Measurement Uncertainty – The very basic

Introduction

Currently many measurement uncertainty (MU) courses and workshops for test laboratories in this region are run by metrology experts instead of practicing chemists. Several laboratory analysts and quality control personnel have found the outcome after attending the two- or three-day presentations rather disillusion, leaving the classroom with their minds even more uncertain. This is because they cannot see how to apply in their routine works as there are no practical worked examples demonstrated to satisfy their needs.

To address this issue, let us go back to the very basic on the subject of measurement uncertainty from the viewpoints of a laboratory analyst.

First of all, we must be clear that we do not *calculate* measurement uncertainty but *estimate* measurement uncertainty as the subject involves statistics and some probability theories. It will be even better to say we *evaluate* measurement uncertainty.

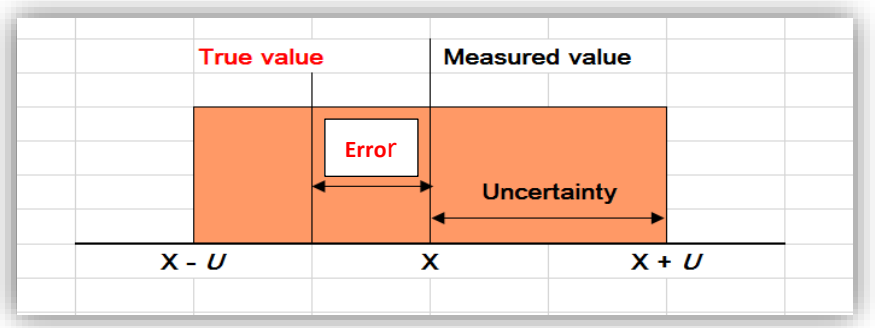
It is also clear to us that laboratory analytical procedures are affected both by **random errors** (i.e., variation of results during analysis) and by **systematic error** (or bias) which shows consistently higher or lower results than the expected, assigned or reference value. It will be ideal if we can provide a single number which describes the uncertainty of these combined effect for the confidence and benefits of our data users. Even the laboratory accreditation standards ISO/IEC 17025 and ISO 15189 also recognize its importance.

So, what is measurement uncertainty?

The definition of the term **uncertainty of measurement** as provided by the ISO *Guide to the expression of uncertainty in measurement* ('the GUM') is:

"A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand."

Simply speaking, the **uncertainty** of a result is a statistical parameter that describes a range of values within which the targeted or true value of the analyte quantity in the sample analyzed is expected to lie, taking into account all sources of error involved in the testing process. That means we can tell the client that the actual analyte concentration of the sample given to us for analysis lies *somewhere* in this range of values after proper uncertainty evaluation with a certain stated degree of confidence, but we are unable to say for sure where it exactly lies!



We can express measurement uncertainty in two ways:

Standard uncertainty (***u***) expressed as a standard deviation is being used throughout in the process of such evaluation until the very last stage of reporting the overall measurement uncertainty in the form of expanded uncertainty.

Hence, **expanded uncertainty** (***U***), also known as measurement uncertainty, is defined as a range that encompasses a large fraction of the values within which the quantity being measured will lie and is obtained by multiplying u by a coverage factor, k, chosen according to the degree of confidence required for the range, i.e., $U = u \times k$.

Since u is analogous to a standard deviation, if k is 2 (which is generally taken as the default value if no other probability information is given), then U gives approximately half-width of the 95% confidence interval. In the laboratory context, we can put it that expanded uncertainty (U) shows a concentration interval around the result of the measurement within which we expect the true value to lie with a reasonably high probability, usually 95%.

Two general approaches to estimating measurement uncertainty

The **bottom-up approach** identifies each separate step of an analysis, including sampling steps whenever necessary, assigns appropriate random and systematic errors to each, and then combines these components using the Law of Propagation of Uncertainty, to give an overall combined u-value before multiplying with a coverage factor k for the expanded uncertainty. This is essentially the familiar ISO **GUM** method as documented in JCGM 100 series. However, this GUM process may not be as simple as it seems.

As even simple analytical processes may involve many individual experimental steps (such as sub-sampling, weighing, digestion, extraction, standard volume preparation, instrument calibrations, sample carry-over, etc. etc.) with possible quantifiable and non-quantifiable errors, we may overlook some of these error sources, and thus arrive at an over-optimistic or unrealistic uncertainty value.

Even if we are able to identify and cover all sources of error, the whole calculation process is expected to be tedious and not practical.

Furthermore, in many laboratories, it may not be necessary to review and make such calculations very often, as an uncertainty estimate made in detail for one analysis may serve as a model for other closely similar analyses cover a period of time. But over time, the laboratories may see a change of technical staff with variable technical competence and newly installed equipment, amongst other changes. The uncertainty value determined earlier may not be realistic in today's situation.

The **top-down method** is a completely different approach. It seeks to look at the holistic performance of the analytical method in terms of its repeatability, intermediate reproducibility and reproducibility, in addition to sampling uncertainty. This approach is particularly appropriate where individual step's uncertainty effects are poorly understood and cannot be quantified.

One of the ways is to use

(1) the uncertainty results in the form of reproducibility (R) reported by some properly run proficiency testing (PT) or inter-laboratory comparison programs participated by a good number of laboratories, and,

(2) the laboratory's own intermediate reproducibility (R') which indicates the long-term within-laboratory precision,

to give estimates of the overall uncertainties of the measurement without necessary trying to identify every individual source of error. This will offer a great saving of effort as compared to the GUM method.

As most PT scheme allow participating laboratories to use a variety of their routine analytical methods instead of an appointed standard method, we might reasonably assume that the uncertainty of results from a single laboratory that has long experience of a single well-established method might be better (smaller) than PT results would suggest.

Today PT schemes are rapidly expanding in number and may provide a real alternative to bottom-up methods in many fields of analysis. However, if a laboratory has not done well in the PT program participated, being flagged as an outlier, it has to review its own performance and find out the errors committed before using this top-down approach.

There are other simpler top-down methods, designed to minimize the workload that use a wide range of analytical procedures for their analytical uncertainty component. They are:

1. Evaluating uncertainties from the overall standard deviations of measurements made in *intermediate reproducibility* (R') conditions, i.e., with different analysts on different days by means of different instruments, using different concentrations and in all relevant matrices, after having established that the method used does not have systematic errors.

2. Even if the method has a bias tendency and cannot be minimized or corrected, the standard uncertainty of bias, u_b can be incorporated as a component of the uncertainty formula.

3. By running replicate measurements on stable and well-characterized authentic samples, reference materials or laboratory control samples, the results may be presented as a quality control chart and the combined standard uncertainty can be evaluated from the mean moving average result calculated.

A list of published international references in relation to the use of top-down approaches, though not exhaustive, can be found on the site: https://consultglp.com/2017/08/09/list-of-published-documents-on-top-down-mu-methods/