



Advances in sample pretreatment and detection of PCBs in the environment

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ABSTRACT

Pollution of the environment by polychlorinated biphenyls (PCBs) continues to be a global concern because of their toxicity, persistence, long-range transport properties and ability to bioaccumulate in fatty tissues. PCBs are classified as 'probable human carcinogens' as well as endocrine-disrupting compounds, and, therefore, their presence in the environment is a threat to human and animal health. Their monitoring in the environment requires novel techniques to achieve detection at very low concentrations that demonstrate harmful effects to the ecosystem. This review discusses conventional and novel sample preparation methods that make use of novel sorbent materials that are aimed at reducing matrix interferences in different environmental and biological matrices. It also focuses on advancements in detection techniques aimed at high selectivity and sensitivity, and low detection limits. These range from conventional chromatographic techniques to sensor technology that facilitates the detection of PCBs at very low concentrations prompting the attainment of cost-effective and reliable methods that promote routine monitoring.

1. Introduction

Environmental pollution remains the world's biggest problem and, more so, in developing countries because many of them either do not have environmental pollution control measures in place or have not put adequate enforcement structures to ensure full compliance with policies. Some of the pollutants that are released to the environment persist in nature long after their utilization and are subsequently toxic, bioaccumulative, and susceptible to long-range environmental transport. Polychlorinated biphenyls (PCBs) portray these characteristics and are classified as persistent organic pollutants (POPs) under the Stockholm Convention (Lallas, 2001). The convention banned the production and use of PCBs, though they continue to be reported in different environmental compartments as a result of leakage from PCBs containing materials, disposal of old electrical appliances, open burning and incineration of PCB containing waste and emission from reservoirs contaminated by PCBs (Faroon et al., 2001; Ndunda and Wandiga, 2020).

Consequently, they have been detected in air (Qu et al., 2019), water (Huang et al., 2020), soil (Liu et al., 2020a), and sediments (Combi et al., 2020). Once in the environment, human beings and animals are exposed to these pollutants as confirmed by reports of PCBs in body tissues of animals, including blood (Garcia-Heras et al., 2017), serum (Chang et al., 2020), and human milk (Müller et al., 2017), where they have the poten-

tial to cause adverse health effects (Loganathan and Masunaga, 2020). Epidemiological studies and reports on accidental exposure to PCBs indicate that PCBs are probable human carcinogens as well as endocrine-disrupting compounds (Diamanti-Kandarakis et al., 2009; Faroon et al., 2001).

Because of their impact on the environment and potential to harm humans and animals, monitoring PCBs is of global importance as a way of addressing environmental pollution. Their determination in the environment follows a series of steps from sample preparation to quantification, and the techniques applied in these steps are continuously improving to achieve the highest sensitivity, low detection limits, and high selectivity. Sample preparation is majorly the rate-limiting step, and conventional liquid-liquid extraction (LLE) and Soxhlet extraction techniques have been replaced by solid-phase microextraction (SPME), liquid-phase microextraction (LPME), pressurized liquid extraction (PLE) and supercritical fluid extraction (SFE) techniques that employ minimized solvent volumes, novel sorbents and solvents achieving substantive removal of interfering matrices, high throughput and enrichment factors, as well as promoting the spirit of green chemistry. On the other hand, detection techniques have advanced from simple high-performance liquid chromatography with ultraviolet-visible detection (HPLC-UV) and gas chromatography with electron capture detection (GC-ECD) to highly sensitive instruments and miniaturized sensor sys-

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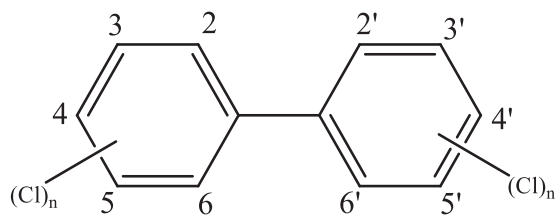


Fig. 1. The general structure of polychlorinated biphenyls.

tems that achieve the required figures of merit in monitoring PCBs. This review aims to highlight these recent developments in sample preparation and detection techniques as well as provide a brief background on PCBs.

2. Polychlorinated biphenyls

2.1. Chemistry and physicochemical properties

Polychlorinated biphenyls (PCBs) are synthetic chlorinated organic compounds consisting of two benzene rings bonded by a single carbon-carbon bond with a general formula of $C_{12}H_{10-n}Cl_n$, where $n = 1$ to 10 (Fig. 1). Each of the ten hydrogen atoms on biphenyl can be substituted with chlorine atoms to yield 209 different compounds (Faroon et al., 2003b) that are named by using either the International Union of Pure and Applied Chemistry (IUPAC) or Ballschmiter and Zell (BZ) system. In the IUPAC system, the PCBs are named according to the number of the carbon to which chlorines are attached and these numbers are listed in sequence followed by the name of the PCB. For example, the PCB congener with chlorines on carbon atoms 2, 2', 3, 4, and 4' is identified as 2,2',3,4,4'-pentachlorobiphenyl. BZ system is the most widely used naming system and uses numbers in reference to specific congeners. Thus, congeners are numbered from PCB 1 to PCB 209 where the structural arrangements of PCBs are correlated in ascending order of the number of chlorine substitutions within each sequential homologue (Mills et al., 2007). For instance, 2,2',3,4,4',5,5'-heptachlorobiphenyl is PCB 180. Among the 209 PCBs congeners, there are the so-called "indicator PCBs" which are recommended for routine monitoring because they were the major components in PCB mixtures and are likely to be detected with the highest frequency (Kim et al., 2004). They include six non-dioxin-like PCBs (PCB 28, 52, 101, 138, 153, and 180) and one dioxin-like PCB (PCB 118) (Table 1).

Non-*ortho* and mono-*ortho* substituted PCBs exhibit a planar structure and are referred to as planar or coplanar PCBs. PCBs with more than two chlorine atoms at the *ortho*-positions exhibit a non-planar structure, thus being classified as non-planar PCBs (Fig. 2).

Planar PCBs are said to be dioxin-like and more toxic, since the phenyl rings of the molecules adopt a planar structure making them display similar toxicity as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Barlow et al., 2016). As a result, the toxicity of dioxin-like PCBs (dl-PCBs) is provided by toxic equivalent factors (TEFs) determined from the most toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin that has a TEF of 1. Non-planar PCBs, are able to rotate and adopt a non-planar conformation far different from that of PCDDs and PCDFs, and are categorized as non-dioxin-like PCBs.

PCBs are generally inert and thermally stable, displaying resistance to disintegration by acids, bases, and heat, hence they persist in the environment for a long period. The hydrophobicity of PCBs is given by the octanol-water partition coefficient (K_{ow}), usually expressed as $\log K_{ow}$, and ranges from 4.09 to 8.18, increasing with the degree of chlorination (Hawker and Connell, 1988). Because PCBs tend to partition in organic solvents, they have very low water solubility ranging from 1.2 to 4.8×10^6 ng L⁻¹ (IARC, 2016). The vapor pressure decreases with an increase in the degree of chlorination ranging from 9.77×10^{-7} to 1.38×10^{-3} mmHg, meaning that the less chlorinated PCBs are more

volatile (Faroon et al., 2003a). The vapor pressure of PCBs is also influenced by the number of chlorine atoms in the *ortho*-positions, whereby it increases with an increase in the number of chlorine substitutions in the *ortho*-positions because of the *ortho*-effect (Nakajoh et al., 2005).

PCBs in the environment can be biologically or abiotically oxidized into toxic PCB derivatives known as hydroxylated polychlorinated biphenyls (HO-PCBs) and methoxylated polychlorinated biphenyls (MeO-PCBs) (Lin et al., 2020). These derivatives exhibit higher toxicity than the corresponding parent PCB, and their toxicity decreases with an increase in the degree of chlorination (Bhalla et al., 2016). PCBs in the environment can also be degraded oxidatively by aerobic bacteria and other microorganisms such as white-rot fungi. PCBs can further be reductively dehalogenated by anaerobic microbial consortia. The biodegradability of PCBs is highly dependent on chlorine substitution, i.e., the number and position of chlorine (Furukawa, 2000).

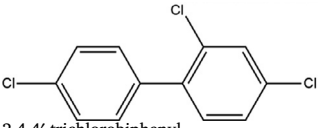
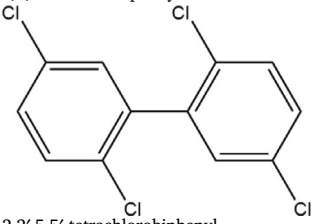
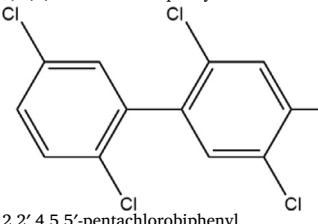
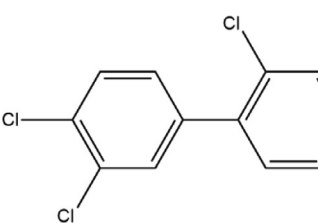
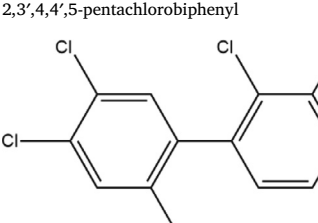
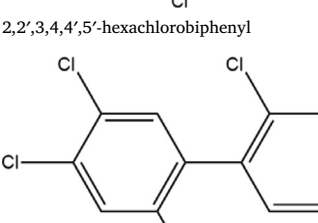
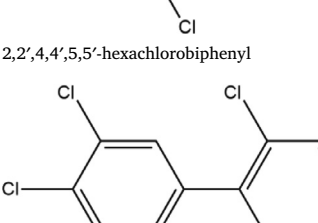
2.2. Levels and environmental effects of PCBs

The commercial production of PCBs began in 1929 and it is estimated that up until 1989 about 1.7 million tonnes had been produced globally (Grossman, 2013). They were typically manufactured as mixtures of individual PCB congeners by the addition of a given percent weight of chlorine to biphenyl, then sold under various trade names, with Aroclor, produced by the Monsanto Company in the USA being the most common (Ahmed, 1976). Because of their extraordinary stability, PCBs were extensively utilized as additives in plastics, paints, pigments, and carbonless paper, and as coolants and lubricants in electrical equipment including transformers and capacitors (Safe, 1994). Their widespread use made PCBs ubiquitous and, hence, they have been detected in almost all environmental compartments as well as in human and animal body tissues.

