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# Low Accelerating Voltage X-ray Microanalysis – Strategies and challenges.

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Low accelerating voltage analysis has become an important strategy in microanalysis because it allows us to push the traditional limitations when attempting to obtain the smallest analytical volumes. Reducing the accelerating voltage reduces the penetrating distance of the beam electrons and thereby reduces the volume being analyzed. Two general strategies have been tried for obtaining the smallest analytical volumes [1]. One approach is to simply use the lowest, reasonable, accelerating voltage that will produce the smallest electron interaction volume. The X-rays will come only from within this volume, and therefore a small analytical volume will be achieved. The optimum accelerating voltage that will produce the smallest interaction volume and still produce a reasonable X-ray count rate, tends to fall in the 5-8 kV range. A lower kV will reduce the penetrating depth of the electrons further. However with lower kV, the diameter of the electron beam itself becomes the critical factor in determining the analytical area, and with a lower kV, the beam diameter becomes larger. Much of this increase in beam diameter comes from the higher required beam current used due to the lower X-ray production rate at the lower kV. Using a lower accelerating voltage also typically requires that a different set of X-ray lines be used in the analysis. Some of the more commonly used X-rays lines are not generated at the low accelerating voltages.

A second strategy involves first determining the preferred X-ray lines to use, and then select a accelerating voltage that is only 1-3 kV greater than the critical ionization energy of the highest energy X-ray line being used. This is called the low-overvoltage method [2]. The beam electrons will typically have a higher energy than the previous method, but the fact that they have such a low overvoltage means that once they have entered the sample they quickly drop below the critical ionization energy. Therefore they can only produce X-rays very close to the surface (Fig. 1), even though the beam electrons continue much deeper into the sample.

Both methods have their advantages and disadvantages, when comparing (a) the analytical volume, (b) minimum detection limits, (c) secondary fluorescence, and (d) the effect of surface coatings and contamination. With care, it is possible to analyze, quantitatively, features that are in the 200 nm range [3]. However, the critical question becomes, how good are the quality of the analyses using the two different methods. One of the big problems is the transition metals, particularly, when switching from using the K$\alpha$ line to the L$\alpha$ line for elements like Fe, Ni, Co, and Mn. The quality of the analyses can drop precipitously when using the L lines over the K lines. Using Fe as an example; the problem with using the L$\alpha$ line in the analysis is that self-absorption of the Fe L lines is very high, and there is an Fe absorption edge that falls between the Fe L$\alpha$ and L$\beta$ lines (Fig.2). Therefore the ratio of Fe L$\alpha$ / Fe L$\beta$ varies with the Fe abundance. This becomes a significant problem when these two lines cannot be separated due the low energy resolution of the spectrometer. This is the case with an energy dispersive spectrometer (EDS), and even with a wavelength dispersive spectrometer when using a layered synthetic microstructure (LDE) for the analyzing crystal. Applying the correct mass absorption coefficient becomes very problematic. An alternative is to use a wavelength dispersive spectrometer (WDS) with a TAP crystal. The two X-ray lines are separate and can be measured independently. However the count rates are much lower than on the layered synthetic microstructure (LDE) analyzing crystal.

There are various strategies that can be used that will help improve the quality of transition metal analyses, even using the L lines when the Lα and Lβ cannot be resolved. One option is to use standards that are more similar in composition to the unknown. This reduces the reliance on the matrix corrections routines and thereby reduces the impact of any error in the absorption calculations. If better standards are not available, then a second option might be to use internal standards. Internal standards are phases in the same sample that are large enough to be analyzed under the normal accelerating voltages. Once the larger grains have been analyzed, then can then be used as standards using the low-kV conditions. These internal standards have the potential advantage of being similar in composition to the unknown, and have the added advantage of being identical in their conductive coating, something that can have an important impact when doing low-kV analyses.

In order to quantitatively analyze sub-micron grains, a lower than normal accelerating voltage must be used, but working at a lower accelerating voltage can offers many challenges. However, good analyses can be obtained, if one understands where the pitfalls exist and work to minimize their effects.

References:

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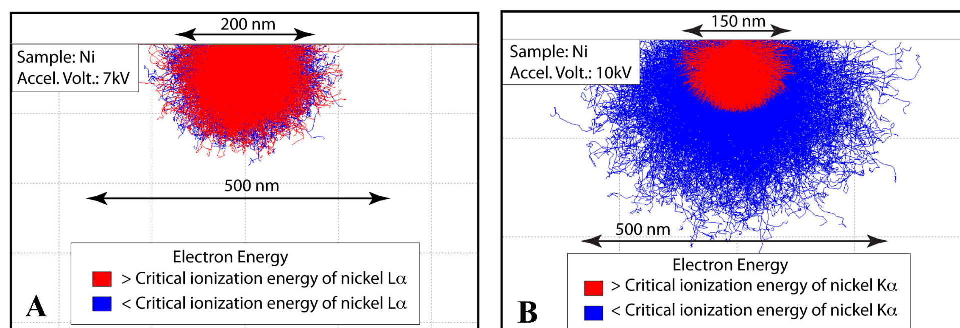


Figure 1. Monte Carlo simulation of the analytical volume for a Ni sample using the low-kV method at 7kV using Ni Lα (a), and the low-overvoltage method at 10kV using Ni Kα (b).

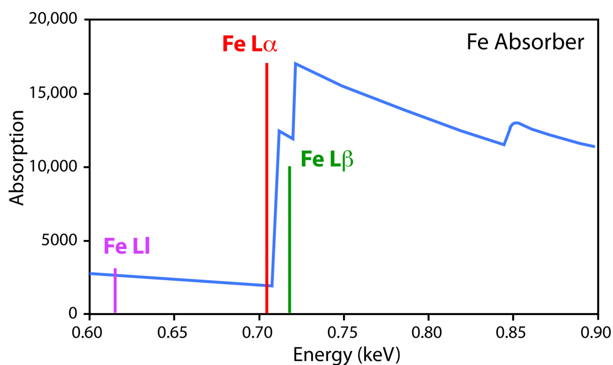


Figure 2. Differences in the amount of absorption of various Fe X-ray lines in an iron absorber.