Glossary of Analytical Terms

Globalization in science, technology and economy causes, amongst other things, problems in derivation, adaptation and acceptance of technical terms in general, and in Analytical Chemistry, too. Both vague and contradictory definitions have been developed and established over the years. Therefore, in the last decade the efforts have been increased to harmonize the use of analytical terms. In particular international organisations like ISO, IUPAC render outstanding services to the fixing and harmonization of essential analytical terms. But also additional activities have been done in this field, e.g., by the Royal Society of Chemistry, the EURACHEM Education and Training Working Group and the Federation of European Chemical Societies (FECS), Division on Analytical Chemistry (DAC) as well as by publications in form of books (e.g., PRICHARD et al. [2001]) and other publications, e.g. the series "*Glossary of Analytical Terms*" (*GAT*) in the journal *Accreditation and Quality Assurance*, see GAT I to X [1996-1998], where multilingual terms are given, and HOLCOMBE [1999/2000].

In the following, definitions of essential analytical terms are compiled, if possible on the basis of international agreements. Attached are sparse references and cross-references. The symbols, being used here, means: $\longrightarrow$ "see also"(cross-references to terms, additional references as well as paragraphs, chapters, equations and figures of this book), and $\times$ is a warning notice.

Accuracy

"Closeness of agreement between the result of a measurement and a true value of the measurand".

ISO 3534-1 [1993]
$\longrightarrow$ Sect. 7.1
$\longrightarrow$ *Trueness*
$\times$ Do not confuse with *Precision*

Analysis (of a sample)

Investigation of a *sample* to identify and/or determine (an) analyte(s) or assay a material.

$\longrightarrow$ Quotation from ANAL CHEM [1975] at the end of the Glossary

Analyte

"The chemical entity being investigated (qualitatively or quantitatively)".

According to PRITCHARD et al. [2001]

Analytical function (*evaluation function*)

Inverse of the calibration function, $x = f^{-1}(y)$, describing the dependence of the analytical values from the measured values.

Analytical method

"Logical sequence of operations, described generally, used in the performance of measurements", e.g., the links of a given analytical technique with particular excitation and detection.

ISO 3524-1 [1993]
$\longrightarrow$ Fig. 7.1

Analytical procedure

"Set of operations, described specifically, used in the performance of particular analytical measurements according to a given method".

ISO 3524-1 [1993]
PRITCHARD et al. [2001]
$\longrightarrow$ Fig. 7.1

Analytical process

Logic sequence of objects linked by general analytical standard operations.

$\longrightarrow$ Fig. 2.1

Analytical result

Analytical value attributed to a measurand, obtained by measurement and completed by information on the uncertainty of measurement.

According to ISO 3524-1 [1993]
$\longrightarrow$ 8.1

Analytical quantity

"Particular quantity subject to analytical measurement".

According to ISO 3524-1 [1993]
$\longrightarrow$ *Measurand*

Analytical technique

"Generic analytical application of a scientific principle".

According to PRITCHARD et al. [2001]
$\longrightarrow$ Fig. 7.1

Assay

Determination of how much of a sample is the material indicated by the name.

$\longrightarrow$ Quotation from ANAL CHEM [1975] at the end of the Glossary
$\longrightarrow$ e.g. analysis of ores

Analytical value

Magnitude of an analytical quantity, x, measured at test samples on the one hand and given for reference samples used for calibration on the other hand.

Background (instrumental background, background signal)

Instrumental background is the null signal, obtained in the absence of any analyte- or interference-derived signal.

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ Background may be set to zero, on the average, for certain instruments

Baseline

"Summation of the instrumental background plus signals in the analyte (peak) region of interest due to interfering species".

IUPAC [1995]; CURRIE [1999]

Bias

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

According to GAT VIII [1997]

Blank

A value, y_B, obtained my measuring a blank sample (in calibration, the intercept of the calibration curve is considered to be equal to the blank).
Blanks may be differentiated into *instrumental blank* (*background* and *baseline*, respectively) and *chemical blank* (*analyte blank*).

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ *Background*
$\longrightarrow$ *Baseline*
$\longrightarrow$ *Chemical blank*

Blank measurement

Procedure by which a measured value is obtained with a sample in that the analyte of interest is intentionally absent.

$\longrightarrow$ According to PRITCHARD et al. [2001]; TAYLOR [1987]; SHARAF et al. [1986]
$\longrightarrow$ *Blank sample*

Blank sample

A sample whose analyte concentration is below the limit of decision of the analytical procedure being used.

