

Review

Food for Thought: A Critical Overview of Current Practical and Conceptual Challenges in Trace Element Analysis in Natural Waters

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Abstract: The practical and conceptual challenges faced by the analysis of trace elements present in natural waters are not merely, as is often thought, an endless race towards lower detection limits or to the development of techniques allowing the determination of any possible chemical species formed by all chemical elements. Rather, as discussed in this paper, they include the development of (i) robust, cheap, and reliable methods that could also be used by laypeople (the experience gained in the development of field kits for As is discussed as an example from which similar developments for other elements may be drawn); (ii) more environmentally-friendly methods (the current guiding criteria probably being too simplistic); and (iii) methods making it possible to follow diel concentration changes and sharp concentration variations caused by the probable increase of heavy rainfall events. This paper also claims that neither the measurement of total concentrations (reliable methods are lacking for many elements of the periodic table of trace elements, as illustrated through the cases of Bi, Te, and Sb), nor chemical speciation analysis, are as mature as often thought. In particular, chemical speciation studies demand the development of a better, comprehensive conceptual framework. A trial is carried out to lay the basis of such a framework.

Keywords: natural waters; freshwaters; seawater; trace elements; chemical speciation; green analytical chemistry; arsenic; antimony; tellurium

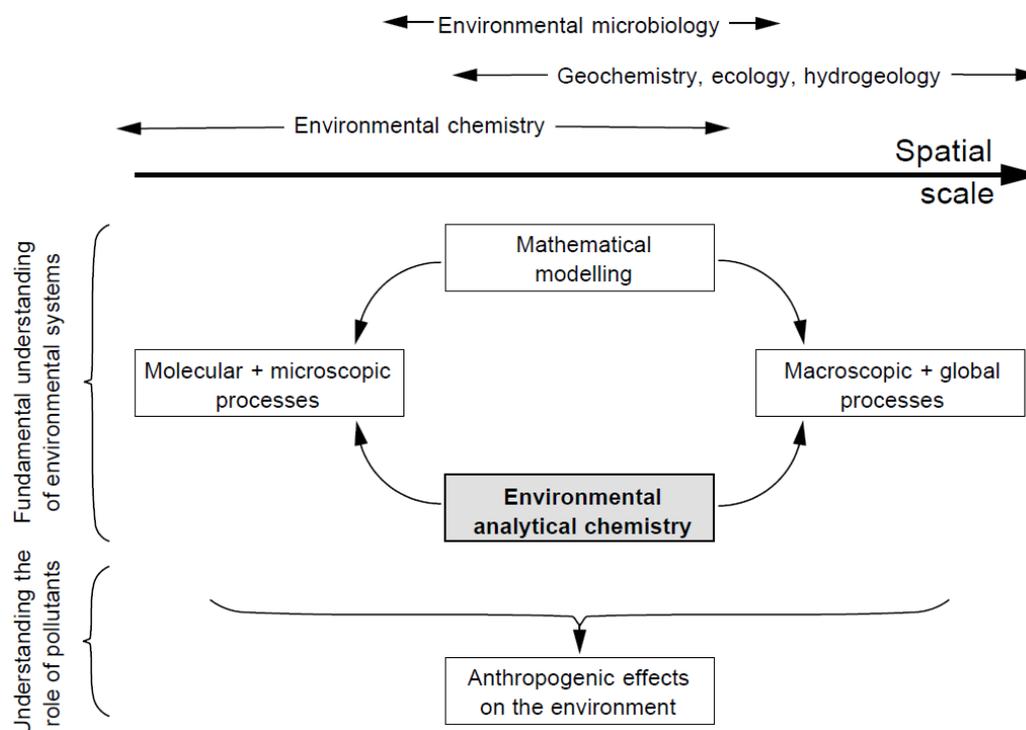
Abbreviations

APDC:	ammoniumpyrrolidinedithiocarbamate
CA:	component additivity
CRM:	certified reference material
DGT:	diffusion/diffusive gradient in thin films
ETTAS:	electrothermal atomic absorption spectrometry
ETV:	electrothermal vaporization
EVISA	European Virtual Institute for Speciation Analysis
GC:	gas chromatography
GC:	generalized composite
HG-AAS:	hydride generation atomic absorption spectrometry
ICP-MS:	inductively coupled plasma mass spectrometry
IUPAC:	International Union of Pure and Applied Chemistry
γ -MPTMS:	γ -mercaptopropyltrimethoxysilane
NAA:	neutron activation analysis
UNICEF:	United Nations Children's Fund
WHO	World Health Organisation
XAD	type of resin

1. Introduction

Analytical chemistry has constantly played a key role in the long road towards understanding the functioning of aquatic systems and solving the problems created by pollution (Figure 1). Analytical chemistry helped face the successive challenges that the 20th century brought in the maintenance of water as a vital resource. We can mention, for instance, freshwater eutrophication in the 1960s and 1970s in Europe and the USA (a problem that, still today, is one of the main causes of degradation of water quality in many parts of the globe), problems associated with acid rain in the 1980s, or pollution by organic micropollutants (with pesticides from the 1970s, PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons) in the 1970s and 1980s, and endocrine disruptors today). In all of these cases, analytical chemistry has made it possible to evaluate the extent of the problem and lay the foundations for understanding and possibly solving them. At present, a debate is needed to define the real needs and perspectives of analytical chemistry in relation to the future of the analysis of natural waters. On the one hand, it is a mature discipline, with a widely consolidated body of knowledge (though not necessarily applied at the same level everywhere) while, on the other hand, new refined and expensive techniques are constantly being developed, especially for analyzing organic compounds and, to a lesser extent, for measuring chemical species of trace elements. What are the real challenges today? Are they reduced to the development of cutting-edge techniques for the determination of organic pollutants, whose number is constantly increasing?

