

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

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## ABSTRACT

The Naval Research Laboratory computer program for quantitative x-ray fluorescence analysis (NRLXRF) is designed to optimize the data reduction scheme for relating measured x-ray intensities to the chemical composition of a wide variety of sample types. The mathematics are versatile and large masses of data can be manipulated. The Usersí Guide introduces the potential user to the program by specifying the input requirements and format for three alternative methods of using the program:

1. To analyze unknown bulk samples using multicomponent standards;
2. To predict effects of particle size and chemical composition on the x-ray intensity emitted by thin samples such as particulate pollution collected on filters; and
3. To predict the relative x-ray intensity for bulk samples.

Annotated example runs of each of these options are given to assist the user in becoming familiar with the program.

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for X-Ray Fluorescence Analysis:  
Users' Guide

INTRODUCTION

The Naval Research Laboratory (NRL) computer program for quantitative x-ray fluorescence analysis employs both fundamental-parameter equations and influence-coefficient equations in order to optimize the matrix corrections for multicomponent samples. In its present form it requires a large computer such as the Digital Equipment Corporation PDP-10 but is very efficient and generally costs between \$0.10 and \$5.00 per sample for analysis (depending, of course, on how computer costs are charged). As a more concrete estimate of costs, all of the examples illustrated in this Users' Guide cost \$3.00 (total) to run in the interactive time-sharing mode on the NRL PDP-10 computer.

The program is extremely versatile in several respects:

- It treats both homogeneous and heterogeneous samples.
- Up to 20 components and 50 standards can be considered simultaneously.
- Components can be either elements or compounds.
- Particle size effects can be treated in bulk powders or thin pollution samples.
- Corrections for background and counting rate (dead time) are made automatically.
- Either pure elements or intermediate standards or a combination of both can be used to analyze the data.
- The amount of a component may be fixed in an unknown (as for fluxes, binders, diluents, dopants, internal standards, minor elements not measured, etc.).
- Either batch processing or time sharing may be used.
- Other capabilities are mentioned in the Reference Manual.

In this Users' Guide, three different kinds of problems are described and illustrated by examples. These are:

Option 1. For bulk samples, analyze an unknown using whatever pure elements and intermediate standards are available.

Option 2. For thin samples such as for pollution analysis, predict effects of particle sizes and composition (requires assumed particle sizes, etc.).

Option 3. For bulk samples, predict the relative x-ray intensities for any assumed composition.

## BACKGROUND

The matrix effects of interelement absorption and secondary fluorescence (enhancement) have been recognized in x-ray analysis for many years. Many approaches for their correction in quantitative analysis have been proposed and used with varying success. The most common approach has been the use of equations in which empirical coefficients representing interelement effects are determined from a set of intermediate standards and then used in equations for analyzing unknown compositions. The limitations of this empirical equation approach include the fact that different standards must be used for each different type of sample, i.e. alloys of similar composition must be used to establish the empirical coefficients for alloys, powders of similar composition and particle size must be used to establish the coefficients for powders, etc. Computers are usually used even with empirical equations for systems of more than three components but generally small dedicated computers suffice.

The less common approach to correct for matrix effects relies on the fundamental parameters such as absorption coefficients, fluorescent yields, jump ratios, and incident spectral distributions. This approach has the important advantage that the standards need not be similar in composition to the unknowns; they may be pure elements or one known compound for each element of interest, or one multi-component standard. It is less necessary to use a different set of standards to analyze some new type of sample, and any number of components can be handled with equal facility. The present program is configured for large computers partly because it is relatively easy to convert from one large computer to another. With extensive revision it probably could run on some minicomputers equipped with floppy-disk storage. (Additional cost per sample to use the more versatile fundamental parameter program compared to using regression equations are negligible in terms of overall analytical costs.)

