Measurement and Monte Carlo simulation of the spatial resolution in element analysis with the FEG-EPMA JEOL JXA-8530F

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Abstract. To get a reliable estimation of the spatial analytical resolution of electron probe micro analysers with field emission electron sources (FEG-EPMA) it is necessary firstly to know the probe diameter, especially for low acceleration voltages, and secondly to calculate the X-ray emitting volume by Monte Carlo (MC) simulations. In the first step of the investigations presented here the probe diameter was determined by recording SE- and BSE-images of a gold-on-carbon high resolution specimen at various acceleration voltages and probe currents. From the rise of the contrast profiles of the gold insulars edges the probe diameter was derived by using the 1 % - 99 % criterion. The obtained probe diameter ranges from 10 nm at 15 kV/10 pA and 20 nm at 5 kV/10 pA to 65 nm @ 5 kV/10 nA. In the next step line scans measured with the FEG-EPMA are compared to corresponding MC-simulations on especially crafted thin layer specimens. The agreement is not well in all cases but MC simulations are suitable to get an approximation of the expected spatial analytical resolution in dependence of the used acceleration voltage, the probe current and the detected X-ray transition. To get useful numbers it is necessary to distinguish between the quantitative and the qualitative spatial analytical resolution. The former refers to applications requiring the quantification of the elements, i.e., the elemental composition is homogenous within the X-ray emitting volume. Therefore, the quantitative resolution is derived from the edge steepness of the line scans using the 1 % - 99 % criterion. At our specimens resolutions suitable for the quantitative analysis down to about 100 nm were observed. The qualitative spatial analytical resolution is evaluated by means of the 16 % - 84 % criterion and applies to the pure recognition of elemental changes in line scans across precipitates or layers whose sizes might be smaller than the X-ray emitting volume. We obtained qualitative spatial analytical resolutions down to several ten nanometres.

1. Introduction
Element analysis with high spatial resolution becomes more important for the investigation of nanoparticles, nanolayers and core-shell-structures in geology, material science and chemistry. The commonly used transmission electron microscopy (TEM) is not suitable in numerous cases where areas with small differences in Z should be imaged or for the precise quantification of medium to heavy weighted elements [1]. In these cases the use of wavelength-dispersive X-ray spectrometers (WDS) in an electron probe microanalyser (EPMA) with their high spectral resolution and sensitivity is advantageous over TEM-analysis. This paper regards bulk EPMA-specimens only, since the specimen preparation then requires less effort compared to the TEM-specimen preparation.
So far the limited spatial analytical resolution is the main drawback of conventional EPMA. In this paper first attempts and measurements are reported to understand the mechanisms that are relevant for the spatial analytical resolution. The main task is to decrease the interaction volume of the emitted and detected signal. This might be done by the decrease of the penetration volume of the electrons by considerably decreasing the acceleration voltage (so called low voltage analysis) or by the decrease of the analytical volume by particularly decreasing the acceleration voltage with respect to the ionisation energy of the detected X-ray transition (so called low overvoltage analysis) [2, 3]. The low overvoltage analysis increases the spatial resolution by the effect that the electrons that still have enough energy to excite the X-ray transition have a small beam spread only. Applying the low overvoltage analysis one accepts that the overvoltage might not have the optimal value to excite the X-ray transition with the highest probability. The focus lies on the optimisation of the spatial resolution.

To compare both methods, the sizes of the penetration volume of all electrons and of the electrons with energy larger than the ionisation energy are determined with Monte Carlo simulations [4]. For the comparison of these simulations with measurements several variables need to be considered additionally. First of all fluorescence has to be regarded unless it is not included in the simulations. Secondly the interaction volume is enlarged by the diameter of the probe. Therefore, the analytical volume is the convolution of the beam diameter with the interaction volume.

The measurements are made using an EPMA with a field emission gun (FEG-EPMA) since only the FEG emits an electron beam with a high brightness allowing a strong focussing even for low acceleration voltages. EPMA with a thermionic electron gun are not suitable for the low voltage analysis at high spatial resolution (but might be used for the low overvoltage–analysis). However, the beam size depends inversely proportional to the acceleration voltage and proportional to the beam currents even for the FEG. Therefore, the probe diameter needs to be determined for all acceleration voltages and currents.

This paper focusses on the optimisation of the analytical resolution in EPMA and leaves problems that might arise for the quantification (by using L- and M-lines) out. Great efforts in understanding the element analysis using L- and M-lines and in the development of solutions have already been made [5-13].

