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REVIEW ARTICLE

Recent advances in the analysis of polycyclic aromatic hydrocarbons in food and water

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Abstract

Polycyclic aromatic hydrocarbons (PAHs), a class of harmful and persistent organic contaminant, are widely distributed in the environment and eventually accumulated in water and food. Also, they are formed in different varieties and varying amounts during processing of food depending on the food composition, cooking method and processing condition. According to the International Agency for Research on Cancer (IARC), various PAHs are classified under Group 1 to 3 category, with Group 1 designated as carcinogenic to humans, Group 2A as probable carcinogen, Group 2B as possible carcinogen and Group 3 as noncarcinogenic. Therefore, it is imperative to develop rapid and highly sensitive analytical methods for determination of PAHs in food and water. This article aims to overview the recent advances of various chromatographic methods as well as electrochemical and SERS-based optical sensing methods for analysis of PAHs in food and water. Initially, several conventional sample preparation methods along with the advanced extraction for isolation of PAHs were summarized, followed by reviewing various gas chromatographic methods coupled with various detection techniques for PAHs analysis in various food products including meat/meat products, seafood, oil, milk/milk products, baby foods, honey, vegetable, cocoa products, tea/coffee, juice, rice, flour, noodle and cake. In addition, high performance liquid chromatographic methods coupled with fluorescence, diode array or mass/tandem mass detection techniques as well as an emerging supercritical fluid chromatographic technique employed for determination of PAHs in different food and water matrices were also overviewed. Finally, various electrochemical sensors and SERS-based optical sensors developed recently for onsite detection of PAHs were tabulated and discussed. Thus, this review article can provide a research update on chromatography and sensor-based analytical methods for PAH analysis as well as enable elucidation of research gaps for future studies.

Keywords: Chromatographic methods, Electrochemical sensors, Polycyclic aromatic hydrocarbons, Sample preparation, SERS sensors

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants originating primarily from natural and anthropogenic sources, with the former can be from fossil fuels, wood fires and volcano eruptions, and the latter from emissions of industrial, mobile transport, domestic and agricultural sources [1,2]. The PAHs originally from these sources are transported through diffusion for deposition in air, water and oil for subsequent contamination into food and human. There are three common routes of PAHs' exposure to humans: (1) absorption by inhalation, skin and gastrointestinal tract, with the highest exposure being from the contaminated food through PAH adherence from the environment, (2) formation in food products during cooking and processing conditions, (3) food preservation by traditional drying and curing methods [3,4]. Most importantly, the formation of PAHs in food products during processing is mainly caused by pyrolysis or incomplete combustion of organic matter including fat, protein and carbohydrate at temperatures >200 °C [5,6]. Also, lipids may

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drip into the flame producing PAHs in the smoke during heating thereby adhering on food surface [7,8]. Accordingly, PAHs can be present in various foods/food products including oils and fats, meat and meat products, leafy and non-leafy vegetables, fruits, cereals and tubers as well as processed products such as sweets, candies and chocolates [9–11]. In addition, non-alcoholic beverages (juices, milk and coffee) and alcoholic beverages can also be the possible food sources for PAH formation [12,13]. The variety and amount of PAH formed in foods/food products during processing depends on various factors such as distance from heat source, fuel composition used, processing condition, cooking duration and methods like reuse, conching, concentration, crushing and storage [4,9,14]. Although not yet comprehensively elucidated, the possible mechanism for formation of PAHs including hydrogen abstraction with acetylene addition (HAM), PAH condensation with HAM, radical-induced PAH formation, Diels–Alder reaction, phenyl addition with cyclization (ACP) and HAM-induced ACP has been reported [5,15,16].

Structurally, PAHs are composed of 2 or more fused aromatic rings with carbon and hydrogen atoms. Several classification of PAH compounds include light-molecular weight PAHs (LMW-PAHs, 2 or 3 aromatic rings) and high-molecular weight PAHs (HMW-PAHs, 4 or more aromatic rings) as well as alternant PAHs (fusion of 6 carbon benzene rings) and nonalternant PAHs (six carbon benzene rings plus <6 carbon ring) [2,17]. The LMW-PAHs are highly volatile compounds with relatively low toxicity, while HMW-PAHs are more stable and toxic as they are resistant to nucleophilic attack due to existence of dense π electrons on aromatic rings. Also, following a rise in MW, the water solubility decreases as well as both melting and boiling points increase due to increase in lipophilicity (octanol–water partition coefficient), making PAHs more susceptible bioaccumulation in living organisms [2].

Different PAHs exhibit varying level of toxicity depending on dose, duration and mode of exposure as well as a person's age and health, with ingestion contributing to the highest cancer risk in humans (98.1–99.3%), followed by skin contact (0.66–1.83%) and inhalation (0.03–0.04%) [18]. Upon ingestion, PAHs are absorbed and eventually undergo metabolic transformation that usually raise their polarity for faster clearance from body [19]. However, such metabolism also generates some reactive intermediates such as hydroxyalkyl derivatives, diolepoxides and quinones that are less polar for faster excretion [16]. Consequently, they form DNA adducts resulting in genotoxic effects and several organs are prone to tumor formation which include stomach, esophageal, colon, pancreas, breast, lung and pancreas [20,21]. Among several biological and cytogenetic markers, 1-hydroxypyrene (1-HP), hydroxynapthalene and hydroxyphenanthrene are the most frequently used to elucidate the relationship between PAH ingestion and cancer risk [19]. In addition, the PAH compounds may also bind to estrogen and androgen receptors affecting reproductive system, as well as bind to aryl hydrocarbon receptors in lymphocytes and accessory cells affecting immune system in human [21].

