1

Sorbent-Based Microextraction Techniques for the Analysis of Phthalic Acid Esters in Water Samples

Miguel Ángel González-Curbelo[1], Javier González-Sálamo[2,3], Diana A. Varela-Martínez[1,2] and Javier Hernández-Borges[2,3]*

[1]Departamento de Ciencias Básicas, Facultad de Ingeniería, Universidad EAN, Bogotá D.C., Colombia
[2]Departamento de Química, Unidad Departamental de Química Analítica, Facultad de Ciencias, Universidad de La Laguna (ULL). Avda. Astrofísico Fco. Sánchez, San Cristóbal de La Laguna, España
[3]Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Universidad de La Laguna (ULL). Avda. Astrofísico Fco. Sánchez, San Cristóbal de La Laguna, España

Abstract

Current society is living in a world in which it is exposed to a broad spectrum of contaminants that can pose different risks for health. In this sense, we are daily bombarded with news related to pollution by plastic residues (especially in the oceans), being one of the main issues that humans must face today, not only because of the direct effects of plastics but also because of the variety of contaminants they can release to the environment. Probably, the most important ones are phthalic acid esters (PAEs), since they easily migrate from the polymeric matrix to the surrounding media, acting as endocrine disruptors in human organisms and resulting in multiple diseases. Their occurrence in water matrices is of especial importance, since it is essential for life, and the presence of PAEs, even at very low levels, can cause serious health problems. This book chapter aims at providing a general and critical overview of the different analytical methodologies that have been developed for the analysis of PAEs in water samples and which are based on the application of sorbent-based microextraction techniques, which is one of the current trends in the Analytical Chemistry field.

**Corresponding author*: jhborges@ull.edu.es

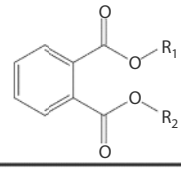
Inamuddin, Mohd Imran Ahamed, Rajender Boddula, and Tauseef Ahmad Rangreez (eds.) Applied Water Science Volume 1: Fundamentals and Applications, (1–62) © 2021 Scrivener Publishing LLC

Keywords: Phthalic acid esters, analytical methods, sample preparation, microextraction techniques, water samples, sorbents

1.1 Introduction

Phthalic acid esters (PAEs) are a group of dialkyl or alkylaryl esters of phthalic acid (see Figure 1.1), commonly known as phthalates, which are widely used as additives in the polymer industry but also added to paints, adhesives, lubricants, and cosmetics, among others [2]. As an example, low-molecular PAEs such as butyl benzyl phthalate (BBP), dibutyl phthalate (DBP), and diethyl phthalate (DEP) are widely used as solvents and emulsifiers to maintain color and fragrance mainly in beauty products and pharmaceuticals, while high-molecular PAEs such as di(2-ethylhexyl) phthalate (DEHP) are highly used as plasticizers to make polymeric materials more workable and flexible. As a result of the extremely high production of such products, especially plastics, PAEs are exorbitantly present in the daily life. Among them, DEHP is the most currently used. In fact, its production as plasticizer is estimated to be a quarter of the total [3, 4]. Due to these widespread applications and intensive production, together with the fact that they are only retained in the polymer structure through weak secondary molecular interactions and not covalently, PAEs can easily migrate to the environment. As a result, PAEs have become ubiquitous contaminants in the environment, in particular, they can be found in natural waters such as lake, river, sea, and ground waters [5, 6], especially those adjacent or downstream from industrial locations [5]. In addition, their possible migration to drinking waters that are in contact with plastic materials like mineral and tap waters must also be taken into account, as well as their final presence in waste waters [5, 7].

It has already been demonstrated that many PAEs act as endocrine disruptors and that they can be toxic for reproduction, even at extremely low concentrations [8–11]. Even more worrying is the fact that certain PAEs can be easily degraded in the environment by bacteria and fungi and their degradation products can also have an important toxicity. Such is the case of DEHP that can be degraded to DBP, DEP, and especially to mono-2-ethylhexyl phthalate (MEHP), which has shown to be more toxic than DEHP [12, 13] (see Figure 1.2). As a result of the high human exposure to PAEs and their metabolites, their potential risks for health and their persistence, several organizations have established an increasingly broad and restrictive legislation. As examples, the European Union has



Name	Abbreviations	R_1 Group	R_2 Group
Dimethyl phthalate	DMP		
Diethyl phthalate	DEP		
Di(2-methoxyethyl) phthalate	DMEP		
Dipropyl phthalate	DPP		
Di(2-ethoxyethyl) phthalate	DEEP		
Benzylbutyl phthalate	BBP		
Dibutyl phthalate	DBP		
Diisobutyl phthalate	DIBP		
Di(2-butoxyethyl) phthalate	DBEP		
Di-n-pentyl phthalate	DNPP		
Diisopentyl phthalate	DIPP		
Dicyclohexyl phthalate	DCHP		
Dihexyl phthalate	DHXP		
Di(2-ethylhexyl) phthalate	DEHP		
Di-n-octyl phthalate	DNOP		
Diisononyl phthalate	DINP		
Diisodecyl phthalate	DIDP		

Figure 1.1 The chemical structures of PAEs. Adapted from [1]. PAEs, phthalic acid esters.

listed several PAEs as compounds suspected to produce endocrine abnormalities [15] and the International Agency for Research on Cancer has classified DEHP in the group 2B (possibly carcinogenic to humans) [16]. Moreover, the US Environmental Protection Agency (EPA) has included several PAEs (BBP, DBP, DEHP, DEP, dimethyl phthalate (DMP), and di-n-octyl phthalate (DNOP)) in its priority list of pollutants and has

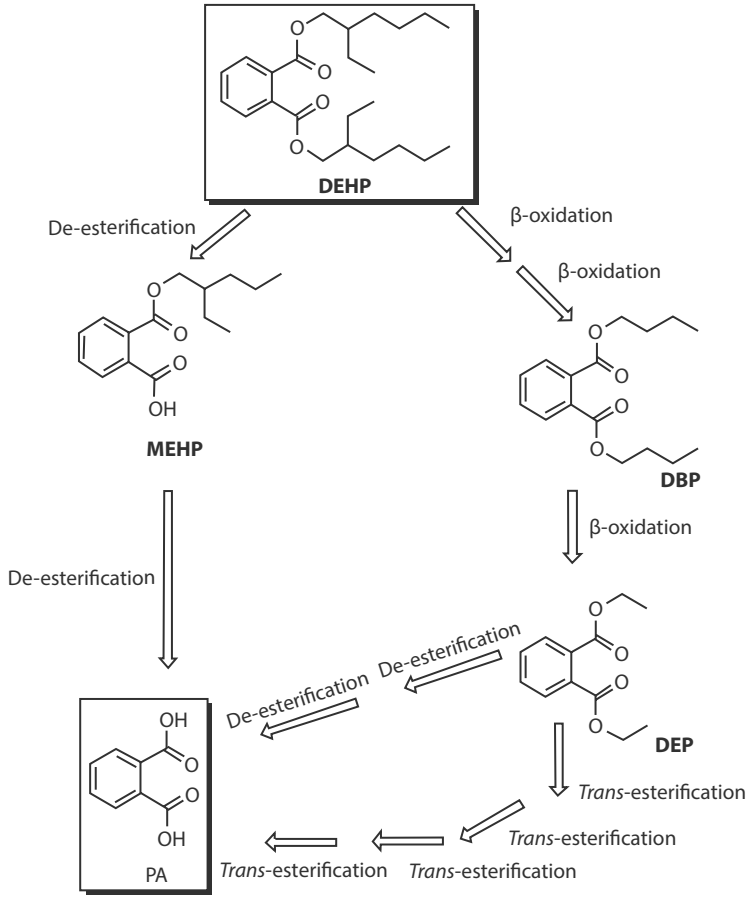


Figure 1.2 DEHP biodegradation pathways to obtain MEHP, DBP, and DEP. Reprinted from [14] with permission from Elsevier. DBP, dibutyl phthalate; DEHP, di-2-ethylhexyl phthalate; DEP, diethyl phthalate; MEHP, mono-2-ethylhexyl phthalate; PA, polyacrylate.

established limits of 6 μg/L and 400 μg/L for DEHP and di(2-ethylhexyl) adipate (DEHA) in drinking water, respectively [17], while this maximum allowed concentration has been established in 8 μg/L for DEHP by the World Health Organization [18] and in 1.3 μg/L in surface waters by the European Union [19]. Considering all the above mentioned, it is clear that there is an increasing need to develop highly sensitive and reliable analytical methods for monitoring trace amounts of PAEs in different samples and, especially, in water.

PAEs have been analyzed in water samples using gas chromatography (GC) coupled to flame ionization detectors (FIDs) [20], mass

spectrometry (MS) [21] and tandem MS (MS/MS) [22], or high-performance liquid chromatography (HPLC) coupled to diode array detectors (DADs) [23], ultraviolet (UV) [24], and MS [25]. Among them, GC is normally the preferred technique since most PAEs are nonpolar and thermostable. It is important to notice that, in all these analytical methods, it has been necessary to include previous sample preparation steps before instrumental analysis to achieve accurate and sensitive results. These steps consist on the isolation and pre-concentration of PAEs since they can be found in water samples at extremely low concentrations. However, since PAEs are not ionizable in water, these samples are normally analyzed directly or after a simple filtration without pH adjustment regardless of the sample preparation technique used in each case [26].

In this context, special attention should be paid to the risk of sample contamination during their analysis, which would result in false positives and/or over-estimated concentrations. As it has already been said, PAEs are ubiquitous contaminants and this includes their possible presence in any laboratory since they can be found in solvents, reagents, filters, etc. Consequently, previous washing steps using PAE-free solvents, if possible (since most organic solvents also contain some PAEs), subsequent heating of non-volumetric glassware at high temperatures (450–550°C) for several hours (4–5 h), washing volumetric or any glassware material with strong oxidizing agents, and, in some cases, even wrapping in heat-treated aluminum foil to avoid adsorption of PAEs from the air are carried out, among others [27–29]. Despite all these precautions, residues of PAEs may finally appear, and the analysis of blanks should be developed on a daily basis in every batch of samples so that background levels can be suitably subtracted [21, 25, 30].

Until very recently, the most widely used sample preparation methods, also for the analysis of PAEs in water samples, have been based on the use of liquid-liquid extraction (LLE) and solid-phase extraction (SPE) [31, 32]. The need for developing quicker, simpler, and miniaturized extraction procedures able to maintain or even to improve the required sensitivity of the analysis has resulted in the development of new sample preparation techniques. In this sense, microextraction techniques have gained notoriety since the extraction is carried out using amounts of extracting phase much smaller than the sample amount (extraction of analytes is not always exhaustive). Microextraction techniques have inherent advantages such as exceptionally high enrichment factors, simplicity, time saving, and the generation of small amounts of organic solvent or reagents wastes, without affecting reproducibility, and compatibility with most analytical

instrumentation [33–36]. Among these new alternatives, sorbent-based microextraction techniques have been widely used due to the great diversity of commercially available sorbents, as well as new extraction sorbents (in particular nanomaterials) that are constantly being proposed for their direct use or after a previous functionalization to enhance their selectivity [35–37].

As a result of the above-mentioned issues, the aim of this book chapter is to provide a general overview of the sorbent-based microextraction techniques applied to the analysis of PAEs in water samples, which mainly include solid-phase microextraction (SPME), dispersive SPE (dSPE), and magnetic dSPE (m-dSPE), among others. The extraction ability to quantitatively and selectively extract these target analytes will be commented and discussed.

1.2 Solid-Phase Microextraction

SPME has been the sorbent-based microextraction technique most used for the analysis of PAEs in water samples (see Table 1.1) probably, among other reasons, because it allows to reduce the risk of PAEs contamination during sample extraction with respect to other conventional extraction techniques. On the one hand, the absence of organic solvents and additional steps reduces PAEs background levels. On the other, water is in many occasions a simple and clean matrix that contains few interferences, so the direct immersion (DI) mode can be used without hardly any impairment of its lifetime (except for waste waters or marine water). Moreover, in SPME, extraction, pre-concentration and direct desorption into analytical instruments can be easily integrated in most cases.

The first studies in which SPME was applied for PAEs extraction from water samples dealt with the direct application of commercial fiber coatings, including polydimethylsiloxane (PDMS), polyacrylate (PA), PDMS-divinylbenzene (DVB), carboxen (CAR)-PDMS, and carbowax (CW)-DVB. As examples, Cao [21] demonstrated the better performance of PDMS-DVB fibers compared to PDMS and DVB-CAR-PDMS fibers for the headspace (HS) SPME extraction of nine PAEs (DMP, DEP, DIBP, DBP, BBP, DHXP, DEHA, DEHP, and DNOP) from bottled water samples, while Polo *et al.* [28] found that PDMS-DVB fibers also give higher extraction efficiency than PDMS, PA, CAR-PDMS, and CW-DVB fibers for DBP, BBP, and DNOP, but CAR-PDMS and PA fibers show a better extraction performance for DMP and DEP, and for DEHP, although the first one provided better results for simultaneous analysis of the target PAEs from bottled,

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples.

