

Achieving Accurate Estimates of Material Composition from Spectrum Images

P. J. Statham

Oxford Instruments NanoAnalysis, High Wycombe, Bucks HP12 3SE, U.K.

Sum peaks and count-rate dependent peak ratios are the result of “pile-up” of unresolved pulse coincidences in the electronics. Electronic methods for detecting and correcting for coincidental arrival of two X-ray photons are fundamentally limited by the uncertainty due to detector noise. If the correction is pushed to minimise sum peaks, pulses may be rejected even if there is only one photon involved and this false correction can be energy dependent. If the correction is conservative, residual pile-up artefacts will remain [1] but if the spectral distribution and count rate for the input data is known, deficiencies in the electronics can be statistically modelled. This is the basis of a software correction for pile-up that uses the spectrum itself as a first estimate of the input spectral distribution [2]. When the beam is scanned over a grid of pixels it is often impractical to apply the software correction at each pixel because of the computational load and the poor correction precision if counts per pixel are low. Normally, the sum spectrum from all pixels is processed to determine what elements are present in the sample and construct element maps but pile-up artefacts give rise to false element identification. Unfortunately, when the field of view contains different materials [Fig.1] software pile-up correction gives a poor result because it is only valid when the input spectrum is constant during the acquisition [Fig.2]. However, by using a clustering technique to aggregate pixels with similar spectral content into groups, spectra can be obtained from each group that are now appropriate for accurate software pile-up correction. To demonstrate this approach, the badly-corrected sum spectrum in Fig.2 was used for automatic element identification (AutoID). Even though there were some false positives and incorrect IDs, X-ray maps were reconstructed and used as input for a new clustering algorithm (“AutoPhaseMap”) that identifies groups of pixels that have a similar pattern of intensities. Spectra from pixels in each group, effectively representing homogeneous material, were summed to form a single aggregate spectrum that was now appropriate for pile-up correction. Fig.3 shows a typical group spectrum where the strong pile-up artefacts have been eliminated by the correction and no longer give rise to false IDs. The, now accurate, lists of elements obtained from all phase groups were used to reconstruct elemental distribution maps showing elemental distribution for elements likely to be in the specimen rather than artefacts of pile-up distortion. If there is a material only present in a small group of pixels, the sum spectrum from the whole field of view dilutes the contribution from those pixels so AutoID can miss some unique elemental peaks from this material. For example, in the original AutoID of the sum spectrum in Fig.4, Cl was not detected. However, after clustering, pile-up correction and AutoID, Cl was now detected in one of the groups as shown in the aggregated spectrum for those pixels in fig.5.

Using summed data from all pixels in a group, rather than attempting to correct each pixel spectrum, improves the precision of pile-up correction. Accurate lifetime correction is required for the summed pixel spectra to be equivalent to a single spectrum obtained from point analysis on the same material and this can be tested by experiment [3]. With correct element designations and relative peak intensities now corrected for pile-up effects, accurate k-ratios are obtained. Matrix “ZAF” corrections can also be applied because each group spectrum is representative of homogeneous material unlike the sum spectrum for the whole field of view. With this segmentation-prior-to-processing approach, a valid compositional analysis can be obtained for each group and combined with the areal fraction of pixels to obtain an accurate summary of elemental abundance and distribution over the sampled field of view.

References

- [1] N.W.M.Ritchie et al., *Microsc. Microanal.* 18 (2012) 892–904
- [2] P.J.Statham, *Microchimica Acta*, 155 (2006) 289-294
- [3] S.R.Burgess et al., *Microsc. Microanal* 13(Suppl 2) (2007) 1432 CD

