APPENDIX

Reliability coefficient R²:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}},$$

$$SS_{tot} = \sum_i (y_i - \underline{y})^2,$$

$$SS_{res} = \sum_i (y_i - f_i)^2,$$

where y_i is the i-th value from the observed dataset, $\underline{y}$ is the mean of observed data, f_i is the predicted value associated with y_i. SS_{tot} is the total sum of squares (proportional to the variance of the data) and SS_{res} is the sum of squares of residuals.

Prediction of x from y:

$$\hat{x}_s = \frac{\bar{y}_s - b_0}{b_1},$$

where $\hat{x}_s$ is the predicted concentration, $\bar{y}_s$ is the mean of m determinations performed on the sample, b_0 is the intercept and b_1 is the slope of calibration curve equation.

$$s_{\hat{x}_s} = \frac{s_e}{b_1}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(\bar{y}_s - \bar{y})^2}{b_1^2 \sum (x_i - \bar{x})^2}},$$

where s_e is an estimate of the variance of the measurements, m is the number of measurements per sample, n is the number of points of the calibration curve, $\bar{y}$ is the mean of all the y observations (grand mean), x_i is the i-th value from the observed dataset and $\bar{x}$ is the mean of all the x observations (grand mean).

Sum of the mean squares of prediction error:

$$\sum_j^k (x_j - \hat{x}_j)^2,$$

where x_j is the reference content of j-th sample and $\hat{x}_j$ is the value of the predicted content of the respective sample.