According to PRITCHARD et al. [2001]
$\longrightarrow$ *Blank measurement*

Calibration

Set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring system and the corresponding values of quantities represented by a material both in form of reference materials and samples. In a wider sense, calibration represents a set of operations that establish relationships between quantities in the sample domain with quantities in the signal domain, viz $y = f(x)$ and $z = f(Q)$.

$\longrightarrow$ ISO 3524-1 [1993]
$\longrightarrow$ GAT IV [1996]
$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ IUPAC [1998]
$\longrightarrow$ Sect. 6.1
$\longrightarrow$ *Sample domain*
$\longrightarrow$ *Signal domain*

Calibration function

Equation for the estimation of the values of a measuring quantity from given values of a analytical quantity. The calibration function may be known a priori by natural laws or estimated experimentally by means of calibration samples.
The calibration function represents that segment of the response function that is chosen for estimating the analytical value of an unknown sample.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ IUPAC [1998]
$\longrightarrow$ SHARAF et al. [1986]
$\longrightarrow$ *Sensitivity*
$\longrightarrow$ *Response function*

Calibration samples

Set of samples characterized by accurate and precise values of the measurand. In a concrete case, calibration samples may be portions of (certified) reference materials, in-house reference materials (laboratory standard samples), or spiked samples, and, in addition, blank samples.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ *Reference material*
$\longrightarrow$ *Certified reference material*

Certified reference material (CRM)

"A reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence".

ISO 3524-1 [1993]
$\longrightarrow$ GAT IV [1996]
$\longrightarrow$ PRITCHARD et al. [2001]

Chemical blank (*analyte blank*)

"Blank which arises from contamination from the reagents, sampling procedure, or sample preparation steps which correspond to the very analyte being sought".

IUPAC [1995], CURRIE [1999]

Coefficient of variation: The term is not recommended by IUPAC;
$\longrightarrow$ **Relative standard deviation**

Concentration domain $\longrightarrow$ Sample domain

One of the dimensions of the sample domain.

Confidence interval (*CI*)

Statistical interval, e.g., of a mean, $\overline{y}$, $cnf(\overline{y}) = \overline{y} \pm \Delta \overline{y}_{cnf}$, which express the uncertainty of measured values. *CI*s are applied for significance tests and to establish quantities for limit values (*CV*).

$\longrightarrow$ Sect. 7.5
$\longrightarrow$ *Critical value*
$\longrightarrow$ *Prediction interval*

Conventional true value

"Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose".

ISO 3534-1 [1993]
$\longrightarrow$ *True value*

Correlation

Stochastic relationship between random variables in such a way that one depends on the other. The degree of relationship may be estimated by the *correlation coefficient*.

Correlation coefficient

The correlation coefficient, r_{xy}, is given by the covariance of two random variables x and y, $\mathrm{cov}(x, y) = s_{xy}$, divided by the standard deviations s_x and s_y, see Eq. (6.3). The correlation coefficient becomes $r_{xy} = 0$ if there is no relationship between x and y, and $r_{xy} = \pm 1$ if there exist a stringent deterministic dependence.

$\longrightarrow$ Sect. 6.1.3
$\times$ The correlation coefficient is not of any relevance in calibration, as a rule. This is because only the measured value is a random variable and, in contrast, the analytical value is a fixed value and not selected randomly

Correlation matrix

Matrix formed by a set of correlation coefficients related to m variables in multivariate data sets, $\boldsymbol{R} = (r_{x_i, x_j})$. It is relevant in multicomponent analysis.

$\longrightarrow$ Eqs. (6.4) and (8.14)

Critical value (CV)

Limit in the signal domain, estimated from the average blank plus its uncertainty, generally according to $y_c = \overline{y}_{BL} + U(\overline{y}_{BL})$, in analytical chemistry frequently according to $y_c = \overline{y}_{BL} + 3s_{BL}$. If the critical value is exceeded, the respective analyte is reliably detected (except for a remaining risk of error α). Therefore, the CV stands for the *guarantee of presence* of an analyte.

EHRLICH and DANZER [2006];
CURRIE [1999]
$\longrightarrow$ Sect. 7.5
$\longrightarrow$ Fig. 7.8
$\longrightarrow$ *Decision limit*

Cross sensitivity (*partial sensitivity*)

Dependence of the measured value (signal intensity), y_A, from other constituents than the analyte A, present in the measuring sample, quantitatively expressed by the respective partial differential quotient.

