MULTI: an Interactive Program for Quantitation in EPMA

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A versatile interactive program for quantifying bulk samples and particles in electron probe microanalysis is presented. The program was developed with the purpose of allowing the analyst to choose among different matrix-correction models and several expressions for the parameters involved. It was written in Pascal and runs on any IBM compatible personal computer with no special requirements. The program was tested on a number of geological and synthetic samples of known compositions. Special applications which show the usefulness of the program are described. Copyright © 1999 John Wiley & Sons, Ltd.

INTRODUCTION

In electron probe microanalysis (EPMA), detected characteristic x-ray intensities I are related to the unknown mass concentrations C by means of the so-called ZAF corrections:[1]

$$\frac{I}{I_0} = \frac{C}{C_0} ZAF \qquad (1)$$

where the subscript 0 refers to standards of known composition. Since ZAF corrections depend on the sample concentrations, an iterative algorithm must be used to obtain the C values. Several computational programs have been developed in order to perform this iterative process.[2–4] Each of these programs has been written on the basis of a particular ZAF correction model; in addition, they are presented as closed packages, and users cannot make decisions about the models for the processes and parameters involved. On the other hand, more recent and complex programs (e.g. DTSA or Ref. 5) permit one to choose among different correction models, although higher computational requirements must be met.

The program MULTI was developed with the purpose of providing an interactive program which allows the user to access different matrix-correction and parameter models. The variety of available models, including standardless peak-to-background analysis, is an important advantage, since each of them is specially suitable for a particular experimental situation related to different overvoltages, mean atomic numbers, lines of interest, kinds of samples, etc. Nevertheless, it must be borne in mind that the good performance of any model always depends on a good experimental strategy and reliable input data.

The program was written in Pascal and runs on any IBM compatible personal computer, with minimum hardware requirement. Spanish and English versions are available free of charge at the Web site http://quechua.fis.uncor.edu/~gean/multi.

DESCRIPTION OF THE PROGRAM

The program starts by an initialization of variables, after which the following data files are read: atomic weights, backscattering coefficients,[6] excitation energies for K, L and M shells,[7,8] emission energies of Kα, Lα and Mα lines,[7] fluorescence yield coefficients,[7] absorption edge jump ratios obtained from expressions given by Heinrich[9] and parameters given by McMaster *et al.*[10] for the assessment of mass absorption coefficients.

After data files have been read, a menu is presented with the following items:

1. Sample composition. The unknown sample may have up to 18 elements. Intensities can be compared with several standards (also up to 18); this comparison may be done by means of using one unique standard containing all the analytes (and eventually other elements), one standard for each analyte or any other combination. Light elements may be taken into account if stoichiometric relationships are provided. Input of elements must be done according to certain rules:

— Elements are input through their symbols, regardless of upper or lower case.
— A sample is built up by 'units,' which may be single elements or compounds (see next item), separated by blank spaces or commas.
— The characteristic intensity of only one element (the heaviest one) must be input for each unit. This detectable element may be associated with one or more lighter elements, in which case the stoichiometric relationship must be indicated, e.g. Ca2(S_0_4) or Ca2S_0_4.

— Except for standardless analysis, the characteristic intensity for each detectable element must be compared with the corresponding value in a standard.

2. Kind of sample. Polished bulk materials and particles are allowed. For particles, a standardless algorithm based on peak-to-background ratios is used, following Trincavelli and Van Grieken.[11] In this case, the sample should be irradiated in a region facing the detector. In this model, it is also assumed that both characteristic and bremsstrahlung photons originate in the same sample region, and that bremsstrahlung is emitted isotropically, just as characteristic radiation.

There are five available models for the continuum spectrum: Reed,[12] Lifshin,[13] Markowicz and Van Grieken,[14] Small et al.[15] and Trincavelli et al.[16]

3. Experimental conditions. Incident energy E_0 of the electron beam, take-off angle, observed line (Kα, Lα or Mα), measured characteristic intensity, live time of spectrum acquisition and beam current i must be input. The last two are given separately for each element in order to allow the use of wavelength- and energy-dispersive modes.

4. Input of data corresponding to the standards used. This is the same as for the sample, including compositions. When the number of standards is set as zero, the standardless algorithm given by Trincavelli and Van Grieken[11] is used; this method can be used for both bulk samples and particles.

