Benefits from bremsstrahlung distribution evaluation to get unknown information from specimen in SEM and TEM

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Abstract. The energy-dispersive X-ray spectrometer (EDS or EDX) is a commonly used device to characterise the composition of investigated material in scanning and transmission electron microscopes (SEM and TEM). One major benefit compared to wavelength-dispersive X-ray spectrometers (WDS) is that EDS systems collect the entire spectrum simultaneously. Therefore, not only are all emitted characteristic X-ray lines in the spectrum, but also the complete bremsstrahlung distribution is included. It is possible to get information about the specimen even from this radiation, which is usually perceived more as a disturbing background. This is possible by using theoretical model knowledge about bremsstrahlung excitation and absorption in the specimen in comparison to the actual measured spectrum. The core aim of this investigation is to present a method for better bremsstrahlung fitting in unknown geometry cases by variation of the geometry parameters and to utilise this knowledge also for characteristic radiation evaluation. A method is described, which allows the parameterisation of the true X-ray absorption conditions during spectrum acquisition. An ‘effective tilt’ angle parameter is determined by evaluation of the bremsstrahlung shape of the measured SEM spectra. It is useful for bremsstrahlung background approximation, with exact calculations of the absorption edges below the characteristic peaks, required for P/B-ZAF model based quantification methods. It can even be used for ZAF based quantification models as a variable input parameter. The analytical results are then much more reliable for the different absorption effects from irregular specimen surfaces because the unknown absorption dependency is considered. Finally, the method is also applied for evaluation of TEM spectra. In this case, the real physical parameter optimisation is with sample thickness (mass thickness), which is influencing the emitted and measured spectrum due to different absorption with TEM measurements. The effects are in the very low energy part of the spectrum, and are much more visible with most recent windowless TEM detectors. The thickness of the sample can be determined in this way from the measured bremsstrahlung spectrum shape.

1. Introduction
The energy-dispersive X-ray spectrometer (EDS) spectrum depends on both the material elements and the measurement geometry of the excited specimen area. The emission intensity of low energy X-rays is influenced significantly both by self-absorption of the generated X-rays inside the specimen and by the surface topography at the analysed point. For example, self-absorption exceeds 70 % for aluminium X-rays in the high absorption case versus 35 % with low absorption (example almandine, electron excitation energy 15 keV, scanning electron microscope (SEM)). It is well known that
bremsstrahlung X-rays are similarly affected. This is utilised in peak-to-background (P/B) quantitative methods to analyse particles and specimens with undefined surfaces. Nevertheless, a good background approximation is necessary for accurate determination of the P/B values for inputs with the P/B-ZAF approach (ZAF is correction for atomic number \( Z \), absorption \( A \), fluorescence \( F \)). The goal of this investigation was to develop a method for better bremsstrahlung fitting in unknown geometry cases by variation of the geometry parameters. It is possible to determine unknown absorption by evaluating the measured bremsstrahlung background shape. This reduces the result uncertainties for specimens with irregular surfaces. The optimised physical parameter is the ‘effective tilt’, which describes the unknown absorption of the sample at the measured surface point [1]. It parameterizes the unknown geometry with an 'equivalent value' for a hypothetical flat sample of the same composition, which would have similar absorption to the investigated sample surface. The theory of this method has been previously reported in [1]. This study provides verification of the method with real measurements.

The method is also applied to transmission electron microscope (TEM) measurements for the first time. With TEM the absorption influences are primarily due sample thickness. Because the typical sample thicknesses are not much higher than 100 nm it affects only the very low energy region of measured X-rays (< 1 keV). The recent innovations with windowless detectors for TEM [2] have triggered a revision of older bremsstrahlung background models, because much more X-rays are now visible in the low energy part of the spectrum [3]. This provides then also more detailed information of the low energy region bremsstrahlung distribution, which is significantly affected by sample thickness. Therefore, the idea is to also apply the absorption evaluation from bremsstrahlung shape to TEM-spectra, but now with variation of the sample thickness.

The used bremsstrahlung background calculation is briefly described in the next section and is based on an earlier publication [6]. There were improvements of the basis method, published in [8], and the dedicated application for TEM spectra was investigated and published in [3]. However, the described method should also be applicable for other bremsstrahlung calculation models.

