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On the significance of Bragg reflections

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Recently Henn & Meindl [*Acta Cryst.* (2010), A**66**, 676–684] examined the significance of Bragg diffraction data through the descriptor $W = \langle I^{1/2}\rangle/\langle\sigma(I)\rangle$. In the Poisson limit for the intensity errors W equals unity, but any kind of data processing (background subtraction, integration, scaling, absorption correction, Lorentz and polarization correction *etc.*) introduces additional error as well as remaining systematic errors and thus the significance of processed Bragg diffraction data is expected to be below the Poisson limit ($W_{\rm Bragg} < 1$). Curiously, it was observed by Henn & Meindl for several data sets that $W_{\rm Bragg}$ had values larger than one. In the present study this is shown to be an artefact due to the neglect of a data scale factor applied to the standard uncertainties, and corrected values of $W_{\rm Bragg}$ applied to Bragg data on an absolute scale are presented, which are all smaller than unity. Furthermore, the error estimation models employed by two commonly used data-processing programs {*SADABS* (Bruker AXS Inc., Madison, Wisconsin, USA) and *SORTAV* [Blessing (1997). *J. Appl. Cryst.* **30**, 421–426]} are examined. It is shown that the empirical error model in *SADABS* very significantly lowers the significance of the Bragg data and it also results in a very strange distributions of errors, as observed by Henn & Meindl. On the other hand, error estimation based on the variance of a population of abundant intensity data, as used in *SORTAV*, provides reasonable error estimates, which are only slightly less significant than the raw data. Given that modern area detectors make measurement of highly redundant data relatively straightforward, it is concluded that the latter is the best approach for processing of data.

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1. Introduction

Carrying out reliable crystal structure determinations from X-ray diffraction data requires both accurate intensities and good estimates of the standard uncertainties corresponding to the individual measurements. Flawed estimation of the errors not only leads to incorrect uncertainties of the refined parameters but will also to some extent bias the obtained values of the refined parameters. In a recent study, Henn & Meindl (2010) (hereafter HM) concluded that there exists a fundamental limit for the significance of diffraction data from X-ray and neutron diffraction experiments, by monitoring the descriptor W throughout the data reduction steps, where $W = \langle I^{1/2}\rangle/\langle\sigma(I)\rangle$ [HM, equation (12)]. In the Poisson limit the standard uncertainty of intensity data is $\langle I^{1/2}\rangle$, and thus $W_{\rm Poisson} = 1$. Any kind of data reduction will lead to an increase in $\langle\sigma(I)\rangle$ while keeping $\langle I^{1/2}\rangle$ unchanged and therefore W becomes smaller than unity for real and processed data. For Bragg diffraction data the net intensities, $I_{\rm net}$, are typically obtained from the raw data, $I_{\rm raw}$, by subtraction of a background intensity. This operation adds the uncertainty from the background estimation to $\sigma(I)$ and therefore the inequality $W_{\rm Poisson} \geq W_{\rm raw} \geq W_{\rm net}$ holds. However, before any kind of structural data modelling can be performed, the net intensities must be reduced to Bragg intensities, $I_{\rm Bragg}$, by a range of data-reduction steps, including scaling, absorption correction, Lorentz and polarization correction *etc*. All these data transformations lead to an increased uncertainty and thus the inequality $W_{\rm Poisson} \geq W_{\rm raw} \geq W_{\rm net} \geq W_{\rm Bragg}$ [HM, equation (8)].

HM analysed the descriptor $W = \langle I^{1/2}\rangle/\langle\sigma(I)\rangle$ for a variety of data sets and surprisingly they observed that in some cases $W_{\rm Bragg}$ not only exceeded $W_{\rm raw}$ but also exceeded unity. They explained this as an effect of a redistribution of σ. In addition they observed that $W_{\rm Bragg}$ differed very significantly when different widespread data-reduction software programs such as *SADABS* (Bruker, 2008) and *SORTAV* (Blessing, 1997) were used to process the same raw data sets. In the present paper we resolve the unphysical issue of $W_{\rm Bragg} > 1$, which simply originates from the failure to work on an absolute scale in the equations of HM. Subsequently, we examine the effect of the error models used by *SADABS* and *SORTAV* on the data significance.

2. The significance of Bragg reflections and the missing scale factor

Owing to the scattering process of X-rays, the significance of intensity data is expected to be limited by Poisson statistics. This led HM to introduce the descriptor $W = \langle I^{1/2}\rangle/\langle\sigma(I)\rangle$, which is smaller than unity for data on an absolute scale. The mean square root of the Bragg intensity represents the minimal achievable (Poisson) error, while additional systematic and random errors arising from the experiment will be included in the final experimental mean standard uncertain-

Table 1
Recalculated Table 1 of Henn & Meindl (2010).

