN
SPEC	COND (from LINE (from MAIN))
MAC	NEXTQ (from MAIN)
DEFIN	MAIN
LINE	MAIN
SPIN	SPEC (from COND (from LINE (from MAIN)))

All keywords are read and checked through NEXTQ, which acts directly on many of the simple commands, and which also handles data associated with some keywords. Most data are checked in through the other subprograms listed above.

APPENDIX I. Program Modification

This Appendix discusses modifications designed mainly to reduce core requirements, either to save running costs or to implement the program on smaller computers -- perhaps even the larger minicomputers, if they have floppy disks or other high-speed multi-channel I/O capabilities. Three approaches will be mentioned: changing array sizes, making separate programs, and eliminating optional features.

Changing Array Sizes

On the NRL DEC-10 system, core requirements can be reduced from about 58K to as little as about 30K just by changes in array sizes. Comment statements at the beginning of the main program are designed to help the programmer make such changes. There are seven integer variables in the labeled common /MXS/ that are set in a DATA statement and then used throughout the program to test input data and calculations against array sizes. These seven parameters include the maximum number of samples that may be treated together, the maximum number of components, etc. The array sizes that are consistent with the values of these parameters are given in comment statements following COMMON statements in the main program, and following many DIMENSION statements elsewhere.

Making Separate Programs

The major functions of the program can be separated into simulation and analysis. The full program combines these two kinds of calculations automatically, under the default analysis option (FULL). However, the analyst may simulate specified hypothetical standards and use them along with measured standards in the empirical regression analysis of unknown materials (see keywords SIMULATE and EMPIRICAL). This analysis scheme can be implemented just as well with two separate programs -- one program would use physical theory as necessary to calculate expected x-ray intensities from standards, and output the results in program-readable form (see keyword DUMP); the other program would use simulated and measured intensities to analyze unknowns, and would not use any "fundamental parameters" or physical formulas. Two separate programs (NRLSIM and NRLEMP) can be created from NRLXRF in a straightforward way, as described below. Each of them requires significantly less core than the full program. The analysis-only program (NRLEMP) offers the greatest savings in core, especially if one also reduces array sizes and drops optional features.

Making a Simulation-Only Program

To convert from NRLXRF to NRLSIM, as discussed above, one eliminates eleven subprograms that apply only to analysis:

UNK
ITER
SETA1
ADJB
GAMBS
COEFS
YBAR
ADJB1
SOLV
SOLV2
SOLV3

One also deletes other sections of coding occurring between pairs of comment statements containing the phrase "OMIT FROM NRLSIM". The resulting program will then not process the keywords ANALYZE, SUM, FULL, EMPIRICAL, THEORETICAL, STEP, COEFFICIENTS, BFIXED, and BFREE. One might also change FORMAT statements in MAIN and NEXTQ to reflect the program changes.

Making an Analysis-Only Program

To convert from NRLXRF to NRLEMP, as discussed earlier, one eliminates 31 subprograms that apply only to calculations using physical theory (i.e., simulation):

COND
SNORM
YNORM
SPEC
MAC
SPIN
PREP
JLDF
AF
WLF
WEF
FLF
YXF
POINT
SORT
SPECW
DOTF
EXP2F
ADJB
SIM
SIM2
SIMP
EXP1F
SIM4
SIMR
SIM6
FHETF
EMACF
CMACF
TUBE
FCHIF

One also deletes other sections of coding occurring between pairs of comment statements containing the phrase "OMIT FROM NRLEMP". The resulting program will then not process the keywords PREDICT, THEORETICAL, FULL, CONDITIONS, SIMULATE, MAC, and NORMALIZE (intensities can be scaled by using the keyword MULTIPLIERS, which remains valid). To avoid the necessity of using EMPIRICAL, change the value of the variable KONT from 1 to 2 in the appropriate data statement in subroutine NEXTQ; also in that subroutine, change one of the IF statements

from `IF ( HTEST.EQ. HRES) KONT= 1`

to `IF ( HTEST.EQ. HRES) KONT= 2`

Also, FORMAT statements in MAIN and NEXTQ should be revised to reflect the program changes.

Eliminating Optional Features

Some reduction in core requirements can be made if some features of NRLXRF are not needed. We offer examples of easy modifications that can be made independently of each other.

MAC keyword to be dropped --
omit subroutine MAC and the reference to it in NEXTQ.

COEFFICIENTS keyword to be dropped --
omit subroutine COEFS and the reference to it in MAIN.

LIST and DUMP keywords to be dropped --
omit subroutine DUMPS and the two references in NEXTQ.

DEFINE keyword to be dropped --
omit subroutine DEFIN and the reference to it in MAIN.

calculation of x-ray tube spectra to be dropped --
omit subroutines TUBE and FCHIF, and in each of subroutines COND and SPIN, omit the section of coding between the pair of comment statements containing the phrase "ONLY IF X-RAY TUBE SPECTRUM IS CALCULATED".

data file XRDATC to be dropped --
in subroutine DEFD, omit the four sections of coding between pairs of comment statements containing the phrase "ONLY IF DATA FILE XRDATC IS USED".

data file XRDATS to be dropped --
in subroutine SPIN, omit the section of coding between the pair of comment statements containing the phrase "ONLY IF DATA FILE XRDATS IS USED".

optional input/output files to be dropped --
in the MAIN program, omit the appropriate "CALL FILIO" statements, according to the comment statements that describe the various I/O devices and unit numbers.

By making all these modifications to NRLXRF, one shortens the source code by more than 700 statements and reduces the core requirements by about 7K bytes. Dropping other features (except for conversions to NRLSIM or NRLEMP) generally would produce little savings or would be more complicated. Much of the core requirement is a result of the flexible input and output features.

INDEX TO PROGRAM-INTERPRETABLE WORDS

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