

Pros and Cons of Low Voltage SEM EDX Elemental Analysis

Ed Boyes
 DuPont Company
 edward.d.boyes@usa.dupont.com

It was Castaing (1) who many years ago lamented "First I realized that in massive samples which concerned the metallurgists I would have to give up the splendid resolving power that I had cheerfully envisaged, as I became aware of the terrific path that my electrons would perform haphazardly in the sample before agreeing to stop. I had to limit my ambitions to analyzing volumes of a few cubic micrometers. This was a big disappointment . . .". In the early days most instruments for imaging and microanalysis of bulk samples were restricted to operating only at relatively high beam energies (~30kV) and for many (and perhaps too many) years this became the accepted operating procedure. However, we now know there are substantial advantages (pros) in using lower, and in some cases much lower, voltages; but also some significant limitations (cons). So what is possible?

The key is that at lower beam energy the electron penetration range into the sample is reduced greatly. For beam energy E_0 the range (R) can be approximated by the Bethe equation (2) with $R \propto E_0^{5/3}$. Changing the beam energy from 20kV to 5kV typically reduces the range by 10x and the excited volume ($\propto E^5$) by 1000x for the same x-ray line energy. The advantages are even greater at higher voltage ratios, e.g. ~100x and ~1,000,000x respectively at 1.5kV. Critically this moves electron microbeam analysis of bulk samples from resolutions at and above 1 micrometer (in this respect the laws of physics remain the same over the past half century), down into

EDS of 0.1µm Thin Film of Al on Si Substrate

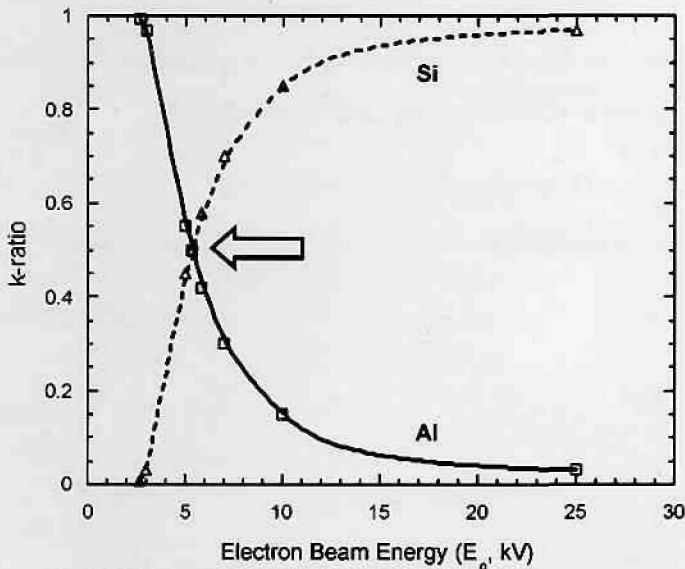


Fig. 1. EDX signals from 0.104µm Al thin film on Si substrate as a function of beam energy (kV).

the exciting sub-micron (1-0.1µm) and nanometer ranges. Many application technologies, including semiconductor microfabrications and pigment and fiber properties, have critical dimensions ~0.1-0.25µm determined by the half wavelength of blue light or soft UV radiation. Low voltage analysis is a key component of defect review tools for these production processes; and increasingly also a powerful research tool in the chemical, materials (3) and biological (4) sciences where many problems are on a similar length scale.

The previous wide gap between high voltage analysis of robust and representative wide area bulk samples in the electron microprobe or SEM at >1µm and thin section STEM for feature sizes <0.1µm is finally closed. In favorable circumstances, such as the analysis of carbon overlayers at 1.5kV, or Ta at 5kV, the need for thin sections is pushed back with demonstrated LVEDX SEM detection sensitivities down to <2nm for thin surface films (5). In addition, it is much easier and quicker to look at a surface film directly in plan view than to have to make a cross-section sample (which is also generally much easier for SEM than (S)TEM). Fortunately, the method is not too sensitive. With careful specimen handling thin surface films from oxidation in air (e.g. on freshly plasma cleaned Cu) do

