

A PROGRAMME FOR ELECTRON PROBE MICRO-ANALYSIS

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ABSTRACT

Quantitative Electron Probe Micro Analysis (EPMA) is carried out by non-dispersive energy analysis or EDAX or by dispersive wave length analysis or WDS. The present paper discusses a computer programme developed in BASIC language for quantitative evaluation of metallographic specimen containing a number of component elements, using the absorption, atomic number (stopping power and reflection power) and fluorescence corrections known as ZAF correction. A comprehensive flow chart and the detailed programme written in basic language are provided in the appendix which can be run in Casio PB 300 personal computer. The programme has been tested for actual quantitative estimation of a steel specimen containing iron, chromium, manganese, carbon and silicon. The x-ray data was obtained from a Double Dispersion Spectroscopy (DDS) attached to a JEOL JSM 35 CF model SEM.

Key Words: EPMA, Computer program, Alloy estimation

INTRODUCTION

Electron Probe Micro Analysis (EPMA) on very small selected areas is carried out by electron bombardment to generate x-rays in the sample to be analysed. From the wave length and the intensity of the lines in the x-ray spectrum, the elements present may be identified and their concentrations estimated [1-4].

In qualitative as well as quantitative analysis, a Double Dispersion X-ray Spectrometer is used, which is normally available as an accessory with any scanning electron microscope. The spectrum is recorded over the range of wave lengths within which relevant lines may be present (1-12Å). The lines are identified by referring to the L-value tables provided by the manufacturer.

In the quantitative analysis, the intensities of the x-ray lines from the specimen are compared with those from standard samples of known composition. It is required that certain instrumental corrections, dependent on the characteristics of the measuring system, as well as the background, the chief source of which is the continuous x-ray spectrum, have to be carried out. After this, certain "matrix corrections", which take account of the various factors governing the relationship between the intensity and the composition, are carried out at the analysed point.

MATRIX CORRECTIONS

The relation between concentration of an element and the corresponding intensity of the emitted x-ray line is not simple, but depends in a complicated manner on the composition of the sample. So a correction, commonly called Matrix corrections, which depend on composition is made and the specimen to specimen standard ratios accordingly are corrected and the correct concentrations are obtained.

If (C') is the uncorrected concentration of each element and (C₀) is the concentration of that element in the standard then,

$C' = C_0 (I/I_0)$, where I and I₀ are the intensities of the specimen and standard respectively.

The matrix effects may be represented by a factor(F) applied as cor-

rection to the intensity. Similarly, a factor (F₀) has to be applied to the standard intensity.

This results in the corrected concentration

$$C = C' (F/F_0)$$

The phenomena upon which matrix corrections depend are:

- absorption of characteristic x-rays emerging from the specimen
- enhancement of the characteristic x-ray intensity due to fluorescence by other lines
- loss of x-ray intensity owing to incident electrons being back scattered out of the specimen and
- variation in the efficiency of x-ray production which is governed by the stopping power of the specimen (a function of atomic number).

These corrections are generally called the Z.A.F. corrections.

Method for quantitative analysis with ZAF method

It has been found with fairly good accuracy that the relative intensity(I) which is simply the intensity ratio of unknown to the standard sample is very nearly equal to the weight fraction C(I) of an element I in unknown sample. The direct experimental result so obtained will be either greater or smaller than the relative intensity corresponding to the concentration as discussed earlier due to effects of atomic number, absorption and x-ray fluorescence. The correction factors of these matrix effects are customarily called the ZAF correction [5].

