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Bremsstrahlung enhancement in electron probe microanalysis for homogeneous samples using Monte Carlo simulation

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Summary

Fluorescence enhancement in samples irradiated in a scanning electron microscope or an electron microprobe should be appropriately assessed in order not to distort quantitative analyses. Several models have been proposed to take into account this effect and current quantification routines are based on them, many of which have been developed under the assumption that bremsstrahlung fluorescence correction is negligible when compared to characteristic enhancement; however, no concluding arguments have been provided in order to support this assumption. As detectors are unable to discriminate primary from secondary characteristic X-rays, Monte Carlo simulation of radiation transport becomes a determinant tool in the study of this fluorescence enhancement. In this work, bremsstrahlung fluorescence enhancement in electron probe microanalysis has been studied by using the interaction forcing routine offered by PENELOPE 2008 as a variance reduction alternative. The developed software allowed us to show that bremsstrahlung and characteristic fluorescence corrections are in fact comparable in the studied cases. As an extra result, the interaction forcing approach appears as a most efficient method, not only in the computation of the continuum enhancement but also for the assessment of the characteristic fluorescence correction.

Introduction

When a finely collimated electron beam impinges on a flat material, several interactions take place. Electron probe microanalysis (EPMA) is based on the comparison of the characteristic intensities emitted by the sample and standards of known composition. This comparison originates in the assumption that the emitted characteristic intensities proportionally relate to the mass concentrations of the corresponding elements, which allows to eliminate geometrical and physical factors that are very difficult to determine (Reed, 1993; Scott *et al.*, 1995). Matrix effects are taken into account by means of the so-called 'ZAF corrections' (Goldstein *et al.*, 2003), originally separated into factors accounting for differences (between sample and standard) in the generation of x-rays and scattering of the incident beam (Z, for atomic number correction), absorption effects (A), and secondary fluorescence enhancement (F).

This last effect originates from ionizations induced by characteristic x-rays or bremsstrahlung photons produced by the primary electron interactions. It is impossible to experimentally determine these intensities separately, since the detector cannot discriminate primary from secondary intensities. For this reason, several models have been proposed to take into account fluorescence enhancement with different levels of approximation (Reed, 1990; Pouchou & Pichoir, 1991). Nowadays, all the quantification routines are based on these models, some of which have been developed under the assumption that bremsstrahlung fluorescence correction is negligible when compared to characteristic enhancement; however, no concluding arguments have been provided in order to support this assumption. Monte Carlo simulations constitute a very important tool for estimating the fluorescence enhancement, and a number of specific situations have already been faced with this approach (Fisher, 1971; Llovet *et al.*, 2003; Fournelle *et al.*, 2005; Tylko, 2015).

The simulation of radiation transport based on the Monte Carlo method consists in generating a particle track as a sequence of free steps governed by the corresponding total and differential cross-sections. Each of these stochastic steps ends in an interaction which changes the particle dynamical state, i.e. its direction of movement and its energy, eventually producing secondary particles. If the number of generated tracks

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is large enough, quantitative information on the transport process may be obtained by averaging over a statistically significant number of trajectories. The PENELOPE routine package (Salvat *et al.*, 2009) has proved to adequately describe EPMA experimental situations (Acosta *et al.*, 1998; Llovet *et al.*, 2003; Salvat *et al.*, 2006); and has been chosen for the simulations carried out along this work.

Disregarding bremsstrahlung enhancement is, in general, not a problem in EPMA when using standards close to the unknowns, since the comparison between characteristic intensities usually cancels out this enhancement in both sample and standard. However, when similar standards are not available, or when standardless quantification is performed, the adequate assessment of this enhancement may become relevant. In addition, the continuum fluorescence enhancement may also become relevant when analysing regions in the vicinity of interfaces, as in the case of thin films (Pouchou & Pichoir, 1993) and particles or microphases (Llovet & Galan, 2003), which is out of the scope of this work.

