Improving the quantification at high spatial resolution using a field emission electron microprobe

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Abstract. The capabilities of field emitter electron microprobes to perform quantitative measurements at high spatial resolution are discussed. Using Fe-Cr-C particles in a bearing steel (SAE 52100) as example, a generic procedure was established to find the optimal analytical conditions (beam energy, beam current and acquisition time). The influence of these parameters on the accuracy, precision and spatial resolution was evaluated using experimental measurements and Monte Carlo simulations. A quantification procedure was developed for soft X-ray lines, taking into account the overlap of high order X-ray lines and background anomalies. The accuracy of K\(\alpha\) and L\(\alpha\)-lines was verified using reference materials. A relationship between experimental and simulated X-ray intensities was determined to evaluate the measurement precision. The spatial resolution of each X-ray line was calculated from the simulated lateral and depth X-ray intensity distribution using simulations integrating experimentally measured beam diameters. The optimal analytical conditions for the studied sample were found to be 5 keV, 10 nA and 10 s acquisition time. Further specialized techniques to improve the spatial resolution are presented: focused ion beam preparation of thin lamella and wedge, and Monte Carlo based reconstruction. The feasibility of the latter to quantify features smaller than the X-ray emission volume was demonstrated.

1. Introduction

By combining the functionality of conventional thermionic gun microprobes with a Schottky field emission gun, field emission microprobes (FE-EPMA) offer new possibilities to characterize smaller features. The higher current density and brightness of this emitter result in a smaller electron probe and extend the analysis range to lower accelerating voltages.

Since their introduction, one decade ago, FE-EPMAs have been used in a wide range of applications from chemical characterisation of micrometeoroids captured on the international space station [1] to partitioning analysis of alloying elements in a cobalt-base superalloy [2]. Several authors combined the improved spatial resolution of FE-EPMA with the spectral resolution of wavelength-dispersive X-ray spectrometers to qualitatively investigate the elemental distribution, including light and trace elements, in various samples by beam and stage mappings [3-8]. Ha et al. [9] performed quantitative analyses on different micrometre-size single phase regions of Mo-Si-B alloys under conventional conditions (15 keV and 20 nA). Ohnuma et al. [10] measured the chemical composition of iron silicate phases using a lower beam energy (6 keV) and the Fe-L\(\alpha\). They estimated the spatial resolution to be below 500 nm. Guo et al. [11] quantified the carbon concentration inside 0.5 µm to 1 µm Co-rich phases of WC-Co alloys. A beam energy of 8 keV and a beam current of...
15 nA were chosen as a compromise between spatial resolution and X-ray yield. The spatial resolution, under these conditions, was evaluated to be 400 nm using the electron trajectories of Monte Carlo simulations and the size of the contamination ring produced by a measurement. Two conclusions can be drawn from this literature review: (1) the use of FE-EPMA to quantitatively analyse sub-micrometre feature is limited, and (2) challenges of low beam energy analyses, as described by Merlet and Llovet [12, 13], are often neglected.

The aim of this work is to establish a generic procedure to optimize the analytical conditions in order to improve the spatial resolution, and to evaluate specialized techniques to further improve the spatial resolution. The quantification of Fe-Cr-C spherical particles inside a bearing steel (SAE 52100) is used as a case study throughout the paper. Section 2 details the sample preparation, instrument and software used. The optimisation strategy is described in section 3 where the influence of the beam energy, beam current and acquisition time on the accuracy, precision and spatial resolution is studied using experimental measurements and Monte Carlo simulations. Finally, section 4 discusses how smaller features can be quantified using Monte Carlo based reconstruction approach or advanced preparation techniques such as milling a wedge or cutting a thin lamella.

