

12.1-7 QUANTITATIVE PHASE ANALYSIS USING THE WHOLE X-RAY POWDER DIFFRACTION PATTERN: Deane K. Smith, Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802 USA

The use of X-ray diffraction methods for quantitative determination of phase composition in a mixture is still the best method for crystalline materials. Although the theory has been established for 40 years, sample preparation difficulties and time consuming data analysis have severely limited its effective application.

With the increased use of automated powder diffractometers, it is a routine matter to collect and store the whole diffractometer trace in computer readable form. By building a data base containing patterns of pure single phases along with their absolute scaling constants, quantitative analysis of mixtures may routinely be accomplished by pattern fitting techniques. For samples which contain orientation effects, pattern adjusting parameters can be used to improve the fit.

This method has been effectively employed to analyze Colorado oil shales and clay minerals. These difficult mineralogical systems involve many minerals which exhibit variable compositions due to solid solution. Such solid solutions need to be represented by several patterns in the data base. The fitting procedures involve selecting the most appropriate pair of representative data base patterns and weighting them properly. The appropriateness of the data base reference pattern to the specific mineral phases under study is one limitation of this approach.

Precision of the method utilizing whole diffraction patterns can be shown to be around 1%, a considerable improvement over techniques using only individual peaks. Accuracy depends on the determination of the absolute scaling factors. These scaling factors have been most effectively determined by whole pattern fitting in patterns of mixtures of reference phases and a standard material such as $\alpha\text{Al}_2\text{O}_3$.

12.1-8 ACCURATE CRYSTALLOGRAPHIC DATA FROM POWDER PATTERNS. By E.J. Sonneveld and J.W. Visser, Technisch Physische Dienst TNO-TH, P.O. Box 155, Delft, The Netherlands.

With the use of a Guinier-Johansson camera or powder diffractometer it is possible to record a powder pattern with high resolution. The use of computers that control the microdensitometer resp. powder diffractometer makes it very easy to collect and store the high quality data. Computer programs are then needed in order to carry out a subsequent evaluation of these data, i.e. determination of position and height of Bragg peaks. Such programs have been made by several authors. If these results are to be used not only for identification purposes but also for refinement of cell constants, accurate quantitative analysis and crystal structure determination, it is important to pay much attention to a proper evaluation, in order to detect all significant Bragg peaks and to determine their position, height, half width and integrated intensity value as accurately as possible. A program for automatic determination of these crystallographic data from the recorded intensity data was developed several years ago. Recent improvements of this program make it possible to find almost all significant reflections. The detection is carried out with the use of the 2nd derivative which gives also an estimate of position, height and half width. A subsequent refinement of these intermediate results using a modified Lorentzian $Y=Y_0/[1+c_s(x-x_0)^2]^{1/2}$ as an appropriate description of the peak profile, is then performed, in order to determine accurate values for these parameters. This refinement gives individual half width values for all peaks that do not overlap too much. Below $2\theta = 30^\circ$, the skewness of the peak profile is accounted for by a 2θ -dependent correction of the modified Lorentzian. However, a better description of the peak profile seems worthwhile for further improvement of detection of peaks and accuracy of the results.

The estimated standard deviation in the peak position is usually smaller than $0.005^\circ 2\theta$. Integrated intensity data and peak heights with an accuracy within a few percent are available for identification, quantitative analysis and crystal structure determination. Plots will be shown of the recorded intensity data, together with the calculated profile after refinement of positions, heights and half widths.

12.1-9 D2B, A NEW HIGH RESOLUTION NEUTRON POWDER DIFFRACTOMETER. By A.W. Hewat and S. Heathman, Institut Laue-Langevin, BP156X, Grenoble 38042 FRANCE.

D2B follows the design principles set out earlier (A.W. Hewat (1975) Nucl. Inst. Methods 127, 361) and improves considerably on the existing machine D1A (A.W. Hewat & I. Bailey (1976) Nucl. Inst. Methods 137, 463). A high monochromator take-off angle $2\theta=135^\circ$ (compared to 120° for D1A) ensures high resolution $\Delta d/d=\Delta\theta\cot\theta$, with the resolution function in 2θ matched to that needed to resolve adjacent lines for a cubic cell of $a_0=18\text{\AA}$. The peak FWHM at focussing $2\Delta\theta=\sqrt{\alpha_1^2+\alpha_3^2}$ is small because 5 minute (instead of 10 minute) collimators α_1 and α_3 are used before both the monochromator and counters. A bank of 64 (instead of 10) collimators and counters at intervals of 2.5° covers the complete scattering range, which can therefore be scanned with only 100 steps each of 0.025° . The loss in intensity ($\Delta\lambda/\lambda$) due to the high take-off angle $2\theta_M$ is compensated by a relatively large monochromator mosaic spread β , since $\Delta\lambda/\lambda=2\beta\cot\theta_M$. The monochromator, 30 strips of squashed germanium, vertically focusses a 300mm high incident beam onto a 50mm high sample: the reactor tube H11 has been enlarged to 200mm diameter to provide such a large beam for focussing. Like D1A, the new machine is controlled by a dedicated PDP11 computer, linked to the central computer, and accessible by remote terminals over the public telephone system. Wavelength, temperature and eventually sample changer will be under computer control. D2B is now working on a neutron guide site, opposite D1A, but will be moved into the reactor to take advantage of the higher flux early in 1985. First tests indicate that D2B will compare favourably with the best possible TOF machine, especially for large structures and d-spacings; it may as well be some-what faster.