Quantitative electron probe microanalysis: State of the art

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Quantitative electron-probe microanalysis (EPMA) has improved due to better instrument design and x-ray correction methods. Design improvement of the electron column and x-ray spectrometer has resulted in measurement precision that exceeds analytical accuracy. Wavelength-dispersive spectrometers (WDS) have layered-dispersive diffraction crystals with improved light-element sensitivity. Newer energy-dispersive spectrometers (EDS) have Si-drift detector elements, thin window designs, and digital processing electronics with x-ray throughput approaching that of WDS systems. Using these systems, digital x-ray mapping coupled with spectrum imaging is a powerful compositional mapping tool.

Improvements in analytical accuracy are due to better x-ray correction algorithms, mass absorption coefficient data sets, and analysis methods for complex geometries. ZAF algorithms have been superceded by $\Phi(\rho z)$ algorithms that better model the depth distribution of primary x-ray production. Complex thin film and particle geometries are treated using $\Phi(\rho z)$ algorithms, and results agree well with Monte Carlo simulations. For geological materials, x-ray absorption dominates the correction and depends on the accuracy of mass absorption coefficient (MAC) data sets. However, few MACs have been experimentally measured, and the use of fitted coefficients continues due to general success of the analytical technique. A polynomial formulation of the Bence-Albee α-factor technique, calibrated using $\Phi(\rho z)$ algorithms, is used to critically evaluate accuracy issues and can be also be used for high speed digital map correction. Accuracy now approaches 1-2% relative and is limited by measurement precision for ideal cases, but for many elements the analytical accuracy is unproven. The EPMA technique has improved to the point where it is frequently used instead of the petrographic microscope for reconaissance work.

Examples of stagnant research areas are: WDS detector design, characterization of calibration standards, and the need for more complete treatment of the continuum x-ray fluorescence correction.

SEM/EDS x-ray spectrum imaging above 100 kHz with the silicon drift detector (SDD), and how to locate the proverbial needle in a haystack, even when you don't know it's a needle that you are seeking!

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Energy dispersive x-ray spectrometry (EDS) performed with conventional semiconductor detectors is limited to output count rates (OCR) below 3 kHz at optimum resolution (~129 eV at MnKα) and 30 kHz with resolution degraded to ~180 eV. Silicon drift detectors (SDD), the newly emerging EDS technology, can deliver OCRs of 15 kHz at 129 eV and >300 kHz with ~180 eV [1]. OCR above 500 kHz may eventually be possible. Such high OCR makes SEM/x-ray spectrum imaging (XSI) routine: a 128x128 pixel image with 10 ms per pixel dwell time and 1.3 ms overhead (for spectrum storage of 2048 10eV-channels, 2-bytes deep and beam positioning) can be accumulated in 185 s. The XSI incorporates all possible elemental information about the region imaged, within the performance limitations of the SDD-EDS. With this extraordinary speed, we are in a position to make much greater use of x-ray mapping for evaluating chemical microstructures. However, an abundance of XSIs will only be useful if we can effciently mine these massive data structures, each 100 Mbyte or larger. XSIs can be considered like a stack of images, each at a different x-ray channel. Bright and Newbury [2] have extended the method of calculating “derived spectra” from the XSI. A “derived spectrum” is a spectrum-like display of intensity vs. channel number in which the intensity at a particular channel is calculated from all or a portion of the counts recorded in that channel image, depending on the algorithm applied. The widely used SUM spectrum adds all the counts in a channel image to represent a particular channel. Peaks in the SUM spectrum represent prominent XSI features. The newly developed MAXPIX spectrum, calculated by finding the maximum value at any pixel within a channel image, is sensitive to rare events, down to the level of single pixel. The MAXPIX spectrum can recover unanticipated, extremely rare XSI features, thus finding an unknown needle in the haystack.

References

[1] Barkan, S. et al. (2004) Microscopy Today **12**, 36-37.
[2] Bright, D. & Newbury, D. (2004) J. Micros. **216** 186-193.