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An Approach for the Uncertainty Evaluation of the Overall Result from Replications of Measurement: Separately Combining Individual Uncertainty Components According to their 'systematic' and 'random' Effects

In Jung Kim,* Byungjoo Kim, and Euijin Hwang

*Korea Research Institute of Standards and Science, Daejeon 305-340, Korea. *E-mail: kimij@kriss.re.kr*
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In our previous articles, an approach has been proposed for the evaluation of the uncertainty of overall result from multiple measurements. In the approach, uncertainty sources were classified into two groups: the first including those giving same 'systematic' effect on each individual measurement and the second including the others giving 'random' effect on each individual measurement and causing a variation among individual measurement results. The arithmetic mean of the replicated measurements is usually assigned as the value for the overall result. Uncertainty of the overall result is determined by separately evaluating and combining an overall uncertainty from sources of the 'systematic' effect and another overall uncertainty from sources of the 'random' effect. This conceptual approach has been widely adopted in chemical metrology society. In this study, further logical proof with more detailed mathematical expressions is provided on the approach

Key Words : Uncertainty, Replications of measurement, Systematic effect, Random effect

Introduction

A result of a measurement is an estimate of the value of a measurand and its associated uncertainty which characterize the dispersion of the value.[1-3] The uncertainty arises from many components related with the operational processes of the measurement. The "Guide to the Expression of Uncertainty of Measurement" (GUM) and its updated version of "Evaluation of measurement data – Guide to the expression of uncertainty in measurement" (JCGM 100:2008) provide general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurements.[1,2] The EURACHEM/CITAC Guide "Quantifying Uncertainty in Analytical Measurement, 2nd ed." illustrates how the concepts in GUM can be applied in the measurement in chemistry.[4]

The result of measurement, in many cases, is determined on the basis of series of repeated observations. And an average value and its uncertainty are usually reported as the overall result of measurement. However examples in the above guides are limited to the evaluation of uncertainty in the results from a single measurement. The 3rd edition of the EURACHEM/CITAC Guide was recently published[5], in which the repeatability of the measurement method was added as an additional uncertainty source without precise consideration of its relationship with other uncertainty sources. In our previous articles,[3,6] an approach for uncertainty evaluation of the average value obtained as the result of replicated measurements has been designed. Uncertainty components are usually categorized into Type A and Type B according to their way of evaluation.[1,2] However they also can be categorized into groups causing 'systematic' effect and 'random' effect to each individual measurement.[1,2,7-10] The 'systematic' sources are such parameters associated with calibration standards, reference data, bias corrections, etc., whose effects are usually common and not altered under repeatability conditions. On the contrary, effects of the 'random' sources are unique to each single measurement and they contribute to the variation among individual measurement results.

In the previous articles, the uncertainty of the average value is determined by separately evaluating and combining an overall uncertainty from the 'systematic' sources and another overall uncertainty from the 'random' sources.[3,6] The approach was designed based on two general ideas: (1) the overall uncertainty from the 'systematic' sources would not be affected or reduced by replication number of measurement owing to the correlation, (2) the overall uncertainty from the 'random' sources could be obtained by combining the uncertainty components in the group, or better estimated by statistical variation among the observations. Logical proof for the approach was described in the articles.[3,6] In this article, the approach is revisited and further logical proof on the approach is provided with more-detailed mathematical expressions, which was not clearly addressed in the previous articles. It was also made clear under what conditions the approach can be applied.

Theory

Uncertainty for Single Measurement. In most cases, measurand Y is determined from k input quantities of X_j's using a functional relationship of f.

$$Y = f(X_1, X_2, \ldots, X_k) \quad (1)$$

Then value of Y from the i^{th} replication of measurement, y_i, is determined as Eq. (2),

$$y_i = f(x_{i1}, x_{i2},..., x_{ik}) \tag{2}$$

where x_{ij} is the estimate of the input quantity of X_{ij}, the j^{th} input quantity in the i^{th} replication of measurement. Then the combined uncertainty of y_i is calculated as Eq. (3),[1,2]

$$u_c^2(y_i) = \sum_{j=1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij}) + 2\sum_{j=1}^{k-1}\sum_{l=j+1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)\left(\frac{\partial f}{\partial x_{il}}\right)u(x_{ij}, x_{il}) \tag{3}$$

where $u(x_{ij})$ is the value of the standard uncertainty of the x_{ij} and $u(x_{ij},x_{il})$ is covariance between x_{ij} and x_{il}, which is estimated by the degree of correlation ($r(x_{ij},x_{il})$) as Eq. (4).

