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Review

Trends in analytical methodologies for the determination of alkylphenols and bisphenol A in water samples

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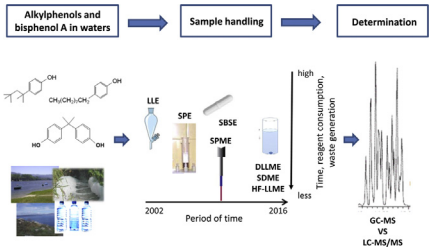
HIGHLIGHTS

- Trends in analytical methods for APs and BPA determination in waters are reviewed.
- Aspects related to sampling, extraction, clean-up and detection are discussed.
- Microextraction techniques are now the most used because of their remarkable advantages.
- Further research is required to achieve an effective method for APs and BPA water analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last decade, the impact of alkylphenols and bisphenol A in the aquatic environment has been widely evaluated because of their high use in industrial and household applications as well as their toxicological effects. These compounds are well-known endocrine disrupting compounds (EDCs) which can affect the hormonal system of humans and wildlife, even at low concentrations. Due to the fact that these pollutants enter into the environment through waters, and it is the most affected compartment, analytical methods which allow the determination of these compounds in aqueous samples at low levels are mandatory. In this review, an overview of the most significant advances in the analytical methodologies for the determination of alkylphenols and bisphenol A in waters is considered (from 2002 to the present). Sample handling and instrumental detection strategies are critically discussed, including analytical parameters related to quality assurance and quality control (QA/QC). Special attention is paid to miniaturized sample preparation methodologies and approaches proposed to reduce time- and reagents consumption according to Green Chemistry principles, which have increased in the last five years. Finally, relevant applications of these methods to the analysis of water samples are examined, being wastewater and surface water the most investigated.

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Contents

1. Introduction

A significant rise in chemical production has aroused special concern during decades because of the worldwide economic progress and technological advances. One clear example are plasticizers, additives used in plastic manufacture to improve its properties (i.e. flexibility, stability, resistance). Some of these additives, such as alkylphenols (APs) and bisphenol A (BPA), are considered endocrine disrupting compounds (EDCs) due to the fact that they can affect the hormonal system of human and wildlife at low concentrations.

Alkylphenols are a great family of organic compounds formed by a substituted phenolic ring and an alkyl chain ($n = 1–12$). The alkyl chain can be attached at various locations around the phenolic ring and therefore, *meta*-, *ortho*- and *para*-alkylphenols (also called 2-, 3- and 4-alkylphenols, respectively) can be distinguished. Among all APs, 4-octylphenols (4-OP) and 4-nonylphenols (4-NP) are the most important APs because of their higher use in industrial and household applications (more than 80% of total APs production) as well as their higher disruption capabilities [1]. These compounds are employed in plastic manufacture such as high density polyethylene (HDPE), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) and also in the production of textiles, paper and agricultural chemical products [2]. Moreover, APs are the main degradation products of alkylphenol ethoxylates (APEOs), one of the most important non ionic surfactants used as detergents, dispersants or solubilizers [3].

Branched and linear isomers can be identified depending on the structure of the octyl- and nonyl- alkyl group. Whereas branched 4-OP (4-*tert*-OP) is a unique compound, more than 211 isomers are part of branched 4-NP (technical mixture). Although linear isomers (4-*n*-OP and 4-*n*-NP) are scarcely used for industrial purposes, they are present in aquatic system and can be bio accumulated in organisms as it was demonstrated in different environmental and ecotoxicological studies [4,5]. For all these reasons, both linear and branched 4-OP and 4-NP have been selected as representative alkylphenols in this critical review.

The other considered compound is BPA, with the chemical name 2,2-(4,4-dihydroxydiphenyl)propane, one of the most important monomers used worldwide in the manufacture of epoxy resins, phenol resins, polycarbonates, polyesters and also in flame retardants. Thus, this EDC is present in electronic components, construction materials, drinking bottles, food containers and medical devices [6].

These pollutants are partially eliminated in wastewater treatments plants (WWTP) and therefore, they enter into the aquatic environment and have negative impacts on surface and marine water bodies. Water is the most affected environmental compartment but of course, because of their physical and chemical properties (Table 1) they can be also associated to sediment and bio accumulated in biota, damaging human health at last step [7–9]. To preserve the environment and guarantee public safety, 4-OPs and 4-NPs have been included in the list of 45 priority substances set in the new European water legislation (Directive 2013/39/EU) [10]. Nevertheless, BPA has not been included in this Directive, although several investigations confirm different effects of this pollutant in organisms and humans such as sexual maturation, altered development and tissue organization of mammary glands [11]. Nowadays, the environmental impact of BPA is still in question and more studies are needed to support an adequate assumption.

Taking into account all the facts mentioned above, research based on the behaviour, distribution and transport of these EDCs in the aquatic system have become a significant issue for environmental and toxicological sciences. To achieve the low environmental levels of APs and BPA, sensitive and selective analytical methodologies are required. Fastness, simplicity and economical aspects are other ideal characteristics for methods, as well as low consumption of reagents and low waste generation. In this context, the main objective of this review is to critically discuss the state of the art and future trends in analytical methods for the determination of linear and branched 4-APs (4-*tert*-OP, 4-*n*-OP, 4-*n*-NP and NP) and BPA in water samples. This detailed recompilation of published methods for the analysis of these EDCs in the aquatic environment could provide significant information for initial assays because characteristics related to sample handling and instrumental detection are mentioned. Although some previous reviews were focused on some of these aspects (i.e. sample preparation, separation techniques) for some selected EDCs [12–14], the detailed information here discussed has not been included in any of them. Consequently, this review can be interesting and helpful for researchers who analyze these compounds (or similar ones) in environmental, food, biological and ecotoxicological studies in order to select an adequate method depending on the aimed application.

Hereby, a total of 75 analytical methods for APs and/or BPA analysis (from 2002 to the present) were recompiled, taking into account their scientific contribution to the topic as well as the number of citations achieved. As it can be seen in Fig. 1, a clear