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A Simple Correction Procedure
For Quantitative Electron Probe
Microanalysis

U.S.
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1972

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A calculation technique for data reduction in quantitative electron probe microanalysis is described. This technique is embodied in a computer program, called MULTI8, written in FORTRAN IV for batch processing. Six chemical elements may be determined simultaneously without redimensioning the program. The relative x-ray intensity data are corrected for atomic number, absorption and secondary fluorescence due to characteristic lines. Options for calculating the mass fraction of one chemical element by difference or by stoichiometry are available in the program.

Key words: Absorption; atomic number; chemical elements; computation procedure; data reduction; electron probe microanalysis; fluorescence; time-sharing; x-ray analysis.

Introduction

This Technical Note details the practical aspects of applying the concepts and models for data reduction which were presented in NBS Technical Note 521 [1] which is reproduced in Appendix II for the convenience of the reader. For the computation of mass fractions of chemical elements in quantitative electron probe microanalysis, we use two calculation techniques, which are contained, respectively, in programs entitled MULTI8 and COR. The MULTI8 program, described herein, was originally

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written in BASIC language for use with a time-shared computer.¹ MULTI8 has had several predecessors dating back to 1965 when we first had access to a time-shared computer. Until recently, all of the quantitative electron probe microanalysis results generated in this laboratory were calculated with these programs. The reduced computation capacity available with the early time-shared computer that we used forced certain simplifications, the most important being the omission of the fluorescence correction for excitation by the continuum. The present version of MULTI8 is a FORTRAN IV program suitable for batch processing.

A more complete treatment of the theoretical models, contained in the program COR, will be the subject of another Technical Note currently in preparation. The COR program includes the correction for fluorescence due to the continuum, and the integration of the stopping power term according to Springer [2] and to Philibert and Tixier [3]. COR requires a larger computer and has therefore not been adapted to time-shared computing. In practice, we usually find little difference between the results from MULTI8 and from the more extensive program COR. However, the input into COR is much simpler and requires less operator time, since the mass attenuation coefficients are internally generated, and all decisions concerning applicability of fluorescence corrections are also made internally.

¹The original BASIC version is available on request.

The number of chemical elements for which mass fractions may be simultaneously calculated by the program MULTI8 is limited only by the size of the computer. In its present form, MULTI8 occupies approximately 3.5 K words of storage and is dimensioned for a maximum of six chemical elements. The background and dead-time corrections as well as the specimen/standard intensity ratios must be precalculated.

MULTI8 performs the following corrections:

1. Absorption correction according to Philibert [4] and Duncumb [5]. The expression for sigma developed by Duncumb has been modified by Heinrich [6].
2. Fluorescence by characteristic lines according to Reed [7].
3. Atomic number correction by the method of Thomas [8] as modified by Heinrich. The backscatter factor, R, is that of Duncumb and Reed. The stopping power is calculated according to Bethe [9], using the mean excitation potentials of Berger and Seltzer [10]. An equivalent electron energy is calculated using an empirical fit obtained by H. Yakowitz. This yields the same result as full integration of the stopping power term according to Springer [2] and Philibert and Tixier [3].

There is no provision for correcting the effects of fluorescence produced by continuous radiation. For this reason, the customary form of correction by multiplicative factors (ZAF procedure) was used.

The iteration procedure followed is that of Criss [11]. However, we have not adopted Criss' suggestion of normalizing the intensity ratios. Only the concentration estimates are normalized before applying the corrections in the iteration. The iteration stops when variations for all elements between

two consecutive loops are less than 0.0001 (0.001%), which almost always is achieved in 3 to 6 loops. Should convergence within the specified limit not occur after 19 loops, the iteration is stopped, the results are listed, and the comment "NO CONVERGENCE" is printed. Failure to converge has not been observed in practice.

The program will accept any number of sets of data and calculate the results in sequence. The following special cases are acceptable:

1. Secondary (fluorescence) excitation of several chemical elements by one element, or of one or more elements by more than one element.

2. One or more elements included in the program may be absent.

3. One element may be determined by difference.

4. One or more elements, although not measured, may be calculated on the basis of stoichiometric relationships with the elements measured and/or with the element determined by difference.

5. The program allows for using different operating voltages in the determination of each element.

With slight modification, this program can also be used for the following cases:

1. The standard used for one or more elements is not an element but a compound;

2. The background and dead-time corrected intensity ratios of a specimen of known or postulated composition can be calculated.

Comments on the Program

The statement numbers below refer to the statement numbers appearing on the program listing.

Main Program

<u>Statements</u>	<u>Comments</u>
START-110	Dimension, formats and related statements.
Between 110 and 120	Read initial data and set up headings. Call input subroutine. Call subroutine to calculate backscatter coefficients. Loop for calculation of the electron absorption coefficient, σ , the h factor of Philibert, and the overvoltage term of Reed's fluorescence correction.
120-150	Write headings and read intensity ratios. Make first estimate of concentration or terminate if end of data has been reached.
150-300	Iteration loop.
150-180	Loop for determination by difference or stoichiometry. Obtain sum of concentration.
180-200	Adjust sum of concentrations to 1 for the purpose of calculating corrections.
200-270	Loop for calculating atomic number, absorption and fluorescence corrections.
220-250	Calculate stopping power terms. Calculate intermediate terms for atomic number, absorption and fluorescence corrections. Calculate characteristic fluorescence correction.

StatementsComments

250-260	Calculate atomic number correction. Calculate $f(\chi)$ values. Calculate the emergent intensity ratios for the assumed concentrations. By hyperbolic fit, obtain new estimates for concentrations, comparing the experimental intensity ratio with the one obtained by calculation.
270-310	Stopping criterion for iteration loop. If not convergent after 19 loops, stop iteration and print "NO CONVERGENCE".
320-370	Print results. Go to next set of data (line 130) Stop.

Input Subroutine

10-30	Dimension, formats and related statements.
Between 30 and 40	Read all data required for each element (but not intensity ratios).
40-END	Print out the characteristic fluorescence correction that has been selected. Return to main program.

Backscatter Subroutine

All	Calculate the backscatter coefficient, R , from the equation of Duncumb (as referenced by Heinrich [1]).
-----	--

Input Requirements

The numbers and letters below each card number are the FORTRAN IV formats for the card. (Card #2 is listed in full.)

Card #1

I1 col 2 number of element - N1 (max. of 6)
F4.1 col 6-9 x-ray emergence angle in degrees - N2
col 15-26 any title

Card #2

a namelist card written as follows beginning in col 1:

X\$NAM1 P=0, 2*1., .24, 4.2, .88, 2*.75, .88\$

Card #3

10F8.4 Read the data for each element:
 (each element requires 5 fields)
 atomic no. A(1,I), atomic weight A(2,I), operating
 kV
 A(3,I), min. excitation potential A(4,I), and
 fluorescence yield A(5,I). (In the input
 subroutine these variables are called AM
 instead of A.)

Card #4

10F8.4 Read mass absorption coefficients needed:
 $\mu(A,A)$, $\mu(A,B)$, $\mu(B,A)$, $\mu(B,B)$
 (first letter is the line - second is the absorber.)
 - M(I,J)

Card #5

10F8.4 Matrix for characteristic fluorescence correction -
 Q(I,J). (In the input subroutine this matrix is
 called QM.)

Card #6

10F8.4 Matrix for stoichiometry calculation. - B(I,J).
The values in this matrix are valences. Let us
assume that we have listed the elements of the
compound $\text{TiO}_2 \cdot \text{BaO}$ in the order: Ti, Ba, O.

