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Analytical Chemistry Today and Tomorrow

Miguel Valcárcel

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1. Introduction

Dealing with Analytical Chemistry in isolation is a gross error [1]. In fact, real advances in Science and Technology —rather than redundancies with a low added value on similar topics— occur at interfaces, which are boundaries, crossroads —rather than barriers— between scientific and technical disciplines mutually profiting from their particular approaches and synergistic effects. Figure 1 depicts various types of interfaces involving Analytical Chemistry.

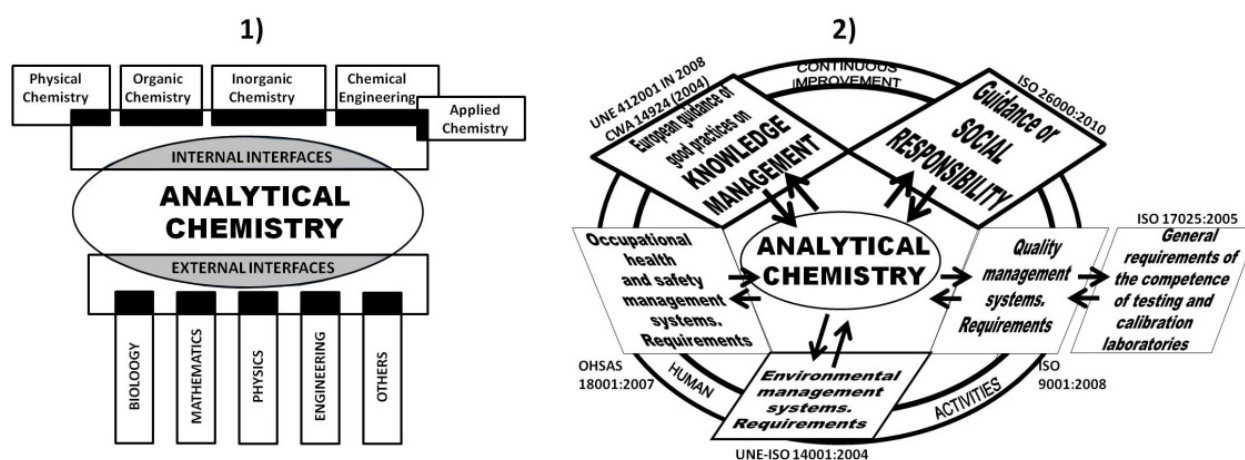


Figure 1. Analytical Chemistry at various interfaces. (1) Internal and interdisciplinary interfaces in the realm of Chemistry. (2) Interfaces with norms and guides. For details, see text.

Analytical Chemistry should in fact be present at a variety of interfaces such as those of Figure 1.1. Two belong to the realm of Chemistry (the framework of reference), namely:

1. *Internal interfaces* with other chemical areas (e.g. organic, inorganic, physical and applied chemistry, chemical engineering). Classifying Chemistry into these disciplines or subdisciplines, which are related via “fading” interfaces (1), has become obsolescent.
2. *External interfaces* with other scientific and technical disciplines such as biology, biochemistry, mathematics, physics or engineering, where Analytical Chemistry can play an active role (e.g. in the determination of enzyme activities or that of drugs of abuse in biological fluids) or a passive one (e.g. in chemometric developments for data processing or the use of immobilized enzymes in analytical processes).

Also, if Analytical Chemistry is to be coherent with its foundations, aims and objectives (see Section 2.2. of this chapter), it should establish two-way relationships with a variety of international written standards (norms and guides) in order to contribute to the continuous improvement of human activities (see Figure 1.2). The classical relationship between Analytical Chemistry and quality has materialized in ISO 17025:2005, which is the reference for laboratory accreditation. This norm contains technical requirements and other, management-related specifications that are shared with those in ISO 9001:2008, which is concerned with quality in general. Also, written standards dealing with knowledge management and social responsibility are highly relevant to the foundations and applications of Analytical Chemistry, even though they have rarely been considered jointly to date. In addition, Analytical Chemistry is very important for effective environmental protection, and occupational health and safety, since the (bio)chemical information it provides is crucial with a view to making correct decisions in these two complementary fields.

2. Cornerstones of modern analytical chemistry

Analytical Chemistry has evolved dramatically over the past few decades, from the traditional notion held for centuries to that of a modern, active discipline of Chemistry. Changes have revolved mainly around new ways of describing the discipline, and its aims and objectives, a broader notion of real basic references, the definition of the results of research and development activities and a holistic approach to analytical properties.

2.1. Definition

Analytical Chemistry can be defined in four simple ways as: (1) the discipline in charge of “Analysis” (the fourth component of Chemistry in addition to Theory, Synthesis and Applications, all of which are mutually related via the vertices of the tetrahedron in Figure 2); (2) the discipline in charge of the production of so named “(bio)chemical information” or “analytical information”; (3) the discipline of (bio)chemical measurements; and (4) the chemical metrological discipline, which is related to the previous definition.

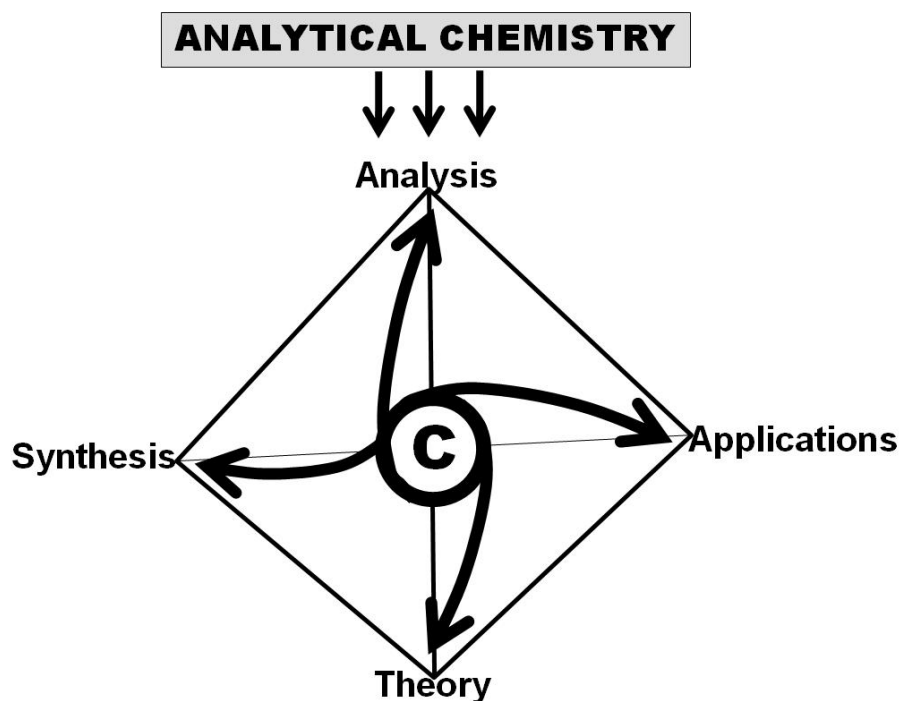


Figure 2. Analytical Chemistry is a discipline of Chemistry (C) inasmuch as it is responsible for “Analysis”, an essential component of Chemistry in addition to theory, synthesis and applications in different fields (e.g. environmental science, agriculture, medicine).

These four general definitions have been used to formulate various more conventional definitions such as the following:

“Analytical Chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time” (Working Party on Analytical Chemistry of the European Federation of Chemical Societies) [2].

“Analytical Chemistry is a metrological discipline that develops, optimizes and applies measurement processes intended to produce quality (bio)chemical information of global and partial type from natural and artificial objects and systems in order to solve analytical problems derived from information needs” [3].

The strategic significance of Analytical Chemistry arises from the fact that it is an information discipline and, as such, essential to modern society. Analytical Chemistry as a scientific discipline has its own foundations, which materialize in keywords such as information, metrology, traceability, analytical properties, analytical problems and analytical measurement processes. Also, it shares some foundations with other scientific and technical areas such as Mathematics, Physics, Biology or Computer Science.

2.2. Aims and objectives

To be coherent with the previous definitions, Analytical Chemistry should have the aims and objectives depicted in Figure 3.

