Quantification of low concentration elements using soft X-rays at high spatial resolution

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Abstract. A review of the remaining challenges in electron probe microanalysis to quantify sub-micrometre features containing elements with a concentration less than 1 wt% is presented. These challenges derive from the equivocal influence of the main experimental parameters (accelerating voltage, beam current, measuring time and X-ray lines) on the achievable spatial resolution and the accuracy and precision of the quantification. This inter-dependence is demonstrated by examples from the literature and from new experimental results. From this survey, five key areas are identified as future research and development topics in order to solve for the discussed challenges and achieve the objective of quantification of low concentration elements using soft X-rays at high spatial resolution.

1. Introduction
This work elaborates on what could arguably be referred to as the two biggest remaining challenges of quantification using electron probe microanalysis (EPMA); as the title suggests, the quantification of elements with (1) a concentration less than 1 wt% at (2) a spatial resolution better than 1 µm. If taken individually, these challenges are not necessarily unheard-of and, for most cases, some solutions already exist for them. It is however more and more common to be confronted with measurements requiring, for instance, the quantification of small phases containing low concentration elements. This situation originates on the one hand from the increased complexity of modern materials and more advanced characterisation needs, but also on the other hand from the improved instrumental and computing capabilities.

Quantification in an electron microprobe or scanning electron microscope is the determination of the composition within a certain volume of a flat polished sample. A model is required to correct for matrix effects within this volume in order to transform measured intensities to concentrations. Up to now, most models assume that the composition within the analysed volume is homogeneous (ZAF) or layered (ϕ(ρz)). Although other models could be developed [1], the following argumentation will imply the use of conventional quantification models, or in other words that the quantified volume is equal to the X-ray excitation volume.

Quantification is influenced by several experimental parameters that can be roughly classified in three categories. First, the fixed parameters are defined by the instrumental setup, such as the type of electron emitter, the type of detector, the take-off angle and solid angle of the detectors, etc. As mentioned in the introduction, changes in these parameters can lead to important improvements of the quantification capabilities. For example, the introduction of field emission guns led to smaller probe size at low accelerating voltage or larger detectors, to improved sensitivity. For the subsequent...
discussion, these parameters will however be considered as constant as they cannot be routinely modified for a given instrument. The second category contains the parameters that are part of the calibration. The pulse height analyser for wavelength-dispersive X-ray spectrometers (WDS) or the energy calibration for energy-dispersive X-ray spectrometers (EDS) are two examples. The assumption that these parameters are properly adjusted will be implied in the following paragraphs. Finally, the third category includes the accelerating voltage, the beam current, the measuring time and the X-ray lines chosen for the analysis. The inter-dependence between the quantification of low concentration elements and the quantification at high spatial resolution results from the fact that variations of these experimental parameters will differently influence the accuracy and precision of the quantification.

These quantification challenges will be explained using examples from the literature and experimental results in the following sections. The inter-dependence will be demonstrated based on two different starting points, the quantification of low concentration elements (Section 2) and the quantification at high spatial resolution (Section 3).

2. Quantification of low concentration elements

Independently of the spatial resolution, the quantification of low concentration elements necessitates high counting statistics and proper determination of the background [2, 3]. High counting statistics translates into high beam currents and/or longer measuring times. In other words, the dose must be increased to increase the number of detected counts and therefore reduce the random uncertainties. Since the peak to background ratio will be close to unity for low concentration, counting statistics applies for both the peak and background evaluation. Furthermore, interferences of other X-ray lines, absorption edges near or below the peak as well as background curvatures have a large influence for the quantification of low concentration elements. Reference samples without the element of interest can be used to assess the effectiveness of the measuring strategy (blank test) [2].

In terms of spatial resolution, increasing the beam current has an adverse effect as the beam diameter increases with the beam current. In a previous work [4], experimental measurements of the beam diameter as a function of the beam current (figure 1) were performed for a field emission microprobe (JEOL JXA8530F).

![Figure 1. Variation of the beam diameter as a function of the beam current for five accelerating voltages (reproduced from [4]).](image)

Based on these measurements, optimal parameters to measure carbide inclusions in a SAE52100 (100Cr6) steel were found using Monte Carlo simulations where the change in the precision as well as the depth and lateral intensity distributions of all X-ray lines were evaluated as a function of the accelerating voltage and beam current. The quantification of carbon in the carbides is a good example where the background determination is crucial due to the absorption edge and interferences of high order lines from Mn, Cr and Fe. Despite these inherent difficulties, the inclusions measured in [4]
were relatively large (≈ 1 µm diameter) and the concentration of all elements was higher than 5 wt%. Finding optimal acquisition parameters would therefore be more challenging for smaller inclusions containing low concentration elements and would inevitably lead to longer measuring times. Nevertheless, the method described in [4] would still be applicable.

