

# Optimization of K-shell intensity ratios in electron probe microanalysis<sup>†</sup>

G. Castellano,<sup>1\*</sup> R. Bonetto<sup>2‡</sup> J. Trincavelli,<sup>1‡</sup> M. Vasconcellos<sup>3</sup> and C. Campos<sup>3</sup>

<sup>1</sup> Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

<sup>2</sup> Centro de Investigación y Desarrollo de Procesos Catalíticos, CONICET–UNLP, Calle 47 No. 257, Cc 59, 1900 La Plata, Argentina

<sup>3</sup> Instituto de Física, Universidade Federal de Rio Grande do Sul, Porto Alegre, Brazil

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**A method for refinement of atomic and experimental parameters was applied to the optimization of K-shell intensity ratios in electron probe microanalysis (EPMA). This kind of procedure, previously used in x-ray diffraction, is shown to be a powerful tool in EPMA. The method consists of minimizing the differences between an experimental x-ray spectrum and a function proposed to account for the bremsstrahlung and characteristic peaks from the corresponding sample, and also for detection artifacts. In this work, the method was used for the determination of transition rates. This procedure was applied to 14 elements with atomic numbers ranging from 20 to 42. The results obtained are in agreement with theoretical and experimental data for  $K\alpha/(K\beta + K\alpha)$  intensity ratios. In addition,  $K\alpha_1$ ,  $K\alpha_2$ ,  $K\beta_1$ , and  $K\beta_2$  relative intensities were compared with experimental data, showing a similar behaviour. Copyright © 2002 John Wiley & Sons, Ltd.**

## INTRODUCTION

The intensity ratios of lines corresponding to decays to a particular atomic shell (or subshell) are atomic parameters very useful in several spectroscopic techniques. Many publications have been devoted to the theoretical prediction,<sup>1,2</sup> tabulation,<sup>3</sup> experimental determinations,<sup>4,5</sup> and polynomial interpolation<sup>6</sup> of intensity ratios. Special attention has been paid to transition rates mainly because reliable experimental values can be used as a straight test for theoretical atomic models. In addition, an adequate knowledge of transition rates may improve the analyses by spectroscopic techniques based on x-ray emission, since peak overlaps between, e.g.,  $K\alpha$  and  $K\beta$  lines of neighbouring elements are frequently a problem for the analyst.

When determining these ratios experimentally, a number of problems arise, since spectrum deconvolution and correction for absorption may be complicated. Therefore, spectra with good statistics may not be enough for determining accurate intensity ratios, especially for energy-dispersive detection systems. These problems were faced in the present work by means of a method for parameter optimization presented previously.<sup>7</sup> Parameter refinement using the whole

spectra is a well known technique in powder x-ray diffraction, and has been used widely in crystalline structural analysis.<sup>8–10</sup> However, the refinement methodology has not yet been extended to other spectroscopic techniques, such as electron probe microanalysis (EPMA) or x-ray fluorescence, except for the results achieved with the codes POEMA<sup>7</sup> and PRAXIS,<sup>11</sup> respectively.

The method consists of performing least-squares fitting of regions in the observed spectrum. An iterative procedure is carried out in order to minimize the differences between the experimental and the calculated spectra. The expressions used for the predicted spectrum are based on fundamental parameters for characteristic lines and bremsstrahlung emission, and take into account detection artifacts. This complicated function involves several parameters related to different sources (x-ray production, x-ray attenuation, sample composition, x-ray detection, etc.). Initial values must be supplied for them, and after a numerical iterative procedure is performed, improved values are achieved. Depending on the particular situation, certain parameters may be known *a priori*, so that they can be fixed allowing the others to vary.

If  $I$  and  $I_c$  denote the experimental and calculated intensities for the energy  $E$ , respectively, the quantity to be minimized can be written as:

$$\chi^2 = \frac{1}{N-P} \sum \frac{(I_c - I)^2}{I}$$

where the summation runs over all  $N$  data points and  $P$  is the number of parameters adjusted. Thus,  $\chi^2$  will depend on the parameters to optimize through the expressions chosen for  $I_c$ . Since these are complicated functions, the procedure involves a non-linear least-squares fitting, and the risk of falling in local minima is not negligible. In order to reduce

\*Correspondence to: G. Castellano, Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.  
E-mail: gustavo@quechua.fis.uncor.edu

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this risk, the initial guess for the parameters must be fairly close to the correct values. An alternative way to overcome the problem is to begin with different estimates and check that the same minimum is achieved.