Figure 1. Situation of analytical chemistry in the context of environmental chemistry. Analytical chemistry links the macroscopic and global processes with those occurring at the molecular and microscopic level under both undisturbed systems and those subject to contamination systems. Adapted from [1] with permission.



The development of new analytical methods has been, and remains, largely driven by ecotoxicity and human toxicity concerns. As is well known, the development of new analytical methods plays a key role in the study of the toxicity of elements or compounds (just remember Minamata [2] or *Silent Spring* [3]). However, the relationship between analytical development, regulation and toxicological tests is complex. For instance, it has been suggested that the phenomenon of the constant decrease of detection limits (vanishing zero creep effect) involved in the continuous improvement of analytical techniques could lead to tighter regulation, regardless of the requirements of toxicological data, with the ensuing unnecessary economic and social costs. A recent study [4], based on the case of the USA, does not seem to confirm this claim, but nonetheless illustrates the complexity of the relationship between regulation, detection limits, cost-benefit analysis, and toxicological data.

Nor should one overlook the role played by non-scientific considerations in the development of new analytical methods. Although the idea that analytical methods are developed by researchers in universities and research centers driven by purely scientific interests still prevails, the fact is that new methods often require the use of expensive equipment and thus necessarily entail that a significant part of the development is carried out either directly by commercial firms or by research groups with strong support from such firms. It is difficult to assess the extent to which purely commercial interests may favor the development of certain techniques over others that generate less profit for the manufacturers. Cause-effect relationships are difficult to prove in this as in closer fields (see, e.g., [5], in the case of the relationship between academic studies and the pharmaceutical industry). However, a quick look at the EVISA (European Virtual Institute for Speciation Analysis) website (“the primary source of

information for speciation analysis”) [6] suggests that the support of commercial firms probably has an effect on the weight given to different analytical techniques.

Ideally, present and future developments of analytical chemistry in the field of analysis of natural waters have to be situated in the context of a broader reflection on water as a necessary resource. Water is often considered a renewable resource because it is thought to be unlimited but this is not strictly true. Groundwaters are a clear example that water is not an unlimited resource in the literal sense of the term, as they are overexploited worldwide and recharge rates are not enough to refill the aquifers. Nor is water a renewable resource in the broader sense because the term “renewable” means restoration of a resource in its previous state and current water pollution, linked to an increasing human pressure, results everywhere in a state far from the initial one. As pointed out by Jerald Schnoor [7], editor of the journal *Environmental Science & Technology*, it is not just the abuse of non-renewable resources which is unsustainable in today’s world but the abuse of renewable resources, which irreversibly diminish as a result of unsustainable practices (e.g., groundwater extraction, pollution, overfishing of the seas, *etc.*). Against this background, the needs that analytical chemistry has to address when applied to natural waters become apparent.

2. Main Challenges

2.1. Total Concentrations

It is generally assumed that determining total element concentrations in water is a “solved” issue, but the fact is that, while this might be true for the most common elements, it is not at all the case for the many that have received less attention; these elements account for a significant part of the periodic table. The lack of appropriate analytical methods for many elements has become a pressing problem in recent years because many everyday objects have become more complex and require the use of an increasing portion of the periodic table. Objects in a household, 20–30 years ago, depended on a total of perhaps 20 elements, but clean energy and information technologies now use most of the first 80 elements of the periodic table. For instance, while computer chips from the 1980s contained 11 elements, growing to 15 in the 1990s, future chips will include up to 50–60 elements. A typical smartphone already contains up to 60 chemical elements [8]. However, no toxicological data are available on many of these “new” elements and, often, analytical methods for detecting and measuring them in natural waters are simply not available. When analyzing some cases in detail, a pessimistic scenario appears. The case of Bi is a good example. This element has been described as an “amazingly green environmentally-minded element” and proposed as nontoxic substitute for other harmful elements such as Pb. However, a recent study [9] has shown that, despite the existence of 125 studies containing Bi concentration values, at present the concentration of the element in fresh and marine waters is not known with any degree of certainty. Discouragingly, the same study showed that most of the analytical methods developed for the determination of Bi in water since 2000 had inadequate detection limits and that, in spite of this, managed to get through the peer-review process and got published.

Unfortunately, this situation is common to many other trace elements. Let us analyze in detail the case of another less-studied element, Te, not just because of the intrinsic interest of the element but

