Prospects for higher spatial resolution quantitative X-ray analysis using transition element L-lines

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Abstract. Lowering electron beam kV reduces electron scattering and improves spatial resolution of X-ray analysis. However, a previous round robin analysis of steels at 5 - 6 kV using Lα-lines for the first row transition elements gave poor accuracies. Our experiments on SS63 steel using Lα-lines show similar biases in Cr and Ni that cannot be corrected with changes to self-absorption coefficients or carbon coating. The inaccuracy may be caused by different probabilities for emission and anomalous self-absorption for the Lα-line between specimen and pure element standard. Analysis using L/(L3-M1)-lines gives more accurate results for SS63 plausibly because the M1-shell is not so vulnerable to the atomic environment as the unfilled M4,5-shell. However, Lβ-intensities are very weak and WDS analysis may be impractical for some applications. EDS with large area SDD offers orders of magnitude faster analysis and achieves similar results to WDS analysis with Lα-lines but poorer energy resolution precludes the use of Lβ-lines in most situations. EDS analysis of K-lines at low overvoltage is an alternative strategy for improving spatial resolution that could give higher accuracy. The trade-off between low kV versus low overvoltage is explored in terms of sensitivity for element detection for different elements.

1. Introduction
The excitation volume for X-rays is essentially determined by the incident electron beam energy and specimen density. In a steel specimen at 20 kV beam voltage, X-rays emerge from a region about 2 µm in diameter whereas at 5 kV, the region is about 300 nm across so there is a big incentive to reduce beam kV to improve spatial resolution. However, at 5 kV and below, the K-lines for many of the first row transition elements are not excited and the lower energy L-line emissions have to be used for x-ray analysis.

Two years ago, a report on an inter-laboratory comparison of electron microprobe analysis (EPMA) analysis of alloy steel using 5 - 6 kV beam voltages demonstrated that quantitative analysis using the transition element L-lines could give rise to large relative errors [1]. Using wavelength-dispersive X-ray spectrometry (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 analysis with energy-dispersive X-ray spectrometry (EDS) there was a wide range of results from the different laboratories with much less consistency and even bigger relative errors. The problems of using these L-lines have been reported by other authors and we have done our own research to corroborate these findings and consider new approaches to obtaining more reliable quantitative results at high spatial resolution.
2. Analysis using WDS

2.1. Conventional analysis using $L_{\alpha_1}$-lines

We first investigated WDS analysis of steel using pure element standards. We chose a steel, SS63 with high Cr and Ni content (Cr: 18.7 %; Fe: 70.5 %; Ni: 9.49 %) and used 5 kV accelerating voltage, 20 nA beam current and acquisition times of 100 seconds for each major element peak. Carbon coating on the standards was measured to be 12 nm by INCA ThinFilmID (Oxford Instruments NanoAnalysis) and k-ratios were processed by Stratagem (SAMx) to give Cr: 15.4 %; Fe: 70.3 % and Ni: 13.0 %. This bad result was in line with the trend observed in [1] with Cr too low and Ni too high and we looked for possible reasons. Figure 1 demonstrates the number of overlaps that can occur with L-line analysis and we took care to choose background measurement points free from peak interference.

Figure 1. WDS scans (log scale) of transition element L-line emissions. Note change of resolution between scans for Mn-L and Fe-L where crystal changes from a synthetic multilayer, LSM60, to TAP.

For the elements Ni and Cr, WDS scans recorded at 5, 10 and 20 kV (figures 2 and 3) show some of the anomalous absorption effects that occur with these L-line series. Both $L_{\alpha_1}$(M3-M5) and $L_{\beta_1}$(L2-M4) are very close in energy to the L3-edge and experience strong self-absorption so that the intensity profile varies as a function of accelerating voltage. Both excitation and absorption may be influenced by the atomic environment which may be different in specimen and standard. Table 1 shows typical values for the mass absorption coefficient, MAC, that are for the most part close to those tabulated by Heinrich [8]. The first three columns are used for conventional analysis using
La$_1$-lines. The self-absorption coefficients Cr-La / Cr, Fe-La / Fe and Ni-La / Ni are those subject to most discussion in the literature and we have replaced the Heinrich values with our own empirical values. For pure elements, empirical MACs can be derived from La$_1$ measurements at different kV [2] but for elements Sc-Cr, WDS cannot resolve the La/L$_\beta_1$ overlap and a single MAC is insufficient to represent the composite effects of two lines where one line is much more strongly absorbed.

