Improved spectrum simulation for validating SEM-EDS analysis

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Abstract. X-ray microanalysis by SEM-EDS requires corrections for the many physical processes that affect emitted intensity for elements present in the material. These corrections will only be accurate provided a number of conditions are satisfied and it is essential that the correct elements are identified. As analysis is pushed to achieve results on smaller features and more challenging samples it becomes increasingly difficult to determine if all conditions are upheld and whether the analysis results are valid. If a theoretical simulated spectrum based on the measured analysis result is compared with the measured spectrum, any marked differences will indicate problems with the analysis and can prevent serious mistakes in interpretation. To achieve the necessary accuracy a previous theoretical model has been enhanced to incorporate new line intensity measurements, differential absorption and excitation of emission lines, including the effect of Coster-Kronig transitions and an improved treatment of bremsstrahlung for compounds. The efficiency characteristic has been measured for a large area SDD detector and data acquired from an extensive set of standard materials at both 5 kV and 20 kV. The parameterized model has been adjusted to fit measured characteristic intensities and both background shape and intensity at the same beam current. Examples are given to demonstrate how an overlay of an accurate theoretical simulation can expose some non-obvious mistakes and provide some expert guidance towards a valid analysis result. A new formula for calculating the effective mean atomic number for compounds has also been derived that is appropriate and should help improve accuracy in techniques that calculate the bremsstrahlung or use a bremsstrahlung measurement for calibration.

1. Introduction
X-ray microanalysis by SEM-EDS requires corrections for the many physical processes that affect emitted X-rays for elements present in the material. These corrections are only applicable under the following conditions: specimen composition must be uniform within the region excited by scattered electrons, the surface must be flat over the region where any X-rays exit towards the detector, the geometry for incident beam, surface and X-ray detector must be known, the incident focussed electron beam must not be affected by specimen charging, the correct elements must be identified and suitable line emissions must be excited and measurable. As analysis is pushed to achieve results on smaller features and more challenging samples it becomes increasingly difficult to determine if all these conditions are upheld and whether the analysis results can be trusted.

If results are calibrated by a standard or beam current measurement, an analytical total close to 100 % gives one level of reassurance. When results are normalized for speed and convenience, an alternative “Check Total” can be used [1] but neither method is infallible and even when the total is...
bad, neither measure provides any information to diagnose the cause. Therefore, we have investigated an idea suggested by Duncumb [2] that it would be useful for the operator to be presented with a theoretical simulated spectrum based on the analysis result. Provided the simulation was accurate, it could indicate problems with the analysis and thus prevent serious mistakes in interpretation. For example, when more than one line emission is generated (e.g., K, L or M), the simulation would show if the observed L/K or M/L ratio was consistent with the theory. If the wrong elements were identified or an element was missing then line ratios or peak/background levels would be different from the observed spectrum. Likewise, specimen charging, inhomogeneity and geometry issues may also be exposed.

2. Current accuracy of theoretical spectrum simulation
To be useful for validating results, the theoretical simulation has to be sufficiently accurate. DTSA-II is a well-known public domain programme that provides SEM-EDS spectrum simulation [11] (Indeed, Fiori’s original DTSA was the first available programme to offer this capability). The 2014 version (Halley 2014-08-01) provides an “instantaneous” simulation based on a series of formulae (“Analytical Model”) or a longer Monte Carlo (MC) simulation that sums the emissions due to many randomized electron trajectories based on various theories for fundamental electron interactions. Figure 1 shows an example of DTSA-II results for a pure Ni specimen compared with experiment where the spectra have been normalized to have the same intensity across a region spanning the Ni K peaks. In figure 1a, whereas the background for the MC simulation is fairly close to that measured, the analytical model shows a large deficit for most of the energy range. In figure 1b, it is apparent that both simulations overestimate the Ni-L\(\alpha\) intensity and the Ni-L\(\alpha\)/L\(\beta\) ratio is higher than that measured.

In figure 2, the results for simulations for pure Au (this time normalized using a region spanning the Au L peaks) again show that the MC simulated background is close to that measured but the analytical model is poor and both types of simulation give a poor match to the Au M intensity in figure 2b.

![Figure 1. a) DTSA-II (2014) Ni simulations 20 kV compared with experiment (X-max80 SDD, red curve). b) Same, low energy region.](image)

For bremsstrahlung background modelling DTSA-II MC looks promising but for characteristic line intensities even the most elaborate MC programmes are limited in accuracy by uncertainty in fluorescence yields and transition probabilities. Furthermore, for a real-time interactive tool, an analytical model is considerably faster to compute so we chose to refine an analytical model to see what could be achieved in terms of accuracy.
Figure 2. a) DTSA-II (2014) Au simulations 20 kV compared with experiment (X-max80 SDD, red curve). b) Same, low energy region.