because it helps to illustrate the problem. Figure 2 shows published values of Te concentration in surface seawaters. The most recent value found, 910 pg L^{-1} , in water “from the Mediterranean” [10] has not been included because it is out of scale. Studies where Te concentrations were below the detection limit of the technique applied are not included. Some immediate features appear: (i) very few values have been published; (ii) a cluster of values is situated around 0.5 pg L^{-1} but all the rest are found in the tenths of pg L^{-1} concentration range; (iii) no value less than 1 pg L^{-1} appears to have been published since 1990 (33 years ago). How can one decide which value is the right one? Accuracy is usually checked by using certified reference materials (CRM) but, in this case, their use is only mentioned in two cases [11,12] and the Te concentrations in the CRM used are much higher than expected seawater concentrations (100 $\mu\text{g mL}^{-1}$ [11] and 1 ng mL^{-1} [12]). Analytical methods used were (number of studies in brackets): colorimetry (1), catalytic polarography (1), HG-AAS (4), NAA (1), ICP-MS (2), ETV-ICP-MS (1), and ETTAS (1), and no apparent relationship seems to exist between the method chosen and the range of Te concentration measured. In fact, as is the case for many elements in seawater [13], most analytical methods are not sensitive enough and preconcentration procedures are needed. In the case of Te, a variety of preconcentration methods were used: coprecipitation with $\text{Mg}(\text{OH})_2$, alkaline precipitation, sorption on XAD-bismuthiol resin, “thiolcotton”, active carbon, γ -MPTMS modified silica coated magnetic nanoparticles, different Separon™ SGX sorbents, and dispersive liquid–liquid microextraction with APDC. Again, no apparent relationship between the type of preconcentration and the level of the values is found. Finally, a further complication exists in the case of Te. This element exists in two redox states and only one, Te(IV), is detectable by some methods (e.g., voltammetry, HG-AAS). This means that it is necessary to reduce any possible Te(VI) present in the sample prior to any measurement and that, if this reduction is performed (as is usually the case) after preconcentration, both Te(VI) and Te(IV) are equally preconcentrated. Not all published studies detail the method used. Different reduction methods have been applied: acid HBr treatment, boiling with HCl, L-cysteine addition (not always under the same conditions and reagent concentrations). It is difficult to judge from the articles whether reduction was complete, analyte was lost during the boiling process, *etc.* My personal experience is that complete reduction is difficult to achieve. As redox speciation of Te in seawater is not yet well characterized, it is impossible to judge the degree of underestimation of total concentrations that might be implied by the lack of a reduction step or by incomplete reduction. Thus, in practice, it is currently impossible to know what the concentration of Te in seawater is and which is the best technique to use.

It might be argued that the two examples discussed, Te and Bi, are “orphan” elements, which is true, and that they do not reflect the overall situation. However, a troubling further case can be added as a further proof of concept. It concerns Sb. Antimony has become a fashionable element to study these last 10–12 years and the number of publications on the environmental behavior of the element have soared. A review published before the current “boom” [14] included the figure reproduced in Figure 3a. This review stated “The observed decrease in antimony concentrations as well as in data scatter with time reflect the parallel improvement of the analytical techniques available” and put forward a tentative value of $184 \pm 45 \text{ ng L}^{-1}$ for seawater from values published after 1985. However, when this set of data is updated, a different picture emerges (Figure 3b) (new points added as red diamonds) with many high, probably unreasonable values having been published recently. These values mostly correspond to analytically-oriented papers where few details are usually given about

sampling points and sample characteristics. How could these disperse values go through the publication system in respected journals? In this case, unlike that of Bi, reasonable values that could have been used as reference by authors, referees and editors exist. Lastly, do we really need more methods for the determination of Sb in seawater?

Figure 2. Published tellurium concentrations for surface seawater as a function of their year of publication. The insight shows the same data with a different scale in the y-axis. Data from [11,12,15–22].

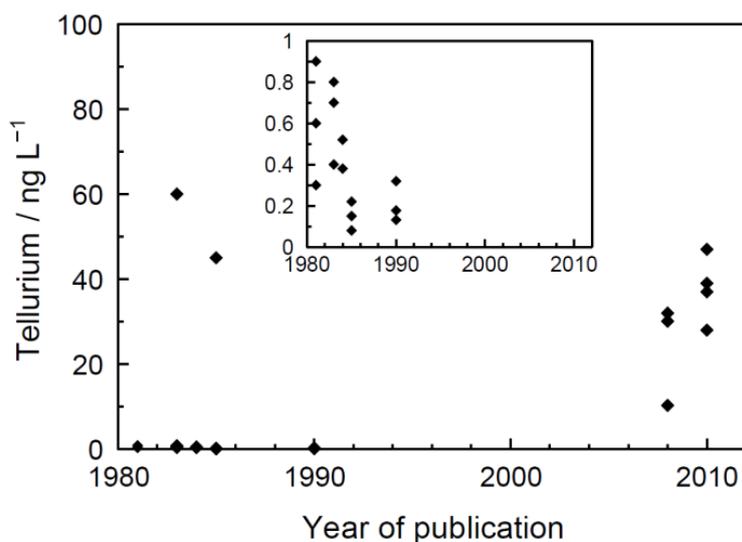
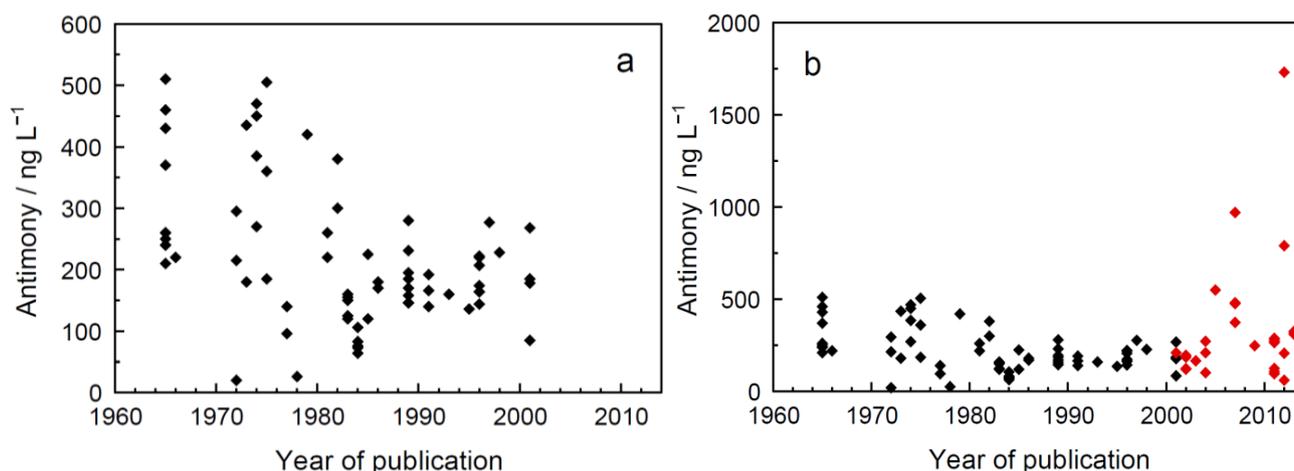


Figure 3. Published antimony concentrations for surface seawater as a function of their year of publication. (a) Figure 1 in [14]; (b) New values published after 2002 added in red, data from [23–40].