$\longrightarrow$ Kaiser [1972]; Danzer [2001]
$\longrightarrow$ Sect. 7.2
$\longrightarrow$ Eq. (3.11)
$\longrightarrow$ *Sensitivity*
$\longrightarrow$ *Sensitivity matrix*
$\longrightarrow$ *Total sensitivity*

Determination

Analysis of a sample to estimate quantitatively the amount (content, concentration) of (an) analyte(s).

$\longrightarrow$ Quotation from Anal Chem [1975] at the end of the Glossary

Evaluation function (*analytical function*)

Inverse of the calibration function, $x = f^{-1}(y)$, describing the dependence of the analytical values from the measured values, being so the basis of analytical evaluation.

Homogeneity

A qualitative term used to describe that the analyte is uniformly distributed through the sample. The degree of homogeneity may also be characterized quantitatively as a result of a statistical test.

$\longrightarrow$ Pritchard et al. [2001]
$\longrightarrow$ *Inhomogeneity*
$\longrightarrow$ Sect. 2.1
$\longrightarrow$ Eq. (2.9)

Hyphenated techniques

Coupling of two (or more) separate analytical techniques via appropriate interfaces and computer with the goal to obtain faster a higher amount of information on the subject under investigation.

$\longrightarrow$ Hirschfeld [1980]
$\longrightarrow$ Kellner et al. [1998]
$\longrightarrow$ By hyphenating analytical methods, the dimension of analytical information will be increased (usually by one)
$\longrightarrow$ Sect. 3.4

Identification

Recognizing of (an) unknown constituent(s) in an analytical test sample.
In contrast, by qualitative analysis it is tested whether (a) known constituent(s) are present or absent.

$\longrightarrow$ Sect. 9.3

Imprecision

A quantitative term to describe the (lack of) "precision" of an analytical procedure (e.g. by *standard deviation*).

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ *Precision*
$\longrightarrow$ *Imprecision of analytical results*, see Sect. 7.1
$\longrightarrow$ *Standard deviation*

Inaccuracy

A quantitative term to describe the (lack of) accuracy of an analytical procedure which comprises the imprecision *and* the bias.

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ *Accuracy*
$\times$ *Inaccuracy* should not be confused with *uncertainty*, see IUPAC [1994a]

Inhomogeneity

"Term used to describe situations where the analyte is unevenly distributed through the sample matrix".
The degree of inhomogeneity may be characterized quantitatively by Eq. (2.9) the value of which becomes negative with the transition from homogeneity to inhomogeneity.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ Sect. 2.1
$\times$ The term *inhomogeneity* should not be confused with *heterogeneity*

Interlaboratory study

"A study in which several laboratories measure a quantity in one or more identical portions of homogeneous, stable materials under documented conditions, the results of which are compiled into a single report".
According to the evaluation types, it is differentiated between:
(1) Method-performance studies.
(2) Laboratory-performance studies.
(3) Material-certification studies.

IUPAC [1994b]
$\longrightarrow$ A minimum of five laboratories should be used to provide meaningful statistical conclusions from interlaboratory studies
$\longrightarrow$ Sect. 8.2.4

Limit of decision ("3σ-limit of detection")

The analytical value (e.g. the concentration) that corresponds to the critical value. The limit of decision is of minor importance in analytical chemistry because the detection at this level of concentration succeeds only in 50% of all cases.

EHRLICH and DANZER [2006]; IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ Sect. 7.5
$\longrightarrow$ Fig. 7.7
$\longrightarrow$ *Critical value*
$\longrightarrow$ *Detection limit*
$\times$ The decision limit should not be used as a performance characteristic of analytical methods and also not as a limit of guarantee of an analyte

Limit of detection (LD)

The analytical value, x_{LD}, that always produce a signal which can be distinguished from the blank (except for a remaining risk of error β).
LD is the limit in the sample domain (analyte domain). It characterizes analytical procedures, in particular with regard to the limit concentration that can be detected. Therefore, the LD stands for the *guarantee of absence* of an analyte.

EHRLICH and DANZER [2006]; IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ Sect. 7.5
$\longrightarrow$ Fig. 7.7
$\longrightarrow$ *Critical value*

Limit of determination $\longrightarrow$ Limit of quantitation

Limit of quantitation (LQ)

An analytical value, x_{LQ}, above which quantitative determinations are possible with a given minimum precision. The condition on precision must be declared in each case. For a given precision $k = x_{LQ}/\Delta x_{LQ}$, the limit of quantification can be estimated by Eqs. (7.48) and (7.49).

