

Glossary of Analytical Terms

ver. 23 May 2018

by

Brian M. Tissue

Abstract

The following glossary defines common terms encountered in analytical chemistry. Many of these terms are used interchangeably in day-to-day language. We use very specific definitions to avoid confusion when describing chemical measurement procedures and results. I follow IUPAC recommendations for most terms, noting any deviations. See references 1 and 2 for extensive listings of terms in various fields of chemistry.^{1,2}

Even with very specific terminology, a given term can have multiple definitions depending on the context. “Resolution” has different meanings depending on whether we are talking about spatial dimensions, an instrument specification, or the separation of peaks in different types of data plots. Similarly, chemical terms will vary in other fields of science and engineering. “Speciation” has a very different meaning for a biologist than it does for a chemist. Use the context to eliminate ambiguity.

The most current version of this document is available online at:

<http://www.achem.org>.

This website and associated files are provided by the author to assist users of the text:

B. M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, (John Wiley: New York, 2013).

Contents	Page
A – B.....	2
C – D.....	3
E – L.....	5
M – Q.....	7
R.....	9
S.....	11
T – Z.....	14
References.....	15

A – B

accuracy

The nearness of an experimental measurement to the true value. For test portions containing unknown amounts of analytes, the accuracy of a given method is inferred from the accuracy when measuring certified reference materials.

analysis, qualitative

The process of making measurements to determine the identity, molecular structure, or physical properties of a substance.

analysis, quantitative

The process of making measurements to determine the purity of a substance or the concentration of one or more analytes in a sample.

analyte

The chemical species to be identified or quantitated. It may be a pure substance or one constituent in a multi-component sample.

background

The detector signal of a physical measurement, spectrum, or chromatogram when no analyte is present. Numerically, the average value of blank measurements. Background or baseline may also refer to the normal or unperturbed concentrations in biological or environmental samples.

baseline

Synonymous with background, but usually in reference to data plotted in a spectrum, chromatogram, or other type of data plot. When the baseline is flat, the numerical value is the average signal level where there are no peaks. When the baseline is sloped, the baseline value at the center of a given peak can be interpolated from the baselines on each side of the peak. For cyclic voltammetry plots, the baseline is extrapolated from the leading baseline before a peak begins. The baseline is illustrated in the figure for the *signal-to-noise ratio* entry.

bias

See *error, systematic*.

blank

A standard that contains no analyte, i.e., a concentration of 0.0. The solvent, electrolyte, and matrix components should match as closely as possible to the test portions being measured. Variations include “method blanks,” “equipment blanks,” and “instrument

blanks,” where these blanks go through all or only part of the sample processing procedures, respectively.

blank, field

A blank prepared in the field that goes through all sample processing and analysis procedures. The field blank is useful to identify sample contamination. A variation is a spiked field blank to monitor loss of analyte during storage, sample processing, etc.

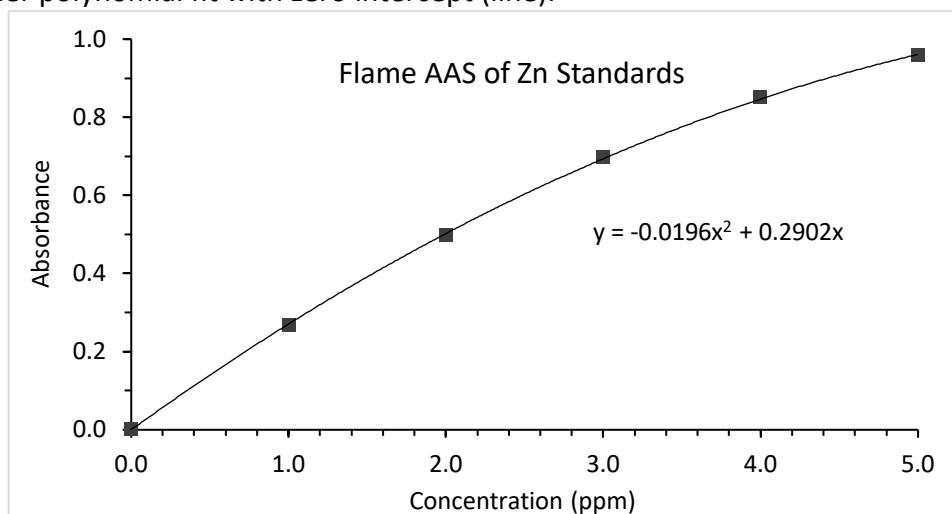
C – D

calibration

The process of measuring a known quantity to determine the relationship between the measurement signal and the analyte amount or concentration. Calibration methods include using external standards, internal standards, and standard addition.

