Appendix

LEAST SQUARES METHOD

One stage of experimental results analysis is determination of kind of functional dependence between measured physicochemical quantities and then determination of parameters of a given equation. Such analysis can be made in a graphical or numerical way which is more accurate and more objective enabling optimal choice of parameters of the function describing the results of measurements.

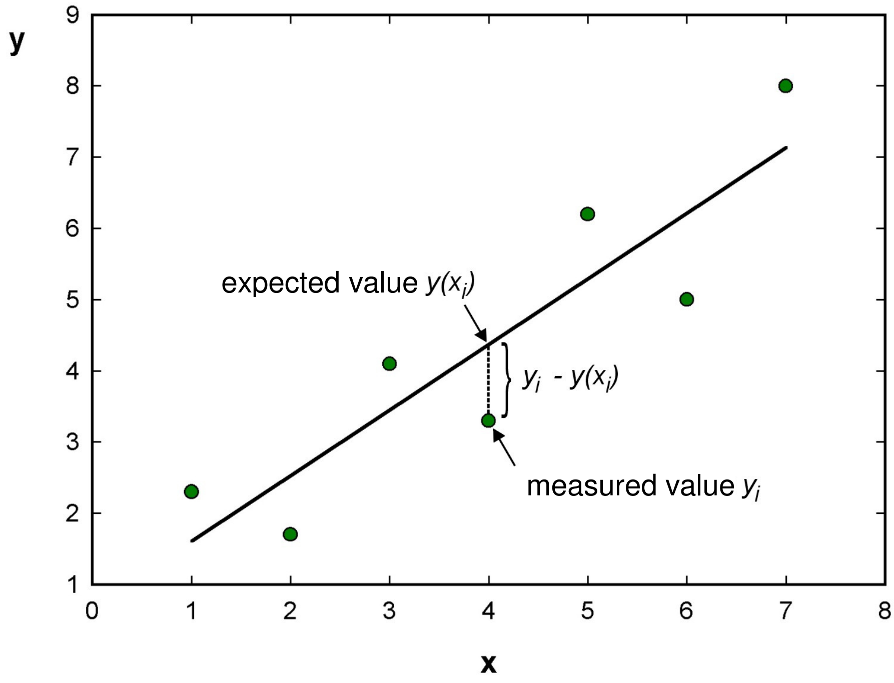
One of the methods of calculating coefficients of known equation is the least squares methods whose use is very simple when between the measured quantities x and y there is the linear dependence:

$$y(x) = ax + b \tag{1}$$

The use of the least squares method for linear equation (1) consists in such choice of parameters a and b that the deviation sum square between the measured quantity y_i and the expected value $y(x_i)$ (see Figure) reaches the minimal value:

$$S = \sum_{i=1}^{n} \left[y_i - y(x_i) \right] = \sum_{i=1}^{n} \left(y_i - ax_i - b \right)^2 \quad \rightarrow \quad \text{minimum} \tag{2}$$

where n – the number of experimental points.



The expected value $y(x_i)$ is calculated using the determined parameters a and b of the linear equation.

Condition (2) consists in finding the minimum of function of two variables $S(a,b)$ that is setting to zero its partial derivatives towards a and b:

$$\left(\frac{\partial S}{\partial a}\right)_b = 0 \qquad \left(\frac{\partial S}{\partial b}\right)_a = 0$$

$$\left(\frac{\partial S}{\partial a}\right)_b = \sum_{i=1}^{n} -2\left(y_i x_i - a x_i^2 - b x_i\right) \tag{3}$$

where

$$\left(\frac{\partial S}{\partial b}\right)_a = \sum_{i=1}^{n} -2\left(y_i - a x_i - b\right) \tag{4}$$

Hence there are obtained two equations with the two unknown, which can be solved on account of a and b:

$$a = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2} \tag{5}$$

$$b = \frac{\sum_{i=1}^{n} x_i^2 \sum_{i=1}^{n} y_i - \sum_{i=1}^{n} x_i y_i \sum_{i=1}^{n} x_i}{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2} \tag{6}$$

The calculation results should be put in the table.

i	x_i	y_i	$x_i\ y_i$		$y(x_i)$	$y_i - y(x_i)$
1 2 . . . n						
$\sum$					$a =$	$b =$

$SD_y =$ $SD_a =$ $SD_b =$

Standard deviation of parameters of the straight line, SD_a and SD_b

$$SD_y = \sqrt{\frac{S}{n-2}}$$

$$SD_a = SD_y \sqrt{\frac{n}{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}}$$

$$SD_b = SD_y \sqrt{\frac{\sum_{i=1}^{n} x_i^2}{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}}$$

The parameters a and b determined from equations (5) and (6) as a result of fitting the straight line to the experimental data results from unavoidable measurement and errors (as well as divergence between the actual course and the assumed rectilinear characteristics) loaded with errors. In the case from the definition of measured values there follows that for $b = 0$, the above considerations are further simplified.

In the measurement error of the dependent variable is not constant, the above equations should take into account suitable statistical weight factors. Generally, if both values i.e. x and y are loaded with measurement errors, there must be found the sum square of points distance from the straight line or the theoretical curve taking into account suitable statistical weights.