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Review

Extraction and preconcentration techniques for chromatographic determination of chlorophenols in environmental and food samples

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ABSTRACT

Methods for chlorophenols (CPs) determination (with low limits of detection) that can be applied to real environmental samples (waters, sediments, soils, biological tissues) and food are reviewed. Special emphasis is given to sampling, storage conditions and the application of preconcentration techniques for the determination of CPs using chromatographic methods. Solid phase extraction, solid phase microextraction, stir bar sorptive extraction, liquid phase microextraction, dispersive liquid–liquid microextraction, liquid–liquid–liquid microextraction and purge and trap methods are considered. Methods for microwave and ultrasonic extraction of CPs from solid matrices are also focused.

Contents

Abbreviations: acetyl, acetylation; AES, atomic emission spectrometry; ASE, accelerated solvent extraction; CAR–PDMS, carboxen–polydimethylsiloxane; CF, continuous flow; CPs, chlorophenols; CRM, certified reference materials; CT, cryogenic trapping; CW-TPR, carbowax-templated resin; DAD, diode array detection; DLLME, dispersive liquid–liquid microextraction; DVB–CAR–PDMS, divinylbenzene–carboxen–polydimethylsiloxane; dw, dry weight; EC, electrochemical detection; ECD, electron capture detection; FCC, ferrocenecarboxylic acid chloride; FID, flame ionization detection; FLD, fluorescence detection; FLLabel, fluorescence labeling; GC, gas chromatography; GCB, graphitized carbon black; HLB, hydrophilic lipophilic balance; HS, headspace; IC, ion chromatography; LC, liquid chromatography; LD, liquid desorption; LLE, liquid–liquid extraction; LLLME, liquid–liquid–liquid microextraction; LODs, limits of detection; LOQs, limits of quantification; LPME, liquid phase microextraction; LVI, large volume injection; MASE, membrane-assisted solvent extraction; mono-CPs, monochlorophenols; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MSPE, magnetic solid phase extraction; MW, microwave; PA, polyacrilate; P-A, purge-assisted; PCP, pentachlorophenol; PDMS, polydimethylsiloxane; PDMS–DVB, polydimethylsiloxane-divinylbenzene; PFBenzoyl, pentafluorobenzoylation; PFBenzyl, pentafluorobenzylation; POLE, polyoxyethylene (10) lauryl ether; PT, purge and trap; PTV, programmed temperature vaporization; QuEChERS, quick, easy, cheap, effective, rugged and safe; SBSE, stir bar sorptive extraction; SD, steam distillation; SDE, steam distillation extraction; S–DVB, styrene–divinylbenzene; SM, stir membrane; SPE, solid phase extraction; SPME, solid phase microextraction; TD, thermal desorption; TEA, triethylamine; UV, ultraviolet detection.

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1. Introduction

The chlorophenols (CPs) are chemicals with high toxicity including estrogenic, mutagenic and carcinogenic effects [1]. Additionally, they have very high acute toxicity, interfering with oxidative phosphorylation and inhibiting ATP synthesis. There is also evidence that CPs are precursors of extremely toxic dioxins and furans either upon incineration [2] or after metabolism in humans [3].

The sources of CPs to the environment are related to their widespread use as pesticides, leather or wood impregnation agents and in various industries. These compounds can be formed during environmental degradation of some pesticides and of the bactericide triclosan [4,5] or during the chlorination of drinking water [1].

Various methods for analysis of CPs in environmental samples have been proposed, mainly based on chromatographic separation. In most cases, a previous preconcentration/cleaning step is necessary. However, even using preconcentration, some of the methods presented relatively high limits of detection (LODs) and, therefore, can be used only for very contaminated samples. For practical purposes, in this paper the LODs of the different methods will be compared to the concentration range for CPs found in real samples.

The concentrations of polychlorinated CPs (biocides) in wood and cork samples is variable, from less than ng g^{-1} to tens ng g^{-1} [6,7] and even μg g^{-1} or more [8,9]. The presence of CPs in food results from environmental contamination or migration from food storage containers treated with biocides. Pentachlorophenol (PCP) has been found in fruits in concentrations from ng g^{-1} to several hundreds ng g^{-1} fresh weight [8]. The levels of CPs in the total diet (Slovak Republic) were on average in the order of ng g^{-1} and several tens of ng g^{-1} fresh weight, the highest values being observed for 2,4-dichlorophenol (2,4-DCP) and 2,6-dichlorophenol (2,6-DCP) [3]. In clam tissues [10] and in honey [11], CPs have been found in the low ng g^{-1} range. CPs have also been found in wines, mainly after bleaching of wooden vessels or treatment with biocides of vessels and cork stoppers. The presence of CPs and of their methylated metabolites chloroanisoles is the reason of a bad flavour of wine [12]. Levels of CPs in the order of ng mL^{-1} were found in wine with such sensory problems [13]. In milk samples, CPs have been found at levels up to several μg L^{-1} [3].

Depending on the type of the wastewater, the concentrations of CPs with different degree of chlorination can be very variable, from ng L^{-1} [5,14–16] to μg L^{-1} [17–22] and even mg L^{-1} range [23]. Most often detected CPs (or those often found at the highest concentrations) include: 2-chlorophenol (2-CP); 2,4-DCP; 4-chlorophenol (4-CP); 4-chloro-3-methylphenol (4-C-3-MP); 2,6-DCP; 2,4,6-trichlorophenol (2,4,6-TCP); 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and PCP. The sewage treatment plants can be considered as sources of these compounds in aquatic environments, especially if the treatment processes cannot remove them effectively. Levels of CPs in landfill leaches are usually about 100 ng L^{-1} or less; higher levels (μg L^{-1} range) were sometimes reported, especially for PCP [24–26].

The concentrations of CPs in open ocean waters are about 5–10 ng L^{-1} or even less [1]. Relatively high concentrations were measured in coastal seawater, up to 1500 ng L^{-1} for both 2,4-DCP and PCP [27]. Much more variable levels have been observed in natural freshwater, from low ng L^{-1} to low mg L^{-1} range [1,19,28–32]. Irrespectively of the huge variation, the medium concentrations are usually very low. For instance, Gao et al. [33] have found medium levels of 5, 2, and 50 ng L^{-1} for 2,4-DCP, 2,4,6-TCP and PCP, respectively, in China's Rivers.

Due to their lipophilic properties, the CPs tend to sorb onto solid material and to accumulate into soils, sediments, sludge and ash samples. Depending on the type of soils and sediments and the pollution sources, the concentration of CPs can range from bellow ng g^{-1} [4] to tens and hundreds ng g^{-1} or even more than μg g^{-1} [34–37]. In sludge samples, 2,4-DCP and 2,4,6-TCP were found in the levels 55–350 ng g^{-1} and 7.5–38 ng g^{-1}, respectively [4]. In ash samples, levels of CPs in the order of tens ng g^{-1} were observed [2].

Some CPs (2-CP, 4-C-3-MP, 2,4-DCP, 2,4,6-TCP, PCP) have been included in the list of priority pollutants established by the US Environmental Protection Agency [36]. European Union legislation has set a maximum admissible concentration (MAC) of total phenols in drinking water to be 0.5 μg L^{-1} and 0.1 μg L^{-1} for individual compounds [32] and 1 μg L^{-1} for PCP in inland and other surface waters [16].

The physical properties of CPs vary greatly, depending on the number of chlorine atoms and their position relative to OH group (see some examples in Table 1), which complicates their simultaneous determination. The current trends of CPs determination in environmental and biological samples using chromatography are summarized in this review. The abbreviation CPs stands for any of the compounds listed in Table 1. However, in the text, whenever necessary, the analytes' type could be specified, like monochlorophenols (mono-CPs) or polychlorinated CPs. Special attention is given to sample storage, pre-concentration of the analytes and quality control. The methods are compared with respect to the matrices, analytes, LODs and sample size.