Owing to the genotoxic, mutagenic and carcinogenic effects of PAHs, several international organizations such as the International Agency for Research and Cancer (IARC), the Joint FAO/WHO Expert Committee on Food Additives, United States Environmental Protection Agency (USEPA) and European Union (EU) have proposed a list of 16 priority PAHs [22–24]. Also, the IARC have categorized PAHs into four groups with group 1 as carcinogenic to humans, group 2A as probably carc-inogenic, group 2B as possibly carcinogenic and group 3 not classifiable as carcinogenic [24] (Table 1). Of all the PAHs, BaP has been recognized by IARC and European Commission as the most carcinogenic PAH and a PAH exposure marker for risk assessment [23]. In addition, the European Food Safety Authority (EFSA) has suggested that a combination of 4 PAHs including BaP, BaA, BbF and CHR as the relevant indicator of PAH contents in food [25]. The EU has set the maximum allowable limits for BaP alone and the sum of 4 PAHs in several processed food products including oil and fats (2 and 10 μg/L), cocoa products (5 and 30 μg/L), smoked meat and meat products (2 and 12 μg/L), smoked seafood (5 and 30 μg/L) and baby foods including processed cereal-based foods, infant and follow-up formula and dietary foods (1 and 1 μg/L) [23]. Also, the analytical method used for determining PAHs in foods should comply with the specific criteria for recovery (50–120%), limit of detection ($\leq$0.30 ng/g) and limit of quantitation ($\leq$0.90 ng/g) along with high specificity, repeatability and reproducibility [23]. Thus, it is imperative to develop rapid and highly sensitive analytical methods for monitoring the level of PAHs in various unprocessed and processed foods as well as environmental waters.

This review article aims to overview the recent advances in development of improved analytical methods for determination of PAHs in food and water. More specifically, several chromatographic methods including gas chromatography (GC), high-performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) as well as onsite

surface enhanced plasmon resonance (SERS)-based optical sensors and electrochemical sensors developed recently for analysis of PAHs were reviewed.

2. Sample preparation methods for PAH analysis

Sample preparation is a vital step in the analysis of PAHs especially in complex food matrices which require efficient extraction and purification steps to isolate PAHs from coexisting matrix components. It usually involves two major steps, (1) extraction of PAHs from the food matrix by adopting an appropriate method and (2) purification of the extract by removing interfering co-extracted compounds [16]. Food samples usually exist in biological solids (meat, fat), liquid/solution and dry powder forms. The PAHs are isolated from solid food samples by solid or liquid extraction followed by a purification method, whereas the liquid samples by liquid–liquid extraction or sorption-based methods [11]. Several combinations of nonpolar solvents (hexane) or low polar solvents (dichloromethane) have been used for PAH extraction. However, the coextraction of unwanted lipophilic compounds is the major drawback requiring further purification to attain an acceptable recovery. Saponification with alcoholic potassium hydroxide (KOH) is one of the foremost extraction methods used for removal of unwanted lipophilic compounds during extraction of PAHs and currently used as a reference method for comparing the extraction efficiency of PAHs with other new methods [11,26]. Some other conventional methods including Soxhlet extraction, ultrasonication and mechanical agitation have been employed or PAH extraction. However, the soxhlet extraction requires a large volume of solvents, while the mechanical agitation method needs long shaking time which can cause measurement errors. On the other hand, ultrasonication involves cavitation forces for PAHs extraction [16,27].

Some advanced extraction techniques such as accelerated solvent extraction (ASE) or pressurized liquid extraction (PLE), supercritical/subcritical fluid extraction (SFE) and microwave-assisted extraction (MAE) methods are employed for efficient isolation of PAHs from food samples [28–31]. In ASE/PLE method, the liquid solvents are subjected to a combination of elevated temperature and pressure enabling deeper penetration to most sample parts for extraction of PAHs by the solvent. Likewise, SFE method combines the high dissolving power of liquid and high diffusion power of gas for deeper penetration into samples for extraction of PAHs. MAE, a relatively cheaper extraction method than SFE, involves application of electromagnetic waves-based thermal radiation energy with a unique heating mechanism for selective extraction of PAHs. In addition, the ultrasound/vortex-assisted extraction (UAE) method is also adopted along with the other extraction techniques [32,33], which utilizes ultrasound cavitation effect to accelerate solvent mobility resulting in a high mass transfer rate through enhanced solvent penetration. After extraction, the extract is usually purified by gel permeation chromatography (GPC), column chromatography with a suitable stationary phase, or solid phase extraction using adsorbents [11,16].

In recent years, both solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) techniques are becoming popular because of their simplicity, short time, high efficiency, cost-effectiveness and green strategy due to low solvent consumption and a less amount of solid sorbents used. Several SPME methods have been used for PAH extraction from food and water, which include fiber SPME, in-tube SPME, stir-bar sorptive extraction (SBSE), microextraction in packed sorbent (MEPS) and thin-film microextraction [31,34]. Likewise, various LPME methods include single drop microextraction (SDME), hallow-fiber LPME (HF-LPME), dispersive liquid–liquid microextraction (DLLME), ultrasound/vortex-assisted LPME and membrane-mediated liquid-phase microextraction (MM-LPME) [31]. Additionally, several other miniaturized dispersive solid phase extraction (dSPE) methods are emerging as potential extraction methods for PAHs. They include QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe), magnetic solid phase extraction (MSPE), fabric phase sorption extraction (FPSE) and pipette-tip solid phase extraction [35,36]. Different kinds of commercial sorbents used in SPME and dSPE techniques were polydimethylsiloxane (PDMS), carboxen (CAR), carbowax (CW), divinylbenzene (DVB), silica gel/alumina, silica nanoparticles, quantum dots, metal/metal-oxide nanoparticles, single-walled/multi-walled carbon nanotubes (SWCNTs/MWCNTs), graphene/graphene oxide (GR/GO), metal organic frameworks (MOFs) and molecularly imprinted polymers (MIPs) [34,37,38]. In addition, supramolecular and green solvents (ionic liquids and deep eutectic solvents) were also used with various SPME and LPME extraction methods [35,36]. The pros and cons of different extraction methods for PAH analysis have been recently summarized by Peng and Lim [39].

3. Chromatographic methods for PAH analysis

HPLC coupled with a fluorescence detector (FLD) and GC with mass spectrometry (GC–MS) are the two main analytical tools frequently used for detection of PAHs in foods. This is mainly due to their sensitivity, accuracy and convenience for determining PAHs content in foods. However, more recently, HPLC-MS/MS, GC–MS/MS and SFC-MS methods are becoming more popular. To meet the requirement of sensitivity, accuracy and precision for PAH determination in foods, EU has specified the regulations (No. 836/2011 and 1881/2006) for LOD and LOQ of PAH4 markers (BaP, BaA, BbF and CHR) to be 0.3 and 0.9 ng/g, respectively, with recovery to be from 50 to 120% and high precision and specificity requiring matrix-free and spectra interference-free analysis [23].