PCBs were first reported as environmental contaminants through the work of Søren Jensen, who detected PCBs in human blood in 1964 (Jensen, 1972). PCBs were further detected in the Great Lakes region at levels ranging from 2300 to 15,400 ng g⁻¹ for Aroclor 1260, and from 18,600 to 22,400 ng g⁻¹ for Aroclor 1254 in fish from Lake Michigan (Veith and Lee, 1971). In 1977, the Michigan Department of Natural Resources reported PCB levels in fish in the range from 2400 to 5040 ng g⁻¹ (Bowden et al., 1981). Subsequently, extensive studies have reported PCBs in almost all parts of the globe, including places where PCBs were never produced. A study on accumulation and time trends of PCBs in finless porpoises from Korean coastal waters from 2003 to 2015 reported levels between 48.5 and 3580 ng g⁻¹ (Jeong et al., 2020). The concentration of PCBs in surface sediments of the Chaobai River in Beijing was reported to be in the range of 0.125 and 0.6 ng g⁻¹ (Yang et al., 2020). In Africa, levels of PCBs between 15 and 60 ng g⁻¹ in plastic resin pellets from six beaches on the Accra-Tema coastline in Ghana have been reported (Tue et al., 2016). Evaluation of PCBs in Umgeni riverbank soil, KwaZulu-Natal, South Africa, reported levels of PCBs ranging between 10.46 and 89.46 ng g⁻¹ (Gakuba et al., 2019). In Tanzania, an assessment of persistent organochlorine compounds contamination in water and sediments from Lake Victoria revealed levels ranging from 950 to 2240 ng L⁻¹ and bdl to 10.28 ng g⁻¹, respectively (Wenaty et al., 2019). Determination of PCB levels in the Nairobi River, Kenya, reported levels below the detection limit (bdl) to 157.64 ng g⁻¹ in sediments and bdl to 718.78 ng L⁻¹ in water (Ndunda and Wandiga, 2020).

PCBs are known to be persistent and are likely to last in the environment for a long time through redistribution in different environmental compartments and can result into production of more toxic congeners through processes such as thermal degradation (Borja et al., 2005). Moreover, the presence of PCBs in the environment, some at concentrations that exceed the recommended levels, is of great concern because of their ability to enter the food chain and cause adverse health effects to humans and animals. There are no safe levels for exposure to PCBs

Table 1The seven indicator PCB congeners and their octanol-water partition coefficients (K_{ow}) (Hawker and Connell, 1988).

Structure/Nomenclature	PCB congener	Molar mass/g mol ⁻¹	log K_{ow} (25 °C)
 2,4,4'-trichlorobiphenyl	PCB 28	257.5	5.67
 2,2',5,5'-tetrachlorobiphenyl	PCB 52	292	5.84
 2,2',4,5'-tetrachlorobiphenyl	PCB 101	326.4	6.38
 2,2',4,5,5'-pentachlorobiphenyl	PCB 118	326.4	6.74
 2,2',3,4,4',5'-hexachlorobiphenyl	PCB 138	360.9	6.83
 2,2',3,4,4',5'-hexachlorobiphenyl	PCB 153	360.9	6.92
 2,2',3,4,4',5,5'-heptachlorobiphenyl	PCB 180	395.3	7.36

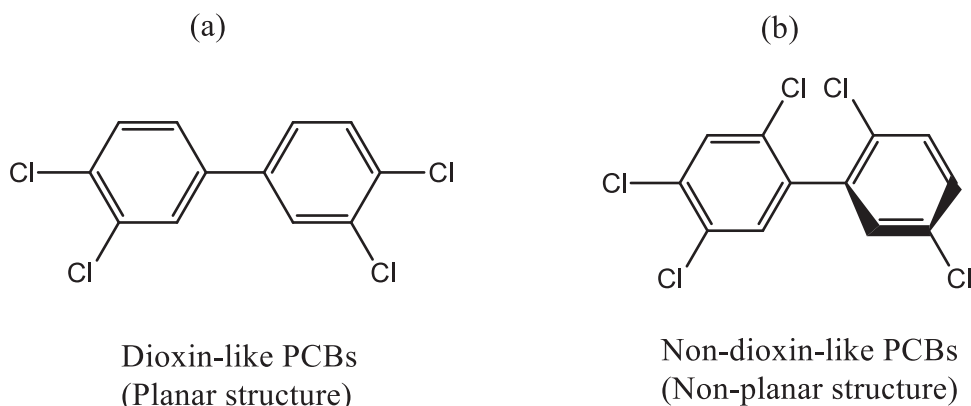


Fig. 2. Examples of (a) planar and (b) non-planar PCBs.

since these compounds are known to bioaccumulative in fatty tissues, so exposure, even at very low concentrations, should be of concern.

2.3. Health implications of PCBs on humans and animals

Human beings and animals are likely to be exposed to PCBs by breathing polluted air (López et al., 2021), exposure to contaminated dust (Abafe and Martincigh, 2015), ingesting contaminated water and food, and incidental and accidental occurrences (Faroon et al., 2000). The United States Environmental Protection Agency (EPA) has a limit of 500 ng L^{-1} for PCBs in drinking water, and the Food and Drug Administration (FDA) has recommended a range of 200 to 300 ng g^{-1} of PCBs in food, whereas the World Health Organization (WHO) allows a PCB intake of 6 ng g^{-1} per day (Ahmad et al., 2019). Exposure to PCBs has been reported to result in adverse health effects on human beings and animals. Consumption of rice contaminated with oil containing PCBs and PCDFs by Japan and Taiwan populations in the 1960s and 1970s, respectively led to manifestations of chloracne, eye discharge, nail and skin pigmentation, and severe liver disease causing death. Fat and liver tissues of patients who died of cancer-related problems were found to have PCBs levels ranging from 100 to 2500 ng g^{-1} (Masuda, 1985). Five years later, blood samples of the victims indicated PCB levels up to 30 ng g^{-1} and 1156 ng g^{-1} in Japan and Taiwan, respectively (Masuda, 1985). High levels of PCBs ranging between 2635 to $10,800 \text{ ng g}^{-1}$ have been reported in human serum in Brescia, Italy (Donato et al., 2006). This highly industrialised town produced PCBs from 1938 to 1984 leading to contamination of the environment and transfer of PCBs into the food chain.

Further investigations have led to PCBs being classified as probable human cancer-causing agents (Ali et al., 2016). Additionally, PCBs have been reported to interfere with the endocrine system and are classified as endocrine-disrupting compounds leading to lower sperm motility, lower birth weight, smaller head circumference, shorter gestational age, delayed puberty among others (Diamanti-Kandarakis et al., 2009; Toft et al., 2004). PCBs have also been reported to influence the psychological development of unborn babies. Women in Taiwan exposed to PCBs in the Yu-Cheng incident gave birth to children with low intelligence quotients (IQ) (Chen et al., 1992). Recently, PCBs have been reported to cause cardiovascular and metabolic diseases (Grimm et al., 2020; Raffetti et al., 2018). Exposure to PCBs has also been associated with a higher risk of dementia characterized by loss of memory, language, problem-solving and other abilities (Raffetti et al., 2020). Likewise, PCBs have been shown to cause adverse health effects in animals reporting endocrine disrupting effects in mice offspring and cancer in dogs (Ferrante et al., 2020; Karkaba et al., 2017). Fish exposed to PCBs have reported moderate hypoxia as well as estrogenic effects (Calò et al., 2010; Sula et al., 2020).

Following the reported effects of PCBs to the environment and human health, the production of PCBs in the United States was banned

by the Toxic Substances Control Act (TSCA) in 1979 and by the Stockholm Convention on POPs in 2004 (Hagen and Walls, 2005). Despite the ban on PCB production and their use in equipment, emissions into the environment still occur. These include emissions from poorly maintained hazard waste sites that contain PCBs, leaks from old transformers containing PCBs that are still in use, and dumping of PCB-containing products, among others (Wolska et al., 2014). From the foregoing, it is clear that monitoring of PCBs in various environmental matrices is still of importance. In particular, newer methods are needed that do not require large volumes of solvents, are less time-consuming and have lower limits of detection.

3. Sample preparation methods for the determination of PCBs

Sample preparation is the pretreatment of a sample before analysis since analytical techniques are often not responsive to analytes in raw form, and interferences may distort the results. It involves pre-concentration and analyte extraction followed by clean-up of the extracts to remove matrix interferences (Mitra and Brukh, 2003). This key step is linked to the positive attributes of reduced matrix interferences, increased sensitivity of analytes, and transfer of analytes into the correct form responsive to analytical instruments (Wen, 2020). Sample preparation methods used in the extraction and preconcentration of PCBs in different environmental matrices have continued to advance to novel protocols that are economical and efficient to attain the low detection limits required for these compounds that occur at trace levels as discussed in the following sections and summarized in Table 2.

