

# Sample preparation procedures for analysis of organochlorinated pollutants and PAHs in surface water samples

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**Abstract:** This review focuses on sample preparation procedures used for chromatographic analysis of the most common organochlorinated pollutants and PAHs in water samples. The studied pollutants have a long persistence in environment, possible carcinogenic effects, and their application has been banned in many countries. The standard ISO procedures with the modern sample preparation procedures were compared in the term of recovery effectiveness for target analytes.

**Keywords:** sample preparation procedures, chromatography, organochlorinated pollutants, PAHs

## Introduction

Sample preparation procedure is a crucial step of trace analysis, which mainly defines the accuracy of the obtained results. Nowadays, traditional sample preparation procedures used for chromatography, e.g. liquid-liquid extraction (LLE) and solid phase extraction (SPE) are slowly replaced by their miniaturized versions. For example, a thin film of sorbent could be coated on a fused-silica fibre (SPME) or a stir bar (SBSE). As to liquid microextraction procedures, the extraction of pollutants is successfully performed on a microdrop of organic solvent suspended from the tip of a microsyringe needle in the case of single-drop microextraction. At the same time, drops of the mixture of a scattering solvent with extraction solvent are used for dispersive liquid-liquid microextraction. Furthermore, separation procedure could be also occurred through flat-sheet and hollow-fibre membrane, where separation mechanisms varies depending on the membrane nature. Size-exclusion mechanism is typical for porous membrane (e.g. polypropylene glycol), both size and charge differences define ion-exchange membrane effectiveness, and partition coefficients are specific parameters for non-porous membrane composed of polymeric film. In addition, membrane pores could be impregnated with a water-immiscible organic solvent to enhance the separation capability. Application of these new sample preparation techniques yields to a significantly reduced consumption of toxic organic solvents, decreased sample amount and improvement of detection limits.

Organochlorinated pollutants and polycyclic aromatic hydrocarbons (PAHs) belong to the most common priority substances defined the European

Water Framework Directive, which mandatory limits of detection in range of ng/l. Organochlorinated pollutants are represented by agricultural insecticides and polychlorinated biphenyls (PCBs). Some of insecticides are persistent in environment due to their problematic degradation by microorganisms, and as a result, their utilization is restricted in many countries. In addition, organochlorinated pesticides are commonly included by International Agency for Research of Cancer (IARC) in Group 2B “possibly carcinogenic to humans”, as well as in Toxic Substances and Disease Registry (U.S. Agency), because of its effects on endocrine, neurological and reproductive human organ systems. One of the first insecticides, dichlorodiphenyltrichloroethane (DDT) have been synthesized in form of two isomers, but only *p,p'*-DDT was used commercially. Dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) are degradation products of DDT, and usually found as contaminants of DDT preparation process. Hexachlorocyclohexanes (HCH) represents the group of 9 isomers, where the special attention should be paid on its  $\gamma$ -form (lindane), whereas the other forms are mostly the byproducts of lindane synthesis. Aldrin is easily converted into dieldrin in environment and living organisms, and characterized by low mobility in soil and advanced bioaccumulation properties. Heptachlor is usually found in stable form of heptachlor epoxide in environmental samples, because of the bacterial influence. In common, endosulfan is not detected in waters, only in agricultural runoff and rivers in industrial zones and hazardous waste localities.

Polychlorinated biphenyls represent a nonpolar organic hydrocarbons group of 209 congeners containing from one to ten chlorine atoms connected

to a pair of linked benzene rings. In the US the mixture of PCBs has the technical name Aroclor with 4 numbers specification, where the first two figures point on the number of carbon atoms in the phenyl rings and the second two indicate the percentage of chlorine by mass in the mixture, e.g. Aroclor 1242, Aroclor 1254 and Aroclor 1260. In other countries PCBs commercial mixtures were marked under other names, e.g. Clophen (Germany), Kanechlor (Japan), Delor (Czechoslovakia) and Sovol (USSR). Coplanar configuration of PCBs is found for those congeners with chlorine substitution at the *para* and at least two *meta* positions on biphenyl nucleus, but for non-*ortho* substitutions. It was reported about high individual toxicities of such PCBs (PCBs 77, 81, 126, 169), but usually these congeners are rarely present in environmental samples (at level of the parts of trillion range). A single *ortho*-chloro substituted PCBs (105, 114, 118, 123, 156, 157, 167, 189) are also relatively coplanar and consequently demonstrate enzyme inducing potencies (McFarland et al. 1989). These non-*ortho*-coplanar and mono-*ortho*-chloro congeners are also called “dioxin-like” or “WHO” PCBs. The toxicity of particular PCB depends on similarity of its molecular spatial configuration to molecular structure 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin). Some di-*ortho* coplanar PCB molecules (128, 138, 158, 166, 168, 170) are also potential toxicants, especially congeners 138 and 153 which are the major components of PCB technical mixtures. In common, environmental samples are usually analyzed for their content of the seven European indicator PCB (28, 52, 101, 118, 138, 153, 180) and the 36 McFarland and Clarke PCBs (18, 37, 44, 49, 52, 70, 74, 77, 81, 87, 99, 101, 105, 114, 118, 119, 123, 126, 128, 138, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 180, 183, 187, 189, 194, 201) (Larsen 1995).

