

COMPUTERIZED DATA TREATMENT
OF LIQUID X-RAY DIFFRACTION STUDIES

by

Sandra C. Habegger

This thesis is submitted in partial fulfillment
of the requirements of the Honors Program of
Ball State University

I. D. 499

Advisor - Dr. R. M. Lawrence

August 27, 1971

This thesis has been accepted in fulfillment
of the requirements of I. D. 499 Senior Honors Project.

Richard M. Lawrence
ADVISOR

27 Aug 71
DATE

SpColl
Thesis
LD
2489
.Z4
1971
.H33

ACKNOWLEDGMENTS

Special thanks are due to my research advisor, Dr. R. M. Lawrence, for his assistance and guidance on this project, Steven Jost, Office of Research, and William Robertson, chemistry graduate student, for their aid with the computer program, and to the National Science Foundation for funding the early research on this project.

TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	THEORY	2
III.	DATA COLLECTION	7
IV.	DATA TREATMENT	9
V.	CONCLUDING REMARKS	28
VI.	REFERENCES	30
VII.	APPENDIX	32

LIST OF FIGURES

I.	RELATIVE INTENSITY CURVE	16
II.	RELATIVE CURVE NORMALIZED TO INDEPENDENT CURVE	19
III.	SI(S) CURVE	21
IV.	INTERPOLATED SI(S) CURVE	22
V.	RADIAL DISTRIBUTION FUNCTION AND $4\pi r^2 \rho_0$ CURVE	24
VI.	RDF COMPUTED WITH PROGRAM AND RDF CONVENTIONALLY DETERMINED	27

I. INTRODUCTION

The structure of liquids has been of interest to man for many decades. Many methods of experimentation have been devised and applied to the search for structural information; among these methods is x-ray diffraction. Although x-ray diffraction studies had been developed early for the crystalline solids and for low pressure gaseous systems, the application of this method to the investigation of liquid systems has been a more recent development.

An elaborate set of manipulations--calculations and graphings--must be carried out on the raw data taken from an x-ray diffractometer to obtain a structurally indicative radial distribution function. The graphings and some of the calculations, performed manually, require several days to complete. Computerization of these calculations and graphings promises the saving of many hours of tedious work and the freeing of the researcher to spend more time interpreting the final form of the data. The computerization of the treatment of liquid x-ray diffraction data became the goal of this research. The result of this project is the subject of this thesis.

II. THEORY

Debye (6) formulated the analytical basis for investigation of liquids by x-ray diffraction methods when he showed that a noncrystalline array of one kind of atoms scatters x-rays with an intensity given in electron units by the equation

$$I_{\text{coh}} = \sum_m \sum_n f_m f_n \frac{\sin sr_{mn}}{sr_{mn}} \quad (1)$$

in which

$$s = (4\pi \sin \theta) / \lambda, \quad (2)$$

θ is the scattering angle, λ is the wavelength of the radiation, f_m and f_n are the atomic scattering factors (12) of the m^{th} and n^{th} atoms. The double summation is taken over all pairs of atoms; no consideration is necessary for directional orientation.

This equation made it possible for early workers in the field to use the experimental intensity function as a test of their a priori assumptions about the atomic configuration of a system. Zernike and Prins (29) were first to suggest a mathematical inversion of the experimental intensity function to a radial distribution function (RDF) by means of the Fourier integral theorem. Modern theory depends on the analysis of the RDF which, in view of the system composition, yields information about the time-averaged environment of particles within

the solution; after such an analysis is made, assumptions about the structure are drawn. The formation of an RDF is based upon the following theory.

Under experimental conditions x-rays are scattered coherently and incoherently by electrons (4). The coherent scattering, modulated by atomic and molecular configuration, can be analyzed to yield information about the short-range ordering of the electrons (27); the incoherent scattering, due to the Compton effect (3), has no dependency on the structure of the sample. Therefore, the incoherent portion of the intensity is theoretically computed and subtracted from the total experimentally observed intensity scaled to absolute units; the remaining coherent intensity scattered by N atoms is expressed per atom as

$$I_{\text{coh}} = I_{\text{tot}} - I_{\text{incoh}} = \frac{1}{N} \sum_m \sum_n f_m f_n \frac{\sin sr_{mn}}{sr_{mn}} \quad (4)$$

It is further desirable to separate the intra-atomic scattering or self-scattering, due to phase differences within an atom, from the rest of the coherent intensity; this can be done because each atom is at zero distance from itself (18). The remaining portion of the coherent intensity is the intra- and inter-molecular scattering and contains the structural information about the system. The separated intensity can be expressed for a polyatomic system (18) as

$$I_{\text{coh}} = \frac{1}{N} \sum_m N_m f_m^2 + \frac{1}{N} \sum_m N_m \sum_n f_m f_n \frac{\sin sr_{mn}}{sr_{mn}} \quad (4)$$

The function $\rho_{ij}(r)$ is introduced (29) where $4\pi r^2 \rho_{ij}(r) dr$ gives the number of atoms of type j at a distance between r and $r + dr$ from an atom of type i (18);

$\rho_{ij}(r)$ is an atomic probability function and is assumed to be continuous. Also, since N is defined as the number of atoms present, $\frac{1}{N} \sum N_i$ can be expressed in an equivalent form as $\sum X_i$ where X_i is the mole fraction of the i th element. Thus, the coherent intensity of a polyatomic system is rewritten as

$$I_{\text{coh}} = \sum X_i f_i^2 + \sum X_i \sum \int_0^{\infty} f_i f_j 4\pi r^2 \rho_{ij}(r) \frac{\sin sr_{ij}}{sr_{ij}}. \quad (5)$$

The double sum now contains the sum of integrals of the f_i functions; the solution is complicated by the fact that these atomic scattering factors are different functions of s (19). Warren, Krutter, and Morningstar (27) approximated a solution to this problem by using the reduced scattering factor f_e . This factor is similar to the scattering factor of one electron, as shown by $f_e = f_i/K_i$ where K_i is the effective number of electrons per atom of type i (17a), and is therefore approximately the same for atoms with similar atomic numbers. Inclusion of the reduced scattering factor, multiplication by s , and rearrangement of equation 5 yields the new expression

$$s(I_{\text{coh}} - \sum X_i f_i^2) f_e^{-2} = \sum X_i \sum K_i K_j \int_0^{\infty} 4\pi r \rho_{ij}(r) \sin sr \, dr. \quad (6)$$

This integral does not converge, but Warren and Gingrich (26) discovered that the addition and subtraction of the integral

$$\int_0^{\infty} 4\pi r \sum X_i \sum K_i K_j X_j \rho_0 \sin sr \, dr \quad (7)$$

would yield the converging integral

$$s(I_{\text{coh}} - \sum X_i f_i^2) f_e^{-2} = \sum X_i \sum K_i K_j \int_0^{\infty} 4\pi r [\rho_{ij}(r) - X_j \rho_0] \sin sr \, dr + \sum X_i \sum K_i K_j X_j \int_0^{\infty} 4\pi r \rho_0 \sin sr \, dr. \quad (8)$$

The additive term is negligible (10). A sine transformation

of the intensity function by the Fourier integral yields the equation

$$4\pi r \left[\sum X_i \sum K_i K_j \rho_{ij}(r) - \sum X_i \sum K_i K_j X_j \rho_0 \right] = \frac{2}{\pi} \int_0^{\infty} s (I_{\text{coh}} - \sum X_i f_i^2) \cdot f_e^{-2} \sin rs \, ds. \quad (9)$$

Equation 9 can be expressed in a more general form as

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\infty} s i(s) M(s) \sin rs \, ds \quad (10)$$

where

$$i(s) = I_{\text{coh}} - \sum X_i f_i^2; \quad (11)$$

$M(s)$ is a modification function of s containing f_e^{-2} and a damping term; $\rho(r)$ is an electronic density function (11) equivalent to $\sum X_i \sum K_i K_j \rho_{ij}(r)$; and ρ_0 , the mean electron density, is expanded to include $(\sum X_i Z_i)^2$, where K_i has been appropriately approximated by Z_i , and thus is now the average electrons squared density.

The term $4\pi r^2 \rho_0$ is the RDF expected for an electronically homogeneous system. The addition of the integral-containing term gives the characteristic form of the RDF of the actual system which is the time-averaged distribution of electrons squared at a distance r from a reference atom. At intermediate values of r , the two curves differ appreciably, but with increasing r , the RDF damps to the $4\pi r^2 \rho_0$ curve because of the lack of long-range ordering in liquids.

Various techniques are used to interpret the nature of the areas under an RDF (18). In general, estimations are made of the number of i - j pairs contributing to a peak, i.e., the number of atoms of type j at a distance r from a reference atom of type i . This time-averaged number of neighbors and

the distance of their approach can sometimes lead to construction of reasonable three-dimensional models of the liquid structure.

III. DATA COLLECTION

This thesis discusses the computer program developed to treat liquid x-ray data. Actual calculations are performed on scattering data from a sample of aqueous 1.2 molar silver nitrate. These data were collected by fellow investigators in the liquid x-ray diffraction laboratory at Ball State University as follows.

First, the sample was carefully prepared with accurately noted weights and volumes; the density was obtained gravimetrically. The solution was placed in a sample holder that allowed the scattering of x-rays from its free surface and was mounted on a specially constructed theta-theta liquid x-ray diffractometer (23).

Second, the scattering pattern of the sample was collected as a molybdenum x-ray source and the detector rotated around an axis through the effective free surface of the sample. The reflected beam was monochromatized by a lithium fluoride monochromator before entering the detector system which included a NaI scintillation crystal, photomultiplier, preamplifier, linear amplifier, pulse height analyzer, scaler, timer, and printer. Disturbances in the sample surface were minimized by the fact that the diffractometer rested on an isolation pad (20).

The data were collected at intervals of, or integral multiples of, $0.5^\circ 2\theta$, where θ is the scattering angle, from a minimum of $4^\circ 2\theta$ to a maximum of $111^\circ 2\theta$. Around $29^\circ 2\theta$, the slit combinations were changed and at $76^\circ 2\theta$ the angular increments were changed from $0.5^\circ 2\theta$ to $1.0^\circ 2\theta$. The observed times were printed out automatically and the slit and increment changes were noted by the investigators (23).

IV. DATA TREATMENT

The typical treatment of x-ray data is discussed in the immediate paragraphs. (This is the method used by another investigator to obtain the hand-calculated radial distribution function from the previously mentioned silver nitrate data and used later.) Unfamiliar terms will be explained more fully in later paragraphs of this section.

The observed intensities are corrected for background, polarization, absorption, and changes in slit combinations in a small computer program. The resultant relative intensity curve is graphed and smoothed. At ten tabulated values of s the independent intensities are calculated and visually matched to the relative intensity curve in the high s region. The rest of the independent intensity curve is drawn and the value of the relative intensity minus the independent intensity is tabulated at small intervals in s . These differences are multiplied by their corresponding s values and the reciprocal of the scaling factor so that the resulting $si(s)$ is placed in absolute units. The $si(s)$ is graphed, smoothed, and visually interpolated at even smaller intervals in s . Another small computer program is used to evaluate the integral and calculate the RDF as given in equation 10. The RDF is graphed and interpretation of the results follows (18,27,28). This may necessitate the calculation of several other curves, among them

the $4\pi r^2\rho$ curve; these are calculated by hand and visually interpolated, if needed. Altogether, many hours of work and much attention to detail are required in this method of converting the observed intensities to a radial distribution function.