3.1. Gas chromatographic methods for PAH analysis

Table 2 shows the various GC methods developed recently for PAH determination in foods. While GC–MS is the frequently used method, some other GC methods such as GC-FID, GC–MS/MS and HPLC-GC/MS are also reported in the literature. Among the various GC columns, DB-5 MS capillary column is used most often for determination of 16 EPA priority PAHs in different food samples [15,32,40–45], with the analysis time ranging from 30.5 to 78.0 min, while with a HP-5MS column, the analysis time can be reduced to 21.0–23.0 min. Nevertheless, some other GC columns are also used for determination of 4–45 PAHs in different food samples with the analysis time ranging from 19 to 93.1 min [27,28,33,46–49].

3.1.1. In seafood and meat/meat products

Marine ecosystems are subjected to severe pollution owing to the increasing anthropogenic activities and release of various contaminants. Obviously, marine organisms including fish, mussels and clams have become the indicators of contaminant accumulation. Likewise, meat and meat products are the protein-rich foods that provide adequate nutrients for human diet. However, meat and meat products can be contaminated by PAHs through water, soil and air as well as the use of contaminated grain-

Table 1. A list of PAHs frequently analyzed in food samples with their abbreviation, chemical formula, molecular weight and IARC toxicity classification.[a,b]

No.	Name	Abbreviation	Chemical formula	Molecular weight	Toxicity (IARC)[c]
1	Naphthalene[d]	NAP	$C_{10}H_8$	128.17	2B
2	Acenaphthene[d]	ACE	$C_{12}H_{10}$	154.21	3
3	Acenaphthylene[d]	ACY	$C_{12}H_8$	152.20	3
4	Anthracene[d]	ANT	$C_{14}H_{10}$	178.23	3
5	Phenanthrene[d]	PHE	$C_{14}H_{10}$	178.23	3
6	Fluorene[d]	FLU	$C_{13}H_{10}$	166.22	3
7	Fluoranthene[d]	FLR	$C_{16}H_{10}$	202.26	3
8	Cyclopental [cd]pyrene	CPP	$C_{18}H_{10}$	226.27	2A
9	Benzo [a]anthracene[d,e]	BaA	$C_{20}H_{12}$	228.29	2B
10	Chrysene[d,e]	CHR	$C_{18}H_{12}$	228.29	2B
11	Pyrene[d]	PYR	$C_{16}H_{10}$	202.26	3
12	Benzo [c]fluorene	BcF	$C_{17}H_{12}$	216.28	3
13	5-methylchrsene	5MCH	$C_{19}H_{14}$	242.31	2B
14	Benzo [a]pyrene[d,e]	BaP	$C_{20}H_{12}$	252.32	1
15	Benzo [a]fluoranthene	BaF	$C_{20}H_{12}$	252.31	2B
16	Benzo [b]fluoranthene[d,e]	BbF	$C_{20}H_{12}$	252.32	2B
17	Benzo [k]fluoranthene[d]	BkF	$C_{20}H_{12}$	252.32	2B
18	Benzo [j]fluoranthene	BjF	$C_{20}H_{12}$	252.30	2B
19	Dibenzo [a,h]anthracene[d]	DBahA	$C_{22}H_{14}$	278.35	2A
20	Benzo [g,h,i]perylene[d]	BghiP	$C_{22}H_{12}$	276.34	3
21	Indeno [1,2,3-cd]pyrene[d]	IP	$C_{22}H_{12}$	276.34	2B
22	Dibenzo [a,e]pyrene	DBaeP	$C_{24}H_{14}$	302.37	3
23	Dibenzo [a,h]pyrene	DBahP	$C_{24}H_{14}$	302.37	2B
24	Dibenzo [a,i]pyrene	DBaiP	$C_{24}H_{14}$	302.37	2B
25	Dibenzo [a,l]pyrene	DBalP	$C_{24}H_{14}$	302.37	2A

[a] Based on United States Environmental Protection Agency (USEPA) (2010) and European Union (2011).
[b] PAHs are arranged in the increasing order of molecular weight.
[c] IARC, international Agency Research on Cancer.
[d] 16 priority PAHs listed by USEPA.
[e] PAH4 markers recognized by EU.

based feed. Furthermore, the accumulation of PAHs in seafood and meat/meat products during processing is inevitable especially for the cooking methods such as grilling, frying, boiling, smoking, barbequing and drying. Consequently, the development of a highly sensitive analytical method for determination of various PAHs in processed meat/meat products is important.

By employing an efficient accelerated solvent extraction, followed by a cleanup GPC and DB-EUPAH column (30 m × 0.25 mm ID, film thickness 0.25 μm), a total of 16 PAHs and 11 chlorinated PAHs were separated in a GC–MS system within 46.0 min with the LOD and recovery ranging from 0.1 to 5.62 ng/g and 42.2–132.6%, respectively [28]. Also, the matrix-matched calibration curves provided high intraday- and interday-precision with the RSD ranging from 0.3 to 16.1% and 0.88–15.1%, respectively. Analysis of 22 fresh water fish samples revealed that the presence of chlorinated derivatives of PHE, PYR and ACE dominated over the other PAHs. In another study, Chiesa et al. [48] developed a QuEChERS-GC-MS/MS method for determination of 4 PAHs (BaA, BaP, BbF and CHR) in mussel and clam samples. Initially samples were extracted by QuEChERS with hexane/acetone as extraction solvent, $MgSO_4$ and NaCl as extraction powder and Z-Sep sorbent as purification powder. For GC–MS/MS analysis, a RXi-XLB fused-silica capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) in SRM mode was employed and a LOQ value of 0.5 ng/g for all the 4 PAHs and recovery ranging from 75 to 88% were reported.