The following descriptors are listed: $W_{raw} = \langle I_{net}^{1/2}\rangle/\langle\sigma(I_{net})\rangle$, $W_{Bragg} = \langle I_{Bragg}^{1/2}\rangle/\langle\sigma(I_{Bragg})\rangle$ and $W_{Bragg}^{corr} = k^{1/2}W_{Bragg}$, where $k^{1/2} = \langle I_{Bragg}/I_{Bragg}^{1/2}\rangle/\langle I_{net}/I_{net}^{1/2}\rangle$. For each data set the upper line represents the values after processing in *SADABS* (Bruker, 2008), and the lower line represents data processed in *SORTAV* (Blessing, 1997).

No.†	W_{raw}‡	W_{Bragg}§	W_{Bragg}^{corr}
1	0.274	2.187	0.179
		0.238	0.261
2	0.183	1.429	0.072
		0.180	0.180
3	0.203	0.934	0.062
		0.144	0.158
4	0.252	0.955	0.102
		0.197	0.223
5	0.939	1.322	0.293
		0.969	0.936
6	0.765	0.766	0.337
		0.759	0.759
7	0.171	4.295	0.064
		0.114	0.122
8	0.451	1.365	0.317
		0.450	0.446
9	0.193	1.839	0.105
		0.184	0.193

† HM Table 1, column 1. ‡ HM Table 1, column 2. § HM Table 1, column 5.

ties. Thus, for sufficiently large data sets this ratio must never be larger than unity, which is the limit corresponding to pure Poisson data without any additional errors. As mentioned above, this is true for data on an absolute scale but cannot be applied directly to processed data that have been scaled. This can be shown as follows [HM, equations (4) and (5)]:

$$I_{Bragg} = kI_{net}, \tag{1}$$

$$\sigma(I_{Bragg}) = k\sigma(I_{net}). \tag{2}$$

Here, the background-corrected intensities I_{net} are used instead of the raw intensities I_{raw}, and I_{Bragg} represents the processed data. Combining these equations gives W for processed data:

$$W = \frac{\langle I_{net}^{1/2}\rangle}{\langle\sigma(I_{net})\rangle} = \frac{\langle k^{-1/2}I_{Bragg}^{1/2}\rangle}{\langle k^{-1}\sigma(I_{Bragg})\rangle}. \tag{3}$$

From this expression it is clear that W depends on the value of the scale factor applied to both the intensities and the uncertainties of the intensities. Therefore, omission of this scale factor in the calculation of W can lead to values of W arbitrarily larger than one, *i.e.* apparently unphysical values. The values presented by HM did not take this scale factor change into account and, thus, the large values of W were incorrectly interpreted as a sign of increased significance.

To correct this view Table 1 lists the W values reported by HM as well as the values calculated by including a scale factor. The scale factor is not explicitly available in the paper, but an indirect scale factor, $k = I_{Bragg}/I_{net}$, can be obtained from the values $\langle I_{Bragg}/I_{Bragg}^{1/2}\rangle = \langle I_{Bragg}^{1/2}\rangle$ and $\langle I_{net}/I_{net}^{1/2}\rangle = \langle I_{net}^{1/2}\rangle$. This scale represents a common scale factor for the whole data set, *i.e.* equation (3) is reduced to

$$W = k^{1/2}\langle I_{Bragg}^{1/2}\rangle/\langle\sigma(I_{Bragg})\rangle. \tag{4}$$

This is an approximation since the individual batches are scaled differently in *SADABS* and *SORTAV*. Furthermore, since *SADABS* uses a scale factor for each data frame, each reflection will have a different scale. However, as shown below this averaging of scale has a much smaller effect on W than the effect of neglecting the scale factor.

Table 1 shows that all W values of the processed data are smaller than for the raw data and that, in all cases, the values are smaller than unity. It remains an important point to monitor how W changes through the data processing and to ensure that, as pointed out by HM, the significance decreases as little as possible when the data are processed.

3. Evaluation of commonly used intensity error models

From the reported values of W obtained using raw data it is clear that the Poisson limit is seldom reached. This happens despite the fact that uncertainties from the commonly used integration procedures in general underestimate the errors of the intensities. The reasons for this and ways to estimate more correct uncertainties have previously been discussed (Abrahams, 1969; Hamilton, 1969; McCandlish *et al.*, 1975; Evans, 2006; Diederichs, 2010; Waterman & Evans, 2010). In general, there are two categories of approaches for achieving the uncertainties: one using a refinable instrument error model and another obtaining errors from the variance of redundant data. In *SADABS* the experimental uncertainties, from the integration routine, are scaled using an empirical error model to obtain standard uncertainties of I_{Bragg}:

$$\text{s.u.}^2(I_{Bragg}) = c\left[\sigma^2(I_{Bragg}) + \left(g\langle I_{Bragg}\rangle\right)^2\right], \tag{5}$$

where

$$\sigma^2(I_{Bragg}) = k\sigma^2(I_{net}). \tag{6}$$

The scale factor k is identical to the one that is applied to the intensities and includes, for example, absorption and frame scale factors. c is an additional scale factor applied to the uncertainties and it is different for each batch of reflections. The error model is included by refining such that $\chi^2 = 1$ in all resolution shells of the data, where

$$\chi^2 = \left\langle\left[N\sum\left(I_{Bragg} - \langle I_{Bragg}\rangle\right)^2\right]\Big/\left[(N-1)\sum\text{s.u.}^2(I_{Bragg})\right]\right\rangle. \tag{7}$$

