

Review

# Analytical Chemistry: Tasks, Resolutions and Future Standpoints of the Quantitative Analyses of Environmental Complex Sample Matrices

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**Abstract:** Currently, the challenges that analytical chemistry has to face are ever greater and more complex both from the point of view of the selectivity of analytical methods and their sensitivity. This is especially true in quantitative analysis, where various methods must include the development and validation of new materials, strategies, and procedures to meet the growing need for rapid, sensitive, selective, and green methods. In this context, given the International Guidelines, which over time, are updated and which set up increasingly stringent "limits", constant innovation is required both in the pre-treatment procedures and in the instrumental configurations to obtain reliable, accurate, and reproducible information. In addition, the environmental field certainly represents the greatest challenge, as analytes are often present at trace and ultra-trace levels. These samples containing analytes at ultra-low concentration levels, therefore, require very labor-intensive sample preparation procedures and involve the high consumption of organic solvents that may not be considered "green". In the literature, in recent years, there has been a strong development of increasingly high-performing sample preparation techniques, often "solvent-free", as well as the development of hyphenated instrumental configurations that allow for reaching previously unimaginable levels of sensitivity. This review aims to provide an update of the most recent developments currently in use in sample pre-treatment and instrument configurations in the environmental field, also evaluating the role and future developments of analytical chemistry in light of upcoming challenges and new goals yet to be achieved.

**Keywords:** environmental analysis; instrument configurations; extraction procedures; environmental applications

## 1. Introduction

In recent years, the increase in production activities in all industrial sectors has led to an increase in the production and consumption of xenobiotic compounds [1]. Specifically, their extensive use has led to the pollution of the environment as a major consequence [2], a fact that represents a direct threat to human health. In this perspective, the Stockholm Convention aims to protect human health and the environment from all activities that produce (and often release in an illegal and/or uncontrolled way) persistent organic

pollutants (POPs), defined based on four criteria: persistence for a long time, toxicity, bioaccumulation, and wide geographical distribution [3].

Along with POPs, another major problem linked to the widespread use of plastic products has recently emerged. The presence of plastic particles in various environmental compartments (water, soil, and air) [4], even of micrometric dimensions (microplastics, MP, with dimensions < 1–5 mm) as part of industrial or domestic products (scrub, peelings, toothpastes, and make-up), and other products deriving from degradation/fragmentation (secondary microplastics) has reached such a level that considerable concentrations of these compounds have been found even in remote places such as Antarctica [5], the Arctic [6], or the deep ocean [7].

This large diffusion is essentially attributable to the fact that the smaller the particle size, the more these particles spread in the environment [8]. Another fundamental problem related to these MPs is that they are able to retain chemical substances on the surface, especially persistent organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochloride pesticides (OCPs), and polybrominated diphenyl ethers (PBDE) [9–11]. These MPs, therefore, act as a sort of pre-concentrator and modify their interactions and their toxicity in living organisms [12,13].

Among the previous classes, PAHs have been well known for some time and have been reported for decades as the main harmful compounds. Since the 1970s, a list of priority pollutants has been drawn up, leading to the identification of 16 PAH Priority Pollutants by the U.S. EPA [14]. This list does not take into account non-polar high-molecular-weight (HMW) PAHs, alkylated PAHs, or polar polycyclic aromatic compounds (PACs) [15]. In the category of polar PACs, it is mandatory to consider nitrate PAHs (NPAH) and oxygenated PAHs (OPAH), which currently, are the most studied [16–18] as their formation can result from reactions between “parent” PAHs and oxidizing agents in the environment. In addition to NPAHs and OPAHs, other polar PACs such as azaarenes (AZA, also referred to as polycyclic aromatic nitrogen heterocycles (PANH)) and polycyclic aromatic sulfur heterocycles (PASH) should also be considered. These compounds, although similar to PAH, NPAH, and OPAH in terms of sources and toxicology [19–21], are mainly related to petrogenic emissions [22,23]. It should be emphasized that all of the compounds reported are being studied by IARC (International Agency for Research on Cancer) and some of them have been classified as possible or probable carcinogens [24]. Regarding this category of pollutants, the very complete review paper by Galmiche et al. [25] appears to be very interesting.

