

Types of precision estimates

When we evaluate the validity of a test result, we are mostly concerned if the performance of the test method used is precise and reproducible enough to fit for a particular purpose or to meet the customer's requirements. That concern also includes in some cases whether the method detection limit is low enough to meet the regulatory or specification limits required.

Precision is defined as "The closeness of agreement between independent test / measurement results obtained under stipulated (repeatability) conditions." as given by ISO 3534-2 : "*Statistics – Vocabulary and Symbols – Part 2: Applied Statistics*". In other words, precision is an estimate of the spread or deviation of the replicated results from the mean value. It is usually expressed as a standard deviation obtained from replicate measurements of an appropriate sample which is stable, sufficiently homogeneous and representative of test samples in terms of the matrix and analyte concentration.

There are 3 types of precision estimate, namely repeatability, intermediate precision (or intermediate repeatability) and reproducibility.

Most, if not all, laboratory analysts do not have much issue to understand the term 'reproducibility' which refers to a precision estimate obtained from replicate analyses carried out in different laboratories by different analysts using different pieces of equipment. This is achievable by carrying out an interlaboratory study.

However, some clearer explanations may be needed for the terms: 'repeatability' and 'intermediate precision'.

'Repeatability' refers to a precision obtained from replicate measurements made in a *laboratory by a single analyst using the same equipment over a short period of time* (that is the so-called stipulated conditions as stated by ISO 3534-2). So, it is a measure of short-term variation in measurement results. It does not consider the variations caused by different analysts and similar equipment over time though in the same laboratory. It is sometimes termed as 'within-sample' variation.

'Intermediate precision' on the other hand refers to a precision estimate obtained from replicate measurements made in a laboratory under more variable conditions from the above mentioned repeatability conditions. Ideally, intermediate precision conditions should reflect, as far as possible, the conditions of the laboratory routine use of the test method (e.g., measurements made on different days by different analysts using different equipment within the same laboratory). It is also known as 'within-laboratory or intermediate reproducibility'.

It follows that the intermediate precision standard deviation reflects the routine performance of the test method used by different analysts and probably by different instruments over a period of time, and thus is expected to be larger than the repeatability standard deviation.

This can be illustrated by the following examples.

Example 1

In a method verification exercise before adopting the standard APHA method for the determination of fluoride content in a waste water, Analyst A conducted a series of eight replicated analyses within a single working day. The analysis results were tabulated as in Table 1.

Table 1: Replicated analysis results of a sample of waste water for F⁻ content in mg/L

Trial #	mg F/L
1	45.5
2	48.7
3	46.7
4	46.3
5	47.6
6	45.9
7	46.3
8	47.9

The sample standard deviation (*s*) equation for a series of *n* values of measurements is:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$

where sample mean value $\bar{x} = \frac{\sum x_i}{n}$. By calculation, it was found that the mean value = 46.9 mg/L with a sample standard deviation of 1.10 mg/L.

Example 2

If the above set of results were to have been obtained by different analysts who carried out the fluoride analysis in duplicates on same water sample, as displayed in Table 2, we would like to see what the standard deviation is going to be.

Table 2: Analysis results as in Table 1 but obtained in duplicates by different analysts

Analyst	a	b	D = (a-b)	D ²
A	45.5	48.7	-3.2	10.24
B	46.7	46.3	0.4	0.16
C	47.6	45.9	1.7	2.89
D	46.3	47.9	-1.6	2.56

The standard deviation equation for duplicates (a 's, b 's) in different sets (k) of data (also known as intermediate precision or intermediate reproducibility) is given by

$$s = \sqrt{\frac{\sum(a_i - b_i)^2}{2k}}$$

By calculation, the mean value was found to be also equal to 46.9 mg/L but the combined standard deviation using the above equation is equal to 1.41 mg/L.

The conclusion in this discussion is that the intermediate precision is expected to be larger than the precision found by a straight run of repeats by a single analyst (re: repeatability). To assess the extent of random error of a test method, it is therefore preferred to check its intermediate precision for its overall performance, instead of repeatability.