**EXPERIMENTAL**

Spectra were measured with two different electron micro-probes, a CAMECA SX-50 and a JEOL JXA-733, both equipped with energy-dispersive detection systems. The spectra were acquired with Si(Li) detectors at energies ranging from 10 to 30 keV and beam current values of 2 and 4 nA for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Zr and Mo (pure samples). In addition, Ca intensity ratios were determined from a dolomite spectrum. Since some of the samples had been coated with a metallic thin film, a comparison was performed between intensity ratios determined from some coated and uncoated samples of the same kind. No appreciable differences were found and, therefore, the effect of coating was neglected in this work.

**OPTIMIZATION OF INTENSITY RATIOS**

The structure of the method rests on two different bases. On the one hand, a full analytical description is given for spectra acquired in EPMA. On the other, a numerical procedure is used to minimize the differences between experimental and calculated spectra. A complete description of these two bases has been given previously by Bonetto *et al.*<sup>7</sup> For the present work, some improvements were introduced: originally only  $K\alpha/(K\alpha + K\beta)$  and  $K\beta/(K\alpha + K\beta)$  were available as optimized outputs; the present version of the program can refine transition rates for any kind of K, L or M line groups. On the other hand, the present version can deal with constraints such as the normalization equation relating all the intensity ratios corresponding to the same atomic shell (or subshell). Finally, an estimate of the errors for each optimized parameter has now been included in the code POEMA.

The experimental spectrum may be regarded as a vector  $y$  whose components are the number of counts at each channel. The parameters to optimize can also be thought of as a vector  $x$ , and the function relating both, as a matrix  $M(x)$ . It can be seen<sup>12</sup> that the uncertainties of the parameters  $x_i$ , arising from the variance-covariance matrix  $V_x$ , can be related to the variance-covariance matrix  $V_y$  for the experimental spectrum by means of

$$V_x = [A^T(V_y)^{-1}A]^{-1}$$

where  $A_{ij} = \partial M_i / \partial x_j$ . The program performs these derivatives numerically in order to yield the matrix  $V_x$ , whose diagonal elements are the searched variances for each parameter  $x_i$ .

In order to predict a spectrum, a complete knowledge of the x-ray bremsstrahlung production, characteristic radiation emission and detection artifacts is required. The continuum spectrum corresponding to the emission of bremsstrahlung  $B$  is predicted by an analytical function of photon energy  $E$ , mean atomic number  $\bar{Z}$  and incident energy  $E_0$  of the electron

beam impinging on the sample, according to Trincavelli *et al.*<sup>13</sup>

$$B = \alpha \sqrt{\bar{Z}} \frac{E_0 - E}{E} \left[ -54.86 - 1.072E + 0.2835E_0 + 30.4 \ln \bar{Z} + \frac{875}{\bar{Z}^2 E_0^{0.08}} \right] A_B R \varepsilon \frac{\Delta\Omega}{4\pi}$$

where  $\alpha$  is a constant proportional to the number of incident electrons,  $A_B$  corrects for x-ray absorption,  $R$  takes into account intensity losses due to electron backscattering,  $\varepsilon$  is the detector efficiency at energy  $E$  and  $\Delta\Omega$  is the solid angle subtended by the detector. This simple analytical function has shown a very good performance for a wide set of experimental spectra as compared with other models.

Spectral peaks are taken into account considering atomic number ( $Z$ ) and absorption ( $A$ ) correction factors from a formalism involving the ionization distribution function  $\phi(\rho z)$  with mass depth  $\rho z$ .<sup>14</sup> The detected characteristic intensity  $P_{j,q}$  of the line  $q$  from element  $j$  in the sample can be written as

$$P_{j,q} = \beta C_j (ZAF)_{j,q} Q_j \omega_j f_{j,q} \varepsilon_{j,q} \frac{\Delta\Omega}{4\pi}$$

where  $\beta$  is a constant proportional to the number of incident electrons,  $C_j$  is the mass concentration of element  $j$ ,  $Q_j$  is the ionization cross-section for element  $j$  at the energy  $E_0$ ,  $\omega_j$  is the fluorescence yield for the considered atomic (sub)shell and  $f_{j,q}$  is the transition rate related to the observed line  $q$ . The applications of the method presented in this work do not include the fluorescence ( $F$ ) correction factor, since it is negligible in these cases. The fluorescence yield coefficients were taken from Hubbell.<sup>15</sup>

