

Electrochemical devices for the detection of priority pollutants listed in the EU water framework directive

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Abstract

Monitoring chemical contamination in water is a must to guarantee the supply to the society of this more and more scarce prized asset. The European Union as well as other bodies have released reports and directives defining lists of substances whose detection in waters should be prioritized and posing limits to the maximum allowable concentrations that drinking water must have. The scientific community has been actively working on the development of analytical tools that could be applied in the detection of hazardous chemical species in waters. Here, an overview of electrochemical devices with the potential of being implemented to the monitoring of the forty five pollutants include in the list of priority substances set in the 2013 EU directive that could be grouped into heavy metals, pesticides, hydrocarbons, halogenated hydrocarbons and alkyl phenols, is given, aiming at showing their benefits and limitations in this scenario.

Keywords: Electrochemical sensor, water, priority pollutants, heavy metal, pesticide, hydrocarbon, alkyl phenol.

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1. Introduction

The last EU directive from the 13th of August, 2013 (2013/39/EU) about the list of priority substances in the field of water policy has been released as an amendment to previous directives (2000/60/EC and 2008/105/EC) that identified a number of water pollutants that should be monitored because they pose a significant risk to, or via, the aquatic environment at the EU territories and, as a consequence, a serious threat to the human health [1]. This list now includes 45 pollutants that can be grouped into five major categories, namely heavy metals, pesticides, hydrocarbons, halogenated hydrocarbons and alkyl phenols. The directive also states the necessity of identifying and pursuing novel monitoring methods that show promise for a future application in the field of water analysis and that meet the performance criteria required by the Union in terms of sensitivity so that pollutant concentrations could be reliably measured at concentration levels below the environmental quality standards (EQS) already set up and enclosed in the mentioned directive.

The EU requires from the Member States to select analytical tools that meet a minimum performance criteria based on an uncertainty of the measurement of the target analyte. The uncertainty of measurement is a parameter defined as the precision of the analysis in real samples and estimated at the EQS values for each hazardous substance in this scenario. The expanded uncertainty of measurement is applied [2], and was set to a value of 50 % or below for a confidence level of 95 % (coverage factor $k = 2$). A limit of quantification equal or below a value of 30 % of these EQS values should also be attained [3]. Additionally, it should be ensured that setting up such monitoring processes do not entail excessive costs. The regulation is thus quite strict and finding approaches that fulfil these criteria proves to be a difficult task that highlights the need for new devices and processes or the adaptation of existing ones.

There exist standard methods available for most of the priority substances as described in the EU technical report 2009-025 Guidance Document No. 19 “Guidance on surface water chemical monitoring under the water framework directive” [4] and in the JRC technical report “Analytical Methods for the new proposed Priority Substances of the European Water Framework Directive” [5]. For some of the latest substances included in the list and reported in the mentioned directive, a standard analytical method has not been established yet, but in this report analytical approaches already identified as possible candidates to be standardized in this scenario are mentioned. All these methods are well established and have often been assessed through collaborative trials that prove their robustness and reliability. However, most of them require bulky and costly instrumentation, and thereby they have to be carried out in a centralized laboratory while samples have to be analyzed by highly skilled users. Also, water sampling has to be carried out and strictly controlled and this includes the use of sample containers, sample preconditioning in field, transport and eventual storage under restrictive conditions before performing the analysis.

Advanced methods for water environmental assessment have been pursued and are under constant evaluation. Among them, electrochemical approaches have shown to be of potential use in the analysis of waters. They are sensitive and inexpensive analytical tools requiring a compact and low-power instrumentation. As such, many of them can be deployed for the in-situ detection of target analytes present in waters. Measuring pollutants in situ using continuous or semi-continuous monitoring processes allowed for increasing the analysis frequency, avoiding errors that could be related to the sample collection and transportation as well as providing with a more efficient detection of contamination outbreaks that helped decide in time the required solutions to avoid environmental damage. In this context, the integration of electrochemical devices in

automatic fluidic systems that enabled sample preconditioning and device calibration is required and should be born in mind when designing new approaches or trying to adapt those reported previously [6,7] . This paper gives an overview about electrochemical analytical tools, mainly reported in the last five years that could fulfill the above-mentioned requirements and have already shown to be applied to the detection of pollutants included in the list set by EU. With the aim of reaching a broad readership, some technical specifications about the most representative devices are also provided.

2. Heavy metals

Heavy metals appear as natural elements of the earth crust but also they have shown to be environmentally persistent contaminants that cannot be degraded [8]. Heavy metals are released into the environment by natural events but mainly by anthropogenic operations, especially mining and industrial activities, and also by the vehicle fleet. They can nowadays be found in underground and surface waters as well as in soils. Because they are bioaccumulative, they pose a serious threat to many living organisms. Among the heavy metals, those listed as priority hazardous substances are cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni), and the maximum allowable concentrations expressed by EQS (MAC-EQS) in surface waters are 0.45-1.5, 14, 0.07, and 34 $\mu\text{g/L}$, respectively [1]. Regarding the minimum performance criteria of the applied analytical methods for water analysis mentioned above, the limit of quantification to be achieved for each of these target analytes should be equal or lower than 0.14, 4, 0.02 and 10 $\mu\text{g/L}$ for Cd, Pb, Hg and Ni, respectively. Conventional methods include inductively coupled plasma – mass spectrometry, graphite furnace atomic absorption spectrometry, atomic fluorescence spectrometry and cold vapor atomic absorption spectrometry [5].

Different electrochemical approaches with the potential to be applied in the detection of all these hazardous species have been developed. These include potentiometric sensors based on solid-state ion electrodes [9, 10], as well as coulometric and voltammetric sensing devices that make use of different of metal and carbon electrode architectures. Among the latter, ion-transfer cyclic voltammetric detection approaches using a liquid-liquid microinterface [11] and stripping detection modes have been reported. The simplicity, sensitivity and multiparametric possibilities of stripping voltammetric techniques have made them of widespread use in the development of electrochemical sensors for heavy metal detection. Coulometric stripping detection approaches have been described [12] but most of them include stripping voltammetric protocols to record the sensor response. These are shown in more detail below.

In stripping voltammetry, an initial step is applied at which the working electrode is held at a set potential or at open circuit potential. During this step the heavy metal species present in solution can be pre-concentrated on the electrode surface. A potential scan is then carried out so that the accumulated metal is stripped off the electrode surface yielding a faradaic current response in the form of peak, whose peak height is directly related to the analyte concentration in the water sample. This technique can be applied to the simultaneous detection of different heavy metals whose resulting voltammetric signals appear at different potentials. Both anodic and cathodic stripping voltammetric approaches can be applied, depending on whether the pre-concentration step involves the reduction of the heavy metal ions to the corresponding metal counterparts and their subsequent anodic oxidation or the formation and accumulation of metal ion complexes produced in solution in the presence of a suitable complexing agent followed by the corresponding cathodic desorption. These are termed anodic and (adsorptive) cathodic stripping voltammetry, respectively.

Initial electrochemical devices using stripping voltammetric approaches for the measurement of Cd(II), Pb(II) and Ni(II) mostly employed hanging Hg drop and Hg film based electrodes. With the increasing concern about the toxicity of Hg, numerous environmentally friendly promising materials are being implemented in the development of electrodes for detecting heavy metal ions in water, including Hg(II). Among them, carbon based electrodes such as glassy carbon electrode (GCE), carbon paste electrode (CPE), and screen printed carbon electrode (SPCE) are the most popular, together with Au electrodes of different configurations. In addition, a wide range of surface electrode modifiers have been applied that provide the resulting device with the appropriate selectivity and sensitivity to the target heavy metal analyte. Recently, Cui et al. [13] gave a comprehensive summary on the various electrode modifiers ranging from inorganic (metallic) to organic structures and bio-materials for electrochemical sensing of heavy metals. Depending on the interaction between the heavy metal and the electrode, most of the reported electrochemical sensor approaches fall into three different categories. Some representative examples are gathered in Table 1, taking into account their analytical figures of merit, such as LOD, linear range and overall response time.

2.1. Cadmium and Lead

These two heavy metal ions are often detected simultaneously by anodic stripping voltammetry (ASV) because they give rise to a faradaic response at a potential that significantly differs from each other but that are in turn close enough to lay within the potential window that is commonly scanned in ASV experiments.

Taking into account the electrode or electrode modifier materials, we have divided the different electrochemical devices for the detection of Cd(II) and Pb(II) into two

different categories. These include the most common approaches based on bismuth (Bi) based electrodes and those based on alternative materials.

2.1.1. Bi-based electrochemical devices

The analytical performance of Bi as electrode material has been widely demonstrated and proved to be very similar to that of the traditional Hg electrodes. In both cases, the response is based on the formation of a "fused alloy" with the reduced heavy metals during the accumulation step. However, the environmentally friendly nature of Bi-based electrodes has made them to grow in popularity for the detection of Pb(II) and Cd(II) as well as Ni(II). Figure 1 displayed typical stripping voltammograms for the determination of Pb, Cd and Ni using carbon electrodes containing Bi nanoparticles.

Several reviews have already been published that summarize the development of Bi based electrodes in electroanalysis. Švancara et al. [33] reviewed the activities and achievements made during the first decade of development of Bi-based electrodes since the pioneering work reported in 2000 [34], especially focusing on the device versatility as well as the significant milestones and break-points in heavy metal determination. From the point of view of miniaturization and disposability of sensor devices for in field application, a wide variety of Bi-based screen printed electrodes (SPEs) and on-chip Bi devices fabricated by photolithography techniques has been presented. Serrano et al. [35] summarized the common design and fabrication approaches for disposable Bi SPEs. Duarte et al. [36] presented an overview about disposable sensors for environmental monitoring of Pb(II), Cd(II) and Hg(II), including a section about the Bi thin-film microelectrode arrays fabricated by lithographic techniques. Among them, almost all the Bi-based sensing platforms can easily meet the analytical requirements for Pb(II) detection at concentration values down to 4 $\mu\text{g/L}$. However, very few of all these

reported electrochemical devices could reach a LOD as low as 0.14 $\mu\text{g/L}$ for Cd(II). For instance, our group [32] has recently synthesized a nanocomposite material made of a carbon xerogel doped with Bi nanoparticles that was applied to the fabrication of a nanocomposite paste electrode for Pb(II) and Cd(II) analysis. The obtained LODs were 0.65 $\mu\text{g/L}$ Pb(II) and 0.81 $\mu\text{g/L}$ Cd(II) for an overall analysis time below 4 min.