If oxygen is determined stoichiometrically,
and the other elements directly, the matrix
B is as follows:

	Ti	Ba	O
TiK α	0	0	0
BaL α	0	0	0
O (stoich.)	4	2	2

Card #7 & above

8F10.5 Intensity ratios ← one card per analysis with
intensities of all elements on each card - K(I).

To calculate intensity ratios from known compositions,
these compositions should be substituted for the k-values on
the appropriate cards and the following changes made to the
main program:

Insert the three statements:

```
DABS = 1/D(J)
WRITE (IO, 70) Z(J), K(J)
WRITE (IO, 90) DABS
```

immediately before the statement which reads GO TO 270 (which
precedes statement 260).

After statement number 270, insert the statement:
GO TO 130

Then the remainder of the main program cannot be reached
and can be deleted except for the END statement.

Dictionary of Variables in MULTI8

The following notations are used:

1. If an * precedes a variable name, that variable must be input.
2. In the list of common symbols, i refers to the iteration number, j to the element number, and q to the measured line.
3. In the list of common symbols, an * in the symbol signifies the analyzed specimen.

Main Program

<u>Variable Name</u>	<u>Common Symbols</u>	<u>Description</u>
* A(1,J)	Z_j	Atomic number of the Jth element.
* A(2,J)	A_j	Atomic weight of the Jth element.
* A(3,J)	E_o	Operating kilovoltage in the determination of the Jth element.
* A(4,J)	E_q ($q=K, L_1, \dots$)	Minimum excitation potential, in keV, for the line used in determining element J.
* A(5,J)	ω_q	Fluorescent yields of elements which excite secondary emission of other elements.
* B(I,J)		Valence of element J used to determine element (I). B(I,I) the valence of element determined by stoichiometry, must be included.
B1		Stoichiometric contribution to concentration.
C(I,J)	C_j	Estimate of concentration of element J in the Ith iteration
CON	C_j	Final concentration of C(I,J).
D(J)	$1/f_p^*$, $1/f(\chi)^*$	Philibert's $1/f(\chi)$ for specimen.
E(I)	$\sum C_j$	Sum of concentrations for Ith iteration.
F(I)	σ	Sigma in Philibert's equation.
G(J)	$1/f_p^{st}$ $1/f(\chi)$	Philibert's $1/f(\chi)$ for the standard.

<u>Variable Name</u>	<u>Common Symbols</u>	<u>Description</u>										
G1		Factor for determining the equivalent electron energy for calculation of stopping power.										
H(I)	h	Philibert's $h = 1.2 \frac{A}{Z^2}$										
I, J, N, N4		Running index numbers in loops.										
IA	Z_j	Integer conversion of A(1, J) (atomic number).										
II		Logical unit number for input (II=5 for card reader).										
IO		Logical unit number for output (IO=6 for line printer).										
J1		Mean ionization potential from Berger-Seltzer equation.										
* K(I)	k	Background and dead-time corrected intensity ratios, in groups ordered according to the sequence of atomic numbers A(1, I). Special cases:										
		<table border="1"> <thead> <tr> <th>Case</th> <th>Value of K(I)</th> </tr> </thead> <tbody> <tr> <td>Element not present</td> <td>0 (Zero)</td> </tr> <tr> <td>Element determined by difference</td> <td>-1</td> </tr> <tr> <td>Element determined by stoichiometry</td> <td>1</td> </tr> <tr> <td>End of data</td> <td>2</td> </tr> </tbody> </table>	Case	Value of K(I)	Element not present	0 (Zero)	Element determined by difference	-1	Element determined by stoichiometry	1	End of data	2
Case	Value of K(I)											
Element not present	0 (Zero)											
Element determined by difference	-1											
Element determined by stoichiometry	1											
End of data	2											
K1		Reed's characteristic fluorescence correction factor.										
K9		$1 + \Sigma(K1)$.										
KK		Integer of the absolute value of K(I).										

<u>Variable Name</u>	<u>Common Symbols</u>	<u>Description</u>
* M(I,J)	$\mu(I,J), \frac{\mu}{\rho}$	Mass absorption coefficient for the line of element I and absorber J.
* N1		Number of elements in specimen.
* N2	ψ, θ	X-ray emergence angle in degrees.
N9		Subscript for selecting the proper characteristic fluorescence ($N9=Q(J,N4)+1$).
O(J)	$\mu(A,B)*$	In line A79: absorption coefficient for the specimen. In line A96: χ/σ for the specimen.
* P(4,1)	$P(k,j)$	Constants of Reed's equation, for $L \rightarrow K$ and $K \rightarrow L$ fluorescence. These are input on the NAME-LIST card NAM1.
* Q(I,J)		Switches for fluorescence of element (I) by element (J).
		Case Value of Q(I,J)
		No fluorescence 0
		K excites K 1
		L " L 2
		K " L 3
		L " K 4
R(I,J)	R	Backscatter factors according to Duncumb equation for radiation I and element J.
R1	R*	Backscatter factor from specimen.
S(IMK)	S	Stopping power factors calculated from Bethe's equation for radiation I and element J.
	$U_B^{-1} \quad 1.67$	
T(I,J)	$\frac{U_B^{-1}}{U_A^{-1}}$	Overvoltage term in Reed's equation.

<u>Variable Name</u>	<u>Common Symbols</u>	<u>Description</u>
U(J)	h^*	Philibert's h-value for the specimen.
U1	E_o/E_q	Overvoltage.
V(J)		Equivalent electron energy in the calculation of stopping power. (Fit by H. Yakowitz).
W(J)	$(R/S)^*$	Atomic number correction for the specimen.
X0		Factor for determining the equivalent electron energy for stopping power calculation.
X1	$(\chi/\sigma)^{st}$	(In Philibert's equation for the standard.)
X5,Y5	x, y	Factors x and y in Reed's equation [7].
Y8,Y9	μ	Mass absorption coefficients in the characteristic fluorescence correction.
Z(J)	k_J	Intensity ratio for element J, calculated in iteration I.
Z1	$\Sigma C_i Z_i$	Effective atomic number of the specimen.
Z9		Intermediate step in hyperbolic approximation of Criss.

Input Subroutine "INP"

Additional Variables

<u>Variable Name</u>	<u>Description</u>
* AM(I,J)	Same as A(I,J) in Main Program.
CH(I)	Variable "K" or "L" as defined by DATA statement B6.
IA	Part of switch for selecting proper printout of characteristic fluorescence correction.
IAM	Integer value of AM(1,J).
IBM	Integer value of AM(1,I).
IC1,IC2	Selected value of CH(I) (either "K" or "L").
IQ	Value of Q(I,J)+1.
IX	IX=5 (from Main Program).
JJ	JJ=N1 (from Main Program).
* QM(I,J)	Same as Q(I,J) in Main Program.

