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To cite this article: X Llovet and F Salvat 2016 IOP Conf. Ser.: Mater. Sci. Eng. 109 012009

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PENEPMA: a Monte Carlo programme for the simulation of X-ray emission in EPMA

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Abstract. The Monte Carlo programme PENEPMA performs simulations of X-ray emission from samples bombarded with electron beams. It is both based on the general-purpose Monte Carlo simulation package PENELOPE, an elaborate system for the simulation of coupled electron-photon transport in arbitrary materials, and on the geometry subroutine package PENGEOM, which tracks particles through complex material structures defined by quadric surfaces. In this work, we give a brief overview of the capabilities of the latest version of PENEPMA along with several examples of its application to the modelling of electron probe microanalysis measurements.

1. Introduction

The Monte Carlo (MC) method is widely recognized as the most reliable tool for the simulation of X-ray emission in electron probe microanalysis (EPMA) [1]. One of the advantages of the method is its ability to handle geometrical configurations that would be difficult to treat by other means and, therefore, it is well suited for the analysis of heterogeneous samples such as small particles, inclusions, interfaces or multilayer films. MC methods are also useful for deducing compositions where current matrix corrections are unable to provide reliable results. Another advantage of MC simulation is that it can incorporate realistic interaction cross-section models, and atomic relaxation parameters, usually in the form of extensive numerical databases, and thus provide highly accurate results. One drawback of MC methods is that simulation results are affected by statistical uncertainties which, in principle, can only be reduced at the expense of increasing the simulation time. However, significant progress has been made in recent years on the application of variance-reduction techniques which, combined with the increasing availability of fast computers, has enhanced the attractiveness of MC simulation.

Various MC programmes aiming at facilitating the application of MC simulation to EPMA, with different capabilities and degrees of sophistication, have been developed over the years (e.g., [2-5]). Our group at the University of Barcelona has developed and maintains the general purpose MC package PENELOPE [6] for the simulation of coupled electron-photon transport in complex material structures. After more than two decades work, PENELOPE has become a mature simulation tool, and has been applied to a wide variety of problems in electron microscopy, radiation metrology, radiotherapy, and other fields. In 2006 we introduced the programme PENEPMA [7], a dedicated version of an earlier main programme called PENMAIN [3], to allow occasional users to perform
simulations of X-ray emission without requiring any programming work. Since then, a number of upgrades have been made to extend the capabilities of the programme and improve its versatility. Nevertheless, a detailed description of PENEPMA has not yet been published.

In this article we provide a brief overview of the latest version of PENEPMA along with some examples of its application to the modelling of EPMA measurements. A more detailed description of the code and its application to EPMA will be published elsewhere. Among the latest extensions of the programme we mention the addition of N x-ray lines of elements with Z > 50 and of X-ray lines with energies as low as 50 eV, the incorporation of the variance-reduction techniques of bremsstrahlung and X-ray splitting, and the possibility of combining independent runs of the same problem to take advantage of multi-core processors. In Section 2 we give a brief description of the physics and structure of the PENELOPE package. The programme PENEPMA is presented in Section 3. Specific examples that illustrate applications of PENEPMA are presented in Section 4. Finally, Section 5 contains some concluding remarks.

2. Brief overview of PENELOPE

As indicated above, the current code PENEPMA is based on the version 2014 of PENELOPE, released in early 2015 [6]. PENELOPE is a general-purpose MC package for the simulation of the coupled transport of electrons and photons in arbitrary materials. This means that the code not only tracks the primary electrons, but also all secondary electrons and photons produced in interactions of the transported particles (i.e., the complete particle shower originated by each primary electron). PENELOPE uses a combination of numerical and analytical differential cross-sections (DCS) to describe the different interaction mechanisms of electrons and photons with matter. For electrons, these include elastic scattering, inelastic collisions (which includes inner-shell ionisation) and bremsstrahlung emission, while for photons the considered interactions mechanisms are coherent (Rayleigh) and incoherent (Compton) scattering, photoelectric absorption, and electron-positron pair production (which is not active at the energies of interest in EPMA). The cross-section models and the electron tracking algorithm implemented in PENELOPE are described in detail in the manual of PENELOPE [6]. Although the interaction databases cover the interval between 50 eV and 109 eV, the accuracy of the physics models worsens when the energy decreases below about 1 keV (see Ref. [6]).