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
SPME								
DMP, DEP, DBP, BBP, DEHP, and DNOP	Mineral, river, industrial port, sewage, and waste waters (10 mL)	SPME using a PDMS-DVB fiber, stirring at 100°C in DI mode for 20 min, and desorption at 270°C for 5 min	GC-MS	0.0067–0.34 μg/L	87–110% at 0.5 and 2.5 μg/L	One sample of each water were analyzed and contained all PAEs at levels from 0.011 to 6.17 μg/L	A multifactor categorical design was used for optimization purposes. PDMS-DVB fiber showed higher extraction efficiency than PDMS, PA, CAR-PDMS and CW-DVB fibers for DBP, BBP, and DNOP, but CAR-PDMS for DMP and DEP, and PA for DEHP. DI-SPME provided better sensitivity than HS mode	[28]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DEHA, DMP, DEP, BBP, DIBP, DBP, DHXP, DEHP, and DNOP	Mineral water (10 mL plus 10 or 30% w/v NaCl)	SPME using a PDMS-DVB fiber, stirring at 90°C in DI mode for 60 min, and desorption at 270–280°C for 5 min	GC-MS	-	-	Eleven samples were analyzed and residues of DEP, DIBP, DBP, and DEHP were found at levels from 0.052 to 1.72 µg/L	PDMS-DVB fiber showed higher extraction efficiency than PDMS and DVB-CAR-PDMS fibers	[21]
DPP, DBP, DIBP, and DNPP	Mineral and tap water (10 mL)	SPME using a MWCNTs-PPy fiber, stirring at room temperature in DI mode for 60 min, and desorption at 250°C for 25 min	GC-FID	0.17–0.33 µg/L	90–113% at 5 and 50 µg/L	Three mineral water samples and 1 tap water were analyzed and contained at least 1 PAE at levels from 0.6 to 7.90 µg/L, except 1 of the mineral water samples	-	[40]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, DAP, and DNOP	Mineral, tap and reservoir waters (12 mL plus 10% w/v NaCl)	SPME using a MIP fiber, stirring at 60°C in DI mode for 30 min, and desorption at 250°C for 10 min	GC-MS	0.0072–0.069 μg/L	94.54–105.34%	One sample of each water were analyzed and contained at least 2 PAEs at levels from 0.07 to 0.53 μg/L	DBP was used as the template molecule. MIP fiber showed higher extraction efficiency than a non-imprinted polymer fiber, and PDMS, PA and CW-DVB fibers	[45]
DMP, DEP, DBP, BBP, DEHP, DINP, and DNOP	Water (5 mL plus 6% w/v NaCl)	SPME using a PA fiber, stirring at room temperature in DI mode for 50 min, and desorption at 270°C for 2 min	GC-MS	0.007–0.027 μg/L	-	Six samples were analyzed and contained at least 2 PAEs at levels from 0.4 to 78.8 μg/L	PA fiber showed higher extraction efficiency than PDMS fiber. Urine was also analyzed	[95]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DIBP, DBP, BMPP, DNPP, DHXP, BBP, DCHP, DEHP, DIPP, DNOP, and DINP	River and tap waters (- mL)	SPME using a bamboo charcoal fiber, stirring at room temperature in DI mode for 20 min, and desorption at 280°C for 10 min	GC-MS	0.013–0.067 µg/L	61.9–87.1% at 0.1, 0.5, and 1 µg/L	One sample of each water were analyzed and no residues were detected	Bamboo charcoal fiber showed greater extraction efficiency than PDMS, PDMS-DVB and PA fibers for DNOP and DINP, but lower for DIBP, DBP, and DNPP	[47]
DBP, DIBP, BBP, and DEHP	Mineral water (9 mL plus 20% w/v NaCl)	SPME using a TiO_2 NPs fiber, stirring at 30°C in DI mode for 75 min, and desorption at 285°C for 5 min	GC-FID, GC-MS	0.17–0.40 µg/L	86–107% at 2 µg/L	One sample was analyzed and residues of DIBP and DEHP were found at 1.0 and 2.2 µg/L, respectively	TiO_2 NPs fiber showed better extraction efficiency than PDMS and poly(3,4-ethylenedioxythiophene)-TiO_2 fibers. DI-SPME provided better sensitivity than HS mode	[39]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, and DEHP	Mineral, river and tap waters (15 mL)	SPME using a SiO_2-PDMS-MWCNTs fiber, stirring at 40°C in DI mode for 30 min, and desorption at 280°C for 2 min	GC-FID	0.033–0.067 µg/L	79.62–109.3% at 10 µg/L	One sample of each water were analyzed and residues of DBP and DEHP were found at 5.26 and 8.47 µg/L, respectively, in the mineral water sample	SiO_2-PDMS-MWCNTs fiber showed better extraction efficiency than PDMS, PA and DVB-CAR-PDMS fibers	[43]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DPP, DIBP, DBP, DNPP, BBP, and DEHP	Mineral and tap waters (10 mL)	SPME using a poly-*o*-aminophenol-MWCNTs fiber, stirring at 35°C in DI mode for 60 min, and desorption at 280°C for 2 min	GC-FID	0.10–0.25 μg/L	91–115% at 5 and 50 μg/L	Three mineral water samples and 1 tap water sample were analyzed and contained at least 2 PAEs at levels from 0.3 ± 0.02 to 8.1 ± 0.19 μg/L, except for 1 mineral water sample	NaCl and dextrose injection solutions were also analyzed	[42]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DBP, BBP, DEHA, DEHP, and DNOP	Tap, barreled drinking and pond waters (10 mL plus 15% w/v NaCl)	SPME using a PS-MWCNTs fiber, stirring at room temperature in DI mode for 60 min, and desorption at 280°C for 5 min	GC-MS/MS	0.0038-0.059 μg/L	73.4-103.8% at 0.05 and 0.2 μg/L	One sample of each water were analyzed and contained at least 1 PAE at levels from 0.038 ± 0.004 to 0.060 ± 0.007 μg/L	A Box-Behnken design was used for optimization purposes	[41]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DPP, DBP, DEHA, and DEHP	Mineral, tanked and tap waters, and boiling water exposed to a PET container (10 mL plus 30% w/v NaCl)	SPME using a G-PVC fiber, stirring at 70°C in HS mode for 35 min, and desorption at 230°C for 4 min	GC-FID	0.2–0.3 μg/L	88–108% at 10 and 20 μg/L	One sample of each water were analyzed and residues of DPP and DBP were found at 2.1 and 1.8 μg/L, respectively, only in the boiling water exposed to a PET container	A central composite design was used for optimization purposes. Sunflower and olive oils were also analyzed	[20]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DIBP, DBP, DMEP, BMPP, DEEP, DNPP, BBP, DHXP, DBEP, DCHP, DPhP, DEHP, DNOP, and DINP	Sea water (10 mL)	SPME using a PDMS fiber, stirring at 35°C in DI mode for 40 min, and desorption at 40°C for 6 min	GC-MS	0.00017–0.0011 µg/L	68.0–114.0%, but 55.4% for DMP, at 100 and 300 µg/L	Eleven sample was analyzed and contained at least 9 PAEs at levels from 0.270 to 1.39 µg/L	Sediment was also analyzed by conventional SPE	[96]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DEP, DIBP, DBP, BBP, and DEHP	River, bottled and mineral waters (4 mL plus 20% w/v NaCl)	SPME using a polyamide6-MnO fiber, stirring at 80°C in HS mode for 30 min, and desorption at 200°C for 5 min	GC-μ-ECD	0.13–0.64 μg/L	90.3–106% at 10 and 100 μg/L	One sample of each water were analyzed and residues of DEP, DIBP and DBP were found at levels from 9.24 to 29.3 μg/L, respectively, in the bottle and mineral waters	Polyamide6-MnO fiber showed better extraction efficiency than PDMS fiber. Soda was also analyzed	[44]
DMP, DEHP, DBP, DNPP, BBP, and DNOP	Tap and sea water (20 mL adjusted at pH 4)	SPME using a GO-1-(3-aminopropyl)-3-vinyl imidazolium bromide/ tetrafluoroborate fiber, stirring at 35°C in DI mode for 30 min, and desorption at 175°C for 5 min	GC-MS	0.017–0.10 μg/L	87.6–101.2% at 1 and 5 μg/L	One sample of each water were analyzed, and no residues were detected	GO-1-(3-aminopropyl)-3-vinyl imidazolium bromide fiber showed higher extraction efficiency than GO-1-(3-aminopropyl)-3-vinyl imidazolium tetrafluoroborate, PA and CAR-PDMS fibers. Coffee was also analyzed	[52]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DEP, DPP, DAP, DBP, BBP, and DEHP	Water (- mL plus 20% w/v NaCl)	SPME using a OH-TPB-COFs fiber, stirring at 105°C in HS mode for 50 min, and desorption at 250°C for 7 min	GC-FID	0.11–1.50 μg/L	78.6–101.9% at 1 and 5 μg/L	Three sample were analyzed and contained at least 4 PAEs at levels from 1.39 to 5.78 μg/L	OH-TPB-COFs fiber showed better extraction efficiency than PDMS fiber	[46]
DMP, DBP, DINP, DEP, BBP, DEHP, DNOP, and DIDP	Mineral water (9 mL)	IT-SPME using AC-PS-DVB monolithic columns, and desorption with 1.5 mL ACN	CE-DAD, UHPLC-UV	0.59–9.83 μg/L	78.8–104.6% at 50 μg/L	One sample was analyzed, and no residues were detected	AC-PS-DVB monolithic column showed better extraction efficiency than AC-poly(BMA-EDMA) monolithic column. ACN showed higher extraction efficiency than MeOH as desorption solvent.	[62]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DAP, BBP, DBP, DNPP, and DCHP	Disposable tableware, plastic cup and river waters (45 mL plus 2% v/v MeOH)	IT-SPME using PDA-melamine-formaldehyde aerogel-carbon-fiber tube, and desorption with MeOH-water for 0.6 mL	HPLC-DAD	0.07–0.16 µg/L	77–120% at 10 and 15 µg/L	One sample of each water were analyzed and residues of DAP, BBP and DNPP were found at levels from 0.12 to 0.99 µg/L in the water in plastic cup	PDA-melamine-formaldehyde aerogel-carbon-fiber tube showed better extraction efficiency than melamine-formaldehyde aerogel-carbon-fiber and bare carbon-fiber tubes	[23]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
SBSE								
DMP, DEP, DBP, BBP, DEHP, and DNOP	Sea and esturiane waters (20 mL plus 30% w/v NaCl and 20% v/v MeOH)	SBSE using a PDMS stir bar, stirring at room temperature for 60–200 min, and thermal desorption at 300°C for 10 min	GC-MS	0.0003–0.063 µg/L	95–124% at 0.1 µg/L	One river water sample and 2 estuarian water samples were analyzed and contained all PAEs at levels from 0.0036 ± 0.0004 to 1.314 ± 0.018 µg/L	A Plackett–Burman and 2 central composite designs were used for optimization purposes. 6 polycyclic aromatic hydrocarbons, 12 polychlorinated biphenyls and 3 nonylphenols were also analyzed	[65]

(*Continued*)

Table 1.1 Some examples of the application of SPME and SBSE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DIBP, DBP, DMEP, DMPP, DEEP, DNPP, DHXP, BBP DBEP, DCHP, DEHP, DPhP, and DNOP	Sea water (25 mL plus 5% w/v NaCl and 10% v/v MeOH)	SBSE using a PDMS stir bar, stirring at room temperature for 120 min, and desorption with 200 µL MeOH and 50 µL ACN by sonication for 50 min	GC-MS	0.00027–1.63 µg/L	-	No samples were analyzed	The stir bar coated with 150 µl PDMS showed higher extraction efficiency than coated with 50 µL and 75 µL PDMS, and 150 µL PDMS over carbon film. A mix MeOH-ACN showed higher extraction efficiency than MeOH and dichloromethane as desorption solvent	[66]

µ-ECD, micro-electron capture detector; AC, activated carbon; ACN, acetonitrile; BBP, benzylbutyl phthalate; BMA, butyl methacrylate; BMPP, bis(4-methyl-2-pentyl) phthalate; CAR, carboxen; CE, capillary electrophoresis; COFs, covalent organic frameworks; CW, carbowax; DAD, diode-array detector; DAP, diallyl phthalate; DBEP, di(2-butoxyethyl) phthalate; DBP, dibutyl phthalate; DCHP, dicyclohexyl phthalate; DEEP, di(2-ethoxyethyl) phthalate; DEHA, di(2-ethylhexyl) adipate; DEHP, di(2-ethylhexyl) phthalate; DEP, diethyl phthalate; DHXP, dihexyl phthalate; DI, direct immersion; DIBP, diisobutyl phthalate; DIDP, diisodecyl phthalate; DINP, diisononyl phthalate; DIPP, diisopentyl phthalate; DMEP, di(2-methoxyethyl) phthalate; DMP, dimethyl phthalate; DMPP, dimethylethyl phthalate; DNOP, di-n-octyl phthalate; DNPP, di-n-pentyl phthalate; DPhP, diphenyl phthalate; DPP, dipropyl phthalate; DVB, divinylbenzene; EDMA, ethylene dimethacrylate; FID, flame ionization detector; G, graphene; GC, gas chromatography; GO, graphene oxide; HPLC, high-performance liquid chromatography; HS, headspace; IT-SPME, in tube-solid-phase microextraction; LOQ, limit of quantification; MeOH, methanol; MIP, molecularly imprinted polymer; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MWCNTs, multi-walled carbon nanotubes; NPs, nanoparticles; PA, polyacrylate; PAE, phthalic acid ester; PDA, poly(dopamine); PDMS, polydimethylsiloxane; PET, polyethylene terephthalate; PPy, polypyrrole; PS, polystyrene; PVC, polyvinylchloride; SBSE, stir bar sorptive extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; TPB, 2,4,6-triphenoxy-1,3,5-benzene; UHPLC, ultra-performance liquid chromatography; UV, ultraviolet.

industrial harbor, river, urban collector, and influent and effluent waste water samples. As expected, the optimal SPME fiber for the extraction of a particular phthalate depends on both the properties of the coating and the PAEs since these compounds differ from each other in terms of polarity and volatility and, therefore, on their distribution between the fiber coating and the matrix. In addition, low-molecular PAEs are more volatile than those of high-molecular weight [38]. As a result, low-molecular PAEs would be expected to be more efficiently extracted when HS mode is used [38]. However, they have a certain solubility in water and, as consequence, they volatilize very slowly from this kind of matrices. Contrary, although high-molecular PAEs are less volatile, they have a lower water solubility and they volatilize faster at higher temperatures than it could be expected [38]. Accordingly, it has been observed that DEHP and DNOP are extracted from different water samples more efficiently than BBP, DEP, and DMP using HS-SPME [28, 39]. Nevertheless, most of the works published on this topic are based on DI-SPME instead of HS-SPME.