To reduce the time and effort required by this method, several small computer programs were developed to perform various portions of these calculations and a method was devised to combine these programs into one large, yet easily-handled program. This computerized method of the foregoing data treatment permits direct calculation of an RDF; the calculations performed by the computer program and their corresponding equations are discussed at length herewith. Easy reference to the actual program contained in the appendix is provided by noting that the following section headings correspond to headings in the program. All computations shown here were performed on an IBM System/360 Model 50 computer with 208K available core; the compiling system was an IBM G level Fortran compiler and a CalComp 563 plotter produced the figures. (The time required for this particular program was 10.55 minutes; approximately 95K core storage was necessary.)

A. VARIABLE DECLARATIONS The implicit statement (21) modifies standard Fortran convention because it causes the computer to treat all variables beginning with H or C as integers instead of real numbers. Since the accuracy of the calculations is limited to three significant figures, this

program is calculated in eight-digit single-precision. When, however, it is desirable to perform the calculations with twice the number of digits per variable, the program is easily changed to double-precision by the addition of ,REAL*8(A-G,P-Z) to the implicit statement.

All variables that must be calculated over a wide range of values and used in further calculations are stored in forty-two one-dimensional arrays. Fifteen of these arrays are initialized to zero in the non-executable data statements.

The statement function RAD(X) is used to convert an angle of X degrees into radian measure--the necessary form for the calculation of the sine or cosine of the angle. The program also calls upon these Fortran IV library functions: absolute value ABS(X), square root SQRT(X), sine SIN(X), cosine COS(X), and exponentiation EXP(X). If the computations are performed in double-precision, these functions must be changed to the corresponding double-precision functions: DABS(X), DSQRT(X), DSIN(X), DCOS(X), and DEXP(X).

B. DATA IDENTIFICATION The first data card contains an eighty-character Hollerith field; by putting information about the solution composition, run numbers of the raw data, values of key variables, etc., on this card, the program user can readily identify the data calculated.

C. SOLUTION COMPOSITION DATA Various equations used in solving for the RDF use mole fractions and atomic numbers of the elements in the sample, e.g., see equations 5 and 9. Weight fractions are needed to calculate the linear absorption

coefficient μ (16). These basic solution composition calculations are performed in this portion of the program in the following manner. The number of elements in the solute, in the solvent, and in the solution, and the atomic weights ATWT, atomic numbers ATNC, and stoichiometric formula coefficients COEF of the elements are supplied as input data. To check for errors, the formula weights and atoms per molecular unit are calculated for the solute and the solvent. For molal solutions, the program user supplies the number of grams of solute per thousand grams of solvent GPTU and the bulk density of the sample DENSI; for molar solutions, the number of grams of solute per liter GPLU and the number of grams of solvent per liter GPLN are supplied.

The following variables are calculated in the molal or molar sections and either are used in later calculations or provide a check on the other variables: molality or molarity FMOLU, moles of solvent FMOLN, bulk density DENSI, total number of moles TCTXI, mole fractions of each element in the solute X and solvent XN, total weight TCTWT, and weight fractions of each element in the solute W and solvent WN. Also included in this set of computations are the number density ENCV and the electrons squared density RHCZE. The number density or mean atomic density of the solution is defined and calculated as the number of atoms per cubic Angstrom, $\frac{N}{V}$ where N is defined as before and V is the volume of the sample in cubic Angstroms. The calculation of the electrons squared density in equation 10 is according to its definition as

the number of electrons in the average atom, squared, and multiplied by the number density, or

$$\rho = \frac{N}{V} (\sum X_i Z_i)^2 \quad (19) \quad (12)$$

in units of electrons squared per cubic Angstrom.

The user of the program must define the mole fraction X_S for each element in the solution as the sum of its mole fractions of the solute and of the solvent, previously calculated as X and XN . In like manner, the weight fraction W_S for each element in the solution is the sum of W and WN for that element. A convention as to the order of the elements must be adopted at this point and be followed throughout the rest of the program. The user also supplies the mass absorption coefficients (μ/ρ) RHO for each element; this furnishes the rest of the necessary information for the calculation of μ . The linear absorption coefficient is calculated as indicated in the equation

$$\mu = \rho \sum W_i (\mu/\rho)_i \quad (13)$$

where ρ is the bulk density of the sample, W_i is the weight fraction of the i th element, and $(\mu/\rho)_i$ is the mass absorption coefficient (16,17b) of the i th element. This quantity provides a validity check in this manner: an overview technique of sample viewing that is dependent on the optics of the machine and the μ of the sample has been developed (20) and eliminates the need for an absorption correction. Samples with a μ of less than three cannot be overviewed and must have the absorption correction applied to them. Since this correction is not a program option, by checking the value

of μ , one can determine the validity of the rest of the computations and suggest a reason for failure of the relative and absolute intensity curves to have the same general form, if this occurs.

D. RELATIVE INTENSITY CURVE The raw data from the x-ray diffractometer are arranged as input in the manner described herewith.

The number of segments NP of data due to changes in slit size, angular increment, or preset count, the Bragg angle α ALPHA of the monochromatizing crystal, the wavelength λ AMBDA of the radiation in Angstroms, and the background radiation BCKGR in counts per minute are supplied first. Preceding each data segment, the overlap index MULT, which is equal to one if the data segment does not overlap an earlier segment, the preset total count COUNT, the lower limit THMIN of angle in degrees 2θ , the upper limit THMAX of angle in degrees 2θ , and angular increment DELTH in degrees 2θ are given. The observed times, in seconds, for that segment for one TCB, two TCB2, or three TCB3 runs are supplied. These times are summed and changed to minutes in the program.

The function s S of the scattering angle is computed as in equation 2. Another function of the scattering angle, the polarization (1) P, is computed according to

$$P(\theta) = (1 + \cos^2 2\alpha \cdot \cos^2 2\theta) / (1 + \cos^2 2\alpha); \quad (14)$$

this is the factor by which the crystal monochromator and the sample reduce the observed intensities.

The relative intensity is then calculated as the intensity in counts per minute and corrected for background scattering and polarization as indicated by

$$I_{\text{rel}}(\theta) = \left(\frac{\text{COUNT}}{\text{TCB}(\theta)} - \text{BCKGR} \right) / P(\theta). \quad (15)$$

The statistical error is equal to the square root of the preset count divided by the preset count and multiplied times the relative intensity.

Since the relative intensity is usually not continuous over the entire angular range of the scattering pattern (because of the changes in slit geometry), a matching factor FMULT is found that brings each succeeding portion of the curve into continuity with the preceding portion. Two continuous arrays, of s values SVAL and of the relative intensity RELINT at these s values, are obtained. A graph of the relative intensity of the silver nitrate solution is shown in Figure 1.

Before the calculations continue, a series of parameters must be supplied as data; these parameters are the tolerable per cent error ETA, the lower SMIN and upper SMAX limits of the integral in equation 10, the delta s value DELS, the lower RMIN and upper RMAX bounds of the interval over which the RDF is to be found, the delta r value DELR, and damping factor BEXP. These terms will be explained in more detail when used later.

E. INDEPENDENT CURVE An array of the independent intensities, at the s values just computed as a function of θ , is calculated; defined as the sum of the intra-atomic

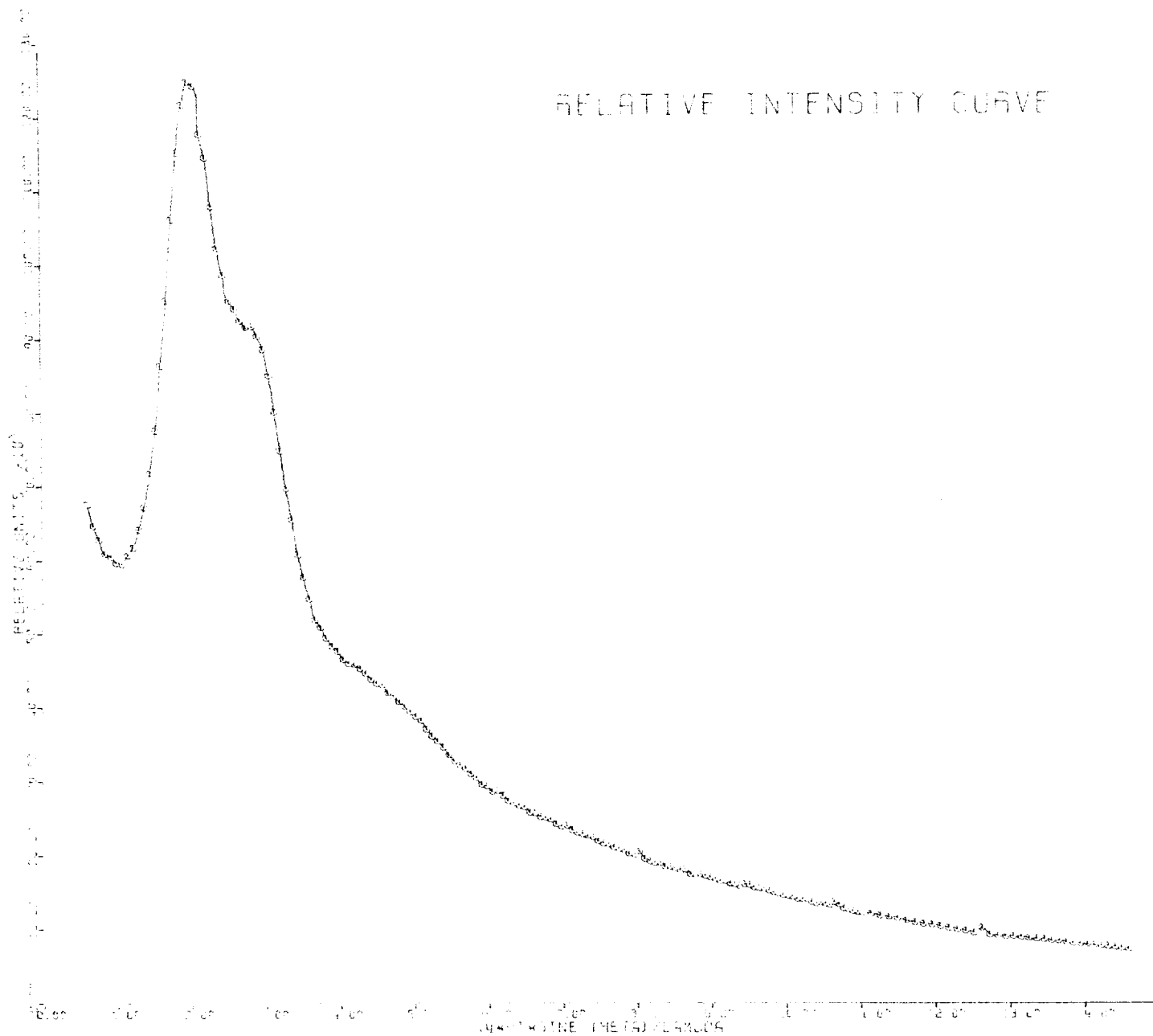


Figure 1.

coherent scattering, it has the equation

$$I_{\text{indep}}(s) = \sum X_i f_i^2(s) + T_f(s) \sum X_i \text{Inc}_i(s) \quad (16)$$

where Inc_i is the incoherent scattering function of element i , T_f is the total correction function, and other symbols are as before.