2. Sampling and storage

2.1. Liquid samples

Water samples are usually collected in amber bottles and stored at 4 °C until analysis [38–44] but storage at 10 °C in darkness has also been reported [45]. CPs have different stability when stored in acidified river water samples at 4 °C and some of them, like 2-CP and 4-CP, suffered 15% losses in 28 days [46]. It is advisable to analyze the samples within 24 h [42] to 48 h after collection [5,47]. It is worth noticing that, in biologically active samples, CPs can be rapidly degraded [48]. To prevent losses and to save storage space, it is advantageous to preconcentrate CPs on solid phase extraction (SPE) cartridges, like Isolute EVN+ (a polystyrene-divinylbenzene polymer) and freeze them before elution and analysis [17]. Other possibility can be static sampling using liquid–liquid–liquid microextraction (LLLME) in which the CPs were extracted into an acceptor phase situated in the lumen of a hollow fibre [49]. Samples can be collected directly in vials, containing NaCl, and acidified and stored at 4 °C until analysis involving

Table 1
Vapour pressures (P_0 at 25 °C), octanol–water partition coefficients ($\log K_{ow}$) and acidity constants (p*Ka*) of different chlorophenols commonly found in environmental and biological samples.

Compound	P_0 (mm Hg)	$\log K_{ow}$	p*Ka*
2-Chlorophenol (2-CP)	1.0–2.4[a]	2.03–2.29[a]	8.3–8.6[c]
3-Chlorophenol (3-CP)	0.25–0.32[a]	2.17–2.63[a]	8.8–9.1[c]
4-Chlorophenol (4-CP)	0.21[a]	2.17–2.88[a]	9.1–9.4[c]
4-Chloro-2-methylphenol (4-C-2-MP)			9.5–10.5[d]
4-Chloro-3-methylphenol (4-C-3-MP)	0.05[a]	2.18–3.10[a]	9.4–9.7[d]
2-Chloro-5-methylphenol (2-C-5-MP)			7.8–9.7[d]
4-Chloro-3,5-dimethylphenol (4-C-3,5-DMP)			9.4–10.6[d]
2,3-Dichlorophenol (2,3-DCP)		3.15–3.19[c]	6.4–7.8[c]
2,4-Dichlorophenol (2,4-DCP)	0.09–0.16[a]	2.87–3.61[a]	7.5–8.1[c]
2,5-Dichlorophenol (2,5-DCP)		3.20–3.24[c]	6.4–7.5[c]
2,6-Dichlorophenol (2,6-DCP)	0.08–0.10[a]	2.34–3.36[a]	6.7–7.8[c]
3,4-Dichlorophenol (3,4-DCP)		3.05–3.68[a]	7.4–8.7[c]
3,5-Dichlorophenol (3,5-DCP)		2.57–3.56[c]	6.9–8.3[c]
2,3,4-Trichlorophenol (2,3,4-TCP)	0.008–0.026[a]	3.51–4.07[a]	6.5–7.7[c]
2,3,5-Trichlorophenol (2,3,5-TCP)	0.022[b]	3.84–4.56[c]	6.8–7.4[c]
2,3,6-Trichlorophenol (2,3,6-TCP)	0.0025[b]	3.88[c]	6.0–7.1[c]
2,4,5-Trichlorophenol (2,4,5-TCP)	0.02–0.057[a]	3.52–4.19[a]	7.0–7.7[c]
2,4,6-Trichlorophenol (2,4,6-TCP)	0.006–0.032[a]	2.67–4.03[a]	6.0–7.4[c]
3,4,5-Trichlorophenol (3,4,5-TCP)	0.0025[b]	4.01–4.39[c]	7.7–7.8[c]
2,3,4,5-Tetrachlorophenol (2,3,4,5-TeCP)	0.00034[b]	4.21–5.03[a]	6.2–7.0[c]
2,3,4,6-Tetrachlorophenol (2,3,4,6-TeCP)	0.004–0.006[a]	4.10–4.45[a]	5.3–6.6[c]
2,3,5,6-Tetrachlorophenol (2,3,5,6-TeCP)	0.00067[b]	3.88–4.90[a]	5.2–5.5[c]
Pentachlorophenol (PCP)	0.00005–0.0017[a]	3.81–5.86[a]	4.7–4.9[c]

[a] [111].
[b] [82].
[c] [112].
[d] [113].

solid phase microextraction (SPME) [29]. The authors reported that the standard solutions in reagent water (ultrapure) were stable in these conditions up to 25 days. For CPs analysis in tap water, sodium thiosulfate pentahydrate, at concentration between 80 mg L^{-1} [29] and 1000 mg L^{-1} [50], has been added just after sampling to prevent the oxidation of the analytes by the residual chlorine. Sodium sulfite (1000 mg L^{-1}) [51] and ascorbic acid (175 mg L^{-1}) [52] have been also used with the same purpose. Wine samples, when not analyzed immediately, can be stored at 4 °C in order to prevent losses from the most volatile analytes [13].

Clear water samples may be analyzed without previous filtration [30,47,53]. However, even for relatively clean samples, filtration can be required to prevent blocking of SPE cartridges [42]. Additionally, if suspended particles are left unfiltered, it is possible that the partitioning of CPs between the particulate and dissolved phases would change during storage. Filters with different pore size in the range 0.22 μm [38,41,54,55]–1.5 μm [39] have been used. It seems there is no consensus about the most suitable pore size of the filters to be used in sample filtration in order to make easier the comparison of field data.

Different filtration materials have been used so far: nylon [19,21,41,43,51,56], glass fibre filters [14,15,20,23,32,33,39,40,57], cellulose [49,54,55,58], cellulose acetate [38] and nitrocellulose [5]. A proper choice of the filtration material is important. For example, filtration of non acidified water samples using nylon filters led to marked losses of CPs, especially the polychlorinated ones, while glass fibre filters could be used without adsorbing or destroying the analytes [15]. However, nylon has been successfully used by other authors to filter samples after acidification [19], or even without acidification [16,41]. Since no consensus over the proper filtration material is achieved, centrifugation of the samples may be an alternative [59].

2.2. Sediment, soil, ash and sludge samples

For the determination of CPs in solid samples there is no consensus regarding the most suitable way of drying and sieving the samples. Literature reports drying of sediment and soil samples by lyophilisation [4,34] or at room temperature [36,37,60–62], 105 °C [63] and 120 °C [64]. Sediment, soil or sludge samples have been sieved to particle size below 2 mm [35,36,60,61], 841 μm [64], 300 μm [4,37,62,63,65] and 120 μm [34]. In most of the cases, the samples have been stored until analysis at 4 °C [34–37,60,61,63], rarely at room temperature [64]. For ash samples, sieving to obtain particle size below 60 μm and storage at 4 °C until analysis have been used [2].

In case of spiking, most researchers agree it is very important to keep the sample spiked with the analytes for a certain period before analysis to allow the equilibrium to be attained. The ageing of the solid samples was carried out at 4 °C for different periods: one day [34], three days [35], three weeks [66], one month [2,37,63], six months [65] as well as at room temperature for one week [61]. Low recoveries were observed for sediment samples after six months of ageing [65]. Another study [62] demonstrated that the recovery of CPs decreases during the first two weeks storage of spiked soil at 4 °C and after that it does not decrease further for ageing times up to two months. The recovery of 2-CP even increased with time after the first two weeks of storage. The authors raise the question of microbial and chemical dechlorination of polychlorinated CPs during storage at 4 °C. To answer this question, experiments with isotope-enriched spikes could be necessary. Ageing of spiked soil was studied by Alonso et al. [34] for storage times between 12 h and 48 h and no significant difference of the recovery was observed. The authors concluded that ageing for 12 h will be enough to attain equilibrium. The discrepancies among works may result from the fact that the ageing process depends not only on the ageing time but also on the matrix. Therefore, a previous optimization of the procedure for each particular kind of samples is recommended.