EHRLICH and DANZER [2006]; IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ *Precision*
$\longrightarrow$ For factual reasons, the limit of quantification cannot be lower than the limit of detection
$\longrightarrow$ The declaration of precision must always be given because it is an inherent component of LQ

Linear dynamic range

The range of concentration in which the response varies linearly with the analyte concentration.

$\longrightarrow$ SHARAF et al. [1986]

Linearity

Ability of an analytical method to give a response which depends linearly on the analyte concentration.

$\longrightarrow$ Pritchard et al. [2001]
$\longrightarrow$ Sharaf et al. [1986]

Matrix

All of the constituents of a sample except the analyte. The matrix is the carrier of the analyte.

$\longrightarrow$ IUPAC Orange Book
$\longrightarrow$ [1997, 2000]
$\longrightarrow$ *Analyte*

Matrix effect

Influence of one or more matrix constituent(s) on the analyte under study. Matrix influences may affect the analyte signal directly by interferences or indirectly by signal depression or amplification.

$\longrightarrow$ Sect. 3.5
$\longrightarrow$ Eqs. (3.12)–(3.14); (3.16); (3.17)

Measurand

"Particular quantity subject to measurement".

ISO 3524-1 [1993]

Measured result

Measured value, obtained by measurement and completed by information on the uncertainty of measurement.

$\longrightarrow$ Sect. 8.1
$\longrightarrow$ *Measured value*
$\longrightarrow$ *Uncertainty*

Measured value

"Outcome of an analytical measurement" or "value attributed to a measurand". A measured value is a "Magnitude of a measuring quantity generally expressed as a unit of measurement multiplied by a number".

ISO 3524-1 [1993]
IUPAC [1995]; Currie [1999]
$\longrightarrow$ *Measuring quantity*

Measuring quantity

"Attribute of a phenomenon … that may be distinguished qualitatively and determined quantitatively".

ISO 3524-1 [1993]

Measuring sample

Sample that is directly introduced into analytical measurement. A measured sample is created from a test sample by conversion into a measurable form by means of a procedure of sample preparation.

$\longrightarrow$ Sect. 2.2

Metrology

"Science of measurement".

ISO 3524-1 [1993]

Monitoring

Continuous or repeated observation, measurement, and evaluation of a process in a certain field of application (e.g., environmental surveillance, health checking, foodstuff inspection, quality assurance in manufacturing), according to given schedules in space and time.

Multicomponent analysis (*multispecies analysis*)

Simultaneous determination of several analytes (species) by means of a multicomponent sensing technique or hyphenated techniques.

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ IUPAC [2004]

Noise

Fluctuations of the baseline- or background record of an (analytical) instrument. Noise do not provide meaningful information, on the contrary, it degrades the quality of signals and, therefore their detectability.

$\longrightarrow$ *Background*
$\longrightarrow$ *Baseline*
$\longrightarrow$ *Signal-to-noise ratio, R/N*, is a measure of the quality of signals
$\longrightarrow$ Sect. 7.5
$\longrightarrow$ Figs. 7.9B and 7.10

Population

"Finite or infinite set of individuals (objects, items). A population implicitly contains all the useful information for calculating the true values of the population parameters", e.g., the mean μ and the standard deviation σ.

FRANK and TODESCHINI [1994]
$\longrightarrow$ *Sample* (in the statistical sense)

Precision

"The closeness of agreement between independent test results obtained under stipulated conditions".
"The precision of a set of results of measurements may be quantified as a standard deviation".

ISO 3524-1 [1993]; GAT II [1996]
$\longrightarrow$ KAISER and SPECKER [1956]
$\times$ In fact, standard deviation characterizes *imprecision*
$\longrightarrow$ Sect. 7.1.1; Eqs. (7.8) and (7.9)

Prediction interval (*PI*)

Statistical interval, e.g., of a mean, $\overline{x}$, $prd(\overline{x}) = \overline{x} \pm \Delta\overline{x}_{prd}$, that express the uncertainty of analytical values which are predicted on the basis of experimental calibration. *PI*s are applied for significance tests and to establish quantities for limit values (*LD*, *LQ*).

$\longrightarrow$ Sect. 7.5
$\longrightarrow$ *Limit of detection*
$\longrightarrow$ *Limit of quantification*
$\longrightarrow$ *Confidence interval*

Proficiency test

"Study of laboratory performance by means of ongoing interlaboratory test comparisons".