Heavy metals also deserve particular attention, which as widely reported in the literature [26,27], not only represent an environmental problem for their presence in soils; superficial, deep, and sea waters; and food (and food supplements and herbal medicines), especially related to the fact that many of them do not have set maximum legal limits and/or are not considered as elements to be monitored and quantified.

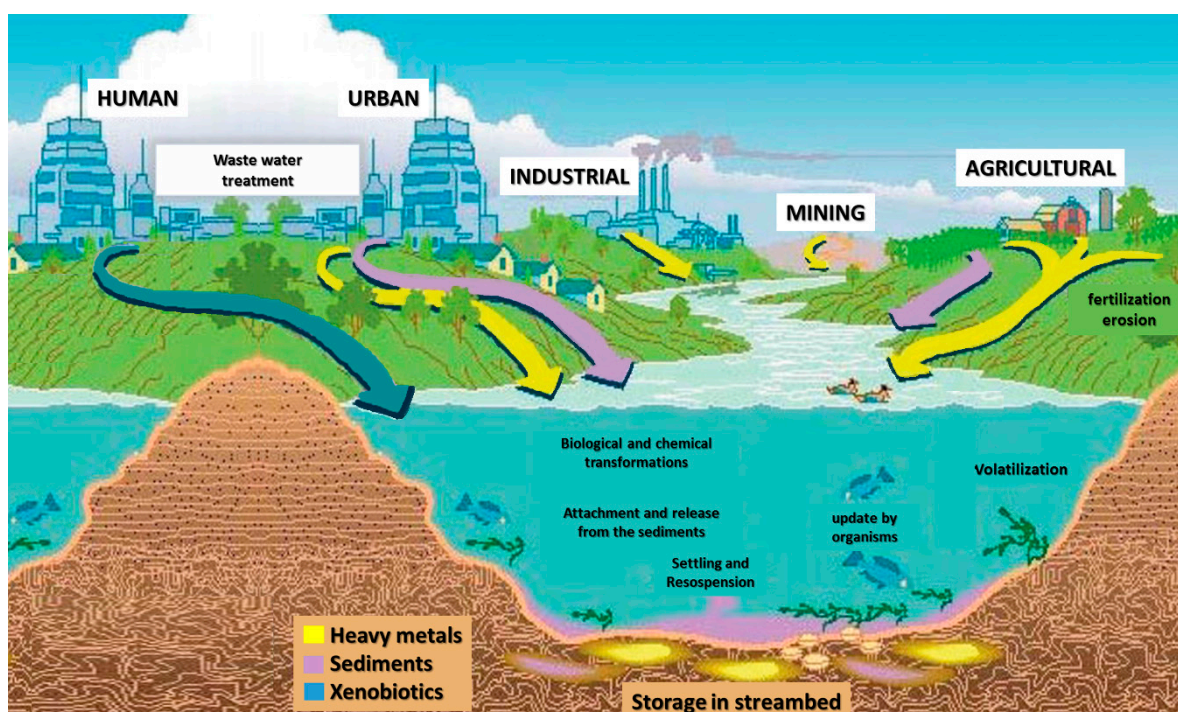
As reported by McGregor and Zhao [28], trichlorethylene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride together with per- and polyfluoroalkyl substances (PFAS) have recently been identified as substances of concern in groundwater. Many of these compounds have also been confirmed as carcinogens or suspected carcinogens and are, therefore, of interest at the level of environmental monitoring. Although there is a variety of technologies for the treatment of chlorinated ethenes, technologies for treating PFAS in groundwater are not widespread and/or developed.