2. Method
The calculation of the bremsstrahlung distribution for background approximations follows Kramer’s law [4], using the modification by Lifshin [5], and was substituted by a quick calculation of the absorption terms \( \varepsilon_{E_v} \) and \( A_{E_v} \) [6]:

\[
N_{E_v}^{br} = \varepsilon_{E_v} A_{E_v} \left[ a \frac{E_0 - E_v}{E_v} + b \frac{(E_0 - E_v)^2}{E_v} \right]
\]

(1)

with:

\( N_{E_v}^{br} \) number of bremsstrahlung counts measured in spectrum-channel with related energy \( E_v \)
\( \varepsilon_{E_v} \) detector efficiency with photon energy \( E_v \) (the fraction which is detected)
\( A_{E_v} \) absorption correction with photons of energy \( E_v \) (the fraction which is not absorbed)
\( a, b \) empirical coefficients for spectra fit (if \( b = 0 \), then \( a \) represents absolute adjustment only)
\( E_0 \) primary electron energy.

It is possible to use as many fit-regions as desired to get the best background fit. The coefficients \( a \) and \( b \) are determined on the real acquired spectrum and are constant during the calculation between two fit regions. The coefficient \( b \) is simply zero between the first spectrum channel and the first fit region. The same is between the last fit region and the last spectrum channel. Therefore, there are \( F+1 \) segments with individual application of (1), where \( F \) is the number of the used fit regions. Each segment is always separately approached by using both boundary fit regions (or only one with the first and last section). Finally, \( F-1 \) pairs of \( a \) and \( b \) are determined with (1) plus 2 times \( a \) only. The measured bremsstrahlung counts for mean energy of a background fit region are determined from the
average of the channel contents. If two measurement points are used, it is possible to determine 2 unknown parameters \((a\) and \(b)\). With one measurement point only (first and last section) then \(b\) is required to be set to zero.

The fit regions are automatically selected in peak-free spectrum regions, with minimum distances predefined, based on a top-hat filter peak-search. The used fit-regions are changeable by the operator, based on a visual inspection of the bremsstrahlung fit compared to the measured spectrum.

The energy dependent self-absorption model is different for SEM- and TEM-spectra. For SEM spectra evaluation, it is possible to describe the absorption part of (1) with \(\varepsilon_{E_V} A_{E_V}\) with only a single absorption formula [6]:

\[
\varepsilon_{E_V} A_{E_V} = e^{\left( k_a \cdot d_{Be,E_v}^{equiv} / E_v^{3.162} \right)}
\]

The absorption for all energies is computable as a function of the energy \(E_v\) with the same exponential absorption formula at each energy \((k_a\) is a constant). A virtual Be material thickness \(d_{Be,E_v}^{equiv}\) is used to describe the total material, which is along the absorption path for all absorbing sample and detector window elements. The basic idea is quite simple. All absorption calculations (mass absorption coefficients (MAC)) have the same characteristic in energy dependence. The only serious differences in energy dependence between the elements are the absorption jumps, which are characteristic for each element. That is why the mass absorption coefficient calculation for beryllium is applicable using an equivalent beryllium thickness. The value \(d_{Be,E_v}^{equiv}\) is constant between absorption edges and is incremented at each edge energy \(E_i\) (start beginning from low energies towards the high energy end of the spectrum).

\[
d_{Be,E_v}^{equiv} = \sum_{E < E_v} d_{Be,E_i}^{equiv}
\]

The increment steps must consider all edges, due both to detector entrance window materials \(\varepsilon_{E_v}\), and all elements inside the specimen \(A_{E_i}\). \(E_i\) is the critical excitation energy of the electron shell (jump energy). The value of the needed \(d_{Be,E_i}^{equiv}\) increments depends on edge energy. They are calculated before the bremsstrahlung computation process. In the case of specimen element edges the formula is [6]:

\[
d_{Be,E_i}^{equiv} = k_b \left( \frac{\mu}{\rho} \right)_{E_i}^{diff} L \left( E_0^2 - E_i^2 \right) c_i E_i^{3.162}
\]

where \(L\) is a numerical value which considers geometry (ratio between absorption path and X-ray emission depth), \(E_0\) is the primary electron energy, \(k_b\) is a constant, \(c_i\) is the mass fraction of the element in specimen and \((\mu/\rho)_{diff}\) is the difference between mass absorption coefficient after and before the regarded edge energy \(E_i\) (all values in keV). Described differently, eq. (4) describes the thickness of an additional virtual beryllium layer which would have the same additional absorption effect (additional contribution to all effects) as the shell-excitation jump of the element at energy \(E_i\).

The calculation of the entire bremsstrahlung deviation (the bremsstrahlung spectrum) starts with an initial energy and value of \(d_{Be,0}^{equiv}\). This initial value is the fictive beryllium thickness, which would have same absorption (at the starting energy) with all absorption effects, from the detector efficiency and from all elements in the specimen, considered together, at the relevant excitation conditions.