Electron elastic scattering is simulated by using numerical DCSs obtained from Dirac partial-wave calculations for the electrostatic potential derived from Dirac–Fock atomic electron densities [8], with the exchange potential of Furness and McCarthy. Inelastic collisions are described by means of DCSs obtained from the Sternheimer-Liljequist generalized oscillator strength model [9, 10], including the density-effect correction. In the 2014 version of PENELOPE ionisations of inner subshells by electron impact are considered as proper inelastic collisions, with the DCSs re-normalized so as to yield a total ionisation cross-section identical to the numerical value obtained from a combination of the distorted-wave Born approximation and the planewave Born approximation [11]. A global renormalisation is also applied to the cross-sections of outer subshells to ensure that the collision stopping power remains unaltered. The energy of bremsstrahlung photons is sampled from numerical energy-loss spectra derived from the scaled cross-section tables of Seltzer and Berger [12], while the angular distribution of radiated quanta is described by an analytical expression consisting of an admixture of two “boosted” dipole distributions [13], with parameters determined by fitting the benchmark partial-wave shape functions of Kissel, Quares and Pratt [14].

Coherent (Rayleigh) scattering of photons is simulated by using the Born DCS with an analytical atomic form factor and theoretical anomalous scattering factors; incoherent (Compton) scattering uses DCSs calculated from the relativistic impulse approximation with analytical one-electron Compton profiles [15]; and photoelectric absorption is described by using total atomic cross-sections and partial cross-sections for the K-shell and L-, M- and N-subshells from the LLNL Evaluated Photon Data Library [16]. The initial direction of photoelectrons is sampled from Sauter’s K-shell hydrogenic DCS.
Electron tracks and photon histories are simulated from the initial energy down to the absorption energies selected by the user, at which the particles are considered to be effectively absorbed in the medium. Secondary particles (electrons and photons) emitted with initial energy larger than the corresponding absorption energy are simulated after completion of each primary electron track. PENELOPE accounts for the emission of characteristic X-rays and Auger electrons that result from vacancies produced in K-shells and L-, M- and N-subshells by photoelectric absorption and Compton scattering of photons and by electron impact. The relaxation of these vacancies is followed until all vacancies have migrated to O- and outer shells. PENELOPE uses radiative and non-radiative transition probabilities extracted from the LLNL Evaluated Atomic Data Library [17]. The energies of X-rays emitted in radiative transitions resulting from vacancies in the K-shell and L-subshells are taken from the compilation by Deslattes et al. [18]. X-ray energies for transitions of vacancies in M-subshells are taken from Bearden’s [19] review. In the case of transitions not included in these compilations, and also in transitions resulting from vacancies in N-subshells, the energy of the X-ray is approximated as \( E_x = U_{S0} - U_{S1} \), where \( U_{S0} \) and \( U_{S1} \) are the ionisation energies of electrons in shell \( S_0 \) where the vacancy has been produced and in shell \( S_1 \) where the vacancy has migrated, respectively. \( U_{S0} \) and \( U_{S1} \) are taken from the LLNL Evaluated Atomic Data Library [17].

Electrons can be simulated by following the usual detailed procedure, i.e., all the interaction events along an electron track are sampled in chronological order, or alternatively, by using a mixed (class II) simulation algorithm [6]. Mixed simulation algorithms are useful when the electrons undergo a very large number of interactions and detailed simulation becomes impractical (e.g., for primary electron energies above \( \sim 100 \text{ keV} \)). Photon histories are simulated in detail, i.e., interaction after interaction.

The practical usefulness of MC simulation lies in its ability to handle samples with complex geometries. PENELOPE contains the subroutine package PENGEOM which automatically tracks particles through arbitrary material systems consisting of homogeneous bodies limited by quadric surfaces. Limiting surfaces can be specified either through their implicit equation, \( f(r) = 0 \), or by means of their reduced form and a few simple geometrical transformations. A Java graphical user interface (GUI) is available [20] to ease the definition and allow the visualisation of the geometrical structure of the sample (see figure 1).