Regarding detection artifacts, escape peaks might become important only for low energies; nevertheless, this occurs for low atomic numbers, for which  $K\alpha$  and  $K\beta$  energies are close enough to have the same probability of producing escape photons in the silicon detector. Therefore, escape peaks were disregarded since their effect was negligible in the determination of intensity ratios. In addition, the detector efficiency is practically the same for all the peaks optimized in each application of the method. On the other hand, the most influential artifact for the determination of intensity ratios is related to the peak asymmetry. Some of the charge carriers produced by a photon arriving at the detector may be 'trapped' before being collected. Thus, the output sent to the amplifier corresponds to an energy lower than the original one. This effect is observed as asymmetric peaks with low-energy tails, departing from the assumed Gaussian shape. Since the highest concentration of traps occurs in a transient region close to the detector surface, between the active volume and the dead layer, peaks appear to be more asymmetric for soft x-ray lines. Therefore, a modification to the Gaussian function is necessary in order to account for this effect. The resulting predicted intensity for the energy  $E$  is

$$I^c = B(E) + \sum_{j,q} P_{j,q} H_{j,q}(E)$$

where  $H_{j,q}$  is the Hypermet modified Gaussian function<sup>7</sup> associated with the peak intensity  $P_{j,q}$ .

For the present work, the strategy followed consisted in the initial refinement of the experimental parameters (calibration coefficients, resolution and peak asymmetry coefficients), as well as scale factors for bremsstrahlung and characteristic line groups. Then, line intensity ratios were refined and the procedure was repeated several times up to convergence. The final step was accomplished allowing all the parameters to vary at the same time, as a test to confirm that a global (not local) minimum was found.

## RESULTS AND DISCUSSION

For all the elements considered,  $K\alpha/(K\beta + K\alpha)$  ratios were obtained and compared to theoretical data given by Scofield,<sup>1</sup> experimental values measured by Bé *et al.*<sup>5</sup> and the data tabulated by Perkins *et al.*<sup>3</sup>

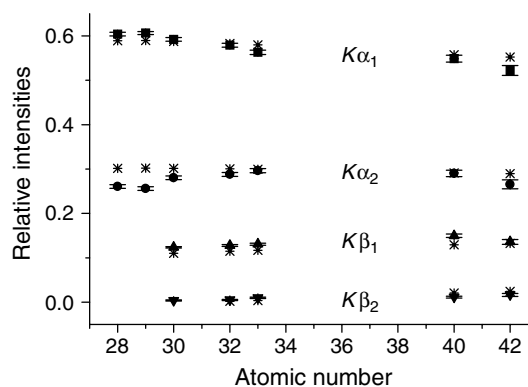
As can be seen in Table 1, the trend followed by Scofield's data was reproduced here: decreasing values with increasing atomic numbers with a more or less constant region from Ti to Zn. There is good agreement between our data and those of Bé *et al.* and Scofield for all the elements except Cu. On the other hand, the values tabulated by Perkins *et al.* show a systematic overestimation compared with the other data sets.

The code POEMA was applied also for determining  $K\alpha_1$ ,  $K\alpha_2$ ,  $K\beta_1$  and  $K\beta_2$  relative intensities for the elements with atomic number above 28. The results obtained are compared in Fig. 1 with those given by Perkins *et al.*<sup>3</sup> As can be seen, the agreement is acceptable even when spectra were acquired with an energy-dispersive system, the resolution of which is insufficient to separate most of the peaks involved.

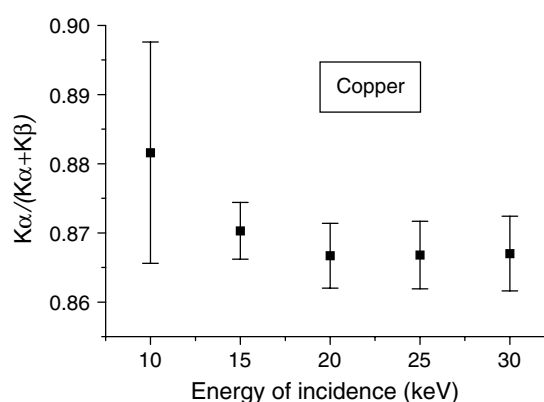
In order to find a possible dependence of transition rates on beam energy,  $K\alpha/(K\alpha + K\beta)$  ratios were determined for a pure copper sample at different overvoltages. The results, plotted in Fig. 2, show a slightly decreasing behaviour with