The total correction function is composed of two functions of s --the Breit-Dirac (2,7) correction factor and the empirical monochromator transmission factor. The former is a correction factor for relativistic effects and has been tabulated (24); the latter reveals the portion of the incoherent scattering that passes through the monochromator and is unique to each laboratory set-up. The latter factor has been tabulated by persons conducting experimental work in this laboratory (20).

Tabulated values of the incoherent (16,24,25) and the coherent (5,16,25) intensities as a function of the scattering angle and wavelength of the radiation are found in several sources. Noticeable differences in the final RDF can be observed that are dependent on the approximation of the atomic scattering factors (18); therefore, the user must choose carefully and consistently those sources which best fit his need. From such tables the user selects n points that give an accurate representation of the curve and notes whether the functions are in units of s (see equation 2) or in units of $x = \sin \theta / \lambda$. This data is entered into the program as the number of points N , the literature index LITS (set equal to one if in units of s ; otherwise, a correction

factor of 4π will be applied to the x value), and then the pairs of points as (y,x) coordinates. These data are first supplied for the incoherent scattering functions of the elements in the predetermined order, then for the total factor, and finally for the coherent scattering functions of the pre-arranged elements.

When the interpolations and the final summation are complete, the resultant independent curve is in units of scattering power.

F. INTENSITY FUNCTION The relative intensity curve is normalized from relative units to absolute units by multiplying it by a scaling factor. The scaling factor is calculated by averaging the factor needed to match the two curves at high values of s where generally little detail occurs in the relative intensity curve. Larger values of s must be selected for those systems with a greater degree of atomic ordering (17a). The values chosen for the lower IA and upper IB limits to the matching interval may be changed as the program user desires. A graphical display of the independent intensity curve with the normalized relative intensity curve oscillating around it is illustrated in Figure 2.

The differential intensity $i(s)$ FOBIND is the same function defined in equation 11 and is found by subtracting the independent curve from the relative curve. Thus, the intra-atomic coherent scattering and the incoherent scattering passed by the detector system are removed from the experimentally determined relative intensities, and the

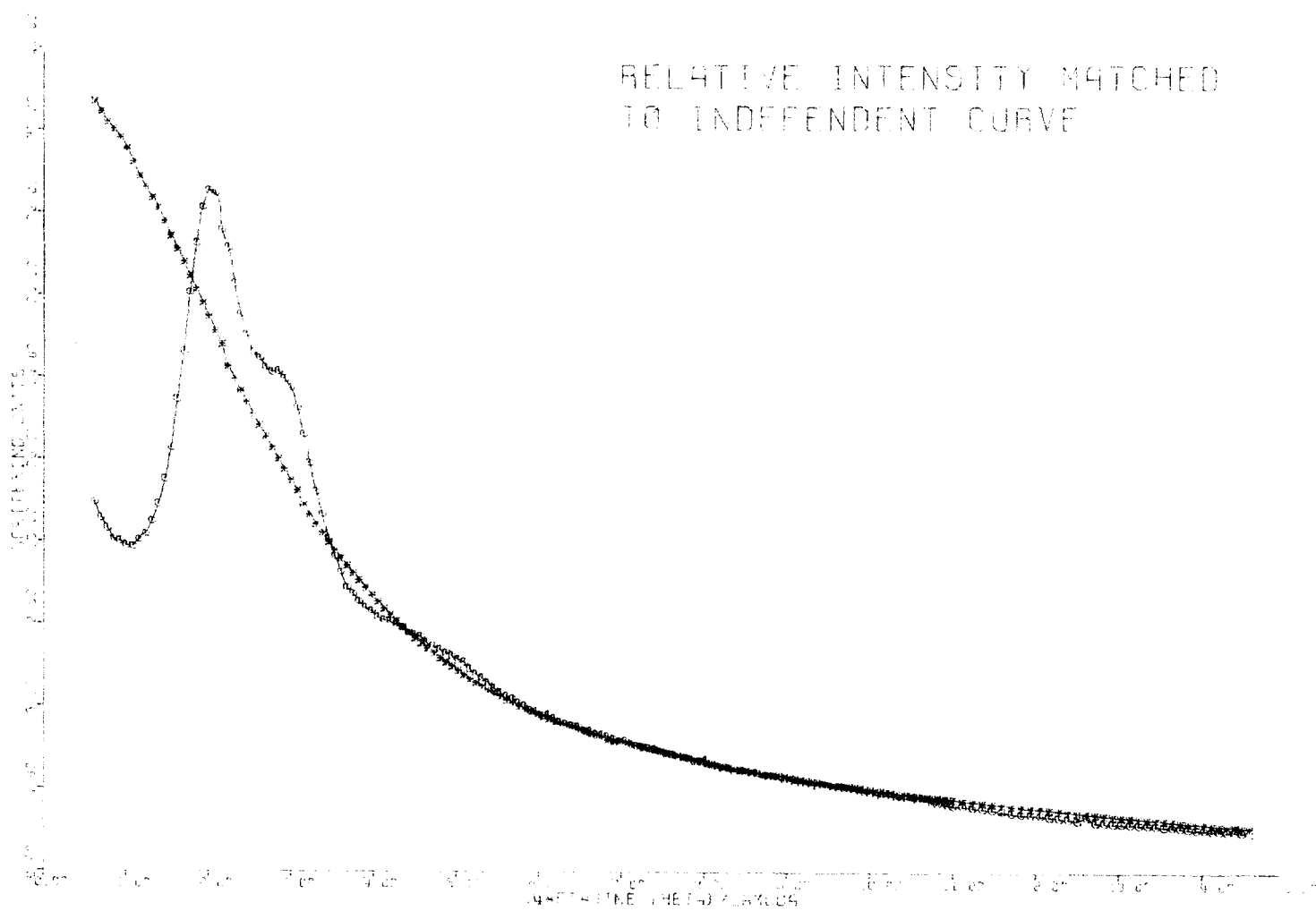


Figure 2.

structurally-sensitive portion of the coherent data, the second term on the right in equation 5, remains.

Multiplication of the differential intensity by its corresponding s value CORRS yields an intensity function $si(s)$ as illustrated in Figure 3. In the evaluation of the integral containing this intensity function, the increments of s must be equal. Since it is assumed that at $s = 0.0$ the relative intensity is equal to the independent intensity, an $si(0.0) = 0.0$ was added to the arrays. All points in the $si(s)$ evaluated from s equal zero to the s equal to or greater than the value of the upper integral limit $SMAX$ were interpolated by the subroutine. Values for the interpolated $si(s)$ SIS from the lower integral limit to the upper integral limit are obtained at equal intervals of s TERPS; the nature of this curve is illustrated in Figure 4. Due to the impossibility of choosing infinity, the upper limit of the integral of equation 10 is chosen at a value of s where the $si(s)$ effectively damps to zero. The value of the lower limit is rarely different from zero.

G. RADIAL DISTRIBUTION FUNCTION This program segment evaluates the radial distribution function $4\pi r^2\rho(r)$ as it is given in equation 10.

The modification function $M(s)$ is calculated first; it consists of the sharpening function f_e^{-2} FMS and a corresponding damping function. The sharpening function was introduced in equation 7 and is approximated according to the expression

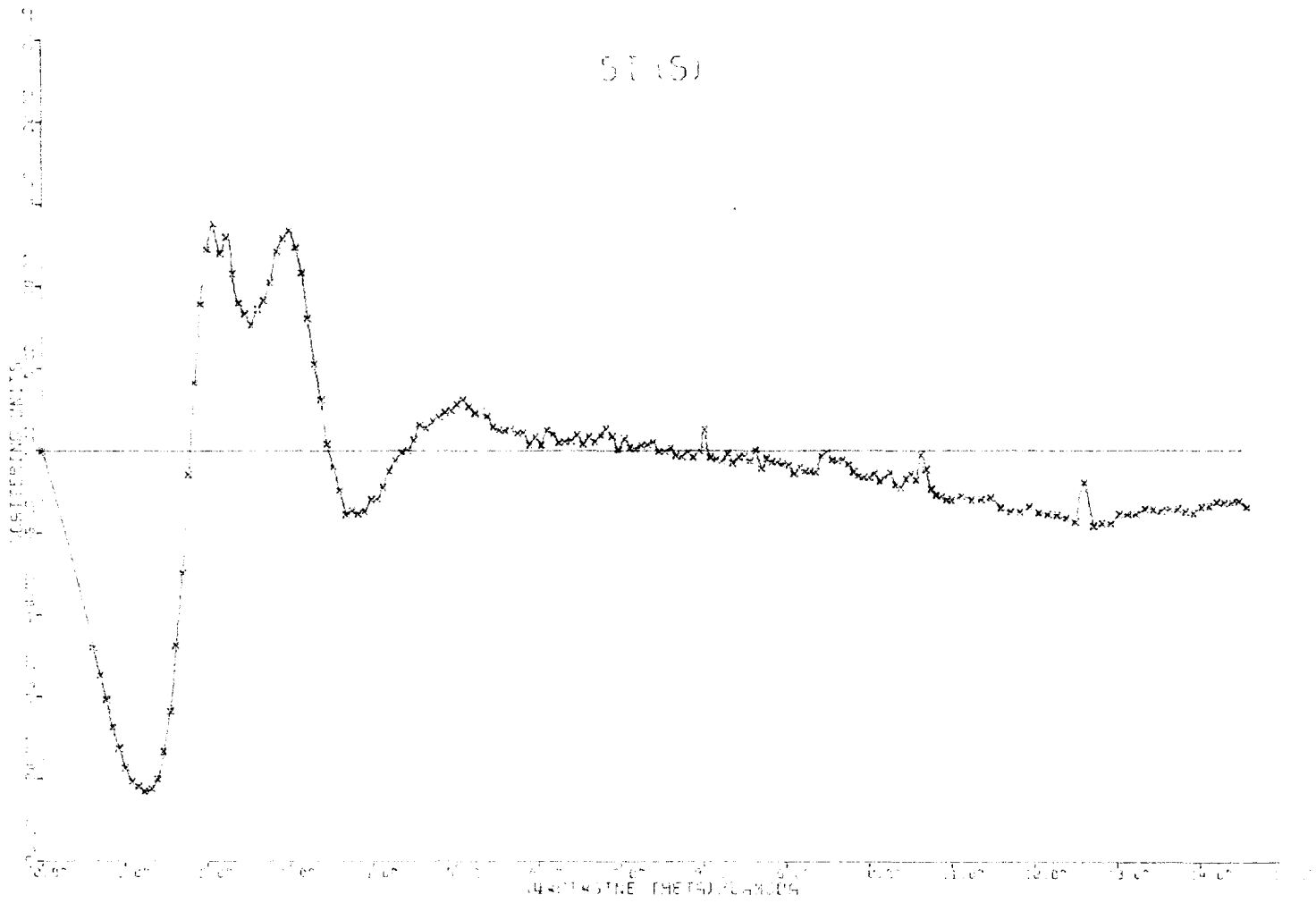


Figure 3.