$$u(x_{ij},x_{il}) = u(x_{ij})u(x_{il})r(x_{ij}, x_{il}) \tag{4}$$

Parameters causing the 'systematic' effect are not correlated with parameters causing the 'random' effect. Hence $u_c(y_i)$ can be decomposed into the 'systematic' and 'random' components and be combined again to give:[3,6]

$$u_c^2(y_i) = u_S^2(y_i) + u_R^2(y_i) \tag{5}$$

where $u_S(y_i)$ and $u_R(y_i)$ are the overall uncertainties from the 'systematic' and the 'random' sources, respectively, in the i^{th} measurement. If the order (or sequence) of the input quantities is rearranged so that X_{ij}'s ($1 \le j \le p$) should be the parameters of the 'systematic' sources and the others ($p < j \le k$) be those of the 'random' sources, then according to Eq. (3) and Eq. (4), $u_S(y_i)$ and $u_R(y_i)$ are respectively given as:

$$u_S^2(y_i) = \sum_{j=1}^{p}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij}) + 2\sum_{j=1}^{p-1}\sum_{l=j+1}^{p}\left(\frac{\partial f}{\partial x_{ij}}\right)\left(\frac{\partial f}{\partial x_{il}}\right)u(x_{ij})u(x_{il})r(x_{ij}, x_{il}) \tag{6}$$

$$u_R^2(y_i) = \sum_{j=p+1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij}) + 2\sum_{j=p+1}^{k-1}\sum_{l=j+1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)\left(\frac{\partial f}{\partial x_{il}}\right)u(x_{ij})u(x_{il})r(x_{ij}, x_{il}) \tag{7}$$

Uncertainty for Replicated Measurements. The individual results, y_1, y_2, $\cdots$, y_n, and their corresponding standard uncertainties, $u_c(y_1)$, $u_c(y_2)$, $\cdots$, $u_c(y_n)$, are obtained from n replications of measurement. The expected value m of M is determined from the individual results of the n measurements using another functional relationship of F.

$$M = F(Y_1, Y_2,..., Y_n) \tag{8}$$

And, in most cases, M is taken as the arithmetic mean of the n replications of measurement.

$$F(Y_1, Y_2,..., Y_n) \equiv \frac{1}{n}\sum_{i=1}^{n} Y_i \tag{9}$$

The combined standard uncertainty of m, based on Eq. (3), is

$$u_c^2(m) = \sum_{i=1}^{n}\left(\frac{\partial F}{\partial y_i}\right)^2 u^2(y_i) + 2\sum_{i=1}^{n-1}\sum_{l=i+1}^{n}\left(\frac{\partial F}{\partial y_i}\right)\left(\frac{\partial F}{\partial y_l}\right)u(y_i, y_l) \tag{10}$$

However, the functional relationship between Y_i's and M can be resolved into another functional relationship of g between the individual input quantities of X_{ij}'s and M,

$$M = g\begin{pmatrix} X_{11} & X_{12} & \dots & X_{1k} \\ X_{21} & X_{22} & \dots & X_{2k} \\ \dots & \dots & \dots & \dots \\ X_{n1} & X_{n2} & \dots & X_{nk} \end{pmatrix} \equiv \frac{1}{n}\sum_{i=1}^{n} f(X_{i1}, X_{i2},..., X_{ik}) \tag{11}$$

Then the combined standard uncertainty $u_c(m)$, based on Eq. (3), is also given in another form as:

$$u_c^2(m) = \sum_{i=1}^{n}\sum_{j=1}^{k}\left(\frac{\partial g}{\partial x_{ij}}\right)^2 u^2(x_{ij}) + 2\sum_{i=1}^{n}\sum_{j=1}^{k-1}\sum_{l=j+1}^{k}\left(\frac{\partial g}{\partial x_{ij}}\right)\left(\frac{\partial g}{\partial x_{il}}\right)u(x_{ij})u(x_{il})r(x_{ij}, x_{il}) + 2\sum_{i=1}^{n-1}\sum_{q=i+1}^{n}\sum_{j=1}^{k}\sum_{l=1}^{k}\left(\frac{\partial g}{\partial x_{ij}}\right)\left(\frac{\partial g}{\partial x_{ql}}\right)u(x_{ij})u(x_{ql})r(x_{ij}, x_{ql}) \tag{12}$$

where,

$$\left(\frac{\partial g}{\partial x_{ij}}\right) = \frac{1}{n}\left(\frac{\partial f}{\partial x_{ij}}\right) \tag{13}$$