In particular, the per- and polyfluorinated alkyl substances (PFAS) are a group of highly stable and degradation-resistant anthropogenic chemicals. These are produced and used in many consumer and industrial products (e.g., food packaging, fire-fighting foams, and textiles) due to their heat-resistant and water-repellent properties. PFAS compounds are persistent, toxic, and potentially harmful to humans, and the leaching and presence of PFAS in our environment have raised serious concerns at a global scale. Exposure to PFAS through drinking water was investigated, leading the European Parliament in December 2020 to adopt the revised Drinking Water Directive (DWD), effective from 12 January 2021,

including the “total PFAS” parameter (all per- and polyfluoroalkyl substances limited to a maximum concentration of 0.5 µg/L).

Regarding the analysis by Shimadzu, the application note is very interesting, providing a direct injection analysis of organofluorine compounds (PFAS) by triple–quadrupole LC-MS/MS [29], although to date, the panorama of pre-treatment procedures is still very limited and not very widespread. With regard to this aspect, the recent review by Winchell and collaborators [30] highlights how much has been developed for the analysis of these analytes and how much still remains to be developed, not only at the monitoring level but also at the level of removal processes. This point highlights that their analysis is very difficult as their advisory limits are in sub ppb to sub ppt levels, showing the emerging challenges to analytical chemists.

In light of what we have seen so far and what is reported in Figure 1, the massive problem inherent in the environmental monitoring of molecules that are harmful (or potentially harmful) both for the environment and for all living organisms is clearly highlighted.



**Figure 1.** Connections and sources of xenobiotics that are poured into the environment as result of human activities.

All of these characteristics have been recently reviewed in the literature [31,32], highlighting the great interest in the area of analytical chemistry and the challenges that await this discipline in the near future. In this scenario, the main role of scientists is to check, follow, and resolve the negative impacts of chemical and biological pollutants on people’s health to protect the supply of clean drinking water, thereby managing their effects on the ecosystems and environment. It should be noted that, in recent years, different factors have been taken into consideration in the development of new instrumental configurations and/or new analysis procedures, in particular, the possibilities of performing miniaturized measurements using low-priced and portable sensors for monitoring biological and chemical pollutants in environmental samples, being easy to use, and having low environmental impact (fundamental concept of green analytical chemistry).

The purpose of this review, as a sort of second “act” to a previously published review [33,34], is to highlight the recent applications developed in the environmental field and aimed at the xenobiotics, POPs, pesticides, heavy metals, and other pollutants monitoring,

and how these can have positive repercussions on future applications, both from the point of view of pretreatment procedures and instrumental configurations (and portable devices).

## 2. Pre-Treatment Procedures

The step following sampling and relative to the treatment of the sample in order to make it suitable for instrumental analysis is a crucial point in practically all analytical methods, especially if the concentration of the analytes of interest is extremely low. Another critical element is the presence of interfering substances often present at high concentrations that can lead to matrix effects and problems related to the correct identification and quantification of the analytes [35]. For an accurate (precise and true) and sensitive determination of the elements present at the level of traces and ultra-traces, a pre-concentration phase is normally required before their detection using different instrumental techniques [36]. In this phase, in addition to being an enormous waste of time, there is the risk of not only obtaining an increase in the analyte signal but also the sample treatment procedure not being carried out correctly: an increase in interferences may be encountered with consequent problems in the instrumental analysis phase.

Another very important component in this phase is the use of solvents of various type, especially organic, that can be toxic and high volatile when used in the classic liquid–liquid extraction (LLE) or solid phase extraction (SPE) techniques for the preconcentration of trace elements prior to total or speciation analysis. Modern analytical methods are increasingly focused on the development of simple, fast, sensitive, and environmentally friendly practices that follow the principles of green chemistry (e.g., replacement of toxic reagents, miniaturization and automation, and development of solvent-free procedures) [37].