![Figure 1. Main window of the GUI [20] provided to help defining and visualising the sample geometry in PENELOPE.](image-url)
3. The programme PENEPMA

Because of its specificity, PENEPMA is not distributed with the PENELOPE package, but it is publicly available from the authors. It is pertinent to also mention that older versions of the code, with limited capabilities, have been incorporated by other researchers into free microanalytical platforms such as CALCZAF, PYPENELOPE or PYMONTECARLO.

As mentioned above, PENEPMA was designed to allow occasional users to simulate EPMA experiments without having to write a PENELOPE main programme. The user can define the details of his or her experiment (electron-beam characteristics, geometrical structure and composition of the target, photon detectors) and set the simulation control parameters by simply editing a single input text file. PENEPMA assumes that primary electrons are emitted from a point source, at a certain position, \( r_0 = (x_0, y_0, z_0) \), with fixed energy. The initial direction of primary electrons is sampled isotropically within a cone of given semi-aperture \( \alpha \) and central axis in the direction \( (\theta_0, \phi_0) \) (see figure 2a). Notice that \( \alpha = 0 \) defines a parallel pencil beam, and \( \alpha = 180^\circ \) corresponds to an isotropic source.

![Diagram](image)

**Figure 2.** a) Definition of the electron-beam geometry. Electrons start off from the position \( r_0 \). The beam is specified by giving the polar and azimuthal angles, \( \theta_0 \) and \( \phi_0 \), of its axis direction, and the semi-aperture \( \alpha \), all in degrees. b) Geometry of the experimental set-up assumed in PENEPMA. Each photon detector is defined by specifying the limiting values of the polar and azimuthal angles, \( (\theta_1, \theta_2) \times (\phi_1, \phi_2) \). Notice that \( \theta \) is the complement of the traditional take-off angle \( \chi \), i.e., \( \chi = \pi - \theta \). The annular detector 1 is useful to obtain fast simulation results in cases where the X-ray flux is axially symmetric. (Reprinted from [7], with kind permission from Springer Science and Business Media).

The user can define a number of ideal photon detectors (up to 25). Each detector covers a solid angle corresponding to a “rectangle”, \( (\theta_1, \theta_2) \times (\phi_1, \phi_2) \), on the surface of the unit sphere centred at the origin of the reference frame (see figure 2b). This particular shape of the active detector surface is useful for normalising the simulated spectrum. The programme delivers energy spectra of photons that enter the various detectors, as well as characteristic line intensities, with fluorescence.
contributions given separately. It is worth mentioning that fluorescence effects are consistently described. The programme also offers the option of scoring the spatial distribution of X-ray emission within the volume of a parallelepiped (the scoring box) with a Cartesian mesh, for selected characteristic lines or for a given interval of X-ray energies.

In actual EPMA measurements, X-ray detectors cover a very small solid angle about a direction \((\theta_d, \phi_d)\) with a take-off angle \(\chi\) relative to the sample surface, i.e., \(\chi = \pi - \theta_d\), of 40°. Simulations with this configuration would be very inefficient, because of the small collection solid angle. In cases where the flux of emerging photons has axial symmetry about the z-axis (e.g., for plane-surface samples that are homogeneous within the interaction volume, and at normal incidence), the efficiency of the simulation can be increased by using an annular detector (with \(\phi_1 = 0\) and \(\phi_2 = 360°\)) that covers a finite interval of polar emission angles \(\theta\) (see figure 2b).

PENEPMA has a dump/resume option which allows the user to stop the simulation at any time, and to resume it from the last dumping point in a completely consistent way. Furthermore, PENEPMA allows the possibility of combining independent runs of the same simulation problem to take advantage of multi-core processors.

The straight simulation of EPMA spectra may be very inefficient, even when using mixed simulation algorithms for electron transport. The reason is that the processes leading to the emission of X-rays (namely, inner-shell ionisation and/or bremsstrahlung emission) occur with exceedingly small probabilities. That is, on average, we need to generate many electron histories to obtain one emerging photon. In addition, as the solid angle subtended by the detector is usually very small, only a tiny fraction of the emerging photons hits the detector and contributes to the spectrum. To cope with this difficulty, PENEPMA takes full advantage of the variance-reduction techniques implemented in PENELLOPE. The most effective of these are interaction forcing and photon splitting. The method of interaction forcing consists of artificially increasing the probability of inner-shell ionisation and bremsstrahlung emission and, at the same time, assigning appropriate statistical weights to the generated secondary particles so that simulation results remain unbiased. Photon splitting consists of considering that during each radiative event several photons are emitted in various directions, with appropriate weights to avoid biasing.