ISO GUIDE 33 [1989]
PRITCHARD et al. [2001]
$\longrightarrow$ *Interlaboratory study*

Qualitative analysis

Testing whether (a) known constituent(s) are present or absent in test samples.
In contrast, identification means recognizing of (an) unknown constituent(s) in a test sample.

$\longrightarrow$ Sect. 9.3

Quantitative analysis

Determination of the amount(s) of (an) analyte(s) in a test sample.

$\longrightarrow$ *Assay*

Random variable

A quantity that appears in a random experiment. Random variables relate events into a set of values.

$\longrightarrow$ SACHS [1992]
$\longrightarrow$ FRANK and TODESCHINI [1994]

Range (in the analytical sense)

"The interval between the upper and the   PRITCHARD et al. [2001]
lower concentration of the analyte in the
sample for which it has been determined
that the method is applicable".

Range (in the statistical sense)

Difference between the greatest and the $\longrightarrow$ PRITCHARD et al. [2001]
smallest values of a series of measure- $\longrightarrow$ Sect. 4.3.2
ments.

Recalibration

Updating of a calibration model in the $\longrightarrow$ *Standard operating proce-*
case that details of the analytical proce-   *dure*
dure are changed.

Reference material

"A material or substance one or more   ISO 3524-1 [1993]
of whose property values are sufficiently $\longrightarrow$ GAT IV [1996]
homogeneous and well established to be $\longrightarrow$ PRITCHARD et al. [2001]
used for the calibration of an apparatus,
the assessment of a measurement method
or for assigning values to materials".

Regression

Statistical method to model a mathemat- $\longrightarrow$ SACHS [1992]
ical equation that describes the relation- $\longrightarrow$ FRANK and TODESCHINI
ship between random variables (usually   [1994]
x and y). The goal of regression analysis $\longrightarrow$ *Regression model*
is both modelling and predicting. $\longrightarrow$ Sect. 6.1.3

Regression coefficients (*regression parameter*)

Coefficients of the predictors in a regres- $\longrightarrow$ Eqs. (6.8) to (6.10)
sion model, e.g., a_x and b_x or a_y and b_y,
respectively, in linear regression models.

Regression model

Mathematical model that describes the relationship between random variables (usually x and y) by means of regression coefficients and their uncertainties as well as uncertainties of model and the prediction.

In linear regression there are two different models:

that of the prediction of y from x

$$\hat{y} = a_x + b_x x \qquad (6.6)$$

and that of the prediction of x from y

$$\hat{x} = a_y + b_y y \qquad (6.7)$$

$\longrightarrow$ Sachs [1992]
$\longrightarrow$ Frank and Todeschini [1994]
$\longrightarrow$ Sect. 6.1.3
$\times$ Eq. (6.7) is not the inverse of Eq. (6.6), viz

$$\hat{x} = a_y + b_y y \neq \frac{\hat{y} - a_x}{b_x}$$

though Eq. (6.7) approximates to Eq. (6.6) in the same degree as the correlation coefficient r_{xy} approximates to 1

Relative standard deviation (RSD)

Standard deviation expressed as a fraction of the mean $s_{rel} = s/\overline{x}$. RSD is a dimensionless quantity; sometimes it is multiplied by 100 and expressed as a percentage.

$\times$ The use of the term "*coefficient of variation*" ("*variation coefficient*") is not recommended by IUPAC
$\longrightarrow$ IUPAC Orange Book [1997, 2000]

Reliability

A qualitative term that covers precision and accuracy as well as robustness (ruggedness).

Repeatability (of results of measurements)

"Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement" (Precision under repeatability conditions).
Repeatability may be expressed quantitatively in terms of suitable dispersion characteristics.

ISO 3524-1 [1993]
$\longrightarrow$ GAT I [1996]
$\longrightarrow$ Sect. 7.1.3
$\longrightarrow$ Repeatability conditions include the same measurement procedure, the same observer, the same measuring instrument, used under the same conditions, the same location, and repetition over a short period of time
$\longrightarrow$ *Repeatability standard deviation*
$\longrightarrow$ *Repeatability interval*

Repeatability standard deviation (s_{repeat})

Experimental standard deviation obtained from a series of n measurements under repeatability conditions.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ The number of measurements should be about $n = 10$

Repeatability interval (repeatability limit)

A confidence interval representing the maximum permitted difference between two single test results under repeatability conditions:

$$r = t_{1-\alpha,v}\sqrt{2} \cdot s_{repeat}$$

$\longrightarrow$ PRITCHARD et al. [2001]
In the given formula, $t_{1-\alpha,v}$ is the quantile of the respective t-distribution (the degrees of freedom v relates to the number of replicates by which s_{repeat} has been estimated)

Reproducibility (of results of measurements)

"Closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement" (Precision under reproducibility conditions).
Reproducibility may be expressed quantitatively in terms of suitable dispersion characteristics.