3.1. Extraction of analytes in liquid matrices

PCBs can be found in the environment in liquid matrices such as water, milk, human blood, and human serum, from where they are pre concentrated and extracted by liquid-liquid extraction, solid-phase extraction and recently solid-phase microextraction, stir-bar sorptive extraction, dispersive solid-phase extraction, liquid-phase microextraction and passive sampling methods as detailed below.

3.1.1. Liquid-liquid extraction

Liquid-liquid extraction (LLE) is a conventional method used to separate compounds based on their solubility differences in two different immiscible liquids, usually a non-polar organic solvent and a polar solvent. LLE involves a mixing step followed partitioning of analytes between the organic and polar phase (Poole and Poole, 2010). LLE has been applied in the extraction of PCBs in river water, attaining recoveries of 78 to 98% (Megahed et al., 2015), and extraction of PCBs in surface water, reporting recoveries of 87.6 and 91.4% (Zaater et al., 2005). Although LLE may be easily applied to extract contaminants from aqueous samples because of its simple operation and availability of apparatus, it is energy-intensive, suffers from emulsion formation, demands large

Table 2

Summary of sample preparation methods applied in the determination of PCBs from different environmental matrices.

Sample preparation techniques	Country	Matrix	Concentration range	Recoveries (%)	Ref
LLE	Egypt	River water	14,000 to 20,000 ng L ⁻¹	78 to 98	(Megahed et al., 2015)
	Jordan	Surface water	300 to 24 000 ng L ⁻¹	87.6 and 91.4	(Zaater et al., 2005)
SPE	Spain	Milk	600 to 500,000 ng L ⁻¹	> 80	(Picó et al., 1995)
	Spain	Seawater	0.5 to 24 ng L ⁻¹	60 to 70	(Dachs and Bayona, 1997)
	Kenya	Solid matrices	0.22 to 6.74 ng g ⁻¹	79.8 to 111.8	(Ndunda et al., 2015)
	China	Vegetables	17.9 ng g ⁻¹	84.5 to 116.5	(Liu et al., 2019)
SPME	Germany	Sediment porewater	0.01 to 0.034 ng L ⁻¹	84 to 91	(Niehus et al., 2019)
	China	Water samples	8.17 to 28.02 ng L ⁻¹	85.56 to 104.30	(Cheng et al., 2019)
SBSE	Germany	Water samples	3 to 1916 ng L ⁻¹	51 to 93	(Popp et al., 2005)
	Belgium	Human serum	–	50 to 60	(Benijts et al., 2001)
	Berlin	Sediment	54 to 390 ng g ⁻¹	62.8 to 91.5	(Vrana and To, 2013)
d-SPE	Australia	Biological matrices	0.16 to 0.44 ng g ⁻¹	70 to 120	(Baduel et al., 2015)
	China	Fishery and aquaculture products	0.00013 to 0.00097 ng g ⁻¹	60 to 140	(Lu et al., 2014)
	USA	Catfish samples	0.23 to 10.3 ng g ⁻¹	70 and 120	(Sapozhnikova and Lehotay, 2013)
	China	Fish samples	0.7292 to 0.813 ng g ⁻¹	73.41 and 114.21	(Du et al., 2014)
LPME	China	Environmental water samples	–	81.9 to 109.7	(Hou et al., 2019)
	Spain	Human breast milk	5000 to 100,000 ng L ⁻¹	85	(Villegas-Álvarez et al., 2020)
	China	Water samples	18,100 ng L ⁻¹	85.9 to 92.0	(Li et al., 2008)
	China	Water samples	10,000 to 300,000 ng L ⁻¹	77.6 to 103.3	(He et al., 2013)
Soxhlet extraction	China	Soil	0.00277 to 8.280 ng g ⁻¹	65 to 130	(Wang et al., 2010)
	Italy	Industrial soil	7000 to 137,000 ng g ⁻¹	98	(Bowadt et al., 1995)
	Spain	Seaweed samples	6.6 to 8.2 ng g ⁻¹	80.34 to 98.73	(Crespo and Yusty, 2005)
QuEChERS	Poland	Breast milk	30.94 ng g ⁻¹	96.46 to 119.98	(Pajewska-Szmyt et al., 2019)
	Ghana	Breast milk	0.08 to 1.30 ng g ⁻¹	82 to 110	(Asamoah et al., 2018)
PLE	Czech Republic	Fish samples	19 to 98 ng g ⁻¹	95 to 115	(Suchan et al., 2004)
	Germany	Soil sample	0.011 to 0.22 ng g ⁻¹	76 to 111	(Klees et al., 2016)
UAE	China	Shellfish	14.12 to 30.61 ng g ⁻¹	80.92 and 93.89	(Zhou et al., 2010)
	India	Fish liver	122.81 to 166.23 ng g ⁻¹	88.5 to 108.4	(Asati et al., 2018)
	Turkey	Sediments	0.145 to 0.644 ng g ⁻¹	90.07 to 100.4	(Kuzukiran et al., 2016)
MAE	China	Soil and fish samples	0.00061 to 8.28 ng g ⁻¹	87 to 112	(Wang et al., 2010)
	Japan	Whale blubber	3.75 to 212 ng g ⁻¹	78 to 103	(Fujita et al., 2009)
	Germany	Seal blubber and cod livers	595 to 2810 ng g ⁻¹	> 90	(Vetter et al., 1998)
SFE	Spain	Seaweed samples	6.6 to 8.2 ng g ⁻¹	54 to 99	(Crespo and Yusty, 2005)
	Spain	Soils and sediments	1.0 to 1.7 ng g ⁻¹ for soil and 0.3 to 0.4 ng g ⁻¹ for sediments	74 to 127	(Corell et al., 2020)
	Colombia	Solid waste	50 ng g ⁻¹	80.2 to 96.0	(Mendes et al., 2018)
	USA	Soil and sediment	> 10,000 ng g ⁻¹	92 to 99	(Hawthorne and Miller, 1995)
MSPD	Greece	Chicken eggs	10 ng g ⁻¹	82 to 110	(Valsamaki et al., 2006)
	Spain	Mussel samples	0.10 to 22.5 ng g ⁻¹	81 to 116	(Carro et al., 2017)

amounts of solvents, and subsequent disposal of the solvents affects the environment (Rawa-Adkonis and Wolska, 2006). Due to these disadvantages, LLE has been largely replaced by other sample preconcentration techniques during the determination of PCBs.

3.1.2. Solid-phase extraction

Solid-phase extraction (SPE) is an alternative to LLE as it tries to minimize solvent usage and does not display some of the limitations experienced when using LLE. SPE consists of a mobile phase and a stationary phase packed in a cartridge, where the difference in the affinity of the solutes between the two phases leads to the separation of analytes. The portion that elutes through the cartridge is either discarded or collected, depending on whether it has the undesired or desired entities respectively (Abdel-Rehim, 2011). SPE based on conventional octadecylsilane (C₁₈) was used in the extraction of selected PCBs in milk, attaining recoveries higher than 80% (Picó et al., 1995) and, also, in pre-concentration of PCBs from seawater with recoveries of 60 to 70% (Dachs and Bayona, 1997). SPE is advantageous since one can store the enriched analytes on solid sorbents until the final determination is carried out at a convenient time and location. Despite these positive attributes, SPE based on C₁₈ sorbent suffers from low recoveries due to the non-selective interactions between the sorbent and the analytes of interest and low adsorption capacities, thus the shift to other reliable

sorbents that offer enhanced properties of robustness, selectivity, and improved recovery rates.

Molecularly imprinted polymers (MIPs) are some of the sorbents that offer the desired selectivity. MIPs are designed to show size, shape, and functional group selectivity to a given target molecule, and are, therefore, excellent materials for sample preparation since they enable a customized sample treatment step before the final determination (Turiel and Martín-Esteban, 2010). SPE based on MIPs (MISPE) has become a novel approach for sample preparation; hence, gaining significant interest in various fields. So far, this novel approach has been employed in the preconcentration of PCBs in river and lake water samples, attaining recovering of 83.5 to 104.4%. (Ndunda et al., 2015)

The advent of nanotechnology has also seen the introduction of nanomaterials as suitable sorbents. Graphene-based nanomaterials as sorbents have remarkable properties of large surface area, excellent electrical conductivity, high thermal conductivity, and high mechanical strength, which are beneficial for the isolation of PCBs from environmental samples. Therefore, graphene aerogel-based monoliths have successfully extracted PCBs from water samples attaining recoveries of 76.3 to 112.5% (Han et al., 2016). Related to graphene are carbon nanotubes that have been applied in the enrichment of PCBs found at trace levels in water samples and have achieved recoveries of 81.1 to 119.1% (Wang et al., 2016). Recently restricted access materials (RAMs) have been introduced. RAMs are sorbents that are designed to capture low

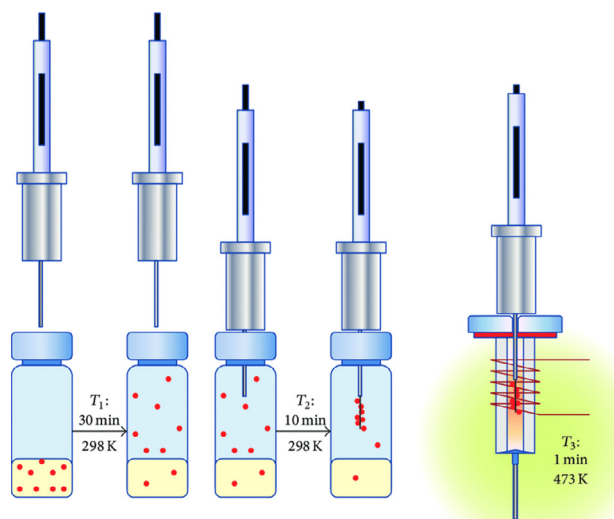


Fig. 3. Scheme illustrating SPME preconcentration and desorption of analytes into analytical equipment (reproduced from (Indelicato et al., 2014)).

molecular weight analytes and primarily exclude macromolecules such as proteins, thereby achieving successful isolation of analytes of interest from sample matrices (de Carvalho Abrão et al., 2019). RAMs as SPE sorbents were used to extract PCBs in water, attaining recoveries of 92 to 98% (Rodríguez-Mozaz et al., 2007).