PAHs as products of incomplete combustion of organic compounds are supplied into the environment in the form of resins, oils, coal, automobile exhaust emissions and cigarette smoke. PAHs show high human carcinogenic and mutagenic effect inducing oxidative stress and oxidative DNA damage, and are easily concentrated through biological chain (Ma et al. 2010). The following 16 PAHs are required by the United States Environmental Protection Agency (US-EPA) to control in water: acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorine, indeno[1,2,3-*c,d*]pyrene, naphthalene, phenanthrene, and pyrene, and 8 of them are also recommended by the EU legislation.

### Sample preparation procedures for organochlorinated pollutants

The ISO 6468:1996 procedure proposed liquid-liquid extraction with hexane, heptane or petrolether as sample preparation procedure for extraction of organochlorine insecticides and polychlorinated biphenyls from surface waters. Previously the acidity of the water samples (30–100 ml) should be regulated to pH 5–7.5 value, whereas for water sample with endosulfane to pH 2. Derouiche et al. tested two commercial solid phase microextraction (SPME) fibres with different thickness of coating such as PDMS (7, 30, 100  $\mu\text{m}$  film thicknesses) and PDMS-DVB (65  $\mu\text{m}$  film thickness) for determination of 15 OCPs and 20 PCBs in aqueous samples (Derouiche et al. 2007). PDMS-DVB fibre was more effective for extraction of high volatile compounds (especially di-, tri- and tetra-PCBs), whereas other target analytes were more effectively concentrated with PDMS fibre (100  $\mu\text{m}$ ) under the selected experimental conditions (Table 1). Camino-Sánchez et al. validated a stir bar sorptive extraction (SBSE) method for the simultaneous analysis of 77 POPs including 10 PCBs in river water (Camino-Sánchez et al. 2012). Preconcentration procedure was carried out from 200 ml of water with 10 g of NaCl by PDMS stir bar (0.5 mm thickness, 20 mm length) for 24 h. It should be noticed that this method provided a possibility to analyze a large number of analytes in one run with very low LOQ values. RSD values increased with increasing number of chlorine atoms in PCB structure, and quantification characteristics of method were sufficient for analysis of such complicated mixture.

In spite of SPME, a micro-drop of organic solvent suspended from the tip of a microsyringe which is used for single drop microextraction (SDME) procedure could be renewed for each experiment. The organochlorine pesticides were successfully extracted by 1.8–2  $\mu\text{l}$  of toluene from 5–10 ml sample during 15–37 min at constant stirring (Lambropoulou et al. 2007; Cortada et al. 2009a). Although the recovery characteristics of used SDME was high for most of studied compounds, the sensitivity of the procedure was lower than for mentioned above SBSE and SPME techniques. Polypropylene hollow fiber (600  $\mu\text{m}$  inner diameter, 200  $\mu\text{m}$  thickness of the wall, 0.2  $\mu\text{m}$  pore size) filled with 10–20  $\mu\text{L}$  toluene as acceptor phase was applied for hollow-fiber liquid-phase microextraction (HF-LPME) for concentration of organochlorine insecticides from 1.8–5 ml of water sample. As the result the obtained LoD values were lower than for SDME (Lambropoulou et al. 2007).

In the case of dynamic hook-type liquid-phase microextraction (DHT-LPME), a polypropylene