For analysis of 16 EPA priority PAHs in smoked meat samples, Al-Thaiban et al. [50] developed a QuEChERS method coupled with GC–MS with LOD, LOQ and recovery ranging from 0.24 to 7.60 ng/g, 00.41–20.01 ng/g and 74–117%, respectively, and reported a total PAH content ranging from 0.63 to 43.00 ng/g in 30 smoked meat samples (turkey, chicken and beef). Initially, homogenized meat samples were extracted by QuEChERS method with acetonitrile as extraction solvent, 3 g $MgSO_4$ and 0.5 g NaCl as extraction powder and Supel Z-sep sorbent (zirconium-coated silica) plus 0.5 g $MgSO_4$ as purification powder. Then, a HP-5MS capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) and helium gas with flow rate at 1 mL/min was used in splitless mode and MS detection by SIM mode with the separation time being 23 min. In a later study, Rascon et al. [32] demonstrated a much lower LOD value ranging from 0.003 to 0.070 ng/g for analysis of 16 EPA priority PAHs by subjecting meat and fish samples to alkaline digestion with 2 M KOH in MeOH, followed by ultrasound-assisted extraction with hexane, purification with a SPE cartridge containing 60 mg of RP-C18 sorbent and GC–MS analysis using a DB-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 μm) with helium as carrier gas at 1 mL/min. A high recovery ranging from 85 to 105% was shown and the total PAHs contents in 32 meat and fish samples were 0.011–6.900 ng/g with NAP, ACE, FLR and PYR being present in large amounts in both meat and fish samples, especially in smoked, roasted and grilled samples compared to the raw ones.

A GC-high resolution mass spectrometry (GC-HRMS) method was also developed for simultaneous determination of 12 PAHs plus 20 chlorinated PAHs [27]. Prior to analysis, a total of 15 meat samples (beef, pork, chicken and pacific saury) were extracted with dichloromethane separately by Soxhlet method, followed by purification using a KOH silica gel column and an activated carbon cartridge with toluene as the elution solvent. Subsequently, the purified extract was injected by splitless mode into a BPX-SXN fused silica capillary column (60 m × 0.25 mm ID) and HRMS detection in SIM mode for analysis within 50 min, with the LOQ and recovery values respectively ranging from 0.025 to 7.8 ng/g and 62–96% for 12 PAHs as well as 0.076 × 10^{-3}-0.082 ng/g and 57–105% for 20 chlorinated PAHs. The contents of total PAHs and chlorinated PAHs ranged from <LOQ-310 ng/g and <LOQ-0.16 ng/g respectively, with charcoal-grilled meat showing a higher total PAH level than gas-grilled meat, and gas-grilled meat generating more chlorinated PAHs than charcoal-grilled meat. The outcome can be attributed to the difference in heating temperature between these two cooking methods.

Two different studies were developed recently by Givechev et al. [47] and Hung et al. [15] for determination of 16 and 23 PAHs within 30 and 78 min in smoked pork and thin-sliced roasted pork, respectively, with both methods employing a QuEChERS technique, followed by GC–MS (SIM mode) using a SLB-5MS column (30 m × 0.32 mm ID, film thickness 0.25 μm) for the former and GC–MS/MS using a DB-5MS column (15 m × 0.25 mm ID, film thickness 0.25 μm) for the latter with splitless injection. Comparatively, although the former method employed Soxhlet and saponification extraction steps prior to QuEChERS and an internal standard Chrysene-D_{12} used for quantification, a lower LOD (0.03–0.3 ng/mL) and LOQ (0.1–0.9 ng/mL) as well as higher recovery (81.2–98.3%) was shown by the latter method with a minimum matrix effect ranging from 1.18 to 1.80 (Table 2), which should be due to

Table 2. Gas chromatography (GC) methods developed recently for PAH determination in food and water.

Analytes	Chromatographic conditions/Detection	Performance characteristics	Analysis time (min)	Food variety/processing	Reference
23 PAHs	HP-5MS quartz capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium Detection: MS/MS (MRM)	Recovery (RSD): 70.0−110.8% (2.1−10.2%) LOD: 0.1−1.0 ng/g LOQ: NS	47	Edible vegetable oils (13 samples from soybean, peanut, olive and corn oils)	[51]
8 PAHs	DB-EUPAH fused silica capillary column 20 m × 0.18 mm, film thickness 0.14 μm Carrier gas: helium (1.2 mL/min) Detection: MS (SIM)	Recovery: 75.0−109.7% Precision: repeatability 2.57−14.13% Intermediate precision 4.36−19.77% LOD: 0.01−0.31 ng/g LOQ: 0.04−0.89 ng/g	27	Cocoa bean (8 samples)	[53]
16 EPA priority PAHs	HP-5MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Recovery (RSD): 74−117% (9−20%) LOD: 0.24−7.60 ng/g LOQ: 0.41−20.01 ng/g	23.0	Meat (turkey, turkey breast, turkey strips, chicken, chicken roll, chicken breast, beef, beef mortadella, smoked beef pastrami)	[50]
18 PAHs (16 EPA priority PAHs + m NAP1, mNAP2)	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS/MS	Recovery (RSD): 71−101% (8−20% LOD: 0.01−0.20 ng/g LOQ: 0.03−0.60 ng/g	45.0	Instant noodles, cakes, dried vegetables, teas, coffees, grilled meats	[44]
4 PAHs	RXi-XLB fused-silica capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: NS Detection: MS/MS	Recovery (RSD): 75−82% (2−6%) LOD: NS LOQ: 0.5 ng/g	65.0	Mussels and clams	[48]
16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Recovery (RSD): 85−105% (4.0−7.4%) LOD: 0.003−0.070 ng/g LOQ: NS	34.3	Meat and fish (chicken, beef, pork, Frankfurt sausage, hake, salmon and prawn/raw, roasted, grilled)	[32]
16 EPA priority PAHs	HP-5MS fused silica column 30 m, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Recovery (RSD): 81.5−100.3% (2.8−11.3%) LOD: 0.29−0.53 ng/g LOQ: 1.05−2.00 ng/g	20.2	Honey (61 commercial samples)	[52]
16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: QqQ-MS (MRM)	Waste frying oil−Recovery (RSD): 66.7−112.9% (0.87−3.34%) LOD: 0.06−0.12 ng/g LOQ: 0.20−0.40 ng/g Oil distillate−Recovery (RSD): 72.5−108.5% (1.06−4.54%) LOD: 0.06−0.13 ng/g LOQ: 0.23−0.43 ng/g	41.0	Waste frying oil (from pumpkin pie, chicken chops, youtiao, chicken wings, chicken thighs, chicken nuggets) Vegetable oil deodorizer distillate (soybean oil, rapeseed oil)	[45]
12 PAHs 20 Cl-PAHs	BPX-SXN fused silica capillary column 60 m, film thickness 0.25 μm Carrier gas: NS Detection: HRMS (SIM)	PAH: recovery (RSD): 62−96% (1−21%) LOD: NS/LOQ: 0.025−7.8 ng/g Cl-PAH: recovery (RSD): 57−105% (1−21%) LOD: NS/LOQ: 0.000076−0.082 ng/g	50.0	Pork, beef, chicken and Pacific saury (gas-grilled and charcoal-grilled)	[27]