A simulated X-ray spectrum corresponds to an ideal detector, and hence, characteristic lines are very narrow, i.e., each line is fully contained in a single channel of the output histogram. In order to obtain a realistic spectrum, which can be compared, e.g., to an experimental spectrum, the effect of the finite energy resolution of the detector must be introduced. The PENEPMA package contains a Fortran programme called CONVOLG that performs this calculation by assuming that the energy-resolution function of the detector is a Gaussian with energy-dependent full-width-at-half-maximum.

4. Examples of the application of PENEPMA

The reliability of PENEPMA and PENELLOPE has been assessed by our group as well as by other researchers through systematic comparisons of simulated and experimental X-ray spectra from bulk samples [21-23], X-ray yields from bulk samples [24-27], \(k\)-ratios from thin films on substrates [28], and \(k\)-ratios from material couples [29, 30]. Examples of recent applications of PENEPMA or PENELLOPE in EPMA include the study of secondary fluorescence effects in bulk samples and near phase boundaries [31, 32], the analysis of inclusions in steel [33], the simulation of energy-dispersive spectra for automated materials identification [34, 35], the determination of the detector efficiency for standard-less analysis [36] or the examination of carbon contamination effects in high-resolution EPMA [37].

In this Section, we present several examples of application of PENEPMA in EPMA that illustrate the capabilities of the code. These examples refer to the simulation of X-ray spectra including N-lines, the determination of the spatial resolution at low energies, the analysis of thin films on substrates and the calculation of secondary fluorescence near phase boundaries.
4.1. *X-ray spectra*

X-ray spectra consist of characteristic peaks superimposed on a continuous background. The background results mostly from bremsstrahlung photons (with a lesser contribution from Compton-scattered characteristic X-rays), while characteristic peaks arise from X-rays emitted in radiative transitions of atoms that have been ionized in an inner shell, either by electron impact, photon absorption or incoherent photon scattering. As already mentioned, the simulation of X-ray spectra is generally difficult because both bremsstrahlung emission and inner-shell ionisation occur with very small probability when compared with the dominant interactions of elastic scattering and outer-shell ionisation (or excitation). Only with the use of variance-reduction techniques [22] can X-ray spectra be generated in reasonably short computer times.

Figure 3a shows an X-ray spectrum from a Pt bulk sample irradiated with a 20 keV electron beam measured with a Si(Li)-detector, compared with the simulation result. The experimental data were taken from Ref. [22]. The spectra are given in absolute units, i.e., as the probability density for detecting a photon per unit photon energy, per unit solid angle and per incident electron. Also shown in figure 3a is the result of convolving the simulated spectrum with the energy-resolution function of the detector, represented by a Gaussian distribution with an energy-dependent width. We see that simulation agrees closely with experiment. Significant differences are visible only at low energies, where the efficiency of the detector, which was considered to be independent of the photon energy, becomes less than its geometrical efficiency.

![Figure 3a](image1.png)

**Figure 3a.** Comparison of simulated and experimental spectra from Pt with a 20 keV electron beam. The dots represent the experimental data and the solid curves represent the simulated raw spectrum (green) and the result of its convolution with the energy-resolution function of a Si(Li)-detector (blue); notice the logarithmic scale on the vertical axis.

Figure 3b shows the spectrum of x rays produced by a 5 keV electron beam, emerging from a W sample for an annular detector covering the angular range $45^\circ < \theta < 55^\circ$. The spectrum is given in absolute units. Since PENEPEMA keeps track of the interaction mechanism that originates each secondary particle, it is able to provide the intensity of characteristic X-rays that reach a detector (i.e., with the bremsstrahlung background removed), along with the different contributions (primary photons resulting from interactions of the beam electrons, characteristic fluorescence and bremsstrahlung fluorescence). Also plotted in figure 3b is the energy spectrum of bremsstrahlung and
characteristic X-rays “generated” within the sample, i.e., at the start of their motion. The characteristic lines observed below 1 keV correspond to N-lines while those above 1 keV are M-lines. A list of the radiative transitions corresponding to the N-lines for W, along with the corresponding X-ray energies and detected line intensities (for the 5 keV incident electron beam) are tabulated in table 1.

