Statistics for Calibration Methods

Lisensky

Linear Least Squares Method for n points (x_i, y_i) fitted to line $y = mx + b$

$$\text{slope} = m = \frac{n\sum(x_i y_i) - \sum x_i \sum y_i}{D}$$

$$y\text{-intercept} = b = \frac{\sum(x_i^2)\sum y_i - \sum(x_i y_i)\sum x_i}{D}$$

$$\text{where } D = n \sum(x_i^2) - (\sum x_i)^2$$

Assuming errors in y are larger than errors in x (known amounts of standards), the uncertainty in the y values is

$$s_y = \sqrt{\frac{\sum(y_i - mx_i - b)^2}{n-2}}$$

Least squares minimizes the numerator: (vertical deviations of y from the line)^2. Notice the $n - 2$ degress of freedom, where n is the number of points.

The uncertainty in m and b come from the uncertainty in y.

$$\text{standard deviation of slope} = s_m = s_y \sqrt{\frac{n}{D}}$$

$$\text{standard deviation of intercept} = s_b = s_y \sqrt{\frac{\sum(x_{i2})}{D}}$$

If use a calibration curve to find x from known y, then standard deviation for x is

$$s_x = \frac{s_y}{|m|}\sqrt{\frac{1}{k} + \frac{n\bar{x}^2 + \sum(x_i^2) - 2\bar{x}\sum x_i}{D}}$$

where $\bar{x}$ is the average value calculated from $y = mx + b$, k is the number of measurements averaged, and n is the number of points in the calibration curve. The confidence intervals will be

$$m \pm t\, s_m \qquad b \pm t\, s_b \qquad x \pm t\, s_x$$

where the t-value depends on the confidence level and $\boldsymbol{n - 2}$ degrees of freedom.

Standard Addition Method Extrapolation

$$x_{\text{extrapolated}} = \frac{b}{m} \qquad s_{x_{\text{extrapolated}}} = \frac{s_y}{|m|}\sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2\sum(x_i - \bar{x})^2}}$$

where $\bar{x}$ and $\bar{y}$ are the averages of the x and y-values and n is the number of points in the standard addition curve (including the point with no standard added). The confidence intervals will be

$$x \pm t\, s_{x_{extrapolated}}$$

where the t-value depends on the confidence level and $\boldsymbol{n - 2}$ degrees of freedom.