12.1-1 MULTI-SCAN X-RAY DIFFRACTOMETRY.

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When collecting data by scanning X-ray diffractometry, a requirement is that the variations of both the generator output and the detector sensitivity are small compared to the statistical fluctuations of the data. If instrumental drift leads to significant periodic variations which are shorter than the scan time, then the linearity of the pattern might be improved if the scan rate is increased and a number of scans are taken. The individual spectra are subsequently added. Recently H.J. Moeck and S.B. Robie reported the use of multi-scanning for detecting small peaks in X-ray diffraction patterns (35th Conference on Applications of X-ray Analysis, Denver, Colorado, August 4-8, 1986), and a device is offered commercially by Scintag Inc., Santa Clara, U.S.A.

In multi-scanning it has been suggested to take 10-300 component scans and sum the data at each point. A belief that multi-scanning reduces the statistical scatter of counts from the scatter obtained from a single scan of equal duration has been propagated, but is fallacious. The statistical standard deviation of a particular point (σ) depends only on the total number of counts recorded (N_{total}) and hence is identical for both multi- and single-scans, provided the total time of scanning is the same. For i component scans we have

$$\sigma_{total} = [\Sigma(\sigma_i)^2]^{\frac{1}{2}} = [\Sigma N_i]^{\frac{1}{2}} = [N_{total}]^{\frac{1}{2}},$$

which is equal to σ for a single measurement of N_{total}.

Improvement in the accuracy of measurements can however be achieved by decreasing the contribution of non-statistical experimental uncertainties. Instrumental drifts can be characterised by the ratio of their period to the total time of each scan. If the ratio is small, the multi-scan technique will improve the linearity and hence enable accurate measurements of relative line areas and other features of interest.

To measure instrumental drifts in our laboratory, counts were collected from a Scintag PAD V diffractometer with a copper anode X-ray tube operated at 40 kV and 40 mA, and a liquid nitrogen-cooled intrinsic Ge detector. The specimen was N.B.S. silicon and counts were measured at fixed angles, corresponding to the (111) and (400) peaks as well as in the background. Data were collected at 512 points of equal dwell time (.1, 1 and 8 seconds), and were analysed for variations greater than those expected from a Poisson distribution.

The data showed an approximately sinusoidal variation of 3% over 30 minutes; similar trends were obtained when repeating the experiments under identical conditions and also with a wide acceptance energy-window set on the detector single-channel-analyser. The stability of the detector and associated electronics was verified with 122 keV γ-rays from a ^{57}Co source; any drifts were less than 0.5% and fluctuations in the data were entirely consistent with a Poisson distribution. Consequently the 30-minute drifts observed appear to arise from generator or anode instabilities.

A more satisfactory solution to the problem of instrumental drifts in a diffractometer is to periodically check the count rate of a reference standard, or to continuously monitor the incident beam intensity (see for e.g. R.A. Coyle, N.F. Hale and C. Wainwright, J. Sci. Instr. 30, 151, 1953).

12.1-2 APPLICATION OF PROFILE FITTING TO A TIME RESOLVED STUDY OF THE REDUCTION OF Fe_2O_3. By

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The potential of profile fitting to analyse data obtained with a position-sensitive detector is demonstrated by applying the technique to a time-resolved study of the reduction of haematite (Fe_2O_3) firstly to magnetite then iron on a diffractometer hot stage in the presence of H_2. This system is an ideal example, as all three phases have major peaks within the angular range of 10°. Owing to severe peak overlap, a reliable analysis of the data requires that a profile-fitting method is used.

Data were obtained at room temperature and then at seven temperatures in the range 300 to 500°C over a period of 34 minutes. The diffraction patterns, obtained with CoKα radiation, were analysed by means of the profile-fitting program PROFIT (J.I. Langford et al, Powder Diff, 1986, 1, 211; E.J. Sonneveld & J.W. Visser, J Appl Cryst, 1975, 8, 1), with peaks modelled by a Pearson VII function. The program decomposes the pattern into its constituent Bragg reflections and gives various parameters to characterise each peak, of which the position, intensity and breadth are used in this instance.

The main quantity used to study the behaviour of each phase during the reaction is the integrated intensity. The reaction started at 330°C with the appearance of the 400 line of the inter-mediate Fe_2O_3 phase (B). The intensity of this line increases to a maximum at 403°C and then decreases to zero at about 460°C. The 110 line of the product of the reaction, Fe(C), first appeared at about 350°C and has a maximum rate of increase in the range 400 to 450°C. Two lines for the Fe_2O_3 precursor (A) occur in the range considered, the 113 and the weak 202. The intensity of the 113 line starts to diminish at 330°C and decreases linearly to zero at about 480°C. Above this temperature there is little change in the intensity from C.

Further information on the reaction can be obtained from the variation of peak positions. For A there is a steady shift towards lower angles as the temperature increases, due to thermal expansion. At the onset of phases B and C there is a sudden shift towards higher angles, due to a 'heave' of the sample, but above about 380°C the displacement is negative, again due to thermal expansion.

Line breadths can give an indication of the variation of crystallite size and strain and were analysed for B and C by the Voigt method (J.I.Langford, J Appl Cryst, 1978, 11, 10; Th.H. de Keijser et al, J Appl Cryst, 1982, 15, 308). For B the apparent crystallite size is constant at about 200 Å for all temperatures, but strain increases to a maximum of 0.0017 at a temperature close to that for maximum intensity, and then decreases. For C, on the other hand, the apparent size and strain both decrease to a minimum (of about 220 Å and 0.0020) at a temperature corresponding to the 'knee' of the intensity curve, and then increase.

These results demonstrate that a position-sensitive detector, coupled with profile fitting, provides a rapid and powerful technique in time-resolved diffraction studies. A wealth of reliable data can be obtained which characterise complex processes in some detail and which can be used to evaluate the kinetic behaviour of chemical reactions.