2. Materials and methods

The bearing steel sample (SAE 52100) and the standards (Cr, Fe, Cr$_{23}$C$_6$, Fe$_3$C) were prepared using mechanical polishing up to 0.05 µm colloidal silica, cleaned with ethanol in an ultrasonic bath and dried under hot air. The samples were left inside the specimen chamber for at least one day before starting the measurements. All measurements were performed on a field emission electron microprobe, JEOL JXA-8530F (JEOL Ltd., Tokyo, Japan). The Cr and Fe K$_\alpha$-lines were measured using LiF crystals on Xe counters, whereas a LDE1 crystal in combination with a P-10 counter was used for their L$_\alpha$-lines. C-K$_\alpha$ was measured using a LDE2 crystal with a P-10 counter. An oxygen jet was used throughout all measurements to reduce the influence of contamination. The efficiency of this anti-contamination device, especially in the case of carbon quantification, has been presented by Bastin and Heijligers [14]. The quantification of the measurements were performed using in-house scripts and the electron probe quantitation library available as part of the NIST DTSA-II software (version Gemini) [15]. Unless otherwise specified, the XPP simplified model [16] and the NIST-Chantler [17] database were respectively selected as the default matrix correction algorithm and mass absorption coefficient (MAC) database. All Monte Carlo simulations were performed using the NISTMonte programme [18], also included inside the NIST DTSA-II software. New distributions were added to the original code to obtain the results in this work.

3. Optimal analytical conditions

3.1. Accuracy

Depending on the selected beam energy, different X-ray lines must be used for the quantification. Many authors reported large inaccuracies when low energy X-ray lines (< 1 keV) are used (e.g., L$_\alpha$-lines for the first row of the transition metals). Inaccurate mass absorption coefficients [19, 20], chemical bonding effects [21], oxidation/contamination effects [22], peak shape alterations [14] and interference problems [23, 24] were identified as potential explanations for the large inaccuracies.

In order to assess the reliability of the quantification of the studied sample, two reference samples with homogeneous composition, Cr$_{23}$C$_6$ and Fe$_3$C, were quantified using K$_\alpha$- and L$_\alpha$-lines of Cr and Fe. To minimize the influence of the aforementioned problems, the quantification was performed using integral intensities (peak areas) obtained from spectrum acquisitions of each X-ray line, detailed background modelling and deconvolution of interfering peaks. Spectra were acquired for each X-ray line with a dwell time of 1.125 s. The step size of each spectrometer was adjusted to keep the total measurement time under 20 min. Pure standards were used for all elements, except for carbon where Fe$_3$C was used to quantify Cr$_{23}$C$_6$ and vice versa.
The background of each spectrum was fitted using a single exponential function, except for C-Kα spectra where the absorption edge below the peak significantly changes the shape of the background. Two exponential functions were then fitted for the background values above and below the absorption edge, and juxtaposed with an error function to create a continuous background function. Figure 1 shows the final background modelling under the C-Kα-peak acquired on Fe3C. This method was privileged over the one described by Rémond et al. [24] since it does not rely on the knowledge of mass absorption coefficients and can correct for the self-absorption of C-Kα X-rays inside the crystal and detector window.

Figure 1. Background modelling below the C-Kα peak acquired on Fe3C (15 keV, 100 nA, 1.125 s dwell time, 3.5 pm step size, LDE2 crystal, P-10 counter).

Overlapping lines were decomposed using a least-square fitting procedure assuming a pseudo-Voigt function for each peak [25]. The pseudo-Voigt function was assumed to be 57 % Gaussian and 43 % Lorentzian as described by Fournier et al. [25]. The optimisation package from the open-source library SciPy [26] was used for the least-square fitting. The initial estimate was manually determined from the peak height, width and position read from each spectrum. For the Cr and Cr23C6 spectra, the Cr-Lα peak was decomposed from the overlapping Lβ- and Ll-lines, whereas for the Fe and Fe3C spectra, the Fe-Lα was decomposed from the Ll-line. In the case of C-Kα, the overlapping correction of the second order X-ray lines of Cr (Lα and Ll) and Fe (Ll) was more difficult due to the poor resolution of the LDE2 crystal. To simplify the fitting procedure, pseudo-Voigt functions of these peaks were first calculated from the pure standard spectra. These functions were then weighted by the nominal Cr and Fe composition of Cr23C6 and Fe3C and subtracted from the spectrum acquired from this sample. Figure 2 shows the fitted Cr-Lα (2) and Ll (2) on pure chromium spectrum and figure 3 the raw and corrected Cr23C6 spectrum. No fitting was used for the Kα-lines. The intensity was directly extracted from the sum of the counts under the peak after background removal.

