Annex 1: Glossary of Terms

Accreditation Formal written acknowledgement that a laboratory is fit and competent to perform one or more given types of analysis. Obtained by subjecting the laboratory to an audit (accreditation process) conducted by personnel external to the laboratory and its parent body.

Absolute error The difference between the value to be qualified and its reference.

Absolute method A type of calculable quantification method that uses no analytical standard.

Absolute method with analytical standards. A calculable method that uses one or more tangible analytical chemical standards.

Absolute trueness An ideal analytical feature and an attribute of chemical information inherent in the target object or sample. Corresponds to the true value

Accuracy – An ideal analytical feature and an attribute of chemical information inherent in the target object or sample. Corresponds to the true value– A capital analytical property of a result or a CMP (the opposite of bias).

Aliquot A well-defined portion (mass, volume) of a sample.

Amount An attribute of an object that can be qualitatively distinguished and quantitatively determined. Amount encompasses "measurand" and "analyte".

Analyse, to – To subject a sample to an analytical process in order to extract information about measurands or analytes.
– To interpret analytical results with a view to producing a report.

Analyser An integrated system consisting of instruments, apparatuses and devices that performs virtually the whole analytical process (CMP).

Analysis In a general sense, "analysis" involves examination, study, acquisition of knowledge to provide information about objects, facts, systems, performance and attitudes. In the chemical realm, "analysis" involves subjecting a sample to an analytical process in order to extract (bio)chemical information about it.

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Analyte A chemical or biochemical species in a sample about which qualitative or quantitative information is required.

Analytical blank A usually artificial sample containing no analyte. In theory, a blank should give no signal if it does it is called the "blank signal".

Analytical Chemistry A metrological science that develops, optimizes and uses measurement processes intended to derive quality (bio)chemical information about natural or artificial objects or systems with a view to solving analytical problems.

Analytical error Broadly speaking, an alteration in analytical information. Analytical errors can be of the random, systematic or gross type.

Analytical fundamentals The cornerstones on which the theoretical and practical sides of Analytical Chemistry stand. Intrinsic to Analytical Chemistry or shared with other scientific and technical areas

Analytical information – Chemical characteristics of an object or system, usually ascribed to its components (analytes) or to the entity as a whole.
– The opposite of "generic uncertainty" and the primary goal of Analytical Chemistry.
Information held as true. That obtained through special testing (e.g., an interlaboratory exercise) or possessed by a CRM. Corresponds to referential quality.
Intrinsic information. That possessed by the object or system to be analysed. Corresponds to ideal quality.
Routine information. That ordinarily produced by laboratories. Corresponds to real quality.

Analytical knowledge Analytical results (information) that are discussed, compared with references, contextualized and accompanied by decision-making proposals. Analytical knowledge materializes in "analytical reports" and is thus at the highest step in the data–information–knowledge ranking.

Analytical method The body of specific operations used in the qualitative or quantitative characterization of an analyte (or analyte family) in a given sample. Entails using a technique (instrument) and is the materialization of a CMP.

Analytical problem An approach to solving the client's information needs by designing and planning a CMP, and interpreting the ensuing results.

Analytical properties Attributes ascribed to results and/or a chemical measurement process (CMP). The quality indicators of Analytical Chemistry.
Basic properties. Those that can be ascribed to a CMP and support capital properties.
Capital properties. Those that can be ascribed to results.

Productivity-related properties. Those that can be ascribed to a CMP and define laboratory productivity.

Analytical quality The degree of excellence in the chemical information supplied with a view to solving an analytical problem. Comprises four components: quality of results, quality of CMPs, quality of analytical tools and quality of work and its organization.

Analytical references Landmarks used in the comparisons inherent in analytical measurements. Can be materials (standards) or methods.

Analytical reports – The body of analytical results (data) and their interpretation in the light of the analytical problem addressed.
– The top level in the information hierarchy.

Analytical results Qualitative and/or quantitative data obtained by mathematical (chemometric) treatment of primary data produced by an instrument in the analytical process.

Analytical schemes Sequential, orderly processes that use separation methods (e.g., precipitation) in Classical Qualitative Analysis to classify species into groups where each analyte can be reliably identified.

Analytical tools Material, strategic and methodological means of varied nature on which chemical measurement processes (CMPs) rely.

Apparatus A system consisting of devices that serves a specific function in a CMP but provides no analytical information. An apparatus produces secondary data.

Applied research in Analytical Chemistry Development of analytical methods based on the "products" of basic research to extract (bio)chemical information with a view to fulfilling information demands. If no effective tool for the intended purpose exists, it must be produced through new basic research.

Audit An instance of external–external assessment conducted by specialists external to the laboratory and its parent body.

Automation Partial or total reduction of human participation in a CMP.

Avogadro's number A chemical standard defined as the number (6.023×10^{23}) of atoms or molecules contained in one mole of any chemical substance.

Balance An instrumental tool primarily used to measure the initial mass of the test sample to be subjected to a CMP or that of the weighed form in gravimetries.

Basic research in Analytical Chemistry Development of new analytical tools (e.g., reagents, solvents, equipment, sensors) and approaches for no specific purpose other than advancement of the discipline

Bias A systematic or determinate error equal to the positive or negative difference between the mean of n results and the value held as true, $\overline{X} - \widehat{X}'$, that can be ascribed to an analytical method and is related to its accuracy.

Binary response – The result (YES or NO) of a qualitative analysis.
– The answer to various questions the most crucial of which are "is it the analyte?" and "is it in the sample?"

Black sample A sample whose composition is completely unknown before analysis.

Blank signal The signal produced by a blank sample.

Blind sample A sample of well-defined composition that is interspersed for quality control purposes with those to be routinely analysed by a laboratory.

Burette An instrumental tool used to measure the volume of titrant solution used in titrations. Burettes can be manual or automatic in operation.

Calculable method One that provides results based on mathematical calculations involving both tabulated data and measurements made during the CMP. May use some or no analytical standard.

Calibration curve A two-dimensional graphical plot showing the variation of the analytical signal with the amount or concentration of analyte (standard). See also "Linear calibration graph".

Capillary electrophoresis A separation process occurring within a capillary under a high electric field. Because the system is equipped with a detector, it can be considered an instrument.

Certified reference material (CRM) A reference material with certified values (specific uncertainties included) for one or more of its properties that are obtained by special procedures (e.g., interlaboratory exercises) under the supervision of a competent, independent body. A CRM should be accompanied by comprehensive documentation.

Characterize, to To identify distinct features in an object or system from analytical results.

Chemical analysis A process by which chemical measurement processes (CMPs) are used to extract information from objects or systems.

Chemical measurement process (CMP) See "Analytical process".

Chemical metrology The science of (bio)chemical measurements.

Chromatograph An analytical system that performs chromatographic separations in a column (gas or liquid chromatography) and includes an on-line detector for continuous monitoring of the fluid emerging from the separation column. Because it provides analytical information, a chromatograph is an instrument.

Chromatography A word that describes a broad range of highly efficient analytical separation techniques based on multiple mass transfer between a mobile phase and a stationary phase.

Gas chromatography. A chromatographic technique where the mobile phase is a gas (into which the sample aliquot is inserted) and the stationary phase is a solid or a liquid supported on an inert solid that is placed in a column.

Liquid chromatography. A chromatographic technique where the mobile phase is a liquid (into which the sample aliquot is inserted) and the stationary phase is a solid or a liquid that is either supported on an inert solid for placement in a column or spread onto a thin layer of a support (in Thin Layer Chromatography).

Classical analysis A type of qualitative or quantitative analysis based on chemical reactions in solution and involving the use of human senses for identification and a balance or burette for quantification.

Classification analysis Classification of samples of similar composition into groups (clusters) that can be distinguished by analysis. Samples can be classified into two groups (e.g., positive and negative samples) by qualitative analysis or into more than two by multiple classification analysis.

Clean-up The process by which interferents in a sample are removed using a separation technique to indirectly enhance selectivity.

Client A general designation applied to an individual or body requiring (bio)chemical information with a view to solving a socio-economic problem.

Coefficient of variation The relative standard deviation in percent form.

Comparative method A type of relative quantification method in which the final result is obtained by comparing the sample signal with that for a sample standard.

Concentration An form of expressing a relative quantitative result: the amount of analyte contained in a given volume or mass of sample.

Cut-off concentration. The concentration chosen by the analyst in establishing a given probability level that a binary response will be correct.

Limiting concentration or **threshold concentration**. Highest or lowest level, established by the client or legislation, to be used in deciding whether a sample or object warrants assignation of a given attribute (e.g., toxic or non-toxic).

Confidence interval A value (concentration) range within which the result of an analytical process can be expected to fall with a given level of confidence. Related to specific uncertainty in the context of precision of a method.

Data processing The body of mathematical calculations leading to the expression of the analytical result from tabulated data (chemical standards, constants, conversion factors) and experimental data produced by a CMP applied to the sample and standards.

Detect, to Of an instrument: To produce a signal and transduce it into an easily measured physical quantity (a primary datum).

Detection The action of detecting. The process of measuring for qualitative purposes.

Determinate error See "Systematic error".

Determination The process by which the amount or concentration of an analyte (or analyte family) in a sample is established.

Deviation The difference between an individual result (x_i) in a set and the mean for the set ($\bar{X}$, the random error).

Device A part of an apparatus, instrument or analyser that can serve one or more of a wide variety of possible functions.

Dialysis The process by which mass transfer between two miscible liquid phases separated by a membrane permeable to the analytes or their interferents takes place.

Disaggregation A substep of the preliminary operations of a CMP involving the fusion of an insoluble solid sample mixed with an acid or alkaline solid reagent.

Dissolution A substep of the preliminary operations of a CMP where a solid (or semi-solid) sample is completely dissolved by treatment with a solvent.

Electrodeposition A gravimetric method performed by an electrochemical device in order to deposit the analyte quantitatively onto one electrode (usually the cathode) that is weighed before and after the process.

End-point In a titration, the volume of titrant added to the solution containing the analyte or standard by the time the indicator system produces a signal in response to which the titration should be stopped.

End-point indicator A system of the visual or instrumental type that exposes the end-point of a titration.

Equipment calibration The process by which a standard containing no analyte is used to check that an instrument (or apparatus) operates as expected. Otherwise, corrections are introduced until the instrument response (or the indication of an apparatus) reaches the value held as true for the standard used.

Equipment verification Equivalent to "Equipment calibration".

Equivalence point In a titration, the theoretical volume of titrant required to react in a quantitative, stoichiometric manner with the analyte or a standard

Error accumulation In a multi-stage process (e.g., the analytical process), the overall error is the arithmetic sum of the variances (standard deviations squared) arising at each stage (sub-process).

Errors in qualitative analysis Deviations from true YES/NO responses. See "False positive" and "False negative".

External manipulation of (bio)chemical information In the context of Social Responsibility in Analytical Chemistry, fraudulent alteration of the composition of a sample in order to obtain spurious results for unethical purposes (e.g., by directly adding a harmless substance to "conceal" the analyte in order to alter a sample and/or an analytical process).

Extraction The process by which one or several substances are separated from a solid or liquid sample.

Liquid–liquid extraction. Treatment of a liquid sample with an immiscible solvent intended to separate the analytes or their interferents.

Liquid–solid extraction. Use of a solid sorbent to retain the analytes or interferents in a liquid sample. Usually called *Solid-phase extraction* (SPE).

Solid–liquid extraction. Treatment of a solid sample with a suitable solvent to dissolve the target analytes. Also called *leaching*.

Supercritical fluid extraction. Treatment of a solid sample with a supercritical fluid to separate the soluble fraction.

False negative An error in Qualitative Analysis that results when a NO response is obtained from a sample that should have yielded a YES response.

False positive An error in Qualitative Analysis that results when a YES response is obtained from a sample that should have yielded a NO response.

Faraday A chemical standard defined as the amount of electricity (96 487.3 C) needed for one equivalent of a redox substance to be electrochemically converted at an electrode.

Generic uncertainty Dubiousness in the chemical composition of an object or sample, that is named "black sample". The opposite of "information".

Good Laboratory Practices (GLPs) The body of rules and procedures that are held as mandatory with a view to assuring quality and correctness in the results produced by laboratories engaged in the analysis and evaluation of substances with direct social implications and as such necessitating regulation.

Gravimetric factor – The ratio of the formula weight of the analyte to the molecular weight of the weighed form in gravimetry (a dimensionless number by which the result of a gravimetric weighing is multiplied in order to determine the analyte weight).
– A combination of chemical standards (atomic weights).

Gravimetry A type of calculable analytical quantification method that uses no analytical standards and is based on measurements of the mass of an analyte or a chemical derivative of the analyte.

Green analytical methods Ecological, environmentally friendly methods of analysis intended to avoid contaminating air, water, soil, etc., by effect of operations of the analytical process.

Grey sample A sample whose composition is known only approximately.

Gross error A large systematic error.

Heterogeneity A property of an object or sample in space or time that poses a problem which must be solved during sample collection if the results produced by the ensuing CMP are to be representative.

Hyphenated techniques Those using a powerful dynamic analytical separation system (e.g., a gas or liquid chromatograph) in combination with an instrument possessing a high information capacity (e.g., a mass spectrometer).

Identification A qualitative analytical process by which the presence of an analyte is ascertained on the basis of chemical or physico–chemical properties of the analyte or a reaction product of the analyte.

Indeterminate error See"Random error".

Information consistency In regard to "analytical problem", suitability of data and results to the client's information requirements.

Instrument
- A measuring system that produces raw (primary) data that can be processed in order to be related to the presence or concentration of one or more analytes in a sample.
- The materialization of an analytical technique.

Instrumental analysis A type of qualitative, quantitative and structural analysis based on the use of instruments other than the balance, burette and human senses.

Interferences Chemical or physical perturbations of various types that systematically alter one or more steps of a CMP and hence the analytical result in terms of selectivity.

Interlaboratory exercise A series of CMPs performed by different laboratories under the supervision of a competent body to analyse aliquots of the same sample for the same analytes. Used to check the results (and their uncertainties) for a variety of purposes (e.g., preparing a CRM).

Internal representativeness In regard to the analytical problem, degree of consistency between the results obtained in the analytical process and the analysed sample, the object from which the sample was taken and the analytical problem addressed by the analytical chemist.

Ion exchange A process by which dissolved ionic species are separated by using an active solid called an "ion-exchange resin".

ISO 17025 A 2005 standard specific to testing laboratories that is entitled "General requirements for the competence of testing and calibration laboratories".

ISO 9000 A general standard for quality entitled "Quality management systems—Fundamentals and vocabulary".

Leaching See "Solid–liquid extraction" under "Extraction".

Limit of detection The analyte concentration yielding an analytical signal that can be statistically distinguished from an analytical blank.

Limit of quantification The analyte concentration yielding a signal that is taken to be the lower limit of the linear range of the calibration curve.

Linear calibration graph A linear (first-order) mathematical function relating the signal with the concentration of standards containing a known analyte concentration that are subjected to the analytical process. It allows the sample signal to be related to the signals for standards in order to calculate the analyte concentration by extrapolation.

Linear range The linear portion of the calibration curve where the sensitivity (slope) remains constant.

Macroanalysis A type of chemical analysis where the initial size of the sample aliquot subjected to the CMP is greater than 100 mg.

Macrocomponents Analytes whose proportions in the sample exceed 1% of their masses.

Masking The use of a reagent to interact chemically in solution with interfering species in a sample in order to avoid their perturbation without the need to physically separate the reaction products from the medium (*pseudo*-separation).

Maximum representativeness In regard to the analytical problem, highest degree of consistency between the results obtained in the analytical process, which is reached when the results are significant both internally (that is, consistent with the sample, object and analytical problem) and with the client's socio-economic problem

Maximum tolerated ratio A parameter that describes the influence of an interfering species in the context of selectivity. The highest interferent-to-analyte concentration ratio that results in no perturbation to a CMP.

Measurand The quantity measured in a CMP, which may be the analyte or some quantity such as pH.

Measurement The process by which a signal yielded by the analyte or a reaction product of the analyte is compared with one produced by a standard.

Method calibration The process by which an analytical standard is used to characterize the response of an instrument in terms of the properties of an analyte or analyte family. Method calibration entails unequivocally relating the signal to the presence or concentration of the analyte.

Method-defined parameter An analytical result that can only be obtained by using a well-defined protocol that constitutes a reference established by law or custom because using another method leads to a different result.

Metrology The science of physical, chemical, biochemical and biological measurements. See "Chemical metrology".

Microanalysis A type of chemical analysis where the initial size of the sample aliquot subjected to the CMP ranges from 10 to 1 mg.

Microcomponents Analytes whose proportions in the sample range from 0.01 to 0.1% of their masses.

Miniaturization A term defining a technological trend to considerably reducing the size of analytical tools, integrating modules of a CMP or both.

Mole A base standard and a base unit of the International System (SI) defined as the amount of substance containing as many elemental units (atoms, molecules, ions, electrons or other individual particles or particle groups) as are in 0.012 kg of the isotope carbon-12.

Nanoanalysis See "Nanoworld analysis".

Nanoworld analysis Extraction of (bio)chemical information (identity, differences, concentration, structure) from objects of nanometric size (1–100 nm).

Negative error A negative difference between the value to be qualified and the reference used to establish it.

Object A system from which chemical information is required and samples are collected for analysis.

Official method A method endorsed and issued by an official body that is to be strictly adhered to.

