

12.X-06 SYSTEMATIC ERRORS IN POWDER DIFFRACTOMETRY

By A.J.C.Wilson, Department of Physics, University of Birmingham, Birmingham B15 2TT, England.

The aberrations ('systematic errors') of a powder diffractometer can be divided into two classes. The *physical aberrations* are inherent in the nature of radiation and its interaction with matter; they can be understood, and their effects allowed for by suitable calculation, but they can be reduced in magnitude only by techniques of monochromatization impracticable at present in routine measurements or ordinary research. The *geometrical aberrations* depend on the finite sizes of any actual sources, specimens, slit systems and detectors, and on the adjustment of the apparatus. Minimization of the aberrations resulting from imperfect adjustment, and other practical matters, are treated in the companion paper by R. Jenkins.

The effects of aberrations on the positions and breadths of powder diffraction maxima have been the subject of many publications, and only a sketch can be given in a short microsymposium paper. There are many review sources, my own probably being the most nearly comprehensive. For detailed treatments and references see:

1. *Mathematical Theory of X-ray Powder Diffractometry*. A.J.C.Wilson, Eindhoven: Centrex, 1963.
2. Note on the aberrations of a fixed-angle energy-dispersive diffractometer. A.J.C.Wilson. *Journal of Applied Crystallography*, 6, 230-237, 1973.
3. *X-ray Diffraction*, Chapter 6. L.V.Azaroff *et al.* New York: McGraw-Hill, 1974.
4. Accuracy in methods of lattice-parameter measurement. A.J.C.Wilson. Pp. 325-351 in *Accuracy in Powder Diffraction*, edited by S. Block and C. R. Hubbard. Washington: US Govt Printing Office, 1980.

Bragg-Brentano (Parrish) diffractometers are discussed in 1, 3 and 4; Seemann-Bohlin in 3 and 4; energy-dispersive in 2.

12.X-07 EXPERIMENTAL MINIMIZATION OF DIFFRACTOMETER ERRORS. By R. Jenkins, Philips Electronic Instruments, Inc., Mahwah, NJ.

In order to obtain accurate d-values with the conventional diffractometer it is important that adequate correction be made for the various experimental errors associated with the measurement. The modern computer controlled diffractometer can do much to minimize systematic errors using procedures which if used in the routine laboratory would be far too tedious to implement with a manual system. For the purpose of this discussion we assume that there are three major sources of error in powder diffractometry: inherent aberrations, alignment errors and errors due to experimental technique. The shape of the curve representing the difference between experimental and theoretical two-theta values can do much to describe the quality of a given alignment procedure.

The major difficulties which can be attributed to experimental technique involve errors due to the placement of the specimen on the focussing circle of the diffractometer, introduction of preferred orientation, and errors in the establishment of peak maxima and conversion to two-theta values. The major problem remaining is that of specimen displacement and this is best handled in a way commensurate with the quality of d-values being sought. In the case of the determination of accurate lattice parameters the best solution lies in the use of a suitable internal standard. In the area of computer search matching Δd over d values of about one part per thousand are required and such accuracy can be obtained using carefully aligned instruments using external standards. Any residual displacement error can be either ignored or compensated for by use of least squares fitting methods.

12.X-08 THE PRECISION OF CELL PARAMETERS DERIVED FROM CALIBRATED GUINIER POWDER PATTERNS. By A. Brown, Studsvik Energiteknik AB, Nyköping, Sweden.

The measurement of line positions in calibrated and indexed powder patterns that have been recorded in Guinier-type focusing cameras is capable of yielding cell parameters with standard deviations at the 0.005 % level, independent of cell symmetry. Whether results of this quality are reproducible in different laboratories depends upon the calibration procedures that are used. Significant factors range from the choice and reliability of the reference material to the form of the calibration curve and the numerical method adopted to correct the measured film distances on the basis of this curve.

With careful application of an internal reference material Guinier focusing cameras offer excellent conditions for the measurement of cell parameters at a level of precision consistent with the calculated standard deviations. For a cassette diameter of 114.6 mm the angular dispersion given by Guinier geometry is $0.5^\circ (2\theta) \text{ mm}^{-1}$, as measured along the recording circle. Resolution within the powder pattern is further assisted by the elimination of the $K\alpha_2$ component of the characteristic radiation when a carefully aligned camera is used with a fine-focus X-ray source. For well-crystallized materials line widths, measured as full width at half maximum height, are less than $0.06^\circ (2\theta)$ in the angular range $20 - 80^\circ (2\theta)$. This is the part of the powder pattern in which the line density is most favourable for the unambiguous detection and indexing of individual X-ray reflections. Visual estimation at 40X magnification gives line positions at a level of $\pm 0.005^\circ (2\theta)$ previous to correction. A well-constructed microphotometer device can easily improve this precision by a factor of two while being less sensitive to subjective errors which may arise when line broadening or partial overlap occur in the pattern. The use of a scale, printed on the film previous to development, is probably unnecessary for the correction of non-uniform shrinkage in present day film base material. These findings are discussed in the light of results of measurements made on Guinier films under a variety of conditions. In this connection, the Likelihood Ratio Method has been used to examine the reliability of the calibration procedure and the least squares reduction of the corrected data. Similarly, interlaboratory comparison has been used to examine the influence of different camera diameters, calibration methods and measurement techniques on the reproducibility of cell parameters derived from Guinier data.