If relative intensity $K_A = I_{\text{sample}}/I_{\text{standard}}$, ZAF calculation is given by

$$C_A = K_A \times \left\{ \frac{f_A(\lambda_A)}{f_{AB}(\lambda_{AB})} \right\} \times \left\{ \frac{R_A}{R_{\text{sample}}} \times \frac{S_A^{\text{stop}}}{S_A} \right\} \times \left\{ \frac{1}{1 + \frac{I_A(f)}{I_A(d)}} \right\} - I$$

where C_A is the true concentration of the element A
 K_A is the relative intensity of the element A

$$\left\{ \frac{f_A(x_A)}{f_{AB}(x_{AB})} \right\}^{-2} \text{ is the absorption correction factor for the element A}$$

$$\left\{ \frac{R_A}{R_{\text{Samp}}} \times \frac{S_A}{S_A^{\text{Samp}}} \right\}^{-3} \text{ is the atomic number correction factor for the element A}$$

and

$$\left\{ \frac{1}{1 + \frac{I_A(f)}{I_A(d)}} \right\}^{-4} \text{ is the fluorescence correction factor for the element A}$$

1. Absorption correction

Absorption correction is one of the major factors in the ZAF corrections. This correction becomes essential because of the fact that x-rays are absorbed in different degrees within unknown and standard samples respectively. So during the computation of the absorption correction factor, one must take into consideration the mass absorption coefficients of the elements in the sample (μ/ρ), energy of the incident electron and the x-ray take off angle, θ . In this case, θ is 35 degrees.

$$f(x) = \frac{f_A(x_A)}{f_{AB}(x_{AB})} = \frac{1 + h_A}{(1 + \frac{x_A}{\sigma_c}) (1 + h_A (1 + \frac{x_A}{\sigma_c}))} \quad \text{--- 5}$$

$$\frac{1 + h_{\text{samp}}}{(1 + \frac{x_{AB}}{\sigma_c}) (1 + h_{\text{samp}} (1 + \frac{x_{AB}}{\sigma_c}))} \quad \text{--- 6}$$

$$x_A = (\mu/\rho)_A^A \times \text{cosec } \theta \quad \text{--- 7}$$

$$x_{AB} = (\mu/\rho)_{\text{Samp}}^A \times \text{cosec } \theta \quad \text{--- 7}$$

$$(\mu/\rho)_{\text{Samp}}^A = \sum C_i \times (\mu/\rho)_A^i \quad \text{--- 8}$$

$$(\mu/\rho)_A^i \quad \text{--- 9}$$

From data book supplied by manufacturers

where μ is the mass attenuation coefficient of the element, ρ is the density of the element

$$h_A = 1.2 \times A_A / Z_A^2 \text{ from the data book where}$$

A_A is the atomic weight of element A

Z_A is the atomic number of the element A

$$h_{\text{samp}} = C_i + h_i$$

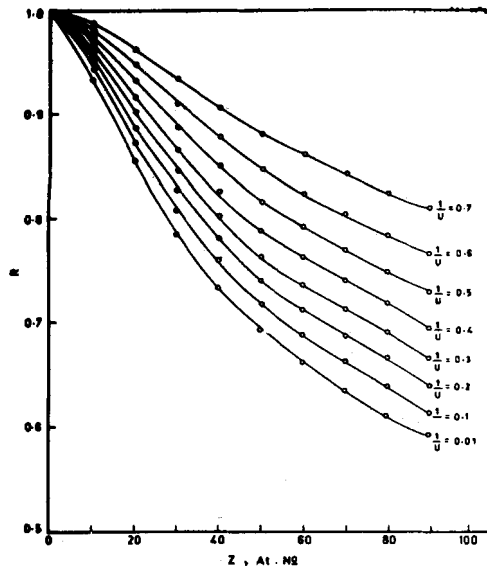
σ_c is the Lenard coefficient and h is given by $h = \sigma/k$ where k is the constant derived from the distribution of angular deflections.

2. Atomic number correction

The penetration and reflection characteristics of the impinging electrons in the sample and the standard do not remain the same. Therefore, this fact has to be taken into consideration and necessary correction has to be provided while computing the concentration. These two factors penetration(S) and reflection (R) tend to cancel each other, and thereby the necessary correction is very small. Atomic number correction factor .

$$\alpha = \frac{R_A^A}{R_A^{\text{Samp}}} \times \frac{S_A^{\text{Samp}}}{S_A^A} \quad \text{--- 10}$$

where R_A^A is the reflection factor of the element A is given in the figure 1 provided by the manufacturer for the particular type of instrument.