Following the model derivations in [6], a basic estimation of a mean generation depth of photons in the specimen was made, based on the Thomson-Whiddington law [7]. The self-absorption is then calculated based on the assumption of a mean emission depth of X-rays with specific energies. Later investigations have shown this simplification limits the accuracy of the calculation for low energy bremsstrahlung of high atomic number elements [8]. There was no way to fit the calculated background to measured spectra with one exponential mass absorption function by modification of the
parameters. This means, a depth distribution is required also for a bremsstrahlung calculation to consider the X-rays that come from different sample depths, which is mathematically a superposition (addition) of several exponential absorption functions.

Figure 1 shows the bremsstrahlung model after modification with a depth distribution consideration. The background fit is improved both in the low energy region and after the absorption edges. The model introduction considering N-shell edges was the final improvement. This is not usual in common published mass absorption coefficient calculation formulae.

![Figure 1](image)

**Figure 1.** Comparison between measured pure element spectrum of Thorium ($E_0 = 20$ keV) and bremsstrahlung background calculation (one single fit region only at 5 keV). The low energy absorption is overestimated if the depth distribution is not accounted for. The model is improved with consideration of a depth distribution of X-rays for bremsstrahlung emission and with including N-jumps into the model (filled line) [8].

For **TEM spectra**, a different X-ray excitation and absorption model is required. Because the TEM specimens are very thin, the absorption calculation $A_{E_i}$ depends primarily on sample thickness and density, and follows a simple X-ray absorption law using a linear approach based on an equal generation of X-rays at all depths. If the same background calculation basic model is used, equation (4) is replaced by (5) for TEM spectra evaluation:

$$d_{{E_i}^{equiv}} = \frac{\rho t_{sample} \left( \frac{\mu}{\rho} \right)_{E_i}^{diff}}{\rho_{Be} \left( \frac{\mu}{\rho} \right)_{Be}^{E_i}} L c_i$$

$$d_{{E_i}^{equiv}} = t_{sample} \frac{\rho_{sample}}{\rho_{Be}} k_a \left( \frac{\mu}{\rho} \right)_{E_i}^{diff} L c_i E_i^{3.162}$$

(5)

where $t$ is the sample thickness and $\rho_{sample}$ the density of sample. $k_a$ is the same constant as in eq. (2).
3. Examples for SEM

Figure 2 compares the absorption effects on almandine spectra simulated for different tilt angles. Different absorptions not only affect the characteristic X-rays, but also the bremsstrahlung background shape. This is also illustrated in figure 3 which shows two different linear intensity scalings to better illustrate the similar absorption effects on both the characteristic lines (a) and on the bremsstrahlung emission (b).

![Figure 2](image_url)

**Figure 2.** Simulation of almandine spectra for a 15 keV primary electron energy at -24° tilt (red bars), 0 tilt (magenta line) and 48° tilt (green line), and the related bremsstrahlung backgrounds (logarithmic y-axis). (Simulation method described in [13]).

It is possible to account for the effect of variation of the tilt-angle by using eqs. (2) and (4). If physical parameter $L$ in eq. (4) is used as an unknown value for the background fitting, then the most affected low energy part of the spectrum can be better adjusted for the non-linear absorption effects than it would be with the two linear parameters $a$ and $b$. Therefore, this is the method of choice to fit the background shape in cases where the specimen surface is not well known, e.g., with unpolished samples.

Although the P/B-ZAF approach is already nearly insensitive for surface geometries [9, 10], application of the physical model based geometry optimisation is required to get reliable measured P/B values, which is always an interpolation and needs as real as possible modelling of the large absorption edges (which depends on specimen composition and excitation). Therefore, iteration is required anyway, which includes the background approximation with perhaps changing weight fraction results until convergence is obtained. With the presented procedure, an optimised approach of
background calculation is also possible with acquired spectra, which are from rough specimen regions and particles with different unknown absorption situations. The calculation is additionally optimised with absorption modelling by fitting the low energy part of background approximation. This is performed by optimising a real physics meaning parameter, the 'effective tilt', which will be optimised additionally to mathematical parameters in equation (1).

The proper 'effective tilt' is searched by variation of absorption with different tilt estimations (setting the azimuth angle to zero) from the most possible negative tilt (high absorption case) towards high positive tilt cases (low absorption). It is a numerical solution by repeated tilt angle variation calculations, searching for the best fitting background in regard of three numerical test criteria within the checked spectrum region between 550 eV (above the oxygen absorption edge at 536 eV) and 4 keV:

- Minimal sum of the deviation squares (least squares) in peak free regions.
- Least squares deviations of all calculated background channels which are above the measured spectrum.