In order to fulfill the strict analytical requirements set by EU in terms of MAC-EQS values, different strategies based on the modification of the working electrode surfaces have been carried out. Herein, various nanomaterials including nanoparticles (NPs), carbon nanotubes (CNTs) and graphene have been employed to modify the electrodes in order to increase the electrochemical active surface area of the device and to offer a synergic effect for enhancing its sensitivity [14,17]. They are commonly integrated on the surface of commercial electrodes aiming at developing different sensor architectures. For instance, Li et al. [14] modified a GCE with a Nafion-graphene composite film in combination with an in-situ plated Bi film for simultaneous detection of Pb(II) and Cd(II), showing estimated LODs to be around 0.02 $\mu\text{g/L}$ for both heavy metals.

From the analytical point of view, one of the advantages of using stripping voltammetric techniques is that accumulation and stripping processes can be tailored to improve the LODs of the sensor devices. Recently, Rutyna et al. [16] reported a double deposition and stripping process on a pair of in-situ plated Bi film electrodes with drastically different surface areas placed at a set distance from each other for the detection of Pb(II) and Cd(II). Extremely low LODs of 0.037 $\mu\text{g/L}$ and 0.005 $\mu\text{g/L}$ for Pb(II) and Cd(II) were achieved, respectively.

The validation of the devices cited above was carried out in most cases by the analysis of real water samples in the laboratory. In order to show the potential for in-situ

measurements, some reports also implemented the developed sensors into a system that could be deployed in a real scenario. For instance, Bi-based miniaturized devices hold great promise for in-field Pb(II) and Cd(II) analysis, as demonstrated by Neagu et al. [37], who developed a set-up in which *Lemna Minor L.* aquatic plant was employed to purify wastewater and a Bi film plated SPCEs sensor was integrated to in-situ measure the efficiency of this plant in the removal of heavy metals. Ninwong et al. [17] incorporated Bi-coated screen printed carbon nanotube electrodes in a sequential injection analysis system for the automated determination of Pb(II) and Cd(II) in drinking water, tap water and pond water samples.

2.1.2. *Non-Bi electrochemical devices*

Other approaches developed to construct electrochemical sensors for the detection of Pb(II) and Cd(II) incorporate functional chemical groups such as amine- and thiol-moieties with the ability to form chelates with heavy metal ions, for the selective accumulation and further detection of these pollutants in aqueous solutions. Sánchez et al. [23] modified a commercial SPCE with amine functionalized mesoporous silica nanoparticles for the determination of Pb(II) at concentration levels down to 0.1 µg/L. Zhao et al. [24] modified the surface of a GCE with a conductive polymer layer containing thiol groups that selectively interacted with Pb(II) and Cd(II). The sensor showed an excellent analytical performance and LODs of 0.3 µg/L Pb(II) and 0.05 µg/L Cd(II), were achieved. Unlike Bi based electrodes, it is worth mentioning here that the multiparametric detection of several metal ions with these modified electrodes faces a potential problem, because of the competition for the binding sites during the pre-concentration step as well as likely saturation, which may hinder their simultaneous detection.

The selective recognition and sensing of a particular ion can also be carried out using imprinted polymers. Polymer imprinting technologies allow for the production of synthetic polymers containing specific binding sites for a target analyte. Sites with specific shape and functional groups complementary to the target analyte are created by cross-linking polymers around a template of this target analyte. Among them, ion imprinted polymers (IIPs), were designed and integrated into electrochemical sensing devices. For instance, Alizadeh et al. [27] constructed a sensor based on a carbon paste electrode impregnated with a Cd(II) imprinted polymer and applied it for highly selective electrochemical detection of Cd(II) in water. This sensor approach showed a good selectivity against potential interfering agents such as Cu(II), Hg(II) and Pb(II) and provide a LOD value of 0.06 $\mu\text{g/L}$ for this metal ion.

2.2. Mercury

Gold (Au) electrodes have shown superior performance for Hg(II) determination in waters. This electrode material form amalgams with Hg and therefore the detection of this highly hazardous compound can be carried out by anodic stripping voltammetry, using a similar measurement protocol to that applied in the detection of Pb(II) and Cd(II). So far, different electrode geometries from bulk to thick-film (screen-printed) and thin film microarrays, have been reported for the determination of Hg(II). However, none of them could meet the requirement imposed by the EU that set a limit of detection (LOD) lower than 0.02 $\mu\text{g/L}$. The lowest reported LOD was 0.17 $\mu\text{g/L}$ using a thin-film Au electrode [38]. In order to enhance it, other electrode architectures have been fabricated, based on the modification of metal or carbon electrodes with other materials. In this context, Gao et al. [38] recently reviewed the different modification strategies that could be found in the literature. Most of the devices incorporate nanomaterials or DNA, but unfortunately once again, few of them achieved the LOD value mentioned

above. Among them, Jena et al. [21] reported a LOD for Hg(II) of 0.02 $\mu\text{g/L}$ on gold nanoelectrode ensembles, which was prepared through binding Au NPs on the surface of Au electrodes previously modified with a thiol-functionalized silicate network. Gong et al. [22] developed a chitosan/graphene/Au NP composite applied as sensing platform for the highly sensitive and selective detection of Hg(II). The sensor combined the advantages of Au NPs and graphene, leading to a remarkable improved sensitivity with a LOD as low as 0.006 $\mu\text{g/L}$. Since Hg(II) can interact specifically with thymine bases (T) to form stable T-Hg(II)-T biomimetic structures, various electrochemical sensors towards Hg(II) detection have been proposed based on T-Hg(II)-T coordination. In this context, Tortolini et al. [30] developed an electrochemical DNA biosensor for the selective determination of Hg(II), achieving a LOD of 0.02 $\mu\text{g/L}$.

Hg(II) ion imprinted polymers were also synthesized aiming at improving the selectivity of the corresponding sensors. Fu et al. [28] prepared a Hg(II) imprinted polymer on a Au NP/CNT modified GCE through electro-polymerization of 2-mercaptobenzothiazole-Hg(II) complex. The resulting ion imprinted polymer showed enhanced response to Hg(II) with no or little influence from other heavy metals such as Ag(I), Pb(II), Cd(II), Zn(II) and Cu(II). A LOD of 0.016 $\mu\text{g/L}$ was achieved.

Although the mentioned approaches show very low LOD and high specificity, the tedious and rigorous fabrication processes together with the lack of stability and reproducibility limit their application in a real scenario. Recently, Yuan et al. [26] reported on the easy fabrication of a sensor based on a GCE modified with layered sodium titanate (Na-TNs) nanosheets that showed satisfactory selective detection towards Hg(II) with a LOD as low as 0.005 $\mu\text{g/L}$. The platform effectively inhibited the interference from other heavy metals ions, due to the preferentially cation exchangeable ability of Na-TNs towards Hg(II).

Overall, it can be stated that in spite of the variety of electrochemical devices reported so far for the selective and sensitive detection of Hg(II), the rather complicated fabrication protocols and their difficult implementation make them unsuitable for an in-field application. Therefore, more research efforts should be put in this regard in order to produce an electrochemical sensor that was simple and reliable, with the in turn potential of being operated in situ.

Simultaneous detection of Pb(II), Cd(II) and Hg(II) proves to be a challenging task. Bi-based electrodes are not suitable for the detection of Hg(II) because Bi shows a standard oxidation potential lower than that of Hg. Therefore, as described above, other electrode materials have to be selected. Although not as sensitive as Bi, carbon-based electrodes could be applied in this context. However, the possible formation of Hg/Pb and Hg/Cd amalgams would give rise to serious interferences and have a negative effect on the analytical performance of the resulting devices. Also, some materials show a high affinity towards the adsorption of specific heavy metal ions, and as such show potential for being incorporated into an electrochemical sensor for these contaminants. Thus, Wei et al. [20] developed highly adsorptive γ -AlOOH(boehmite)@SiO₂/Fe₃O₄ porous magnetic microspheres that could selectively interact with Zn(II), Cd(II), Pb(II), Cu(II) and Hg(II). These spheres were applied to the fabrication of an electrochemical sensor based on a glassy carbon electrode coated with the mentioned microspheres. Figure 2 illustrates the SWASV responses of this device recorded in a solution containing the different heavy metals. Again, the device suffered from interferences when the analysis was performed simultaneously because of the competition for the adsorption sites of the microspheres. Nevertheless, very low LODs were achieved for each heavy metal when these were measured individually.

2.3. Nickel

The development of electrochemical sensors for Ni(II) detection is scarce. Most of them are based on the use of Bi-modified carbon electrodes and the application of adsorptive cathodic stripping voltammetric technique (AdCSV). In a typical analytical process, Ni(II) is firstly complexed with a chelating agent, mainly dimethylglyoxime (DMG) in the aqueous solution and then the Ni(DMG)₂ metal complex is adsorbed on the surface of the Bi electrodes at a fixed potential during the accumulation step. Afterwards, the potential is scanned in the cathodic direction, thereby reducing the Ni(II) ion and in turn inducing the complex desorption from the electrode and the generation of a current response, as shown in Figure 1. All the Bi-based sensors reported so far fulfill the analytical requirements set by the EU to detect Ni(II) in waters at concentration values lower than 10 µg/L. For instance, Dal Borgo et al. [18] developed a macroporous Bi film screen printed carbon electrode for the determination of Ni(II) and achieved a very low LOD of 0.094 µg/L. This device was successfully validated in sewer water samples. Kokkinos et al. [39] obtained a LOD of 0.1 µg/L for Ni(II) determination using an integrated on-chip Bi film electrochemical device. More importantly, these electrochemical sensors were shown to adequately perform for on-line Ni(II) monitoring. For instance, Economou et al. [19] described an on-line automatic analyzer for Ni(II) as well as Pb(II) and Cd(II) detection by combining a Bi film electrode with a hybrid flow-injection/sequential injection system.