Then

$$R_A^{\text{Samp}} = \sum C_i \times R_A^i$$

$$S_A^A = \frac{Z_A}{A_A} \times \ln(1.166 \times \frac{E}{J_A})$$

where A_A is the atomic weight of the element A

Z_A is the atomic number of the element A

E is the energy of the X-ray

where $E = 1/2$ (Excitation energy + Accelerating voltage)

J_A = Ionisation potential, given in the standard tables

$$S_A^{\text{Samp}} = \sum C_i \times S_A^i$$

Fluorescence correction

Fluorescence correction is only necessary if the characteristic x-ray line of an element, say B, lies on the short wavelength side of the absorption edges of line of the concerned element, A. The x-ray photon of the element B, therefore, has the possibility to excite the element A in the sample. The effect of continuum x-rays emitted may also be similar, but the amount of error introduced due to this will be generally very small and always neglected.

Fluorescence correction factor

$$\gamma = \left\{ \frac{I_A(f)}{I_A(d)} \right\}_B = C_B \times J(A) \times D \times \frac{(\mu/\rho)_B^A}{(\mu/\rho)_{\text{Samp}}^A} \times \{g(x) + g(y)\} \quad \text{--- 11}$$

where J(A) is energy for excitation obtained from standard tables

D = a function depending on the accelerating voltage and the atomic number difference between A and B and is provided by the manufacturer

$$x = \frac{(\mu/\rho)_A^{\text{Samp}}}{(\mu/\rho)_B^{\text{Samp}}} \times \text{cosec } \theta \quad \text{--- 12}$$

$$y = \frac{\sigma_c}{(\mu/\rho)_B^{\text{Samp}}} (\sigma_c \text{ of element B}) \quad \text{--- 13}$$

$$g(x) = \frac{\ln(1+x)}{x} \quad \text{--- 14}$$

$$g(y) = \frac{\ln(1+y)}{y} \quad \text{--- 15}$$

From the foregoing description of the ZAF correction it may be clearly seen that the calculation is monotonous with involvement of many variables and data. The calculation once made gives out new corrected concentrations factor which is again to be treated as the starting values to effect correction. Such iterations carried out many times will give the approaching value of 1 for the sum of concentrations of all components.

EXPERIMENT

Carbon-manganese steel sample was taken. This specimen contained Cr, C, Mn, Si and Fe and was subjected to quantitative analysis in the DDS attached to the JSM 35CF model S.E.M. The specimen was polished to less than a micron roughness and a probe current of 1×10^{-8} amperes was used. Probe diameter was less than 5 microns. The intensity values were taken for the individual elemental components in the sample and also for the corresponding standards. After carrying out the background corrections, these values were used for the computations.

Computation of concentrations after ZAF correction

A programme has been written in the basic language suitable for loading in PB 300 Casio personal computer. The flow diagram for the programme is shown in Appendix I. The detailed programme listing is given in the Appendix II. A few points were borne in mind before carrying out the required correction. In this sample, carbon x-rays are not absorbed by the other constituents. So, there is no need of absorption correction for carbon. Fe is the atomically heaviest element in this specimen and so it has no fluorescence. The fluorescence correction for Mn is negligible. In the case of Si and C, x-ray energies are very much lower than the x-ray energies of the other elements. Hence, chromium alone has fluorescence with Fe x-rays and is computed.

Program

The program contains three subroutines for calculating absorption correction factor, atomic number correction factor and fluorescence correction factor respectively. The program repeats five times for calculating correction factors of the five elements (Fe, Mn, Cr, C, Si, the constituents of the sample analysed). During the program execution, the computer first calculates the sum of the relative intensities of the constituents. Then, in the first cycle, it will calculate (a) absorption (b) atomic number and (c) fluorescence correction factors for the first element. In the subsequent cycles, the evaluation of the correction factors is carried out until for all the five elements the correction is done.

