The concept of measurement uncertainty – a new perspective

Actually the term "measurement uncertainty" has been referred to being analytical uncertainty by most, if not all, testing laboratories since the very first edition of ISO/IEC 17025:1999 accreditation standards set the requirement for measurement uncertainty. However, since the publication of the newly revised ISO/IEC 17025:2017, measurement uncertainty evaluation has expanded its coverage to include sampling uncertainty as well because ISO has recognized that sampling uncertainty can be a serious factor in the final test result obtained from a given sample. Indeed, sampling may not be considered as a standalone activity because its activities always be associated with testing and calibration.

One must not be mistaken that by taking many random samples from a population and analyze each of the samples for the targeted analyte once, the confidence interval (i.e. standard error of mean, SEM) of the population mean is the sampling uncertainty, using Student's t-distribution equation:

$$\mu = \bar{x} \pm t_{(\alpha,n-1)}\frac{s}{\sqrt{n}}$$

In fact, the factor $SEM = t_{(\alpha,n-1)}\frac{s}{\sqrt{n}}$ is just a measurement of sampling error.

To evaluate sampling uncertainty, we must at the same time consider the analytical uncertainty in order to present the overall picture of measurement uncertainty.

Eurachem/CITAC Guide (2007) "*Measurement Uncertainty arising from Sampling*" and Nordtest Technical Report TR 604 (2007) "*Uncertainty from Sampling*" have proposed few empirical methods for such evaluation.

The empirical approach is intended to obtain a reliable uncertainty estimate without necessarily knowing any of the sources individually. It is **to study the overall reproducibility estimates** (in-house or inter-organizational sampling and measurement trials), being a top-down method.

The simplest approach is to draw at least 8 samples randomly from a population and analyze each sample twice. The data obtained from this simple split experimental design are subject to one-way ANOVA (analysis of variance) which leads us to get the sampling standard uncertainty as well as the analytical uncertainty. In fact, by this method, we are actually evaluating the sampling and analytical precisions. If bias does exist in sampling or analysis, or both, we can add these bias uncertainties as another uncertainty components in the overall measurement uncertainty estimation.

Let's examine an example of taking 10-hourly beverage samples from a bottling process for the analysis of their total sugars contents (% m/v). The analytical data obtained were summarized below:

Table 1: Total sugar contents (%m/v) of 10-hourly samples in a beverage bottling process

Hours	1	2	3	4	5	6	7	8	9	10
Duplicate 1	6.88	6.11	6.69	6.32	5.92	6.44	6.32	6.65	6.94	6.10
Duplicate 2	6.53	6.58	6.87	5.95	6.54	6.79	6.75	6.43	6.58	6.24
Mean	6.71	6.35	6.78	6.14	6.23	6.62	6.54	6.54	6.76	6.17

The overall mean = 6.48 %m/v. By applying the one-way ANOVA on the MS Excel® Analytical Tool, the following outcomes were obtained:

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Hour 1	2	13.41	6.705	0.06125
Hour 2	2	12.69	6.345	0.11045
Hour 3	2	13.562	6.781	0.016562
Hour 4	2	12.27	6.135	0.06845
Hour 5	2	12.46	6.23	0.1922
Hour 6	2	13.23	6.615	0.06125
Hour 7	2	13.07	6.535	0.09245
Hour 8	2	13.08	6.54	0.0242
Hour 9	2	13.52	6.76	0.0648
Hour 10	2	12.34	6.17	0.0098

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Hours	1.080601	9	0.120067	1.711786	0.207138	3.020383
Within Hours	0.701412	10	0.070141			
Total	1.782013	19				

From the ANOVA results, we conclude that:

1. As the calculated *F*–value of 1.712 was lower than the critical value of 3.020, there was no significance difference between the sampling and analytical errors.
2. The Mean Square (within hours), which is also known as Mean Square (within sample) or Variance (within sample) or analysis variance = 0.070. It follows that the standard uncertainty of analysis expressed as standard deviation, $u_{analysis} = \sqrt{0.070} = 0.265$ %(m/v)
3. Mean Square (between hours), also known as Mean Square (between samples) or Variance (between samples) = 0.120.
4. The variance in (3) for the measurement covers both sampling variance and analysis variance. In other words, $\sigma^2_{measurement} = \sigma^2_{sampling} + n\sigma^2_{analysis}$
5. Hence, Mean Square (sampling) or sampling variance = (0.120–0.070)/2 = 0.025. It follows that the standard uncertainty of sampling expressed as standard deviation $u_{sampling} = \sqrt{0.025} = 0.158$ %m/v.
6. Since combined standard measurement uncertainty = $\sqrt{u^2_{sampling} + u^2_{analysis}}$, we have $Combined\ u = \sqrt{0.158^2 + 0.265^2} = 0.31$ %m/v
7. The expanded uncertainty = 2 x 0.31 = 0.62 %m/v.
8. Report as : Total sugars content, %m/v = 6.48 ± 0.62 with a coverage factor of 2 with 95% confidence