hollow fibre with hook shape inserted into a microsyringe filled with 35  $\mu\text{L}$  of 1-hexanol was placed in the headspace above 10 ml of water sample. The extraction occurs on a large drop (13–14  $\mu\text{L}$ ) formed inside the fibre. The LoD value (2–5 ng/L) for the proposed analytical procedure was near to those required by ISO 6468:1996 technique (Chen et al. 2009). The modified version of DHT-LPME, dynamic headspace time-extended helix liquid-phase microextraction (DHS-TEH-LPME) procedure utilized the microsyringe with 13  $\mu\text{L}$  portion of 1-octanol revolved around with hollow fibre with 1-octanol impregnated pores (Huang et al. 2009). Such equipment was applied for headspace preconcentration from a 110 ml aqueous sample. Since 10  $\mu\text{L}$  of the received extract should be injected, special inlet is required. The promising results were received for *o,p'*-DDT and aldrin, for which observed LoD was lower than 1 ng/L. Dispersive liquid-liquid microextraction (DLLME) with 10  $\mu\text{L}$  of tetrachloroethylene (extraction solvent) and 1 mL of acetone (disperser solvent) was used for extraction procedure of 10 ml of water sample (Cortada et al. 2009b). After centrifugation procedure of cloudy solution, 2  $\mu\text{L}$  of extractant was recovered and injected into the GC-MS instrument. This procedure provided much improved sensitivity for organochlorine insecticides compared to SDME. In spite of HF-LPME, membrane-assisted extraction (MASE) utilizes non-porous membrane since porous membrane has adsorption effects (Lambropoulou et al. 2007). Also up to 1 ml of solvent could be immobilized in this case, whereas only 10–20  $\mu\text{L}$  of solvent in HF-LPME. The membrane is commonly inexpensive and could work as a filter to prevent extraction of larger molecules and interferences for sample clean-up procedures (Lambropoulou et al. 2007) e.g. flat membrane from low-density polyethylene glycol (Hauser et al. 2001), dense polypropylene bags (Hauser et al. 2004). Nonpolar solvents (heptane, cyclohexane) were preferred as acceptor phase. It should be noticed that in comparison with the ISO procedure, better LoDs were received with MASE for most of target compounds. The main disadvantages of MASE procedure were long extraction time (12 h) and its limitation for polar compounds, because of the nonpolar character of the used membrane. In dispersive liquid-liquid microextraction with solidification of a floating organic drop (DLLME-SFO), a single microdroplet (2  $\mu\text{L}$ ) or a few droplets (total volume 10  $\mu\text{L}$ ) could be used for extraction (Yamini et al. 2008; Leong et al. 2009). Nonpolar hexadecane or polar 1-dodecanol organic solvents were applied for 5–20 ml of water

sample. In both cases, the sample was cooled by inserting into an ice bath, and 1–2  $\mu\text{L}$  of extract was injected. Similarly to DLLME-SFO, small amounts of solvent were required (13  $\mu\text{L}$  of mixed organic solvent (TCE:TBME = 4:6) in dispersive liquid-liquid microextraction with little solvent consumptions (DLLE-LSC) for 10 ml of sample (Tsai et al. 2009). High recoveries were received in this case (90.5–109.4 %). Ultrasonic radiation was efficient for acceleration of mass transfer process between two immiscible phases (Ozcan et al. 2009; Regueiro et al. 2008). Extraction with chloroform (100–200  $\mu\text{L}$ ) was performed from 10 ml of water sample in an ultrasonic water bath for 5–10 min. In general, LoDs of the determined compounds were higher than the recommended values by ISO procedure, but the improved recoveries (83–103 %) were obtained with DLLME-SFO procedure.

As to PCBS the PDMS fibre (30  $\mu\text{m}$  film coating) was used for concentration of the congeners from water sample in presence of PAHs and phthalate esters (Cortazar et al. 2002). In this case, a larger amount of water sample was required for extraction, but much worse LoD values were received compared to the other similar investigations. Polydimethylsiloxane (PDMS, 100  $\mu\text{m}$ ) SPME fiber and porous polypropylene hollow fibre (PC-HFME) with 2,5-substituted pyridine were compared for the extraction of PCB congeners from a 10 ml coastal sea water sample (Basheer et al. 2007). Although the developed method of PC-HFME demanded utilization of desorption procedure with 100  $\mu\text{L}$  of hexane and ultrasonication, it was highly reproducible with better extraction efficiency than SPME. A single drop of immiscible solvent suspended in a sample (SDME) and extraction through a membrane (MASE) were applied for concentration of PCB congeners from environmental samples (Table 1) (Lambropoulou et al. 2007). 5 ml of sample was extracted with a 1.6  $\mu\text{L}$  drop of toluene during 15 min in the case of SDME, and whereas 15 ml of the NaCl saturated aqueous sample was concentrated into 800  $\mu\text{L}$  of cyclohexane through polypropylene membrane during 30 min at constant shaking in MASE. In this case, SDME preconcentration procedure was more effective as to the received LoD and recovery values. Razaeei et al. (Razaeei et al. 2008) tried DLLME with 500  $\mu\text{L}$  acetone as dispersive solvent and 10.0  $\mu\text{L}$  of chlorobenzene as extraction solvent for 5 ml of PCBs spiked water sample. LoD values of this procedure were improved compared to previously described SPME (Cortazar et al. 2002), SDME (Lambropoulou et al. 2007) and MASE (McFarland et al. 1989) sample preconcentration techniques.

