Appendix: How to assess and correct instrument bias using this SRM

When looking for instrumental problems, the peaks should be considered jointly, not individually. First, plot control bands as $1 \pm U$ over the range of 2Θ, where U is the relative uncertainty ($U = 0.0612$ if peak areas were used, or 0.0785 if peak heights were used). Next, plot the ratio of each new measurement to the certified value on the vertical axis against the 2Θ peak location on the horizontal axis. As long as these ratios fall within the control bands and are patternless, the system cannot be labelled "out of control."

However, if there is a pattern in the ratios, then the device is introducing a systematic error, even if all of the ratios fall within the control bands. This systematic error should be corrected by modelling the ratios as a function of peak location and using the model to correct future observations on unknowns.

Let the measured relative intensities on the 12 peaks be y_i and the certified values be c_i, so the ratios to model are

$$r_i = \frac{y_i}{c_i}.$$

Fit a simple model, using ordinary least squares regression, which describes these ratios adequately as a function of peak location (x_i). The fitted model has m parameters: m=1 for a horizontal straight line, m=2 for a slanted straight line, m=3 for a quadratic, etc. The residual sum of squares from the fit, plus an allowance for the uncertainty in the certified values on the certificate, is:

$$RSS_{full} = \sum_{1}^{n}(r_i - \hat{r}_i)^2 + (n-m)\frac{(RSD)^2}{25}$$

and the residual degrees of freedom for this "full" model are n - m. The RSD = 0.0206 if peak areas were used, or 0.0262 if peak heights were used. The residual sum of squares for the horizontal line at 1 (which describes "ideal" data), plus an allowance for the uncertainty in the certified values on the certificate, is:

$$RSS_1 = \sum_{1}^{n}(r_i - 1)^2 + (n-1)\frac{(RSD)^2}{25}$$

and the residual degrees of freedom are n - 1. Then if the test statistic

$$F = \frac{\left\{RSS_1 - RSS_{full} + (m-1)\frac{(RSD)^2}{25}\right\} / (m-1)}{\left\{RSS_{full} + (n-m)\frac{(RSD)^2}{25}\right\} / (n-m)}$$

is larger than the upper 0.05 percentage point from the F distribution with m-1 numerator and n-m denominator degrees of freedom (commonly provided in table form in introductory statistics texts), the correction model is needed.

To use the correction model: A new peak angle x^* and a new relative intensity y^* are measured on an unknown sample. If $\hat{r}^*$ is the predicted value of the fitted model at x^*, the corrected relative intensity for the new peak angle on the unknown sample is

$$\text{corrected relative intensity} = \frac{y^*}{\hat{r}^*}.$$