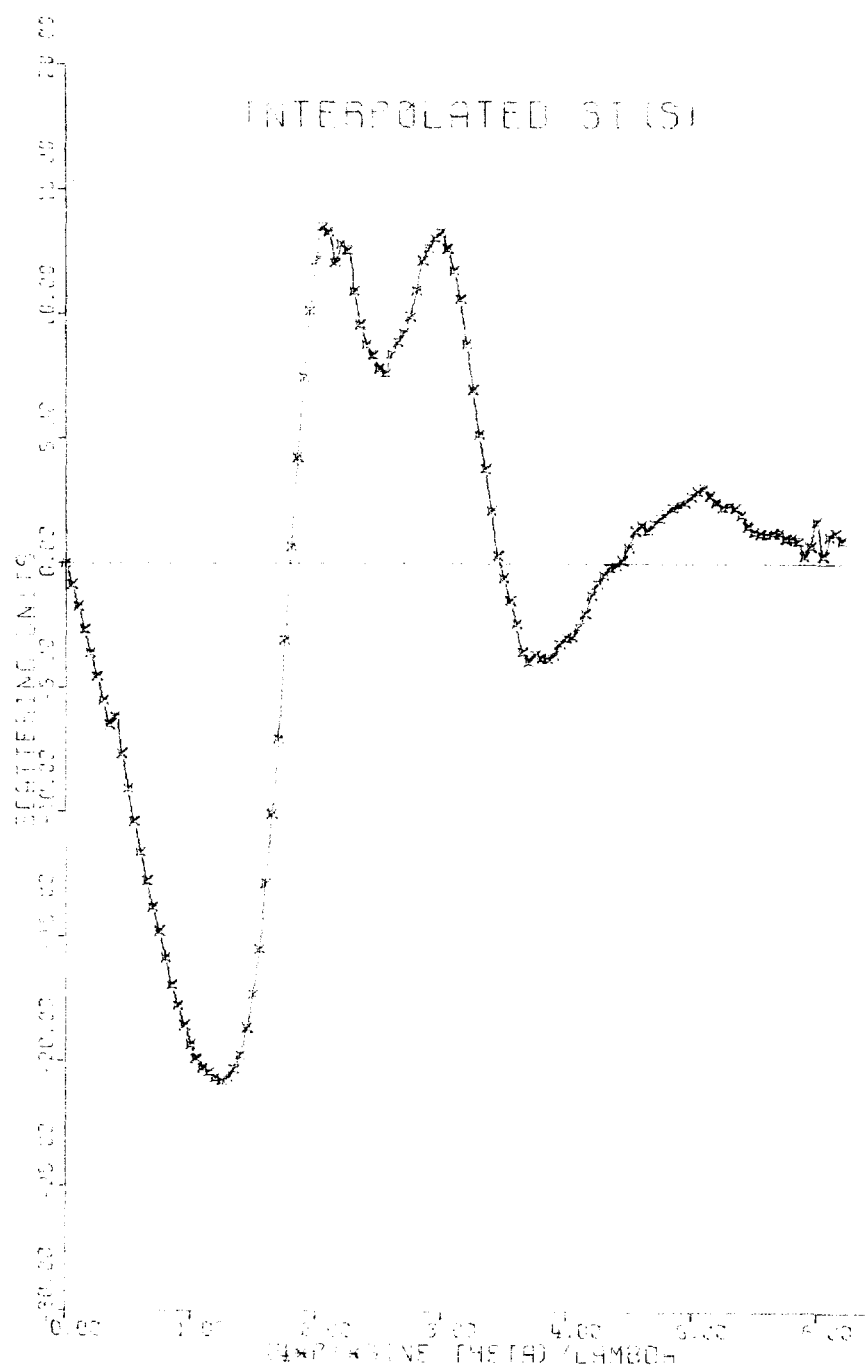


Figure 4.

$$f_e^{-2}(s) = \left[\sum X_i f_i(0) / \sum X_i f_i(s) \right]^2 \quad (17)$$

where all symbols retain their previous meaning. An analytical approximation (9) of the atomic scattering factor of the form

$$f_i(s) = A_i e^{-a_i s^2} + B_i e^{-b_i s^2} + C_i \quad (18)$$

has been adopted for use in this program. The five parameters CAPA, A, CAPB, B, and CAPC for each element are the last bits of information supplied by the program user. If desired, the program can be easily modified to include the scattering factors approximated when forming the independent intensity curve. The damping term, or artificial temperature factor, included in the modification function FMSEXP, is calculated as e^{-bs^2} where b BEXP is the damping constant introduced earlier. Finbak (8) developed this term to reduce the emphasis given to high s values by the sharpening function which possibly introduces spurious maxima in the RDF.

The differential radial distribution function RFINT has the form $(2r/\pi) \int_0^{s_{\max}} si(s)M(s) \sin rs \, ds$. The integral is evaluated by Simpson's rule for irregular integrals (13). If an even number of divisions occur in the $si(s)$, the final segment is evaluated by the trapezoidal rule. The calculation of the homogeneous radial distribution function or $4\pi r^2 \rho_0$ curve RHCZR2 is a separate entity so as to maintain a reference for the structurally-affected curve. The sum of the differential RDF and the homogeneous RDF yields the final RDF, shown in Figure 5, with the parabolic $4\pi r^2 \rho_0$ curve.

As a matter of interest, the pair correlation function $g(r)$ (11) GCFR is calculated by the equation

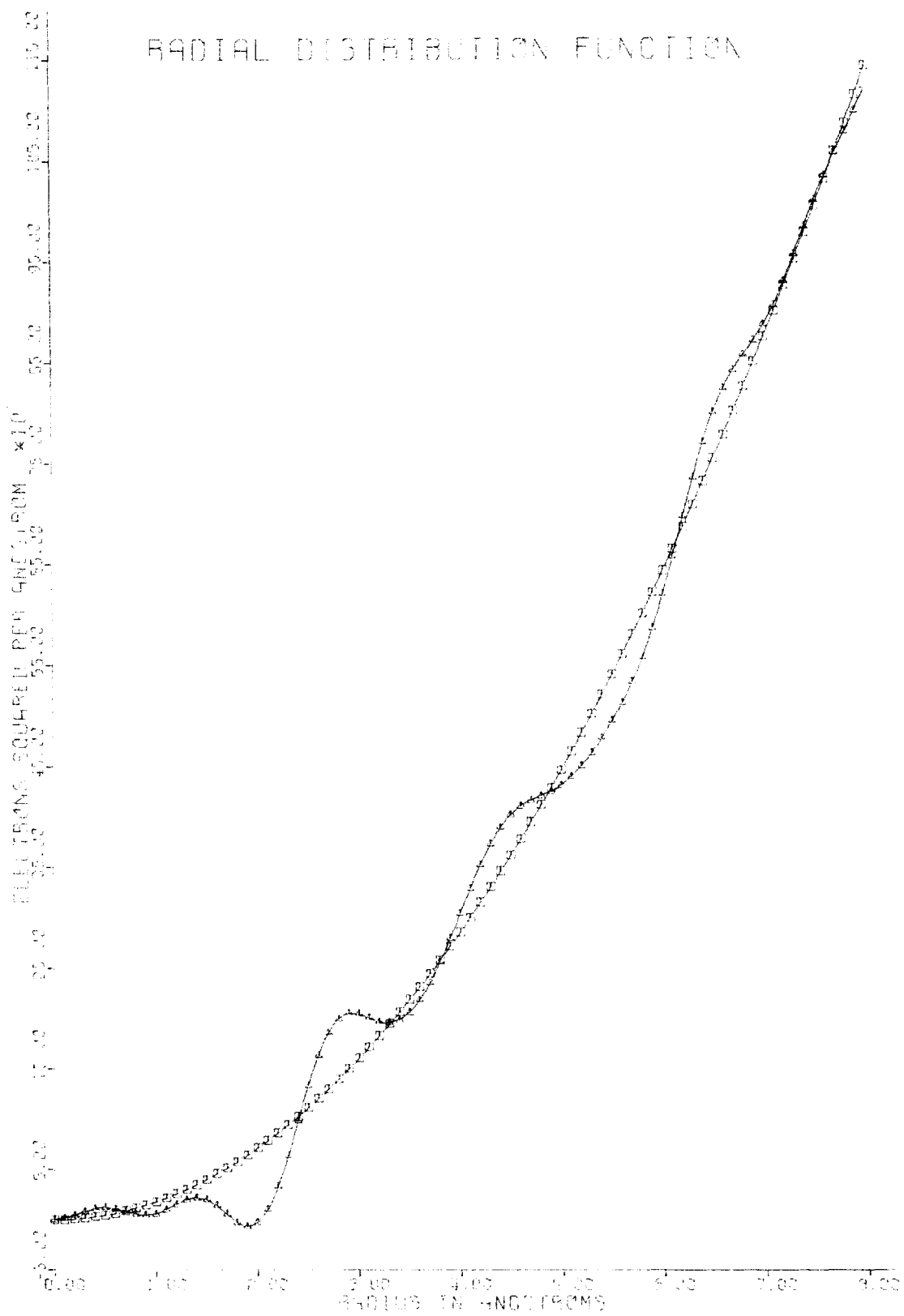


Figure 5.

$$g(r) = \rho(r)/\rho_0 ; \quad (19)$$

it can be used as an aid in the determination of interaction distances at larger r due to its extreme sharpening.

H. FORMAT SPECIFICATIONS The formats used in this program are grouped in numerical order for easy reference.

I. SUBROUTINE The subroutine TERPOL interpolates using Aitken's method of iterated interpolation by approximating polynomials (14). The arguments passed into the subroutine are the number of given points N , two arrays containing the x and the corresponding y coordinates Z and F of the points, a percentage error limit ETA , the number of points at which interpolation is to occur $NPTBC$, and the x coordinates $TERPS$ of these points. The given points are first rearranged in order of increasing differences between the given x values and the x value of the point to be interpolated. The evaluation of a cross-product followed by a division yields an interpolated value corresponding to a polynomial approximation of the highest possible degree (one less than the number of points used), and it is into this evaluation the given points are then fed. The sequence of approximations terminates when two successive approximations (of orders t and $t + 1$ and using $t - 1$ and t points, respectively) differ by less than the maximum tolerable error--the percentage error limit. If the sequence fails to "effectively converge" by the time it reaches its highest order approximation (either of an order one less than the number of given points or of order twenty, whichever is smaller), it is denoted as such in the written output and

the value of the quadratic approximation is assumed for the interpolated value.