Table 1 gives the quantification results in weight fraction for the Cr23C6 and Fe3C reference samples measured at 3 and 15 keV. For both reference samples, accurate quantification was obtained using the Kα-lines at 15 keV and the Lα-lines at 3 keV. In the case of Cr, the large errors on the quantification with the Lα-lines at 15 keV are related to the mass absorption coefficients. The accuracy of the MAC is critical due to the large absorption correction at high overvoltage ratio. If the MAC database from Pouchou and Pichoir [16] is used instead of the one from NIST-Chantler, the Cr and C concentration are closer to the nominal values (95.54 % and 5.9 % respectively, total of 101.44 %). Incorrect MAC values could potentially explain the errors for the Fe-Lα, but no improvement was observed by selecting a different MAC database.
Figure 2. Carbon Kα background-corrected spectrum acquired on Cr showing the pseudo-Voigt fitting of the Cr-Lα (2) and -Ll (2) (15 keV, 100 nA, 1.125 s dwell time, 3.5 pm step size, LDE2 crystal, P-10 counter).

Figure 3. Carbon Kα background-corrected spectrum acquired on Cr23C6 before (raw) and after the correction for the overlap of the Cr-Lα (2) and -Ll (2) (15 keV, 100 nA, 1.125 s dwell time, 3.5 pm step size, LDE2 crystal, P-10 counter).

Table 1. Quantification of Cr23C6 and Fe3C reference samples (all values in weight percent).

| Line | Cr23C6 | Fe3C |
|------|--------|------|
|      | C      | Total | C    | Total |
| Nominal | —     | 94.32 | 5.68 | 100.00 | 93.31 | 6.69 | 100.00 |
| 15 keV  | Kα   | 94.30 | 6.00 | 100.29 | 93.13 | 6.41 | 99.54 |
| 3 keV   | Lα   | 95.12 | 6.62 | 101.74 | 93.40 | 6.18 | 99.58 |
| 15 keV  | Lα   | 104.89 | 6.76 | 111.64 | 119.12 | 8.55 | 127.66 |

Databases from Henke [27] and Heinrich [28] were tested as well. Other matrix correction models, PAP [16] and Proza96 [29], did not improve the results. Problems with the mass absorption coefficients of the Fe-Lα were also reported by Llovet et al. [19] and Gopon et al. [20].

Based on these results, both Kα- and Lα-lines of Cr and Fe could be used to quantify the Fe-Cr-C particles, if the overvoltage on the Lα-lines is small. This example, however, illustrates the importance of evaluating the quantification accuracy of low energy lines with appropriate standards before measurements on unknown samples.
3.2. Precision

The precision of a quantitative measurement is determined by the combination of systematic and random uncertainties [30]. Systematic uncertainties can typically be minimized by rigorous calibration of the spectrometers, good sample preparation, and use of accurate standards. On the other hand, random uncertainties are unavoidable. Following Poisson statistics, they are equal to the square root of the number of detected X-rays. For an integral acquisition, the on and off peak intensities are obtained from the same spectrum. The uncertainty ($\sigma$) is thus equal to the square root of the total intensity ($I$) under a peak (sum of net and background ($I_B$) intensities). As the intensity is proportional to the electron dose, increasing the beam current and/or the acquisition time reduces the relative uncertainty ($\varepsilon$) of the measurement. The beam energy has also an influence on the intensities as the ionisation distribution function, $\phi(\rho z)$, is energy dependent. The relative efficiency can be calculated using eq. 1 for an integral acquisition. The total intensity ($I$) is equal to the area under the peak over a defined interval, whereas the background intensity ($I_B$) is the area under the fitted background over the same interval.

$$
\varepsilon = \frac{n\sigma}{I - I_B} = \frac{n\sqrt{I}}{I - I_B}
$$

where $n$ is the confidence index.

