

Challenges and New Approaches for Quantitative X-Ray Analysis in SEM at Low Beam Voltages

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The excitation volume for X-rays is determined by the incident electron beam energy, critical excitation potential and specimen density. In a steel specimen at 20kV beam voltage, X-rays emerge from a region about 2 μm in diameter whereas at 5kV, the region is about 300nm. Therefore there is a big incentive to reduce kV to improve spatial resolution. However, at 5kV and below, the K lines for most first row transition elements (Sc-Zn) are not excited and lower energy L line emissions have to be used for X-ray analysis. With EDS, deconvolution by peak fitting can only resolve overlaps if peak shapes are accurately known. Even with the improved resolution of WDS, peak overlaps make choice of regions for peak and background measurement critical (Fig.1). Furthermore, in this unusual series, the $L\alpha$ and $L\beta_1$ line energies are within the fine-structure range of the L3 absorption edge and experience unusually high self absorption. As a consequence, the relative intensities of the L series emissions changes markedly with kV as shown for example in Fig. 2(a) for Fe L and Fig. 2(b) for Ni L. For Cu L, the $L\alpha$ absorption is not so severe, but the effect of the changing $L\beta_1$ peak is to shift the apparent position of the main peak in Fig. 2(c). The accuracy in determining k-ratios by EDS is improved by automatically correcting relative line intensities so that the peak shape adjusts for the kV of excitation. The high self-absorption effects mean that the relative line intensities are also affected if there are big changes in concentration for that element. For example, errors due to differential absorption affecting analysis of Cu L in Cu-Au alloys at 20kV have been reported [1]. The absorption effects on L lines are very much reduced when analysing at 5kV but there are additional problems to address. In Ferromagnesian minerals it has been noted that self-absorption of Fe $L\alpha$ and $L\beta_1$ X-rays varies as a function of bonding and empirical correction may be required [2] and in the transition element series the 3d electrons from the M4,5 shells make the production of X-rays sensitive to chemical bonding environment [3]. These observations suggest that for low kV analysis, some prior knowledge of the specimen may be needed to obtain the same accuracies that can be achieved with K lines at higher voltages.

A recent inter-laboratory comparison of epma analysis of alloy steel using 5-6kV beam voltages demonstrated that quantitative analysis using the transition element L lines could give rise to large relative errors [4]. Using WDS, one laboratory discovered a systematic trend with composition in a range of 15 steels where Cr analysis was systematically low by about 14% relative whereas Ni was 22% too high. For EDS there was a wide range of results from the different laboratories with much less consistency and even bigger relative errors. We have also analysed steel specimens. Using default factory settings for WDS analysis at 5kV, the SS63 standard (Cr:18.7% , Ni:9.49%) gave Cr:15.5% and Ni:12.2%, in line with the trend observed above. EDS analysis was slightly better for Cr but still showed the same excess for Ni. Again, chemical effects seem a more likely cause of bias. In practice, with WDS, peak and background regions have to be selected carefully to avoid overlaps, both with other L lines and with commonly-occurring O $K\alpha$ at 523eV (Fig.1). Furthermore, relative overlap can alter in the switchover between a TAP crystal and synthetic multilayer diffractor. Whereas at low kV, cps/nA is low for WDS, high count rates are easy to achieve with a large area SDD detector and if there are only a few elemental overlaps, good statistical precision can be obtained in seconds rather than the minutes required for WDS.

Although analysis at low kV is unlikely to deliver the routine quantitative capability that can be achieved at 20kV, as instrumentation and software improves we obtain more useful elemental information to understand and characterise features at resolution well below 1 μm . While new methods are being developed to address L line analysis, it has been suggested that errors are reduced by using K line analysis at low overvoltage to achieve improved spatial resolution [3]. However, at low overvoltage, excitation is reduced and any surface layer, such as carbon contamination or superficial oxide, has a big influence on intensity because of the effect on slowing down of incident electrons. The trade-off in precision between L and low-overvoltage K line analysis at the same spatial resolution has therefore been investigated using multi-layer spectrum simulation software (“LayerProbe”).