Unfortunately, longer measuring times are not only synonym to more costly measurements, but phenomena of contamination and beam damage become predominant. The formation of a carbonaceous deposit under and around the electron beam decreases the landing energy and increases the absorption path of the outgoing X-rays. Especially for soft X-rays, contamination can lead to significant artefacts in the quantification. Anti-contamination devices (e.g., plasma cleaning, cold trap, gas jet) can reduce the effects of contamination, but cannot completely eliminate the deposition of cracked hydrocarbons on the surface of the sample [5]. For high spatial resolution measurements where measurement locations are closely spaced, it is important to realize that the contamination leftover by previous neighbouring measurements has a large influence on the measurement of the following locations.

One way to evaluate this influence is to look at the precision of carbon measurements on steel reference samples. The precision on the carbon concentration can be evaluated using the standard deviation calculated from several measurement points. As the samples are homogeneous, the observed fluctuations originate from the combination of random uncertainties due to counting statistics (Poisson distributed) and systematic uncertainties, which strongly depends on the contamination behaviour. By keeping the counting time constant, similar random uncertainties are obtained and the influence of contamination can be observed from the variations in the systematic uncertainties [6]. This experiment was performed on pure iron and four low alloyed steel reference materials containing up to 1 wt% C. Line scans with a step size of 40 nm and 20 µm were run at 15 kV and 100 nA with a counting time of 5 s per point. An oxygen gas jet was used as an anti-contamination device throughout the measurements. Under these conditions a ring-shaped carbonaceous deposit is formed with a diameter of approximately 4 µm [5]. There is, therefore, a strong overlap between the deposits for the 40 nm line scan. Measured intensities were converted to concentrations using the quantification procedure described in [6]. Figure 2 shows the variations of the random and systematic uncertainties for the different samples and step sizes. The full height of each column corresponds to the total measured uncertainty. In all cases, the systematic uncertainties dominate the random uncertainties. This confirms the influence of contamination on the measurements of carbon. Fluctuations in the systematic uncertainties for both line scans indicate that the contamination varies from one measurement to another. This instability is higher for closely spaced measurements as illustrated by the stronger variations of the systematic uncertainties for the overlapping-spot line scan. Nevertheless, these measurements demonstrate that high resolution carbon measurements can be performed up to a detection limit of 0.05 wt% C in low alloyed steels despite the influence of contamination. Measuring lower carbon concentrations would require a better control of the contamination behaviour.

Apart from the anti-contamination devices, the influence of contamination on the measurements can be reduced by other methods. If the carbonaceous deposit is assumed to be a simple carbon film and there is no carbon in the sample of interest, a thin-film correction algorithm (e.g., STRATAGEM [7]) can be used to correct for the absorption in the carbonaceous film by measuring the carbon intensity [8]. When WDS are used, one method to minimize the measuring time is to skip the measurement of the background positions, either by using a calibration curve [9, 10], a pre-determined background [6] or a calculated background (e.g., mean atomic number [11]). For all these strategies, interferences and changes of the background curvature due to total reflection [12] must be carefully considered.

Beam damage comes in different flavours: ablation of the conductive coating layer of non-conductive specimens [13], ion migration [2, 14], volatilisation, sample degradation, etc. Solutions have been proposed to minimize the amount of beam damage: replacing the conductive carbon coating...
Figure 2. Random and systematic uncertainties on carbon concentrations for line scans performed with two different step sizes.

with metallic coatings [14-16], using lower beam currents [17], using higher accelerating voltages [14], or cooling the sample using a cryo-stage [18]. All except perhaps the last solution are detrimental to the objective of quantification of low concentration elements at high spatial resolution. Metallic coatings and lower beam currents worsen the detection limits, whereas higher accelerating voltages increase the emission volume.

One last consideration regarding the quantification of low concentration elements is the phenomenon of fluorescence. The emission of fluorescent X-rays far from the electron beam essentially expands the X-ray emission volume and thus worsens the spatial resolution. Although the fluorescence probability is low in most cases, this effect becomes less negligible when quantifying low concentration elements [19, 20]. Lowering the accelerating voltage can only provide a small improvement [21]. Correction based on Monte Carlo simulations [19, 20] or semi-analytical models [22] is a promising solution to improve the spatial resolution.