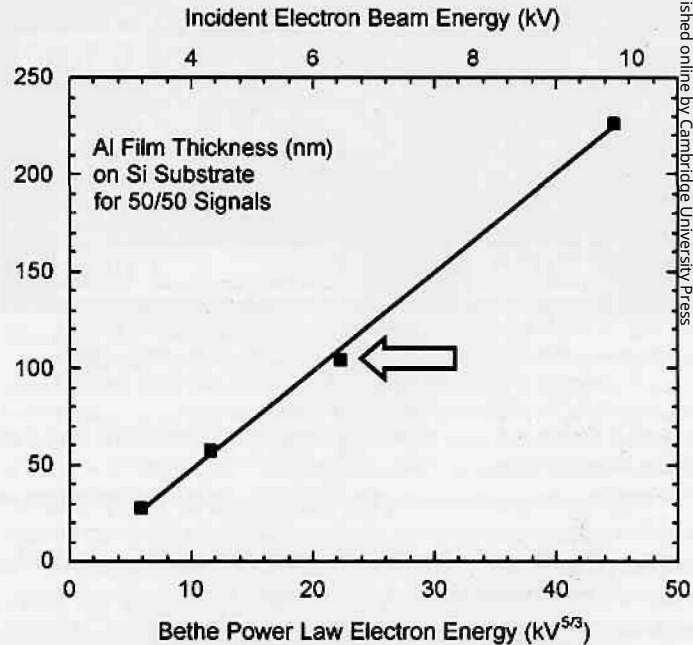


Fig. 2. Equal (Al, Si) EDX signals from Al thin films of various thickness on Si substrates with kV – the arrowed value is the 50/50 data transferred from Fig. 1

not create undue problems. For samples heterogeneous on a fine sub-micron scale the effect of geometry on the reported chemistry can be much greater than the traditional ZAF x-ray corrections. Fig. 1 shows the measured k-ratios for a 0.104µm thin film of Al on a Si wafer as a function of electron beam energy. Many of the properties of these two materials are similar and we can think of this as being a physically homogeneous sample with a buried chemical interface parallel to the surface. Sets of such data for different film thicknesses can be interpreted to show good agreement with the Bethe equation (Fig. 2). The arrows indicate the point of coincidence between Figs 1 and 2. The improvements in volumetric sensitivity extend well down into the nanometer dimension range and there is a corresponding dramatic improvement in the spatial resolution of x-ray maps at low voltages. Fig 3 (ZrO₂/ SiO₂ composite at 5kV) includes features down to 50nm or less in size recorded at an original magnification of 15,000x and far removed from the prior art. The special DuPont/Hitachi S5000SPX FESEM used here also provides ~1nm (2.5x) electron image resolution at 1kV and superior (0.3sr or 15x) EDX sensitivity. A potential downside of low voltage analysis is the increased energy density in the sample. This is the origin of the improved analytical resolution (pro) but it can also have undesirable (con) side effects including damage creation in sensitive samples. The total injected energy per x-ray count generated is increased only modestly (~2x) with kV and on a temporal or rate basis it is

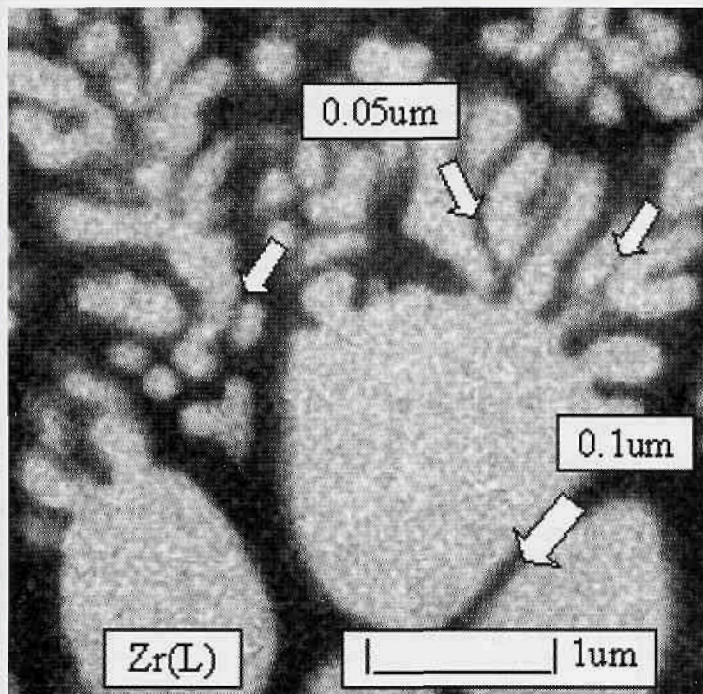


Fig. 3. High resolution chemical image map of ZrO_2 in SiO_2 matrix using $Zr(L)$ x-ray line at 5kV, 0.2nA/2nm probe, 256 x 256 spectral image recorded in 11 minutes live time on SPX system at 15,000x original magnification.

reduced. Contamination is also probably more prevalent, and it is certainly more visible, at low voltages.