Although briefly described in the previous sections, it should be mentioned here that one of the main shortcomings of the above described sensor devices for heavy metal detection is related to the lack of selectivity or the presence of other interferents when the sensors are applied in real water samples. Although the electrochemical signals for these heavy metals are well defined and thoroughly studied, some other metal species

that may be present in solution produce overlapped electrochemical signals that cannot be resolved depending on the heavy metal relative concentrations [32]. One of the most studied ones is the interference of Co in the detection of Ni. In other cases, the big differences in the relative concentrations of the different metal species in solution or the organic matter content, which mask the presence of heavy metals, produced a negative influence on the accumulation step of the target analyte heavy metals. Such an effect was studied in the detection of Pb and Cd when Cu or Zn were present in solution at relatively high concentrations [32].

3. Pesticides

Eight out of the twelve new priority substances listed in the EU Directive are pesticides (Table 2) [1]. Pesticides include a wide range of chemical compounds used to prevent, destroy, repel, or mitigate the growth of harmful animals, invasive plants, weeds, fungi, bacteria, viruses and prions. According to their use, pesticides can be divided into four categories: herbicides, fungicides, insecticides and bactericides.

Although most of the pesticides included in the list of priority substances are banned in EU [40], they are still found in waters due to their widely use in the past and their persistence in the environment. Indeed, fifteen of them are included in the list of persistent organic pollutants (POPs) due to their ability to remain in the environment, to be bioaccumulative and biomagnifying, and to show long-range transport capacity (Stockholm Convention on Persistent Organic Pollutants) [41]. Conventional methods employed for pesticide detection include different gas and liquid chromatography techniques coupled to mass spectrometry. These powerful analytical tools allow for the determination of pesticides at sub $\mu\text{g/L}$ level providing the sensitivity, selectivity, and specificity set by EU directive [42]. However, as mentioned in the introduction section,

they are bench-top techniques using sophisticated and expensive instrumentation, and therefore, although well-suited for laboratory analysis, they cannot be applied for *in situ* measurements.

The electrochemical detection of pesticides has been widely described in the literature and includes two clear strategies. One is the direct electrochemical detection of redox-active pesticides using appropriate electrodes. The other one is the fabrication of biosensors that include a biorecognition element (i.e. enzymes, antibodies, etc.) immobilized onto a suitable electrochemical transducer, for the indirect detection of pesticides through their interaction.

3.1. Direct Electrochemical Detection

Stripping voltammetry is undoubtedly the most reported electrochemical technique for pesticide determination. As shown in the previous section, this technique has been widely used for metal ion analysis due to its high sensitivity, and as such can also be applied for the determination of small organic molecules such as pesticides. Despite the number of works related to direct electrochemical detection of pesticides that have been published over the last years, few of them fulfil the analytical requirements set by the EU Directive (Table 2).

The alachlor herbicide was detected at concentrations down to 0.0016 $\mu\text{g/L}$ by differential pulse cathodic stripping voltammetric (DP-CSV) using a hanging mercury drop electrode (HMDE) [43]. A thin-film mercury electrode generated on a glassy carbon electrode in the presence of thiocyanate, was developed for the determination of the atrazine triazine pesticide [44]. The presence of thiocyanate induced an adsorptive effect on the protonated atrazin molecule and a very low detection limit was attained (0.024 $\mu\text{g/L}$) by means of CSV. Chlorfenvinphos (0.0015 $\mu\text{g/L}$) organophosphorus

insecticide was also detected by CSV using a HMDE [43]. Although Hg electrodes show the best analytical performance for stripping analysis, it is very desirable to find alternative less-toxic electrode materials. In recent years, nanotechnology has allowed to develop new electrode materials showing excellent electroanalytical performance.

A highly sensitive determination of chlorpyrifos (DP-CSV, LOD 0.0014 $\mu\text{g/L}$) was reported by Sreedhar et al. [45] using a novel Ag/Cu alloy nanoparticle and graphene nanocomposite paste electrode. A glassy carbon electrode modified with multiwalled carbon nanotubes (MWCNT), polyaniline (PANI) and polypyrrole (PPY) was used for the determination of isoproturon at concentrations down to 0.1 $\mu\text{g/L}$ by differential pulse anodic stripping voltammetric (DP-ASV) [46]. A sodium montmorillonite clay-modified glassy carbon electrode was also employed for the determination of isoproturon herbicide by DP-ASV [47]. Montmorillonite was shown to be a suitable matrix for the accumulation of the pesticide on the electrode surface and a limit of detection of 1 $\mu\text{g/L}$ was achieved. A highly sensitive electrochemical device has been reported by Mirabi-Semnakolai et al. [48] based on a copper nanowire modified carbon paste electrode and applied to the detection of trifluralin at concentrations down to 0.002 $\mu\text{g/L}$.

Regarding the direct electrochemical detection of organochlorine and diphenyl ether pesticides, very few reports show devices sensitive enough to detect these hazardous species at the MAC-EQS levels (Table 2). Dicofol, whose MAC-EQS was not established by EU, was detected at concentrations down to 0.05 $\mu\text{g/L}$ by DP-ASV using the MWCNT /PANI/PPY modified GCE previously described for isoproturon analysis [46].

Almost all works described above allowed for the sensitive determination of different pesticides and adequately performed in water matrices [43, 44, 45-47]. However, the

selective detection of the corresponding target analyte was not assessed in most cases, considering that the electrode response was only evaluated in the presence of inorganic interferences, or organic pollutants with a very different electrochemical/ adsorption behavior. It should be noted that major interferences in stripping analysis are overlapping stripping peaks, caused by compounds exhibiting similar redox potentials, and the presence of surface-active substances that adsorb on the electrode surface (i.e. pesticides with similar structures). To overcome selectivity problems in the direct electrochemical detection of pesticides two interesting alternatives have been proposed. One of them was the novel differential pulse voltammetry method developed by Qiu et al. [49] for the simultaneous determination of four triazine pesticides (including atrazine and simazine). The method relies on the application of chemometric techniques to solve the complex voltammograms and extract the results. The approach compared well with the chromatographic techniques for the simultaneous analysis of these herbicides in water. Limits of detection of 0.8 $\mu\text{g/L}$ and 0.13 $\mu\text{g/L}$ were calculated for atrazine and simazine, respectively.

The other alternative for the simultaneous determination of triazines was developed by Islam et al. [50]. A capillary electrophoresis microfluidic chip with pulse amperometric detection was designed for the determination of atrazine, simazine and ametryn. The triazine compounds were separated due to their differential migration through an agarose gel under the influence of an electric field (20V/cm) and then detected within an assay time of 1.25 min using a gold electrode. Limits of detection below the MAC-EQS values specified in the new EU Directive were determined for atrazine (0.1 $\mu\text{g/L}$) and simazine (0.07 $\mu\text{g/L}$).

3.2. Electrochemical biosensors

A number of different biological recognition elements (i.e. enzymes, antibodies, bacteria) have been employed for the fabrication of pesticide biosensors [51]. Although to a lesser extent, examples of the use of biomimetic receptors such as molecularly imprinted polymers (MIPs) have also been found in literature.

As mentioned above for the direct electrochemical detection of pesticides, nanotechnology has allowed the construction of new bioelectrochemical interfaces with improved stability of the immobilized bioreceptor, faster electronic transfer rates and overall enhanced analytical performance [52, 53]. Also, a variety of electrochemical techniques have been explored in the development of pesticide biosensor approaches, including differential pulse voltammetry, square-wave voltammetry, amperometry, potentiometry and electrochemical impedance spectroscopy .

The ability of some pesticides to inhibit the activity of certain enzymes has been exploited in the development of electrochemical enzymatic biosensors [54]. Enzymes use as receptors were usually immobilized onto the electrode surface and their catalytic activity was electrochemically monitored through the generation of an electroactive enzymatic product. Highlighted publications on enzymatic biosensors for pesticide determination are listed in Table 3. As seen in this table, enzyme inhibition assays have been widely studied as potential alternatives to chromatographic methods for organophosphorous pesticide determination. Organophosphorus insecticides have a high acute toxicity to human health and ecosystems caused by their ability to inhibit the activity of cholinesterase enzymes. An excellent review of pesticide determination based on acetylcholinesterase inhibition has been recently published by Punder and Chauhan [55]. More sensitive electrochemical approaches for the organophosphorus insecticides chlorfenvinphos [56, 57] and chlorpyrifos [58-62] are shown in Table 3.

Based on the inhibitory effect of atrazine on tyrosinase activity, a very sensitive amperometric enzymatic sensor for this triazine herbicide was described by Kim et al. [63]. A limit of detection of 0.00035 $\mu\text{g/L}$ was achieved. It is clear from Table 3 that the incorporation of nanomaterials in the design of enzymatic biosensors for pesticide detection has attracted enormous attention in recent years. Taking into account that the performance of an enzymatic biosensor mainly depends on the catalytic activity preservation after the enzyme immobilization onto the electrode surface, different immobilization strategies have been explored. Covalent bonding was the most widely used procedure for enzyme immobilization [56, 58, 62, 63]. To this end, different functional groups were created on the transducer surface through the incorporation of polymers [56] or modified nanostructures [58, 62, 63]. In addition to covalent coupling, physical entrapment [59, 61] and the use of microspheres as enzyme carriers [60] were also reported.

Similar to the direct electrochemical detection, the lack of selectivity is the main disadvantage of the reported enzymatic biosensor approaches for pesticide determination, since one enzyme can be inhibited by several pesticides. Another important problem that limits the application of this kind of biosensors is the irreversible loss of enzyme activity upon pesticide inhibition. To solve this drawback in most of the enzymatic biosensors found in literature based on acetylcholinesterase inhibition, the enzyme was reactivated upon the addition of nucleophilic oximes [56, 58, 60-62]. Another way to renew the enzyme following one analysis was the use of enzyme functionalized magnetic beads. The same transducer can be reused for several analyses by simply removing the magnetic beads and incorporating fresh ones to the electrode surface [57].