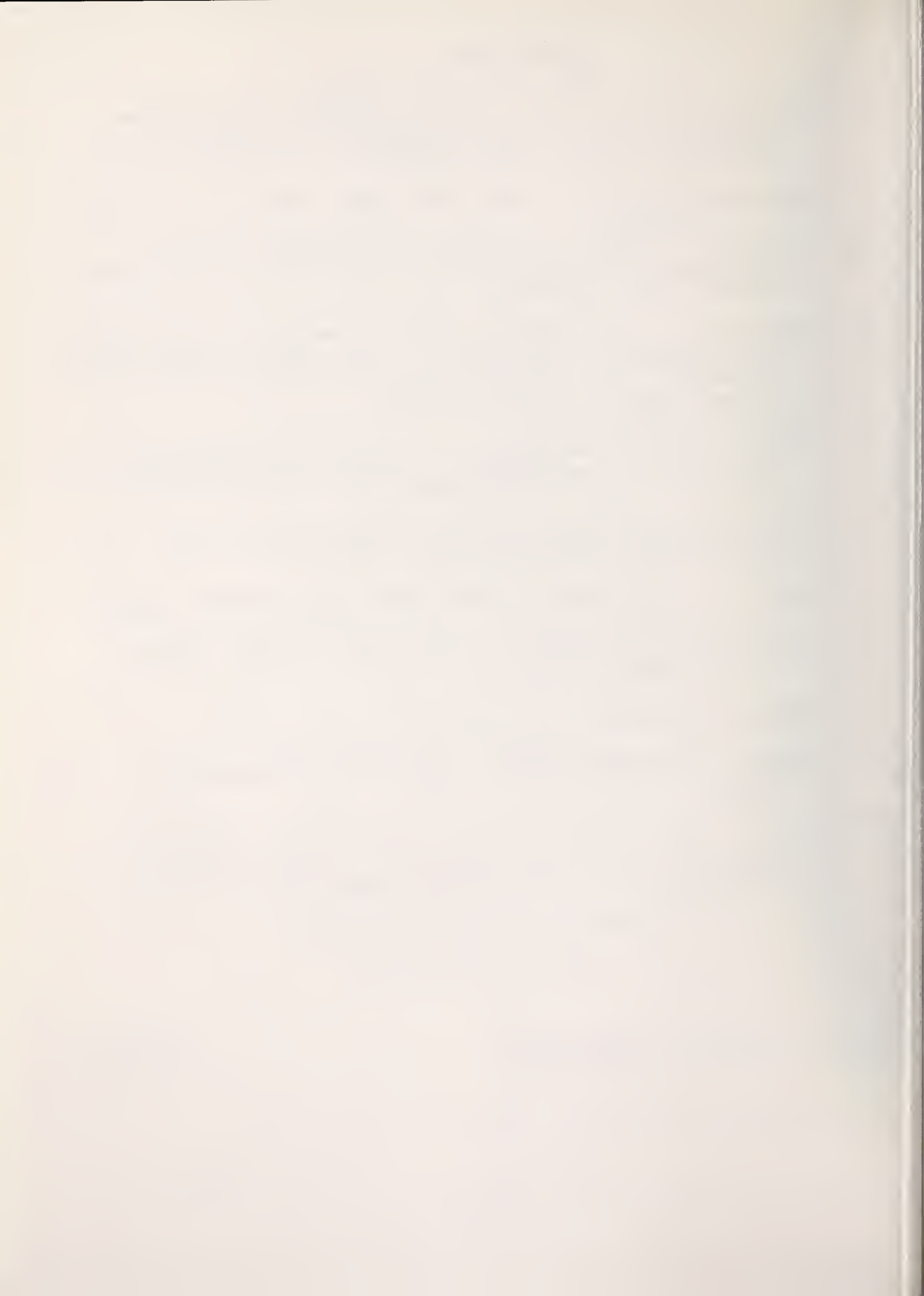
Backscatter Subroutine "BACK"

Additional Variables

R1,R2,R3 R4,R5,T1 T2,T3,T4,T5	Temporary factors used in the calculation of the backscatter factors R(I,J).
W	Reciprocal of the overvoltage (E_q/E_o).
W2,W3,W4,W5	W^2 , W^3 , W^4 , and W^5 respectively

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APPENDIX I

Program and an Example for MULTI8



2 52.5 AULA - CUKA
 THE L -LINE OF 79 EXCITES THE K -LINE OF 29

Z1= 29 EO = 20.0

Z2= 79 EO = 20.0

	K	C	F(X)
SPECIMEN NUMBER	1		
	.8401	.8060	.9746
	.1570	.1973	.9487
TOTAL	=1.0033	ITERATION	4
SPECIMEN NUMBER	2		
	.6622	.6059	.9658
	.3323	.3976	.9543
TOTAL	=1.0035	ITERATION	4
SPECIMEN NUMBER	3		
	.4634	.4015	.9573
	.5286	.5991	.9600
TOTAL	=1.0006	ITERATION	4
SPECIMEN NUMBER	4		
	.2462	.2008	.9491
	.7525	.8030	.9655
TOTAL	=1.0038	ITERATION	4

Figure 1. Results of MULTI8 calculation of mass fractions (C) from relative x-ray intensities (K). F(X) is the absorption correction factor. Total mass fraction and iteration number are also printed out.

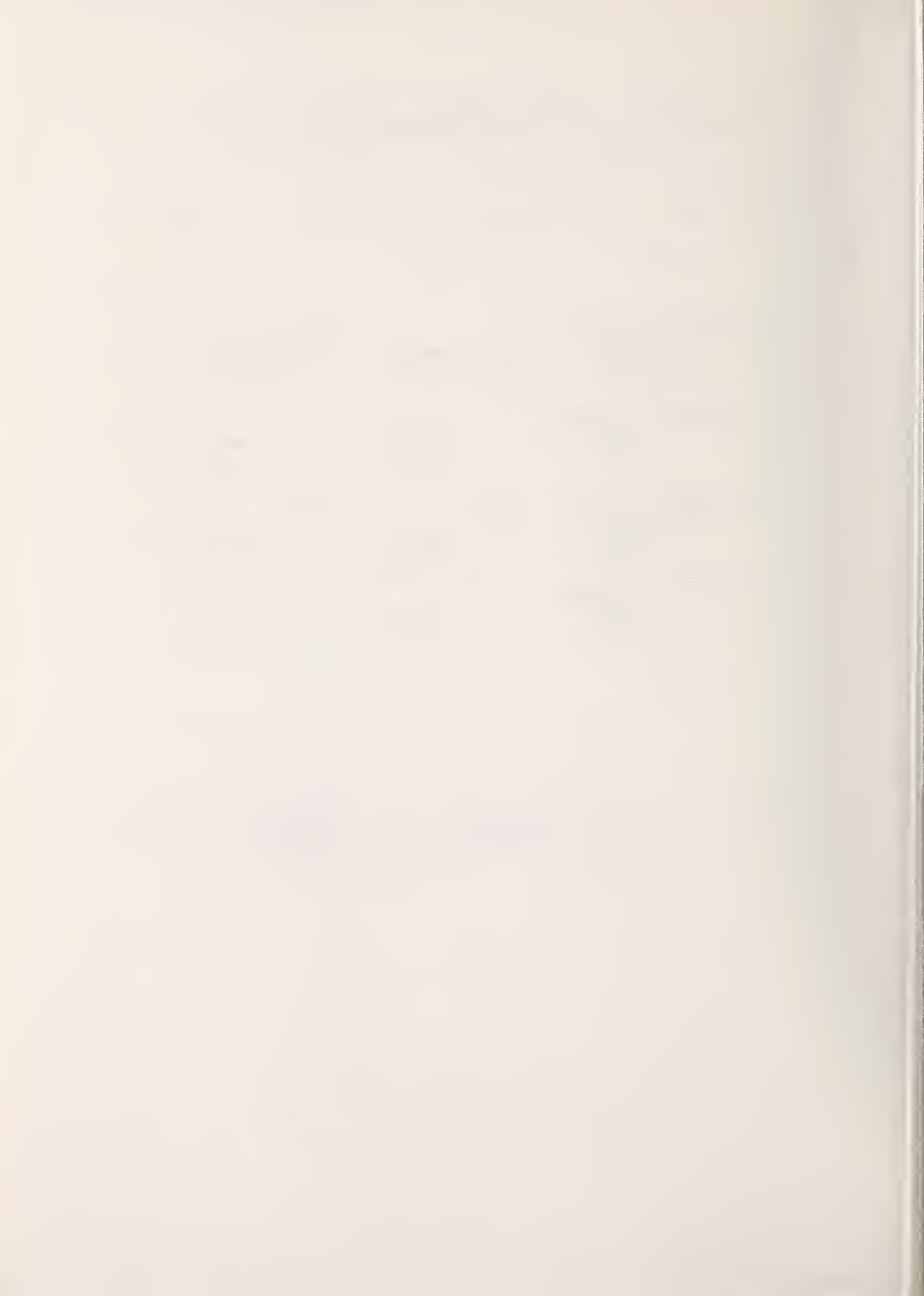
2 52.5 AULA - CUKA
 THE L -LINE OF 79 EXCITES THE K -LINE OF 29