2.3. Biological tissues and food

The biological tissues and food samples generally require low storage temperatures. For analysis of CPs in cork, the samples were ground and stored at −20 °C [7,13] or 4 °C [6]. Clam tissues samples

were freeze dried, homogenized in a grinder and stored at −20 °C until analysis [10]. Food samples (total diet) were homogenized and deep-frozen [3]. The homogenization of biological samples like algae, for example, can be difficult and freezing it with liquid nitrogen and subsequent grinding is recommended [67].

After storing in the dark for 8 weeks, the average extraction recovery of CPs from cork and wood samples decreased from 104% to 58% [68] and, therefore, similar to the other solid samples, the ageing is recommended to attain equilibrium since it will be more representative of the natural condition of the samples. For the determination of CPs in soft tissues no ageing of the spiked samples was carried out [3,10,67].

3. Analytical methods

For determination of the CPs listed in Table 1, the methods that have been used, as well as the degree of chlorine substitution in each compound and the respective LODs are summarized in Table 2 for the case of liquid samples, like water and wine, in Table 3 for non-biological solid samples and in Table 4 for biological solid samples. When the procedures have also been used for other analytes this is stated in notes below Tables 2–4. From the concentrations of CPs found in real samples (see Section 1), target LODs for CPs can be established. For waters, methods with LODs below 10 ng L^{-1} can be considered useful for practical application in environmental analysis. For wine samples, the LODs should be less than about 100 ng L^{-1}; 1 ng g^{-1} being the limit set for food samples and 10 ng g^{-1} for solid non-biological samples and wood.

3.1. Water samples

In certain waters with difficult matrices, like wastewaters, liquid chromatography (LC) has been used without preconcentration of the analytes. For example, capillary LC with electrochemical detection (EC) was used to determine 2-CP by direct injection of the samples and provided a LOD of 1 μg L^{-1} [18]. Different CPs were directly determined in tap and wastewater by LC with fluorescence detection (FLD) after fluorescence labeling (FLLabel) with coumarin-6-sulphonyl chloride [69], the LODs being in the range 100–900 ng L^{-1}. The direct analysis is simple and rapid, which is an important advantage over the time-consuming preconcentration techniques. Nevertheless, direct injection methods are not widely applied owing to relatively high LODs. However, their sensitivity could be improved, for example, by proper selection of FLLabel reagent [70,71].

3.1.1. Solid phase extraction

SPE is an exhaustive extraction method that, compared to the previously widely used liquid–liquid extraction (LLE), minimizes the use of organic solvents. However, it requires at least 100 mL of water sample in order to attain sufficiently low LODs (Table 2). The necessary sample volume is determined by both the breakthrough volume of the cartridge and the need to reduce the analysis time. Different sorbent materials have been used for SPE of CPs from water samples.

Styrene–divinylbenzene (S–DVB) based resins for preconcentration of free CPs and graphitized carbon black (GCB) for preconcentration of acetylated CPs [72–74] have been used in combination to gas chromatography (GC) with different detectors. S–DVB based resins and GCB were applied for preconcentration of free CPs and the analysis of the extracts was carried out by LC with ultraviolet detection (UV) [17,39,46]. A recent study by Elci et al. [32] used S–DVB cartridges to preconcentrate CPs from water samples and to analyze by GC with atomic emission spectrometry (AES) detection. However, instead of using chlorine emission lines, the authors derivatized the CPs by ferrocenecarboxyl acid chloride and used the much more sensitive and selective iron emission leading to LODs from 1.6 to 3.7 ng L^{-1}.

In recent years, conductive polymeric sorbents have been used for SPE of free CPs. Polyaniline [75], poly-N-methylaniline [76] and polypyrrole [77] resins have been used to preconcentrate non-derivatized CPs. Acetylation was carried out after SPE and the extracts were analyzed using GC with electron capture detection (ECD) or mass spectrometry (MS) detection and the obtained LODs were in the ng L^{-1} and tens ng L^{-1} range. Polyaniline has enhanced performance only for the analysis of polychlorinated CPs, while poly-N-methylaniline and polypyrrole showed quantitative recoveries for all CPs. Important advantage of polypyrrole sorbent is very low consumption of desorption solvent which made possible its application on-line with LC-UV without derivatization, having LODs between 10 and 90 ng L^{-1} [51].

The hydrophobic divinylbenzene and the hydrophilic N-vinylpyrrolidone have been used in hydrophilic lipophilic balance (HLB) cartridges. Free CPs from acidified samples [19,67] or at neutral pH [30] were preconcentrated and determined by LC–MS [19,67] or LC with tandem mass spectrometry (MS/MS) [30]. Very high breakthrough volumes (2 L) were found, depending on the quantity of HLB sorbent in the cartridge, and CPs with different degree of chlorination were determined with relatively high recoveries. LODs in the order of several ng L^{-1} were obtained. A recent study demonstrated that coupling of HLB and C18 cartridges could be used for the simultaneous extraction of analytes with very different polarities [20]. After silyl derivatization of the extracts and analysis by GC–MS, the LODs were in the range 4–44 ng L^{-1}.

New materials for SPE have been used in recent years for CP determination with quantitative recoveries, such as multi-walled carbon nanotubes [54] or co-polymers, molecularly imprinted with 2,4,6-TCP as a template molecule to increase the selectivity of SPE [42]. The extracts were analyzed by LC-UV and LODs from a hundred to a thousand ng L^{-1} were obtained.

Silica particles covered with dialkylated cationic surfactant were excellent sorbents for CPs with different degree of chlorination, leading to LODs between 20 and 100 ng L^{-1} when LC-UV was used to analyze the extracts [59]. The sorption of CPs was based on both electrostatic and hydrophobic interaction. In contrast, when anionic surfactant was used (alumina covered with sodium dodecyl sulfate) only hydrophobic interactions took place, leading to lower recovery of more polar mono- and di-CPs [78].

Nanosized sorbents have high extraction capacity. Unfortunately, it is difficult to pack the small particles into cartridges. Magnetic solid phase extraction (MSPE) has been used recently. Nanoparticles with magnetic properties (Fe_3O_4) were covered with cationic surfactants or ionic liquids [41,55] or combined with clay particles with high sorption capacity [22] and suspended in the water sample for SPE of CPs. After the extraction, the magnetic particles were isolated using a strong magnet. The analysis of the extracts was carried out by LC–MS or LC-UV with LODs of about a few hundreds ng L^{-1}. Quantitative recoveries were obtained. The suspension SPE method was fast because the loading of sample to the SPE cartridge was avoided.

3.1.2. Purge and trap (PT)

In PT techniques, the analytes are preconcentrated and separated as completely as possible from the sample matrix using purging agent (inert gas or water vapor) after which they are sorbed into a suitable solid or liquid trap. It is required that the analytes are volatile at the purging conditions used.

For instance, CPs were acetylated to reduce their polarity and increase the volatility and were subsequently purged by a flow of helium into a Tenax GC trap [79]. Care should be taken when choosing the right trap material since a recent study demonstrated that Tenax TA can cause decomposition of acetyl-CP species [80]. The

Table 2
Methods for analysis of chlorophenols in liquid samples.