**Tab. 1.** Sample preparation procedure for organochlorine insecticides.

Sample preparation	Compounds	Type of water	Analysis	LoD (ng/l)	Recovery (%)	RSD (%)	Ref.
SPME	aldrin	River water	GC-MS	4.5	96.2	11.34	Derouiche et al. 2007
	dieldrin	River water	GC-MS	8.1	91.5	15.86	
	<i>p,p'</i> -DDT	River water	GC-MS	26.3	76.3	19.7	
	<i>o,p'</i> -DDE	River water	GC-MS	0.4	83.6	16.45	
	<i>p,p'</i> -DDE	River water	GC-MS	1.0	89.7	16.45	
	<i>o,p'</i> -DDD	River water	GC-MS	7.2	87.2	20.64	
	$\gamma$ -HCH	River water	GC-MS	1.6	101.2	11.64	
	hexachlorobenzene	River water	GC-MS	16.2	105.1	13.94	
	heptachlor	River water	GC-MS	22.0	105.2	11.79	
	heptachlor epoxide	River water	GC-MS	4.3	96.3	6.12	
PCBs	An artificial sea water, spiked tap water	GC-MS	0.13–4.63	83–93	4.4–15.7	Basheer et al. 2007	
	Water	GC-MS	30–110		8–14	Cortazar et al. 2002	
SBSE	aldrin	River water	GC-MS	0.25*	111	8	Camino-Sánchez et al. 2012
	dieldrin	River water	GC-MS	0.25*	100	16	
	endrin	River water	GC-MS	1.50*	92	14	
	<i>p,p'</i> -DDT	River water	GC-MS	0.25*	101	10	
	<i>p,p'</i> -DDT + <i>p,p'</i> -DDD	River water	GC-MS	0.50*	97	14	
	<i>o,p'</i> -DDT	River water	GC-MS	0.25*	103	15	
	$\alpha$ -endosulfan	River water	GC-MS	0.25*	100	13	
	$\beta$ -endosulfan	River water	GC-MS	1.50*	96	16	
	$\alpha$ -HCH	River water	GC-MS	0.25*	98	14	
	$\beta$ -HCH	River water	GC-MS	1.50*	99	12	
	$\delta$ -HCH	River water	GC-MS	1.50*	100	16	
	heptachlor	River water	GC-MS	0.25*	100	10	
	heptachlor epoxide	River water	GC-MS	0.25*	98	12	
	pentachlorobenzene	River water	GC-MS	0.25*	101	24	
	hexachlorobenzene	River water	GC-MS	2.50*	105	11	
	PCBs	River water	GC-MS	10*	76–105	6–24	
SDME	aldrin	Water, wastewater	GC-MS	53	90±8	9.9	Cortada et al. 2009a
	dieldrin		GC-ECD	5	96.7–96.1	5.7	Lambropoulou et al. 2007
	dieldrin	Water, wastewater	GC-MS	53	90±8	9.9	
	dieldrin	Water, wastewater	GC-MS	22	78±8	6.3	Cortada et al. 2009a
	endrin	Water, wastewater	GC-MS	68	78±6	9.8	
	<i>p,p'</i> -DDT	water, tap, reservoir water	GC-ECD	200	90.5–92.6	9.6	Lambropoulou et al. 2007
	<i>p,p'</i> -DDT	Water, wastewater	GC-MS	101	50±10	7.8	Cortada et al. 2009
	<i>p,p'</i> -DDE	water, tap, reservoir water	GC-ECD	50	94.2–98.3	5.4	Lambropoulou et al. 2007
	<i>p,p'</i> -DDE	Water, wastewater	GC-MS	25	43±5	9.0	Cortada et al. 2009
	<i>p,p'</i> -DDD	Water, wastewater	GC-MS	22	47±7	6.9	
	$\alpha$ -endosulfan	water, tap, reservoir water	GC-ECD	200	83.3–90.4	4.6	Lambropoulou et al. 2007
		Water, wastewater	GC-MS	64	47±6	7.6	Cortada et al. 2009a
	$\beta$ -endosulfan	Water, wastewater	GC-MS	71	52±5	7.9	
	$\alpha$ -HCH	Water, wastewater	GC-MS	87	103±8	6.7	