Outlier A datum not belonging to a set obtained under reproducible or repeatable conditions that exhibits a significantly greater or smaller difference from the mean of the set than do the other data in the set.

Paradigm A body of essential, crucial, unarguable notions that set the guidelines for some activity. Analytical chemical paradigms are thus essential landmarks of Analytical Chemistry and, as such, change with time.

Positive error A positive difference between the value to be qualified and the reference used to establish it.

Precision The degree of mutual agreement of a set of results. The opposite of dispersion of the results around their mean, which is the reference used to calculate individual deviations (random errors).

Preconcentration A process by which sensitivity is indirectly enhanced through a separation. Involves reducing the original volume of a sample containing the analytes at low concentrations.

Preconcentration factor A dimensionless number greater than unity that is obtained by dividing the original volume into the reduced volume obtained upon application of an analytical separation technique to a sample. Multiplying by the original analyte concentration gives the final concentration of the aliquot subjected to the second step of the CMP.

Preliminary operations
- The body of actions performed in the first step of an analytical process (CMP).
- The link between the uncollected, unmeasured, untreated sample and the principal measuring instrument.
- The first step in a CMP.

Primary data
- Those produced by instruments in measurement processes.
- The most elementary form of information and the foundation of the results.
- The third step in the analytical information hierarchy.
- The results of detecting and sensing.

Primary method The type of method with the highest metrological quality.

Procedure A detailed specification of an analytical method.

Productivity A characteristic of a laboratory defined as the combination of its productivity-related analytical properties (expeditiousness, cost-effectiveness, and personnel safety and comfort).

Proficiency testing A form of external assessment of quality in the results of an analytical laboratory that involves participation in a specially designed interlaboratory exercise in order to compare its results with those of the other participating laboratories.

Qualimetrics The triple interface where Computers, Chemometrics and Quality in the laboratory converge.

Qualitative analysis
- A type of chemical analysis by which the analyte or analytes in a sample are identified.
- The result is a YES/NO binary response.

Quality The body of characteristics or abilities of an entity that make it better, equal to or worse than others of the same kind. In practice, quality is identified with client satisfaction.

Quality assessment Specific activities (audits) carried out by personnel from outside a laboratory to examine both the results produced and the laboratory as such and in regard to its quality control systems.

Quality assurance The body of activities performed in order to assure quality in the results produced by an analytical laboratory. Involves specific control, assessment and correction activities.

Quality assurance unit (QAU) A unit associated to GLPs that is independent of the laboratory, answerable to the president or manager of the parent body, and responsible for implementing, controlling and assessing quality in addition to proposing improvement actions.

Quality control The body of specific activities carried out by laboratory personnel in order to—basically—examine, in a direct manner, the results obtained and tools used by the laboratory.

Quality indicator A qualitative and quantitative aspect into which some characteristic or ability of an entity meeting a client's requirements materializes.

Quality manual A detailed written description of a laboratory and its activities (particularly quality control and assessment).

Quality system A series of coordinated activities performed on various elements (procedures, documents, structures) in order to assure quality in the products or services delivered by a given organization.

Quantitative analysis A type of chemical analysis by which the proportion (concentration) or amount of each analyte in a sample is determined. The result is a numerical response.

R&D&T in Analytical Chemistry Research, development and transference of analytical knowledge and technology.

Random error
- An error that can be ascribed to positive or negative (random) fluctuations typical of experimental operations.
- The basis on which precision and specific uncertainty are established.
- Also called "indeterminate error".

Reagent A chemical species that is added to a sample or standard in order to yield a reaction product with the analyte(s).

Group reagent. One that separates a small number of analytes from those present in the sample. Used in the framework of analytical schemes in Classical Qualitative Analysis.

Identification reagent. One that reacts with the analyte to produce an external effect that can be readily identified by the human senses (e.g., in Classical Qualitative Analysis) or detected by an instrument.

Masking reagent. One that reacts in solution with species accompanying the analyte in the sample in order to cancel their interferences.

Reference material A material or substance one or more properties of which are sufficiently uniform and well known for use to calibrate an instrument or apparatus, assign values to materials and systems or assess CMPs.

Reference method A method that is used to compare the accuracy and uncertainty of routine methods.

Relative error The ratio of an absolute error to the reference value used to calculate it. Multiplying a relative error by 100 gives a percent error.

Relative interpolation and extrapolation methods Relative quantification methods based on a signal–concentration relation (a calibration curve).

Relative method In Quantitative Analysis, a method based on comparisons between measurements of the sample and of one or a set of analytical standards. The output of such comparisons is the result.

Relative standard deviation An expression of the standard deviation in relative terms (as a fraction of unity with respect to the mean for the set of results).

Reliability
- A characteristic of a method (CMP) defined as its ability to retain its accuracy and precision over time. Related to robustness and transferability.
- The proportion of correct identifications in individual qualitative tests performed on aliquots of the same sample.
- A capital property in Qualitative Analysis that combines accuracy and precision, and is assigned to binary responses.

Repeatability A manner of expressing precision. Defined as the dispersion of the results of mutually independent tests using the same method as applied to aliquots of the same sample, at the same laboratory, by the same operator, using the same equipment over a short interval of time.

Representativeness A capital analytical property related to consistency between the results, the samples received, the object, the analytical problem and the socio-economic problem addressed.

Reproducibility A manner of expressing precision. Defined as the dispersion of the results for mutually independent tests performed by applying the same method to aliquots of the same sample under different conditions: different operators, equipment, days or laboratories.

Robustness An analytical property of a CMP that reflects its resistance to slight changes in the experimental conditions under which it is performed.

Safety An attribute of a laboratory or CMP related to the absence of hazards to human health and/or the environment.

Sample A part (aliquot) of an object potentially containing the analyte.
Bulk sample or **primary sample**. The result of the first selection from the object. Usually of a large size.

Composite sample. The result of combining several portions of a bulk sample.
Convenience sample. One selected in terms of availability, cost-effectiveness, efficiency, etc.
Laboratory sample. A portion of the object that is submitted, in an appropriate container, to the laboratory for analysis.
Random sample. One selected in such a way that any portion of the object will have a specified probability (e.g,. 95%) of being withdrawn.
Representative sample. A portion of the object that is selected by applying a sampling plan consistent with the analytical problem addressed.
Selective sample. A sample that is collected by following a guided sampling procedure.
Stratified sample. One withdrawn from a stratum or well-defined zone of the object.
Test sample or **aliquot**. The object portion that is eventually subjected to the analytical process.

Sample collection See "Sampling".

Sample custody chain The action or series of actions that ensures an unequivocal relationship between the sample aliquot subjected to a CMP and the result it produces (sample traceability).

Sample matrix Structure and chemical composition of the sample to be analysed. Includes the analytes and all other components.

Sample throughput A measure of expeditiousness of CMPs. The number of samples that can be processed per unit time (e.g., hour, day).

Sample treatment A general term used to refer to the substeps of the preliminary operations of the CMP performed in order to prepare the test sample or aliquot for measurement of the analytical signal (second step of the CMP).

Sampling An operation by which one or more portions (aliquots) of an object are chosen for individual or joint subjection (following size reduction) to a CMP. Sampling can be of the intuitive, statistical, directed or protocol-based type.

Sampling error A deviation in the representativeness of the collected sample. Sampling errors can be accidental, systematic or random in nature

Sampling plan The strategy to be used in order to ensure that the analytical results will be representative of the analytical problem addressed.

Screening of analytes A process used to systematically identify analytes or analyte families in samples.

Screening of samples Classifying a set of samples into two groups according to (bio)chemical composition.

Secondary data – Items of non-analytical information that characterize the performance of apparatuses and instruments in the analytical process.
– The lowest level in the information hierarchy.

Selectivity A basic analytical property of an analytical method that is defined as the ability of the method to produce results exclusively dependent on the analyte for its identification or quantification in the sample.

Selectivity factor A parameter describing the selectivity of a method with respect to another. Defined as the quotient of the tolerated interferent-to-analyte ratios obtained by using the two methods to determine the same analyte in the same sample.

Semi-microanalysis A type of chemical analysis where the initial size of the sample aliquot subjected to the CMP ranges from 100 to 10 mg.

Sense, to To use a device responding to the presence or concentration of an analyte in a sample. Entails interacting with an instrument proper.

Sensitivity – A basic analytical property defined as the ability of a method (CMP) to detect (qualify) and determine (quantify) small amounts of analyte in a sample.
– The ability of a CMP to distinguish between similar concentrations (amounts) of analyte.

Sensor A portable, easy to use miniature device or instrument that responds to the presence or concentration of an analyte (or analyte family) in a sample. Usually connected to or integrated in an instrument.

Separation An operation involving mass transfer between two phases. A crucial element of the preliminary operations of a CMP. Discrete or continuous in nature.

Chromatographic separation. One where distribution between phases reaches equilibrium many times (e.g., in a column, thus significantly enhancing the separation efficiency.
Non-chromatographic separation. One where mass transfer between phases reaches equilibrium only once or a small number of times.

Simplification A technological trend to reducing the number of steps traditionally involved in CMPs in order to increase expeditiousness and decrease costs.

Social responsibility (SR) – Awareness of organizations (e.g, private and public bodies) and individuals of the impact (consequences) of their actions and decisions, which may directly or indirectly affect stakeholders—who can in turn influence such actions and decisions or those who make them.
– The next step to ultimate Quality: a perfect mankind.

Social responsibility in Analytical Chemistry The impact of (bio)chemical knowledge resulting from the analysis of objects and systems on society at large, and on human and animal health, the environment, nutrition, industry, etc.

Social responsibility principles Cornerstones of Social Responsibility: answerability, transparency, ethical conduct, meeting stakeholders' expectations, and complying with national and international laws and norms.

Socio-economic problem – A question posed by the client that is to be answered by delivering appropriate information.
– The origin of the analytical problem.

Spatial analysis Extraction of (bio)chemical information from different zones of an object or system or from objects and systems in outer space.

Speciation A type of analysis that provides qualitative and quantitative information about the different forms in which an analyte may occur in a (usually environmental) sample.

Specific uncertainty The range of values where a result, a mean of such values and the value held as true may fall with a given probability. Similar to, but not the same, as precision. Can be absolute, partial or zero.

Stakeholders In the context of Social Responsibility (applicable ISO norms), the individuals, groups, NGOs, etc., potentially affected by the decisions and actions of a body, in which they can participate through ordinary procedures.

Standard A tangible or intangible reference used to support or perform analytical chemical measurements.

Base standard. A standard that coincides with one of the seven SI base units. Only the kilogram prototype is of the tangible type, however.
Chemical standard. A standard that can acts as a traceability link between base (SI) standards and analytical chemical standards.
Analytical chemical standard. Any of the standards used in ordinary analytical practice. Of the primary or secondary type.

Standard deviation A statistical parameter that reflects the precision of a set of results according to the theory of Gauss.

Standard method A method that is developed, validated and specified in detail by a competent body.

Standard operating procedure (SOP) A detailed description of how each individual laboratory activity should be conducted. Each activity should have an associated SOP. SOPs are related to Good Laboratory Practices (GLP).

Standard sample An artificial, naturally occurring or modified natural material intended to simulate as closely as possible an actual sample that possesses the properties of a reference material or certified reference material.

Structural analysis A type of chemical analysis by which the structure of a sample (viz., the spatial distribution of its constituents) or a pure analyte is established

Sustainable development That meeting current needs without compromising the ability of future generations to fulfil their own.

Systematic error An error ascribed to well-defined operational alterations in a CMP that has the true value or the value held as true as reference. Consistently positive or negative in sign. Can be assigned to a result or a CMP.

Technique A scientific principle used to obtain analytical information by using an instrument.

Titrant A reagent solution containing a referential concentration (that is, one prepared from primary and analytical standards) which is used in a titrimetry.

Titration See "Titrimetry".

Titration curve A logarithmic or linear plot of the monitored signal as a function of the titrant volume used in a titration.

Titrimetry A classical quantification technique involving an absolute method based on the use of analytical standards that relies on accurate measurements of the volume of titrant solution required to react, in a quantitative manner, with the analyte present in a sample. Can be of the direct or indirect type and performed in a manual, semi-automatic, automatic or automated manner.

Total index A measurand describing the presence and/or concentration of a family of analytes (e.g., total polyphenols in tomatoes).

Trace analysis An analytical process especially suitable for the identification or quantification of analytes present in proportions lower than 0.01% (100 ppm) in the sample.

Traceability An attribute that characterizes various analytical concepts. An abstract concept that integrates two notions: tracing (the history of production or performance) and relationship to standards.

> **Traceability of an aliquot**. An unequivocal relationship of a sample aliquot subjected to a CMP to both the socio-economic problem (representativeness) and the result (sample custody chain) which thus assures consistency between the problem and the result (cyclic traceability).
>
> **Traceability of an instrument**. The documented history of the performance of an instrument (installation, malfunctioning, repairs, servicing, calibration, correction, hours of use, samples processed, etc.). Through calibration, the relationship to standards implicit in traceability is established.
>
> **Traceability of a result**. A property of a result or of the value of standard through which the result or value is related to well-established national or international references via an unbroken chain of comparisons characterized by their respective uncertainties.

Traceable method A method whose results (and uncertainties) are linked to a well-known standard (e.g., a CRM).

Traces A word used to designate analytes present in proportions lower than 0.01% (100 ppm) in the sample.

Transducing The process by which a raw signal produced by an instrument is transformed into a (usually electrical) measurable signal.

Transfer in Analytical Chemistry The process by which basic and applied knowledge and technology developed at Analytical Chemistry R&D centres is supplied to routine analytical laboratories.

Transfer weights Objects of fixed mass used to calibrate balances. Available in various classes dependent on their uncertainty and issuer.

Transferability An attribute of a CMP that reflects its ability to provide consistent results on application to the same samples in different laboratories. Related to robustness and reliability.

True value The value corresponding to absolute trueness: the analyte concentration in a sample with zero uncertainty. Corresponds to ideal quality.

Ultra-microanalysis A type of chemical analysis where the initial size of the sample aliquot subjected to the CMP is less than 1 mg.

Uncertainty range A concept used in Qualitative Analysis instead of specific uncertainty (Quantitative Analysis) even though it has a different meaning. A feature of binary responses defined as the concentration range around the threshold value where errors (false positives and negatives) are made.

Validated method A method whose properties have been thoroughly studied and specified

Validation
- The experimental, documented demonstration that an overall process (CMP) or a particular step (e.g., sampling, data processing) has developed and will continue to develop as expected.
- The experimental, documented demonstration that an object (e.g., an apparatus, an instrument) possesses and will continue to possess specific properties.

Value held as true A datum (accompanied by its uncertainty) derived by chemometric treatment of the results obtained by having many different laboratories process aliquots of the same sample (a CRM) to determine the same analyte. Corresponds to referential quality.

Volatilization A separation technique occasionally used for gravimetric purposes that relies on the mass difference of the sample prior to and after controlled heating in the presence or absence of a reagent.

Volumetric factor A dimensionless number by which the approximate concentration of a titrant solution prepared from a secondary standard is to be multiplied in order to calculate the actual concentration. Obtained by experimentation and computation.

White sample A sample with well-defined properties which, with few exceptions, remain virtually constant on the whole.

Annex 2: Answers to the Questions

Chapter 1. Principles of Analytical Chemistry

1.1. Tick the type of determination corresponding to each of the following examples:

Answer:

Examples	Determination of		
	Traces	Micro components	Macro components
Determination of pesticides in urine	X		
Determination of calcium in a milk sample		X	
Determination of proteins in beef			X

1.2. Tick the correct statements among the following:

Answer:

[ ] The word "analysis" refers to the analyte
[X] Analysis of traces. ***Accepted, but incorrect***
[ ] Microanalysis of copper
[X] Qualitative analysis comes before quantitative analysis

1.3. What type of information regarding quality can be assigned to the result for a certified reference material?

Answer:

Information held as true or referential information, which possesses the highest level of quality that can be reached with special experimentation: certification of the analyte content of a sample (a certified reference material, CRM) through an interlaboratory exercise.

M. Valcárcel Cases et al., *Foundations of Analytical Chemistry*,
DOI 10.1007/978-3-319-62872-1

1.4. Explain the two types of quality trade-offs to be made in response to contradictions between aims or objectives in Analytical Chemistry.

Answer:

One should distinguish between aims and objectives here.

Aims: A decision must be made if a high metrological quality, in the form of high accuracy and low specific uncertainty, is to prevail over fulfilment of the information requirements or vice versa.

Objectives: The decision here is whether to maximize the amount of information and its quality or minimize the use of sample and reagents, time, effort and risks.

The laboratory and the client should share some quality trade-offs.

1.5. What are the most salient differences between Analytical Chemistry and other disciplines of Chemistry?

Answer:

Analytical Chemistry is responsible for producing reliable (bio)chemical information about natural and artificial objects and systems. It lies at the third apex of the basic triangle of Chemistry, which includes Synthesis and Theory.

1.6. When does analytical knowledge not suffice to solve problems? With what should it be replaced in those cases?

Answer:

A need exists to push boundaries towards interdisciplinarity and to create new paradigms in order to address the new problems to be faced by today's world (e.g., exploring the Nanoworld).