2.2. Chemical Speciation

Although today it seems to be generally accepted that the effects of trace elements in organisms (accumulation, nutrition, toxicity) depend on their chemical speciation, reaching such acceptance has been a lengthy process. For example, in the first edition (1970) of the classic book in the environmental field *Aquatic Chemistry* by Stumm and Morgan [41], the term “chemical speciation”

does not appear in the index while in the third, and last, edition (1996) [42], it not only appears but can be read in the introduction: “The notion of chemical speciation is central in equilibrium and kinetics aspects of aquatic chemistry, as will be evident throughout the book.” The contrast between the two editions perfectly reflects the progress made by the concept in the field of environment studies over the years that separate the two editions. However, it has to be mentioned that the first tentative steps in developing chemical speciation studies were met with misunderstanding and disagreement in the scientific community, to the extent that a well-known scientist wrote in 1991: “Speciation is the titillating effort to speciate among the different definitions of speciation to identify the correct meaning of the term speciation” [43] and forced IUPAC (International Union of Pure and Applied Chemistry) to clarify meanings and concepts in 2000 [44].

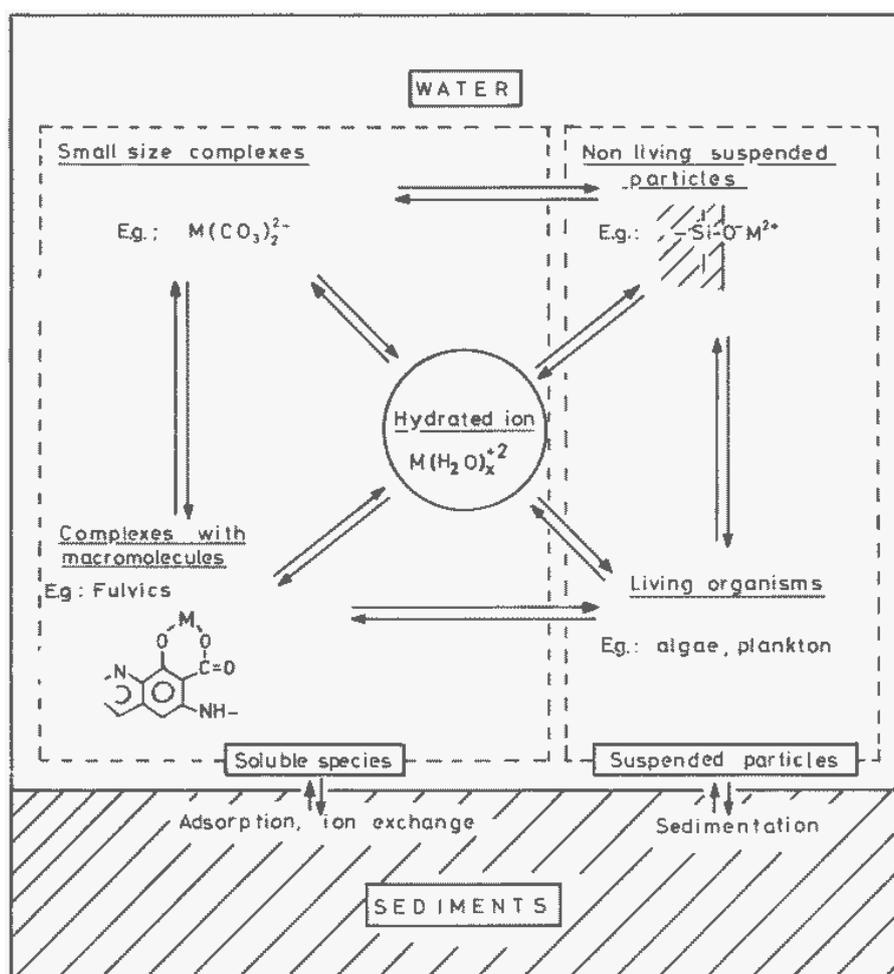
Today, the “speciation community” is characterized by a deep internal division between groups developing, and using, methods applicable to “labile” species (whether in equilibrium or dynamic), and those that use methods that only allow the detection of “inert” species. An interesting feature of the increasing application of chemical speciation concepts and techniques in environmental studies has been the progressive loss of the weight of electroanalytical techniques (compare the contents of the first book published where the terms “trace element speciation” and “surface waters” appeared in the title [45] with the contents of the EVISA webpage) and, in general, of “labile” techniques (probably with the exception of DGT) compared to hyphenated methods (adapted to “inert” species). This is accompanied by a split of the scientific community into two relatively impermeable communities. For instance, not a single mention of techniques other than hyphenated ones appears in a recent volume of the *Journal of Analytical Atomic Spectrometry* [46], which was intended to provide an overview of the latest developments in the field. On the other hand, the community devoted to thermodynamic modeling and dynamic techniques totally ignores hyphenated techniques: they are not mentioned in a recent article on “How well can we predict and measure chemical speciation in freshwaters?” [47]. Since environmental problems are very wide ranging, the techniques needed should be equally wide-ranging but, at present, the choice of the technique used is often made according to the group to which one belongs rather than to considerations related exclusively to the problem to solve. Some voices are starting to be raised against this situation (see, e.g., [48]), but they are still very few.