Sample preparation	Compounds	Type of water	Analysis	LoD (ng/l)	Recovery (%)	RSD (%)	Ref.
	$\beta$ -HCH	Water, wastewater	GC-MS	93	100 $\pm$ 8	6.5	
	$\gamma$ -HCH	water, tap, reservoir water	GC-ECD	20	97.2	3.2	Lambropoulou et al. 2007
		Water, wastewater	GC-MS	45	102 $\pm$ 8	6.5	
	$\delta$ -HCH	Water, wastewater	GC-MS	66	101 $\pm$ 8	8.2	
	PCBs	Distilled water, river, lake, tap water	GC-ECD	2.5	88–102	6.8–7.9	
HF-LPME	aldrin	rainwater	GC-MS (SIM)	59	79.3–98.7	2.01	Lambropoulou et al. 2007
		Water, seawater	GC-MS (SIM)	6		8.6	
		seawater	GC-MS (SIM)	59	83.6–89.5	2.01	
	dieldrin	Water, seawater	GC-MS	1		5.7	
		rainwater	GC-MS	47	74.9–87.3	2.32	
		seawater	GC-MS	47	91.4–97.1	2.32	
	edrin	Water, seawater	GC-MS	8		4.7	
		rainwater	GC-MS	33	85.6–93.1	1.93	
		seawater	GC-MS	31	89.3–90.0	5.50	
	<i>p,p'</i> -DDT	rainwater	GC-MS	17	81.6–97.6	1.66	
		seawater	GC-MS	17	81.7–94.7	1.66	
		Water, seawater	GC-MS	1		7.4	
	<i>p,p'</i> -DDE	Water, seawater	GC-MS	1		10.6	
	<i>p,p'</i> -DDD	rainwater	GC-MS	28	85.0–108.4	2.28	
		seawater	GC-MS	28	92.1–95.2	2.28	
		Water, seawater	GC-MS	1		7.4	
	endosulfan	rainwater	GC-MS	28	79.4–90.1	3.13	
		seawater	GC-MS	28	92.0–93.3	3.13	
	$\alpha$ -HCH	rainwater	GC-MS	17	86.1–106.7	13.72	
		seawater	GC-MS	17	91.8–93.6	13.72	
		water, seawater	GC-MS	1		6.6	
	$\beta$ -HCH	rainwater	GC-MS	29	87.4–111.6	10.29	
		seawater	GC-MS	29	85.3–91.3	10.29	
		water, seawater	GC-MS	5		5.5	
	$\gamma$ -HCH	rainwater	GC-MS	13	93.4–112.6	14	
		seawater	GC-MS	13	84.1–86.52	14	
		water, seawater	GC-MS	3		6.5	
	$\delta$ -HCH	water, seawater	GC-MS	2		5.5	
	simazine	Deionized water	GC-MS	10	94.3–104.5	0.78–2.68	
DHT-LPME	dieldrin	Deionized, rainwater	GC-MS	2	84.2	14.4	Chen et al. 2009
	<i>o,p'</i> -DDT	Deionized, rainwater	GC-MS	4	94.4	6.5	
	<i>p,p'</i> -DDE	Deionized, rainwater	GC-MS	4	99.6	10	
	$\alpha$ -endosulfan	Deionized, rainwater	GC-MS	5	85.8	12.2	
DHS-TEH-LPME	aldrin	Water, river water	GC-MS/MS	0.33		10.9	Huang et al. 2009
	dieldrin	Water, river water	GC-MS/MS	25	106 $\pm$ 12	16.3	
	<i>o,p'</i> -DDT	Water, river water	GC-MS/MS	0.37	98 $\pm$ 15	17.4	
	$\alpha$ -endosulfan	Water, river water	GC-MS/MS	19	109 $\pm$ 15	12.5	
DLLME	aldrin	Distilled, river tap, surface water	GC-MS	9	81–97	7	Chen et al. 2009