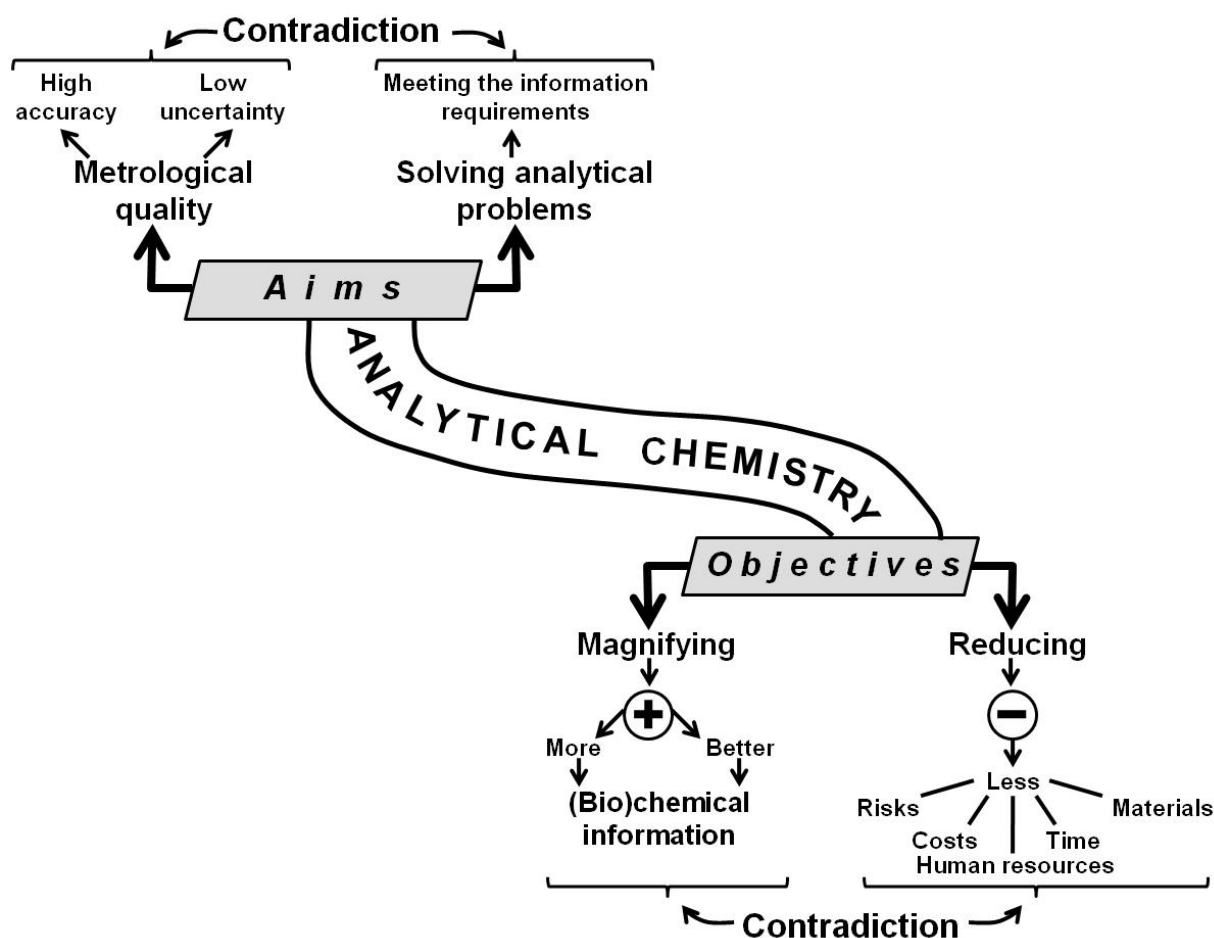


Figure 3. Primary aims and objectives of Analytical Chemistry. For details, see text.

Analytical Chemistry has two essential aims. One, which is intrinsic, is the obtainment of as high metrological quality as possible (i.e. of as true as possible analytical information with as low as possible uncertainty). The other, extrinsic aim is solving analytical problems derived from (bio)chemical information needs posed by “clients” engaged in a great variety of activities (health, general and agrifood industries, the environment).

The main magnifying objectives of Analytical Chemistry are to obtain a large amount of (bio)chemical information of a high quality, and its main reducing objectives to use less material (sample, reagents), time and human resources with minimal costs and risks for analysts and the environment.

The aims and objectives of Analytical Chemistry share its two sides (basic and applied); these are usually in contradiction and require appropriate harmonization. Thus, ensuring a high metrological quality may be incompatible with obtaining results in a rapid, economical manner. In fact, obtaining more, better (bio)chemical information usually requires spending more time, materials and human resources, as well as taking greater risks. Balancing the previous two aims and objectives requires adopting quality compromises [4] that should be clearly stated before specific analytical processes are selected and implemented.

2.3. Basic analytical standards

Analytical Chemistry relies on the three basic standards (milestones) shown in Figure 4 [5]. The two classical standards, which have been around for centuries, are tangible measurement standards (e.g. pure substances, certified reference materials) and written standards (e.g. the norms and guides of Figure 1, official and standard methods). A modern approach to Analytical Chemistry requires including a third standard: (bio)chemical information and its properties it should have to facilitate correct, timely decisions. Without this reference, analytical laboratory strategies and work make no sense. In fact, it is always essential to know the level of accuracy required, how rapidly the results are to be produced, and the maximum acceptable cost per sample (or analyte), among other requirements.

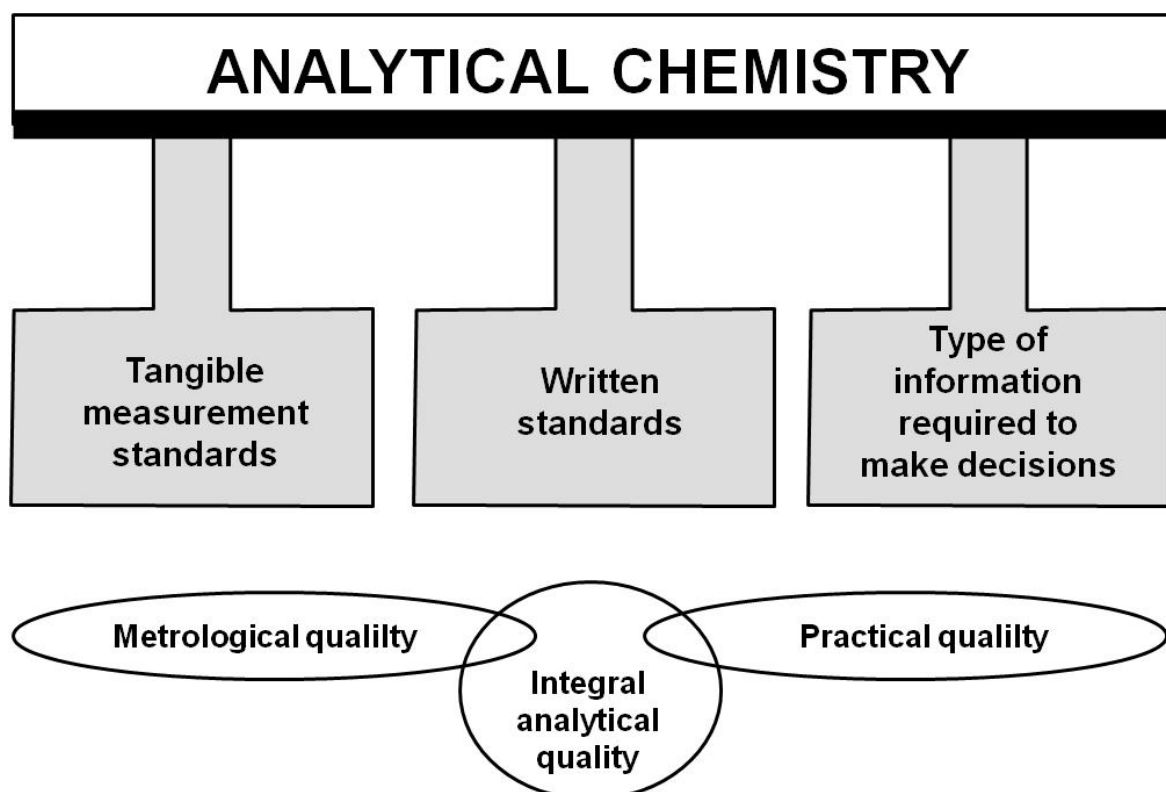


Figure 4. Basic standards supporting the Analytical Chemistry building and analytical quality related concepts. For details, see text.

As can be seen in Figure 4, conventional basic standards are related to so named “metrological quality”, whereas (bio)chemical information and its required characteristics (the third basic standard) are related to “practical quality”. Combining both concepts in so named “integral analytical quality” requires balancing two contradictory forces, which in turn entails the adoption of “quality compromises” (see Section 4 of this chapter).