Z1 = 29 EO = 20.0

Z2 = 79 EO = 20.0

	K	C	F(X)
SPECIMEN NUMBER	1		
	.8378	.8060	.9746
	.1565	.1973	.9487
SPECIMEN NUMBER	2		
	.6603	.6059	.9658
	.3311	.3976	.9543
SPECIMEN NUMBER	3		
	.4631	.4015	.9573
	.5282	.5991	.9600
SPECIMEN NUMBER	4		
	.2453	.2008	.9491
	.7489	.8030	.9655

Figure 2. Results of MULTI8 calculation of relative x-ray intensities (K) from mass fractions (C). F(X) is the absorption correction factor.



Complete Listing of Program MULTI8



C		MULTI8	A	1
C			A	2
C		MAIN PROGRAM - THIS PROGRAM DETERMINES CHEMICAL CONCENTRATIONS	A	3
C		FROM RELATIVE X-RAY INTENSITY DATA MEASURED ON AN ELECTRON PROBE	A	4
C		MICROANALYZER.	A	5
		REAL M,N2,H,K,J1,K9,K1	A	6
		DIMENSION A(5,6),M(6,6),R(6,6),S(6,6),C(20,6),B(6,6),Q(6,6),T(6,6)	A	7
	1,	P(5,2),V(6),E(20),K(6),H(6),F(6),W(6),U(6),O(6),G(6),D(6),Z(6)	A	8
		COMMON II,IO	A	9
		NAMELIST /NAM1/ P	A	10
10		FORMAT (1H1)	A	11
20		FORMAT (1X,I1,3X,F4.1,5X,'TITLE OF RUN')	A	12
30		FORMAT (1H0,'Z',I1,'=',I3,5X,'EO =',F5.1)	A	13
40		FORMAT (1H0,9X,'K',15X,'C',13X,'F(X)')	A	14
50		FORMAT (1H0,'NO CONVERGENCE')	A	15
60		FORMAT (1H ,7X,F6.4,9X,F6.4)	A	16
70		FORMAT (1H+,T40,'N.D.')	A	17
80		FORMAT (1H+,T38,F6.4)	A	18
90		FORMAT (1H0,'TOTAL =',F6.4,' ITERATION ',I2/)	A	19
100		FORMAT (8F10.5)	A	20
110		FORMAT (1H0,'SPECIMEN NUMBER ',I3)	A	21
		II=5	A	22
		IO=6	A	23
C		READ INITIAL DATA AND SET UP HEADINGS	A	24
		WRITE (IO,10)	A	25
		READ (II,20) N1,N2	A	26
		WRITE (IO,20) N1,N2	A	27
		READ (II,NAM1)	A	28
C		CALL SUBROUTINE TO READ INPUT DATA	A	29
		CALL INP (A,M,Q,B,5,N1)	A	30
C		CALL SUBROUTINE TO CALCULATE BACKSCATTER COEFFICIENTS	A	31
		CALL BACK (A,R,N1)	A	32
C		CALCULATE THE ELECTRON ABSORPTION COEFFICIENT,SIGMA,THE H-FACTOR	A	33
C		OF PHILIBERT, AND THE OVERVOLTAGE TERM OF REEDS FLUORESCENCE	A	34
C		CORRECTION	A	35
		DO 120 I=1,N1	A	36
		IA=A(1,I)	A	37
		WRITE (IO,30) I,IA,A(3,I)	A	38
		H(I)=1.2*A(2,I)/(A(1,I)**2)	A	39
		F(I)=4.5E5/(A(3,I)**1.65-A(4,I)**1.65)	A	40
		DO 120 J=1,N1	A	41
120		T(I,J)=(((A(3,J)-A(4,J))*A(4,I))/((A(3,I)-A(4,I))*A(4,J)))*1.67	A	42
C		WRITE HEADINGS AND READ INTENSITY RATIOS. MAKE THE FIRST ESTIMATE	A	43
C		OF CONCENTRATION OR TERMINATE IF END OF DATA HAS BEEN REACHED.	A	44
		WRITE (IO,40)	A	45
		NS=0	A	46
130		READ (II,100) (K(I),I=1,N1)	A	47
		NS=NS+1	A	48
		DO 150 I=1,N1	A	49
		IF (K(I)-2.0) 140,370,140	A	50
140		C(1,I)=K(I)	A	51

	KK=INT(ABS(K(I)))	A 52
	IF (KK.EQ.1) C(1,I)=.5	A 53
150	CONTINUE	A 54
	WRITE (IO,110) NS	A 55
C		A 56
C	BEGIN ITERATION LOOP	A 57
C		A 58
	DO 300 I=1,20	A 59
	Z1=0	A 60
	E(I)=0	A 61
C	LOOP FOR THE DETERMINATION AN ELEMENT BY DIFFERENCE OR	A 62
C	BY STOICHIOMETRY. OBTAIN THE SUM OF CONCENTRATIONS.	A 63
	DO 180 J=1,N1	A 64
	IF (K(J).LT.0.) GO TO 180	A 65
	IF (K(J)-1.0.LT.0.) GO TO 170	A 66
	C(I,J)=0	A 67
	DO 160 N=1,N1	A 68
	IF (J-N.EQ.0) GO TO 160	A 69
	B1=C(I,N)/A(2,N)*A(2,J)*B(J,N)/B(J,J)	A 70
	C(I,J)=C(I,J)+B1	A 71
160	CONTINUE	A 72
170	E(I)=E(I)+C(I,J)	A 73
180	CONTINUE	A 74
C	ADJUST THE SUM OF CONCENTRATIONS TO 1 FOR THE PURPOSE OF	A 75
C	CALCULATING CORRECTIONS.	A 76
	DO 190 J=1,N1	A 77
	IF (K(J).GE.0.) GO TO 190	A 78
	C(I,J)=1-E(I)	A 79
	E(I)=1	A 80
190	CONTINUE	A 81
	DO 200 J=1,N1	A 82
	C(I,J)=C(I,J)/E(I)	A 83
200	Z1=Z1+C(I,J)*A(1,J)	A 84
	DO 270 J=1,N1	A 85
	IF (ABS(K(J))-1.0) 210,260,210	A 86
210	W(J)=0	A 87
	U(J)=0	A 88
	S1=0	A 89
	O(J)=0	A 90
	R1=0	A 91
	G1=0	A 92
	K9=1	A 93
	U1=A(3,J)/A(4,J)	A 94
	IF (Z1/A(1,J).GT.1) GO TO 220	A 95
	G1=.225-.722*Z1/A(1,J)+.789*(Z1/A(1,J))**2-.291*(Z1/A(1,J))**3	A 96
220	X0=(1+G1)*(.0604*ALOG(50*U1-16)+.1262)	A 97
	V(J)=X0*A(3,J)+(1-X0)*A(4,J)	A 98
	IF (C(I,J)) 230,260,230	A 99
230	DO 250 N4=1,N1	A 100
C	CALCULATE MEAN EXCITATION POTENTIAL J.	A 101
	J1=9.76*A(1,N4)+58.5*A(1,N4)**(-.19)	A 102
C	CALCULATE STOPPING POWER.	A 103
	S(J,N4)=1/V(J)*A(1,N4)/A(2,N4)*ALOG((1166*V(J))/J1)	A 104
	O(J)=O(J)+C(I,N4)*M(J,N4)	A 105
	U(J)=U(J)+C(I,N4)*H(N4)	A 106
	N9=Q(J,N4)+1	A 107