1.7. Why are the two classical standards of Analytical Chemistry insufficient? What is the third?

Answer:

Because one of the goals of Analytical Chemistry is to fulfil (bio)chemical information requirements. This obviously entails knowing the type and characteristics of the information to be delivered. Hence, the information required is the third basic standard of Analytical Chemistry in addition to the classical (tangible and written) standards.

1.8. Explain with appropriate examples the importance of interdisciplinarity to Analytical Chemistry.

Answer:

The future of Chemistry lies in an interdisciplinary approach linking it to Biology, Medicine, Physics, Engineering and other scientific and technical areas at the boundaries of which major innovations can be expected to arise.

Analytical Chemistry cannot evade this trend. In order to reach its goals and objectives, it must connect to other areas of knowledge.

Thus, analysing the Nanoworld requires cooperating with physicists capable of designing the analytical instruments needed for this purpose (e.g., transmission electron microscopes).

Also, there is a growing trend to using immunoreagents to detect or determine traces of analytes on the grounds of their high sensitivity and selectivity. These reagents are synthesized in close cooperation with biochemists.

1.9. Explain and exemplify the most salient written standards for Analytical Chemistry.

Answer:

Analytical Chemistry uses two major types of written standards, namely:

- ***Official, standard methods issued by government agencies or by prestigious national or international bodies (e.g., AOAC, EU, OECD)***.
- ***Norms and guides issued by international organizations (e.g., ISO) that are adapted by a competent national body for application in each country. These standards provide the framework for managing analytical quality (e.g., ISO 17025:2010) or implementing Social Responsibility in Analytical Chemistry (ISO 26000:2010)***.

1.10. What are the areas influenced by (bio)chemical information? Give an example for each area in Slide 1.26.

Answer:

HEALTH. Enzymatic determination of creatinine in blood serum to monitor patients with chronic renal disease.

NUTRITION. Analysis by a customs laboratory of a batch of bottled Russian liquor in order to quantify its content in methanol, which is a toxic substance.

HYGIENE. Determination of the concentration of hydrochloric acid in harsh cleaning products.

TRANSPORTATION. Analysis of aviation fuel for banned polluting additives.

DRESSING. Determination of a marker such as lithium deliberately added during the production of branded sportswear in order to fight the growing fraud of counterfeiting.

SPORTS. Analysis of athletes' urine to determine substances banned by the International Olympic Committee.

CULTURE. Dating of works of art by C-14 radiometry.

NEW TECHNOLOGIES. Determination of the exact purity of ultrapure silica used in wafers for TIC equipment.

HOUSEHOLD. Analysis of sofa and carpet stain removers to ensure that they contain no banned toxic solvents. Unbranded removers are not guaranteed to be completely safe.

BUILDING. Determination of the titanium dioxide content of dirt-repelling nanomodified concrete for use outdoors.

SUSTAINABLE DEVELOPMENT. Determination of the components of acid rain (sulphur and nitrogen oxides) in air from thermal power stations. The analytes react with water vapour in the atmosphere to form nitric and sulphuric acid, which destroy plants, erode monuments and damage animals' lungs.

1.11. Relate two hierarchies of analytical terms.

Answer:

In the analyser–instrument–apparatus–device hierarchy, the analyser is associated to the process and the instrument to the technique.

In the data–information–knowledge hierarchy, instrument signals are data, results constitute information and reports convey knowledge.

1.12. Rank the following concepts according to representativeness:

Answer:

The particular information requirements lead to the choice of an analytical process that is applied to a well-defined object in a specific sample.

Place	Concept: representativeness of
4	The sample
1	The information requirements
2	The analytical problem
3	The object

1.13. Illustrate the distinction between object availability and sample availability with several examples.

Answer:

A readily available object is a macro- or microscopically sized entity (e.g., a river) from which samples are withdrawn for analysis. Objects such as the Nanoworld and the earth's outer space are much more difficult to analyse.

A readily available sample is one that can be easily withdrawn from a macro- or micro-sized object. Thus, baby's blood is less easily available than horse urine. Also, it is more difficult to date a piece of artwork from Roman times than a painting from the XV century.

1.14. State the parts (items) of the paper by Whitesides mentioned in Slide 1.42 and recommended as reading. What aspect of Chemistry did you find the most surprising?

Answer:

The paper emphasizes the importance of (bio)chemical information. Also, it underlines the significance of Analytical Chemistry in the chemical realm and deems it a bottleneck for major scientific and technical developments.

1.15. Give two real-life examples other than those depicted in Slide 1.29 and identify the information requirement, object, sample and analyte in each.

Answer:

Example 1:

- ***Information required: The pesticide concentration, in ppb, of a tomato batch from Almeria, Spain. If the concentration is lower than the maximum tolerated level in the applicable EU Directive, the batch will be fit for export***.
- ***Object: A tomato batch ready for export***.
- ***Samples: Aliquots (tomatoes) withdrawn from boxes according to a specific sampling plan***.
- ***Analytes: The pesticides concerned***.

Example 2:

- ***Information required: The point in time a bioreactor should be stopped because more than 95% of the target product (glucose) will have by then been produced***.
- ***Object: The bioreactor and its contents***.
- ***Samples: Aliquots of the reactor contents taken at preset intervals***.
- ***Analyte: Glucose***.

1.16. Justify the designation "Trace Analysis".

Answer:

Technically, the definition is not strictly correct because the analytes (traces) are not "analysed" but rather "determined".

However, the designation "Trace Analysis" remains widely used, so, for historical reasons, it can be retained. The term designates special analytical processes for preventing contamination that are conducted in clean rooms by operators wearing appropriate apparel (caps, gloves, masks) and using ultra-pure reagents. Organic and inorganic traces are analysed with rather different methods.

1.17. Give several examples of real-life situations where the sample and analyte differ in nature.

Answer:

- ***Analysis of soils to determine pesticides.***
- ***Determination of calcium in milk.***
- ***Analysis of oil crude to determine vanadium.***
- ***Determination of traces of organic compounds in atmospheric air.***
- ***Analysis of blood to determine iron.***

1.18. Is the designation "Analytical Separation Techniques" correct?

Answer:

Strictly, this designation is incorrect because a technique uses a measuring instrument. Thus, liquid–solid extraction and filtration are not "techniques" because they use no measuring instrument.

Two correct designations for analytical separations as a whole are "Analytical Separation Systems" and "Analytical Separation Processes".

"Analytical Separation Techniques" is correct when a detector is coupled to a gas chromatograph, liquid chromatograph or capillary electrophoresis system, for example.

1.19. What are the differences between the following?

1. (Bio)chemical information and analytical information.
2. Chemical information and biochemical information.

Answer:

1. ***The two terms are completely equivalent. There is no difference.***
2. ***Differences can arise from the nature of the sample (e.g., a lunar rock and plant tissue) or the analyte (e.g., iron and an enzyme).***

1.20. How many pathways can applied research in Analytical Chemistry follow? Why?

Answer:
Basically, two.

- ***The more simple pathway involves using the body of processes, techniques and strategies supplied by basic research as adapted to the sample–analyte pair concerned***.
- ***The more complex pathway must be followed when an unusual analytical problem that cannot be solved with the means of basic research is addressed and directed, more specific research is required instead***.

1.21. When do analytical chemical R&D centres have to contact the clients requiring (bio)chemical information or vice versa? Give some examples.

Answer:
In principle, clients requiring some (bio)chemical information use routine analytical laboratories to monitor raw materials, intermediates and end-products. Only rarely (e.g., when diversifying production) do new information requirements arise that can only be fulfilled by developing new analytical processes for use by routine laboratories. In these situations, a direct connection between clients and research centres may be advisable.

1.22. What is the meaning of the four general paradigms of today's and tomorrow's Analytical Chemistry?

Answer:
The paradigms define the correct way of approaching Analytical Chemistry today and in the future. In their light, Analytical Chemistry is defined as the discipline of (bio)chemical information; one that seeks interdisciplinarity with other scientific and technical areas, and that possesses R&D&I of its own where analytical knowledge and technology transfer plays a prominent role.

Chapter 2. Analytical Properties

2.1. Tick the correct statements in relation to the dynamic range of a calibration curve obtained in the photometric determination of iron in wines:

Answer:

[ ] The sensitivity remains constant
[X] The lower limit coincides with the limit of detection
[X] The sensitivity is always greater than zero
[ ] The lower limit coincides with the limit of quantification

2.2. To which analytical properties are the following concepts directly related?

Answer:

TRACEABILITY	[ ] Precision	[X] Accuracy	[ ] Sensitivity
ROBUSTNESS	[ ] Expeditiousness	[X] Precision	[ ] Sensitivity
PRODUCTIVITY	[X] Expeditiousness	[X] Cost-effectiveness	[ ] Representativeness

2.3. Distinguish dynamic range from linear range in a calibration curve.

Answer:

Sensitivity as defined according to IUPAC's criteria is greater than zero throughout the dynamic range; however, it differs among zones in the range. In the linear portion of the dynamic range, the sensitivity is also greater than zero, but it is a constant value, so the analytical signal (X) is linearly related to the concentration and the calibration curve is linear as a result.

2.4. State whether the following statements are true (T) or false (F).

Answer:

[T] Precision decreases with increasing standard deviation
[F] Accuracy decreases with decreasing relative error
[T] Sensitivity increases with decreasing limit of detection and quantification
[F] Selectivity increases with increasing interference

2.5. Define the analytical property robustness.

Answer:

Robustness is the resistance of a method to its results changing by effect of slight changes in the experimental conditions.

2.6. Define "bias" in relation to errors in Analytical Chemistry.

Answer:

In the context of accuracy, bias is the deviation of the mean result of a method from the value held as true $(\widehat{X}')$***. The deviation is a positive or negative error depending on whether the mean is greater or smaller, respectively, than*** $\widehat{X}'$.

2.7. Tick the correct statements in the dynamic concentration range of the calibration curve for the photometric determination of calcium in milk:

Answer:

[ ] The sensitivity remains constant
[X] The sensitivity is always non-zero
[X] The sensitivity is not always the same
[X] The sensitivity decreases at the end of the range

2.8. Which datum is needed to assess the accuracy of an analytical result?

Answer:

[ ] The mean of n results
[X] The value held as true
[ ] The standard deviation

2.9. State whether the following statements are true (T) or false (F).

Answer:

[T] Selectivity increases with decreasing interference
[F] Sensitivity increases with decreasing slope of the calibration curve
[T] Accuracy increases with increasing precision
[F] Precision increases with increasing standard deviation

2.10. Distinguish generic and specific uncertainty.

Answer:

Generic uncertainty is the overall dubiousness in the composition of a sample or object and arises from a complete lack of knowledge about it. On the other hand, specific uncertainty restricts the dubiousness to a specific range where the result obtained by repeating the analytical process will fall with a given probability.

2.11. What are the differences between "repeatability" and "reproducibility"?

Answer:

These are two ways of calculating precision experimentally. Repeatability is assessed by using the same experimental conditions (time, instrument, operator, laboratory, etc.) each time the analytical process is performed. On the other hand, reproducibility is assessed by changing some experimental condition between replications of the process. Obviously, reproducibility is a more rigorous statistical concept than is repeatability.

2.12. What kind of reference is used to calculate (a) the accuracy of the result for a sample and (b) the precision of a method?

Answer:

(a) ***The value held as true*** $(\widehat{X}')$.
(b) ***The mean of a set of results*** $(\overline{X})$.

2.13. State whether the following statements about accuracy and precision are true (T) or false (F).

Answer:

[F] Both analytical properties can be ascribed to results
[F] The two are unrelated
[F] Good precision can only be obtained with good accuracy
[T] Good accuracy can only be obtained with good precision

2.14. Name the four types of relationships between analytical properties.

Answer:

1. ***Hierarchical***.
2. ***Foundation***.
3. ***Contradictory***.
4. ***Complementary***.

2.15. What are the similarities and differences between systematic errors and gross errors?

Answer:

– ***Similarities***:

1. ***Both are associated to accuracy***.
2. ***Both can be positive or negative***.
3. ***Both arise from well-defined changes during the analytical process***.

– ***Differences***:
In magnitude: systematic errors are typically much smaller than gross errors.

2.16. Two methods A and B are used to determine the same analyte in aliquots of a sample with a certified value of 1.23 ± 0.05 mg/L. The experimental result is 1.27 ± 0.03 mg/L with method A and 1.29 ± 0.01 mg/L with method B. Which method is the more accurate? Which is the more precise? Why?

Answer:
Method A is the more accurate because its result is closer to the value held as true, $\widehat{X}'$. Thus, $e_A = 0.04 < 0.06 = e_B$. On the other hand, method B is the more precise because its uncertainty range is narrower: 0.01 < 0.03.

2.17. Why stating the accuracy of a result is meaningless if its precision is unknown?

Answer:
If the precision is inadequate (too low), the probability of obtaining the same result when the analytical process is repeated will also be very low.

2.18. Can productivity-related properties be more important than capital and basic properties?

Answer:
Yes. In fact, the importance of analytical properties depends on the particular analytical problem. If the problem requires prioritizing cost-effectiveness, expeditiousness and safety, it will be at the expense of accuracy and the basic analytical properties (e.g., precision, sensitivity and selectivity).

2.19. What is a "blank"? What is the "blank signal"?

Answer:
A "blank" is a sample not containing the target analyte. The "blank signal is the signal produced by a blank subjected to the analytical process.

2.20. Which are the references needed to define the following analytical properties in mathematical and conceptual terms? Tick the correct choices.

Answer:

	Set of blanks	Value held as true	Mean of *n* results	Interferences from other systems
Accuracy		X		
Precision			X	
Limit of detection	X			
Selectivity				X

2.21. State whether the following statements as regards accuracy and precision are true (T) or false (F).

Answer:

[F] Both analytical properties can be assigned to results
[T] The two are mutually related
[T] Good precision cannot be obtained without good accuracy
[T] Good accuracy cannot be obtained without good precision

2.22. Why does accuracy rest on precision?

Answer:
There can be no accuracy without good precision. Otherwise, the probability of obtaining identical or similar results when the analytical process is repeated will be low.

2.23. Tick the correct boxes in this comparison of precision and robustness.

Answer:

	Same sample aliquot	Same method	Supports accuracy	Basic analytical property
Robustness	X		X	X
Precision	X	X	X	X

2.24. How are the facets of sensitivity related?

Answer:

The lower are the limits of detection (C_{LOD}) and quantification (C_{LOQ}), the higher is the sensitivity (S, IUPAC) and the greater is the ability of a method to discriminate between similar analyte concentrations.

2.25. Two methods A and B for determining aflatoxins in milk are compared in terms of sensitivity by analysing two different certified reference materials with certified values of 0.25 ± 0.01 and 0.28 ± 0.01 ppb. Based on method A, both CRMs contain aflatoxins. Based on method B, both CRMs contain aflatoxins and the second CRM contains a slightly greater amount than the first. Which is the more sensitive method? Why?

Answer:

Method B is the more sensitive because it can discriminate between samples with similar concentrations of the analyte.

2.26. What is the lower limit of the linear range of the calibration curve?

Answer:

The limit of quantification (C_{LOQ}).

2.27. What is the "maximum tolerated ratio"? To which analytical property does it relate?

Answer:

The maximum tolerated ratio (MTR) is the highest interferent-to-analyte concentration ratio not altering a result. MTR is associated to the basic analytical property selectivity.

2.28. Give an example of analysis (state the sample and analyte) where accuracy is to be favoured over productivity-related properties?

Answer:

The determination of the purity of a gold batch directly imported from a mining company. Gold is the analyte and the mined batch is the sample.

2.29. Is it correct to assign accuracy to an analytical process? Why?

Answer:

It is not because accuracy is a capital analytical property that characterizes results.

2.30. The sensitivity of a method is 1.02×10^{-3} AU mL ng^{-1}. What are the units for the following parameters?

Answers:

Blank signal: ***AU***
Standard deviation of the blank: ***AU***
Limit of detection: ***ng/mL***
Limit of quantification: ***ng/mL***
Analyte concentration: ***ng/mL***

2.31. Complete the following table comparing the analytical properties "accuracy" and "precision".

Answer:

	Accuracy	Precision
Type of analytical property	***Capital***	***Basic***
A typical property of	***Results***	***The analytical process***
Parameters used to measure it	***Errors***	***Standard deviation***
An indispensable numerical reference for calculating the parameters	***The value held as true*** $(\widehat{X}')$	***The mean of a set of results*** $(\overline{X})$
Mutually dependent	***Depends on precision***	***Does not depend on accuracy***

2.32. (1) Discuss the ideal situation and (2) describe the real situation in independently subjecting n aliquots of sample to an analytical process in order to obtain n results.

Answer:

(1) ***The individual results*** (x_i) ***are identical with one another, with the mean and with the value held as true*** $\left(x_i = \overline{X} = \widehat{X}'\right)$.

(2) ***The individual results*** (x_i) ***are different from one another, from the mean and from the value held as true*** $\left(x_i \neq \overline{X} \neq \widehat{X}'\right)$.

2.33. Classify errors in Analytical Chemistry according to (1) form of expression; (2) direction; and (3) sources, references and magnitude.

Answer:

1. ***Absolute and relative***
2. ***Positive and negative***
3. ***Random, systematic and gross***.

2.34. A method provides accurate results. May it not be precise?

Answer:

No. Properly defining the accuracy of a method requires knowing its precision. If the precision is poor, the results can only be accurate by chance.

