



# Microwave-assisted extraction of pharmaceuticals, personal care products and industrial contaminants in the environment



Maria Llompart <sup>a,\*</sup>, Maria Celeiro <sup>a</sup>, Thierry Dagnac <sup>b</sup>

<sup>a</sup> Department of Analytical Chemistry, Nutrition and Food Science, Faculty of Chemistry, E-15782, Campus Vida, Universidade de Santiago de Compostela, Santiago de Compostela, Spain

<sup>b</sup> Agronomic and Agrarian Research Centre (AGACAL-CIAM), Unit of Organic Contaminants, Apartado 10, 15080, A Coruña, Spain

## ARTICLE INFO

### Article history:

Available online 8 May 2019

### Keywords:

Microwave assisted extraction  
Pharmaceuticals  
Veterinary drugs  
Personal care products  
Plasticizers  
Flame retardants  
Phenolic compounds  
Bisphenol A

## ABSTRACT

Microwave-assisted extraction (MAE) is a well-established automated green extraction technique, offering many advantages such as the combined reduction of the extraction time, solvent and energy consumptions, as well as the possibility of performing simultaneous multiple extractions, thus increasing the number of samples processed daily. This review provides a comprehensive description of the most relevant analytical methods and applications, proposed from year 2012, for the extraction of selected emerging pollutants, including pharmaceuticals and veterinary drugs, personal care products, as well as industrial contaminants, in environmental matrices. The novel developments and last technological trends such as the implementation of organic solvent-free extraction methods, the use of surfactants and ionic liquids, the combination with microextraction approaches or the introduction of systems that sequentially process the samples, are also addressed. Overall, MAE appears to be an excellent alternative for the determination of emerging organic pollutants, thereby enabling its application within the regulatory environmental field.

© 2019 Elsevier B.V. All rights reserved.

## 1. Introduction

Sample preparation methods keep on playing an essential role in modern analytical chemistry, but most analytical instruments are unable to handle matrices directly and some pre-treatment steps are required to extract and to isolate the analytes [1].

Main trends in analyte isolation include less solvent consumption, higher recoveries and better reproducibility, repeatability and detection limits. The implementation of traditional solvent extraction for this purpose may cause significant pollution by releasing high solvent amounts into the environment.

In this context, some green solvent extraction techniques have been developed and among them microwave-assisted extraction (MAE) also called microwave-assisted solvent extraction (MASE) [2,3]. MAE is a process consisting of the transfer of solutes from a solid matrix into a solvent allowing a rapid extraction and a high throughput with yields comparable/higher than/to those obtained by many classical techniques. From a green chemistry point of view, the main advantages of MAE consist of significantly

decreasing the solvent and sample amounts required, as well as the extraction time, thereby reducing waste generation, energy consumption, solvent release into the environment and then human exposure [4–6].

The use of microwave energy in sample preparation first emerged in the early 1970s for sample digestion under pressurized conditions for elemental analysis [7]. The development of MAE took place later, and the first application of microwave energy for the extraction of organic compounds was described by Ganzler et al. [8] in 1986, using a domestic equipment. The first patent dealing with the extraction of a natural product using microwaves was filed by Pare in 1991 (US 5002784, *Microwave-assisted natural products extraction*). This technology became very popular in the 90s, with the introduction of MAE devices in the laboratory, particularly for the extraction of contaminants and natural products, reaching a peak in 2008 in terms of published articles number.

The use of MAE for the extraction of pollutants from environmental matrices has attracted considerable interest. The first applications dealt with the determination of pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in soils and sediments [8–11] and, since then, many other environmental contaminants have been efficiently extracted

\* Corresponding author.

E-mail address: [maria.llompart@usc.es](mailto:maria.llompart@usc.es) (M. Llompart).

**Abbreviations**

ACN	Acetonitrile	MS	Mass spectrometry
APCI	Atmospheric pressure chemical ionization	MSPD	Matrix solid-phase dispersion
APEO	Alkylphenol ethoxylate	MS/MS	Tandem mass spectrometry
BFR	Brominated flame retardant	MW	Microwave
BPA	Bisphenol A	MWCNT	Multi-walled carbon nanotube
BSA	Benzenesulfonamide	NOR	Norfloxacin
BSTFA	N,O-bis (trimethylsilyl)trifluoroacetamide	NPEO	Nonylphenol ethoxylate
BT	Benzothiazole	NPEO2	Nonylphenol diethoxylate
BTR	Benzotriazole	NP1EC	Nonylphenolmonocarboxylate
CIP	Ciprofloxacin	NSAID	Non-steroidal anti-inflammatory drug
CPE	Cloud point extraction	OPE	Organophosphate
DAD	Diode array detector	OPEO	Octylphenol ethoxylate
DLLME	Dispersive liquid–liquid microextraction	PAE	Phthalic acid ester
DVB	divinylbenzene	PBB	Polybrominated biphenyl
ECD	Electron capture detector	PBDE	Polybrominated diphenyl ether
EDC	Endocrine disruptor compound	PUF	Polyurethane foam
EDTA	(ethylenedinitrile)-tetraacetic acid	PVC	Polyvinylchloride
ENR	Enrofloxacin	PCP	Personal care product
ESI	Electrospray ionization	PDMS	Polydimethylsiloxane
FID	Flame ionization detector	PFR	Phosphorus flame retardant
FL	Fluorescence	PLE	Pressurized liquid extraction
FR	Flame retardant	PPCP	Pharmaceutical and personal care product
GC	Gas chromatography	PPT	Part per trillion
GPC	Gel permeation chromatography	Q	Quadrupole
HF-L/SME	Hollow-fiber-liquid/solid phase microextraction	QuEChERS	Quick, easy, cheap, effective, rugged and safe
HPH	High-pressure homogenizer	RSD	Relative standard deviation
HRMS	High resolution mass spectrometry	SA	Sorbent-assisted
HS	Headspace	SAR	Sarafloxacin
HTAB	Hexadecyltrimethylammonium bromide	SAS	Sulfonamides
ICP	Inductively coupled plasma	SBSE	Stir bar sorptive extraction
IL	Ionic liquid	SFE	Supercritical fluid extraction
LC	Liquid chromatography	SPE	Solid-phase microextraction
LDTD	Laser diode thermal desorption	SPME	Solid-phase microextraction
LEVO	Levofloxacin	TA	Tenax
LLME	Liquid–liquid microextraction	TEP	Triethyl phosphate
LOD	Limit of detection	THF	Tetrahydrofuran
LOQ	Limit of quantification	TMP	Trimethyl phosphate
MABE	Microwave assisted back extraction	TOF	Time of flight
MAE	Microwave-assisted extraction	TPPO	Triphenyl phosphine oxide
MAME	Microwave-assisted micellar extraction	UAE	Ultrasound assisted extraction
MeOH	Methanol	US	Ultrasound
MRM	Multiple reaction monitoring	UV	Ultraviolet
		WWTP	Wastewater treatment plant

[12–14]. Since more than one decade, the EPA method 3546 ‘Microwave Extraction’ provides a valuable protocol for the extraction of semivolatile organic compounds, including organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, phenoxyacid herbicides, substituted phenols, PCBs, and PCDDs/PCDFs, which may then be analyzed by different chromatographic procedures [15]. This protocol may also be applicable for the extraction of additional target analytes, provided that the analyst demonstrates adequate performance for the intended application [16].

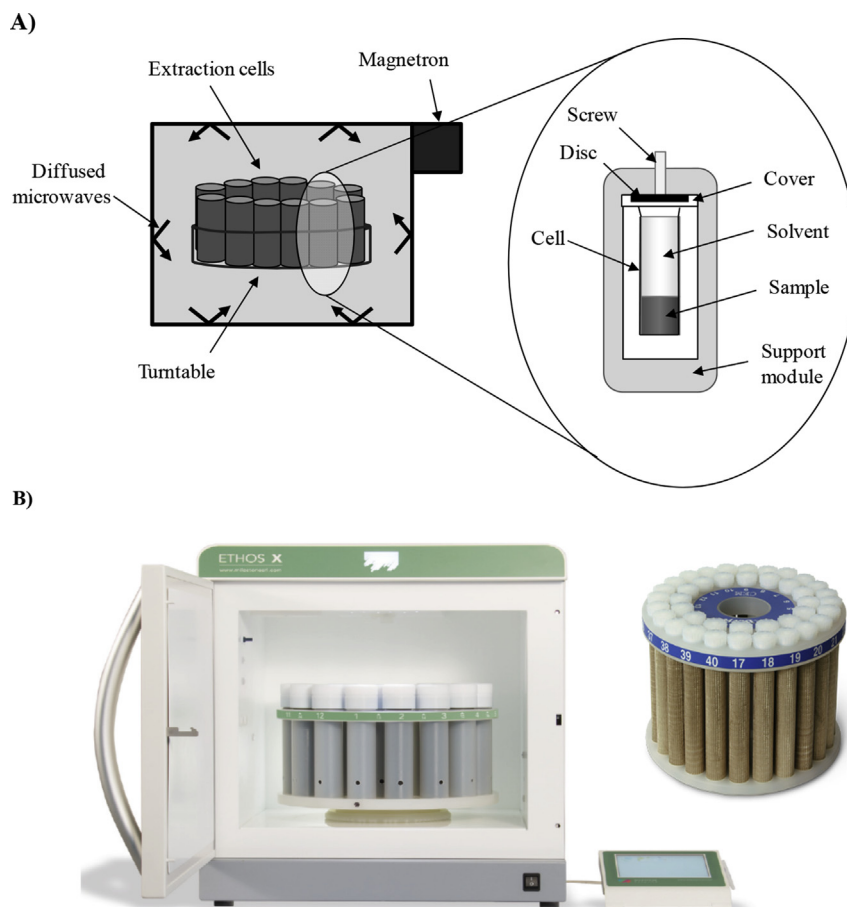
More recently, the use of microwaves for the extraction of emerging micropollutants from environmental matrices has been strongly growing [6,17]. MAE was then successfully adopted for various classes of organic pollutants (e.g. flame retardants, surfactants, pharmaceutical and personal care products) due to relative easiness for conducting the optimization of the parameters affecting the extraction. The automation ability, high efficiency and high sample throughput constitute other advantages related to the MAE use.

### 1.1. Principles, MAE systems and factors affecting extraction

MAE combines the use of traditional solvent extractions with microwave energy, which is used to heat the solvents in contact with the samples, achieving the partition of the target compounds from the sample into the solvent. However, only materials or solvents with permanent dipoles can get heated under microwaves. Consequently, the effect of the microwave energy strongly depends on the nature of the solvent/matrix binomial.

More details are provided in: Microwave-Assisted Extraction, *Encyclopedia of Analytical Science* [18].

Microwave systems used for extraction in the laboratory exist in two main configurations: either in closed extraction vessels/multi-mode microwave ovens or in ‘open’ focused microwave ovens. Nowadays, the most used systems are the closed vessel-like (see Fig. 1A), for which the extraction yield is governed by both the pressure and temperature applied. The pressure achieved depends



**Fig. 1.** (A) Schematic view for a closed-vessel MAE system and (B) Commercial MAE instrument from Milestone and Carousel with 40 positions (Reproduced with permission of Milestone, Inc.).

on the extraction temperature, the solvent (type and volume), and the sample characteristics and size. The temperature should be optimized, and it is usually set between 60°C and 120°C. The drawbacks or limitations of closed vessel systems include the risk induced using high pressures and temperatures with the possible risk of analyte degradation. The commercial equipments include several security mechanisms to avoid overpressures and to detect solvent leaks, and they allow processing several samples simultaneously. New MAE multimode systems allow the simultaneous extraction of up to 40 samples in only 10–15 min (see Fig. 1B). Recently, the use of new vessels made of Weflon™ (Milestone), equipped with inexpensive and disposable glass vials inside, avoid the need of cleaning the vessel after each extraction, improving significantly the sample preparation throughput. Besides, modern sample MAE platforms incorporate two magnetrons allowing performing the extraction at up to 2000 W. New automatic configurations for sequential analysis are also available. These systems incorporate an autosampler to run extraction sequences of up to 24 samples, which considerably accelerates the method optimization since each extraction can be conducted under different experimental conditions.