(*continued on next page*)

Table 2. (continued)

Analytes	Chromatographic conditions/Detection	Performance characteristics	Analysis time (min)	Food variety/processing	Reference
16 PAHs 11 Cl-PAHs	DB-EUPAH column 30 m × 0.25 mm, film thickness, 0.25 μm Carrier gas: NS Detection: MS	PAH–recovery (RSD): 42.2–132.6% (1.6–19.8%) LOD: 0.10–5.62 ng/g/LOQ: NS Cl-PAH–recovery (RSD): 45.1–33.7% (2.7–18.3%) LOD: 0.15–1.77 ng/g/LOQ: NS	54.3	Fish (carp, black carp, silver carp, grass carp, crucian, blunt-snout, rainbow trout, catfish, islanderfish, and tamban)	[28]
7 PAHs	HP5-MS fused silica capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: nitrogen Detection: FID	Recoveries: 84–110% RSD: 1.8–8.23% LOD: 0.02–0.14 ng/mL LOQ: NS	25.0	Water (drinking and mineral) Tea (beverage and infusion) White rice, Tapioca flour, Corn flour	[54]
5 PAHs	HP5-MS fused silica capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: nitrogen Detection: FID	Recovery (RSD): 88–116.1% (4.3–9.8%) Water, orange & apple juice LOD: 8.47–55.96 ng/mL) LOQ: 28.23–186.54 ng/mL Rice LOD: 2.98–30.22 ng/g LOQ: 9.04–91.59 ng/g/ME: 0.57–3.47%	26.0	Water Rice Orange juice Apple juice	[55]
4 PAHs	Selected PAHs® capillary column 15 mx0.15 mm, film thickness 0.10 μm Carrier gas: helium Detection: MS (SIM)	Recovery (RSD): 83.8–93.5% (7.9–11.8%) LOD: 0.03–0.05 ng/g LOQ: 0.10–0.16 ng/g ME: −19.4 to −11.6%	30.4	Yoghurt	[46]
16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Recovery (RSD): 86.1–100.3% (3.2–10.1%) LOD: 0.04–0.06 ng/g LOQ: 0.121–0.181 ng/g	35.5	Butter and yoghurt	[42]
16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Recovery (RSD): 91.2–101.7% (4.1–10.6%) LOD: 0.020–0.080 ng/g LOQ: 0.063–0.242 ng/g	30.5	Mushroom (fried and grilled)	[43]
23 PAHs	DB-5 MS capillary column 15 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1.25 mL/min) Detection: MS/MS (MRM)	Recovery (RSD): 81.2–98.3% (3.7–12.63%) LOD: 0.03–0.3 ng/mL LOQ: 0.1–0.9 ng/mL/ME: 1.18–1.80	78.0	Dried pork (thin slices/roasted)	[15]
16 EPA priority PAHs	SLB-5 MS GC column 30 m × 0.32 mm, film thickness 0.25 μm Carrier gas: helium Detection: MS (SIM)	Recovery (RSD): 71–120% (1.7–7.6%) LOD: 0.27–5.74 ng/g LOQ: 0.81–17.22 ng/g	30.0	Pork meat (smoked)	[47]
16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium (1 mL/min) Detection: MS (SIM)	Milk–Recovery: 80–107% Precision: Intra-day 5.0–10.2% Inter-day 6.9–11.3% LOD: 1–100 ng/kg LOQ: 3.3–330 ng/kg/ME: -19-19% Butter–Recovery: 85–107% Precision: Intra-day 5.9–9.8% Inter-day 8.5–11.5% LOD: 0.002–0.200 ng/g LOQ: 0.007–0.660 ng/g/ME: −19 to 14%	36.0	Milk (milk, yogurt, cheese, custard, cream and milkshakes) Butter (butter and margarine)	[40]

16 EPA priority PAHs	DB-5 MS capillary column 30 m × 0.25 mm, film thickness 0.25 μm Carrier gas: helium Detection: MS (SIM)	Recovery (RSD): 93.4–101.6% (6.7–10.7%) LOD: 0.06–1.12 ng/g LOQ: 0.18–3.38 ng/g	35.5	Baby foods (Rice-, wheat-, mixed wheat and rice-, mixed wheat and honey-, mixed wheat and date-mixed almond porridge and fruit-, mixed wheat and fruit-, mixed five cereal- and almond porridge-based baby foods)	[41]
22 PAHs (EPA + EU priority PAHs)	DB-XLB capillary column, 60 m × 0.25 mm, film thickness 0.25 μm Carrier gas: hydrogen (3 mL/min) Detection: MS (SIM)	Recovery (RSD): 35–106% (3–15%) LOD: 0.02–0.06 ng/g LOQ: 0.07–0.15 ng/g	41.5	honey	[33]

PAHs, polycyclic aromatic hydrocarbons; EPA, Environmental Protection Agency; EU, European Union; LOD, limit of detection; LOQ, limit of quantitation; MS, mass spectrometry; FID, flame ionization detection; MS/MS, tandem mass spectrometry; SIM, selected ion monitoring; MRM, multiple reaction monitoring; HRMS, high resolution mass spectrometry; mNAP1, 1-methylnaphthalene; mNAP2, 2-methylnaphthalene; RSD, relative standard deviation; NS, not specified; ME, matrix effect.

the more efficient QuEChERS and higher sensitivity of the GC–MS/MS method [15].