If the specimen has any element that needs fluorescence correction, then we must choose the elements in the order of higher atomic number to lower atomic number. During the end of each cycle, it is so arranged in the programme that the absorption correction factor (AF), atomic correction factor (ZF) and the fluorescence correction factor (FF) of the computing element are displayed. If the element has no fluorescence correction or has no absorption correction, then the appropriate factors will be displayed as 1 (one).

At the end of the fifth cycle, the name of each element and its concentration are displayed. Then it will display the total concentration. In the next step, if the total concentration is ≤ 1 it will send for normalisation. And the programme will go to end.

The given programme holds good for specimens containing five elements and it can be extended for the specimens containing less than or more than five elements. The entire programme has been written in the basic language suitable for feeding PB 300 portable computer [6].

RESULTS

The relative intensities of the elements got from the EPMA for the sample is given below:

Fe = 0.97, Mn = 0.0083, Cr = 0.0008, Si = 0.0032
C = 0.0077 and the total = 0.99

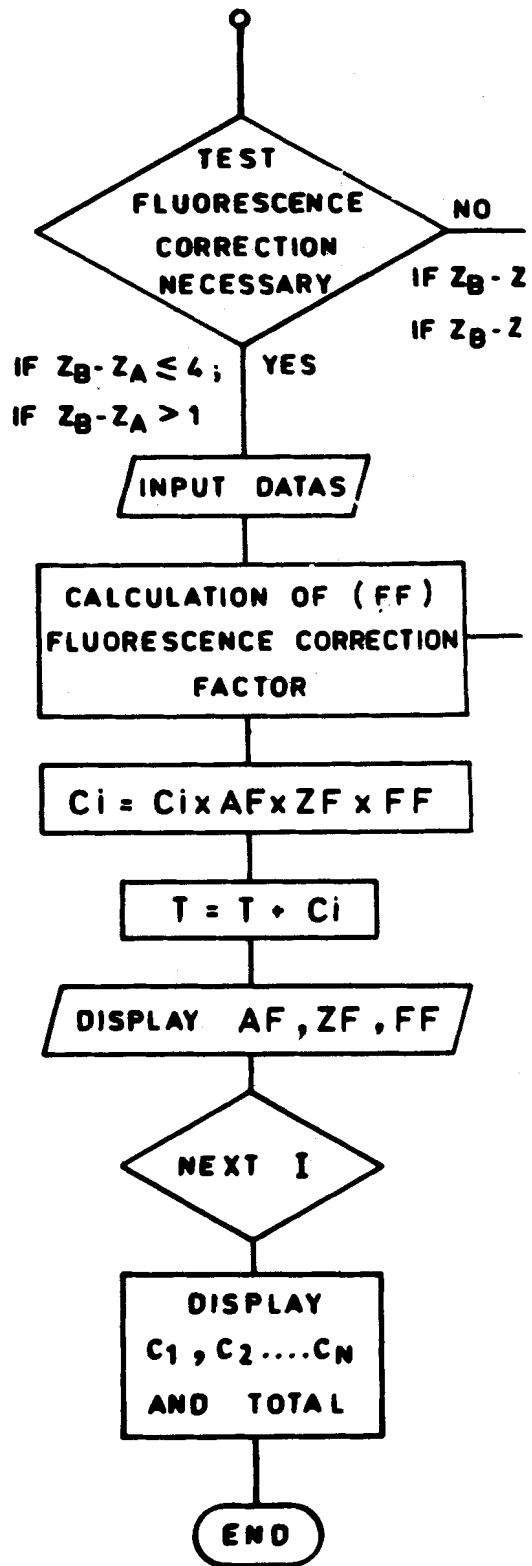
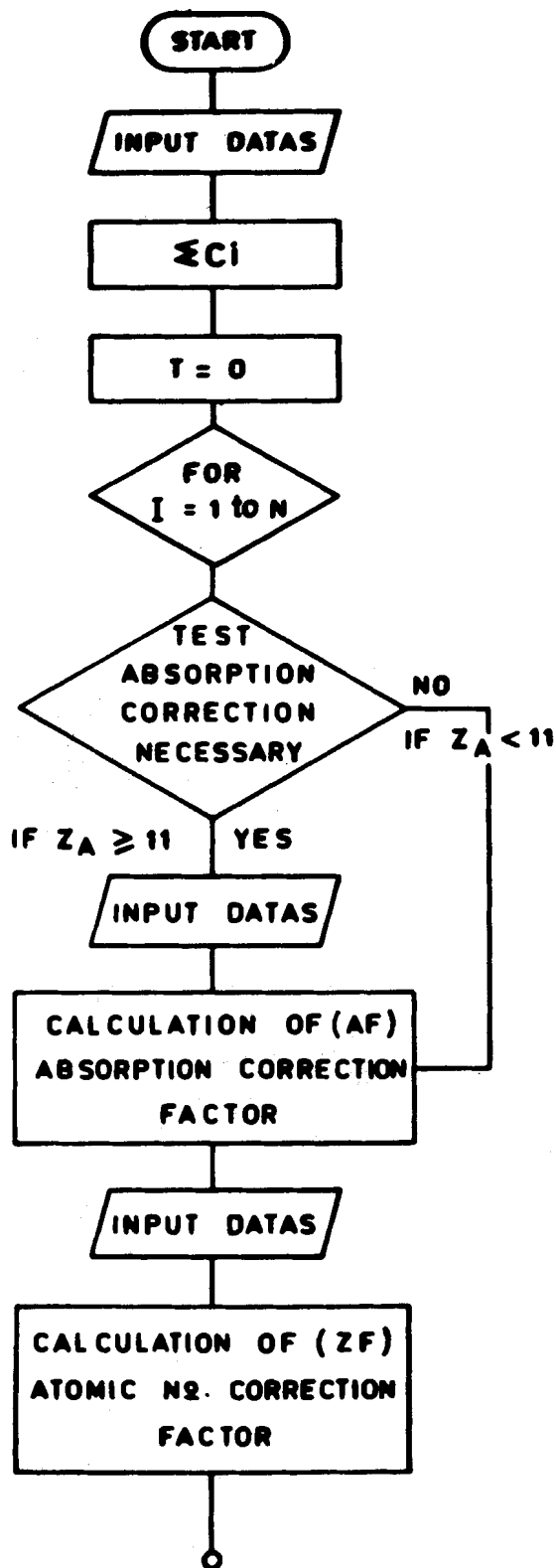
After doing the ZAF corrections, the true concentrations of the individual elements are tabulated.