Analytical technique	Sample type (volume)	Number of Cl atoms in CPs	LOD (ng L^{-1})	Reference
SPME-GC–MS	Landfill leaches (12 mL)	1–5	1–40	[25]
Acetyl-HS-SPME-GC–MS	Wastewater (12 mL)	1, 2[a] 3–5	1–36 (LOQ) 2–21 (LOQ)	[89]
PFBenzoyl-SPME-GC-ECD	Groundwater (3 mL)	1–3, 5	5–800	[88]
MW-HS-SPME-GC-ECD	Landfill leaches (20 mL)	2–5	100–2000	[24]
SPME-GC–MS	Landfill leaches (2 mL)	1–5[a]	5–1000	[82]
SPME-GC-FID	River water (8 mL)	1–3, 5	5–276	[58]
HS-SPME-GC-FID	Well, tap water (15 mL)	1–3, 5[a]	700–58,000	[86]
SPME-silylation-GC–MS	River, wastewater (20 mL)	2, 3[a]	2–4 (LOQ)	[40]
P-A/HS-SPME-GC–MS	Landfill leaches (0.1 mL)	2–5	10–40	[26]
SPME-GC–MS	Reservoir, tap, groundwater (20 mL)	1–5[a]	53–4100	[29]
SPME-GC–MS/MS	Tap water, wine, lemon juice (5 mL)	3, 4[a]	0.25–0.30	[90]
HS-SPME-GC–MS	Lake water (10 mL)	1, 2[a]	40–60	[85]
Acetyl-HS-SPME-GC–MS/MS	River, reservoir, wastewater (10 mL)	2, 3[a]	13–21	[14]
SPME-GC-ECD	Deionised water (4 mL)	3, 5[a]	500	[84]
Acetyl-HS-SPME-GC–MS	Wastewater, landfill leaches (5 mL)	1–5[a]	11–27	[23]
Acetyl-HS-SPME-GC-ECD	River, estuarine, wastewater (10 mL)	1–5	0.1–120	[15]
SPME-LC-EC	Drinking water (20 mL)	1–5	5–9	[9]
SPME-LC-EC	River and wastewater (4 mL)	1–3, 5[a]	13–60	[21]
SPME-LC-DAD	Sea, ground, wastewater (4 mL)	1–3, 5[a]	1000–6000	[38]
Acetyl-SBSE-TD-GC–MS	Lake, groundwater (10 mL)	1–3, 5[a]	100–400	[31]
Acetyl-SBSE-TD/CT-GC–MS	River, tap water (10 mL)	2–5	1–2	[28]
SBSE-LD-silylation-LVI-GC–MS	Well, tap, river, wastewater (15 mL)	1–3, 5[a]	6–65	[5]
SBSE-LC-DAD	Tap, sea, wastewater (50 mL)	1, 2[a]	720–1370	[91]
SBSE-TD/CT-GC–MS/MS	Tap water, wine, lemon juice (5 mL)	3, 4[a]	0.06–0.27	[90]
Acetyl-LPME-GC–MS	River water (1 mL)	1–3[a]	10–21	[114]
Acetyl-LPME-GC–MS	River, mineral, tap water (10 mL)	1–5[a]	5–210	[95]
LPME-silylation-GC–MS	Reservoir, sea, tap water (5 mL)	2, 5[a]	15	[27]
LPME-silylation-GC–MS	River water (3 mL)	1–3, 5[a]	4–61	[56]
SM/LPME-silylation-GC–MS	River, tap water (30 mL)	1–3	15–23	[44]
LPME-tosylation-GC–MS	River, lake, wastewater (5 mL)	1–3[a]	200–280	[96]
MASE-LVI-GC–MS	Groundwater (15 mL)	1–3, 5[a]	9–595	[45]
MW-HS-LPME-GC-ECD	Landfill leaches (10 mL)	2–5	40–700	[94]
HS-LPME-LC-UV	Lake, tap water (10 mL)	1, 2	6000–23,000	[93]
SPE-methylation-HS-LPME-LC-DAD	River, tap, groundwater (40 mL)	1–3, 5[a]	40–80	[52]
LPME-LC-DAD	Lake, ground, wastewater (20 mL)	1–3, 5	100–300	[43]
LLLME-LC-UV	Tap, river, ground, wastewater (15 mL)	1–3	500–1000	[99]
LLLME-LC-UV	Ground, lake, river, wastewater (15 mL)	1–3	300–400	[49]
LLLME-LC-UV	Seawater (10 mL)	1–3, 5[a]	20–100	[53]
SM/LLLME-LC-UV	River, well, tap water (20 mL)	1–3[a]	198–453	[115]
LLLME-LC-DAD	Reservoir, tap water (14 mL)	1–3, 5	49–81	[98]
CF/LLLME-LC-DAD	River, tap water (100 mL)	1–3, 5	20–90	[50]
DLLME-acetyl-GC-ECD	Well, tap, river water (5 mL)	1–5	10–2000	[47]
SPE-DLLME-acetyl-GC-ECD	Well, tap, river water (100 mL)	1–5	0.5–100	[97]
SPE-acetyl-GC-ECD	River water (75 mL)	1–3, 5	3–110	[75]
SPE-acetyl-GC-ECD	River water (250 mL)	1–3, 5[a]	1–40	[76]
SPE-acetyl-GC–MS	River water (250 mL)	1–3[a]	15–75	[77]
SPE-acetyl-GC–MS/MS	Wastewater (250 mL)	1–3, 5[a]	10–30	[16]
SPE-silylation-GC–MS	Wastewater (2 L)	1–5[a]	4–44	[20]
SPE-FCC-GC-AES	Lake, tap water (10 mL)	1–3	1.6–3.7	[32]
SPE-LC–MS/MS	River, lake, drinking water (2 L)	1–3, 5	1–7	[30]
SPE-LC–MS	Groundwater (500 mL)	1–3, 5[a]	10–25	[67]
SPE-LC–MS	River, wastewater (100 mL)	1, 2	5–48 (LOQ)	[19]
SPE-LC-UV	River, tap, wastewater (10 mL)	1–3, 5[a]	570–1080	[42]
SPE-LC-UV	River water (200 mL)	1–2[a]	3300–3700	[116]
SPE-LC-UV	River, tap water (200 mL)	1–3, 5	80–800	[54]
SPE-LC-UV	River, tap water (100 mL)	1–3[a]	10–90	[51]
SPE-LC-UV	River, groundwater (500 mL)	1–5	20–100	[59]
SPE-LC-UV	Wastewater (150 mL)	1[a]	200–480 (LOQ)	[57]
micro SPE-LC-UV	River, tap, wastewater (60 mL)	1–3, 5[a]	560–4500	[117]
MSPE-LC-UV	River, wastewater (150 mL)	1	170–220	[22]
MSPE-LC-DAD	River, spring, tap water (200 mL)	1, 2, 5	200–350	[55]
MSPE-LC–MS	River, tap, ground, wastewater (700 mL)	1–3, 5	110–150	[41]
Acetyl-PT-GC-AES	Tap water (5 mL)	1–3	23–150	[79]
Acetyl-HS-PTV-GC–MS	Tap, river, seawater (5 mL)	1–3	5–8	[80]
Capillary LC-EC	Wastewater (2 μL)	1[a]	1000	[18]
FLLabel-LC-FLD	Tap, reservoir, wastewater (500 mL)	1–3[a]	100–900	[69]
SPE-acetyl-GC-ECD	Cork macerate (100 mL)	3–5	<10	[101]
SPE-acetyl-GC-ECD	Wine (1 L)	3–5[a]	8–20	[100]
SPE-acetyl-LVI-GC–MS/MS	Wine (1 L)	3–5[a]	0.2–0.5	[100]
Acetyl-HS-SPME-GC-ECD	Cork macerate (5 mL)	3–5	0.8–1.5	[101]
Acetyl-HS-SPME-GC-ECD	Wine (8 mL)	3–5	3–20	[12]
Acetyl-DLLME-GC–MS	Wine (5 mL)	1–5[a]	4–40	[13]
HS-SPME-GC-ECD	Milk (0.5 mL)	3–5[a]	560–1010	[102]

[a] Other compounds also analyzed.

Table 3
Methods for determination of chlorophenols in sediment, soil, sludge and ash samples.