In Eq. (12), $r(x_{ij}, x_{ql})$ satisfies following relations; (1) $r(x_{ij}, x_{ql}) = r(x_{ql}, x_{ij})$, (2) if (j or $l > p$, $i \ne q$) then $r(x_{ij}, x_{ql}) = 0$ since the 'random' sources obtained from different observations cannot be correlated to each other either to the 'systematic' sources, (3) if (j, $l \le p$) then $r(x_{ij}, x_{qj}) = 1$ and $r(x_{ij}, x_{ql}) = r(x_{0j}, x_{0l})$ since the 'systematic' sources cause the same effects on Y_i and Y_q. Thus if $u_c(m)$ is decomposed into $u_S(m)$ and $u_R(m)$, just as in Eq. (5), and be combined again, then it is given as:

$$u_c^2(m) = u_S^2(m) + u_R^2(m) \tag{14}$$

$$u_S^2(m) = \frac{1}{n^2}\sum_{j=1}^{p}\left\{\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_{ij}}\right)u(x_{ij})\right\}^2 + \frac{2}{n^2}\sum_{j=1}^{p-1}\sum_{l=j+1}^{p}\left\{\sum_{i=1}^{n}\sum_{q=1}^{n}\left(\frac{\partial f}{\partial x_{ij}}\right)\left(\frac{\partial f}{\partial x_{ql}}\right)u(x_{ij})u(x_{ql})r(x_{0j}, x_{0l})\right\} \tag{15}$$

$$u_R^2(m) = \frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=p+1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij}) + \frac{2}{n^2}\sum_{i=1}^{n}\sum_{j=p+1}^{k-1}\sum_{l=j+1}^{k}\left(\frac{\partial f}{\partial x_{ij}}\right)\left(\frac{\partial f}{\partial x_{il}}\right)u(x_{ij})u(x_{il})r(x_{ij},x_{il}) = \frac{1}{n^2}\sum_{i=1}^{n} u_R^2(y_i) \tag{16}$$

where $u_R(y_i)$ is given in Eq. (7). However, if the probability distribution of the observations could be properly evaluated, $u_R(m)$ can be evaluated also from the probability distribution;

$$u_R(m) = \frac{1}{\sqrt{n}} s(y_i) \tag{17}$$

where $s(y_i)$ is the estimated standard deviation of the individual results.

Results and Discussion

One of the idea, on which the approach[3,6] was designed, is that the overall uncertainty from the 'random' sources could be obtained by combining the uncertainty components in the group, or better estimated by statistical variation among the observations. It is trivial that overall uncertainty from the 'random' sources could be determined by Eq. (16), if there were no unrecognized terms[6] or inexactly known influent quantities[1,2,11] such as inhomogeneity of analytical sample or repeatability/reproducibility of the measurement procedure, *etc.* However, if any unrecognized terms or inexactly known influence quantities were involved in the measurement, then Eq. (16) would cause underestimation of the overall uncertainty from the 'random' sources. A good consistency between $u_R(m)$s estimated by Eq. (16) and Eq. (17) would be obtained only when a measurement were made on very well homogenized analytical sample under good repeatability conditions.[14] However, in many cases, it is not easy to eliminate those unrecognized or inexactly known influence quantities. Thus $u_R(m)$ would be best estimated by Eq. (17), if statistical variation among the observations could be properly evaluated.

Another idea, based on which the approach[3,6] was designed, is that the overall uncertainty from the 'systematic' sources should not be reduced by increasing number of replicates of measurement, since each of them are strongly correlated to itself. Eq. (15) is mathematical expression of the idea. However, Eq. (15) is too much complex for practical use. And it is found that it can be simplified under certain conditions: (1) uncertainties of the 'systematic' sources are nearly constant at every replication of measurement, $u(x_{ij}) \approx u(x_{0j})$ ($j \le p$), (2) different 'systematic' sources are not correlated to each other, $r(x_{0j}, x_{0l}) = 0$ ($j, l \le p, l \ne j$).

Case I: $u(x_{ij}) \approx u(x_{0j})$ ($j \le p$). If $u(x_{ij}) \approx u(x_{0j})$ for any j ($j \le p$), then, according to Eq. (6) and Eq. (15), it is naturally satisfied that $u_S(m) \approx u_S(y_0)$, where and $u_S(y_0)$ is given as:

$$u_S^2(y_0) \equiv \sum_{j=1}^{p}\left(\frac{\partial f}{\partial x_{0j}}\right)^2 u^2(x_{0j}) + 2\sum_{j=1}^{p-1}\sum_{l=j+1}^{p}\left(\frac{\partial f}{\partial x_{0j}}\right)\left(\frac{\partial f}{\partial x_{0l}}\right)u(x_{0j})u(x_{0l})r(x_{0j}, x_{0l}) \quad (18)$$

