



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.

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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,

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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 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. 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

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