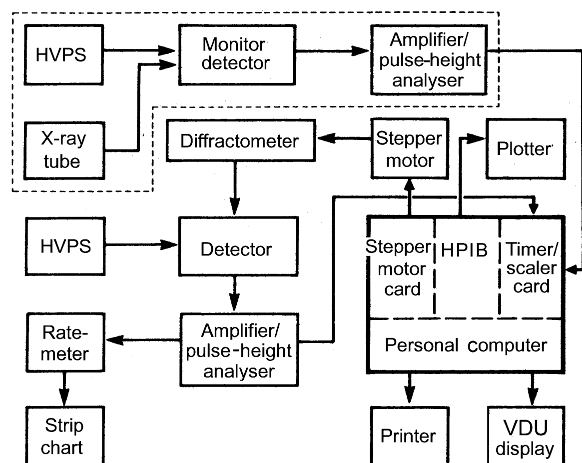
International Tables for Crystallography (2006). Vol. C, Section 2.3.3.6, pp. 64–65.

continuous scanning with read-out on the fly, or slewing to selected angles to read particular points. Step scanning is the method most frequently used. It is essential that absolute registration and step tracking be reliably maintained for all experimental conditions.

The step size or angular increment $\Delta 2\theta$ and count time t at each step, and the beginning and ending angles are selectable. For a given total time available for the experiment, it usually makes no difference in the counting statistical accuracy if a combination of small or large $\Delta 2\theta$ and t (within reasonable limits) is used. A minimal number of steps of the order of $\Delta 2\theta \simeq 0.1$ to 0.2 FWHM is required for profile fitting isolated peaks. It is clear that the greater the number of steps, the better the definition of the profile shape. The step size becomes important when using profile fitting to resolve patterns containing overlapped reflections and to detect closely spaced overlaps from the width and small changes in slopes of the profiles. A preliminary fast run to determine the nature of the pattern may be made to select the best run conditions for the final pattern. Will *et al.* (1988) recorded a quartz pattern with 1.28 Å synchrotron X-rays and 0.01° steps to test the step-size role. The profile fitting was done using all points and repeated with the omission of every second, third, and fourth point corresponding to $\Delta 2\theta = 0.02$, 0.03 and 0.04°. The R(Bragg) values were virtually the same (except for 0.04° where it increased), indicating the experimental time could have been reduced by a factor of three with little loss of precision; see also Hill & Madsen (1984). Patterns with more overlapping would require smaller steps. Ideally, the steps could be larger in the background but this also requires a prior knowledge of the pattern and special programming.



(*a*)

ROUTING: Analyse previous runs? ____
Initiate active runs? ____ Present position? ____
Define active runs? ____ How many? ____

RUN ID ____ Comment ____

EXPERIMENTAL: Start angle: ____ End angle: ____
Step increm: ____ Count time: ____

ANALYSIS: Peak search? ____ Profile fit? ____
Std. dev: ____ Min peak ht: ____

(*b*)

Fig. 2.3.3.5. (*a*) Block diagram of typical computer-controlled diffractometer and electronic circuits. The monitor circuit enclosed by the dashed line is optional. HPIB is the interface bus. (*b*) A full-screen menu with some typical entries.

A typical VDU screen menu for diffractometer-operation control is shown in Fig. 2.3.3.5(*b*). A number of runs can be defined with the same or different experimental parameters to run consecutively. The run log number, date, and time are usually automatically entered and together with the comment and parameters are carried forward and recorded on the print-outs and graphics to make certain the runs are completely identified. The menu is designed to prompt the operator to enter all the required information before a run can be started. Error messages appear if omissions or entry mistakes are made. There are, of course, many variations to the one shown.

2.3.3.6. *Counting statistics*

X-ray quanta arrive at the detector at random and varying rates and hence the rules of statistics govern the accuracy of the intensity measurements. The general problems in achieving maximum accuracy in minimum time and in assessing the accuracy are described in books on mathematical statistics. Chapter 7.5 reviews the pertinent theory; see also Wilson (1980). In this section, only the fixed-time method is described because the fixed-count method takes too long for most practical applications.