Sample preparation	Compounds	Type of water	Analysis	LoD (ng/l)	Recovery (%)	RSD (%)	Ref.
	dieldrin	Distilled, river tap, surface water	GC-MS	4	82–100	9	Cortada et al. 2009b
	endrin	Distilled, river tap, surface water	GC-MS	4	81–102	8	
	<i>p,p'</i> -DDT	Distilled, river tap, surface water	GC-MS	4	75–93	11	
	<i>p,p'</i> -DDE	Distilled, river tap, surface water	GC-MS	2	81–99	7	
	<i>p,p'</i> -DDE	Distilled, river tap, surface water	GC-MS	4	84–96	8	
	$\alpha$ -endosulfan	Distilled, river tap, surface water	GC-MS	5	83–95	6	
	$\beta$ -endosulfan	Distilled, river tap, surface water	GC-MS	25	85–103	15	
	$\alpha$ -HCH	Distilled, river tap, surface water	GC-MS	3	101–113	7	
	$\beta$ -HCH	Distilled, river tap, surface water	GC-MS	5	96–112	25	
	$\gamma$ -HCH	Distilled, river tap, surface water	GC-MS	8	96–111	5	
	PCBs	Well, river, seawater	GC-ECD	1.0–1.5	92–103	4.1–11.0	Rezaei et al. 2008
MASE	alachlor	Milli-Q, drinking water	GC-MS	10	72.3	10.7	Lambropoulou et al. 2007
	aldrin	Bidistilled water	GC-MS	5		10.9	Hauser et al. 2004
	dieldrin	Bidistilled water	GC-MS	2		7.3	
	endrin	Bidistilled water	GC-MS	2		7.0	
	<i>p,p'</i> -DDT	Bidistilled water	GC-MS	2		9.5	
	<i>o,p'</i> -DDT	Bidistilled water	GC-MS	2		7.9	
	<i>p,p'</i> -DDE	Bidistilled water	GC-MS	2		4.7	
	<i>p,p'</i> -DDD	Bidistilled water	GC-MS	2		6.8	
	$\beta$ -endosulfan	Bidistilled water	GC-MS	10		7.4	
	$\alpha$ -HCH	Milli-Q, drinking water	GC-MS	0.01	81.8	15.5	Lambropoulou et al. 2007
		Deionized, river, drinking water	GC-MS	10–25	107.6	5.2	
		Reagent water, groundwater	GC-MS	20	89	6	Hauser et al. 2001
		Bidistilled water	GC-MS	5		5.7	Hauser et al. 2004
	$\beta$ -HCH	Milli-Q, drinking water	GC-MS	0.02	73.8	16.7	Lambropoulou et al. 2007
		Reagent water, groundwater	GC-MS	10			Hauser et al. 2001
		Bidistilled water	GC-MS	10		4.8	Hauser et al. 2004
	$\gamma$ -HCH	Milli-Q, drinking water	GC-MS	0.04	98.5	16	Lambropoulou et al. 2007
		Reagent water, groundwater	GC-MS	10	93	9	Hauser et al. 2001
		Bidistilled water	GC-MS	10		6.0	Hauser et al. 2004
	$\delta$ -HCH	Milli-Q, drinking water	GC-MS	0.01	68.7	17.1	Lambropoulou et al. 2007
		Reagent water, groundwater	GC-MS	25	105	8	Yamini et al. 2008
		Bidistilled water	GC-MS	2		5.4	Hauser et al. 2004
	hexachlorobenzene	Milli-Q, drinking water	0.02	47.3	2.6		Lambropoulou et al. 2007
		Reagent water, groundwater	10	93	9		Yamini et al. 2008
		Bidistilled water	2		6.0		Hauser et al. 2004

Sample preparation	Compounds	Type of water	Analysis	LoD (ng/l)	Recovery (%)	RSD (%)	Ref.
	PCBs	Drinking water		10.0	72.3	10.7	Lambropoulou et al. 2007
DLLME-SFO	aldrin	Deionized, tap, river, agriculture water	GC-ECD	7		5.4	Yamini et al. 2008
		Tap, lake water	GC-ECD	21.5	90.2–94.8	8.5	Leong et al. 2009
	dieldrin	Deionized, tap, river, agriculture water	GC-ECD	19		6.4	Yamini et al. 2008
	endrin	Deionized, tap, river, agriculture water	GC-ECD	14		7.2	
	<i>p,p'</i> -DDT	Deionized, tap, river, agriculture water	GC-ECD	16		5.5	
	<i>o,p'</i> -DDT	Tap, lake water	GC-ECD	25.1	85.1–90.0	8.8	Leong et al. 2009
	<i>p,p'</i> -DDE	Deionized, tap, river, agriculture water	GC-ECD	10		6.3	Yamini et al. 2008
		Tap, lake water	GC-ECD	28.3	86.3–102.5	7.2	Leong et al. 2009
	<i>p,p'</i> -DDD	Deionized, tap, river, agriculture water	GC-ECD	8		4.9	Yamini et al. 2008
	$\alpha$ -endosulfan	Deionized, tap, river, agriculture water	GC-ECD	16		5.5	
		Tap, lake water	GC-ECD	12.1–19.7	87.0–96.2	7.6	Leong et al. 2009
	$\beta$ -endosulfan	Deionized, tap, river, agriculture water	GC-ECD	9		5.9	Yamini et al. 2008
Tap, lake water		GC-ECD	12.9	85.5–93.5	5.8	Leong et al. 2009	
$\gamma$ -HCH	Deionized, tap, river, agriculture water	GC-ECD	11		5.8	Yamini et al. 2008	
DLLE-LSC	aldrin	River, reservoir water	GC-MS	0.6–1.2	93.9–104.5	4.1–7.1	Tsai et al. 2009
		River, reservoir water	GC-MS	0.4–1.1	93.6–100.5	8.2–8.9	
	$\alpha$ -endosulfan	River, reservoir water	GC-MS	0.4–0.8	99.5–102	5.6–9.7	
	$\beta$ -endosulfan	River, reservoir water	GC-MS	1.3–2.5	93.1–101.6	6.0–8.2	
USAEME	aldrin	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–6	90–98		Ozcan et al. 2009
		Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	83–94		
	endrin	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	94–103		
	<i>p,p'</i> -DDT	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	75–83		
	<i>p,p'</i> -DDE	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	98–100		
	<i>p,p'</i> -DDD	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	95–100		
	$\alpha$ -endosulfan	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	94–101		
	$\beta$ -endosulfan	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	90–101		
	$\alpha$ -HCH	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	100–103		
	$\beta$ -HCH	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	98–100		
$\gamma$ -HCH	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	100–103			
	Ultrapure, tap water	GC-MS	21	103–109	6–9	Regueiro et al. 2008	
$\gamma$ -HCH	Distilled, tap, well, surface water	GC- $\mu$ ECD	2–16	100–102		Ozcan et al. 2009	
PC-HFME	PCBs	An artificial sea water, spiked tap water	GC-MS	0.04–0.21	83–93	1.6–8.6	Basheer et al. 2007