2. Experimental and results

2.1. Measurement of the probe diameter

SE- and BSE-images of a gold-on-carbon high resolution specimen were recorded at various accelerating voltages (3, 5, 8, und 15 kV) and probe currents in steps from 10 pA to 100 nA using a FEG-EPMA JEOL JXA8530F (figure 1). The probe diameter is derived from these images in correspondence with ISO/TS 24597 by the analysis of the contrast profile of the gold insulators. The programme “Image” by FEI (figure 2) has been used since it allows freely choosing the thresholds and averaging over many grains and orientations. The programme „Image“ determines the beam diameter from the image sharpness which is calculated following the derivative method specified in the standard ISO/TS 24597. The derivative method fits error functions to edge profiles extracted from the SEM image. The image needs to contain of as many Au particles, so that at least 2000 edge profiles with a homogenous distribution of orientations contribute to the calculated mean value. In our case images with about 30000 edge profiles were analysed.

The analytical resolution is determined by the convolution of the probe diameter with the interaction volume. Since Monte Carlo simulations of the interaction volume trace the electron path until the complete stopping of the electrons, the probe diameter is determined from the line profile with a 1 % to 99 % criterion as well. Usually resolution measurements using profile scans are evaluated using the 16 % - 84 % criterion corresponding to the full-width-half-maximum (FWHM) of
of a Gaussian function convoluted with an abrupt edge, i.e., the Gaussian beam diameter [5]. In figure 3 the different criterions are compared with the occasionally used 30 % - 70 % criterion. In figure 4 the measured edge steepness’s are plotted for different acceleration voltages, e.g., 15 nm for 15 kV and 10 pA or 31 nm for 8 kV and 1 nA. For high analytical resolution low beam currents and high acceleration voltages are required. These data correspond with the specifications as provided by the JEOL Company [14].
2.2. Monte Carlo simulation and measurements of the quantitative spatial analytical resolution

In the next step measurements of the analytical resolution are compared to predictions from Monte Carlo (MC) simulations obtained from the programme CASINO (version 2.48) [15]. Three specimens were specially made for this purpose consisting of thin layers or sharp transitions of pure elements. The specimens are designed to allow both low voltage and low overvoltage measurements. Cross-sections are prepared by classical metallography or by use of a focused Ga-ion beam (FIB, FEI Helios NanoLab600). WDX line scans of particular X-ray transitions are recorded across the element interfaces (FEG-EPMA, JEOL JXA 8530F). Assuming a Gaussian beam profile and a Gaussian distribution of emitted X-rays, the line scans have a sigmoidal shape corresponding to the integral of the Gaussian function. Unfortunately the real beam profiles and the X-ray distribution have more complex shapes and might not be easily fitted at least for the 1 % - 99 % criterion to analyze the edge steepness. Therefore, the measured line scans are smoothed over 5 points and the analytical resolution is estimated as the distance between points having 1 % and 99 % of the maximum signal respectively. This 1 % - 99 %-criterion is necessary to determine the analytical resolution for a quantitative analysis. In this case it is guaranteed that all detected photons are emitted from a homogenous volume of the sample. We call this the quantitative analytical resolution (see sections 2.2.1 - 2.2.3). Additionally it is interesting to know the minimum size of features (having another element distribution) that can be detected by WDX line scans. In this case the source area of emitted photons might be larger compared to the size of the feature. We call this the qualitative analytical resolution (see section 2.3). It is determined by analyzing the steepness of line scans with a 16 % - 84 % criterion which corresponds to the full width half maximum (FWHM) of a Gaussian function convoluted with a step function.

The MC simulations are performed for the same specimen and measurement conditions, i.e., the same X-ray transitions, element configuration, acceleration voltages and beam currents. Furthermore, the simulations consider the particular probe diameters (as determined in sect. 2.1) as a parameter. The simulated line scans are analysed with the 1 % - 99 %-criterion to apply for comparisons with the measurements.
quantitative analytical resolution. Moreover the 1% - 99% criterion offers the possibility to compare the measurements with MC simulations that consider a complete stopping of the electrons.

2.2.1. First example: Fe-Ni interface. At the metallographic prepared cross-section of an electroplated Fe-Ni interface (figure 5) we measured line scans of the Ni-Lα transition with accelerating voltages of 15, 8 and 5 kV and a beam current of 5 nA. 450 points were analysed with a step size of 10 nm and a dwell time per point of 3 s. The Ni Lα-line (0.851 keV) was measured with the TAP-crystal.

