

Bence-Albee Corrections and Secondary Standards: A Part of Art Chodos' Legacy of High Quality Microprobe Analysis that Needs to be Revived

*J. T. Armstrong

* American University, Department of Chemistry, 4400 Massachusetts Ave., NW, Washington, DC 20016; AAES Consulting, 9112 Roundleaf Way, Gaithersburg, MD 20879

Electron microprobe analysis was validated in the late 1960's and 1970's as a versatile technique for high-accuracy quantitative elemental analysis by the types of results obtained on geological, lunar and meteoritic specimens by microprobe laboratories like that of Art Chodos at Caltech. The electron microprobe proved to be one of the most reliable and versatile tools for the characterization of the returned lunar samples from the Apollo missions. The results obtained in Chodos' laboratory were of exceptional quality and there was excellent agreement among the various microprobe laboratories analyzing different sections of the same lunar rocks [e.g., 1]. Among the reasons for this were (1) a common use of one of two well-defined correction procedures for the microprobe data and (2) an inter-laboratory cooperative sharing of mineral and glass standards and the measurement of selected secondary standards at each analytical session for quality control. During this period, each user of the electron microprobe in the Caltech laboratory analyzed one of two secondary standards each day, and a collective record of all of the raw and processed standard data was maintained. As a result, there was a reasonable degree of traceable data comparability among users over the years within the Caltech laboratory as well as in those other microprobe labs that used the standards provided by Art Chodos.

Most geological laboratories used either a correction procedure developed at Caltech by Bence and Albee [2] based on semi-empirical "a-factors" or a ZAF correction procedure based on a choice of algorithms outlined by Sweatman and Long [3]. Most laboratories had access to both procedures and there was considerable inter-comparison of the results obtained by each. The Bence-Albee a-factors were calculated from the ZAF corrections, but were modified by fitting to experimental data when the corrections were found to produce systematic errors in certain mineral systems – a refinement that was much easier to achieve with the a-factor method than the ZAF method.

The a-factor method was based on the observation, first made by Castaing, that the relation between relative intensity, k_{AB}^A , and relative concentration, C_{AB}^A , in a binary system can be approximated by a hyperbolic curve: $(1 - k_{AB}^A) / k_{AB}^A = [(1 - C_{AB}^A) / C_{AB}^A] a_{AB}^A$, where the a-factor, a_{AB}^A , gives the degree of curvature. This expression can be rearranged as: $(C_{AB}^A / k_{AB}^A) = a_{AB}^A + (1 - a_{AB}^A) C_{AB}^A$; thus the a-factor can be determined by the intercept and (1 – slope) of a linear plot of measured values of (C_{AB}^A / k_{AB}^A) vs. known C_{AB}^A . Alternatively, the a-factor can be made from a single measurement of k_{AB}^A for a known C_{AB}^A by the relation: $a_{AB}^A = [(C_{AB}^A / k_{AB}^A) - C_{AB}^A] / (1 - C_{AB}^A)$. Using this expression, the a-factor can be calculated for different concentrations in a system and the validity of the hyperbolic approximation can be tested [4]. For multi-component systems, C/k can be calculated by a linear combination of concentration-weighted a-factors for the individual binary components [2]. The a-factor method has not widely been used for metal or semiconductor systems due to the inadequacy of the hyperbolic approximation for systems with large fluorescence corrections (or very large atomic number and absorption corrections), but has been widely used by the geological and ceramics communities – particularly in the 1960's-1980's, and to a lesser but still considerable extent today.

Over the years, it became clear that there were a number of silicate and oxide systems for which the simple hyperbolic approximation of the original Bence-Albee procedure resulted in systematic errors. Albee and Bence noted this problem in their early papers and Armstrong proposed a polynomial a-factor algorithm that appears versatile enough to accurately fit all of the commonly used ZAF, Phi-Rho-Z, and Monte Carlo corrections [4-9]. A database of high precision analyses of secondary standards in the system MgO-Al₂O₃-SiO₂-CaO measured in Art Chodos' laboratory was used to develop a set of refined empirical polynomial a-factors for this important geological system that significantly improved analyses compared to any of other then available correction procedures [4-5]. However, the use of a-factor corrections, particularly in the automation software of newer electron microprobes and EDS systems, diminished as improved laboratory computers eliminated program size and computational speed as significant factors. Today, many different algorithms are employed, the method documentation and publication of secondary standard analyses are rarer, and direct comparison of data from one laboratory to another has become more difficult [9].

The a-factor approach, so successfully implemented by Art Chodos, still has significant advantages and should continue to be developed. 1) The polynomial a-factor equation is versatile enough that it can near-perfectly fit C/k ratios calculated by any of the currently used correction procedures and thus be a high speed clone. Tables of calculated a-factor coefficients can serve as a permanent archive for back-calculation of the corrections applied. 2) Most practical microprobe applications involve a limited number of major or minor elements in the presence of a limited number of other major elements. For those cases, calibration curve data from secondary standards can be used to refine the specific a-factors involved; much easier than can be done using a limited set of data to change quasi-theoretical correction algorithms. 3) There are growing applications for accurate analysis of specimen types (particles, layered specimens, etc.) and analytical conditions (non-normal beam incidence, multiple accelerating potentials, etc.) for which conventional correction algorithms do not apply. Monte Carlo calculations are now more often applied to such types of specimens, but the calculations are too extensive and the programs too operator-intensive at this time to be practically employed as a real-time correction procedure. However, these calculations can be made off-line, the results tabulated, and matrices of a-factors determined which then could be used (and archived) for rapid, simple data correction. 4) a-factor plots using different correction procedures can be readily compared to each other as well as measured data to determine systems or conditions for which various correction models may produce significant errors. Each of these applications for a-factors has significant demonstrable advantages over the current crop of widely used corrections. The analytical legacy of Art Chodos is still valuable and relevant today.

References

- [1] S. R. Taylor, *Lunar Science: A Post Apollo View*, Pergamon Press, New York, 1975.
- [2] A.E. Bence and A.E. Albee, *J. Geology* 76 (1968) 382.
- [3] T.R. Sweatman and J.V.P. Long, *J. Petrology* 10 (1969) 332.
- [4] J.T. Armstrong, *J.T. Microbeam Analysis – 1984*, 208-212, 1984.
- [5] J.T. Armstrong, *Microbeam Analysis - 1988*, 469-476, 1988.
- [6] J.T. Armstrong, J.T. In: *Electron Probe Quantitation*, Heinrich, K.F.J. & Newbury, D.E. (eds), Plenum Press, New York, 261 – 315, 1991.
- [7] J.T. Armstrong, *Microbeam Analysis 2* (1993) S25.
- [8] P. Carpenter and J.T. Armstrong, (1998) *Microsc. Microanal.* 4 (Suppl. 2), 224.
- [9] J.T. Armstrong, *Microsc. Microanal.* 10 (Suppl. 2) (2004) 121.