As it has already been said, the fiber coating plays a key role in the SPME of PAEs from water samples. However, the types of commercial fibers are still limited, which reduces their application field. In addition, under certain conditions they have low thermal and chemical stability. Furthermore, they are fragile since they are based on fused silica supports. Consequently, most of the subsequent studies have been focused on developing new highly selective, efficient, inexpensive, and robust SPME fibers with controllable thickness through different coating techniques. For this purpose, a wide variety of new fibers based on the use of carbon-based nanomaterials [40–43], metal oxide nanoparticles (NPs) [39, 44], molecular imprinted polymers (MIPs) [45], covalent organic frameworks (COFs) [46], and bamboo charcoal [47] have been reported, among others.

The development of carbon-based coatings for stainless-steel fibers has been an important research field as a result of the exceptional properties these materials have, such as great chemical and thermal stability, high surface area and great capacity to establish π-π interactions with the aromatic groups of the PAEs [37, 48, 49]. Moreover, they can be easily dispersed in a polymer matrix to obtain coatings that provide considerably better characteristics than those of virgin polymers. Among them, multi-walled carbon nanotubes (MWCNTs) have been the most used, which are large molecules composed by numerous electronically aromatic delocalized carbon atom layers and rolled up into a cylinder. As examples of the use of this kind of coatings for the extraction of PAEs from water samples, Asadollahzadeh *et al.* [40] made a fiber coated with an oxidized MWCNTs-polypyrrole (PPy) composite while Behzadi *et al.* [42] used MWCNTs-poly-*o*-aminophenol,

both obtained through electrochemical polymerization, for the extraction of mineral water samples. Song *et al.* [41] also prepared a MWCNTs-polystyrene (PS) material via electrostatic interactions as SPME coating, and Zhang *et al.* [43] developed a SiO_2-PDMS-MWCNTs fiber by a sol-gel method. In both cases, drinking and environmental water samples were analyzed. All these fiber coatings presented a porous structure with very large surface areas where both phases (the MWCNTs and polymer) took part in the extraction procedure, enhancing the final adsorption capacity of the fiber. Moreover, in the last work, the organic-inorganic bilayer structure was designed to increase the stability and durability of the coating. In particular, a stainless-steel fiber was coated with a SiO_2 layer, which was used as support for the chemical bonding of the second layer of PDMS-MWCNTs (see Figure 1.3). The first coating with a SiO_2 layer is a general procedure widely used for coating different surfaces or particles [50, 51]. Compared with commercial PDMS, PA, and DVB-CAR-PDMS fibers, this new coating showed better extraction efficiency and longer lifetimes (150 vs. 50–100 times) for the extraction of DMP, DEP, DBP, and DEHP. It is also noteworthy to mention the extensive study that was conducted by these authors to evaluate the influence of salt addition on the extraction efficiency. It was observed that the addition of different kinds of salts such as

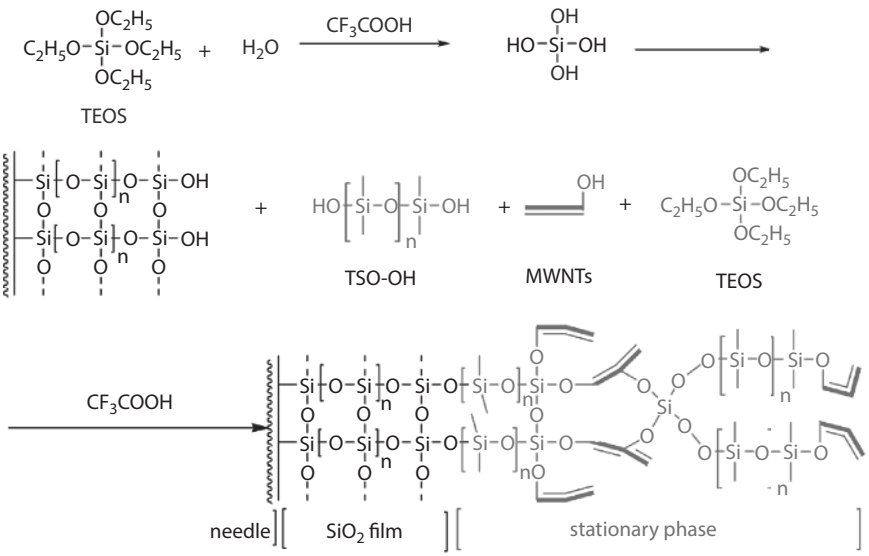


Figure 1.3 Schematic representation of the SiO_2-PDMS-MWNTs fiber preparation. Reprinted from [43] with permission from The Royal Society of Chemistry. MWNTs, multi-walled carbon nanotubes; TEOS, tetraethoxysilane; TSO-OH, hydroxyl terminated silicone oil.

NaCl, $CaCO_3$, $FeCl_3$, and $MgCl_2$ at different concentrations (0%, 5%, 10%, and 15%, w/v) can have a negative or a negligible effect on the recovery values. Therefore, no salt was added to the samples, as in the vast majority of the published works on this topic (see Table 1.1).

Graphene is another of the allotropic forms of carbon that has been used as SPME coating. It consists of a monolayer of sp^2 hybridized carbon atoms arranged in a 2D network. Like MWCNTs, graphene has a high surface area, high chemical and thermal stability as well as a high affinity for hydrophobic and aromatic compounds. Then, graphene-polymer nanocomposites have also been used as excellent SPME fiber coatings for the extraction of PAEs. Such is the case of the work developed by Amanzadeh *et al*. [20] in which a stainless-steel fiber was coated using a new graphene/polyvinylchloride (PVC) material and evaluated successfully as a SPME fiber for the extraction of dipropyl phthalate (DPP), DBP, DEHA, and DEHP from drinking waters and sunflower and olive oil samples. However, even though it was used in the HS mode, a single fiber could be used only 60 times without a significant decrease in the extraction efficiency. As a very interesting experiment, these authors also determined these PAEs in boiling water exposed to a polyethylene terephthalate (PET) bottle. Although the water used did not contain residues of any of the target PAEs at the beginning, residues of DPP and DBP were found at 2.1 and 1.8 μg/L, respectively, after filling this bottle with the same water just after boiling (it was analyzed after cooling). That is, the PAEs with low molecular weight (250.2 g/mol for DPP and 278.3 g/mol for DBP compared to 370.5 g/mol for DEHA and to 390.5 g/mol for DEHP) have larger water solubility, so these kinds of PAEs migrated more easily from PET bottles containing hot water.

Another example of the benefits of using graphene, is the work of Tashakkori *et al*. [52] who prepared SPME fibers based on the use of the ionic liquid (IL) 1-(3-aminopropyl)-3-vinyl imidazolium bromide and 1-(3-aminopropyl)-3-vinyl imidazolium tetrafluoroborate grafted onto graphene oxide (GO) previously deposited onto stainless-steel wires. On the one hand, GO disperses more easily for the first preparation step and inherits the mechanical properties of graphene but with a moderate decrease of mechanical parameters (Young's modulus and intrinsic strength) due to the alterations produced in the sp^2 structure [53, 54]. On the other hand, ILs can be structurally customized based on diverse procedures to tune the extraction performance [55]. In fact, ILs can establish a broader variety of interactions with the analytes such as π-π, dipolar, hydrogen bonding, and ionic/charge-charge [56]. As a result, they are also suitable for the extraction of hydrophobic compounds and aromatic

analytes like PAEs. Consistently, the first GO-IL fibers showed better extraction efficiency for the analysis of DMP, DEHP, DBP, DNPP, BBP, and DNOP in tap and sea water samples (also in instant coffee samples) than other lab-made fiber, as well as commercial PA and CAR-PDMS fibers, using DI mode in all cases.

MIPs also provide a great improvement in selectivity since they have cavities specifically designed for a particular compound or group of analogous compounds [57, 58]. That is to say, retention occurs through a molecular recognition mechanism based on their size, shape and three-dimensional distribution of functional groups [59]. He *et al.* [45] demonstrated that MIPs are quite suitable as SPME fiber coatings for the successful extraction of low (DMP, DEP, DBP, and diallyl phthalate -DAP-) and high-molecular PAEs (DNOP) simultaneously, from bottled, tap, and reservoir water samples, although it is true that the latter was poorly extracted since DBP was used as template molecule during the synthesis of the polymer. Moreover, the peak areas obtained using the MIP fiber were much higher than those using a non-imprinted fiber prepared with the same protocol (without the addition of the template molecule), but also better compared to commercial PDMS, PA, and CW-DVB fibers (see Figure 1.4). These results indicate that the MIP fiber provided a better selectivity for the structural analogues of DBP, while commercial SPME coatings are more susceptible to undesirable interferences in the extraction process.

Another variant of SPME which has also been applied for PAEs extraction is in-tube (IT)-SPME [60]. In this format, a very thin tube is coated in its inner walls and the extraction and desorption are carried by the introduction and extraction of the sample inside the tube several times [61]. As in conventional SPME, the combination of materials with high surface areas and polymers afford a high extraction capability, while its porous structure provides suitable dynamic transport during extraction. As examples, Wang *et al.* [23] used poly(dopamine) (PDA) to functionalize melamine formaldehyde aerogel on carbon fibers and were packed inside IT-SPME tubes for the extraction of seven PAEs from drinkable and surface water, while the performance of this process embedding activated carbon (without any chemical modification) in different polymers (e.g., poly(butyl methacrylate-co-ethylene dimethacrylate) (poly(BMA-EDMA)) and PS-DVB) was investigated by Lirio *et al.* [62]. In this last work, low extraction recovery values were obtained when a solution containing eight PAEs was collected using monolithic columns with native poly(BMA-EDMA) and PS-DVB. On the contrary, the presence of increasing amounts of activated carbon provided a higher extraction efficiency under the same conditions. Moreover, the activated

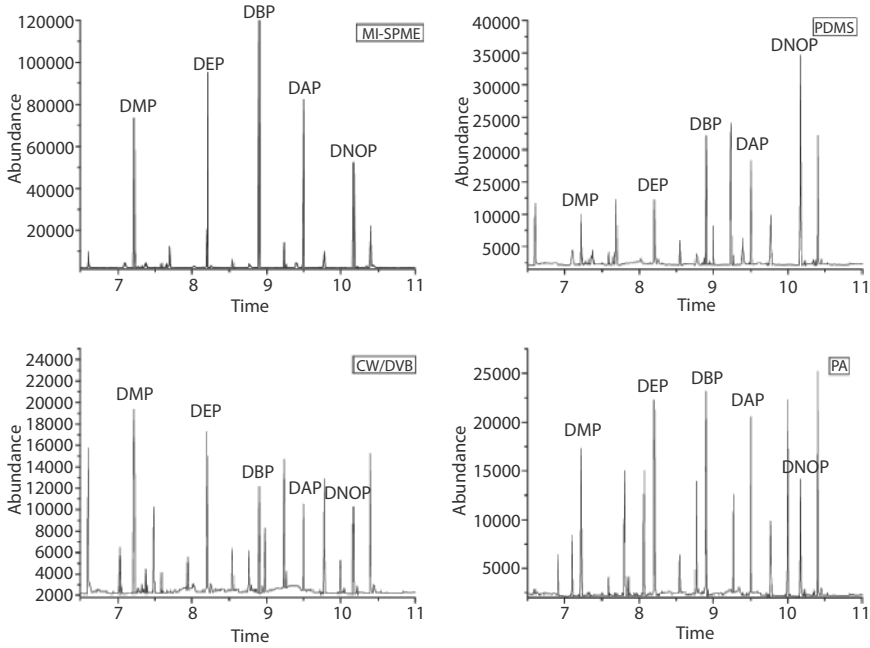


Figure 1.4 Extraction yields with different fibers (MI-SPME, PDMS, CW/DVB, and PA) in water samples. Extraction conditions: 12 ml of spiked pure water including NaCl content of 10% w/v, stirring at 60°C in DI, adsorption time 30 min, desorption at 250°C for 10 min. Reprinted from [45] with permission from Elsevier. CW, carbowax; DAP, diallyl phthalate; DBP, dibutyl phthalate; DEP, diethyl phthalate; DMP, dimethyl phthalate; DNOP, di-n-octyl phthalate; DVB, divinylbenzene; MI, molecular imprinted polymer; PA, polyacrylate; PDMS, polydimethylsiloxane; SPME, solid-phase microextraction.

carbon-PS-DVB monolithic column exhibited better extraction performance than the activated carbon-poly(BMA-EDMA) one. Therefore, the first was applied in the IT-SPME of mineral water samples obtaining recovery values in the range of 78.8%–104.6% at 50 μg/L.