The chemical speciation literature is also often plagued with misconceptions such as taking for granted that measuring the concentration of the element present in one redox state is synonymous with measuring a species or believing in the physical existence of complexing ligands whose “existence” is based on a mathematical treatment of water titration data. Understanding the degree of operability of most of the methods applied, and its consequences, appears to be a major problem.

The field needs a better conceptual framework to be developed wherein the current practices can find their role. The discussion that follows is an attempt to stir up discussion and establish common ground for further conceptual development. It is common to use schemes like the one shown in Figure 4a [49], where the reactions of a metal ion with different types of aquatic constituents are shown. This scheme has obviously been developed thinking of (i) the case of transition elements such as copper; (ii) a system where all species are in thermodynamic equilibria. However, this type of scheme does not take into account that: (i) water is a ligand that does not behave in the same way towards all elements (*i.e.*, not all elements form true aquo complexes $[M(OH_2)_n]^{z+}$; water molecules may also lose protons spontaneously and be transformed into hydroxo or oxo ligands); (ii) elements

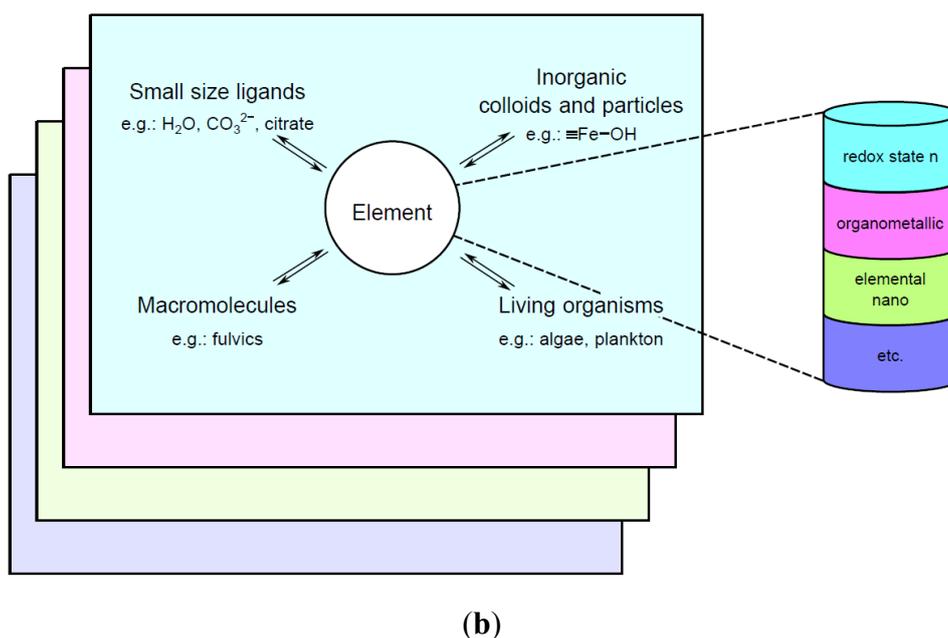
can be covalently bound to carbon forming organometallic entities which will behave in a way equivalent to a “naked” element *vis-à-vis* complexation, thus forming different chemical species; (iii) elements can be present in forms not known in the past such as metallic nanoparticles (e.g., nano silver) or in entities such as quantum dots. A better conceptual framework is provided by the alternative scheme shown in Figure 4b, where water appears as a ligand and the central entity does not need to be always an element of the periodic table but can also be any entity where an element is present that can participate in outer sphere or inner sphere coordination. This entity may have been formed by an irreversible reaction (e.g., organometallic compounds), engineered processes (e.g., nanoparticles) or be the redox state of a given element (and, thus, be interconvertible to another redox state through more or less fast equilibrium processes). It goes without saying that this description remains thermodynamic. Kinetics, of course, will also be present and needs to be considered in each layer of the scheme and sometimes between.

Figure 4. (a) Schematic representation of the interactions of a metal with different types of aquatic systems constituents, reproduced with permission from [49]; (b) Proposed new schema that takes into account aspects discussed in the text.



(a)

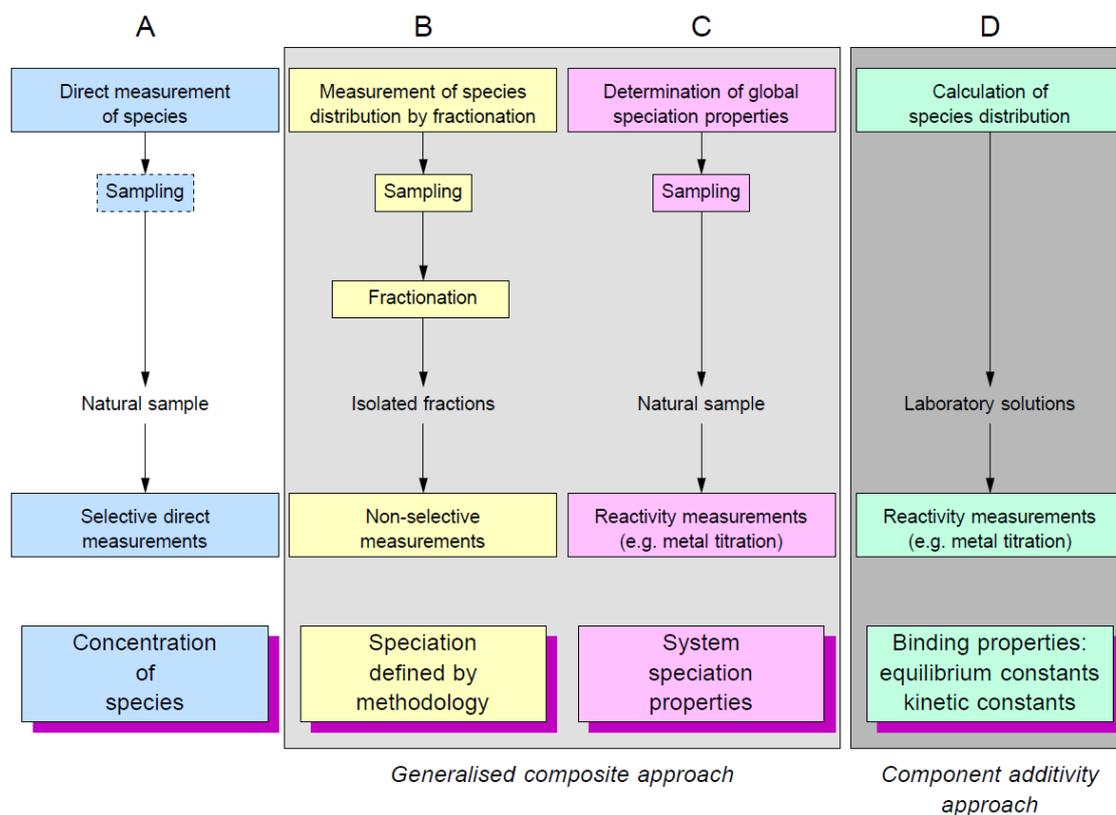
Figure 4. Cont.



