COSMIC PROGRAM # DOD-00065

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

Users' Reference Manual and General Documentation

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COSMIC PROGRAM # DOD-00065

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

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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IN REPLY REFER TO: 6680JWC

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
58313       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.

```
 1345C: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
  1011      BLOCK DATA
  1021      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.

```
 34134C: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
 3209        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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IN REPLY REFER TO:

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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IN REPLY REFER TO:

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.