calibration curve

A plot of signal versus analyte amount or concentration for calibrating a measurement over an extended range. Good practice is to measure five to ten standards that are equally spaced through the measurement range. The following figure shows a calibration curve for flame atomic absorption of zinc solutions (square markers) and a 2nd-order polynomial fit with zero intercept (line).



calibration function

The mathematical equation that is the best fit to a calibration curve. The function can vary depending if the measurement range is in a linear or non-linear region.³

carry over

Residual analyte in a sample preparation or measurement step that causes a measurement to be higher than the true value. See *memory effect*.

certified reference material (CRM)

A material that is verified to contain a known amount of analyte(s) or to have known physical properties. Usually available from commercial suppliers. Also referred to simply as reference material (RM).⁴ See <https://www.nist.gov/srm/srm-definitions> for more details.

chromatogram

A plot of signal versus time that corresponds to the amount of each analyte as they elute from a separation column.

contaminant

A substance, which can include the analyte itself, that is introduced unintentionally into a sample or test portion during collection, processing, or measurement.

control chart

A plot of measurement results of control samples versus time. Usually maintained over days, weeks, or months to verify that an instrument is working properly. The plot can include upper and lower limits to specify if a method or instrument is “within control” or “out of control.” An “out of control” condition requires instrument repair or recalibration.

control samples (quality control samples)

The blanks, standards, and spiked test portions that are measured to determine the accuracy of a measurement or instrument.

dark current or dark signal

The detector output when the detector is shielded from any input.

dark spectrum

The dark signal as a function of wavelength or energy. Measured and stored (with a reference spectrum if measuring absorbance) in array-detector spectrometers to calculate the spectrum of the test portion.

detection limit

See *limit of detection* or *method detection limit*.

detector

A device that responds to the presence of analyte, usually generating an electrical output.

difference spectrum

A spectrum obtained by subtracting a reference spectrum from a measured spectrum to show changes between the two spectra. Peaks can be positive or negative.

drift

The gradual change in blank measurements over time.

duplicate sample

A sample that is split into two portions to monitor method variability. A method will often specify analysis of duplicate samples at some frequency based on time or number of collected samples. See also *replicate measurements*.

dynamic range

The ratio of the maximum to the minimum measurable analyte concentration. The maximum is determined by the point at which the signal no longer increases with increasing analyte concentration. The minimum is chosen as the limit of detection (LOD). For linear dynamic range, the maximum is the point at which the signal deviates from linearity. See also *range, measurement*.

E – L***electrolyte***

A substance that makes an electrically conductive solution when it is dissolved in a solvent, typically a soluble ionic salt. This definition includes molten inorganic salts and organic ionic liquids, which serve as their own solvent. Solid electrolytes are usually termed ionic conductors. In medical terminology, electrolytes are the ions in body fluids.

electrolyte, strong and weak

A strong electrolyte is a soluble compound that dissociates completely, or nearly so, when dissolved in solution. Weak electrolytes are substances that dissociate only partially, e.g., weak acids and weak bases. The conductivity of a solution will depend on the concentration of the electrolyte and the extent to which it dissociates.

electrolyte, supporting

The electrolyte added to a solution to make it electrically conductive for making electroanalytical measurements. The supporting electrolyte is generally at a high concentration compared to the analyte. It should not undergo redox reactions over the voltage range of the measurement.