The situation becomes complex when experimental speciation methods are taken into consideration. Since being able to determine any possible chemical species formed by an element in a given medium is an unrealistic objective, different approaches have been developed. In a very few cases, a “real” chemical species can be determined (which, according to IUPAC is “speciation analysis” [44]). This corresponds to column A in Figure 5. Many cases that at first glance appear to belong to this category actually do not. Remember, before classifying any method, that As(V) or methylmercury are not chemical species but a group of species where As is present in this redox state or containing MeHg^+ , respectively. Otherwise, from a methodological point of view, there are two possible strategies (which, according to IUPAC [44] would correspond to “fractionation”): (i) the component additivity (CA) approach (column D in Figure 5) based on the idea that, by decomposing any system into its parts and identifying their interactions, it is possible to reconstruct their global functioning and (ii) the generalized composite (GC) approach (columns B and C in Figure 5), where the system is taken as a whole and fractionation or other global techniques are applied.

The best example of the CA approach is provided by speciation modeling where, by knowing the main components of a natural water—cations, anions, natural organic matter, *etc.*—and the stability constants of the equilibria established among them, the concentration of the species formed is calculated. This approach is conceptually appealing but faces some fundamental problems: (i) it is not possible to know “all” the components of any natural water; (ii) the approach is based on the idea that complexing agents such as natural organic matter and mineral particles do not interact among themselves, which is far from reality [50]; (iii) the description of metal complexation by natural organic matter and, to a lesser extent, by mineral particles has proved difficult and controversial [51–54]; (iv) the control by kinetics is not considered. Thus, this approach, although useful, will never produce the “final” answer (like all of the other approaches!).

Figure 5. Schematic representation of different approaches used to study the speciation of trace elements in water.



Most of the existing speciation techniques fall under the GC approach. Speciation methods usually consist of separation techniques associated with a measuring method that detects total concentrations and has no inherent speciation capabilities. Separation techniques fractionate samples on the basis of size, charge, *etc.* and include filtration, centrifugation, ion exchange, chromatographic techniques, *etc.* In all cases, the results obtained are dependent on the methodology used and give fractions or method-dependent results (e.g., metal size classes, DGT labile metal concentrations, so-called “redox” species, *etc.*). All techniques can only “see” species, or groups of species, that are inert enough to remain unchanged all along the procedure. For this reason, hyphenated techniques, so popular nowadays, can only measure relatively inert species or groups of species but rarely provide information about the real species that exist.

Finally, some methods give a measure of the overall response of the system (for instance, towards binding [55]) without trying to identify what type of compounds are responsible for the response (column C in Figure 5). The calculation of partition coefficients or the determination of operational fractions (e.g., “soluble”, “reactive”, “bioavailable”, *etc.*) fall into this category. These methods might be useful to characterize the state of a given system but have a low predictive value.

3. Other Challenges

Analytical chemistry is by definition a problem oriented discipline and, as such, new developments should be guided by existing needs. Some aspects requiring further research in the field of trace element analysis are discussed in this section.

3.1. Cheap, Simple, and Reliable Analytical Methods

The need for cheap and reliable analytical methods is general but the problem becomes more acute in the case of developing countries where purchasing, and also maintaining, analytical equipment is plagued with difficulties [56,57]. Unfortunately, this issue is rarely discussed in scientific journals. For instance, a quick review of the articles recently published in journals such as *Trends in Analytical Chemistry* or *Analytical Chemistry* shows that the subject is far from being a main concern of researchers in the field. In fact, a significant, and increasing, gap exists between the current development of highly sophisticated analytical methods and the reality of the analyses that are performed in many places, even in developed countries. Although the solution to the problem is not solely scientific, but mostly lies on the political or economic side, the fact remains that the increasing development of sophisticated techniques requiring expensive instrumentation exacerbates it. Cheap and robust analytical methods, which do not require advanced analytical expertise and instrumentation would be most welcome.