5. Choice of models for atomic number and absorption corrections ZA. Five algorithms have been implemented in the program: the quadrilateral model,[17] the parabolic model,[18] the Gaussian model[19] modified by Bastin and co-workers[20,21] and by Riveros and co-workers (see, e.g., Ref. 22). All of them are combined with Reed's fluorescence correction factor F.[23] When a particular model for ZA correction is chosen, the expressions for mass absorption coefficients and mean ionization potential, and also the method of averaging mean values for different parameters, are selected automatically, taking into account the original model. Nevertheless, these options can be changed by the user.

6. Choice of models for mean ionization potential and mass absorption coefficients. Several expressions[22] may be selected for the former, whereas both the MAC30[9] and McMaster et al.[10] algorithms for mass absorption coefficients are available.

7. Averaging. Mean values for several parameters involved in calculations may be weighted with atomic or mass concentrations.

8. Tolerance for convergence of iterations may be changed for each analysis.

9. Choice for output using elementary or compound concentrations.

10. Configuration file. Option to save or read choices.

11. Perform the iterations for analysis (when all necessary options have been set).

12. Output of results to a file or printer.

Since no normalization is carried out, except for standardless analysis, the program output displays the sum of calculated concentrations as a test of the analysis quality.

Each line of every menu is accompanied by an illustrative help, including references for publications.

SOME EXAMPLES

The program MULTI has been extensively checked on known samples at the University of Antwerp (UIA) and different Argentinian centres and it has been implemented at the Serveis Científico-Tècnics of the University of Barcelona, where it is used at present for routine microprobe quantitations.

Routine analysis

Fourteen samples of different kinds were analysed in a CAMECA SX50 microprobe at the University of Barcelona with a wavelength-dispersive system. Samples were measured with a take-off angle of 40°, incident energies of 15, 20 and 25 keV and beam currents of 15 and 20 nA, as can be seen in Table 1. This set of samples includes analytes with concentrations ranging from 10 ppm to 64.317% and atomic numbers from 11 to 90; oxygen concentrations were obtained by stoichiometry. The lines analysed were Kα (for atomic numbers from 11 to 30), Lα (from 38 to 77) and Mα (for thorium).

Table 1. Samples of known composition used for conventional analyses

Sample	Elements	i (nA)	E_0 (keV)
Sodalite	O, Na, Al, Si, S, Cl, K, Ca, Ti, Fe	15	15
Sphalerite	S, Fe, Cu, Zn, Ag, Cd	20	20
Laurite	S, Cr, Fe, Ru, Os, Ir	20	25
Erlichmanite	S, Cr, Fe, Ru, Os, Ir	20	25
Feldespar 1	O, Na, Al, Si, K, Ca, Ti, Fe	15	15
Feldespar 2	O, Na, Al, Si, K, Ca, Ti, Fe	15	15
Wollastonite	O, Mg, Si, K, Ca, Ti, Mn, Fe	15	15
Olivine	O, Mg, Al, Si, Cr, Mn, Fe, Ni	20	15
Orthopyroxene	O, Na, Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, Ni	20	15
Clinopyroxene	O, Na, Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, Ni	20	15
Feldespar 3	O, Na, Al, Si, K, Ti, Fe, Ni, Sr, Ba	20	15
Allanite	O, Mg, Al, Si, Ca, Mn, Fe, Y, La, Ce, Nd, Sm, Eu, Gd, Th	15	20
Spinel	O, Mg, Al, Si, Ti, Cr, Mn, Fe	20	15
Feldespar 4	O, Na, Al, Si, K, Ca, Ti, Fe, Sr	20	15

Table 2. Concentrations (%) obtained with MULTI and nominal values in three samples containing water

Element	Allanite		Biotite		Muscovite	
	MULTI	Nominal	MULTI	Nominal	MULTI	Nominal
Na Kα	—	—	0.187	0.187	0.022	0.023
Mg Kα	0.497	0.468	6.189	6.241	0.661	0.672
Al Kα	8.723	8.516	10.241	10.297	17.675	17.904
Si Kα	14.420	14.442	16.350	16.450	22.251	22.358
K Kα	—	—	7.515	7.660	8.884	8.982
Ca Kα	7.641	7.636	—	—	0.008	0.007
Ti Kα	—	—	1.318	1.323	—	—
Mn Kα	0.304	0.308	0.169	0.169	0.008	0.008
Fe Kα	9.521	9.480	14.681	14.548	1.364	1.341
Y Lα	0.074	0.062	—	—	—	—
La Lα	5.066	5.258	—	—	—	—
Ce Lα	9.792	9.841	—	—	—	—
Nd Lα	2.101	2.238	—	—	—	—
Sm Lα	1.037	1.047	—	—	—	—
Eu Lα	0.442	0.451	—	—	—	—
Gd Lα	1.400	1.418	—	—	—	—
Th Mα	1.458	1.572	—	—	—	—
O (oxides)	35.238	35.193	38.547	38.739	43.727	44.074
H_2O	2.085[a]	1.585	4.803[a]	3.966	5.400[a]	4.512

[a] Determined by difference from 100%.