Immunosensors are potentially useful for the rapid detection of pesticides due to their intrinsic advantages, such as high sensitivity, and specificity. This affinity biosensors rely on the binding of a target analyte (antigen, Ag) to its specific antibody (Ab), thus requiring the production of a particular Ab for each antigen determination. Provided that the production of antibodies against small molecules such as pesticides is a difficult and costly process, most of the work developed in this area has been focused on the detection of atrazine, for which specific antibodies have been developed and thoroughly assessed (Table 3) [64-71]. Examples of electrochemical immunosensors for chlorpyrifos [72], diuron [73, 74], isoproturon [75] and endosulfan [76] have also been found in the literature (Table 3). As stated above for enzymatic biosensors, covalent bonding was the most reported strategy for immunoreagent immobilization either on the electrode surface [65, 66, 68 71, 72, 74-76] or on magnetic beads [67].

Among the immunosensor formats applied for pesticide analysis, label-free reagentless approaches should be mentioned [70, 71, 76]. Label-free and reagentless immunosensors are systems capable to measure a target analyte after the corresponding affinity interaction without the need of additional reagents. Reagentless immunosensors for the detection of pesticides were constructed by immobilizing a redox probe on the electrode surface [70, 76] or by measuring the changes produced on the double layer capacitance at the solid/liquid interface after immunocomplex formation [71]. A schematic representation of the label-free and reagentless immunosensor developed by Liu et al. [76] for the determination of endosulfan is shown in Figure 3. label-free and reagentless sensors are shown to be the most promising alternative for on-site detection of small molecules in environmental monitoring. Most of the label-free strategies listed in Table 3 require, however, the addition of redox probes (i.e. $[\text{Fe}(\text{CN})_6]^{3-/4}$) to get the electrochemical signal [65,66,68,72]. Electrochemical detection for these label-free

immunosensors was based on the change of electron transfer kinetics of the redox-probe at the electrode-solution interface, due to the corresponding affinity reaction [65, 66, 68, 72].

Different types of DNA biosensors have also been developed for the screening of pollutants based on the damage that some pesticides produce to the DNA double helix and/or its structural components. Less studied than enzymatic and immunosensor devices, most of the DNA sensors found in the literature showed a lack of sensitivity. One example that meets the EU requirements was the DNA sensor described by Wu et al. [77] for hexachlorobenzene (LOD 0.008 $\mu\text{g/L}$). This organochlorine pesticide was detected on a double-stranded DNA modified gold electrode using methylene blue as redox indicator by means of differential pulse voltammetry. The biosensor response was based on the strong interaction between hexachlorobenzene and dsDNA (stacking, hydrogen bonding and hydrophobic interaction). This interaction produces conformational changes in the DNA structure that blocks the intercalation of methylene blue redox probe, resulting in a decrease of the biosensor signal. In addition to the low sensitivity showed for pesticide analysis, the selectivity of DNA-based sensors was not very high, since pesticides with similar chemical structures may share the mechanism of interaction with DNA and thus the same response.

Microbes (e.g., algae, bacteria, and yeast) offer a very interesting alternative to enzymes, Ag/Ab or DNA in the fabrication of biosensors. Compared to biological recognition elements described above microbial cells can be easily produced at large scale. Furthermore, they can be manipulated in order to obtain a specific response for a target analyte through selective cultivation conditions or genetic engineering [78, 79]. Another advantage of whole-cell sensors, widely exploited in recent years for environmental analysis, is their ability to provide information about the bioavailable

fraction of toxic compounds. Although the work on whole-cell sensors has been mainly focused on optical detection, examples of pesticide biosensors with electrochemical detection can also be found in literature. In fact, an electric cell-substrate impedance sensing system suitable for environmental monitoring is commercially available (Applied BioPhysics, Inc.) [80, 81]. This device measures toxicant-induced changes in the electrical impedance of mammalian cells attached onto the surface of eight small gold electrodes. Cholinesterase enzyme from *Arthrospira platensis* was used for the sensitive conductometric detection of diuron herbicide at concentrations down to 0.0002 $\mu\text{g/L}$ [82]. *Arthrospira platensis* whole cells were immobilized on gold interdigitated electrodes and conductivity changes were recorded in the presence of acetylthiocholine chloride. A highly sensitive, selective, and rapid, whole-cell electrochemical biosensor was developed by Prathap et al. [83] for the determination of hexachlorocyclohexane. Genetically modified *E. coli* cells capable to degrade this insecticide were immobilized onto a polyaniline modified gold interdigitated electrode. The HCl generated during pesticide degradation produced a change in conductivity that was monitored by pulsed amperometry. A 0.002 $\mu\text{g/L}$ limit of detection was achieved. The sensor was found to be selective to all the isomers of hexachlorocyclohexane and to pentachlorocyclohexane but did not respond to other aliphatic and aromatic chlorides or to the corresponding end product of the pesticide degradation.

The lack of specificity of pesticide sensors based on biocatalytic or affinity receptors may be overcome through the identification and use of artificial ligands such as molecularly imprinted polymers (MIPs), whose production process is analogue to that described for the ion imprinted polymers applied to the detection of heavy metals [84]. A MIP-based potentiometric sensor for γ -hexachlorocyclohexane was developed by Anirudhan and Alexander [85]. The changes in the potential produced at a MIP-

modified Cu working electrode compared to a reference one before and after pesticide interaction with the MIP structure provided the basis of the sensor response. The limit of detection of this sensor was worse than those reported for this insecticide using DNA or bacterial sensors, but it showed enhanced selectivity.

4. Hydrocarbons

In this group of priority substances, all the aromatic compounds, showing one ring (benzene), two rings (naphthalene) or more rings (anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)-pyrene) in their chemical structures, are included. They are named after PAHs and are listed in Table 4. These compounds can occur naturally but the largest amounts of PAHs released into the environment are due to anthropogenic processes related to the incomplete combustion of organic matter, by-products of industrial processing and cooking foods. PAHs have been identified as carcinogenic and mutagenic, as well as teratogenic [86]. The compound di(2-ethylhexyl)phthalate (DEHP) has also been included in this group. Due to its suitable properties and low cost, DEHP is widely used as plasticizer in manufacturing of articles made of polyvinyl chloride, among other industrial applications. Although DEHP has low acute toxicity, it is considered pollutant of concern for its potential as endocrine disruptor. The standard methods to determine all these compounds are based on bench-top laboratory instruments such as high-pressure liquid chromatography with fluorescence detection or gas chromatography / mass spectrometry.

In Table 5, we have summarized those electrochemical approaches found in the literature that show a LOD equal or below the MAC-EQS values for inland surface waters, shown in Table 4. Direct oxidation of these organic compounds using metal or

carbon-based electrodes proved to be unfeasible given that the high potentials required are outside the potential window defined by the hydrolysis of water for these devices. In this context, one approach has been developed up to now for the direct oxidation of benzo(a)pyrene [95]. This was possible using a boron-doped diamond electrode that shows a wider potential window so that the oxidation of water does not interfere. Using square-wave stripping voltammetry, the benzo(a)pyrene yielded a well-defined voltammetric response at +1.07 V (vs. Ag/AgCl) after 120 s accumulation at +0.10 V. Although the obtained LOD for the pollutant was 0.72 $\mu\text{g/L}$, it could be easily improved by increasing the deposition time in order to accomplish the 0.27 $\mu\text{g/L}$ value set by the EU directive for this pollutant. In addition, a study of interferences is needed to verify that the benzo(a)pyrene peak is well resolved from that of other organic compounds that may be present in the sample. Other strategies have been mostly applied that are based on the use of electrochemical receptors that selectively interact with the target analyte and whose corresponding redox processes are attenuated upon this interaction. In addition, indirect detection approaches that rely on electrochemical biosensors have also been pursued.

The application of an electrochemical impedance spectroscopy detection approach enabled the direct measurement of DEHP plasticizer in water. A pair of gold planar interdigitated electrodes, fabricated using standard photolithographic techniques on a silicon substrate, was used as the electrochemical probe [93]. A LOD of 2 $\mu\text{g/L}$ was achieved, which is close to the 1.3 $\mu\text{g/L}$ value set by the EU directive. By modifying the design of the digits, the promising outcome of this research is the improvement of the sensor's sensitivity and selectivity.

Apart from these works, most of the devices developed so far make use of organic receptors with redox activity or biomolecules that could selectively interact with the target pollutants. These are shown below.

4.1. Electrochemical devices based on electroactive receptors

As mentioned above, PAHs can be detected using recognition elements with redox activity. The ones reported so far show a planar polycyclic structure and can interact with PAHs through synergistic non-covalent charge transfer and π - π stacking forces [94]. These interactions modulate the electrochemical response of the receptor and a decrease in the oxidation and reduction peaks is recorded that is directly related with the PAH concentration. Recently, two compounds have been proposed for quantifying PAHs in water samples, namely thionine and benz(a)anthracene-7,12-dione. Thionine was incorporated into a composite with graphene sheets to determine the total amount of phenanthrene and anthracene [91]. This molecule can selectively interact with these tricyclic aromatic hydrocarbons and as a consequence, its electroactivity is partially blocked. On the other hand, benz(a)anthracene-7,12-dione, whose molecular structure is shown in Figure 4, was electrodeposited, together with a polypyrrole film, on an electrode surface and the resulting device was applied to the detection of benzo(k)fluoranthene [92]. Given the specific interaction between the probe and the pollutant, no other common PAH interfered in the voltammetric sensor response. The reduction of the two ketone groups to hydroxyl groups in the probe is a quasi-reversible process, whose peaks decreased upon the interaction with the target analyte. However, it was reported that the oxidation peak current was more sensitive and so, it was used as the sensor response to obtain the corresponding calibration curve (Figure 4) [92]. A linear response in the semi-logarithm plot was produced, and this behavior was related

to the non-covalent interactions taking place between the sensor and the target analyte [6].

Other redox-active probes of biological origin were also applied to the development of electrochemical sensors for PAHs. Del Carlo et al. [96] used single stranded DNA immobilized on the surface of an electrode to detect anthracene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene and benzo(a)pyrene. This device is based on the non-covalent interactions between PAHs and DNA. The modulation of the guanine base oxidation peak upon interaction with the target analyte was used as the analytical sensor signal. Unlike those related works described above [91, 92], this device lacks selectivity so that a cross response of all PAHs present in the sample is obtained. However, the sensitivity of detection is different depending on the pollutant. A feasible approach to work out this drawback is the use of an array of different DNA chains as redox probes and the application of multivariate chemometric tools, such as artificial neural networks or partial-least squares, to clearly measure the signal for each pollutant. These non-specific chains would respond to all PAHs, but with different selectivity and sensitivity. As in the case of an electronic tongue, the concentration of each single PAH could be extracted from the multidimensional data generated by the DNA chains.

