

# Is my uncertainty estimate realistic?

**Analysts' estimates of the uncertainty of their results are often somewhat low. How do we know? By looking at the results of interlaboratory studies such as collaborative trials and proficiency tests. These studies are designed to make explicit any latent contributions to uncertainty. The results can be helpful in assessing the validity of our uncertainty estimates.**

Consider a hypothetical example. Suppose we have group of laboratories, each of which analyses the same homogeneous material for a minor constit

We can draw two immediate conclusions from a situation such as that in Figure 2:

- § There are sources of error contributing to the dispersion of results that many, perhaps most of the participants did not take into account in their uncertainty budgets.
- § Until these additional sources of error are understood and properly incorporated into the individual uncertainty estimates, the estimates cannot be regarded as adequate or realistic.

## Interlaboratory studies

A collaborative trial is designed to explore the performance of a particular analytical method applied to a specified type of test material. All of the participant laboratories apply the same closely defined analytical procedure to the same set of materials. The main outcome of the study is separate estimates of repeatability and reproducibility standard deviations ( $\sigma_r$  and  $\sigma_R$  respectively), which are regarded as characteristics of the method. Repeatability conditions are those prevailing within a single analytical run. A standard deviation based on repeated results obtained under repeatability conditions can never incorporate all the factors that are relevant to an uncertainty estimate. The reproducibility (or between-laboratory) standard deviation, however, also takes account of variation due to

- § different interpretations of the method protocol in the various laboratories;
- § different occasions (runs) when the method is used within a laboratory, perhaps due to different analysts, different equipment and new calibration curves.

## How large are these additional effects?

On average, we find in collaborative trials for a single method that

$$\text{Eq 1} \quad \sigma_r \approx 0.5\sigma_R,$$

which is an indication of the magnitude of the 'missing' uncertainty.

We can also estimate the possible biases associated with particular analytical methods. These can arise, for example, through variations in the recovery when the analyte is transferred from the test material into the test solution, and uncorrected interference effects.

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Furthermore, diagrams showing individual uncertainties have not so far been common in routine proficiency tests. Nevertheless, there is good evidence to show that the underlying situation is very often exactly as shown.

In real life (as opposed to the specially designed studies considered above) there may be further sources of error that may need to be