2.35. Define a parameter representing the analytical property "selectivity".

Answer:

Selectivity can be assessed in terms of the highest tolerated interferent-to-analyte ratio not leading to error:

$$S = (TR)_{max} = \frac{C_{int}}{C_{an}}$$

2.36. Solve the different parts of the following problems.

Problem A

An analytical method for determining copper traces in feed is characterized as follows:

(1) Using the method to analyse standards of increasing concentrations of analytes provides the following results:

$[Cu^{2+}]$, ppb	0.0	1.0	2.0	3.0	4.0	5.0
Signal, AU	0.030	0.050	0.102	0.149	0.201	0.250

(2) Independently subjecting 5 aliquots of a reference standard with a certified concentration of 3.30 ± 0.10 ppb gives the following results, in ppb: 3.40, 3.39, 3.50, 3.27 and 3.35.

Questions:

(a) What is the blank signal? What are its units?

Answer:

The blank signal must be expressed in the same units as the instrument signal. Since the instrument was used to measure absorbance, the blank signal should be expressed in absorbance units (AU).

Based on the definition of "blank", the blank signal will be that corresponding to a copper concentration [Cu^{2+}] = 0 ppb. This datum is contained in the table. Therefore, the blank signal will be

$$Signal\left(\left[Cu^{2+}\right] = \mathbf{0\,ppb}\right) = \mathbf{0.030\ AU}$$

(b) What is the signal corresponding to the certified copper concentration in the standard?

Answer:

Calculating the signal corresponding to the analyte concentration of the CRM entails constructing a calibration curve and using it to calculate the following parameters:

1. ***The sensitivity of the method, which will coincide with the slope of the curve. A few data pairs from the table are applied the IUPAC criterion to calculate the corresponding S values. The mean of the more similar values is taken to be the slope of the calibration curve***:

$$S = \frac{\Delta X}{\Delta C}$$

$$S_1 = \frac{(\mathbf{0.050} - \mathbf{0.030})\ \mathbf{AU}}{(\mathbf{1.0} - \mathbf{0.0})\ \mathbf{ppb}} = \mathbf{0.020\ AU/ppb}$$

$$S_2 = \frac{(\mathbf{0.149} - \mathbf{0.102})\ \mathbf{AU}}{(\mathbf{3.0} - \mathbf{2.0})\ \mathbf{ppb}} = \mathbf{0.047\ AU/ppb}$$

$$S_3 = \frac{(\mathbf{0.201} - \mathbf{0.250})\ \mathbf{AU}}{(\mathbf{5.0} - \mathbf{4.0})\ \mathbf{ppb}} = \mathbf{0.049\ AU/ppb}$$

Using S_2 and S_3, which are the more similar values, allow one to calculate the sensitivity of the method as their mean:

$$S = \frac{(\mathbf{0.047} + \mathbf{0.049})\ \mathbf{AU/ppb}}{\mathbf{2}} = \mathbf{0.048\ AU/ppb}$$

2. ***The equation of the calibration curve, which is established from the blank signal and the previously calculated sensitivity, is***

$$\mathbf{Signal}(\mathbf{AU}) = \mathbf{0.030} + \mathbf{0.049} \cdot \left[\mathbf{Cu}^{\mathbf{2}+}\right]$$

The signal corresponding to the CRM can now be calculated by substituting the certified copper concentration into the previous equation:

$$\mathbf{Signal}(\mathbf{CRM}) = (\mathbf{0.030} + \mathbf{0.049} \cdot \mathbf{3.30})\ \mathbf{AU} = \mathbf{0.193\ AU}$$

(c) Can the precision of the method be calculated? Why? If it can, what is it?

Answer:

In fact, the precision of the method can be calculated from the set of results obtained by applying the analytical process to aliquots of a CRM sample. Since no confidence level was provided, the precision is assessed in terms of the standard deviation of the results:

$$s_c = \pm\sqrt{\frac{\sum\left(c_i - \overline{C}\right)^2}{n-1}}$$

The precision of the method is thus $s_c = \pm\ \mathbf{0.09\ ppb}$.

(d) Can the accuracy of the result be calculated? Why? If it can, what is it?

Answer:

The accuracy of the result can also be calculated because a certified value that can be taken to be the value held as true is known. Thus, the accuracy can be defined in terms of the error of the method, which can be calculated as the difference between the mean of the results and the certified value:

$$e = \overline{X} - \widehat{X}' = (\mathbf{3.38} - \mathbf{3.30})\ \mathbf{ppb} = +\mathbf{0.08\ ppb}$$

$$e(\%) = \frac{\overline{X} - \widehat{X}'}{\widehat{X}'} \cdot \mathbf{100} = \frac{(\mathbf{3.38} - \mathbf{3.30})\ \mathbf{ppb}}{\mathbf{3.30\ ppb}} \cdot \mathbf{100} = +\mathbf{2.43\%}$$

The error of the method is thus positive and equal to 2.43%.

(e) If the client's imposed limit is 0.1 ppb copper, is the method suitable for qualifying (detecting) and quantifying the analyte if the deviation of the blank signal is 2.3×10^{-3} AU?

Answer:

The sensitivity and deviation of the blanks can now be used to calculate the limits of detection and quantification:

$$C_{LOD} = \frac{3 \cdot s_B}{S} = \frac{3 \cdot 2.3 \times 10^{-3}\ \text{AU}}{0.049 \cdot \text{AU/ppb}} = 0.14\ \text{ppb}$$

$$C_{LOQ} = \frac{10 \cdot s_B}{S} = \frac{10 \cdot 2.3 \times 10^{-3}\ \text{AU}}{0.049\ \text{AU/ppb}} = 0.46\ \text{ppb}$$

Graphically comparing C_{LOD} and C_{LOQ} with the stated legal limit, C_{LL}, reveals that both exceed the stated legal limit. Therefore, the method is not valid for detecting or quantifying the analyte.

– *Problem B*

An analytical process for determining pesticides (P) in water is applied through the following tests:

(1) Subjecting a total of 10 blanks to the process gives the following results in absorbance units (AU):

0.031	0.033	0.041	0.029	0.035	0.037	0.040	0.032	0.030	0.037

(2) A calibration curve is constructed from a set of standards of increasing hydrocarbon concentrations. The equation for the curve is

$$Signal(AU) = 0.035 + 1.07[P]$$

where $[P]$ is the pesticide concentration in ng/mL.

Questions:

(a) Can the precision of the method be calculated? Why? Explain your answer.

Answer:

The precision of this method cannot be calculated because no set of results allowing calculation of its precision is available. Although the results of the analysis of blanks cannot be used to assess precision, their standard deviation allows the actual precision to be estimated.

(b) Express the sensitivity of the method through three different parameters.

Answer:

The sensitivity of a method can be expressed in the form of IUPAC's parameter (S), and also as the limit of detection (C_{LOD}) and the limit of quantification (C_{LOQ}). The sensitivity is directly proportional to the former parameter and inversely proportional to the latter two.

The IUPAC sensitivity (S) can be directly extracted from the statement of the problem as it coincides with the slope of the calibration curve:

$$S = 1.07\ \text{AU mL/ng}$$

The limits of detection and quantification can be calculated from the standard deviation of the blank signals:

$$s_B = \pm\sqrt{\frac{\sum\left(X_{i,B} - \overline{X}_{i,B}\right)^2}{n-1}} = \pm 0.004\ \text{AU}$$

$$C_{LOD} = \frac{3 \cdot s_B}{S} = \frac{3 \cdot 0.004\ \text{AU}}{1.07\ \text{AU mL/ng}} = 0.011\ \text{ng/mL}$$

$$C_{LOQ} = \frac{10 \cdot s_B}{S} = \frac{10 \cdot 0.004\ \text{AU}}{1.07\ \text{AU mL/ng}} = 0.037\ \text{ng/mL}$$

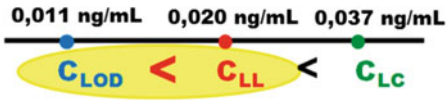
In summary, the sensitivity of the method can be expressed in the following three forms:

$$\begin{aligned} S &= 1.07\ \text{AU mL/ng} \\ C_{LOD} &= 0.011\ \text{ng/mL} \\ C_{LC} &= 0.037\ \text{ng/mL} \end{aligned}$$

(c) If the legal limit for pesticides in water is 2 ng/mL, is the method useful for their detection and quantification?

Answer:

Graphically comparing the previously calculated limits of detection and quantification with the legal limit,



allows one to conclude that the method is valid for detecting the analyte but not for quantifying it because the limit of quantification exceeds the legally tolerated limit.

– *Problem C*

The precision of an analytical process for determining copper traces in seawater is assessed in three tests involving different experimental conditions, namely:

(1) Processing a single aliquot of sample and introducing six portions of the treated aliquot into the measuring instrument.
(2) Independently processing six aliquots of the same sample and introducing them into the measuring instrument on the same day.
(3) As in (2), but having six different analysts perform the analytical process on different days.
(4) The results obtained are as follows:

Test	Results (mg/L)					
1	1.32	1.31	1.32	1.33	1.30	1.31
2	1.28	1.36	1.30	1.27	1.31	1.33
3	1.35	1.45	1.21	1.37	1.30	1.28

Calculate the specific uncertainty at the 95% confidence level for each test and plot it. Use the uncertainty values to discuss the precision achieved in each case, and identify the facet that can be characterized with each test.

Answer:

The specific uncertainty at the 95% confidence level is

$$U_R = k \cdot s_R, \quad \textit{where} \quad k(95\%) = 2$$

Since the standard deviation is given by

$$s_R = \pm\sqrt{\frac{\sum\left(X_R - \overline{X}_R\right)^2}{n-1}}$$

the respective specific uncertainties are as follows:

$$U_A = k \cdot s_A = \pm 2 \cdot 0.02\,\mathrm{mg/L} = \pm 0.04\,\mathrm{mg/L}$$
$$U_B = k \cdot s_B = \pm 2 \cdot 0.04\,\mathrm{mg/L} = \pm 0.08\,\mathrm{mg/L}$$
$$U_C = k \cdot s_C = \pm 2 \cdot 0.09\,\mathrm{mg/L} = \pm 0.18\,\mathrm{mg/L}$$

If the results are expressed in the form

$$R \pm U_R \quad \textit{where} \quad R = \overline{X}_R,$$

then:

$$\textit{Method A} : 1.32 \pm 0.04\,\mathrm{mg/L}$$
$$\textit{Method B} : 1.31 \pm 0.08\,\mathrm{mg/L}$$
$$\textit{Method C} : 1.33 \pm 0.18\,\mathrm{mg/L}$$

Method A is therefore seemingly the most precise. However, it was used incorrectly because it was applied to the whole sample rather than to aliquots. Therefore, the calculated precision is spurious and should be discarded.

Method B is the most precise after A. The analytical process was performed correctly, so the calculated precision can be deemed valid. However, the precision corresponds to repeatability and is thus scarcely rigorous.

Method C is the least precise. The analytical process was performed correctly, so its calculated precision can be deemed valid. Also, it corresponds to reproducibility and is therefore more rigorous than that of Method B.

In summary, Method B, which was performed under repeatable conditions, is the most precise. Method C is less precise than B but more rigorous because it was performed under reproducible conditions. Finally, Method A was performed under neither repeatable nor reproducible conditions, so its results can hardly be valid.

Chapter 3. Reference Materials

3.1. What are the main purposes of a sample matrix standard with a certified analyte content (a CRM)? Tick the correct answers.

Answer:

[ ] Calibrating an instrument
[X] Globally assessing an analytical process
[ ] Calibrating a method
[ ] Standardizing secondary analytical chemical standards

A CRM can also be used to calibrate a special instrument such as an X-ray spectrometer.

3.2. What is a matrix standard? What is its main use?

Answer:

A matrix standard is a high-quality material mimicking the composition of a sample and having the value of an associated quantity certified by a competent body. Matrix standards are certified reference materials (CRMs) that are typically used to globally assess analytical methods but can also be useful to calibrate special instruments.

3.3. What are the essential requirements for establishing the traceability of an instrument?

Answer:

The two basic requirements for establishing traceability in an instrument coincide with the notions inherent in traceability, namely:

- ***Linking the instrument to its calibration standards, which in turn must be connected to standards of a higher quality (e.g., certified reference materials)***.
- ***Tracing the "history" of the instrument by recording the time it was installed, its usage and users, its routine calibrations, any servicing or repairs, etc. This facet is closely related to analytical quality***.
- ***The two are related by the history of the instrument's calibration***.

3.4. Tick the type correct type of standard in each case.

Answer:

	Standard			
	Basic	Chemical	Analytical chemical	
			Primary	Secondary
Carbon-12		X		
A 0.1 mol L^{-1} solution of $KMnO_4$				X
Potassium hydrogen phthalate			X	
Ultrapure silver	X	X		
The faraday		X		

3.5. Describe the traceability network among standards relevant to Analytical Chemistry with emphasis on the connections between basic, chemical and analytical chemical standards.

Answer:

This traceability network comprises linear and branching links among base (SI) standards, chemical standards and the analytical chemical standards used in practice.

There is a linear traceability chain connecting the mole (a base standard), the mass of carbon-12, atomic weights (chemical standards), and primary and secondary analytical chemical standards.

The linear link backbone branches as follows:

(1) ***The mole is defined in terms of the kilogram, a base (SI) standard***.
(2) ***The faraday (an operational chemical standard) is related to the mass of carbon-12 through Avogradro's number (N), and also to the ampere and the second (two base standards)***.

3.6. How would you define "traceability of an analytical method (CMP)"?

Answer:

An analytical method or (bio)chemical measurement process (CMP) is traceable if it can be linked to a reliable reference. Such is the case, for example, with

- ***a certified reference material (CRM) if the results of subjecting it to the CMP coincide with the certified value; and***
- ***the result of an intercomparison exercise—one managed by a prestigious national or international organization—if the result of the laboratory concerned does not differ substantially from the mean for the body of participating laboratories and its uncertainty***.

Proven traceability in the results of a method can be included in a laboratory's reports in order to persuade clients of the quality of the method.

3.7. The total free acid content of a wine sample is determined by acid–based titration with a sodium hydroxide solution previously standardized with potassium hydrogen phthalate. What standards are used in the process?

Answer:

Chemical: ***Atomic weights used in calculations***
Primary analytical chemical: ***Potassium hydrogen phthalate***
Secondary analytical chemical: ***Sodium hydroxide***

3.8. Define "equipment calibration" and relate it to or distinguish it from "method calibration".

Answer:

Equipment calibration is intended to assure proper performance of an instrument or apparatus used in the second step of the analytical process. Equipment is calibrated by using reference materials not containing the analyte to record their signals. If the signals depart from the expected values, the instrument is adjusted as required (e.g., by replacing the lamp in a spectrophotometer).

Method calibration differs from equipment calibration in the following respects:

(a) ***The target is an analytical method rather than an instrument or apparatus***.
(b) ***A signal is related to the presence or concentration of the analyte through a calibration curve***.
(c) ***A standard containing the analyte is used***.
(d) ***It is performed after equipment calibration***.

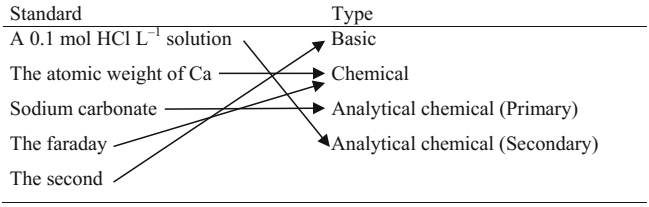
3.9. What are the purposes of equipment calibration (verification)? Tick the correct answer(s).

Answer:

[ ] Constructing a calibration curve
[X] Adjusting faulty equipment
[ ] Globally assessing an analytical method
[ ] Distinguishing error types in Analytical Chemistry

3.10. Connect each of the following standards to its type in the column on the right.

Answer:



3.11. Rank the reliability of the following types of standards with a score from 1 (least reliable) to 4 (most reliable).

Answer:

Standard	Reliability
Secondary analytical chemical standard	***4***
Chemical standard	***1***
CRM	***2***
Primary analytical chemical standard	***3***

3.12. What role do analytical chemical standards play in the traceability of a result?

Answer:

Traceability of results cannot be assured without analytical chemical standards, which play two crucial roles, namely:

(a) ***Certified reference materials (CRMs) are the ultimate references***.
(b) ***Primary standards are intermediate links in the traceability chain connecting a result to a CRM***.

3.13. What type of standard (basic, chemical or analytical chemical) has the greatest associated uncertainty? Why?

Answer:

Uncertainty is greatest in analytical chemical standards because they constitute the last link in the traceability (comparison) chain among the standards that are relevant to Analytical Chemistry.

3.14. A sample of powdered milk with a protein content certified in a document issued by a renowned independent organization is

Answer:

[ ] A primary standard
[X] A certified reference material
[ ] A secondary standard
[ ] A reference material

3.15. Name the types of chemical standards, state their differences and give some examples.

Answer: There are two main types of chemical standards:

- ***Non-operational (tabulated) standards such as the mass of Carbon-12, atomic weights, among others***.
- ***Operational standards (e.g., the Faraday), which are established through experimentation***.

3.16. Give an example of each complementary criterion used to classify analytical chemical standards.

Answer:

The standards used in chemical processes can be classified in a non-excluding manner according to nature (physical, chemical), stability and/or purity (primary, secondary), and the certifying authority (reference materials and certified reference materials).

