Approaches of Evaluating Measurement Uncertainty – General Discussion

Despite of exhaustive literature information, many analysts are still unsure in evaluating the uncertainty of measurement, mainly because of the intrinsic difficulties in choosing an appropriate approach and/or of an inadequate background in statistics and metrology fundamentals. Sometimes, additional problems, at present under debate such as how to relate measurement uncertainty to the compliance of specification, make their efforts even more stressful. General discussions of the various approaches are appended below:

The ISO GUM approach

The current popular approach in estimating measurement uncertainty is largely based on the "**G**uide to the Expression of **U**ncertainty in **M**easurements" by ISO/IEC Guide 98.

This Guide, known as **GUM** in short, has been extensively used and followed closely by those personnel in calibration and metrology community since its first publication in 1995.

The GUM method supposes that a mathematical model is available or can be derived that describes the functional relationship between the measurand and the influence quantities.

In a laboratory analysis method, we usually have a mathematical equation comprising all the values collected in the various steps to calculate the final value to be measured.

For example: In an analytical method, we may have involved in:

- the weight of sample used for analysis, W gm
- the prepared sample solution, V ml
- a dilution factor, D
- result of the prepared sample solution from the instruction calibration, Abs mg/L

and hence, the concentration of the analyte of interest in the sample, C is calculated as:

$$C = \frac{Abs \times D \times V}{W}$$

Note: all values in these various steps form the functional relationship for the final value.

Now, we need to gather and consider the contributions of these individual uncertainties and other additional possible effects for the final outcome. The overall uncertainty is then estimated via the "law of propagation of uncertainty", following identification and quantification of uncertainties in individual influence factors or 'budgets'.

As this component-by-component approach builds upon the basic steps of the analysis, it is also known as the "bottom-up" approach.

Other Schools of Thoughts

In order to simplify the evaluation process, many other attempts have been made by different technical working groups of accreditation and professional bodies to apply the basic GUM principles in chemical measurements in more simplified manners, generally based on the overall performance of the test method. This is sometimes known as holistic approach:

- The earliest and most referred one is from the Eurachem group which published a guide called "Quantifying Uncertainty in Analytical Measurement" (3rd edition) in the year 2012. You may check the Internet at http://eurachem.org/index.php/publications/guides/quam

- The Nordic Committee of Food Analysis in the Scandinavian countries is also trying to propose alternative approach to this problem. Search the NMKL Procedure No. 5 (2003) on "Estimation and expression of measurement uncertainty in chemical analysis" at http://www.nmkl.org

- The ISO Technical Committee ISO/TC 69, *Applications of Statistical Methods*, Sub-committee SC, *Measurement Methods and Results*, has also been working actively to come out with more guidance for measurement uncertainty estimation.

  The recently adopted ISO 21748:2010 is named as "Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation".

All these so-called simplified methods attempt to evaluate the uncertainty by determining the overall performance parameters in experiments. Such experiments are practical and form the basis for most in-house method validation. They use measures of QA/QC data such as precision as the basis for estimating uncertainty that are well known in the testing community. These measures include reproducibility ,repeatability and accuracy. The use of a dynamic control chart moving range data is another technique for evaluating the uncertainty of an established test method.

These measures are standard deviations derived from the analysis of experimental data, and if the reproducibility experiment is designed in such a way that variability due to all of the major sources of uncertainty is simplified, then reliable estimates of uncertainty can be based entirely on experiment without having to resort to the mathematics and theory found in the GUM that so many people find daunting.

In fact, the ISO GUM states explicitly (Section 3.4.1) that "If all the quantities on which the results of a measurement depends are varied, its uncertainty can be evaluated by statistical means" strongly suggesting that a reconciliation between the two is possible in principle. There are however, significant difficulties in applying the GUM methodology generally in analytical chemistry. In particular, it is common to find that the largest contributions to uncertainty arise from the least predictable effects, such as matrix effects on extraction or response, sampling operations, and interferences. And, the GUM assumes no systematic error which may occur frequently in analytical chemistry.

Hence, using the established QA/QC data as the 'top-down' approach also has its merits and shortcomings. This will be discussed in the subsequent write-up.