Y8=0	A 108
Y9=0	A 109
DO 240 N=1,N1	A 110
Y8=Y8+C(I,N)*M(J,N)	A 111
Y9=Y9+C(I,N)*M(N4,N)	A 112
S1=S1+C(I,N4)*S(J,N4)	A 113
R1=R1+C(I,N4)*R(J,N4)	A 114
X5=(Y8/Y9)/SIN(N2/57.2958)	A 115
Y5=F(J)/Y9	A 116
CALCULATE SECONDARY FLUORESCENCE CORRECTION.	A 117
K1=.5*A(5,N4)*P(N9,1)*C(I,N4)*P(N9,2)*A(2,J)*T(J,N4)	A 118
K1=K1/A(2,N4)*(ALOG(1+X5)/X5+ALOG(1+Y5)/Y5)*M(N4,J)/Y9	A 119
K9=K9+K1	A 120
DETERMINE ATOMIC NUMBER CORRECTION.	A 121
W(J)=(R(J,J)*S1)/(S(J,J)*R1)	A 122
CALCULATE ABSORPTION FACTOR.	A 123
X1=M(J,J)/F(J)/SIN(N2/57.2958)	A 124
O(J)=O(J)/F(J)/SIN(N2/57.2958)	A 125
G(J)=(1+X1)*(1+H(J)*(1+X1))/(H(J)+1)	A 126
D(J)=(1+O(J))*(1+U(J)*(1+O(J)))/(U(J)+1)	A 127
CALCULATE THE EMERGENT INTENSITY RATIOS FOR THE ASSUMED CONCENTRATIONS.	A 128
Z(J)=C(I,J)/W(J)*K9*G(J)/D(J)	A 130
Z9=K(J)*C(I,J)*(1-Z(J))	A 131
BY HYPERBOLIC FIT, OBTAIN NEW ESTIMATES FOR CONCENTRATIONS, COMPARING THE EXPERIMENTAL INTENSITY RATIO WITH THE ONE OBTAINED BY CALCULATION.	A 132
C(I+1,J)=Z9/(K(J)*(C(I,J)-Z(J))+Z(J)*(1-C(I,J)))	A 133
GO TO 270	A 134
C(I+1,J)=C(I,J)	A 135
CONTINUE	A 136
IF (I.EQ.1) GO TO 300	A 137
STOPPING CRITERION FOR ITERATION LOOP. IF NOT CONVERGENT AFTER 19 LOOPS, STOP ITERATION AND PRINT 'NO CONVERGENCE'.	A 138
PRINT RESULTS.	A 139
DO 280 J=1,N1	A 140
IF (ABS(C(I,J)-C(I-1,J)).GT..00001) GO TO 290	A 141
CONTINUE	A 142
GO TO 320	A 143
IF (I.EQ.19) GO TO 310	A 144
CONTINUE	A 145
WRITE (IO,50)	A 146
DO 360 N=1,N1	A 147
CON=C(I,N)*E(I)	A 148
WRITE (IO,60) K(N),CON	A 149
IF (ABS(K(N))-1.0) 330,340,330	A 150
IF (C(I,N)) 350,340,350	A 151
WRITE (IO,70)	A 152
GO TO 360	A 153
DABS=1/D(N)	A 154
WRITE (IO,80) DABS	A 155
CONTINUE	A 156
WRITE (IO,90) E(I),I	A 157
GO TO NEXT SET OF DATA (LINE 130).	A 158
GO TO 130	A 159
STOP	A 160
END	A 161
	A 162
	A 163
	A 164-

	SUBROUTINE INP (AM,M,QM,B,IX,JJ)	B	1
C	THIS SUBROUTINE READS ALL THE REQUIRED DATA FOR A CALCULATION.	B	2
	INTEGER CH	B	3
	REAL M	B	4
	DIMENSION AM(IX,JJ),M(6,6),QM(6,6),B(6,6),CH(2)	B	5
	COMMON II,IO	B	6
	DATA CH(1),CH(2)/1HK,1HL/	B	7
10	FORMAT (1H , 'THE ',A2, '-LINE OF',I3, ' EXCITES THE ',A2, '-LINE OF',	B	8
	1I3)	B	9
20	FORMAT (1H , 'NO FLUORESCENCE CORRECTION')	B	10
30	FORMAT (10F8.4)	B	11
C	READ DATA FOR EACH ELEMENT.	B	12
	READ (II,30) AM	B	13
	READ (II,30) ((M(I,J),I=1,JJ),J=1,JJ)	B	14
	READ (II,30) ((QM(I,J),I=1,JJ),J=1,JJ)	B	15
	READ (II,30) ((B(I,J),I=1,JJ),J=1,JJ)	B	16
	IA=0	B	17
	DO 80 I=1,JJ	B	18
	DO 80 J=1,JJ	B	19
	IQ=QM(I,J)+1	B	20
	IC1=CH(1)	B	21
	IC2=CH(1)	B	22
	GO TO (80,70,60,50,40), IQ	B	23
40	IC1=CH(2)	B	24
	GO TO 70	B	25
50	IC2=CH(2)	B	26
	GO TO 70	B	27
60	IC1=CH(2)	B	28
	IC2=CH(2)	B	29
70	IAM=AM(1,J)	B	30
	IBM=AM(1,I)	B	31
C	PRINT OUT THE CHARACTERISTIC FLUORESCENCE CORRECTION THAT HAS	B	32
C	BEEN SELECTED.	B	33
	IF (IQ.GT.1) WRITE (IO,10) IC1,IAM,IC2,IBM	B	34
80	IA=IA+QM(I,J)	B	35
	IF (IA.EQ.0) WRITE (IO,20)	B	36
C	RETURN TO MAIN PROGRAM.	B	37
	RETURN	B	38
	END	B	39

	SUBROUTINE BACK (A,R,N1)	C	1
C	THIS SUBROUTINE CALCULATES THE BACKSCATTER COEFFICIENT, R, FROM	C	2
C	THE EQUATION OF DUNCUMB.	C	3
	DIMENSION A(5,N1),R(6,6)	C	4
	DO 10 I=1,N1	C	5
	W=A(4,I)/A(3,I)	C	6
	W2=W**2	C	7
	W3=W**3	C	8
	W4=W**4	C	9
	W5=W**5	C	10
	DO 10 J=1,N1	C	11
	R1=(-.581+2.162*W-5.137*W2+9.213*W3-8.619*W4+2.962*W5)*1E-2*A(1,J)	C	12
	R2=(-1.609-8.298*W+28.791*W2-47.744*W3+46.54*W4-17.676*W5)*1E-4*A(C	13
	11,J)**2	C	14
	R3=(5.4+19.184*W-75.733*W2+120.05*W3-110.7*W4+41.792*W5)*1E-6*A(1,	C	15
	1J)**3	C	16
	R4=(-5.725-21.645*W+88.128*W2-136.06*W3+117.75*W4-42.445*W5)*1E-8*	C	17
	1A(1,J)**4	C	18
	R5=(2.095+8.947*W-36.51*W2+55.694*W3-46.079*W4+15.851*W5)*1E-10*A(C	19
	11,J)**5	C	20
10	R(I,J)=1+R1+R2+R3+R4+R5	C	21
	RETURN	C	22
	END	C	23-



