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SHORT COMMUNICATION

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An uncertainty evaluation for multiple measurements by GUM

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Abstract An approach for uncertainty evaluation is proposed to determine the overall uncertainty by combining the uncertainties of the individual results from multiple measurements. It is accomplished by the separate combinations of the individual random and systematic components of the uncertainties of the individual results. The approach is useful when the individual results are not statistically different. It is recognized that, owing to the correlation, the uncertainty resulting from systematic effects is not reduced by multiple measurements. On the contrary, the uncertainty resulting from random effects can be reduced.

Keywords Uncertainty · Covariance · Uncertainty Propagation · GUM

Introduction

Measurement is defined as "*set of operations having the object of determining a value of a quantity*" according to the "*International Vocabulary of Basic and General Terms in Metrology*"(VIM) [1]. Therefore, a measurement procedure should be understood as a whole process including sample treatment, instrumental analysis and data treatment (personal correspondence with Paul De Bièvre at IRMM) . A result of a measurement is an estimate of the value of a measurand and, to be complete, should be accompanied by an uncertainty statement. The "*Guide to the Expression of Uncertainty of Measurement*" (GUM) provides general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurements [2]. The EURACHEM/CITAC Guide "*Quantifying Uncertainty in Analytical Measurement*" illustrates how the concepts in GUM can be applied in chemical measurement [3]. The examples in GUM and the EURACHEM Guide are limited to a specific analytical determination using *one* specific measurement procedure. Until now, almost all of the examples for uncertainty in measurement have been based on the result of a *single* measurement. However, it is quite often for the analytical chemist to carry out multiple measurements in order to report an average value and its uncertainty as a result. Here, we are proposing an approach to uncertainty evaluation which determines the overall uncertainty by combining the uncertainties of the individual results from multiple measurements.

Uncertainty evaluation based on GUM

A measurand Y is not measured directly but is determined from N other input quantities X_i using a functional relationship f.

$$Y = f(X_1, X_2, \ldots, X_N) \tag{1}$$

where input quantities X_1, X_2, ..., X_N upon which the output quantity Y depends may themselves be viewed as measurands and may themselves depend on other quantities.

The estimated standard deviation associated with each input estimate x_i of X_i, is termed the standard uncertainty $u(x_i)$. There are two approaches to estimate the standard uncertainty based on the evaluation method: Type A evaluation is based on statistical treatment on a series of observations, and Type B evaluation is based on all means other than statistical one such as data from certificates, manufacturer's specifications, previous experimental data, experience or knowledge, etc. For convenience, standard uncertainty estimated by Type A evaluation is sometimes called Type A standard uncertainty. The same applies for the Type B component. However, it is worthwhile considering that both Type A and Type B uncertainties can be due to a "random effect" as well as to a "systematic effect" in nature. Random effect gives rise to variations in repeated observations. Systematic effect is the recognized effect of an influence quantity on a measurement result, which causes systematic error. The estimated standard deviation associated with output estimate y of Y, termed combined standard uncertainty, $u_c(y)$, is:

$$u_c^2(y) = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left(\frac{\partial f}{\partial x_i}\right)\left(\frac{\partial f}{\partial x_j}\right)u(x_i, x_j) \quad (2)$$

where $u(x_i, x_j)$, covariance between x_i and x_j, is estimated by the degree of correlation

$$u(x_i, x_j) = r(x_i, x_j)\, u(x_i)\, u(x_j) \quad (3)$$

Although $u_c(y)$ can be universally used to express the uncertainty of a measurement result, it is often required to give a measure of uncertainty that defines an interval about the measurement result that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand. This additional measure of uncertainty is termed the expanded uncertainty, U, and it is determined, in general, by multiplying $u_c(y)$ by a coverage factor k=2 [3].

$$U = k\, u_c(y) \quad (4)$$

An approach to combining uncertainties from multiple measurements

This approach is useful when the individual results are not statistically different. The individual results, $y_1, y_2, ..., y_n$ and their corresponding uncertainties, $u(y_1), u(y_2), ..., u(y_n)$, are obtained by n measurements. The expected value m of M is taken as the arithmetic mean of n measurements.

$$M = \frac{1}{n}\sum_{k=1}^{n} Y_k = \frac{Y_1 + Y_2 + \ldots + Y_n}{n} \quad (5)$$

The combined standard uncertainty, based on Eq. (2), is

$$u_c^2(m) = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial y_i}\right)^2 u^2(y_i) + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left(\frac{\partial f}{\partial y_i}\right)\left(\frac{\partial f}{\partial y_j}\right)u(y_i, y_j) \quad (6)$$

According to GUM, an individual standard uncertainty $u(y_i)$ for the given single measurement has already been evaluated by combining the uncertainties from Types A and B evaluations. It can be recomposed into random $u_R(y_i)$ and systematic $u_S(y_i)$ components and be combined again to give:

$$u(y_i) = \sqrt{u_R^2(y_i) + u_S^2(y_i)} \quad (7)$$

where $u_R(y_i)$ and $u_S(y_i)$ are the individual standard uncertainties due to random and systematic effects, respectively, of ith measurements. The separate combinations of random and systematic components for n measurements give the overall combined standard uncertainty

$$u_c(m) = \sqrt{u_R^2(m) + u_S^2(m)} \quad (8)$$

where $u_R(m)$ and $u_S(m)$ are the overall combined standard uncertainties due to random and systematic effects, respectively, for n measurements.

Since the individual uncertainties due to random effects in n measurements are not correlated, $r(y_i, y_j)$=0 in Eq. (6), the combined standard uncertainty due to random effects $u_R(m)$ is:

$$u_R(m) = \sqrt{\frac{u_R^2(y_1) + u_R^2(y_2) + \ldots + u_R^2(y_n)}{n^2}} \quad (9)$$

On the contrary, the individual uncertainties due to systematic effects in n measurements are fully correlated, $r(y_i, y_j)$=1 in Eq. (6), therefore, the combined standard uncertainty due to systematic effects $u_S(m)$ is:

$$u_S(m) = \sqrt{\frac{u_S(y_1) + u_S(y_2) + \ldots + u_S(y_n)}{n}} \quad (10)$$

With the same measurement procedure under repeatability conditions, the uncertainties of the individual results are expected to be similar and, especially, the uncertainties due to systematic effects are supposed to be the same for n measurements. Therefore, Eq. (6) can be expressed as

$$u_c(m) = \sqrt{\frac{u_{R,P}^2(y)}{n} + u_S^2(y)}$$

where $u_{R,P}(y) = \sqrt{\frac{u_R^2(y_1) + u_R^2(y_2) + \ldots + u_R^2(y_n)}{n}}$

$$u_S(y) = u_S(y_1) = u_S(y_2) = \ldots = u_S(y_n) \quad (11)$$

Conclusions

This paper has described how to determine the overall uncertainty from the uncertainties of the individual results of n measurements. It is accomplished by the separate combinations of the uncertainties arising from systematic and random effects. It is recognized that, owing to the correlation, the uncertainty resulting form systematic effects is not reduced by n measurements. On the contrary, the uncertainty arising from random effects can be reduced by increasing the number of measurements. Further work is needed to combine the results of multiple measurements when the individual results are statistically different.

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