

## 2.4 ZAF CORRECTION METHOD

The ZAF correction method determines the mass concentration  $C_A$  of an element A from the following equation:

$$C_A^{UNK} = K_A^{UNK} \times G_Z \times G_A \times G_F$$

$$= K_A^{UNK} \times \frac{R_A^{STD} \times P_A^{STD}}{R_A^{UNK} \times P_A^{UNK}} \times \frac{f_A^{STD}(\chi_A)}{f_A^{UNK}(\chi_A)} \times \frac{1}{1 + \frac{I_A(f)}{I_A(d)}}$$

where  $K_A^{UNK} = \frac{I_A^{UNK}}{I_A^{STD}}$  and  $I_A$  are the X-ray intensities (in cps) per unit current of element A after dead-time correction and background correction; UNK indicates the unknown sample; STD indicates the standard sample; and  $G_Z$ ,  $G_A$ , and  $G_F$  are atomic-number correction coefficient, absorption correction coefficient, and fluorescence correction coefficient, respectively.

The following are brief descriptions of atomic-number correction, absorption correction, and fluorescence correction.

- Atomic number correction (Z)

Atomic-number correction deals with differences in the behavior of incident electrons between an unknown sample and a standard sample. This correction is usually considered in two factors: the P factor, including the stopping power term, which indicates penetration of electrons into the sample, and the R factor which indicates the backscattering of electrons from the sample. The two factors tend to cancel each other, so that the correction factors are not very large in most cases.

- Absorption correction (A)

Absorption correction deals with differences in the degree of X-ray absorption between an unknown sample and a standard sample. This correction gives consideration to the mass absorption coefficient, incident electron energy, and X-ray take-off angle.

- Fluorescence correction (F)

Fluorescence correction needs to be considered if the characteristic X-rays from an element, B, are at the short-wavelength (high-energy) side of the absorption edge of another element, A. In this case, the X-rays from element B may excite element A. The same is true with fluorescence excitation by continuous X-rays, but the effect usually is negligible.

### 2.4.1 Atomic Number Correction

The basic equation of atomic number correction is

$$G_z = \frac{R^{STD}}{R^{UNK}} \times \frac{P^{STD}}{P^{UNK}}$$

where R is the backscattering factor and P is the penetration factor.  
The backscattering factor of an unknown sample is determined from:

$$R = \sum_j C_j R_{ji}$$

$$R_{ji} = R(Z_j, U_i)$$

where  $C_j$ : concentration of element j,  $\sum C_j = 1$

$Z_j$ : atomic number of element in matrix

$U_i$ : over-voltage ratio ( $= E_0/E_{Ki}$ )

$E_{Ki}$ : K-shell excitation energy of element i

$E_0$ : accelerating voltage

The value  $R_{ji}$  is determined by calculating the values\*, that are given by Duncumb-Reed, through the method of least squares:

$$R(Z_j, U_i) = 1 - X \cdot V \left[ -0.187204 + 1.67366V - 1.51187V^2 + 0.707063V^3 \right. \\ \left. + X \left\{ 3.63547 - 1.9914V - 1.6539V^2 + 0.477246V^3 \right\} \right. \\ \left. + X^2 \left\{ -4.04514 - 4.11268V + 9.26509V^2 - 2.79199V^3 \right\} \right. \\ \left. + X^3 \left\{ 1.54054 + 3.43134V - 5.22007V^2 + 1.23353V^3 \right\} \right]$$

where  $X = Z_j/100$ ,  $V = 1 - 1/U_i$

The penetration factor  $P_i$  is given by

$$P_i = \frac{1}{M} \left[ (U_i - 1) \frac{1}{W_i} \ln W_i \left\{ Li(U_i W_i) - Li(W_i) \right\} \right]$$

where  $Li(x)$  is a logarithmic differential function expressed as

$$Li(x) = C + \ln |\ln x| + \sum_{r=1}^{\infty} \frac{(lnx)^r}{r \cdot r!} \quad C: \text{Euler's constant}$$

$$\ln W_i = \frac{1}{M} \sum_j C_j \frac{Z_j}{A_j} \ln \frac{1.166 E_{Ki}}{J_j} \quad i: \text{emitter, } j: \text{absorber}$$

\* P. Duncumb. and S. J. B. Reed, NBS Special Publication, 298, P. 133 (1968)

$$M = \sum_j C_j \frac{Z_j}{A_j}$$

$A_j$ : atomic weight of element j

$J_j$ : average ionization potential of  
element J (eV)

$$J_j = 9.76Z_j + 58.8Z_j^{-0.19} \quad (\text{Berger-Seltzer}^*)$$

$$= Z_j (9.76 + 58.8Z_j^{-1.19})$$

For each element, the atomic weight is given in the file atom.asc in the directory /opt/epma/phys, while the excitation energy is given in the file abs\_edge.dat in the same directory.