APPENDIX II

NBS TECHNICAL NOTE 521



PRESENT STATE OF THE CLASSICAL THEORY OF
QUANTITATIVE ELECTRON PROBE MICROANALYSIS*

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Although the foundations for a procedure of data reduction in quantitative electron probe analysis have not been changed for several years, there has been progress in the choice of expressions, parameters, and constants. A brief account of recommended expressions and procedures is given. Reference is made to the Standard Reference Materials of Au-Ag and Au-Cu alloys issued for electron probe microanalysis. These are especially useful for investigating the application of correction procedures.

Key words: corrections; electron probe microanalysis; quantitative analysis; x-ray spectroscopy.

INTRODUCTION

In his doctoral thesis, published in 1951 [1], Castaing laid the groundwork for a theory of quantitative electron probe microanalysis. He pointed out that the intensity of characteristic primary radiation generated in multi-element specimens is approximately proportional to the mass fraction of the emitting element. He therefore proposed that the corrections which need to be applied to measured x-ray intensity ratios to obtain mass fractions ("concentrations") were as follows:

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1. An absorption correction, which takes into account the absorption of x-rays emerging from the specimen, and
2. A fluorescence correction which cancels the effects of indirect x-ray generation.

Castaing also suggested that for accurate analysis the proportionality between concentration and intensity of emission may have to be considered an insufficient approximation. Hence, he proposed a form of atomic number correction to correlate more accurately the mass fraction with the measured intensity of x-ray emission.

This "classical" scheme of data reduction has essentially remained the commonly used approach to quantitative analysis. It has been described in many publications, including the National Bureau of Standards Special Publication 298 (1968) [2], which contains several references used in this paper. In the recent past there has been considerable discussion of the choice of parameters and constants to be employed within the framework of this procedure. The problem remains if, instead of the classical procedure, a Monte-Carlo method or a transport equation procedure is used to calculate the mass-fractions of the elements being measured.

It is the purpose of the present publication to give an account of the specific choices of parameters and constants which are available at present for the computation of corrections for quantitative electron probe microanalysis. For a general description of the correction procedures, as well as for a detailed discussion of the origin of these expressions, the reader is referred to the cited literature.

ATOMIC NUMBER CORRECTION

Thanks to the work of many investigators [*e.g.* 2-6] the processes resulting in primary x-ray emission are now quite well understood. The number of ionizations produced by a single electron coming to rest within the target can be written as follows* ;

$$n_A = N_{Av} \cdot \rho \cdot \frac{C_A}{A} \int_{E_0}^0 \frac{Q}{-dE/dx} dE \quad (1)$$

For the ionization cross-section, Q , and the stopping power, $-dE/d(\rho x)$, we can substitute in the above equation the expressions proposed by Bethe *et al.* [7,8]:

$$Q = b \cdot \pi e^4 \cdot z_l \cdot \frac{\ln U}{U} \cdot E^{-2} \quad (2)$$

$$S \equiv -\frac{1}{\rho} \cdot \frac{dE}{dx} = 2\pi e^4 \cdot N_{Av} \cdot \frac{Z}{A} \cdot \frac{1}{E} \ln \left(\frac{\alpha E}{J} \right) \quad (3)$$

The values of some parameters of these equations are, however, poorly known. Héroc has concluded from the study of experimental results on the ionization cross section that the value $b = 0.76$ can be considered valid for all levels of ionization [9]. The value of the coefficient α in equation (3) was frequently considered to be equal to two. However, according to Nelms [10], for electrons the value $\alpha = 1.166$ should be used.

There is some controversy concerning the best expression for the mean ionization potential, J . The value ($J = 11.5Z$), used frequently in the past, is certainly inaccurate. We use at present an expression obtained by Berger and Seltzer [11], who averaged a large number of experimental observations by several authors:

$$J = 9.76 Z + 58.5 Z^{-0.19} \quad (4)$$

* A list of symbols used is appended.

Another expression for J has been proposed by Duncumb *et al.* [12]:

$$J/Z = 14.0 [1 - \exp(-0.1 Z)] + 75.5/Z^{Z/7.5} - Z/(100 + Z) \quad (5)$$

This equation has been derived empirically to optimize the results of a large number of electron probe analyses of specimens of known composition. We withhold judgment on the best choice of expression for J, pending further investigations.

In order to obtain an algebraic expression for ionization within a multi-element target, we introduce the variables M and V, defined by the following equations:

$$M = \sum_i C_i \frac{Z_i}{A_i} ; \quad V = \exp \left[\frac{1}{M} \sum_i C_i \frac{Z_i}{A_i} \ln \left(\frac{\alpha E}{J_i} \right) \right] \quad (6)$$

As shown by Springer [13], if one introduces equations (2), (3), and (6), the integration of equation (1) yields the expression

$$n_A = \frac{1}{2} \frac{C_A}{A} z_\ell b \frac{1}{M} \left\{ U_0 - 1 - \frac{\ell_n V}{V} [EI(\ell_n(U_0 V)) - EI(\ell_n V)] \right\} \quad (7)$$

in which EI is the exponential integral:

$$EI(x) = \text{const.} + \ell_n x + \sum_{s=1}^{s=\infty} \frac{x^s}{s \cdot s!} \quad (8)$$

Expression (7) is used in an extensive program for data processing in quantitative electron probe microanalysis, called COR, recently developed by Hénoch and Heinrich at the National Bureau of Standards [14].

A further correction is necessary to take account of the effects of electron backscattering. A fraction of the impinging electrons is reemitted with energies sufficient to excite x-rays. This reduces the generated x-ray intensity by a fac-

tor R (backscatter effect), which decreases rapidly with increasing atomic number. The average number of ionizations per impinging electron is thus $n_A R$. We believe that the most reliable expression for the factor R is that proposed by Duncumb [15]:

$$\begin{aligned}
 R = & 1.0000 + \\
 & + (-.581+2.162W-5.137W^2+9.213W^3-8.619W^4+2.962W^5) \times 10^{-2}Z + \\
 & + (-1.609-8.298W+28.791W^2-47.744W^3+46.540W^4-17.676W^5) \times 10^{-4}Z^2 + \\
 & + (5.400+19.184W-75.733W^2+120.050W^3-110.700W^4+41.792W^5) \times 10^{-6}Z^3 + \\
 & + (-5.725-21.645W+88.128W^2-136.060W^3+117.750W^4-42.445W^5) \times 10^{-8}Z^4 + \\
 & + (2.095+8.947W-36.510W^2+55.694W^3-46.079W^4+15.851W^5) \times 10^{-10}Z^5
 \end{aligned} \tag{9}$$

where $W = 1/U_0 = E_0/E_k$. This expression agrees well with the experimental measurements of the factor R by Dérian [16].