4.2. Electrochemical immunosensors

Biosensor devices based on the use of antibodies as specific receptors have been applied to some extent in the detection of PAHs. Lin et al. [87] reported on an electrochemical approach based on a competitive immunoassay using magnetic beads coated with antibodies to PAH and a PAH-horseradish peroxidase (HRP) conjugate. Amperometric detection was carried out using electroactive 3,3',5,5'-tetramethylbenzidine as HRP mediator. Using a similar detection strategy the same authors developed an

electrochemical immunosensor for benzo(a)pyrene based on a PAH-modified transducer [88]. Here, spheres modified with anti-PAH and HRP label were applied together with hydroquinone HRP mediator in order to get the corresponding amperometric sensor response. Zhang et al. fabricated a label-free immunosensor for the detection of naphthalene [89] and benzo(a)pyrene [90] based on the immobilization of Prussian blue redox probe and the respective antibody receptors onto a glassy carbon electrode. This configuration provides a great experimental simplicity. Here, the interaction of the corresponding analyte with the recognition element generates an inert layer that blocks the electron and mass transfer and concomitantly decreases the peak currents of Prussian blue, which was used as analytical signal.

Provided the specificity of the immunoreactions, the electrochemical devices mentioned above do not suffer from interference problems. Furthermore, custom-made antibodies could be obtained for other PAHs and thus similar sensor strategies could be applied for their determination. However, they also present several drawbacks, mainly related to their applicability as systems for remote and on-line monitoring. One of them is the conditions and the time of analysis. Generally, the immunosensors need to work under optimal conditions of pH, supporting electrolyte, temperature and time of incubation. These incubation times, prior to analytical measurement, ranged from 15 min for the direct immunoassay [89] up to 2 ½ h for the competitive immunosensor [88]. Another important limitation of these systems is their operational stability, given that immunosensors must be stored at 4 °C when not in use and also for the irreversibility of the immunological reactions. Although in some cases the immunosensor could be regenerated [89, 90], the number of measurements carried out with the same device is usually very limited.

5. Halogenated hydrocarbons

In this group of priority substances, all the organic solvents and precursors (1,2-dichloroethane, dichloromethane, hexachlorobutadiene and chloroform), flame retardants (brominated diphenylethers, chloroalkanes C₁₀₋₁₃ and hexabromocyclododecanes) as well as dioxins are included. Some of these halogenated hydrocarbons occur naturally, being synthesized by halogenation reactions occurring during combustion of biomass. However, most of these species are synthetic and are manufactured as industrially useful materials, or are incidentally produced as a by-product during industrial chemical reactions, or during the incineration of municipal waste. For example, chlorinated hydrocarbons are associated with contamination problems, because most of these chemicals are persistent in the environment, and they accumulate in organisms, sometimes causing toxicity. Dioxins and dioxin-like compounds are by-products of various industrial processes, and are commonly regarded as highly toxic compounds and persistent organic pollutants. They include the polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls, among others. The perfluorooctanesulfonic acid synthetic surfactant has also been included in this group. It is a persistent, bioaccumulative and toxic pollutant. For some of these compounds, there is not currently an available standardized method for their determination in water. In the case of 1,2-dichloroethane, dichloromethane, hexachlorobutadiene and chloroform, standard methods are based on bench-top laboratory instruments such as gas chromatography with mass spectrometric detection or gas chromatography with electron capture detector.

Given the chemical structure of this family of pollutants, no approaches based on direct electrochemical methodologies have been found in the literature for the determination of the flame retardants, dioxins or 1,2-dichloroethane and hexachlorobutadiene compounds. Just an electrochemical approach has been reported for quantifying

halomethanes, such as dichloromethane and trichloromethane (chloroform) in water. It was based on a three-step stripping analysis that entailed (1) direct electrochemical reduction of a halomethane at a silver cathode to form halide ions in an aqueous sample containing tetraethylammonium benzoate, (2) capture of the released halide ions as a silver halide film on the surface of a silver gauze anode, and (3) cathodic reduction and quantification of the silver halide film by means of differential pulse voltammetry [97]. The standard addition was used to analyze sample solutions of each halomethane. Chloroform was successfully measured in 30 min at concentrations down to 6.0 µg/L. Presumably, this value could be improved by increasing the time of electrolysis and deposition to reach the 2.5 µg/L value set by the EU directive. The main drawback of this method is the lack of selectivity, since the total amount of halide ions arising from all halogenated compounds present in the sample was actually measured.

6. Alkylphenols

The alkylphenols considered as priority substances are 4-nonylphenol and 4-tert-octylphenol. They are used extensively as precursors of detergents, as additives for fuels and lubricants, polymers, and as components in phenolic resins. However, they have been identified as endocrine disruptors, are persistent in the environment, and liable to bioaccumulate. According to the current EU directive, the standard method to determine these two compounds in water is based on gas chromatography with mass spectrometry.

Alkylphenols are electroactive and as such can be detected by irreversible oxidation of the hydroxyl group of the basic molecule structure. However, direct detection using conventional electrochemical devices lack the required sensitivity to detect these pollutants at the levels required by the EU directive. Then, most of the devices reported so far make use of different strategies to enhance the sensitivity, and are mainly based

on implementing the means to pre-concentrate the analyte on the sensor surface or to carry out the analyte electrocatalytic oxidation. Three devices found in the literature that show LOD equal or below the MAC-EQS values shown in Table 4, are explained in detail below.

Wan et al. [98] constructed a voltammetric sensor approach for the sensitive detection of 4-tert-octylphenol. A glassy carbon electrode was firstly coated with CNTs and then, a poly(L-lysine) film was electrodeposited. On one hand, the CNTs conferred higher active area and also a high catalytic activity to the electrode. On the other hand, the deposited conductive polymer provides with a porous structure capable of accumulating the analyte by electrostatic interactions. A LOD of 0.1 $\mu\text{g/L}$ was obtained. The device was applied to the detection of this pollutant in spiked lake and river water samples. The same strategy was used by Zhou et al. [99] for the successful determination of 4-nonylphenol. In this case, the catalytic element was the reduced graphene and chitosan was applied to accumulate the pollutant. A LOD of 1.1 $\mu\text{g/L}$ was obtained with the sensor being applied in spiked milk and honey samples. Although in both works an interference study was performed with different inorganic ions and short-chain molecules, other alkylphenols with similar chemical structure that could have a significant influence on the response of these electrodes must have been tested. In order to avoid this important interference, Chen et al. [100] applied a molecularly imprinted polymer film selective to 4-nonylphenol, generated on to the electrode surface. The use of molecularly imprinted polymers had been utilized in previous works, but in this case an enhanced LOD was obtained. A detailed diagram of the whole process of the sensor fabrication is depicted in Figure 5. A LOD of 0.0035 $\mu\text{g/L}$ was obtained that was almost three-decades lower than that required by the EU.

Two more devices have been reported that show a LOD of 2.2 $\mu\text{g/L}$ for nonylphenol, only 10 % higher than the required by the EU directive, shown in Table 4. A cetyltrimethylammonium bromide was used to form a hydrophobic bilayer on the surface of a carbon paste electrode. This layer interacted with the alkyl part of the pollutant and was applied to preconcentrate the analyte [101]. A second device is a biosensor based on the use of reduced graphene and ss-DNA. While graphene had an electrocatalytic effect on the detection of nonylphenol, this could also be accumulated on the sensor surface thanks to the intercalation and electrostatic binding with the ss-DNA [102]. Finally, it is worth mentioning the work of Liu et al. [103], who reported on a new sensor device for nonylphenol that was in turn incorporated into an automated analysis system type flow-injection analysis showing the potential of the developed sensor for in-field analysis of this pollutant.

7. Conclusions

Electrochemical sensor devices based on a variety of configurations have been developed and applied to the detection of water pollutants, including those identified by the EU and other bodies, such as World Health Organization and the Environmental Protection Agency, to be prioritized and thus primarily controlled in waters. Device implementation involves high sensitivity below the EQS values, selectivity and long-term stability together with amenability to be integrated in automatic systems and thus be applied in field. While electrochemical sensors for inorganic compounds, that is, heavy metals, can be envisaged as potentially deployable in the near future, other approaches for organic molecules required further development, especially in terms of selectivity and stability. Thus, despite the high sensitivity, low-cost and rapid response associated with direct electrochemical detection of pesticides and alkyl phenols, their

lack of selectivity makes them difficult to apply to real sample analysis. Electrochemical biosensors are however expected to play an expanding role in the development of rapid, simple, selective, and low-cost systems. The main challenge for transferring biosensors for these target analytes from the laboratory to the marketplace is related to the stability and selectivity of biological receptors. The development of appropriate antibodies with desired specificity, the use of genetically modified microorganisms or the synthesis biomimetic receptors (MIPs, aptamers, etc.) are the most promising alternatives to circumvent the selectivity problem. Regeneration of the biosensor device upon one measurement is another important drawback that could be overcome by mass production of low-cost single-use biosensors by different production processes such as screen- or inkjet printing, and implementation of biosensor arrays in analytical systems for semi-continuous monitoring processes. Nevertheless, the field of environmental analysis is highly demanding and scientists working in technological approaches to carry out pollutant analysis put a great effort to tackle these issues and produce analytical tools in general and electrochemical devices in particular that helped in the implementation of the corresponding directives and thus controlled water resources to contribute to a better life.

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Figure captions

Figure 1. Stripping voltammograms, recorded by square-wave voltammetry with Bi NP- carbon based electrodes for the detection of, (A) Pb(II), Cd(II) in a concentration range of 1-100 $\mu\text{g/L}$, and (B) Ni(II) in a concentration range of 10-150 $\mu\text{g/L}$. Voltammograms in black are the blank responses. Adapted with permission from ref. [32].

Figure 2. (A) TEM image $\gamma\text{-AlOOH@SiO}_2\text{/Fe}_3\text{O}_4$ ion-imprinted microspheres. (B) SWASV responses illustrating the simultaneous detection of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II), using the microsphere-based electrochemical sensor. Concentrations: Zn(II) (0.04-0.56 μM), Cd(II) (0.01-0.14 μM), Pb(II) (0.002-0.48 μM), Cu(II) (0.03-0.28 μM) and Hg(II) (0.02-0.28 μM). The black dotted line corresponds to the blank response. Reprinted with permission from ref. [20].