As is well-known, one of the main problems in developing countries is access to safe drinking water. According to the United Nations, more than one in six people worldwide—894 million—do not have access to improved water sources [58]. Today 2.5 billion people, including almost one billion children, live without even basic sanitation. Thus, the primary water-quality problem is waterborne disease and, understandably, pollution by trace elements has so far been a lower priority. However, the massive pollution of water by As in Bangladesh, where as many as 35–50 million people are exposed to toxic levels, has put trace element pollution on the agenda. Ironically, as is well-known, the problem arose in Bangladesh because during the 1970s UNICEF promoted the installation of tubewells to reduce risks associated with the use of microbially contaminated surface water. It needs to be added that problems related to As contamination are not exclusive to Bangladesh [59], and that contamination by other toxic trace elements is likely to increase in many countries if the current pressure to exploit more mineral resources continues. Episodes of pollution linked to mining in countries where no pollution control exists at all (e.g., countries in Central Africa) or where economic development trumps environmental considerations (e.g., some countries in South America) are becoming more and more common. In this context, the development of cheap and easy-to-use methods that untrained—even local—people could use becomes extremely important. However, this is not an easy endeavor as the case of the development of As kits for Bangladesh—briefly described below—illustrates.

The most common mitigation option followed in rural areas in Bangladesh has been well switching [60]. This involves switching from an As contaminated tubewell to a safe tubewell nearby. An As testing campaign targeting five million wells in regions identified to be at risk for As contamination was initiated in 2001 and completed by 2004 (wells tested represented about half the existing ones). By 2005, 1.4 million tubewells were found to have levels of As above $50 \mu\text{g L}^{-1}$ (Bangladesh standard; current WHO guideline concentration is $10 \mu\text{g L}^{-1}$) and were painted red, while another 3.5 million wells were found to be below the standard and painted green [58]. However, the number of wells approximately doubles every two years [61], and most of the wells installed since the national testing campaign remain untested in many areas today [62]. Testing every individual tubewell is necessary because results of past test campaigns indicate a high landscape and depth variability of As contamination [63]. The need for test methods that facilitate extensive and continuous As

monitoring by local people was soon understood when the problem became known; the use of laboratory-based tests had to be excluded because of their costs and the logistics involved in sampling, transport and communicating results. Many studies have been published over the last 15 years either describing new field kits or comparing existing ones ([64] and references therein). The ideal test should be affordable, robust, mobile, safe for the user, environmentally friendly, and easy to operate. Somewhat surprisingly, the results of all these efforts have been the commercialization of colorimetric field kits that rely on a more than 100-year-old reaction, the Gutzeit reaction [65]: generation of volatile arsine (AsH_3) gas and then detecting and quantifying it with a mercuric bromide impregnated paper. Arsine gas generates a yellow to brown or black color spot that is quantified using a color chart. Table 1 lists some problems identified and corresponding improvements. Certain widely-used commercial field tests have been criticized for insufficient sensitivity and high rates of false-positives and false-negatives [66]. It is also clear that a method that produces a toxic gas such as arsine, uses toxic and difficult-to-dispose-of reagents (e.g., mercury, lead, tin, *etc.*), requires long reaction times (20–40 min), and has a somewhat subjective detection system, will never fulfil many of the requirements listed above. The troubling question that arises is that, if in the case of As, where a huge amount of money and effort has been put into quantifying the element, developing simple and reliable methods has not yet been fully achieved, developing tests for other—presumably lower-profile—elements might prove extremely difficult. Hopefully, the lessons learned from the case of As will guide new developments. It is for this reason that Table 1 has been prepared and included here.

Table 1. Arsenic field kits. Problems involved and actions taken.

Problem	Consequence	Action taken
Water representativeness	Meaningless results	Adequate purging of the borehole and pipework
Water turbidity	Scattering in colorimetric methods, clogging	Filtration; however filtration is not recommended in Bangladesh campaigns
Precipitation of Fe oxide flocs	Loss of As	None; redissolution under the acidic conditions of the test
Presence of As in metallic Zn	Early As testing had high detection limits because of Zn contamination	Use of low-As Zn; use of NaBH_4 (unstable over long periods of time)
Grain size of Zn	Grain size of Zn affects the kinetics of H_2 production and AsH_3 transport	Use 10-100 mesh granules
Different arsine production rates by As(V) and As(III)	As(III) generates AsH_3 more rapidly than As(V)	Incorporation of a pre-reduction step (addition of few drops of concentrated KI and SnCl_2 solution; concentrated HCl and NaSCN diluted in NaCl); use of NaBH_4 (unstable over long periods of time)
Toxicity of AsH_3	Hazard for operator	Leakage prevented by modification of the absorbing device
Strong acid used (often 6 mol/L HCl)	Problems during transport; dangerous for use by people not trained in chemistry	Replacement with sulfamic acid in solid form (its acidity is lower and longer reaction time are needed)

Table 1. Cont.

Problem	Consequence	Action taken
Organoarsenicals not measured	Underestimation of As concentrations	Oxidation treatment prior to analysis by the test kit
Interference by H ₂ S	H ₂ S reacts with HgBr ₂ in the test paper	Removal by using a scrubber (cotton soaked in lead acetate); oxidation of H ₂ S to sulfate (potassium peroxymonopersulfate)
Interference by Se, Te, Sb	–	–
Long reaction time and dependence of results on reaction time	Production of false-negatives and false-positives	Waiting longer has been reported to reduce inconsistencies
Difficulty in detecting weak yellow color by human eye	Production of false-negatives and false-positives	Use of a detector
Reaction products are photosensitive; they tend to dark	Production of false-negatives and false-positives	Work in the shadow
Disposal of toxic reagents	–	–

3.2. “Green” Analytical Methods

Chemical analytical methods need reagents, solvents and energy and they generate waste. Classical wet analytical chemistry was characterized by the use of large volumes of a wide variety of analytical reagents and solvents, whose use posed health risks in many cases, besides causing contamination if the waste was left untreated. Since the 1980s, the increasing use of instrumental techniques has led to a significant decrease in the amount of solvents and reagents needed for measurements. This reduction slightly preceded the first description of the principles of green analytical chemistry in the 1990s [67] and, in some ways, showed the way towards more sustainable analytical practices. Although, analytical analysis is usually considered a small-scale activity, as noted by Koel and Kajurand [68], there are many state controlling and monitoring laboratories that analyze a huge number of samples daily. Therefore, concern about the use of non environmentally-friendly procedures is fully justified. In addition, even if often chemical analysis remains a small-scale activity in absolute terms, the use of “green” methods is always justified when the end-users of a method are local people, such as for the arsenic field kits mentioned above.