Unfortunately, both bremsstrahlung production and ionization by photons are rather unlikely processes; for this reason, it becomes necessary to make use of variance reduction techniques, which allow to achieve high statistics within reasonable CPU times. Several options for variance reduction are available in the PENELOPE package, interaction forcing being the most adequate when dealing with bremsstrahlung production. This particular technique is based in the multiplication of a very low cross-section for an event by a factor, `IFORCE`, artificially improving its probability, hence producing high statistics related to it. All the distributions of interest are then properly normalized in order not to introduce any bias (Bielajew & Rogers, 1988; Salvat *et al.*, 2009).

In this work, the fluorescence enhancement by bremsstrahlung in EPMA has been studied and compared with characteristic enhancement, by using the interaction forcing technique offered by PENELOPE. Since the primary intensity I_p directly generated by the electron beam is enhanced by the secondary intensity I_s corresponding to ionizations produced by other photons present in the sample, the total intensity I_t can be written as

$$I_t = I_s + I_p = F\, I_p,$$

where the fluorescence correction factor, F, can be assessed as

$$F = 1 + \frac{I_s}{I_p}. \tag{1}$$

If the errors associated with I_p and I_s are, respectively, σ_p and σ_s, the estimation of the uncertainty in F is given by

$$\sigma_F = (F-1)\sqrt{\left(\frac{\sigma_p}{I_p}\right)^2 + \left(\frac{\sigma_s}{I_s}\right)^2}. \tag{2}$$

In order to analyse the dependence of the statistical uncertainties of F with the `IFORCE` parameter, the secondary intensities I_s were studied for different compositions in Fe-Ni binary alloys. Three typical incident energies (10, 15 and 20 keV) were selected in order to perform the simulations. In addition, to validate the method, the obtained results were compared to those originally given using the splitting technique (Kahn & Harris, 1951).

Materials and methods

The program PENSLAB from 2003 PENELOPE distribution was modified to classify all kinds of enhancement (Petaccia *et al.*, 2015); this new code was updated to fulfil the PENELOPE 2008 requirements, and take advantage of the variance reduction techniques offered by this distribution. For this study, the possibility of using interaction forcing was included in order to take into account secondary fluorescence by bremsstrahlung photons. The resulting code initiates each shower when an electron hits the sample, simulating the primary electrons first, while secondary particles are saved into a stack. Once the primary track is completed, the simulation of second-generation particles begins. Every time a characteristic x-ray is produced after ionization by photons, the program classifies it according to its origin, through the free particle identifier `ILB(5)` (Salvat *et al.*, 2009).

To verify that the distributions of interest are not distorted when `IFORCE` increases, several surveys were carried out for different values of this forcing factor by analysing a single type of interaction each time: on the one hand, bremsstrahlung production and on the other hand, ionization by electrons. These two possible interactions were afterwards combined, with different `IFORCE` values, to obtain good statistics in primary as well as secondary photons. Starting with `IFORCE` = 50 for both processes, the forcing factor was step by step increased in order to verify that no distortions arose in the different kinds of enhancement. The final values chosen were: `IFORCE` = 1000 for electron ionizations and `IFORCE` = 10 000 for bremsstrahlung production. It is worth mentioning that it is also possible to favour ionizations by photons: its direct implementation in the PENELOPE package would favour all possible ionizations in a body, particularly Ni ionizations by bremsstrahlung. This alternative was avoided in this study since Ni concentrations are 50% or above, and all simulations were planned for fixed total CPU times.

The adopted values for the simulation parameters were chosen to take advantage of the CPU time, i.e. simulating electrons above the Fe-K ionization energy and photons slightly below the Fe-Kα characteristic energy; this was accomplished by setting the absorption energies to `EABS(1)`=7.11 keV for electrons and `EABS(2)`=6.399 keV for photons. The choice for the average angular deflection produced by multiple elastic scattering along a path length equal to the mean free path between consecutive hard elastic events was $C_1 = 0.05$; the maximum average fractional energy loss between consecutive hard elastic events was set to $C_2 = 0.05$; the cut-off energy loss for hard