At NRL we have devoted considerable effort to developing, improving, and simplifying a combination approach which uses the fundamental parameters plus whatever standards the analyst cares to supply. The estimate of composition of the unknown is obtained by iteration loops in which hypothetical standards are generated internally and adjusted to agree with the real standards. For highest accuracy, at least one multicomponent standard similar to the unknown is required.

The present version of the program contains many built-in capabilities which are deliberately concealed from the user unless he requests them explicitly. It has been prepared so that an inexperienced user can carry out the most-wanted options readily without worrying about details that are of no interest to him. By this means he can become familiar with, and confident in the use of, the method in the most painless fashion. We believe that once a user has tried the program he will find it far more convenient and accurate than less sophisticated approaches.

#### A NOTE ON INCIDENT SPECTRA

The program as issued in 1977, contains in data files the accurate spectral distributions for specific x-ray tubes (Cr target-Philips FAQ 60/1; Rh target-Machlett SEG 50H; W target-Philips FAAQ 60/3.5) operated at 45 kV. If appropriate to the analytical conditions used, one of these spectra may be called for by specifying CR45C, RH45C or W45C as illustrated in some of the examples following. The use of targets other than those three elements and/or voltages other than 45 kV is facilitated by the capability in the program to calculate spectra for any target element at any operating voltage and for specific geometrical considerations (x-ray take-off angle and Be window thickness). While these calculated spectra are good approximations, their use is most dependable for the case where at least one multicomponent standard similar to the unknowns is used to mitigate the uncertainties in the fundamental parameters (including the primary spectrum) used in the calculation. If a multicomponent standard is not available, the accuracy will suffer due to these uncertainties.

The user may call for any monochromatic primary radiation (fluorescer emission or effective primary wavelength) by specifying the element line designation, e.g. MO KA, the desired wavelength, e.g. 0.711  $\approx$ , or the energy, e.g. 17.4 keV. In addition, the analyst may add any other spectra to the data file by using procedures described in the Reference Manual.

#### INSTALLING THE PROGRAM

The other documentation supplied with this program includes suggestions for its installation on the user's computer. It is presumed that the x-ray analyst will have initial help from someone versed in computer usage who will instruct him on how to call for the program on time sharing or how to supply data for batch processing.

## EXAMPLES SHOWING THREE OPTIONS

When the program is called for in an interactive mode it will identify itself and then type a symbol (in the illustrations, a small star) at the beginning of a line indicating it is ready to receive information. The user may first type RESET followed by # OPTION 1 (or whatever heading he wishes), followed by another blank line. He is then ready to start entering data. The type of data entered and the form in which it should be entered is shown in the annotated examples below. It should be noted that the user must leave a blank line after each set of data so that the program will know that the set of data is complete.

If the program is used in batch mode, keyword cards, data cards, and blank cards for separating sets of data replace the direct interaction via teletype. There should be one card for each star shown in the examples but the cards should not contain the stars.

It is suggested that the user repeat the illustrations as shown and then repeat again with data from his own samples to become familiar with the procedure.

Option 1: The first option to be illustrated is that which calculates the composition of a bulk unknown using measured x-ray intensities and whatever standards are furnished. This is the option which will be most useful for analysts concerned with alloy specimens or other bulk samples. Note that each line must be measured in some standard but that a single multicomponent standard may suffice. The program will utilize whatever standards or reference samples are supplied.

The first example of Option I illustrates a simple type of input for a bulk steel sample.

\* RESET  
\* #OPTION 1

"OPTION 1" or any other label may be input if desired. Must be preceded by "#" to indicate a remark so that the computer will not act on it.