In the spirit of miniaturization, a miniaturized form of SPE is micro solid-phase extraction (μ -SPE) that consists of adsorbent packed in a sealed porous membrane, which is immersed in the sample followed by desorption into an appropriate solvent. A hollow-fiber membrane with metal-organic frameworks (MOFs) as an adsorbent in μ -SPE for pre-concentration of PCBs in water reported recoveries between 80.6 and 115.9% and low limits of detection (LODs) (Zang et al., 2013).

3.1.3. Solid-phase microextraction

Solid-phase microextraction (SPME) is a sample preparation step that is deemed to be solvent-free and incorporates a fiber coated with an extracting phase as a sorbent material (Boyaci et al., 2015). It can extract different analytes, including volatile and non-volatile ones, from gas or liquid phases (Risticvic et al., 2009). During sample extraction, the fiber is immersed in a liquid sample or exposed to the headspace of a liquid sample (headspace-SPME) to allow the analytes to partition between the extraction phase and the sample matrix. The subsequent step involves desorption of the concentrated extracts into an analytical instrument as shown in Fig. 3 (Indelicato et al., 2014).

SPME comes as an attractive technique that can be automated to an analytical instrument, eliminating several procedures witnessed in other techniques. SPME based on fused-silica fibers coated with conventional polydimethylsiloxane (PDMS) was applied in the extraction of PCBs in aquaculture fish feed and cultured marine species attaining recoveries of 78 to 101% (Li et al., 2015), extraction of PCBs in sediment pore water, attaining recoveries of 84 to 91% (Niehus et al., 2019), and in the preconcentration of PCBs in snail extracts achieving recoveries of 55 to 80% (Al-Alam et al., 2020).

Novel fiber coatings in SPME that offer high adsorption surface area, stability, shortened equilibrium extraction time, and sensitivity have been reported. Tailored multimodal porous carbons as sorbents in SPME were used in water samples attaining recoveries for PCBs of 86% to 104% (Cheng et al., 2019). A polypropylene membrane coated with multiwalled carbon nanotubes functionalized with chitosan was used as an SPME sorbent to determine the levels of PCBs in water, attaining recoveries of 82.4 to 98.6% (Bashir et al., 2020). The use of fiber-coated carbon nanotubes as sorbent materials in SPME has resulted in a tremen-

dous improvement in the sample preparation step, as reported by Guo et al. (Guo et al., 2020), who used metal-organic framework-derived nitrogen-doped carbon nanotube cages as an efficient SPME coating for extraction of PCBs. The technique reported better performance than commercial PDMS/DVB and unmodified carbon nanotube fibers due to π - π interactions, the hollow cage structure, and a high number of active sites.

Some of the drawbacks of SPME include restricted operating temperatures, swelling in solvents, breakage of the fiber, cost of fibers, removal of fiber coatings, slow sorption process of analytes on the fiber, and carryover of analytes between runs (Pawliszyn, 2002). An alternative polydopamine-based MOF (DPA-MIL-53 (Fe))-coated stainless steel fiber showed better performance and higher stability in ultrasonic-assisted head-space solid-phase microextraction (US-HS-SPME) than conventional PDMS/DVB/carboxen fibers in preconcentration of PCBs in soil (Lv et al., 2017).

3.1.4. Stir-bar sorptive extraction

Stir-bar sorptive extraction (SBSE), introduced as an alternative to SPME, is also a solvent-less method that utilizes a coated stir bar to adsorb both volatile and non-volatile analytes from aqueous or solid samples through immersion or in the headspace followed by thermal desorption into the analytical equipment or liquid desorption into an appropriate solvent for analysis. Analytes are adsorbed into a PDMS polymer layer coated on a magnetic stir rod rather than a fiber, whereby this layer is much bigger than in SPME and consequently increases the sensitivity and extraction efficiency (Aly and Górecki, 2020).

The main disadvantage of SBSE is that it requires a special device for thermal desorption and, also, conventional PDMS adsorbs mainly non-polar compounds (Abdulra, 2014). Several studies employing SBSE as a green alternative have been reported, including determination of PCBs in water samples (Popp et al., 2005), analysis of PCBs in human serum (Benijts et al., 2001), and quantification of PCBs in sediment (Vrana and To, 2013). SBSE offers the possibility of avoiding the clean-up step, thus providing an attractive green option. Improvement on PDMS and polyacrylate (PA) as the conventional coating materials to more selective coatings has involved the use of MOFs that offer high surface area, large pore size, excellent affinity, and selectivity (Aly and Górecki, 2020). SBSE coated with MOFs for the determination of PCBs in fish samples gave excellent results in addition to being reusable (Lin et al., 2015a). Others include the selective immobilization of an aptamer on a MOF as a coating for SBSE in the determination of PCBs in fish samples (Lin et al., 2015c), and a polyaniline/cyclodextrin composite coated on SBSE for determination of PCBs in water, attaining enrichment factors of 39.8 to 68.4% and recoveries of 72.6 to 121% for spiked water samples at 48 to 220 ng L⁻¹ limits of detection (Lei et al., 2016).

3.1.5. Dispersive solid-phase extraction

Dispersive solid-phase extraction (d-SPE) is an emerging alternative to conventional SPE procedures supported by the advantages of simple operation, low solvent consumption, and high efficiency. In d-SPE, the sorbent is directly added to the sample extract, and the resulting mixture is shaken to achieve rapid interaction between the sorbent and the sample matrix. Therefore, the contact between the two phases is immediate and more effective in the extraction and clean-up of analytes before quantification and it avoids the numerous steps in SPE (Socas-Rodríguez et al., 2015). d-SPE has been used to extract PCBs in biological matrices with a zirconium dioxide-based sorbent attaining recoveries of 70 to 120% (Badel et al., 2015). Elsewhere, d-SPE has been applied to determine PCBs in fishery and aquaculture products for both extraction and clean-up of the samples before GC-MS analysis. Typical sorbents were silica, acidified silica, Florisil, and alumina. Recoveries in the range of 60 to 140% were obtained (Lu et al., 2014). Multi-residue analysis of PCBs in fish using a zirconium-based sorbent in d-SPE as a sample preparation method coupled to GC-MS in the analysis of catfish

samples reported recoveries between 70 and 120% (Sapozhnikova and Lehotay, 2013).

To enhance the separation of the adsorbent from the samples as well as enhance the adsorption capacity, sorbents can be modified by incorporating magnetic properties. Multi-walled carbon nanotubes modified with dummy-template magnetic molecularly imprinted microspheres as a sorbent were applied in the extraction of PCBs from fish samples, attaining recoveries in the range between 73.41 and 114.21% (Du et al., 2014). Magnetic MOFs and graphene oxide have also been successfully applied in the extraction of PCBs from water samples (Chen et al., 2013). MIPs bring along properties of robustness, selectivity, and reusability, and have been used together with reduced graphene oxide (rGO) to produce sorbents that display additional properties of large surface area and increased adsorption due to π - π stacking interactions (Lin et al., 2015b).

3.1.6. Liquid-phase microextraction

Liquid-phase microextraction (LPME) or solvent microextraction (SME) is a recently introduced miniaturized form of LLE that greatly reduces the volume of solvent used to just a few microliters (Pacheco-Fernández and Pino, 2020). There are different categories of LPME developed to achieve high enrichment factors, stabilization of the extracting phase, and improve analyte selectivity (Yamini et al., 2019). Dispersive liquid-liquid microextraction (DLLME) involves the dispersion of fine droplets of extraction solvent into an aqueous sample by using a disperser solvent miscible with both phases, thereby achieving efficient extraction due to increased contact between the sample surface and extracting solvent (Quigley et al., 2016). The cloudy solution is then centrifuged to provide the extraction phase containing the analytes of interest which is reduced to the appropriate volume for instrumental analysis. DLLME is known for its simplicity, low cost due to reduced solvent and apparatus, high extraction efficiency (achieving 540-fold enrichment factor), and short extraction time (Rezaei et al., 2008). It has been applied in the determination of PCBs in environmental water samples achieving recoveries in the range of 81.9 to 109.7% (Hou et al., 2019). Though DLLME is simple and fast, the use of a disperser solvent comes with complications of decreased partition coefficients of analytes into the extracting solvent and a complicated phase separation process due to the formation of emulsions (Pacheco-Fernández and Pino, 2020).

Vortex-assisted liquid-liquid microextraction (VALLME), as well as ultrasound-assisted emulsification microextraction (USAEME) protocols, have also been applied in the analysis of PCBs in water and wastewater attaining recoveries of 96% at optimized conditions of 5 mL of water sample, 200 μ L of chloroform as extracting solvent, 2 min vortex extraction time at 3000 rpm, and 5 min centrifugation at 4000 rpm (Ozcan, 2011), and above 80% recovery at optimized conditions of 10 mL sample, 200 μ L of chloroform, 10 min of extraction at 25 °C, and 5 min of centrifugation at 4000 rpm, respectively (Ozcan et al., 2009). Other modifications involve DLLME based on solidification of the floating organic droplet (DLLME-SFO) that enables the use of an extracting solvent that is less dense than water and able to melt at temperatures below or near room temperature, and that is compatible with the analytical equipment (Lana et al., 2013).