![Figure 5. Backscattered electrons image of the Fe-Ni interface and direction of the line scan.](image)

Figure 6 compares simulated and measured line scans for the three acceleration voltages. As expected the analytical resolution increases as the acceleration voltage is decreased. Considering the measurements the resolution is getting better from 800 nm at 15 kV to 200 nm at 5 kV. At 15 kV simulations and measurements coincide quite well. But for lower accelerating voltages simulation and measurement deviate from each other and the underestimation of the simulation increases with the decrease of the voltage. The reason for this discrepancy is not clear yet. Maybe the simulation is not optimized for low energies since radial distributions of emitted X-rays, which were simulated with CASINO showed a maximum several nanometre out of the centre but not at the centre. The simulation at 5kV would coincide with the measurement if a beam diameter of 120 nm is postulated. According to the measurements (figure 4) the beam diameter has a value of 56 nm and there is no reason to assume a deviance of more than a factor of 2. In any case fluorescence is not responsible for the effect, since the energy of all Fe L-lines (0.60 - 0.72 keV) is well below the Ni-L ionisation energy (0.853 keV).

2.2.2. Second example: Ag-Au-Ag interface. This second specimen is suitable for the comparison of low voltage and low overvoltage analysis. Two silver (500 nm) layers with an intermediate gold layer (75 nm) were deposited on a silicon wafer with a sputter coater. Afterwards a 15 µm wide cross-section was prepared using the FIB. The top layer visible in figure 7 is a platinum layer necessary during the FIB-preparation. On the layers cross-section, a line scan with 15 kV and 5 kV and 1 nA was measured using the beam scan with a step size of 3 nm and a dwell time of 20s. The Au Mα- and the Au Lα-signal were recorded with the TAP and the LIFH crystal respectively.

First an acceleration voltage of 15 kV was used allowing the excitation of the Au Mα- and the Au Lα-transitions. The later transition is excited with a low overvoltage. From Monte Carlo simulation curves (figure 8) we get an estimated resolution of 375 nm for the Au Mα-signal and 144 nm for the Au Lα-signal. Figure 9 plots the measured line scans with evaluated resolutions of 200 nm and 360 nm for comparison. We found a quite good accordance for the Au Mα-signal but a
Figure 6. Comparison of MC simulated and measured line scans of Ni-Lα across the Fe-Ni interface at 15, 8 and 5 kV.
Figure 7. In-lens SE-image of the Ag-Au-Ag interface and direction of the line scan.

Figure 8. MC simulated line scans of Au-Mα and Au-Lα across the Ag-Au-Ag interface at 15 kV.

Figure 9. Measured line scans of Au-Mα and Au-Lα across the Ag-Au-Ag interface at 15 kV.
clear 25 %-underestimation for the Au Lα-signal. Again this discrepancy is not understood yet. It might be caused by the roughness of the interface which worsens the resolution. This effect has a different influence on Au Mα- and Au Lα-photons. Apparently, the measured Au signals are additionally not in saturation even in the middle of the gold layer, i.e., that the volume of the emitted photons exceeds the thickness of the gold layer. Therefore, the line scans were repeated at an acceleration voltage of 5 kV. Now only the Au Mα-signal occurs and it is excited with a low voltage.

The reduction of the acceleration voltage to 5 kV improves the analytical resolution by decreasing the range of electrons. Additionally it might be used for the comparison of low voltage and low overvoltage analysis. From figures 8 and 9 at 15 kV it is already visible that the detection of the Au Lα-signal enables a better resolution. The reason for this is that only few (sharply localized) electrons have enough energy to excite L-transitions (ionisation energy 11.92 keV) while many electrons from a wide excitation area might excite the M-transitions (ionisation energy 2.21 keV).

The question is: How does the Au Lα-line scan recorded at 15 kV compares to the Au Mα-line scan at 5 kV? The MC simulation in figure 10 shows that the range of electrons nearly has the same size as the thickness of the gold layer since the Au Mα-signal is in saturation at the centre. Unfortunately simulation and measurements do not coincide very well again. Probably CASINO includes the fluorescence of Au-Mα (2.21 keV) excited by Ag-Lα (2.98 keV) not in a suitable way since most matrix correction models consider fluorescence ratios smaller 1.25 only. In our case it has a value of 1.35. Furthermore, it is not clear whether the measured Au-signal has reached the saturation.

