Precision data from validation

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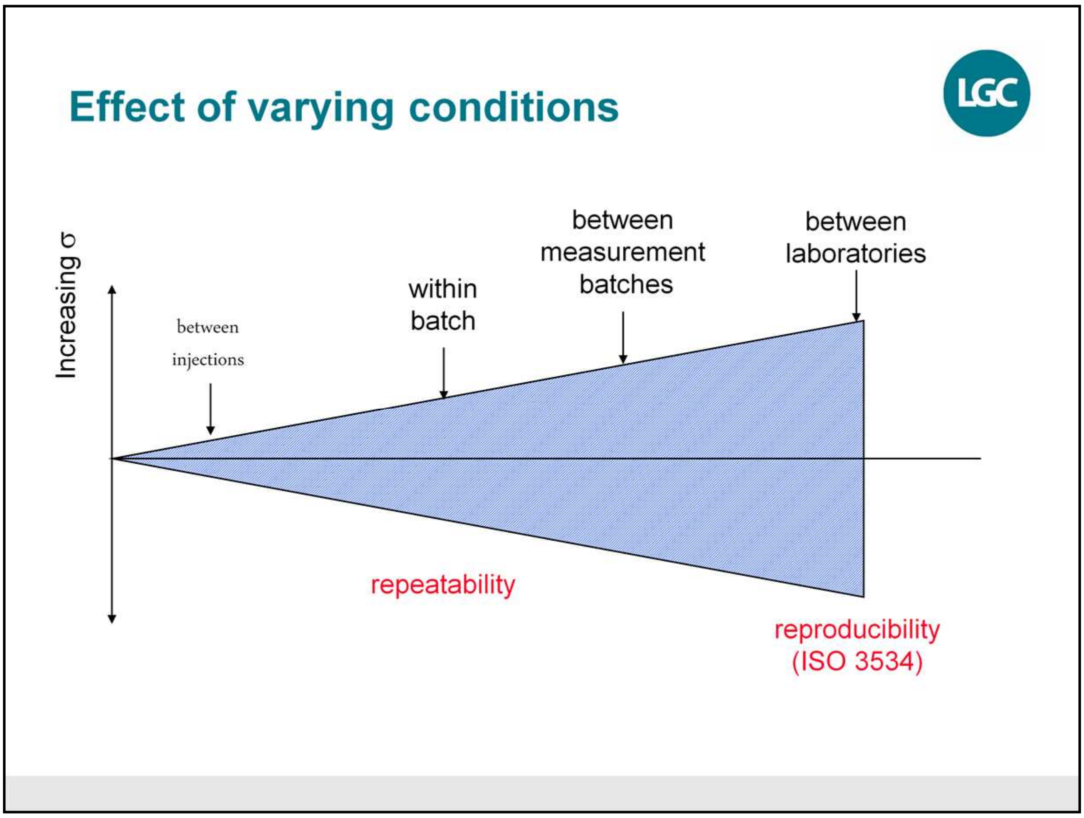
Overview

- Different types of precision estimate
- Measurement uncertainty and precision studies
- Forms of precision data
- Contribution of precision to overall uncertainty



Precision measures depend greatly on the things that are are allowed to vary. It is vital to understand which parameters were, or were not, held constant during a particular precision experiment.

Simply re-injecting the same prepared extract usually gives a much smaller spread of results than repeating the whole method, extractions and all, even within a short period of time. Interlaboratory variability is always larger than typical within-laboratory variation for the same method. So it is important to know the conditions under which the precision value was obtained.

Two frequently encountered sets of conditions are **repeatability**, where essentially all conditions (analyst, time, equipment, laboratory) for a single method are maintained constant, and **reproducibility**, where conditions are allowed to vary. The most common definition of reproducibility conditions (ISO 3534) specifically refers to variation of results from different laboratories using the same method and applied to the same material.

Some sectors also recognise the term **intermediate precision**, representing the extreme of variation within a single laboratory, or some other intermediate set of conditions.

In practice it is permissible to calculate precision under any particular set of conditions but those conditions must be stated if the precision value is to have any useful meaning.

