Specimen homogeneity requirements for EDS in high count rate mode

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Abstract. This work describes limits with pile-up correction considering EDS spectra evaluation in the case of processing high count rate spectra from inhomogeneous specimen areas. The pulse processor pile-up rejection has some limitations with detection of X-ray event coincidences. Therefore, remaining pile-up artefacts are always present in measured spectra and it is necessary to consider these artefacts to avoid mistakes in qualitative and quantitative results. Any pile-up calculation is based on probabilities for coincidences of X-rays, some of which cannot be resolved by pile-up rejection due to the constantly limited time resolution. A fundamental assumption with all calculation approaches is the time-related random distribution of emitted X-rays. This rule is violated with spectra from inhomogeneous specimen areas. Examples are shown and opportunities to avoid the fundamental shortcoming are discussed.

1. Introduction
One of the major benefits of ‘silicon drift detectors’ (SDD) in electron microscopes is their ability to process very high count rates during collection. Thus it is possible to collect spectra at each point while scanning the electron beam at high speed. As previously described, ‘Smart PileUp Consideration’ (SPUC) [1] can evaluate spectra collected at rates greater than 200 kcps, considering the pile-up distribution in the spectrum during all qualitative and quantitative evaluation processes. Therefore, the published automated qualitative analysis with EXpertID [2] which also incorporates SPUC can also deal with very high count rate spectra.

Often one adds single pixel spectra from selected specimen areas into one “sum” spectrum for evaluation. However, if the specimens are heterogeneous, the sum-spectrum from areas of different elemental composition is not the same as a spectrum with the same elements from a homogenous specimen. The well-known differences are due to variation in excitation and absorption of X-rays. The combination of high count rates and spectra summed from heterogeneous samples presents a substantial additional challenge for quantitative analysis. SPUC and other pile-up corrections assume the detected X-rays are emitted randomly within a given time interval and therefore follow probability estimations about X-ray detection and processing [1]. But this assumption is not the case for inhomogeneous specimen surfaces with sum-spectrum from area with different element composition.
2. Problem
The basic theory is that the probability of an un-rejected pile-up pulse \( P_{\text{pu}}^{\text{C1+C2}} \) (pile-up event in channel \( C1+C2 \), at sum of both energies) is calculated in the following way:

\[
P_{\text{pu}}^{\text{C1+C2}} = P_{\text{C1}} \times P_{\text{C2}} \times CR \times PPR
\] (1)

where \( P_{\text{C1}} \) is the probability of an event in energy channel \( C1 \) considering all X-ray counts being measured, \( P_{\text{C2}} \) is the same for events in channel \( C2 \), CR is count rate, and \( PPR \) is the average pulse pair resolving time (determined by the fast channel). Therefore, \( CR \times PPR \) describes the probability that another measured X-ray quantum is detected before the fast channel is open to recognize additional events. Following [1] eq. (1) is possible to transform into (2):

\[
N_{\text{pu}}^{\text{C1+C2}} = N_{\text{C1}} \times N_{\text{C2}} \times CR \times PPR / TC
\] (2)

Actually this is a calculation of the contribution of the pile-up distribution to the measured spectra, based on the spectrum itself, where \( N_{\text{C1}} \) and \( N_{\text{C2}} \) are the counts actually measured in channel \( C1 \) and \( C2 \) of the spectrum and \( TC \) is total number of counts in the spectrum. But all these calculations are based on the probabilities of X-ray emission being randomly based. This assumption is not satisfied if the electron beam excitation involves areas of different specimen constituent (composition). Sometimes X-rays from two different elements will never be detected at the same time, because the elements are in one phase but not in the other. Then these sum energy peaks will never be present in the inhomogeneous specimen spectrum. More generally, the probabilities for emission are not constant, but depend on the concentration of the element in different phases. This is not in agreement with the basic approach (eq. 1). Moreover, it is not possible to cover the variable probabilities with a pile-up distribution calculation. This results in spectra evaluation issues, even if SPUC is applied.

3. Example with simulation of \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) spectra
\( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) spectra were simulated [3] with a 50 kcps count rate assumed (figure 1). A simple addition of both spectra includes no Al+Si sum peak in the summed spectrum (figure 2), because both element characteristic lines will never be detected by EDS at same time. But the pile-up approximation based on this sum-spectrum does not fit. The fundamental reason is the calculated pile-up distribution assumes wrongly that the probability for X-ray emission is constant for each type of radiation.

