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Review

Recent advances in analytical methods for the determination of 4-alkylphenols and bisphenol A in solid environmental matrices: A critical review

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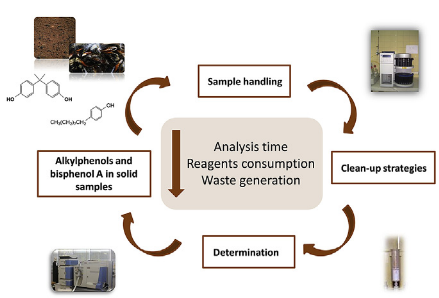
HIGHLIGHTS

- Analytical methods for APs and BPA determination in sediments and biota are reviewed.
- Aspects related with extraction, clean-up and determination steps are critically discussed.
- Ultrasound assisted extraction followed by SPE clean-up is still the most used procedure.
- New trends include simultaneous extraction and clean-up (e.g. Selective PLE, QuEChERS).
- Further research is required to have an ideal methodology for the analysis of APs and BPA.

GRAPHICAL ABSTRACT



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ABSTRACT

The problem of endocrine disrupting compounds (EDCs) in the environment has become a worldwide concern in recent decades. Besides their toxicological effects at low concentrations and their widespread use in industrial and household applications, these pollutants pose a risk for non-target organisms and also for public safety. Analytical methods to determine these compounds at trace levels in different matrices are urgently needed. This review critically discusses trends in analytical methods for well-known EDCs like alkylphenols and bisphenol A in solid environmental matrices, including sediment and aquatic biological samples (from 2006 to 2018). Information about extraction, clean-up and determination is covered in detail, including analytical quality parameters (QA/QC). Conventional and novel analytical techniques are compared, with their advantages and drawbacks. Ultrasound assisted extraction followed by solid phase extraction clean-up is the most widely used procedure for sediment and aquatic biological samples, although softer extraction conditions have been employed for the latter. The use of liquid chromatography followed by tandem mass spectrometry has greatly increased in the last

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Sample handling
Mass spectrometry determination

five years. The majority of these methods have been employed for the analysis of river sediments and bivalve molluscs because of their usefulness in aquatic ecosystem (bio)monitoring programs. Green, simple, fast analytical methods are now needed to determine these compounds in complex matrices.

Contents

1. Introduction

Society and the scientific community have examined many high-volume industrial chemicals in recent decades that affect both the land and the aquatic environment, as a major environmental issue. Some are estrogenic endocrine disrupting compounds (EDCs) which have potential adverse effects at low concentrations on the normal function of the reproductive system of wildlife and humans, mimicking or inducing estrogen-like responses in organisms [1]. Among these estrogenic EDCs, alkylphenols (APs) and bisphenol A (BPA) (Fig. 1) raise concern on account of their estrogenic potency (estradiol equivalent factors between 1.4E-006 and 2.5E-005, Table 1), their large-scale production, and their ubiquity and persistence.

Alkylphenols are a large family of organic compounds formed by an alkyl chain ($n = 1–12$) normally attached in the *para-* position of a phenolic ring (called *para*-alkylphenols or 4-alkylphenols). APs are employed in industrial, household and institutional applications, especially in the production of plastics, pesticides and textiles. These compounds are derived from microbial degradation of the non-ionic surfactants alkylphenol polyethoxylates (APEOs) [2]. Nonylphenol polyethoxylates account for 80% of the total production of APEOs (500,000 tons/year) and octylphenol polyethoxylates for about 20% [3]. This critical review therefore considers 4-nonylphenols and 4-octylphenols as representative APs.

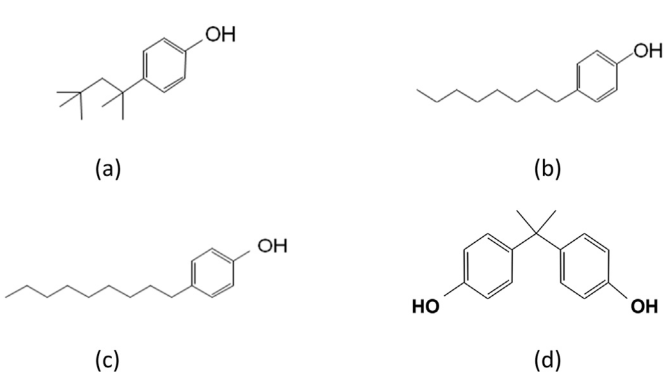

Fig. 1. Chemical structures of target endocrine disrupting compounds: (a) 4-*tert*-octylphenol (b) 4-*n*-octylphenol (c) 4-*n*-nonylphenol and (d) bisphenol A.

Branched or 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, there are more than 211 isomers in branched 4-NP (technical mixture). In comparison with branched isomers, linear isomers (4-*n*-OP and 4-*n*-NP) are rarely used for industrial purposes; however, they are also considered in this work, as they are present in aquatic systems and can bio-accumulate in organisms.

Bisphenol A, with the chemical name 2,2-(4,4-dihydroxydiphenyl)propane, is one of the major monomers employed worldwide in plastic manufacture. More than two million tons/year of BPA are used for the synthesis of polycarbonates, epoxy resins and PVC [4]. Secondary applications include the production of rubbers, flame retardants and materials for dental care [5].

These EDCs are discharged in the aquatic environment through direct emission or from industrial and wastewater treatment plants where they are not completely eliminated, and distribute into water bodies. Depending on their physical and chemical properties (Table 1), they tend to be associate with suspended particulates and sediments, and also accumulate in aquatic biota species [6-10]. Consequently all these matrices need to be analyzed to control chemical pollution and avoid loss of habitats and biodiversity, and to avoid harm to public health, according to the Directive 2013/39/EU [11] and the Marine Strategy Framework Directive (Directive 2008/56/EC) [12]. Both legislations examine a list of 45 priority substances in water policy, including 4-nonylphenols and 4-

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