To evaluate the precision for the studied sample under different analytical conditions, a simple model was developed based on intensities calculated by Monte Carlo simulations and the assumption that the simulated intensities are directly proportional to the experimental ones. The proportionality is only valid for a specific X-ray line as the detector efficiency changes based on the selected crystal and type of counting detector as well as the solid angle, based on the crystal position. The premise also disregards possible inaccuracy in fundamental parameters such as the ionisation cross-section and fluorescence yield [31]. Despite these restrictions, the model allows to quickly estimate the experimental precision from simulated intensities without the need of experimental measurements at each analytical condition.

To calculate the proportionality constant for each X-ray line, the integral intensities measured for the accuracy assessment were compared to the characteristic X-ray and background intensities obtained from the simulations. The background intensities were obtained by summing the X-ray counts over a certain energy range. For the experimental values, the fitted background function of each experimental spectrum was used and for the simulated ones, the simulated energy dispersive spectrum of an ideal detector without characteristic X-ray peaks. Figure 4 shows the relationship between experimental and simulated intensities for the Cr-K$\alpha$, Cr-L$\alpha$, and C-K$\alpha$ in Cr$_2$C$_6$.

**Figure 4.** Relationship between experimental and simulated intensities for the Cr-K$\alpha$ (left axis), Cr-L$\alpha$ (right axis), and C-K$\alpha$ (right axis) in Cr$_2$C$_6$. Measurements of net and background intensities at 5, 8 and 15 keV are shown.
Figure 5 displays the variation of the relative uncertainty ($2\sigma$) of the Cr-K$\alpha$, Cr-L$\alpha$ and C-K$\alpha$ in Cr$_2$C$_6$ as a function of the beam energy and dose. The Cr-K$\alpha$ and Cr-L$\alpha$ follow a similar trend where the uncertainties decrease as the overvoltage and dose increase. In the case of C-K$\alpha$, the uncertainties do not decrease as the beam energy increases. The high absorption of C-K$\alpha$ X-rays in Cr$_2$C$_6$ limits the increase of the characteristic X-ray intensity at high beam energies, keeps the peak to background ratio constant ($\approx 2.3$) and prevents the decrease of the uncertainties. From Figure 5, an electron dose of 100 nC would be required to obtain relative uncertainties less than 1 % for all X-ray lines.

![Figure 5](image1.png)

**Figure 5.** Relative uncertainty ($2\sigma$) as a function of the beam energy and dose of the a) Cr-K$\alpha$, b) Cr-L$\alpha$, and c) C-K$\alpha$ in Cr$_2$C$_6$.

The composition also affects the precision. A higher dose is required to measure minor and trace concentration of an element. Figure 6 illustrates this effect where the concentration of Cr was varied from 0.1 wt% to 10 wt% in a Fe-Cr-C compound for a fixed beam energy of 10 keV. Doubling the dose from 100 nC to 200 nC has the effect of reducing the relative uncertainty by a factor equal to the square root of 2. Since the composition of a sample is usually unknown prior to the measurement, the dose required to obtain a given precision level could be evaluated from a preliminary semi-quantitative analysis.
3.3. Spatial resolution

The emission volume of a characteristic X-ray line is defined as the volume from which X-rays are generated and can escape the sample. The dimensions of this volume depend on the beam energy and composition of the sample.

Figure 7 shows the variation of the depth resolution for the Cr-Kα, Cr-Lα and C-Kα in Cr₂₃C₆. The depth resolution was calculated by Monte Carlo simulations and is defined as the depth where 90% of the X-rays are emitted. The density of Cr₂₃C₆ was assumed to be 6541.5 kg m⁻³. The depth resolution of all X-ray lines, except C-Kα, increases approximately linearly with the overvoltage. C-Kα X-rays are strongly absorbed by Cr atoms which limit their escaped depth. Above 10 keV the depth resolution of C-Kα X-rays is smaller than the one of Cr-Kα despite the larger overvoltage (3.5 versus 1.4 at 10 keV).