3.17. Comment on the tracing facet of traceability of a result. What should it be consistent with?

Answer:

The tracing facet of an analytical result, which is complementary to the relation to references, requires that a laboratory result be invariably accompanied by information allowing questions such as the following to be answered: Who performed the analysis? When was it performed? How? What tools were used? Under which environmental circumstances was it conducted? etc.

This facet is fully consistent with the quality systems to be implemented in analytical laboratories. One essential aspect of quality systems is the production of documents facilitating characterization of past results—in order, for example, to meet auditors' requests.

3.18. Describe a procedure for assessing (validating) a new analytical method in terms of its relationship to matrix-type certified reference materials.

Answer:

Ideally, new analytical methods should be validated with a certified reference material (CRM) whose matrix is identical with that of the sample to be analysed and comes with a certified analyte concentration and its uncertainty.

A total of* n *aliquots of the CRM are subjected to the analytical process to be validated, and the ensuing result and its specific uncertainty are compared with those of the CRM. The following conclusions can be made if they coincide statistically:

- ***the method is validated (that is, deemed valid for the intended purpose); and***
- ***the method is traceable to the CRM used.***

3.19. What is the main limitation of CRMs for establishing the traceability of methods?

Answer:

The greatest constraint of CRMs is their scarcity in commercial form (only 5–10% of the CRMs required by analytical laboratories are commercially available). This entails using alternative procedures to assure traceability in analytical methods (e.g., participating in intercomparison exercises involving a large number of laboratories).

3.20. What types of standards prevail among (a) reference materials (RMs) and (b) certified reference materials (CRMs)?

Answer:

Most RMs are physical or chemical (e.g., pure or mixed substances), whereas most CRMs are chemical and of the sample matrix type.

3.21. Which base standard is the most relevant to Chemical Metrology? Why?

Answer:

The ultimate base (SI) chemical standard is the mole, which is defined in terms of the kilogram. Several other base standards are also relevant to Metrology in Chemistry, however. The importance of the mole arises from the fact that it is related to the mass of carbon-12, to atomic weights and to primary and secondary standards, through a traceability chain.

3.22. Why are secondary standards used even though they have unsuitable properties (e.g., instability, impurity)?

Answer:

Because they possess unique chemical properties. Such is the case with sodium hydroxide, a very strong base that is highly suitable for titrating both strong and weak acids.

3.23. What are the requirements for a matrix-type CRM?

Answer:

- ***The material should be homogeneous and stable***.
- ***It should be very similar to the target sample in composition***.
- ***It should come with a certified value and its uncertainty or be assigned the two in an interlaboratory exercise (the relational facet of traceability)***.
- ***The material should come with a detailed history of its origin (natural or artificial), stability and homogeneity, and information about the certifying campaign including the results of all participating laboratories (the tracing facet of traceability)***.

3.24. What are the three most salient general uses of analytical chemical standards?

Answer:

1. ***Equipment and method calibration***.
2. ***Overall assessment (validation) of chemical measurement processes (CMPs)***.
3. ***Standardization of secondary standards with primary standards***.

3.25. What are the three principal meanings of traceability of an analytical result?

Answer:

1. ***Relationship to references (standards)—the most orthodox***.
2. ***Tracing facet: documented history of production***.
3. ***Practical facet: Comparison and harmonization of analytical laboratories***.

3.26. How is an analytical method assessed to assure reliability?

Answer:

By subjecting n aliquots of a certified reference material (CRM) to the method (analytical process) and comparing the result and its uncertainty with the certified values. If they coincide, the method can be reliably used for the intended purpose.

In the absence of an appropriate CRM, the best choice is to take part in an intercomparison exercise. If the result obtained by the laboratory concerned is consistent with the mean for the body of participating laboratories, the method can be deemed reliable.

3.27. What analytical properties are related to traceability? Explain your answer.

Answer:

Traceability is related to the capital properties (accuracy and representativeness).

Accuracy is associated to the relationship to traceability references and representativeness is associated to the traceability of the sample aliquot subjected to the analytical process.

3.28. On what should mutual recognition of the results of two or more laboratories rest?

Answer:

On the comparability of the results obtained by analysing the same CRM and/or on consistency of their results with the mean of an intercomparison exercise where the two have participated.

3.29. What feature and twofold meaning does traceability of the sample aliquot subjected to an analytical process have?

Answer:

Traceability to samples is an unorthodox concept because it includes the tracing facet but excludes the relational facet (that is, the linkage to references).

Because of the dual nature of traceability, the sample aliquot should be related to both the information required and the result of an analytical process.

Chapter 4. Generalities of the Analytical Process

4.1. What question does the development of an analytical process essentially answer regarding extraction of (bio)chemical information from an object: what, how, when or where?

Answer:

Essentially, it answers the following question: How is the information extracted?

The other questions are intended to identify the analyte (what?), and the place (where?) and time (when?) the sample is obtained.

4.2. Why do analytical processes invariably use measurement standards? How are they used?

Answer:

Analytical Chemistry is the chemical and biochemical metrological science. In other words, it is the science of (bio)chemical measurements. Measuring involves comparing and comparing requires using a reference (e.g., a standard). The analytical process is therefore meaningless unless appropriate standards are used for equipment and method calibration.

4.3. A manufacturing process leads to an error in the quality-related parameters for the product that requires analytical control. What kind of sampling should be done in this situation?

[ ] Intuitive
[ ] Statistical
[X] Directed
[ ] Protocol-based

Explain why.

Answer:

After the error is identified, only the samples leading to the error are resampled. Hence the sampling is of the directed type.

4.4. What is the difference between "dissolution" and "disaggregation" of a solid sample?

Answer:

Both operations are related to the preparation of solid samples.

Dissolution uses a solvent (e.g., an acid) to solubilize a solid solute (e.g., a calcareous rock) until none remains suspended or in the bottom of the vessel. Leaching (solid–liquid extraction) is used to selectively dissolve a given component of a solid sample.

Disaggregation is a drastic dissolution operation used when attack with a solvent proves ineffective. The sample is mixed with an acid flux such as $KHSO_4$ or an alkaline one such as Na_2CO_3 and melted at a high temperature in a platinum or nickel crucible. Then, the molten mass is allowed to cool for easy dissolution in an appropriate solvent.

4.5. Give four definitions of "sampling" or "sample collection".

Answer:

(1) ***The body of operations used to select a portion (aliquot) of the object from which (bio)chemical information is to be extracted***.
(2) ***The first substep in the preliminary operations of the analytical process***.
(3) ***The link between the object and the analytical process***.
(4) ***The foundation of the capital analytical property "representativeness", which, together with "accuracy", characterizes the quality of analytical results***.

4.6. How does the availability of materials and equipment (reagents, solvents, apparatuses, instruments, etc.) influence the choice of an analytical process for a specific sample–analyte pair? Use one or more examples.

Answer:

In the following example, the information required is the content, in ppb, of aflatoxins of whole milk from cows fed with contaminated feed.

The analytical process will be very simple, expeditious and reliable—but also very expensive—if a specific immunoassay is used; also, the sample will require little processing. In the absence of a direct test, the sample treatment will be a complex, time-consuming process using a liquid chromatograph interfaced to a mass spectrometer. This equipment is unaffordable for many laboratories. In fact, a modest peripheral laboratory at a dairy cooperative will hardly be able to obtain the information needed to confirm whether its milk is contaminated with aflatoxins.

4.7. What factors dictate the choice of an analytical method? What is usually the most important?

Answer:

The most important factor is the analytical information required (and its characteristics). Thus, the method of choice will differ depending on whether

- ***overall or discriminate, individual information about a mixture of analytes from the same family (e.g., polyphenols in food) is needed;***
- ***a high accuracy is indispensable (e.g., in the determination of the purity of an imported gold batch);***
- ***the results are to be obtained within a short time (e.g., determining the fat content of an olive batch in order to establish the price to be paid to members of an agricultural cooperative)***.

4.8. Tick the true statements about the preliminary operations of the analytical process:

Answer:

[X] They are equivalent to so-called "sample treatment"
[X] They typically account for 50–70% of the length of a CMP
[ ] They come after measurement and transducing of the analytical signal
[ ] They have little impact on the quality of the final result

4.9. Why is sampling important in chemical measurement processes? Tick the correct answers.

Answer:

[ ] Because it influences selectivity and sensitivity
[X] Because it is essential to assure representativeness in the final result
[ ] Because it is a key to robustness in CMPs
[ ] Because it has a direct impact on the accuracy of the results of CMPs

4.10. Are equipment and method calibration part of a CMP? Why?

Answer:

Both are in fact essential components of CMPs. Thus, it is crucial to ensure proper functioning of the instruments and apparatuses used (equipment calibration) and to unequivocally relate the presence and/or concentration of the analyte to an instrumental signal through, for example, a calibration curve (method calibration).

4.11. Name at least five features of the preliminary operations of CMPs. Is any of them positive?

Answer:

- ***Variable***
- ***Complex***
- ***Difficult to automate and control***
- ***Sources of error***
- ***Sources of hazards to operators and the environment***
- ***Slow***

In principle, none of these features is positive.

4.12. What are the positive contributions of the preliminary operations of CMPs?

Answer:

They allow samples to be prepared for measurement. In fact, most samples cannot be analysed directly—the ideal situation in Analytical Chemistry as it would allow the adverse effects of preliminary operations to be circumvented.

4.13. How are instruments classified according to the nature of the raw signals they provide?

Answer:

Instruments can be

- ***Optical (e.g., atomic or molecular absorption or emission spectrophotometers)***.
- ***Electrochemical (e.g., potentiometers, voltammeters)***.
- ***Thermal (e.g., thermogravimeters, differential thermal analysers)***.
- ***Mass (e.g., balances, mass spectrometers)***.
- ***Magnetic (e.g., nuclear magnetic resonance spectrometers)***.

Various other types of instruments are also used, albeit less commonly, in Analytical Chemistry.

4.14. What are the two information sources for the third step of the analytical process (data processing and result delivery)?

Answer:

(1) ***Experimental data obtained by subjecting samples, standards and blanks to an analytical process***.
(2) ***Tabulated, non-experimental data required for computations (e.g., atomic weights, statistical factors)***.

4.15. Name the five factors governing the development of an analytical measurement process.

Answer:

The choice of an existing CMP—and the development of a new one, if needed—essentially depends on the type of (bio)chemical information to be obtained from the target object or sample. The choice may also be influenced by factors associated to the sample (e.g., availability, nature, state of aggregation), the analyte (e.g., nature, concentration) and whether absolute or relative measurements are to be made.

4.16. What are the two main purposes of the preliminary operations of CMPs?

Answer:

1. ***To facilitate the analytical process (by making the sample ready for measurement)***.
2. ***To improve analytical properties (sensitivity and selectivity, mainly)***.

4.17. Why is variability a negative connotation of analytical processes?

Answer:

Because each sample–analyte combination requires a specific sample treatment. This precludes generalization, so

- ***it entails developing an analytical process and sample treatment suited to each situation; and***
- ***it precludes the development of affordable all-purpose commercial equipment except for widespread determinations such as that of Kjeldahl nitrogen***.

4.18. How is automatability related to the preliminary operations of the analytical process?

Answer:

The mechanical complexity of some preliminary operations of sample treatment (e.g., precipitation, disaggregation, extraction) precludes their automation—which would provide highly interesting advantages such as reduced human involvement and operator risks. Some techniques such as solid-phase extraction (SPE) have benefited from the development of multi-extraction equipment that is highly appreciated by routine laboratories receiving large numbers of samples each day.

4.19. What is the most sluggish, labour-intensive and error-prone step of an analytical process?

Answer:

That of preliminary operations (sample collection and treatment here). According to some authors, sampling does not belong in the analytical process.

4.20. What should be balanced in designing a sampling plan?

Answer:

The number of samples to be collected from the object, which should be as small as possible in order to maximize productivity-related analytical properties, and representativeness (a capital analytical property), which should be as high as possible.

4.21. What are the four types of sampling arising from the overall sampling plan?

Answer:

- ***Intuitive sampling (designed by an experienced analyst)***
- ***Statistical sampling (based on statistical probability rules)***
- ***Directed sampling (when a specific type of information is sought)***
- ***Protocol-based sampling (established by the client or official regulations)***

4.22. What names are samples given according to size and nearness to the object?

Answer:

Bulk sample, aggregate (composite) sample, laboratory sample and test sample (aliquot).

4.23. Distinguish "object" and "sample".

Answer:

The object is the entity about which (bio)chemical information is required (e.g., a river, a mine, an agricultural field).

The sample is an aliquot of the object that is collected according to a specific sampling plan.

4.24. When and why must organic matter in a sample be destroyed in the preliminary operations of the analytical process?

Answer:

Organic matter is destroyed by using an appropriate wet or dry procedure in order to prevent it from interfering with the determination of inorganic analytes.

4.25. What basic properties are favourably affected by separation techniques? What capital property is also favoured? What basic property can be adversely affected?

Answer:

(a) ***Sensitivity (through preconcentration) and selectivity (through interference removal)***.
(b) ***Accuracy, which rests on sensitivity and selectivity***.
(c) ***Precision (random errors increase as more preliminary operations are needed)***.

4.26. How are instruments classified according to the nature of the analytes to be determined?

Answer:

There are two types of instruments according to analyte nature, namely:

Active instruments, which interact with the analyte to have it respond in some form (e.g., by producing fluorescence).

Passive instruments (e.g., a potentiometer), which receive a response from the analyte without the need to previously excite it.

4.27. How are sampling and representativeness related?

Answer:

The capital analytical property "representativeness" rests on the atypical basic property "proper sampling".

4.28. What are the main types of analytical separation systems?

Answer:

There are two types of systems, namely:

- ***Batch systems***.
- ***Continuous systems, which can be chromatographic or non-chromatographic***.

Chapter 5. Quantitative Analytical Processes

5.1. The determination of pyrethrins in a food sample gives a concentration of 10 μg/kg. Express it in ppb and as a percentage.

Answer:

Expressing the stated concentration in ppb entails using a conversion factor. Since 1 ppb is equivalent to 1 μg/kg, then

$$10\,\frac{\mu g}{kg}\cdot\frac{1\ ppb}{1\,\frac{\mu g}{kg}}=10\ ppb$$

Expressing the concentration as a percentage requires using the definition of "ppb" (one part per billion) in order to establish a proportion (a fraction of unity that is then multiplying by 100 to obtain the percentage):

$$10\ ppb\equiv\frac{10\,parts}{10^9\,parts}\rightarrow\frac{10\,parts}{10^9\,parts}\times 100=10^{-6}\%$$

5.2. An amount of 0.231 mg of a compound of molecular weight 114 g/mol is added to a volume of 500 mL of water. Calculate the resulting concentration in (a) mol L^{-1}, (b) ppb and (c) μg/g water.

(a) mol L^{-1}

Answer:

The mass is divided into the molecular weight to obtain an amount of substance (mol) and then by the volume of water used to dissolve it because the resulting solution volume is assumed to be very similar to the volume of water used to prepare the solution:

$$0.231\times10^{-3}\ g\cdot\frac{1\ mol}{114\ g}=2.03\times10^{-6}\ mol$$

$$Concentration\left(mol\ L^{-1}\right)=\frac{2.03\times10^{-6}\ mol}{0.5\ L}=4.06\times10^{-6}\ mol\ L^{-1}$$

(b) ppb

Answer:

Since* 1 ppb *is equivalent to* 1 μg/kg *and, on the assumption that the solution will be so highly dilute that is density will virtually coincide with that of water* (1 g/mL), *then

$$\mathbf{0.231\,mg \equiv 231\,\mu g}$$
$$\mathbf{500\,mL \equiv 500\,g \equiv 0.5\,kg}$$
$$\textit{Concentration}(\mathbf{ppb}) = \frac{\mathbf{231\,\mu g}}{\mathbf{0.5\,kg}} = \mathbf{461\,ppb}$$

(c) μg/g

Answer:

The concentration in ppb obtained in (b) is multiplied by an appropriate conversion factor:

$$\mathbf{461\,ppb} = \frac{\mathbf{461\,\mu g}}{\mathbf{1\,kg}} \cdot \frac{\mathbf{1\,kg}}{\mathbf{1000\,g}} = \mathbf{0.461}\ \frac{\mu g}{g}$$

5.3. How do titrimetries differ from gravimetries? Tick the correct answers.

Answer:

[ ] Titrimetries are not classical method of analysis
[ ] They are not quantitative methods
[X] They use analytical chemical standards ***(only titrimetries do)***
[ ] They are not absolute methods
[ ] They use no atomic weights as chemical standards

5.4. Which features would you associate with titrimetries and gravimetries? Tick the correct answers.

Answer:

Feature	Titrimetries	Gravimetries
Absolute methods using no analytical chemical standards		X
Absolute methods using analytical chemical standards	X	
Relative quantification methods		
Only use atomic weights as standards		X
Use analytical chemical standards	X	
Use base standards	X	X
Have the shortest traceability chain		X

5.5. Briefly describe the foundation of a back-titration.

Answer:

A back-titration must be performed when no direct titration is possible. Essentially, it involves adding excess titrant in order to ensure that the whole amount of analyte present will react and then titrating unreacted titrant with an appropriate reagent.

5.6. Which of the following methods use no analytical chemical standards?

Answer:

[ ] Titrimetries
[ ] Relative interpolation methods
[X] Gravimetries

5.7. What are the key features of absolute analytical methods?

Answer:

Absolute analytical methods possess two main features, namely:

- ***They use base and chemical standards—and also analytical chemical standards in some cases***.
- ***They are used in both Classical and Instrumental Analysis***.