The extraction time is strongly lowered when applying MAE because microwaves directly heat the solution, whereas with classical extraction techniques, a finite period is needed to heat the vessel before heat is transferred to the solution. This allows keeping the temperature gradient to a minimum and accelerating the heating speed. Additionally, as already commented, MAE allows for the possibility of simultaneously running multiple

samples. Therefore, MAE largely complies with the minimum criteria required for modern sample preparation techniques and provides a very attractive alternative to the conventional techniques. The main parameters influencing the MAE performance include: solvent and matrix types; solvent volume; microwave power; exposure time; sample size and moisture and temperature [19–21]. The use of experiment designs allows decreasing the number of experiments needed to assess the influence of these factors on the MAE process and to find out the optimal extraction conditions. Multivariate approaches like response surface methodology-RSM can be used to develop, improve and optimize the design process [13,22]. The extraction solvents for MAE are usually limited to those that absorb microwaves (solvents with permanent dipole leading), although the use of solvent mixtures (with and without dipoles) extend MAE applications to a larger variety of analytes (polar and non-polar). Recently, some alternative solvents, such as ionic liquids (ILs), have been proposed for MAE of environmental pollutants. ILs are composed of bulky organic cations and inorganic or organic anions, and they exist in the liquid state around room temperature. They have attracted much interest for a variety of research applications, thanks to their excellent physico-chemical properties: negligible vapor pressure, good thermal stability, wide liquid range, tunable viscosity and miscibility with water and organic solvents, as well as good solubility and extractability for various organic compounds. Besides, the use of aqueous phases, water and surfactants have also been proposed as attractive ‘green’ alternatives to conventional volatile organic solvents.

## 2. Analysis of emerging pollutants in the environment

Emerging pollutants were defined as compounds that were not currently covered by existing environmental quality regulations, have not been thoroughly studied before, and were suspected to threaten ecosystems and human health and safety [23]. They encompass many groups of compounds, including pharmaceuticals, steroids and hormones, veterinary drugs, personal-care products (PCPs), surfactants, perfluorinated compounds, flame retardants such as polybrominated diphenyl ethers (PBDEs), industrial additives and agents, petrol additives, and more recently nanoparticles.

Emerging contaminants can reach the environment because of human and industrial activities through several pathways, being their final fate many different environmental compartments (see Fig. 2).

The use of MAE to extract emerging pollutants from environmental matrices has attracted considerable interest due to its high efficiency and low time and solvent consumptions. However, owing to the low levels of emerging pollutants to be monitored, pre-treatment steps are usually required to extract and isolate the target analytes. In most cases, substantial analyte enrichment is mandatory to isolate the target compounds from the matrix and to achieve the lowest limits of detection (LODs). Derivatization can be also necessary if the final analysis involves gas chromatography [22–25].

Conventional extraction techniques (liquid–liquid extraction, Soxhlet, Soxtec, Ultrasound-Assisted Extraction (UAE), mechanical shaking, etc) were traditionally employed for the extraction of emerging pollutants from solid or liquid environmental matrices. Nevertheless, large consumption of sample and reagents, generation of large amounts of waste (including solvents) and long preparation time are common drawbacks of these traditional techniques.

Over the past twenty years, new green solvent extraction techniques such as Solid-Phase Extraction (SPE), Solid-Phase-Microextraction (SPME), Pressurized Liquid Extraction (PLE), Supercritical Fluid Extraction (SFE), Matrix Solid-Phase Dispersion (MSPD), or MAE have then been developed to mitigate these downsides. These green techniques have been successfully applied

to the extraction of many classes of emerging pollutants, from solid, semi-solid or even liquid samples. Regarding analysis, both gas chromatography (GC) and liquid chromatography (LC) were employed. In the last decade, more selective and sensitive detectors (MS, MS/MS, Orbitrap–MS, QTOF) are being used, allowing the identification and quantification of emerging pollutants and their transformation products at trace levels in a broad range of environmental matrices.

In the next sections, the most recent environmental applications of MAE, published from 2012 to 2018 for the analysis of pharmaceuticals, personal care products and industrial pollutants are summarized.

### 2.1. Pharmaceuticals and veterinary drugs

More than 3000 different substances are used as pharmaceutical ingredients for the treatment of human or animals' diseases, including antibiotics, antidiabetics, betablockers, contraceptives, lipid regulators, anti-depressants or non-steroidal anti-inflammatory drugs (NSAIDs). Pharmaceuticals for human use and their metabolites enter urban wastewater treatment plants (WWTPs), from domestic and hospital sewage, where they are not completely removed. Therefore, their final fate usually involves different environmental compartments (like water, sediments, but also biota). Regarding veterinary drugs, the animals excrete them together with their metabolites, and they can be accumulated in soils, filtered through them to reach ground waters, or directly transferred to surface water by run-off.

The use of MAE for extracting pharmaceuticals from environmental matrices has attracted considerable interest. Table 1 summarizes the most recent environmental applications of MAE for the extraction of different pharmaceuticals intended for human and veterinary use. These applications are briefly commented below.

#### 2.1.1. Pharmaceuticals

The analytical methods based on MAE to determine pharmaceuticals have been mainly applied to sewage sludge samples from wastewater treatment plants (WWTP). In this context, a large class of pharmaceutical compounds, including steroid hormones [24–29], non-steroidal anti-inflammatory drugs (NSAIDs) [29–32],

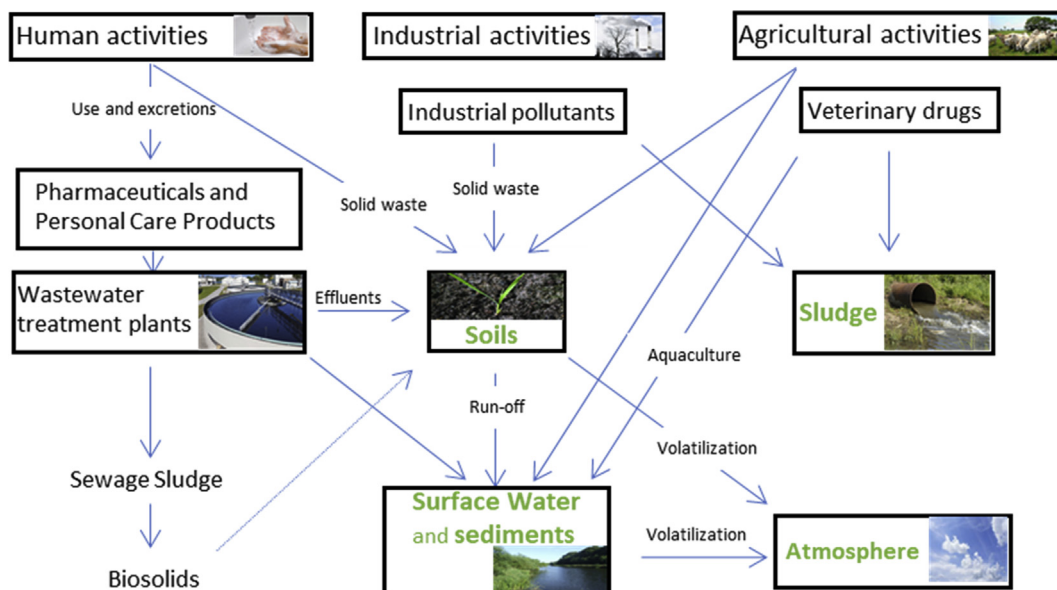


Fig. 2. Common pathways of pharmaceuticals, personal care products and industrial pollutants to reach the environment.

**Table 1**  
Pharmaceuticals and veterinary drugs.

Analyte	Sample	Sample pretreatment	MAE conditions	Extract treatment	Determination	Recovery (%)	LOD	RSD (%)	Year	Ref
<i>Pharmaceuticals</i>										
15 sex hormones and corticosteroids	Sludge (0.1 g)	Freeze-dried	10 mL MeOH MAE (500 W, 65°C, 4 min)	Filtration, evaporation and reconstitution (MeOH)	LC–MS/MS	>71	1.1 to 7.9 ng g <sup>-1</sup>	<23	2016	[24]
20 synthetic and natural steroids and their related metabolites	Sediment (3 g)	MeOH addition and vortex stirring	5 mL MeOH MAE (10 min ramp time up to 90°C and held 5 min) × 2 cycles.	Combination of the 2 fractions. Evaporation up to 0.2 mL	LC–MS	90–100	0.07–1.87 ng g <sup>-1</sup>	<60	2013	[25]
E1, E2, E3, EE2, DES, among others	Sewage sludge (1 g)	Homogenization and air-dried	5 mL MeOH MAE (300 W, 10 min)	Dilution, and SPE	LC–MS/MS	75–98	0.1–0.5 ng g <sup>-1</sup>	<8.3	2013	[26]
T, 19-norethindrone, DES, norgestrel, EE2, E2, E3, E1, among others	Sewage sludge (1 g)		5 mL MeOH MAE (200 W, 6 min)	Filtration, dilution, and SPE	LC–MS/MS	75–102	0.1–0.7 ng g <sup>-1</sup>	<9	2013	[27]
E1, E2, EE2, among other PCPs, alkylphenols, phenylphenols, bisphenol A	Soil, sediment, sludge (1 g)	Freeze-dried and homogenized	10 mL MeOH/water (3:2, v/v) MAE (500 W, 6 min)	Filtration and evaporation. Reconstitution. SPE and derivatization	GC–MS	92–98	4.7–5.1 ng kg <sup>-1</sup>	<5.1	2012	[28]
8 NSAIDs and 5 estrogenic hormones	Soil, sediment, sludge (5 g)	Dried, homogenization and sieved	10 mL water MAE (400 W, 115°C, 15 min)	Evaporation, reconstitution, SPE and derivatization	GC–MS	>50	0.3–5.7 ng g <sup>-1</sup>	<14	2015	[29]
5 NSAIDs, 3 steroids and PCPs	Sewage sludge	Digestion and freeze-dried	25 mL water/MeOH (1:1, v/v) MAE (110°C, 10 min)	SPE	LC–MS/MS	90–100	0.05–4.81 ng g <sup>-1</sup>		2016	[30]
18 multiclass pharmaceutical and illicit drugs	Sludge (1 g)	Digestion and freeze-dried	30 mL MeOH/water (1:1, v/v) MAE (1200 W, 120°C, 30 min)	Centrifugation and SPE	Chiral–LC–MS	91–124	300–1160 ng g <sup>-1</sup>	<10	2015	[31]
Acetylsalicylic acid, NAP, IBU and gemfibrozil	Wastewater, sludge		5 mL MeOH MAE (500 W, 6 min)		LC–FL	79 (wastewater), 69 (sludge)	13–1338 ng L <sup>-1</sup> (wastewater), 1–86 ng g <sup>-1</sup> (sludge)		2016	[32]
CBZ	Wastewater sludge (0.5 g)	Freeze-dried, homogenization	20 mL MeOH MAE (1200 W, 10 min ramp up to 110°C, held 10 min)	Concentration and redissolution (water)	LDTD–APCI–MS/MS	98–113 (water) 96–107 (sludge) 73–96	12 ng L <sup>-1</sup> (wastewater) 3.4 ng g <sup>-1</sup> (sludge)	<5	2012	[33]
LEVO, NOR, CIP, ENR, SAR	Marine sediment, sewage sludge (2 g)	Air-dried	15 mL of 5% HTAB MAME (500 W, 15 min)		LC–FL		0.15–0.55 ng g <sup>-1</sup>	≤8	2012	[34]
13 quinolone antibiotics	Sewage sludge (0.5 g)	Dried and sieved	10 mL of extraction buffer solution (pH = 3) MAE (1000 W, 87°C, 17 min)	Centrifugation, evaporation, redissolution and centrifugation	LC–MS/MS	978–105	1–5 ng g <sup>-1</sup>	0.3–6.7	2013	[35]
Fluoroquinolones	Compost (0.3 g)	Air-dried, homogenization and sieved	10 mL Mg(NO <sub>3</sub> ) <sub>2</sub> × 6H <sub>2</sub> O and NH <sub>3</sub> aqueous solution MAE (200 W, 135°C, 20 min)	Dilution and SPE	LC–MS/MS	70–112	2.2–3 ng g <sup>-1</sup>	<13	2015	[36]
25 multiclass antibiotics	Aquifer sediment	Air-dried and sieved	MeOH MAE 5 min ramp up to 60°C (held 25°C), 100 W	Centrifugation and SPE	LC–Q–Orbitrap–MS	>70	0.1–3.8 mg kg <sup>-1</sup>	<21	2016	[37]
Fluoroquinolones, sulfonamides, tetracyclines, anfenicols, and NSAIDs	Fish (0.5 g)	Lyophilization	50 µL Proteinase-K solution + 5 µL formic acid + 5 mL ACN/H <sub>2</sub> O (1:1, v/v) MAE (5 min)	Evaporation and reconstitution (water)	LC–MS/MS	70	0.6–12 ng g <sup>-1</sup>	<15	2018	[38]
	Fish (10 g)				LC–HRMS	56–120		<17	2017	[39]