Table 1. List of radiative transitions corresponding to the N-lines for W implemented in PENEPMA. The column $S_0$ corresponds to the subshell where the vacancy has been produced, $S_1$ is the shell to which the vacancy migrates and $E$ is the energy of the N X-ray line. The columns $I$ and ‘unc’ are the intensity and statistical uncertainty (at 3σ level), respectively, of the N X-ray lines detected by an annular detector covering the angular range $45° < \theta < 55°$ (i.e., a take-off angle $\chi$ of 40°) for an incident electron beam of 5 keV. This simulation took 2.5 h on an Intel Core i7 2.93 GHz processor with a RAM size of 8 Gb.

<table>
<thead>
<tr>
<th>$S_0$</th>
<th>$S_1$</th>
<th>$E$ (eV)</th>
<th>$I$ (1/(sr×electron))</th>
<th>unc</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 N2</td>
<td>96.09</td>
<td>$2.14 \times 10^{-8}$</td>
<td>$4.9 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N3 N4</td>
<td>159.57</td>
<td>$4.96 \times 10^{-8}$</td>
<td>$7.4 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N1 N3</td>
<td>165.08</td>
<td>$1.65 \times 10^{-7}$</td>
<td>$1.3 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N3 N5</td>
<td>172.28</td>
<td>$5.91 \times 10^{-7}$</td>
<td>$2.6 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N5 O3</td>
<td>201.69</td>
<td>$2.66 \times 10^{-7}$</td>
<td>$1.7 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N5 N6</td>
<td>201.73</td>
<td>$5.88 \times 10^{-8}$</td>
<td>$8.0 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N4 O2</td>
<td>204.80</td>
<td>$1.76 \times 10^{-7}$</td>
<td>$1.4 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N4 O2</td>
<td>204.09</td>
<td>$1.13 \times 10^{-6}$</td>
<td>$3.5 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N4 O3</td>
<td>214.40</td>
<td>$2.62 \times 10^{-8}$</td>
<td>$5.4 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N4 N6</td>
<td>214.44</td>
<td>$7.15 \times 10^{-8}$</td>
<td>$2.8 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N2 N4</td>
<td>228.52</td>
<td>$8.14 \times 10^{-7}$</td>
<td>$3.0 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N3 O1</td>
<td>334.48</td>
<td>$4.22 \times 10^{-7}$</td>
<td>$2.2 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N2 O1</td>
<td>403.47</td>
<td>$2.34 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>N3 O4</td>
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<td>$6.43 \times 10^{-9}$</td>
<td>$2.7 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N3 O5</td>
<td>412.21</td>
<td>$2.56 \times 10^{-9}$</td>
<td>$5.3 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N2 O4</td>
<td>480.34</td>
<td>$5.66 \times 10^{-9}$</td>
<td>$2.5 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>N1 O2</td>
<td>528.68</td>
<td>$1.33 \times 10^{-7}$</td>
<td>$1.2 \times 10^{-8}$</td>
<td></td>
</tr>
</tbody>
</table>

Published quantitative measurements of N-line X-ray intensities emitted by electron impact are very scarce. Scheffel et al. [38] have reported measurements with an energy-dispersive X-ray spectrometer of the intensity ratio of the $N_{4,5}N_{6,7}$-line $I(N_{4,5}N_{6,7})$ to the $M\alpha\beta$ line $I(M\alpha\beta)$. Although an absolute comparison of the measured $I(N_{4,5}N_{6,7})/I(M\alpha\beta)$ ratio with results from MC simulation would require knowledge of the detector efficiency at the energies of both X-ray lines, it is possible to compare the relative shape of the $I(N_{4,5}N_{6,7})/I(M\alpha\beta)$ curve versus the electron beam energy. This comparison is presented in figure 4. We see that the agreement between simulation and experiment is quite good in relative terms. Multiplication of the simulation results by a factor of 1.46 to account for the different detector efficiencies at the energies of the $N_{4,5}N_{6,7}$ (E ~ 0.2 keV) and $M\alpha\beta$ (E ~ 1.7 keV) lines would give a perfect match between simulation and experiment. There is obviously a need for absolute N-line intensity measurements to assess the reliability of simulations of such X-ray lines.
4.2. Spatial resolution of EPMA