The corollary of the limited interaction range for x-ray production with low voltage beams is the similar reduction in the x-ray escape path length, also by factors of $>10x$. This is generally much more important than differences in take-off angle. It can lead to a significant reduction, and in many cases the effective elimination, of matrix absorption (A) and fluorescence (F) in x-ray corrections. In this regard, but not in others (Z), there are some basic similarities to thin section corrections in the (S)TEM (6). However, in the SEM the "thin section" is created in the context of the surface of the wide area native sample by restricted penetration of the electron beam into the bulk, without the physical separation or reduction required for (S)TEM. Light element analysis is generally much improved, with better and more proportionate low Z representation, in spectra obtained at low beam voltages.

OK, if low voltages have all these wonderful advantages (pros) why was it not used much more widely and earlier? Well, there are some serious problems/snags (cons) too. Firstly, let us consider the fundamental physics. To excite an x-ray line with energy E_x requires we use a beam energy E_0 at least $1.3x E_x$; or an over voltage $U = E_0/E_x > 1.3$. There needs to be available a characteristic x-ray line at an accessible (for a signal) and useful (low enough for the application penetration range) energy. It should also have a workable fluorescent yield; for example with a 5kV beam Cu(L) does but Ti(L) is problematic. Secondly, the peak to background (P/B) ratios and kilocounts per second per nanoamp (kcps/nA) both decline significantly as the beam energy is reduced. For Si(K) the factor is $\sim 6x$ between 20kV and 5kV (fig.4). This reduces the actual mass sensitivity improvement due to geometry from $\sim 1000x$ to $\sim 150x$. Not catastrophic, in fact very useful; but not quite

as good as is first promised. In a new instrument (DuPont/Hitachi S5000SPX FESEM) we have more than compensated for the loss in kcps/nA by improving the EDX detection sensitivity by $\sim 15x$ over previous practice. This would apply across the kV range, except the 50kcps/nA and 2nm probe with Al at 5kV, and 10kcps with the 0.2nA we prefer, translates into an unmanageable $>1Mcps/nA$ for Pt at 30kV. By the way, it is clear signal strength (counts) matters more than a few eV energy resolution in low voltage analysis and larger area EDX detectors (30mm² etc.) are always preferred with FESEMs. Light elements in a heavier matrix will always be better represented in low voltage spectra irrespective of lateral resolution because of the reduction in matrix absorption and fluorescence. Thirdly, at lower analysis voltages, the corrections for Z become a strong function of the exact accelerating voltage translated to the sample (so no charging, please). For each system (element + microscope + detector etc.) this should be a one time determination using simple elemental standards or equivalent calculations. This is much more manageable than the alternative need at high voltages for large, variable (including sensitivity to local take-off angle) and complex A and F corrections (17x for O in SiO_2 at 30kV) at every analysis point. Depending on the detector characteristics, SiO_2 analyzes correctly below 10kV. The latter value is for a perfect detector – which does not exist (not close, yet) – and 3-5kV is typical for a good lo-Z system today.

It helps, especially for unknown samples, if the majority of elements can be analyzed at one beam voltage and 5kV fulfills this need with only a few exceptions; the most important of which is Barium. In principle 7kV covers everything; but as always with differing yields. At voltages in the 5-7kV range conductive coatings are often required to stabilize conditions at the specimen surface. We currently use thin (2-5nm) sputtered or evaporated Carbon and this is on the verge of detection at 5kV. At useful thickness ($>5nm$) metal coatings produce too many overlapping x-ray lines. This is a general problem even without a contribution from the coating be-

Si Wafer EDS Sensitivity and P/B as F(E_0, U)