2.4. R&D analytical “products”

The basic side of Analytical Chemistry encompasses a variety of R&D activities aimed at improving existing methods and/or developing new ones in response to new, challenging

information needs. These activities can produce both tangible and intangible tools such as those of Figure 5 [6]. Typical tangible analytical tools include instruments, apparatus, certified reference materials, immobilized enzymes and engineering processes adapted to the laboratory scale (e.g. supercritical fluid extraction, freeze-drying). Analytical strategies, basic developments (e.g. calibration procedures) and chemometric approaches (e.g. new raw data treatments, experimental design of analytical methods) are the intangible outputs of analytical R&D activities. Transfer of technology in this context is more closely related to tangible R&D tools, whereas transfer of knowledge is mainly concerned with intangible R&D analytical tools; in any case, the two are difficult to distinguish.

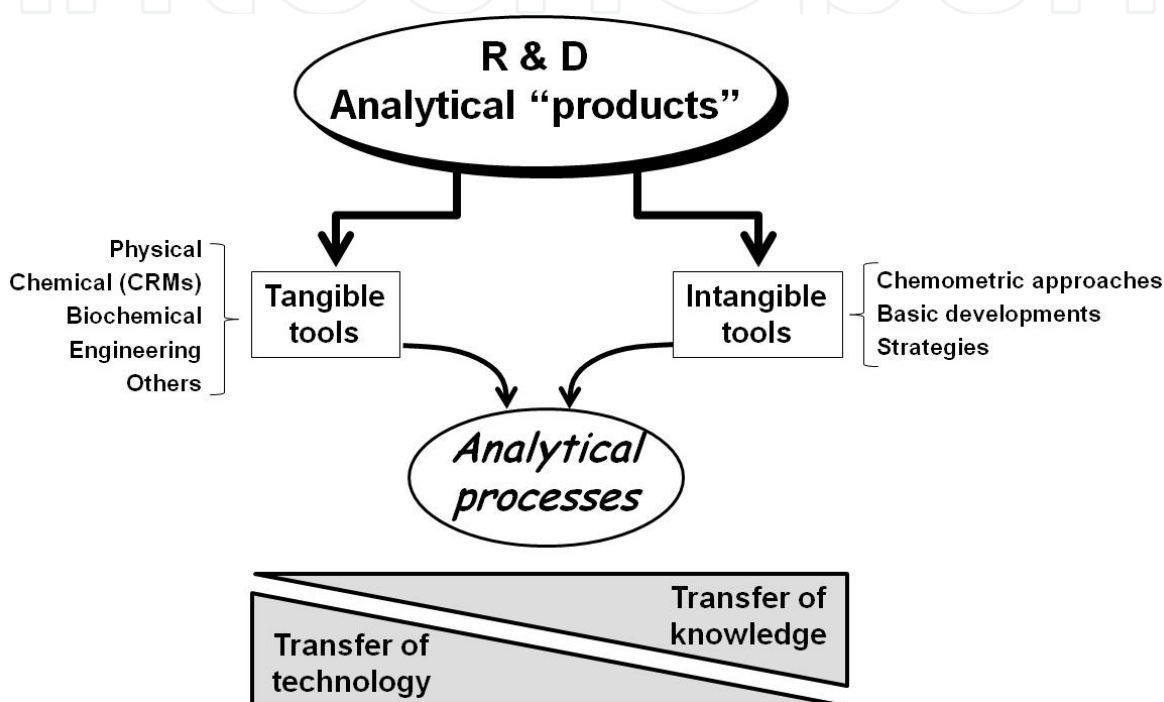


Figure 5. Main outputs of research and development (R&D) in Analytical Chemistry, transfer of knowledge and technology included. For details, see text.

2.5. Quality indicators

Analytical properties are quality indicators for the great variety of systems, tools and outputs of (bio)chemical processes that allow one to compare and validate analytical processes and the results they provide. Traditionally, they have been dealt with separately, with disregard of the high significance of their mutual relationships. Figure 6 provides a holistic view of analytical properties [7] as classified into three groups (capital, basic and productively-related) that are assigned to analytical results and analytical processes.

Top or capital analytical properties (accuracy and representativeness) are characteristics of the quantitative results of measurement processes. Accuracy is related to two classical metrological properties: traceability and uncertainty. In qualitative analysis, this property must be replaced with “reliability”, which includes precision (a basic property). Capital properties can be defined in simple terms as follows:

Accuracy is the degree of consistency between a result (or the mean of several) and the true value or that considered as true (viz. the value for a certified reference material) in quantitative analyses. Any differences between the two constitute systematic errors.

Reliability is the proportion (percentage) of right yes/no answers provided by independent tests for analyte identification in aliquots of the same sample in qualitative analyses.

Representativeness is the degree of consistency of the results with the samples received by a laboratory, the overall sample or object studied, the particular analytical problem and the information required by the client.

Basic analytical properties (precision, robustness, sensibility selectivity) are attributes of analytical processes and provide support for capital properties. Thus, it is impossible to obtain highly accurate results if the analytical process is not precise, sensitive and selective enough. These properties can be defined as follows:

Precision is the degree of consistency among a set of results obtained by separately applying the same analytical method to individual aliquots of the same sample, the mean of the results constituting the reference for assessing deviations or random errors.

Robustness in an analytical method is the resistance to change in its results when applied to individual sample aliquots under slightly different experimental conditions.

Sensitivity is the ability of an analytical method to discriminate between samples containing a similar analyte concentration or, in other words, its ability to detect (qualitative analysis) or determine (quantitative analysis) small amounts of analyte in a sample.

Selectivity is the ability of an analytical method to produce qualitative or quantitative results exclusively dependent on the analytes present in the sample.

Productivity-related properties (expeditiousness, cost-effectiveness and personnel-related factors) are attributes of analytical processes with a very high practical relevance to most analytical problems.

Expeditiousness in an analytical method is its ability to rapidly develop the analytical process from raw sample to results. Expeditiousness is often expressed as the sample frequency (i.e. in samples per hour or per day).

Cost-effectiveness is the monetary cost of analyzing a sample with a given method and is commonly expressed as the price per analyte-sample pair. This property has two basic economic components, namely: the specific costs of using the required tools and the overhead costs of the laboratory performing the analyses.

Personnel-related factors. Strictly speaking, these are not analytical properties but are occasionally essential towards selecting an appropriate analytical method. These factors include the risks associated to the use of analytical tools and the analyst's safety and comfort.

As illustrated by Figure 6, quality in the results should go hand in hand with quality in the analytical process. In other words, capital analytical properties should rely on basic properties as their supports. It is a glaring error to deal with analytical properties in isolation as it has been usual for long. In fact, these properties are mutually related in ways that can be more consequential than the properties themselves. Their relationships are discussed in detail in Section 4. Each type of analytical problem has its own hierarchy of analytical properties, which materializes in the above-described “quality compromises”.