![Figure 3. WDS scans of pure Cr metal standard. Note the appearance of oxygen peak from superficial oxide at low kV.](image)

Table 1. MAC (cm$^2$/gm) for emitters and absorbers involved in the steel analysis.

| Emitter | Cr La$_1$ energy keV | Cr La$_1$ MAC | Fe La$_1$ energy keV | Fe La$_1$ MAC | Ni La$_1$ energy keV | Ni La$_1$ MAC | Cr L$\ell$ energy keV | Cr L$\ell$ MAC | Fe L$\ell$ energy keV | Fe L$\ell$ MAC | Ni L$\ell$ energy keV | Ni L$\ell$ MAC |
|---------|----------------------|----------------|----------------------|----------------|----------------------|----------------|----------------------|----------------|----------------------|----------------|----------------------|----------------|
| Cr MAC  | 0.573                | 3100           | 0.705                | 17122          | 0.851                | 11139          | 0.500                | 3479           | 0.615                | 19904          | 0.743                | 15208          |
| Fe MAC  | 0.573                | 3317           | 0.705                | 3200           | 0.851                | 13726          | 0.500                | 4394           | 0.615                | 2865           | 0.743                | 15979          |
| Ni MAC  | 0.573                | 4221           | 0.705                | 2713           | 0.851                | 3500           | 0.500                | 5623           | 0.615                | 3632           | 0.743                | 2424           |

It is possible that this uncertainty in MAC values and the potential for carbon contamination build up during analysis could be responsible for the systematic bias in results. Therefore, the effects on results of changing the La$_1$ MACs and also the estimated thickness of carbon on the specimen are shown in Table 2. Column C uses empirical values from ref. [2] and Column H from ref. [1]. Column G is an attempt to use the values from various sources to give the best analysis. Although there is no combination here that overcomes the huge under-estimate in wt% of Cr and over-estimate of Ni, it should be noted that while the self-absorption MACs have been studied in some detail, there are still very high and questionable values for absorption of Fe- and Ni-lines in Cr and Fe.

The physics of L X-ray emission from nickel is complicated and an anomalous La absorption resonance has been demonstrated and shown to be less prevalent in some Ni compounds [3]. Such anomalous absorption occurs when the incident energy is close to that required to move an electron from one shell to another unfilled shell and this produces line type absorption in addition to the normal absorption step across the L$3$-edge. Thus, the composite absorption effect on Ni-La depends on what fraction of emission is subject to the much higher resonance absorption. The overall intensity measured for Ni-La is therefore going to be affected by spectrometer resolution and whether the
Table 2. Weight% results for SS63 analysis obtained in different tests where the same set of Lα₁ k-ratios was corrected using Stratagem with different MACs and carbon thickness estimates.

| Test | A  | B  | C  | D  | E  | F  | G  | H  |
|------|----|----|----|----|----|----|----|----|
| Carbon nm | 12 | 12 | 12 | 15 | 15 | 15 | 15 | 15 |
| Cr Lα₁ / Cr | 3100 | 3850 | 3850 | 3850 | 3850 | 3850 | 3100 | 3612 |
| Fe Lα₁ / Fe | 3200 | 3200 | 3350 | 3350 | 3350 | 3350 | 3200 | 3559 |
| Ni Lα₁ / Ni | 3500 | 3500 | 3500 | 3500 | 3500 | 3500 | 4227 | 4227 |
| Fe Lα₁ / Cr | 17121 | 17121 | 17121 | 17121 | 15409 | 17121 | 18833 | 17121 |
| Ni Lα₁ / Cr | 11123 | 11123 | 11123 | 11123 | 11123 | 11123 | 11123 | 11123 |
| Ni Lα₁ / Fe | 13707 | 13707 | 13707 | 13707 | 13707 | 13707 | 13707 | 13707 |
| Cr (18.7)% | 15.8 | 15.4 | 15.4 | 15.6 | 15.6 | 15.5 | 15.5 | 15.7 |
| Fe (70.5)% | 70.0 | 70.3 | 70.3 | 70.0 | 70.8 | 71.6 | 70.4 |
| Ni (9.5)% | 12.8 | 13.0 | 13.0 | 12.9 | 13.0 | 12.4 | 11.6 | 12.5 |