**Figure 3.** Same as with figure 2 but linear y-scale to show better the absorption influences with characteristic lines (a) compared to background shape (b).
• Statistical criteria, the calculated background should be never higher than acquired counts, all channels, plus 3 times the square root of channel content. The best fitting background is found per a decision tree which combines the three criteria. This tilt angle is then used as the found result for the 'effective tilt’. The described procedure provides both the background spectrum shape with all important low energy edges in irregular surface cases, and provides the best fit angle with beneficial use in quantitative model calculations for final concentration determination with characteristic radiation evaluation.

The search for unknown absorption is with an additional free parameter with additional result uncertainties. Therefore, this should be performed only if the specimen surface is not perfectly flat. It is always better to avoid this with well-polished and positioned specimen, but the daily praxis in SEM labs is often not with this ideal case.

4. Results with SEM measurements
First some simulated 'almandine' spectra were evaluated to test the method in regarding reliability. The absorption is known and can be compared with determined values. This allows a good assessment about abilities of the method.

Figure 4 presents the calculated tilts with bremsstrahlung background fit versus known values of the simulation between -30° and +48°. The uncertainty in determination of the tilt angle by bremsstrahlung background fitting (taken as unknown) is high for low absorption cases (high positive tilts), because it is then less sensitive. Fortunately, where the tilt determination has higher uncertainties the influences of those tilt uncertainties to the quantitative results are also less (also low absorption case). But for the much more important high absorption case (low and negative tilts) all determined results are reasonably aligned with the real values. So, this is all in good agreement with the needs. The determination of the ‘effective tilt angle’ itself is not the final goal, but reduction of the entire result uncertainty.

The determined tilt angle for an unknown geometry is even beneficial for a classical net-counts evaluating ZAF correction, which it is usually only possible to apply for polished specimens. But figure 5 demonstrates the possibility of the evaluation of irregular surfaces even with such a classical ZAF correction. Because the low X-ray energy elements are much more absorbed in high absorption cases, the results contain an underestimation if not considered (figure 5a). This provides too low
element concentrations at negative tilts (means high absorption case in a rough surface). The low absorption influenced elements like Iron show the opposite behaviour, due to normalisation effects. The individual quantitative results differ up to 100 % relative (Fe result variation between 20 - 43 %) depending on the absorption situation.

By using the additional knowledge of the already calculated ‘effective tilt angle’ the results are much more stable (see figure 5b). Therefore, even the quantitative results of ZAF-based evaluations depend less on the actual absorption case, if the absorption parameter is used which was almost independently ascertained. The usually small mutual dependence from specimen composition is solved by iteration.

With the second step, the method was tested with measured spectra of a Nb/Ni alloy specimen (figure 6). To make an assessment possible, again a flat surface specimen was used to compare the evaluation results of calculated tilt with a known measurement tilt. If this succeeds, then it is certain also improving the results in real irregular surface cases.

All quantitative evaluations were performed by evaluating the L-line series for Nb and the K-lines for all other elements. Figure 7 presents the determined tilts vs. known. In some cases there are two different result values for each angle, because due to iteration with slightly different quantitative results, the best fit angles can differ slightly between the P/B-ZAF based and ZAF-based standardless analysis. These also contain higher uncertainties in small absorption cases. These calculated values for tilt also vary little with selection of background fit regions.

The results for P/B-ZAF based evaluation [11-13] are presented with figure 8 and the net-count based ZAF results [14] are within figure 9. In both cases the final quantitative result changes in the right-hand parts of the figure are much reduced with the optimised tilt, compared to the left-hand part where all was calculated with the assumption of zero tilt.

Figure 5. ZAF based evaluation [14] of almandine simulated spectra with -30° to +48° specimen tilt (normalised results, oxygen by stoichiometry); a) without considering the different self-absorption in ZAF model; b) with considering the ‘effective tilt’ angle which was determined by bremsstrahlung background fit.
Figure 6. Comparison of spectra from a Nb/Ni alloy measured at three tilt angles: -4°, +10°, and +40°.

Figure 7. Comparison of real tilt angles (y-axis) with results, determined by background optimisation (x-axis) for measured Nb/Ni alloy spectra.

It is apparent that even the P/B method needs background optimisation by varying the absorption. This is demonstrated well with figure 10, where the background calculation performed for zero tilt is compared to calculation using the optimised tilt. The background shape differs most below Si-K and Nb-L X-ray line series. This is what influences the P/B value determination and it does not matter that the final P/B-model correction does not depend much on absorption. The difficulties are already with determination of the measured P/B values.

