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Single Atom Detection by XEDS in the Aberration Corrected AEM: Is it Feasible?

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With the recent advances in aberration corrected electron microscopes the prospect of ultra-high/atomic spatial resolution microanalysis in materials is becoming a realistic expectation. The ability to create sub-angstrom probes, however, is not the only criterion essential to fully realizing this capability. A number of important technological materials and processes, such as the study of active sites in catalysts, needs not only structural imaging, but also the requires that an investigator uniquely identify the existing elemental components and at near atomic dimensions. While high angle annular dark field images contains Z contrast information this is not always sufficient to uniquely characterize a material. The use of analytical spectroscopy remains one of the unambiguous methods of verifying the composition and signatures of the various elemental species. X-ray energy dispersive spectroscopy (XEDS) in the AEM is among the methods which can achieve this, and to this end we are interested in assessing the ability of using XEDS to detect and identify *single* or *clusters* atoms localized by a sub-angstrom probe. In a perfect system this is an experiment which requires one to adjust the probe and enable the appropriate detector and simply acquire the spectra. The question becomes under what conditions is this practical in terms of experimental parameters, i.e. what is the intensity of the spectroscopic signal as a function of accelerating voltage, beam current, atomic number, detector characteristics and analysis time.

To determine this feasibility we calculate from first principles the x-ray generation by an incident electron probe in the analytical electron microscope as a function of atomic number (Z) and accelerating voltage (Eo). The basic relation for which is given by the following:

$$I_A^{K\alpha} = \left[\sigma_A^K(E_o)\omega_A^K\Gamma_A^{K\alpha}\right] \bullet \left(C_A \frac{N_o \rho\, t}{W_A}\right) \bullet (\eta) \bullet \left(\varepsilon_A^{K\alpha}\Omega\right)$$

Here, σ_A, ω_A, Γ_A are respectively the Kth shell ionization cross-section, fluorescence yield and radiative partition function; C_A, N_o, ρ, W_A, t the composition, Avagadro's number, density, atomic weight and thickess of atom/element A; $\eta = i{*}T$ is the incident number of electrons (equivalently beam current * time) while ε_A and Ω are respectively, the relative detector efficiency and collection solid angle for the x-ray signal being measured. [1]. Setting the composition to unity and the thickness to the nominal dimension of a single atom we calculate the results shown in Figure 1. Here we plot the total number of x-rays produced per atom per nanoampere, per sterradian per second from selected $K\alpha$ and $L\alpha$ lines for a range of elements (Al, Ni, Mo, La, Pt, Ag) and at various accelerating voltages. For the purposes of generality we have assumed a detector with $\varepsilon_A = 1$ at all energies. In this way this data can be scaled to the performance of any XEDS detector by simply multiplying by its relative efficiency for the line in question. Because we are calculating the emission from a single atoms or small clusters which are solely excited by the incident electron beam, the effects of absorption and fluorescence can safely be ignored. For the purposes of this calculation, we have also implicitly assumed that the clusters are supported on a substrate of low atomic number and negligible thickness so that scattering and background effects are minimal.

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In figure 1, we can see that for a given element over the range of 100-300 kV, the calculated count rate changes by not more than factor of 2 which is not a large variation. This immediately allows us to conclude that that the key parameter which will control the feasibility of a measurement is not the accelerating voltage (albeit there is a moderate advantage at 30-50 kV operation) or the element being studied. Realistically and not surprisingly the controlling factors which one must optimize become the analysis time, beam current and solid angle. Increasing the analysis time can be problematic although new generations of low drift stages are being developed [2]. Aberration corrected instruments improve the probe current performance of AEMs, however, there is a limit to which this can be exploited as electron sputtering associated radiation damage effects can develop [3]. The only parameter which can be improved upon, without deleterious effects is the detector solid angle[4]. X-ray detectors in use on the current generation AEMs have a range of solid angles which vary from 0.05-0.5 sr which means we are collecting at best 4% of the total x-ray emission. Thus, improvements to detector design will have the greatest practical advantage, and larger gaps potentially available in aberration corrected instruments should help facilitate this in the near future.

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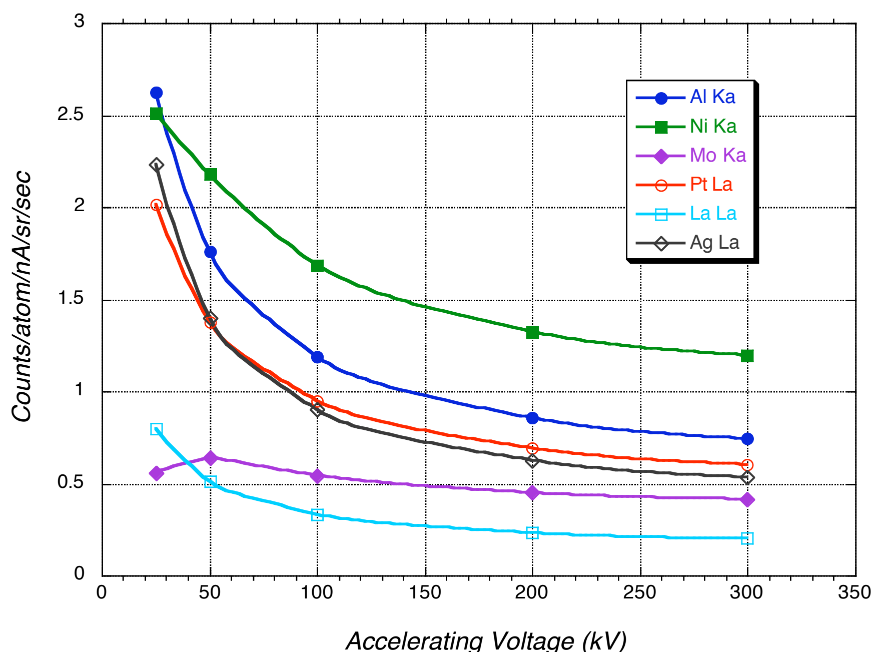

Figure 1. Calculated x-ray emission per atom for Al, Ni, Mo, Pt, La and Ag as a function of accelerating voltage (kV). These values should be scaled to the relative detection efficiency (ε) of the detector used for comparison to any experimental measurements.

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