Lα₁ peak intensity or the total peak area is measured. Furthermore, since the overall absorption factor is a non-linear function of the MACs, the determination of an empirical MAC based on measurements at different kV will also be affected by the range of kVs used. These effects may account to some extent for the different empirical MAC values for pure Ni reported in references [1], [2] and [3]. In the calculations used for Table 2, the same MAC is assumed for both the pure element standard and the SS63 specimen. In the case of Ni it has been shown that the effective self-absorption MAC for Ni-Lα₁ in NiAl is much less than for pure Ni [3]. However, using such a different Ni MAC for the specimen has virtually no effect in the current case because Ni absorption in SS63 is dominated by Fe. For Ni at least, it is difficult to see how the analysis can be improved by any further adjustment of MACs. It has been suggested that Ni-Lα₁ intensity in compounds is enhanced due to increased occupancy of the 3d band [3] and the effects of bonding on the partially filled M4,5-shells may be apparent in any of the first row transition elements [4]. Such effects add to the potential problems that may occur with Lα₁-line analysis of transition elements.

2.2. Analysis using Lℓ-lines

A vacancy in the L3-shell can be produced by direct ionisation. At 5 kV there are no Auger transitions that could give rise to additional L3-vacancies following a K-shell ionisation but internal Coster-Kronig transitions from L1- and L2-shells are possible. When there is a vacancy in the L3-shell there are a number of possible transitions that could produce an X-ray. As suggested above, the probability of a transition that gives rise to Lα₁(L3-M5) or Lα₂(L3-M4) may be affected by the different occupancy of the M4,5-shells. However, the more tightly bound M1-shell is fully occupied so the probability of emission of an Lℓ(L3-M1) transition should be much less affected by the local atomic environment. Furthermore, the Lℓ-line is well away from the L3-absorption edge and does not experience any anomalous resonance absorption effects. Therefore, we tried using the Lℓ/(L3-M1)-lines to see if that would improve the accuracy in our SS63 example. As is clear from figures 2 and 3, the Lℓ-line is at energy well below the range of Lα and Lβ spectrometer positions normally made available for analysis with WDS. We therefore had to set new peak and background positions, taking particular note of potential overlaps suggested by figure 1. Furthermore, the Lℓ-intensity can be much less than that for Lα₁ so we needed to extend analysis times to a few hundred seconds for some lines. Since the depth distribution of Lℓ and Lα₁ should be the same because they are instigated by ionisation of the same L3-shell, MACs from Table 1 for Lℓ were substituted in Stratagam for the normal Lα₁-values to provide for absorption of the Lℓ-lines. The new results for analysis with Lℓ-lines are shown in figure 4 and compared with a typical result using Lα₁-lines. The
vertical extent of the symbol has been scaled to correspond to twice the calculated statistical standard deviation and the results of the four repeated analyses with L_\ell-lines appear to be consistent within this expected experimental error. With L_\ell-lines, the Cr results are 11 % higher and the Ni results 27 % lower than the results using L_{\alpha_1}-lines. Although the Cr values are still 9 % below the expected value, the Ni results are now very close to the expected concentrations.

![Figure 4. Diamonds show results using L_\ell-lines. Squares use L_{\alpha_1} and conditions as for Test C in Table 2. Horizontal lines show expected concentrations for SS63 standard. Symbol height = 2\sigma statistics.](image)

Whereas this is a promising result and suggests that analysis with L_\ell-lines may be a route to improved quantitative analysis at low kV, there are some caveats. In our experiments we used 20 nA beam current and still required long acquisition times that made each analysis take over 20 minutes. Achieving high currents at low kV inevitably involves using large probe diameter and in order to exploit the advantages of low kV in reducing the excitation volume, it is essential that the probe diameter does not become the dominant factor in limiting spatial resolution.