Element	RI	AF	ZF	FF	Corrected concentration
Fe	0.97	1.000045	1.00025	1	0.9740
Mn	0.0083	1.0067	0.9723	1	0.0082
Cr	0.0008	1.0174	0.9814	0.7817	0.0006
Si	0.0032	2.9079	0.9890	1	0.0092
C	0.0077	1	1.019	1	0.0080
Total					1.0000

PROGRAM

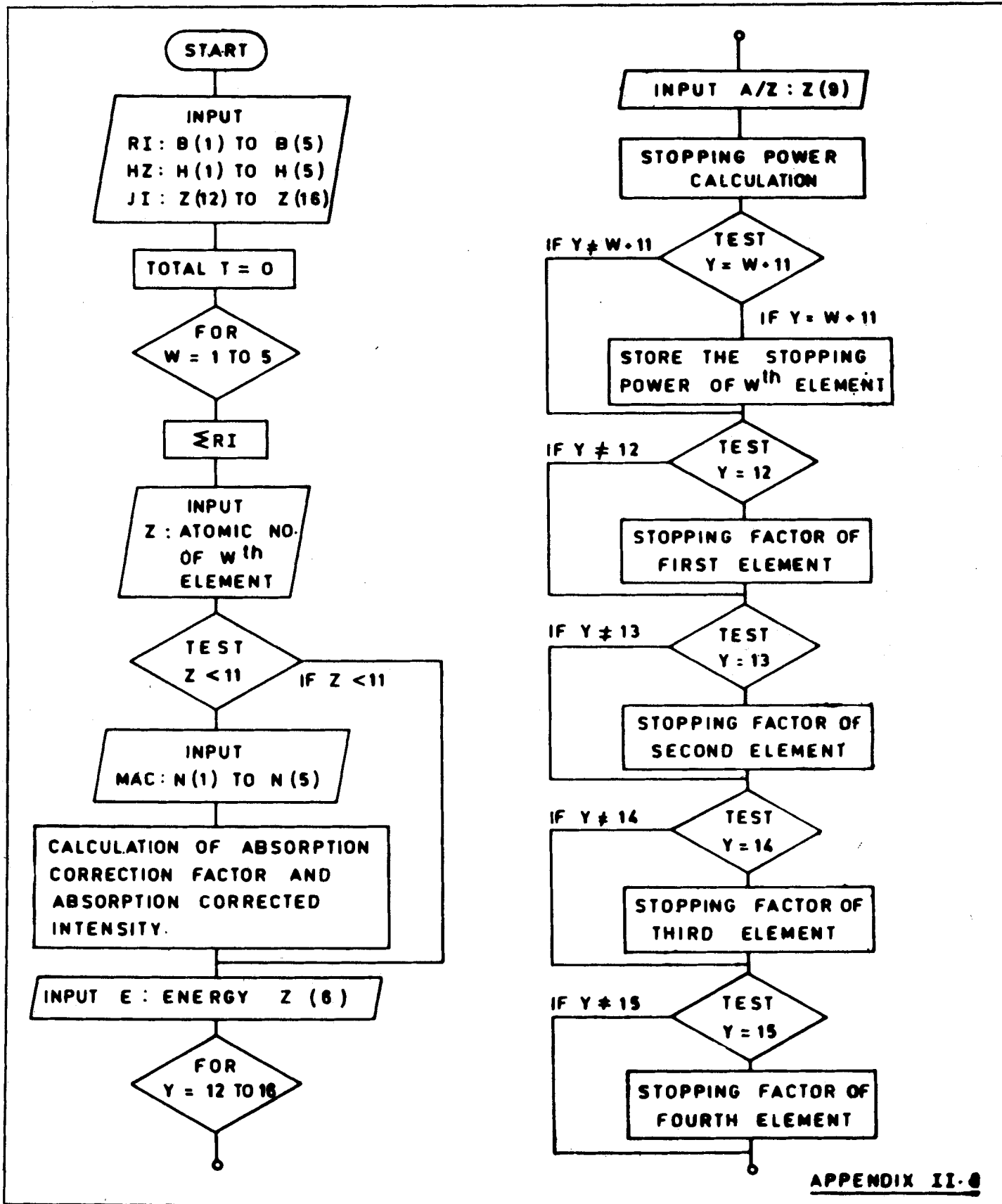
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10 INPUT "F,M,CR,S,C; RI", B(1), B(2), B(3), B(4), B(5)
20 INPUT "F,M,CR,S,C; HI", H(1), H(2), H(3), H(4), H(5)
30 INPUT "F,M,CR,S,C; JI", Z(12), Z(13), Z(14), Z(15), Z(16)
40 T = 0
50 FOR W = 1 TO 5
60 B = B(1) + B(2) + B(3) + B(4) + B(5)
70 A = 1
80 INPUT "Z", Z
90 IF Z < 11 THEN 160
100 INPUT "F,M,CR,S,C; MAC", N(1), N(2), N(3), N(4), N(5), "X", X
110 N = (N(1) * B(1) + N(2) * B(2) + N(3) * B(3) + N(4) * B(4) + N(5) * B(5))/B
120 H = (H(1) * B(1) + H(2) * B(2) + H(3) * B(3) + H(4) * B(4) + H(5) * B(5))/B
130 U = N(W)/X/SIN 35°
140 V = N/X/SIN 35°
    
