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Communications

An Error Model for the Evaluation of Uncertainty in Calibration Process

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When the result of an analysis or measurement is reported, it is obligatory that some quantitative indication of the quality of the result be given. The use of the *Guide to the Expression of Uncertainty in Measurements* (GUM)[1] is one of the prerequisites for the expression of the quality because it has been internationally accepted as an unified standard for communicating uncertainty. It has been widely applied to many fields of chemical analysis and measurements as an authentic standard.[1-3]

One of the general assumption in ordinary least square (OLS) method[4,5] is that the reference values in calibration have no uncertainty. This assumption is seriously impractical because the uncertainty in reference is one of the major sources. But, the calibration processes are generally assisted by OLS in most of all the fields without any serious consideration of errors. The purpose of this paper is to present a modified error model in calibration and how to calculate the uncertainty using the model strictly following the idea of GUM. The procedure developed can be applied to the results treated using OLS without any consideration on whether the reference values have uncertainties or not.

The model generally assumed in OLS[4,5] is

$$y_i = f(x_i) + \varepsilon_i^o \tag{1}$$

, where y_i is a variable of ith reading and x_i is a variable of ith reference. The model can be successfully used in OLS if the data obtained has the following characteristics.

i. The x_i value are controlled and/or observed without error.

ii. The errors are mutually independent.

iii. The errors have the same variance whatever be the value of y_i

iv. The errors are normally distributed.

v. The polynomial equation of calibration curve can be expressed like

$$y = f(x) = b_0 + b_1x + \cdots\cdots + b_m x^m \tag{2}$$

And the coefficients are calculated by OLS and uncertainty of unknown sample obtained using the equation (1) and (2). Matrix form of the coefficients of mth polynomial equation ($f(x)$) is given by

$$\boldsymbol{b} = (\boldsymbol{X}' \cdot \boldsymbol{X})^{-1} \cdot \boldsymbol{X}' \cdot \boldsymbol{y} \tag{3}$$

In case that both the reference and reading values have uncertainties, the error model of equation (1) can be expressed as

$$y_i + \varepsilon_{y_i} = f(x_i + \varepsilon_{x_i}) + \tau_i \tag{4}$$

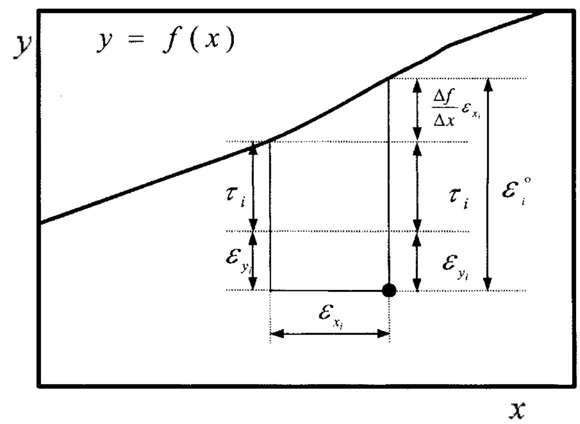

Figure 1. Illustration of measurement errors.

This correlation of the error model is presented in Figure 1. The errors between a solid data point and calibration curve can be divided into 3 vector quantities: ε_{x_i}, ε_{y_i}, τ_i. The figure shows that the equation (4) can be derived as

$$y_i = f(x_i) + \frac{\Delta f}{\Delta x}\varepsilon_{x_i} + \varepsilon_{y_i} + \tau_i \tag{5}$$

The error presented in the equation (1) is same as the sum of errors in the equation (4), so that

$$\frac{\Delta f}{\Delta x}\varepsilon_{x_i} + \varepsilon_{y_i} + \tau_i = \varepsilon_i^0 \tag{6}$$

And, the sum of squared errors is given by

$$Q = \sum_{i=1}^{n}\left(\frac{\Delta f}{\Delta x}\varepsilon_{x_i} + \varepsilon_{y_i} + \tau_i\right)^2 = \sum_{i=1}^{n}(\varepsilon_i^0)^2 = \sum_{i=1}^{n}\{y_i - f(x_i)\}^2 \tag{7}$$

, where the n is the number of the reference point used for calibration.

If the method of OLS is applied to data, then the coefficients of equation can be obtained by taking the partial differential of Eq. (7) and minimizing the Q. Therefore, the coefficients obtained through OLS are same as those obtained by new approach with model equation (4). In the modified error model, the polynomial equation of calibration curve can be expressed as

$$y = f(x) + \tau = b_0 + b_1 x + \cdots\cdots\cdots + b_n x^n + \tau \tag{8}$$

, where y is measurand, x is reading value of an unknown and the function is mth polynomial equation. And the coefficients of polynomial equation are same as those in equation (3). Practically, the equation (8) and (3) are used for the calculation of uncertainty strictly following the concept of GUM.