In Eq. (18), $u(x_{0j})$ can take any value of $u(x_{ij})$ obtained from a series of measurement. In some cases, each $u_S(y_i)$ would be automatically obtained from individual replicate by the assist of spreadsheets or analysis programs, etc. then $u_{S'}(m)$ given as Eq. (19) could be taken as the value of $u_S(m)$ instead.

$$u_{S'}(m) \equiv \frac{1}{n}\sum_{i=1}^{n} u_S(y_i) \quad (19)$$

Case II: $r(x_{0j}, x_{0l}) = 0$ ($j, l \le p, l \ne j$). If $r(x_{0j}, x_{0l}) = 0$ ($j, l \le p, l \ne j$) is applied to Eq. (6) and Eq. (15), then $u_S(y_i)$ and $u_S(m)$ are simply given as:

$$u_S^2(y_i) = \sum_{j=1}^{p}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij}) \quad (20)$$

$$u_S^2(m) = \frac{1}{n^2}\sum_{j=1}^{p}\left[\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_{ij}}\right)u(x_{ij})\right]^2 \quad (21)$$

Minkowski inequality[12] provides a simpler way to estimate $u_S(m)$ as:

$$\sqrt{\sum_{j=1}^{p}\left[\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_{ij}}\right)u(x_{ij})\right]^2} \le \sum_{i=1}^{n}\sqrt{\sum_{j=1}^{p}\left(\frac{\partial f}{\partial x_{ij}}\right)^2 u^2(x_{ij})} \quad (22)$$

or

$$u_S(m) \le u_{S'}(m) \quad (23)$$

the equation of inequality (22) or inequality (23) is satisfied when $u(x_{ij})$ is constant independent of i for any js, or $u(x_{ij}) = u(x_{0j})$. Thus $u_{S'}(m)$ given in Eq. (19) can be taken as the estimated value of $u_S(m)$ instead, also in this case.

Therefore, once the condition of $u(x_{ij}) \approx u(x_{0j})$ or $r(x_{0j}, x_{0l}) = 0$ ($j, l \le p, l \ne j$) is satisfied, $u_c(m)$ can be determined as Eq. (24):[6]

$$u_C^2(m) = u_{S'}^2(m) + \frac{s^2}{n} \quad (24)$$

Those conditions are not rare but usually satisfied in many cases of measurement. In most of cases, the magnitudes of $u(x_{ij})$ ($j \le p$) is very similar among replicates ($i = 1$ to n). Even in many of cases, x_{ij} and $u(x_{ij})$ are same for all replicates when the measurements are performed under well controlled repeatable conditions.[13,14] One example of the cases is concentration of standard solution used for calibration for all replicates of samples, and its uncertainty is inherently the same for all replicates. Any parameters would have the correlation among them when they rise from a series-of-procedure[1,2] or whose functional form share more than one input quantity of variable.[15,16] However the correlation can be eliminated by immersing them into a new parameter, so that the new one would not be correlated with the others any more. One example of the cases is the correlation between concentrations of internal standard and calibration standard being added up to prepare a calibration solution. The correlation is simply eliminated by immersing them into a new parameter of their mass-ratio, and that scheme is a usually applied. Thus application of the approach[3,6] would not be limited much by the conditions. The approach may cause $u_c(m)$ be over-estimated by a little bit in some cases, but would provide convenience.

Conclusion

An approach[3,6] proposed to evaluate uncertainty of overall result from replicates of measurement is revisited. In the approach, uncertainty sources were classified into two groups: the first including those giving same 'systematic' effect on each individual measurement and the second including the others giving 'random' effect on each individual measurement and causing a variation among individual measurement results. The arithmetic mean of the replicated measurements was assigned as the value for the overall result, and whose uncertainty was determined by separately evaluating and combining an overall uncertainty from the 'systematic' sources and another overall uncertainty from the 'random' sources.[3,6] In this study, it is shown that the approach provides simple and convenient way to estimate uncertainty of the overall result from replicates of measurement but that it works under certain conditions which was not declared in the original papers. The required condition is (1) uncertainties of the 'systematic' sources are nearly constant at every replication of measurement or (2) different 'systematic' sources are not correlated to each other. However it is considered that application of the approach would not be limited much by the conditions, since these conditions are usually satisfied in many practical measurement cases. The approach discussed in this paper is a bottom-up design for uncertainty evaluation. Hence the approach would not be proper for usual laboratories to apply since it would take more effort than top-down approaches. However this kind of approach would be helpful for those who are looking for better understanding of a certain measurement and for improvement of their measurement quality.

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