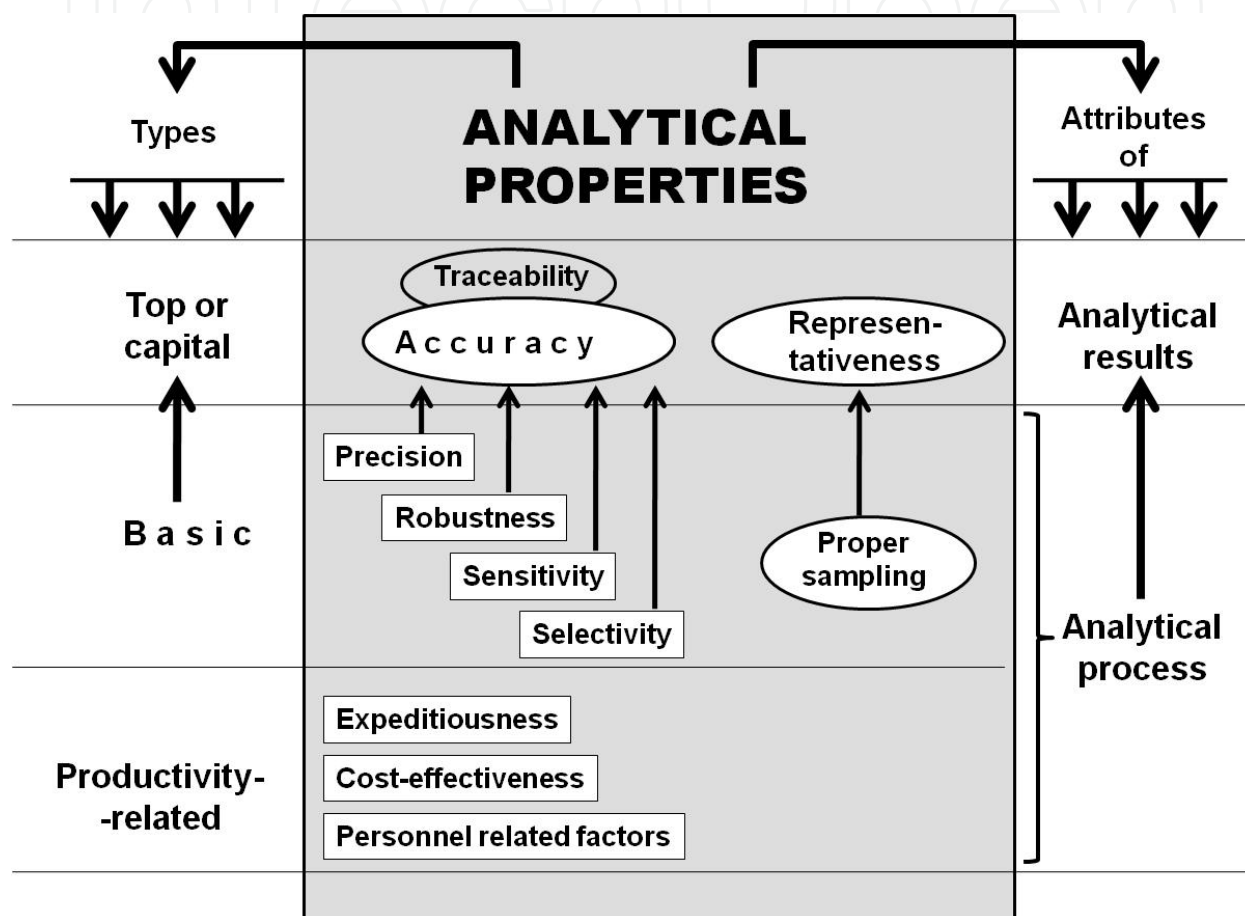


Figure 6. Holistic view of analytical properties as classified into three major groups and of their relationships with quality of the results and the analytical process. For details, see text.

3. (Bio)chemical information

The main output of (bio)chemical measurement processes is analytical or chemical/biochemical information, which is used to describe objects and systems for a variety of purposes, but especially to (a) understand processes and mechanisms in multidisciplinary approaches; and (b) provide support for grounded, efficient decision-making in a great variety of scientific, technical and economic fields. “Information” is probably the most important keyword for Analytical Chemistry, which has been aptly defined as an “information discipline” [8]. As shown below, (bio)chemical information lies in between raw data and knowledge; also, it has evolved markedly over the past few

centuries and eventually become highly influential on human life and the environment by virtue of the increasing importance attached to social responsibility in Analytical Chemistry.

“(Bio)chemical information” and “analytical information” are two equivalent terms in practice. In fact, the difference between chemical and biochemical analysis is irrelevant as it depends on the nature of the analyte (e.g. sodium or proteins), sample (e.g. soil or human plasma) and tools involved (e.g. an organic reagent or immobilized enzymes).

3.1. Contextualization

Information is the link between raw data and knowledge in the hierarchical sequence of Figure 7. *Primary* or *raw data* are direct informative components of objects and/or systems, whereas *information* materializes in a detailed description of facts following compilation and processing of data, and *knowledge* is the result of contextualizing and discussing information in order to understand and interpret facts with a view to making grounded, timely decisions. Einstein [9] has proposed *imagination* as an additional step for the sequence in critical situations requiring the traditional boundaries of knowledge to be broken by establishing new paradigms.

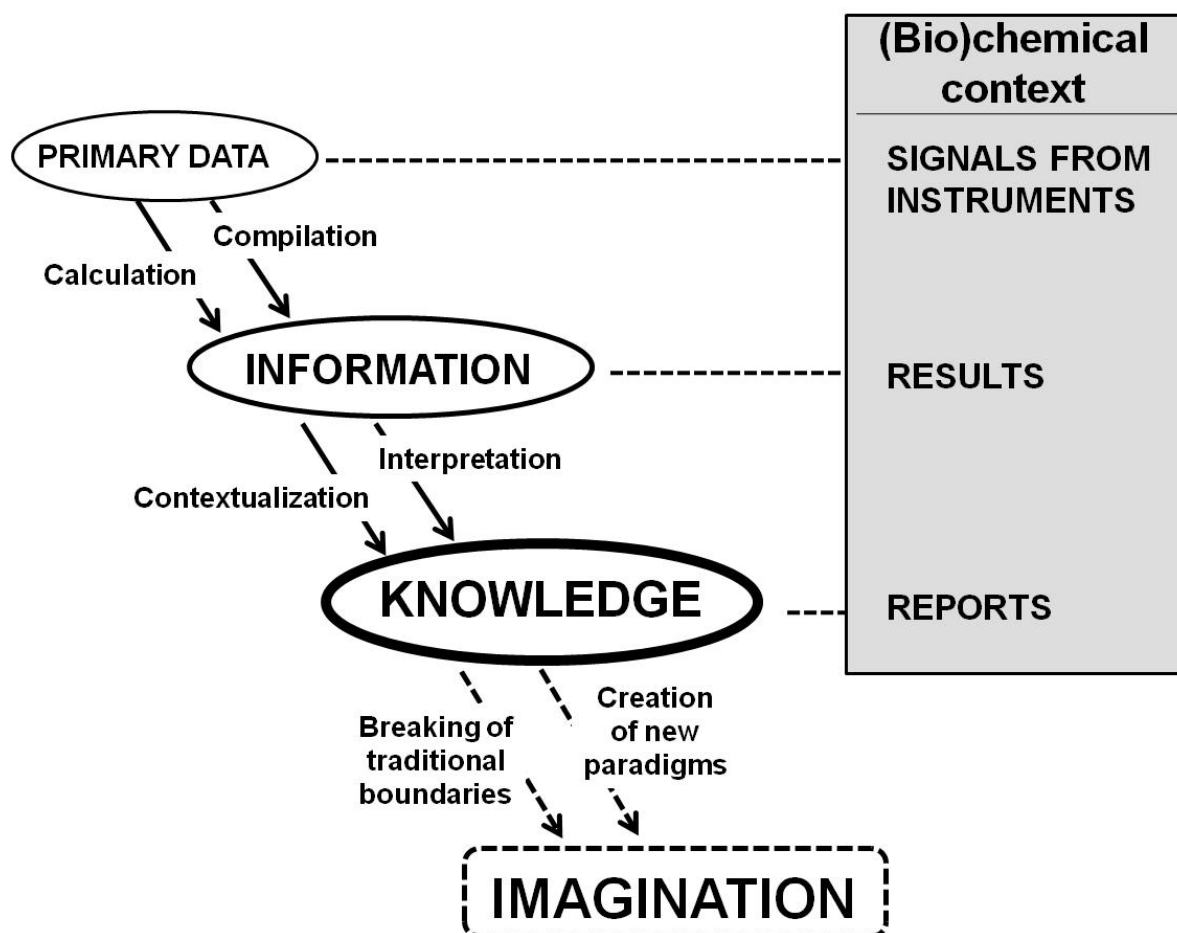


Figure 7. “Information” as an intermediate step between “raw data” and “knowledge”, and their significance in the context of chemistry and biochemistry. For details, see text.

In a (bio)chemical context, “raw data” coincide with the primary “signals” provided by instruments (e.g. absorbance, fluorescence intensity, electrical potential readings). Also, “information” corresponds to the “results” of (bio)chemical measurement processes, which can be quantitative or qualitative. Finally, “knowledge” corresponds to “reports”, which contextualize information, ensure consistency between the information required and that provided, and facilitate decision-making.

3.2. Types

Figure 8 shows several classifications of (bio)chemical information according to complementary criteria such as the relationship between the analyte(s) and result(s), the nature of the results, the required quality level in the results in relation to the analytical problem and the intrinsic quality of the results [10].