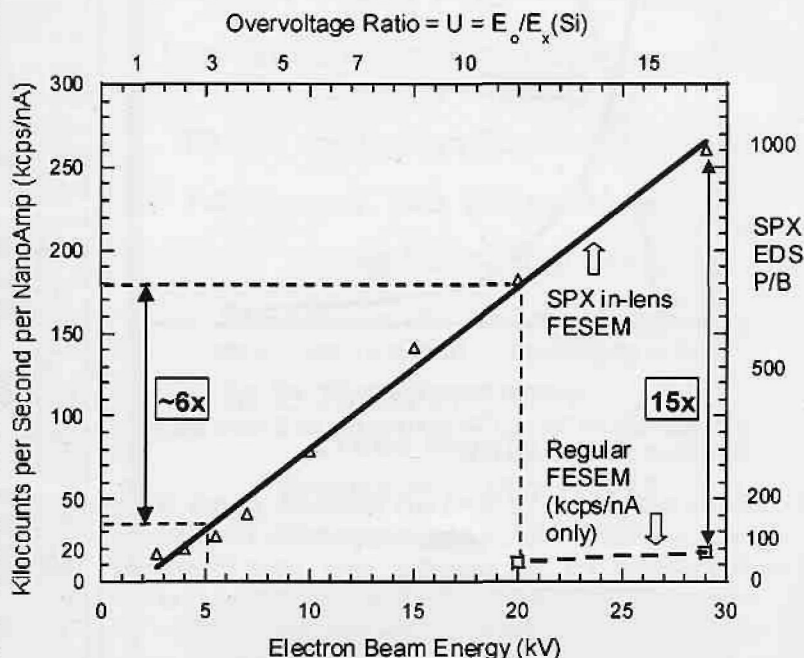


Fig. 4. Experimental x-ray yield and P/B ratio for Si with kV. Values from special SPX system but the slope with kV is universal.

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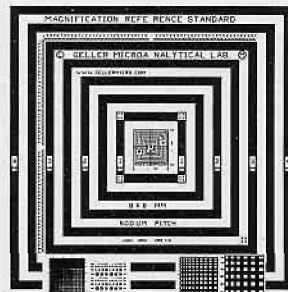
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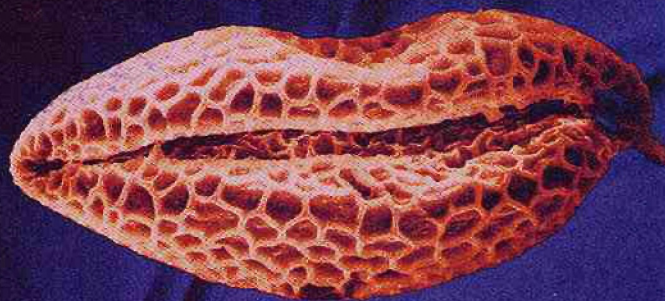
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Happy Valentine's Day



Jennifer LaPlante, '00, Ohio Wesleyan University

Jennifer is currently in medical school at the University of Florida. Image was taken using a LEO 435VP at the G.W. Burns SEM Laboratory. Submitted by Laura Tuhela-Reuning, OWU.

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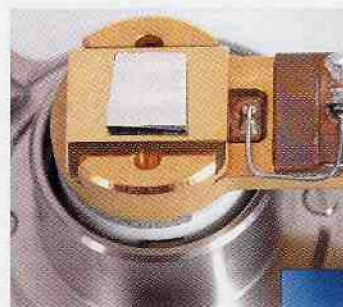
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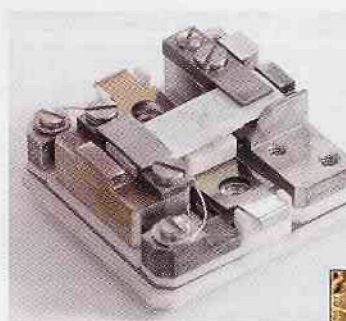


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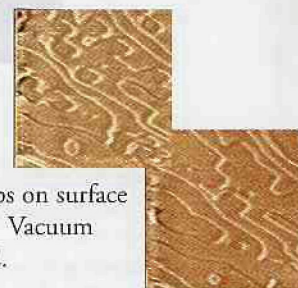