The development of innovative procedures and materials reflect the actual trend in sample preparation field for analytical applications. Specifically, currently, the application of nanomaterials has become a valuable tool for sample preparation methods, especially in SPE, leading to many advantages, especially with regard to their high surface-volume ratio, chemical stability, and the possibility of functionalization of the sample surface in order to increase selectivity [38]. In this scenario, certainly, the development of new materials, also based on the molecularly imprinted polymer concept, allow for obtaining high performances in terms of sample clean up and interference removal. Coupled with these materials, often based on polymer technologies, the implementation of alternative solvents supported on solid nanomaterials can be considered a further interesting approach (and development) to providing a high surface area by increasing their extraction efficiency [39], with a reduction in solvents/sample volume consumption.

Recently, Oviedo et al. [40] reported an exhaustive and complete overview of the pre-concentration and determination of trace elements using alternative solvent systems such as ionic liquids (IL), surfactants, deep eutectic solvent (DES), as well as their combinations with new nanomaterials, summarizing and underlining the progress observed from 2017 to date in the extraction and clean-up procedures with the use of these green solvents.

In Table 1, different and more recent developments related to extraction methods are reported.



**Table 1.** Most key developments in extraction methods.

Matrix	Analyte/S	Material	Phase System/Fields/Technique	Sensitivity (in Terms of LOD)	Ref.	
Environmental	Pollutants	Engineered enzyme-conjugated materials	Dehalogenating enzymes	Lower than 2 ppt	[32]	
Water	Metals	ILs	DLLME	$10\text{--}4.0 \times 10^{-4}$ ppb	[40]	
Water	Metals	Surfactants	CPE	$0.5\text{--}1.1 \times 10^{-3}$ ppb		
Water	Metals	DESs	DLLME/LLME	2.9–0.12 ppb		
Water	Metals	Nanomaterials combined with alternative solvent system	MSPE/D- $\mu$ -SPE	$0.11\text{--}1.1 \times 10^{-3}$ ppb		
Water	Pesticides		Graphene-based nanosorbents	MSPE/SPE/DSPE		-
Water	Fungicides		Graphene-based nanosorbents	MSPE/SPE/DSPE		-
Water	Herbicides		Graphene-based nanosorbents	MSPE/SPE/DSPE		-
Environmental	Pesticides	Carbon nanomaterials	Enzyme-based Antibody-based Aptamer-based MIP-based General	$99\text{--}2.5 \times 10^{-5}$ ppb 8 ppb $1.1\text{--}4.0 \times 10^{-5}$ ppb $470\text{--}4.2 \times 10^{-3}$ ppb $905\text{--}6.5 \times 10^{-4}$ ppb	[41]	
Water	Glimepiride	LAY-FOMM 60	SPE sorbent 3D-printed	-	[42]	
Water	As, Se	BV-007 resin and TiO <sub>2</sub> NPs	Column holders 3D-printed	-	[43]	
Water	Fe	Clear photoactive resin	Disk-based SPE 3D-printed	-	[44]	
Groundwater and leachate	14 trace metals	Clear photoactive resin	Extraction disks 3D-printed	1.3–0.03 ppb	[45]	
Water	Organophosphate pesticides	ILs	[C4MIm][NTf <sub>2</sub> ]	$5\text{--}16 \times 10^{-3}$ ppb	[46]	
Water	4- <i>n</i> -nonylphenol 4- <i>Tert</i> -octylphenol Bisphenol A Phenol	ILs	DDAC	$3 \times 10^3$ ppb	[47]	
Water	Metals	ILs	[OPy] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup>	0.1 ppb	[48]	
Wastewater	Fluoxetine and Citalopram	MSPE	Fe <sub>3</sub> O <sub>4</sub> @PPy-GO	1.6 ppb	[49]	
Water	Pirimicarb and Fenitrothion	FPSE	PCL-PDMS-PCL	3 ppb	[50]	
Water	Propoxur and Fenitrothion	MSPE	Decanoic Acid Modified	1.4 ppb	[51]	
Water	4-Cyanophenol and 3-Nitrophenol	SPE	MWCN	0.1 $\mu$ g	[52]	
Soil	Epoxiconazole, Fluroxypyr Metribuzin Oxyfluorfen	ILs	(VBHDIM-NTf <sub>2</sub> ) [ViC <sub>10</sub> OHIM][Nf <sub>2</sub> T]	0.4 ppb	[53]	

