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Quantitation Procedures for Electron Probe Microanalysis of Polished Materials, Thin Films and Particles: The Past and Next Thirty Five Years

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Thirty five years ago, when Joe Goldstein organized the first Lehigh Short Course on Scanning Electron Microscopy and X-ray Microanalysis, quantitation procedures for thick, polished materials were already well developed. The correction procedures first proposed by Castaing had been tested and modified, and the seminal papers describing the "ZAF" corrections (still in use) had all been published [e.g., 1]. Various computer programs incorporating the ZAF correction procedures had been developed by researchers like Joe Goldstein, John Colby and John Ruckledge and were in common use by most of the microprobe community. An alternate "a-factor" correction scheme, developed by Ziebold and Ogilvie for metals and adapted by Bence and Albee for silicates and oxides, was gaining in popularity in the geological microprobe community.

Both ZAF and a-factor correction procedures gave reasonably satisfactory results for the type of specimens most commonly analyzed. Although at the yearly meetings of the Electron Probe Analysis Society of America, various researchers reported new measurements of the correction parameters and suggested improvements of the procedures themselves, most attention was devoted to the widely increasing range of applications and developments in instrumentation. Microprobe quantitation appeared to be fairly mature. As Castaing wrote some twenty years later, "At this time it (electron probe x-ray analysis) was already an old story; now it looks like prehistory." [2, p.1].

During the past thirty-five years, the state-of-the-art in electron microprobe quantitation has considerably increased in many areas and foundered in others. For thick polished specimens, the ZAF corrections (and to a lesser extent the a-factor corrections) have continued to be used with only modest improvements in the algorithms and parameters employed. However, a plethora of alternate correction procedures have been published based on Monte Carlo calculations and various schemes for Gaussian or parabolic fits to $\phi(\rho z)$ curves. These procedures in many cases have enabled superior accuracy for many specific types of materials – particularly in the areas of low voltage and soft x-ray analysis. However, a number of these corrections were formulated with empirical factors to best fit specific sets of data, often resulting in relatively poor accuracies for other types of "problem samples". Many different combinations of correction algorithms and parameter sets are employed in the various programs in current use. Unlike the early years, when the choice of computer program was the decision of the microprobe operators, who had source codes of the program and might well make their own refinements, most laboratories today use the commercial software supplied with their instruments – sometimes using unpublished proprietary corrections and often poorly documented. As a result various laboratories could analyze the same materials with the same standards, obtain the same raw data, and report significantly different results. Some attempts were made (many of these in association with the Lehigh School) to develop stand-alone software that would enable the analyst to compare and evaluate the various correction procedure alternatives – programs like NIST's DTSA, David Joy's Monte Carlo programs, and this author's CITZAF [3-5].

Significant efforts have been made by the commercial x-ray detector manufacturers (particularly of EDS systems) to simplify analysis methods and lower the required skill level needed, including development "standardless" analysis programs that utilize spectral generation calculations to simulate standards or adapt stored standard spectra. These programs vary considerably in the accuracy obtained depending on the analytical conditions and composition of the sample. Currently, efforts are underway to design "smart systems" that provide users recommendations of the analytical conditions to employ for their specific analytical needs.

The greatest advances in quantitation made during this time were with respect to the variety of sample types for which reasonably accurate analyses could be performed. Advances in Monte Carlo calculations and $\phi(\rho z)$ correction models led to robust correction procedures for analysis of light elements as well as thin films and layered specimens [3]. Several competitive procedures were developed that enabled accurate analysis of individual microparticles [6]. All of these new developments became part of the curriculum of the Lehigh short courses.

Many worthy tasks in refining x-ray microanalysis quantitation await the next 35 years. Monte Carlo calculations are likely to continue to develop with respect to flexibility, ease of use, and versatility. It is very likely that they will form the basis for the next generation of correction procedures for layered specimens, particles, inclusions, grain boundaries and irregular surfaces. One can imagine combining image analysis, pixelization, and Monte Carlo methods to combine spectral and image data together for accurate analysis. Monte Carlo methods may replace ZAF and $\phi(\rho z)$ methods for bulk specimens. If so, better measurements of the fundamental parameters that are utilized by these models must be made as well as further refinement of the electron scattering, ionization cross section and electron energy loss models employed. Undoubtedly, further work will be done in simplifying microanalysis software and developing more sophisticated standardless analysis procedures. These too will need additional fundamental measurements. The use of multiple accelerating potential and multiple specimen tilt measurements in more fully automated instruments to characterized layer thin films and other multiphase samples will require better data sets on which to refine correction methods. Perhaps most importantly, we need to continue to train new analysts about x-ray microanalysis in fresh and creative ways and not turn it into a routine, "mature", stagnant method. For these challenges, Joe Goldstein's combination of creative development of microanalysis methods, creative science using microanalysis, and creative teaching of the state-art-the-art to generations on microprobe analysts remains as a shining example.

References

[1] Quantitative Electron Probe Microanalysis, K.F.J. Heinrich, ed., NBS Special Publication 298, U.S. Gov. Printing Office, Washington, D.C. (1968).
[2] Electron Probe Quantitation, K.F.J. Heinrich and D.E. Newbury, eds., Plenum Press, NY (1991).
[3] J.A. Small, D.E. Newbury, and J.T. Armstrong, J. T., in Handbook of X-ray Spectrometry, 2nd ed., R. Van Grieken and A.A. Markowicz, eds., Marcel Dekker, Inc., NY, (2002) pp. 811-926.
[4] D.C. Joy, Monte Carlo Modeling for Electro Microscopy and Microanalysis, Oxford University Press, New York (1995).
[5] J.T. Armstrong, *Microbeam Analysis* 4, (1995) 177-200.
[6] J.T. Armstrong, in Electron Probe Quantitation, *op. cit.*, p261-315.

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