Analytical technique	Extraction procedure	Number of Cl atoms in CPs	LOD (ng g^{-1})	Reference
SPE-LC-UV	MW, CH_3OH/H_2O (4/1) + 2%TEA; soil 10 g	1–3, 5[a]	30–80	[34]
SPE-LC–MS	MW, CH_3OH/H_2O (4/1) + 2%TEA; soil 10 g	1–3, 5[a]	0.007–0.4	[34]
SPE-silylation-GC–MS/MS	MW, acetone/CH_3OH (1/1); sludge 0.5 g	2, 3[a]	0.8 (LOQ)	[4]
SPE-silylation-GC–MS/MS	MW, acetone/CH_3OH (1/1); sediment 1 g	2, 3[a]	0.4 (LOQ)	[4]
SPE-GC-FID	MW, 10^{-5} M NaOH; sediment 5 g	1, 2, 5[a]	1.3–10.6	[37]
LC-UV	MW, 2% POLE; sediment 2 g	1–3, 5[a]	2.4–25	[65]
GC–MS	MW-acetyl, *hexane/acetone (1/1)*; ash 1 g	1–5	2–5 (LOQ)	[2]
GC-ECD	MW-SD-acetyl-SPE; soil 3 g	1–5	13–194	[61]
SPE-LC–MS	Ultrasound, *CH_3OH/H_2O (4/1) +5%TEA*; sediment 30 g	1–3, 5[a]	1	[67]
Acetyl-SBSE-TD-GC–MS	Ultrasound, *CH_3OH*; soil 1 g	1–3, 5[a]	0.2–0.9	[35]
Acetyl-SBSE-TD-GC–MS	Ultrasound, *CH_3OH/CH_2Cl_2 (9/1)*; sediment 0.5 g	2, 3, 5	1.8–3.8	[103]
SDE-GC-FID	Ultrasound, *0.1 M NaOH*; soil 15 g	1, 3[a]	100	[81]
Acetyl-PT-GC-AES	Ultrasound probe, *5% K_2CO_3*; soil 7 g	1–3	0.08–0.54	[79]
SPME-GC–MS	ASE, *H_2O + 5% CH_3CN*; soil 10 g	1–5	1.1–6.7	[36]
Acetyl-GC–MS/MS	QuEChERS, *CH_3CN/H_2O (2/1) +1% acetic acid*; soil 10 g	1, 3, 5[a]	0.5–3	[60]
Acetyl-HS-SPME-GC–MS; soil 1 g	–	1–5[a]	0.07–0.92	[63]
MW-HS-SPME-GC-ECD; soil 1 g	–	2–5	0.1–2	[64]

[a] Other compounds also analyzed.

Table 4
Methods for determination of chlorophenols in solid biological samples.

Analytical technique	Extraction	Number of Cl atoms in CPs	LOD[b] (ng g^{-1})	Reference
Acetyl-LLE-GC-ECD	*Pentane*; cork	3–5[a]	0.5–1.7	[7]
GC–MS	Acetyl *(hexane)*; wood	1–5	<20	[8]
GC–MS	Acetyl *(hexane)*; fruit	1–5	<2	[8]
Acetyl-LLE-GC-ECD	MW, *CH_3OH*; cork	3–5[a]	0.1–0.5	[6]
SPME-GC–MS	MW, *0.5% POLE*; wood	1–5	2–120	[68]
Acetyl-DLLME-GC–MS	Ultrasound probe, *pentane*; cork	1–5[a]	0.02–0.11	[13]
Acetyl-LLE-GC-ECD	Ultrasound, *hexane/acetone (1/1)*; worms	2–5	20–130	[105]
SPE-LC–MS	Ultrasound, *CH_3OH/H_2O (4/1) + 5%TEA*; algae	1–3, 5[a]	2.5–5	[67]
SPE-IC-MS	Ultrasound, *CH_3OH/H_2O (4/1) + 5% TEA*; clam	1–3, 5	0.05–0.5 dw (LOQ)	[10]
SBSE-TD-GC–MS	Ultrasound, *ethanol/H_2O (3/1)*; cork	3–5[a]	0.7–380	[104]
PFBenzyl-SPE-GC-ECD	Alkaline digestion-SDE; food	2–5	0.5–1 (LOQ)	[3]
SPME-LC-EC; wood	–	5	45	[9]
Acetyl-HS-SPME-GC-AES; honey	–	1–5	0.1–2.4	[11]

[a] Other compounds also analyzed.
[b] LOD expressed to fresh weight, except otherwise stated.

analytes were thermally desorbed by heating the trap and purged into GC-AES for analysis. The method required only 30 min/sample. The LODs were between 23 and 150 ng L^{-1} but PCP was not volatile enough to be purged, even after the acetylation. The steam distillation extraction (SDE) method [81] used the volatility with water vapor of the non-derivatized CPs. Here, the purging agent was water vapor and the trapping was carried out by simultaneous LLE of the CPs from the condensate, with diethyl ether. The hydrophobicity of chlorine-substituted phenols strongly enhanced the extraction efficiency and quantitative recoveries were obtained. The organic extracts were analyzed by GC with flame ionization detection (FID) and LODs of 10 μg L^{-1} were obtained. The method has potential to be applied to real samples when using more sensitive and selective detectors. The steam distillation required about 90 min/sample but can be accelerated using microwave (MW) heating.

3.1.3. Microextraction methods

The microextractions are non-exhaustive methods that strongly minimize or even completely eliminate the use of organic solvents. The extraction is not complete but the extracted quantity is proportional to the concentration of CPs in the sample. They generally require 1–20 mL of sample which is an important advantage having in mind storage space and limited sample availability, especially in model studies.

3.1.3.1. Headspace evaporation. This method, although similar to the purge and trap techniques, will be considered together with the other microextraction techniques because it is also a non-exhaustive method. Pavón et al. [80] reported that acetyl-CPs were purged from the headspace and cryogenically trapped into empty or packed liners using programmed temperature vaporization (PTV). The analytes were analyzed using fast GC–MS after flash-heating of the liner to desorb the analytes. Since Tenax TA sorbent destroyed the acetyl-CPs, an empty liner was used. The LODs are between 5 and 8 ng L^{-1}.

3.1.3.2. Solid phase microextraction (SPME). Due to the polar nature of the CPs, a polar polyacrilate (PA) fibre was used for sampling of the non-derivatized analytes. The fibre was immersed in the sample at pH about 2, in the presence of NaCl or Na_2SO_4, during 40–60 min. Then the CPs were desorbed from the fibre in the hot GC injector. The detection was carried out using MS [25,29,82,83] or ECD [84]. However, the direct sampling of CPs using PA fibre may depend on the sample matrix, like the presence of surfactants and humic acids, but a simple increase of the extraction time could be sufficient to eliminate the matrix effect [83].

To decrease the matrix interferences and to increase the fibre life-time, sampling from the headspace was tested but it did not result for TeCPs and PCP when conventional heating of the samples was used [24,82]. When MW energy was used to heat the sample, the SPME procedure was completed in about 5 min and it was possible to determine CPs from the headspace, including TeCP and PCP [24]. Similar results were obtained by purging the sample with nitrogen and fast headspace extraction (30 min) of CPs (including TeCP and PCP) [26].

Laboratory-made fibers have been also tested. Carbon monolith fibre permitted short extraction time and displayed high capacity to phenolic compounds [85]. Polyaniline fibers could be prepared

by highly reproducible electropolymerization process. Such fibers were used for headspace (HS) sampling of phenols with different degree of chlorination, even PCP, but they had low thermal stability [86]. It was found that calixarene and carbon aerogel fibers had higher thermal stability and presented no carry-over problems, usually encountered when PA fibers were used, especially for PCP [58,83,87].

Without derivatization, the LODs, depending on the analyte, have been, in most cases, between several ng L^{-1} and several μg L^{-1} (Table 2) [24–26,29,58,82,84–86]. Such values are not sufficiently low to determine CPs in most environmental water samples. When the analytes were converted to less polar and more volatile analytes, chromatographic separations were improved and the LODs were usually enhanced (Table 2) [14,15,23,40,89].