7 NSAIDs, 8 sedatives, 12 sulfonamides, 8 quinolones, and PCPs		Lyophilization and homogenization	Octanol/toluene (1:1, v/v) MAE–HF–L/SME (100 W, 60°C, 12 min)				0.01 –0.50 ng g <sup>-1</sup>			
6 antibiotics	Fish (2 g)	Cleaning and homogenization	8 mL ACN MAE (5 min, 50°C)	Solid-phase purification and DLLME	LC–MS/MS	>87	4.5 –101 pg kg <sup>-1</sup>	<4	2016	[40]
E1, E2, E3, EE2 and alkylphenols	Fish (2 g)	Lyophilization and homogenization	MeOH MAE (110°C, 20 min)		GC–MS	55–100	0.3–0.7 ng g <sup>-1</sup>	<13	2012	[41]
TC, DC, OTC, CTC and PCPs	Soil, sludge, atmospheric particulate matter (1 g)		5 mL MeOH + $\mu$ SPE device MAE (400 W, 60°C, 20 min)	Sonication with MeOH	LC–UV	71–110	0.1–6.3 ng g <sup>-1</sup>	<15	2015	[42]
<i>Veterinary drugs</i> OTC, TC and CTC	Agricultural soil (1 g)	Air-dried, homogenization and sieved	ACN/McIlvaine buffer/0.1 M EDTA (2:1:1, v/v/v) MAE (400 W, 60°C, 10 min)	SPE	LC–MS/MS	101–110	1.7–2.5 ng g <sup>-1</sup>	<9	2018	[43]
7 veterinary pharmaceuticals	Agricultural soil (1 g)	Air-dried, homogenized and sieved	10% Mg(NO <sub>3</sub> ) <sub>2</sub> /NH <sub>4</sub> Cl (9:1) + 0.5 mL MeOH MAE (400 W, 60°C, 10 min)	SPE	LC–MS/MS	73–127	1.0–3.3 ng g <sup>-1</sup>	<12	2017	[44]
ENR, DAN and their photoproducts	Agricultural soil (1 g)	Dried, homogenization and sieved	8 mL aqueous 20% (w/v) Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + 2% (v/v) NH <sub>3</sub> solution MAE (1600 W, 80°C, 20 min)	Centrifugation and acidification	LC–FL	70–130		1–6	2012	[45]
MNC, OTC, TC, ENR, CEF	Sediment, sludge	Sediment: Freeze- dried. Sludge samples: Frozen, centrifugation, and freeze-dried	MeOH-formic MAE (40°C, 20 min)	Centrifugation, evaporation and reconstitution	LC–DAD	81			2013	[46]
8 veterinary pharmaceuticals	Sediment (1 g)	Dried, crushed and sieved	15 mL MeOH/water (80:20, v/v) MAE (65°C, 15 min)	Decantation, evaporation and reconstitution (MeOH)	LC–DAD	40–100	5–460 ng L <sup>-1</sup>	<5	2016	[47]
9 SAs	Sediment, soil		MeOH, 45 min	Filtration	LC–MS/MS	>80		<20	2014	[48]
10 SAs	Agricultural soil, sediment, sludge (2 g)	Dried and homogenization	Triton X114 (1.5 v/v) at 1.5 mL min <sup>-1</sup> MAME (800 W)	Centrifugation	LC–UV	70–102	0.42 –0.68 ng g <sup>-1</sup>	<7	2016	[49]
Oxibendazole	Agricultural soil (1 g)	Air-dried, and sieved	20 mL Genapol X-080 (0.5%) MAE (1000 W, 2 min)	Centrifugation	LC–FL	87–95	0.10 $\mu$ g g <sup>-1</sup>	<7.7	2012	[50]
4 SAs	Environmental waters (2 mL)		IL MAE (240 W, 90 s)	Separation of the IL (freezing) and centrifugation	LC–UV	75–116	0.33 –0.85 mg L <sup>-1</sup>	<12	2014	[51]

ACN: Acetonitrile. CBZ: Carbamazepine. CEF: Ceftriaxone. CIP: Ciprofloxacin. CTC: Chlortetracycline. DAD: Diode array detector. DAN: Danofloxacin. DC: Deoxytetracycline. DES: Diethylstilbestrol. E1: Estrone. E2: 17 $\beta$ -Estradiol. E3: Estriol. EE2: 17 $\alpha$ -ethynylestradiol. ENR: Enrofloxacin. FL: Fluorescence detector. GC: Gas chromatography. HF-L/SME: Hollow-fiber-liquid/solid phase microextraction. HTAB: Hexadecyltrimethylammonium bromide. IBU: Ibuprofen. LC: Liquid chromatography. LDTD–APCI: Laser diode thermal desorption–atmospheric pressure chemical ionization. LEVO: Levofloxacin. LOD: Limit of detection. MAE: Microwave-assisted extraction. MAME: Microwave-assisted micellar extraction. MeOH: Methanol. MNC: Minocycline. MS: Mass spectrometry. MS/MS: Tandem mass spectrometry. NAP: Naproxen. NOR: Norfloxacin. NSAIDs: Nonsteroidal anti-inflammatory drugs. OTC: Oxytetracycline. PCPs: Personal care products. RSD: Relative standard deviation. SAR: Sarafloxacin. SAs: Sulfonamides. SPE: Solid-phase extraction. T: Testosterone. TC: Tetracycline. UV: Ultraviolet detector. W: Watts.

anti-epileptic drugs [33], and antibiotics [34,35] have been studied in this matrix. In addition, the use of MAE has been also successfully employed to determine pharmaceuticals in other solid matrices such as compost [36], sediments [37] and biota [38–41] or in air samples [42].

Estrogens are the most important group of steroid hormones and their release in the environment, especially in the aquatic environment can cause serious effects for the aquatic organisms. MeOH [24,25,27], water [29] and the mixture MeOH/water (3:2, v/v) [28] were the extraction solvents mainly employed for conducting the MAE optimization of steroid hormones in sewage sludge and sediments. After MAE, extract evaporation and reconstitution in MeOH was employed as concentration step prior the LC–MS analysis of 15 sex hormones and corticosteroids in sludge [24], and 20 synthetic and natural steroids and their related metabolites in sediments [25]. SPE was also employed as an additional clean-up step prior analysis [26,27]. In all cases, satisfactory recoveries between 71 and 102% were achieved as well as LODs at the low  $\text{ng g}^{-1}$  [24–27].

When the analysis of steroids in sewage sludge was performed by GC–MS, a derivatization step was included after the MAE procedure [28,29]. N,O-Bis (trimethylsilyl)trifluoroacetamide (BSTFA) was employed as derivatizing agent for the analysis of 3 steroid hormones together with PCPs, alkylphenols, phenylphenols, and bisphenol A [28], and for the determination of 5 estrogens and NSAIDs in soils, sediments and sludge [29]. In both cases, satisfactory recoveries and precision, and very low LODs at part per trillion (ppt) levels were obtained.

The simultaneous multiresidue analysis of pharmaceuticals in sewage sludge employing MAE followed by LC analysis, has also been proposed [30–32]. Two analytical methodologies based on MAE–LC–MS/MS were successfully developed to determine 5 NSAIDs, 3 steroids and PCPs including parabens, and UV filters [30], and chiral pharmaceuticals [31]. MAE, followed in this case by LC–FL has been also successfully proposed for the simultaneous analysis of acetylsalicylic acid, 2 NSAIDs, and gemfibrozil (fibrate drug) in sewage and sludge samples [32]. In the three cases, the MAE conditions involved the use of MeOH/water (1:1, v/v) or MeOH as extraction solvent, at 110–120°C for 6–30 min. Besides, after the MAE procedure, a SPE clean-up step was carried out. Satisfactory recoveries, precision, and low LODs were obtained in all cases for most compounds.

Carbamazepine is the most employed pharmaceutical in the treatment of epilepsy and neuropathic pain. A rapid and reliable method based on MAE followed by laser diode thermal desorption–atmospheric pressure chemical ionization (LDTD–APCI) coupled to MS/MS, has been proposed to determine this compound in wastewater sludge. MeOH was employed as extraction solvent, and MAE conditions involved 1200 W at 110°C for 10 min [33]. MAE efficiency was compared with that of ultrasound-assisted extraction (UAE) and pressurized liquid extraction (PLE). PLE and MAE showed the best recoveries, probably due to the higher extraction temperature (140°C, and 110°C, respectively), in comparison with UAE.

Antibiotics are pharmaceuticals that fight bacterial infections. Among them, fluoroquinolones are probably the most important class of synthetic antibiotics due to their broad activity spectrum and good oral absorption. They have been detected in wastewater effluents and they can accumulate in sediments or sludge due to their lipophilic character. MAE has been successfully employed to extract fluoroquinolones from sewage and wastewater sludge [34,35] and compost [36]. A MAME method has been proposed for the determination of levofloxacin (LEVO), norfloxacin (NOR), ciprofloxacin (CIP), enrofloxacin (ENR), and sarafloxacin (SAR). Experimental conditions involved the use of water containing

hexadecyltrimethylammonium bromide (HTAB) as surfactant, and 500 W of microwave radiation for 15 min. Good recoveries, and low LODs ( $<0.55 \text{ ng g}^{-1}$ ) were obtained [34]. The extraction efficiency of MAE was compared with that of UAE and PLE for the simultaneous determination of 13 quinolone-based antibiotics in sewage sludge [35]. In this case, a buffer solution (pH = 3) was employed as extractant. For all the studied compounds, quantitative recoveries and LODs lower than  $5 \text{ ng g}^{-1}$  were obtained. Owing to its higher extraction yield, easy implementation, shorter analysis time and high automation degree, MAE was considered the best option. Fluoroquinolones have been also successfully extracted from compost samples employing MAE [36]. In this case, an aqueous solution of  $\text{Mg}(\text{NO}_3)_2$  at 200 W and 135°C for 20 min were selected as extraction conditions. The method exhibited quantitative recoveries and low RSD values.

MAE has successfully extracted other antibiotics such as tetracyclines from soil, sludge and atmospheric particulate matter [42], or multiclass antibiotics from aquifer sediments [37].

A comparison between MAE– $\mu$ SPE procedure and classical MAE was carried out for the determination of 4 tetracycline antibiotics in soil, sludge and atmospheric particulate matter [42]. For the MAE– $\mu$ SPE procedure, MeOH was employed as extraction solvent and the  $\mu$ SPE device (copper (II) isonicotinate in an enclosed microporous polypropylene membrane) was irradiated with microwave energy (400 W) at 60°C for 20 min. Afterwards, the  $\mu$ SPE device was taken from the solution, and analytes were desorbed by sonication with MeOH. This procedure was compared with conventional MAE under the same conditions. Both procedures showed good recoveries and low RSD values, although lower LODs ( $<6.3 \text{ ng g}^{-1}$ ) were achieved employing MAE– $\mu$ SPE.

MAE procedure followed by UHPLC–Q-Orbitrap–MS analysis has been proposed as an effective method to determine 25 multiclass antibiotics, including fluoroquinolone- and tetracycline-derivatives, in aquifer sediments [37]. The optimized MAE conditions involved the use of MeOH at 100 W and 60°C for 5 min. After the validation, the proposed method was applied to real aquifer sediment samples taken at different depths. Results revealed the presence of chlorotetracycline and ofloxacin at relative high concentrations (53 and  $19 \text{ mg kg}^{-1}$ , respectively) in the deeper level (18 m).

For the simultaneous determination of 8 steroid and phenolic endocrine disrupting compounds in biological samples, an improved MAE method was developed employing MeOH and 110°C for 20 min and an automated clean-up was performed by gel permeation chromatography (GPC). A satisfactory method performance was demonstrated by its application on tissues from fish exposed to high concentration of EDCs [41].