5.8. Convert the following concentrations into percentages:

Answer:

Concentration	%
1 ppm	10^{-4}
1 ppb	10^{-7}
1 µg/L	10^{-7}
1 mg/L	10^{-4}
1 ng/L	10^{-10}

5.9. What are the differences between gravimetry and titrimetry in the following respects?

Answer:

	Gravimetry	Titrimetry
Type of analytical method used	***Absolute calculable***	***Absolute calculable***
Standards used	***Base, chemical***	***Base, chemical, analytical chemical***
Analytical properties	***High accuracy, short traceability chain***	***Low accuracy, high simplicity, high expeditiousness***

5.10. Explain the differences between "absolute" and "relative" quantification methods.

Answer:

Absolute methods use a mathematical law in combination with a tabulated constant to calculate the amount of analyte present in a sample.

On the other hand, relative methods compare experimental signals for standards with that for the analyte in order to calculate the amount of analyte.

5.11. What analytical properties apply to Quantitative Analysis?

Answer:

The three types discussed in Chap. 2***, namely***:

- ***Capital properties: accuracy and representativeness***.
- ***Basic properties: precision, sensitivity, selectivity, robustness and proper sampling***.
- ***Productivity-related properties: expeditiousness, safety and cost-effectiveness***.

5.12. What are the instruments typically used in Classical Quantitative Analysis?

Answer:

Basically, the classical burette in titrimetries and the two-pan balance in gravimetries.

5.13. Name the two types of calculable methods and give an example (analytical process) of each.

Answer:

	Calculable methods	Example
1	***Absolute methods using no analytical standards***	***Gravimetry***
2	***Absolute methods using analytical standards***	***Titrimetry***

5.14. Describe several ways of expressing the results in Quantitative Analysis.

Answer:
A quantitative result can be expressed in two different forms, namely:

- ***Absolute (as a mass)***.
- ***Relative: as a proportion (e.g., %, ppm, ppb), a mass–volume ratio (e.g., g/L) or as a mass–mass ratio (e.g., g/kg)***.

5.15. What type of quantitative analytical method requires no method calibration? Why? Give an example.

Answer:
Method calibration is unnecessary in absolute methods using no analytical standards (e.g., gravimetries) because they have a very short traceability chain and their results can be directly related to base and chemical standards.

5.16. What is the gravimetric factor? Tick the correct answer.

Answer:

[X] A ratio of molecular or atomic weights.
[X] A dimensionless number that is multiplied by the gravimetric weighing to calculate the mass of analyte
[ ] A number by which the atomic weight of the analyte is multiplied to express the result
[X] A factor calculated from the molecular weight of the weighed form

5.17. What are the five requirements to be fulfilled by a chemical reaction to be useful for titrimetric purposes?

Answer:

(1) ***A well-defined stoichiometry***.
(2) ***Developing to completion (that is, having a large product formation constant)***.
(3) ***Being fast***.
(4) ***Being selective***.
(5) ***Having an appropriate end-point indicator***.

5.18. Name the three types of visual indication systems in titrimetry.

Answer:

(1) ***Auto-indicators***.
(2) ***Chemical substances interacting with the analyte***.
(3) ***Chemical substances interacting with the titrant***.

5.19. Is Classical Quantitative Analysis possible with a relative method? Why?

Answer:
No. The instruments used in Classical Analysis produce no signals. Therefore, they do not allow the use of a relative method to compare the signal for the sample with that for a standard.

5.20. Why does sensitivity in gravimetries increase with decreasing gravimetric factor?

Answer:
Because the smaller the gravimetric factor is, the greater is the molecular weight of the weighted form relative to the analyte—and hence the smaller is the amount of analyte that can be detected in a given gravimetric weighing.

5.21. What is a titrimetry? Tick the correct answer.

Answer:

[ ] A quantitative method for identifying analytes
[ ] A relative interpolation method
[X] An absolute quantitative method using analytical standards
[ ] An absolute quantitative method using no analytical standards

5.22. Explain the relationship between gravimetric factor and sensitivity in gravimetry.

Answer:

$$P_A = G \cdot P_g$$

The smaller the gravimetric factor (G) is, the higher is the sensitivity of a method (that is, the smaller is the amount of analyte it can detect with a gravimetric weighing).

Chapter 6. Qualitative Analytical Processes

6.1. Does the qualitative analysis of samples fit in Classification Analysis?

Answer:

Yes. This is the simplest form of classification analysis. Samples are classified into two groups depending on whether they give a YES response or a NO response. Dubious samples may be included in a third group.

6.2. What name is usually given to qualitative analytical processes?

Answer:

Test (or assay).

6.3. Tick the analytical properties that are not applicable to Qualitative Analysis.

Answer:

[ ] Representativeness
[X] Accuracy
[X] Precision
[ ] Sensitivity ***(only the limit of detection can be used)***

6.4. Two methods for the qualitative analysis of milk samples possibly contaminated with pesticides provide wrong information. Thus, method A gives false positives and method B false negatives. Which would you use? Why?

Answer:

Method A because

(a) ***it gives no false negatives; and***
(b) ***any false positives it provides can be ascertained by using an appropriate confirmation technique***.

6.5. What are the main differences between Qualitative Analysis and Quantitative Analysis? Tick the correct answers.

Answer:

[X] The binary response
[ ] A classical method of analysis
[ ] The use of analytical chemical standards
[X] The analytical property "reliability"
[ ] Selectivity

6.6. What are the differences between binary and multiple classification in Qualitative Analysis?

Answer:

Binary classification splits the body of samples into two groups only according to whether they give a YES response or a NO response. On the other hand, multiple classification provides more than two groups according to various criteria (e.g., the origin of wine samples).

6.7. What are the factors dictating the following parameters?

Answer:

(a) Limit of detection ***(The analytical process, CMP)***
(b) Cut-off concentration ***(The laboratory)***
(c) Threshold concentration ***(Applicable legislation and the client)***

6.8. What is a false positive in Qualitative Analysis? Give an example.

Answer:

A YES response which should have been NO.

Example: A YES response to an analyte concentration of 1.5 ppb by a method with C_{LOD} = 2 ppb is a false positive.

6.9. What is a false negative in Qualitative Analysis? Give an example.

Answer:

A NO response which should have been YES.

Example: A NO response to an analyte concentration of 2.5 ppb by a method with C_{LOD} = 2 ppb is a false negative.

6.10. An immunochemical test (method A) and a chemical spot test (method B) are used to detect the same analyte in the same sample. The results of analysing 100 samples are as follows:

	Reliability (%)	False positives (%)	False negatives (%)
Method A	95	2	3
Method B	94	6	0

Which method provides the better results? Why?

Answer:

Method B. Although it is less reliable, its proportion of false negatives is 0%, which makes it highly reliable. Also, any false positives it provides can be ascertained by using a confirmation technique.

6.11. What analytical properties are applicable to quantitative determinations but not to qualitative tests? Why?

Answer:

Accuracy, precision and two sensitivity-related parameters (IUPAC's S and the limit of quantification, C_{LOQ}).

6.12. What are "analytical systems with group separation" in Classical Qualitative Analysis?

Answer:

Analytical schemes that are used to classify analytes experimentally (e.g., by chemical precipitation). The resulting groups allow the analytes in them to be determined individually (that is, without interference from the others in the group).

6.13. What are the differences between group, identification and masking reagents in Classical Qualitative Analysis?

Answer:

Group reagents ***allow a mixture of analytes to be separated into groups where each individual analyte can be reliable detected***.

Identification reagents ***react with the analyte to produce an external effect (e.g., a colour change, formation of a gas or precipitate) that can be identified by the human senses***.

Masking reagents ***form stable, soluble, colourless chelates with interfering species***.

6.14. Name two identification (Qualitative Analysis) procedures used in dynamic instrumental systems (e.g., chromatography).

Answer:

- ***Use of an internal standard to make standardized measurements***.
- ***Addition of a standard of the analyte to the sample***.

6.15. Tick the words directly connected with Qualitative Analysis:

Answer:

[X] Detection
[ ] Quantification
[X] Identification
[X] Qualification

6.16. How does a "white" sample differ from a "black" sample?

Answer:

A white sample is a sample whose properties are quite well-known or predictable (e.g., water from a spring). On the other hand, a black sample is one whose properties are completely unknown (e.g., a previously never analysed lunar rock).

6.17. Is Qualitative Analysis important to modern Analytical Chemistry? Why?

Answer:

Qualitative Analysis in its classical and instrumental forms continues to be in wide use today because most of the analytical information required is of the binary type.

6.18. What are the three quantitative landmarks for the binary response in Qualitative Analysis?

Answer:

The limit of detection (C_{LOD}), the cut-off concentration (C_C) and the threshold concentration (C_L).

6.19. One brand of canned tuna fish contains 4 ppm tin. A qualitative test with $C_{LOD} = 1$ ppm for the metal gave a positive (YES) response. What type of error was made?

Answer:

[X] None
[ ] A false positive
[ ] A false negative

6.20. What type of error is the more crucial in Qualitative Analysis? Why? Give an example.

Answer:
A false negative because a NO response terminates the process whereas a YES response requires confirmation.

6.21. Is "specific uncertainty" applicable to Qualitative Analysis? Why?

Answer:
No. It must be adapted to the singularities of Qualitative Analysis in the form of an unreliable range around the threshold or cut-off concentration within which errors (false positives and false negatives) occur.

6.22. What are the three most important limitations of Classical Qualitative Analysis in relation to Instrumental Qualitative Analysis?

Answer:

- ***A low sensitivity***
- ***A low selectivity***
- ***A narrower scope***

6.23. What are the three types of reagents used in Qualitative Analysis? What is their purpose? Give an example of each.

Answer:

	Name	Purpose	Example
Type 1	***Identification***	***Recognition***	***Detection of Pb^{2+} with I^-***
Type 2	***Group***	***Grouping species to avoid interferences***	***Separation of Ag^+, Pb^{2+} and Hg_2^{2+} with Cl^-***
Type 3	***Masking***	***Avoiding interferences***	***CN^- to detect Cd^{2+}***

6.24. What are the three main features of so-called "analytical schemes without group separation"?

Answer:

- ***They use highly sensitive and selective reagents***
- ***Their operational sequence must be strictly followed***
- ***They occasionally require using a separation technique***

6.25. What is the difference between a dynamic and a static instrumental system in Qualitative Analysis?

Answer:
In a dynamic system, the instrumental signal is time-dependent; in a static system, it does not change with time.

6.26. What analytical properties are applicable to Qualitative Analysis?

Answer:

- ***Capital (accuracy and representativeness)***.
- ***Basic (sensitivity, selectivity, precision and robustness)***.
- ***Productivity-related (expeditiousness, cost-effectiveness and safety)***.

6.27. Are both types of calibration applicable to Qualitative Analysis?

Answer:

Method calibration [X] Yes [ ] No
Equipment calibration [X] Yes [ ] No

6.28. What types of instruments does Classical Qualitative Analysis use?

Answer:
It uses the human senses (sight and smell, mainly) as instruments.

6.29. What are masking reagents? In what context are they used?

Answer:
Masking reagents are substances forming stable, soluble, colourless chelates with interfering substances which enable the reliable identification of a species in a group or a sample without the need for separation. They are typically used in Classical Qualitative Analysis.

6.30. Define "reliability" in Qualitative Analysis. To which classical analytical properties does it relate?

Answer:

- ***The proportion of correct YES/NO answers obtained by subjecting a large number of aliquots from a standard sample to a qualitative process (a test)***.
- ***A combination of the properties "accuracy" and "precision", which are used in Quantitative Analysis***.

6.31. Instrumental Qualitative Analysis relies on a triple comparison of signals to be subjected to the analytical process. What do the three signals belong to?

Answer:

- ***A sample standard containing the analyte***.
- ***A blank (that is, a sample not containing the analyte)***.
- ***A sample***.

Chapter 7. Analytical Problem-Solving

7.1. Identify the binary interfaces between Analytical Problem-Solving, Analytical Quality and Social Responsibility.

Answer:

	Analytical Problem-Solving	Analytical Quality	Social Responsibility
Analytical problem-solving	×	***Analytical properties as indicators Satisfying information requirements***	***Satisfying information requirements as an internal connotation of Social Responsibility***
Analytical quality	***Analytical properties as indicators Satisfying information requirements***	×	***Quality as a general approach to Social Responsibility***
Social responsibility	***Satisfying information requirements as an internal connotation of Social Responsibility***	***Quality as a general approach to Social Responsibility***	×

7.2. What is the third basic standard in Analytical Chemistry? How is it related to the analytical problem?

Answer:

The third basic Standard of Analytical Chemistry is "required information", which constitutes the foundation, core and goal to be fulfilled in order to solve the analytical problem: the analytical problem delivers the required information.

7.3. How would you define "fitness for purpose"? To which facet of representativeness is it related? Is it related to chemical metrology?

Answer:

"Fitness for purpose" is the suitability of the information or results delivered for the intended purpose and is related to the highest level of representativeness in the results, which arises in the socio-economic (external) realm. However, it is completely unrelated to chemical metrology, where representativeness bears an orthodox, internal meaning, namely: consistency of the relationship of the results with the sample or aliquot used to obtain them.

7.4. Describe the roles of the analytical problem in the basic and applied sides of Analytical Chemistry.

Answer:

On the basic side, the analytical problem operates as a support and as an incentive to improve the intrinsic foundations of Analytical Chemistry (analytical properties, sampling). Also, it facilitates harmonization and communication among the different branches of Science for effective transfer of information and mutual recognition of their results.

On the applied side, the analytical problem is a means for fulfilling clients' information needs. In fact, correctly solving the analytical problem provides a solution to a real-life socio-economic problem.

7.5. How does the analytical problem relate the analytical chemist to the client?

Answer:

The analytical problem is the communication interface between clients and analytical chemists, and the link between the following pairs of elements:

(1) ***The socio-economic problem and the analytical process. The analytical process is designed in accordance with the specificities of the analytical problem, which in turn is conceived with the requirements of the particular socio-economic problem to be solved in mind***.
(2) ***The information needs and analytical properties. The information required by clients is converted into objectives to be fulfilled in order to solve the analytical problem—and the objectives contain the analytical properties needed to solve it***.
(3) ***External quality and internal (analytical) quality. Internal quality reflects quality in the results and in the analytical process with a view to solving the analytical problem. It should match external quality, which is required by the client to solve the originating socio-economic problem***.

7.6. What are the components of the concept hierarchy containing the analytical problem? What place does the analytical problem take in it?

Answer:

The analytical problem is at the top of the scope hierarchy:
Analytical problem > Object > Sample/Aliquot > Analyte.

7.7. How would you relate the analytical problem to the leading concepts "reports", "external quality" and "to analyse" in other hierarchies?

Answer:

The analytical problem requires a solution that is provided by results that are obtained by analysing and contained in a report. The quality of the results should match the external quality needed for the socio-economic problem to be properly solved.

7.8. Distinguish "orthodox" representativeness from "maximum" representativeness. Which traceability chain does each belong to?

Answer:

"Orthodox representativeness", which is that implicit in chemical metrology, is the consistency between the results and the sample or aliquot analysed to obtain them. Therefore, it applies to traceability of the results to the sample or aliquot.

"Maximum representativeness" comprises consistency between the results and the sample or aliquot used to obtain them, and also between the analytical problem and the socio-economic problem. The concept includes fitness for purpose, which pertains to the applied, socio-economic side of Analytical Chemistry only. Therefore, maximum representativeness is associated to the traceability chain results–sample (aliquot)–analytical problem–socio-economic problem; also, it is the result of a mixed (orthodox–heterodox) approach to traceability of the sample (aliquot).

7.9. A river is suspected to be polluted with toxic organic waste that may be having adverse effects on the nearby population. This hypothesis is verified by collecting 200 samples of water at different depths along the river for analysis. The method used has a limit of detection of 0.7 ppm and a limit of quantification of 2.1 ppm. The effects of the organic waste are felt at concentrations above 3 ppm. The concentration of waste obtained with the chosen method as the average of 200 individual values is 2.7 ppm.

(a) Complete the following table.
(b) Can the socio-economic problem addressed be correctly solved?
(c) Does the analytical method require any corrective actions?

Answer:

(a)

Socio-economic problem	***Checking whether the river is contaminated with toxic organic waste***
Analytical problem	***Detecting and determining organic compounds with potentially detrimental effects on the population***
Object	***The river***
Sample/aliquot	***Water from the river as collected at a variable depth at different points along its course***
Analyte(s)	***Toxic organic compounds***
Limit of detection (C_{LOD})	**0.7 ppm**
Limit of quantification (C_{LOQ})	**2.1 ppm**
Legal limit (C_{LL})	**3 ppm**
Result ($C_{obtained}$)	**(2.7 ± 0.1) ppm**

(b)

Yes. The socio-economic problem can be solved because the analytical process allows the presence of toxic organic compounds to be confirmed and their concentration, which is close to the legally accepted limit, determined.

(c)

No corrective actions are needed because the limits of detection (C_{LOD}) and quantification (C_{LOQ}) are valid for detecting and quantifying the analytes—both are lower than the legal limit (C_{LL}).

7.10. What are the intangible elements of an analytical problem? How do they relate to the steps of the analytical problem-solving process?