<pre> * LINES * 1 FE KA 57 40 W45C * 2 NI KA * 3 CR KA * * COMPOSITION SRM1171 * FE 68.3 * NI 11.2 * CR 17.4 * MN 1.80 * * INTENSITIES SRM1171 * 1 265900 20 340 20 2.2 * 2 146271 100 28 10 2.2 * 3 124266 20 281 20 2,2 * 4 512.33 1 0 1 0 * * INTENSITIES STEEL * 1 243676 20 356 20 2.2 * 2 89613 100 28 10 2.2 * 3 149572 20 281 20 2.2 * 4 600 1 0 1 0 * * ANALYZE STEEL </pre>	<pre> "LINEs" identifies the first group of input as the x-ray lines of interest. After the first x-ray line one puts the analysis conditions for that line: incidence angle is 57°, take off angle is 40°, and the primary spectrum is from a W tube, at 45 kV (from the data file). Subsequent lines need no conditions unless they change. A blank line (after the star) indicates that the first input group is ended.  COMPOSITION in percent and name of the one multicomponent standard are entered. The name of this standard is "SRM1171". (The computer only recognizes first eight characters of sample name; samples must be distinguished from one another within these eight characters.)  INTENSITIES are given for the standard, In this example, raw intensities are entered in the following sequence; Line number. Total counts (signal plus background), Time in seconds (signal plus background), Total counts (background), Time in seconds (background), and Dead Time in micro- seconds. Line 4 is given in counts per second, already corrected for background and dead-time.  INTENSITIES for the unknown sample (named "STEEL") are entered in the same format.  Computer instructed to "ANALYZE STEEL" </pre>
---	---



COMPONENT	AMOUNT	Computer prints out the composition of "STEEL" in percent.
FE	66.57	
NI	6.86	
CR	21.77	Operator can call for additional digits (usually they are not significant) by using procedures described in the Reference Manual.
MN	2.13	
(TOTAL)	97.32	

The second example of Option I is a minor variation on the first. In this case, the analytical conditions are specified for all the measurements by using the keyword "CONDITIONS", at any point in the input sequence. Here, the incident spectrum is to be calculated. Note that the conditions can be input following the designation of each line, negating the requirement for the "CONDITIONS" keyword, also permitting different conditions to be used for different lines (see first example of Option 3).

```
* RESET
* CONDITIONS 57 40 W 45 26 1
```

Incidence angle is 57°, take-off angle is 40°, and the primary spectrum is calculated for a W-target tube operated at 45 kV, having a 26° x-ray take off angle and a 1 mm Be window (should be equivalent to measured spectrum used in preceding example).

```
* LINES
* 1 FE KA
* 2 NI KA
* 3 CR KA
* 4 MN KA
*
```

LINES, COMPOSITION of standard and INTENSITIES of standard and unknown are entered as before.

```
* COMPOSITION SRM1171
* FE 68.3
* NI 11.2
* CR 17.4
* MN 1.80
*
```

```
* INTENSITIES SRM1171
* 1 265900 20 340 20 2.2
* 2 146271 100 28 10 2.2
* 3 124266 20 281 20 2.2
* 4 512.33 1 0 1 0
*
```

```

* INTENSITIES STEEL
* 1 243676 20 356 20 2.2
* 2 89613 100 38 10 2.2
* 3 149572 20 340 20 2.2
* 4 600 1 0 1 0
*

```

```

* ANALYZE STEEL Computer told to ìANALYZE STEELî.

```

COMPONENT	AMOUNT	
FE	66.63	Results appear remarkably similar to the previous set, indicating the adequacy of a calculated spectrum when a multi-component standard similar to the unknown is used.
NI	6.86	
CR	21.80	
MN	2.13	
(TOTAL)	97.42	

A third example illustrates the use of pure element standards along with a multicomponent standard.

```

* RESET
* LINES LINES and conditions are input
* 1 FE KA 57 40 W45C Before.
* 2 NI KA
* 3 CR KA
* 4 MN KA
*
* COMPOSITION IRON COMPOSITION and INTENSITIES for
* FE 100 the standards are given. Each
standard is identified by a
name. IRON is the Fe standard,
etc. COMPOSITION is in weight
percent.
* INTENSITIES IRON
* 1 490524 20 708 20 2.2
* COMPOSITION NICKEL
* NI 100
*
* INTENSITIES NICKEL
* 2 2626800 100 336 10 2.2
* COMPOSITION CHROMIUM
* CR 100
*

```

\* INTENSITIES CHROMIUM  
 \* 3 504406 20 818 20 2.2  
 \*

As illustrated in previous examples, pure standards are not required. It is recommended that they be used to provide fixed end points in the calibration.