EPA action level

The concentration of a contaminant in the environment or water, or as residue on food, that requires a response such as public notification, exposure monitoring, or remediation.

error, random

The spread in replicate measurements due to random fluctuations. These fluctuations will be both higher and lower than the true value.

error, systematic

A consistent difference either higher or lower between an experimental measurement and the true value. Can differ from sample to sample depending on variability in sample matrix effects. Identifying these systematic errors, or bias, is a primary goal of method validation.

false positive

Determination that an analyte is present in a sample that had no analyte. Causes include sample contamination and memory effects.

false negative

Inability to detect an analyte that is present above the detection limit. Causes include analyte loss during sample processing or matrix effects that reduce the true signal.

good laboratory practice (GLP)

Specific regulations in the Code of Federal Regulations by which laboratories must conduct, verify, and maintain their procedures, results, and records. See for example:

- <https://www.fda.gov/ICECI/EnforcementActions/BioresearchMonitoring/ucm135197.htm>
- <https://www.epa.gov/compliance/good-laboratory-practices-standards-compliance>
- <http://www.oecd.org/chemicalsafety/testing/good-laboratory-practiceglp.htm-monitoring-program>

interference

“A systematic error in the measure of a signal caused by the presence of concomitants in a sample.” The interference may cause the measurement to be higher or lower than the true value. Interferences can occur due to signal from non-analyte species, overlap of peaks, or chemical conversion of the analyte to a form that is not detected or is detected with a different sensitivity. Interference usually refers to a bias caused by a specific species rather than a systematic error caused by the summation of matrix effects. [Italicized terms from IUPAC Gold Book.¹]

interferent

The specific component that is in or is introduced into a test portion that causes an interference. Interference is often used interchangeably to refer to an interferent.

IUPAC (International Union of Pure and Applied Chemistry)

A non-governmental agency that recommends standardization of chemical nomenclature, terminology, and chemical and physical data.

limit of detection (LOD)

The minimum measured concentration at which an analyte may be reported as being detected in the test portion or sample. There are several accepted methods to determine an LOD. A simple method is to calculate the concentration that corresponds to a signal level that equals the baseline plus 3 times the noise. See also *method detection limit*.

limit of linearity (LOL)

The concentration at which the signal deviates from linearity.

limit of quantitation (LOQ)

The minimum measured concentration at which an analyte concentration may be reported. A simple method is to calculate the concentration that corresponds to a signal level that equals the baseline plus 10 times the noise.

linear range

Nominally the concentration range over which the analytical signal is directly proportional to analyte concentration. The lower limit may be taken as zero and the upper limit is where the signal versus concentration deviates from linearity. Some measurement devices, such as ion-selective electrodes, respond to the logarithm of analyte activity. More generally, the linear range is the concentration range for which the calibration curve is linear.

linear regression

A calculational method using least squares to determine the best linear equation to describe a set of x and y data pairs.

M – Q***masking reagent***

A reagent added to a test portion to prevent sample components from interfering in an analytical method. An example is the chelating ligand in total ionic strength adjustment buffer (TISAB) that is used with a fluoride ion selective electrode (ISE). The ligand prevents metal ions such as Fe^{3+} and Al^{3+} from forming fluoride complexes.

matrix effect

A systematic error due to physical or chemical interactions from non-analyte components in the sample. Can cause the measurement to be higher or lower than the true value and varies sample-to-sample. Specific species that are known to cause a systematic error are called interferents.

memory effect

An increase in signal in an instrumental measurement due to contamination or carry-over from a previous test portion. May be determined by running blanks in between the measurements of test portions. Unidentified memory effects will produce erroneously high measurements.

method detection limit (MDL)

...the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. [Italicized terms from 40 CFR 136 Appendix B.] See also reference.⁵

method development

The process of determining the experimental conditions for sample collection, preparation, and measurement that give accurate and repeatable results.

method validation

Performing control experiments to verify the *accuracy, sensitivity, specificity, and reproducibility of test methods.* [Italicized terms from 21 CFR 211.165 (e).]

noise

Random fluctuations in the signal. Often quantified using the standard deviation of multiple measurements of a blank. See the definition of the *signal-to-noise ratio* for an illustration of noise in a spectrum.

precision

The repeatability in making replicate measurements. Imprecision, or the lack of precision, is probably a better term to describe the repeatability of measurements, but precision is the more common term. Quantitative measures include standard deviation, standard error, and confidence limits.

protecting reagent

A reagent added to a test portion to prevent the analyte(s) from being lost or otherwise not detected. An example is a weak complexing agent to prevent metal ions from precipitating as insoluble hydroxides at high pH.

qualitative and quantitative analysis

See *analysis*, *qualitative* and *analysis*, *quantitative*.

quality assurance

Auditing of methods and procedures to ensure accurate results.

quality control

A system of instrument calibration and method validation procedures to produce accurate results.