To overcome the limitations of DLLME, hollow fiber liquid-phase microextraction (HF-LPME) employs a hollow fiber as an extracting device (majorly polypropylene) containing the extraction solvent, which is then placed in contact with the liquid sample, is considered a preferred alternative. Dynamic HF-LPME ensures increased diffusion rates are achieved, and large particles, which may be present in the sample, do not block the pores of the hollow fiber (Pacheco-Fernández and Pino, 2020). Optimization of HF-LPME for PCBs in human breast milk achieved average recoveries of 85% (Villegas-Álvarez et al., 2020) and 85.9 to 92.0% for PCBs in water with 718 to 840-fold enrichment factors (Li et al., 2008). Closely related to HF-LPME is membrane-assisted solvent extraction (MASE) that uses a membrane bag mainly made of propylene to allow the transfer of analytes from the aqueous phase into or small volume of organic solvent. This method is cheap, uses a low

volume of extractant, and eliminates interferences (Carro et al., 2009). Single-drop microextraction (SDME) involves the use of an organic solvent suspended on the tip of the microsyringe, which then achieves extraction of analytes from the aqueous phase through direct immersion (DI-SDME) or headspace (HS-SDME) modes. After extraction, the organic solvent in the form of a micro-drop is drawn back into the syringe for analysis (Sarafraz-Yazdi and Amiri, 2010). Green ionic liquids in HS-SDME achieved excellent recoveries of 77.6 to 103.3% and LODs of 0.005 to 0.07 μ g L⁻¹ in the determination of trace levels of PCBs in water, thereby providing an alternative to organic solvents (He et al., 2013).

3.1.7. Passive water sampling

Passive water sampling is a sampling method based on difference in concentration of the analyte between two media. The flow of analytes from one medium to the other continues until equilibrium is established in the system or until the sampling session is terminated by the user (Gořecký and Namiešník, 2002). Passive sampling has the advantages of attaining high pre-concentration factors, especially for analytes that occur at trace levels, and also eliminates the logistics required to transport large volumes of water samples (Vrana et al., 2005). Besides, the method provides time-weighted average (TWA) concentrations important for risk assessment, selectively preconcentrates residues from the sampling medium, and can detect changes in concentration of contaminants which may not be possible with grab sampling. Semi-permeable membrane devices (SPMDs) made from non-porous low-density polyethylene (LDPE) that eliminate large molecules and only allow dissolved components to diffuse through the membrane are mainly applied for organic pollutants (Vrana et al., 2005). Other passive samplers that have displayed favourable results similar to conventional methods in monitoring PCBs include polyethylene (PE), polyoxymethylene (POM) and XAD-resin (Burgess et al., 2015; Choi et al., 2009; Perron et al., 2013). Passive samplers based on activated carbon fiber provide high adsorption capacity with results comparable to conventional LLE, thereby displaying their potential for application in monitoring of PCBs in water (Cerasa et al., 2020). Novel and more selective approaches that involve molecularly imprinted membrane (MIM) passive samplers are being introduced as reported by Mkhize et al., who showed that the approach could be deployed for monitoring PCBs as it was able to achieve detection of congeners that could not be detected in grab samples (Mkhize et al., 2019).

3.2. Extraction of analytes from solid matrices

PCBs were traditionally extracted from solid matrices such as soils, sediments, seaweed, human and animal tissues by soxhlet extraction but more efficient methods that include QuEChERS, pressurized liquid extraction, ultrasound-assisted extraction, microwave-assisted extraction, supercritical fluid extraction and matrix solid-phase dispersion have been adopted as described below.

3.2.1. Soxhlet extraction

Soxhlet extraction is used to extract analytes from different solid matrices such as soils, sediments, animal tissues, and plants (Reddy et al., 2019). It has been in use for the longest period because of its affordability; however, a long duration is required to achieve complete extraction of analytes and involves excessive solvent consumption, making the method expensive. The disposal of these solvents can lead to great concern in pollution of the environment (Al-Saqrati et al., 2019). Soxhlet extraction has been applied in the extraction of PCBs in soil, industrial soil, and seaweed samples, attaining recoveries of 65 to 130%, 98%, and 80.34 to 98.73%, respectively (Bowadt et al., 1995; Crespo and Yusty, 2005; Wang et al., 2010). To reduce the amount of time required to process samples and the cost of extraction, other environmentally friendly techniques that demonstrate increased throughput have been introduced.

3.2.2. QuEChERS

QuEChERS was introduced in 2003 to offer a method that is quick, easy, cheap, effective, rugged, and safe (so the name QuEChERS) (Anastassiades and Lehotay, 2003). The method involves two stages: first is the extraction of analytes from the sample to an organic solvent aided by inorganic salts (MgSO_4 and NaCl), followed by a dispersive solid-phase extraction (dSPE) step to remove interfering components that may include pigments and lipids. Removal of these components is crucial to increase the sensitivity and reproducibility in the instrumental analysis. QuEChERS has been applied in isolating PCBs from breast milk of Polish women at recoveries of 96.46 to 119.98% by using GC-MS for quantification (Pajewska-Szmyt et al., 2019), and breast milk of Ghanaian mothers reporting recoveries of 82 to 110% with GC-MS/MS detection (Asamoah et al., 2018). However, the method is limited to the extraction of polar analytes and besides being tedious, a large volume of solvent is used, and loss of analytes may occur (Darvishnejad and Ebrahimzadeh, 2019).

3.2.3. Pressurized liquid extraction

Pressurized liquid extraction (PLE), also known as accelerated solvent extraction (ASE), or pressurized fluid extraction (PFE), or pressurized solvent extraction (PSE), was introduced as an efficient alternative for Soxhlet extraction. PLE is an automated sample preparation method that uses elevated temperature and pressure to achieve an exhaustive extraction of analytes from solid matrices within a record time of 15 to 30 min and with an extraction solvent volume of 10 to 30 mL. PLE can be considered as an environment-friendly technique, generating small volumes of waste and reducing costs and time while achieving high extraction efficiencies (Carabias-Martínez et al., 2005). PLE is a useful sample preparation method applicable to the extraction of POPs from various matrices with excellent recoveries. Extraction of PCBs in fish samples attained recoveries of 95 to 115% (Suchan et al., 2004), while analysis of PCBs in the soil reported recoveries of 76 to 111% (Klees et al., 2016), and determination of PCBs and PCDD/Fs in street dust samples reported recoveries of 78 to 92% (Klees et al., 2013). Miniaturized PLE, which offers a reduced sample amount to 100 mg, solvent consumption of 3.5 mL, and extraction in a single run of 17 min, has been reported to achieve PCB recoveries comparable to those of Soxhlet extraction (98% vs. 108%) (Ramos et al., 2007). To achieve one-step extraction and clean-up, PLE provides room for further modification by including an in-cell clean-up of samples through the addition of fat removal adsorbents, such as Florisil or alumina, to the cell and including a carbon column in the extraction cell to selectively adsorb dioxin-like compounds (Haarich and Orkamp, 2013). Copper(II) isonicotinate as a clean-up sorbent for the determination of PCBs in food samples, including chicken meat, clam meat, and pork, demonstrated better purification as a result of selective adsorption (Jiao et al., 2016).

3.2.4. Ultrasound-assisted extraction

Ultrasound-assisted extraction (UAE) is an extraction method easily applied in the extraction of analytes from solid matrices taking advantage of faster kinetics and an increase in extraction efficiency. UAE is useful in extracting thermolabile compounds since it can be operated at low temperatures favourable for such compounds. The UAE system is affordable and easy to operate compared to other sample preparation methods, thus offering a simple, efficient, and inexpensive sample preparation method. UAE in the extraction of PCBs in shellfish reported recoveries between 80.92 and 93.89% (Zhou et al., 2010). Also, the determination of OCPs and PCBs in fish liver achieved recoveries of 88.5 to 108.4% (Asati et al., 2018). UAE followed by dispersive liquid-liquid microextraction tends to eliminate the clean-up step by providing clean extracts ready for instrumental analysis. The method was reported in the determination of PCBs in sediments by GC-MS with recoveries of 90.07 to 100.4% and limits of detection between 0.021 to 0.057 ng g^{-1} (Kuzukiran et al., 2016).

3.2.5. Microwave-assisted extraction

Microwave-assisted extraction (MAE) involves heating the solvent via the absorption of microwave energy to increase the penetration of the solvent into the sample matrix. Its extraction time ranges between 20 and 30 min and uses a small amount of solvent between 5 and 30 mL (Tatke and Jaiswal, 2011). MAE requires an additional clean-up step and demonstrates low extraction efficiencies for non-polar compounds (Lahmanov and Varakina, 2019). A comparative study on the use of MAE, Soxhlet extraction, and PLE in the determination of PCBs in soil and fish samples showed that PLE and MAE provide better recoveries than Soxhlet extraction. The reported recoveries were 86 to 111%, 87 to 112%, and 65 to 130% for PLE, MAE, and Soxhlet extraction, respectively (Wang et al., 2010). Validation of a high-throughput system with MAE and gas chromatography coupled to an electron capture detector (GC-ECD) for determination of PCBs in whale blubber afforded recoveries of 78 to 103% (Fujita et al., 2009). MAE combined with gel permeation chromatography for clean-up in the determination of PCB 153, 138, 180, HCB, and p,p'-DDE in seal blubber and cod livers reported recoveries of 90 to 100% (Vetter et al., 1998).