![Figure 10. Comparison of MC simulated and measured line scans of Au-Mα and Ag-Lα across the Ag-Au-Ag interface at 5 kV.](image)

Obviously, the low voltage analysis delivers in both cases a better resolution compared with the low overvoltage analysis. The further decrease of the overvoltage in figures 8 and 9 will increase the resolution but the detected signal will further decrease. In addition it should be mentioned that the low overvoltage analysis might not be optimal for the later quantification of the revealed small structures. Using an acceleration voltage of 15 kV to measure the Au Lα-line gives an overvoltage ration of 1.25 only whereas it should have a value of 2.5 ... 3 to maximize the excitation. From this point of view it is more suitable to use the Au Mα-line at 5 kV (overvoltage ration of 2.6), i.e., the low voltage analysis is preferable due to the better spatial resolution and due to the better quantification.
2.2.3. Third example: Si-Au-C interface. In the next step the analytical resolution is examined in the presence of light elements. A 75 nm thick gold layer was deposited by sputter coating on a silicon wafer substrate. A 275 nm thick carbon layer was then added by electron beam evaporation on top. The line scan (200 points with step size 3 nm and dwell time 20 s) was measured at a cleaved cross-section of the specimen (figure 11) with 5 kV (1 nA). Here, the Au-M$_{\alpha}$ signal was recorded with the PETH crystal, but similar results were obtained with the TAP crystal.

![Figure 11. Layout and backscattered electrons image of the Si-Au-C interface and direction of the line scan.](image)

By comparing both line scans in figure 12 it is clear that there is a poor agreement between simulation and measurement. The measured Au M$_{\alpha}$-line scan shows a strong but reasonable asymmetry since the gold layer is embedded in silicon (left) and carbon (right). In contrast, the simulation is nearly symmetric. Obviously the density of the electron beam evaporated carbon film differs too much from the density of bulk carbon used by the simulation. In addition the simulation might include the absorption of Au-M$_{\alpha}$ in Si which is ten times higher compared to the absorption in C not in a suitable way.

2.3. Measurements of the qualitative spatial analytical resolution

In some applications it is not necessary to quantify the elements but only to trace small areas with another elemental composition. Then, it is sufficient that the WDX-signals change along the line scan well above noise [16]. Therefore, it is reasonable here to define a qualitative analytical resolution. This value is a measure for the size of structures that might be detected using the WDX-signal. Then it is meaningless to use the 1 % - 99 % criterion to analyze the steepness in line scans. In figure 13 the Au-M$_{\alpha}$ and the Si-K$_{\alpha}$ line scans from the third specimen are re-analysed by fitting Gaussian and sigmoidal functions respectively. From these fitting functions the edge steepness is measured using the $16\%$ - $84\%$ criterion corresponding to the FWHM of the Gaussian beam convoluted with a sharp transition of elements. With this commonly used criterion a (qualitative) analytical resolution of 26 nm for the Au M$_{\alpha}$-line and 45 nm for the Si K$_{\alpha}$-line is obtained. From the clear contrast of the Au M$_{\alpha}$-signal it might be derived that even thinner layers with a better analytical resolution are detectable.
Figure 12. Comparison of MC simulated and measured line scans of Au-Mα, Si-Kα and C-Kα across the Si-Au-C interface at 5 kV. Right: The measured line scans are smoothed over 5 points and the markers for the edge steepness’s are set by hand.

Figure 13. Measured line scans of Au-Mα and Si-Kα across the Si-Au-C interface at 5 kV and indicated quantitative and qualitative analytical resolution. The Au Mα-signal is fitted by two Gaussian functions considering the two interfaces. The Si Kα-signal is fitted with a sigmoidal function. The 16 % - 84 % analysis is obtained from the fitting function while the 1 % - 99 % analysis is obtained from the smoothed measurements figure 12 right.

3. Conclusions
The FEG-EPMA has a significantly increased analytical resolution compared to EPMAs with thermionic electron emitter reaching values down to several ten nanometres. When measuring the analytical resolution two applications should be distinguished. On the one hand, the quantitative analytical resolution is considered as a measure allowing the quantification of the elements since the analysed structures are larger than the area of emitted photons. The quantitative analytical resolution is determined by steepness of line scans with a 1 % - 99 % criterion. Here we measured values of about 100 nm. On the other hand, for some applications it is enough just to detect small elemental
changes using the WDX-signal. Then the qualitative analytical resolution is regarded which is derived from line scans with a 16 % - 84 % criterion. This resolution value was found to be in the order of tens of nanometres. At particular samples the recognition of even 10 nm thin layers seems to be feasible.

For the prediction of both kinds of analytical resolutions, MC simulations are helpful. Appropriate simulations consider the actual probe diameter which needs to be measured for all individual acceleration voltages and probe currents as an input parameter for the simulation. Commonly Au-on-C reference specimens are used for these measurements. If the quantitative analytical resolution is required then also the probe diameters are determined with the 1 % - 99 % criterion.

At three specially made specimens we compared resolutions derived from MC simulations with measurements under different measurement conditions. In most cases, the MC simulations are suitable to get an approximation of the expected resolution but often they differ by 25 % to 33 % from the measurements. The discrepancy seems to be larger for small accelerations voltages and large differences in the atomic number. In the future further attempts to understand the differences are necessary.

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