R

range, measurement

The range from the minimum to the maximum measurable analyte concentrations. The minimum may be taken as zero or chosen as the limit of detection (LOD). The maximum is determined by the point at which the signal no longer increases with increasing analyte concentration. For linear dynamic range, the maximum is the point at which the signal deviates from linearity. Not to be confused with *dynamic range*, which is a ratio.

Recovery

The fraction or percentage of analyte retained after performing one or more sample preparation steps. The recovery is determined by processing control samples with a known amount of analyte.

reference spectrum (for instrument operation)

The spectrum of a pure solvent or reference substance. Measured and stored in array-detector spectrophotometers to calculate the absorption or reflectance spectra of test portions. Also used to convert measured spectra to difference spectra.

reference spectrum (of a material)

The spectrum of a certified reference spectrum. Useful for comparison to identify or determine the purity of test portions.

repeatability

Comparison of replicate measurements made on the same sample or test portion and performed under identical conditions. A typical descriptor is the standard deviation of the measurements.

replicate measurements

Multiple measurements of the same laboratory sample. Replicate measurements are made by dividing the sample into several test portions and measuring each portion separately. Doing replicate measurements provide a measure of precision of the

method and can identify outliers due to gross errors (blunders) such as omitting one step in a procedure, one-time instrument glitches, or recording a value incorrectly.

reproducibility

Comparison of replicate measurements made on the same test sample by different analysts in different laboratories. The calculation of precision is the same for repeatability and reproducibility, the difference is the source of the measurement results.

resolution, chromatography

The numerical value, R_S , determined from the distance between two adjacent peaks divided by the average baseline widths of the peaks:

$$R_S = \frac{t_{R2} - t_{R1}}{0.5(w_{b2} + w_{b1})}$$

where t_R is retention time, w_b is baseline width, and the 1 and 2 refer to two consecutive eluting peaks. The calculation is the same when working in terms of retention volume. Two adjacent peaks are baseline resolved at values of $R_S \approx 1.5$ and larger.

resolution, spatial

The minimum distance in surface analytical measurements, laterally or depth-wise, for which measurements can be made without overlap. In microscopy, the minimum size of features that can be determined in an image.

resolution, spectral

The minimum difference in x-axis units between two spectral peaks that are determined to be separated.

resolution, spectrometer

The minimum bandpass of a spectrometer.

resolving power

A measure of resolution in mass spectrometry, usually calculated as $m/\Delta m$. The criterion for determining Δm must be specified as there are multiple conventions.

response

The signal output from a detector for a given amount of analyte at specified measurement conditions. Detector response can vary with experimental parameters such as temperature, scan rate, and detector settings. See also *sensitivity*.

response factor or relative detector response factor (f)

The relative sensitivity of a detector for an analyte and a standard. May be less than or greater than 1.0. Commonly used in chromatography with calibration using an internal standard.

robustness

See *ruggedness*.

ruggedness

The degree to which variable experimental conditions, such as temperature, pH, ionic strength, etc, will affect the accuracy and precision of a measurement result.³ See also *reproducibility*.

S

sample

A portion of material selected from a larger quantity of material. [Italicized terms from IUPAC Gold Book.]

sample, laboratory

A sample as delivered to the testing laboratory.

sample, test

A sample that has been processed in the laboratory and is ready to divide into test portions.

sampling plan

The method by which samples are collected from a population or physical location. Common sample selection methods use random, systematic or grid, stratified, or judgmental strategies.⁶

selectivity

The ability of a method or instrument to measure an analyte without interference from other constituents in the sample or test portion.⁷

sensitivity

The slope of the calibration function, i.e., the change in detector signal versus the change in amount of analyte.³ For non-linear calibration functions, the sensitivity will be a function of concentration. Not to be confused with *limit of detection*. A higher sensitivity may allow measurement of a lower analyte concentration, depending on the signal-to-noise ratio.