Answer:

Intangible elements: planning, design, evaluation and correction, which are connected to the steps of the analytical problem-solving process as follows:

1. ***"planning" to the first and second step (identification, confirmation and definition of the information requirements);***
2. ***"design" to the third step (planning of the analytical strategy);***
3. ***"evaluation" to the fourth step (monitoring and validation of the results); and***
4. ***"correction" to the fifth step (corrective actions)***.

7.11. Define and briefly describe the five steps of the analytical problem-solving process. Give an example of socio-economic problem and describe the steps needed to solve it.

Answer:

First step: Identification of the information requirements, which rests on effective communication between the client and the analytical chemist in order to define the characteristics of the information needed. Example: the client asks the analytical chemist to determine whether a salmon batch is fit for marketing based on its pinkish colour.

Second step: Specifying the analytical information required. Conversion of the socio-economic information requested in the first step into analytical information. Example: the analytical chemist associates the pinkish colour of salmon to the concentration of astaxanthin.

Third step: Planning the analytical strategy. Development of the methodology to be applied (an appropriate analytical process). Example: The analytical chemist develops a method by which samples are subjected to solid–liquid extraction, elution with acetone and liquid–liquid extraction with hexane in order to isolate astaxanthin free of interferences from other substances. The pinkish colour is determined by using a photometer to measure the absorbance at 470 nm of the hexane extract.

Fourth step: Monitoring the results, which involves assessing them against internal and external references. If the results are correct, the analytical process will have been solved; otherwise, a fifth step will be needed. Example: The experimental result is compared with a tabulated reference and the analyte percent recovery as determined by adding a known amount of astaxanthin as internal standard to a sample.

Fifth step: Corrective actions. Identifying errors in the previous steps and correcting them. After each corrective action, the process returns to step 4 until the analytical problem is solved. Example: if the results are not acceptable, the solvent used in either or both extractions may have to be changed with a similar one where astaxanthin is more readily soluble.

7.12. Why is fluent communication between the analytical chemist and the client important in the first step of the analytical problem-solving process?

Answer:

Because it is the origin of the integral definition of "required information" and hence the only way in which the analytical chemist can know what the client needs and how to supply it.

7.13. Name three essential items of information needed to identify the analytical information required in the second step of the analytical problem-solving process.

Answer:

- ***The characteristics of the sample (sampling + sample size)***.
- ***The type of analyte or measurand sought, and the type of analysis to be performed***.
- ***The required levels of analytical properties***.

7.14. What is the purpose of the third step of the analytical problem-solving process? What are the factors influencing selection and design of a CMP?

Answer:

The third step involves designing and developing an analytical process suited to the client's information needed in order to obtain useful results for the intended purpose.

The factors influencing the choice of an existing process or the development of a new one include

- ***the type of information required (general or analytical);***
- ***the specific analyte or measurand;***
- ***the laboratory's human, technical and economic resources; and***
- ***the agreed cost (overall or per analysis)***.

7.15. What are the references used to assess the results in the fourth step of the analytical problem-solving process? How are they related to quality?

Answer:

Results are assessed with respect to two main references, namely:

(1) ***The minimum levels of analytical properties required by the client, which may or may not be fulfilled by the laboratory. This reference is associated to internal (analytical) quality in the results because it pertains to the analytical realm***.

(2) ***The information required by the client (the intended purpose). The results must be validated and properly interpreted in order to solve the originating socio-economic problem. This reference is associated to external quality in the results because it falls outside the scope of the analytical laboratory: the analytical information delivered must be interpreted by the client or expert professionals in order to solve the socio-economic problem***.

7.16. When is the fifth step of the analytical problem-solving process needed? Why?

Answer:

The fifth step (corrective actions) is needed when the results of a CMP are not valid (that is, when they do not meet the required levels of quality and analytical properties or do not allow the socio-economic problem to be solved).

This step is intended to correct errors made in the previous ones. Such errors may arise from poor communication between the client and the analytical chemist, misidentification of the analytical information needed or use of a CMP whose results do not allow the socio-economic problem to be solved.

7.17. How can delivered information be in relation to required information? Give an example of each situation.

Answer:

The following situations are possible:

(1) ***Delivered information = Required information. The two are completely identical. Example: A client requires the content in vitamin C of a given fruit juice and the analytical chemist provides the amount of ascorbic acid (that is, vitamin C) present.***

(2) ***Delivered information $\neq$ Required information. The two are completely different: what is delivered is not what was expected. Example: A client requires the content of vitamin C in a fruit juice and the analytical chemist provides the amount of retinol (vitamin A) in it.***

(3) ***Delivered information < Required information. The client is supplied with inadequate information. Example: A client needs the amounts of vitamins A and C in a juice but the analytical chemist only provides the amount of retinol (vitamin A) present.***

4) ***Delivered information > Required information. The client receives more information than is needed for the intended purpose. Example: A client needs the amount of vitamin C but the analytical chemist additionally supplies those of retinol (vitamin A) and cyannocobalamin (vitamin B12), both of which are superfluous for the intended purpose.***

7.18. In order to decide whether a person should be pronounced guilty of murder, a laboratory is asked to perform a comparative analysis of a blood sample from the defendant and one containing a mixture of blood from the defendant and the victim blood found in the crime scene. The analysis involves determining the DNA sequence of the defendant, the victim and the mixed blood sample. Please complete the following table by identifying the different elements.

Answer:

Socio-economic problem	***Whether the defendant is guilty or not guilty***
Analytical problem (1st step)	***A comparative analysis of blood from the victim and the defendant with that found in the crime scene***
Analytical information (2nd step)	***A qualitative (comparative) characterization of the blood samples for DNA***
CMP to be used (3rd step)	***– Individual analyses of blood from the victim and the defendant*** ***– Analysis of the mixed blood sample found in the crime scene and of an artificial mixture containing blood from the victim and the defendant*** ***– Separation of the two types of blood contained in the mixture for individual analysis***
Verification of the results (4th step)	***Comparison of the results for the victim-defendant mixed blood sample and the crime scene sample*** ***Comparison of the DNA profile for the defendant with that for the mixed sample not containing blood from the victim***

Chapter 8. Analytical Chemistry and Quality

8.1. To what analytical chemical concepts do the basic and applied sides of quality relate?

Answer:

The relationship between Analytical Chemistry and Quality has two sides: a basic side and an applied side. On the basic side, Quality is defined as the body of characteristics, properties, attributes or abilities of an entity that make it better, worse than or equal to, other entities of the same type. Consequently, the basic side relates the major analytical chemical concepts (analytical properties) with Quality in its broadest sense.

On the applied side, Quality is understood as the body of characteristics of an entity that allow it to fulfil specific or implicit requirements of clients or legislation. This side has to do with the implementation of Quality Systems in analytical laboratories and is therefore related to the analytical problem.

8.2. What types of indicators are used to assess quality?

Answer:

The comparisons inherent in the very notion of Quality can be made by using various types of indicators. Thus, there are quantitative (numerical data), qualitative (e.g., opinions) and integral indicators (combinations of the previous two). Obviously, the last are the most comprehensive. For example, properly characterizing a natural environment involves more than simply checking that the typical parameters (e.g., temperature, pollutant concentrations in air, water and soil) fall within acceptable or legally set ranges. The human perception of well-being is different in technical "clean", appropriate places. Also, a given type of agri-food may fulfil all applicable regulations and yet lack the quality needed for marketing owing to an unappealing appearance, colour or flavour.

8.3. How are the quality expected and that perceived by the "client" related to the quality planned and designed a body or organization?

Answer:

Achieved quality falls at the boundary between external and internal quality. The primary aim of an entity is to have achieved quality fully coincide with designed quality. On the other hand, clients expect perceived quality to surpass or at least match expected quality—the former may increase expenses for the entity concerned. The most critical comparison is that of expected and perceived quality. Ideally (total quality), the three types of quality should coincide.

8.4. Distinguish external and internal quality, and relate the two, through two examples: (*a*) a government environmental agency and (*b*) analytical laboratory.

Answer:

Quality can be classified in various ways. One divides quality into internal and external. Internal quality is quality in the entity delivering products or services, whereas external quality is that in the client receiving them.

Example (a)

In an environmental agency, internal quality refers to quality of the agency itself, which influences its management and staff, whereas external quality refers to client satisfaction. For example, the clients of an environmental certification agency may be firms seeking certification of their environmental management and quality, professionals attending training courses taught by the agency, individuals or firms commissioning environmental studies, etc.

Example (b)

In an analytical laboratory, external quality refers to quality of the client or user (e.g., a farmer needing to have his irrigation water analysed, members of a residents' community wishing to have the quality of their pool water assessed). On the other hand, internal quality coincides with analytical quality, which is that leading to external quality by fulfilling information requirements. Internal quality rests on quality in the results, analytical processes, work and its organization, and the analytical tools used.

8.5. What are quality trade-offs? Give some examples in various fields.

Answer:

Quality is not utopic. Ideally, a body should reach a high level of internal properties in an expeditious, economical and safe manner. In practice, however, internal, economic, and time- and safety-related features are frequently contradictory and require adopting some trade-off. Thus, if quality is to be achieved by maximizing intrinsic properties, costs can be expected to rise, processes to be slower and staff involvement to increase.

One clear example in the field of clinical analysis is that of a patient admitted to the emergency department of a hospital. The patient will have to be correctly diagnosed (e.g., with a blood analysis for various parameters) in order to be properly treated. This situation will require expeditiousness at the expense of other analytical properties and also greater staff involvement.

One other example is that of the determination of inorganic nitrogen in a fertilizer. If a very large number of samples is to be analysed each day, the laboratory may seek to minimize costs by using an appropriate tool from a wide range of choices from a straightforward burette to a sophisticated neutron activation analyser, for example. The particular tool or technique of choice will also depend on the intrinsic properties the results are to have, the availability of staff to implement it and the time taken by each individual analysis.

Finally, the determination of the gold content of a jewel in order to assess its purity should prioritize accuracy because the jewel price will depend considerably on it. This will entail maximizing intrinsic properties at the expense of increased costs—the increase may be offset by rising the jewel price as well, however—longer analysis times and greater staff involvement.

8.6. What are the structural landmarks in the quality of a body or organization?

Answer:

First, the body or organization should have a Quality Policy in the form of a document endorsed by the top decision organ. The Policy materializes in Quality Management elements and operational systems that are realized in Quality Assurance, which encompasses all activities performed in order to assure quality in the body or organization concerned. Such activities include Quality Control, which involves direct assessment of the body or organization in terms of quantitative indicators mainly; Quality Assessment, which involves examining both the body or organization and its activities; and internal corrections deriving from the previous two types of activities.

8.7. Explain some direct or indirect benefits of implementing a Quality System.

Answer:

The direct benefits of a Quality System are improved characteristics of the product, system or service. The improvements can be expected to increase client satisfaction, and also the supplier's credibility and prestige. For example, satisfied clients are bound to recommend the services of laboratories they trust to their acquaintances and their positive opinions are bound to increase the prestige of the recommended laboratories as a result.

As regards indirect benefits, implementing a Quality System can lead to new jobs (e.g., staff for the Quality Assurance Unity of Good Laboratory Practices). One other potential benefit is more rational work avoiding superfluous repetitive tasks by careful planning of laboratory activities in developing the Quality Manual. Any deficiencies and mistakes arising during operation will thus be clearly exposed. Also, using a Quality System makes it easier to establish and clarify goals, helps reduce indecision and facilitates fluent communication.

8.8. In what way is Analytical Quality related to analytical properties? To which properties are (*a*) quality of results and (*b*) quality of the analytical process related?

Answer:

In its basic definition, Quality is a body of characteristics or properties. As a result, analytical properties are directly related to analytical quality and allow its different facets to materialize. Thus, the quality of analytical results is related to the capital analytical properties (accuracy and representativeness), integration of which is indispensable.

Also, basic and productivity-related analytical properties are attributes of the analytical process. Thus, the basic properties (robustness, precision, sensitivity, selectivity and proper sampling) provide support for the capital properties, whereas the productivity-related properties (expeditiousness, cost-effectiveness and safety) characterize laboratory productivity.

8.9. What is the relationship of quality to analytical quality?

Answer:

Quality can be defined as a body of properties and is thus related to analytical quality through analytical properties. Analytical properties play a central role in the materialization of the characteristics of required analytical information—a crucial reference for assessing results.

Also, properly solving an analytical problem entails fulfilling the client's information needs and ensuring consistency between required analytical information and laboratory-delivered information (that is, ensuring the degree of analytical quality required to achieve external quality). In the analytical chemical realm, this entails comparing with standards, whether written or otherwise, and also with the client's information needs.

8.10. Distinguish external and internal corrective actions in the framework of Quality Assurance.

Answer:

Quality Assurance comprises Quality Assessment, Quality Control and, if needed in view of the quality of the results, Internal Corrective Actions. Such actions may lead to partial or total changes in control activities. Quality Assurance activities of the three types frequently raise the need for corrective (external) actions initially involving the laboratory. Such actions must assure quality in the analytical processes performed by the laboratory through properly organized and conducted work, and the use of effective analytical tools. In any case, corrective actions should lead to improved quality in the laboratory's analytical results and ability to solve analytical problems.

8.11. What Quality Assurance elements examine an analytical laboratory?

Answer:

Quality Assurance involves examining both Quality Control activities and the analytical laboratory—in addition to the results it produces and its ability to solve specific analytical problems. Quality Control essentially involves examining the laboratory and its results.

8.12. Comment on the cyclic nature of Quality Assurance activities in the analytical chemical realm.

Answer:

The activities inherent in the three elements of Quality Assurance are in fact cyclic in nature. Thus, Quality Control, which comes into play before and during the analytical process, involves examining the analytical laboratory and the results it produces. By contrast, Quality Assessment takes place during and after the analytical process. Finally, Corrective Actions are usually performed after the analytical processes if judged necessary from the outcome of the assessment and can lead to changes in control activities or the adoption of new ones the next time the analytical process is conducted.

8.13. On what standards and elements do Quality Systems applied to analytical laboratories rest?

Answer:

The main frameworks for developing quality systems in analytical laboratories are as follows:

- ***The general standard ISO 9000 (Quality Management Systems. Fundamentals and Vocabulary)***.
- ***The specific standard 17025 ("General Requirements for the Competence of Testing and Calibration Laboratories), which, as implied by its title, applies to testing and calibration laboratories only***.
- ***Good Laboratory Practices (GLPs), which comprise Standard Operating Procedures (SOPs) and the Quality Assurance Unit (QAU)***.

Quality systems can also be developed from combinations of major standards, Total Quality Systems and Critical Point Systems, among others.

8.14. What are the goals of ISO 17025?

Answer:

The main goals of ISO 17025 are as follows:

(a) ***To establish a Quality Management System requiring no external recognition***.

(b) ***To have technical competence recognized by clients, regulation authorities or accreditation bodies***.

8.15. What are Good Laboratory Practices?

Answer:

Good Laboratory Practices (GLPs) are bodies of rules, operational procedures and practices established by a given institution such as the Organization for Economic Cooperation and Development (OECD) or the European Union (EU) that are deemed compulsory with a view to assuring quality and correctness in laboratory results.

GLPs are issued by international bodies and adopted by national governments through publication in their official state gazettes and are typically binding for laboratories performing socially influential analyses such as those of pharmaceuticals, cosmetics, foodstuffs and products with a potential environmental impact.

8.16. What are Standard Operating Procedures? Where are they used?

Answer:

A Standard Operating Procedure (SOP) is a detailed description of each individual activity to be performed by a laboratory (e.g., sample handling; control of reagents, reference materials, equipment and methods; archiving).

8.17. What is the Quality Assurance Unit?

Answer:

The Quality Assurance Unit (QAU) is an essential element of Good Laboratory Practices. The Unit consists of staff belonging to the laboratory's parent body but not to the laboratory itself and is answerable to the body's management only. The QAU's roles include implementing, controlling and assessing quality with a view to proposing improvement actions.

8.18. What is a primary method? How does it affect analytical quality?

Answer:

Primary quantification methods are at the top of the metrological quality ranking. According to the Consultative Committee for the Amount of Substance (CCQM), a primary method is "a method having the highest metrological qualities, whose operations can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units and whose results are, therefore, accepted without reference to a standard of the quantity being measured".

In summary, a primary method possesses a high metrological quality, is completely described and understood, is subject to well-defined uncertainty in terms of SI base standards and requires no analyte standard.

8.19. What is the difference between an official method and a standard method?

Answer:

An official method is a quantification method described in detail and issued by a government body such as the US Environmental Protection Agency (EPA) for legal adoption with a view to sanctioning the results of laboratories. Some official methods are used as reference methods, however.

On the other hand, a standard method is a method developed, validated and issued by a standardization body (ISO, CEN) or an association supporting Analytical Chemistry (e.g., the AOAC).

8.20. What activities does quality control involve?

Answer:

Quality Control is a body of planned, documented actions to be performed by laboratory staff in order to directly examine the laboratory's work, the tools it uses and the results it produces. Such activities typically include the following:

(a) ***Implementing and using control charts based on reference materials***.
(b) ***Examining and correcting instruments and apparatuses to ensure that they operate as they should***.
(c) ***Examining the purity and stability of the reagents and solutions used in CMPs***.
(d) ***Examining experimental laboratory conditions such as temperature, relative humidity, cleanliness and presence of contaminants***.
(e) ***Examining the sample custody system in order to ensure correlation between samples and results***.
(f) ***Using RMs and CRMs to examine CMPs at specific points***.
(g) ***Examining any changes in the results arising from the use of a CMP to determine specific analytes in a given sample by different staff or with different analytical tools***.