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\* M. J. Berger and S. M. Seltzer, *Nat. Acad. Sci.*, Nat. Res. Council. Publ. 1133, P. 205 (1964)

## 2.4.2 Absorption Correction

Absorption correction uses the following Philibert formula:

$$f(x) = \frac{1+h}{\left(1+\frac{x}{\sigma}\right)\left\{1+h\left(1+\frac{x}{\sigma}\right)\right\}}$$

where

$$h = 1.2 \frac{A}{Z^2} \quad A: \text{atomic weight}$$

Z: atomic number

$$\sigma = \frac{4.5 \times 10^5}{E_0^{1.65} - E_K^{1.65}} \quad (\text{Lenard's coefficient}) \quad E_0: \text{accelerating voltage (in keV)}$$

$E_K$ : K-shell excitation energy (in keV)

$$x = (\mu / \rho) \operatorname{cosec} \theta \quad \theta: \text{X-ray take-off angle}$$

$\mu/\rho$ : mass absorption coefficient

The mass absorption coefficient is determined as follows:

- $Z < 10$  (wavelength  $\lambda$  is more than  $12\text{\AA}$ ): The values given by Henke\* are used.
- $Z \geq 10$  (wavelength  $\lambda$  is  $12\text{\AA}$  to  $0.7\text{\AA}$ ): The values calculated by Heinrich method\*\* are used.

### ● Heinrich method

- The mass absorption coefficient of characteristic X-rays (radiation) from an element for the absorber is given as:

$$\mu / \rho = C_i(Z) \lambda_R n_i(Z)$$

where  $C_i(Z)$  and  $n_i(Z)$  are values that depend on the atomic number (Z) of the absorber. The value i varies with the relation between the X-ray wavelength  $\lambda_R$  and the absorber's absorption edge.

- The wavelengths and coefficients needed for calculation are as follows:

Wavelength as a function of Z:	wavelength of X-rays ( $K\alpha$ , $K\beta$ , $L\alpha$ , $L\beta$ , $M\alpha$ , $M\beta$ )
Absorber as a function of Z:	wavelength of absorption edge ( $K$ , $L_1$ , $L_2$ , $L_3$ , $M_1$ , $M_2$ , $M_3$ , $M_4$ , $M_5$ )
	coefficient $C_i$ ( $C_K$ , $C_{KL}$ , $C_{L1}$ , $C_{L2}$ , $C_{LM}$ , $C_{M1}$ , $C_{M2}$ , $C_{M3}$ , $C_{M4}$ , $C_{MN}$ )
	coefficient $n_j$ ( $n_K$ , $n_{KL}$ , $n_{LM}$ , $n_{MN}$ )

\* B. L. Henke, *Adv. X-ray Anal.*, 9, 460 (1966)

B. L. Henke et al., *Atomic Data and Nuclear Data Tables*, vol 27, No.1 (1982)

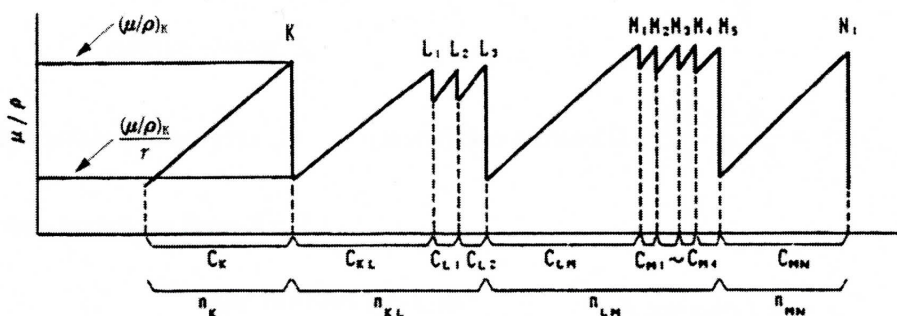
\*\* K. F. J. Heinrich, *The Electron Probe* (New York, Wiley), P. 296 (1966)

All of these values are approximated by the quartic equation for the atomic number:

$$X = \exp \{ A(0) + A(1)Y + A(2)Y^2 + A(3)Y^3 + A(4)Y^4 \}$$

where  $Y = \ln(Z)$   
 $A(i)$ : constant

- The suffix  $i$  in  $C_i(Z)$  and  $n_i(Z)$  is determined by placing the absorption edges relative to the order of wavelength and identifying the positions of wavelength,  $\lambda_R$ , of characteristic X-rays, as shown below.



