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Measurement uncertainty arising from sampling: the new Eurachem Guide

Chemical analysis is undertaken to support a decision about the target* material, such as its commercial value or whether it is within specification. The decision is based on the measurement result and its uncertainty. But chemical measurement nearly always includes a primary sampling step, which generates its own contribution to the overall uncertainty on the result. As the customer needs to know the combined uncertainty of the whole measurement process (including sampling) to make an optimal decision about the target, the inclusion or exclusion of a contribution from sampling can make a critical difference to the reliability of a decision.

Although standard procedures for obtaining a representative sample have been laid down for many types of material, few methods have been validated in the way that allows the sampling uncertainty to be estimated. Moreover, until recently there was little information about how sampling uncertainty should be addressed. This is unfortunate because in many instances sampling makes a substantial or even dominant contribution to the combined uncertainty of the measurement.

The Eurachem Guide to sampling uncertainty was drawn up to address this shortcoming. It advocates a logical sequence of events familiar to analytical chemists, namely: (i) to validate a method by examining its uncertainty; (ii) to check that the uncertainty is consistent with fitness for purpose; and (iii) to check by quality control procedures that the uncertainty is not deteriorating during routine use of the method. Of course, in all of this, we have to recognise that sampling uncertainty will vary with the concentration of the analyte. While many of the methods described in the Guide are recognisable analogues of quality procedures in chemical analysis, there are some important differences that have to be taken into account.

Unique feature of uncertainty from sampling

Firstly, much of the uncertainty of sampling springs from the heterogeneity of the target, and the degree of heterogeneity may vary from target to target. We cannot therefore base validation on a single target. Moreover, when an unusually heterogeneous target is encountered in routine operations, it is possible for a measurement result to be unfit for purpose even though the method was applied exactly as specified in the validated procedure. This fact makes routine quality control of sampling exceptionally important.

Secondly, while sampling precision can be addressed by simple replication, sampling bias is difficult to assess. The sampling analogue of a reference material can sometimes be made, but it could be prohibitively costly to prepare and maintain. Seemingly the best that can be managed in this area is the comparison of a 'quick-and-dirty' sampling method with a more elaborate procedure that is thought *a priori* to be unbiased. At present it is often impracticable to assess sampling bias and its contribution is omitted from the uncertainty budget.

Finally, sampling variation can be explored only via chemical analysis which adds its own variation to the results. That means that experiments in sampling validation are necessarily more elaborate than in analytical validation.

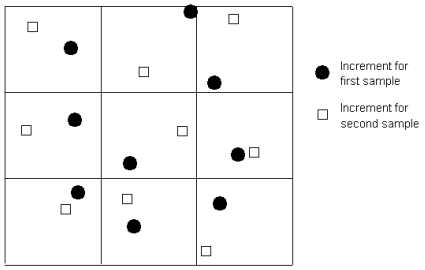

Figure 1. An example of randomised duplicate sampling. The sampling target is divided into 'strata', and the increments for the duplicate composite samples are extracted at random positions within each stratum.

The modelling and empirical approaches to sampling precision

The Eurachem Guide recognises and gives examples of two rather different approaches to estimating sampling precision. The modelling approach follows the GUM method for estimating uncertainties by breaking down the sampling procedure into elementary operations in the form of a 'cause-and-effect' (fishbone) diagram, estimating the uncertainty resulting from each contribution, and then combining them in the usual fashion. Another modelling possibility that can be applied to targets in which the material is consistently well-defined (in terms of the range of particle sizes and shapes and distribution of the analyte among them) is based on the sampling theory of Pierre Gy.

* 'Target' is used in the defined technical sense of 'portion of material, at a particular time, that the sample is intended to represent'.

A general problem with the modelling approach is that it relies on having a lot of information about the nature of the target. It is therefore mainly of use when the qualities of the target material are rather predictable, as in many processed materials.