ISO 3524-1 [1993]
$\longrightarrow$ GAT I [1996]
$\longrightarrow$ Sect. 7.1.3
$\longrightarrow$ Reproducibility conditions are characterized by changing conditions such as: observer, measuring instrument, conditions of use, location, time, but applying the same method
$\longrightarrow$ Reproducibility standard deviation
$\longrightarrow$ Reproducibility interval

Reproducibility standard deviation (s_{repro})

Experimental standard deviation obtained from a series of measurements under reproducibility conditions.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ The number of measurements should be sufficiently large to estimate a representative reproducibility standard deviation

Reproducibility interval (reproducibility limit)

A confidence interval representing the maximum permitted difference between two single test results under reproducibility conditions:

$$R = t_{1-\alpha,v}\sqrt{2} \cdot s_{repro}$$

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ In the given formula, $t_{1-\alpha,v}$ is the quantile of the t-distribution (the degrees of freedom v relates to the number of replicates by which s_{repro} has been estimated)

Resolution

Process by which a composite signal is split up into individual forms. The resolution can be related to:

$\longrightarrow$ Sect. 6.4.1
$\longrightarrow$ Sect. 7.6

(i)   Signal overlappings and fine structure (z-scale)
(ii) Signals in close succession in time and space

Resolution limit

The smallest difference Δz at which two adjacent signals can be separately observed, i.e., their overlap does not exceed a threshold of 50% of the individual profiles.

$\longrightarrow$ SHARAF et al. [1986]
$\longrightarrow$ In case (ii) of resolution of the resolution problem, Δt and Δl are the crucial parameters
$\longrightarrow$ Sect. 7.6

Resolution power

Ability of an analytical procedure to detect signals of small differences as separate signals. Resolution power is inversely proportional to resolution limit, e.g., $R = z/\Delta z$

$\longrightarrow$ SHARAF et al. [1986]
$\longrightarrow$ Sect. 7.6

Response

Output of an analytical system as a reaction to a certain stimulus.

$\longrightarrow$ Stimulus
$\longrightarrow$ The output may be an observable or measurable effect

Response function

Relationship between the response of the analytical system and the amount of analyte. The overall response function is frequently nonlinear.

$\longrightarrow$ SHARAF et al. [1986]
$\longrightarrow$ Calibration function

Response variable (dependent variable)

$\longrightarrow$ *Measuring quantity, measured value*

Robustness

Property of an analytical procedure that indicates insensitivity against changes of known operational parameters on the results of the method and hence its suitability for its defined purpose.

$\longrightarrow$ BURNS et al. [2005]
$\longrightarrow$ ICH [1996]
$\longrightarrow$ Robustness may be quantified by means of quantities characterizing signal effects
$\longrightarrow$ Eq. (7.31)

Round robin test $\longrightarrow$ interlaboratory study

Ruggedness

Property of an analytical procedure that indicates insensitivity against changes of known operational variables and in addition any variations (not discovered in intra-laboratory experiments) which may be revealed by inter-laboratory studies.

$\longrightarrow$ BURNS et al. [2005]
$\longrightarrow$ Ruggedness may be quantified by means of quantities characterizing signal effects
$\longrightarrow$ Eq. (7.33)

Sample (in the analytical sense)

Portion of the object under study (the material submitted for analysis).
A sample consists of the analyte and the matrix.

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ There are various types of samples within given sampling schemes, e.g., bulk samples > primary samples > gross samples > subsamples > test samples > measuring samples
$\longrightarrow$ Fig. 2.4

Sample (in the statistical sense)

"Subset of a population that is collected in order to estimate the properties of the underlying population", e.g., the sample parameters mean $\overline{x}$ and standard deviation s. In the ideal case of representative sampling, the sample parameter fit the parameter of the population μ and σ, respectively.

FRANK and TODESCHINI [1994]

Sample domain (*analyte domain*)

> Field of analytical operation that is characterized by samples' properties such as type of analytes, Q, and their amount, x_Q. The transition to signal domain is done by calibration and analytical measurement.