3.2.6. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is an effective green sample preparation method with improved recoveries achieved by optimizing temperature and pressure when using a supercritical fluid as the extractant. Analytes are extracted from solid matrices with a supercritical fluid, commonly CO_2 , which is sometimes modified by co-solvents, such as ethanol or methanol, to increase the polarity and enhance extraction efficiencies of most organic pollutants. SFE gives rise to clean extracts free from interferences in cases that involve complex matrices (Lahmanov and Varakina, 2019). CO_2 as the supercritical fluid has low toxicity, low viscosity, high diffusion coefficients, and low flammability and, hence, is superior to organic solvents used in other techniques and promotes the ideas of green chemistry. The primary disadvantage of this extraction is that it requires a higher capital and operation cost because the extraction must be operated at high pressure to maintain the solvent in the supercritical state (Reddy et al., 2019). SFE followed by GC-ECD has been applied in the determination of PCBs in seaweed samples attaining recoveries of 54 to 99% (Crespo and Yusty, 2005), extraction of PCBs in contaminated soils and sediments and quantification by thermal desorption-GC-MS reporting recoveries of 74 to 127% (Corell et al., 2020), and in the determination of total PCBs in solid waste by GC-MS reporting recoveries of 80.2 to 96.0% (Mendes et al., 2018). SFE has been applied for extraction of PCBs from soil and sediment attaining recoveries of 92 to 99% at optimized conditions of 300 °C, 50 atm, and an extraction time of 5 min. The main drawback of SFE is the additional steps required to transfer analytes into a collection solvent that is compatible with the quantification instrument (Hawthorne and Miller, 1995).

3.2.7. Matrix solid-phase dispersion (MSPD)

Matrix solid-phase dispersion (MSPD) introduced in the 1980s offers the possibility of combining extraction and clean-up at the same time, thus reducing the amount of solvent, analysis time, and sample handling procedures (Carro et al., 2017). MSPD is applicable for the extraction of analytes from solid, semi-solid, and viscous samples. In MSPD, the samples are blended with sorbent (Florisil, C_{18} , silica gel, or alumina), which plays the role of supporting and adsorbing analytes, to obtain a homogeneous mixture then transferred into a chromatographic column packed with a sorbent, and a solvent is passed through the column to achieve elution of analytes from the matrix (Xijuan and Wenbin, 2018). MSPD has been applied in the determination of PCBs in chicken eggs using Florisil as the sorbent material, attaining average recoveries ranging from 82 to 110% (Valsamaki et al., 2006). Miniaturization of MSPD to micro-MSPD contributes to reduced sample, solvent volume, and the amount of sorbent used. An optimized method based on micro-MSPD with Florisil as the adsorbent for the determination of PCBs in mussel

samples attained recoveries in the range of 81 to 116% (Carro et al., 2017). The optimized method used only a 0.5 g sample, 1 mL of extracting solvent, and 0.5 g of Florisil. The advantages of MSPD are favourable extraction conditions, few and simple operation steps, minimal organic solvent, low cost, and no need for expensive instrumentation. However, one of the drawbacks is the non-usability of the extraction column, where the column cannot be reused after the first extraction (Xijuan and Wenbin, 2018).

3.3. Extraction of analytes in air

PCB constituents in air are normally collected through passive air sampling (PAS) by making use of polyurethane foam (PUF) disks, semipermeable membrane devices (SPMDs), polymer-coated glasses (POGs), XAD-2 resin, and organic-rich soil (Shoeib and Harner, 2002; Valsamaki et al., 2006). These materials are then taken through Soxhlet extraction and clean-up steps for the quantification of PCBs (Battermana et al., 2009). PAS is a low-cost method that is easily deployed to remote areas compared with high volume active air sampling (Hi-Vol AAS) (Qu et al., 2018) that is reported to use Amberlite XAD-2 resin and a styrene-divinylbenzene copolymer in the collection of high-volume air samples for the determination of PCBs (Hu et al., 2011). To improve the sorption capacity of PUFs, Kim and Park, 2014, tried impregnation of XAD-4 powder into PUFs to produce sorbent-impregnated PUFs to prolong PAS deployment duration and increase detection frequency of chemicals at low concentrations (Kim and Park, 2014). Recently, passive samplers based on polyoxymethylene reported results on levels of PCBs in a confined disposal facility comparable to HiVol AAS (Odetayo et al., 2020).

3.4. Clean-up of sample extracts

Clean-up is usually an additional sample preparation step for complex matrices and it is done to remove interferents present in the matrix before quantification of analytes. Clean-up ensures that ultra-trace level detection of analytes is achieved for pollutants that are found in trace amounts and also spares the instrument from extra loading by interferences. It can be achieved by gel permeation chromatography (GPC), adsorption chromatography with different sorbents packed in glass columns or SPE cartridges, or through D-SPE, using sorbents such as a primary-secondary amine (PSA), C₁₈, and graphitized carbon black (GCB) (Guo et al., 2017).

3.4.1. Gel permeation chromatography

Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) is a traditional clean-up method that is based on size exclusion where large molecules are eluted from a gel, usually Bio-Beads S-X3, followed by smaller molecules, with an appropriate solvent. It is a good method for removal of sulfur, lipids, proteins, and other high molecular weight interferences from complex samples, which due to their large size are unable to enter into the pores of the polymer and are eluted first from the column in the mobile phase followed by the analyte molecules lodged in pores (Lahmanov and Varakina, 2019). GPC based on S-X3 has been used for clean-up of soils, sediment, and waste oil in the determination of PCBs (Czuczwa and Alford-Stevens, 1989), but it is mostly used in pre-clean-up to remove lipids before further clean-up is done to fractionate different classes of compounds (He et al., 2017). Though the column might be efficient for removal of lipids, it utilizes a large amount of solvent, and sample throughput is limited.

3.4.2. Adsorption chromatography

Adsorption chromatography has been applied in clean-up through the partitioning of compounds between adsorbents packed in glass or SPE columns, and the mobile phase. Alumina (Al₂O₃) in its deactivated form has been used in clean-up procedures to separate PCBs from interfering components and lipids in stormwater sediments (Cao et al.,

2019) as well as to fractionate dl-PCBs from PCDD/Fs (Haarich and Orkamp, 2013). Activated silica gel is often used as a secondary column in separating interfering polar compounds, such as pesticides, during the determination of PCBs, and was successfully used in multi-residue analysis achieving successful separation of PCBs from polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OPCs) (Ozcan et al., 2008). Acidified silica gel (SiO₂-H₂SO₄) has come in handy for the removal of lipids and has been applied for the clean-up of extracts that contain fatty residues (Aganbi et al., 2019). Sulfur, found mostly in soils and sediments, is known to interfere with instrumental detection and must be removed during the clean-up steps. To this end, silica gel impregnated with silver nitrate (SiO₂-AgNO₃) is effective (Fan et al., 2017). Florisil is the other adsorbent used to remove interferences from extracts before analysis and is usually applied in combination with other absorbents as it has been shown that on its own, it may not achieve efficient removal of extractives in fish tissue (achieved only 24% removal) compared with a two-step SPE column packed with C₁₈ and primary secondary amine (PSA) (Lourencetti and Ricci, 2020). C₁₈ as an adsorbent in SPE columns followed by neutral alumina clean-up has also been applied in clean-up in the determination of PCBs and OCPs in virgin olive oil (Yagüe et al., 2005). To achieve thorough purification of extracts, the three sorbents are usually packed in chromatographic columns to provide multilayered columns. Such a multi-layered column, consisting of alumina, silica gel and Florisil, achieved simultaneous determination of WHO-12 PCBs and dioxins in soil, sediment, air and fly ash (Robinson et al., 2004). Also, a dual column of acidified silica and alumina successfully isolated PCBs and PBDEs in human adipose tissues (Naert et al., 2006).

The aforementioned clean-up sorbents are characterized by the use of a large amount of solvent and portray poor selectivity. To this end, materials that overcome these challenges have been introduced. MIPs are materials that are robust and selective towards particular target analytes and provide attractive options as sorbents in sample clean-up in SPE mode (Ashley et al., 2017). A reusable dual-column consisting of acidified silica and MIPs has been used in clean-up in the determination of PCBs in soil and sediment (Ndunda et al., 2015). A commercial molecularly imprinted solid-phase extraction (MISPE) cartridge was used in the fractionation of hydroxylated PCBs and polybrominated diphenylether derivatives in animal tissue (Roszko et al., 2015).

3.4.3. Dispersive solid-phase extraction

Dispersive solid-phase extraction (d-SPE) in clean-up operates on the same principle as D-SPE for the extraction of analytes in aqueous samples. Multiwalled carbon nanotubes (MWCNTs), PSA, C₁₈, Florisil, and acidified silica gel have been used as sorbents to achieve the desired removal of interfering matrices. D-SPE involving the use of acidified silica has reported better removal of lipids and recoveries of target analytes at 72 to 105% compared with lipid removal of 52% using MSPD during the analysis of PCBs and PBDEs in fishery and aquaculture products (Lu et al., 2014). Some of the improvements in the performance of these sorbents have included the use of carboxylated-MWCNTs in the determination of 18 PCBs in vegetables attaining recoveries of 84.5 to 116.5% and limits of detection of 0.3–1.4 µg kg⁻¹ with GC-MS (Liu et al., 2019), use of mixed sorbents consisting of PSA, C₁₈, and Florisil provided satisfactory recoveries of 85.9 to 119.8% in the determination of PCBs and OCPs in Chinese mitten crab by GC-MS (Liu et al., 2020b). For the removal of sulfur in sediment or soil extracts, D-SPE using activated copper or tetrabutylammonium sulfite has been applied (Bawana et al., 2020; Ndunda et al., 2015).

4. Analytical techniques for quantification of PCBs

After sample preparation, extracts are analyzed to determine the concentrations of PCBs by making use of either HPLC or GC coupled with different detectors. More recently, sensors have found their novel use. This section discusses these techniques in detail and provides a summary in Table 3.

Table 3
Summary of different analytical techniques for quantification of PCBs in environmental matrices.

