Proximate Particles in a Variable Pressure/Environmental SEM

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Quantitative microanalysis of particles is always more difficult than microanalysis of bulk samples. Many of the basic assumptions of quantitative microanalysis no longer hold. The excitation volume maybe comparable or smaller than the material volume; the beam does not necessarily strike the surface at a normal; and the absorption path length is not easy to calculate. Performing the measurement in a variable pressure or environmental SEM further complicates the issue. Some of the most effective techniques that are commonly applied to facilitate quantitative analysis of particles are less effective. For example, it is common to normalize the analysis results to 100% to compensate for volumetric effects. However if a fraction of the beam is deflected into the skirt, the normalization will involve both electrons that strike the sample and electrons that strike the regions around the sample. However this note will focus on a slightly different complication that also is a results from the electron skirt.

This note will consider the influence of close or adjacent particles to the spectrum of a particle of interest. For example, consider a stainless steel particle adjacent to a molybdenum-rich particle. Is it possible to determine the presence or absence of molybdenum potentially at the 1 to 2% level in the stainless steel particle? Will the electrons from the skirt that strike the adjacent molybdenum-rich particle contribute a similar number of x-rays to the spectrum?

One possible way to address this question might be to start with a semi-empirical model of the electron skirt. Integrate this model over the area of the adjacent particle to estimate the fraction of electrons that are likely to strike the adjacent particle. Finally, compare the spectral contribution due to these electrons and those that are likely to strike the particle of interest. While this model is likely to provide reasonable results, I chose an alternative model based on Monte Carlo modeling of electron trajectories and x-ray generation.

Microanalytical Monte Carlo models track the trajectory of individual electrons through multiple scattering events as they bury themselves in a sample. Monte Carlo models have the potential to be extremely accurate models of electron transport, x-ray generation and spectrum formation. The behavior of the electrons can be based on sophisticated models of electron / atom interactions, the x-ray generation models can be based on the best expressions for ionization cross section and the x-ray absorption can be based on the precise location of the x-ray generation and the resulting absorption path length.

Most Monte Carlo models for microanalytical processes make a simplifying assumption about the electron interactions. They assume that all electron/atom scattering events are e*lastic* (meaning the electron does not loose measurable amounts of energy) and that electron energy loss can be modeled using the *continuous slowing down* approximation. This approximation is justified by comparing the angular distribution of elastic and inelastic scattering events. Elastic events are the result of electrons scattering off of the much heavier atomic nucleus. Inelastic events are the result of interactions with the atomic electrons. Figure 1 shows the differential cross section for elastic and inelastic processes for argon at an electron energy of 10 keV. The elastic cross section is modeled using the NIST Electron Elastic-Scattering Cross-Section Database[1] and the inelastic cross section is modeled using the simple expression of Colliex and Mory[2]. This figure shows behavior that is common to all elements and microanalytical energies, the inelastic cross section is peaked at lower scattering angles than the elastic cross section. Thus inelastic events are likely to involve small deflections while elastic events are likely to involve larger deflections. Most of the time the small inelastic events can be rolled into a single analytical expression modeling the average energy loss.

However, the variable pressure situation is a little unusual. Small deflections can have large effects when those deflections occur in the gas between the electron optics and the sample. Because the density of gas is likely to be small, the total number of scattering events

