16.2-9 LEAST-SQUARES DETERMINATION OF SAMPLE CENTERING AND INSTRUMENT ERRORS FOR FOUR-CIRCLE DIFFRACTOMETERS.* W.R. Busing, Chemistry Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, TN 37831, USA.

Methods for the least-squares determination of lattice and orientation parameters have been described in detail by Busing and Levy (Acta Cryst., 1967, 22, 457-464; Crystallographic Computing, 1970, ed. by Ahmed, Hall & Huber, 319-330, Munksgaard). This early work assumed the sample crystal to be correctly centered on a perfect diffractometer well aligned with respect to the primary beam. Others have described ways of calculating centering errors and beam-direction errors from the angles observed for a reflection using eight settings of the diffractometer (Hamilton, International Tables for X-ray Crystallography, 1974, IV, 282-284, Kynoch; King & Finger, J. Appl. Cryst., 1979, 12, 374-378). This report describes a way of including these error parameters in a general orientation least-squares calculation. The procedure has been included in program ORDIF which controls four-circle X-ray and neutron diffractometers. Although the instrument axes can usually be adjusted to be parallel or perpendicular to each other using optical or mechanical measurements (Samson & Schuelke, Rev. Sci. Instr., 1967, 38, 1273-1283), the deviations from perfect adjustment have also been included as optional parameters in this program.

Maximizing the intensity of a reflection and centering it in the counter produces three independent observations. These are the instrument angle which establishes the Bragg condition and two other angles which center the reflection horizontally and vertically. The least-squares parameter list includes the wavelength, six crystal-lattice parameters, eight angles (five of them redundant) which define the sample orientation, three angle-dial zero corrections, three sample-centering errors, and three parameters which define the source and counter displacements. In addition to these 24 quantities an option is provided to include three translational errors and three orientational errors for each of the four axes, making a total of 48 parameters.

It is the task of the least-squares program to use the trial values of these parameters, the reflection indices, and those instrument angles which serve as independent variables to calculate an angle to be compared with its observed value. The matrix mathematics involved in making this calculation will be described elsewhere. Numerical differentiation is used to compute the contribution of each observation to the matrix and vector of the normal equations. Because the problem is nonlinear, two or three cycles are usually required for convergence.

Lattice parameters may be constrained to conform to crystal symmetry, and the user is allowed complete freedom in the selection of variables. Care must be taken in this selection, however, to avoid redundancies and poorly determined combinations of parameters. In the refinement of instrument errors the size of the data set and the choice of the reflections included has some effect on which parameters can be determined. In order to facilitate the selection of variables and to diagnose problems when they occur, the program can be made to perform principal-component analysis. In this procedure the eigenvalues and eigenvectors of the matrix of normal equations are obtained. Small eigenvalues indicate a poorly conditioned matrix, and the corresponding eigenvectors can be used to identify groups of variables which are nearly redundant. This procedure makes it easy to obtain the reliable least-squares results needed to center the sample and align the instrument.

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16.2-10 NEW PROGRAM SYSTEM FOR FOUR-CIRCLE DIFFRACTOMETER. Christer Svensson, Inorganic Chemistry 2, Chemical Center, University of Lund, Sweden.

A new general purpose four-circle diffractometer system has been built at the Chemical Center. It was designed around a sturdy Huber goniometer working with a step size of 0.0005 deg and 5 deg s^{-1} slew speed. The other modules of the system are a Siemens switched X-ray HV generator, a LeCroy multichannel analyzer with Camac, and a Digital Equipment personal computer. The diffractometer is equipped with two detectors that can be used concurrently: a NaI(Tl) scintillation detector and an 80 mm $Xe(CO_2)$ linear position sensitive detector, with appropriate detector electronics. The different units of the diffractometer are interconnected on a general purpose interface bus (GPIB).

A program system has been developed for use of the diffractometer in crystal structure analysis. It is written almost entirely in (readable) Fortran 77.

The user interacts with the diffractometer through a single program with some 140 commands. The other programs are invoked as needed and run in the background. They communicate using the message facilities and event flags managed by the real-time operating system.

Some of the features of the program system are:

- extensive on-line help facility
- log file for significant data and events
- resident COMMON for data collection parameters and other pertinent data
- data files are shared, allowing multiple access
- terminal colour graphics is used for display of profiles, standards and data summaries
- setting angles are precalculated and stored in the reflection file; this allows sorting, and measurement, in any user-defined order
- indexed reflection data file for quick retrieval of of data on one of five keys
- all input/output that is specific to the diffractometer hardware is collected in a driver program; the program system should be fairly simple to modify for a different diffractometer
- data collection with step scans, continuous scans, or two-dimensional ω-2θ scans
- profile evaluation in multichannel analyzer, which uses standard firmware for set-up, data acquisition, smoothing, and data display; optional interactive evaluation on personal computer
- the load on the personal computer by the data collection program is negligable; other calculations and/or program development can run simultaneously
- concurrent absorption correction

The experience so far with the instrument, its design and general characteristics as well as its functioning in some representative data collections, will be described.

The program system, which now comprises a total of more than 15 000 lines of text (source code and help texts), will be made available to other interested crystallographers.

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