CPE: cloud point extraction; DES: deep eutectic solvents; DLLME: dispersive liquid–liquid micro extraction; DSPE: dispersive solid phase extraction; FPSE: fabric phase sorptive extraction; ILs: ionic liquids; LLME: liquid–liquid microextraction; MSPE: magnetic solid phase extraction; MWCN: multi-walled carbon nanotubes; SPE: solid phase extraction; SPME: solid phase micro extraction.

As indicated in Table 1, it is noted that recent literature and scientific research is directed, above all, towards pre-treatment systems based on techniques that exploit the interaction between membranes or chemically functionalized particles in order to maximize the selectivity of the method, while still few are the applications that resort to liquid phases with green solvents (ionic liquids) [40,46–48,53].

It should be emphasized that, among the membrane-based techniques, FPSE has recently proved to be a very promising technique as it allows for not only the pre-treatment of a sample but also its conservation for subsequent confirmatory analyses. This technique is also very promising as it has been shown to have analytical performances that allow for the analysis with dated, robust, and well-known instrumental configurations (HPLC-PDA) of xenobiotic traces in complex matrices, obtaining quantification limits comparable with well-known configurations with respect to more complex and expensive and requiring trained personnel (for example, LC interfaced with mass spectrometry). These techniques are also easy to perform since, once the membrane has been activated, it is sufficient to proceed after optimization of the main parameters (sample volume, extraction and back-extraction time, solvent, and back-extraction volume) with sampling and the subsequent instrumental analysis, as highlighted in the literature [54,55].

Currently, only techniques based on solvents and/or functionalized particles have been applied in the analysis of heavy metals, opening up areas of research in the field of membranes capable of selectively adsorbing these analytes for environmental applications.

### 3. Instrumental Configurations and New Materials

Concurrent with the development of the new sample treatment procedures, new materials, and new solvent systems presented above, there has also been the development of new instrumental configurations and new techniques for quantitative measurements. These elements, often combined in order to minimize the manipulation of the original sample (to minimize errors and analyte losses), have recently improved with the development of new carbon-based nanomaterials such as diamond, graphene, amorphous carbon, C60 fullerene, carbon nanotubes, carbon dots (CD), and materials for organic structures that allowed for the simultaneous extraction of the analyte and its fluorimetric detection [56–60]. Such systems could directly or indirectly recognize target analytes by generating fluorescence signals (FRET, IFE, and electron transfer mechanism) [61–63] in a single system and simultaneously. At present, however, the structural integrity, chemical/thermal stability, and surface microenvironment of carbon nanomaterials, which greatly influence their practical applications and signal intensity, still need to be “resolved” and/or standardized in order to make the procedure maximally reproducible.

It should be emphasized that, in addition to carbon nanomaterials, other materials for fluorescence (e.g., quantum dots of semiconductors, metallic nanoclusters, and luminescent materials of higher conversion) have seen wide application in the analysis of pesticides through integration with recognition units in the benchtop or portable configuration [64,65] that exploit the use of new sensors [41]. Metal–organic frameworks are a versatile and remarkable class of crystalline functional materials with many unique features and huge potential for numerous applications. There are four main categories of luminescent MOFs: lanthanide-based MOFs, transition metal-based MOFs, heterometal–organic frameworks, and main group metal–organic frameworks. In the field of environmental pollutant analysis, LMOFs have shown their potential as suitable candidates for detecting temperature, pH, nitroaromatic explosives, small molecules, metallic cations, as well as inorganic anions.

