Supporting Information

Quantifying Uncertainty of Determination by Standard Additions and Serial Dilutions

Methods Taking into Account Standard Uncertainties in Both Axes

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Unified equations for the slope, intercept and their standard uncertainties of the regression line

According to the York et al. approach, the process of straight line fitting can be reduced to the following compact set of four WLR equations:

\[
\begin{align*}
    a &= \frac{\sum_{i=1}^{n} w_i \lambda_i (y_i - \bar{y})}{\sum_{i=1}^{n} w_i \lambda_i (x_i - \bar{x})} \quad (S-1) \\
    b &= \bar{y} - a \bar{x} \quad (S-2) \\
    u(a) &= s_{y/x} \left[ \frac{1}{\sum_{i=1}^{n} w_i (X_i - \bar{X})^2} \right]^{1/2} \quad (S-3) \\
    u(b) &= s_{y/x} \left[ \frac{1}{\sum_{i=1}^{n} w_i} + \bar{X}^2 u^2 (a) \right]^{1/2} \quad (S-4)
\end{align*}
\]

where

\[
\begin{align*}
    w_i &= \frac{w(x_i) w(y_i)}{w(x_i) + a^2 w(y_i) - 2ar_i \sqrt{w(x_i) w(y_i)}} \quad \text{(weight of \(i\)-th data point)} \quad (S-5) \\
    w(x_i) &= \frac{1}{u^2 (x_i)} \quad \text{(weight of the \(x_i\) value)} \quad (S-6) \\
    w(y_i) &= \frac{1}{u^2 (y_i)} \quad \text{(weight of the \(y_i\) value)} \quad (S-7)
\end{align*}
\]

\(r_i\) – correlation coefficient between uncertainties in \(x_i\) and \(y_i\)
\[ \lambda_i = w_i \left[ \frac{(x_i - \bar{x})}{w(y_i)} + \frac{a(y_i - \bar{y})}{w(x_i)} - \frac{(a(x_i - \bar{x}) + (y_i - \bar{y}))}{\sqrt{w(x_i)w(y_i)}} \right] \]  
(S-8)

\[ \bar{x} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i} \]  
(mean value of the observed \( x \) values)  
(S-9)

\[ \bar{y} = \frac{\sum_{i=1}^{n} w_i y_i}{\sum_{i=1}^{n} w_i} \]  
(mean value of the observed \( y \) values)  
(S-10)

\[ \bar{X} = \frac{\sum_{i=1}^{n} w_i X_i}{\sum_{i=1}^{n} w_i} \]  
(mean value of the expected values of \( x \))  
(S-11)

\[ \bar{Y} = \frac{\sum_{i=1}^{n} w_i Y_i}{\sum_{i=1}^{n} w_i} \]  
(mean value of the expected values of \( y \))  
(S-12)

\[ X_i = \bar{x} + \lambda_i \]  
(expected value of \( x \_i \), least-squares-adjusted value)  
(S-13)

\[ Y_i = \bar{y} + a\lambda_i \]  
(expected value of \( y \_i \), least-squares-adjusted value)  
(S-14)

\( n \) is the number of data points for the calibration line (pairs of \( x \) and \( y \) observations)

and

\[ s_{y/x} = \sqrt{\frac{\sum_{i=1}^{n} w_i (y_i - ax_i - b)^2}{n - 2}} \]  
is the residual standard deviation  
(S-15)
When the standard uncertainties of the predictor variable \((u(x_i))\) are set to 0 and the standard uncertainties in the response variable \((u(y_i))\) are statistically equal, then all weighting factors of experimental points \((w_i)\) will be the same and equal 1, and eqs. (S-1) – (S-4) become identical to those obtained for the OLR method. For the further considerations it is justified to recall the corresponding OLR equations:

\[
a = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n} (x_i - \bar{x})^2} \quad (S-16)
\]

\[
b = \bar{y} - a\bar{x} \quad (S-17)
\]

\[
u(a) = s_{y/x} \sqrt{\frac{1}{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \quad (S-18)
\]

\[
u(b) = s_{y/x} \sqrt{\frac{1}{n} + \bar{x}^2 u^2(a)} \quad (S-19)
\]

where

\[
s_{y/x} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - ax_i - b)^2}{n - 2}} \quad (S-20)
\]