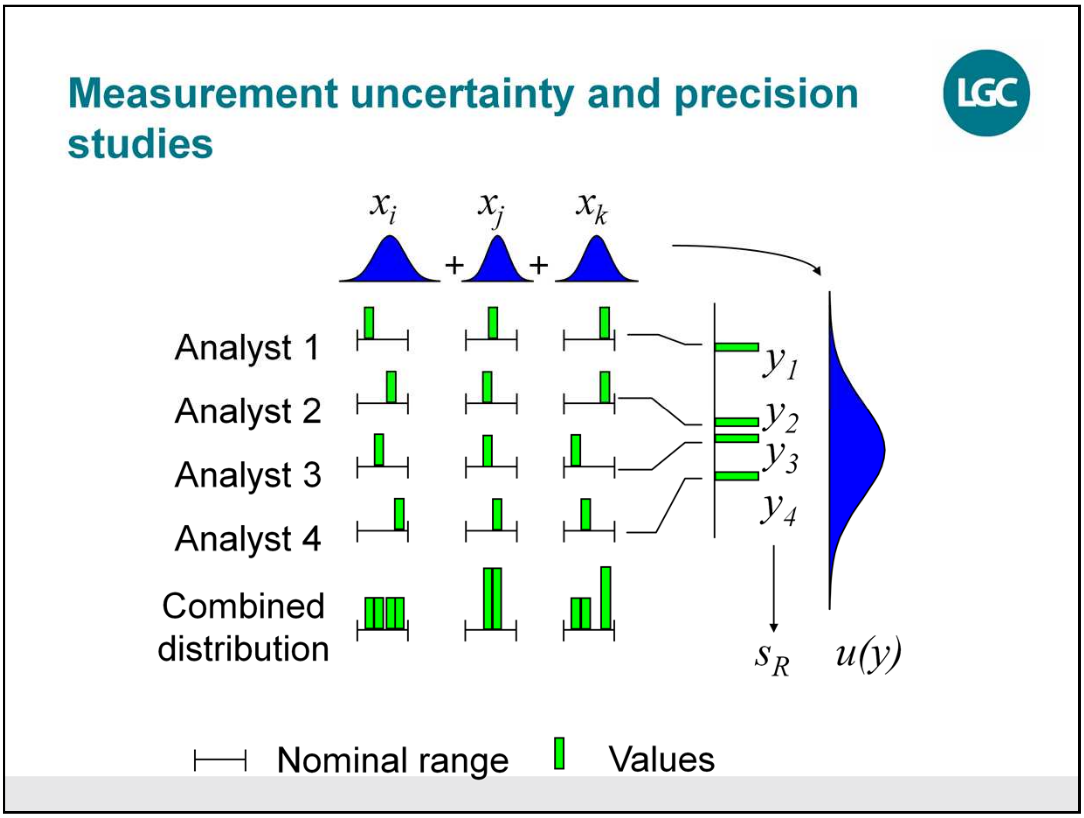
What varies?

	Repeatability	Between batch	Reproducibility
Sample prep	●	●	◐
Extraction	●	●	●
Reagents	○	◐	●
Environment	○	◐	●
Equipment	○	◐	●
Operator	○	◐	●
Matrix effect	○	○	○

Different factors vary under different conditions. The table above shows some examples of factors and the conditions under which they typically vary.

Clearly, precision measured under each set of conditions gives different information. None is the "right" precision; measurement uncertainty estimation can employ precision measures effectively for all or part of a procedure.

In general, a better idea of the full variability of a method under all conditions is obtained under reproducibility conditions. But even here, important factors may be missing. Collaborative studies usually use homogenised materials, reducing the effects of sample preparation, and reproducibility figures are almost invariably quoted for single matrices, neglecting systematic matrix effects.



The diagram shows a model of the relationship between measurement uncertainty and precision experiments. The example is based on a multi-analyst study, but the same concepts apply to any set of results.

In this view, the analysts' results (y_1 to y_4) vary because each result for each analyst arises from a particular collection of all the effects operating (represented by x_i to x_k, here). Each of these effects can take a range of values. The combined effect of this near-random selection of all these effects is the spread of values y_1 to y_4.

Measurement uncertainty can be thought of as an estimate of the spread really caused by all the effects operating, if each took its full range of values. In principle, this could be done by randomly varying all the input effects across their real range. In practice, this is usually very time-consuming; that is why measurement uncertainty estimation often involves the evaluation of effects that have not been varied during an experiment.

The diagram also illustrates (see x_j) effects that do not take their full range of values during the experiment, perhaps because of consistent training practices or more consistent environmental conditions.

One important corollary of this view is that IF everything relevant is varied representatively, including things that might normally be considered 'systematic effects', the spread of *y* values includes all the relevant contributions.

Implication:

A factor that is representatively varied during the course of a precision experiment requires no further study

If the precision experiments are properly done, there is less work to do in evaluating uncertainty

... but MAKE SURE OF WHAT IS VARIED!