An analytical methodology based on MAE–LC–MS/MS has been recently developed for the determination of antibiotics [40], and for multiresidue pharmaceutical analysis, including fluoroquinolones, sulfonamides, tetracyclines, anfenicols and NSAIDs [38] in fish tissues. In both cases, acetonitrile [40] and the mixture acetonitrile/water (1:1, v/v) [38] were employed as extraction solvents and the MAE procedure only took 5 min. Extract evaporation and reconstitution with water was performed before multiresidue analysis of pharmaceuticals [38], whereas a further step including solid-phase purification and dispersive liquid–liquid microextraction (DLLME) was necessary for the antibiotic determination [40]. Very low LODs at the  $\text{pg kg}^{-1}$  level, were obtained in this last case for all the studied antibiotics.

The use of new approaches such as MAE combined with hollow-fiber-liquid/solid phase microextraction (HF-L/SME) has been recently proposed as a suitable tool to extract 54 multiclass pharmaceuticals (NSAIDs, sedatives, sulfonamides, quinolones and other common drugs) and PCPs from fish samples [39]. In this case,

a synthesized SPME fiber showed high capacity, concentration rate and efficiency, and microwave energy was applied during the HF-L/SME procedure. This combination allows improving the rate of the target compounds diffusion, thereby decreasing the extraction time (12 min). LODs between 0.01 and 0.50 ng g<sup>-1</sup> were obtained for all compounds.

### 2.1.2. Veterinary drugs

A huge diversity of veterinary pharmaceutical compounds is employed in food-animal agriculture worldwide for the purposes of treating or preventing infectious and non-infectious diseases, managing reproductive processes and promoting growth. Most papers reporting MAE applications for the determination of veterinary drugs in the environment are referred to solid samples [43–50] especially agricultural soils [43–45,49,50]. Only few studies on aqueous matrices have been published [51]. The latest environmental MAE application to determine veterinary drugs are summarized in Table 1 and commented below.

MAE of veterinary drugs from agricultural soils using different extraction solvents was reported. Recently, the combination of ACN:McIlvaine buffer containing 0.1 M of EDTA (2:1:1, v/v/v) has been successfully employed for the determination of three tetracycline-derivatives [43], whereas an aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>/NH<sub>4</sub>Cl was selected as extractant for the determination of 7 multiclass veterinary pharmaceuticals [44]. In both cases, the MAE conditions were 400 W at 60°C for 10 min. Both methodologies achieved quantitative recoveries, and LODs lower than 3.3 ng g<sup>-1</sup> [43,44].

Apart from determining the target compounds, it is also important to analyze the formation of photoproducts, which can be more toxic than the original compounds. Thus, a method based on MAE–LC–FL has been proposed for the determination of two fluoroquinolone-antibiotics, enrofloxacin and danofloxacin, and their photoproducts in agricultural soils. An aqueous solution containing Mg(NO<sub>3</sub>)<sub>2</sub>, 1600 W of microwave power, 80°C and 20 min as extraction time have been selected as optimal experimental MAE conditions [45].

MAE showed a high extraction efficiency for the simultaneous determination of multiclass veterinary drugs, including tetracycline-, fluoroquinolone- and cephalosporin-derivatives, among other, in sediments and sludges [46,47]. In this study, MAE conditions involved the use of MeOH-formic at 40°C for 20 min [46] and MeOH/water at 65°C for 15 min [47], respectively.

The extraction and analysis of sulfonamides (SAs) in agricultural soils, sediments and sludges were also successfully carried out employing MAE [48,49]. Some SAs such as sulfamethoxazole or sulfamerazine are among the most widely used antibiotics in animal husbandry. These compounds can easily be accumulated in soils after fertilization of agricultural fields by manure application. Classical solvents, such as MeOH were employed to perform the MAE procedure for the extraction of 9 SAs from sediments and soils [48]. However, the use of aqueous surfactant solutions as extracting phase is one of the trends in these last years. The term microwave-assisted micellar extraction (MAME) was suggested to name this particular procedure, capable of offering high recovery efficiencies and reducing costs. In this context, a high-throughput MAME method has been proposed for the determination of 10 SAs in agriculture soils, sediments, and sludge [49]. Triton X-114 is continually flowing through the extraction vessels where the sample is contained, under 800 W of microwave power, and LODs lower than 0.7 ng g<sup>-1</sup> were achieved. The total preparation time for 15 samples was 18 min, and the results demonstrated that 8 out of the 10 target SAs persist in the soils for 3 months. Other analytical method based on MAME has been described for the determination of the anthelmintic drug oxibendazole in agricultural soils [50]. In

this case, experimental conditions involved the use of the non-ionic surfactant Genapol X-080 (Oligoethylene glycol monoalkyl ether) (0.5%), and 1000 W of microwave irradiation power for 2 min. After MAME procedure, the final extract was centrifugated, and the supernatant was directly injected in the LC–FL system. The extraction efficiency was compared with those of mechanical agitation and UAE, showing MAME the highest extraction efficiency in comparison with the other two extraction techniques.

One of the few MAE-based methods reported for environmental waters in last years, implies the combination of MAE and liquid–liquid microextraction (MAE–LLME) for the analysis of 4 SAs [51]. This method is based on the solidification ability of the ionic liquid (IL) 1-ethyl-3-methylimidazolium hexafluorophosphate at room temperature. After microwave irradiation at 240 W for 90 s, the IL was separated by freezing and centrifugation and the target sulfonamides showed satisfactory recoveries and LODs lower than 0.85 mg L<sup>-1</sup>.

### 2.2. Personal care products

PCPs have gained increasing interest due to their huge consumption and potentially harmful concentration in environmental compartments. Their environmental concentrations and toxicity have been largely overlooked in comparison to pharmaceutical compounds [52]. PCPs, which are used in large volumes, are persistent in the environment, bioaccumulative, and with designed bioactivity like that of synthetic musk fragrances, UV filters, and antimicrobials. Their high polarity and thermal lability in some cases, and relatively low environmental concentrations, together with their interaction with a host of complex environmental matrices, make their analysis challenging. PCPs are continuously released in urban wastewater at relatively high concentration; therefore, they can be found in sewage, as well. The study of this matrix is essential to evaluate the efficiency of sewage treatments to remove these emerging contaminants.

Several methodologies based on MAE have been proposed for the extraction of solid samples such as sludge, sediment, soil and biota. In lesser extend, MAE has been applied to the determination of PCPs in air and water. In many of these studies, MAE was compared with other extraction techniques demonstrating the benefits of microwave extraction. In some of these studies several families of PCPs are considered, and the determination of PCPs is conducted simultaneously with pharmaceuticals and other endocrine disrupting agents.

Table 2 summarizes the most recent applications of MAE for the determination of PCPs in environmental samples, and some of them are discussed below.

MAE has been employed for the simultaneous extraction of seven parabens and two alkylphenols from soil [53]. Target compounds were derivatized with BSTFA and analyzed by GC–MS. A glass sample holder, inside the microwave cell was used to allow the simultaneous extraction and clean-up of samples. In most of the analyzed samples, methylparaben and butylparaben were detected at levels between 0.5 and 8.0 ng g<sup>-1</sup>.

In several applications, a SPE clean-up step was included after MAE and prior analytical determination. Thus, a multi-residue methodology has been proposed for the analysis of 90 emerging contaminants, including parabens, triclosan, benzophenone UV filters, and pharmaceuticals in sewage sludge [30], reaching LOQs under 1 ng g<sup>-1</sup>. A recent study describes MAE followed by on-line SPE–GC–MS analysis, for the simultaneous determination of EDCs, including parabens, triclosan and other phenols in soil, sediment, and sludge [28]. A systematic comparison of the MAE results with those of ultrasound-assisted and Soxhlet extraction showed that MAE provides the highest extraction efficiency (close



**Table 2**  
Personal care products.

Analyte	Sample	Sample pretreatment	MAE conditions	Extract treatment	Determination	Recovery (%)	LOD	RSD (%)	Year	Ref
7 parabens and 2 alkylphenols	Soil (2 g)	Dried, sieved and homogenization	2 g Na <sub>2</sub> SO <sub>4</sub> + 2.5 g florisil. 10 mL ACN MAE (80°C, 10 min ramp up to 80°C (held 5 min)	Derivatization	GC–MS	78–112	0.4–1.1 ng g <sup>-1</sup>		2012	[53]
5 benzophenones and 2 phototransformation products	Sediment (4 g)	Dried	30 mL MeOH/acetone (1:1, v/v) with formic acid (5%) MAE (800 W, ramp up to 150°C, 10 min)	Centrifugation, evaporation, dilution, SPE and derivatization	GC–MS	80–99	0.1–1.4 ng g <sup>-1</sup>		2014	[54]
7 BTRs	Marine sediment, sewage sludge (1 g)	Filtration	2 mL ACN MAE (300 W, 5 min)	Filtration, on-line SPE	LC–MS/MS	50–87	0.053–0.1 ng g <sup>-1</sup>	<16	2013	[55]
2 BTRs, 3 BTs, 2 BSAs	Soil		6 mL MeOH MAE (120°C, 10 min)	Evaporation, reconstitution	LC–UV	72–119	100 ng g <sup>-1</sup> (LOQ)	<11	2016	[56]
33 EDCs	Wastewater, sewage sludge (0.5 g)	Filtration	25 mL MeOH/water (1:1, v/v) MAE (110°C, 30 min)	SPE	LC–MS/MS	11–187	2 ng g <sup>-1</sup> (LOQ)		2018	[57]
Nitro muks	Indoor dust (0.8 g)	Sieved	8 mL hexane + 4 mL H <sub>2</sub> SO <sub>4</sub> (1 M) ascorbic acid (0.10%, w/w) MAE (10 min)	Centrifugation, dried, shaken and filtration	GC–μECD	88–97	1–3.3 ng g <sup>-1</sup>	<8.5	2012	[58]
Polycyclic- and nitromusks	Air (1.6 m <sup>3</sup> )	Analytes adsorption (PUF glass fiber filter)	60 mL cyclohexane/acetone (1:1, v/v) MAE (85°C, 60 min)	Evaporation, reconstitution	GC–MS/MS	65–120	0.48 ng m <sup>-3</sup>		2014	[59]
BSAs, BTRs, BTs	Surface waters (50 mL)	d-SPE	5 mL MeOH/ethyl acetate/ acetic acid (10:70:20, v/v/v) MAE (250 W, 160°C, 20 min)		LC–MS/MS	70–116	30–170 ng L <sup>-1</sup>	<7	2017	[60]
13 UV filters and BPA	Wastewater (10 mL)	Filtration	DLLME (50 μL chloroethylene + 1 mL acetone), silylation MAE (600 W, 5 min)		GC–MS	82	2–30 ng L <sup>-1</sup>	<22	2015	[61]
Hydroxyl UV filters	Wastewater, river, tap water (1 mL)	Filtration	0.5 mL acetone + D <sub>0</sub> /D <sub>3</sub> -MIAA + 0.1 mL chloroform MADLLME (240 W, 80°C, 3 min)	Centrifugation, evaporation, reconstitution	LC–MS/MS	93–104	0.5–18.8 ng L <sup>-1</sup>	<3	2017	[62]
4 Polycyclic and nitro-musks	Fish (2 g)	Cleaning	4 mL MeOH + 15 mL water (4 g NaCl) MAE–HS–SPME (80 W, 5 min)		GC–MS	80–92	0.4–1.2 ng g <sup>-1</sup> (LOQ)	<9	2013	[63]
2 Polycyclic musks	Oyster (5 g)	Homogenization	10 mL water + 3 g NaCl MAE–HS–SPME (180 W, 4 min)		GC–MS	80–89	0.04 ng g <sup>-1</sup>	<9	2012	[64]

BSAs: Benzenesulfonamides. BTRs: Benzotriazoles. BTs: Benzothiazoles. ACN: Acetonitrile. BPA: Bisphenol A. GC: Gas chromatography. LC: Liquid chromatography. LOD: Limit of detection. LOQ: Limit of quantification. MAE: Microwave-assisted extraction. MeOH: Methanol. MS: Mass spectrometry. MS/MS: Tandem mass spectrometry. RSD: Relative standard deviation. SPE: Solid-phase extraction. SPME: Solid-phase microextraction. UV: Ultraviolet detector. W: Watts. D<sub>0</sub>/D<sub>3</sub>-MIAA: D<sub>0</sub>-/D<sub>3</sub>-1-methylindole-3-acetic acid. ECD: Electron capture detector. EDC: Endocrine disruptor compound. DLLME: Dispersive liquid–liquid microextraction. MADLLME: Microwave-assisted DLLME.

to 100%) with the shortest extraction time (3 min). The sewage sludge samples were found to contain all target compounds at concentration ranging from 36 to 164 ng kg<sup>-1</sup>.