The spatial (lateral) resolution of EPMA is generally estimated by means of the penetrative range of primary electrons, $R_x$, which is defined as the average path length (distance) travelled by a primary electron before slowing down to rest (or more precisely to an energy equal to the ionisation energy $E_i$ of the atomic shell which originates the X-rays of interest). $R_x$ is the difference between the ranges of electrons with energies $E_0$ and $E_i$:

$$R_x = \int_{E_0}^{E_i} \frac{dE}{dE/ds}$$  \hspace{1cm} (1)

where $dE/ds$ is the stopping power of the material. Approximate analytical expressions for $R_x$ obtained from experimental measurements have been developed which are used in practice. Eq. (1) assumes that the beam has a negligible size, which is plausible for moderately high-beam energies. However the width of the electron beam may become comparable to the electron range at low-beam energies, and therefore its effect should be accounted for at such energies.

Experimentally, the lateral resolution of EPMA can be measured as edge resolution, i.e., by means of an integrated X-ray intensity profile obtained by scanning the electron probe across the boundary of two materials separated by a plane interface perpendicular to the surface of the specimen. The edge resolution is then quoted as the distance between points corresponding to 10 % and 90 % of the total intensity (or sometimes the 16 % to 84 % distance). Figure 5 shows a comparison between measured and simulated integrated X-ray profiles for the Ni-$\text{L}_\alpha$ line across the boundary of a Fe-Ni couple, obtained with a 5 keV electron beam having a diameter $d$ of 54 nm. The experimental data are from [39]. Agreement between simulation and experiment is satisfactory. Measurements of this kind, although scarce, are very useful for the purpose of assessing the reliability of MC simulations.

It is possible to investigate the effect of the beam size on the spatial (lateral) resolution of EPMA by simulating the X-ray distribution as a function of the radial $r$ distance from the beam centre (radial X-ray distribution). Figure 6 compares radial X-ray distributions for Si-$\text{K}_\alpha$ X rays generated in Si and 4 keV electron beams with different beam diameters. The full-width-at-half-maximum of a radial distribution is often regarded as a measure of the lateral resolution of a given imaging technique. In this case, the X-ray distributions are seen to consist essentially of two components, a central sharp peak superimposed onto a much broader contribution. Figures 6b-6d display X-ray distributions as functions of both the radial distance $r$ and the depth $z$ within the specimen, and allow a 2D visualisation of the beam spread within the sample. In the studied cases, the 2D X-ray distributions have been generated by scoring the number of Si-$\text{K}_\alpha$ X-rays that have been generated within a $0.4 \times 0.4 \times 0.4$ $\mu$m$^3$ scoring box, whose edges are parallel to the axes of the laboratory frame, and integrating over the y coordinate.
4.3. Thin films
EPMA is conventionally used for the analysis of samples which are homogeneous at the micrometre-scale; however, it can also be used for determining the thickness and composition of thin films deposited on substrates and multilayer films, with thicknesses ranging from a few nanometres up to few micrometres. In order to analyze these kinds of samples, k-ratio measurements are performed at varying incident electron energy and they are processed with the help of a suitable thin-film analysis programme. The latter determines the composition and thickness of the film or multilayer by fitting the predictions of an X-ray emission model to the measured k-ratios.

Extensive experimental databases have become available in recent years for the purpose of assessing the reliability of thin film programmes [40]. Evidently, they can also be used to assess the performance of MC simulation programmes [28]. Figure 7 shows one such example, in which a comparison between simulated and experimental Al and Pd k-ratios emitted from Al and Pd films deposited on a wide variety of single-element substrates spanning the periodic table, as a function of substrate atomic number. The experimental data were taken from Bastin and Heijligers’s database [41, 42]. The results from PENEPMA agree satisfactorily with the measured k-ratios.

4.4. Secondary fluorescence
As mentioned previously, the penetrative range $R_x$ of an electron beam with an energy in the keV range is of few micrometres, depending on the beam energy and the material. However, the range of both characteristic and bremsstrahlung X-rays can be one-to-two orders of magnitude greater than that of primary electrons. Consequently, X-rays can also be generated by fluorescence of characteristic and bremsstrahlung X-rays absorbed in a non-excited material far away from the point of impact of the electron beam. This contribution is known as secondary fluorescence (SF) and it can be significant in certain situations, both quantitatively and qualitatively. We would like to mention that this contribution is not accounted for by conventional matrix correction methods.