\* COMPOSITION MANGANESE  
 \* MN 100  
 \*

\* INTENSITIES MANGANESE  
 \* 4 255080 10 3443 100 2.2  
 \*

\* COMPOSITION SRM1171  
 \* FE 68.3  
 \* NI 11.2  
 \* CR 17.4  
 \* MN 1.80  
 \*

COMPOSITION in weight percent is given for the multicomponent standard (named 'SRM1171').

\* INTENSITIES SRM1171  
 \* 1 265900 20 340 20 2.2  
 \* 2 146271 100 28 10 2.2  
 \* 3 124266 20 281 20 2.2  
 \* 4 600 1 0 1 0  
 \*

INTENSITIES for the multicomponent standard are given.

\* INTENSITIES STEEL  
 \* 1 243676 20 356 20 2.2  
 \* 2 89613 100 38 10 2.2  
 \* 3 149572 20 340 20 2.2  
 \* 4 600 1 0 1 0  
 \*

INTENSITIES for the unknown (named 'STEEL') are given.

\* ANALYZE STEEL

Computer instructed to "ANALYZE STEEL".

COMPONENT	AMOUNT
FE	66.57
NI	6.85
CR	21.81
MN	2.13
(TOTAL)	97.37

Again the results are very similar to the previous two examples.

A fourth example of Option 1 deals with the homogeneous sample which results from the fusion of a geological, mineralogical or similar type of material (which may be heterogeneous before fusion) using any of the borate materials. The flux is conventionally added to the sample in a known amount and is an example of the use of a "fixed" component. The example shown here illustrates sample components which are not independent elements (viz. they are compounds).

\* RESET

\* LINES

\* 1 SI KA 60 80 CR 30 26 .3  
\* 2 TI KA  
\* 3 FE KA  
\*

LINES as before.

Here, incidence angle is  $60^\circ$  and take-off angle is  $80^\circ$ , the primary radiation is a Cr tube at 30 kV, having  $26^\circ$  take-off angle and 0.3 mm Be window.

\* DEFINE SIO2 2.64 AT

\* SI 1  
\* O 2  
\*

Components of the sample are compounds which must be defined. First compound is  $\text{SiO}_2$ , its density is  $2.64 \text{ g/cm}^3$  and its definition is given in atomic proportions (AT) rather than weight (WT) proportions.

\* DEFINE TIO2 4.5 AT

\* TI 1  
\* O 2  
\*

Other components of the sample are  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ .

\* DEFINE FE2O3 5.1 AT

\* FE 2  
\* O 3  
\*

\* DEFINE BORATE 1.4 AT

\* LI 2  
\* B 4  
\* O 7  
\*

The flux (named "BORATE") is Lithium Tetraborate.

\* COMPOSITION PELLETT

\* SIO2 ?  
\* TIO2 ?  
\* FE2O3 ?  
\* BORATE 75  
\*

The COMPOSITION of sample (named "PELLET") is unknown except for 75% "BORATE".

\* INTENSITIES PELLETT

\* 1 .083 0  
\* 2 .0065 0  
\* 3 .092 0  
\*

Use of zero for counting time indicates that intensities of the unknown are given as relative x-ray intensity (RXI). RXI is the intensity of a given line in a multielement sample divided by the intensity of the same line from a pure sample of same element. No data for standards need be input.