Benzophenone and benzotriazole derivatives, used as UV filters, have been also extracted from sediments and sludge using microwave energy [30,54,55]. MAE followed by automatic SPE on-line purification and preconcentration has been proposed for the analysis of seven benzotriazole UV stabilizers in sewage sludge and marine sediments [55]. After conducting the optimization of the MAE experimental conditions 2 mL of acetonitrile was employed as extractant solvent at 300 W for 5 min. The concentrations in real samples were between 0.18 and 24 ng g<sup>-1</sup>. Another study describes a procedure for determining five benzophenone-type UV filters in surface waters and sediments [54]. The proposed analytical method involves MAE of sediment samples followed by derivatization before GC–MS analysis. The analysis of environmental samples revealed the presence of the target UV filters at concentrations up to 650 ng g<sup>-1</sup>. Fast low-pressurized microwave-assisted extraction (120°C, 10 min) has been proposed for the simultaneous extraction of benzotriazole, benzothiazole and benzenesulfonamide compounds from soil samples. Efficient extractions were achieved using only 6 mL of MeOH and satisfactory recoveries, intra-day and inter-day precisions were obtained for all the compounds. The entire procedure has been successfully applied to the analysis of real soil samples [56].

MAE followed by LC coupled with time of flight mass spectrometry (LC–ESI–TOF–MS) has been recently proposed for targeted analysis of 33 EDCs in diverse solid environmental samples, as well as to identify and quantify several metabolites using post-acquisition data monitoring. MeOH/water (1:1, v/v) was used as extractant and the MAE conditions were 110°C for 30 min. Satisfactory recoveries were obtained in most cases, and LOQs were lower than 2 ng g<sup>-1</sup> for all the studied compounds. Several of the 33 analyzed EDCs, including benzophenone-UV filters, preservatives or polycyclic musks were found in the digested sludge [57].

As it was previously mentioned, MAE of PCPs from environmental matrices has been mainly focused on the analysis of solid samples. However, several applications have been developed for the analysis of air and water samples, showing that MAE was a very suitable extraction technique to determine these emerging pollutants in these matrices. Solid sorbents, such as polyurethane foam (PUF), Tenax (TA<sup>®</sup>), and XAD<sup>®</sup>, have been successfully employed for the sampling of synthetic musks in indoor air [58,59]. MAE using the mixture cyclohexane/acetone was performed at 85°C for 60 min for extracting the sorbent retained analytes [59].

A novel analytical method has been recently developed for the simultaneous extraction of benzenesulfonamides (BSAs), benzotriazoles (BTRs), and benzothiazoles (BTs) from surface water. The extraction was performed using dispersive SPE with multi-walled carbon nanotubes (MWCNTs) followed by MAE. Only 5 mL of the mixture cyclohexane/acetone (1:1, v/v) were employed as extraction solvent and MAE was conducted at 250 W, 160°C for 20 min. Recoveries and precision were satisfactory for all the studied compounds, proving that MWCNTs offer a valid alternative to other common sorbents, both in terms of cost and sorption capacity. The application to real surface water samples showed that concentrations of these contaminants ranged from 0.1 to 2 µg L<sup>-1</sup> [60].

The use of MAE combined with other microextraction techniques such as DLLME has been proposed as an effective tool to determine PCPs in environmental aqueous matrices [61,62]. A multi-residue DLLME followed by rapid microwave-assisted silylation was proposed for the simultaneous determination of trace levels of 13 UV-filters and BPA in wastewater samples. Different experimental parameters governing the extraction and derivatization steps were evaluated to achieve the highest yield. Under the

optimal conditions, mean extraction efficiency of 82%, and low LODs were reached [61]. Recently, a sensitive method using stable isotopic labeling (SIL) and microwave-assisted dispersive liquid–liquid microextraction (MADLLME), was developed for the determination of hydroxyl-UV filters in different environmental waters including wastewater, river and tap water. The optimal MAE conditions implied working at 240 W, and 80°C. The whole sample treatment (including analyte extraction, pre-concentration and isotope labeling) was carried out in only 9 min [62]. Other authors propose a rapid and solvent-free procedure using microwave-assisted headspace SPME (MA-HS-SPME) for the extraction of six commonly used synthetic polycyclic musks in different matrices including fish and biota [63,64]. The analytes were efficiently extracted from the samples, mixed with 10 mL water, by a polydimethylsiloxane–divinylbenzene (PDMS–DVB) fiber placed in the headspace whereas the system is microwave irradiated at 180 W for 4 min. The accuracy and precision were evaluated, and the method suitability for the determination of the target analytes was demonstrated. Mean recoveries ranged from 85% to 96% and LODs from 0.04 to 0.1 ng g<sup>-1</sup>. Authors pointed out many advantages of using MA-HS-SPME after comparing it with other techniques, in the sense that it provides higher throughput without additional clean-up steps and appears as a good and eco-friendly alternative for the extraction of musks in environmental samples.

MAE has also been combined with other microextraction techniques such as HF-L/SME for the successful extraction of PCPs from biota. The MAE–HF-L/SME environmentally friendly method was developed for the simultaneous extraction of 54 multiclass PPCPs from fish samples. The method showed a low matrix interference and high enrichment factor [39].

### 2.3. Industrial pollutants

Industrial contaminants is a very wide category that includes those compounds produced, manufactured and emitted by the industry, or appearing into the environment because of the industrial development. This group comprises substances used in industrial processes and production, as well as the chemical industry. The entry into the environment is continuous; in a big extent as solid waste, but also through gas emissions and water discharges. Belonging to this category, plasticizers, surfactants and flame retardants are considered emerging environmental pollutants.

#### 2.3.1. Plasticizers and flame retardants

Phthalates (phthalic acid esters, PAEs) are used to improve the plasticity of industrial polymers but they have many other uses. They are widely employed in the production of plastics and resin, such as soft polyvinylchloride (PVC) plastics, non-polymers, adhesives and personal care products. Because of their widespread application, these compounds are ubiquitous in the environment, and the concern about their toxic effects, such as endocrine disruption and carcinogenicity, is increasing.

Flame retardants (FRs) are chemicals added to potentially flammable materials; a variety of different chemicals is often combined to increase effectiveness. Brominated flame retardants (BFRs) are used in plastics, paints, varnishes and textile materials to prevent flammability. Polybrominated diphenyl ethers (PBDEs) have been a popular ingredient in flame retardants since the polybrominated biphenyls (PBBs) were banned about 30 years ago. Nevertheless, various scientific observations suggested that PBDEs might act as endocrine disruptors, and the Stockholm Convention banned the production of PBDEs as well as their use in commercial products in 2009. However, PBDEs are still present in many consumer products, and they are still released into the environment

[65]. These compounds pose a great risk to the environment and their presence in all environmental compartments, both abiotic and biotic have been documented [66].

Since the ban of some brominated flame retardants (BFRs), phosphorus flame retardants (PFRs) are often proposed as alternatives [67]. Several esters of phosphoric acid (organophosphates, OPEs) are extensively employed as flame-retardant additives as well as plasticizers. Although toxicity of OPEs is relatively low compared with that of BFRs, their increasing use and some negative effects reported, have increased the concern about possible long term effects associated to a chronic exposure to these species [68].

All these industrial contaminants are ubiquitous in the environment and the development of reliable analytical methods to study their occurrence and environmental behavior is of high interest. Environmental MAE applications have been mainly developed for the analysis of solid samples [66,69–72], and to a lesser extent for particulate matter and air [73,74], water [75,76], and biological samples [77]. Recent MAE based methodologies are summarized in Table 3 and commented below.

FRs have been mainly determined in complex solid samples, such as sewage sludge. This analysis provides valuable information about the risks associated with the reuse as biosolids for land application. MAE followed by GC–ICP–MS was proposed for the determination of six PBDEs in sewage sludge [69]. The analytes were efficiently extracted by applying MAE with 0.1 mol L<sup>-1</sup> HCl in methanol, and the subsequent addition of Tris-citrate buffer and iso-octane. This procedure showed good performance and high sensitivity with LODs below 0.3 ng g<sup>-1</sup>.

A fast method based on sorbent-assisted microwave-assisted extraction (SA-MAE) was proposed for the determination of PBDEs in sediments [70]. The extraction efficiency was compared with other sorbent-assisted based methods such as pressurized liquid extraction (SA-PLE) and ultrasound assisted extraction (SA-UAE), showing the SA-MAE methodology the highest extraction efficiency and LOQs at the low ng g<sup>-1</sup> level. The presence of BFRs has been also investigated in soils collected at fire sites where extinguishing procedures were used. Two different extraction techniques (PLE and UAE) were compared with MAE for the determination of 7 PBDEs. Analytical determination was carried out employing two different capillary columns in parallel with  $\mu$ -ECD detection [66].

MAE is usually recommended for the extraction of PFRs from sediments, since it is faster and requires less solvent than other methods. A novel and selective method based on MAE coupled with silica gel/alumina multilayer SPE clean-up, has been proposed for the determination of 11 OPEs in soil samples, showing a good performance with LOQs lower than 2.4 ng g<sup>-1</sup>. The developed method was successfully applied to different soil samples, where 6 out of the 11 target OPEs were present in all the analyzed samples [71].

MAE was optimized and applied to study the distribution of 15 PAEs in sediments and suspended particles from lakes. Extractions were performed employing a mixture of MeOH and ethyl acetate. Recoveries were quantitative for all analytes in both type of samples. The distribution of PAEs was associated to the anthropogenic activities in the region [72].

The presence of several disrupting compounds, including PAEs and bisphenol A, in atmospheric particulate matter has been studied using a  $\mu$ -SPE device with copper(II) isonicotinate as sorbent material coupled with MAE [73].

In indoor air, the human exposure due to PFR concentrations appears to be higher than exposure due to PBDE concentrations [67]. Recently, a green protocol based on the combination of MAE and SPME has been proposed for the quantification of OPEs bound to airborne particulate matter. An experimental design was used for

the multivariate optimization of the parameters affecting the MAE as well as SPME. The satisfactory performance reached makes the proposed method a green and high-throughput alternative for OPE analysis [74].

For the analysis of environmental waters, novel microextraction approaches focus on the use of 'green' methodologies. In this context, combinations of MAE with ILs and surfactants have been introduced for the determination of industrial contaminants in different types of waters. Regarding PAEs analysis, an IL-based microwave-assisted DLLME method showed to be suitable for their determination in environmental matrices [75]. The use of surfactants was also explored for the extraction of PAEs from water employing cloud point extraction using a micellar extracting phase coupled with microwave assisted back extraction (CPE–MABE) [76]. The analytes were entrapped in the micelles of the non-ionic surfactant Triton X-114 and removed from the bulk phase by centrifugation. The resulting surfactant-rich phase was treated with water-immiscible solvents, and the target analytes were back extracted by short-term microwave application.

Recently, an innovative procedure based on HF-SBSE followed by microwave desorption has been proposed for determination of PAEs in environmental and biological matrices, allowing selective extraction of phthalate esters with low consumption of organic solvents and without the need of further clean-up steps [77].

### 2.3.2. Phenolic compounds

Phenolic compounds are among the most widely used chemicals in the world. Bisphenol A (BPA), used in the production of flame retardants and many other products, has estrogenic activity and belongs to category 1 of the EDCs priority list for wildlife and human health [78]. BPA, as one typical endocrine disrupter, has been ubiquitously detected in the aquatic environment, soils and sediments, and it has often been included in analytical methods developed for the determination of phenolic surfactants. Alkylphenol ethoxylates (APEOs) are one of the most widely used classes of surfactants, particularly, octylphenol ethoxylates (OPEOs) and nonylphenol ethoxylates (NPEOs), that are two of the most common non-ionic surfactants in the marketplace. APEOs are discharged to wastewater treatment facilities or directly released into the environment. During biological treatment, they are partially converted to more persistent metabolites such as nonylphenol diethoxylate (NPEO2) and nonylphenolmonocarboxylate (NP1EC), which belong to categories 1 and 2, respectively, of the EDCs priority list for wildlife and human health [79].

Methodologies based on the application of microwaves to the analysis of BPA, APEOs, and phenolic derivatives are summarized in Table 3. Several phenolic compounds such as BPA have been determined together with PPCPs (e.g. parabens, triclosan) [28] or with PAEs [73].