1.3 Stir Bar Sorptive Extraction

As a technique derived directly from SPME, SBSE is based on the same principles of distribution of the analytes between the sorbent and the sample. This technique, introduced by Baltussen *et al.* [63], is based on the use of a small device consisting of a magnetic bar which is introduced in a glass tube coated by PDMS in most cases, generally using around 50–300 times larger PDMS amounts as coating, so SBSE significantly increases

the enrichment factors compared to SPME, providing at the same time a higher extraction efficiency as a consequence of its larger volume and surface area. Moreover, SBSE desorption can be directly developed in a thermal desorption unit in many GC systems, so it maintains one of the main advantages derived from the use of SPME [64]. Since then, this technique has evolved and a wide variety of laboratory made coatings have been developed in order to extend the field of application of SBSE, especially to the extraction of polar compounds, as well as to improve its selectivity [64]. Up to now, few works have used SBSE for the determination of PAEs in water samples (see Table 1.1). This is the case of the work of Prieto *et al.* [65], who analyzed six PAEs together with sixteen polycyclic aromatic hydrocarbons (PAHs), twelve polychlorinated biphenyls (PCBs) and three nonylphenols in sea and estuarine waters, and that of Si *et al.* [66], who extracted fifteen PAEs from sea water. In both works, commercial PDMS-coated stir bars of 0.5- and 1-mm thickness were used, respectively. In both cases, the addition of methanol (MeOH) to the water sample (20% for 0.5-mm thickness fibers and 10% for 1-mm thickness fibers, v/v) was crucial to avoid PAEs adsorption on the glass walls and to improve the extraction efficiency, particularly for long chain PAEs. In the last work, four commercially available stir bars containing different amounts of PDMS were evaluated in terms of extraction capacity. The results showed that the stir bar containing the highest amount (150 μL vs. 50, 75, and 150 μL over carbon) provided the largest peak areas, which was consistent with the principles of the process. However, the sensitivity for the higher-molecular weight PAEs (i.e., DNOP and DEHP) was notably lower, which is probably caused by the fact that this kind of nonpolar compounds establish strong interactions with the PDMS coating which could result in an incomplete desorption and the consequent higher LODs and LOQs. The combination of SBSE with GC-MS systems using single quadrupoles operated in the SIM mode allowed obtaining high extraction efficiency as well as high sensitivity (0.1–489 ng/L) in general.

1.4 Solid-Phase Extraction

One of the most important advantages of SPE compared to SPME is the availability of a wider range of relatively cheap commercial sorbents. However, the low rate of diffusion and mass transfer between the packed sorbents and the target analytes generally results in a slow extraction process. Moreover, in some cases, cartridges can be blocked when complex matrices are analyzed, leading to process failure. Besides, a previous

cartridge conditioning is required which also lengthens the extraction process. In order to solve these problems, dSPE—as a miniaturized version of SPE in many cases—emerged as an alternative based on the direct addition of the sorbents (without preconditioning) to samples or extracts [67, 68], improving the contact area between sorbent and the sample/extract solution. Consequently, the analytes are extracted much faster by simple manual, vortex, or ultrasound agitation, while most interferences remain in the solution (depending on the selectivity of the sorbent). Then, the sorbent can be separated by its retention into a SPE column [25] or by centrifugation and the subsequent supernatant decantation [69]. In the first case, the analytes are later eluted as in conventional SPE, while in the second, the analytes have to be desorbed under agitation, centrifugation, and decantation. Therefore, this variant saves time, efforts, and solvents, with the consequent economic savings that this entails [70, 71]. The few dSPE methods developed for the extraction of PAEs from water samples (see Table 1.2) have been based on the application of graphene [72], GO-MIP [69], MIPs microbeads [73], a commercial metal-organic framework (MOF) [25], and a temperature-sensitive polymer [74]. In this last case, a lab-synthesized β-cyclodextrin-poly(N-isopropylacrylamide) (β-CD-PNIPAM) polymer was used to carry out the extraction of three short-chain PAEs from tap and mineral water. This kind of polymers are characterized by showing a reversible phase transition in aqueous samples at a certain temperature known as low critical solution temperature (LCST). In this case, the LCST is at 32°C, so the polymer behaves as a liquid below that value while it is a solid when the temperature exceeds it. Taking advantage of this fact, the authors introduced 20 mL of β-CD-PNIPAM into the sample and mixed. Then, the temperature was increased up to 50°C obtaining a floating solid phase, which was collected after Na_2SO_4 addition in order to favor the salting-out effect. This extraction methodology, in combination with GC-MS, allowed obtaining good extraction efficiency and sensitivity, especially for DBP, which makes think about the potential of this procedure for the determination of long-chain PAEs. It is important to mention that, from an operational point of view, the use of this kind of polymers implies that the extraction step is developed in the same way as a LLE procedure and, as consequence, it could be not considered as a sorbent-based extraction methodology for some authors. However, the second part involve a desorption of the analytes from the solid polymer, since that reversible phase transition just takes place when it is into the water sample. In order to provide a better vision of this procedure, Figure 1.5 shows a scheme of a similar procedure used by Chen *et al.* in a previous work for the determination of different phenolic compounds—no PAEs were included [75].

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples.

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DIBP, DBP, DMEP, BMPP, DEEP, DNPP, DHXP, BBP, DBEP, DCHP, DEHP DNOP, and DNP	River and sea waters (20 mL)	dSPE using 3 mL colloidal G and vortex for 2 min, centrifugation at 3800 rpm for 5 min, and desorption with 5 mL ethyl acetate and 2 g sodium sulfate by vortex for 30 s	GC-MS	5–20 µg/L	72–117% at 20 and 50 µg/L	Nine river and 2 sea waters samples were analyzed and contained at least 1 PAE at levels from 2 to 78 µg/L	Ethyl acetate showed higher extraction efficiency than ACN, acetone and hexane as desorption solvent	[72]
DEHP	Rain, lake and river waters (600 mL)	dSPE using 20 mg GO-MIP and agitation for 30 min, centrifugation at 12000 rpm for 10 min, and desorption (twice) with 2.5 mL acetone by vortex for 1 min and subsequent sonication for 5 min	HPLC-UV	2.82 µg/L	82-92% at 5, 50, and 500 µg/L	One sample of each water were analyzed and residues were found at 0.32 ± 0.08 and 1.56 ± 0.32 µg/L in lake and river waters, respectively.	DEHP was used as the template molecule. Acetone showed higher extraction efficiency than MeOH as desorption solvent	[69]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, BBP, DEHP, and DNOP	Bottle water (200 mL)	dSPE using 60 mg DMIMs and stirring for 90 min, and desorption with 5 mL dichloromethane by sonication for 15 min	GC-MS	1.03–1.35 μg/L	92.4–99.0% at 25 μg/L	Two samples were analyzed and residues of DEHP were found at 10.06 ± 0.84 and 11.90 ± 1.70 μg/L	DEP was used as the dummy template. Dichloromethane showed higher extraction efficiency than acetone, MeOH, chloroform, ethyl acetate and hexane as desorption solvent. DMIMs-dSPE method showed higher recovery values compared with non-imprinted polymers	[73]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, and DBP	Tap and mineral waters (20 mL)	dSPE using 20 mg β-cyclodextrin-poly (N-isopropylacrylamide) and water bath at 50°C for 25 min., addition of sodium sulfate for polymer condensation purposes, and desorption with 200 µL ethyl acetate by sonication for 15 min.	GC-MS	0.021–0.350 µg/L	82.2–105.6% at 5, 100, and 600 µg/L	One sample of each water were analyzed and all PAEs were found at levels from 0.14 to 4.97 µg/L	Ethyl acetate showed higher extraction efficiency than hexane, acetone and dichloromethane as desorption solvent.	[74]
BBP, DBEP, DIPP, DNPP, DCHP, DEHP, DNOP, DINP, and DEHA	Milli-Q, pond, tap and waste waters (50 mL)	dSPE using 120 mg Basolite® F300 MOF and shaking for 5 min, vacuum-dried using a SPE column for 30 min, and elution with 15-mL ACN	HPLC-MS	0.022–0.069 µg/L	70–118% at 0.375 and 1.875 µg/L	Eight samples were analyzed and residues of DEHP were found at levels from 0.21 ± 0.26 to 4.04 ± 0.23 µg/L in all samples	ACN showed higher extraction efficiency than dichloromethane, acetone, cyclohexane and MeOH as elution solvent	[25]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DPP, DIBP, DBP, DNPP, DHXP, BBP, DEHP, DHP, DCHP, DPhP and DNOP	Drinking water (200 mL)	m-dSPE using 20 mg MWCNTs-m-NPs under agitation for 2 min, a magnet was used for decantation, and elution with 1 mL toluene–acetone (1:4, v/v)	GC-MS/MS	0.03–0.1 μg/L	86.6-100.2% at 5 μg/L	Three samples were analyzed and no residues were detected	Toluene showed higher extraction efficiency than acetone, MeOH, hexane and ethyl acetate as elution solvent. To reduce the toxicity of toluene, different proportions toluene-acetone (1:1, 1:4 and 1:9, v/v) were tested and the mix toluene–acetone (1:4, v/v) gave similar results	[76]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DEP, DPP, DBP, DCP, and DEHP	Bottled and river waters (300 mL)	m-dSPE using 25 mg G-Fe_3O_4 under agitation for 15 min, a magnet was used for decantation, and elution (in triplicate) with 0.5 mL acetone by vortex for 10 s	HPLC-UV	0.03–0.1 µg/L	80.0-106.0% at 0.5 and 5 µg/L	One sample of each water were analyzed and residues of DBP and DEHP were found at 0.12 and 0.15 µg/L, respectively, in the river water sample	Acetone showed higher extraction efficiency than MeOH and ACN as elution solvent. Coca-Cola and green tea samples were also analyzed	[78]
DMP, DEP, DAP, DIBP, and BBP	River, reservoir and sea waters (300 mL)	m-dSPE using 36 mg layered carbon-Fe_3O_4 under agitation for 10 min, a magnet was used for decantation, and elution (in triplicate) with 0.5 mL acetone by vortex for 10 s	HPLC-UV	0.27–0.33 µg/L	88.0–104.7% at 5 and 10 µg/L	One sample of each water were analyzed and residues of DAP and DIBP were found at 0.52 and 0.86 µg/L, respectively, in the river water sample	Acetone showed higher extraction efficiency than MeOH and ACN as elution solvent	[26]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DIBP, DBP, DMEP, BMPP, DEEP, DNPP, DHXP, BBP, DBEP, DCHP, DEHP, DIPP, DNOP, and DNP	Mineral and tap waters (9.8 mL plus 0.2 mL MeOH)	m-dSPE using 0.1 mL suspension of MWCNTs-m-NPs in water (40 mg/ml) under vortex for 3 min, a magnet was used for decantation, and elution with 1 mL acetone	GC-MS	0.016–0.13 µg/L	79.6–125.6% at 5 µg/L	Two mineral and 1 tap water samples were analyzed and contained at least 3 PAEs at levels from 0.36 to 3.3 µg/L	Acetone showed higher extraction efficiency than MeOH, ethyl acetate and hexane as elution solvent. Juice and carbonated drinks, and one perfume sample were also analyzed	[77]
DMP, DEP, DIBP, DBP, DEHP, BBP, and DNOP	River and pond waters (10 mL)	m-dSPE using 20 mg G-Fe_3O_4 under vortex for 15 min, a magnet was used for decantation, and elution with 0.4 mL ethyl acetate and 0.5 g anhydrous sodium sulfate by sonication for 15 min	GC-MS	0.035–0.19 µg/L	88–110% at 10,000 µg/L	One sample of each water were analyzed and residues of all PAEs except DMP were found at levels from 22.2 to 150.8 µg/L	Ethyl acetate showed higher extraction efficiency than acetone and chloroform as elution solvent	[79]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, BBP, and DNOP	River, tap and mineral waters (20 mL)	m-dSPE using 20 mg Fe_3O_4-ZIF-8 MOF under sonication for 8 min, a magnet was used for decantation, and elution with 1 mL MeOH by sonication for 8 min	HPLC-DAD	0.3–0.8 µg/L	85.6–103.6% at 1, 10, and 100 µg/L	One sample of each water were analyzed and at least 2 PAEs at levels from 5 to 60 µg/L were detected in the river and tap water samples	Methanol showed higher extraction efficiency than ACN, chloroform and tetrahydrofuran as elution solvent	[85]
DMP, DEP, DIBP, DBP, DEHP, BBP, DNOP, DMEP, DEEP, DNPP, BMPP, DHXP, DBEP, DCHP, DPhP, and DINP	Tap and lake waters (20 mL)	m-dSPE using 20 mg Fe_3O_4-polypyrrole under agitation for 40 min, a magnet was used for decantation, and elution with 2 mL ethyl acetate by sonication for 60 min	GC-MS	0.018–0.068 µg/L	80.4–108.2% at 5 and 100 µg/L	One sample of each water were analyzed and at least 5 PAEs at levels from 0.10 to 6.90 µg/L were detected	An orthogonal fraction factorial design was used for optimization purposes. Ethyl acetate showed higher extraction efficiency than acetone and isopropanol as elution solvent	[81]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DEP, DPP, DBP, DIPP, DNPP, BBP, DCHP, DEHP, DNOP, DINP, DIDP and DEHA	Mineral, tap, pond and waste waters (25 mL adjusted at pH 6)	m-dSPE using 60 mg Fe_3O_4-PDA under agitation for 1 min, a magnet was used for decantation, and elution with 6 mL dichloromethane by agitation for 30 s	GC-MS/MS	0.009–0.02 μg/L	71–120% at 0.5 and 5 μg/L	One sample of each water were analyzed and residues of DEP and DBP were found at levels from 0.36 ± 0.46 to 4.20 ± 0.52 μg/L in the mineral, tap and waste waters	Dichloromethane showed higher extraction efficiency than acetone, MeOH and ACN as elution solvent	[22]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, BBP, and DBP	Carbonated, mineral and soda waters (25 mL)	m-dSPE using 30 mg poly(1-vinyl-3-butylimidazolium bromide)-PS m-NPs under vortex for 2.5 min, a magnet was used for decantation, and elution with 7 mL ACN by sonication	HPLC-DAD	0.017-0.047 μg/L	77.8-102.1% at 2 and 20 μg/L	One sample of each water were analyzed and residues of DEP were found at 25.8 and 15.5 μg/L in the carbonate and soda waters, respectively	ACN showed higher extraction efficiency than acetone, petroleum ether and MeOH as elution solvent	[82]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DAP, DIBP, and DBP	Tap and well waters (5 mL plus 15% w/v NaCl)	m-dSPE using 15 mg Fe_3O_4-MIL-101(Cr) MOF under agitation for 20 min, a magnet was used for decantation, and elution with 1 mL hexane/acetone (1:1 v/v) by vortex for 3 min	GC-MS	0.3–0.5 μg/L	90.1–106.7% at 5 and 50 μg/L	One sample of each water were analyzed and no residues were detected	The use of Fe_3O_4-MIL-101(Cr) MOF showed higher enrichment capacity than Fe_3O_4 and MIL-101(Cr) MOF separately. Hexane/acetone (1:1 v/v) showed higher extraction efficiency than ethyl acetate, hexane, acetone and hexane/ethyl acetate (1:1 v/v) as elution solvent. Human plasma was also analyzed	[86]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, BBP, DEHP, and DNOP	Tap, drinking and mineral waters (10 mL)	m-dSPE using 15 mg Fe_3O_4-MIL-100 MOF and 15-mg Fe_3O_4-SiO_2-polythiophene under sonication for 1 min and oscillation for 15 min, a magnet was used for decantation, and elution with 1 mL ACN by agitation for 10 min	GC-MS	1.1-2.9 µg/L	76.9–109.1% at 1, 10 and 50 µg/L	One sample of each water were analyzed and no residues were quantified	A combination of 15-mg Fe_3O_4-MIL-100 MOF and 15-mg Fe_3O_4-SiO_2-polythiophene gave better extraction efficiency than using 30-mg each separately. ACN showed higher extraction efficiency than acetone, ethyl acetate and hexane as elution solvent	[88]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DBP, BBP, DCHP, and DEHP	Tap and lake waters (100 mL adjusted at pH 6)	m-dSPE using 30 mg poly(1-vinylimidazole)-carboxy-latocalix[4] arene m-NPs under sonication for 15 min, a magnet was used for decantation, and elution with 0.5 mL MeOH by sonication for 5 min	HPLC-UV	0.05–0.11 μg/L	89.9–110.0% at 0.5, 1, and 5 μg/L	One sample of each water were analyzed and contained at least 1 PAE at levels from 0.4 to 8.9 μg/L	Methanol showed higher extraction efficiency than ACN and chloroform as elution solvent. The use of poly(1-vinylimidazole)-carboxy-latocalix[4] arene m-NPs showed higher enrichment capacity than Fe_3O_4 and poly(1-vinylimidazole) separately.	[83]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
							m-dSPE using poly(1-vinylimidazole)-carboxy-latocalix[4]arene m-NPs showed better results compared with SPE with C_{18} and Cleanert SCX cartridges. Drinks, tonic lotions, and human serum were also analyzed	
DBP, DMP, DCHP, BBP, and DEP	River water (10 mL)	m-dSPE using 30 mg 3D N-Co-C/HCF MOF under agitation for 20 min, a magnet was used for decantation, and elution with 6 mL ACN by sonication for 10 min	HPLC-UV	0.077–0.377 µg/L	92.4–104.2% at 1, 10, and 50 µg/L	One sample was analyzed and contained DMP and DEP at 0.075 and 0.081 µg/L, respectively	Green tea, sports beverage and white spirit were also analyzed. ACN showed higher extraction efficiency than acetone, MeOH, and ethanol as elution solvent	[87]