3.1.2. In oil samples

Owing to their lipophilic nature, the level of PAHs in oil- and fat-rich foods has become a serious concern as a recent survey showed that 35% of common edible oil and half of rapeseed, sunflower and corn oil samples from Brazilian market exceeded the EU safety limit 2 and 10 ng/g for BaP and PAH4, respectively. The contamination of oil with PAH is mainly due to three following routes: (1) absorption of PAHs by oil crops, (2) high-temperature heating and organic solvent treatment during oil processing, (3) food-contact during packaging/storage/transport. Moreover, PAHs can be further generated during oil storage and deep-frying with the PAH level increasing with frying time and temperature compared to the any other cooking methods. Following extraction with hexane-saturated acetonitrile, Zhou et al. [51] evaluated a GC–MS/MS method with MRM mode for analysis of 23 PAHs in 13 edible vegetable oils from 4 oil varieties including soybean, peanut, olive and corn oil by using a HP-5MS quartz capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) and helium as carrier gas with programmed column temperature. All the 23 PAHs were analyzed within 47 min and a good linear response was shown in the PAH concentration range of 2–100 ng/mL, with the LOD and mean recovery ranging from 0.1 to 1.0 ng/g and 70.0–110.8%, respectively.

To overcome the existing challenges in PAH analysis in oily matrices, Sun & Wu [45] reported a QuEChERS method combined with GC–MS/MS for determination of 16 EPA priority PAHs within 41 min in 12 oily samples. Following QuEChERS extraction with acetonitrile/acetone (3:2, v/v) as the extraction solvent, 6 g $MgSO_4$ and 1.5 g NaOAc as the extraction powder and 1 g EMR-lipid plus 1.6 g $MgSO_4$ and 0.4 g NaCl as the purification powder, the GC–MS/MS analysis was performed in a DB-5MS capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) with helium as carrier gas at 1 mL/min in splitless mode and detection by MRM mode, the recovery, LOD and LOQ were 66.72–112.87%, 0.06–0.13 ng/g and 0.20–0.43 ng/g, respectively, with the total PAH levels ranging from 39.21 to 197.44 ng/g and 1219.34–1482.25 ng/g in waste frying oil and vegetable oil deodorizer distillates, respectively.

3.1.3. In milk and milk products

Milk and milk products are nutritionally essential for infants, children and adults due to the presence of macro and micronutrients with yogurt and butter playing a vital role in human diet. This issue has

posed a serious concern on PAH contents and safety due to contamination during production, transport, and storage of milk and milk products. For analysis of PAH4 markers (BaP, BaA, BbF and CHR) in yoghurt, Akdogan et al. [46] used a saponification method combined with toluene extraction and a subsequent SPE purification with a silica cartridge with toluene as the elution solvent. By using a Select PAHs® column (15 m × 0.15 mm ID with film thickness 0.10 μm), helium as carrier gas (1.54 mL/min) and MS detection at SIM mode, the 4 PAHs could be separated and detected within 30.4 min with the recovery, LOD and LOQ being from 83.8 to 93.5%, 0.03–0.05 ng/g and 0.10–0.16 ng/g, respectively.

In a later study, a MSPE/GC–MS method was developed by Kiani et al. [42] who employed acetonitrile-methanol (70:30, v/v) plus 1 M KOH as the extraction solvent followed by preconcentration with 10 g of MWCNTs-MNPs for sample preparation. Then, a DB-5 MS capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) with helium gas (1 mL/min) and temperature programming was used to separate 16 PAHs within 35.5 min. A high recovery (86.1–100.3%) as well as low LOD (0.040–0.060 ng/g) and LOQ (0.121–0.181 ng/g) were shown with the total PAHs higher in butter (6.87 ng/g) than in yogurt (3.82 ng/g).

More recently, Colon et al. [40] adopted a liquid–liquid extraction method with DMF/water (9:1, v/v) plus ethanol or hexane a solvent depending on sample type, followed by semi-automated SPE purification using the RP-C18 packed adsorbent and 2-propanol plus triphenyl phosphate as the elution solvent. For GC–MS analysis, a HP-5MS capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) was used with helium as carrier gas at 1 mL/min in splitless mode for analysis of 16 PAHs within 36 min with the injection temperature at 300 °C and MS detection in SIM mode. The LOD as low as 0.001–0.1 ng/g and 0.002–0.2 ng/g was reported for milk/milk products and butter/margarine respectively, while their corresponding recovery ranged from 80 to 107% and 85–107%. Also, the RSD for intraday- and interday precision for all the tested samples respectively ranged from 5 to 10.2% and 6.9–11.5%. Application of this method to analyze 30 dairy products on the market revealed the presence of PAH concentration ranging from 0.007 to 1.9 ng/g with mostly detected PAHs being NAP, ACE, FLU and PHE.

3.1.4. In baby foods

Baby food is one of the most sensitive foods that needs to be monitored for carcinogenic toxins. Cereal-based baby food has recently become a vital nutrient source of a baby's daily diet and regardless of cultural/religious concerns, baby foods deserve a high priority in devising strategies for managing food safety and promoting child health. Thus, by taking into child's immature immune system, it is highly essential to constantly monitor possible contaminants in baby foods. Moazzen et al. [41] developed a MSPE method coupled with GC–MS for determination of 16 EPA priority PAHs in 36 baby food samples from 9 varieties sold on Iran's market. Following extraction with acetonitrile-methanol (70:30, v/v) and KOH, 10 mg of MWCNTs-MNPs was added and vortex-mixed for 5 min for PAH enrichment for subsequent GC–MS analysis by SIM mode. A DB-MS column (30 m, 0.25 mm ID, film thickness 0.25 μm) and helium as carrier gas at 1 mL/min were used with the recovery, LOD and LOQ ranging from 93.4 to 101.6%, 0.06–1.12 ng/g, and 0.18–3.38 ng/g, respectively. The mean value of carcinogenic BaP (0.29 ng/g) was shown to be lower than that recommended by USEPA for baby foods (1 ng/g for BaP). Also, the mean value for 6 PAHs was the highest for cereal-based baby food (5.06 ng/g) and lowest for date-based baby food (3.03 ng/g), revealing that the tested baby foods in Iran were safe for consumption.

