In practice, there is usually a background count N_B. The net peak count $N_{P+B} - N_B = N_{P-B}$ is dependent on the P/B radio as well as on N_{P+B} and N_B separately. The relative error ε_D of the net peak count is

$$\varepsilon_D = \frac{[(N_{P+B}\varepsilon_{P+B})^2 + (N_N\varepsilon_B)^2]^{1/2}}{N_{P-B}}, \qquad (2.3.3.9)$$

which shows that ε_D is similarly influenced by both absolute errors $N_{P+B}\varepsilon_{P+B}$ and $N_B\varepsilon_B$. The absolute standard deviation of the net peak height is

$$\sigma_{P-B} = (\sigma^2_{P+B} + \sigma^2_B)^{1/2} \qquad (2.3.3.10)$$

and expressed as the per cent standard deviation is

$$\sigma_{P-B} = \frac{(N_{P+B} + N_B)^{1/2}}{N_{P-B}} \times 100. \qquad (2.3.3.11)$$

The accuracy of the net peak measurement decreases rapidly as the peak-to-background ratio falls below 1. For example, with $N_B = 50$, the dependence of σ_{P-B} on P/B is

P/B	σ_{P-B} (%)
0.1	205
1	24.5
10	4.9
100	1.43.

It is obviously desirable to minimize the background using the best possible experimental methods.

2.3.3.7. *Peak search*

The accurate location of the 2θ angle corresponding to the peak of the profile has been discussed in many papers (see, for example, Wilson, 1965). Computers are now widely used for data reduction, thereby greatly decreasing the labour, improving the accuracy, and making possible the use of specially designed algorithms. It is not possible to present a description of the large number of private and commercial programs. The peak-search and profile-fitting methods described below have been successfully used for a number of years and are representative of the results that can now be obtained. They have greatly improved the results in phase identification, integrated intensity measurement, and analyses requiring precise profile-shape determination. It is likely that even better programs and methods will be developed in this rapidly changing field.

There are two levels of the types of data reduction that may be done. The easiest and most frequently used method is usually called 'peak search'. It computes the 2θ angles and intensities of the peaks. The results have good precision for isolated peaks but give the values of the composite overlapping reflections as they appear, for example, on a strip-chart recording. The calculation is virtually instantaneous and is often all that is needed for phase identification, lattice-parameter determination, and similar analyses. The second, profile fitting, described below, is a more advanced procedure that can resolve overlapping peaks into individual reflections and determines the profile shape, width, peak and integrated intensities, and reflection angle of each resolved peak. This method requires a prior knowledge of the profile-fitting function. It is used to determine the integrated intensities for analyses requiring higher precision such as crystal-structure refinement and quantitative analysis, and profile-shape parameters for small crystallite size, microstrain and similar studies.

To measure weak peaks, the counting statistical accuracy must be sufficient to delineate the peak from the background. When the intensity and peak-to-background ratio are low, the computing time is much increased. Since powder patterns often contain a number of weak peaks that may not be required for the analysis, computer programs often permit the user to select a minimum peak height (MPH) and a standard deviation (SD) that the peak must exceed to be included in the data reduction. For example, MPH = 1 would reject peaks less than 1% of the highest peak in the recorded pattern, and SD = 4 requires the intensity to exceed the background adjacent to the peak by $4B^{1/2}$. The number of peaks rejected depends on the intensity and peak-to-background ratio as illustrated in Fig. 2.3.3.7, where the cut-off level was set at $\bar{B} + 4\bar{B}^{1/2}$ for two recordings of the same pattern with about a 40 times difference in intensities. All visible peaks are included in the high-intensity recording and several are rejected by the cut-off level selected in the lower-intensity pattern.

Before carrying out the computer calculations, it may be desirable to subtract unusual background such as is caused by a glass substrate in a thin-film pattern.

The following method was developed using computer-generated profiles having the same shapes as conventional diffractometer (Fig. 2.3.1.3) profiles and adding random counting statistical noise (Huang & Parrish, 1984; Huang, 1988). The best results were obtained using the first derivative ($dx/dy = 0$) of a least-squares-fitted cubic polynomial to locate the peaks, combined with the second derivative (d^2y/dx^2 = minimum) of a quadratic/cubic polynomial to resolve overlapped reflections (Fig. 2.3.3.8). Overlaps with a separate ≥ 0.5 FWHM can be resolved and measured and the accuracy of the peak position is 0.001° for noise-free profiles. Real profiles with statistical noise have a precision of ±0.003 to 0.02° depending on the noise level. The Savitzky & Golay (1964) method (see also Ateiner, Termonia & Deltour, 1974; Edwards & Willson, 1974) was used for smoothing and differentiation of

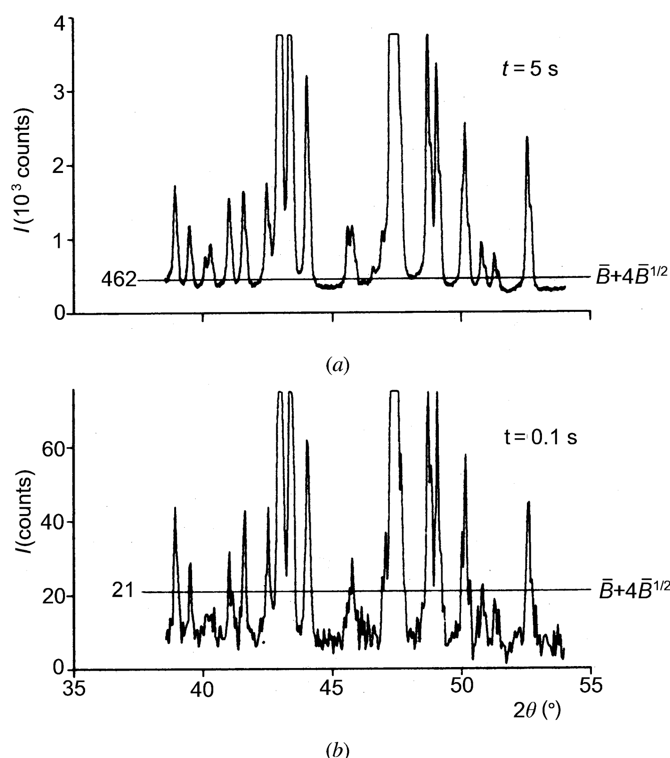

Fig. 2.3.3.7. Effect of 4σ maximum peak height (horizontal line) on dropping weak peaks from inclusion in computer calculation. Step scan with (*a*) $t = 5$ s and (*b*) $t = 0.1$ s. Five-compound mixture, Cu $K\alpha$.

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