A method to carry out the derivatization of the analytes was on-fibre silylation after direct SPME of the CPs with polar (PA) or bipolar (polydimethylsiloxane–divinylbenzene (PDMS–DVB)) fibers [40]. The fibre with the sorbed CPs was exposed to N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide for 10 min and after thermal desorption the derivatives were separated and detected using GC–MS. Limits of quantification (LOQs) of 2–4 ng L^{-1} were obtained. Another tested approach was the in situ derivatization, using direct SPME at pH about 11, by pentafluorobenzoyl chloride previously sorbed on PDMS–DVB fibre [88]. The separation and detection were performed by GC-ECD. The LODs, depending on the analyte, were from 5 to 800 ng L^{-1}. Also in this case, additional step of 10 min was required for the sorption of the derivatizing agent to the fibre, before SPME.

Acetylation has been another type of in situ derivatization, carried out by adding acetic anhydride to the sample at alkaline pH, maintained by alkaline metal carbonates [15], bicarbonates [23,89] or hydrogen phosphates [14]. Since the derivatization occurred in the water sample, the number of analytical steps was minimized. The use of hydrogen phosphates had the advantage of preventing bubble formation (carbon dioxide) and eventual overpressure during the extraction. Owing to the high volatility and low polarity of the acetylated derivatives, it is convenient to sample them from the headspace using bi-polar PDMS–DVB [15], carboxen–polydimethylsiloxane (CAR–PDMS) [89], divinyl-carboxen-polydimehtylsiloxane (DVB–CAR–PDMS) [14] or non-polar polydimehtylsiloxane (PDMS) fibers [23,89]. Non-polar fibers are more appropriate to determine polychlorinated CPs owing to their low polarity [89]. CAR–PDMS fibre suffers from strong carry-over [15,23]. To simultaneously determine CPs with different degree of chlorination in water samples after acetylation, the best fibre seems to be PDMS–DVB [15]. The detection has been carried out by MS [89], MS/MS [14] and ECD [15]. The LODs obtained, depending on the analyte, were from less than ng L^{-1} to a hundred ng L^{-1}.

SPME with carbowax-templated resin (CW-TPR) fibre was coupled with LC after on-line desorption using the mobile phase [38] or off-line desorption in a small volume (40–60 μL) of organic solvent mixture [9] or a micellar solution [38]. Using diode array detection, the LODs obtained were 1–6 μg L^{-1} [38]. With amperometric electrochemical detection, the LODs were 5–9 ng L^{-1} but marked carry-over was observed with CW-TPR fibre [9]. Static desorption of the CPs from PA fibre in the injector of the LC-EC solved the carry-over problems and permitted to attain LODs from 13 to 60 ng L^{-1} [21].

3.1.3.3. Stir bar sorptive extraction (SBSE). A drawback of SPME is the small volume of enrichment phase attached to the fibre (0.5 μL). In SBSE, a magnetic bar is covered with much larger quantity of acceptor phase which strongly enhances the extraction efficiency [5]. As with SPME, carry-over problems can be an important limitation caused by repeated analysis with the same stirring bar.

The acetylated derivatives of CPs, due to their low polarity, can be more efficiently sorbed into a stir bar covered with PDMS phase. In a work from Montero et al. [31], after the extraction, the bars were heated in a thermal desorption unit and the desorbed derivatives analyzed by GC–MS, providing LODs between 100 and 400 ng L^{-1} or even two orders of magnitude less if the analytes were cryofocused after the thermal desorption [28]. The SBSE with PDMS coated bar has also been used to extract non-derivatized CPs. After the extraction, the CPs were desorbed into ethylacetate and the extracts were silylated and analyzed by GC–MS using large volume injection [5]. The LODs were between 6 and 65 ng L^{-1}. Lower LODs (0.06–0.27 ng L^{-1}) were obtained using thermal desorption with cryofocusing and GC–MS/MS detection [90]. However, the method of liquid desorption is less expensive because avoids the use of thermodesorption device.

Until recently, only non-polar PDMS coatings for SBSE were available, thus limiting the selectivity of the method [5]. However, the new SBSE coatings, like poly(vinylpyrrolididone-divinylbenzene) monolithic material (VPDB) [91] or polyurethane foams [92] have much higher affinity to non-derivatized CPs than PDMS coating do, which is a promising future development of the CPs determination.

3.1.3.4. Liquid phase microextraction (LPME). Compared to SPME and SBSE, the LPME has the advantage of not to suffer from carry-over effects. It requires very small amounts of organic solvents. One approach to reduce the solvent consumption during the traditional LLE can be the use of membrane-assisted solvent extraction (MASE) [45]. A small volume (less than 1 mL) of organic solvent was put into a membrane bag made of dense polypropylene and the membrane was placed into the sample. After the extraction, the analysis was carried out by GC–MS equipped with large volume injector and the LODs obtained were between 9 and 595 ng L^{-1}. Recent study demonstrated that integrated stirring into the extraction unit could provide much better performance compared to the case of separated extraction and stirring units [44].

Larger reduction of solvent consumption was obtained using single drop microextraction and hollow fibre LPME. A single drop of 50% solution of acetonitrile in water was exposed to the headspace above the sample and heated with the help of ultrasound energy [93]. Due to the limited drop volume of about 5 μL, and to the difficulties to cool the solvent drop, the efficiency of this extraction procedure was relatively small. For this reason, the sampling from the headspace was carried out in 10 μL of 50% acetonitrile, placed in the bottom of a PCR tube inserted into the vial cap with the bottom upwards. The bottom of the PCR tube was placed out of the vial and was cooled in an ice bath, which together with the larger volume of the acceptor solvent increased greatly the efficiency of the process [93]. The use of ultrasound enabled a decreasing of the extraction time to only 25 min. However, the analysis was carried out by LC-UV and relatively high LODs, in the range 6–23 μg L^{-1}, were obtained.

Other possibility in order to increase the volume of organic phase is the application of polytetraflourethylene (PTFE) sleeve over the needle of the syringe [43,52]. Vesicle-based coacervate drops with large volume (30 μL) were used as solvents, compatible with LC analysis [43]. These multifunctional coacervate drops interact with CPs by hydrophobic, π-cation and hydrogen bond interactions and have the ability to solubilize analytes with wide range of polarity. LODs in the range 100–300 ng L^{-1} were reported [43].

Sampling from the headspace of non-derivatized CPs using disposable hollow fibre LPME could be achieved using MW energy [94]. In these conditions, very short extraction times (10 min) were required even for polychlorinated CPs. However, efficient cooling system was necessary to prevent solvent evaporation from the

hollow fibre and to increase the extraction efficiency. The analysis of the extract was carried out by GC-ECD with LODs in the range 40–700 ng L^{-1}.

The CPs have been acetylated in situ and the derivatives extracted in a microdrop of butylacetate on the tip of a syringe needle [51] or in a floating drop of 1-undecanol which, after the fast extraction, solidified upon cooling [95]. Another type of derivatization, especially suitable for solvent microextraction techniques owing to the small volume of extractant required, is the silylation in the hot injector after the injection of the extract [27] or silylation inside the syringe before the injection [56]. Using GC–MS for analysis of drops, LODs in the order of tens ng L^{-1} were obtained for both acetylation and silylation derivatization [27,56,95]. The derivatization could be carried out inside the drop simultaneously with the extraction. For instance, the CPs were transported from the sample, containing ion-pair agent, to the drop of the organic solvent containing tosyl chloride to derivatize the CPs [96]. After GC–MS analysis, the LODs were from 200 to 280 ng L^{-1}.

Sampling from the headspace with a single drop (10 μL) was applied after methylation of the CPs with dimethyl sulfate in alkaline media [52]. The methylation was required to both increase the volatility of the analytes for the headspace sampling and improve separation in the subsequent LC-UV analysis. Thus, despite derivatization has been mainly used for GC analysis, it can also improve LC performance. When combined with SPE, this method permits to attain relatively low LODs, between 40 and 80 ng L^{-1}.

