Simplifying the calculation for the law of propagation of uncertainty

In an experimental work, the quantity to be determined is often calculated from a combination of many steps with observable quantities such as:

- weight,
- titre,
- dilution factor,
- uncertainty given by certified calibration standard chemicals,
- instrumental calibration uncertainty, etc.

The final calculation may involve taking the sum, difference, product (multiplication) or quotient of two or more quantities or the raising of any quantity to a power.

When we want to estimate an ***uncertainty*** *of our measurement, we have to consider the total measurement error incurred.* The **total error** of an analytical process is combined by the *independent* error contributions of *all steps* of the analytical procedure (e.g. sampling, sample preparation, dissolution, separation, extraction, measurement, etc). The combination of individual errors to give the total error is determined partly by statistics and partly by functional relationships of the form:

$$y = f(x_1, x_2, x_3, \ldots.) \qquad (1)$$

The total standard uncertainty u_y, in terms of variance, can be estimated according to the general law of propagation of errors for ***independent*** variables $x_1, x_2, x_3, \ldots., x_n$ with associated respective standard deviations, $u(x_1), u(x_2), u(x_3), \ldots., u(x_n)$:

$$u_y^2 = \sum_{i=1}^{n} \left[\frac{\partial f}{\partial x_i} \right]^2 u(x_i)^2 \qquad (2)$$

$\left[\frac{\partial f}{\partial x_i} \right]$ is called sensitivity coefficient, represented by symbol c_i， i.e. $c_i = \partial f / \partial x_i$。

If $x_1, x_2, \ldots$ have interaction with each other, the propagated uncertainty is then

$$u_y^2 = \sum \left(\frac{\partial f}{\partial x_i} \right)^2 u(x_i)^2 + \sum \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} Cov(x_i, x_j) \qquad (3)$$

In chemical analysis, the steps taken in the test method are mutually independent and hence the equation (2) can be applied, i.e.

$$u_y^2 = \sum \{ [\partial f / \partial x_1]^2 u(x_1)^2 + [\partial f / \partial x_2]^2 u(x_2)^2 + [\partial f / \partial x_3]^2 u(x_3)^2 + \ldots. \} \qquad (2a)$$

or

$$u_y^2 = \sum \{ c_1^2 u(x_1)^2 + c_2^2 u(x_2)^2 + c_3^2 u(x_3)^2 + \ldots. \} \qquad (2b)$$

Hence, u_y is an estimate of combined standard uncertainty. In the process of uncertainty evaluation, x_1, x_2,…can be concentration C, volume v, weight w, dilution factor D, etc。

Example 1: If the relationship between y and C, v and w is

$$y = \frac{C \times v \times 1000}{w}$$

Then, by differentiating the above equation, we have

$$\frac{dy}{dC} = \frac{v \times 1000}{w} \quad ; \quad \frac{dy}{dv} = \frac{C \times 1000}{w} \quad ; \quad \frac{dy}{dw} = -\frac{C \times v \times 1000}{w^2}$$

If $C = 0.45 mg/L$, $v = 10 ml$, $w = 1.5682 g$,

and standard uncertainties are $u(C) = 0.05 mg/L$, $u(v) = 0.08 ml$, $u(w) = 0.002 g$

$$y = \frac{C \times v \times 1000}{w} = \frac{0.45 \times 10 \times 1000}{1.5682} = 2{,}870 \mu g / L$$

The individual sensitivity coefficients are separately:

$$c_c = \frac{dy}{dC} = \frac{10 \times 1000}{1.5682} = 6376.74$$

$$c_v = \frac{dy}{dv} = \frac{0.45 \times 1000}{1.5682} = 286.95$$

$$c_w = \frac{dy}{dw} = -\frac{0.45 \times 10 \times 1000}{1.5682^2} = -1829.83$$

Hence : $u_y^2 = \{c_c^2 u(C)^2 + c_v^2 u(v)^2 + c_w^2 u(w)^2\}$

$= \{6376.74^2 \text{x} 0.05^2 + 286.95^2 \text{x} 0.08^2 + (-1829.83)^2 \text{x} 0.002^2\} = 102197$

$u_y = 320 \mu g/L$

Let's take a look at various situations:.

a. Addition/Subtraction

If $y = mA + nB + pC$

and their associated standard uncertainties are: u_A, u_B, u_C

then, the combined variance as from Eq (2) is: $u_y^2 = m^2u_A^2 + n^2u_B^2 + p^2u_C^2$ (4)

Example 2

If the analytical balance of a laboratory was found to have a standard uncertainty of $11.8mg$.

In an experiment, the weight of a weighing bottle as given by this balance was $m_1 = 24.9845$g, and the weight of weighing bottle + a portion of sample was $m_2 = 35.3460$g

Hence the weight of sample was $m = m_2 - m_1 = 35.3460 - 24.9845 = 10.3615$g

and the combined variance of this weighing process was $u_m^2 = 11.8^2 + 11.8^2 = 278.48$

It follows then that the combined standard uncertainty of this portion of sample taken for experiment was $u_m = 16.7mg = 0.0167g$

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b. Multiplication / Division

If the relationship between y and A, B, C was: $y = m\dfrac{AB}{C}$ where m is a constant

By applying Eq (2) and after differentiation, we have

$$u_y^2 = \left(m\frac{B}{C}\right)^2 u_A^2 + \left(m\frac{A}{C}\right)^2 u_B^2 + \left(-m\frac{AB}{C^2}\right)^2 u_C^2 \qquad (5)$$

If we were to divide the left side of Eq (5) by y^2, and the right side by $\left(m\dfrac{AB}{C}\right)^2$, we have:

$$\left(\frac{u_y}{y}\right)^2 = \left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2 + \left(\frac{u_C}{C}\right)^2 \qquad (6)$$

Eq (6) shows that we can directly use the square of coefficient of variation CV of each of the components involved and this has largely simplified the more complicated calculus calculations.

Example 3

Let's re-look at the Example 1 and we shall see how easy we can evaluate the final combined standard uncertainty as follows:

$$y = \frac{c \times v \times 1000}{w} = \frac{0.45 \times 10 \times 1000}{1.5682} = 2{,}870 \mu g / L$$

Since the various standard uncertainties were: $u_c = 0.05 mg/L$, $u_v = 0.08 ml$, $u_w = 0.002 g$,

we have:

$$\left(\frac{u_y}{2870}\right)^2 = \left(\frac{u_c}{c}\right)^2 + \left(\frac{u_v}{v}\right)^2 + \left(\frac{u_w}{w}\right)^2 = \left(\frac{0.05}{0.45}\right)^2 + \left(\frac{0.08}{10}\right)^2 + \left(\frac{0.002}{1.5682}\right)^2$$

Hence,

$$u_y = 320 \mu g/L$$