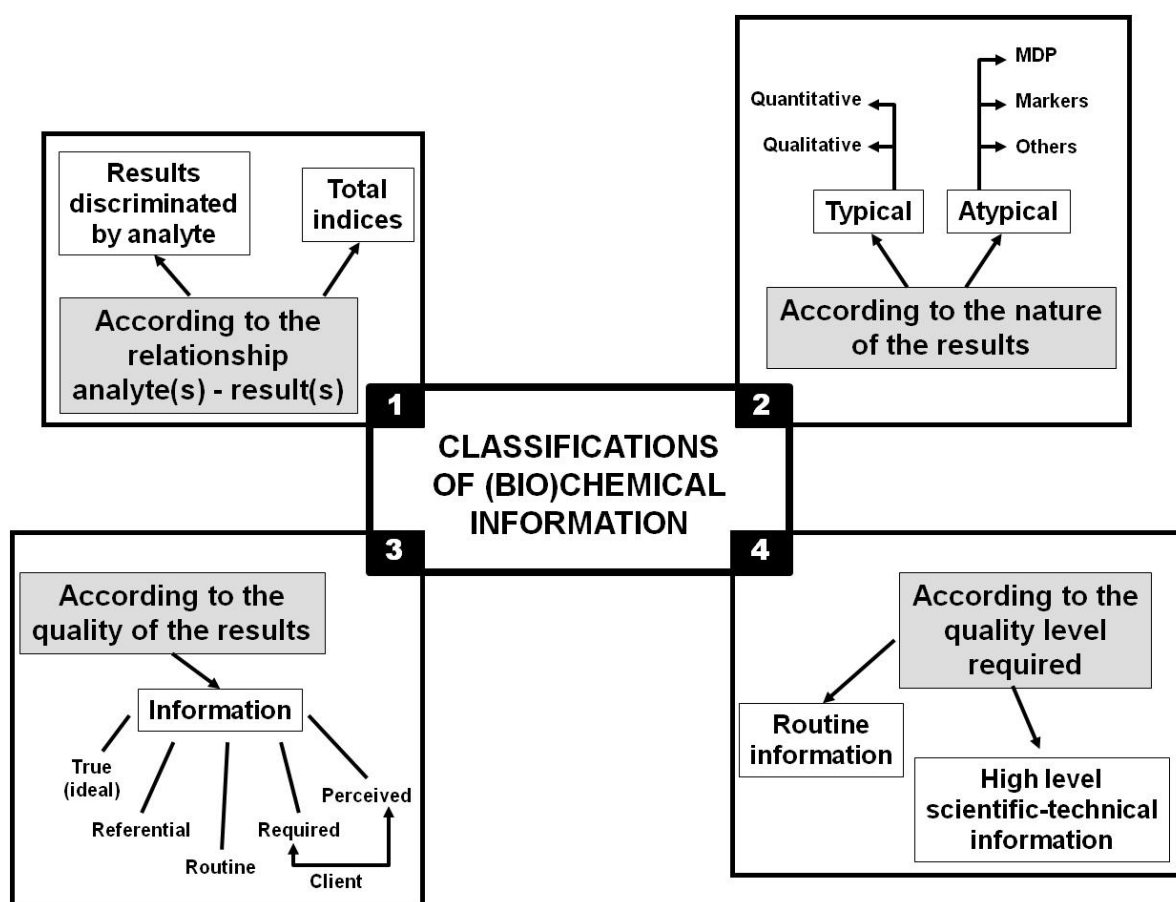


Figure 8. Four complementary classifications of (bio)chemical information based on different criteria. For details, see text.

Based on classification 1 in Figure 8, results can be discriminated by analyte (one analyte–one result), which is the most frequent situation when a separation (e.g. chromatographic, electrophoretic) is involved or when the measurement process is highly selective (e.g. immunoassays). Of increasing interest in this context are “total indices” [11], which can be defined as parameters representing a group of (bio)chemical species (analytes) having a

similar structure/nature (e.g. greases, polyphenols, PAHs, PCBs) and/or exhibiting a similar operational behavior or effect (e.g. toxins, antioxidants, endocrine disruptors). More than 50% of the information required for decision-making is of this type. A large number of validated analytical methods produce this peculiar type of output. Probably, the greatest problem to be solved here is to obtain appropriate metrological support.

Classification 2 in Figure 8 establishes two types of results: typical and atypical. Typical (ordinary) results can be quantitative (viz. numerical data with an associated uncertainty range) and qualitative (e.g. yes/no binary responses); the latter have gained increasing importance in recent times. There are also atypical results requiring the use unconventional metrological approaches in response to specific social or economic problems. Thus, so named “method defined parameters” (MDPs) [12] are measurands that can only be obtained by using a specific analytical method — which, in fact, is the standard — and differ if another method is applied to the same sample to determine the same analyte. Usually, MDPs are total indices expressed in a quantitative manner (e.g. 0.4 mg/L total phenols in water; 0.02 mg/L total hydrocarbons in water). In some cases, MDPs are empirical (e.g. bitterness in beer or wine). Some can be converted into yes/no binary responses (e.g. to state whether a threshold limit imposed by legislation or the client has been exceeded). Markers [13] are especially important analytes in terms of information content (e.g. tumor markers, saliva markers to detect drug abuse).

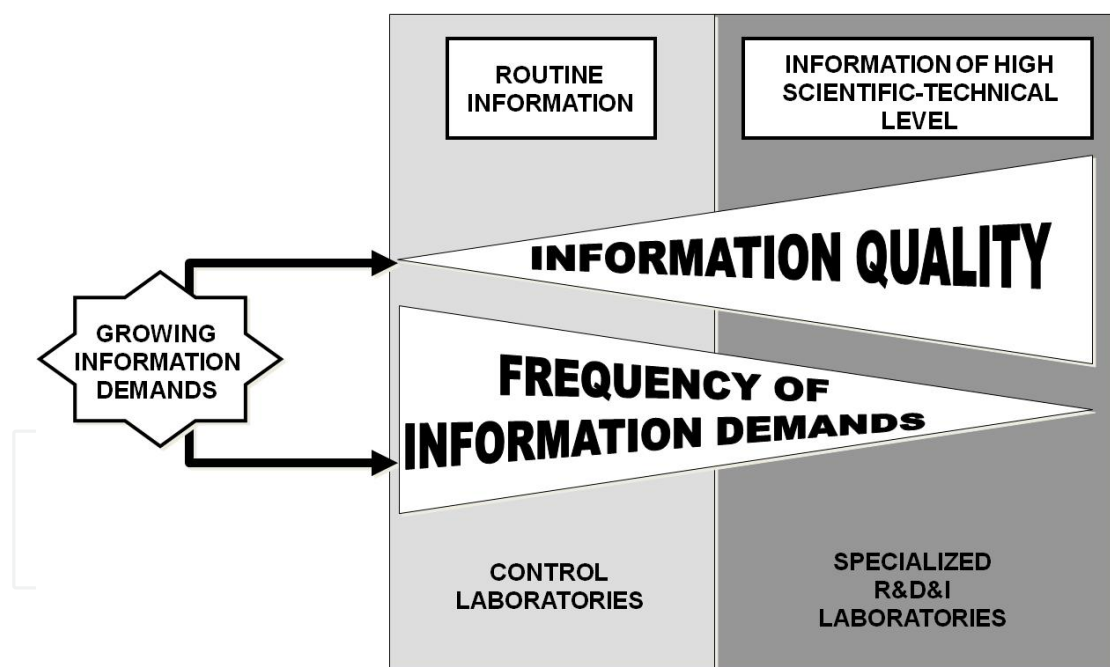


Figure 9. Contradiction between the frequency of information demands and the level of quality required in a situation of growing demands for (bio)chemical information. For details, see text.

Classification 3 in Figure 8 is based on the quality level of the results required in response to the client’s information needs and comprises (a) routine information provided by control laboratories analyzing environmental, industrial, clinical or agrifood samples, for example; and (b) information of a high scientific and technical level that can only be obtained by using sophisticated instrumentation in specialized laboratories usually involved in R&D activities.

The frantic recent changes in social and economic activities have promoted an impressive expansion of (bio)chemical information about objects and systems. As can be seen in Figure 9, the quality of (bio)chemical information increases from routine laboratories to specialized laboratories, whereas the frequency of information demands decreases in the same direction. A compromise must often be made between these two contradictory notions. The panoramic view of Figure 9 is essential to perceive all connotations of analytical information. Classification 4 in Figure 8 is based on the intrinsic quality of the results and is examined in detail in Section 4 of this chapter.

3.3. Evolution

The routine information provided by control laboratories has evolved dramatically in the last decades. Figure 10 summarizes the most salient general trends in this context, which are commented on briefly below.