Technique	Place	Sample matrix	Concentration range	Detection limit	Ref
HPLC-UV	China	Water samples	880 to 55,100 ng L ⁻¹	48 to 220 ng L ⁻¹	(Lei et al., 2016)
GC-ECD	Turkey	River water	111 to 6700 ng L ⁻¹	110 to 620 ng L ⁻¹	(Al-Janabi, 2016)
	China	Surface sediments of urban rivers	7.90 to 30.21 ng g ⁻¹ and 5.53 to 32.67 ng g ⁻¹ in the winter and summer, respectively	0.1 to 0.9 ng g ⁻¹	(Qadeer et al., 2019)
	Russia	Bering flounder	24.7 to 279 ng g ⁻¹	0 to 0.8 ng g ⁻¹	(Lukyanova et al., 2018)
	Nigeria	Water	23,000 ng L ⁻¹	100 ng L ⁻¹ and 0.10 ng g ⁻¹	(Folarin et al., 2018)
GC-MS	Pakistan	Soil	27.3 ng g ⁻¹		
		Dust	272.6 ng g ⁻¹		
		Sediment	510.6 ng g ⁻¹		
		Surface water	0.03117 to 0.1752 ng L ⁻¹	2.0 × 10 ⁻⁵ to 1.5 × 10 ⁻⁴ ng L ⁻¹ (water), 3.0 × 10 ⁻⁵ to 1.0 × 10 ⁻⁴ ng g ⁻¹ (soil), 2.0 × 10 ⁻⁵ to 1.0 × 10 ⁻⁴ ng m ⁻³ (air)	(Ullah et al., 2020)
HRGC-HRMS		Soil	n.d. to 1.908 ng g ⁻¹		
		Air	0.0298 to 0.0944 ng m ⁻³		
	South Africa	Fresh root and leafy vegetables	90.9 to 234 ng g ⁻¹	10 to 22 ng g ⁻¹	(Olatunji, 2019)
	Japan	Surface water	32.17 to 199.4 ng L ⁻¹	10 to 22 ng L ⁻¹	(Habibullah-Al-Mamun et al., 2019)
Immunomagnetic electrochemical sensor	Spain	Surface water	0.13 to 0.50 ng L ⁻¹	0.01 to 0.1 ng L ⁻¹	(Domínguez et al., 2017)
	Germany	Sea water and mussels	2 to 26 ng L ⁻¹ and n.d. to 9.130 ng g ⁻¹	1.0 × 10 ⁻⁵ to 1.18 × 10 ⁻³ ng L ⁻¹ (sea water), 1.0 × 10 ⁻⁵ to 3.3 × 10 ⁻⁴ ng g ⁻¹ (mussels)	(Telli-Karakoc et al., 2002)
	Greece	Human hair	0.61 to 38.74 ng g ⁻¹	0.6 to 1.3 ng g ⁻¹	(Barbounis et al., 2012)
	Italy	Soil samples	–	300 to 800 ng L ⁻¹	(Centi et al., 2005)
Electrochemical aptasensor	China	Water samples	–	0.22 ng L ⁻¹	(Fan et al., 2019)
Fluorescent aptasensor	China	Water and soil samples	–	3.5 ng L ⁻¹	(Wang et al., 2018)

n.d. – not detected.

4.1. High performance liquid chromatography

High performance liquid chromatography (HPLC), and recently ultra-high performance liquid chromatography (UHPLC), is a type of column chromatography where the solvent, which is the mobile phase, is allowed to flow through a column filled with an adsorbent under pressure. The separation of components is based on their different degrees of interaction with the stationary phase, which leads to different elution rates for various components (Kupiec, 2004). The recently introduced UHPLC guarantees high throughput and improved separation efficiency comparable to that of gas chromatography (Ol'sovská et al., 2010). The two systems can be connected to a UV detector, photodiode-array detector (DAD), fluorescence detector, mass spectrometer (MS), or tandem mass spectrometer (MS/MS) detector for quantification of analytes after separation (Swartz, 2010). Studies that involved the determination of PCBs in water samples by means of HPLC-UV reported concentrations between 880 and 55,100 ng L⁻¹ for the total PCBs analysed and detection limits of 48 to 220 ng L⁻¹ (Lei et al., 2016). Similarly, determination of PCBs in river water by HPLC with UV detection reported concentrations ranging from 111 to 6700 ng L⁻¹ and a detection limit of 110 to 620 ng L⁻¹ (Al-Janabi, 2016). As evidenced by some of these studies, HPLC coupled to normal detectors reports high detection limits, and its application is limited by the low sensitivity to volatile compounds since they are irreversibly adsorbed and the need for large quantities of expensive solvents (Tamayo et al., 2007). Improved detection limits of 1.6 to 3.1 ng L⁻¹ have been reported by the use of HPLC coupled to a more sensitive tandem mass spectrometer (LC-MS/MS) in the determination of PCBs in surface water, tap water, and wastewater (Moukas et al., 2014).

4.2. Gas chromatography electron capture detector

Gas chromatography coupled to an electron capture detector (GC-ECD) is a favourable technique for the analysis of halogenated compounds in different environmental matrices and is mostly used for such

studies because of its availability. Some of the advantages of GC-ECD include high sensitivity to halogenated compounds; however, it is limited to volatile molecules and suffers from matrix interferences, especially from sulfur found in sediment samples. Studies that have used GC-ECD include determination of PCBs in surface sediments of urban rivers, where PCBs levels ranged from 7.90 to 30.21 ng g⁻¹ and 5.53 to 32.67 ng g⁻¹ in the winter and summer, respectively at detection limits of 0.1 to 0.9 ng g⁻¹ (Qadeer et al., 2019). Also, the determination of PCBs in Bering flounder from the Okhotsk Sea revealed levels of PCBs ranging from 24.7 to 279 ng g⁻¹ and detection limits of 0 to 0.8 ng g⁻¹ (Lukyanova et al., 2018). Distribution of PCBs in water, soil, dust, and sediment samples from an electrical power station reported average values of 23,000 ng L⁻¹, 27.3 ng g⁻¹, 272.6 ng g⁻¹, and 510.6 ng g⁻¹ respectively, with the method achieving a detection limit of 0.10 ng g⁻¹ and 100 ng L⁻¹ (Folarin et al., 2018).

4.3. Gas chromatography-mass spectrometry

Gas chromatography coupled to mass spectrometry (GC-MS) is a tool mainly used to analyze very low concentrations of pollutants and also to perform confirmatory studies. GC-MS offers good sensitivity, high resolution, high precision, accuracy, and reproducibility. GC-MS can be operated in electron impact (EI) ionization, positive chemical ionization (PCI), or negative chemical ionization (NCI) modes, with the latter being more sensitive for halogenated compounds compared with GC-ECD (Zhao et al., 2007). Ions that are produced may be separated by different mass analyzers that include quadrupole and time-of-flight (TOF). For ultimate sensitivity, accuracy, and selectivity, gas chromatography-tandem mass spectrometry (GC-MS/MS) is employed, providing results comparable to those of GC- high resolution mass spectrometry (HRMS) (Gao et al., 2020). It consists of two scanning mass analyzers, i.e., quadrupole ion trap (QIT) and triple quadrupole (QqQ-MS/MS) techniques, with QqQ-MS/MS being the robust technique demonstrating high selectivity, wide linear range, and sensitivity (Lu et al., 2014). Despite the aforementioned attractive properties, the acquisition of

these instruments requires heavy investment and competent personnel (Coutinho et al., 2009).

This technique has been used to assess trace levels of PCBs in surface water, soil, and air matrices where the levels ranged from 0.031 to 0.175 ng L⁻¹, not detected (n.d.) to 1.908 ng g⁻¹ and 0.0298 to 0.0944 ng m⁻³, respectively with detection limits of 2.0×10^{-5} to 1.0×10^{-4} ng m⁻³ for air, 2.0×10^{-5} to 1.5×10^{-4} ng L⁻¹ for water, and 3.0×10^{-5} to 1.0×10^{-4} ng g⁻¹ for soil samples (Ullah et al., 2020). Evaluation of selected PCB congeners in fresh root and leafy vegetables had concentrations ranging between 90.9 and 234 ng g⁻¹ and detection limits of 10 to 22 ng g⁻¹ (Olatunji, 2019), and also the distribution of PCBs in surface water revealed concentrations of PCBs ranging between 32.17 and 199.4 ng L⁻¹ and detection limits of 10 to 22 ng L⁻¹ (Habibullah-Al-Mamun et al., 2019). Determination of PCBs in marketed seafood by GC-MS/MS reported LODs from 0.011 to 0.014 ng g⁻¹ (Li et al., 2017). Miniaturization of the GC-MS system to achieve on-site detection of PCBs was reported by Zhang et al. (Zhang et al., 2016). Though the method detection limit was very high, the tool is appropriate for the screening of PCBs in contaminated soils, providing fast data for immediate action.

4.4. High resolution gas chromatography-high resolution mass spectrometry

Capillary or high-resolution gas chromatography (HRGC) enables the achievement of trace level detection and improved separation of analytes for quantitation. Coupled with a high-resolution mass spectrometer, the technique achieves very low limits of detection and is highly recommended for analysis of dl-PCBs (Špánik and Machyňáková, 2017). There are only limited studies that have employed this technique in the analysis of PCBs, probably due to its limited availability since it is costly to acquire and maintain. Some of the reported studies include ultra-trace determination of PCBs in surface water where the concentrations of PCBs ranged between 0.13 and 0.50 ng L⁻¹ and detection limits of 0.01 to 0.1 ng L⁻¹ (Domínguez et al., 2017), determination of PCBs in seawater and mussels at a concentration of 2 to 26 ng L⁻¹ and not detected (n.d.) to 9.130 ng g⁻¹, respectively, at detection limits of 1.0×10^{-5} to 1.18×10^{-3} ng L⁻¹ and 1.0×10^{-5} to 3.3×10^{-4} ng g⁻¹ (Telli-Karakoc et al., 2002), and assessment of PCBs in human hair where the levels ranged between 0.61 and 38.74 ng g⁻¹ with detection limits of 0.6 to 1.3 ng g⁻¹ (Barbounis et al., 2012). HRGC-HRMS has established itself as a powerful tool, reporting very low detection limits, thus offering a better alternative to conventional techniques (Kanan and Samara, 2018).