3. Improved theoretical model
We started with an earlier parameterized analytical model [3] and extended it to incorporate differential absorption of emission lines and differential excitation of shells, including the effect of Coster-Kronig transitions. Thus, for an element $A$ of mass fraction $C_A$, the average characteristic intensity emitted per electron per unit solid angle for a given line is

$$I_A = (\omega_A \rho_A) \cdot R_{\text{el}} N_0 C_A / A_A \int Q \cdot S \cdot dE \cdot f(\chi) A \cdot (1 + F) \cdot (1 + G) \cdot CK_{ss} \quad (1)$$

where $\omega_A$ is the fluorescence yield for element $A$ for the appropriate shell, and $\rho_A$ is the proportion of emission for the line. $A_A$ is the atomic weight of element $A$, and $N_0$ is Avogadro’s number. $(1 - R)$ is the intensity fraction lost by backscatter. $S = -dE/d(\rho x)$ is the stopping power or rate of electron energy loss with mass thickness $\rho x$ where $\rho$ is the density. Absorption factor $f(\chi)_A$ is for radiation travelling towards the detector and fluorescence enhancement factors $(1 + F)$ and $(1 + G)$ are for characteristic and bremsstrahlung continuum radiation respectively. The cross-section used follows the form in [3],

$$Q = q_i \cdot m \cdot (\ln U) / (E_c^2 \cdot U^m) \quad (2)$$

where $E_c$ is the critical excitation potential for the analysed peak and $U$ is the overvoltage ratio $E/E_c$. $m$ is a constant adjusted for each shell and $q_i$ is a multiplier set by experiment to match the observed intensities from each shell to one another and to those results for which the intensities are known in absolute terms. $CK_{ss}$ is the enhancement factor for primary vacancies due to Coster-Kronig non-radiative transitions. For the L1, L2, L3 sub-shells, $CK_{L1} = 1$, $CK_{L2} = I + \text{f}_{12} \cdot N_1 / N_2$ and $CK_{L3} = I + (\text{f}_{13} + \text{f}_{23} \cdot \text{f}_{12}) \cdot N_1 / N_2 + N_3 \cdot N_2 / N_3$, where $\text{f}_{ij}$ is the probability for shifting a vacancy from subshell $i$ to $j$ and $N_i$ is the relative number of primary vacancies in subshell $i$ [4]. As in [3], the bremsstrahlung continuum intensity is represented by the following parameterized form

$$I_v = q_e \cdot Z \cdot F \cdot (U - 1)^P \quad (3)$$

where $F$ and $P$ are parameterized functions of $Z$ and $E_0$ and $q_e$ is an overall multiplier used to match predicted intensity to a specific absolute measurement. Additional corrections for absorption and backscatter are applied as in [3]. In [3] the parameterisation was optimized to achieve a best-fit to a large set of measurements of the ratio of peak intensity to total background intensity thus avoiding the need to correct for beam current. In the present work we have made frequent reference measurements
on a pure element standard so that we could independently optimize the models for characteristic emissions and bremsstrahlung background.

A source of inaccuracy in previous published attempts to generate a parameterized spectral form is the assumed detector efficiency as a function of energy. Although a parameterisation may work well for one particular detector, if the efficiency is not correct the analytical formulae may not work so well on a different detector. In the current study, rather than rely on an estimate based on an assumed structure for the detector and window, an efficiency characteristic was measured using the method described in [5] for a reference X-Max 80 SDD detector. Using this efficiency-calibrated detector, 124 spectra were acquired from a large set of reference material standards at both 5 kV and 20 kV covering elements $Z = 4 - 92$.

Published tables (e.g., Johnson and White [6]) only provide “nominal” relative line intensities because these depend on specimen and excitation method. For previous work to improve accuracy for peak shapes at low kV [7], 603 line intensities were optimized using experimental data and these results were incorporated in the current work to improve simulation accuracy. To deal with differential absorption of individual lines, 56 empirical mass attenuation coefficients were also determined by fitting to spectra obtained at different kV. For 233 element emission series (K, L or M), a computed background was fitted, interpolated and subtracted to obtain total intensity cps for the series. The fluorescence yield for Co-K was fixed at the value deduced from previous measurements at known beam current using a grid-free Be window detector and a machined collimator at measured distance from the specimen. The parameterisation for ionisation cross-section and remaining fluorescence yields were optimized to give the best fit to the ratio of intensity to that for a pure element measured at the same beam current (Si for 5 kV data, Co for 20 kV data). Fluorescence yields were interpolated for elements where no measurement was available. For lines with sufficient intensity, (K for $Z > 3$, L for $Z > 20$, M for $Z > 46$), the mean absolute relative error in the new simulation was 3.4 %.