Figure 3. Schematic diagram of the reagentless label-free immunosensor for endosulfan detection. The electrochemical response of the attached ferrocene group is modulated by the binding event between surface-bound endosulfan antibodies and endosulfan to reach the detection purpose. Adapted with permission from ref. [76]. Copyright 2012 American Chemical Society.

Figure 4. (A) Chemical structure of the benzo(a)anthracene-7,12-dione electrochemical probe, and (B) Differential pulse voltammograms recorded with the corresponding probe-based sensor in solutions containing increasing concentrations of benzo(k)fluoranthene, from *a*: 1.0×10^{-12} M to *h*: 1.0×10^{-9} M. Reprinted with permission from ref. [92].

Figure 5. Detailed diagram of the procedure applied for the fabrication of an electrochemical sensor for 4-nonylphenol. Reprinted with permission from ref. [100].

Figure 1

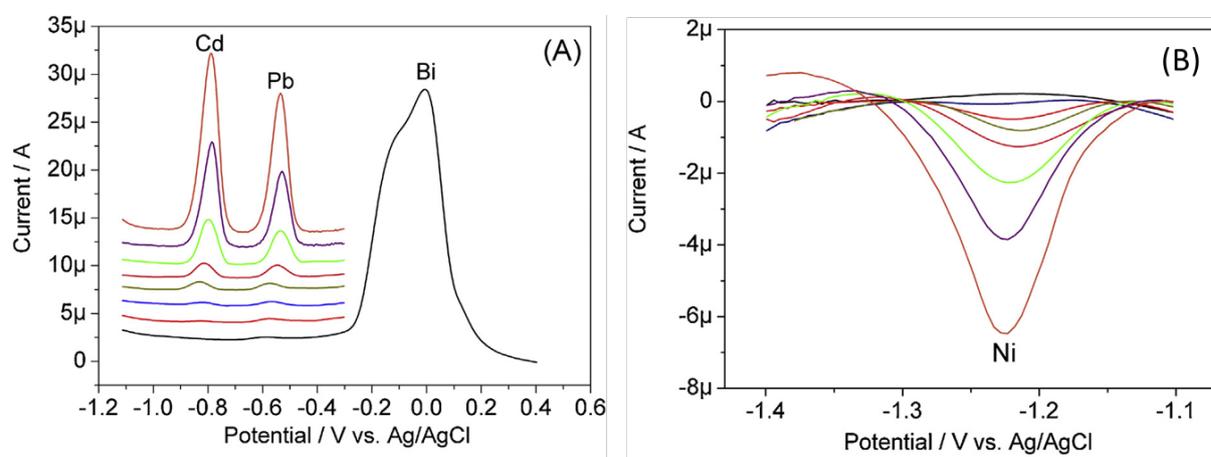


Figure 2

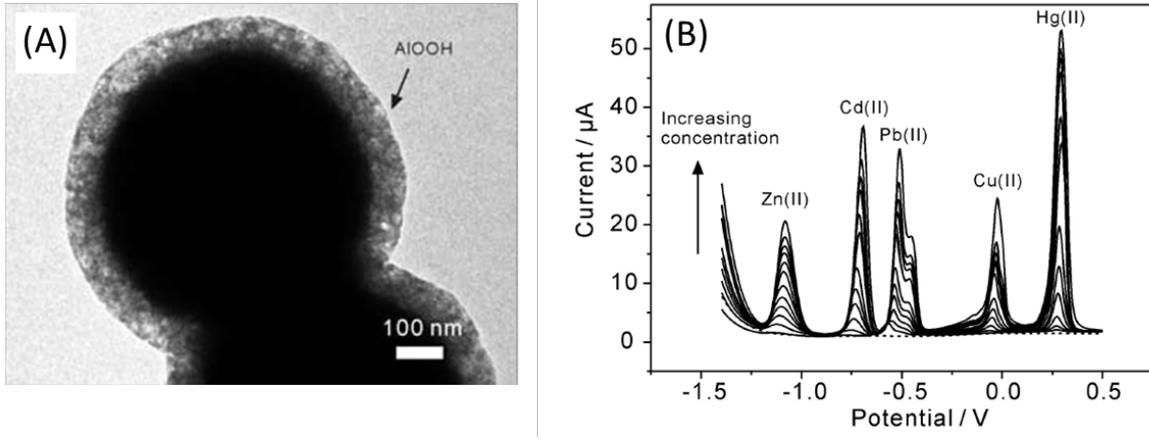


Figure 3

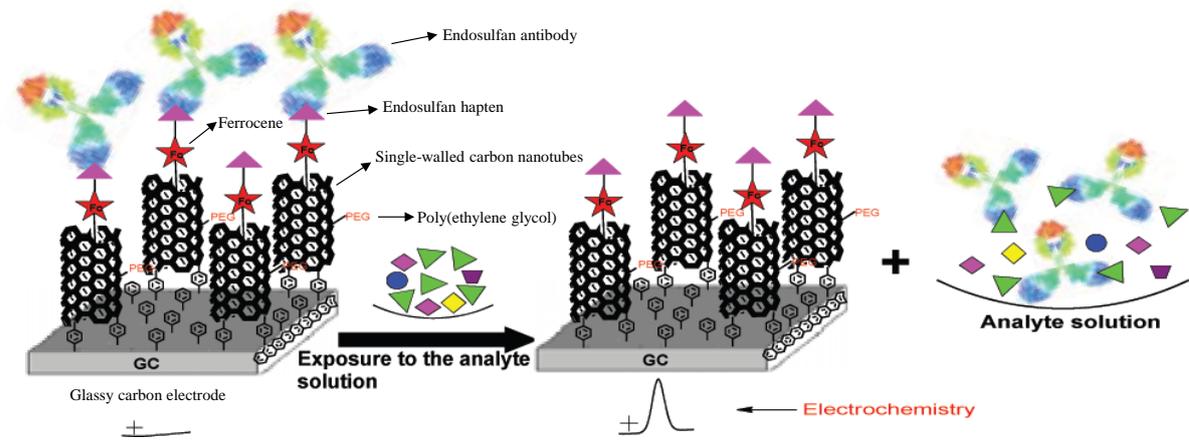


Figure 4

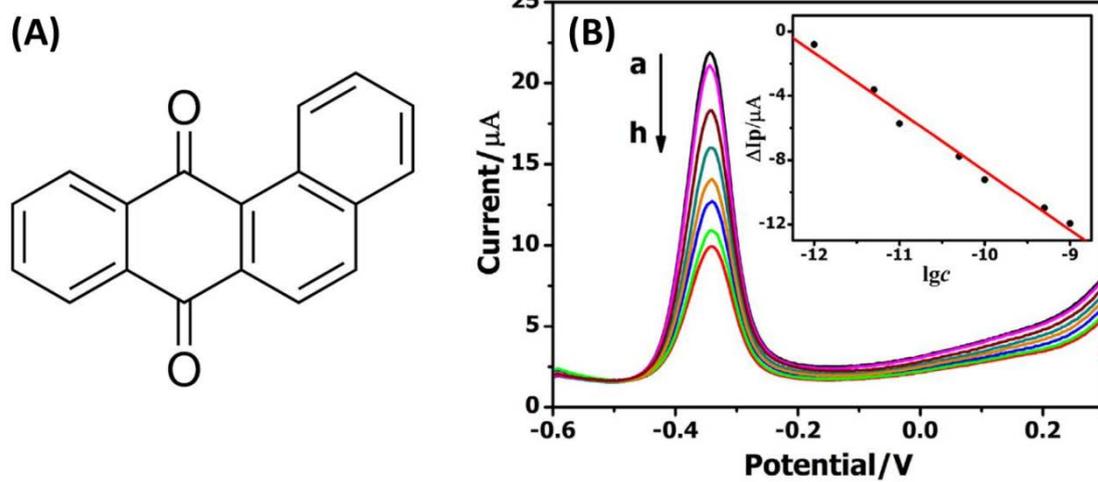


Figure 5

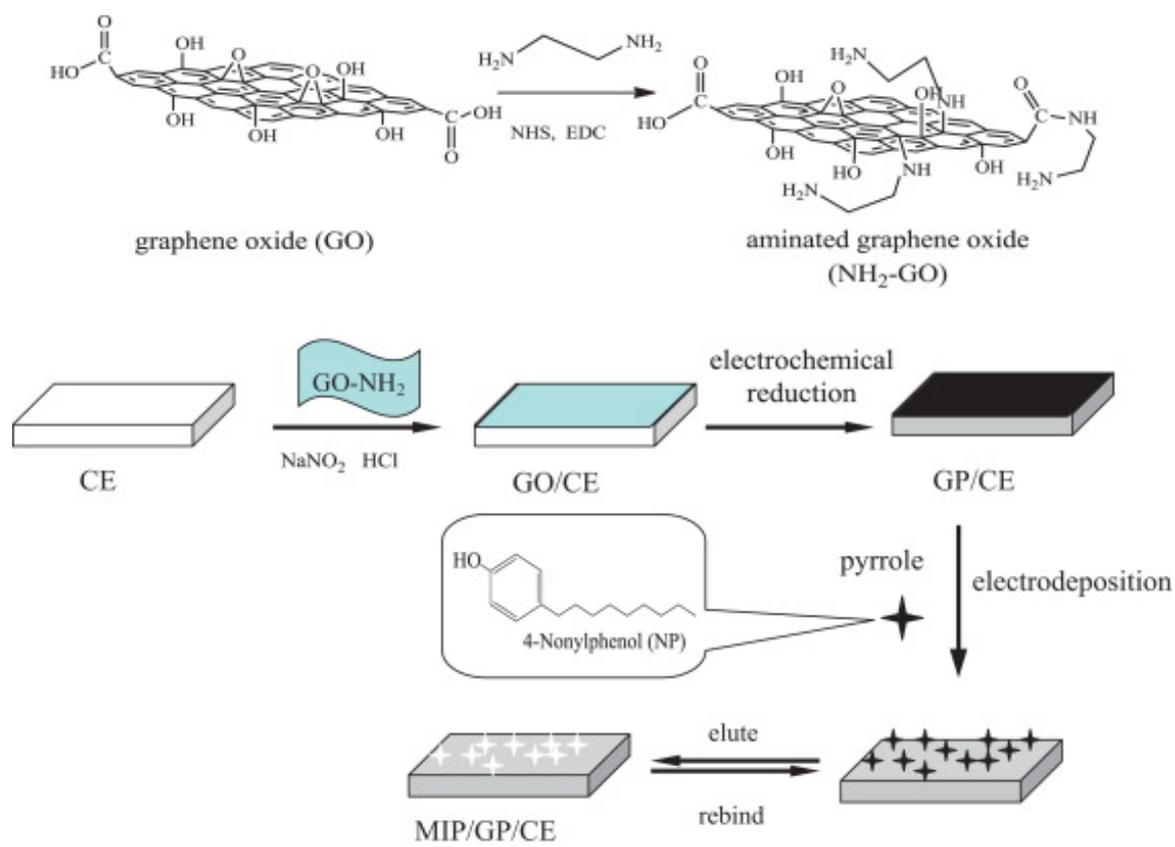


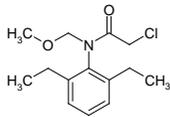
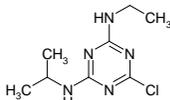
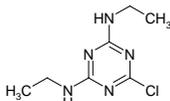
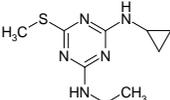
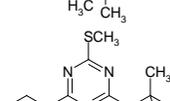
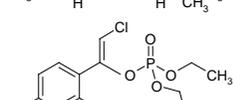
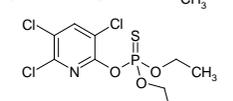
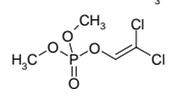
Table 1. Electrochemical devices for the detection of Pb(II), Cd(II), Ni(II) and Hg(II) that fulfill the performance criteria of the EU directive in terms of LOD.

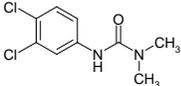
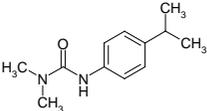
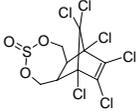
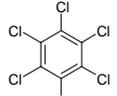
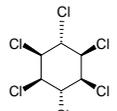
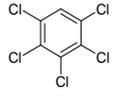
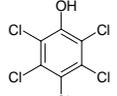
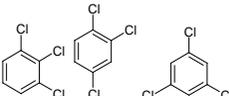
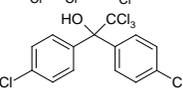
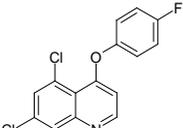
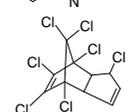
Detection Mechanism	Electrodes	Analyte	Transduction mode	Response time	Linear Range ($\mu\text{g/L}$)	LOD ($\mu\text{g/L}$)	Tested Samples	Ref.
Formation of “fused alloy” of heavy metals with the electrode material	Bi film modified graphene/ Nafion composite electrode	Pb(II), Cd(II)	<i>DPASV</i>	120 s	0.5-50 Pb(II), 1.5-30 Cd(II)	0.02 for both Pb(II) and Cd(II)	Lake water	[14]
	Bi bulk electrode	Pb(II), Cd(II)	<i>SWASV</i>	180 s	10-100 for both Pb(II) and Cd(II)	Individual analysis, 0.093 for Pb(II), and 0.054 for Cd(II)	River water	[15]
	Bi film Electrode (double deposition and stripping process)	Pb(II), Cd(II)	<i>SWASV</i>	300 s + 120 s	n.r.	Simultaneous: 0.18 for Pb(II) and 0.045 for Cd(II)	Fresh water	[16]
	Bi film/Screen printed carbon nanotube electrodes (SPCNTes)	Pb(II), Cd(II)	<i>SWASV</i>	11 min	Two linear ranges of 0.5-15, 15-70 for both Pb(II) and Cd(II)	0.01 for both of them	Drinking, pond, tap water	[17]
Adsorption of heavy metals	Macroporous Bi on SPCE	Ni(II)	<i>SWAdSV</i>	180 s	1-10	0.027	Sewer water	[18]
	Bi film together with hybrid flow-injection/sequential injection mode	Ni(II)	<i>SWAdSV</i>	180-240 s	0-35	1	Iron ore water	[19]
	Porous magnetic Microspheres	Pb(II), Cd(II), Hg(II)	<i>SWASV</i>	100 s	Individual: 1-20 Cd(II), 0.2-40 Pb(II), and 2-30 Hg(II)	Individual: 0.002 for Cd(II), 0.002 for Pb(II), 0.003 for Hg(II)	Reservoir water	[20]
Metal - metal affinity or organics – metal complex	Au nanoelectrode ensembles	Hg(II)	<i>SWASV</i>	100 s	0.1-14	0.02		[21]
	Au graphene modified GCE	Hg(II)	<i>SWASV</i>	120 s	0.0008-0.05 and 0.1-60	0.006	River water	[22]
	Functionalized mesoporous SiO ₂ NPs modified SPCE	Pb(II)	<i>SWASV</i>	300 s + 120 s	1-30	0.1	Tap, river and underground water	[23]