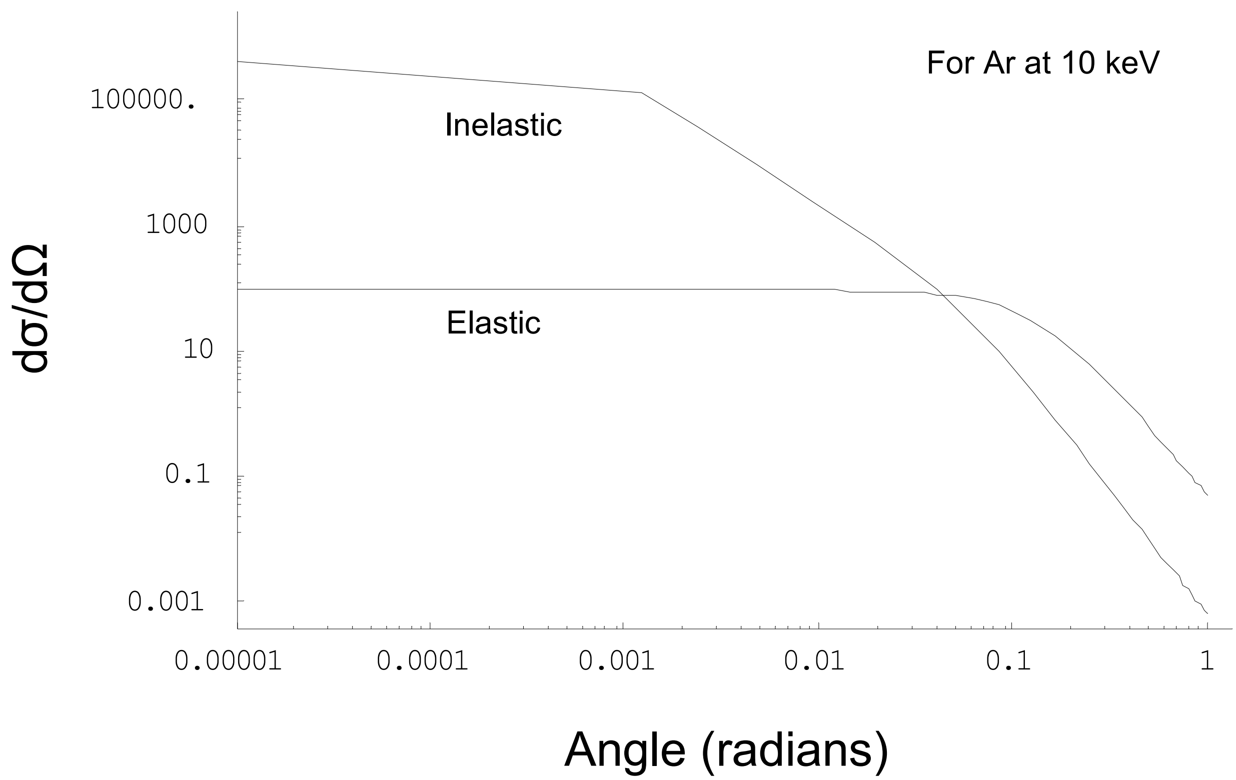

Figure 1: Comparing the elastic and inelastic scattering cross sections for an electron at 10 keV incident on a argon atom.

1 A. Jablonski, F. Salvat, C. F. Powell, *NIST Electron Elastic-Scattering Cross-Section Database* - version 3.1, National Institute of Standards and Technology, Gaithersburg, MD (2003)

2 C. Colliex, C. Mory, in *Quantitative Electron Microscopy*, ed J. N. Chapman & A. J. Craven, SUSSP Publications, Edinburgh (1984)

is likely to be of the order of one. In addition, the electron path length is relatively long (~ 1 cm) and the critical sample dimensions are typically a few orders of magnitude smaller (~1 μm), small angle scattering events are actually very important. A milliradian deflection over a path length of 1 cm can lead to a radial deflection of ~10 μm. The shape of the skirt is likely to be strongly influenced by both the elastic and inelastic scattering events.

NISTMonte[3] is a new implementation of a Monte Carlo model. NISTMonte is written in Java for platform independence and the source code is freely available from the author. NISTMonte features arbitrarily complex sample geometries, interchangeable physics, multiple interchangeable detection schemes, and is typically scripted in Jython, a Java-based scripting language. NISTMonte has been enhanced to include inelastic scattering events when the interaction material is a gas.

A simple model of two adjacent particles, the primary one of material and the secondary, adjacent particle of another was constructed in NISTMonte. The two particles were placed on a matrix of a third material. The radius of the primary particle was held at 1 μm and the secondary particle is varied in size between 1 and 100 μm. The incident beam energy was 20 keV and the path length 1 cm. Figure 2 shows the variation in primary beam fraction and the ratio of the electron flux on the secondary and primary particles as the pressure in the chamber is varied. The figure shows that even at a incident fraction of about 60%, the number of electrons striking the secondary particle is only about 1% of the number