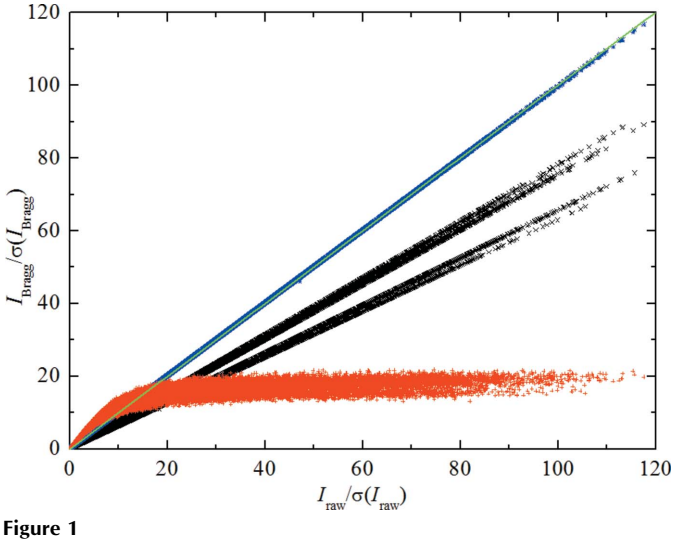

Figure 1
Low-temperature synchrotron data on a single crystal of K_2SO_4 (unpublished data) showing the significance of the processed data $[I_{Bragg}/\sigma(I_{Bragg})]$ *versus* the significance of the raw data $[I_{raw}/\sigma(I_{raw})]$. The blue stars are for *SORTAV*, the red plus signs are for *SADABS* with an error model included in the processing, and the black crosses are for *SADABS* without an error model. The green line represents no change in significance after data processing.

Clearly, this error model affects the significance of the intense reflections a lot compared with the significance of the raw data and of the data processed in *SORTAV*. From equation (5) it is clear that the significance will reach a plateau when the second term dominates, and that is exactly what we see in Fig. 1, which displays the significance of processed data *versus* raw data for K_2SO_4 (unpublished data). The data were collected at a synchrotron source using a very small crystal, meaning that extinction and absorption effects in the data are relatively small. However, the choice of data is not critical for the arguments made. It is clearly seen in Fig. 1 that the error model applied in *SADABS* (red plus signs) introduces a plateau of the significance of the Bragg reflections $[I_{\rm Bragg}/\sigma(I_{\rm Bragg})]$ leading to a majority of the reflections having almost equal significance. These significances are far from reflecting the significance of the raw unprocessed data. Furthermore, it may be noted that some of the low-significance reflections actually become more significant than the raw data after application of the model. This behaviour of the significance was also noted by HM, but not further discussed.

In an attempt to study the effect of the error model, the value of g was forced to be equal to zero, whereby the error model is suppressed. The result is shown in Fig. 1 as black crosses. All reflections are now less significant and fall into four groups (lines), one for each of the data batches. This splitting of the data is caused by the additional batch scale factor, c, which is only applied to the uncertainties and not to the intensities. This appears to be a bug in *SADABS* in the case where it is forced to run without an error model by setting $g = 0$. In this case the program should not refine the standard uncertainties to get χ^2 closer to unity.

The data processed by *SORTAV* (blue stars) are close to the significance of the raw data (green line) but consistently slightly lower. This is due to the uncertainty introduced by least-squares refinement of the batch scale factors. This appears trivial but clearly illustrates the point discussed above, *i.e.* a scaling should not drastically change the significance. It is possible to apply an empirical error model in *SORTAV*; however, it is not possible to refine this model. Several tests with different values suggest that the influence of this error model does not change the significance nearly as drastically as the processing in *SADABS*.

Once the uncertainties of the processed, non-averaged data have been determined, the next step is to estimate the uncertainties of the unique averaged reflections. In *SORTAV*, it is possible to use the distribution of equivalent reflections to derive reasonable standard uncertainties. Seen from an experimentalist's point of view this represents the best way of obtaining reliable uncertainties as they are calculated directly from the measurements. This approach depends on the availability of redundant data which intrinsically include the errors, both random and systematic. However, highly redundant data can now routinely be obtained by the use of fast area detectors. It may be that use of error models is in fact a convenient leftover from the days when Bragg intensity data were measured very slowly with point detectors, and thus the redundancy was low. In the present case it should be noted that the effect of the error estimation by *SADABS* does not appear to have a significant effect on the final model in a charge-density refinement (data not shown).

4. Conclusion

It has been shown that the significance descriptor, W, recently introduced by HM has to be modified to include changes in the scale of the data in question. Omitting this can lead to unphysical values and, thus, erroneous conclusions. Furthermore, it has been shown that applying an empirical error model, using *SADABS*, drastically influences the significance of the data, thereby lowering the value of W. Suppressing this error model leads to serious errors in the scaling of the standard uncertainties. At this point it seems that the best estimates of errors in Bragg diffraction data are obtained by measuring highly redundant data and then calculating the error from the variance of the population of measurements.

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