\*ANALYZE

COMPONENT	AMOUNT
S1O2	23.42
T1O2	0.21
FE2O3	2.11
BORATE	75.0000 (FIXED)
(TOTAL)	100.74

Computer is told to ANALYZE.  
Sample name is omitted. Last sample named (PELLET) will be treated.  
Computer prints out the composition of "PELLET" in terms of the components which were defined. Since no multicomponent standard was used, these results are purely fundamental parameter.

\* ELEMENTS

SI	10.9450
TI	0.1237
FE	1.4788
O	62.8619
LI	6.1547
B	19.1781

After "ANALYZE" the results can be called for in terms of the ELEMENTS also.

A fifth example of Option 1 calculates the composition of a bulk heterogeneous unknown using measured x-ray intensities and whatever standards are furnished. This option requires that the analyst have some knowledge, or can make some reasonable assumptions, of the degree of heterogeneity of the samples such as particle sizes and voids fractions.

\* RESET

\* LINES

\* 1 SI KA 60 80 .496 A  
\* 2 TI KA  
\* 3 FE KA  
\*

LINES as before.

The primary radiation is defined by its wavelength.

\* DEFINE SIO2

\* SI 1  
\* O 2  
\*

Since "RESET" was used components must be redefined.

\* DEFINE TIO2 4,5 AT

\* TI 1  
\* O 2  
\*

\* DEFINE FE2O3 5.1 AT

\* FE 2  
\* O 3  
\*

COMP RAWMIX PARTIC 100 .1 10 Parameters of importance in  
 SIO2 ? 30 describing heterogeneity need  
 TIO2 ? 5 to be given, including particle  
 FE2O3 ? 20 sizes of compounds. Sample is  
 thick (100 g/cm<sup>2</sup>), has 10% voids  
 (0.1) and void size is 10 µm.  
 Unknown percentage of components  
 is listed as î?î, their particle  
 sizes are 30,5 and 20 µm,  
 respectively.

\* INTENSITIES RAWMIX INTENSITIES of the lines from  
 \* 1 .23 0 "RAWMIX" are given in RXI for  
 \* 2 .017 0 this example. Again, no  
 \* 3 .31 0 multicomponent standard is used.  
 \*

\* ANALYZE RAWMIX

COMPONENT	AMOUNT
SIO2	59.72
TIO2	2.52
FE2O3	37.66
(TOTAL)	99.89

The computer prints out the  
 results of the calculation.

Option 2 is used for particulate samples deposited on a thin substrate at small mass-thickness (small enough so that it can be assumed the particles do not shadow each other); the program predicts the effects of particle size and chemical composition on the emitted x-ray intensity. This option is particularly applicable to environmental samples such as the particulate material collected out of air or water on filters or impactor stages. The analyst must estimate particulate sizes and chemical composition for the material which he expects to deposit on his collection substrate.

\* RESET

\* # OPTION 2

\* LINES LINES as before. This time the  
 \* 1 S KA 57 40 CR45C tabulated Cr tube is used.  
 \*

```

* DEFINE N2H4SO4 1.796 AT      A particular material of interest
* N 2                          is defined [(NH4)2SO4, ammonium
* H 8                          sulfate].
* S 1
* O 4
*
* COMP SULFATE SEPARATE      COMPOSITION of the compound
* N2H8SO4 1.E-6 10          (here named "SULFATE") is
*                             identified as SEPARATE particles
*                             at 10-6 g/cm2 mass per unit area
*                             and 10 μm in size.

* PREDICT SULFATE           The computer then prints out the
                             intensity XI for the defined sample
                             divided by the intensity XI0 for
                             the same mass per unit area at zero
                             particle size (i.e. without
                             absorption effects).

LINE XI/XI0
1 S KA 0.782840

```

Option 3: The third option to be illustrated is that which predicts relative x-ray intensities for bulk samples of any assumed composition. This option is useful for establishing the intensity-versus-composition relation for a set of simulated standards, for examining the effect of filters placed in the primary x-ray beam, the effect of primary spectra, etc.