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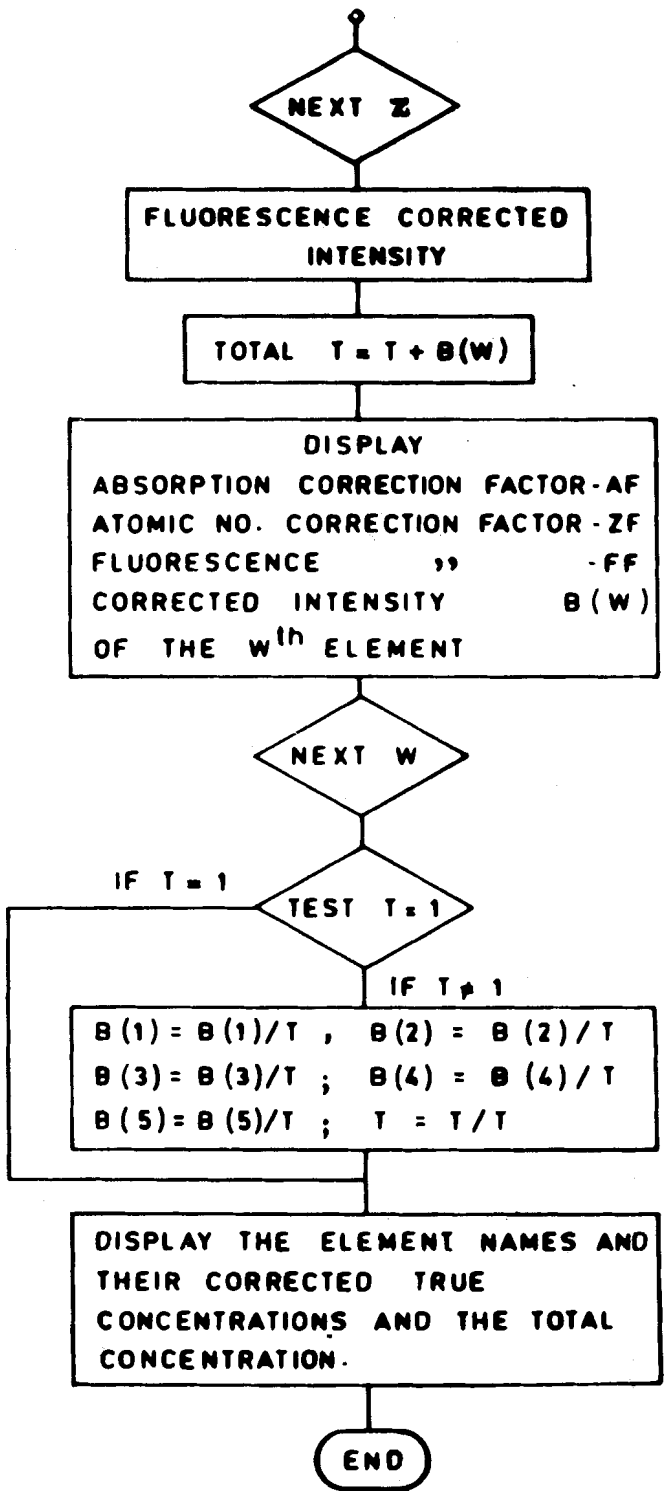
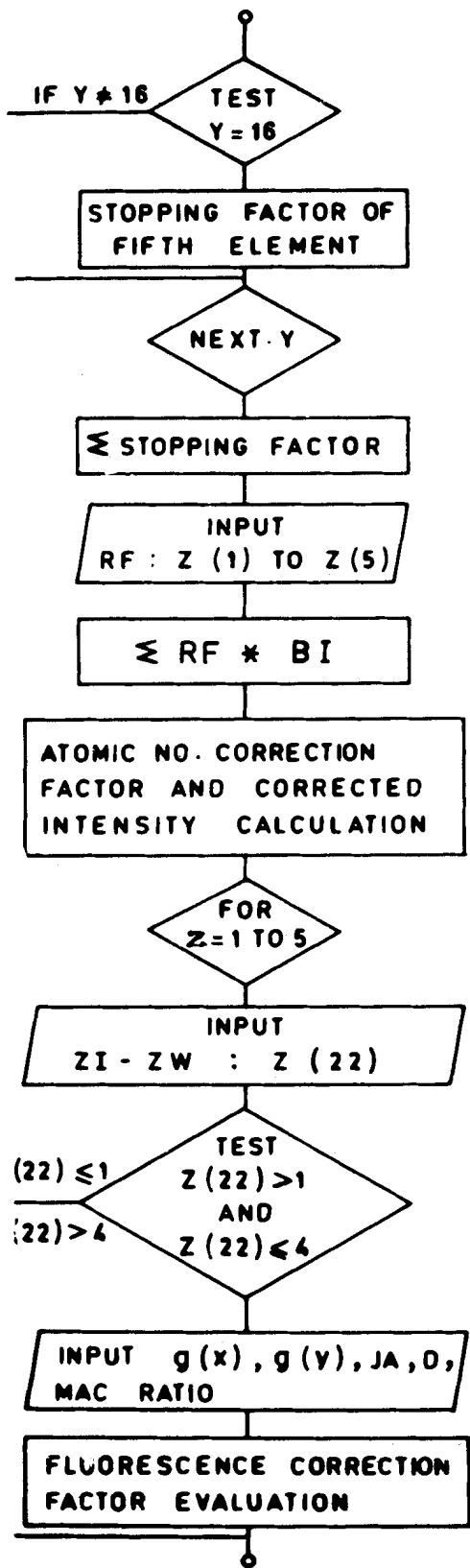