### *Sample preparation for PAHs analysis*

Two ISO sample preparation procedures (ISO 17993:2002 and ISO 28540:2011) based on LLE with hexane are commonly used for PAHs analysis by GC and HPLC techniques. In both cases, one liter of water sample is dechlorinated with sodium thiosulfate, and pH of water is adjusted to value 2 with sodium thiosulfate for HPLC analysis. Extract for GC analysis is cleaned through the cartridge filled with silica, and in the case of HPLC, extract is eluted from cleanup column including silica gel with mixture of dichloromethane/hexane (1:1). A number of alternative sample preparation procedures were developed for PAHs extraction with gas chromatography (Table 2). Multi-walled carbon nanotubes (MWCNTs) were used as a novel adsorbent for SPE procedure of 16 PAHs from environmental water samples (Ma et al. 2010). In this procedure, a 500 ml water sample was loaded at the flow rate of 5.0 ml/min, and after 30 min under vacuum (to remove residual water), analytes were eluted by 15 ml of *n*-hexane at the flow rate of 1 ml/min. Lower recoveries (about 10 %) were found for C18 sorbent material compared to MWCNTs. PAHs as nonpolar compounds can be easily adsorbed on MWCNTs than on C18, because the delocalized  $\pi$ -bond interaction between PAHs and MWCNTs is much stronger than the hydrophobic interaction between PAHs and C18 group. In the addition, low LoD was received in this case. Additionally, 24 PAHs were concentrated from wastewater by SBSE with a 10-mm long stir bar coated with a 0.5 mm film thickness layer of PDMS. Extraction procedure was carried out from 50 ml of non-filtered wastewater with 10 % of methanol to prevent PAHs adsorption on the glassware during 4 h (Barco-Bonilla et al. 2011). Huertas et al. (Huertas et al. 2007) used two times longer stir bar for extraction of 7 PAHs in the presence of other priority substances from the European Water Framework Directive in seawater. However, in this case the increased amount of water sample (100 ml) as well as a long extraction time (12 h) were required. Consequently LoD values of PAHs were decreased in one order of magnitude. SBSE and SPME procedures were compared by Popp et al. (Popp et al. 2003). One hundred micrometer PDMS SPME fibre or a 10 mm stir bar coated with a 0.5 mm layer of PDMS was used for 10 ml of water sample during 1 h. Since SBSE is characterized by higher phase ratio (volume of water phase to the volume of the PDMS phase), it results in higher recoveries and lower LoD values than SPME. The same fibre was tested for monitoring of degradation of PAHs after ultrasonic treatment from 5 ml of spiked water sample (Psillakis et al. 2003), however the much