signal

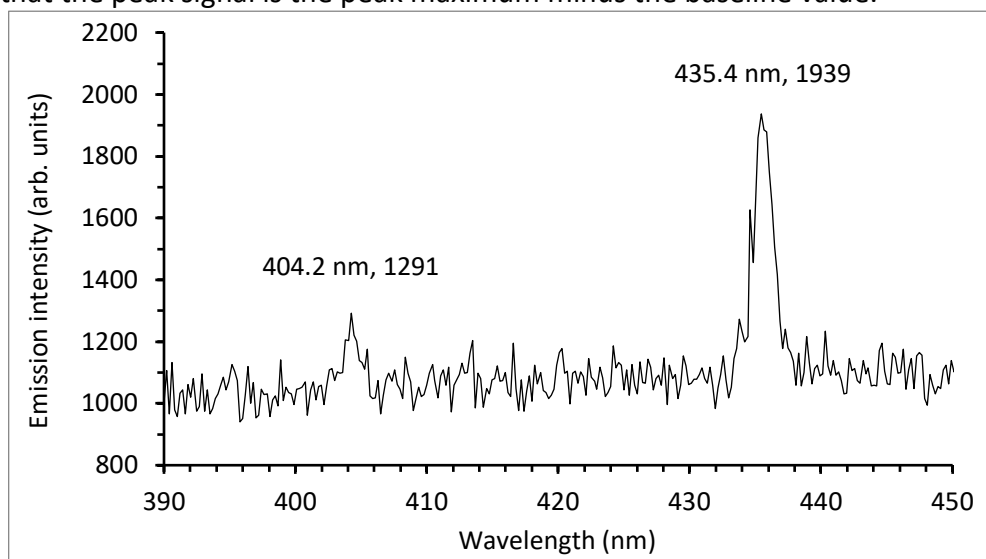
The detector output that is displayed or recorded.

signal-to-noise ratio (S/N or SNR)

The simple mathematical ratio of the average or peak signal to a measure of the noise. For repetitive measurements, S/N is usually reported as the average signal divided by the standard deviation. For spectra and chromatograms, the S/N will be different for each peak. In the following figure, the baseline value is found from the average of the data points between 410 and 430 nm, which is 1079 ± 50 . Using the standard deviation as a measure of the noise, the two peaks in this spectrum have S/N of:

- 404.2 nm: $S/N = (1291 - 1079)/50 = 4.2$
- 435.4 nm: $S/N = (1939 - 1079)/50 = 17.2$

Note that the peak signal is the peak maximum minus the baseline value.



signal averaging

Recording and averaging a signal for some number of measurements or for some period of time to improve the signal-to-noise ratio. The test portion is not changed, which distinguishes signal averaging from making replicate measurements.

smoothing

Averaging adjacent points in a spectrum or plot to reduce the apparent noise.

speciation analysis

The determination of the specific forms of an analyte. Common examples are elemental mercury versus organomercury and different oxidation states such as As^{3+} , AsO_3^{3-} , and AsO_4^{3-} .⁸

species

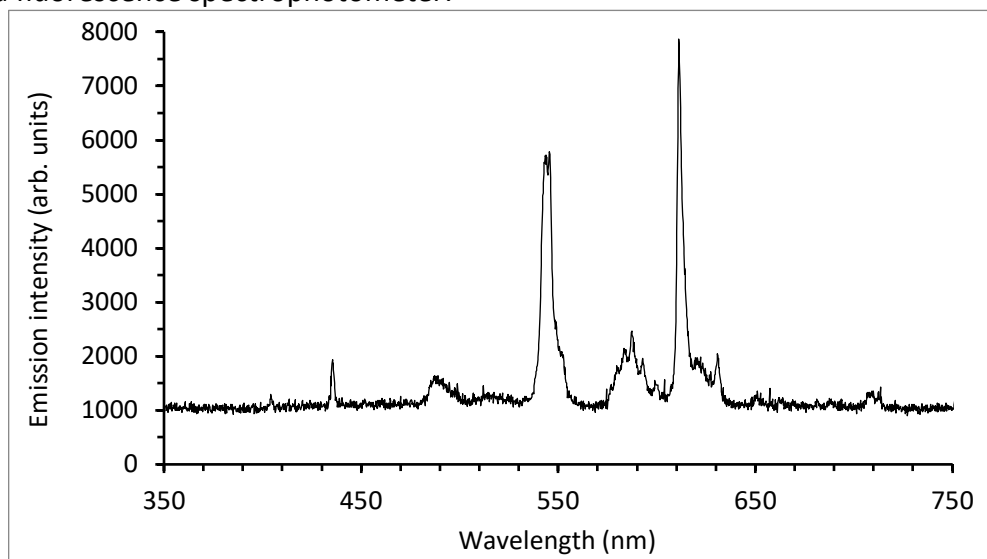
One specific form of an atomic or molecular entity. IUPAC uses “chemical species (of an element)”.⁸ Use the term “chemical species” if there is potential for confusion with biological species.

