EDATA2: A FORTRAN IV COMPUTER PROGRAM FOR PROCESSING WAVELENGTH- AND/OR ENERGY-DISPERSIVE ELECTRON MICROPROBE ANALYSES

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The development of EDATA2 was stimulated by the proliferation of mixed energy dispersive/wavelength dispersive equipped electron microprobes. For such systems to be operated most efficiently and conveniently, a data reduction program is required that can handle energy-dispersive, wavelength-dispersive, or a mixture of both kinds of data. This requirement has become particularly pressing with the widespread introduction of a high degree of automation, which permits either kind of data to be gathered rapidly and reliably. If the reduction of data to give the compositional information ultimately required is not to present a bottleneck, software must be versatile, running times short, and costs low.

In the development of EDATA2 (Fig. 1) the design philosophy of its predecessor, "EDATA," was retained in that an automatic rather than an interactive program was constructed. In any laboratory where an appreciable part of the operation involves producing large numbers of analyses, it is desirable that minimal intervention be required during data processing. EDATA1 was developed to process only energy-dispersive analyses, and was limited to handling analytical data for elements of atomic number 11 (Na) to 30 (Zn), plus Zr and Ba. These elements cover the compositions of most silicates, as well as many other minerals. However, EDATA2 permits the specification of any suite of up to 22 analyzed elements (from Z = 9 to 92).

An empirical expression for the relationship of continuum intensity to atomic number, continuum energy, and accelerating potential has now been reinvestigated for an accelerating voltage of 15 kV, continuum energies up to 10 keV, and for atomic numbers up to 92; the following new expression was obtained:

\[ I_v = k \sum_i \{ C_i \left[ (E_v - E_{1v}) / E_{1v} \right]^{n_i} \} \]

where \( x_i = a - 0.00145(Z_i - E_v) \) and the constant \( a \) = 1.5, \( Z_i \) = atomic number of element \( i \), \( C_i \) is the concentration of element \( i \), \( I_v \) = continuum intensity at an energy \( E_v \), and \( n_i = E_v \left[ (0.0739 - 0.0051 \ln Z_i) + p \right] \), where \( p \) is a constant. Although this expression differs somewhat from that proposed by Smith,2 its value is very similar within the atomic-number range then investigated. The new expression is incorporated into EDATA2. It has been tested to date only at one operating voltage (15 kV) and one take-off angle (52.5°), but facilities to test it under various analytical conditions have now been built into the program. The dependence on atomic number of both exponents (that is, \( n \) on \( Z \) and \( x \) on the energy term) was looked for but not observed by Smith et al. in the more limited atomic-number range then investigated, although Rao-Sahib and Wittry suggested such a dependence.3

Since spectra can be acquired at different probe currents and for different counting times, the calculated background must be scaled to the sample spectrum. In EDATA2, a new approach has been taken to this scaling: the ratio of calculated background to sample spectrum is determined for each channel, so that a 'histogram' is produced (Fig. 2). The program finds the ratio at the smoothed maximum of this 'histogram' and scales using this factor. A parameter is printed reflecting the histogram peak width—a measure of the success of estimation of background shape.

EDATA used stored values for such parameters as mass absorption coefficients, emission wavelengths, and absorption edge energies. With the extension to \( Z = 92 \), space and data entry requirements become very severe. Expressions published by Springer and Nolan were therefore used to calculate these parameters.4 Continuum fluorescence corrections used by Springer were also incorporated.

The other principal improvement in the capability of EDATA2 over EDATA is its capacity to handle wavelength-dispersive as well as energy-dispersive data. This facility is de-

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FIG. 1. – Flow diagram for EDATA2. Subroutine names are shown underlined.
FIG. 2.--Background scaling histograms for rutile (excellent fit) and fluorapatite (poorer fit). "Ratio parameter" is the ratio of sample spectrum to computed background, calculated for each channel as a multiple of the lowest average ratio found for 10 adjacent channels ("min. ratio").
each system. WDA data are therefore given priority. Furthermore, if an element is specified as having been analyzed by WDA, but no standard information is supplied, the program automatically defaults to EDA. If no EDA standard data were acquired, the program turns to EDA default standard values—values measured previously, corrected for matrix effects, and stored.