(*Continued*)

Table 1.2 Some examples of the application of SPE for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DPP, DBP, DCHP, DEHP, DNOP, DIDP, BBP, DINP, DIPP, DNPP, and DEHA	Sea water (50 mL adjusted at pH 6)	m-dSPE using 120 mg Fe_3O_4-PDA under agitation for 1 min, a magnet was used for decantation, and elution with 1 mL dichloromethane by agitation for 30 s	GC-MS	0.0018–0.319 μg/L	79–116% at 0.4, 1, and 1.6 μg/L	Ten samples were analyzed and no residues were quantified	Sea sand was also analyzed.	[80]

MeOHMeOHMeOHMeOHMeOHACN, acetonitrile; BBP, benzylbutyl phthalate; BMPP, bis(4-methyl-2-pentyl) phthalate; DAD, diode-array detector; DAP, diallyl phthalate; DBEP, di(2-butoxyethyl) phthalate; DBP, dibutyl phthalate; DCHP, dicyclohexyl phthalate; DEEP, di(2-ethoxyethyl) phthalate; DEHA, di(2-ethylhexyl) adipate; DEHP, di(2-ethylhexyl) phthalate; DEP, diethyl phthalate; DHP, diheptyl phthalate; DHXP, dihexyl phthalate; DIBP, diisobutyl phthalate; DIDP, diisodecyl phthalate; DINP, diisononyl phthalate; DIPP, diisopentyl phthalate; DMEP, di(2-methoxyethyl) phthalate; DMIMs, dummy molecularly imprinted microbeads; DMP, dimethyl phthalate; DNOP, di-n-octyl phthalate; DNP, dinonyl phthalate; DNPP, di-*n*-pentyl phthalate; DPhP, diphenyl phthalate; DPP, dipropyl phthalate; dSPE, dispersive solid-phase extraction; G, graphene; GC, gas chromatography; GO, graphene oxide; HCF, hierarchical carbon framework; HPLC, high-performance liquid chromatography; LOQ, limit of quantification; m-dSPE, magnetic solid-phase extraction; MeOH, methanol; MIL, Material of Institute Lavoisier; MIP, molecularly imprinted polymer; m-NPs, magnetic nanoparticles; MOF, metal organic framework; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MWCNTs, multi-walled carbon nanotubes; PAE, phthalic acid ester; PDA, poly(dopamine); PS, polystyrene; SPE, solid-phase extraction; UV, ultraviolet; ZIF, Zeolitic Imidazolate Framework.
MeOHMeOHMeOHMeOHMeOH

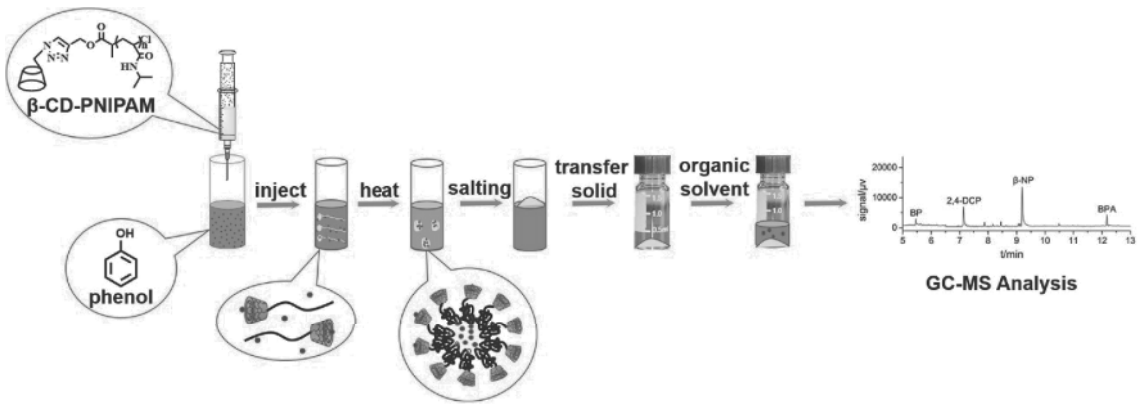


Figure 1.5 Scheme of a similar extraction procedure carried out by Chen *et al.* [75] using the same β-CD-PNIPAM temperature-sensitive polymer as extractant for the determination of phenolic compounds in river water samples. Reprinted from [75] with permission of Elsevier. Peak identification: phenol (BP), 2,4-dichlorophenol (2,4-DCP), β-naphthol (β-NP), and bisphenol A (BPA).

Despite the simplicity of the dSPE, the whole procedure can be even improved and simplified if the sorbent particles can be manipulated with a magnet. Such dSPE mode is called m-dSPE and is based on the use of magnetic NPs (m-NPs), which can be applied as synthesized (though in very few cases), although they are generally functionalized or coated with other chemical species or materials, resulting in many cases a "core-shell" structure, in order to improve their selectivity, or even embedded them in the extraction sorbent to provide it with magnetic properties [50]. Despite the extraction step is performed in a similar way as in dSPE, in this case, the magnetic sorbent containing the analytes is retained in the extraction recipient using an external magnet while the sample matrix is easily discarded without the need of an additional centrifugation step or the retention of the sorbent in an empty column. Finally, the analytes are desorbed from the magnetic sorbent using a suitable solvent and, once more, the sorbent is retained with the magnet to separate the solvent containing the analytes by decantation for their determination with a suitable technique.

Although a wide variety of metals, metal oxides and alloys can be used to provide magnetic properties to the sorbent, Fe_3O_4 NPs have been used as the main support with this purpose due to their extraordinary magnetic features and the possibility of being modified by anchoring certain chemical species or materials to obtain sorbents that provide different selectivity. Therefore, as in the rest of the sorbent-based microextraction techniques, the preparation of appropriate sorbents is one of the most important aspects to be considered. In this regard, carbon-based nanomaterials like MWCNTs [76, 77] and graphene [26, 78, 79], combined with m-NPs have once again been one of the most used for the extraction of PAEs from water samples due to their well-known properties in terms of high surface area-to-volume ratio that guarantees high extraction efficiency. As an example, MWCNTs were functionalized via chemical modification by Jiao *et al.* [76]. Figure 1.6 shows the scanning electron microscopy and transmission electron microscopy images of m-NPs successfully combined with MWCNTs. The authors used this sorbent to study a large set of thirteen PAEs, paying special attention to the elution step because PAEs may not be easily desorbed due to the strong interaction between the sorbent and analytes. For this purpose, different common organic elution solvents (i.e., acetone, MeOH, n-hexane, ethyl acetate, and toluene) were evaluated, finding that the use of toluene provided higher recovery percentages compared to non-aromatic solvents, particularly for BBP and diphenyl phthalate (DPhP), since they contain two and three benzene rings, respectively. However, since toluene is highly toxic, toluene-acetone mixtures

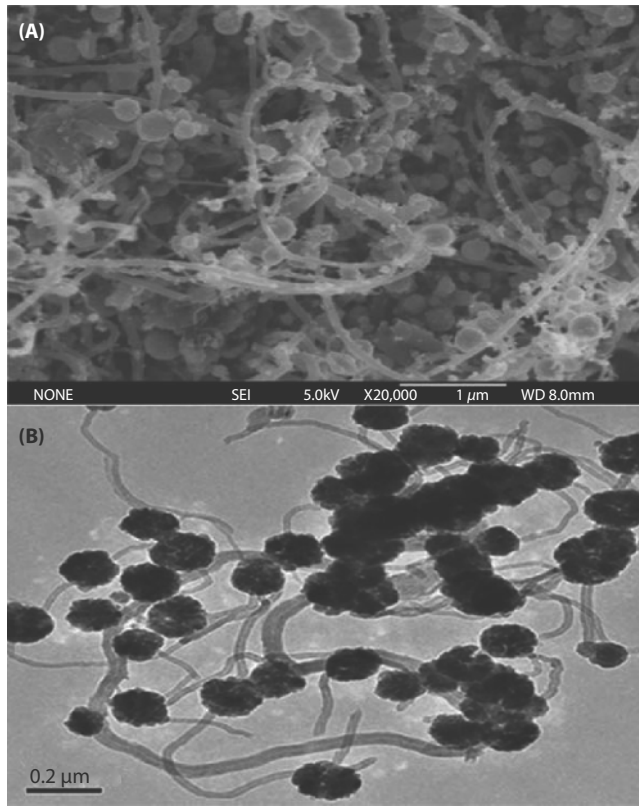


Figure 1.6 Scanning electron microscope image (A) and transmission electron microscope image (B) of the MWCNTs coated m-NPs. Reprinted from [76] with permission from Royal Society of Chemistry. m-NPs, magnetic nanoparticles.

were also evaluated in different proportions (1:1, 1:4, and 1:9, v/v), obtaining that toluene-acetone (1:4, v/v) kept satisfactory recovery values, while the use of toluene-acetone (1:9, v/v) decreased them. Finally, the viability of this method was demonstrated for the extraction of the selected PAEs from drinking water, showing an extraordinary extraction capacity which, in combination with the inherent advantages of m-dSPE, becomes this methodology an excellent alternative to be explored for the analysis of other pollutants. Similarly, Luo *et al.* [77] immobilized m-NPs onto MWCNTs by ultrasound application as a simpler alternative to chemical functionalization (see Figure 1.7). In particular, appropriate amounts of the previously synthesized Fe_3O_4 NPs and MWCNTs were dispersed in dimethylformamide and sonicated, achieving the spontaneous assembling of both materials resulting in a magnetic composite. Finally, it was