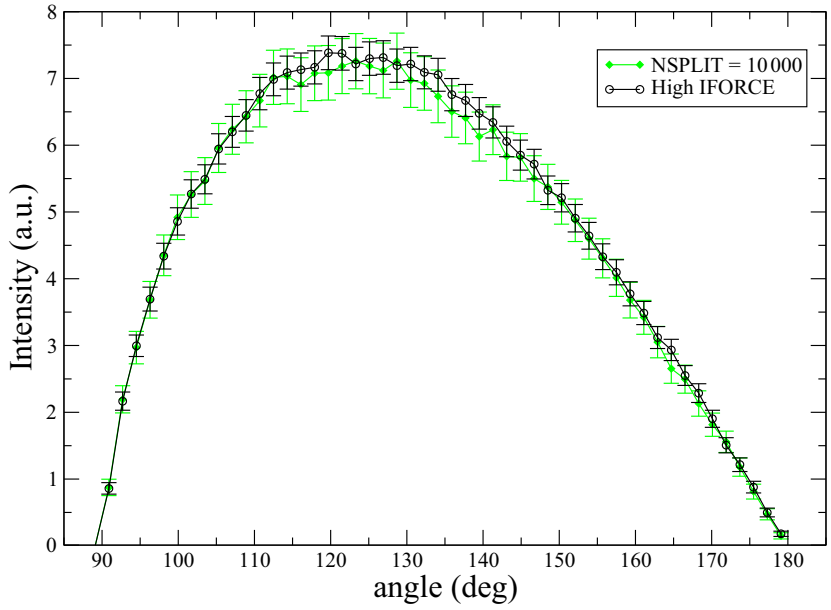

Fig. 1. Angular distribution (relative to the beam direction) of simulated secondary characteristic Fe-Kα photons induced by bremsstrahlung in an Fe1%-Ni binary alloy for a 10-keV beam energy. Circles: high interaction forcing; diamonds: strong splitting.

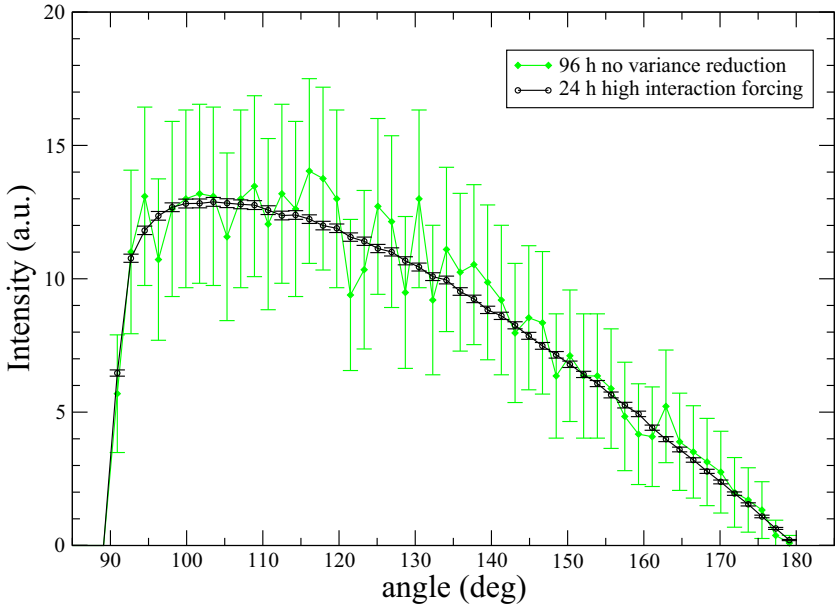

Fig. 2. Angular distribution (relative to the beam direction) of simulated primary characteristic Fe-Kα photons in an Fe3%-Ni binary alloy for a 15-keV beam energy. Hollow circles: 24 h run with high interaction forcing (`IFORCE`=1000 for ionizations by electrons and `IFORCE`=10 000 for bremsstrahlung production); diamonds: 96 h run, no variance reduction.

inelastic collisions was chosen as $W_{cc} = 100$ eV and the selected value for the cut-off energy loss for hard bremsstrahlung emission was $W_{cr} = 100$ eV (Salvat *et al.*, 2009).