Currently, in this scenario, luminescent metal–organic structures (LMOFs) represent an important sub-category of MOFs in which photon emission occurs following the absorption of radiative excitation energy with great potential for practical applications [66,67]. In fact, LMOFs have proven to be a unique basis for chemical detection thanks to their characteristics such as the size, shape, chemical composition, and surface specifications of the pores, which can be finely controlled [68,69]. These elements are reflected in the fact

that porosity allows for the adsorption of molecules, increases interactions, preconcentrates the target molecule [69,70], and consequently allows for an increase in sensitivity.

The possibility of monitoring the level of environmental pollution in real time using selective and sensitive techniques is the main objective today in light of a growing introduction of polluting compounds due to anthropogenic activity. There are indeed a large number of organic pollutants and metal ions in water and soil, and there are many volatile organic chemicals in the atmosphere, which pose a serious threat not only to the environment but also, especially, to human health. Many organic molecules show high toxicity values and are able to influence physiological and pathophysiological functions [71,72] to such an extent that their rapid and sensitive detection is of great importance.

At present, the main pollutant detection methods include ultraviolet (UV) spectrophotometry techniques and methods [73], high-performance liquid chromatography (HPLC) [74] coupled with various types of detectors (especially mass spectrometry, MS), Fourier transform infrared spectroscopy (FTIR) [75], near infrared spectroscopy (NIR) [76], and surface-enhanced Raman spectroscopy (SERS) [77]. All of the configurations indicated show high sensitivity and accuracy, but often, the high purchase/maintenance cost and the lack of a “portability” feature limit their practical application.

Surely, the optical detection method, thanks to its high sensitivity, portability, short response times, and low cost, represents the most used configuration in the field of environmental pollutants detection, especially through procedures that increase the luminescence (“ignition”), switch off the luminescence (“switching off”), and measure the luminescence ratio [69,78].

With regard to the development of new devices, currently, analytical chemistry increasingly uses three-dimensional (3D) printing [79], especially for the production of microfluidic systems, electrochemical sensors, and biosensors, as well as the production of instruments applied in the fields of separation sciences, sample pretreatment, and wearable sensors [80,81]. Compared with traditional techniques, microfluidic techniques have many advantages, including the low cost and small footprint that allow for their portability, high analysis speed, reduced consumption of sample and solvents, and integration of various components [82,83].

Regarding microfluidic systems, the application proposed by Li et al. is very interesting. Using a system in a Y-shaped configuration with colorimetric detection, they determined the content of iron in water [84] or nitrates in soil [85]. Mattio et al. developed a similar device in 3D using poly (methyl methacrylate) (PMMA), improving the portability, simplicity, and low-cost determination of lead in natural water [86]. SLA 3D printing has also been employed for the construction of a fourth-generation microflow injection analysis system for metal and glucose trace detection in complex samples and other applications [87], while Fornells et al. exploited different materials integrated on a 3D-printed microfluidic device for the detection of ammonium in ambient water samples [88].

In Table 2, the different key developments in instrument configurations applied in environmental analyses are reported.

**Table 2.** List of key developments in instrument configurations.

Matrix	Analyte/S	Instrument Configuration	Sensitivity	Ref.
Water	Organophosphate pesticides	GC-MS	$5\text{--}16 \times 10^{-3}$ ppb	[46]
Water	4-n-nonylphenol 4-Tert-octylphenol Bisphenol A Phenol	UV/Vis spectroscopy	$3 \times 10^3$ ppb	[47]
Water	Metals	ICP-MS or AFS	0.1 ppb	[48]
Wastewater	Fluoxetine and Citalopram	HPLC-PDA	1.6 ppb	[49]

Table 2. Cont.

