

TERMINOLOGY - THE KEY TO UNDERSTANDING ANALYTICAL SCIENCE PART 1: ACCURACY, PRECISION, AND UNCERTAINTY

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September 2003

amc technical brief

Analytical Methods Committee

No. 13 Sep 2003

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Terminology - the key to understanding analytical science. Part 1: Accuracy, precision and uncertainty.

Over the last two decades, considerable strides have been made in constructing a single, self-consistent, conceptual scheme for quality in chemical measurement (and, indeed, all measurement). In the course of that effort, concepts are being clarified and refined, and the corresponding terminology is necessarily following suit. Terms that were vague or ambiguous are being eliminated or redefined. As a result it is now easier for us analytical chemists to say exactly what we mean, and we should make every attempt to do so, especially in formal writing. Nicety in the use of terminology is not just pedantry. If we misuse words, then we run the risk of confusing others and, just as importantly, ourselves.

Unfortunately we are still somewhat lax about terminology. How often do we say *accuracy* when we mean *trueness, error* when we mean *uncertainty, precision* when we mean *standard deviation*, or *measurement* when we should be saying *result of a measurement*? This paper provides a brief account of the state of play.

Accuracy and error

Accuracy The closeness of agreement between a test result and the accepted reference value.

Note – The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component. [ISO 3534: 3.11]

AMC comments

- Accuracy is essentially absence of error. A result of higher accuracy has a smaller error.
- Accuracy should not be used in contrast to precision a result is unlikely to be accurate if the results in general are not precise.
- Notice also that, strictly, accuracy applies to results and not more general entities such as analytical methods, laboratories or individuals, and should only be used that way in formal writing.
- See also *measurement uncertainty* (below)

Error (of measurement) The result of a measurement minus the true value of the measurand.

Note – Since a true value cannot be determined, in practice a conventional true value is used. [VIM: 3.10]

Random error (of a result) A component of the error which, in the course of a number of test results for the same characteristic, varies in an unpredictable way.

Note – It is not possible to correct for random error. [ISO 3534: 3.9] *Systematic error* A component of the error which, in the course of a number of test results for the same characteristic, remains constant or varies in a predictable way.

Note – Systematic errors and their causes may be known or unknown. [ISO 3534: 3.10]

Trueness and bias

Trueness Closeness of agreement between the average value obtained from a large series of test results and an accepted reference value. [ISO 3534: 3.12]

Bias The difference between the expectation of the test results and an accepted reference value.

Note – Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value. [ISO 3534: 3.13]

AMC comments

- Trueness is equivalent to absence of bias. Notice that bias is a type of systematic error.
- Trueness, unlike accuracy, may be correctly contrasted with precision.

Precision

Precision The closeness of agreement between independent test results obtained under stipulated conditions.

Notes - 1. Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

- 2. The measure of precision usually is expressed in terms of imprecision and computed as a standard deviation of the test results. Less precision is reflected by a larger standard deviation.
- 3. *Independent test results* means results obtained in a manner not influenced by any previous results on the same or similar test object. Quantitative measures of precision depend critically on the stipulated conditions. Repeatability and reproducibility conditions are particular sets of extreme stipulated conditions. [ISO 3534: 3.14]

AMC comments

Because precision depends on the conditions of measurement, the conditions must be specified when referring to an estimate of precision. The following terms are in common use to describe the conditions of measurement. Note that several terms have slightly different definitions depending on the ISO standards referenced.

Repeatability conditions 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. [ISO 3534: 3.15]

Reproducibility conditions Conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment. [ISO 3534: 3.20]

AMC comments

- Repeatability conditions involve repeat execution of the entire method from the point at which the test portion is taken from the laboratory sample, and not just repeat instrumental determinations on prepared extracts.
- VIM distinguishes between repeatability and reproducibility by referring to the former when successive measurements are made under the same conditions, and the latter when measurements are made under changed conditions of measurement. For repeatability conditions, the VIM and ISO 3534 definitions are almost identical.
- The VIM definition of reproducibility conditions, however, is more general than the ISO 3534 definition, and includes within-laboratory measurements over extended time periods and/or even measurements using different principles of measurement. This more general terminology is increasingly common. For this reason, it is recommended that the conditions of measurement be *always* indicated in references to reproducibility.