Regarding the radial resolution, the beam diameter must be considered as it enlarges the emission volume. One advantage of a Schottky field emission source is the smaller beam diameter [32]. However, the actual width of the beam changes with the analytical conditions. To study this effect and obtain quantitative values for the beam diameter, secondary electron (SE) images of gold flakes on a carbon substrate were taken at different beam energies and beam currents. The resolution of an image was measured using its Fourier transform where it is defined as the extent of the low frequency region [33]. For each image, the Fourier transform was calculated for five regions of interest (512x512 pixels) and the threshold of the low frequency region was manually selected from each
power spectrum image following the instructions from Joy [33] and Probst et al. [34]. Since the interaction volume of secondary electrons is small in comparison to the measured resolutions (< 5 nm), the beam diameter was assumed to be equal to the resolution.

For all beam energies, the beam diameter increases with the beam current (figure 8). At 100 nA the beam diameter is at least 80% larger than at 10 nA. Furthermore, for a fixed beam current, the beam diameter decreases with the beam energy. This effect is more clearly shown in figure 9 where the beam diameter was measured as a function of the beam energy for a beam current of 10 nA. The smallest beam diameter was therefore obtained at the highest beam energy (15 keV) and the lowest beam current (10 nA). From figure 9, the broadening of the beam diameter is more pronounced at low beam energies (< 6 keV), which limits the improvement of the resolution. Regardless of the size of the emission volume, the smallest detectable feature can never be smaller than the beam diameter. Reducing the beam current to values lower than 10 nA would result in a smaller beam diameter, but as shown in the previous section, the uncertainties on the measurements would increase unless the acquisition time is increased. Sample drift may however limit the practical increase of the acquisition time.

Figure 8. Variation of the beam diameter as a function of the beam current for five beam energies.

Figure 9. Variation of the beam diameter as a function of the beam energy for a 10 nA beam current.

To evaluate the radial resolution of the different X-ray lines, Monte Carlo simulations were performed at different beam energies using the beam diameters measured at 10 nA. A Gaussian distribution was assumed for the simulated beam with the standard deviation equal to half of the
experimental beam diameter. The radial distribution was constructed by collecting the intensities of each emitted X-ray into bins according to the radial distance between the X-ray generated site and the centre of the beam. The width of the bins was calculated to ensure that all bins have an equal area, i.e., an equal probability of collecting an X-ray. As for the depth, the radial resolution was defined as the radius where 90% of the X-rays have been emitted (figure 10a). For comparison, the same simulations were run with a theoretical beam diameter of 0 nm (figure 10b). The influence of the beam diameter is seen for beam energies less than 10 keV where the decrease of the emission volume is counter-balanced by the larger broadening of the beam. This shows a practical limitation of low beam energy analyses. The comparison of figures 7 and 10a reveals that the spatial resolution is primarily determined by the lateral resolution, especially at beam energies lower than 10 keV. The increase of the beam diameter at low energies does not influence the depth resolution which monotonously decreases with the beam energy. Assuming perfectly spherical Fe-Cr-C particles, the lateral resolution defines the size of the smallest particles that can be measured.

Figure 10. Radial resolution as a function of the beam energy for the Cr-Kα, Cr-Lα and C-Kα in Cr23C6 using a) the experimental beam diameters measured at 10 nA, and b) a theoretical beam diameter of 0 nm.

To evaluate the influence of Fe addition on the radial resolution, simulations were performed using different Fe/Cr ratios from 0.1 to 10 at 10 keV (figure 11). There is a small resolution improvement for Cr-Lα and C-Kα with higher Fe content due to the higher mass absorption coefficients of these X-ray lines in Fe.