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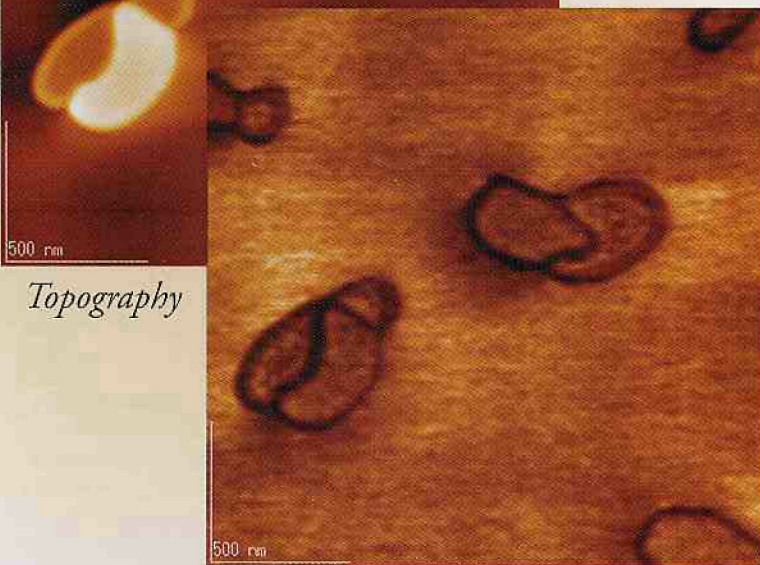
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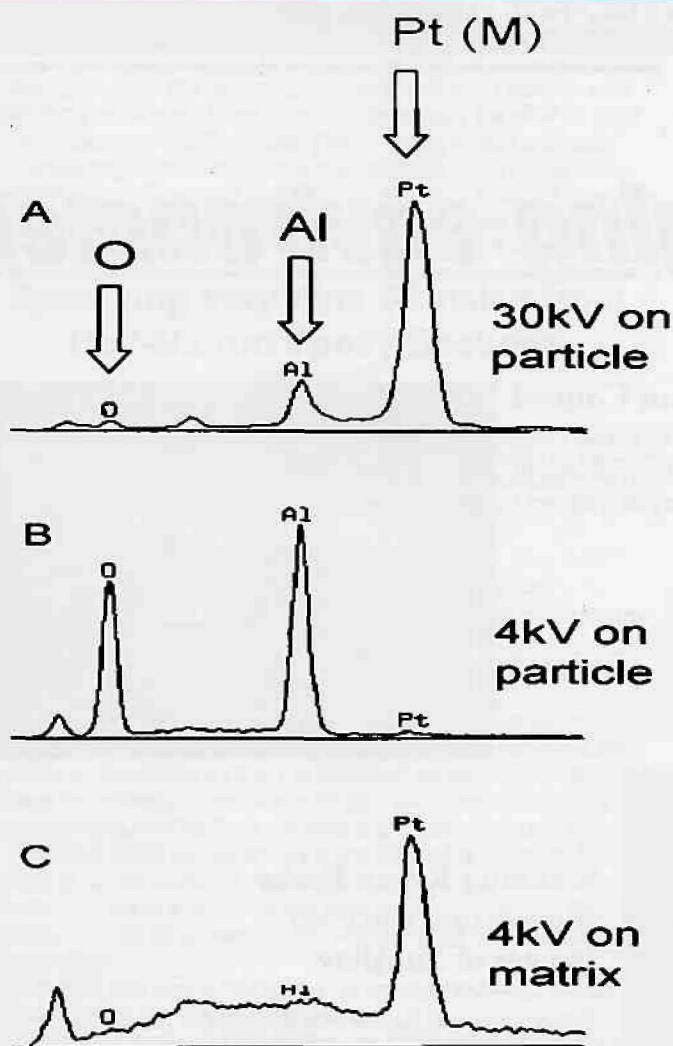


Fig. 5. Analysis of initially unknown particle (Al_2O_3) in Pt matrix with kV

voltage analysis is the proper representation of the oxygen light element component of the particle chemistry. With a complete forensic characterization it is possible to go look for effective solutions to the problem; or at least methods to ameliorate the negative consequences in key applications. In this case the quick solution was to coat the apertures on both sides with Pt or (much easier) Au-Pd; just like any other recalcitrant high voltage SEM sample.

The challenge now is to turn low voltage analysis into a more general quantitative procedure (10), including (more) reliable parameters for the lower energy x-ray lines, and to exploit the potential improvements in accuracy; especially for light elements in heavier matrices. The much higher spatial resolution at low voltages helps with one key condition for accurate quantitative analysis: the need to isolate homogeneous analysis volumes in a sample heterogeneous on a fine, sub-micron or nanometer, scale. Almost any SEM can be used for thin film depth analysis. Extending this to three dimensions is assisted by improved instrument configurations. As well as (10) this will be the subject of a future publication.