1. *Simplification.* Instead of delivering large amounts of high-quality information (a classical paradigm in Analytical Chemistry), there is a growing trend to delivering the information strictly required to make grounded decisions while avoiding time-consuming efforts to obtain oversized information that is useless in practice. Specially relevant here is the third basic standard supporting Analytical Chemistry (see Figure 4). The situation is quite common in routine laboratories but should be minimized or avoided altogether. Such is the case, for example, with the determination of hydrocarbons in tap water, the legal threshold limit for which is 0.1 ng/mL total hydrocarbons. Using a classical method involving several steps (e.g. filtration, cleanup, solvent changeover) and sophisticated equipment (e.g. a gas chromatograph and mass spectrometer) allows a long list of aliphatic and aromatic hydrocarbons with their concentrations —usually at the ppt or even lower level— to be produced which is utterly unnecessary to make grounded decisions, especially when a simplified method (e.g. one involving extraction into Cl_4C and FTIR measurement of the extract) can be used instead to obtain a total index totally fit for purpose.

2. *Binary responses.* Qualitative Analysis has been revitalized [14] by the increasing demand for this type of information; in fact, clients are now more interested in yes/no binary responses than in numerical data requiring discussion and interpretation. This trend is related to the previous one because obtaining a simple response usually entails using a simple testing method. The greatest challenge here is to ensure reliability in the absence of firm metrological support. In any case, false negatives should be avoided since they lead to premature termination of tests; by contrast, false positives can always and are commonly confirmed by using more sophisticated quantitative methodologies (see Section 5.4 and Figure 14).

3. *Total indices.* Based on classification 1 in Figure 8, a result can be a total index [11] representing a group of analytes having a common structure or behavior. This type of information is rather different from classical information, which is typically quantitative and discriminated by analyte. For example, the total antioxidant activity of a food can be easily determined with a simple, fast method using a commercially available dedicated analyzer. This avoids the usual

procedure for determining antioxidants in foodstuffs, which involves time-consuming sample treatment and the use of sophisticated instruments (e.g. a liquid chromatograph coupled to a mass spectrometer). This trend is also related to simplification and is rendering the classical paradigm of Analytical Chemistry (viz. maximizing selectivity) obsolete.

4. *Increasing importance of productivity-related properties.* The holistic approach to analytical properties of Figure 6, which considers hierarchical, complementary and contradictory relationships between them, and systematically using information needs as the third basic analytical reference (Figure 4), provide solid support for the increasingly popular productivity-related analytical properties (expeditiousness, cost-effectiveness and personnel-related factors). These properties are in contradiction with capital and basic analytical properties. Thus, achieving a high accuracy is not always the primary target and, in some cases, productivity-related properties are more important than capital properties. Such is the case with so named “point of care testing” approaches [15], the best known among which is that behind the glucose meter used to monitor the glucose level in blood at home. Glucose meter readings are inaccurate but rapid and convenient enough to control diabetes.



Figure 10. Major trends in the characteristics of (bio)chemical information provided by routine laboratories. For details, see text.

5. *Use of positive approaches to produce reports from results.* Analysts tend to emphasize negative aspects in delivering results and reports. A dramatic impulse of their “marketing abilities” to communicate with clients is therefore needed. One case in point is the word “uncertainty”, inherited from Metrology in Physics and introduced in Metrology in Chemistry during the last few decades. This word can lead to wrong interpretations in chemistry nonmajors (e.g. politicians, economists, managers, judges) and raise global doubts about results. Simply replacing “uncertainty” with “confidence interval”, which has the same scientific and technical meaning, can facilitate interpretation and acceptance of the results [16]. One other typical case is the use of “false positives” and “false negatives” to describe errors in binary responses. There is an obvious need to revise the terms related with (bio)chemical information and find alternatives emphasizing positive aspects rather negative connotations.

4. Analytical quality

An integral approach to quality should rely on the following essential components: (1) the basic connotations of the concept as related to a set of features and comparisons, which in Analytical Chemistry materialize in analytical properties (Figure 6) and the three basic standards (Figure 4); (2) the practical connotations of fulfilling the (bio)chemical information needs posed by clients, which is one of the essential aims of Analytical Chemistry (Figure 3); and (3) the measurability of quality in terms of the capital, basic and productivity-related properties for analytical methods and their results.

Classification 3 in Figure 8 allows (bio)chemical information types to be depicted as shown in Figure 12, which additionally shows their mutual relationships via a tetrahedron. The arrows in the figure represent tendencies to converge –in the ideal situation, the tetrahedron could be replaced with a single, common point. Below is briefly described each member of the tetrahedron.

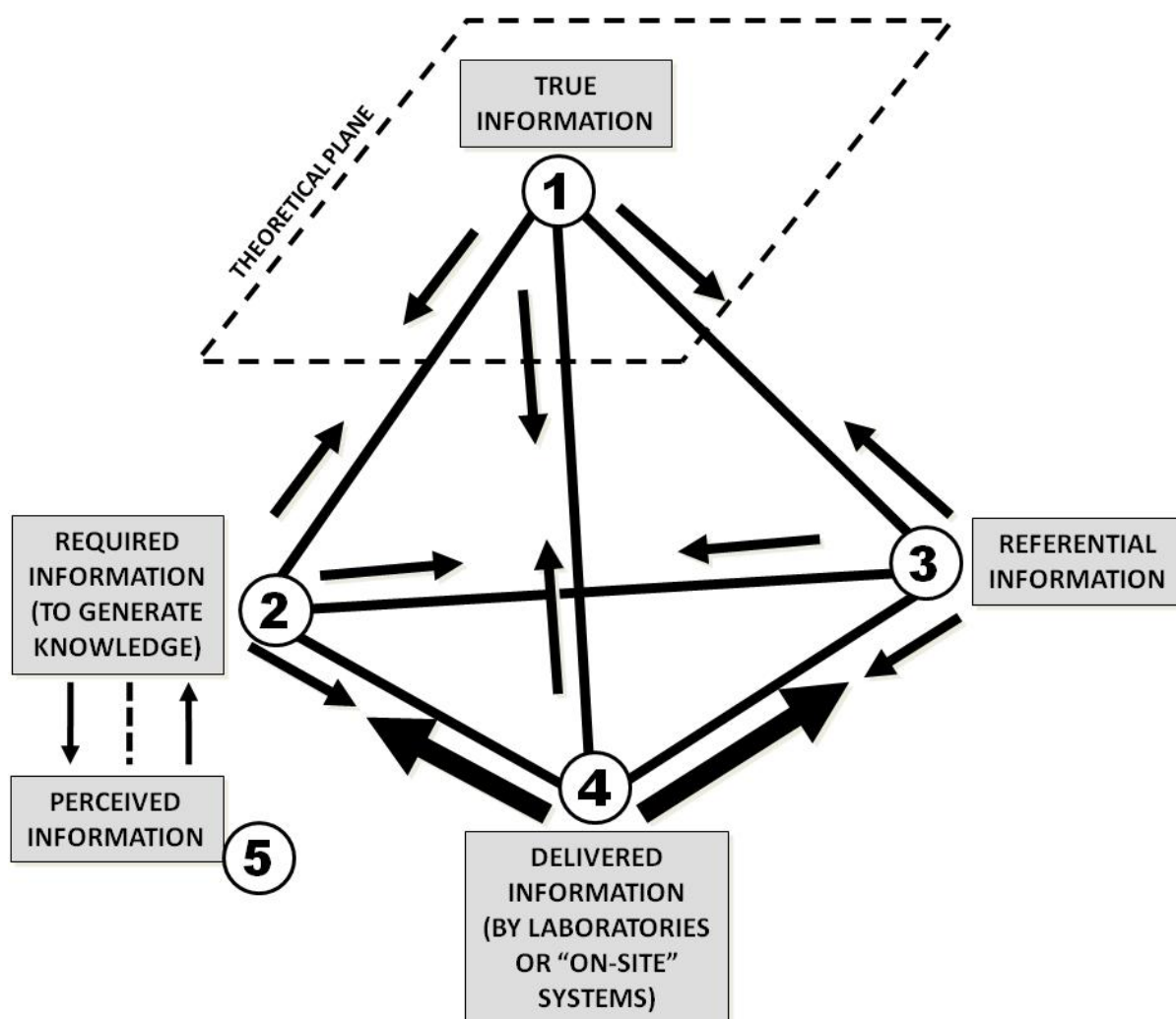


Figure 12. Types of analytical information according to quality and location in a tetrahedron. (1) denotes the ideal situation, in clear contrast with the other types (triangle 2–3–4). The triangles 1–2–4 and 1–3–4 represent problem solving and Metrology in Chemistry, respectively. For details, see text.