Figure 11. Radial resolution as a function of the Fe/Cr ratio at 10 keV and 10 nA.
Based on these results, Fe-Cr-C spherical particles larger than 250 nm in diameter can be measured using the Cr- and Fe-L\(\alpha\) (assuming a similar emission volume for Fe), the C-K\(\alpha\) and a beam energy of 5 keV. Measurements at 7 keV using the Cr-K\(\alpha\) could also be possible, but as shown in figure 5a, large uncertainties at these low overvoltages would limit the precision of the measurements.

3.4. Quantification of Fe-Cr-C particles
To visualize the distribution and size of Fe-Cr-C particles, qualitative mappings were performed using a beam energy of 10 keV, a beam current of 10 nA and a dwell time of 150 ms (figure 12). The C- and Fe-K\(\alpha\) were acquired using large crystals. The mapping shows no segregation within the particles. Based on the spatial resolution calculations, not all particles can be quantitatively analysed. Sample drift may also limit the measurement of particles with a diameter close to the resolution. The quantification was therefore performed on the largest particles (≈ 1.5 µm).

![Figure 12. Qualitative mapping of bearing steel sample (SAE 52100) at 10 keV and 10 nA with a dwell time of 150 ms of the a) Cr-K\(\alpha\), b) Fe-K\(\alpha\), and c) C-K\(\alpha\). The raw counts are shown.](image-url)
6 keV (figure 10a). If the C-Kα intensity is still measured at 6 keV, the overall spatial resolution does not worsen. This example demonstrates an alternative acquisition strategy where different elements are measured at different beam energies to achieve the best spatial resolution and quantification.

A semi-quantitative analysis of the particle revealed a Fe/Cr ratio of approximately 7 and a carbon concentration of a few wt%. For this composition and a beam current of 10 nA, an acquisition time of 10 s is required to obtain relative uncertainties (2σ) less than 1 % on all X-ray lines (figure 5). For integral intensities, an acquisition time of 10 s would approximately be equal to a dwell time of 25 ms per step (assuming 400 steps under each peak). In the present case, the fitting algorithm used to decompose overlapped peaks requires a certain level of precision from the experimental intensities. Otherwise, the accuracy of the fits, and consequently of the quantification, would decrease. A dwell time of 500 ms was selected for the acquisitions to give a total acquisition time of approximately 10 min. The influence of the dwell time and step size on the fitting procedure should, however, be further investigated to increase the speed of integral acquisitions. The MAC database from Pouchou and Pichoir [16] was used.

Table 2 gives the quantification results of two particles: one analysed using the Kα-lines and the other with the Lα-lines. The calculated compositions are comparable. The higher total concentration using the Lα-lines may be explained by inaccuracies in the mass absorption coefficients for Cr and Fe Lα-lines as previously noted. The lower Cr-concentration obtained using the Lα-lines (approx. 15 %) is in line with the findings of Llovet et al. [19], which reported an under-estimation of Cr-concentration in stainless steels. The high Fe-Cr ratio correlates with the low intensity measured in the mapping (figure 12). These results confirm the proper selection of the analytical conditions to measure these particles.

Table 2. Composition of Fe-Cr-C particles (all values in weight percent).

| Line | Fe   | Cr   | C    | Total |
|------|------|------|------|-------|
| Kα   | 81.66| 11.65| 7.58 | 100.89|
| Lα   | 83.72| 9.95 | 7.66 | 101.32|

4. Specialized techniques

4.1. Monte Carlo based reconstruction

Under the analytical conditions used to quantify Fe-Cr-C particles, the emission volume is completely inside the particles and conventional matrix correction algorithms can be used to convert intensities into mass concentrations. Thin film reconstruction algorithms have been successfully developed to calculate the thickness and composition of horizontal layers on a substrate, even when the thickness is much smaller than the emission depth. Can this method be extended to other three-dimensional structures (vertical layers, predefined shaped particles, etc.) in order to quantify smaller features?