Acetylated derivatives of the CPs have been extracted from water samples by means of a water soluble disperser solvent, containing small quantity of water insoluble and dense extraction solvent. After addition of the disperser solvent to the sample, a finely dispersed emulsion (microdrops of the extraction solvent) was formed leading to practically immediate extraction, called dispersive liquid–liquid microextraction (DLLME) [47]. After centrifugation, the lower layer was analyzed by GC-ECD and the LODs varied 10 ng L^{-1} to 2 μg L^{-1}. The highest LODs values were obtained for mono-CPs due to the lower sensitivity of ECD to these compounds. MS detection may improve the sensitivity of the method for mono-CPs. Additional improvement of the method was attained by combining it with SPE [97]. The elution solvent during the SPE phase should be chosen carefully because it should also play the role of disperser solvent during DLLME. With GC-ECD, the LODs were in the range 0.5–100 ng L^{-1}. Advantage of DLLME is its extreme rapidity, decreasing strongly the time and cost of the analysis.

Additional improvement in selectivity can be obtained using LLLME of non-derivatized CPs. For this purpose, the CPs were extracted from the acidified sample, in their molecular forms, into an organic solvent (1,2,4-trichlorobenzene [98] or polar ionic liquid [53,99]) impregnating the hollow fibre membrane from where the CPs diffuse into 10–15 μL alkaline acceptor phase. There, the CPs were transformed into their respective anions which cannot return back into the membrane and are concentrated into the acceptor phase. The analysis was carried out by LC-UV and the LODs were 500–1000 ng L^{-1} [99] or several tens ng L^{-1} [53,98]. In the work of Lin and Huang [98] alkaline mobile phase was used, since the CPs anions provided better ultraviolet spectra than did uncharged CPs. Disk-shaped supported liquid membranes, impregnated with dichloromethane, were used for LLLME from the sample to alkaline acceptor phase using continuous flow (CF) operation, offering high enrichment factor and very good stability of the liquid membrane [50].

3.2. Other liquid samples

Some of the methods used for water sample analysis could be applied for CPs determination in other liquid samples (Table 2). For instance, SPE was used for determination of CPs in wine samples. A large volume (1 L) of red wine was successfully preconcentrated on HLB cartridges and after acetylation the extracts were analyzed using GC–MS/MS obtaining LODs in the range 0.2–0.5 ng L^{-1} [100].

The CPs from wine and cork macerate samples were acetylated and analyzed by HS-SPME-GC-ECD with PDMS fibre [12,101] with quantitative recoveries for most of the CPs studied (compared to standards in hydroalcoholic solution). However, it is possible that PCP determination in wine depends on the matrix, since one of the studies reported very strong matrix effect from white wine, while it was possible to determine it in cork macerate [101]. The other study reported successful PCP determination in red wine using the same method [12].

A similar HS-SPME-GC-ECD method, but with PA fibre and without derivatization, was used to determine the CPs in human milk samples, obtaining LODs from 560 to 1010 ng L^{-1} [102]. The samples were acidified with perchloric acid in order to de-conjugate the CPs.

3.3. Solid samples

3.3.1. Extraction of chlorophenols from a solid matrix

Shaking of the sample with organic solvent is cheap and effective in some cases but most often is time consuming or presents low recoveries. For instance, shaking for 30 min with hexane with simultaneous acetylation of CPs was applied to aqueous slurry of fruits and wood samples [8]. The recoveries were quantitative for fruits but only between 42% and 58% for the wood samples. Cork samples were extracted with hexane by shaking for 90 min [7] with quantitative recoveries, except for PCP (57–76%).

An alternative shaking method, which was classified by the authors [60] as a quick, easy, cheap, effective, rugged and safe (QuEChERS) procedure was reported. Extraction was carried out with a mixture acetonitrile/water (2/1) acidified with acetic acid (0.66%) for 1 h. After salting out, the acetonitrile layer was removed. Quantitative recoveries were obtained, possibly because the method does not require evaporation step. However, further validation studies are necessary, since the authors did not apply their procedure to certified reference materials (CRM) and did not mention if ageing of the spiked samples was used in the validation protocol.

Accelerated solvent extraction from soil samples with water containing 5% acetonitrile as organic modifier permitted to minimize the use of organic solvents and took only 30 min [36]. The recoveries were in the range 42–82%, the lowest ones being found for polychlorinated CPs. Most of the researchers opted to use ultrasound or microwave-assisted extraction to enhance the efficiency of the extraction or to speed-up the process, as will be detailed below.

3.3.1.1. Ultrasonic extraction. Organic solvents were widely used in ultrasonic extraction of CPs. Sediment and soil samples were ultrasonically extracted using methanol/dichloromethane (9/1) for 15 min [103], methanol for 30 min [35] and methanol/water (4/1) containing 5% triethylamine (TEA) for 20 min [67]. In the last case, TEA prevented the losses of CPs in the subsequent evaporation of methanol. Recoveries higher than 80% were obtained with the exception of PCP (about 70%) which is, generally, the most problematic CP species to extract from the solid matrix due to its high hydrophobicity.

Soil samples were extracted with 0.1 M NaOH for 60 min in ultrasonic bath [81] or with 5% potassium carbonate using ultrasound probe for 30 s [79]. Both alkaline extraction methods provided recoveries higher than 75–80% but TeCP and PCP were not analyzed.

The ultrasonic extraction of CPs from biological tissues generally displays less recovery problems than in the cases of sediments or soil samples. Extraction from cork samples with ethanol/water

(3/1), involving ultrasonication and shaking for about one day [104], or with pentane, using ultrasound probe for 3 min [13], provided quantitative recoveries, including for PCP. For algae samples, extraction for 20 min using methanol/water (4/1) containing 5% TEA [67] led to recoveries of CPs in the range 70–90%, the lowest value being observed for PCP.

CPs from soft biological tissues (worms) were ultrasonically extracted for 10 min with hexane/acetone (1/1) after acidification with sulfuric acid [105]. For clam tissues, 20 min of extraction with methanol/water (4/1) containing 5% TEA was used [10]. Recoveries higher than 80%, including for PCP, were obtained with both methods.

3.3.1.2. Microwave (MW) extraction. A MW extraction process requires optimization of the following parameters: composition and volume of the solvent, pressure or temperature, MW power and time of extraction and, possibly also, derivatization reagents quantities.

Most of the methods for MW extraction use organic solvents. The extraction time for CPs using this process was between 16 min [106] and 90 min [6] and the organic solvent volume was between 15 mL [106] and 50 mL [34]. Either acid or base additives to the solvent were found sometimes useful to increase the recovery. MW extraction was carried out both in closed [2,4,6,106] and open vessel systems [34].

Methanol was used for extraction of CPs from cork samples with about 90% recoveries for polychlorinated CPs [6]. Acetone/hexane (1/1) was used for soils [106] or with simultaneous acetylation, in the presence of TEA as a base, for the case of ash samples [2]. Recoveries between 72 and 94% were obtained for ash samples; the lowest values were found for 2,6-DCP. Acetone/methanol (1/1) containing 1% formic acid was used for sludge and sediments [4] and the recoveries were independent on the matrix, between 85% and 94% on average, even for sludge samples containing very high levels of organic matter. Methanol/water (4/1) in the presence of 2% TEA was used for soil samples with recoveries higher than 77%, including for PCP [34].

Alkaline and micellar extractions have the advantages of completely eliminate the use of organic solvents and strongly decrease the extraction times. A solution of NaOH (pH 9) was used in closed vessels to extract CPs from sediments in 6 min [37]. A possible drawback of alkaline extraction could be the interference of humic material, co-extracted with CPs at high pH [36].

Micellar solution of polyoxyethylene-10-lauryl ether was used in closed vessels to extract CPs from soil [62] or sediment samples [65] or in open vessels for wood samples [68]. It was possible to work without addition of acids or bases to the extraction medium. The method for CPs extraction showed higher recoveries than the Soxhlet extraction with organic solvent and the extraction time was only 2–3 min. Recoveries were quantitative and independent of the matrix, both for soil and sediments [62,65].

