

SOFTWARE NOTICE

A practical interactive least-squares cell-parameter program using an electronic spreadsheet and a personal computer*

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ABSTRACT

A program using single-page electronic-spreadsheet templates has been developed for Microsoft EXCEL version 1.5 on an Apple Macintosh SE computer or Microsoft EXCEL version 2.0 for the MS DOS environment to facilitate the efficient calculation of unit-cell parameters for each of the six crystal systems. Input can be as simple as wavelengths of the radiation used and a set of up to 40 indexed 2θ values for well-defined reflections. Output includes both direct and reciprocal cell parameters refined by the methods of least-squares, estimated standard errors of the cell parameters, d observed and calculated, and $Q(hkl)$ observed and calculated, as well as Δd and ΔQ . Individual hkl 's can be quickly modified, and systematic errors in 2θ can be corrected. Refined data for a monoclinic amphibole, kaersutite, from the Cima volcanic field located in the eastern Mojave Desert in California are presented and compared with results of the 1973 Appleman-Evans cell-parameter program run on a MS DOS system.

The templates—one for each crystal system—are ideal for instruction in mineralogy, X-ray diffraction, or computer applications and programming in geology and are well suited for research. In either the Macintosh or MS DOS environments, one simply opens the EXCEL application and a least-squares template for the required crystal system and substitutes new data (2θ and hkl) for the given example data. These six templates along with operational documentation are public domain and are available from the authors.

INTRODUCTION

Electronic-spreadsheet programs for personal computers were first introduced with VISICALC for the Apple computer in 1980. Initially, spreadsheets were intended primarily for business applications; however, evolution of these programs toward the inclusion of numerous algebraic, trigonometric, statistical, and logical functions and, especially, matrix operations, accompanied by advances in microcomputing hardware, have made it possible to use spreadsheets for a variety of scientific applications. Microsoft EXCEL and other comparable spreadsheet programs have certain features that make them powerful research tools and teaching aids: they can be easily presented as tables in publications; formulas reside behind individual spreadsheet cells or array functions behind groups of cells; they have many automatic graphing and charting capabilities; finally, and probably most important, they possess a user-friendly macro programming language, analogous to BASIC, that allows development of complex user-defined functions and interactive programs within the spreadsheet environment.

TEMPLATE DESIGN

Six different least-squares single-page templates (one for each crystal system) have been developed on an Apple Macintosh SE computer using the spreadsheet software EXCEL version 1.5 by Microsoft. These least-squares templates with minor modification can also be used on MS DOS computers with Microsoft EXCEL version 2.0. The set of templates occupies approximately 400K of a 3½-inch floppy disk.

Figure 1 is the screen-dump of the monoclinic least-squares spreadsheet template with example data of a kaersutite megacryst from the Cima volcanic field of eastern California (Colville and Novak, unpub. data). Input data consists of 38 pairs of 2θ values measured on a Philips 1840 powder diffractometer along with the appropriate hkl value for each observation. Each EXCEL template for the other crystal systems is set up in a similar fashion. Although essentially transparent to the user, all calculations rely on the technique of naming cells and arrays rather than using relative or absolute cell references. For example, one of the terms of the coefficient matrix needed for the monoclinic least-squares evaluation is $\text{SUM}(h*k^2*l)$, where the summation is over the complete set of hkl data. By naming the data blocks of the individual sets of h , k , and l values “ h ,” “ k ,” and “ l ” respectively, the formula to evaluate the sum of the products and squares within this data array simply is $\{=\text{SUM}(h*k^2*l)\}$. The special symbols $\{\}$ indicate that the enclosed function is array specific. Values of 2θ are converted to d_{obs} following Bragg's law using the input wavelengths of X-radiation. Again all cells (such as those containing α and α_1 values) and all arrays (such as that containing 2θ values) are given specific names. The program is set up to use $\text{CuK}\alpha$ for 2θ less than or equal to 40° and $\text{K}\alpha_1$ for 2θ greater than 40° , but both wavelengths and their limits can be changed. The quadratic, Q observed, values are determined as $1/d_{\text{obs}}^2$.

The template for each crystal system contains an array on the lower left part of the sheet with the various summation terms needed for the least-squares refinement. For example the monoclinic template has 13 unique summations, whereas there are only 5 unique least-squares summation terms required for the tetragonal case. The four normal equations for monoclinic least-squares are presented in matrix form, $\mathbf{X} * \mathbf{A} = \mathbf{Y}$ with the coefficient matrix designated \mathbf{X} , and the matrix of unknowns designated \mathbf{A} . Standard matrix algebraic inversion using matrix functions of EXCEL produces the reciprocal cell parameters listed in the “results” box on the template. These are then algebraically converted to the direct parameters of the unit cell that are then used to determine D_{calc} and Q_{calc} values. Δd and ΔQ values subsequently lead to estimates of the average deviation in Δd and the standard deviation in ΔQ . Disparity of the average deviation from zero might be indicative of systematic errors such as film shrinkage for powder-camera data or the need for alignment of the diffractometer. A 2θ correction factor is built into each template and can be used by replacing the default value of 0.00 with the desired value. Estimated standard deviations (esd's) in both reciprocal and direct cell parameters are calculated by using the

* Copies of the six templates as well as user documentation may be obtained from the authors by sending one standard double-sided double-density 3½-inch (Macintosh) or 5¼-inch floppy disk (IBM) and a self-addressed mailer.

TABLE 1. Least-squares examples

Crystal system	Mineral	Locality	Reference
Triclinic	Microcline (maximum)	Pellotsalo, Russia	Borg and Smith (1969)
Monoclinic	Kaersutite	Cima volcanic field, California	Colville and Novak (unpub. data)
Orthorhombic	Enstatite (ordered)	Bamle, Norway	Pollack and Ruble (1964)
Tetragonal	Stishovite	Meteor Crater, Arizona	Chao et al. (1962)
Hexagonal	Benitoite	San Benito County, California	Laird and Albee (1972)
Cubic	Spessartine	Synthetic	Yoder and Keith (1951)

methods discussed in the *International Tables of Crystallography* on propagation of errors techniques.

The six least-squares refinement templates each contain a built-in set of example diffraction data. With the exception of the kaersutite data discussed above, all data are taken from the literature, with 2θ observed calculated from published d -spacing data. These examples are listed in Table 1.

Although data entry time is a function of user skill, inexperienced students require approximately 15 to 30 min to input a new set of 2θ and hkl data. Calculation time is essentially instantaneous, or at most requiring a few seconds of cpu time. The kaersutite diffraction data were also refined using the Appleman and Evans (1973) program modified to run on an AT clone by Benoit (1987). This refinement resulted in statistically identical cell parameters and associated estimated standard errors when compared to the EXCEL refinement.

DISCUSSION

These least-squares templates can be conveniently used in various aspects of mineralogical instruction in higher education. They are interactive programs and can be readily modified. All calculations are based on transparent formulas that can be made visible upon command. These formulas are designed to help explain to students the theory and application of least-squares to cell-parameter refinement. The templates can be used by individual students at microcomputer workstations or they can be efficiently displayed by a video projection system for classroom demonstration. Finally, these templates can be used in miner-

alogical or crystallographical research. They offer a quick, efficient, and "user-friendly" mode for cell-parameter refinement with the advantage that the spreadsheet can be easily modified and laser-printed as a figure or table for publication.

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