The value of error (τ) should be zero and the uncertainty and degree of freedom can be estimated from the ANOVA represented in Table 1. If error propagation law is applied to Eq. (6), Eq. (9) can be derived.

$$s^2\left(\frac{df}{dx}\varepsilon_{x_i} + \varepsilon_{y_i} + \tau_i\right) \cong s^2(\varepsilon_i^0) \cong s^2(\varepsilon_{y_i}) + s^2\left(\frac{df}{dx}\varepsilon_{x_i}\right) + s^2(\tau_i) \tag{9}$$

Therefore, standard uncertainty of error ($u(\tau)$) is obtained

Table 1. ANOVA table

Expected variance	Experimental variance	Degrees of freedom
$\sigma^2\left(\frac{df}{dx}\varepsilon_{x_i} + \varepsilon_{y_i} + \tau_i\right)$	$\frac{\sum_{i=1}^{n}(y_i - y_i^o)^2}{n-m-1}$	$n-m-1$
$\sigma^2(\varepsilon_{y_i})$	$\frac{\sum_{i=1}^{n} u^2(y_i)\times v_{y_i}}{\sum_{i=1}^{n} v_{y_i}}$	$\sum_{i=1}^{n} v_{y_i}$
$\sigma^2\left(\frac{df}{dx}\varepsilon_{x_i}\right)$	$\frac{\sum_{i=1}^{n}\left(\frac{df}{dx}\right)^2 u^2(x_i)\times v_{x_i}}{\sum_{i=1}^{n} v_{x_i}}$	$\sum_{i=1}^{n} v_{x_i}$

y_i^o is obtained from $y_i^o = f(x_i)$.

using

$$u^2(\tau) = \frac{\sum_{i=1}^{n}(y_i - y_i^0)^2}{n-m-1} - \frac{\sum_{i=1}^{n}\{u^2(y_i)\times v_{y_i}\}^2}{\sum_{i=1}^{n} v_{y_i}} - \frac{\sum_{i=1}^{n}\left\{\left(\frac{df}{dx}\right)^2 u^2(x_i)\times v_{x_i}\right\}^2}{\sum_{i=1}^{n} v_{x_i}} \tag{10}$$

The effective degree of freedom (v_{eff}) can be obtained from Welch-Satterswaite formula.[1,2] Thus,

$$\frac{u_c^4(y)}{v_{eff}} = \sum_{i=1}^{n}\frac{u_i^4(y_i)}{v_i} \tag{11}$$

Therefore, degree of freedom on error (τ) can be calculated with equation (12) and Table 1.

$$\frac{u^4(\tau)}{v(\tau)} = \frac{u^4(\varepsilon_i^o)}{v(\varepsilon_i^o)} + \frac{u^4(\varepsilon_{y_i})}{v(\varepsilon_{y_i})} + \frac{u^4\left(\frac{df}{dx}\varepsilon_{x_i}\right)}{v\left(\frac{df}{dx}\varepsilon_{x_i}\right)} \tag{12}$$

Because of all the input data including those of the error (τ) quantified, we can calculate combined standard uncertainty and effective degrees of freedom of output variable (y). In the equation (8), the coefficients are expressed with the functions of all the variables of the reading and reference variables so that the equation is independently described by all the reading and reference values, reading value of unknown, and the error (τ) :

$$y = f(x, x_1, x_2, \cdots, x_n, y_1, y_2, \cdots, y_n) + \tau \tag{13}$$

The combined standard uncertainty is obtained from the principle of error propagation. Therefore, the combined uncertainty (u_c) of y is obtained from

$$\begin{aligned} u_c^2 = {} & \left(\frac{\partial f}{\partial x_1}\right)^2 \cdot u(x_1)^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \cdot u(x_2)^2 \cdots\cdots\cdots + \left(\frac{\partial f}{\partial x_n}\right)^2 \cdot u(x_n)^2 \\ & + \left(\frac{\partial f}{\partial y_1}\right)^2 \cdot u(y_1)^2 + \left(\frac{\partial f}{\partial y_2}\right)^2 \cdot u(y_2)^2 \cdots\cdots\cdots + \left(\frac{\partial f}{\partial y_n}\right)^2 \cdot u(y_n)^2 \\ & + \left(\frac{\partial f}{\partial x}\right)^2 \cdot u(x)^2 + \left(\frac{\partial f}{\partial \tau}\right)^2 \cdot u(\tau)^2 \end{aligned} \tag{14}$$

Contrary to uncertainty treatment in OLS, all the uncertainty of reading and reference value and the error (τ) should be propagated to the final out variable (y) because of the initial assumption at which both the reading and reference values have uncertainties.

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