Mean value: 0.998
Std. dev.: 0.048
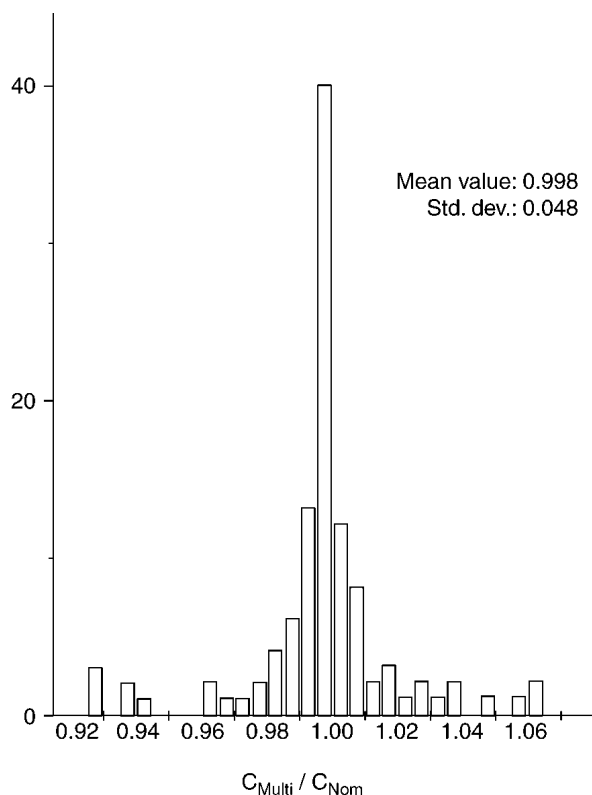
C_{Multi} / C_{Nom}

Figure 1. Histogram of the ratios between calculated and nominal concentrations for 110 analytes shown in Table 1 (three data have been excluded because they departed from the mean value by more than three times the standard deviation).

A comparison between certified and calculated concentrations is shown in Fig. 1. For these assessments *ZAF* corrections given by Riveros and Castellano[22] or by Pouchou and Pichoir[18] were employed, using mass absorption coefficients given by Heinrich[9] or by McMaster *et al.*,[10]

alternatively. For the 113 calculated concentrations, only three differ by more than 8% from nominal values and 12 differ more than 5%; both numbers appear to be statistically acceptable.

Determination of elements by subtraction

Table 2 shows the analysis of three samples: allanite, biotite and muscovite. In these cases, the sum of concentrations is lesser than 100%. This was to be expected, since in all the three samples certified values show the presence of water.

The concentrations of water determined by subtraction from 100% are good first approximations to the nominal values. Although they are indeed overestimated, it must be emphasized that no influence of water has been taken into account in the matrix corrections for any element. This means that the mass absorption coefficient of the sample for each characteristic line does not include the contribution of water. Therefore, the amount of emerging radiation and hence the factor *A* in Eqn (1) are greater than they should be. For this reason, most calculated concentrations are slightly underestimated, which implies an overestimation of water when determining it by subtraction from 100%.

Further work will be carried out on this aspect, and it will be incorporated in subsequent versions of MULTI.

Standardless algorithm

Usually, quantitation programs available to microanalysts do not contain peak-to-background standardless algorithms. MULTI includes this option, applicable to both bulk samples and particles. Standardless quantification can be carried out by means of the algorithm developed by Trincavelli and Van Grieken[11]. For the present example,

Table 3. Concentrations (%) obtained by a peak-to-background standardless algorithm[11] and certified values[a]

Constituent	Group 1 ($d = 1$–2 μm)	Group 2 ($d = 2$–3 μm)	Group 3 ($d = 3$–4 μm)	Group 4 ($d = 4$–7 μm)	Certified
Pb (%)	77 ± 2	74 ± 1	74 ± 2	72 ± 2	74.3
Si (%)	8.3 ± 0.9	9.5 ± 0.4	9.4 ± 0.8	10.0 ± 0.8	9.0
O (%)	15 ± 1	16.6 ± 0.8	16.5 ± 1	17.5 ± 1	16.3