Plotting subroutines (22) are interspersed throughout the main program to produce the first five figures used in this paper. Although the program can perform its calculations without these plots, they are an invaluable aid in picturing the computations performed and in checking for errors in the calculations.

Now that the discussion of the program computations is complete, it seems appropriate to remark on the results of the program as compared with results obtained traditionally. The final radial distribution functions of a 1.2 molar aqueous silver nitrate solution obtained from the same raw data (referred to in Sections III and IV) but by the two different methods are plotted together in Figure 6. It can readily be observed that beyond an r value of 2.2, the curves are very well matched. The average percent difference of this portion of the curve, containing the major peaks, is only two percent. The great deviation at the smaller r values has several sources, but is mainly due to the differences in the computed and hand-calculated $s_i(s)$, which in turn has great effect on the integral at small r . Since this portion of the curve contains no structural information, the value of the overall result is not lessened by the deviations, and the researcher uses its shape only to determine the nature of errors present in the relative intensities or the data treatment (8).

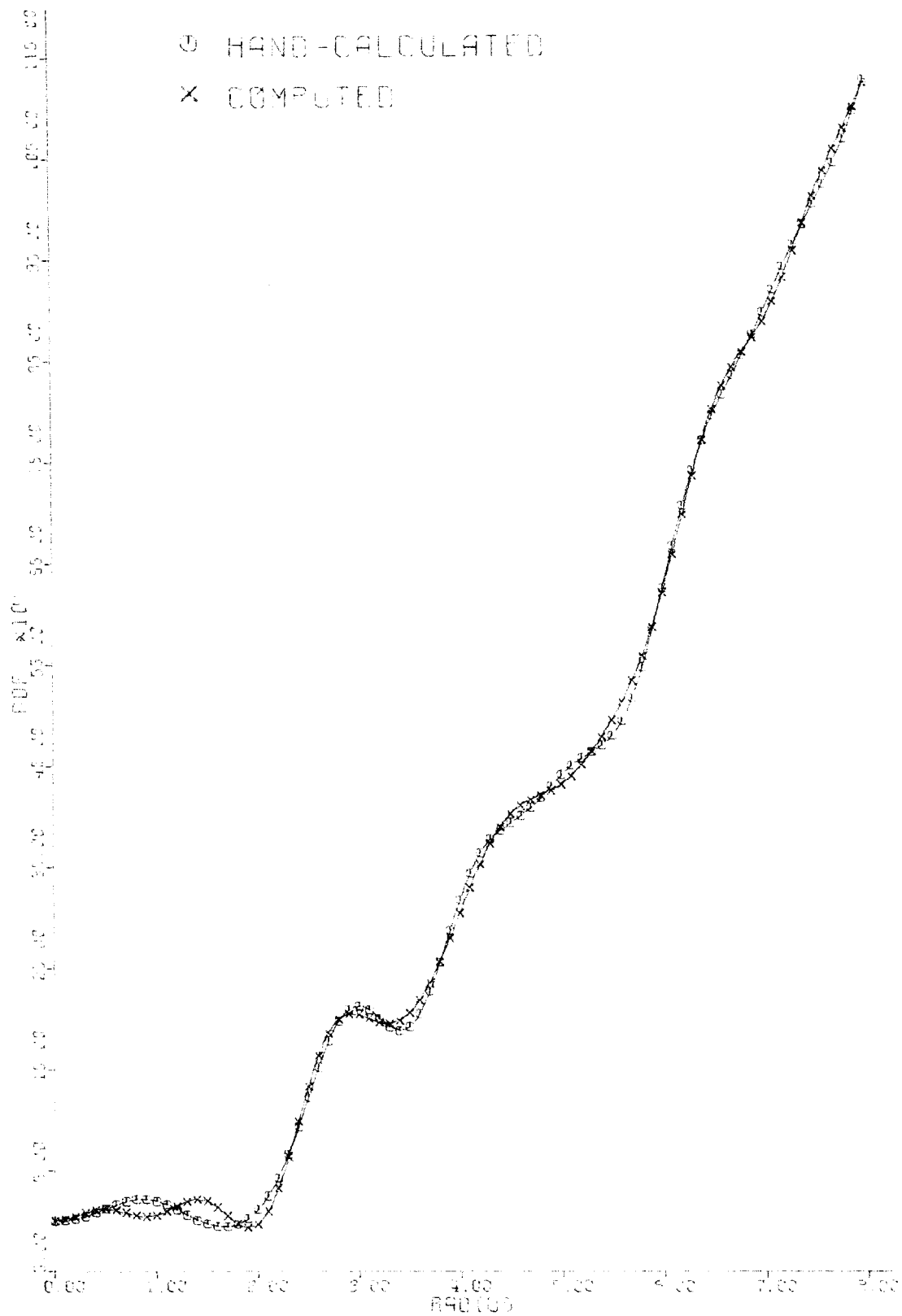


Figure 6.

V. CONCLUDING REMARKS

As mentioned previously, the computer program contained in the appendix was developed to eliminate tiresome, lengthy hand calculations and graphings associated with the treatment of liquid x-ray data, and an example of comparable results from the two methods is given. However, as in all first developments, there are areas which could be improved and refined. This section includes suggestions to make the program more efficient, easier to use, and more valuable to the researcher.

Suggested further improvements include the following: (a) simple manner of correcting obviously erroneous points in the relative intensity curve and $si(s)$, (b) alternate method of approximation involving exponential expressions, (c) easy selection of coherent scattering factors from the various tabulated values, (d) inclusion of the absorption correction if the sample is not overviewed, and (e) calculation of s_{max} from a formula such as $\int_0^{s_{max}} si(s) = 0.0$ (15). The time and storage required for the execution of this program also could be minimized. And, as laboratory techniques are refined, the program must be kept abreast of these developments.

Thus one can conclude that the program accomplishes its objective--computerizing the treatment of liquid x-ray diffraction data to reduce the time and effort needed to obtain the final structurally significant RDF--with results extremely compatible to those obtained traditionally.

VI. REFERENCES

- (1) Azároff, L. V., Acta Crystallogr., 8, 701 (1955).
- (2) Breit, G., Phys. Rev., 27, 362 (1926).
- (3) Compton, A. H., Phys. Rev., 21, 715 (1923); 22, 409 (1923).
- (4) Compton, A. H. and Allison, S. W., "X-Rays in Theory and Experiment," D. Van Nostrand Co., Princeton, N. J., 1935.
- (5) Cromer, D. T. and Waber, J. T., Acta Crystallogr., 18, 104 (1965).
- (6) Debye, P., Ann. Phys., 46, 809 (1915).
- (7) Dirac, P. A. M., Proc. Roy. Soc., 8, 405 (1926).
- (8) Finbak, C., Acta Chem. Scand., 3, 1279 (1949); 3, 1293 (1949).
- (9) Forsyth, J. B. and Wells, M., Acta Crystallogr., 12, 412 (1959).
- (10) Gingrich, N. S., Rev. Mod. Phys., 15, 90 (1943).
- (11) Gruebel, R. W. and Clayton, G. T., J. Chem. Phys., 46(2), 639 (1967).
- (12) Guinier, A., "X-Ray Diffraction," W. H. Freeman and Co., San Francisco, 1963, Chapt. 1.
- (13) "Handbook of Chemistry and Physics," 49th ed., Chemical Rubber Company, Cleveland, Ohio, 1968, pp. A256 to A259.
- (14) Hildebrand, F. B., "Introduction to Numerical Analysis," McGraw-Hill Book Co., Inc., New York, 1956, pp. 49-50.
- (15) Hultgren, R., Gingrich, N. S., and Warren, B. E., J. Chem. Phys., 3, 351 (1935).
- (16) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Chapt. 3.
- (17a) Klug, H. P. and Alexander, L. E., "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, 1954, pp. 588-612.