$\longrightarrow$ Fig. 2.12
$\longrightarrow$ *Signal domain*

Sampling

> "Sequence of selective and non-selective operations ending with the selection of one or several test portions submitted to the analytical process in their entirety. Their physical properties (maximum particle size, mass, etc) are specified in the analytical procedure." Sampling covers sampling (in the narrow sense) and sample reduction.

$\longrightarrow$ Gy [1992]
$\longrightarrow$ Sect. 2.1
$\longrightarrow$ Fig. 2.4

Screening

> Testing of (a large number of) objects in order to identify those with particular characteristics.

$\longrightarrow$ Sect. 1.2
$\longrightarrow$ Fig. 1.5

Selectivity

> The extent to which n given analytes can be measured simultaneously by (a least) n sensors (detecting channels) without interferences by other components and, therefore, can be detected and determined independently and undisturbedly.

$\longrightarrow$ KAISER [1972]; DANZER [2001]
$\longrightarrow$ Sect. 7.3
$\longrightarrow$ Eq. (7.24)
$\times$ *Selectivity* should not be merged with *specificity*: *selectivity* relates to multicomponent analysis and *specificity* to single component analysis

Sensitivity

> "Change in the response of a measuring instrument divided by the corresponding change in the stimulus". In analytical measurements is this, in fact, the differential quotient of the measured value to the analytical value.

ISO 3435-1 [1993]; GAT VII [1997]
$\longrightarrow$ Sect. 7.2
$\longrightarrow$ Eq. (7.12)
$\times$ *Sensitivity* should not be confused with *limit of detection*

Sensitivity matrix (*Matrix of partial sensitivities*)

Matrix that contains all the sensitivities and cross sensitivities of a multicomponent (multidetector) analytical system.

$\longrightarrow$ KAISER [1972]; DANZER [2001]
$\longrightarrow$ Sect. 7.2
$\longrightarrow$ Eq. (7.17)
$\longrightarrow$ *Cross sensitivity*

Signal

"Response of a device (usually an instrument or a module of an instrument) to certain stimuli". A signal is characterized by at least three parameters: position, intensity, and width (symmetry, shape).

SHARAF et al. [1986]
$\longrightarrow$ Sect. 3.3
$\longrightarrow$ Fig. 3.6

Signal domain (*response domain*)

Field of analytical operation that is characterized by signal properties such as signal position, z, and signal intensity, y_z. The transition to sample domain is done by analytical evaluation (signal decoding).

$\longrightarrow$ Fig. 2.12
$\longrightarrow$ *Sample domain*

Signal function

Record of signal intensity in dependence of the signal position over a certain range of the z-scale: $y = f(z)$.

Signal-to-noise ratio

Measure of the precision of signal measurement, expressed mostly by the ratio of the net signal value to a noise parameter (standard deviation or peak-to-peak distance).

$\longrightarrow$ Sect. 7.1, Fig. 7.2
$\longrightarrow$ Eqs. (7.1)–(7.6)

Specificity

The extent to which *one individual* analyte can be measured undisturbedly in a real sample by a specific reagent, a particular sensor or a comparable specific measuring system.

$\longrightarrow$ KAISER [1972]; DANZER [2001]
$\longrightarrow$ Sect. 7.3
$\longrightarrow$ Eq. (7.26)
$\longrightarrow$ *Selectivity*
$\times$ *Specificity* should not be merged with *selectivity*

Specimen

Fraction of a lot (batch sample) taken without respecting the rules for sampling correctness or under unknown conditions.

Gy [1992]

Standard deviation (SD)

Dispersion parameter for the distribution of measured values, s_y, or analytical results, s_x, for a given sample or the population, σ_y and σ_x. The SD is the square root of the variance.

$\longrightarrow$ IUPAC [1995]; CURRIE [1999]
$\longrightarrow$ SACHS [1992]
$\longrightarrow$ DIXON and MASSEY [1969]
$\longrightarrow$ Sect. 4.1.2
$\longrightarrow$ Eqs. (4.12)–(4.14)

Standard error

The term "standard error" is not explicitly introduced. It is used sometimes (a) synonymously for standard deviation and (b) for the residual standard deviation in modelling and calibration.

$\longrightarrow$ SACHS [1992]
$\longrightarrow$ FRANK and TODESCHINI [1994]
$\times$ The term standard error should be avoided

Stimulus

Property of an analytical system to produce a response of an observation- or measuring system. Rousing effect of an analyte that can be characterized qualitatively and quantitatively.