![Figure 1](image1.png)

**Figure 1.** Simulated \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) spectra (50 kcps) displayed together with pile-up (blue).
Therefore, any pile-up correction will fail to correctly evaluate this spectrum (as a model for adding spectra from areas in specimen of different composition). Al+Al, Si+Si and Si+O are underestimated. Moreover, the Al+Si sum is overcorrected with a common pile-up correction or could be displayed, if SPUC [1] is used, as an anomalous feature in reconstruction which is not really present in the spectrum (figure 3).

The pile-up was properly calculated in the low energy region of the spectrum up to about 1.5 keV, because both individual spectra are similar in this energy region. Thus all calculated pile-up fits the sum-spectrum up to the O+O sum peak energy, but not at higher energies where the sum events with Al and Si X-rays are incorrectly considered.
4. Example with real measurements of a Kiruna mineral stone

Another example is with real measured spectra from different phases of a Kiruna stone, see phase map image (figure 4) below. Each phase is distinguished by colour. The sum-spectrum examples were obtained from pure phase pixel spectra summation. The evaluation of these high count rate spectra (~ 150 kcps) uses a proper consideration of the pile-up effects (figure 6).

![Phase map of Kiruna mineral with mean count rate about 150 kcps. Three different phase areas were selected as examples for sum-spectrum of homogeneous phases, marked with number 1, 2 and 3.](image1)

**Figure 4.** Phase map of Kiruna mineral with mean count rate about 150 kcps. Three different phase areas were selected as examples for sum-spectrum of homogeneous phases, marked with number 1, 2 and 3.

![Enlarged image of a specimen area near mark 2 in figure 4. The inhomogeneous area outlined in green encloses the pixels from which the sum-spectrum shown in figure 7.](image2)

**Figure 5.** Enlarged image of a specimen area near mark 2 in figure 4. The inhomogeneous area outlined in green encloses the pixels from which the sum-spectrum shown in figure 7.
Figure 6. Examples of the evaluation of three spectra from mineral phases in Kiruna. The blue line reconstruction includes pile-up consideration. The most severe pile-up regions are labelled +pu+.
There is a different result when collecting all pixel spectra from a sample area which is not a homogeneous, such as that marked in figure 5. The pile-up consideration in the evaluation has uncertainties for element identification due to violations the pile-up calculation pre-assumptions (see spectra evaluation of this sum-spectrum in figure 7).

![Figure 7](image_url)  

**Figure 7.** Evaluation of the Kiruna sum-spectrum from the area of inhomogeneous composition delineated in figure 5 using SPUC to consider the pile-up counts. There are remaining questions, also for element identification, due to violation of pile-up calculation pre-assumptions (X-ray emission not constant).

False positive element identification is one of the results. Also, incorrect consideration of the pile-up will have additional effects for quantification. This is further to the incorrect calculation of all excitation and absorption effects in the ZAF correction. The quantitative results will not only depend on element distribution and area fractions of single phases, but also on the count rate.

Although SPUC is not able to handle the inhomogeneous specimen case, this is much better than other commonly used pile-up corrections (see figure 8), where overcorrection makes the entire spectrum unusable for any further evaluation. This advantage is due to SPUC self adjustment, which finally in most cases produces some underestimation of the correction, rather than overcorrection.

**Conclusions**

EDAX’s Smart Phase Mapping [4] or other methods, based on PCA (principle component analysis) [5], supports the operator by selecting regions of uniform composition to avoid acquiring a sum-spectrum from inhomogeneous area. However, even if the selected area is inhomogeneous, the SPUC [1] still addresses the issue reasonably and generally avoids over-correction, which occur with other pile-up correction solutions and helps to provide the user with the best possible results. But basically, the usual pile-up detector artefacts are not possible to take exactly into account for
Figure 8. Evaluation of the Kiruna sum-spectrum from the area of inhomogeneous composition delineated in figure 5 using common pile-up correction. Overcorrection occurs at several points due to violation of pile-up calculation pre-assumptions (X-ray emission not constant).

qualitative and quantitative analysis with a spectrum from inhomogeneous specimen area. Therefore this should be avoided.

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EDAX’s Smart Phase Mapping [4] or other methods, based on PCA (principle component analysis) [5], supports the operator by selecting regions of uniform composition to avoid acquiring a sum-spectrum from inhomogeneous area. However, even if the selected area is inhomogeneous, the SPUC [1] still addresses the issue reasonably and generally avoids over-correction, which occur with other pile-up correction solutions and helps to provide the user with the best possible results. But basically, the usual pile-up detector artefacts are not possible to take exactly into account for qualitative and quantitative analysis with a spectrum from inhomogeneous specimen area. Therefore this should be avoided.

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