- (17b) Ibid., pp. 677-678.
- (18) Kruh, R. F., Chem. Rev., 62, 319 (1962).
- (19) Lawrence, R. M., Diss. Abstr., 26, 4268 (1965).
- (20) Lawrence, R. M., Relford, J. R., and Habegger, S. C., Rev. Sci. Instrum. (in press).
- (21) Murrill, P. W. and Smith, C. L., "An Introduction to Fortran IV Programming," International Textbook Company, Scranton, Pa., 1970, Chapt. 8.
- (22) "Programming CalComp Pen Plotters," California Computer Products, Inc., Anaheim, Calif., Sept. 1969, pp. 1-25.
- (23) Relford, J. R., Master's Thesis, Ball State University, Muncie, Indiana, 1971.
- (24) Sagel, K., "Tabellen zur Röntgenstrukturanalyse," Springer-Verlag OHG., Berlin, 1958, pp. 165-167.
- (25) Tavad, C., Nicolas, D., and Rouault, M., J. Chim. Phys., 64, 540 (1967).
- (26) Warren, B. E. and Gingrich, N. S., Phys. Rev., 46, 368 (1934).
- (27) Warren, B. E., Krutter, H., and Morningstar, C., J. Amer. Ceram. Soc., 19, 202 (1936).
- (28) Waser, J. and Schomaker, V., Rev. Mod. Phys., 25, 671 (1953).
- (29) Zernike, F. and Prins, J. A., Z. Phys., 41, 184 (1927).


```
C *HEAD IS AN 80-CHARACTER ALPHANUMERIC ARRAY. SUGGESTED DATA
C *INCLUDES SOLUTION NAME, DATA RUN NUMBERS, DATE, VALUE OF SMAX AND
C *BEXP, ETC.
017 READ(5,501) HEAD
018 WRITE(6,502) HEAD
C
C C. SOLUTION COMPOSITION DATA
C
C 1. GENERAL CALCULATIONS
C
C *JC IS THE NUMBER OF ELEMENTS IN THE SOLUTE, KC EQUALS JC + 1, LC
C *IS THE NUMBER OF ELEMENTS IN THE SOLVENT, AND O IS THE NUMBER OF
C *DIFFERENT ELEMENTS IN THE ENTIRE SOLUTION.
019 READ(5,272) JC,KC,LC,O
C *ATWT, ATNO, AND COEF ARE ARRAYS CONTAINING THE ATOMIC WEIGHTS,
C *ATOMIC NUMBERS, AND TOTAL FORMULA COEFFICIENTS OF EACH ELEMENT IN
C *THE SOLUTE AND OF EACH ELEMENT IN THE SOLVENT.
020 READ(5,225)(ATWT(I),ATNO(I),COEF(I), I=1,JC)
021 READ(5,225)(ATWT(I),ATNO(I),COEF(I), I=KC,LC)
022 WRITE(6,226)
023 WRITE(6,227)(ATWT(I),ATNO(I),COEF(I), I=1,JC)
024 WRITE(6,227)(ATWT(I),ATNO(I),COEF(I), I=KC,LC)
025 FRWTU=0.0
026 ATPMU=0.0
027 DO 8 I=1,JC
028 ATPMU=ATPMU+COEF(I)
029 8 FRWTU=FRWTU+ATWT(I)*COEF(I)
030 FRWTN=0.0
031 ATPMN=0.0
032 DO 9 I=KC,LC
033 ATPMN=ATPMN+COEF(I)
034 9 FRWTN=FRWTN+ATWT(I)*COEF(I)
035 WRITE(6,228)
036 WRITE(6,229) FRWTU,ATPMU,FRWTN,ATPMN
C *IF A MOLAR SOLUTION WAS RUN, GPLU AND GPLN (GRAMS OF SOLUTE PER
C *LITER AND GRAMS OF SOLVENT PER LITER) ARE READ IN. IF A MOLAL
C *SOLUTION WAS RUN, GPTU AND DENSI (GRAMS OF SOLUTE PER 1000 GRAMS
C *OF SOLVENT AND THE SOLUTION DENSITY) MUST BE READ IN.
037 READ(5,231) GPLU,GPLN,GPTU,DENSI
038 WRITE(6,232)
039 WRITE(6,233) GPLU,GPLN,GPTU,DENSI
040 11 IF(GPLU-GPTU) 13,12,22
041 12 WRITE(6,234)
042 STOP
C
C 2. CALCULATIONS FOR MOLAL SOLUTION
C
043 13 WRITE(6,235)
```

```

044      FMOLU=GPTU/FRWTU
045      FMOLN=1000./FRWTN
046      WRITE(6,237)
047      WRITE(6,238) FMOLU,DENSI,FMOLN
048      TOTXI=0.0
049      DO 14 I=1,JC
050 14     TOTXI=TOTXI+FMOLU*COEF(I)
051      DO 15 I=KC,LC
052 15     TOTXI=TOTXI+FMOLN*COEF(I)
053      WRITE(6,240) TOTXI
054      WRITE(6,242)
055      DO 16 I=1,JC
056      X(I)=FMOLU*COEF(I)/TOTXI
057 16     WRITE(6,245) X(I)
058      DO 17 I=KC,LC
059      XN(I)=FMOLN*COEF(I)/TOTXI
060 17     WRITE(6,245) XN(I)
061      TOTWT=FRWTU*FMOLU+FRWTN*FMOLN
062      WRITE(6,247) TOTWT
063      WRITE(6,248)
064      DO 18 I=1,JC
065      W(I)=COEF(I)*ATWT(I)*FMOLU/TOTWT
066 18     WRITE(6,245) W(I)
067      DO 19 I=KC,LC
068      WN(I)=COEF(I)*ATWT(I)*FMOLN/TOTWT
069 19     WRITE(6,245) WN(I)
070      ENOV=(FMOLU*ATPMU+FMOLN*ATPMN)/TOTWT*DENSI*0.602252
071      WRITE(6,239) ENOV
072      SUM=0.0
073      DO 119 I=1,JC
074 119    SUM=SUM+X(I)*ATNO(I)
075      DO 120 I=KC,LC
076 120    SUM=SUM+XN(I)*ATNO(I)
077      RHOZE=ENOV*SUM**2
078      WRITE(6,270) RHOZE
079      GO TO 30

```

C
C
C

3. CALCULATIONS FOR MOLAR SOLUTION

```

080 22     WRITE(6,250)
081      FMOLU=GPLU/FRWTU
082      FMOLN=GPLN/FRWTN
083      DENSI=(GPLU+GPLN)/1000.
084      WRITE(6,251)
085      WRITE(6,238) FMOLU,DENSI,FMOLN
086      TOTXI=0.0
087      DO 23 I=1,JC
088 23     TOTXI=TOTXI+FMOLU*COEF(I)

```

```

089      DO 24 I=KC,LC
090      24 TOTXI=TOTXI+FMOLN*COEF(I)
091      WRITE(6,240) TOTXI
092      WRITE(6,242)
093      DO 25 I=1,JC
094      X(I)=FMOLU*COEF(I)/TOTXI
095      25 WRITE(6,245) X(I)
096      DO 26 I=KC,LC
097      XN(I)=FMOLN*COEF(I)/TOTXI
098      26 WRITE(6,245) XN(I)
099      TOTWT=GPLN+GPLU
100      WRITE(6,247) TOTWT
101      WRITE(6,248)
102      DO 27 I=1,JC
103      W(I)=ATWT(I)*COEF(I)*FMOLU/TOTWT
104      27 WRITE(6,245) W(I)
105      DO 28 I=KC,LC
106      WN(I)=ATWT(I)*COEF(I)*FMOLN/TOTWT
107      28 WRITE(6,245) WN(I)
108      ENOV=(FMOLU*ATPMU+FMOLN*ATPMN)*.602252/1000.
109      WRITE(6,239) ENOV
110      SUM=0.0
111      DO 125 I=1,JC
112      125 SUM=SUM+X(I)*ATND(I)
113      DO 126 I=KC,LC
114      126 SUM=SUM+XN(I)*ATND(I)
115      RHOZE=ENOV*SUM*SUM
116      WRITE(6,270) RHOZE

```

C
C
C

4. DEFINITION OF XS AND WS ARRAYS

117

30 CONTINUE

C *IN THE FOLLOWING STATEMENTS THE PROGRAM USER MUST DEFINE THE
C *WEIGHT FRACTION ARRAY WS FOR THE DIFFERENT ELEMENTS IN HIS
C *PARTICULAR SOLUTION AS SUMS OF THE WEIGHT FRACTIONS PREVIOUSLY
C *CALCULATED AS THE WEIGHT FRACTIONS OF EACH ELEMENT IN THE SOLUTE
C *W(1-JC) AND OF EACH IN THE SOLVENT WN(KC-LC). IN LIKE MANNER THE
C *USER MUST ALSO DEFINE THE MOLE FRACTION ARRAY XS FOR THE 0
C *DIFFERENT ELEMENTS. IN THESE AND LATER CALCULATIONS THE 0
C *DIFFERENT ELEMENTS MUST ALWAYS BE IN THE SAME ORDER SO THAT THE
C *NTH SUBSCRIPT ALWAYS REFERS TO THE SAME ELEMENT.

```

118      XS(1)=X(1)
119      XS(2)=XN(4)
120      XS(3)=X(2)
121      XS(4)=X(3)+XN(5)
122      WS(1)=W(1)
123      WS(2)=WN(4)
124      WS(3)=W(2)

```

```
25      WS(4)=W(3)+WN(5)
26      WRITE(5,248)
27      WRITE(6,231) (WS(I), I=1,0)
28      WRITE(6,242)
29      WRITE(6,231) (XS(I), I=1,0)
C
C      5.  CALCULATION OF FMU
C
C      *RHO IS THE ARRAY OF THE MASS ABSORPTION COEFFICIENTS OF THE 0
C      *DIFFERENT ELEMENTS.
130     READ(5,262) (RHO(I), I=1,0)
131     WRITE(6,263)
132     WRITE(6,245) (RHO(I), I=1,0)
133     FMU=0.0
134     DO 32 I=1,0
135 32  FMU=FMU+WS(I)*RHO(I)
136     FMU=DENSI*FMU
137     WRITE(6,266) FMU
C
C      D.  RELATIVE INTENSITY CURVE
C
138     PI=3.14159
C      *NP IS THE NUMBER OF SEGMENTS OF RAW DATA DUE TO CHANGES IN SLIT
C      *SIZE, COUNT, OR ANGLE INCREMENTS.  ALPHA IS THE BRAGG ANGLE OF THE
C      *MONOCHROMATOR CRYSTAL, AMBDA IS THE WAVELENGTH OF THE RADIATION,
C      *AND BCKGR IS THE BACKGROUND RADIATION IN COUNTS PER MINUTE.
139     READ(5,511) NP,ALPHA,AMBDA,BCKGR
140     WRITE(6,511) NP,ALPHA,AMBDA,BCKGR
141     COMP= COS(RAD(2.*ALPHA))**2
142     SCOMP=4.*PI/AMBDA
143     JREL=0
144     DO 60 K=1,NP
C      *EACH SEGMENT OF DATA MUST HAVE DEFINED THMIN (MINIMUM VALUE OF TH,
C      *WHERE TH IS TWICE THE SCATTERING ANGLE), THMAX (MAXIMUM VALUE OF
C      *TH), DELTH (INCREMENTS OF TH), COUNT (TOTAL PRESET COUNT), AND
C      *MULT (AN INDEX WHICH IS SET EQUAL TO 1 IF THE DATA DOES NOT
C      *OVERLAP A PREVIOUS DATA SEGMENT).
145     READ(5,511) MULT,COUNT,THMIN,THMAX,DELTH
146     WRITE(6,511) MULT,COUNT,THMIN,THMAX,DELTH
147     JOLD=JREL
148     N=(THMAX-THMIN)/DELTH+1.001
149     TH=THMIN-DELTH
150     PCORR= SQRT(COUNT)/COUNT
C      *TOB IS THE OBSERVED TIME IN SECONDS.  IF TWO OR THREE RUNS ARE
C      *MADE, ADDITIONAL READ STATEMENTS MUST BE SUPPLIED FOR ARRAYS
C      *TOB2 AND TOB3.
151     READ(5,101) (TOB(I),I=1,N)
152     WRITE(6,101) (TOB(I),I=1,N)
```

```

153      DO 35 I=1,N
154      TOB(I)=(TOB(I)+TOB2(I)+TOB3(I))/60.
155      TH=TH+DELTH
      C
      C      1. FUNCTION OF SCATTERING ANGLE
      C
156      S(I)=SCOMP* SIN(RAD(TH/2.))
      C
      C      2. POLARIZATION CORRECTION
      C
157      P(I)=(1.+COMP* COS(RAD(TH))**2)/(1.+COMP)
      C
      C      3. BACKGROUND CORRECTION
      C
158      35 FIREL(I)=(COUNT/TOB(I)-BCKGR)/P(I)
      C
      C      4. MATCHING FACTOR
      C
159      IF(K.EQ.1.OR.MULT.EQ.1) GO TO 37
160      FMULT=(FIOLD1/FIREL(1)+FIOLD2/FIREL(2)+FIOLD3/FIREL(3)+FIOLD4/FIRE
161      37 IF(K.EQ.1) FMULT=1.00000
162      38 WRITE(6,522) FMULT
163      41 DO 45 I=1,N
164      FIREL(I)=FIREL(I)*FMULT
      C
      C      5. ERROR LIMITS
      C
165      EIREL(I)=FIREL(I)*PCORR
166      JREL=I+JOLD-5
167      IF(K.EQ.1.OR.MULT.EQ.1) JREL=JREL+5
168      RELINT(JREL)=FIREL(I)
169      SVAL(JREL)=S(I)
170      45 WRITE(6,533) I,S(I),P(I),EIREL(I),FIREL(I)
171      IF(K.EQ.1.OR.MULT.EQ.1) GO TO 55
      C
      C      6. DATA OVERLAP
      C
172      RELINT(JOLD-4)=(RELINT(JOLD-4)+FIOLD1)/2.
173      RELINT(JOLD-3)=(RELINT(JOLD-3)+FIOLD2)/2.
174      RELINT(JOLD-2)=(RELINT(JOLD-2)+FIOLD3)/2.
175      RELINT(JOLD-1)=(RELINT(JOLD-1)+FIOLD4)/2.
176      RELINT(JOLD)=(RELINT(JOLD)+FIOLD5)/2.
177      55 FIOLD1=FIREL(N-4)
178      FIOLD2=FIREL(N-3)
179      FIOLD3=FIREL(N-2)
180      FIOLD4=FIREL(N-1)
181      FIOLD5=FIREL(N)