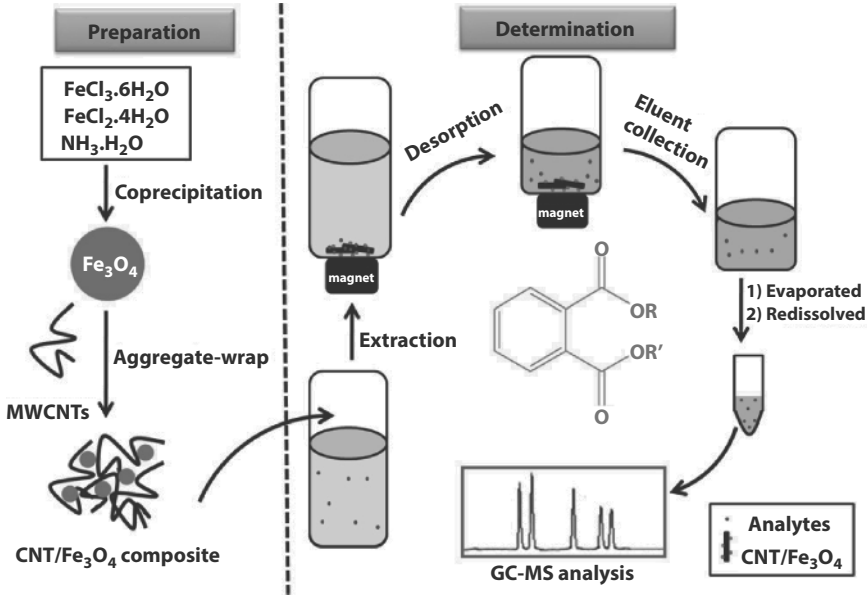


Figure 1.7 Schematic illustration of the preparation strategy for m-NPs and the m-dSPE procedure for the determination of PAEs. Reprinted from [77] with permission from Elsevier. CNT, carbon nanotubes; GC, gas chromatography; MS, mass spectrometry; MWCNTs, multi-walled carbon nanotubes.

washed with water and suspended in water at 40 mg/mL, taking a certain volume of it for the extraction procedure. Next, the usual m-dSPE procedure was carried out for the enrichment of sixteen PAEs from mineral and tap water, juice and carbonated drinks as well as one perfume sample. The combination of this extraction procedure with GC-MS allowed obtaining a good extraction capacity in relatively short times as well as high sensitivity, becoming this methodology an interesting alternative to be considered.

Graphene is also able to establish strong π stacking interactions with benzene rings which already was demonstrated when it was used as sorbent in dSPE for PAEs extraction [72]. However, graphene is difficult to remove from the sample in which it has been dispersed because it is an ultralight material. Therefore, if magnetic properties are provided, its subsequent separation will be greatly facilitated while retaining its excellent adsorption capacity. Such is the case of the work developed by Wu *et al.* [78] in which graphene-coated m-NPs were first used for the extraction of PAEs from bottled and river water samples as well as from a soft drink and green tea samples. In this case, graphene was previously obtained from the

graphite oxide exfoliation to obtain GO, which was subsequently reduced. Then, it was suspended in the alkaline solution used to synthesize the Fe_3O_4 NPs by a chemical coprecipitation process, obtaining the desired magnetic sorbent. As expected, the developed m-dSPE procedure provided high extraction efficiency, besides high enrichment factors, which resulted in LODs in the range of few μg/L, even though a HPLC-UV system was used for analytes separation and detection.

Despite carbon-based nanomaterials have been widely combined with m-NPs in a good number of applications, polymeric coatings have been, without any doubt, the most extensively used in m-dSPE because of the versatility and advantages they provide. In consequence, and as it could not be otherwise, polymer-coated m-NPs have also been widely used for the extraction of PAEs from water samples. The polymer coating protects m-NPs from oxidization and undesirable aggregation that occurs after their synthesis improves their stability and maintains their magnetic properties. Consequently, surface functionalization will also improve m-NPs dispersion while different kinds of interactions with PAEs take place, at the same time that enhances their selectivity. As several examples, Hernández-Borges' group first applied PDA-coated m-NPs for the isolation and enrichment of PAEs from mineral, tap, pond, and waste waters [22] as well as in sea water and sea sand samples [80], using in both cases a chemical co-precipitation method to obtain the Fe_3O_4 m-NPs and taking advantage of the self-polymerization capacity of DA in weak alkaline water solutions to create a magnetic core-shell sorbent; while Zhao *et al.* [81] demonstrated the applicability of synthesized PPy-coated m-NPs through a chemical oxidation method which allowed the combination of both materials for the determination of sixteen PAEs in lake and tap water samples, while Liu *et al.* [82] and Zhou *et al.* [83] employed the highly hydrophilic ILs 1-vinyl-3-butylimidazolium bromide and 1-vinylimidazole to modify PS and carboxylatocalix[4]arene coated m-NPs, respectively. In these last two works, the immobilization of polymerized ILs onto m-NPs surface improved the dispersion and extraction efficiency in drinking and environmental water samples significantly due to the additional hydrogen bonding and π-π interactions. In addition, the developed sorbents could be reused at least 12 and 30 times, respectively, without a significant decrease in their adsorption capacity or carry-over.

Finally, m-NPs have also been combined with MOFs and used as sorbents in m-dSPE. In fact, and specifically concerning the extraction of PAEs, it has been the main field of application of MOFs among all sorbent-based microextraction techniques. MOFs are considered one of the nanoporous materials with the largest surface areas, characterized by

highly ordered cavities and tailorable chemistry by coordinated bounds of a large variety of metal cations and organic ligands [84]. Various types of MOFs combined with the magnetic core have arouse special interest in this topic, as it is the case of Liu *et al.* [85], who coated Fe_3O_4 m-NPs with Zeolitic Imidazolate Framework-8 (ZIF-8) resulting in a core-shell structure. These modified m-NPs were successfully applied to the extraction of five PAEs from river, mineral and tap water samples, showing an excellent extraction capacity (recovery in the range 84%–104%) for all the analytes independently of the matrix. On contrary, Dargahi and co-workers [86] proposed other alternative sorbent based once again on the combination of Fe_3O_4 m-NPs and a MOF, but in this case, the Material of Institute Lavoisier-101 (MIL-101) was used as support on whose surface the m-NPs were deposited. This sorbent was applied to the m-dSPE of five short-chain PAEs from well water and human plasma samples, showing promising results. However, MOFs are not always used as synthesized, but they are sometimes used as the basis to create highly porous sorbents with different features. A clear example of this fact is the work of Wang *et al.* [87], in which they synthesized what they called a "three-dimensional magnetic porous N-Co@carbon dodecahedron/hierarchical carbon framework" (3D N-Co@C/HCF) which was used as sorbent for the extraction of five PAEs from river water, green tea, a sports beverage, and white spirit samples. The first step consisted in the synthesis of a 3D carbon-based structure based on sodium carbonate and glucose. Then, it was combined with $Co(NO_3)_2$ and 2-methylimidazole under stirring, obtaining a composite of ZIF-67 and the HCF, which was finally calcined at 700°C under N_2 atmosphere to obtain the desired 3D N-Co@C/HCF. This magnetic nanoporous sorbent demonstrated to provide an excellent extraction efficiency for all the target PAEs and matrices thanks to its large surface-to-volume ratio.

Apart from the previous works, the combination of MOF and polymer-coated m-NPs has also been found beneficial for the extraction of PAEs. In this sense, Li *et al.* [88] prepared Fe_3O_4@MIL-100 and Fe_3O_4@SiO_2@polythiophene as mixed sorbents for m-dSPE extraction of six PAEs (DMP, DEP, DBP, BBP, DEHP, and DNOP) from tap and mineral water samples. Although PAEs contain both benzene rings and alkyl chains, the use of the MOF-coated m-NPs alone did not show enough extraction efficiency particularly for both DMP and DEP. This was attributed to the greater water solubility of these low-molecular PAEs as well as lower hydrophobic interaction with this sorbent. When the polymer-coated m-NPs were used, it did not show good adsorption capacity for the PAEs that contain longer alkyl chains, especially DNOP. This was associated to the negative effect of these long alkyl chains on the π-π interactions with the sorbent. Instead,

both sorbents in a 1:1 (w/w) ratio were combined under sonication, and the mixture was used as sorbent, giving satisfactory extraction recovery values for all the PAEs and matrices.

1.5 Others Minor Sorbent-Based Microextraction Techniques

Although dispersive versions of SPE have been widely used due to the well-known advantages they offer, as it has been already mentioned, trends in sorbent-based extraction techniques are also focused on the miniaturization of the extraction devices, which has given place to the appearance of new modifications of conventional SPE but with reduced amounts of sorbent or slight changes on extraction devices. Some of these alternative methodologies have also been successfully applied to the analysis of PAEs in water samples (see Table 1.3).

In this sense, microextraction by packed sorbent (MEPS) is considered as a miniaturized technique derived directly from SPE which can be coupled directly to the chromatographic systems without any additional modification. MEPS only use 1–2 mg of sorbent to adsorb the analytes successfully. Concretely, it is packed between frits inside a microsyringe and extraction is performed within it by subsequent suction. After the analytes are trapped, the packed sorbent is washed with water to remove the interferences. Finally, the target analytes are eluted by appropriate solvent aspiration into the microsyringe [89]. Amiri *et al.* [90] used only 2 mg of synthesized hydroxyapatite NPs packed inside a 0.5-ml microsyringe for the rapid extraction of five PAEs from river, mineral and tap water samples. To evaluate the extraction efficiency, the effect of multiples drawing-ejecting cycles in the range 10–60 cycles were performed in the same vial containing 8 ml of spiked sample at 50 μg/L. The results showed that the maximum peak areas were achieved using 40 cycles for all the target analytes and then kept constant. When the same process was repeated using 8 mL of spiked sample at 100 μg/L discarding each 0.5 mL load to another vial (16 cycles), the results did not improve. Therefore, 40 cycles of draw-eject in a same vial was the best approach in terms of simplicity. With it, the developed methodology showed good sensitivity, repeatability, and relative recovery values, being a really interesting alternative to conventional SPE procedures.

As it is well-known, thin film microextraction (TFME) initially emerged as an alternative to classical SPME, which provides a higher

Table 1.3 Some examples of the application of other sorbent-based extraction techniques for the analysis of PAEs in water samples.

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DIBP, DBP, DMP, and DEP	Water (20 mL)	4-mg poly m-aminophenol/ nylon6/GO nanofiber previously conditioned with 2 mL 2-propanol, the sample was passed at 1 mL/ min, washing with 2 mL water, and desorption with 400 μL 2-propanol at 0.05 mL/min	GC-MS	0.3–0.5 μg/L	96–101% at 20 and 100 μg/L	Two samples were analyzed and no residues were detected	The poly m-aminophenol/ nylon6/GO nanofiber gave better results than poly m-aminophenol/ nylon6 nanofiber. 2-propanol showed higher extraction efficiency than MeOH, ethanol, chloroform and ACN as desorption solvent. Milk was also analyzed	[93]

(*Continued*)

Table 1.3 Some examples of the application of other sorbent-based extraction techniques for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DBP, BBP, DEHP, and DNOP	Bottle water (20 mL)	10 mg of MIL-101(Cr) MOF were introduced in a porous polypropylene membrane and stirred for 35 min; desorption into 0.5 mL MeOH by sonication for 15 min	GC-MS	0.01–0.07 μg/L	76.8–111.6% at 1, 4, and 10 μg/L	Two samples were analyzed and contained at least 1 PAE at levels from 0.28 to 2.85 μg/L	MIL-101(Cr) showed higher extraction efficiency than AC and MIL-101(Fe) as extraction sorbent, and MeOH than acetone and ACN as desorption solvent. A computational modeling method accurately predicted the extraction efficiency of MOFs-based materials toward the PAEs	[94]

(*Continued*)

Table 1.3 Some examples of the application of other sorbent-based extraction techniques for the analysis of PAEs in water samples. (*Continued*)

PAEs	Matrix (sample amount)	Sample pretreatment	Separation technique	LOQ	Recovery study	Residues found	Comments	Reference
DMP, DEP, DIBP, DBP, and DEHP	River, bottled mineral and tap waters (8 ml plus 20% w/v NaCl)	MEPS using 2 mg of nano-hydroxyapatite previously conditioned with 0.5 mL MeOH followed by 0.5 mL of deionized water, draw-ejecting of the sample for 40 cycles, washing with 1 mL water, and desorption with 60 µL dichloromethane by solvent aspiration into the syringe	GC-FID	0.07 and 0.25 µg/L	85.5–99.2% at 0.25, 5, and 50 µg/L	One sample of river and tap waters, and 3 mineral water samples were analyzed and contained at least 2 PAEs at levels from 0.5 to 5.3 µg/L	Dichloromethane showed higher extraction efficiency than MeOH, ethyl acetate, hexane, and ACN as desorption solvent	[90]

µ-SPE, micro-solid-phase extraction; AC, activated carbon; ACN, acetonitrile; BBP, benzyl butyl phthalate; DBP, dibutyl phthalate; DEHP, di(2-ethylhexyl) phthalate; DEP, diethyl phthalate; DIBP, diisobutyl phthalate; DMP, dimethyl phthalate; DNOP, di-n-octyl phthalate; FID, flame ionization detector; GO, graphene oxide; GC, gas chromatography; LOQ, limit of quantification; MEPS, microextraction in packed syringe; MeOH, methanol; MIL, Material of Institute Lavoisier; m-NPMOF, metal organic framework; MS, mass spectrometry; PAE, phthalic acid ester; PSTFME, thin film microextraction.

volume of extractive phase as well as a larger surface-to-volume ratio compared to SPME fibers, which results in an improved sensitivity with relatively shorter extraction times [91, 92]. However, such an interesting alternative extraction method has been adapted and applied in different ways which can be considered as SPE variants more than SPME modifications. As an example, Mehrani *et al.* [93] developed a membrane by peeling a piece of poly m-aminophenol-nylon6-GO nanofiber and supported it in a circular holder in order to emulate a miniaturized version of a conventional SPE device. Then, the analytes were extracted by pushing the sample through the membrane with a syringe. After a washing step, the analytes were eluted with 2-propanol. In this case, a GC-MS system was used for the separation and detection of the analytes. This methodology was successfully applied to the analysis of four PAEs from water and milk samples, with LODs in the range 0.1–0.15 μg/L for all the studied analytes.

