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Determination of hormones, a plasticizer, preservatives, perfluoroalkylated compounds, and a flame retardant in water samples by ultrasound-assisted dispersive liquid–liquid microextraction based on the solidification of a floating organic drop

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ABSTRACT

Dispersive liquid–liquid microextraction based on the solidification of a floating organic drop (DLLME-SFO) is a novel extraction technique commonly applied for the extraction on a specific group of compounds. In this paper, the applicability of ultrasound-assisted DLLME-SFO for multiresidue extraction has been evaluated. A method for the simultaneous extraction of four hormones (17α-ethinylestradiol, 17β-estradiol, estriol and estrone), a plasticizer (bisphenol A), three preservatives (methyl-, ethyl- and propylparaben), six perfluoroalkylated compounds (perfluorooctane sulfonic acid and five perfluoroalkyl carboxylic acids, from C4 to C8), and a brominated flame retardant (hexabromocyclododecane) has been developed and validated for their extraction from surface water and tap water. Determination was carried out by high-performance liquid chromatography–tandem mass spectrometry in negative ionization mode. Recoveries of the target compounds were highly dependent on their log K_{ow} values. Linear relationship between recoveries and log K_{ow} values was observed for compounds from the same group (hormones, preservatives and perfluoroalkylated carboxylic acids). The lowest recoveries were obtained for the less hydrophobic compounds (estriol (43%), methylparaben (32%), ethylparaben (45%) and the perfluorinated compounds of shorter alkyl chain (C4: 17%, C5: 41% and C6: 57%)). Recoveries of the other pollutants were higher than 80%. Precision, expressed as relative standard deviation, was in the range from 1% to 16%. Method detection limits were in the range 0.001–1.126 μg L^{-1}, for surface water, and 0.001–1.446 μg L^{-1} for tap water. No important matrix effect was observed.

1. Introduction

In the last years, special attention has been paid to the development of miniaturized extraction methods faster, simpler, cheaper and more environment-friendly than traditional methods. Special attention has been focused in the dispersive liquid–liquid microextraction (DLLME) method developed by Rezaee et al. [1] because it is fast, inexpensive, easy to operate and requires low volume of organic solvents. In spite of it being a novel extraction technique, several papers have already been reported about DLLME evolution and its applications [2–5]. Conventional DLLME is based on a three component solvent system, the aqueous sample, a high density solvent (extraction solvent) and a water-miscible polar solvent (disperser solvent). The mixture of extraction and disperser solvents is rapidly introduced into the aqueous sample and a cloudy solution is formed. Finally, the extraction solvent is separated by centrifugation. The main disadvantages of DLLME are the use of highly toxic extraction solvents, normally chlorinated solvents, and the difficulty to collect the extraction solvent that ends us at the bottom of the extraction tube as a tiny drop. To overcome these drawbacks, a dispersive liquid–liquid microextraction method based on the solidification of a floating organic drop (DLLME-SFO) was firstly reported by Leong and Huang [6]. The main advantages of DLLME-SFO are the easy collection of the organic drop that ends up solidified at the top of the solution and the use of organic solvents more environment-friendly than the chlorinated ones used in conventional DLLME. The dispersive liquid–liquid microextraction method based on the solidification of a floating organic drop (DLLME-SFO) has already been successfully applied to the extraction of specific groups of pollutants in environmental aqueous samples such as halogenated compounds [6], phthalate esters [7], polycyclic aromatic hydrocarbons [8], chlorinated anilines [9], polychlorinated biphenyls [10], steroid hormones [11], bisphenol A [12] and triclosan and its

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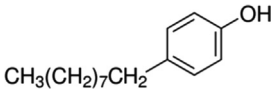
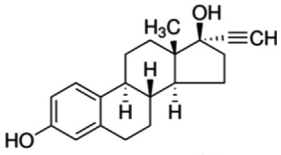
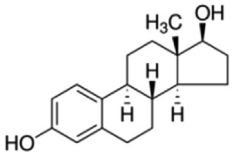
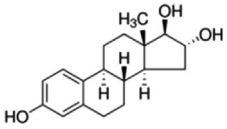
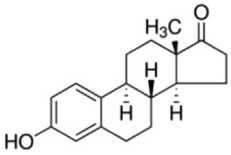
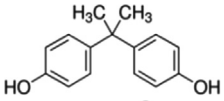
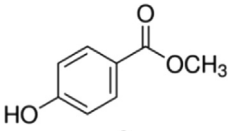
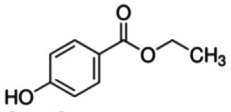
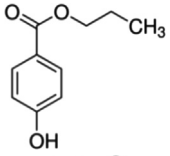
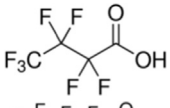
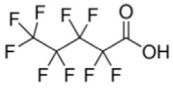
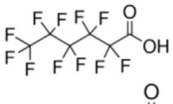
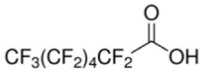
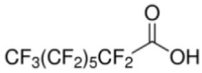
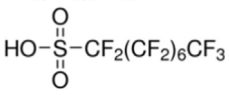
Table 1
Chemical structures and log K_{ow} values of target compounds.

Family	Compound	Abbreviation	Structure	Log K_{ow}
Surfactant	Nonylphenol	NP		4.5[a]
Hormones	17α-Ethinylestradiol	EE2		3.90[b]
	17β-Estradiol	E2		3.75[b]
	Estriol	E3		2.67[b]
	Estrone	E1		4.31[b]
Plasticizer	Bisphenol A	BPA		4.04[b]
Preservatives	Methylparaben	MeP		1.67[b]
Preservatives	Ethylparaben	EtP		2.03[b]
	Propylparaben	PrP		2.55[b]
Perfluoroalkylated compounds	Perfluorobutanoic acid	PFBuA		2.43[c]
	Perfluoropentanoic acid	PFPeA		3.40[c]
	Perfluorohexanoic acid	PFHxA		4.37[c]
	Perfluoroheptanoic acid	PFHpA		5.33[c]
	Perfluorooctanoic acid	PFOA		6.30[c]
	Perfluorooctane sulfonate	PFOS		5.25[d]