- ISO 5725 additionally discusses intermediate measures of precision, and provides a notation for conditions in which time, calibration, operator and equipment are varied.
- With the help of these specified conditions and some other common terms, it becomes straightforward to describe estimates of precision. Some important examples follow.

Repeatability Precision estimated under repeatability conditions. [ISO 3534: 3.151

Reproducibility Precision under reproducibility conditions. [ISO 3534: 3.20]

Run-to-run precision Precision obtained where independent test results are obtained in separate runs in the same laboratory by the same method and on the same material.

Run Period during which analyses are conducted under repeatability conditions, and factors affecting accuracy are effectively constant. Note that separate runs are usually distinct in time, and usually involve some recalibration of an instrument.

Instrumental precision Precision estimated by repeated measurements on a single prepared test solution, with no instrumental adjustments, in a short period of time.

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- Terms such as repeatability standard deviation are used to qualify specific measures of precision, such as standard deviation, under the
- Analytical chemists should avoid using precision to refer to a standard deviation, relative standard deviation or variance. In short, do not say 'the precision was 3%'.
- Instrumental precision is not an ISO definition, but is a type of precision frequently encountered in instrument specifications. It differs from repeatability in that it does not include repetition of a whole analytical method; only the instrumental measurement itself, often not even with instrumental adjustments.
- Run-to-run conditions form a specific case of reproducibility conditions in the VIM definition, and correspond with intermediate conditions defined in ISO 5725. It is a practically useful descriptive term for use by analytical chemists, and is encountered in practice in routine internal quality control.
- The run is sometimes loosely called a batch, but that terminology should be avoided because batch has other meanings in quality

Uncertainty

Uncertainty i) An estimate attached to a test result which characterises the range of values within which the true value is asserted to lie. [ISO 3534: 3.25] ii) (of measurement) Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand. [GUM: 2.2.3]

Measurand A quantity subjected to measurement. [ISO 3534: 3.5]

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- Definitions i) and ii) above differ in philosophy, but for most practical purposes may be considered equivalent.
- An estimate of uncertainty must incorporate both what is known about random effects and what is known about uncertainties associated with systematic effects on the measurement process.
- Because uncertainty estimates incorporate uncertainties from all possible effects, an estimate of uncertainty is probably the most appropriate means of expressing the accuracy of results.

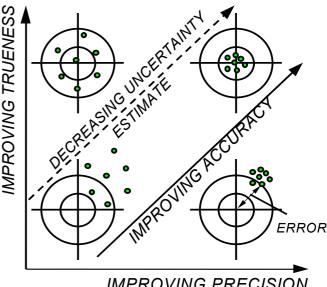
- In most chemical measurements, the *measurand* is a concentration, mass fraction or similar quantity.
- In routine analysis, the uncertainty associated with an individual result will usually be estimated from prior studies, including validation studies, and will not involve an individual estimate for each result

Standard uncertainty Uncertainty of the result of a measurement expressed as a standard deviation. [GUM: 2.3.1]

Expanded uncertainty Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand. [GUM: 2.3.5]

Postscript

The classical illustration of accuracy and precision in terms of a pattern of shots on a target no longer correctly describes accuracy. Accuracy refers to a combination of systematic and random errors, not just the systematic errors. The following is therefore closer to the mark.



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Bibliography

Attributed definitions are taken from the following sources:

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ISO Guide 43 -1: Proficiency testing by inter-laboratory comparisons. ISO 5725 -1: Accuracy (trueness and precision) of measurements methods and

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