Standard operating procedure (SOP)

"A set of written instructions that document a routine or repetitive activity followed by an organization".

EPA [2001]
$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ Fig. 7.1

Test

Process of analyzing the sample to recognize (an) analyte(s) and/or determine the amount(s) of (an) analyte(s).

$\longrightarrow$ PRITCHARD et al. [2001]
$\longrightarrow$ Quotation from ANAL CHEM [1975] at the end of the Glossary

Total sensitivity (*total multicomponent sensitivity*)

Sensitivity of a multicomponent analysis. In the simplest case it is given by the determinant of the sensitivity matrix.	$\longrightarrow$ SHARAF et al. [1986] $\longrightarrow$ MASSART et al. [1988] $\longrightarrow$ Sect. 7.2 $\longrightarrow$ Eqs. (7.18)–(7.20)

Traceability

"The property of a result of measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons".	GAT I [1996] $\longrightarrow$ ISO 3435-1 [1993] $\longrightarrow$ All the standards used should have stated uncertainties

Trackability

"The property of a result of a measurement whereby the result can be uniquely related to the sample".	GAT I [1996]

True value

"Value consistent with the definition of a given particular quantity" and "value which characterizes a quantity perfectly defined in the conditions which exist when that quantity is considered".	ISO 3534-1 [1993] GAT III [1996] $\longrightarrow$ *Conventional true value* $\longrightarrow$ Sect. 7.1

Trueness

"Closeness of agreement between the average value obtained from a large series of test results and an accepted reference value". Trueness has been referred to as "accuracy of the mean".	IUPAC ORANGE BOOK [1997, 2000] $\longrightarrow$ CODEX ALIMENTARIUS COMMISSION [1997] $\longrightarrow$ Sect. 7.1.3

Uncertainty of measurement

"Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand". The uncertainty should combine both statistical and non-statistical contributions to the variation of the measured values which may occur in all steps of the analytical process.

ISO 3524-1 [1993]
EURACHEM [1995]
GAT I [1996]
$\longrightarrow$ The uncertainty of measurement may be expressed by the combined or extended uncertainty, $u(y)$ or $U(y)$, respectively
$\longrightarrow$ Sect. 4.2
$\longrightarrow$ Eqs. (4.25), (4.26) and (4.29) to (4.32)

Uncertainty of an analytical result

Interval, e.g., of a mean, $U(\overline{x})$, that express the uncertainty of analytical values considering statistical and non-statistical variations within the measurement process plus uncertainties of experimental calibration.

$\longrightarrow$ Sect. 4.2
$\longrightarrow$ Eq. (4.32)

Validation (of an analytical method)

"Process by which it is established, by laboratory studies, that the performance characteristics of the method meet the requirements for the intended analytical applications".

USP XXII < 1225 > [1990]
WEGSCHEIDER [1996]
EURACHEM [1998]
$\longrightarrow$ Typical performance characteristics that should be considered in the validation are: *precision, accuracy, limit of detection, limit of quantitation, selectivity, range, linearity, robustness, ruggedness*

Variable

"Characteristic of an object that may take on any value from a specified set".

FRANK and TODESCHINI [1994]
$\longrightarrow$ There are several types of variables, e.g., *categorical, dependent* and *independent, experimental* and *theoretical, manifest* and *latent, random, standardized variables*

Variance

Dispersion parameter for the distribution of measured values, s_y^2, or analytical results, s_x^2, for a given sample or the population, σ_y^2 and σ_x^2. Statistically defined as the second moment about the mean.

$\longrightarrow$ IUPAC [1995]; Currie [1999]
$\longrightarrow$ Sachs [1992]
$\longrightarrow$ Dixon and Massey [1969]
$\longrightarrow$ Sect. 4.1.2
$\longrightarrow$ Eqs. (4.8); (4.10)

Working range $\longrightarrow$ *Range* (in the analytical sense)

Analysis, Identification, Determination, and Assay (quoted from Anal Chem [1975])

"While most chemists probably realize the difference between the terms *analyze*, *identify*, and *determine*, they are frequently careless when using them. Most frequently the term *analysis* is used when *determination* is meant.

A study of the nomenclature problem indicates that only samples are *analyzed*; elements, ions, and compounds are *identified* or *determined*. The difficulty occurs when the sample is nominally an element or compound (of unknown purity). 'Analysis of . . .' (an element or compound) must be understood to mean the identification or determination of impurities. When the intent is to determine how much of such a sample is the material indicated by the name, *assay* is the proper word."

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