All the simulations for secondary fluorescence distributions were run in an Intel® Quad CPU Q8400 @ 2.66 GHz processor during 24 h in order to bring to evidence the influence of `IFORCE` in the resulting statistical uncertainties for a fixed CPU time.

Results and discussion

As displayed in Figure 1, the predicted angular distributions of secondary characteristic Fe-Kα photons (relative to the beam

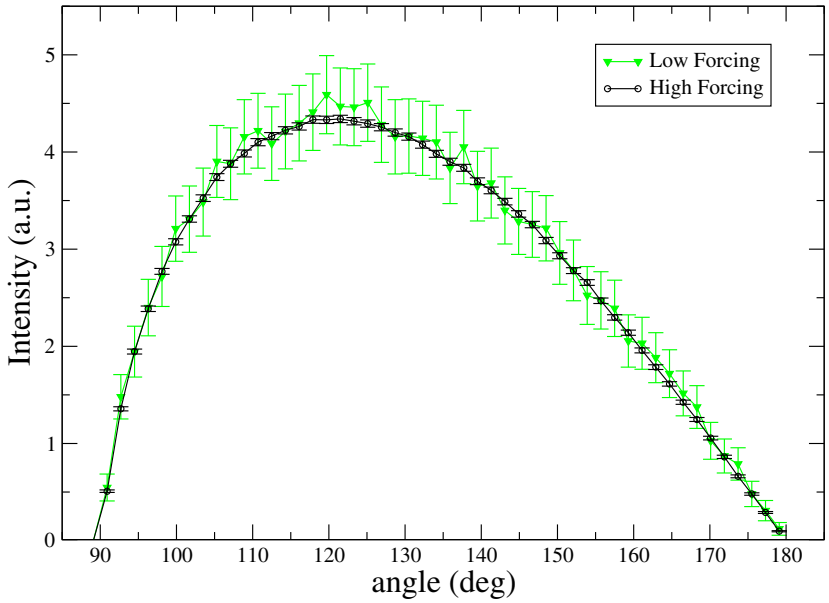

Fig. 3. Angular distribution (relative to the beam direction) of simulated secondary characteristic Fe-Kα photons induced by bremsstrahlung in an Fe10%-Ni binary alloy for a 20-keV beam energy. Hollow circles: high interaction forcing (`IFORCE`=1000 for ionizations by electrons and `IFORCE`= 10 000 for bremsstrahlung production); triangles: low interaction forcing (`IFORCE`=50 for both cross-sections).

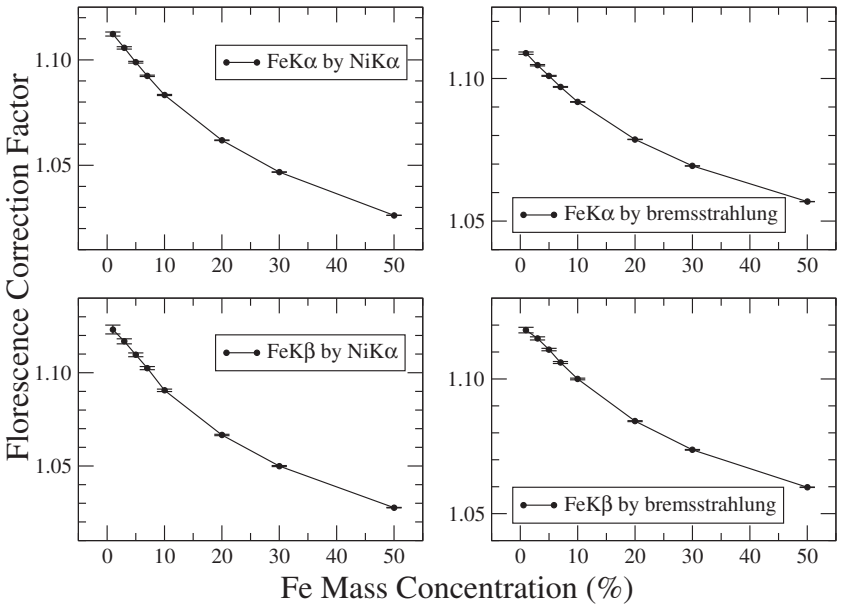

Fig. 4. Fluorescence correction factors at 10 keV in a binary Fe-Ni alloy.