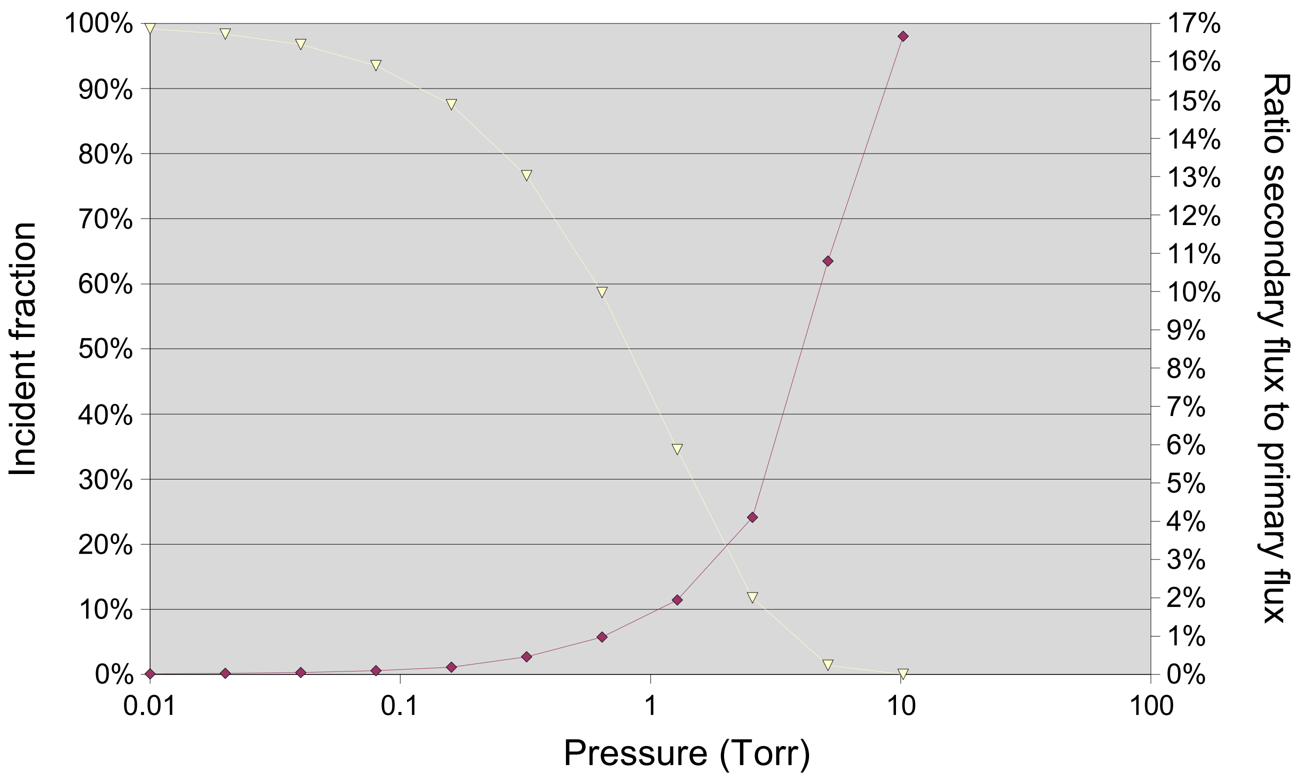

Figure 2: The variation in primary beam fraction (yellow) and secondary particle electron flux to primary particle electron flux (red) for primary and secondary particles of 1 μm radius and a beam energy of 20 keV.

3 N. W. M. Ritchie, *Surf. Interface Anal.* 2005; **37**: 1006-1011

of particles striking the primary particle. Figure 3 shows the model results if the path length and pressure are held constant at 1 cm and 0.5 Torr but the size of the adjacent particle is varied between 1 μm and 100 μm.

These figures and other similar calculations suggest that unless the secondary particle covers substantial amounts of area then it will not contribute significantly to the spectrum of the primary particle. This may be intuitive given that the dimensions of the skirt are so much larger than the dimensions of the particle. It does suggest that an undeflected incident beam and a deflected skirt is a useful model. In the case of Figure 2, we see that even when the skirt consists of ~40% of the incident beam only ~1% of the skirt actually strikes the adjacent particle. On the other hand our intuition seems to suggest that there would be substantially more electrons that were deflected by very small amounts because either they interacted weakly with an atom in the gas or scattered close to the sample. According to this model, more electrons are scattered at smaller angles but because the actual area covered is so small the contribution remains small.