For absolute intensities, the new simulation was tested against a few experimental data points derived from plots obtained by Procop [8] and table 1 shows that the agreement is within a few percent.

| X-ray peak | kV | New simulation | Procop expt [8] |
|------------|----|----------------|----------------|
| Cu-Kα      | 18 | 6.8 E-05       | 7.1 E-05       |
| Cu-Kα      | 20 | 9.5 E-05       | 9.8 E-05       |
| Ge-Kα      | 20 | 5.0 E-05       | 5.3 E-05       |
| Si-Kα      | 20 | 7.3 E-04       | 7.4 E-04       |

For pure elements, the bremsstrahlung background intensity depends on atomic number, Z. For compounds a common approach is to use the mass fraction average $Z$ instead, but this does not take into account the physics of bremsstrahlung generation. Calculations of the bremsstrahlung per atom using a screened Coulomb potential [9] show that the emission is not quite proportional to $Z^2$. The data from [9] for Al and Au for incident electron energies of 10 keV and 50 keV suggests that the intensity for 5 keV bremsstrahlung varies approximately as $Z^{1.75}$. When an electron passes through a thin layer of material, the bremsstrahlung emission is the sum of contributions weighted according to the number of atoms of each element and the total emission along the whole electron path is found by integrating the product of this sum with $(I/S)$. The stopping power $S_{\text{compd}}$ for a compound is the mass
fraction average of the stopping power for individual elements \(j\) and using Joy and Luo’s form for \(S\) [10], the stopping power is given by

\[
S_{\text{empd}} \propto \sum_j [C_j \cdot Z_j / A_j \ln (1.166 [E/J + k])]
\]

(4)

If, following [10], the values \(k = 0.8, J = 9.76Z + 58.8Z^{0.19}\) for \(Z \geq 7\) and \(J = 11.5Z\) for \(Z < 7\) are used, the term \(\ln (1.166 [E/J + k])\) can be approximated by \(0.66 \cdot E^{0.273} / Z^{0.25}\) \((E\) in keV\) so that the terms involving \(Z_j\) can be separated from those involving \(E\) when forming the path integral. Since the number of atoms of element \(j\) per unit volume is given by \(\rho C_j . N_0 / A_j\), the \(Z\)-dependence of the bremsstrahlung can be expressed by using an effective \(Z\) for a compound given by

\[
Z_{\text{eff}} = \left( \sum_j [C_j \cdot Z_j^{1.75} / A_j] \right) / \left( \sum_j [C_j \cdot Z_j^{0.75} / A_j] \right)
\]

(5)

This expression was tested by measuring the integrated background intensity from 7.4 - 8.2 keV in spectra from pure elements and compounds (BN, Al2O3, CaF2, NaCl, MgO, GaP, FeS2, KBr, InAs, SrF2, HgTe, BaF2, LaB6, CeO2, PbTe) obtained at 20 kV and normalising to the Co-K intensity from the reference standard. At these energies, there is little matrix absorption and the results should fall on a smooth curve that is a function of \(Z_{\text{eff}}\). It is clear from figure 3a that this is not the case when \(Z_{\text{eff}}\) is represented by the concentration-weighted average \(Z\). However, using the new expression (5) for \(Z_{\text{eff}}\) brings the results for compounds into line with those for pure elements. The improvement is most noticeable for compounds involving elements with large difference in \(Z\) (LaB6, BaF2, CeO2).

![Bremsstrahlung vs mean Z](image1)

![Bremsstrahlung vs Z_{eff}](image2)

**Figure 3.** a) Use of conventional mass average \(Z\). b) Eq. (5) used for \(Z_{\text{eff}}\).

All peak-free regions were identified in spectra and the parameterisation optimized, making use of the new expression for \(Z_{\text{eff}}\) to minimize sum of mean absolute relative errors over all spectra and for all peak-free energy regions. Thus, a mean absolute relative error of 6.3 % was achieved in the predicted background intensity for energies from 90 eV up to half the beam energy \(E_0\).