direction) bear the expected behaviour. These distributions are equivalent to those obtained using another variance reduction technique, i.e. splitting (Kahn & Harris, 1951), which have proved to provide adequate values for the characteristic fluorescence correction factors (Petaccia *et al.*, 2015). It can be seen that the uncertainties are slightly lower in the case of interaction forcing. However, it is worth emphasizing that interaction forcing allows to simultaneously obtain primary intensities with small errors, whereas with splitting two separate simulations are needed to achieve reasonable uncertainties, since primary photons must be simulated with no splitting (Petaccia *et al.*, 2015). Nevertheless, primary intensities obtained following the strategy suggested in this previous work bear uncertainties much larger than those achieved with interaction forcing, as displayed in Figure 2, despite the rather longer CPU time devoted (96 h against 24 h).

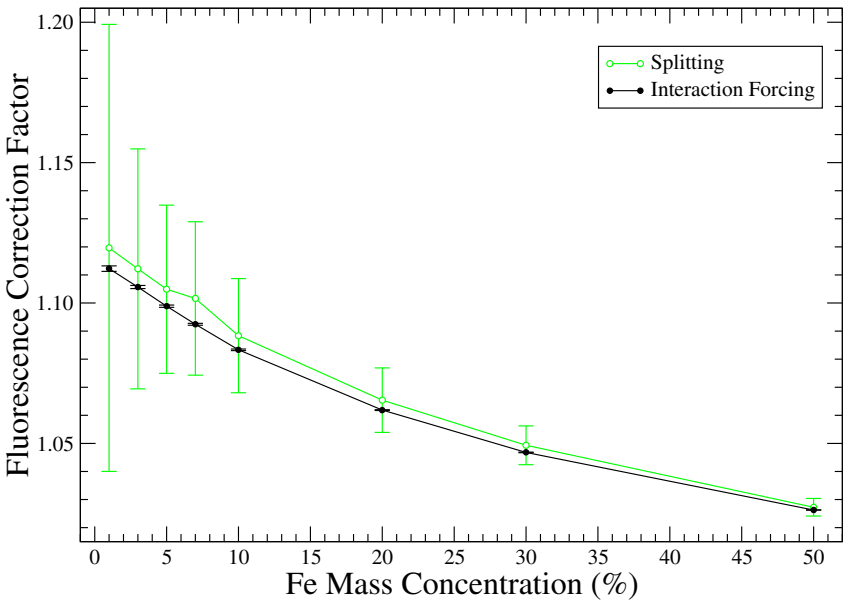

Fig. 5. Comparison between the F-values obtained by interaction forcing and splitting technique.

Table 1. Bremsstrahlung fluorescence enhancement for FeKα as a function of composition and beam energy.

C	10 keV	15 keV	20 keV
1	1.1089 ± 0.0004	1.0688 ± 0.0002	1.0593 ± 0.0002
3	1.1047 ± 0.0002	1.0673 ± 0.0001	1.05779 ± 0.00009
5	1.1009 ± 0.0002	1.06505 ± 0.00008	1.05628 ± 0.00007
7	1.0971 ± 0.0002	1.06320 ± 0.00007	1.05495 ± 0.00006
10	1.0918 ± 0.0001	1.06077 ± 0.00006	1.05310 ± 0.00004
20	1.07863 ± 0.00007	1.05453 ± 0.00004	1.04848 ± 0.00003
30	1.06934 ± 0.00006	1.05016 ± 0.00003	1.04533 ± 0.00002
50	1.05685 ± 0.00004	1.04456 ± 0.00002	1.04130 ± 0.00002

Figure 3 shows the comparison between the angular photon distribution of Fe-Kα photons enhanced by bremsstrahlung for low and high forcing. It can be observed that no distortion arises when incrementing the `IFORCE` value within the range covered, whereas error bars accordingly reduce. Similar results are obtained for all energies and compositions.

