Low-Overvoltage Microanalysis: an Alternative High Resolution Strategy to Low-Voltage Microanalysis

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When improved spatial resolution for microanalysis is a critical requirement, the two leading strategies are (1) the thin specimen/high beam voltage option of analytical electron microscopy (AEM) and (2) the thick specimen/low beam voltage option of low-voltage scanning electron microscopy (LV-SEM).[1] If the specimen must be studied in bulk form, only option 2 is viable. However, with currently available wavelength dispersive (WDS) and semiconductor energy dispersive (Si-EDS) x-ray spectrometry techniques, the analyst frequently encounters severe constraints upon the suite of elements that can be effectively measured.[2] The choice of low voltage (defined as $V_0 \leq 5$ kV) greatly restricts the atomic shells that can be excited, which frequently forces the analyst to choose x-ray peaks with low fluorescence yields, e.g., Ti-L rather than Ti-K and Ba-M rather than Ba-L. WDS has sufficient spectral resolution to resolve most interferences encountered in low-voltage x-ray spectrometry and to produce a sufficiently high peak-to-background (P/B) for effective detection of most elements, even those with low fluorescence yield. However, the overall efficiency of the conventional WDS is so poor that it is not practical to operate with the low beam currents (typically $\leq$ nA) available in high resolution LV-SEM instruments. Si-EDS has adequate efficiency, but spectral resolution is so poor that low yield peaks are often not discernible above background, especially with the added complication of interfering carbon and oxygen K-peaks, a situation that is frequently encountered in practical materials.[2]

Low-overvoltage microanalysis offers an alternative route to achieving improved spatial resolution, but with the added advantage of utilizing the conventional choices for analytical peaks. This method is based upon the observation that the x-ray production range collapses very rapidly as the overvoltage, $U = E_0/E_c$, where E_0 (keV) is the incident beam energy and E_c (keV) is the critical excitation energy, decreases toward unity:

$$R \text{ (nm)} = [(27.6 \, A)/(\rho \, Z^{0.89})] \, [E_0^{1.68} - E_c^{1.68}] \qquad (1)$$

A and Z are atomic weight and number, and ρ is the density.[1] Thus, the strategy consists of choosing an x-ray peak with high yield, e.g. K rather than L, L rather than M, and then selecting a beam energy that provides a low overvoltage, $U \leq 1.25$, for that peak. As an example, consider the range of production for copper K-shell x-rays ($E_c = 8.98$ keV) in copper. For $U = 1.15$, the range for Cu K production is about 100 nm, and with $U = 1.25$ ($E_0 = 11.2$ keV), the production range is 175 nm. By comparison, utilizing a low-voltage microanalysis strategy with a beam energy of $E_0 = 2.5$ keV, which would provide an overvoltage of 2.7 for the Cu L shell, gives an x-ray production range of 37 nm, while $E_0 = 5$ keV ($U = 5.4$) gives an x-ray range of 138 nm.

Are low-overvoltage EDS spectra useful? Figure 1 shows an example of a spectrum for a 70Cu – 30Zn brass, for which the K-edges of Cu (8.98 keV) and Zn (9.66 keV) are sufficiently close to

simultaneously satisfy the low overvoltage condition for both the Cu K and Zn K x-ray peaks. The Si-EDS spectrum was recorded with a resolution of 129 eV (Mn Kα) at a beam energy of 11 keV, which gives an overvoltage of $U = 1.22$ for Cu and $U = 1.14$ for Zn. This level of excitation provides a peak-to-background (at 1.2 FWHM) of 6.15 for Cu and 1.86 for Zn. These P/B values and peak count rates (for a deadtime of 30%) result in limits of detection of 0.0098 mass fraction for Cu and 0.017 for Zn in this alloy with a single 100 s spectrum accumulation. Thus, major constituents ($C > 0.1$ mass fraction) are readily measurable under these conditions, while the full range of minor constituents ($0.01 \leq C \leq 0.1$) would require increased measurement time. Trace elements ($C < 0.01$) would only be accessible with high dose measurement conditions.

While there are other examples of technologically interesting combinations of elements with similar excitation edges, e.g., Fe-Cr-Ni alloys, GaAs, and InSb, that would be directly amenable to this low-overvoltage microanalysis strategy, the analyst will be confronted most often with mixtures of elements having excitation edges that span a broad range of energy. The low-overvoltage strategy can still be applied in this case through the use of two or more beam energies chosen to give similar overvoltage values for all peaks of interest. While procedurally more difficult, such a measurement strategy is entirely feasible with a modern computer-controlled instrument where even the beam position is well maintained while changing voltage. Moreover, there exist matrix correction procedures, such as NIST COR 2, that can calculate corrections when the suite of k-values is determined with different energies.[3] Moreover, low-overvoltage conditions result in matrix correction factors that tend strongly toward unity since absorption and fluorescence are negligible and backscattering effects are minimized.

References
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[3] J. Henoc,, K.F.J. Heinrich, and R.L. Myklebust, A Rigorous Correction Procedure for EPMA (COR 2), NIST (NBS) Technical Note 769, (Gaithersburg, MD, 1973).
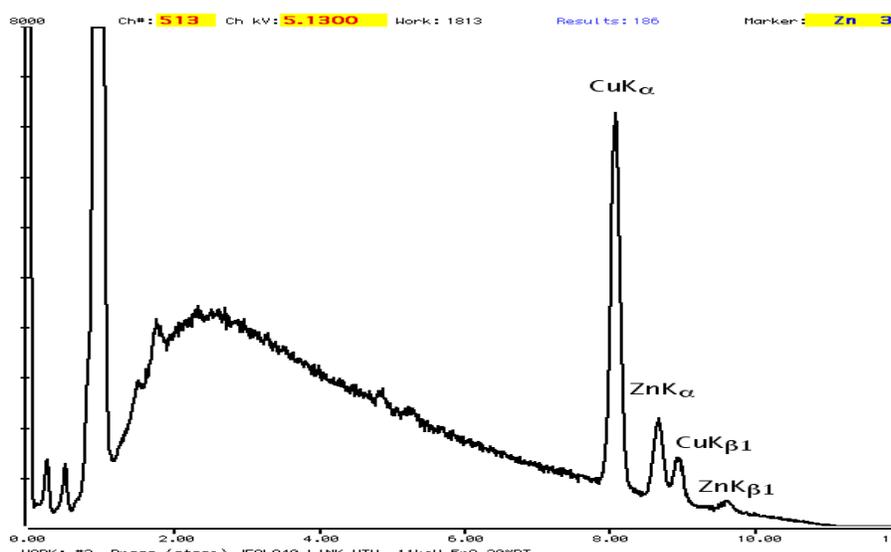
Figure 1 Low-overvoltage spectrum of brass (70Cu-30Zn), $E_0 = 11$ keV, 30% deadtime