$$\frac{50}{C^{\frac{1}{2}}} \leq R \leq \frac{50}{C^{\frac{1}{2}}} \left\{\frac{\tau+1}{\tau-1}\right\}^{\frac{1}{2}} .$$

Although peak to background ratios of less than two are not uncommon these will usually be associated with very small structure factors which will have very little effect on R. A working assumption is to take the extreme value of τ equal to two. With this assumption

$$\frac{50}{C^{\frac{1}{2}}} \leq R \leq \frac{85}{C^{\frac{1}{2}}}$$

For most stereochemical purposes an R value of 10 % is perfectly acceptable, implying that from

$$2500/R^2 \leq C \leq 7225/R^2$$
$$25 \leq C \leq 72 .$$

It is difficult to conceive what the purpose of collecting to an R of better than 1 % would be at the present state of diffractometry and for this

$$2500 \leq C \leq 7225 .$$

Consequently, for most purposes, to collect more than a few thousand counts per reflexion in a constant count experiment would be difficult to justify, as in a real experiment the non-random errors of setting, extinction and absorption probably limit R to above 1 % independent of the value C. Indeed, ignoring these non-random errors, it is possible to modify the constant count experiment so that an agreement analysis would give constant values with $\langle|F(\mathbf{h})|\rangle$ and $\langle\sin\theta\rangle$ as variables. In order to do this it is only necessary to make C a function of τ,

$$C(\tau) = \left(\frac{50}{R}\right)^2 \left\{\frac{1+1/\tau}{1-1/\tau}\right\}, \qquad (1)$$

or in terms of the integral peak count

$$N(\tau) = \left(\frac{50}{R}\right)^2 \left\{\frac{(1+1/\tau)}{(1-1/\tau)^2}\right\}. \qquad (2)$$

Table 1 gives the values of $C(\tau)$ and $N(\tau)$ to yield an R value of 10 %. These counts must be multiplied by 100 to give the corresponding values for an R of 1 %.

Equations (1) and (2) are the basic planning equations for a constant agreement analysis diffractometer experiment.

References

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Structure analysis based on inadequate data – a cautionary tale.

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A plausible structure analysis, based on a 7-fold excess of three-dimensional data to parameters and refined to an R value of 12%, proved to have many errors in molecular dimensions – some of them as much as 6 times their estimated standard deviations.

We have recently (1967) completed an X-ray structure analysis of potassium hydrogen di-aspirinate, $KH(C_9H_7O_4)_2$. Our final results were based on some 2700 diffractometer intensity data (Mo radiation); with R reduced to 9·9 % and a 19-fold excess ratio of observations to parameters, our average estimated standard deviations of position, $\sigma(r)$, were 0.0026 Å for O, 0·0033 for C, and 0·06 for H atoms.

Our experience at an earlier stage of this work seems worth setting down. We performed a preliminary refinement based on 700 non-zero reflexions (Cu radiation, careful visual estimation of intensities, $h0l$ to $h3l$ with b = 7·2 Å). In this we had a 7-fold excess of observations and R was reduced to 12.3 %. Average values of $\sigma(r)$ are included in Table 1. By these criteria, we expected the preliminary results to be reasonably reliable, at least so far as positional parameters were concerned.

Table 1. *Average standard deviations in preliminary analysis and average shifts after final analysis* (Å)

$X' = xa \sin\beta$; $Z' = xa \cos\beta + zc$)

	X'	Y	Z'
Preliminary analysis, $\sigma(r)$:			
O atoms	0·005	0·009	0·005
C atoms	0·008	0·014	0·008
Shifts to final parameters:			
O atoms	0·010	0·015	0·007
C atoms	0·014	0·029	0·015

This expectation is not borne out by the changes in absolute coordinates whose average values are also shown in Table 1. Bond lengths derived from the preliminary analysis were in error by up to 0·045 Å (C–O) and 0·070 (C–C). The greatest shifts, naturally, were in Y; but those in X' and Z' averaged about double the respective standard deviations.

Exercising hind-sight, we can now see good reasons for the fallibility of the preliminary analysis. (Such reasons are our failure to correct for absorption, when μ was 30·6 cm^{-1} and the crystal a thin plate of notably anisometric cross-section, and our use of intensity data with limited coverage of reciprocal space in the $\mathbf{b}^*$ direction. In such circumstances estimates of standard deviations seem to be much too optimistic.) Nevertheless many analyses with credentials that look less plausible are on record in the literature – some of them by one of us.

Reference

Manojlović, Lj. & Speakman, J. C. (1967). *J. Chem. Soc.* p. 971.