The characteristics of low voltage analysis include:

- Superior spatial resolution (>10x) and volume sensitivity (>1000x)
- Reduction or elimination of complex A and F matrix corrections at every point
- Proper representation of light elements in spectra - but still no magic for C in W or Si matrices
- Potentially more accurate quantitative analyses, especially of light elements - but a long way to go yet
- Restriction in x-ray lines (E_x) and beam energies (E_0) for analyses per element - we use a 130% minimum ratio for $U = E_0/E_x$
- Some low energy x-ray lines have poor fluorescent yields
- Z corrections are more dependent on accelerating voltage (E_0) at low over voltage (U) - but one time determination per system and set up using standards
- Yields and P/B ratios decline with lower kV, even for K and L lines - and P/B ratios are already lower for M lines
- Most elements are in principle accessible at 5kV, all of them at 7kV and a useful number of light and 3D transition elements at 1.5kV - and this is much more than Castaing had accessible in the first microprobe
- Multiple voltages can be used to deconvolute the depth dimension with trends in convergent chemistry
- New technology spectrometers will transform low voltage analysis by making a wider range of elements accessible through low and very low energy x-ray lines, and improving the P/B ratios and analytical sensitivity 10x or more
- Some of the limitations are fundamental but others can be improved with new approaches
- Overall we conclude that low voltage EDX analysis is a powerful new tool. In most, but not all, cases the pros outweigh the cons; especially on the sub-micron scale or for light elements.

The bottom line with low voltage methods is the minimum detectable mass is typically improved by >100x, and the volume sensitivity by >1000x, but for homogeneously distributed material the minimum mass fraction is degraded by up to 10x, but usually rather less. The method is best used to analyze the major constituents, especially lo-Z, in small volumes; rather than more widely distributed minor components of heavier elements. A series of very useful new methods have been added to the micro and nano analysis toolbox and they amount to much more than just very high resolution (~50nm) chemical image x-ray maps (useful as they are). ■

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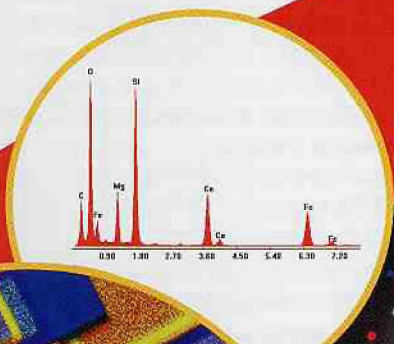
cause peak separations (e.g. Ta(M) and Si(K), $\Delta E_x \sim 31\text{eV}$) can be less than the 60-200eV energy resolution of the EDX detector. Overlap of the L lines of 3D transition elements, such as Cr, with light element K lines, such as O, is a problem in specific cases, as is the 60-80eV separation of adjacent 3D L lines. Classical WDX spectrometers have adequate energy resolution (~10eV) but their inefficiency in kcps/nA sensitivity requires the brutal high current beam conditions of a microprobe which may be specimen destructive for light (and not so light) elements (7). The advent of x-ray optics combined with parallel beam spectrometers (8), and eventually microcalorimeters (9), should help significantly with resolution of this problem. With the correct processing we have shown cold FEG systems can have both the emission stability (<1%/hr variation) and current (0.2-1nA at 5kV) for serial data collection, including spectral imaging maps (fig 3).

Fig.5 is an example of a surface containing an embedded rogue particle. In the high voltage (30kV) analysis (a) the particle chemistry is mixed up with major contributions from the surrounding matrix, in this case a heat treated Pt EM aperture. By reducing the beam energy to 4kV the matrix Pt(M) line is still adequately excited, if with its usual rather low P/B ratio (c) but the analysis on the particle (b) is now contained within the volume of that component. This is established by convergence of the chemistry as the voltage is reduced, since the embedded depth is initially unknown. Even if perfect separation cannot be achieved, the trend allows the component chemistries to be separated. A modern computer controlled instrument can (and should) be operated at a variety of voltages to best effect. The source of the contamination by alumina and other ceramics in this and other Pt applications may be due to incomplete reprocessing of recycled auto exhaust catalyst materials. A further benefit of the low

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