3. Quantification at high spatial resolution

Approaching the initial challenges from the perspective of the high spatial resolution, the most influential parameter is the accelerating voltage. Lowering the accelerating voltage has the combined effects of decreasing the electron interaction volume and additionally, due to the lower overvoltage, the X-ray emission volume. As for the beam current, the beam diameter is not constant as the accelerating voltage is decreased. The experimental measurements from [4] show a large increase of the beam diameter below 6 kV (figure 3). Practically this puts a limit on the spatial resolution improvement achievable by the current generation of field emission microprobes. Using Monte Carlo simulations, the authors have estimated that there is no advantage to use accelerating voltages below 5 kV in most cases.

Inevitably at lower accelerating voltages X-ray lines with lower excitation energy must be used to quantify the elements inside a sample. This has several implications, which also apply to all soft X-rays, including the Kα (K-L3) lines of the ultra-light elements (e.g., B, C, N and O). First X-rays are produced from transitions involving electrons taking part in chemical bonding [23-25]. This effect was extensively studied by [25] for borides, carbides, nitrides and oxides. Using standards with similar chemistry as the unknown is the typical solution, since chemical effects are not considered by any model used in the quantification procedure. The second implication is that low energy X-rays are more affected by surface effects such as oxidation and contamination due to increased absorption
Figure 3. Variation of the beam diameter as a function of the beam energy for a 10 nA beam current (reproduction from [4]).

Although these effects can be minimized by proper sample preparation and anti-contamination devices, they can never be completely avoided. Finally, inaccuracies in the matrix correction models lead to errors in the quantification. Large errors were observed using the $\text{L}_\alpha$ (L3-M5) lines for alloyed steels [27–29], iron silicides [13], and Ni-base metallic glass [30]. Two examples are given in figure 4 where the quantification of alloyed steels (Acerinox, S.A.) using the $\text{L}_\alpha$-line results in relative errors up to 32% at an accelerating voltage of 5 kV.

Figure 4. Quantification of two alloyed steels at an accelerating voltage of 5 kV using the $\text{L}_\alpha$- and $\text{L}_\beta$-lines. Cr and Fe were measured on a LDE1 crystal, whereas a TAP crystal was used for Ni. Pure standards, DTSA-II [31] and mass absorption coefficients from Chantler et al. [32] were used for the quantification.

It should however be pointed out the anomalies related the $\text{L}_\alpha$-lines seem to only influence the quantification of first-row transition metals. Measurements on binary alloys of Au-Cu and Pt-Rh at 5 kV gave accurate results even if the $\text{M}_\alpha$-lines were used for Au and Pt and $\text{L}_\alpha$-lines for Cu and Rh (figure 5).

One solution to the $\text{L}_\alpha$-quantification problem is to use the $\text{L}_\beta$ (L3-M1) X-ray line. Authors [13, 28, 29] showed satisfactory results for the major elements using this line. This improvement was attributed to the absence of absorption edges near the X-ray line and valence electrons involved in the X-ray transition [13, 28]. The improved quantification results for the major elements (Cr, Fe and Ni) can be seen in figure 4.
Figure 5. Quantification of 7 binary alloys at 5 kV using the Cu-Lα, Rh-Lα, Pt-Mα and Au-Mα. Measurements on Au-Cu alloys were performed at 300 nA using TAP (Cu) and PETJ (Au) crystals. Measurements on Pt-Rh were performed at 250 nA using PETJ crystals (Pt and Rh). Nominal concentrations for Au-Cu were taken from the NIST SRM482 whereas for Pt-Rh concentrations were measured at 15 kV. Pure standards, DTSA-II [31] and mass absorption coefficients from Chantler et al. [32] were used for the quantification.