worse quantification characteristics were received in this case. Another commercial fibre (65- $\mu$ m PDMS/DVB) was used for concentration of 27 parent and alkylated PAHs with diverging polarities (Fernández-González et al. 2007). It was found that organic modified (e.g. methanol) which is usually recommended for prevention of PAHs adsorption on the glass walls, has negative influence on recoveries of PAHs. In addition, solution ionic strength and sample pH has shown little effect on the extraction of analytes. In general very low values of LoD comparable with best results of SBSE procedure was received. Alternative SPME fibre coating, such as electrochemically prepared dodecylsulfate-doped polypyrrole with a porous structure was applied for extraction of 8 PAHs (Mohammadi et al. 2005). Although NaCl was added to 10 ml of water sample, LoDs were too high in comparison with other sample preparation techniques. Rezaee et al. (Rezaee et al. 2006) tested different combinations of an extraction solvent (carbon disulfide, carbon tetrachloride and tetrachloroethylene) and dispersive solvent (acetone, acetonitrile and methanol) for effective concentration of 16 PAHs by DLLME method. As the result, the higher extraction effectiveness was reached with tetrachloroethylene, whereas variations of recoveries for tested disperse solvents were not remarkable, but acetone is less toxic and cheaper. 8.0  $\mu$ l of tetrachloroethylene as extraction solvent and 1.00 ml of acetone as disperser solvent were injected into 5.00 ml of water solution and centrifuged for 1.5 min. The increased volume of extraction solvent decreased the enrichment factor and recovery. Cloudy state is not formed at a low volume of acetone, whereas at the high volume of acetone, the solubility of PAHs in water increases, therefore the extraction efficiency decreases. In comparison with LPME and SPME, DLLME was faster, simpler and inexpensive procedure with sufficient quantitative characteristics for PAH determination.

The SBSE and SPME sample preparation procedures were applied for HPLC analysis of PAHs (Table 3). The peak areas of the compounds in the SBSE chromatograms were 3- to 10- fold higher than those of the SPME chromatogram, and similarly LoD characteristics were better for SPME procedure (Popp et al. 2003). In-tube SPME device coated with PDMS was used for preconcentration of 4 PAHs from 10 ml of water sample (Bagheri et al. 2004). In this case nearly all the sample reacts with sorbent because of frequent withdrawing and ejecting the water sample from/into a vial. The received results were compatible with classical SPME procedure. Ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) method was



**Tab. 2.** Sample preparation procedures for PAHs before GC analysis.

Sample preparation	Type of water	Analysis	LoD (ng/L)	Recovery (%)	RSD (%)	Ref.
SPE	Spiked real water	GC-MS	2.0–8.5	80.5–127	1.2–12.1	Ma et al. 2010
SBSE	Wastewater	GC-MS	2–10	62–118	2–26	Barco-Bonilla et al. 2011
	Seawater	GC-MS	0.1–7.3	90.2–97.3	2.7–14.7	Huertas et al. 2007
	Spiked ater	GC-MS	0.05–0.5	29–95	2.5–21.7	Popp et al. 2003
SPME	Water spiked	GC-MS	0.2–1.2	11–45	3.0–16.8	
	Spiked water	GC-MS	10–700			Psillakis et al. 2003
	Tap, well, superficial water, seawater	GC-MS	0.07–0.76	59–103	6.1–11.8	Fernández-González et al. 2007
	Sea water	GC-MS	50–160		2.6–7.6	Mohammadi et al. 2005
DLLME	Surface water	GC-FID	7.0–30.0	82.0–111	1.4–10.2	Rezaee et al. 2006

**Tab. 3.** Sample preparation procedures for PAHs before HPLC analysis.

Sample preparation	Type of water	Analysis	LoD (ng/L)	Recovery (%)	RSD (%)	Ref.
SBSE	Spiked water	HPLC-MS	0.3–2			Popp et al. 2003
SPME	Water spiked	HPLC-MS	1.0–10			
	Snow sample	HPLC-FLD	1–6		2.6–6.3	Bagheri et al. 2004
UASEME	Tap, rain, waste water	HPLC-FLD	0.6–62.5	73–120	1.8–10.8	Cheng et al. 2011

applied for determination of PAHs in tap, river and waste waters (Cheng et al. 2011). It was found that the emulsification temperature and the equilibrium time have no significant effect on the extraction efficiency of the PAHs. 1-octanol, 1-dodecanol, *n*-tetradecane and cyclohexane were tested as extraction solvents, and the last one provides the best recoveries. It was found that nonpolar PAHs were more easily emulsified by the non-ionic surfactant (Tween 80 and Triton X10) than as ionic surfactant (SDS, CATB). At the result 20 µl of cyclohexane and 10 µl of Tween 80 were added to 5 ml of aliquot of water containing 6 % of NaCl. The LoDs of PAHs were in wide range 0.6–62.5 ng/L.

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