1. *True information* corresponds to intrinsic information about objects or systems. It is subject to no uncertainty and hence equivalent to trueness, which is unavailable to analysts. It is also known as “ideal analytical quality”.

2. *Referential information* corresponds to the highest quality level that can be achieved in practice, with the information about a certified reference material (CRM) as the most typical example. Referential information is usually obtained in interlaboratory exercises where nonroutine laboratories analyze the same sample under the supervision of a renown organization (e.g. NIST in USA). Certified reference materials and their associated values are essential with a view to assuring quality in analytical methods and their results. The main problem here is their limited availability. In fact, only 3–5% of current needs for CRMs in (bio)chemical analysis have been met, in clear contrast with up to 90–95% in Metrology in Physics. Under these conditions, analysts are very often compelled to use alternative strategies to validate new analytical methods (e.g. standard addition procedures involving pure analytes).

3. *Routine information* is that produced by control laboratories or on-site systems operating outside the laboratory and largely used to control the quality of foodstuffs, industrial products or the environment.

4. *Required information* is that demanded by clients to make grounded, timely decisions and constitutes the third basic analytical standard (see Figure 4), which is frequently disregarded despite its high relevance to the major aims and objectives of Analytical Chemistry (see Figure 3).

5. *Perceived information*, which can be of a similar, higher or lower quality than that actually required by the client. Ideally, a client's perceived and required information should coincide. In some cases, the information delivered falls short of that required and can thus be deemed of low quality. Such is the case, for example, with the toxicological characterization of seawater by potential mercury contamination. The total mercury concentration is inadequate for this purpose because the toxicity of mercury species differs with their nature (inorganic, organometallic). It is therefore necessary to provide discriminate information for each potentially toxic mercury species.

The sides of the tetrahedron of Figure 12 represent the relationships between the different types of analytical information [19]. There are two contradictory relationships (forces) arising from delivered analytical information of great significance to Analytical Chemistry, namely: (1) the relationship between required and delivered information (2–4 in Figure 12), which represents problem solving and is related to the second aim of the discipline (see Figure 3); and (2) that between routinely delivered information and referential information (3–4 in Figure 12), which coincide at the highest metrological quality level — the first aim of Analytical Chemistry (Figure 3). One other significant distinction is that between required and perceived information on the client's side. Analytically, the most convenient situation is that where both types of information coincide in their level of quality — even though it is desirable that the client's perception surpass the actual requirements.

There are thus two contradictory facets of Analytical Chemistry that coincide with the its two aims, namely: a high level of metrological quality and fulfilling the client's information needs (see Figure 3). Analytical Chemistry is located at their interfaces [4]. There are some apparent conflicts, however, including (1) contradictory relationships of capital and basic analytical properties with productivity-related properties (see Figure 6); (2) failing to include required information among basic standards (see Figure 4); and (3) conceptual differences in analytical excellence between metrology and problem solving.

5. Major challenges

Achieving the general aims and objectives of Analytical chemistry in today's changing world requires producing tangible (reagents, sorbents, solvents, instruments, analyzers) and intangible means (strategies, calibration procedures, advances in basic science) to facilitate the development of new analytical methods or improvement of existing ones. This, however, is beyond the scope of this section, which is concerned with general trends in this context.

1. A sound balance between metrological and problem solving approaches for each information demand. The situation in each case depends strongly on the specific type of information and its characteristics (see Figure 8). With routine information, the challenge is to adopt well-defined quality compromises, which usually involves selecting and adapting analytical processes to fitness for purpose. Obtaining information of a higher scientific–technical level (e.g. that for materials used in R&D&I processes) calls for a high metrological quality level, as well as for exhaustive sample processing and sophisticated laboratory equipment.

2- Information required from objects/systems far from the ordinary macroscopic dimensions. These target objects or systems are directly inaccessible to humans because of their location or size. The size of such objects can fall at two very distant ends: nanomatter and outer space.

Analyzing the nanoworld is a real challenge for today's and tomorrow Analytical Chemistry. Extracting accurate information from nanostructured matter requires adopting a multidisciplinary approach. Nanotechnological information can be of three types according to nature; all are needed to properly describe and characterize nanomatter. Figure 13 shows the most salient types of physical, chemical and biological information that can be extracted from the nanoworld. Nanometrology, both physical and chemical, is still at an incipient stage of development. There is a current trend to using powerful hybrid instruments affording the almost simultaneous extraction of nanoinformation by using physical (e.g. atomic force microscopy, AFM) and chemical techniques (Raman and FTIR spectroscopies, electrochemistry).

The extraction of accurate information from objects and systems in outer space is a challenge at the other end of the "usual" range. This peculiar type of analysis uses miniaturized instruments requiring little maintenance and energy support. There are three different choices in this context, namely: (a) remote spectrometric analyses from spacecrafts with, for example, miniaturized X-ray spectrometers [20] or miniaturized mass spectrometers for the analysis of cosmic dust [21]; (b) analyses implemented by robots operating on the

surface of other planets (e.g. to find traces of water in Mars [22], by using laser ionization-mass spectrometers [23]); or (c) monitoring of the inner and outer atmospheres of spacecrafts [24,25].

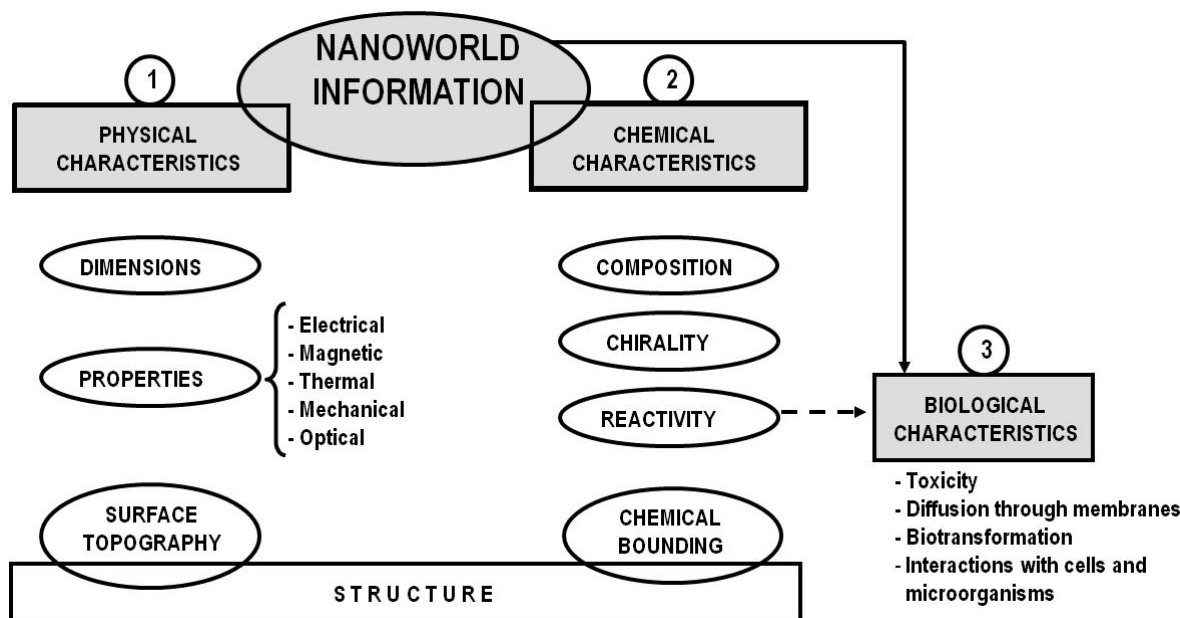


Figure 13. Types of information that can be extracted from the nanoworld. For details, see text.

3. *Breaking the traditional boundaries of the analytical laboratory.* To be consistent with its present aims and objectives (Figure 3), Analytical Chemistry cannot be exclusively confined inside the laboratory walls. In fact, it is necessary to open laboratory doors and analysts' minds in at least two complementary ways, namely:

(a) Analytical Chemistry should play an active role in activities preceding and following the development of analytical processes. Analytical chemists should play a twofold external role here by participating in the design and control of sampling procedures, and also in the discussion and interpretation of analytical results with other professionals in a multidisciplinary approach to transforming information (results) into knowledge (reports).

(b) Analytical Chemistry is increasingly focusing on the production of primary data from (automated) analytical processes implemented with so named "on site" systems outside the laboratory. These systems accumulate or send the requested primary data or results to a central laboratory. In the industrial field, on site monitoring can be performed "in-line" or "on-line". In clinical analysis, points of care testing systems (POCTs) [15] are extensively used for this purpose. The development of robust, reliable sensors for a broad range of analytes in a variety of sample types is a major challenge in this context, where automated calibration and quality control are the two greatest weaknesses.