	Polymeric thiadiazole film modified GCE	Pb(II), Cd(II)	<i>DPASV</i>	300 s + 30 s	1-200 Pb(II), and 0.5-200 Cd(II)	0.3 for Pb(II) and 0.05 for Cd(II)	Tap and river water	[24]
	3D porous graphene/ Polypyrrole composite film modified Au electrodes	Hg(II)	<i>SWASV</i>	20 min + 60 s	0.1-110	0.03	Waste water	[25]

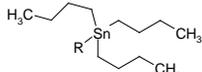
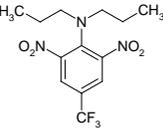
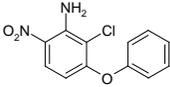
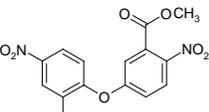
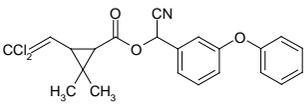
Layered titanate nanosheets modified GCE	Hg(II)	<i>SWASV</i>	10 min + 80 s	0.008-0.7 and 2-40	0.005	River water	[26]
CPE modified with Cd(II) ion imprinted polymer	Cd(II)	<i>DPASV</i>	20 min + 30 s	0.1-50	0.06	Tap, river, lake water	[27]
Hg(II) ion imprinted polymer Au NPs/ SWCNTs modified GCE	Hg(II)	<i>DPASV</i>	12 min + 60 s	0.08-20	0.016	River and tap water	[28]
DNA with Pb(II) aptamer based biosensor	Pb(II)	<i>DPASV</i>	>30 min	0.02-200	0.015	River water	[29]
DNA with Hg(II) aptamer based biosensor	Hg(II)	<i>SWASV</i>	>60 min	0.05-20	0.02	Tap, bottled, and river water	[30]
DNA/NEase with Hg(II) aptamer based biosensor	Hg(II)	<i>SWASV</i>	>120 min	0.02-100	0.017	Tap water	[31]

DPASV – Differential-pulse anodic stripping voltammetry. *SWASV* – Square-wave anodic stripping voltammetry. *SWAdSV*- Square-wave adsorptive stripping voltammetry.
n.r. – not reported

Table 2. Pesticides included in the EU list of priority substances.

Family	Common name	Structure	Type	WHO Classification ¹ Use in EU	MAC ² Inland surface waters	MAC ² Other surface waters
Chloroacetanilide	Alachlor		Herbicide	Moderately hazardous Not approved		0.7
Triazine	Atrazine		Herbicide	Slightly hazardous Not approved		2.0
	Simazine		Herbicide	Unlikely to present acute hazard in normal use Not approved		4.0
	Cybutryne		Herbicide	Restricted		0.016
	Terbutryn		Herbicide	Slightly hazardous Not approved	0.34	0.034
Organophosphorus	Chlorfenvinphos		Insecticide	Highly hazardous Not approved		0.3
	Chlorpyrifos		Insecticide	Moderately hazardous Approved		0.1
	Dichlorvos		Insecticide	Highly hazardous Not approved		710 ⁻⁴

Substituted Urea	Diuron		Herbicide	Slightly hazardous Approved	1.8	
	Isoproturon		Herbicide	Moderately hazardous Approved	1.0	
Organochlorine	Endosulfan ³		Insecticide	Moderately hazardous Not approved	0.01	0.004
	Hexachlorobenzene ³		Fungicide	Extremely Hazardous Not approved	0.05	
	Hexachlorocyclohexane ³		Insecticide	Moderately hazardous Not approved (gamma isomer)	0.04	0.02
	Pentachlorobenzene ³		Fungicide	Not approved	0.007 ⁴	0.0007 ⁴
	Pentachlorophenol		Insecticide Fungicide	Highly hazardous Not approved	1.0	
	Trichlorobenzenes		Insecticide		0.4 ⁴	
	Dicofol		Acaricide	Moderately hazardous Not approved	-	
Quinoxifen		Fungicide	Unlikely to present acute hazard in normal use Approved	2.7	0.54	
Heptachlor ³ and heptachlor epoxide		Insecticide	Not classified Not approved	310 ⁴	310 ⁵	

Organotin	Tributyltin compounds		Biocide	Restricted		0.0015
Dinitroanilines	Trifluralin		Herbicide	Unlikely to present acute hazard in normal use Not approved		0.03 ⁴
Diphenyl ethers	Aclonifen		Herbicide	Unlikely to present acute hazard in normal use Approved	0.12	0.012
	Bifenox		Herbicide	Unlikely to present acute hazard in normal use Approved	0.04	0.004
	Cypermethrin		Herbicide	Moderately hazardous Approved	610 ⁻⁴	610 ⁻⁵

¹ World Health Organization recommended classification of pesticides by hazard. ² MAC: maximum allowable concentration ($\mu\text{g/L}$). ³ Included in the list of persistent organic pollutants (POPs). ⁴ MAC values are not applicable. The AA-EQS (Annual average environmental quality standards) values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.