Finally, the use of miniaturized extraction devices based on membrane-protected sorbents has also been explored for the analysis of PAEs in water. That is the case of Wang and co-workers [94], who developed a small device (1 cm × 1.5 cm) using a polypropylene membrane sheet as a kind of heat-sealed bag containing 10 mg of sorbent. The extraction was developed introducing the extraction device in the sample and stirring for a certain time while the device tumbled freely. Then, the device was taken out with a pair of tweezers, dried with a tissue paper and the analytes were desorbed with MeOH in a vial. After that, the device was washed with MeOH and this volume was combined with the desorption portion. In this case, three materials were evaluated as possible sorbents in terms of enrichment factors, MIL-101(Cr), MIL-100(Fe) and powdered activated carbon. MIL-101(Cr) showed the strongest adsorption ability for the extraction of the six PAEs selected from bottled water samples, providing suitable extraction recovery.

1.6 Conclusions

The use of sorbent-based microextraction techniques is a current trend in sample preparation that will surely continue its consolidation during next years as a result of their inherent advantages related with Green Analytical Chemistry principles. Such techniques have also been applied with success for the extraction of PAEs from different types of water samples. Among them, SPME has been mostly used, followed by dSPE. SBSE, as a variation of SPME, has also been applied but in extremely few occasions together

with other small variants of each of the technique. Though commercial sorbents can also be used for such purpose, the latest achievements in this field have been done using laboratory made coatings, mainly using nanomaterials such as MWCNTs, graphene, GO, coated m-NPs, etc., as well as new polymers or nanoporous materials such as MOFs. In this last case, a suitable characterization of them using different surface characterization techniques is necessary as well as clear demonstration of their stability and batch-to-batch reproducibility. In all probability, this will constitute an active research area in the near future.

Once suitably optimized, the application of all these extraction procedures has demonstrated that PAEs are present in nearly any type of water sample as a result of their capacity to migrate from plastics, which is probably their main source. Further studies should also continue to be assessed in order to continue monitoring their presence in all environmental compartments.

Acknowledgements

J.G.S. would like to thank "Cabildo de Tenerife" for the Agustín de Betancourt contract at the Universidad de La Laguna.

References

1. Feng, C.-H., Jiang, S.-R., Micro-scale quantitation of ten phthalate esters in water samples and cosmetics using capillary liquid chromatography coupled to UV detection: effective strategies to reduce the production of organic waste. *Microchim. Acta*, 177, 167, 2012.
2. Rahman, M., Brazel, C.S., The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Prog. Polym. Sci.*, 29, 1223, 2004.
3. Ceresana. Market study: Plasticizers (5th edition), 2019.
4. Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. *Environ. Sci. Technol.*, 49, 4019, 2015.
5. Gao, D., Li, Z., Wang, H., Liang, H., An overview of phthalate acid ester pollution in China over the last decade: Environmental occurrence and human exposure. *Sci. Total Environ.*, 645, 1400, 2018.
6. Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., Occurrence and effects of plastic additives on marine environments and organisms: A review. *Chemosphere*, 182, 781, 2017.

7. Ding, M., Kang, Q., Zhang, S., Zhao, F., Mu, D., Zhang, H., Yang, M., Hu, J., Contribution of phthalates and phthalate monoesters from drinking water to daily intakes for the general population. *Chemosphere*, 229, 125, 2019.
8. Benjamin, S., Masai, E., Kamimura, N., Takahashi, K., Anderson, R.C., Faisal, P.A., Phthalates impact human health: Epidemiological evidences and plausible mechanism of action. *J. Hazard. Mater.*, 340, 360, 2017.
9. Arcadi, F.A., Costa, C., Imperatore, C., Marchese, A., Rapisarda, A., Salemi, M., Trimarchi, G.R., Costa, G., Oral toxicity of bis(2-ethylhexyl) phthalate during pregnancy and suckling in the long–Evans rat. *Food Chem. Toxicol.*, 36, 963, 1998.
10. Latini, G., De Felice, C., Verrotti, A., Plasticizers, infant nutrition and reproductive health. *Reprod. Toxicol.*, 19, 27, 2004.
11. Benson, R., Hazard to the developing male reproductive system from cumulative exposure to phthalate esters—dibutyl phthalate, diisobutyl phthalate, butylbenzyl phthalate, diethylhexyl phthalate, dipentyl phthalate, and diisononyl phthalate. *Regul. Toxicol. Pharmacol.*, 53, 90, 2009.
12. Lhuguenot, J.-C., Mitchell, A.M., Milner, G., Lock, E.A., Elcombe, C.R., The metabolism of di(2-ethylhexyl) phthalate (DEHP) and mono-(2-ethylhexyl) phthalate (MEHP) in rats: In vivo and in vitro dose and time dependency of metabolism. *Toxicol. Appl. Pharmacol.*, 80, 11, 1985.
13. Jonsson, S., Ejlertsson, J., Ledin, A., Mersiowsky, I., Svensson, B.H., Mono- and diesters from o-phthalic acid in leachates from different European landfills. *Water Res.*, 37, 609, 2003.
14. Jornet-Martínez, N., Muñoz-Ortuño, M., Moliner-Martínez, Y., Herráez-Hernández, R., Campíns-Falcó, P., On-line in-tube solid phase microextraction-capillary liquid chromatography method for monitoring degradation products of di-(2-ethylhexyl) phthalate in waters. *J. Chromatogr. A*, 1347, 157, 2014.
15. Commission of the European Communities. *Communication from the Commission to the Council and the European Parliament on the implementation of the community strategy for endocrine disrupters—a range of substances suspected of interfering with the hormone systems of humans and wildlife*, COM1999, Brussels, 1999.
16. International Agency for Research on Cancer. *Agents Classified by the IARC Monographs*, Volumes 1–123, 2018.
17. US Environmental Protection Agency. *National Primary Drinking Water Regulations*, Federal register, Part 12, 40 CFR Part 141, 1991.
18. *Guidelines for Drinking-Water Quality, third ed.* World Health Organization, Volume 1, 2008.
19. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending

Directive 2000/60/EC of the European Parliament and of the Council. *Off. J. Eur. Union*, L 348, 84, 2008.
20. Amanzadeh, H., Yamini, Y., Moradi, M., Asl, Y.A., Determination of phthalate esters in drinking water and edible vegetable oil samples by headspace solid phase microextraction using graphene/polyvinylchloride nanocomposite coated fiber coupled to gas chromatography-flame ionization detector. *J. Chromatogr. A*, 1465, 38, 2016.
21. Cao, X.-L., Determination of phthalates and adipate in bottled water by headspace solid-phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr. A*, 1178, 231, 2008.
22. González-Sálamo, J., Socas-Rodríguez, B., Hernández-Borges, J., Rodríguez-Delgado, M.Á., Determination of phthalic acid esters in water samples using core-shell poly(dopamine) magnetic nanoparticles and gas chromatography tandem mass spectrometry. *J. Chromatogr. A*, 1530, 35, 2017.
23. Wang, X., Feng, J., Tian, Y., Li, C., Ji, X., Luo, C., Sun, M., Melamine-formaldehyde aerogel functionalized with polydopamine as in-tube solid-phase microextraction coating for the determination of phthalate esters. *Talanta*, 199, 317, 2019.
24. Zhou, Q., Fang, Z., Liao, X., Determination of phthalate esters from environmental water samples by micro-solid-phase extraction using TiO_2 nanotube arrays before high-performance liquid chromatography. *J. Sep. Sci.*, 38, 2526, 2015.
25. González-Sálamo, J., González-Curbelo, M.Á., Hernández-Borges, J., Rodríguez-Delgado, M.Á., Use of Basolite® F300 metal-organic framework for the dispersive solid-phase extraction of phthalic acid esters from water samples prior to LC-MS determination. *Talanta*, 195, 236, 2019.
26. Wang, W., Wu, Q., Zang, X., Wang, C., Wang, Z., Extraction of phthalate esters in environmental water samples using layered-carbon magnetic hybrid material as adsorbent followed by their determination with HPLC. *Bull. Korean Chem. Soc.*, 33, 3311, 2012.
27. Hadjmohammadi, M.R., Ranjbari, E., Utilization of homogeneous liquid–liquid extraction followed by HPLC-UV as a sensitive method for the extraction and determination of phthalate esters in environmental water samples. *Int. J. Environ. Anal. Chem.*, 92, 1312, 2012.
28. Polo, M., Llompart, M., Garcia-Jares, C., Cela, R., Multivariate optimization of a solid-phase microextraction method for the analysis of phthalate esters in environmental waters. *J. Chromatogr. A*, 1072, 63, 2005.
29. González-Sálamo, J., Socas-Rodríguez, B., Hernández-Borges, J. Analytical methods for the determination of phthalates in food. *Curr. Opin. Food Sci.*, 22, 122, 2018.
30. González-Sálamo, J., González-Curbelo, M.Á., Socas-Rodríguez, B., Hernández-Borges, J., Rodríguez-Delgado, M.Á., Determination of phthalic acid esters in water samples by hollow fiber liquid-phase microextraction

prior to gas chromatography tandem mass spectrometry. *Chemosphere*, 201, 254, 2018.
31. Lv, X., Hao, Y., Jia, Q., Preconcentration procedures for phthalate esters combined with chromatographic analysis. *J. Chromatogr. Sci.*, 51, 632, 2013.
32. Tsochatzis, E.D., Tzimou-Tsitouridou, R., Gika, H.G., Analytical methodologies for the assessment of phthalate exposure in humans. *Crit. Rev. Anal. Chem.*, 47, 279, 2017.
33. Lord, H., Pawliszyn, J., Microextraction of drugs. *J. Chromatogr. A*, 902, 17, 2000.
34. Sajid, M., Płotka-Wasylka, J., Combined extraction and microextraction techniques: Recent trends and future perspectives. *TrAC Trends Anal. Chem.*, 103, 74, 2018.
35. González-Sálamo, J., Socas-Rodríguez, B., Hernández-Borges, J., Rodríguez-Delgado, M.Á., Nanomaterials as sorbents for food sample analysis. *TrAC Trends Anal. Chem.*, 85, 203, 2016.
36. Socas-Rodríguez, B., González-Sálamo, J., Hernández-Borges, J., Rodríguez-Delgado, M.Á., Recent applications of nanomaterials in food safety. *TrAC Trends Anal. Chem.*, 96, 172, 2017.
37. González-Sálamo, J., Varela-Martínez, D.A., Cairós, C., González-Curbelo, M.Á., Hernández-Borges, J., Nanomaterials have come to stay: An overview of their use as sorbents in sample preparation. *LG-GC North Am.*, 37, 22, 2019.
38. Cousins, I.T., Mackay, D., Parkerton, T.F., Physical-chemical properties and evaluative fate modelling of phthalate esters, *in: BT - Series anthropogenic compounds: Phtalate esters,* C.A. Staples (Ed.), pp. 57–84, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003.
39. Banitaba, M.H., Davarani, S.S.H., Pourahadi, A., Solid-phase microextraction of phthalate esters from aqueous media by electrophoretically deposited TiO_2 nanoparticles on a stainless steel fiber. *J. Chromatogr. A*, 1283, 1, 2013.
40. Asadollahzadeh, H., Noroozian, E., Maghsoudi, S., Solid-phase microextraction of phthalate esters from aqueous media by electrochemically deposited carbon nanotube/polypyrrole composite on a stainless steel fiber. *Anal. Chim. Acta*, 669, 32, 2010.
41. Song, X.-L., Chen, Y., Yuan, J.-P., Qin, Y.-J., Zhao, R.-S., Wang, X., Carbon nanotube composite microspheres as a highly efficient solid-phase microextraction coating for sensitive determination of phthalate acid esters in water samples. *J. Chromatogr. A*, 1468, 17, 2016.
42. Behzadi, M., Noroozian, E., Mirzaei, M., Electropolymerization of carbon nanotubes/poly-ortho-aminophenol nanocomposite on a stainless steel fiber for the solid-phase microextraction of phthalate esters. *RSC Adv.*, 4, 50426, 2014.
43. Zhang, M., Huang, J., Zeng, J., Zhang, C., Silicon dioxide–poly(dimethylsiloxane) with a bilayer structure, incorporating multi-walled carbon nanotubes,