8.21. Why is labelling quality assessment activities as external or internal confusing?

Answer:

Depending on the assessor (that is, on the human factor), Quality Assessment is classified as internal or external. This classification, however, can be confusing because it rests on at least two different criteria. Thus, assessors may members of the laboratory staff, its parent body or an external entity. It is therefore preferable to classify Quality Assessment according to the following two alternative criteria:

- ***Whether the assessors belong to the laboratory. Their assessment will be of the internal type if they do and of the external type if they do not. In the latter case, Quality Assessment will be external–internal if the assessors are members of the parent body but not of the assessed laboratory and external–external if they belong to another body***.
- ***Whether the assessors belong to the assessed body. Their assessment will be internal if it is conducted by staff from the laboratory or its parent body, and external if performed by staff from another body***.

8.22. What are the goals of interlaboratory exercises? Where do they fall in the analytical quality realm?

Answer:

Interlaboratory exercises constitute a mode of external–external quality assessment. Each participating laboratory analyses the same sample to determine the same analyte(s) in order to have its results quantitatively assessed by comparison with those of the other laboratories.

The main goal of an interlaboratory exercise is to compare results and their uncertainty, and its primary objectives are (a) to have inexperienced laboratories learn to conduct specific CMPs; (b) to validate CMPs developed in response to new information needs; (c) to have the values and uncertainties for a given CRM certified; and (d) to have the quality of the results produced by the participating laboratories assessed.

8.23. Why are documentation and archiving activities the bottleneck in implementing quality in a laboratory?

Answer:

Documentation and archiving activities are in fact the bottleneck of Quality Assurance programmes and the greatest hindrance to implementing and monitoring Quality Systems in analytical laboratories. Thus, documentation and archiving are two time-consuming activities that frequently make laboratory staff reluctant to adopt a Quality System.

A laboratory having a Quality System must document and archive everything as stated in a Standard Operating Procedure (SOP) describing how each

laboratory operation is to be performed. Also, the laboratory must record sample custody chains and how its equipment performs after it is installed; also, it must monitor materials, SOPs, primary data, results, reports and documentation activities themselves, all of which demand a strong commitment.

8.24. What is external–external assessment? Give some examples and distinguish it from external–internal assessment.

Answer:

External–external assessment is performed by experts from a body other than that being assessed and hence doubly external to the laboratory. The activities to be performed for this purpose are known as "audits" in the realm of Quality. Audits can be conducted on systems (qualitative, visual and documental examination), performance (quantitative) or both (integral audits). In the analytical realm, audits can be of two main types, namely: (a) direct, which lead to accreditation of laboratories; and (b) indirect (e.g., proficiency testing).

One example of external–external assessment is that of a laboratory wishing to be accredited for performing a given type of clinical analysis. The auditors should belong neither to the candidate laboratory nor to its parent; rather, they should pertain to a certified national auditing body, whether public or private.

One other example is that of a laboratory wishing to assess a method it is using to determine benzene by participating in an interlaboratory exercise in order to compare its results with those of other laboratories analysing the same sample for the analyte. Usually, the body coordinating the exercise will be independent of the interested laboratory's parent body. Therefore, the laboratory will be subjected to external–external assessment of its results.

In external–internal assessment, the assessors are staff members of the interested body but not of its laboratory. One example is that of an agri-food multinational firm having several factories each with its own quality control laboratory in the same country. The body's headquarters may set up an intercomparison exercise involving the different quality control laboratories, whose results will be assessed by staff from the body but not from any of the laboratories.

8.25. Who accredits analytical laboratories? What is laboratory accreditation based on?

Answer:

Laboratories are accredited by a public or private body from their country using internationally accepted standards issued by EU, OECD or ISO, for example.

8.26. Define "accreditation". What are the main features of analytical laboratory accreditation?

Answer:

In the quality realm, "accreditation" is defined as "the formal recognition in writing that a laboratory is fit and competent to perform a given analysis or specific group of analyses".

The accreditation of analytical laboratories is (a) voluntary (done at their request), (b) temporary (it holds for a specified length of time only) and (c) partial (it applies to specific activities or groups of activities rather than to the laboratory as a whole).

8.27. What does the process of accrediting a laboratory involve?

Answer:

A laboratory can be accredited if it has a Quality System that has materialized in a Quality Manual. The accreditation process is started by the auditors conducting a documental and visual (qualitative) inspection and producing a report. If the report is unfavourable, the laboratory can challenge it; if it is favourable, the laboratory will be awarded a Certificate of Accreditation to be paid at its own expense.

The Certificate carries the twofold commitment of maintaining the existing quality systems and allowing the auditors free access to perform periodic controls during its validity period. Because accreditation is temporary, it must be renewed after the validity period has expired or if the laboratory undergoes any substantial changes in the meantime. Renewing accreditation involves repeating the whole accreditation process; however, the new audit may be made easier by the auditors' prior knowledge of the laboratory to be re-accredited.

8.28. What does analytical quality assurance rest on?

Answer:

First of all, Quality Assurance (QA) in an analytical laboratory is impossible without human contribution. In fact, QA requires support from the management of the laboratory's parent body and willing acceptance by the laboratory staff. Also, auditors must have a constructive attitude in their work to facilitate sustained improvement in the laboratory.

Successfully implementing a Quality System in a laboratory entails providing it with the required technical means and training its staff in the new way of working. The supports for QA in a laboratory include computers, participation in interlaboratory exercises, and documentation and archiving activities.

Computer hardware and software play a crucial role in implementing Quality Assurance. Quality control and analytical equipment control software can be highly useful for this purpose. At the boundary of Computers, Chemometrics and Quality is Qualimetrics, which influences analytical information, and the

optimization of analytical processes and Quality Systems. Chemometrics enables validation of primary data and comparison of results—which is the basis for Quality Control and Quality Assessment systems—whereas interlaboratory exercises facilitate assessment of laboratory proficiency.

Finally, documenting and archiving all activities, and having a standard operating procedure (SOP) for each, is crucial for proper performance in a laboratory possessing a Quality System. The laboratory should also keep a record of sample custody chains, equipment performance from installation, monitoring of other materials, SOPs, primary data, results, reports and documenting activities themselves.

8.29. Comment on the problems potentially arising in implementing quality assurance in analytical laboratories.

Answer:

Successfully establishing and maintaining Quality Assurance may require solving various problems such as the following:

- *Lack of leadership. The laboratory's parent body should have clear-cut goals (leadership). Also, the laboratory should be committed to quality and the inspiring Quality Assurance principles be supported by a Quality Policy. The body's management should encourage and support quality-related activities*.
- *The human factor. This is one of the cornerstones of effective laboratory quality systems. Motivating laboratory staff is in fact essential to have them accept the burden of some labour-intensive tasks involved in keeping the system working. Although some duties may initially be imposed by management, the system will fail in the long term in the absence of an awareness of the significance of Quality*.
- *Costs. Implementing a Quality System requires starting and maintenance investments that should be carefully considered before its establishment is addressed*.
- *Abrupt implementation. Abruptly adopting a Quality System may elicit outright rejection from by the staff concerned. Rather, the system should be implemented in a gradual manner in order to give the staff the opportunity to get acquainted with specific activities (e.g., keeping sample custody chains, developing and adhering to SOPs, validating charts) before development of the Quality Manual and subjection to internal audits (creation of the Quality Assurance Unit for Good Laboratory Practices) and external audits (accreditation and intercomparison exercises) are undertaken in a second step*.
- *Compatibility with routine work. The tasks involved in implementing a Quality System should be compatible with the laboratory's primary goal, namely: to produce quality analytical information within the applicable deadline and at the agreed cost*.
- *Lack of constancy. Implementing a Quality System is a long-distance race in which the staff should not exhaust their energy at the start if they are to retain*

their willingness to perform the more labour-intensive tasks (e.g., documentation and archiving). The outcome of internal and external audits can help preserve staff motivation.

– ***Complex literature. The literature on Quality is atypical, contradictory, and occasionally plagued with acronyms and rules that may raise a high initial barrier for staff to overcome***.

Chapter 9. Social Responsibility in Analytical Chemistry

9.1. Relate SR in Analytical Chemistry to

- analytical quality (Chap. 8); and
- analytical problem-solving (Chap. 7).

Answer:

Social Responsibility in Analytical Chemistry is related to analytical quality because the latter is essential with a view to the sustainable production of truthful information.

Social Responsibility in Analytical Chemistry is also related to analytical problem-solving because both involve supplying (bio)chemical information to make grounded, timely decisions.

In other words, SR is the materialization of the social and environmental connotations of analytical problem-solving and quality.

9.2. What are the keywords defining Social Responsibility? Which are especially significant because they are shared by many definitions of SR?

Answer:

The keywords for SR are "responsibility", "stakeholders", "quality of life" and "sustainability", and its most common dimensions "stakeholders" and "social".

9.3. Define "stakeholders" in the context of SR, and of ISO guides and norms.

Answer:

Stakeholders are individuals or groups of individuals that may be affected by the activities or decisions of a body or area of knowledge but may also influence or take part in such activities or decisions. Stakeholders constitute a key element of Social Responsibility.

9.4. Describe the cycle of concepts that provides an integral definition of SR in an individual, an organization and a scientific or technical area.

Answer:

The cycle of Social Responsibility concepts is a series of mutually connected actions that start and end at the binding "commitment" of an entity to systematically support SR.

The commitment comprises the following sequence of actions:

- ***designing and developing an SR implementation strategy;***
- ***managerial changes;***
- ***recognizing social and environmental concerns;***

- ***expanding classic stakeholders with new stakeholders such as NGOs;***
- ***objectively balancing SR support and the goals of the entity or area of knowledge concerned so that their fulfilment is not hindered by the adoption SR; and***
- ***ensuring responsibility and sustainability in the entity or area concerned***.

9.5. Highlight four of the five principles governing SR. Which is the most important? Why?

Answer:

The most salient principles of SR are accountability, transparency, ethical conduct and respect for stakeholders' interests, the last of which is the most important because it ensures fulfilment of SR.

9.6. Can marketing SR be

(a) positive?
(b) negative?
(c) neither positive nor negative?

Justify your answer.

Answer:

(a) ***Yes. Example: integral SR is systematically publicized by the entity or area of knowledge concerned***.
(b) ***Yes. Example: SR is only publicized with anecdotal actions such as stating that each consumer buying a given brand of yoghourt will be thus supporting a humanitarian cause***.
(c) ***Yes. Example: when support of SR is not systematically publicized***.

9.7. What is the most important element of the cyclic succession of SR concepts? Why is it more important than the others?

Answer:

The commitment that starts and ends the cyclic succession of concepts leading to the establishment of SR in a body or area of knowledge. It is more important than the other elements because no integral SR system can be successfully established without the commitment of those involved.

9.8. Are the following statements true or false?

(a) Ethical principles encompass SR.
(b) Implementing SR in a scientific or technical area encompasses quality systems.
(c) For many organizations and businesses, SR is merely a window-dressing opportunity.

Justify your answers.

Answer:

(a) ***False. SR rests largely on ethical conduct—it encompasses ethical principles***.
(b) ***True. SR can be considered an extension of Quality Systems***.
(c) ***Unfortunately true. Some organizations and businesses market SR without supporting it systematically and wholeheartedly***.

9.9. Why are SR in Analytical Chemistry and SR in (bio)chemical information equivalent?

Answer:

Because the main output of Analytical Chemistry is (bio)chemical information on objects and systems. If Analytical Chemistry is socially responsible and sustainable, so will be the production and dissemination of (bio)chemical information.

9.10. What are the internal and external connotations of SR in (bio)chemical information? Are they related in any way? How?

Answer:

The internal connotations are the sustainable production of quality (bio)chemical information (that is, of information that is consistent with reality).

The external connotations can be the summarized as the correct dissemination of such information to society through reports in order to derive knowledge.

There is an obvious relationship between the two: the external connotations can never be fulfilled unless the internal connotations are satisfied. For example, no reliable knowledge can be produced without quality (bio)chemical information.

9.11. Explain the differences between the transfer of data (signals), results (information) and reports (knowledge) to society.

Answer:

They key is who interprets them. Thus, if transferred data and results are interpreted by society or the media, they may be misinterpreted—and reality distorted as a consequence—through poor knowledge or disinterest. On the other hand, the facts behind contextualized transferred knowledge are bound to be correctly interpreted by society and to help decision-making.

9.12. Which of the three sources of distortion in the transfer of (bio)chemical information is the most important? Rank them according to significance.

Answer:

Although the significance of each potential source of distortion differs depending on the particular situation, the following three are usually the most important:

(a) ***Malicious external manipulation of the object or sample***.
(b) ***The type of information required***.
(c) ***A poor knowledge of the required information and its features***.

The latter two sometimes exchange their place in the significance ranking.

9.13. Are the two internal connotations of SR in Analytical Chemistry related? Which is the more important? Why?

Answer:

The internal connotations of SR in Analytical Chemistry are the reliable, sustainable production of quality (bio)chemical information. In principle, they are unrelated. SR provides a relational framework for the two.

9.14. What is the difference between the two models of quality in (bio)chemical information (the second facet of external connotations of SR in Analytical Chemistry)?

Answer:

The model comprising three facets of quality (namely, intrinsic, referential or held as true and routine) is more simple. Also, it constitutes one side of the tetrahedron including required information (the third basic standard for Analytical Chemistry) as a fourth facet in addition to perceived quality as a fifth.

The most salient difference between the two models is that the latter is much more comprehensive than the former.

9.15. Why can the type of information delivered be important with a view to facilitating effective communication between analytical laboratories and clients requiring information?

Answer:

Because it is not the same to deliver primary data, results (information) or knowledge (contextualized, interpreted data). The probability of clients properly understanding what they receive from laboratories grows from primary data to results to knowledge. Therefore, it is more reliable to transfer knowledge than results.

9.16. Can using a communication office to deliver information from a laboratory have a positive effect on the parent body? Why?

Answer:

The main function of the communication office of the laboratory's parent body is to facilitate communication by delivering a message that can be easily interpreted by society. The office should therefore avoid triggering false alarms and raising false expectations. Ultimately, the communication office is concerned with the tough task of disseminating analytical science and technology.

9.17. How is the choice of an analytical process dictated by the potential impact of the (bio)chemical information to be delivered?

Answer:

One essential requirement for performing a given analysis is knowing the potential consequences of the information or knowledge to be produced, which influence the choice of the analytical process. In choosing, one should be aware that specific uncertainty may be highly consequential. For example, a few tenths in the purity of a 500-kg gold batch can be more consequential on price than a few units in the percent moisture content of animal feed.

9.18. Explain the sentence "quality in information transfer depends on both the producer and the receiver of the information". Discuss the significance of the information required by the receiver.

Answer:

Honesty and professionalism in the transfer of (bio)chemical information rests both on the producer (the analytical chemist) and the receiver (the client)—which may or may not coincide with the requester. This is especially important when interpreting the information with a view to proposing or making decisions.

The difference between the information required and that received falls outside the analytical chemical realm but is extremely important. The two can be intentionally mismatched for dishonest purposes. Thus, a firm may be informed that its vegetable produce contains small amounts of a pesticide and yet ignore the analytical information and give its produce the green light for export. This misconduct is not be expected if effective administrative controls (e.g., certification by an accredited laboratory) are established.

9.19. How important can experience in the dissemination of science be to transfer (bio)chemical information? Why?

Answer:

It is crucial with a view to avoiding errors in transferring (bio)chemical information that might lead to false alarms or expectations. The only limitation arises from the communication office being pressed to produce information simply highlighting the importance of its parent body.

9.20. How can SR in Analytical Chemistry be assured?

Answer:

Through the commitment of laboratories and their parent bodies. Social Responsibility is a voluntary prior commitment which, however, is indirectly required by public administrations and society (e.g., NGOs).

9.21. Explain the "transparency principle" supporting SR in Analytical Chemistry.

Answer:

As per ISO Guide 26000:2010, transparency is one the principles of SR. Transparency in the conduct of an analytical chemist or laboratory implies the following:

- ***as regards the external connotations of SR in Analytical Chemistry, establishing a Quality System, and ensuring that all activities are sustainable, recorded and easily accessed by auditors;***
- ***in regard to the internal connotations, ensuring that results and reports are based on objective, easily assessed data***.

9.22. Describe the two main ways in which a sample can be tampered with in order to have it give spurious results for fraudulent purposes.

Answer:

(1) ***An extraneous analyte may be deliberately added to the sample so that the object from which it is extracted is spuriously deemed "contaminated". One example is pollution of a bay with mercury. If mercury is deliberately added to the water from a ship, the coastal environment may be declared polluted and unsafe for bathing and/or fishing. This may boost tourism and fishing in an unpolluted competing area***.

(2) ***A harmless substance may be added to the sample in order to conceal the presence of the analyte in either of two ways***:

- ***By having it interact with the analyte (e.g., to form a compound that will be retained during the preliminary operations and prevented from reaching the measuring instrument)***.
- ***By having it interact with the object in order to eliminate the analyte (e.g., using a diuretic to remove any traces of anabolic steroids or drugs of abuse taken by an athlete)***.