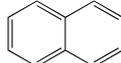
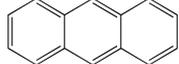
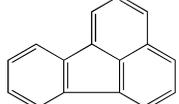
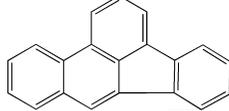
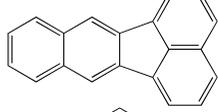
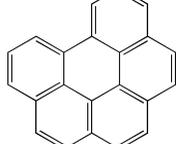
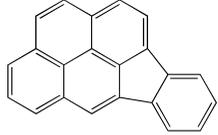
Table 3. Electrochemical devices for pesticide detection that fulfill the performance criteria of the EU directive in terms of LOD.

Type	Pesticide	Receptor	Transducer	Transduction mode	Assay	LOD($\mu\text{g/L}$)	Ref.	
Enzymatic	Chlorfenvinphos	AChE / (poly(SNS-NH ₂)/ MWCNTs	Graphite	Amperometry		0.0049	[56]	
		Ni-IDA- MBs	SPCE	Amperometry		0.0046	[57]	
	Chlorpyrifos	AChE/L-Cys/ HGNs/Chit	GCE	Amperometry		0.06	[58]	
		AChE -CLDH/GN-AuNPs	GCE	DPV	Inhibition/Substrate: ATCl	0.05	[59]	
		AChE-AuNPs-CaCO ₃ /Silica-sol gel	Gold	Amperometry		0.03	[60]	
		Chit-PB- MWNTs-HGNs	Gold	DPV		0.01	[61]	
		AChE /PANI/ssDNA-SWCNT	Gold	SWV		0.0003	[62]	
Atrazine	Tyrosinase-AuNPs	GCE	Amperometry	Inhibition/ Substrate: catechol	0,00035	[63]		
Immunosensor	Atrazine	Ag (Glass slide)	Gold IDE	Conductometric	Competitive/Enzymatic label	0.22	[64]	
		mAb/ AuNPs	Gold	DPV	Direct/Label-free [Fe(CN) ₆] ^{3-/4}	0.016	[65]	
		Ab-SSA-PANI	SPCE	EIS	Direct/Label-free [Fe(CN) ₆] ^{3-/4}	0.01	[66]	
		Ab-MBs	Graphite-Epoxy	Amperometry	Competitive/Enzymatic label HRP/H ₂ O ₂ -HQ	0.006	[67]	
		Ab-AuNPs-BMIM-BF ₄ (IL)-MWCNTs	GCE	FFT-SWV	Direct/Label-free [Fe(CN) ₆] ^{3-/4}	0.004	[68]	
		Ab-MBs	SPCE	Chronoamperometry	Non competitive/ Enzymatic HRP(mAb)/Pyrocatechol	0.0002	[69]	
		poly(JUG-HATZ)	GCE	SWV	Competitive/Label-free	0.0002	[70]	
		Ab-Nanoporous alumina membrane	Gold	EIS	Direct/Label-free	110-5	[71]	
		Chlorpyrifos	mAb/MWCNTs-THI-CHIT	GCE	Amperometry	Direct/Label-free [Fe(CN) ₆] ^{3-/4}	0.046	[72]
		Diuron	Ag/PB/AuNPs	Gold	SWV	Competitive/Enzymatic label AP/ 1-naphthyl phosphate	0.001	[73]
		Ag-CNT	SPCE	DPV	Competitive/Enzymatic AP/ 1-naphthyl phosphate	0.0001	[74]	
	Isoproturon	Ag-UltraBind TM membrane	SPCE	Amperometry	Competitive/Enzymatic HRP/H ₂ O ₂ -OPD	0.84	[75]	
	Endosulfan	Ag/FDMA/SWNTs/Aryldiazonium salts	GCE	SWV	Direct/ Label-free	0.01	[76]	
DNA	Hexachlorobenzene	dsDNA	Gold	DPV	MB (Redox probe)	0.008	[77]	

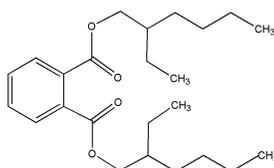
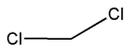
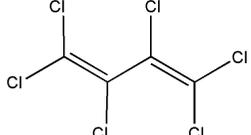
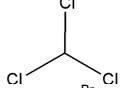
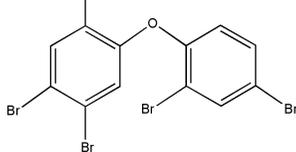
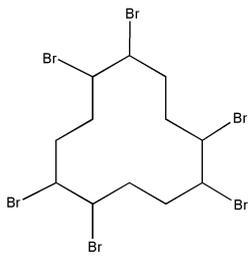
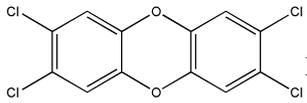
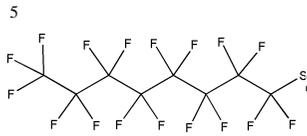
Bacterial	Diuron	AChE(<i>Arthrospira platensis</i>)/PAH/ AuNPs	Gold IDE	Conductometric	Inhibition Substrate: ATCl	0.0002	[82]
	Hexachlorocyclohexane	<i>E. coli</i> /PANI	Gold IDE	Amperometry		0.002	[83]
Biomimetic	Hexachlorocyclohexane	MWCNT-MIP(Agarose gel)	Cu	Potentiometry		0.02	[85]

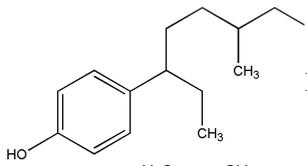
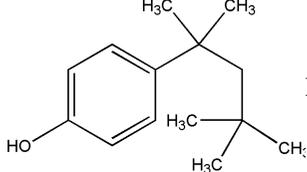
AChE: acetylcholinesterase; AP: alkaline phosphatase; ATCl: acetylthiocholine chloride; BMIM-BF₄(IL): 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid; CLDH: Cu-Mg-Al calcined layered doublehydroxide; dsDNA: double-stranded DNA; EIS: Electrochemical impedance spectroscopy; FDMA: ferrocenedimethylamine; FFT-SWV: fast Fourier transformation; GN: graphene nanosheet; HGNS: hollow gold nanospheres; HRP: horseradish peroxidase; IDA: iminodiacetic acid; JUG-HATZ :poly[N-(6-(4-hydroxy-6-isopropylamino-1,3,5-triazin-2-ylamino)hexyl)5-hydroxy-1,4-naphthoquinone-3-propionamide]; IDE: interdigitated electrodes; PANI: polyaniline; PB: prussian blue; PAH: poly(allylamine Hydrochloride); PVA: poly(vinyl acetate); MB: methylene blue; MBs: magnetic beads; MBT: mercaptobenzothiazole; MIP: molecular imprinted polymers; ssDNA: single strand oligonucleotide; SSA: styrene sulphonic acid; THI: thionine; OPD: o-phenylenediamine.

Table 4. Hydrocarbons included in the EU list of priority substances.

Family	Name	Structure	Type	MAC ¹	
				Inland surface waters	Other surface waters
Hydrocarbons	Benzene		Aromatic		50
	Naphthalene		PAH		130
	Anthracene		PAH		0.1
	Fluoranthene		PAH		0.12
	Benzo(a)pyrene		PAH	0.27	0.027
	Benzo(b)fluoranthene		PAH		0.017
	Benzo(k)fluoranthene		PAH		0.017
	Benzo(g,h,i)perylene		PAH	8.2 10 ⁻³	8.2 10 ⁻⁴
	Indeno(1,2,3-cd)-pyrene		PAH		1.7 10 ⁻⁴ 2

Halogenated hydrocarbons

Di(2-ethylhexyl)phthalate		Plastizicer		1.3 ²
1,2-dichloroethane		Solvent / precursor		10 ²
Dichloromethane		Solvent / precursor		20 ²
Hexachlorobutadiene		Solvent / precursor		0.6
Trichloromethane		Solvent / precursor		2.5 ²
Brominated diphenylethers (tetra ³ , penta ³ , hexa and heptabromodiphenylethers)		Flame retardant	0.14	0.014
Chloroalkanes C ₁₀₋₁₃	$C_xH_{(2x-y+2)}Cl_y$ where x = 10-13 and y = 1-13	Flame retardant		1.4
Hexabromocyclododecane ³		Flame retardant	0.5	0.05
Dioxin and dioxin-like compounds ³ (polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls)		By-products	-	
Perfluorooctane sulfonic acid and its derivates ³		Surfactant	36	7.2

Alkylphenols	4-nonylphenol		Detergent	2.0	
	4-tert-octylphenol		Detergent	0.1 ²	0.01 ²

¹ MAC: maximum allowable concentration ($\mu\text{g/L}$).² MAC values are not applicable. The AA-EQS (Annual average environmental quality standards) values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute.³ Included in the list of persistent organic pollutants (POPs) by the Stockholm Convention.⁴ The structure depicted corresponds to the pentabromodiphenylether.⁵ The structure depicted corresponds to the 2,3,7,8-tetrachlorodibenzodioxin.

Table 5. Different electrochemical approaches for hydrocarbon detection that fulfill the performance criteria of the EU directive in terms of LOD.

Priority substance	Electrochemical device	Transduction mode	LOD ($\mu\text{g/L}$)	Real samples	Ref.
PAH	Magnetic beads-based immunoassay	CV	0.02	Spiked tap water	[87]
Benzo(a)pyrene	Fe_3O_4 /polyaniline/Nafion and multienzyme-antibody functionalized highly-carbonized spheres - based immunosensor	CV	0.001	Spiked water	[88]
Naphthalene	Prussian blue and Au nanoparticles-based immunosensor	CV	0.06	Spiked river water	[89]
Benzo(a)pyrene	Prussian blue and Au nanoparticles-based immunosensor	CV	0.08	Spiked waste water from coke-oven plant	[90]
Anthracene	Thionine-graphene composite-based sensor	DPV	1.1×10^{-4}	Spiked waste water from coke-oven plant	[91]
Benzo(k)fluoranthene	Polypyrrole and Benzo(a)anthracene-7,12-dione - based sensor	DPV	2.5×10^{-5}	Spiked waste water from coking plant	[92]
Di(2-ethylhexyl)-phthalate	Au planar interdigital sensor on Si substrate	EIS	2	Energy drinks	[93]