The empirical approach

Empirical methods rely entirely on the replication of sampling to estimate the precision. Of course, the replication has to be randomised in some way, or at least a good approximation to randomised, to obtain a valid precision estimate. For instance, if the sampling protocol requires the collection of a number of increments to form a composite sample, the increments must be collected at random points in the target. For a duplicate sample, the increments must be taken at a new set of random points. Figure 1 schematically shows how this might be done in a stratified target.

Duplicate sampling of a number of typical targets is the most efficient design, so that a validation experiment would look like Figure 2. Hierarchical analysis of variance can then provide estimates of the sampling and analytical standard deviations σ_{sam}, σ_{an}. A robust procedure could be used to moderate the influence of an unexpected atypical target.

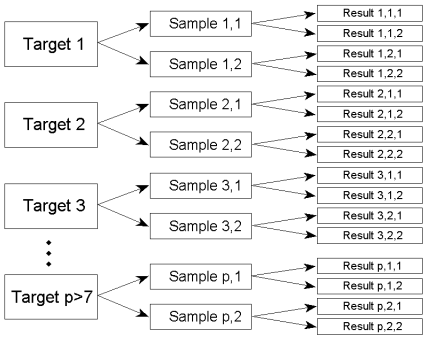

Figure 2. Design for the estimation of sampling precision from a randomised replicated experiment.

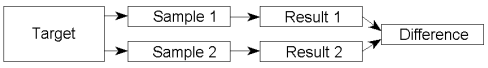

Figure 3. Design for sampling quality control.

Internal quality control

To conduct sampling quality control, subsequent targets are sampled in duplicate and each duplicate analysed once (Figure 3). The standard deviation of the difference between the two results[†]

$\sigma_{diff} = \sqrt{\left(\sigma_{sam}^2 + \sigma_{an}^2\right)/2}$ can be used to set up control limits at $\pm 2\sigma_{diff}, \pm 3\sigma_{diff}$. If sampling uncertainty were dominant, such a chart would represent primarily variations in sampling. Figure 4 shows an example.

[†] If there is substantial variation in the concentration of the analyte in successive targets, the difference may need to be scaled to accommodate the concomitant variation in uncertainty.

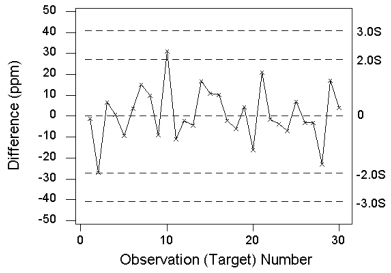

Figure 4. Routine internal quality control chart for combined analytical and sampling variation for the determination of aluminium in animal feed. The training set (used to define the control limits) comprises the first nine observations.

Between-sampler variation

Rather more elaborate designs can be undertaken to address variation between individual samplers, which can sometimes be shown to exist. This is a way of including some components of sampling bias into estimates of measurement uncertainty. The sampling analogues of the collaborative trial and the proficiency test have been investigated essentially as feasibility studies. These exercises are certainly feasible, but they are complex and costly to carry out and it is not clear yet whether they will find regular use.

Further reading

- *Measurement uncertainty arising from sampling—a guide to methods and approaches* (2007) 102pp. The Guide is the joint production, under the Chairmanship of Prof M H Ramsey, of Eurachem, CITAC, Eurolab, Nordtest and the Analytical Methods Committee. It contains chapters on fundamental concepts, estimation of sampling uncertainty, and management issues. Six practical examples are examined in detail. (Free download available from the Eurachem website www.eurachem.org/guides)
- *Uncertainty from sampling, in the context of fitness for purpose.* M H Ramsey and M Thompson (2007) *Accred Qual Assur* **12**:503-513. (A review of quality concepts and practice in sampling. Easy reading.)
- *Eurachem Workshop on Uncertainty from Sampling* in Berlin (April 2008). PowerPoint presentations from the Workshop are available gratis on www.eurolab-d.bam.de

This Technical Brief was prepared for the Analytical Methods Committee by the Sampling Uncertainty/ Sampling Quality Subcommittee under the Chairmanship of M H Ramsey.

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