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Extension of the standard addition method by blank addition

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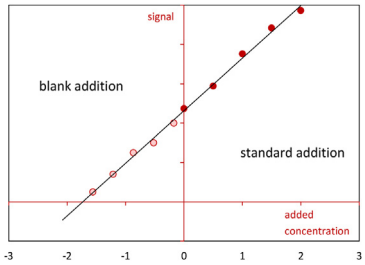
GRAPHICAL ABSTRACT



ABSTRACT

Standard addition involves adding varying amounts of the analyte to sample portions of fixed mass or fixed volume and submitting those portions to the sample preparation procedure. After measuring the final extract solutions, the observed signals are linearly regressed on the spiked amounts. The original unknown amount is estimated by the opposite of the abscissa intercept of the fitted straight line [1]. A limitation of this method is that only data points with abscissa values equal to and greater than zero are available so that there is no information on whether linearity holds below the spiking level zero. An approach to overcome this limitation is introduced.

- Standard addition is combined with blank addition.
- Blank addition means that defined mixtures of blank matrix and sample material are subjected to sample preparation to give final extract solutions.
- Equations are presented to estimate the original unknown amount and to calculate the 1-2α confidence interval about this estimate using the combined data set.

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Method details

Suppose that a liquid sample contains a particular compound of interest at unknown concentration. To determine this concentration, n aliquots of the sample are spiked with the analyte at concentration levels $(x_i)_{i=1,\ldots,n}$. Furthermore, sample material is diluted with blank matrix to give mixtures with sample volume fractions of $(k_j)_{j=1,\ldots,m}$ (ratios of sample volume to volume of total mixture). From each solution of the two series an aliquot of the same volume is taken and submitted to chemical analysis. The observed measurement values $y_1, \ldots, y_{n+m}$ are considered as realizations of random variables $Y_1, \ldots, Y_{n+m}$. Our statistical model is

$$\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \tag{1}$$

where

$$\mathbf{Y} = \begin{pmatrix} Y_1 \\ \vdots \\ Y_n \\ Y_{n+1} \\ \vdots \\ Y_{n+m} \end{pmatrix}, \quad \mathbf{X} = \begin{pmatrix} 1 & x_1 \\ \vdots & \vdots \\ 1 & x_n \\ k_1 & 0 \\ \vdots & \vdots \\ k_m & 0 \end{pmatrix}, \quad \boldsymbol{\beta} = \begin{pmatrix} \beta_0 \\ \beta_1 \end{pmatrix} = \begin{pmatrix} \beta_1 x^* \\ \beta_1 \end{pmatrix}$$

and

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 \\ \vdots \\ \varepsilon_n \\ \varepsilon_{n+1} \\ \vdots \\ \varepsilon_{n+m} \end{pmatrix}$$

x^* designates the unknown initial concentration of the analyte. The parameter β_1 is the slope and the parameter β_0 is the ordinate intercept of the straight line that relates the expectation of the signal to the spiked concentration. Note that β_0 is equal to $\beta_1 x^*$. Put another way, the functional relationship between the expectation of the signal and the totally present concentration is supposed to be given by a straight line through the origin. ε is the vector of the measurement errors. We assume that $\varepsilon_1, \ldots, \varepsilon_{n+m}$ is a sequence of independent and identically normally distributed random variables with expectation value zero and variance σ^2. Minimizing the sum of the squared deviations provides an estimator $\mathbf{b}$ for the parameter vector β:

$$\mathbf{b} = \begin{pmatrix} b_0 \\ b_1 \end{pmatrix} = (\mathbf{X}'\mathbf{X})''\mathbf{X}'\mathbf{Y} \tag{2}$$

that is

$$b_0 = \frac{\sum_i x_i^2 \left(\sum_i Y_i + \sum_j Y_{n+j} k_j\right) - \sum_i x_i Y_i \sum_i x_i}{\sum_i x_i^2 \left(n + \sum_j k_j^2\right) - \left(\sum_i x_i\right)^2} \tag{3}$$