Precision in ASTM Test Methods

What Precision Means

By John Carson

Q What is precision and how is it interpreted in the context of ASTM test methods?

A From ASTM standard E177, Practice for Use of the Terms Precision and Bias in ASTM Test Methods, we have this definition of precision:

Precision, n — the closeness of agreement between independent test results obtained under stipulated conditions.

What we actually measure is imprecision, typically by means of the standard deviation, which has an inverse relationship with precision. For a process in statistical control with only common cause and no special cause variation, and following the normal distribution, the standard deviation (denoted by σ) is an excellent measure of spread.

The phrase "obtained under stipulated conditions" is quite important. The standard defines commonly stipulated conditions as:

Repeatability conditions, n — conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.

Reproducibility conditions, n — conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Intermediate precision conditions, n — conditions under which test results are obtained with the same test method using test units or test specimens taken at random from a single quantity of material that is as nearly homogeneous as possible, and with changing conditions such as operator, measuring equipment, location within the laboratory and time.

The stipulated conditions give rise to different types of standard deviations and precisions with corresponding names.

It is usually true that repeatability (*r*) precision is greater than intermediate precision (*I*), which is in turn greater than reproducibility precision (*R*). However, for poorly performing laboratories, the estimated intermediate precision, or even the estimated repeatability precision, may be worse than the stated reproducibility from an interlaboratory study for a given test method.

For the standard deviation, since it has an inverse relationship with precision, the relations go the other way:

$$\sigma_r < \sigma_I < \sigma_R$$

In fact, moving from repeatability conditions to intermediate conditions to reproducibility conditions results in additional complexity and sources of variation that are added at each step, i.e., repeatability conditions have fewer sources of common cause variation than intermediate conditions, which are fewer than those in reproducibility conditions. In the context of testing, common cause variation is a major component of measurement error. The repeatability and reproducibility standard deviations are estimated as part of an ILS, as described in E691, Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

Laboratory-specific repeatability and intermediate standard deviations can be determined by designed experiments and/or by routine analysis and control charting of quality control samples (E2554). The process sigma estimated for a control chart based on repeated measurement of a QC sample is commonly determined under within-laboratory precision conditions.

Table 1 — Description of Types of Precision

Type of Precision	Factor Levels				Components of Variance
	Analyst	*Instrument*	*Day*	*Site*	
Repeatability	Single	Single	Single	Single	σ_r^2
Multi-Operator, Single-Day-Apparatus Precision	Multiple	Single	Single	Single	$\sigma_r^2+\sigma_{Anal}^2$
Single-Operator-Apparatus, Multi-Day Precision	Single	Single	Multiple	Single	$\sigma_r^2+\sigma_{Day}^2$
Within-Laboratory Precision	Single or Multiple	Single or Multiple	Multiple	Single	$\sigma_r^2+\sigma_{Anal}^2+\sigma_{Instr}^2+\sigma_{Day}^2$
Within-Organization Precision	Multiple	Multiple	Multiple	Multiple, within organization	$\sigma_r^2+\sigma_{Anal}^2+\sigma_{Instr}^2+\sigma_{Day}^2+\sigma_{Site}^2$
Within-Industry Sector Precision	Multiple	Multiple	Multiple	Multiple, within industry sector	$\sigma_r^2+\sigma_{Anal}^2+\sigma_{Instr}^2+\sigma_{Day}^2+\sigma_{Site}^2+\sigma_{Org}^2$
Reproducibility	Multiple	Multiple	Multiple	Multiple, across industry sectors	$\sigma_r^2+\sigma_{Anal}^2+\sigma_{Instr}^2+\sigma_{Day}^2+\sigma_{Site}^2+\sigma_{Org}^2+\sigma_{Sector}^2$

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In the setting of multiple laboratories within a division or corporation, within-organization precision, a form of interlaboratory precision that is narrower in scope than reproducibility, is important. The within-organization standard deviation is used to set limits for internal proficiency testing programs. The specified conditions and formulas for the (population) standard deviations associated with repeatability, various types of relevant intermediate precision and reproducibility are summarized in Table 1. As the scope of the precision expands, the components of variance terms must be understood as averages over increasingly wider domains. As alluded to above, the repeatability standard deviation estimated for an individual laboratory may be quite different from what is published in the method.

DEPENDENCE OF PRECISION ON SAMPLE MATRIX

Repeatability precision often varies substantially by sample matrix. Generally, more complex matrices have lower repeatability precision. For example, precision of testing for drinking water will tend to be higher than that for natural surface water, which in turn will tend to be higher than that for wastewater. This makes it highly advisable to chart different matrices on separate control charts.

When it comes to repeated testing of a routine sample, rather than a homogenized control sample material, the precision of results is highly dependent on the degree of heterogeneity in the sample.

DEPENDENCE OF PRECISION ON ANALYTE CONCENTRATION

One universal feature of data derived from analytical chemistry measurements is non-constant error variance. Error standard deviation in analytical chemistry has been demonstrated[1,2] to be reasonably approximated by a power law over a wide range (six orders of magnitude) of concentrations. This has been demonstrated in data from thousands of collaborative trials involving all analytical technologies and matrices that are found in food, pharmaceutical and environmental analysis.

Based on a large set of collaborative trials, each with enough data to estimate the exponent in the power law, the estimates of its value tend to be near 0.85.[3] Therefore, the error standard deviation in analytical chemistry tends to be an increasing function of concentration that increases more slowly than a constant coefficient of variation would indicate. As a consequence of this, control samples that have different concentrations must be charted separately.

There are, however, cases in which the expected concentration range for a specific application of an analytical method is sufficiently narrow that constant error standard deviation can be a useful approximation. However, even at a fixed concentration, a minor modification to something as simple as sample prep can change the error variance. Constant error variance must not be assumed but rather demonstrated over the expected range of the data by means of an F-test (or other statistical test) comparing the variance of replicates at the lower end of the expected range of the application with the variance of replicates at the higher end.

References

1. Horwitz, W., Kamps L.R., Boyer K.W., Quality assurance in the analysis of foods and trace constituents. *Journal of the Association of Official Analytical Chemists*, Vol. 63, No. 6, 1980, pp. 1344-1354.
2. Horwitz, W., "Evaluation of analytical methods used for regulation of foods and drugs," *Analytical Chemistry*, Vol. 54, 1982, pp. 67A-76A.
3. Thompson, M., "The Amazing Horwitz Function," AMC Technical Brief No.17, Royal Society of Chemistry, 2004. www.rsc.org/images/horwitz-function-technical-brief-17_tcm18-214859.pdf.

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