Figure 8a compares simulated and measured k-ratio profiles for a non-diffused couple consisting of two homogeneous alloys, namely Co (4.1 wt% Cu) and Cu (2.1 wt% Co), as a function of the distance from the beam to the boundary. The electron beam impacts on the Cu (2.1 wt% Co) alloy. Material couples of this kind have been used as starting materials for diffusion experiments using the diffusion couple technique. The measured Co-Kα X-ray intensity has a primary contribution (from electron impact on the Cu (2.1 wt% Co) alloy itself) and a contribution from secondary fluorescence due to the interaction of both Co characteristic X-rays and bremsstrahlung within the adjacent Co (4.1 wt% Cu) alloy. Simulated and measured fluorescence intensities agree very well with each other.
Figure 6. a) Radial distribution of Si-Kα X-ray emission in Si for a 4 keV electron beam with increasing beam radii, as indicated in the legends. b) 2D Si-Kα X-ray distribution in the $x - z$ plane generated within a Si sample with a 4 keV electron beam with diameters $d = 0$ nm (upper left), 50 nm (upper right), 100 nm (lower left), and 200 nm (lower right).
Figure 7. Comparison of measured and simulated $k$-ratios for Al (a) and Pd (b) films deposited on different single-element substrates, versus substrate atomic number. $t$ is the mass thickness of the films. Experimental data were taken from [41, 42].

Figure 8. a) Comparison of measured and simulated Co-Kα $k$-ratios versus electron beam distance to the interface for a Co (4.1 wt% Cu)-Cu (2.1 wt% Co) couple. The beam impacts on the Cu (2.1 wt% Co) alloy (right-hand side of the couple). The measured and simulated values are represented by open squares and crosses joined by continuous lines for visual aid. The experimental data were taken from [43]. Notice that these two slabs of alloy have been joined together under cold conditions and no atoms have diffused. b) Effect of the position of the spectrometer on the SF profile for a Fe-Cu couple. See text for details.

Because of the much higher range of primary X-rays, absorption of fluorescent X-rays within the sample may be sensitive to the relative position of the X-ray spectrometer, as discussed by Fournelle et al. [44]. Figure 8b illustrates this dependence for a Fe-Cu couple, with the electron beam impacting on the Cu side of the couple. Three simulated SF profiles are compared, namely one obtained by using an annular X-ray detector, i.e., with limiting polar and azimuthal angles of $(\theta_1 = 45°, \theta_2 = 55°) \times (\phi_1 = 0°, \phi_2 = 360°)$, a second one with a detector with polar and azimuthal...
angles \((\theta_1 = 45^\circ, \theta_2 = 55^\circ) \times (\phi_1 = -90^\circ, \phi_2 = 90^\circ)\), i.e. facing towards the Cu-side of the couple (labelled A in figure 8b), and a third one placed with polar and azimuthal angles \((\theta_1 = 45^\circ, \theta_2 = 55^\circ) \times (\phi_1 = 90^\circ, \phi_2 = 270^\circ)\), i.e. facing towards the Fe-side of the couple (labelled B in figure 8b). The differences between the different profiles are mainly caused by the different absorption of Fe-K\(\alpha\) X-rays in Fe and in Cu. The observed differences between the three profiles indicate that accurate correction of SF requires knowledge of the position of the spectrometer with respect to the couple boundary.

5. Conclusion
We have provided an overview of the MC simulation programme PENEPMA. The programme uses the general-purpose MC simulation package PENELOPE, which implements the most realistic interaction cross-section models available today. These models are generally described by extensive numerical databases. Examples have been provided to demonstrate the reliability of the programme in simulations of X-ray spectra including N-lines, for the determination of the spatial resolution of EPMA at low energies, for the analysis of thin films and in the calculation of secondary fluorescence across phase boundaries.

Acknowledgements
Financial support from the Spanish Ministerio de Economía y Competitividad and ERDF (project no. FPA2013-44549-P) and from the Generalitat de Catalunya (grant 2014 SGR 846) is gratefully acknowledged.

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