FLOW DIAGRAM

APPENDIX - I



APPENDIX II.8



APPENDIX II-D

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150  A = (1 + H(W))/((1 + U) * (1 + H(W) * (1 + U)))
      (1 + H)/((1 + v) * (1 + H * (1 + V)))
160  INPUT "E", Z(6)
170  FOR Y = 12 TO 16
180  INPUT "A/Z", Z(9)
190  Z(10) = Z(9) * LN (1.166 * Z(6)/Z(Y))
200  IF Y ≠ W + 11 THEN 220
210  Z(11) = Z(10)
220  IF Y ≠ 12 THEN 240
230  Z(17) = Z(10) * B(1)
240  IF Y ≠ 13 THEN 260
250  Z(18) = Z(10) * B(2)
260  IF Y ≠ 14 THEN 280
270  Z(20) = Z(10) * B(3)
280  IF Y ≠ 15 THEN 300
290  Z(29) = Z(10) * B(4)
300  IF Y ≠ 16 THEN 320
310  Z(30) = Z(10) * B(5)
320  NEXT Y
330  Z(8) = (Z(17) + Z(18) + Z(20) + Z(29) + Z(30))/B
340  INPUT "F,M,CR,S,C: RF", Z(1), Z(2), Z(3), Z(4), Z(5)
350  Z(7) = (Z(1) * B(1) + Z(2) * B(2) + Z(3) * B(3) + Z(4) * B(4) + Z(5)
      * B(5))/B
360  Z(19) = Z(W) * Z(8)/Z(7)/Z(11)
380  Z(24) = 0
390  FOR Z = 1 TO 5
400  INPUT "ZI — ZW", Z(22)
410  IF Z(22) ≤ 1; IF Z(22) > 4 THEN 450
420  INPUT "G(Y)", Z(21), "G(X)", Z(25), "JA", Z(26), "D", Z(27), "BI
      * NI/N", Z(23)
430  Z(28) = Z(23) * Z(26) * Z(27) * (Z(21) + Z(25))/B
440  Z(24) = Z(24) + Z(28)
450  NEXT Z
460  Z(24) = 1/(1+Z(24))
480  B(W) = B(W) * Z(24) * A * Z(19)
490  T = T + B(W)
500  PRINT "AF", A, "ZF", Z(19), "FF", Z(24), "MAC", N
510  NEXT W
520  IF T = 1 THEN 570
530  FOR N = 1 TO 5
540  B(N) = B(N)/T
560  NEXT N
570  PRINT "F", B(1), "M", B(2), "CR", B(3), "S", B(4), "C", B(5)
580  END

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