3. EDS analysis at low kV compared with low overvoltage

We repeated the SS63 analysis at 5 kV using EDS X-max^5 150 SDD, INCA software) using the same pure element standards. To correct for background and overlaps, filtering and least squares fitting were used to fit the spectrum to L-peak shapes matching those of pure elements at 5 kV. The total L-series intensity was assumed to correspond to L_{\alpha_1}. Since the L_{\alpha_1}-peak still dominates the L-series, it is perhaps not surprising that the EDS results (Cr: 16.8 %; Ni: 12.0 %) showed similar biases to the WDS analysis using L_{\alpha_1}. However, it was immediately apparent that count rates were at least two orders of magnitude higher with the large area SDD detector and analyses could be accomplished in seconds rather than the 10’s of minutes required for WDS.

The problems of uncertainty in MACs and difficult peak overlaps can be overcome by using higher beam kV and a low overvoltage to reduce the interaction volume [4, 5]. Figure 5 shows how the range of X-ray generation [6] changes with beam kV for a material with the same density as silicon. The nanometre range will be less for denser material like steel because the range is inversely proportional to the density. It can be seen that similar range and spatial resolution can be achieved with Cu K-radiation using 11 kV or with Cu L-radiation using 5 kV. Spectra under these two conditions for the same beam current are compared in figure 6. It is immediately apparent that the Cu K-peak using 11 kV is considerably smaller than the Cu L-peak obtained using 5 kV with the same current. However, when these spectra are scaled, it is also apparent that the background is higher in the 5 kV case so it is not immediately obvious which condition is best for analysis. Therefore, a few examples
have been studied by spectrum simulation to see what EDS spectrum analysis would achieve in terms of peak area and statistics. The ratio of peak counts/statistical sigma ultimately determines the detection limit and is, therefore, one measure of sensitivity. The results are plotted in figure 7 and show two points for each elemental line corresponding to conditions that give 200 nm and 400 nm range in figure 5. As expected, sensitivity is improved at poorer spatial resolution. For Cu, it appears that greater sensitivity is achieved with low kV and L-line analysis, whereas for Cr, K-line and low overvoltage is more sensitive. Whereas this gives an idea of the trade-offs for sensitivity, for quantitative analysis the presence of any superficial layers has a greater effect on the low-overvoltage measurements.

Figure 5. Range of X-ray generation for different element lines in a matrix with density 2.33 gm/cm^3. Note: range scales inversely with density of matrix.

Figure 6. X-ray spectrum from Cu at 5 kV and 11 kV using same beam current and acquisition time.
Figure 7. Results from spectrum simulation for SDD (124 eV fwhm at Mn-Kα) with polymer window, take-off-angle 35°, for 1 % of element in a silicon matrix using same beam current and time. Peak counts are obtained by filter-fit method and statistical sigma (standard deviation) is calculated as in ref. [7]. Vertical axis units are arbitrary and scale with time 0.5. In each case, two points are calculated corresponding to kV values that gives rise to 200 and 400 nm range according to figure 5.

4. Conclusions
The inaccuracy in analysis using La-lines of transition elements for steel appears likely to be due different probabilities for emission and anomalous self-absorption for the La-line between specimen and pure element standard. This is a serious barrier to accurate low kV analysis because it means that each new type of material will require a set of standards showing similar chemical effects if relative errors much less than 20 % are required. Analysis using the Lf-line rather than La appears to be a promising strategy to improve accuracy because emission is less affected by the atomic environment. However, Lf-intensities are very weak and WDS analysis may be impractically slow for some applications. EDS with large area SDD offers orders of magnitude faster analysis and achieves similar accuracy to WDS analysis with La-lines but energy resolution precludes the use of individual Lf-lines in most situations. For selected elements, EDS analysis of K-lines at low overvoltage is an alternative strategy for improving spatial resolution that could give higher accuracy. However, peak intensity and peak-to-background ratio changes with element so the best approach depends on whether qualitative sensitivity or quantitative accuracy is more important.

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