[a] Particles were divided into four groups according to their diameter d. Each averaged value displayed corresponds to about 10 particles.

analyses were performed on a set of standard spherical particles. Experimental determinations were carried out using a Jeol 733 microprobe at UIA; the particles were grouped according to their diameter: 1–2 μm (group 1), 2–3 μm (group 2), 3–4 μm (group 3) and 4–7 μm (group 4). Each group is composed of about 10 particles. The model for the bremsstrahlung used in these assessments is that given by Trincavelli *et al.*[16]

As can be seen in Table 3, the results are close to the certified concentrations, with no systematic deviation.

CONCLUSIONS

The program MULTI is a versatile, fast and efficient software tool for EPMA quantitation. Several correction models are available to the user by means of an interactive menu, making the program more understandable than conventional commercial programs. It also includes a standardless algorithm applicable to both bulk samples and particles.

The results presented in this paper show that MULTI is an interesting and practical tool for a number of different experimental situations, including determinations of concentrations of a few ppm, analysis of Mα and Lα lines and peak-to-background quantification.

REFERENCES

1. D. Ugarte, J. Trincavelli, G. Castellano, M. del Giorgio and J. Riveros, *X-Ray Spectrom.* **16**, 249 (1987).
2. R. Myklebust, C. Fiori and K. Heinrich, ''FRAME C. A compact procedure for quantitative energy-dispersive electron probe x-ray analysis.'' *Nat. Bur. Stand. Tech.* Note 1106, US Dept. Commerce, Washington.
3. G. Bastin and H. Heijligers, in *Electron Probe Quantitation*, edited by K. Heinrich and D. Newbury, p. 145. Plenum Press, New York (1991).
4. J. Pouchou and F. Pichoir, in *Electron Probe Quantitation*, edited by K. Heinrich and D. Newbury, p. 31. Plenum Press, New York (1991).
5. J. Donovan, M. Rivers and J. Armstrong, *Am. Mineral.* **77**, 444 (1992).
6. S. Reed, in *Electron Microprobe Analysis*, edited by M. Woolfson and F. Ziman, p. 223. Cambridge University Press, Cambridge (1975).
7. J. Robinson, *Handbook of Spectroscopy*, Vol. 1. CRC Press, Boca Raton, FL (1974).
8. B. Henke, P. Lee, T. Tanaka, R. Shimabukuro and B. Fujikawa, *At. Data Nucl. Data Tables* **27**, 1 (1982).
9. K. Heinrich, in *X-Ray Optics and Microanalysis*, edited by J. Brown and R. Packwood, p. 67. University of Western Ontario, Ontario (1987).
10. W. McMaster, N. Kerr del Grande, J. Mallet and J. Hubbell, *Compilation of X-Ray Cross Sections*, Doc. Report UCRL 50174, Sect. 2. Lawrence Radiation Laboratory, Livermore, CA (1969).
11. J. Trincavelli and R. Van Grieken, *X-Ray Spectrom.* **23**, 254 (1994).
12. S. Reed, *X-Ray Spectrom.* **2**, 16 (1975).
13. E. Lifshin, in *Proceedings of the 9th Annual Conference of the Microbeam Analysis Society, Ottawa, Canada*, 1974, paper 53 (available from San Francisco Press, San Francisco, CA).
14. A. Markowicz and R. Van Grieken, *Anal. Chem.* **56**, 2049 (1984).
15. J. Small, S. Leigh, D. Newbury and R. Myklebust, *J. Appl. Phys.* **61**, 459 (1987).
16. J. Trincavelli, G. Castellano and J. Riveros, *X-Ray Spectrom.*, **27**, 81 (1998).
17. D. Sewell, G. Love and V. Scott, *J. Phys. D* **18**, 1245 (1985).
18. J. Pouchou and F. Pichoir, presented at the 11e Congrès d'Optique des Rayons X et de Microanalyse (ICXOM 11), London, Canada (1986).
19. R. Packwood and J. Brown, *X-Ray Spectrom.* **11**, 187 (1982).
20. G. Bastin, H. Heijligers and J. Van Loo, *Scanning* **8**, 45 (1986).
21. G. Bastin and H. Heijligers, Scanning **12**, 225 (1990).
22. J. Riveros and G. Castellano, *X-Ray Spectrom.* **22**, 3 (1993).
23. S. Reed, *Br. J. Appl. Phys.* **16**, 913 (1965).