References

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 [3] J.T.Armstrong and K.L.Crispin, *Microsc. Microanal.* 18 (Suppl 2) (2012) 1726
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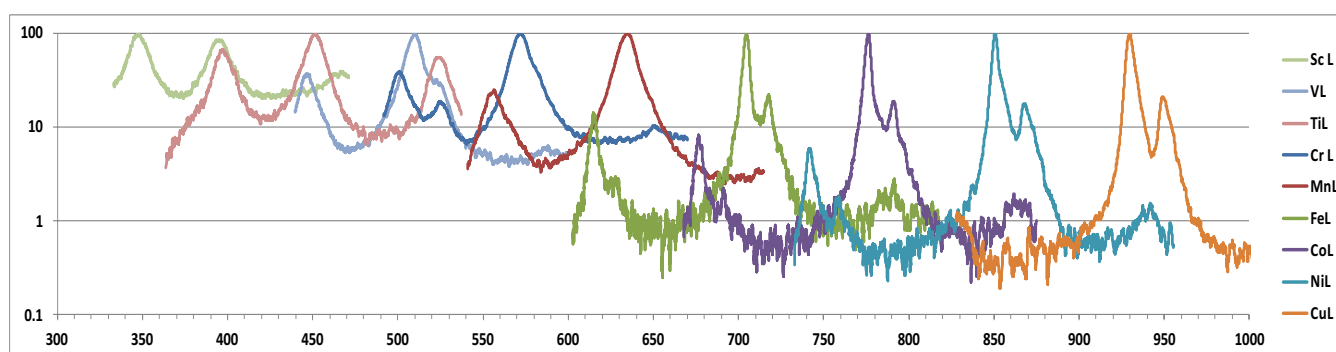


FIG. 1. WDS energy scans for ScL – CuL series showing interferences that influence background

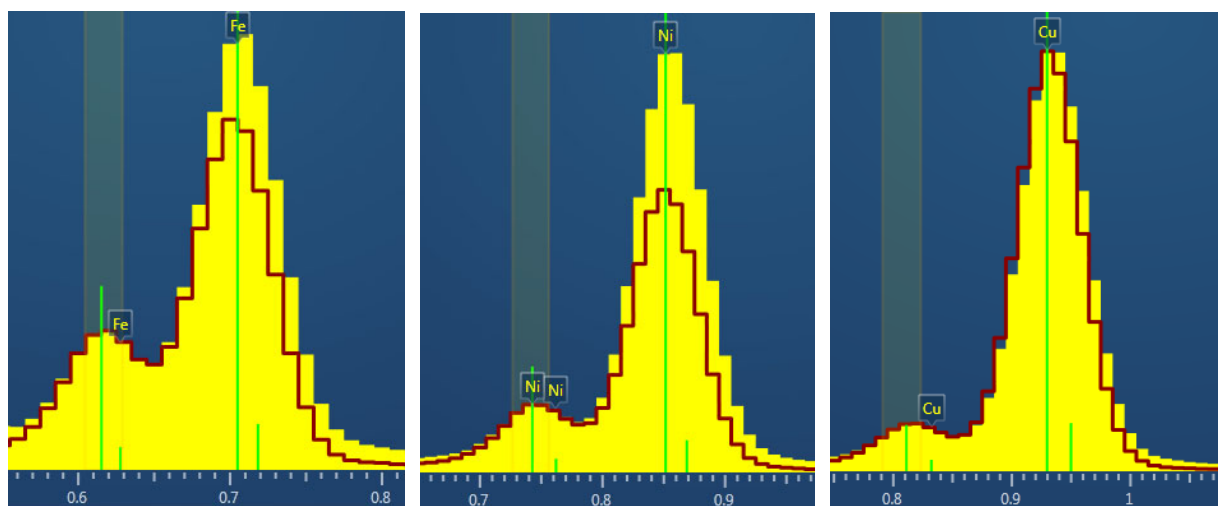


FIG.2. (a) Fe L series (b) Ni L series (c) Cu L series
 Yellow bars=5kV, Red line=20kV EDS spectra recorded from bulk specimens with SDD