The approach to overlap corrections used in EDATA has been retained. Values are obtained for overlap coefficients by using the program itself to determine the extent of overlap of each element into the analytical region for every other element to be analyzed. These coefficients are corrected for background-and matrix effects. Overlap coefficients of elements to be determined by WDA must also be included. Comparison of coefficients for elements from F to Zn reported on previously with those obtained recently by means of the revised background correction clearly indicates that minor misfits at the low-energy end of spectra for elements of higher atomic number have largely vanished.

Several other new features have been incorporated into EDATA2. A review of archival tape records of every analytical run between May 1975 and September 1976 revealed a progressive change in the measured ratio of Zn L to Zn K intensities in the Zn2SiO4 calibration standard spectrum, owing to gradual contamination of the detector Be window with pump oil. Based on Zn K : Zn L intensity ratios observed for the calibration standard, EDATA2 now corrects all spectra back to the intensities which would be observed with an ideally clean Be window.

Escape peak stripping is performed by use of a modification of an expression suggested by Statham. However, this modification has been tested only for normal incidence of x rays onto the detector; if variable, non-normal incidence is used, Statham’s unmodified expression should be reintroduced together with an opportunity to enter appropriate angles for each analysis.

EDATA2 has retained most of the other features of EDATA, such as automatic measurement of energy miscalibration based on a calibration standard, and correction of all spectra back to ideal calibration. Peak integration ranges are established on the basis of current resolution measured on the calibration standard. A peak-seeking routine locates and identifies peaks. Their FWHM, approximate intensities, peak to background ratios, and identities are reported in the program output.

Although experience suggests that 15 kV is a good accelerating potential for most purposes, any potential may now be used in combination with a chosen width and number of channels. However, when any of these parameters is changed the program must be recalibrated in terms of the background-intensity expression, overlap coefficients, and default standard values. Thus, once values for these parameters have been chosen, the analyst will not wish to change them without good reason.

A feature of EDATA is the presence of two subroutines, AJST and CALC. The former calculates the concentration of elements not analyzed (e.g., oxygen) either on the basis of input information or by difference from 100%. Calculations made in AJST are iterated along with ZAP corrections, etc., until convergence is achieved. On the other hand, CALC is called only once, at the end of data processing, and manipulates corrected data and presents them in whatever form is most-useful for the user. In EDATA2 more complex and sophisticated AJST and CALC programs have been incorporated and offer the user a much wider range of options.

The success of the new program can be judged in several ways. For example, background corrections can be tested by plotting the calculated background and the background-subtracted spectrum, as has been done for four substances of varying atomic number and complexity in Fig. 3. In each case residuals are trivial.

Table 1 shows analyses of basaltic glass processed by several options. First, the 'normal' procedure of analyzing samples against standards measured during the same run, with a calibration standard at the beginning and end, was adopted. Second, the same procedure was used except that only one calibration standard was read, at the beginning of the run. Third, standards measured during the run were not used, but sample intensities were measured against 'default' values. In this case, not only were 'default' standard values used, but also no calibration standard was used and samples and standards were made to self-calibrate.
FIG. 3.—Calculated background and background-subtracted spectra for kaersutite [Ca₂(Na,K)(Mg,Fe)₃Ti(Si₆Al₂O₂₋)(O,OH,F)₃]; cobalt and silver metals, and uranium silicide [U₃Si]. Note that the small peak centered at about 1.5 keV in the silver spectrum with a small valley on either side may be an artifact of the escape peak correction and result from the different widths of the escape and parent peaks.
### TABLE 1.

Composition of basaltic glass. I; best available independent information; II; EDATA2 analytical standards and a calibration standard at the beginning and end of run; III; same as II but without second calibration standard. IV; without either analytical or calibration standards, i.e., using the sample spectrum itself to determine stretch and shift corrections, and 'default' (i.e., stored) values instead of analytical standards. All analyses recalculated H₂O-free to 100% from analytical totals in parenthesis. Oxygen determined by stoichiometry.

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### References