supported on stainless steel wire as a solid-phase microextraction fiber for the determination of trace phthalate esters in drinking water sample. *RSC Adv.*, 4, 12313, 2014.
44. Eskandarpour, N., Sereshti, H., Electrospun polycaprolactam-manganese oxide fiber for headspace-solid phase microextraction of phthalate esters in water samples. *Chemosphere*, 191, 36, 2018.
45. He, J., Lv, R., Zhan, H., Wang, H., Cheng, J., Lu, K., Wang, F., Preparation and evaluation of molecularly imprinted solid-phase micro-extraction fibers for selective extraction of phthalates in an aqueous sample. *Anal. Chim. Acta*, 674, 53, 2010.
46. Guo, H., Song, N., Wang, D., Ma, J., Jia, Q., A modulation approach for covalent organic frameworks: Application to solid phase microextraction of phthalate esters. *Talanta*, 198, 277, 2019.
47. Zhao, R.-S., Liu, Y.-L., Zhou, J.-B., Chen, X.-F., Wang, X., Bamboo charcoal as a novel solid-phase microextraction coating material for enrichment and determination of eleven phthalate esters in environmental water samples. *Anal. Bioanal. Chem.*, 405, 4993, 2013.
48. Herrera-Herrera, A., Asensio-Ramos, M., González Curbelo, M.Á., Hernández-Borges, J., Carbon nanotubes applications in solid-phase extraction, *in: Carbon Nanotubes: Synthesis, Properties and Applications*, A.K. Mishra (Ed.), pp. 1-42, Nova Science Publishers, 2013.
49. González-Curbelo, M.Á., Rodríguez-Delgado, M.Á., Hernández-Borges, J., *Nuevas aportaciones en el tratamiento de muestra para el análisis de plaguicidas*, Servicio de Publicaciones de la Universidad de La Laguna, 2015.
50. González-Sálamo, J., Herrera-Herrera, A. V, Fanali, C., Hernández-Borges, J., Magnetic nanoparticles for solid-phase extraction. *LC GC Eur.*, 29, 180, 2016.
51. Ríos, Á., Zougagh, M., Recent advances in magnetic nanomaterials for improving analytical processes. *TrAC Trends Anal. Chem.*, 84, 72, 2016.
52. Tashakkori, P., Erdem, P., Merdivan, M., Bozkurt, S.S., Determination of phthalate esters in water and coffee by solid-phase microextraction using vinyl terminated imidazolium based ionic liquid grafted on graphene oxide coatings. *Chemistry Select*, 4, 2307, 2019.
53. Socas-Rodríguez, B., González-Sálamo, J., Hernández-Borges, J., Chapter 2 Carbon Nanomaterials in Sample Preparation, *in: Carbon-based Nanomaterials in Analytical Chemistry*, C.D. García, A.G. Crevillén, A. Escarpa (Eds.), pp. 37–68, The Royal Society of Chemistry, 2019.
54. Liu, L., Zhang, J., Zhao, J., Liu, F., Mechanical properties of graphene oxides. *Nanoscale*, 4, 5910, 2012.
55. Singh, S.K., Savoy, A.W., Ionic liquids synthesis and applications: An overview. *J. Mol. Liq.*, 297, 112038, 2020.
56. Anderson, J.L., Ding, J., Welton, T., Armstrong, D.W., Characterizing ionic liquids on the basis of multiple solvation interactions. *J. Am. Chem. Soc.*, 124, 14247, 2002.

57. Włoch, M., Datta, J., Chapter Two - Synthesis and polymerisation techniques of molecularly imprinted polymers, *in: MIP Synthesis, Characteristics and Analytical Application*, vol. 86, M. Marć (Ed.), pp. 17–40, Elsevier, 2019.
58. Kosheleva, R.I., Mitropoulos, A.C., Kyzas, G.Z., Chapter 7 - New trends in molecular imprinting techniques, *in: Advanced Low-Cost Separation Techniques in Interface Science*, vol. 30, G. Kyzas, A. Mitropoulos (Eds.), pp. 151–172, Elsevier, 2019.
59. Zaidi, S.A., Molecular imprinting polymers and their composites: a promising material for diverse applications. *Biomater. Sci.*, 5, 388, 2017.
60. Costa Queiroz, M.E., Donizeti de Souza, I., Marchioni, C., Current advances and applications of in-tube solid-phase microextraction. *TrAC Trends Anal. Chem.*, 111, 261, 2019.
61. Eisert, R., Pawliszyn, J., Automated In-Tube Solid-Phase Microextraction Coupled to High-Performance Liquid Chromatography. *Anal. Chem.*, 69, 3140, 1997.
62. Lirio, S., Fu, C.-W., Lin, J.-Y., Hsu, M.-J., Huang, H.-Y., Solid-phase microextraction of phthalate esters in water sample using different activated carbon-polymer monoliths as adsorbents. *Anal. Chim. Acta*, 927, 55, 2016.
63. Baltussen, E., Sandra, P., David, F., Cramers, C., Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcolumn Sep.*, 11, 737, 1999.
64. Soares da Silva Burato, J., Vargas Medina, D.A., de Toffoli, A.L., Vasconcelos Soares Maciel, E., Mauro Lanças, F., Recent advances and trends in miniaturized sample preparation techniques. *J. Sep. Sci.*, 43, 202, 2020.
65. Prieto, A., Zuloaga, O., Usobiaga, A., Etxebarria, N., Fernández, L.A., Development of a stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry method for the simultaneous determination of several persistent organic pollutants in water samples. *J. Chromatogr. A*, 1174, 40, 2007.
66. Si, Q., Li, F., Gao, C., Wang, C., Wang, Z., Zhao, J., Detection of phthalate esters in seawater by stir bar sorptive extraction and gas chromatography–mass spectrometry. *Mar. Pollut. Bull.*, 108, 163, 2016.
67. Socas-Rodríguez, B., Herrera-Herrera, A. V, Asensio-Ramos, M., Hernández-Borges, J., Dispersive solid-phase extraction. *Anal. Sep. Sci.*, 1525, 2015.
68. Khezeli, T., Daneshfar, A., Development of dispersive micro-solid phase extraction based on micro and nano sorbents. *TrAC Trends Anal. Chem.*, 89, 99, 2017.
69. Cheng, L., Pan, S., Ding, C., He, J., Wang, C., Dispersive solid-phase microextraction with graphene oxide based molecularly imprinted polymers for determining bis(2-ethylhexyl) phthalate in environmental water. *J. Chromatogr. A*, 1511, 85, 2017.
70. González-Curbelo, M.Á., Asensio-Ramos, M., Herrera-Herrera, A. V, Hernández-Borges, J., Pesticide residue analysis in cereal-based baby foods

using multi-walled carbon nanotubes dispersive solid-phase extraction. *Anal. Bioanal. Chem.*, 404, 183, 2012.
71. González-Curbelo, M.Á., Herrera-Herrera, A. V, Hernández-Borges, J., Rodríguez-Delgado, M.Á., Analysis of pesticides residues in environmental water samples using multiwalled carbon nanotubes dispersive solid-phase extraction. *J. Sep. Sci.*, 36, 556, 2013.
72. Wu, X., Hong, H., Liu, X., Guan, W., Meng, L., Ye, Y., Ma, Y., Graphene-dispersive solid-phase extraction of phthalate acid esters from environmental water. *Sci. Total Environ.*, 444, 224, 2013.
73. Özer, E.T., Osman, B., Yazıcı, T., Dummy molecularly imprinted microbeads as solid-phase extraction material for selective determination of phthalate esters in water. *J. Chromatogr. A*, 1500, 53, 2017.
74. Chen, X., Xin, L., Xu, Y., Liu, J., Li, Z., Wang, Y., Zhao, J., (2019) Polymer phase transition characteristics coupled with GC-MS for the determination of phthalate esters. *J. Sep. Sci.*, 42, 3095, 2019.
75. Chen, X., Guo, Z., Wang, Y., Liu, Y., Xu, Y., Liu, J., Li, Z., Zhao, J., Temperature sensitive polymer-dispersive liquid–liquid microextraction with gas chromatography–mass spectrometry for the determination of phenols. *J. Chromatogr. A*, 1592, 183, 2019.
76. Jiao, Y., Fu, S., Ding, L., Gong, Q., Zhu, S., Wang, L., Li, H., Determination of trace leaching phthalate esters in water by magnetic solid phase extraction based on magnetic multi-walled carbon nanotubes followed by GC-MS/MS. *Anal. Methods*, 4, 2729, 2012.
77. Luo, Y.-B., Yu, Q.-W., Yuan, B.-F., Feng, Y.-Q., Fast microextraction of phthalate acid esters from beverage, environmental water and perfume samples by magnetic multi-walled carbon nanotubes. *Talanta*, 90, 123, 2012.
78. Wu, Q., Liu, M., Ma, X., Wang, W., Wang, C., Zang, X., Wang, Z., Extraction of phthalate esters from water and beverages using a graphene-based magnetic nanocomposite prior to their determination by HPLC. *Microchim. Acta*, 177, 23, 2012.
79. Ye, Q., Liu, L., Chen, Z., and Hong, L., Analysis of phthalate acid esters in environmental water by magnetic graphene solid phase extraction coupled with gas chromatography–mass spectrometry. *J. Chromatogr. A*, 1329, 24, 2014.
80. Jiménez-Skrzypek, G., González-Sálamo, J., Varela-Martínez, D.A., González-Curbelo, M.Á., Hernández-Borges, J., Analysis of phthalic acid esters in sea water and sea sand using polymer-coated magnetic nanoparticles as extraction sorbent. *J. Chromatogr. A*, 1611, 460620, 2019.
81. Zhao, H., Huang, M., Wu, J., Wang, L., He, H., Preparation of Fe_3O_4@PPy magnetic nanoparticles as solid-phase extraction sorbents for preconcentration and separation of phthalic acid esters in water by gas chromatography–mass spectrometry. *J. Chromatogr. B*, 1011, 33, 2016.
82. Liu, G., Su, P., Zhou, L., Yang, Y., Microwave-assisted preparation of poly(ionic liquids)-modified polystyrene magnetic nanospheres for phthalate esters extraction from beverages. *J. Sep. Sci.*, 40, 2603, 2017.

83. Zhou, S., Song, N., Lv, X., Jia, Q., Preparation of carboxylatocalix[4]arene functionalized magnetic polyionic liquid hybrid material for the pre-concentration of phthalate esters. *J. Chromatogr. A*, 1565, 19, 2018.
84. Rocío-Bautista, P., González-Hernández, P., Pino, V., Pasán, J., Afonso, A.M., Metal-organic frameworks as novel sorbents in dispersive-based microextraction approaches. *TrAC Trends Anal. Chem.*, 90, 114, 2017.
85. Liu, X., Sun, Z., Chen, G., Zhang, W., Cai, Y., Kong, R., Wang, X., Suo, Y., You, J., Determination of phthalate esters in environmental water by magnetic Zeolitic Imidazolate Framework-8 solid-phase extraction coupled with high-performance liquid chromatography. *J. Chromatogr. A*, 1409, 46, 2015.
86. Dargahi, R., Ebrahimzadeh, H., Asgharinezhad, A.A., Hashemzadeh, A., Amini, M.M., Dispersive magnetic solid-phase extraction of phthalate esters from water samples and human plasma based on a nanosorbent composed of MIL-101(Cr) metal–organic framework and magnetite nanoparticles before their determination by GC–MS. *J. Sep. Sci.*, 41, 948, 2018.
87. Wang, Y., Tong, Y., Xu, X., Zhang, L., Developed magnetic multiporous 3D N-Co@C/HCF as efficient sorbent for the extraction of five trace phthalate esters. *Anal. Chim. Acta*, 1054, 176, 2019.
88. Li, H., Cao, Z., Cao, X., Jiang, Z., Abd El-Aty, A.M., Qi, Y., Shao, H., Jin, F., Zheng, L., Wang, J., Magnetic solid-phase extraction using a mixture of two types of nanoparticles followed by gas chromatography-mass spectrometry for the determination of six phthalic acid esters in various water samples. *RSC Adv.*, 8, 39641, 2018.
89. Abdel-Rehim, M., Microextraction by packed sorbent (MEPS): A tutorial. *Anal. Chim. Acta*, 701, 119, 2011.
90. Amiri, A., Chahkandi, M., Targhoo, A., Synthesis of nano-hydroxyapatite sorbent for microextraction in packed syringe of phthalate esters in water samples. *Anal. Chim. Acta*, 950, 64, 2017.
91. Olcer, Y.A., Tascon, M., Eroglu, A.E., Boyacı, E., Thin film microextraction: Towards faster and more sensitive microextraction. *TrAC Trends Anal. Chem.*, 113, 93, 2019.
92. Reyes-Garcés, N., Gionfriddo, E., Gómez-Ríos, G.A., Alam, M.N., Boyacı, E., Bojko, B., Singh, V., Grandy, J., Pawliszyn, J., Advances in Solid Phase Microextraction and Perspective on Future Directions. *Anal. Chem.*, 90, 302, 2018.
93. Mehrani, Z., Ebrahimzadeh, H., Moradi, E., Poly m-aminophenol/nylon 6/graphene oxide electrospun nanofiber as an efficient sorbent for thin film microextraction of phthalate esters in water and milk solutions preserved in baby bottle. *J. Chromatogr. A*, 1600, 87, 2019.
94. Wang, T., Wang, J., Zhang, C., Yang, Z., Dai, X., Cheng, M., Hou, X., Metal–organic framework MIL-101(Cr) as a sorbent of porous membrane-protected micro-solid-phase extraction for the analysis of six phthalate esters from drinking water: a combination of experimental and computational study. *Analyst*, 140, 5308, 2015.

95. Lee, M.-R., Lai, F.-Y., Dou, J., Lin, K.-L., Chung, L.-W., (2011) Determination of trace leaching phthalate esters in water and urine from plastic containers by solid-phase microextraction and gas chromatography-mass spectrometry. *Anal. Lett.*, 44, 676, 2011.
96. Zhang, Z.-M., Zhang, H.-H., Li, J.-L., Yang, G.-P., Determination of Phthalic Acid Esters in Seawater and Sediment by Solid-phase Microextraction and Gas Chromatography-Mass Spectrometry. *Chinese J. Anal. Chem.*, 45, 348, 2017.