Matrix	Analyte/S	Instrument Configuration	Sensitivity	Ref.
Water	Pirimicarb and Fenitrothion	HPLC–PDA	3 ppb	[50]
Water	Propoxur and Fenitrothion	HPLC-PDA	1.4 ppb	[51]
Water	4-Cyanophenol and 3-Nitrophenol	CE	0.1 µg	[52]
Soil	Epoxiconazole, Fluroxypyr Metribuzin Oxyfluorfen	GC–MS	0.4 ppb	[53]
Water	Metformin	CE	10 <sup>4</sup> ppb	[89]
Water	Heavy metals	Portable sensing–optical	0.5 ppb	[90]
Water	Heavy metals	Portable sensing–colorimetric	3 ppb	[91]
Water	Heavy metals	Portable sensing–electrochemical	0.15 ppb	[92]
Water	Heavy metals	SWASV	0.0096 µM	[93]
River water	Methyl parathion	DPV	0.015 µM	[94]
Water	Nitrite	Amperometry	0.03 µM	[95]

AFS: atomic fluorescence spectrometry; CE: capillary electrophoresis; DPV: differential pulse voltammetry; GC–MS: gas chromatography–mass spectrometry; HPLC–PDA: high-performance liquid chromatography–photodiode array detector; ICP–MS: inductively coupled plasma mass spectrometry; SWASV: square wave anodic stripping voltammetry.

In this panorama, it should also be highlighted how, in the environmental field, instrumental configurations that resort to electrochemical (bio) sensors based on carbon cloth and carbon paper are increasingly used, combining their characteristics such as their interesting features and their highly efficient, versatile, and disposable design for biomolecules, biomarkers, and hazardous and chemical compound detection in environmental samples. The advantage of an easy integration in miniaturized and portable devices envisages their successful application in point-of-care diagnostics and in situ measurements through the development of portable, space-saving, and high-performance devices in terms of sensitivity and specificity [96,97].

The improvement at the level of the analytical parameters related to the detection of various water pollutants in different ecosystems and/or remote locations is strongly correlated with the development of convenient, portable, simple, and sensitive systems that are easy to use even by untrained personnel. In this context, the possibility of coupling portable devices for measurement (based on sensors) with an efficient and easy-to-use platform, such as a smartphone, have opened a very important line of research for the development of configurations and procedures for in situ analysis [98,99]. Exploiting mobile applications and cameras with very good performance and light sensors, many fascinating biosensors have been developed based on smartphones [100–105].

Regarding the techniques/processes based on (bio)sensors, fundamental points in their study and development are based on (i) evaluating the different analytical signals that can be used for quantitative purposes by means of different electrochemical and optical sensors, (ii) developing different molecularly imprinted probes to increase the selectivity of the procedure, and (iii) exploiting the possibility of nanomaterials being incorporated into and used in portable sensors.

#### 4. Conclusions

In this article, only the most recent developments in the field of environmental analysis that have led to a rapid increase in the application potential of analytical techniques in this sector have been reported. It should be noted that many developments observed in a specific application field are, however, used as ideas for other sectors, and this leads to a greater choice of procedures that can be applied to analytical problems that are often very “distant” from the original intent. Specifically, however, it can be observed that, in



recent years, more and more attention has been paid to all of the techniques that allow for a reduction in the impact of human activities on the environment and to the development of green procedures and of devices for *in situ* analyzes.

As depicted in Figure 1, the close connection between the environment, human activity and health is even more evident. These are sectors that, even if at first glance could be limited in their “boundaries”, in reality involve strong reciprocal influences linked to the life cycle of the molecules and their degradation/metabolism processes. It can be fairly concluded that it is possible to apply, after appropriate verification of the analytical performance (and in this case, a new validation process in the new matrix), methods created for different purposes. If we combine this element with the continuous interest in green and high throughput procedures, we can understand how analytical chemistry plays a predominant role in all fields where chemical processes are involved.

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