Precision

Overview

- What is precision
- Expression of precision
- Different types of precision
- Determining precision
- Useful application of precision data
- Pitfalls in determining precision

This lecture will describe precision, what it is, how it is calculated and the different ways it can be expressed. The different types of precision will be discussed, together with potential uses and the common pitfalls that analysts encounter when dealing with precision.

Precision

"The closeness of agreement between independent test/measurement results obtained under stipulated conditions"

[ISO 3534-2:2006]

The ISO definition is shown above. Different sources agree pretty well on this definition. It is important to note are that test results need to be independent and that precision is defined for stated conditions. Both of these issues are dealt with in more detail later.

Precision is...

- A measure of the spread of results
- Calculated and reported for particular conditions
- Possibly dependent on
  - analyte concentration
  - sample matrix

Precision is a measure of the spread of the results, in other words how different the results are from each other. Precision in isolation has nothing to do with the closeness of a value to a "true" value. Precision is dependent upon the conditions under which it is determined and so it should always be calculated and reported for stated conditions.

Precision may be either a function of, or independent of, analyte concentration or property value. In general, the relative precision of a measurement becomes larger, i.e. worse, the lower the analyte concentration.

Precision is also usually matrix dependent.

For any validation experiment it is normal to determine precision for a number of sets of conditions, at a number of concentrations and for a variety of representative sample matrices.

Expression of precision

- Usually calculated as a standard deviation from the results of replicate analyses, for a given set of conditions
- May be stated in a variety of ways, e.g.:
  - standard deviation
  - relative standard deviation (rsd, CV)
  - limit (R, r, l)

Precision determinations start with replicate analyses made within a given set of conditions. The simplest form of expression is to state the standard deviation (*s*) so obtained. Assuming normal distribution, 95% of values should lie within ±2*s* of the mean.

Dividing the standard deviation by the mean value gives the relative standard deviation (rsd). This may also be expressed as a percentage and quoted as the CV (coefficient of variation). The main danger with the use of relative values is the loss of units, which exposes the risk of comparing like with unlike (for example if the value of *s* from determining the boiling point of water is 1°C or 1K, then depending on which scale you use the CV is either 1% or 0.27%.

Reproducibility limit R and repeatability limit r involve multiplying the appropriate *s* by $t\sqrt{2}$, where *t* is the Student's *t* value for the appropriate number of degrees of freedom. Further explanations of these limits are given later.

Different precision estimates

- Repeatability
  - same laboratory, analyst, equipment, short time interval
  - typically used for studying variation within a batch of analyses
- Intermediate precision
  - within lab variation - different days, analysts, equipment
  - can be in a number of forms - user defined
- Reproducibility
  - different laboratories, analysts, equipment
  - typically used to study between laboratory variation in measurements

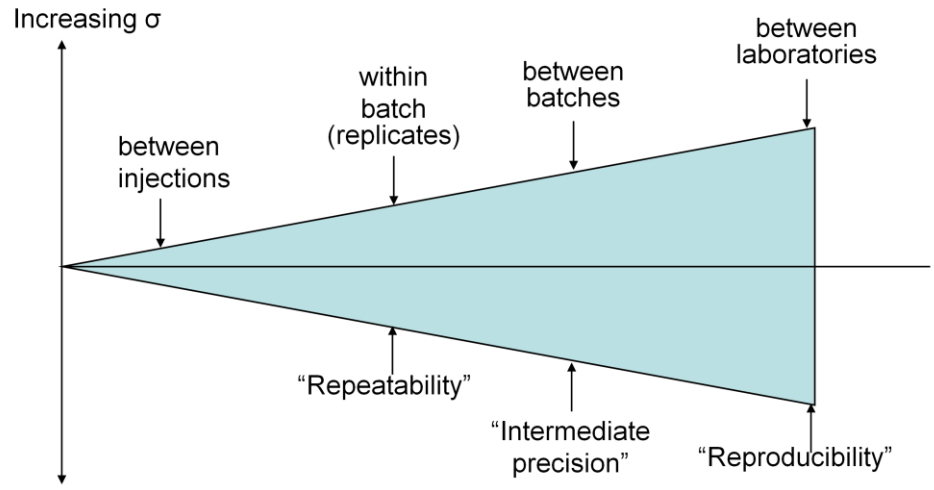
Repeatability represents the tightest extreme of independent precision measurements, describing as it does the sort of precision one might expect from a set of replicate measurements made one after the other, in a single laboratory, by a single analyst on a single instrument. Over such conditions one would not expect results to be affected by drift. The time interval may well be a period of several days for methods where each determination takes several hours.

Intermediate precision is a less widely accepted term compared to repeatability and reproducibility. However, where a single laboratory uses several analysts or equipment sets for a particular method, it has a great practical value, as it probably gives the most appropriate precision value for setting quality control limits.

There are various combinations of conditions for intermediate precision and the conditions used in the calculations should always be stated.

Reproducibility represents the widest extreme of precision, describing the variation that one might expect within a set of measurements made on a sample over an extended time period, in several laboratories, by a number of different analysts on different instruments. One would expect reproducibility to reflect variation in the method from all possible sources, i.e. the sort of variation expected in a method used to measure a sample in several different laboratories.

Effect of varying conditions



In general the more conditions you vary within a particular method the larger the precision value will become. Thus you will normally expect repeatability precision to be smaller (i.e. more precise) than intermediate precision which will in turn be smaller than reproducibility. Also a failure to analyse replicates that are appropriately independent will lead to misleadingly good precision data.

To get a representative estimate of the precision of an analytical method the replicate determinations made must be sufficiently independent.

For example: determination of the precision of a method starting with a dry sample, involving an extraction stage and a measurement stage. For this study, 10 replicates were required.

The replicate results, obtained by taking one test-portion from the sample, dissolving and extracting it, and analysing the resultant extract 10 times are **NOT** sufficiently independent. This merely gives the precision of the measurement stage.

The replicate results, obtained when one test-portion is dissolved, 10 aliquots are taken from it, individually extracted and measured are **NOT** sufficiently independent.

For 10 independent replicates it is necessary for 10 individual portions of sample to be weighed, each dissolved and the resultant solutions individually extracted and measured. Thus at all stages in the determination, the replicates are independent.

Summary

- Precision is a measure of closeness of results to one another
- Precision bears no relationship to “true” value
- Precision is recorded for specified conditions
- Precision can be expressed in a number of ways depending on requirements
- Several different precision estimates may be needed in a given validation
- Nested designs may be used to minimise effort