4. *Vanguard–rearguard analytical strategies* [26]. As can be seen from Figure 9, the demand for (bio)chemical information has grown dramatically in the past decade and will continue to grow in the next. As a consequence, conventional analytical laboratories have been rendered unable to accurately process large numbers of samples each day. This has raised the need

for a new strategy (an intangible R&D&I analytical product according to Figure 5) intended to minimize the negative connotations of conventional sample treatment steps and facilitate the adoption of quality compromises between metrology and problem solving. This strategy uses a combination of vanguard (screening) systems and rearguard (conventional) systems as illustrated in Figure 14.

Vanguard analytical systems are in fact sample screening systems (SSS) [27,28] which are used in many activities where information is rapidly needed to make immediate decisions in relation to an analytical problem. Their most salient features are as follows: (a) simplicity (*viz.* the need for little or no sample treatment); (b) a low cost per sample–analyte pair; (c) a rapid response; (d) the production of atypical results (binary responses, total indices, method-defined parameters); and (e) reliability in the response. These systems act as mere sample filters or selectors and their greatest weakness is the low metrological quality of their responses —however, uncertainties up to 5–15% are usually accepted as a toll for rapidity and simplicity, which are essential and in contradiction with capital analytical properties. Sample screening systems provide a very attractive choice for solving analytical problems involving high frequency information demands. If these systems are to gain widespread, systematic use, they must overcome some barriers regarding accuracy (*viz.* the absence of false negatives for rapid binary responses), metrological support (traditionally, norms and guides have focused almost exclusively on quantitative data and their uncertainties) and commercial availability (e.g. in the form of dedicated instruments acting as analyzers for determining groups of analytes in a given type of sample such as antioxidants in foodstuffs or contaminants in water).

Rearguard analytical systems are those used to implement conventional analytical processes. Their most salient features are as follows: (a) they require conventional, preliminary operations for sample treatment and these involve intensive human participation and are difficult to automate (e.g. dissolution, solid and liquid extraction, solvent changeover); (b) they also usually require sophisticated instruments (e.g. GC–MS, GC–MS/MS, GC–FTIR/MS, LC–MS, LC–ICP–MS, CE–MS); (c) they afford high accuracy as a result of their excellent sensitivity and selectivity; (d) they use powerful primary data processing systems supported by massive databases easily containing 5000 to 50 000 spectra for pure substances, which ensures highly reliable results; (e) they usually provide information for each individual target analyte in isolation; and (f) they are expensive and operationally slow, but provide information of the highest possible quality level.

An appropriate combination of these two types of systems allows one to develop *vanguard–rearguard analytical strategies* (see Figure 14). With them, a large number of samples are subjected to the vanguard (screening) system to obtain binary or total index responses in a short time window. The output is named “crash results” and can be used to make immediate decisions. In fact, the vanguard system is used as a sample “filter” or selector to identify a given attribute in a reduced number of samples (e.g. a toxicity level exceeding the limit tolerated by law or by clients) which are subsequently processed systematically with the rearguard analytical system to obtain quantitative data and their uncertainty for each

target analyte. The rich information thus obtained can be used for three complementary purposes, namely: (1) to confirm the crash results of vanguard systems (e.g. positives in binary responses to ensure that they are correct); (2) to amplify the simple (bio)chemical information provided by vanguard systems and convert global information about a group of analytes into discriminate information for each for purposes such as determining relative proportions; and (3) to check the quality of vanguard systems by using them to process a reduced number of randomly selected raw samples according to a systematic sampling plan.

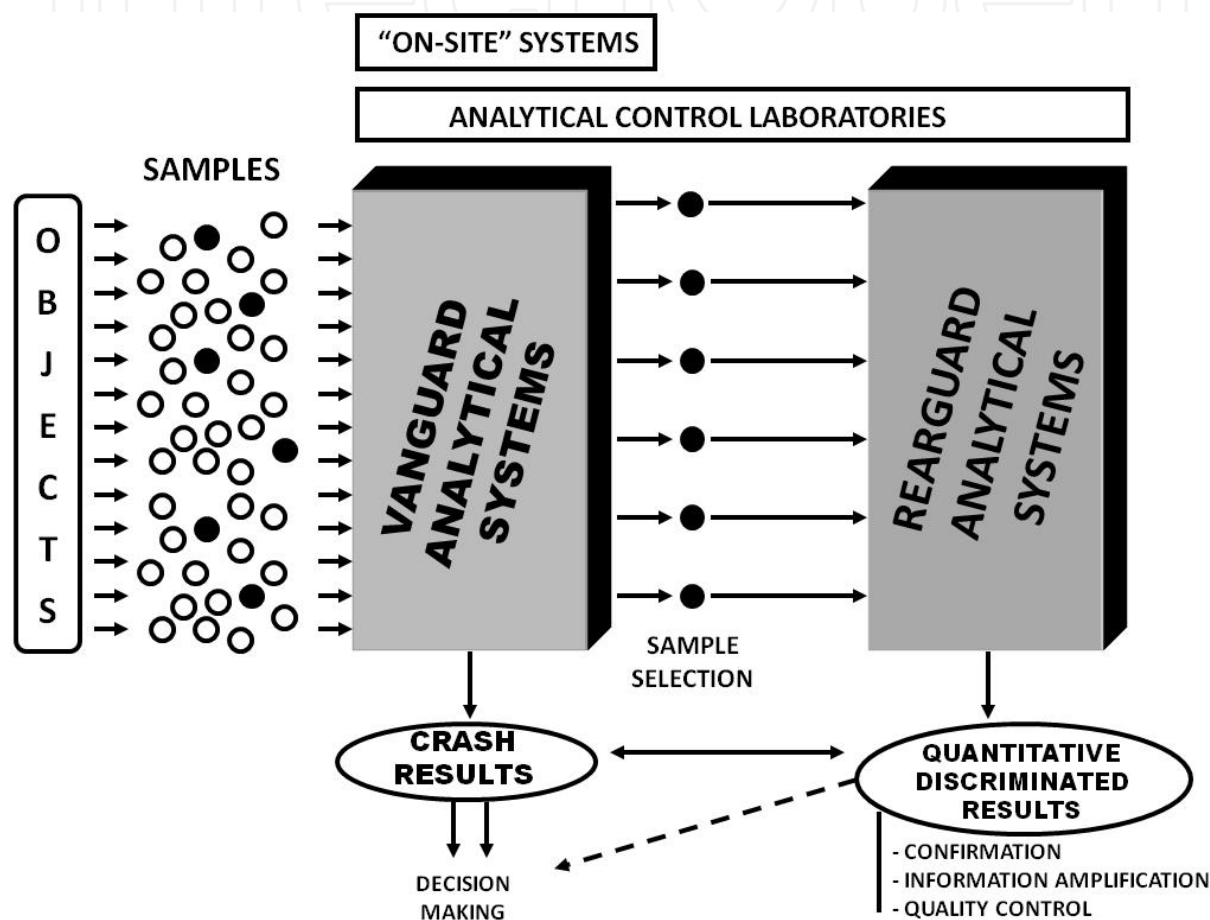


Figure 14. Vanguard–rearguard analytical strategies for the systematic analysis of large numbers of samples. For details, see text.

List of acronyms

R&D&I	Research, Development and Innovation
ISO	International Organization for Standardization
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
MDPs	Method Defined Parameters
FTIR	Fourier Transform Infrared Spectroscopy
SR	Social Responsibility

SRAC	Social Responsibility of Analytical Chemistry
CRM	Certified Reference Material
NIST	National Institute of Standards and Technology (USA)
AFM	Atomic Force Microscopy
POCTs	Point-of-Care-Testing
SSS	Sample Screening Systems
GC-MS	Gas Chromatography – Mass Spectrometry coupling
GC-MS/MS	Gas Chromatography – Mass Spectrometry / Mass Spectrometry coupling
GC-FTIR/MS	Gas Chromatography – Fourier Transform Infrared Spectroscopy / Mass Spectrometry coupling
LC-MS	Liquid Chromatography – Mass Spectrometry coupling
LC-ICP-MS	Liquid Chromatography – Inductively Coupled Plasma Spectrometry – Mass Spectrometry coupling
CE-MS	Capillary Electrophoresis – Mass Spectrometry coupling

Author details

Miguel Valcárcel

Faculty of Sciences of the University of Córdoba, Spain

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