Let $\bar{N}$ be the average of N, the number of counts in a given time t, over a very large number of determinations. The spread is given by a Poisson probability distribution (if $\bar{N}$ is large) with standard deviation

$$\sigma = \bar{N}^{1/2}. \qquad (2.3.3.7)$$

Any individual determination of N or the corresponding counting rate n $(= N/t)$ will be subject to a proportionate error ε which is also a function of the confidence level, *i.e.* the probability that the result deviates less than a certain percentage from the true value. If Q is the constant determined by the confidence level, then

$$\varepsilon = Q/N^{1/2}, \qquad (2.3.3.8)$$

where $Q = 0.67$ for the probable relative error ε_{50} (50% confidence level) and $Q = 1.64$ and 2.58 for the 90 and 99% confidence levels (ε_{90}, ε_{99}), respectively. For a 1% error, $N = 4500$, 27 000, 67 000 for ε_{50}, ε_{90}, ε_{99}, respectively. Fig. 2.3.3.6 shows various percentage errors as a function of N for several confidence levels.

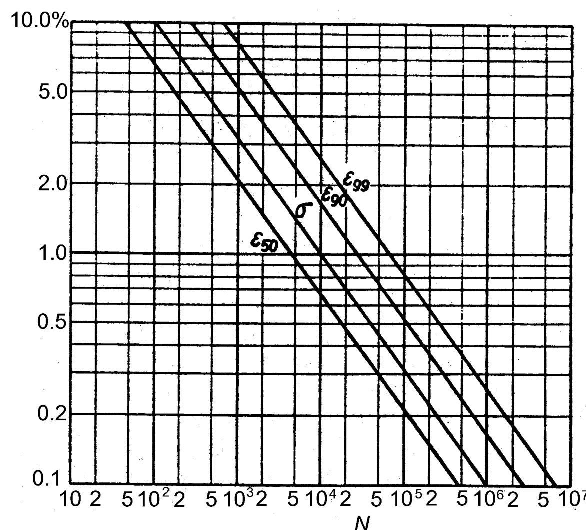


Fig. 2.3.3.6. Percentage error as a function of the total number of counts N for several confidence levels.

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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

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

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 $(d^2y/dx^2 = \text{minimum})$ 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

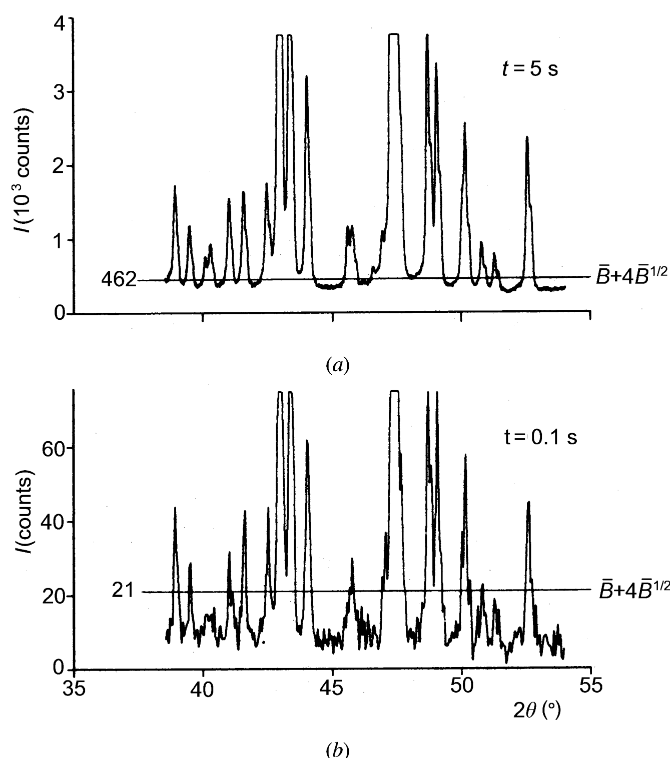

Fig. 2.3.3.7. Effect of 4σ maximum peak height (horizontal line) on dropping weak peaks from inclusion in computer calculation. Step scan with (*a*) $t = 5$ s and (*b*) $t = 0.1$ s. Five-compound mixture, Cu $K\alpha$.

references