MAE has been proposed for the simultaneous determination of 11 EDCs, including alkylphenolic compounds, BPA, and various steroidal hormones, in sewage sludge samples [27]. A MAE based method for the determination of 15 alkyl, aryl, and halogenated phenols in sewage sludge and biosolids samples were also developed. Several experimental parameters, such as extraction solvent, temperature, and time were evaluated. The method was extensively applied to determine phenolic compounds in over 150 sludge and biosolids samples [80].

An analytical method, including MAE, SPE, derivatization and GC–MS analysis, was developed to detect BPA in sludge collected from five WWTPs and the concentrations found were above 100 ng g<sup>-1</sup>. This study also demonstrated that a large proportion (89%) of residual BPA entered the environment via the effluent [81].

Four extraction procedures, MAE, PLE, UAE, and high-pressure homogenizer (HPH), were compared for the isolation of BPA from

**Table 3**  
Industrial pollutants. Plasticizers, flame retardants and phenolic compounds.

Analyte	Sample	Sample pretreatment	MAE conditions	Extract treatment	Determination	Recovery (%)	LOD	RSD (%)	Year	Ref
<i>Plasticizers and flame retardants</i>										
6 PBDEs	Sludge (0.5 g)	Dried	10 mL MeOH (HCl (0.1 mol L <sup>-1</sup> )) MAE (1200 W, 90°C, 5 min)	Tris-citrate buffer solution (pH = 6) + 2 mL isoctane and mechanical shaking	GC-ICP-MS	95–104	0.2–0.3 ng g <sup>-1</sup>	<6	2016	[69]
9 PBDEs	Sediment (1 g)	Mixture with Florisil, alumina and acidic silica	10 mL hexane/acetone (1:1, v/v) MAE (150 W, ramp up to 130°C in 5 min (held 20 min))	Filtration, evaporation and redissolution	GC-MS/MS	71–118	0.5–10 ng g <sup>-1</sup> (LOQ)	<10	2016	[70]
7 PBDEs 11 OPEs and plasticizers	Soil Soil				GC-μECD GC-MS	52–87	0.09–2.4 ng g <sup>-1</sup> (LOQ)		2017	[66] [71]
15 PAEs	Sediment (1 g) and suspended particles	Air-dried, ground, homogenization and sieved	10 mL MeOH/ethyl acetate (1:1, v/v) MAE (150°C, 20 min)	Evaporation and reconstitution	GC-MS	84–109 (sediments) 91–109 (suspended particles)			2014	[72]
3 PAEs and BPA	Atmospheric particulate matter	Filtration	10 mL MeOH + μSPE device MAE (400 W, 40°C, 15 min)	Rinse, sonication, filtration, evaporation and reconstitution	LC-UV	82–119	2.0–8.5 ng L <sup>-1</sup>	<10	2015	[73]
10 OPEs 5 PAEs	Particulate matter Water		EtOH/water (1:1, v/v) MAE IL-based MADLME MAE (60°C, 2 min)	SPME	GC-MS/MS LC-DAD	81–117 85–103	0.7–1.9 μg L <sup>-1</sup>	<15 <6	2018 2013	[74] [75]
6 PAEs	Mineral water	Entrapment in Triton X-114 micelles and centrifugation	CPE-MABE: Surfactant-rich phase treated with solvents MAE		GC-FID	89–96	12–19 μg L <sup>-1</sup>	<6	2014	[76]
4 PAEs	Soil, water, food and biological samples				GC-MS	65–113	0.003 ng mL <sup>-1</sup>	<9	2017	[77]
<i>Phenolic compounds</i>										
15 Alkyl-, aryl- and halogenated phenols	Sewage sludge and biosolids	Dried	30 mL acetone/hexane (1:1, v/v) + 0.5 mL glacial acetic acid MAE (600 W, 80°C, 15 min)	Filtration, evaporation, reconstitution and acetylation	GC-MS	71–105	5–200 ng g <sup>-1</sup>	<6	2016	[80]
BPA	Sludge (1 g)	Freeze, grounded, sieved (sludge)	3 mL MeOH MAE (500 W, 3 min) (×4)	Clean-up	GC-MS	83–101	1 ng g <sup>-1</sup>		2015	[81]
BPA	Sewage sludge (2 g)	Dried	10 mL hexane/acetone (1:1, v/v) MAE (600 W, 110°C, 10 min) (×3)		LC-UV	86	100 ng L <sup>-1</sup> (wastewater) 100 ng g <sup>-1</sup> (sludge)	<4	2013	[82]
BPA and chlorinated derivatives	Sewage sludge (1 g)	Dried	10 mL ethyl acetate + 0.4 mL water MAE (1000 W, 90°C, 10 min)	Centrifugation, evaporation, reconstitution and centrifugation	LC-MS/MS	98–103	2–9 ng g <sup>-1</sup>	<6	2012	[83]
8 BPA analogs	Sediment (1 g)	Freeze, dried and sieved	10 mL THF/MeOH (1:1, v/v) MAE (150 W, 60°C, 5 min)	Filtration, concentration and reconstitution	LC-MS/MS	58–83	0.1–0.5 ng mL <sup>-1</sup>	<6	2017	[84]
Alkylphenols, butylparaben, BPA among others	Sediment (0.1 g)		5 mL 40 mM [C16MIM] [Br] solution FMAE (140 W, 90°C, 6 min)	Centrifugation and filtration	LC-DAD	67	100–800 ng g <sup>-1</sup> (LOQ)	<19	2012	[85]
Alkylphenols, butylparaben, BPA among others	Sediment (0.1 g)	Sieved	3 mL aqueous solution of CTAB FMAE (140 W, 90°C, 6 min)	Derivatization, agitation and centrifugation	GC-MS	107	20–360 ng g <sup>-1</sup>	<8	2012	[86]
8APs	Water		SPME-MAE (80 W, 5 min)		GC-MS	74–88	0.005–0.05 ng L <sup>-1</sup> (LOQ)	<8	2012	[87]

ACN: Acetonitrile. BPA: bisphenol A. CPE-MABE: Cloud point extraction-microwave-assisted back-extraction. DAD: Diode array detector. EtOH: Ethanol. FID: Flame ionization detector. FL: Fluorescence detector. GC: Gas chromatography. HF-L/SME: Hollow-fiber-liquid/solid phase microextraction. ICP: Inductively coupled plasma. LC: Liquid chromatography. LDTD-APCI: Laser diode thermal desorption-atmospheric pressure chemical ionization. LOD: Limit of detection. LOQ: Limit of quantification. MADLME: Microwave-assisted dispersive liquid-liquid microextraction. MAE: Microwave-assisted extraction. MAME: Microwave-assisted micellar extraction. MeOH: Methanol. MS: Mass spectrometry. MS/MS: Tandem mass spectrometry. OPEs: Octylphenols. PAEs: Phthalic acid esters. PBDE: Polybrominated diphenyl ethers. RSD: Relative standard deviation. SPE: Solid-phase extraction. UV: Ultraviolet detector. W: Watts. 4-CP: 4-cumylphenol. 4-t-OP: 4-tert-octylphenol.

activated sludge samples. MAE showed the highest recovery among the four extraction methods tested, with an average value of 86% for all samples [82]. The extraction efficiency of MAE was also compared with UAE and PLE for the determination of BPA and its chlorinated derivatives in complex sewage sludge matrices [83]. For each technique, the extraction parameters were optimized, offering the use of ethyl acetate/water, 1000 W, 90°C and 10 min the highest extraction efficiency. The statistical comparison of the methods did not demonstrate any significant differences between the extraction techniques.

MW- and US-assisted methods based on a quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample preparation approach followed by LC–MS/MS, were developed for the determination of 8 bisphenol analogs in sediments. The optimal MAE parameters implied the use of THF/MeOH as extractant solvent, 150 W at 60°C for 5 min. The proposed MW-QuEChERS method was successfully applied to 7 sediment samples and 20 serum samples allowing the biomonitoring of bisphenols [84]. A MAE method has been developed for the simultaneous extraction of two alkylphenols and seven parabens from soil and compared with a MSPD procedure [53]. Extracts were derivatized with BSTFA and analyzed by GC–MS. A glass sample holder put inside the microwave cell was used to allow the simultaneous extraction and clean-up of the samples. Both procedures showed good recoveries and sensitivity.

An innovative concentration strategy based on the use of IL and focused MAE for the preconcentration and extraction of organic contaminants from sediments, including 5 alkylphenols, the preservative butylparaben and 3 PAHs, has been proposed [85,86]. The main purpose of this study was to expand the applicability of preconcentration procedures with IL-based surfactants towards complex solid samples. This was the first description of an extraction/preconcentration procedure based on the use of the IL surfactant 1-hexadecyl-3-methylimidazoliumbromide for the determination of the target compounds.

The combination of MAE with other microextraction techniques, such as SPME has been proposed for the determination of 4-tert-octylphenol and 4-nonylphenol isomers in water samples. The method involved in-situ acetylation during the MAE-(HS)-SPME-procedure and the MAE conditions were 80 W for 5 min. The method demonstrated good performance and it was successfully applied to several environmental water samples [87].

### 3. Conclusions and trends

MAE technique has been successfully applied to the extraction of many chemical families of emerging pollutants (pharmaceuticals, PCPs, and industrial pollutants), from a wide range of environmental samples. MAE offers an easy to implement, powerful and rapid technology that provides good extraction yields similar (or often higher) to those obtained with classical techniques (e.g. Soxhlet). In addition, MAE performance is similar to that of recent extraction techniques such as SFE or PLE. Main features such as the great reduction of the extraction time, energy and solvent consumption, as well as the opportunity to perform multiple extractions, then increasing the number of samples processed daily, must be underlined. The reasonable cost of the equipment should be taken into account, as well.

The optimization of MAE conditions is an easy task owing to the full control that can be exerted on the main influential parameters (i.e., matrix moisture, nature of the solvent, extraction time, power applied and temperature in closed vessels). Chemometrical approaches by means of response surface methodology are often implemented to develop, improve and optimize the MAE process.

Most of the applications for emerging pollutants conducted the extraction at high temperature and high pressure using polar solvents. Modern MAE instruments enable performing the extraction

at powers up to 2000 W. In some cases, the use of water as extraction phase provided an efficient extraction, avoiding or minimizing the use of organic solvents.

Recent applications of MAE describe the simultaneous multi-analyte extraction (PCPs, pharmaceuticals, industrial pollutants...) as well as novel concentration strategies based on the use of non-organic solvents. In this context, the use of aqueous solutions, ILs or surfactants such as  $\mu$ SPE, DLLME, or LPME, has been showed to be successful for the extraction of antibiotics and plasticizers from a broad range of aqueous samples and air.

Another trend consists of implementing solvent-free extraction methods such as the one that associates MAE with SPME, already developed for the determination of pharmaceuticals, PCPs and industrial pollutants in water and in different solid environmental and biological matrices.

Recent smart batch microwave systems now include libraries of predefined methods and they are able to count the number of samples and to recognize the vessel type loaded. In the oldest systems, a temperature sensor was inserted into only one of the vessel assemblies, containing a sample with a solvent, to create a feedback control and then to regulate the microwave input power. The main drawback of this kind of device is that it supposes microwave energy is homogeneously absorbed by all samples in the system. This technology has recently switched to floor-mounted temperature sensors measuring the sample temperatures at the time they rotate inside the system. The average value of all the measured temperatures is then taken into account to regulate the microwave input power, thereby improving the control over the whole extraction process.

In addition, more flexible microwave devices that sequentially process the sample extractions have been recently introduced, providing many potential benefits versus batch style microwave systems. This approach enables operators to select an accurate temperature for every sample or to handle different sample types with different extracting solvents, all within the same rack. However, to achieve a batch-style approach, the main remaining obstacle is always at the sample–solvent separation after the extraction phase.

The most recent MAE instruments are even supplied with vessels of Weflon™, which allows the use of disposable glass vials inside them, avoiding the need to clean the vessel after each extraction. Most of the future application fields are likely to focus on improving the flexibility of the latest introduced sequential systems. For example, by giving the operator the capacity to manage the extraction conditions for each individual sample.

These improvements should enable scientists to develop and validate robust and reproducible methods suited for different chemicals in different environmental matrixes. Overall, MAE appears to be an excellent alternative, as green extraction method, for the determination of various families of emerging organic pollutants in many matrixes, thereby enabling its application within the regulatory environmental field.