3.1.5. In honey

Nectar and pollen are the two important constituents of honey that can be contaminated with environmental pollutants during production of honey from bee, with the latter being more susceptible to PAH contamination than the former constituent possessing low level of lipid. Although a maximum permissible limit of PAHs is not yet set for honey, it is vital to evaluate if bees act as a carrier of environmental contaminants especially PAHs. With this in mind, Petrovic et al. [52] developed a QuEChERS method coupled with GC–MS for determination of 16 EPA priority PAHs in 61 commercial honey samples in Serbia by using a HP-5M fused silica column (30 m × 0.25 mm ID, film thickness 0.25 μm) with splitless mode and programmed column temperature as well as both the injector and MS temperature at 280 °C. Prior to analysis, a QuEChERS method was adopted by using 3 mL of acetonitrile as the extraction solvent, 3 g $MgSO_4$ and 1 g NaOAC as the extraction powder and 150 mg of $MgSO_4$, 100 mg of primary secondary amine (PSA) and 50 mg of C18 as the purification powder. The LOD, LOQ, recovery, as well as RSD of repeatability and reproducibility were reported to be from 0.29 to 0.5 ng/g, 1.05–5.00 ng/g, 81.5–100.3%, 2.8–11.3% and 3.3–14.2%, respectively, while 6.6% of all the honey samples was

found unsafe due to presence of higher level of some PAHs including CHR (140.6 ng/g), BghiP (136.3 ng/g), BaP (120.1 ng/g), BaA (87.2 ng/g) and BkF (79.6 ng/g).

In a later study, an ultrasound-vortex-assisted DLLME (USVA-DLLME) method combined with a GC–MS method was employed for simultaneous determination of 22 PAHs in 57 honey samples in Italy by using a DB-XLB column (60 m × 0.25 mm ID, film thickness 0.25 μm) and hydrogen as carrier gas at 3 mL/min with the injector and MS temperature at 250 °C and 290 °C respectively [33]. Following sample preparation by the USVA-DLLME method, all the 22 PAHs were separated within 41.5 min with a relatively lower recovery from 35 to 106% being shown as well as a higher sensitivity in terms of LOD (0.02–0.06 ng/g) and LOQ (0.07–0.15 ng/g) when compared to the above method. Through cluster analysis and principal component analysis, the sampling area was reported to be constantly exposed to BaA and PHE due to combustion as well as to NAP due to beekeeping practices.

3.1.6. In vegetable and cocoa products

The processing of cocoa-derived products usually involves drying fermented beans by natural or artificial method, followed by packing and transportation. The contamination of cocoa beans by PAHs frequently occurs during drying on asphalt or bitumen under sun or on artificial dryers using burned firewood/fossil fuel and transportation in mineral oil-treated bags. An ASE method coupled with GC–MS was optimized for determination of 8 PAHs (BaA, CHR, BbF, BkF, BaP, IP, DahA and BghiP) in cocoa beans [53]. Following 3 min agitation with hexane:dichloromethane (85:15, v/v) as the extraction solvent, purification by column chromatography with 16 g of silica gel as the adsorbent and PAH elution with 15 mL of hexane, a linear response was shown in the range of 0.5–8.0 ng/g for BaP and 0.75–8.0 ng/g for the other 7 PAHs, with the LOD and LOQ being from 0.01 to 0.31 ng/g and 0.04–0.89 ng/g, respectively, through separation in a DB-EUPAH fused silica capillary column (20 m × 0.18 mm ID, film thickness 0.14 μm) with helium gas at 1.2 mL/min and MS detection in SIM mode. Although a significant matrix effect was found for CHR and BbF, this method showed high precision in terms of RSD of the repeatability (2.57–14.13%) and intermediate precision (4.36–19.77%) as well as high accuracy with an acceptable recovery (74.99–109.73%) in 8 different cocoa bean samples.

PAHs are usually accumulated in plants tissues through soil, air and water as well as the surface of vegetable wax, which can adsorb PAHs from air with the total PAH concentration in vegetables being from 0.01 to 0.50 ng/g (in some cases even 5 ng/g) [43]. Moreover, some more varieties of PAHs may be generated during processing of vegetables depending on fuel type, cooking method/temperature/time and ingredient composition. Due to the presence of high protein content and essential elements, edible mushrooms are becoming a popular alternative to animal proteins and consumed widely for their beneficial health-promoting effects. With an aim to determine the level of 16 PAHs in raw, fried and grilled mushrooms, Shariatifar et al. [43] developed a MSPE method coupled with GC–MS by extraction of PAHs from mushroom samples initially with an equal volume (7.5 mL) of 1 M KOH and 30% MeOH-ACN, followed by adding 10 mg of MWCNTs-MNPs and 500 mg of NaCl for preconcentration of PAHs and subsequent analysis by GC–MS. The application of a magnet was shown to facilitate separation of PAH-enriched MWCNTs-MNPs after an equilibrium time of 10 min. By employing a DB-5MS capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm) and helium gas at a flow rate of 1 mL/min, a total of 16 EPA priority PAHs were separated within 30.5 min and detected through MS in SIM mode with the interface, quadrupole and source temperatures at 300, 150 and 230 °C, respectively. The LOD, LOQ and recovery values ranged respectively from 0.02 to 0.08 ng/g, 0.1–250 ng/g and 91.2–101.7%, while the level of total PAHs ranged from 0.82 to 6025 ng/g with ACY dominating (0.84 ng/g) and PAHs including BaP, ACE, PHE, DBahA, BaA, FLR, IP and BghiP remaining undetected. Furthermore, the total PAHs was shown to be present in the highest amount in fried mushrooms, followed by grilled and raw ones.

3.1.7. In mixed variety of samples

There are also several GC-FID and GC–MS methods developed for PAH analysis in mixed varieties of food matrices including grilled meats, rice, noodle, cake, dried vegetable, tapioca flour, corn flour, orange juice, apple juice, tea, coffee and water. In a study dealing with analysis of 18 PAHs in 6 different food types, Tran-Lam et al. [44] reported that a QuEChERS method coupled with GC–MS/MS by using acetonitrile as the extraction solvent, 4 g $MgSO_4$ and 1 g NaCl as the extraction powder and 0.9 g $MgSO_4$/0.3 g PSA/0.3 g C18 as the purification powder for subsequent separation in a DB-5 MS capillary column (30 m × 0.25 mm, film thickness 0.25 μm) with helium gas at 1 mL/min and detection in electron ionization mode with GC–MS interface temperature at 310 °C. A total of 18 PAHs including 16 EPA priority PAHs, 1-methylnaphthalene (mNAP1) and 2-

methylnaphthalene (mNAP2) were separated within 45 min with the validation parameters LOD, LOQ and recovery being from 0.01 to 0.20 ng/g, 0.03–0.60 ng/g and 71–101%, respectively. Analysis of 198 samples from 6 different food types in Hanoi city of Vietnam showed that the mean PAH levels ranged from 1.43 to 25.2 ng/g for grilled meat, 9.3–9.6 ng/g for instant noodle, 0.22–2.48 ng/g for cake, 0.91–4.83 ng/g for dried vegetable, 5.14–23.32 ng/g for tea and 4.82–24.35 ng/g for coffee, with the total PAH levels in the first two food types (grilled meat and instant noodle) exceeding the EU recommended maximum limits of 35 μg/kg for total PAHs and 5 μg/kg for BaP.