Using soft X-ray lines has also an impact on the quantification of low concentration elements, and unfortunately an adverse impact affecting both the needs for high counting statistics and proper background determination. First, the emission probability of soft X-ray lines is normally smaller than the one of high energy lines, due to lower fluorescence yield, lower ionisation probability and higher absorption. To illustrate this point, intensities for different X-ray lines of Ti, Fe and Au from 3 to 30 kV were calculated using Monte Carlo simulations (DTSA-II/NISTMONTE [33]). The results are plotted in figure 6 as the factors required obtaining the same precision as the one at 20 kV using the conventional X-ray line (Kα for Ti and Fe, Lα for Au). The measuring time or beam current would need to be multiplied by these factors to get the same precision. At 5 kV, this would be equivalent to 54 times for Ti-Lα, 21 for Ti-Ll, 7 for Fe-Lα, and 20 for Fe-Ll, whereas the same precision can be achieved by the Au Mα than the Au Lα at 20 kV. For Ti and Fe, it then becomes obvious that low concentration quantification can only be done using the most intense low energy X-ray line, in occurrence the Ti-Ll and Fe-Lα.

Figure 6. Variation of the equivalent precision factor as a function of the accelerating voltages for different X-ray lines of Ti, Fe and Au. The factors are defined as the multiplication factor in order to obtain the same precision than Ti-Kα, Fe-Kα and Au-Lα at 20 kV. Intensities used in the calculations are obtained by Monte Carlo simulations.
Secondly, the use of soft X-ray lines complicates the determination of the background. For WDS, synthetic layered dispersive crystals become necessary for X-ray lines with an energy lower than 0.7 keV (≈ Fe-Lα). The commercially available crystals are typically optimized for high reflectivity (high intensity) but at the expense of the spectral resolution. Combined with the fact that the energy separation between low energy X-ray lines is significantly reduced, overlapping and interference problems between adjacent X-ray lines are therefore common. Figure 7 shows an overlay of five WD spectra acquired on pure standards of Cr, Mn, Fe, Co and Ni on a LDE1 crystal. These elements which are very common in different steel grades would all require interference corrections. The latter would be substantial for the Ll-lines as the interfering lines (mainly Lα-lines) have a higher intensity than the interfered lines. Pinard et al. [29] obtained large errors (3 to 4 wt%) on the Mn-concentration in high Cr containing steels using the Mn Ll-line.

![Five WD spectra acquired on pure standards of Cr, Mn, Fe, Co and Ni at 5 kV, 50 nA using a LDE1 crystal.](image)

This interference problem is even more challenging for EDS, although this technique has the advantage that deconvolution is performed on the whole spectrum [34]. In the case of the first-row transition metals, it is however unlikely, due to the energy resolution, that the intensity of Ll-lines could be correctly extracted [28]. In most cases, the $k$-ratios obtained from EDS spectra are constructed using all lines within a family.

For completeness, another approach to reduce the emission volume and therefore increase the spatial resolution is to adjust the accelerating voltage in order to have a small overvoltage ratio for each X-ray line measured [35, 36]. In principal, this strategy circumvents many of the previously mentioned problems with the low energy X-ray lines as conventional, well-established X-ray lines can be used. Limitations for low concentration quantification still exist since the emitted intensity decreases with lower overvoltage, thus worsening the counting statistics. As shown by [36], instrumental stability and other experimental considerations also complicate the practicality of this approach.

4. Conclusion

The quantification of elements with a concentration less than 1 wt% at a spatial resolution better than 1 µm pushes the frontiers of EPMA. Review from the literature and new experiments revealed limited improvements to this objective when the accelerating voltage, beam current, measuring time and/or X-ray lines of analysis are changed. Each parameter will either have a positive effect on the quantification of low concentration elements or on the spatial resolution, but never for both. Five problems or areas of future research were identified to overcome these shortcomings: (1) better focussing optics to reduce the broadening of the beam diameter at high beam currents and low...
accelerating voltages, better understanding and minimisation of the (2) contamination and (3) beam damage phenomena, (4) higher spectral resolution crystals with good reflectivity, less total reflection for low energy X-ray lines and low intensity of high order X-ray lines, and (5) better matrix correction models and/or fundamental physical parameters to quantify using soft X-rays.

To leave the reader on a hopeful note, solutions to the presented challenges are under development. To sidestep the quantification problems of soft X-rays, standards with similar composition as the unknown could be used, if such reference samples exist. Moving away from soft X-rays, quantification at high spatial resolution using conventional X-ray lines is possible if the sample is a thin lamella [37] or if multiple accelerating voltages are used to reduce the overvoltage [36]. Another idea is to eliminate the constraint for chemical homogeneity inside the X-ray excitation volume by modelling X-ray emission in arbitrary geometries and iteratively reconstructing the composition of each constituent [1]. Needless to say all these solutions have advantages and disadvantages as well as their own challenges.

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