These improvements should enable scientists to develop and validate robust and reproducible methods suited for different chemicals in different environmental matrixes. Overall, MAE appears to be an excellent alternative, as green extraction method, for the determination of various families of emerging organic pollutants in many matrixes, thereby enabling its application within the regulatory environmental field.

These improvements should enable scientists to develop and validate robust and reproducible methods suited for different chemicals in different environmental matrixes. Overall, MAE appears to be an excellent alternative, as green extraction method, for the determination of various families of emerging organic pollutants in many matrixes, thereby enabling its application within the regulatory environmental field.

### Acknowledgments

This work was supported by FEDER funds 2007–2013, and GPC2017/04 (Consolidated Research Groups Program, Xunta de Galicia).



## References

- [1] L. Chen, D. Song, Y. Tian, L. Ding, A. Yu, H. Zhang, Application of on-line microwave sample-preparation techniques, *TrAC – Trend. Anal. Chem.* 27 (2) (2008) 151–159.
- [2] T.M.E. Destandau, C. Elfakir, *Microwave-Assisted Extraction*, Royal Society of Chemistry Publishing, Cambridge, United Kingdom, 2013, p. 113e115.
- [3] P. Tatke, Y. Jaiswal, An overview of microwave assisted extraction and its applications in herbal drug research, *Res. J. Med. Plant.* 5 (1) (2011) 21–31.
- [4] M. Letellier, H. Budzinski, Microwave assisted extraction of organic compounds, *Analysis* 27 (3) (1999) 259–270.
- [5] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namienik, Green analytical chemistry in sample preparation for determination of trace organic pollutants, *TrAC – Trend. Anal. Chem.* 28 (8) (2009) 943–951.
- [6] L. Sanchez-Prado, C. Garcia-Jares, M. Llopart, Microwave-assisted extraction: application to the determination of emerging pollutants in solid samples, *J. Chromatogr. A.* 1217 (16) (2010) 2390–2414.
- [7] A. Abu-Samra, J.S. Morris, S.R. Koityohann, Wet ashing of some biological samples in a microwave oven, *Anal. Chem.* 47 (8) (1975) 1475–1477.
- [8] K. Ganzler, A. Salgo, K. Valko, Microwave extraction: a novel sample preparation method for chromatography, *J. Chromatogr. A.* 371 (1986) 299–306.
- [9] V. Lopez-Avila, R. Young, W.F. Beckert, Microwave-assisted extraction of organic compounds from standard reference soils and sediments, *Anal. Chem.* 66 (7) (1994) 1097–1106.
- [10] F.I. Onuska, K.A. Terry, Microwave extraction in analytical chemistry of pollutants: polychlorinated biphenyls, *J. High Resolut. Chromatogr.* 18 (7) (1995) 417–421.
- [11] F.I. Onuska, K.A. Terry, Extraction of pesticides from sediments using a microwave technique, *Chromatographia* 36 (1) (1993) 191–194.
- [12] O. Donard, B. Lalere, F. Martin, R. Lobinski, Microwave-assisted leaching of organotin compounds from sediments for speciation analysis, *Anal. Chem.* 67 (23) (1995) 4250–4254.
- [13] M.P. Llopart, R.A. Lorenzo, R. Cela, J.R.J. Paré, J.M.R. Balanger, K. Li, Phenol and methylphenol isomers determination in soils by in-situ microwave-assisted extraction and derivatisation, *J. Chromatogr. A.* 757 (1–2) (1997) 153–164.
- [14] M. Llopart, R.A. Lorenzo, R. Cela, K. Li, J.M.R. Balanger, J.R.J. Paré, Evaluation of supercritical fluid extraction, microwave-assisted extraction and sonication in the determination of some phenolic compounds from various soil matrices, *J. Chromatogr. A.* 774 (1–2) (1997) 243–251.
- [15] EPA, SW-846, *Microwave Extraction, 2007*. Available at: <https://www.epa.gov/hw-sw846/sw-846-test-method-3546-microwave-extraction>.
- [16] K. Li, J.M.R. Balanger, M.P. Llopart, R.D. Turpin, R. Singhvi, J.R.J. Paré, Evaluation of rapid solid sample extraction using the microwave-assisted process (MAP [TM]) under closed-vessel conditions, *Spectrosc. Ott.* 13 (1997) 1–14.
- [17] L. Sanchez-Prado, C. Garcia-Jares, T. Dagnac, M. Llopart, Microwave-assisted extraction of emerging pollutants in environmental and biological samples before chromatographic determination, *TrAC – Trend. Anal. Chem.* 71 (2015) 119–143.
- [18] M. Llopart, C. Garcia-Jares, M. Celeiro, T. Dagnac, *Extraction|Microwave-Assisted Extraction*, Encyclopedia of Analytical Science, third ed., 2019, pp. 67–77. Oxford.
- [19] K. Madej, Microwave-assisted and cloud-point extraction in determination of drugs and other bioactive compounds, *TrAC – Trend. Anal. Chem.* 28 (4) (2009) 436–446.
- [20] V. Camel, Microwave-assisted solvent extraction of environmental samples, *TrAC – Trend. Anal. Chem.* 19 (4) (2000) 229–248.
- [21] V. Camel, Recent extraction techniques for solid matrices-supercritical fluid extraction, pressurized fluid extraction and microwave-assisted extraction: their potential and pitfalls, *Analyst* 126 (7) (2001) 1182–1193.
- [22] M. Llopart, R.A. Lorenzo, R. Cela, J.R.J. Paré, Optimization of a microwave-assisted extraction method for phenol and methylphenol isomers in soil samples using a central composite design, *Analyst* 122 (2) (1997) 133–137.
- [23] B. Petrie, R. Barden, B. Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring, *Water Res.* 72 (2015) 3–27.
- [24] R. Guedes-Alonso, S. Santana-Viera, S. Montesdeoca-Esponda, C. Afonso-Olivares, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Application of microwave-assisted extraction and ultra-high performance liquid chromatography-tandem mass spectrometry for the analysis of sex hormones and corticosteroids in sewage sludge samples, *Anal. Bioanal. Chem.* 408 (24) (2016) 6833–6844.
- [25] D.D. Snow, T. Damon-Powell, S. Onanong, D.A. Cassada, Sensitive and simplified analysis of natural and synthetic steroids in water and solids using on-line solid-phase extraction and microwave-assisted solvent extraction coupled to liquid chromatography tandem mass spectrometry atmospheric pressure photoionization, *Anal. Bioanal. Chem.* 405 (5) (2013) 1759–1771.
- [26] T. Vega-Morales, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Evaluation of the presence of endocrine-disrupting compounds in dissolved and solid wastewater treatment plant samples of Gran Canaria Island (Spain), *Biomed. Res. Int.* 2013 (2013).
- [27] T. Vega-Morales, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, The use of microwave assisted extraction and on-line chromatography-mass spectrometry for determining endocrine-disrupting compounds in sewage sludges, *Water Air Soil Pollut.* 224 (3) (2013) 1486.
- [28] A. Azzouz, E. Ballesteros, Determination of 13 endocrine disrupting chemicals in environmental solid samples using microwave-assisted solvent extraction and continuous solid-phase extraction followed by gas chromatography-mass spectrometry, *Anal. Bioanal. Chem.* 408 (1) (2016) 231–241.
- [29] J. Kumirska, N. Migowska, M. Caban, P. Aukaszewicz, P. Stepnowski, Simultaneous determination of non-steroidal anti-inflammatory drugs and oestrogenic hormones in environmental solid samples, *Sci. Total Environ.* 508 (2015) 498–505.
- [30] B. Petrie, J. Youdan, R. Barden, B. Kasprzyk-Hordern, Multi-residue analysis of 90 emerging contaminants in liquid and solid environmental matrices by ultra-high-performance liquid chromatography tandem mass spectrometry, *J. Chromatogr. A.* 1431 (2016) 64–78.
- [31] S.E. Evans, P. Davies, A. Lubben, B. Kasprzyk-Hordern, Determination of chiral pharmaceuticals and illicit drugs in wastewater and sludge using microwave assisted extraction, solid-phase extraction and chiral liquid chromatography coupled with tandem mass spectrometry, *Anal. Chim. Acta* 882 (2015) 112–126.
- [32] A. Morales-Toledo, C. Afonso-Olivares, S. Montesdeoca-Esponda, R. Guedes-Alonso, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Optimization and development of ultra-high performance liquid chromatography for the determination of acetylsalicylic acid, naproxen, ibuprofen and gemfibrozil in sewage and sludge samples, *Curr. Anal. Chem.* 12 (6) (2016) 545–552.
- [33] D.P. Mohapatra, S.K. Brar, R.D. Tyagi, P. Picard, R.Y. Surampalli, Carbamazepine in municipal wastewater and wastewater sludge: ultrafast quantification by laser diode thermal desorption-atmospheric pressure chemical ionization coupled with tandem mass spectrometry, *Talanta* 99 (2012) 247–255.
- [34] S. Montesdeoca-Esponda, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Combination of microwave-assisted micellar extraction with liquid chromatography tandem mass spectrometry for the determination of fluoroquinolone antibiotics in coastal marine sediments and sewage sludges samples, *Biomed. Chromatogr.* 26 (1) (2012) 33–40.
- [35] N. Dorival-García, A. Zafra-Gomez, F.J. Camino-Sanchez, A. Navalón, J.L. Vilchez, Analysis of quinolone antibiotic derivatives in sewage sludge samples by liquid chromatography-tandem mass spectrometry: comparison of the efficiency of three extraction techniques, *Talanta* 106 (2013) 104–118.
- [36] A. Speltini, M. Sturini, F. Maraschi, S. Viti, D. Sbarbada, A. Profumo, Fluoroquinolone residues in compost by green enhanced microwave-assisted extraction followed by ultra performance liquid chromatography tandem mass spectrometry, *J. Chromatogr. A.* 1410 (2015) 44–50.
- [37] L. Tong, H. Liu, C. Xie, M. Li, Quantitative analysis of antibiotics in aquifer sediments by liquid chromatography coupled to high resolution mass spectrometry, *J. Chromatogr. A.* 1452 (2016) 58–66.
- [38] J. Kazakova, R. Fernandez-Torres, M.A. Ramos-Payan, M.Á.N. Bello-Lopez, Multiresidue determination of 21 pharmaceuticals in crayfish (*Procambarus clarkii*) using enzymatic microwave-assisted liquid extraction and ultrahigh-performance liquid chromatography-triple quadrupole mass spectrometry analysis, *J. Pharm. Biomed. Anal.* 160 (2018) 144–151.
- [39] Y. Zhang, W. Guo, Z. Yue, L. Lin, F. Zhao, P. Chen, W. Wu, H. Zhu, B. Yang, Y. Kuang, Rapid determination of 54 pharmaceutical and personal care products in fish samples using microwave-assisted extraction-hollow fiber-liquid/solid phase microextraction, *J. Chromatogr. B.* 1051 (2017) 41–53.
- [40] P. Huang, P. Zhao, X. Dai, X. Hou, L. Zhao, N. Liang, Trace determination of antibacterial pharmaceuticals in fishes by microwave-assisted extraction and solid-phase purification combined with dispersive liquid-liquid microextraction followed by ultra-high performance liquid chromatography-tandem mass spectrometry, *J. Chromatogr. B.* 1011 (2016) 136–144.
- [41] J. Liu, X. Pan, B. Huang, K. Fang, Y. Wang, J. Gao, An improved method for simultaneous analysis of steroid and phenolic endocrine disrupting chemicals in biological samples, *Int. J. Environ. Anal. Chem.* 92 (10) (2012) 1135–1149.
- [42] Z. Jiao, Z. Guo, S. Zhang, H. Chen, Microwave-assisted micro-solid-phase extraction for analysis of tetracycline antibiotics in environmental samples, *Int. J. Environ. Anal. Chem.* 95 (1) (2015) 82–91.
- [43] P. Lukaszewicz, A. Bialk-Bielinska, J. Dolzonek, J. Kumirska, M. Caban, P. Stepnowski, A new approach for the extraction of tetracyclines from soil matrices: application of the microwave-ramos extraction technique, *Anal. Bioanal. Chem.* 410 (6) (2018) 1697–1707.
- [44] P. Lukaszewicz, J. Kumirska, A. Bialk-Bielinska, J. Dolzonek, P. Stepnowski, Assessment of soils contamination with veterinary antibiotic residues in Northern Poland using developed MAE-SPE-LC/MS/MS methods, *Environ. Sci. Pollut. Res.* 24 (26) (2017) 21233–21247.
- [45] A. Speltini, M. Sturini, F. Maraschi, A. Profumo, A. Albin, Microwave-assisted extraction and determination of enrofloxacin and danofloxacin photo-transformation products in soil, *Anal. Bioanal. Chem.* 404 (5) (2012) 1565–1569.
- [46] P.N. Carvalho, A.N. Pirra, M.C.P. Basto, C.M.R. Almeida, Multi-family methodologies for the analysis of veterinary pharmaceutical compounds in sediment and sludge samples: comparison among extraction techniques, *Anal. Methods* 5 (22) (2013) 6503–6510.
- [47] D. Drijaca, D. Asperger, M. Ferencak, M. Gavranic, S. Babie, I. Mikac, M. Ahel, Comparison of four extraction methods for the determination of veterinary pharmaceuticals in sediment, *Chromatographia* 79 (3–4) (2016) 209–223.