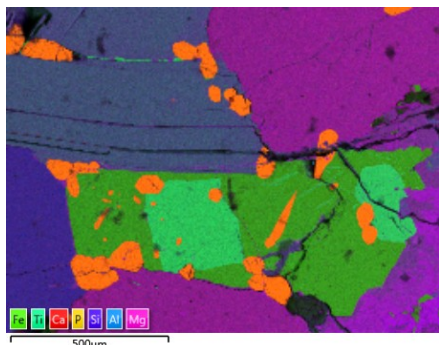


FIG. 1. Colour X-ray map overlay for specimen with multiple phases

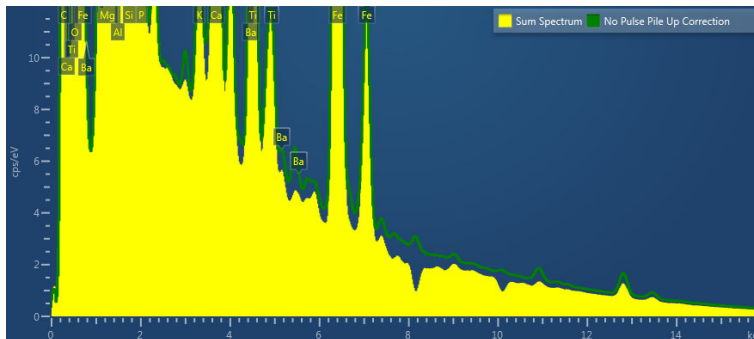


FIG. 2. Sum spectrum for whole field of view. Green: original Yellow bars: corrected for pile-up. Pile-up correction is inaccurate because of variable pixel spectral content.

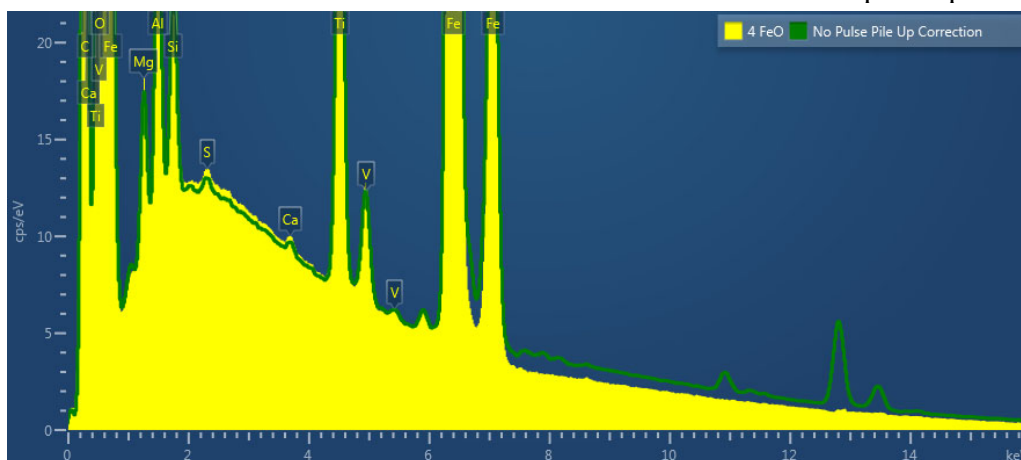


FIG. 3. Spectrum from the Fe-rich phase. Green: original, Yellow bars: corrected for pile-up. Pile-up correction is now accurate because all pixel spectra are from similar material

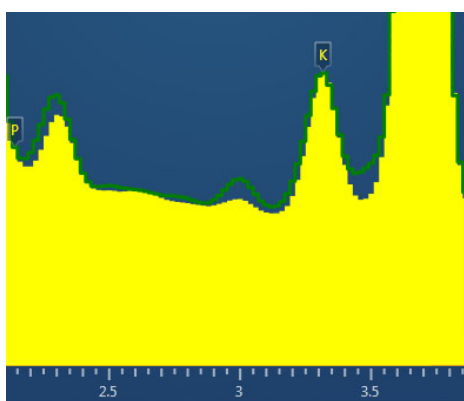


FIG. 4. Sum spectrum from all 49152 pixels. Green: original, Yellow: pile-up corrected

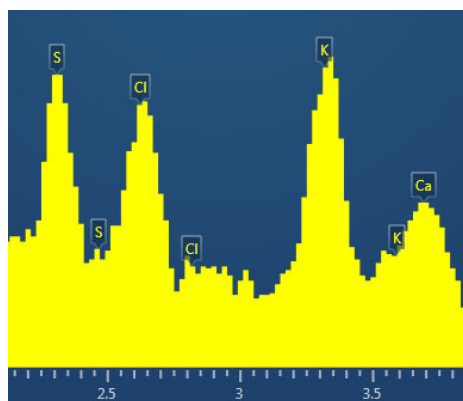


FIG. 5. Spectrum from phase with only 14 pixels shows strong Cl K peak