The first example of Option 3 predicts the relative x-ray intensities for a bulk homogeneous sample.

```

* RESET

* # OPTION 3                  Identify # OPTION 3.

LINES                          LINES and measuring conditions
1 V KA 57 40 W45C             introduced as for OPTION 1.
2 CR KA
3 FE KA
4 W LA1 57 40 W45C NI .03     For the W LA1 calculation a Ni
                               primary beam filter, 0.03 g/cm2
                               in thickness, is assumed. If a
                               calculated spectrum were used, the
                               filter and its thickness would
                               be listed after the complete
                               specification for the tube (e.g.
                               following the CR 30 26 .3 in the
                               line for Si in the example on the

```

```

* COMPOSITION STEEL
* V 3
* CR 5
* FE 73
* W 19
*
* PREDICT STEEL

```

Next keyword indicates that COMPOSITION of sample will be given. ("STEEL" is a name which identifies the sample.) Each line lists an element and its concentration in percent

Computer is told to PREDICT RXI for the ìSTEELî sample.

LINE		RXI	
1	V KA	0.026741	Computer prints out the calculated RXI for each LINE.
2	CR KA	0.051762	
3	FE KA	0.565698	
4	W LA1	0.14170	

The second example of Option 3 predicts relative x-ray intensities for bulk heterogeneous samples for any composition and defined heterogeneity. This example requires that parameters such as particle sizes and voids fractions be used to characterize the heterogeneity.

```

* RESET
* LINES
* 1 SI KA 60 80 MN KA
* 2 TI KA
*
* DEFINE SIO2 2.64 AT
* SI 1
* O 2
*
* DEFINE TIO2 4.5 AT
* TI 1
* O 2
*
* DEFINE FE2O3 5.1 AT
* FE 2
* O 3
*

```

LINES entered as before. Here, incidence angle is 60°, take-off angle is 80°, and primary radiation is Mn K $\alpha$ .

As in the previous example, the components of interest need to be defined.



\* COMP RAWMIX PARTIC 100 .1 10 COMPosition of the sample to  
 \* SIO2 80 30 be predicted is given.  
 \* TIO2 3 5 Name of the sample is  
 \* FE2O3 17 20 "RAWMIX"; it is PARTICulate,  
 infinitely thick (100 g/cm<sup>2</sup>),  
 has 10% voids (.1) of 10 μm  
 diameter. "RAWMIX" by weight  
 is 80 parts SiO<sub>2</sub>, 3 parts TiO<sub>2</sub>  
 and 17 parts Fe<sub>2</sub>O<sub>3</sub>; the particle  
 sizes are 30, 5 and 20 μm  
 respectively.

\* PREDICT RAWMIX

	LINE	RXI	Computer prints out RXI for
1	SI KA	0.247651	the two lines input at the
2	TI KA	0.043261	start. (No Fe line was input
			so no RXI is predicted, but the
			Fe <sub>2</sub> O <sub>3</sub> , must be considered.)

\* PREDICT RAWMIX HOMOGENEOUS For comparison, calculation of  
 RXI for a homogeneous sample  
 of same composition can be made.

	LINE	RXI	Computer prints out RXI for
1	SI KA	0.194917	the homogeneous sample.
2	TI KA	0.039748	

## CONCLUSION

The purpose of this Users' Guide is to help get the x-ray analyst started and familiar with the common kinds of problems which the computer program can handle. Therefore the examples have been put in very simple form. However, the program has many additional capabilities which have not been illustrated in this Users' Guide but which the analyst will find discussed in the Reference Manual which is a separate document. One of the most important of the additional capabilities is performing the multivariate error analysis of the data so the analyst can see just what limitations in final accuracy arise from the experimental x-ray measurements themselves as distinguished from the mathematical treatment of the data. Hopefully, the analyst will explore the Reference Manual after becoming experienced with the examples contained in this Users' Guide.