- [48] V.K. Balakrishnan, K.N. Exall, J.M. Toito, The development of a microwave-assisted extraction method for the determination of sulfonamide antibiotics in sediments and soils, *Canad. J. Chem.* 92 (5) (2014) 369–377.
- [49] H. Wang, J. Ding, L. Ding, N. Ren, Analysis of sulfonamides in soil, sediment, and sludge based on dynamic microwave-assisted micellar extraction, *Environ. Sci. Pollut. Res.* 23 (13) (2016) 12954–12965.
- [50] M.a. del Mar Gil-Diaz, A. PÁrez-Sanz, M.a.C. Lobo, Validation of a microwave-assisted micella retraction method for the oxibendazole determination in soil samples, *Afinidad* 69 (559) (2012).
- [51] Y. Song, L. Wu, C. Lu, N. Li, M. Hu, Z. Wang, Microwave-assisted liquid-liquid microextraction based on solidification of ionic liquid for the determination of sulfonamides in environmental water samples, *J. Sep. Sci.* 37 (23) (2014) 3533–3538.
- [52] R. Loos, R. Carvalho, D.C. Antonio, S. Comero, G. Locoro, S. Tavazzi, B. Paracchini, M. Ghiani, T. Lettieri, L. Blaha, EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents, *Water Res.* 47 (17) (2013) 6475–6487.
- [53] R.A. Pérez, B. Alberio, E. Miguel, C. Sánchez-Brunete, Determination of parabens and endocrine-disrupting alkylphenols in soil by gas chromatography-mass spectrometry following matrix solid-phase dispersion or in-column microwave-assisted extraction: a comparative study, *Anal. Bioanal. Chem.* 402 (7) (2012) 2347–2357.
- [54] K. Kotnik, T. Kosjek, U. Krajnc, E. Heath, Trace analysis of benzophenone-derived compounds in surface waters and sediments using solid-phase extraction and microwave-assisted extraction followed by gas chromatography-mass spectrometry, *Anal. Bioanal. Chem.* 406 (13) (2014) 3179–3190.
- [55] S. Montesdeoca-Esponda, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Microwave-assisted extraction combined with on-line solid phase extraction followed by ultra-high-performance liquid chromatography with tandem mass spectrometric determination of benzotriazole UV stabilizers in marine sediments and sewage sludges, *J. Sep. Sci.* 36 (4) (2013) 781–788.
- [56] A. Speltini, M. Sturini, F. Maraschi, A. Porta, A. Profumo, Fast low-pressurized microwave-assisted extraction of benzotriazole, benzothiazole and benzenesulfonamide compounds from soil samples, *Talanta* 147 (2016) 322–327.
- [57] L. Lopardo, A. Rydevik, B. Kasprzyk-Hordern, A new analytical framework for multi-residue analysis of chemically diverse endocrine disruptors in complex environmental matrices utilising ultra-performance liquid chromatography coupled with high-resolution tandem quadrupole time-of-flight mass spectrometry, *Anal. Bioanal. Chem.* 411 (3) (2019) 689–704.
- [58] R. Barro, C. Garcia-Jares, M. Llompart, Indoor air sampling, in: J. Pawliszyn (Editor), *Comprehensive Sampling and Sample Preparation*, Elsevier, Netherlands, 2012.
- [59] I.T.I. Wang, S.-F. Cheng, S.-W. Tsai, Determinations of airborne synthetic musks by polyurethane foam coupled with triple quadrupole gas chromatography tandem mass spectrometer, *J. Chromatogr. A.* 1330 (2014) 61–68.
- [60] A. Speltini, F. Maraschi, M. Sturini, M. Contini, A. Profumo, Dispersive multi-walled carbon nanotubes extraction of benzenesulfonamides, benzotriazoles, and benzothiazoles from environmental waters followed by microwave desorption and HPLC-HESI-MS/MS, *Anal. Bioanal. Chem.* 409 (28) (2017) 6709–6718.
- [61] S.C. Cunha, A. Pena, J.O. Fernandes, Dispersive liquid-liquid microextraction followed by microwave-assisted silylation and gas chromatography-mass spectrometry analysis for simultaneous trace quantification of bisphenol A and 13 ultraviolet filters in wastewaters, *J. Chromatogr. A.* 1414 (2015) 10–21.
- [62] X. Li, G. Chen, J. Liu, Y. Liu, X. Zhao, Z. Cao, L. Xia, G. Li, Z. Sun, S. Zhang, A rapid, accurate and sensitive method with the new stable isotopic tags based on microwave-assisted dispersive liquid-liquid microextraction and its application to the determination of hydroxyl UV filters in environmental water samples, *Talanta* 167 (2017) 242–252.
- [63] M.W. Wu, P.C. Yeh, H.C. Chen, L.L. Liu, W.H. Ding, A microwave-assisted headspace solid-phase microextraction for rapid determination of synthetic polycyclic and nitro-aromatic musks in fish samples, *J. Chin. Chem. Soc.* 60 (9) (2013) 1169–1174.
- [64] S.-F. Wu, L.-L. Liu, W.-H. Ding, One-step microwave-assisted headspace solid-phase microextraction for the rapid determination of synthetic polycyclic musks in oyster by gas chromatography-mass spectrometry, *Food Chem.* 133 (2) (2012) 513–517.
- [65] S.D. Richardson, S.Y. Kimura, Water analysis: emerging contaminants and current issues, *Anal. Chem.* 88 (1) (2015) 546–582.
- [66] M. Vavrova, L. Mravcova, I. Vondrackova, M. Hroch, J. Caslavsky, H.Z. Gargosova, V. Vecerek, Brominated flame retardants in soils from fire places, *Fresenius Environ. Bull.* 21 (11) (2012) 3267–3271.
- [67] I. Van der Veen, J. de Boer, Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis, *Chemosphere* 88 (10) (2012) 1119–1153.
- [68] M.A.-E. Abdallah, G. Pawar, S. Harrad, Human dermal absorption of chlorinated organophosphate flame retardants; implications for human exposure, *Toxicol. Appl. Pharm.* 291 (2016) 28–37.
- [69] P. Novak, T. Zuliani, R. Milačić, J. Ščančar, Development of an analytical method for the determination of polybrominated diphenyl ethers in sewage sludge by the use of gas chromatography coupled to inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 915 (2016) 27–35.
- [70] S. Song, M. Shao, H. Tang, Y. He, W. Wang, L. Liu, J. Wu, Development, comparison and application of sorbent-assisted accelerated solvent extraction, microwave-assisted extraction and ultrasonic-assisted extraction for the determination of polybrominated diphenyl ethers in sediments, *J. Chromatogr. A.* 1475 (2016) 1–7.
- [71] K. Cui, J. Wen, F. Zeng, X. Zhou, S. Li, Z. Zeng, Determination of organophosphate ester flame retardants and plasticizers in soil samples by microwave-assisted extraction coupled with silica gel/alumina multilayer solid-phase extraction and gas chromatography-mass spectrometry, *Anal. Methods* 9 (6) (2017) 986–993.
- [72] X. Zheng, B.-T. Zhang, Y. Teng, Distribution of phthalate acid esters in lakes of Beijing and its relationship with anthropogenic activities, *Sci. Total Environ.* 476 (2014) 107–113.
- [73] Z. Jiao, Z. Guo, S. Zhang, H. Chen, H. Xie, S. Zeng, Novel extraction for endocrine disruptors in atmospheric particulate matter, *Anal. Lett.* 48 (8) (2015) 1355–1366.
- [74] A. Naccarato, A. Tassone, S. Moretti, R. Elliani, F. Sprovieri, N. Pirrone, A. Tagarelli, A green approach for organophosphate ester determination in airborne particulate matter: microwave-assisted extraction using hydroalcoholic mixture coupled with solid-phase microextraction gas chromatography-tandem mass spectrometry, *Talanta* 189 (2018) 657–665.
- [75] R. Wang, P. Su, Y. Yang, Optimization of ionic liquid-based microwave-assisted dispersive liquid-liquid microextraction for the determination of plasticizers in water by response surface methodology, *Anal. Methods* 5 (4) (2013) 1033–1039.
- [76] Y.-K. Lv, W. Zhang, M.-M. Guo, F.-F. Zhao, X.-X. Du, Centrifugal micro-extraction tube-cloud point extraction coupled with gas chromatography for simultaneous determination of six phthalate esters in mineral water, *Anal. Methods* 7 (2) (2015) 560–565.
- [77] J. Li, Y.B. Wang, Q. Su, S. Wu, L. Wu, Hollow fiber stir bar sorptive extraction for determination of phthalic acid esters in environmental and biological matrices, *J. Sep. Sci.* 40 (4) (2017) 893–900.
- [78] J.R. Rochester, A.L. Bolden, Bisphenol S and F: a systematic review and comparison of the hormonal activity of bisphenol A substitutes, *Environ. Health Perspect.* 123 (7) (2015) 643–650.
- [79] S. Esteban, M. Gorga, M. Petrovic, S. Gonzalez-Alonso, D. Barceló, Y. Valcarcel, Analysis and occurrence of endocrine-disrupting compounds and estrogenic activity in the surface waters of Central Spain, *Sci. Total Environ.* 466 (2014) 939–951.
- [80] H.-B. Lee, M. Lewina Svoboda, T.E. Peart, S.A. Smyth, Optimization of a microwave-assisted extraction procedure for the determination of selected alkyl, aryl, and halogenated phenols in sewage sludge and biosolids, *Water Qual. Res. J. Can.* 51 (4) (2016) 344–356.
- [81] J. Zhang, B.-W. Yang, B. Song, D.-Q. Wang, N.-Q. Ren, Bisphenol A in wastewater and sewage sludge from five wastewater treatment plants of Guilin, China, *Fresenius Environ. Bull.* 24 (11) (2015) 3609–3615.
- [82] B. Banihashemi, R.L. Droste, Trace level determination of bisphenol-A in wastewater and sewage sludge by high-performance liquid chromatography and UV detection, *Water Qual. Res. J. Can.* 48 (2) (2013) 133–144.
- [83] N. Dorival-García, A. Zafra-Gómez, A. Navalón, J.L. Vilchez, Analysis of bisphenol A and its chlorinated derivatives in sewage sludge samples. Comparison of the efficiency of three extraction techniques, *J. Chromatogr. A.* 1253 (2012) 1–10.
- [84] S. Song, M. Shao, W. Wang, Y. He, X. Dai, H. Wang, L. Liu, F. Guo, Development and evaluation of microwave-assisted and ultrasound-assisted methods based on a quick, easy, cheap, effective, rugged, and safe sample preparation approach for the determination of bisphenol analogues in serum and sediments, *J. Sep. Sci.* 40 (23) (2017) 4610–4618.
- [85] B. Delgado, V. Pino, J.L. Anderson, J.H. Ayala, A.M. Afonso, V. González, An in-situ extraction-preconcentration method using ionic liquid-based surfactants for the determination of organic contaminants contained in marine sediments, *Talanta* 99 (2012) 972–983.
- [86] B.r. Delgado, V.n. Pino, J.H. Ayala, A.M. Afonso, V. González, A novel preconcentration strategy for extraction methods based on common cationic surfactants: an alternative to classical coextractive extraction, *J. Chromatogr. A.* 1257 (2012) 9–18.
- [87] Y.P. Wu, Y.C. Wang, W.H. Ding, Rapid determination of alkylphenols in aqueous samples by in situ acetylation and microwave-assisted headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry, *J. Sep. Sci.* 35 (16) (2012) 2122–2130.