When the optimized new model is used to simulate the same Ni and Au spectra as used for figures 1 and 2, the background shape and line intensities are now close to the experimental spectra as seen in figures 4 and 5.
4. Examples of application

When analysing an unknown, the measured composition given by the analytical results can now be used to simulate a “Theoretical Spectrum” overlay (cyan line) that is accurate enough to show up inconsistencies exceeding 10%. This overlay differs from the conventional “Fitted Spectrum” (magenta line, as in figure 9) that shows the result of least squares fitting of peaks and background to the spectrum. The following examples show how a theoretical spectrum can be useful in avoiding mistakes in routine microanalysis.

Figure 6 shows a colour image derived from spectrum image data and figure 7 shows a single spectrum that has been reconstructed from pixels from a rectangular region that seems to be within what appears to be a homogeneous band of material. However, the theoretical spectrum based on the analysis result is inconsistent with the Ga and In peak heights. This warns that the analysis is unreliable and warrants further investigation. In this case 20 keV scattered electrons can excite X-rays in layers adjacent to the layer in question and some emerging X-rays also travel through different material on the way to the detector (which is on top in this field of view). In the Ga-K X-ray map in figure 8, the blurring due to electron scattering is more apparent. However, when many maps are combined with the sharp secondary electron image, the layers look distinct and imply a small information volume. The theoretical spectrum mismatch is therefore a useful prompt to check out the other data to see if X-rays are confined to the layer.
Figure 6. Series of colour X-ray maps overlaid on a secondary electron image of a sectioned semiconductor sample recorded at 20 kV. The white rectangle shows a region of interest and the spectrum in figure 7 is the result of summing all pixel spectra within this region.

Figure 7. a) Sum spectrum for boxed region in figure 6. b) Same, region near Ga-K peak.

Figure 8. Individual X-ray maps for same field of view as for figure 6.
Figure 9 shows a spectrum of Ni-based superalloy where the conventional fitted spectrum overlay (magenta) is a good match. Including Sr-L improves the fit at 1.8 keV and Zn-K has been chosen in preference to Re-L at 8.6 keV. The analysis total in table 2 is only slightly high, but the theoretical spectrum in figure 10 shows that if Zn were present at 0.92 %, there should be a Zn-L peak at 1 keV. When Zn and Sr are removed and replaced with Re, figure 11 shows much better agreement with the theoretical spectrum and the analytical total in table 3 is also improved.

![Figure 9. Spectrum from Ni-based superalloy (yellow) overlaid with result of spectrum fitting (magenta).](image)

![Figure 10. Theoretical spectrum for table 1 composition overlaid on original spectrum. Note differences near Zn-L, Ta-M.](image)

**Table 2.** Results for figure 10.

| Elmt | Wt%   |
|------|-------|
| Al   | 5.22  |
| Ti   | 0.72  |
| Cr   | 6.31  |
| Co   | 9.63  |
| Ni   | 62.36 |
| Zn   | 0.92  |
| Sr   | 2.93  |
| Mo   | 0.71  |
| Ta   | 4.72  |
| W    | 9.25  |
| **Total** | **102.77** |

At low kV, some lines may not even be excited so that analysis results normalized to 100 % can conceal gross errors. The conventional fitted spectrum (magenta) is a good match in both figures 12 and 13. In figure 12, a 4 kV spectrum of Quartz (SiO₂), the theoretical spectrum is also a good match. However, for figure 13 when the analysis results, Si: 44 % O: 56 %, are used to calculate the theoretical spectrum, the inconsistent peak heights warn of a serious problem so the operator should not assume this is also SiOₓ. The analysis is wrong here because at 4 kV the Ca-K peak from Wollastonite (CaSiO₃) is not excited so Ca is not even detected.
| Elmt | Wt%  |
|------|------|
| Al   | 5.26 |
| Ti   | 0.72 |
| Cr   | 6.30 |
| Co   | 9.62 |
| Ni   | 62.30|
| Mo   | 0.67 |
| Ta   | 4.63 |
| W    | 8.76 |
| Re   | 2.37 |
| Total| 100.63|

**Table 3.** Results for figure 11.

5. Conclusion

To give some confidence in a compositional analysis result, the operator is usually presented with the result of fitting peaks and background to the spectrum but a good fit can often be achieved even when the elements or composition results are wrong. However, with a sufficiently accurate theoretical model, a simulated spectrum corresponding to the measured elemental composition can be overlaid on the measured spectrum and, unlike the curve showing results of fitting, this theoretical spectrum can expose some non-obvious mistakes and help avoid bad conclusions. In this work, we have developed a parameterized theoretical model that is sufficiently accurate to provide useful diagnostics and some expert guidance towards a valid analysis result. A new formula for calculating the effective mean
atomic number for compounds has also been derived that is appropriate and should improve accuracy for techniques that calculate the bremsstrahlung or use a bremsstrahlung measurement for calibration.

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