The number of photons of the x-ray line n, generated by ionization of the electron shell m, is obtained by multiplying the number of ionizations, $n_A R$, with the fluorescence yield, ω_m , and with the ratio of the intensity of the line of interest to the intensity of all lines originating from this shell (weight of the line, p_{mn}):

$$I'_{Ap} = n_A \cdot R \cdot \omega_m \cdot p_{mn} \tag{10}$$

THE ATTENUATION OF PRIMARY RADIATION

The attenuation of primary radiation on emergence from the specimen can be calculated using an equation proposed by Philibert [17]

$$1/f(\chi) = (1 + \frac{\chi}{\sigma})(1 + \frac{h}{1+h} \cdot \frac{\chi}{\sigma}); \quad h = 1.2 \frac{A}{Z^2}; \tag{11}$$

The factor $f(\chi)$ is the ratio between attenuated and unattenuated primary radiation: $F(\chi) = I_p/I'_p$. Expressions for the coefficient σ , which depends on the electron energy, were pro-

posed by Duncumb and Shields [18] and by Heinrich [19]. We presently use the following equation:

$$\sigma = \frac{4.5 \times 10^5}{E_o^{1.65} - E_k^{1.65}} \quad (12)$$

We have not evaluated an alternative equation for the absorption correction, by Wittry and Andersen [20].

The attenuation of primary radiation is large when x-rays of low photon energy are measured. It is important to note, however, that the magnitude of this effect, and hence, the uncertainty of its computation, depends upon experimental conditions under our control. Primary absorption can be minimized by working at low electron energies and using high x-ray emergence angles; and these conditions are desirable when soft x-rays are measured. It should be added that further experiments on the depth distribution of primary x-rays should be encouraged. The uncertainties in the absorption correction have been analyzed by Yakowitz and Heinrich [21] who suggested that the experimental conditions should be adjusted, wherever possible, to maintain the value of $f(\chi)$ above 0.8.

SECONDARY RADIATION EXCITED BY CHARACTERISTIC LINES

The effects of secondary radiation excited by characteristic lines are usually treated according to the equation proposed by Castaing [1]:

$$r_f \equiv \frac{I_{fA}}{I_{pA}} = C_B \cdot \frac{I'_{pA}}{I'_{pA}} \cdot \frac{r_A - 1}{r_A} \cdot \frac{\omega_B}{2} \cdot \frac{\mu(A, BK_{\infty})}{\mu(AB, BK_{\infty})} \cdot \frac{A}{B} \left[\frac{\ell_n(1+u)}{u} + \frac{\ell_n(1+v)}{v} \right] \quad (13)$$

In this equation, r_f is the ratio of the attenuated fluorescent radiation to the attenuated primary radiation of the element which is being determined. I'_{pB}/I'_{pA} is the ratio of the gener-

ated (not attenuated) primary emissions of the exciting and the excited lines as obtained from pure elements. Castaing proposed to approximate this ratio by the ratio of the absorption edge wavelengths of these elements, while Reed [22] replaced it by the expression $[(U_B - 1)/(U_A - 1)]^{1.67}$ in which U_A and U_B are the corresponding overvoltage ratios.

This procedure is amenable to several improvements which were incorporated in the program COR. In this program, the ratio I_B/I_A is fully calculated, using equation (10) for primary intensities, just as in the atomic number correction. This simplifies the calculation of fluorescence of K lines by L lines and *vice versa*, as well as the calculation of fluorescence of $K\alpha$ lines by $K\beta$ lines, which is performed separately. As pointed out by Criss [23], the exponential approximation to primary distribution in depth of x-ray emission, used by Castaing to calculate the term v in equation (13), can be replaced by a more accurate model. We use in COR the model contained in Philibert's calculation for the function $f(\chi)$ [17]. With the computer facilities presently available to most analysts, this more rigorous approach is possible without an excessive increase in the cost of computation.

SECONDARY RADIATION EXCITED BY THE CONTINUUM

Hénoch has described a method for calculating the effects of secondary radiation excited by the continuum [24]. In order to perform the formal integration of the expressions contained in his procedure, he had to make the simplifying assumption that between absorption edges the mass attenuation coefficients vary with the cube of wavelength. However, the wavelength dependence of mass attenuation coefficients is always less than cubic [25]. This has been taken into account in the modification of Hénoch's original method incorporated

in the program COR. The formal integration is replaced by a numerical integration, using the parameters for attenuation coefficients published in reference [25].

The main practical difficulty in performing the correction for fluorescence excited by the continuum is that the position of the absorption edges of all elements contained in specimen and standard must be taken into account. Each wavelength range between adjacent absorption edges must be calculated separately. Therefore, the procedure is lengthy, and in machine computation it requires extensive data input. Errors in the input occur frequently and may escape detection, since it is difficult to acquire an intuitive feeling for the magnitude of this correction.

In the program COR the relations between lines and absorption edges are inspected by the computer which selects the wavelength ranges for the integration. These decisions are made and the computer completes the calculation without active intervention of the operator. In the same process, the computer also determines which operations must be performed for calculating secondary excitation by characteristic lines. This enormously simplifies the execution of the fluorescence corrections, and renders unnecessary further attempts to simplify them, as advocated by Springer [26].

THE ITERATIVE PROCESS

We will now discuss how the individual corrections are combined in calculating the composition of the specimen.

The usual form employs multiplicative correction factors:

$$C^* = k \cdot k_Z^* \cdot k_A^* \cdot k_F^* \quad (14)$$

This procedure is based on the concept that ideally the method should yield a linear correction curve. The multiplicative factors correct for deviations from the ideal model. However, the values of the correction factors depend on the composition of the specimen, which is unknown. The problem is traditionally resolved by using an estimate of composition to calculate the correction factors, and using the resulting mass fractions as a new estimate of composition and iterating until convergence of results is obtained.

As stated by Criss [23], the formulation of the correction by multiplicative factors unnecessarily complicates the structure of the correction equations, and obscures the underlying physical events. Moreover, the iteration frequently fails to converge, as observed by Reed [27]. For these reasons, the program COR uses a different iterative concept, first proposed by Criss and Birks [28], and somewhat modified by Hénoc and Heinrich.

Each iteration contains two steps. In the first step, we establish an estimate of the specimen composition and calculate the intensity ratios to be expected for each element, according to the theory. The intensity ratios are obtained by the simple relation

$$K = \frac{I^*}{I} = \frac{I_p^* + I_c^* + \Sigma I_f^*}{I_p + I_c + \Sigma I_f} \quad (15)$$

The correction procedures previously discussed are used to calculate the absolute intensities (in photons per electron) due to direct and indirect excitation. As a first estimate of the specimen composition we assume that the weight fractions of the elements are proportional to the experimentally obtained x-ray intensity ratios. This estimate, as well as the subsequent estimates is normalized so as to render the sum of mass fractions equal to unity. Thus, in each iteration, we calculate

the signal intensities to be expected from a theoretically possible composition.

Since equation (15) does not yield an explicit term for mass fractions, we must use another relation to obtain, in the second step of each iteration, a new estimate of composition. We use for this purpose a hyperbolic approximation to the analytical calibration curve for each element:

$$\frac{1-k}{k} = a \frac{1-C}{C} \quad (16)$$

Ziebold and Ogilvie observed that the analytical curves in electron probe microanalysis are indeed approximately hyperbolic [29]. On the plot of intensity ratio *versus* mass fraction for each element, the hyperbola can be defined by three points (0,0), (1,1), and (C,k), where C and k are the estimate of mass fraction used in the iteration, and of the intensity ratio calculated for it. Our next estimate for the mass fraction, C_m , corresponding to the observed intensity ratio, k_m , can thus be calculated by the equation

$$C_m = \frac{k_m \cdot C(1-k)}{k_m(C-k) + k(1-C)} \quad (17)$$

Contrary to the procedure suggested by Criss, we do not normalize the observed intensity ratios k in equation (16), or the final results after convergence. Thus, if the presence of an element has been overlooked, or if there are experimental errors or failures of the correction procedures, this will become apparent since the calculated mass fractions fail to sum to unity.