```

```

182      60 CONTINUE
183      WRITE(6,544)
184      WRITE(6,555) (I,SVAL(I),RELINT(I),I=1,JREL)
      C
      C
      C **PLOTTER SUBROUTINES FOR RELATIVE INTENSITY CURVE
185      SVAL(JREL+1)=0.0
186      SVAL(JREL+2)=01.00
187      RELINT(JREL+1)=0.0
188      RELINT(JREL+2)=1000.0
189      CALL PLOTS(IBUF,2000,1)
190      CALL PLOT(0.0,1.0,-3)
191      CALL FACTOR(.48)
192      CALL AXIS(0.0,0.0,24H(4*PI*SINE THETA)/LAMBDA,-24,15.0,0.0,0.0,1.)
193      CALL AXIS(0.0,0.0,14HRELATIVE UNITS,14,13.0,90.0,0.0,1000.C)
194      CALL FLIN(SVAL,RELINT,-JREL,1,1,1)
195      CALL SYMBOL(7.0,12.0,.28,24HRELATIVE INTENSITY CURVE,0.,24)
196      CALL PLOT(20.0,0.0,-3)
      C
      C *ETA IS THE PERCENT ERROR ALLOWED IN THE INTERPOLATION OF VARIOUS
      C *FUNCTIONS OF S. SMIN IS THE LOWER LIMIT OF THE INTEGRAL AND IS
      C *GENERALLY 0.0, DELS IS THE INCREMENT SIZE AND IS USUALLY .LE.0.10,
      C *SMAX IS THE UPPER LIMIT OF THE INTEGRAL AND USUALLY OCCURS AT THE
      C *POINT THE SI(S) LOSES ITS DETAIL. RMIN AND RMAX ARE THE LOWER AND
      C *UPPER BOUNDS OF THE RDF AND DELR IS THE INCREMENT OF R. BEXP
      C *RANGES FROM 0.0 TO 0.1 AND DETERMINES THE STRENGTH OF THE
      C *DAMPENING TERM.
197      READ(5,104) ETA,SMIN,DELS,SMAX,RMIN,DELR,RMAX,BEXP
198      WRITE(6,104) ETA,SMIN,DELS,SMAX,RMIN,DELR,RMAX,BEXP
      C
      C E. INDEPENDENT CURVE
      C
199      JOE=2*0+1
200      DO 77 NELT=1,JOE
201      OE=NELT-(0+1)
      C *Z IS THE ARRAY OF N S VALUES AND F IS THE ARRAY OF CORRESPONDING
      C *FUNCTIONS OF S. LITS IS AN INDEX SET EQUAL TO 1 IF THE S VALUES
      C *ARE IN UNITS OF (4*PI*SINE THETA)/LAMBDA. THE PAIRS OF ARRAYS
      C *SHOULD BE ORDERED TO INCLUDE THE INCOHERENT FUNCTION OF THE 0
      C *DIFFERENT ELEMENTS, THEN THE TOTAL FACTOR FUNCTION, AND FINALLY
      C *THE COHERENT FUNCTIONS OF THE 0 ELEMENTS.
202      READ(5,117) N,LITS,(F(I),Z(I),I=1,N)
203      IF(LITS.EQ.1) GO TO 396
204      DO 394 I=1,N
205      394 Z(I)=4.000*PI*Z(I)
206      396 WRITE(6,127) N,LITS,(F(I),Z(I),I=1,N)
207      CALL TERPOL (ETA,F,Z,N,SVAL,TERPI,JREL)
208      WRITE(6,104) (SVAL(I),TERPI(I),I=1,JREL)

```

```
209      DO 88 J=1,JREL
      C
      C      1.  CALCULATION OF INCOHERENT PORTION
      C
210      IF(NELT.LE.0) ARRAY2(J)=ARRAY2(J)+XS(NELT)*TERPI(J)
      C
      C      2.  CORRECTION FOR TOTAL FACTOR
      C
211      IF(NELT.EQ.(0+1)) ARRAY2(J)=ARRAY2(J)*TERPI(J)
      C
      C      3.  CALCULATION OF COHERENT PORTION
      C
212      IF(NELT.GE.(0+2)) ARRAY1(J)=ARRAY1(J)+XS(OE)*TERPI(J)**2
      C
      C      4.  CALCULATION OF TOTAL CURVE
      C
213      FINDEP(J)=ARRAY1(J)+ARRAY2(J)
214      88 CONTINUE
215      WRITE(6,525) (SVAL(J),FINDEP(J),J=1,JREL)
216      77 CONTINUE
217      WRITE(6,526) (SVAL(J),FINDEP(J),J=1,JREL)
      C
      C F.  INTENSITY FUNCTION
      C
      C      1.  CALCULATION OF THE SCALE FACTOR
      C
218      FACT=0.0
219      IA=76
220      IB=116
221      DO 388 I=IA,IB
222      388 FACT=FINDEP(I)/RELINT(I)+FACT
223      TEMP=IB-IA+1
224      FACT=FACT/TEMP
225      WRITE(6,130) FACT
      C
      C      2.  TABULATION OF DIFFERENTIAL INTENSITY
      C
226      DO 389 I=1,JREL
227      RELINT(I)=RELINT(I)*FACT
228      FCBIND(I+1)=RELINT(I)-FINDEP(I)
229      389 CORR(S(I+1)=SVAL(I)
230      FCBIND(1)=0.0000
231      CORR(S(1)=0.0000
232      JRELL=JREL+1
233      WRITE(6,527) (CORR(S(J),FCBIND(J),J=1,JRELL)
      C
      C
      C      **PLOTTER SUBROUTINES FOR RELATIVE CURVE MATCHED TO INDEPENDENT
```

```
234 SVAL(JREL+1)=0.0
235 SVAL(JREL+2)=1.00
236 RELINT(JREL+1)=0.0
237 RELINT(JREL+2)=4.0
238 FINDEP(JREL+1)=0.0
239 FINDEP(JREL+2)=4.0
240 CALL PLOT(0.0,1.0,-3)
241 CALL FACTOR(.48)
242 CALL AXIS(0.0,0.0,24H(4*PI*SINE THETA)/LAMBDA,-24,15.0,0.0,0.0,1.)
243 CALL AXIS(0.0,0.0,16HSCATTERING UNITS,16,10.0,90.0,0.0,4.0)
244 CALL FLINE(SVAL,FINDEP,-JREL,1,1,11)
245 CALL FLINE(SVAL,RELINT,-JREL,1,1,1)
246 CALL SYMBOL(7.0,9.5,.28,26HRELATIVE INTENSITY MATCHED,0.,26)
247 CALL SYMBOL(7.0,9.0,.28,20HTO INDEPENDENT CURVE,0.,20)
248 CALL PLOT(20.0,0.0,-3)
```

C
C
C
C

3. TABULATION OF INTENSITY FUNCTION

```
249 DO 397 I=1,JRELL
250 397 FOBIND(I)=FOBIND(I)*CORRS(I)
251 WRITE(6,528) (CORRS(J),FOBIND(J),J=1,JRELL)
```

C
C
C

**PLOTTER SUBROUTINES FOR SI(S)

```
252 FOBIND(JRELL+1)=-25.0
253 FOBIND(JRELL+2)=5.0
254 CORRS(JRELL+1)=0.0
255 CORRS(JRELL+2)=1.0
256 YARRAY(JRELL+1)=-25.0
257 YARRAY(JRELL+2)=5.0
258 CALL PLOT(0.0,1.0,-3)
259 CALL FACTOR(.48)
260 CALL AXIS(0.0,0.0,24H(4*PI*SINE THETA)/LAMBDA,-24,15.0,0.0,0.0,1.)
261 CALL AXIS(0.0,0.0,16HSCATTERING UNITS,16,10.0,90.0,-25.0,5.0)
262 CALL FLINE(CORRS,FOBIND,-JRELL,1,1,10)
263 CALL LINE(CORRS,YARRAY,JRELL,1,0,3)
264 CALL SYMBOL(6.8,9.5,.28,5HSI(S),0.,5)
265 CALL PLOT(20.0,0.0,-3)
```