The extraction under MW field is a very rapid method that may solve the problem of poor recoveries of polychlorinated CPs. However, it is necessary to check if catalytic reactions on the solid matrix induced by MW radiation occur [34], which could lead to poorer recoveries of some analytes. CPs were found stable in MW field during alkaline extraction of sediments [37] but studies for other procedures and other matrices are yet to come.

3.3.2. Extracts' clean-up

In the case of extraction with organic solvents, after evaporation, the extracts have been purified using SPE with Isolute EVN [34] or, more recently, with Oasis HLB cartridges [10,67], followed of analysis using LC, without any further treatment. However, most often GC was used even if it required more complicated treatment, like derivatization. When the matrices of the samples are very complex, the cleaning may require several steps. Removal of basic and neutral interferences by back-extracting them from an alkaline solution was used to clean-up extracts from sludge and sediment samples [4]. After that, SPE was used with Oasis HLB cartridges and the extracts were finally silylated before analysis.

If water miscible solvents were used, the extracts could be diluted with water and the CPs preconcentrated using SBSE with in situ acetylation [35,103] or without any derivatization [104]. The organic extracts, containing the CPs to be analyzed could be evaporated [6,13] or purified by extraction into alkaline solution [7,105] and the CPs could be acetylated in aqueous medium. Then, the derivatives were re-extracted with organic solvent using LLE [6,7,105] or DLLME [13]. It seems to be possible to acetylate the CPs directly into the organic solvent used for the extraction of the solid sample, in the presence of pyridine as base [60].

Extracts in organic solvent of acetyl-CPs, obtained after simultaneous extraction and acetylation from fruits and wood [8] and ash samples [2] were analyzed using GC–MS without further treatment, apart from possible evaporation of the organic solvent.

The extraction with organic solvent usually required its evaporation, which, in conjunction with high toxicity and negative environmental impact, could lead to possible losses of the analytes. In contrast, the extracts of solid samples with alkaline and neutral aqueous media could be compatible with LC [62,65], SPME [36,68], PT [79] or SDE [81] without further purification of the extract. However, for some complex sample matrices, especially when alkaline water was used for extraction, the extracts should be cleaned-up [37].

3.3.3. Extraction–preconcentration integrated procedures

3.3.3.1. Steam distillation extraction (SDE). The SDE of solid samples can be integrated with liquid extraction or SPE, although it has to be carried out *off-line* to the main analytical device. Such procedure was applied to total diet food samples, which were de-conjugated in alkaline conditions and, after acidification, distilled with water vapor with simultaneous extraction with toluene for 1 h [3]. After that, the CPs were derivatized with pentafluorobenzyl bromide for 3 h, the solution cleaned-up with Florisil and analyzed by GC-ECD. The method was very sensitive, in spite of being time consuming, with LOQs between 0.5 and 1 ng g^{-1} (Table 4) and quantitative recoveries were obtained. Microwaves can be used to speed-up the SDE. In another case [61], a soil sample was mixed with water, the CPs were acetylated and the acetyl-CPs were distilled with water vapour using MW energy. The distillate passed through *on-line* SPE cartridge. Both C18 and ENVI-18 were used and provided quantitative recoveries, mainly as a result of the lower polarity of the derivatized analytes. The whole distillation process took about 16 min. The analysis was carried out with GC-ECD and the LODs were between 13 and 194 ng g^{-1} (Table 3).

3.3.3.2. Solid phase microextraction (SPME). To analyze acidified slurries of solid samples SPME can be used, which eliminates a previous extraction step. It can be easily automated to be carried out *on-line* with the main analytical device. SPME requires less amount of sample than usual methods to extract CPs from solids and it is much faster. Direct SPME with PA fibre was applied to determine 3-chlorophenol in slurry of contaminated soil, using GC-FID for analysis [107]. A CW-TPR fibre and analysis by LC-EC were used for PCP in wood slurry [9]. As adsorption of CPs to the fibre is a relatively slow process, non-equilibrium SPME has also been used, applying a suitable internal standard, given that it would reach equilibrium for the same time as the analytes [107]. However, as relatively high LODs were obtained (for instance, 45 ng g^{-1} for PCP in wood [9]) direct SPME could be used to analyze only relatively contaminated samples.

Transfer of CPs with different degree of chlorination from the acidified slurry to the headspace could eliminate the matrix effects encountered with complex soil matrices [64]. The extraction from the headspace using PA fibre was accelerated by using microwaves and accomplished in less than 10 min, even for the least volatile PCP, after which the analysis was carried out with GC-ECD. Another approach for fast headspace SPME was to combine it with in situ acetylation. This method was applied for soil slurry analysis [63] and honey samples [11]. The acetyl-CPs from the soil slurry were preconcentrated using the PDMS fibre at 100 °C and analyzed by GC–MS. At this temperature, the extraction time profile had a very peculiar shape, the analytical response being maximal at 20 min and strongly decreasing afterwards. The authors proved that this behavior was a consequence of the soil matrix. The acetyl-CPs from the honey sample were adsorbed to PDMS–DVB fibre and analyzed by GC-AES. The equilibrium was reached in 30 min at 90 °C. The LODs for headspace SPME methods for solid samples were in the order of ng g^{-1}, or less, and can be used even for the analysis of non-contaminated samples.

4. Quality control

The Federal Institute for Materials Research and Testing [108] and Institute for Reference Materials and Measurements [109] sell industrial soils certified for PCP and, in some cases, also with 3,4-DCP and 2,4,5-TCP, and wood samples certified for PCP. Especially good source of environmental reference materials is the Resource Technology Corporation [110] which sells a rich variety of materials, namely lake sediment, sewage sludge, soils with different matrices and levels of contamination. CRM from Resource Technology Corporation (RTC) contain one or more of the following CPs: 4-C-3-MP; 2-CP; 2,4-DCP; 2,6-DCP; 2,4,6-TCP; 2,4,5-TCP and PCP. Unfortunately, for water and food samples, there are no certified reference materials, and in such cases the accuracy has been estimated by spiking. To our knowledge, the ageing of the CPs spiked into solid food samples was not evaluated but at least one day ageing is advisable, based on the properties of CPs to undergo slow equilibration with solid matrices. Due to the very high price, even if the CRM are available, only a limited number of studies have included analysis of CRM into method development [61–63,79,103]. Participation into inter-laboratory exercises has been also reported [9].

5. Conclusions

A lot of recent methods aimed at the simultaneous determination of CPs with different degree of chlorination. However, the sampling storage, despite of being an important step of analytical process, has been largely underestimated in the literature. Application of organic solvent-free (or minimal solvent) techniques has been used in the last decade.

The target LODs for CPs in water samples (in low ng L^{-1} range or lower) can be attained only if a preconcentration step (microextraction or solid phase extraction) with derivatization is included, and the analysis is carried out using GC with a sensitive detector, like ECD or MS. Apart from lower cost and easier maintenance, ECD has no advantage over MS detector because it is less sensitive for mono-CPs. The MS detector has also the advantage of making possible the use of stable isotope-labeled surrogate standards. This enables to work with very difficult matrices and to check out for eventual CPs transformation during sample storage and analysis. The use of LC does not require derivatization but preconcentration and use of sensitive detectors (MS or EC) are necessary to analyze CPs in real water samples. More widespread detectors, like UV, can still be used successfully if high preconcentration is achieved with SPE or LLLME techniques. In non-biological and biological solids and wine samples, almost all cited methods permit attaining LODs suitable for real sample applications. The main trend in solid sample analysis has been the development of fast methods for CPs withdrawal from the solid matrices, like MW extraction, that are able to disrupt the strong interaction between the matrix and the lipophilic CPs, especially PCP. An alternative of extraction methods, integrating into one step extraction and analysis of solid samples, is a very attractive future trend.

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