Most of the “green” methods published in the literature concern the analysis of organic micropollutants; the examples in the analysis of trace elements being much less abundant [69]. Probably the best known case is the search for alternatives to the use of mercury in electroanalysis. Since the invention of polarography by Heyrovský, the Hg electrode was established as the preferred electrode for use in electrochemistry due its properties as well as the renewability of the electrode surface. International regulations concerning the use of Hg have led to the search of competitive electrodes manufactured using minimal amounts of Hg or using other materials [70,71]. However, Hg still has many advantages over solid electrodes and its complete elimination should be avoided [72]. With respect to this, it should be pointed out that the total amount of Hg used in electroanalysis is very low, particularly if we compare it with the new use of Hg in compact fluorescent light bulbs.

Although among the strategies for greener analytical methods, the “use of alternative sample treatments consuming less energy” is routinely mentioned, in practice, the emphasis is always put into

consuming less reagents and producing less waste or treating it appropriately [69,73]. It is paradigmatic that a very recent publication proposing an analytical eco-scale for assessing the greenness of analytical procedures [74] considers energy consumption per analysis based only on three values taken from a communication to a conference. Astonishingly, the same reference is the only one given in a recent chapter on “energy savings in analytical chemistry” [75]. In fact, it is somewhat surprising that methods that involve the use of sophisticated apparatus, such as an ICP-MS, can be considered “green”. The reason is that the usual type of assessment plainly neglects the energy that was required to manufacture the device. This is especially important for high-tech products, such as analytical equipment, that are produced using extremely material- and energy-intensive manufacturing processes. At the same time, it is extremely difficult to obtain reliable and up-to-date figures on the energy consumed during the production phase of high-tech products. A life cycle analysis of such products is very complex due to the large number of parts, materials, and processing techniques involved, most life cycle analyses are out-dated by the time they are published and many just do not exist. To my knowledge such analyses do not exist for analytical instrumentation, but life cycle analyses of computers and mobile phones show that their total energy use is dominated by production rather than use. This aspect needs to be considered in any sound evaluation. The issue of the carbon footprint associated with any process is also closely linked to energy consumption. Again, no data on the carbon footprint associated with analytical methods seem to be available. Calculation of carbon footprints is extremely complex [76] and no serious attempt to calculate carbon footprints of analytical instrumentation appears to have been made.

A final point that needs to be taken into account when evaluating the greenness of an analytical method is the fact that analytical equipment needs to be considered a source of e-waste. The release of toxic substances from controlled and uncontrolled e-waste disposal and recycling is becoming a serious issue nowadays [77,78] and cannot be ignored when evaluating the “greenness” of any instrumental method. In conclusion, the development of environmentally-friendly methods and strategies needs to be encouraged but better criteria need to be developed. These will inevitably penalize the use of sophisticated instrumentation and probably favor *in situ* analysis.

3.3. Analytical Methods for Measuring “Continuously”

Many studies have noted that diel cycles confound efforts to monitor contamination in streams using once-per-day sampling strategies [79]. Since sunlight is the main energy source of the ground surface, many biogeochemical phenomena affecting water follow a 24-h photocycle in response to sunlight. These processes produce regular changes in many physical and chemical characteristics of water, especially under stable water conditions. The changes throughout the day not only affect variables such as pH and dissolved oxygen but also concentrations of trace elements. In some cases, their amplitude can be as high as that observed on an annual scale [80]. When diel changes are substantial and persistent, conclusions based on point measurements may be uncertain or even wrong. This may be the case for a wide variety of studies covering issues as varied as the determination of background environmental conditions, identification of sources of pollution, detection of long-term trends, assessment of potential risks to aquatic organisms, *etc.* To partially alleviate this problem, using integrated 24 or 96 h samples has been proposed, but this often entails problems related to sample

conservation and complicates sampling strategies. Alternatives include the use of either *in situ* methods (sensors located in the water, without a sampling phase) and automated methods that include online sampling method pre-processing and off line measurement. However, at present, the number of existing techniques applicable to trace metals is very low. It should be added that, in practice, real-time monitoring of all systems and elements will never be possible (and is probably unnecessary) but that designing sampling which is optimally adapted to a given problem requires continuous measurement techniques to be available to enable testing when needed. For instance, not all elements display diel concentration variations (e.g., copper typically does not show distinct diel cycles) and variations depend on the season and system considered.

Continuous measuring methods are also required to properly evaluate the impact of heavy rainfall events. These events have a strong impact on the quality of water used in the production of drinking water and in the ecological health of aquatic systems through the surge transport of suspended solids, organic matter, chemicals (natural and anthropogenic), and pathogens [81]. It is increasingly accepted that one of the consequences of climate change is the increase in frequency and intensity of such events [82]. In this context, it is necessary to develop analytical tools adapted to the rapid assessment of the vulnerability of water resources and the monitoring of abrupt changes in concentrations.

4. Conclusions

The analysis of trace elements in natural waters is far from being an “obsolete” field, merely covering routine water analysis methods with research devoted to the endless race towards the reduction of detection limits. To the contrary, the maintenance of waters as a necessary resource requires significant research efforts to be deployed for many aspects ranging from the development of new cheap, robust, and easy to use methods to the elaboration of new conceptual frameworks in order to unshackle progress in key fields such as trace element speciation.

Conflict of Interest

The authors declare no conflict of interest.

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