To assess the feasibility of the reconstruction, a similar methodology as the work of Peter Statham for multi-layered thin films [35] was applied to the Fe-Cr-C case study. Two unknown parameters, x and y, (e.g., the diameter and the carbon concentration of the particles) were varied and plotted against the residuals between the simulated intensities (I) obtained for each combination of parameters and those of a single reference set of parameters, x₀ and y₀. Residuals were calculated using eq. 2, where m is the number of elements present in the sample (particle and matrix):
The two-dimensional parameter space was discretized into a 20 by 20 grid. Monte Carlo simulations were used to obtain the simulated intensities since no analytical model exists for this geometry. The simulations were run with a beam energy of 10 keV, a beam diameter of 50 nm and 5000 electron trajectories to achieve reasonable precision. Only the intensities from Kα-lines were considered. Table 3 summarizes the three test cases studied.

### Table 3. Parameters of feasibility study.

| Parameter # 1                      | Parameter # 2                      | Composition        |
|------------------------------------|------------------------------------|--------------------|
| Particle diameter (d) (d = 200 nm) | Carbon concentration (x)           | Fe Cr<sub>1-x</sub>C<sub>x</sub> |
| (x = 5.5 wt% C)                    |                                    |                    |
| Fe/Cr ratio (α) (α = 1)            | Carbon concentration (x)           | Fe (Fe-Cr)<sub>1-x</sub>C<sub>x</sub> |
| (x = 5.5 wt% C)                    |                                    |                    |
| Fe/Cr ratio (α) (α = 0.1)          | Particle diameter (d) (d = 200 nm) | Fe (Fe-Cr)<sub>23</sub>C<sub>6</sub> |
| (d = 200 nm)                       |                                    |                    |

The residual plot of the first test case (figure 13a) shows a pronounced minimum at the reference point which confirms the feasibility to determine the composition and diameter of a 200 nm particle at the chosen analytical conditions. This is an improvement over the experimental resolution where only a 550 nm particle could be measured under the same conditions. From figure 13b, the addition of Fe inside the particle results in a sharp minimum along Fe/Cr ratio direction and a less pronounced minimum along the carbon concentration direction. This example, where one element is present in both the particle and matrix, proves that the reconstruction can be successful for a known particle diameter. No minimum is observed for the last case (figure 13c) even if a low Fe/Cr ratio was selected as the reference point. Instead, a saddle is visible around the reference point indicating a non-unique solution. More measurement points (e.g., line scan) could be taken into account to overcome this ambiguity. Nonetheless, these examples prove the feasibility of using Monte Carlo based reconstruction to determine the dimensions and composition of small structures, although certain constraints are necessary, and thus improve the spatial resolution of quantitative microanalysis.

### 4.2. Thin lamella

In a thin lamella, commonly used in transmission electron microscope (TEM) analysis, the broadening of the electron beam is almost negligible due to the lower amount of scattering processes. The emission volume is thus reduced. To demonstrate this effect, a multi-layered structure consisting of alternating Si and Al layers with thicknesses of respectively 390 nm and 300 nm was prepared in two different ways: (1) a bulk sample where the cross-section was polished using a focussed ion beam (FIB) after cleavage, and (2) a thin lamella (≈ 150 nm thick) was cut using a conventional FIB routine for TEM sample preparation. On both samples, a line profile (figure 14) was acquired across the layered structure at 10 keV, 100 nA and a dwell time of 500 ms. Al-Kα intensities were respectively collected using a TAP crystal in combination with a P-10 counter. Stronger variations in the Al-Kα intensities are visible in the lamella due to the improved spatial resolution. With the larger emission volume, X-rays are also emitted from neighbouring layers in the bulk sample, which worsens the
Figure 13. Residual plots for the three studied cases: a) particle diameter and carbon concentration, b) Fe/Cr ratio and carbon concentration, and c) Fe/Cr ratio and particle diameter.

Figure 14. Al-Kα intensity profile across a Al-Si multi-layered structure prepared from a cleaved cross-section (bulk) and lamella (10 keV, 100 nA, 500 ms dwell time and 20 nm step size, TAP crystal, P-10 counter).