- ✍ The values  $C_i$  and  $n_i$  are given in a table by Heinrich. The constants for  $A(0)$  to  $A(4)$  are determined so that they may come close to the values in the table. However,  $C_{M4}$  is unknown.
- ✍ In  $C_i$ , the values  $C_{L1}$  and  $C_{L2}$  are proportional to  $C_{KL}$ , while the values  $C_{M1}$ ,  $C_{M2}$ ,  $C_{M3}$  and  $C_{M4}$  are proportional to  $C_{LM}$ . Therefore, only  $C_K$ ,  $C_{KL}$ ,  $C_{LM}$  and  $C_{MN}$  are calculated in the quartic equation; the others are determined by multiplying them with the proportional constants.
- ✍ For  $n_i$ , Heinrich always specifies  $n_{LM} = 2.6$  and  $n_{NM} = 2.22$ .
- ✍ The values for the absorption edge and wavelength are also calculated with the quartic equation of  $Z$ .

These mass absorption coefficient values are stored in the following files in the directory /opt/epma/phys/mac: Ka.mac, Kb.mac, La.mac, Lb.mac, Ma.mac, and Mb.mac.

### 2.4.3 Fluorescence Correction

Fluorescence correction usually refers to determining the value  $^{fl}\gamma_A$  in the equation below. Assuming the specimen is a binary element system in which element A is excited by element B, we have:

$$^{fl}\gamma_A = \frac{I_A(f)}{I_A(d)} = \frac{1}{2} C_B \frac{r_K^A - \ln(\mu/\rho)_B^A}{r_K^A (\mu/\rho)_B^{AB}} W_K^B \frac{A_A}{A_B} \left( \frac{U_0^B - 1}{U_0^A - 1} \right)^{1.67} \left\{ \frac{\ln(1+x)}{x} + \frac{\ln(1+y)}{y} \right\}$$

where

- $I_A(d)$ : intensity of primary X-rays of element A subject to direct excitation
- $I_A(f)$ : intensity of X-rays due to fluorescence excitation of the other element B
- $C_B$ : concentration of element B
- $r_K^A$ : absorption edge jump factor for element A
- $(\mu/\rho)_B^{AB}$ : specimen's mass absorption coefficient for X-rays from element B
- $(\mu/\rho)_B^A$ : element A's mass absorption coefficient for X-rays from element B
- $W_K^B$ : K-shell fluorescence absorption rate of element B
- $A_A$ : atomic weight of element A
- $A_B$ : atomic weight of element B

$$U_0^A = E_0 / E_K(A)$$

$$U_0^B = E_0 / E_K(B)$$

$$x = \left\{ (\mu/\rho)_A^{AB} / (\mu/\rho)_B^{AB} \right\} \text{cosec}\theta$$

$$y = \sigma / (\mu/\rho)_B^{AB}$$

Considering the excitation caused by other X-rays, Reed transformed the above equation to the following:

$$^{fl}\gamma = C_B J_A D \frac{(\mu/\rho)_B^A}{(\mu/\rho)_B^{AB}} \{g(x) + g(y)\}$$

where

$$J(A) = \frac{1}{2} P_{ij} \frac{r_{K(L)}^A - 1}{r_{K(L)}^A} W_{K(L)}^A \frac{A_A}{A_B}$$

$$D = \left( \frac{U_0^B - 1}{U_0^A - 1} \right)^{1.67}$$

$$g(x) = \frac{\ln(1+x)}{x}$$

- $P_{ij}$ : constant related to difference in generation of K-line and L-line

The values  $J(A)$  are given by Reed in a table.

The values are stored in the file `Reed_JA.dat` in the directory `/opt/epma/phys`.

- ✍ Whether fluorescence excitation occurs is checked by comparing the wavelengths at the absorption edges of each element and the wavelengths of all other X-rays generated from other elements.
- ✍ Fluorescence excitation can be caused by X-rays not even intended to be measured. This software also takes such X-rays into account in the correction calculations.