It must be emphasized that the fluorescence enhancement is finally assessed by computing the F factor given by Eq. (1). From the results shown above, the uncertainties in both I_p and I_s, decrease as `IFORCE` is increased, thus σ_F given by Eq. (2) decreases as well.

As mentioned above, some of the current quantification algorithms disregard the continuum fluorescence enhancement, assuming it is negligible when compared to other enhancement situations, no matter the beam energy and sample composition. Figure 4 shows four fluorescence correction factors at 10 keV: FeKα|NiKα, FeKα|Br, FeKβ|NiKα and FeKβ|Br; similar results are obtained at 15 and 20 keV. The situations where the NiKβ photons enhance the FeKα or FeKβ signals are not displayed in the figure due to its negligible contribution to both F and its standard deviation; for example, the F factor corresponding to KαKβ enhancement for 1%Fe runs from 1.3% at 10 keV to 3.5% at 20 keV, with relative errors below 10^{-5}. The comparison in this figure clearly evidences that the different enhancement contributions are comparable, and no arguments can be given to neglect the bremsstrahlung fluorescence correction factor. This enhancement can therefore be disregarded only in those cases in which an unknown sample is compared to a standard with similar composition; however, when the analysis is performed using a standard of different composition or in the case of a standardless quantification the bremsstrahlung fluorescence correction can clearly become relevant.

In Table 1, the behaviour of the bremsstrahlung fluorescence enhancement is displayed for several compositions and beam energies. It becomes evident that the bremsstrahlung enhancement becomes relevant for higher mean atomic number samples at low beam energies: in these samples, the continuum emission is favoured, increasing the probability of ionizing the element of interest.

The interaction forcing approach was also applied to the case of characteristic enhancement. Figure 5 shows a comparison between the F values obtained by interaction forcing and splitting technique evidencing the improvement achieved in the present simulations. The comparisons in all characteristic enhancement situations are similar, i.e. uncertainties are

quite smaller in the case of interaction forcing; in addition, it must be emphasized that the present simulations allow the assessment of secondary as well as primary intensity distributions and therefore the fluorescence correction factor in a single simulation with very good statistics.

The results obtained so far encourage to devote shorter times for these simulations, for example, a 6-h simulation would provide similar results with twice the corresponding uncertainties for primary and secondary intensities. In the most unfavourable case, the relative error in F would become 0.5%.

Conclusions

A Monte Carlo simulation programme was implemented in order to study the continuum fluorescence enhancement by bremsstrahlung in EPMA. The variance reduction technique of interaction forcing offered by the PENELOPE package was chosen. The obtained results for primary and secondary intensities follow the same trend that those previously obtained by using the splitting technique (Petaccia *et al.*, 2015); however, the assessed bremsstrahlung correction factors F bear quite smaller errors.

The comparison among the different possible enhancements clearly evidences that no arguments can be given to neglect the bremsstrahlung fluorescence correction factor. This enhancement can be disregarded only when an unknown sample is compared to a standard with similar composition, but when the analysis is performed using a standard of different composition or in the case of a standardless quantification, it must be clearly taken into account, as in the programs XPP and PAP (Pouchou & Pichoir, 1991) and XPHI (Merlet, 1994). Particularly, bremsstrahlung enhancement could become relevant for high mean atomic number samples at low beam energies, since these conditions favour the abundance of continuum photons capable to induce the ionizations of interest, relative to the primary characteristic photons.

The interaction forcing approach was also applied to the case of characteristic enhancement. The comparison with the F-values obtained by splitting technique evidences the improvement achieved in the present simulations. It must be emphasized that the present approach allows the assessment of secondary as well as primary intensity distributions and therefore the fluorescence correction factor in a single simulation with very good statistics which allows to achieve better results with shorter CPU times.

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