This iteration procedure has been extensively tested. We have never observed failure to converge. In fact, the convergence is always rapid, as is to be expected in view of the good fit of the hyperbolic model observed by Ziebold and Ogilvie.

The program COR can also compute results of analysis with use of multi-element standards; furthermore it can determine one element by difference or several unmeasured elements on the basis of stoichiometric relations.

STANDARD REFERENCE MATERIALS

In spite of the progress made in recent years, there are still uncertainties in several aspects of the correction procedures. I believe that the availability of reliable standard reference materials will be instrumental in pointing out the areas in which further investigation is most needed. For this reason, the National Bureau of Standards has devoted considerable effort to preparing and characterizing materials specially selected for electron probe microanalysis [30]. Recently, NBS certified and issued an alloy of nominal composition 0.8 W, 0.2 Mo, a series of binary alloys in the Au-Ag system, in nominal steps of 0.2 (20 weight percent), and a similar series of alloys in the system Au-Cu. All these alloys were carefully analyzed chemically by several laboratories, and painstakingly investigated for homogeneity. They should be particularly useful in testing the atomic number correction. Extension of the studies of oxydic systems is presently in progress.

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List of Symbols

A,B	atomic weights of elements A, B
C	mass fraction ("concentration")
E	kinetic energy of the electron
E_0	initial kinetic energy of the electron, operating voltage
E_k	excitation potential of line k
I	attenuated (emergent) intensity of radiation
I'	intensity of generated radiation, before attenuation
J	mean ionization potential
M	variable used for stopping power calculation (eq. 6-7)
N_{Av}	Avogadro's number
Q	ionization cross-section
R	correction factor for electron backscattering
S	stopping power
U	= E/E_k
U_0	= E_0/E_k
V	variable used for stopping power calculation (eq. 6-7)
W	= $1/U_0$
Z	atomic number
a	constant in the hyperbolic approximation
b	constant in the calculation of the ionization cross-section
c	constant in the calculation of σ
e	charge of electron

$f(\chi)$	correction factor for absorption of primary radiation
h	$= 1.2(A/Z^2)$ in Philibert's equation. For multi-element targets, $h = \sum_i C_i A_i / Z_i^2$
EI	exponential integral
\ln	natural logarithm
n_A	number of ionizations produced by one electron which comes to rest within the specimen
p_{mn}	relative frequency of the line n , generated on ionization of the shell m , with respect to generation of all lines originating from shell m
r	absorption edge jump of the absorption coefficient
r_f	intensity of emerging fluorescent radiation, relative to emerging primary radiation of the same line
s	tally in the exponential integral
k	relative intensity of emergent radiation
k_Z, k_A, k_F	correction factors for atomic number, absorption, and fluorescence effects
u, v	auxiliary variables for attenuation of fluorescent radiation
α	constant in Bethe's equation for energy loss of electrons
θ	emergence angle of measured x-rays
μ	x-ray mass attenuation coefficient
$\mu(AB, AK\alpha)$	mass attenuation coefficient of specimen containing elements A and B, for $K\alpha$ radiation of element A
ρ	density of specimen
σ	coefficient for electron energy effect in Philibert's equation
χ	$= \mu \operatorname{cosec} \theta$
ω	$=$ fluorescence yield

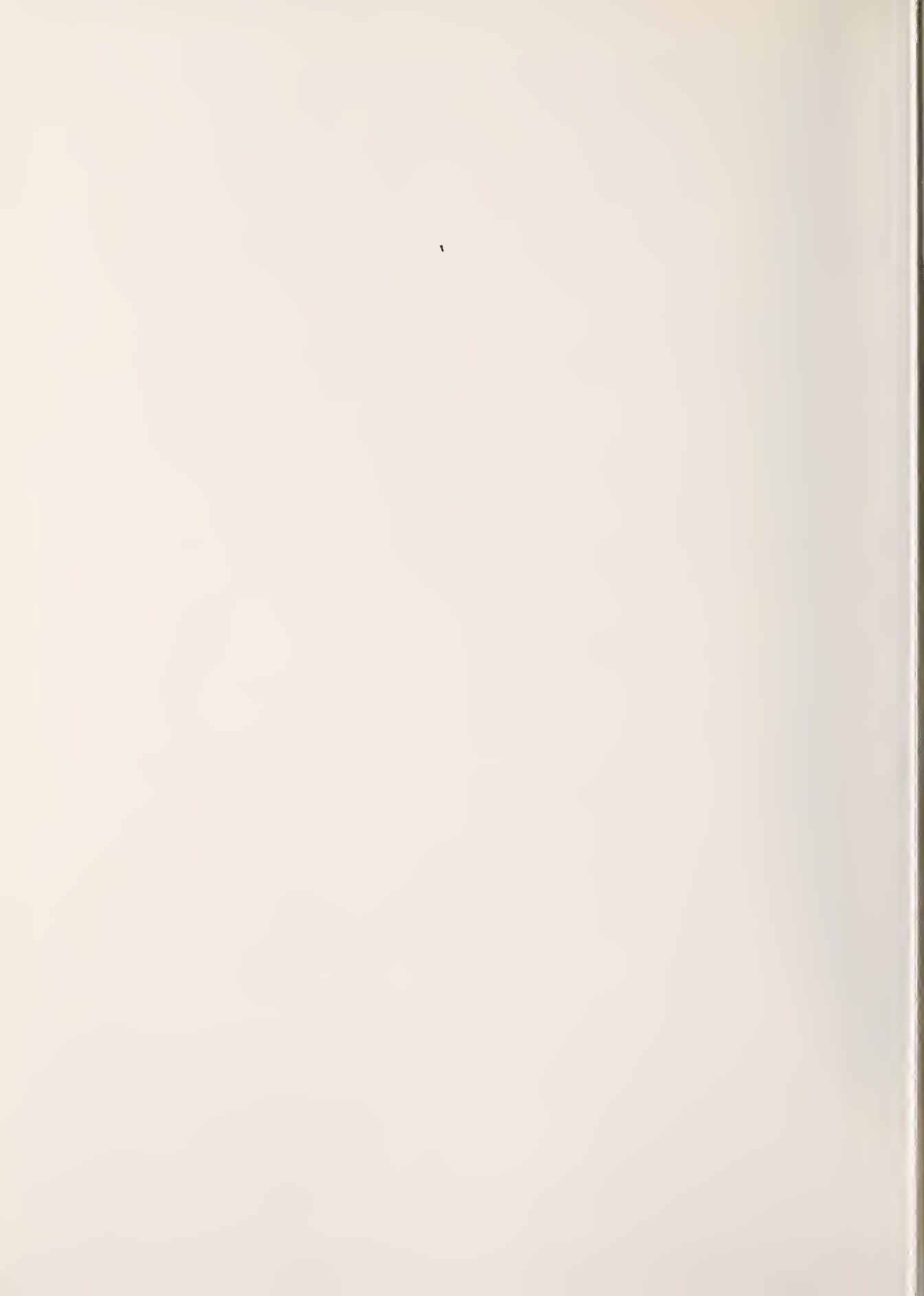
Subscripts and superscripts:

A,B elements A, B
i tally in integration
l electron shell l
* composition dependent

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