**Table 1.** Comparison between  $K\alpha/(K\beta + K\alpha)$  ratios determined in this work and experimental and theoretical data given in the literature

Element	This work	Bé <i>et al.</i> <sup>5</sup>	Perkins <i>et al.</i> <sup>3</sup>	Scofield <sup>1</sup>
Ca	0.891 ± 0.003	—	0.904	0.884
Ti	0.881 ± 0.003	0.880 ± 0.001	0.898	0.881
V	0.881 ± 0.003	0.878 ± 0.001	0.896	0.880
Cr	0.882 ± 0.002	0.877 ± 0.001	0.897	0.882
Mn	0.884 ± 0.002	0.878 ± 0.001	0.893	0.878
Fe	0.873 ± 0.004	0.8757 ± 0.0015	0.892	0.878
Co	0.877 ± 0.004	0.878 ± 0.001	0.891	0.883
Ni	0.865 ± 0.006	0.878 ± 0.001	0.891	0.877
Cu	0.862 ± 0.006	0.878 ± 0.001	0.892	0.879
Zn	0.872 ± 0.006	—	0.890	0.876
Ge	0.867 ± 0.006	—	0.883	0.869
As	0.859 ± 0.007	—	0.879	0.865
Zr	0.839 ± 0.011	—	0.849	0.839
Mo	0.848 ± 0.015	—	0.842	0.835



**Figure 1.**  $K\alpha_1$ ,  $K\alpha_2$ ,  $K\beta_1$  and  $K\beta_2$  intensity lines normalized with respect to all the K lines as a function of atomic number. Data tabulated by Perkins *et al.*<sup>3</sup> (\*) are also displayed.



**Figure 2.**  $K\alpha/(K\alpha + K\beta)$  intensity ratios for a pure copper sample as a function of the electron beam energy.

$E_0$ , but this trend is hidden by the uncertainties and more precise measurements should be made in order to confirm this dependence.

## CONCLUSIONS

A versatile method for parameter optimization was applied to the determination of K-line intensity ratios. The results obtained show good agreement with theoretical and experimental published data and also indicate some systematic overestimation in the tabulated data of Perkins *et al.*<sup>3</sup>

The performance achieved for close lines, unresolved because of the detection resolution, suggests that the methodology proposed here may become a powerful tool for the refinement of fundamental atomic magnitudes such as L and M radiative decay rates, Coster–Kronig yields, fluorescence yields, mass attenuation coefficients for low photon energies, etc. Measurements in a wavelength-dispersive system will further enhance these possibilities.

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## REFERENCES

1. Scofield J. *Phys. Rev. A* 1974; **9**: 1041.
2. Scofield J. *Phys. Rev. A* 1974; **10**: 1507.
3. Perkins S, Cullen D, Chen M, Hubbell J, Rathkopf J, Scofield J. *Tables and Graphs of Atomic Subshells and Relaxation Data Derived from LLNL Evaluated Atomic Data Library (EADL), Z = 1–100*. Report UCRL-50400, Lawrence Livermore National Laboratory: Livermore, CA; 1991; 30.
4. Trincavelli J, Montoro S, Van Espen P, Van Grieken R. *X-Ray Spectrom.* 1994; **22**: 372.
5. Bé M-M, Lépy M-C, Plagnard J, Duchemin B. *Appl. Radiat. Isot.* 1998; **49**: 1367.
6. Khan Md. R, Karimi M. *X-Ray Spectrom.* 1980; **9**: 32.
7. Bonetto R, Castellano G, Trincavelli J. *X-Ray Spectrom.* 2001; **30**: 313.
8. Rietveld H. *Acta Crystallogr* 1966; **20**: 508.
9. Rietveld H. *Acta Crystallogr* 1967; **22**: 151.
10. Rietveld H. *J. Appl. Crystallogr* 1969; **2**: 65.
11. Carreras A, Bonetto R, Trincavelli J, Castellano G. *X-Ray Spectrom.* in press.
12. Young R. *The Rietveld Method*. International Union of Crystallography, Oxford University Press: Oxford; 1993.
13. Trincavelli J, Castellano G, Riveros JA. *X-Ray Spectrom.* 1998; **27**: 81.
14. Riveros J, Castellano G, Trincavelli J. *Mikrochim. Acta* 1992; **12**: (Suppl.) 99.
15. Hubbell J. Bibliography and current status of K, L and higher shell fluorescence yields for computations of photon energy-absorption coefficients. NISTIR 89-4144. National Institute of Standards and Technology: Gaithersburg MD, 1989.