4.5. Sensor technology

Sensors are gaining more attention as they are perceived to offer several advantages such as cost-effectiveness, simplicity, and the possibility for real-time and on-site analysis. Thus, sensors provide the best alternative to high-cost instrumentation techniques while achieving the required figures of merit. Concerted efforts have brought about sensors that can be used to detect pollutants in the environment achieving quantification of PCBs in different environmental matrices (Chobtang et al., 2011). The earliest form of sensor reported for detection of PCBs is the chemical-activated luciferase gene expression (CALUX) bioassay that measures the ability of chemical mixtures to activate certain genes in biological fluids. The CALUX bioassay was reported to provide comparable toxic equivalence (TEQ) similar to chemical analysis by GC-ECD (Pauwels et al., 2000). This type of bioassay is limited by the high level of expertise and equipment needed to carry out cell cultures, thereby creating room for the development of other bioassay formats like enzyme-linked immunosorbent assays (ELISA). A commercially available ELISA kit evaluated toxic equivalents (TEQs) for dl-PCBs in retail fish reporting low detection limits (10 ng mL⁻¹) and results comparable to TEQs determined by means of HRGC-HRMS (Tsutsumi et al.,

2006). The application of these biosensors is limited by the need for antibodies/enzymes that entail a high cost of production and are unstable in harsh conditions.

As an alternative, chemical sensors that withstand harsh analytical conditions have been reported. These chemical sensors have the potential to be modified using different recognition elements to offer the desired selectivity and achieve trace detection of pollutants. A quartz crystal microbalance (QCM) sensor with oligopeptides as recognition elements could easily distinguish between dioxins and PCBs providing a tool for screening of PCBs before instrumental analysis using HRGC-HRMS (Mascini et al., 2005). A fluorescent aptasensor for PCB detection revealed a detection limit of 3.5 ng L⁻¹ and average recoveries of 93.4 to 109.7% and 83.2 to 118.5% for water and soil samples, respectively (Wang et al., 2018).

Electrochemical sensors have been widely explored due to their easy of fabrication in addition to being versatile tools that can be miniaturized for on-site and real time detection. To this end, a disposable immunomagnetic electrochemical sensor has been fabricated for the detection of PCBs in spiked soil samples with detection limits of 300 ng L⁻¹, 400 ng L⁻¹, 500 ng L⁻¹, 800 ng L⁻¹ for Aroclors 1242, 1248, 1254, 1016, respectively (Centi et al., 2005). A label-free and highly selective electrochemical aptasensor based on nickel hexacyanoferrate nanoparticles (NiHCF NPs)/reduced graphene oxide (rGO) hybrids demonstrated high sensitivity and selectivity for detection of PCB-77 in water samples at a detection limit of 0.22 ng L⁻¹ with the results comparable to those of HPLC (Fig.4) (Fan et al., 2019). Recently, an electrochemical aptasensor based on diamond-gold nanocomposite exhibited good linearity from the femtomolar to micromolar range and a very low detection limit of 0.32 fM for PCB-77 and recoveries between 98% and 106% for spiked samples. The sensor demonstrated its superiority to other sensors by achieving trace detection of PCB-77, being selective, and reusable (Yuan et al., 2020).

Modification using biologically generated materials has been shown to provide sensors with very low detection limits but their production is costly and such sensors are not robust enough to withstand very harsh conditions encountered when analysing environmental samples. To overcome these challenges, an electrochemical impedance sensor for determination of PCB-77 based on a single-walled carbon nanotube/pyrenecyclodextrin (SWCNT/PyCD) hybrid has been reported to detect PCB-77 up to 1 nM (Wei et al., 2011). Similarly, an electrochemical sensor in which the working electrode was modified with β -cyclodextrin polymer and reduced graphene oxide composite (β -CDP/rGO) achieved the detection of PCBs in form of Aroclors in sediment core at detection limit of 0.0005 nM and a linear range of 0.001–10,000 nM, providing similar results as GC-ECD (Zheng et al., 2016). In all these cases, β -cyclodextrin was applied to achieve host-guest complex and increase the selectivity of the analyte and graphenes and nanoparticles were used to increase the electrode conductivity to enhance the sensor signal.

The detection limits and the performance of these sensors are comparable to those reported by the use of conventional analytical equipment suggesting their potential for widespread routine monitoring of PCBs. Sensors are cost-effective and offer opportunities for further modification to enhance their sensitivity and selectivity for the detection of components from trace to ultra-trace levels. Materials that include MOFs, graphene oxides, carbon nanotubes, and MIPs have been reported to demonstrate high adsorption capacities, large surface area and selectivity, thus putting them in the right position for their application as recognition elements in sensors.

5. Conclusions and future perspectives

Continuous monitoring of PCBs in the environment is paramount to protect the environment and humans from the adverse effects of the PCBs. As discussed above sample preparation steps that aim at ensuring that the analytes are in the right form for instrumental quantification

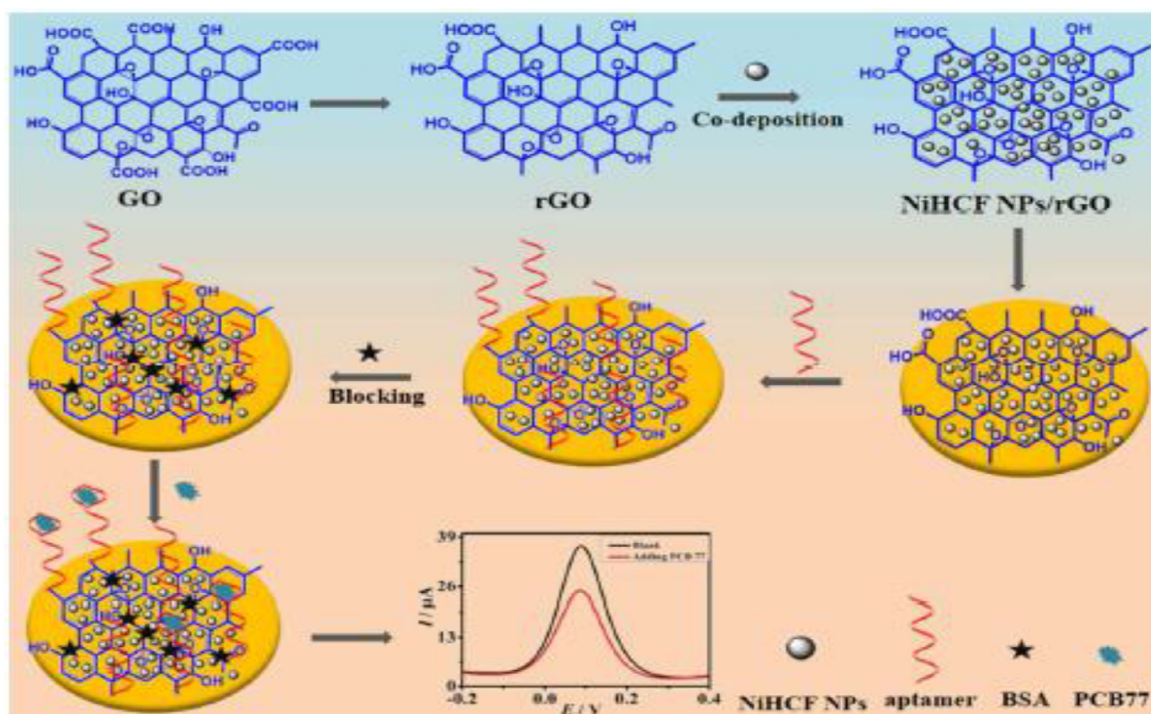


Fig 4. Fabrication of electrochemical aptasensor for PCB-77 (Reproduced from (Fan et al., 2019), Copyright 2019, with permission from Elsevier).

have advanced to green and miniaturized technologies, such as SPME, SBSE and LPME, that are rapid, consume less solvent, and do not suffer from matrix interferences, thereby facilitating the detection of PCBs at trace to ultra-trace levels. Likewise, techniques for the detection of PCBs have advanced to high-resolution systems such as HRGC–HRMS that are highly selective and achieve ultra-trace level detection of PCBs. Despite this advancement, HRGC–HRMS is costly in terms of investment, thereby limiting frequent monitoring of PCBs. This has necessitated innovative sensor technology that is affordable and achieves the required figures of merit promptly. Prospects in selective enrichment of PCBs involves the use of highly selective materials such as MIPs in SPE, SPME and SBSE, while detection techniques that have been miniaturized to sensors have the potential to achieve ultra-trace detection of PCBs by integration with nanomaterials such as carbon nanotubes, MIPs and MOFs as recognition elements, to provide robust systems towards affordable and routine monitoring of PCBs. The design of MIPs has recently incorporated computational analysis to provide MIPs with smart properties and eliminate the trial-and-error method usually applied. So far, a number of studies have reported successful application of such rationally designed MIPs in sample preparation, implying the potential for such novel computational analysis to be extended in design of MIPs selective to PCBs and their subsequent application in sample enrichment and sensors for environmental monitoring of PCBs.

Declaration of Competing Interest

The authors declare no conflict of interest.

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