It should be remembered that this result is based on a simplified model of the inelastic scattering cross section in which the details of the atomic shell structure are not considered. One might expect that the smallest angular deflections might result from interactions on the outer extremities of the atom. These interactions would depend highly on atomic shell structure and are thus were not well modeled. To truly address the issue of the smallest angle scattering events will require either careful measurement of the smallest angle scattering

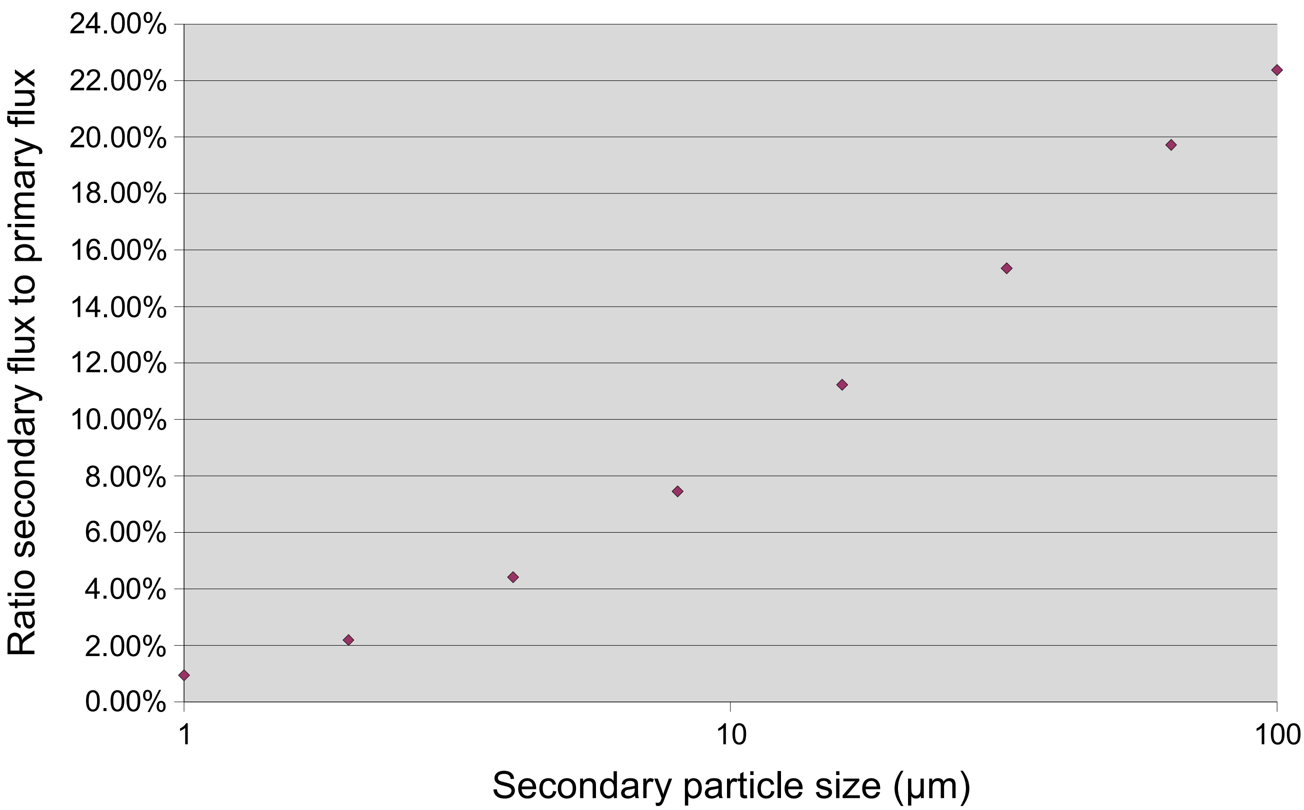

Figure 3: Shows the variation in electron flux on the secondary particle as a fraction of the flux on the primary particle as secondary particle size is varied.

events or a more sophisticated model of the inelastic scattering process.

It is also important to remember that we only considered the case of two adjacent particles. More often a particle of interest is located on a particle covered sample. In this case, a better quantity of merit is the area coverage fraction. If the surrounding particles cover a small (<1%) fraction of the total surface area, then it is likely there contribution can be neglected. However, if the surrounding particles cover 10% of the total area and 40% of the incident beam is scattered into the skirt, we could expect to see approximately a 4% contribution from the neighboring particles.