Al-Kα signal. Thin samples lead to higher spatially resolved measurements, although the longer specimen preparation, the lower precision and the need for adapted quantification procedures may counterbalance this improvement.
4.3. Bevel surface  
Another sample preparation strategy is to create a wedge using the FIB to characterize laterally homogeneous structures inside a sample [36, 37]. With this geometry, the resolution primarily depends on the milled angle (limited by the divergence angle of the ion beam) and to a lesser extent the beam diameter. To study the spatial resolution improvement of the bevel technique over the conventional cross-section analysis, a multi-layered structure consisting of alternating Ni- and Cr-layers with thicknesses of respectively 57 nm and 56 nm was prepared using both sample preparation methods. Intensity profiles of Ni-K\(_\alpha\) and Cr-K\(_\alpha\) (figure 15) were acquired at a beam energy of 10 keV, 15 nA and a dwell time of 10 s on the bevel, and 10 eV, 10 nA and 2 s on the cross-section. LiF crystals on Xe counter were used for both X-ray lines. The interfaces are more clearly visible in the bevel profile due to the kinks, which are characteristic features of this technique caused by the abrupt change of the concentration at the interface. The oscillations are much smaller in the cross-section profile. This comparison confirms the advantages of the bevel technique to identify interfaces without any knowledge of the beam profile. Using a modified thin film algorithm, quantification of finer structures as a function of depth is therefore possible [36].

![Cr-K\(_\alpha\) and Ni-K\(_\alpha\) profile across a Ni-Cr multi-layered structure prepared as a) a bevel (10 keV, 15 nA, 10 s dwell time and 52 nm step size, LiF crystals, Xe counters), and b) a cross-section (10 keV, 10 nA, 2 s dwell time and 9 nm step size, LiF crystals, Xe counters).](image)

5. Conclusion  
Using Fe-Cr-C particles in a bearing steel as example, a generic procedure was developed to find the optimal analytical conditions to achieve the best spatial resolution. It can be summarized in four points. First, the accuracy of low energy lines should be checked with homogeneous reference materials. If no reference sample is available, verification could be performed on the unknown sample using the high energy lines, as shown for the Fe and Cr K\(_\alpha\)-lines. Integral acquisitions, overlapping corrections and advanced background modelling may be required to obtain accurate intensities for all analysed elements. Secondly, the precision can be estimated from simulated intensities and predetermined calibration factors. This evaluation becomes critical in the presence of elements in minor or trace concentration. Thirdly, the beam diameter must be considered in the evaluation of the spatial resolution. The results in this work showed that the improvement of the spatial resolution at low beam energies is limited by the focussing capabilities of the electron column. Once the beam diameter has been measured at different beam energies and currents, the radial and depth resolutions can be obtained from Monte Carlo simulations. Finally, the analytical conditions (beam energy, beam current and acquisition time) cannot be independently determined as they differently influence the
accuracy, precision and spatial resolution. One must consider all of them together in combination with practical considerations such as carbon contamination and sample drift to select the optimal conditions for a measurement.

Other strategies can be used to further improve the spatial resolution. A feasibility study demonstrated the possibility to resolve features smaller than the emission volume using a non-linear optimisation algorithm coupled with Monte Carlo simulations. To reduce the risk of ambiguous solutions, either the information content of the measurement (e.g., more measuring points at different conditions) or the number of constraints (prior knowledge of the material structure) have to be sufficiently increased. Both the thin lamella and bevel techniques were shown to improve the spatial resolution due to the shallower emission volume and reduced sensitivity to the lateral X-ray intensity distribution, respectively. The longer and more costly sample preparation is however a disadvantage of these techniques.

Other factors not directly considered in this work, e.g., the reproducibility of the stage movement in serial measurements and automatic beam drift correction, play an important role in defining the analytical spatial resolution. Nevertheless, the present results corroborate the potential of field emission microprobes as accurate and precise instruments for the chemical characterisation of sub-micrometre structures.

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