C

```
266 JCUT=1
267 DO 398 I=2,JRELL
268 JCUT=JCUT+1
269 FOBIND(JCUT)=FOBIND(I)
270 CORRS(JCUT)=CORRS(I)
271 IF(CORRS(I).GE.SMAX) GO TO 399
272 398 CONTINUE
273 399 WRITE(6,528) (CORRS(J),FOBIND(J),J=1,JCUT)
```

```
C
C 4. INTERPOLATION OF INTENSITY FUNCTION
C
```

```
274 NS=(SMAX-SMIN)/DELS+1.001
275 ES=SMIN-DELS
276 DO 390 I=1,NS
277 ES=ES+DELS
278 390 TERPS(I)=ES
279 WRITE(6,104) (TERPS(I),I=1,NS)
280 CALL TERPOL(ETA,FOBIND,CORRS,JCUT,TERPS,SIS,NS)
281 WRITE(6,529) (TERPS(I),SIS(I),I=1,NS)
```

```
C
C
C **PLOTTER SUBROUTINES FOR INTERPOLATED SI(S)
```

```
282 YARRAY(JRELL+1)=0.0
283 YARRAY(JRELL+2)=0.0
284 YARRAY(NS+1)=-30.0
285 YARRAY(NS+2)=5.0
286 TERPS(NS+1)=0.0
287 TERPS(NS+2)=1.0
288 SIS(NS+1)=-30.
289 SIS(NS+2)=5.0
290 CALL PLOT(0.0,1.0,-3)
291 CALL FACTOR(.65)
292 CALL AXIS(0.0,0.0,24H(4*PI*SINE THETA)/LAMBDA,-24,6.5,0.0,0.0,1.0)
293 CALL AXIS(0.0,0.0,16HSCATTERING UNITS,16,10.0,90.0,-30.0,5.0)
294 CALL FLINE(TERPS,SIS,-NS,1,1,10)
295 CALL LINE(TERPS,YARRAY,NS,1,0,3)
296 CALL SYMBOL(1.4,9.5,.21,18HINTERPOLATED SI(S),0.,18)
297 CALL PLOT(20.0,0.0,-3)
```

```
C
C
C G. RADIAL DISTRIBUTION FUNCTION
```

```
C
C *THE FIVE COEFFICIENTS OF THE ANALYTICAL APPROX. OF THE ATOMIC
C *SCATTERING FACTORS BY FORSYTH AND WELLS MUST BE SUPPLIED FOR THE
C *O DIFFERENT ELEMENTS.
```

```
298 READ(5,203) (CAPA(I),A(I),CAPB(I),B(I),CAPC(I),I=1,0)
299 WRITE(6,203) (CAPA(I),A(I),CAPB(I),B(I),CAPC(I),I=1,0)
300 NR=(RMAX-RMIN)/DELR+1.001
301 CONST1=(4.**2)*(PI**2)
302 ES=SMIN-DELS
303 WRITE(6,93)
304 DO 94 I=1,NS
305 FE(I)=0.0
306 ES=ES+DELS
307 DO 92 J=1,0
```

```
C
```

```
C      1.  CALCULATION OF SHARPENING FUNCTION
C
308 - 92 FE(I)=FE(I)+XS(J)*(CAPA(J)* EXP(-A(J)*ES**2/CONST1)+CAPB(J)* EXP(-
309      1B(J)*ES**2/CONST1)+CAPC(J))
      FMS=(FE(1)/FE(I))**2
C
C      2.  INCLUSION OF DAMPENING FUNCTION
C
310      FMSEXP(I)=FMS* EXP(-BEXP*ES**2)
311 94 WRITE(6,204)I,ES,FE(I),FMS,FMSEXP(I)
312      WRITE(6,97)
313      RHOZE=4.0*PI*RHOZE
C
C      3.  EVALUATION OF DIFFERENTIAL RADIAL DISTRIBUTION FUNCTION
C
314      CONST2=DELS*2./3./PI
315      R(1)=RMIN
316      GOFR=0.0
317      DO 96 J=1,NR
318      IF(J.EQ.1) GO TO 3
319      R(J)=R(J-1)+DELR
320 3 SUM=0.
321      I=1
322      ES=0.0
323 1 SUM=SUM+SIS(I)*FMSEXP(I)* SIN(ES*R(J))
324      I=I+1
325      ES=ES+DELS
326      SUM=SUM+SIS(I)*FMSEXP(I)* SIN(ES*R(J))*4.0
327      I=I+1
328      ES=ES+DELS
329      SUM=SUM+SIS(I)*FMSEXP(I)* SIN(ES*R(J))
330      IF(I.LE.(NS-2)) GO TO 1
331      IF(I.EQ.NS) GO TO 2
332      SUM=SUM+3./2.*(SIS(I)*FMSEXP(I)* SIN(ES*R(J))+SIS(I+1)*FMSEXP(I+1)
333      1* SIN((ES+DELS)*R(J)))
334      I=I+1
335 2 FINT=SUM*CONST2
      RFINT=R(J)*FINT
C
C      4.  CALCULATION OF HOMOGENEOUS SYSTEM RDF
C
336      RHOZR2(J)=RHOZE*R(J)**2
C
C      5.  COMPUTATION OF RADIAL DISTRIBUTION FUNCTION
C
337      RDF(J)=RFINT+RHOZR2(J)
338      IF (J.EQ.1) GO TO 96
C
```

```
C      6.  CALCULATION OF PAIR CORRELATION FUNCTION
C
339      GOFR=RDF(J)/RHOZR2(J)
340      96 WRITE(6,5102) J,I,R(J),FINT,RFINT,RHOZR2(J),RDF(J),GOFR
C
C
C      **PLOTTER SUBROUTINES FOR RDF AND 4*PI*R*R*RHO-ZERO
341      R(NR+1)=0.0
342      R(NR+2)=1.0
343      RDF(NR+1)=-50.0
344      RDF(NR+2)=100.0
345      RHOZR2(NR+1)=-50.0
346      RHOZR2(NR+2)=100.0
347      CALL PLOT(0.0,1.0,-3)
348      CALL FACTOR(0.65)
349      CALL AXIS(0.0,0.0,19HRADIUS IN ANGSTROMS,-19,8.25,0.0,0.0,1.0)
350      CALL AXIS(0.0,0.0,30HELECTRONS SQUARED PER ANGSTROM,30,12.5,90.0,-
351      150.0,100.0)
352      CALL FLINE(R,RHOZR2,-NR,1,1,0)
353      CALL FLINE(R,RDF,-NR,1,1,2)
354      CALL SYMBOL(1.00,12.0,.21,28HRADIAL DISTRIBUTION FUNCTION,0.,28)
      CALL PLOT(12.0,0.0,999)
C
C
C H.  FORMAT SPECIFICATIONS
C
355      93 FORMAT (//3X,'COUNTER',9X,'S',8X,'FE',7X,'FMS',3X,'FMS*EXP'/)
356      97 FORMAT (//3X,'COUNTER',16X,'R',7X,'FINT',6X,'RFINT',5X,'RHOZR2',8X
357      101 FORMAT (8F10.1)
358      104 FORMAT(8F10.4)
359      117 FORMAT(2I5/(2F10.4))
360      127 FORMAT('1'/6X,'NO. OF POINTS = ',I2,3X,'LITS = ',I1//9X,'FUNCTION
361      130 FORMAT(//T25,'SCALE FACTOR = ',1PD16.7)
362      203 FORMAT (10X,5F10.3)
363      204 FORMAT (I10,7F10.4)
364      225 FORMAT(F10.5,F10.1,F10.0)
365      226 FORMAT (/T6,'ATOMIC WEIGHT',T21,'ATOMIC NUMBER',T35,'FORMULA COEFF
366      227 FORMAT(T8,F10.3,T23,F10.1,T43,F10.2)
367      228 FORMAT(//T6,'SOLUTE',T42,'SOLVENT'/T6,'FORMULA WEIGHT',T22,'ATOMS/
368      229 FORMAT(T5,F14.4,T21,F14.2,T45,F14.4,T58,F14.2)
369      231 FORMAT(4F10.4)
370      232 FORMAT(//T6,'MOLAR SOLUTION',T41,'MOLAL SOLUTION'/T6,'SOLUTE',T24,
      1'SOLVENT',T41,'SOLUTE',T53,'DENSITY'/T10,'GRAMS/LITER',T27,'GRAMS/
      2LITER',T44,'GRAMS/1000')
```

```
371      233 FORMAT(T10,F10.4,T27,F10.4,T43,F10.4,T55,F10.4)
372      234 FORMAT(2X,'INSUFFICIENT DATA FOR STATEMENT ELEVEN')
373      235 FORMAT(//T6,'MOLALITY CALCULATIONS')
374      237 FORMAT(//T6,'MOLALITY',T21,'DENSITY',T36,'MOLES OF SOLVENT')
375      238 FORMAT(3X,3F15.5)
376      239 FORMAT(//T6,'NUMBER DENSITY=',E16.9)
377      240 FORMAT(//T6,'TOTAL NUMBER OF MOLES PRESENT=',T36,F10.4)
378      242 FORMAT(//T6,'MOLE FRACTIONS')
379      245 FORMAT(7X,F8.4)
380      247 FORMAT(//T6,'TOTAL WEIGHT OF SOLUTION=',T32,F9.4)
381      248 FORMAT(//T6,'WEIGHT FRACTIONS')
382      250 FORMAT(//T6,'MOLARITY CALCULATION')
383      251 FORMAT(//10X,'MOLARITY',8X,'DENSITY',3X,'MOLES OF SOLVENT'/)
384      262 FORMAT(F10.5)
385      263 FORMAT(//T6,'INPUT DATA---MU OVER RHO')
386      266 FORMAT(//T6,'FMU=',F8.4)
387      270 FORMAT(//T6,'RHO ZERO IS ',1P016.7,3X,'FOR THIS SOLUTION')
388      272 FORMAT (4I10)
389      501 FORMAT (20A4)
390      502 FORMAT (1H1//////////T5,20A4/1H1)
391      511 FORMAT (I10,4F12.4)
392      522 FORMAT (T25,'MATCHING FACTOR IS ',F9.6)
393      525 FORMAT (3(2F12.4,3X))
394      526 FORMAT(//10X,'INDEPENDENT CURVE'/(15X,2F12.4))
395      527 FORMAT (//10X,'SCALED RELATIVE CURVE MINUS INDEPENDENT CURVE'/(15X
1,2F12.4))
396      528 FORMAT(//10X,'SI OF S BEFORE INTERPOLATION'/(15X,2F12.4))
397      529 FORMAT(//10X,'INTERPOLATED SI OF S'/(15X,2F12.4))
398      533 FORMAT (13X,I6,4F12.2)
399      544 FORMAT (///T35,'ONE DIMENSIONAL ARRAYS'/T26,'OF RELATIVE INTENSITY
1 AT CORRESPONDING S'//T41,'SVAL',4X,'RELINT'/)
400      555 FORMAT (25X,I3,8X,F6.2,2X,F8.2)
401 5102 FORMAT (I10,I6,6F11.2)
402      STOP
403      END
```

```

C
C I. SUBROUTINE
C
C 1. ARGUMENT LIST
C
C *TERPS, NPTBC, N PAIRS OF DATA (Z,F), AND AN ERROR PERCENTAGE ETA
C *ARE ALL GIVEN TO FIND THE Y VALUE OF NPTBC PAIRS OF DATA (TERPS,
C *TERPI) BY AITKEN'S METHOD OF ITERATIVE INTERPOLATION.
001 SUBROUTINE TERPOL(ETA,F,Z,N,TERPS,TERPI,NPTBC)
002 IMPLICIT INTEGER*4(H-G)
003 DIMENSION F(N),Z(N),X(300),Y(300),TERPS(NPTBC),TERPI(NPTBC)
004 DO 67 J=1,NPTBC
C
C 2. ARRAY REARRANGEMENT
C
C NA=N-1
C DO 3 JILL=1,NA
C MARY=JILL
C MARYA=JILL+1
C DO 2 I=MARYA,N
005 2 IF( ABS(Z(I)-TERPS(J)).LT. ABS(Z(MARY)-TERPS(J))) MARY=I
006 SAVE=F(JILL)
007 F(JILL)=F(MARY)
008 F(MARY)=SAVE
009 SAVE=Z(JILL)
010 Z(JILL)=Z(MARY)
011 3 Z(MARY)=SAVE
012 32 X(1)=Z(1)-TERPS(J)
013 Y(1)=F(1)
014 K=2
015 37 L=K-1
016 X(K)=Z(K)-TERPS(J)
017 Y(K)=F(K)
018 DO 47 M=1,L
019 47 Y(K)=(Y(M)*X(K)-Y(K)*X(M))/(X(K)-X(M))
C
C 3. PRECISION CONTROL
C
C IF( ABS(Y(K)-Y(L)).LE.( ABS(ETA*Y(L)))) GO TO 57
025 K=K+1
026
C
C 4. DEGREE LIMITATION
C
C IF(K.GT.21) GO TO 55
C IF(K.LE.N) GO TO 37
027
028
C
C 5. QUADRATIC ASSIGNMENT
C

```