The empirically observed linear relationship between relative x-ray intensity and relative concentration is the basis for a simplified approach to electron microprobe data reduction which is compatible with computer control of the x-ray spectrometers. Element oxide matrix effects, predetermined using empirical and theoretical techniques, are concentration weighted in a polycrystal phase analysis. Successive iterations refine the matrix correction factor for each characteristic x-ray line measured. These correction factors define the relationship between relative x-ray intensity and relative concentration for each element. [The SCP indicates that this paper has been cited over 230 times since 1966.]

A. E. Bence
Department of Earth and Space Sciences
State University of New York
Stony Brook, NY 11794

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"When this project was conceived at California Institute of Technology in early 1967, the impact of the electron microprobe in mineralogy was just being felt. However, its utilization as an everyday analytical technique was stifled by two factors. First, data collection in polycrystal systems (9-10 elements in some common rock-forming minerals) was a laborious task, and second, the complicated data reduction techniques needed to correct for matrix effects were time consuming and required access to large computers with their inherently slow turn around times. The combination of these precluded the rapid turn around of analyses and few laboratories utilized the probe to its full capacity. Those that did relied on large libraries of mineral standards whose analyses were of variable and, quite frequently, dubious quality. Our objectives, in this joint effort, were twofold: to develop simplified data reduction procedures that could be carried out on the hand calculators then available, and to lay the groundwork for computer control of the x-ray spectrometers thus permitting online control and real time data reduction

"The fundamentals for the matrix correction procedures were established in 1964 by T. Ziebold and R. Ogilvie who noted that in simple binary metallurgical systems, where fluorescence was not severe, an approximately linear relationship existed between relative x-ray counts and relative concentration. This relationship, C/K = \(\alpha + (1-\alpha)C\), introduced an aggregate matrix effect, \(\alpha\), which includes the three corrections, absorption, atomic number effect, and fluorescence. In polycrystal systems, the correction factor for each x-ray signal, assuming no second order effects, is the sum of the concentration weighted \(\alpha\)-factors for that radiation.

"We applied this technique to silicate and oxide systems by amassing a library of natural and synthetic standards and then measuring \(\alpha\)-factors in binary systems for which sufficient standards were available. In systems where sufficient standards were not available, correction factors were calculated from the theoretical/empirical relationships currently in use in microprobe data reduction. Extrapolation into ternary systems was then made. Nearly 18 months went into obtaining and testing the data. With the basic data collected, refinement and upgrading, using improved theoretical approaches, became a relatively simple process. Furthermore, as small computers appeared, the step to automation and online data reduction became simplified. The first automated electron microprobes to be established in mineralogical laboratories used this reduction procedure. In the succeeding years, as more precise analytical data were desired, continual refinement of the \(\alpha\)-factors occurred.

These data now reveal that a truly linear relationship in some binary systems is an oversimplification and polynomial expressions should be used.

"The success of the technique is attested to by the number of laboratories that use it to reduce their data. We are gratified that this approach, conceived out of frustration, became so readily accepted."