But as expected, the net-count based results fluctuate more due to changing absorption cases. But it can be shown for the first time even those are possible to improve if irregular surfaces are measured and the proposed method is used to determine the unknown specimen self-absorption. The resultant fluctuation was reduced both for the P/B method (Si 27% → 7%; Nb 15% → 5%) and for ZAF based quantification (Si 33% → 14%; Nb 25% → 8%). Nevertheless, the P/B method remains the better choice for irregular surfaces.
Figure 8. P/B-ZAF based evaluation of the measured alloy spectra with -4° to +40° specimen tilt (normalised results); a) without considering the different self-absorption for background calculation; b) with performing the ‘effective tilt’ angle determination by bremsstrahlung background fit.

Figure 9. Same as with figure 8, but all results are net-count based ZAF quantifications; a) without considering the different self-absorption in ZAF model; b) with considering the ‘effective tilt’ angle which was determined by bremsstrahlung background fit.
Figure 10. Measured alloy spectrum with +40° tilt (automatically determined fit regions for background approximation are visible); a) with using a zero degree tilt for background fit; b) the background fit is performed with the described additional ‘effective tilt angle’ optimisation.

5. Examples for TEM
It is also possible to beneficially apply the same method for TEM-EDS spectra evaluation. The thickness of the TEM sample is almost always unknown at the location where the analysis is performed. The improved ability to evaluate low-energy X-rays with new types of detectors [2] now makes the small absorption effects visible. Following the proven method with SEM-EDS spectra, it is possible to determine the unknown specimen thickness (the mass thickness) automatically from the measured TEM-EDS bremsstrahlung shape, not the absorption by tilt variation (as with SEM, eq. (4)) but by variation of a specimen thickness parameter for TEM samples (eq. (5)).

The effect of different thicknesses on the bremsstrahlung background shape is demonstrated in figure 11. Because the very thin samples thickness affects only the low energy X-ray part of the spectrum, the parameter optimisation is typically performed by fitting spectrum energy range below 2 keV.

6. Results with TEM measurements
TEM measurements with FIB lamella were performed along a chain of points (figure 12) with determination of thickness by automatic fitting of the low energy spectrum part of the bremsstrahlung distribution by variation of the specimen thickness parameter. The expectations were thicknesses between about 40 and 100 nm. The results with automatic thickness determination have met the expectation (figure 13).
Figure 11. MnSi2 TEM spectrum background calculation always with first fit region at 3 keV but with different sample thickness parameter assumptions, from 0 nm until 120 nm (density 3 g/cm³).

Figure 12. TEM image of FIB lamella with a chain of measurement points for EDS spectra.
The accuracy of the thickness determination is expected to be in the range ±15 to 20 nm. However, the goal is not primarily to calculate thickness, but to automatically determine values for better background fitting for improved automated qualitative analysis of TEM-spectra [3] with EXPertID [15] (automatic element identification). Finally, this optimised spectrum evaluation with thickness determination should also be beneficial for reduction of uncertainties with quantitative results, as it is with SEM spectra evaluation. Figure 14 gives an example of spectrum background evaluation for ‘EDS Spot1’ in figure 12.

**Figure 13.** Plot of the calculated thicknesses (with assumed density of 4.23 g/cm³) by evaluation of bremsstrahlung spectra for different measurement spots marked in figure 12.

**Figure 14.** TEM spectrum from ‘EDS Spot1’ in figure 12 evaluation with optimisation of bremsstrahlung spectrum shape by automatic variation and optimisation of TEM sample thickness (with assumed density of 4.23 g/cm³).

### 7. Conclusions

This work demonstrates the advantages, reasonability and the justifications to calculate the bremsstrahlung distribution with evaluation of EDS spectra. The used bremsstrahlung model was outlined for SEM and for the first time also for TEM applications. It was then demonstrated that the bremsstrahlung distribution (shape) is usable to ascertain the real specimen absorption situation during EDS spectrum acquisition, for both SEM and TEM spectra. This is beneficial and applicable for the exact background approximation for non-flat sample surfaces (SEM) and unknown TEM sample thicknesses. It was shown that it is also possible to use as an additional knowledge for ZAF correction.
because the final analytical results become much more reliable. The application for TEM with included automatic sample thickness determination was presented for the first time. The thickness results were also in the expected range and provide extra knowledge. However, the primary goal with TEM sample thickness determination was to optimise and improve the spectrum background fit to make all following spectra evaluation steps more reliable and with less uncertainties.

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