specificity

See *selectivity*.

spectrum

A plot of signal versus wavelength, energy, frequency, or another independent variable. The following figure shows the emission spectrum of a fluorescent lamp as recorded with a fluorescence spectrophotometer:



spike

An internal standard or standard addition added to a test portion or blank.

stability

The retention of analyte over time or during sample preparation and measurement steps. Analyte loss can occur due to volatility, chemical degradation, precipitation, etc. Stability testing is a related concept, but usually refers to determining the shelf life of a pharmaceutical or other consumer product as a function of temperature, humidity, light exposure, etc. For instrument stability see the definitions for *drift* and *repeatability*.

standard

A sample or test portion of known composition prepared from a certified reference material (CRM).

standard, external

A standard that is measured independently of other test portions. Usually multiple external standards are measured to generate a calibration curve. This method of calibration is suitable when the method does not suffer from bias due to sample matrix effects.

standard, internal

A standard that is added directly to the test portion. The internal standard is then measured simultaneously with the analyte(s). When added before performing sample preparation procedures, the internal standard can correct for bias due to analyte recovery being less than 100 %.

standard, primary

A reagent that is extremely pure, stable, has no waters of hydration, and has a high formula weight.

standard, secondary

A standard that is prepared in the laboratory or by a third party for a specific analysis. It is usually standardized against a primary standard.

standard-addition method

A calibration method of adding a known amount of the analyte, a spike, to the sample to provide an “internal” calibration to the measurement.

standard operating procedure (SOP)

A document containing the instructions to perform an analytical procedure or to use an instrument.

T – Z***test portion***

A portion of a sample that is tested or analyzed.

trace analysis

Measurement of analyte concentrations of less than approximately 100 ppm.

ultra-trace analysis

A term with no standard definition. Typically used for measurement of analyte concentrations of less than approximately 1 ppb or less.

unknown

A term with no standard definition. The source of a test sample is usually known. Calling a sample an “unknown” is common usage to indicate that the analyte concentration in a test solution or the molecular identify of a sample is unknown.

validation

See *method validation*.

References

- ¹ *IUPAC Compendium of Chemical Terminology - the Gold Book* (International Union of Pure and Applied Chemistry: Research Triangle Park, NC, 2005-2014); available: <http://goldbook.iupac.org/index.html>, 2014-02-24: Release 2.3.3.
- ² *IUPAC Compendium on Analytical Nomenclature* (1997); available: http://old.iupac.org/publications/analytical_compendium/.
- ³ Currie, L. A. “Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities,” *Pure & Appl.Chem.* **1995**, 67(10), 1699–1723.
- ⁴ NIST Standard Reference Materials: Definitions. <http://nist.gov/srm/definitions.cfm>.
- ⁵ Analytical Detection Limit Guidance & Laboratory Guide for Determining Method Detection Limits, Wisconsin Department of Natural Resources Laboratory Certification Program, April 1996, PUBL-TS-056-96; available: <http://dnr.wi.gov/regulations/labcert/documents/guidance/-lodguide.pdf>.
- ⁶ EPA, Selecting a Sampling Design. <https://www.epa.gov/quality/selecting-sampling-design>.
- ⁷ Vessman, J. et al. “Selectivity in analytical chemistry (IUPAC Recommendations 2001),” *Pure & Appl.Chem.* **2001**, 73(8), 1381–1386.
- ⁸ Templeton, D. M. et al. “Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000),” *Pure & Appl.Chem.* **2000**, 72(8), 1453–1470.