Later in two different studies from the same research group, Hui et al. [54] and Nazir et al. [55] developed a GC-FID method by using the same HP5-MS fused silica capillary column (30 m × 0.25 mm, film thickness 0.25 μm) with nitrogen as carrier gas (30 mL/min) in splitless mode and injector/detector temperature set at 300/330 °C. In the first study, a total of 7 PAHs (ACE, FLU, PHE, FLR, PYR, BaA and BaP) were separated within 25 min in 13 samples from 5 different food matrices (white rice, corn flour, tapioca flour, tea and water) by a dispersive liquid phase microextraction technique involving poly (β-cyclodextrin-ionic liquid)-grafted MNPs and supramolecular solvent 1-octanol, followed by GC-FID analysis. This method provided a linear response in the range of 0.1–150 ng/mL with the LOD, recovery and RSD of intraday/interday precision being from 0.02 to 0.07 ng/mL, 84–110% and 1.80–7.56%/2.97–8.23%, respectively. In the second study, Nazir et al. [55] utilized spent tea leaves as a sorbent from porous tea-filter bags for micro-solid phase extraction (μ-SPE) of 5 PAHs (FLU, FLR, PYR, CHR and BaP) from food (rice, organic juice and apple juice) and water (river, tap and well waters), followed by GC-FID analysis. With an optimized μ-SPE conditions by using 5 mg of adsorbent, 5 mL of sample volume, adsorption time of 12 min, 0.5 mL of hexane as eluent and desorption time of 10 min, all the 5 PAHs were separated within 26 min and a linear response in the PAH concentration range of 50–100 ng/mL was shown with a recovery ranging from 88 to 116%, and LOD and LOQ ranging respectively from 8.47 to 55.96 ng/mL and 28.23–186.54 ng/mL for water/juice samples as well as 2.98–30.22 ng/g and 9.04–91.59 ng/g for rice samples.

3.2. High performance liquid chromatographic methods for PAH analysis

Table 3 summarizes the HPLC methods recently developed for PAH determination in foods. The HPLC coupled with various detectors including fluorescence (FLD), diode-array detector (DAD), mass spectrometer (MS) and tandem mass spectrometer (MS/MS) were used. Detection with FLD involving molecular absorption and emission enables on-line monitoring PAHs due to its higher sensitivity and selectivity. Several HPLC methods have been reported to determine PAHs in food providing high sensitivity, accuracy and precision to meet the regulation set by various authorities and are discussed below.

3.2.1. With DAD detection

Two diode array detection-based HPLC methods were reported for analysis of 4 PAHs (1-hydroxypyrene (1-HP), PYR, BaA and BaP) in milk samples [56] and 15 PAHs in pork, fish, bacon, coffee and water samples [57]. An efficient hallow fiber supported ionic liquids based liquid phase microextraction method (IL–HF–LPME) was combined with HPLC-DAD method for determination of 4 PAHs in milk samples [56]. More specifically, a 3:1 ratio of 1-octyl-3-methylimidazolium hexafluorophosphate and lauric acid immobilized as ionic liquid into the pores of a polypropylene hollow fiber was used an extraction solvent. With the extraction solvent volume at 20 μL, hallow fiber length at 6 cm, extraction time at 3 min and temperature at 30 °C, a good linear response in the range of 5–1000 ng/mL with the LOD and LOQ being from 0.14 to 0.71 ng/mL and 0.40–1.80 ng/mL respectively was attained. Also, a high recovery (93.6–102.8%) was shown for the tested 4 PAHs in milk samples. In a later study, a facile and sensitive method for preconcentration of 15 PAHs from different food samples was developed by Li et al. [57], who employed core–shell magnetic iron oxide–Benzidine/1,3,5-triformylphloroglucinol covalent organic framework (Fe_3O_4@COF-TPB) hybrid microspheres as an excellent adsorbent of PAHs, followed by efficient separation using a magnet. Prior to adding Fe_3O_4@COF-TPB, meat samples were hydrolyzed by KOH in ethanol–water followed by ultrasonic-assisted acetonitrile extraction, while coffee samples were diluted with hot water and water samples were directly used. Upon adding Fe_3O_4@-COF-TPB to the extract, a high enrichment efficiency with rapid kinetics attaining an equilibrium within 12 min was shown and a subsequent analysis by HPLC-DAD using a Thermo Hypersil Gold RP-18 column (150 × 4.6 mm, particle size 3 μm) and a gradient mobile phase of 5% acetonitrile in water (A) and acetonitrile (B) at flow rate of 1 mL/min and detection wavelength at 254 nm showed a LOD and LOQ ranging from 0.83 to 11.7 ng/L and 2.76–39.0 ng/L respectively in the linear range of 1–100 ng/mL. A

high recovery (84.3–105.1%) and precision (intra-day RSD, 1.7–3.7%; interday RSD, 2.5–4.3%) was also shown for the developed method.

3.2.2. With FLD detection

FLD is one of the most frequently used detection methods for HPLC analysis of PAHs in food and water. In two different studies, both Nucleosil LC-PAH and Spheri-5 ODS columns with the same dimension (250 × 4.6 mm, particle size 5 μm) were used for HPLC-FLD analysis of 6 PAHs including PHE, ANT, BaA, CHR, BeP and BaP in fish tissue/shrimp samples [58] and 4 PAHs including BaA, BbF, BkF and BaP in bovine tissue [59] within 26 and 30 min respectively by employing a gradient mobile phase of acetonitrile (A)/water (B) and an isocratic mobile phase of methanol/water (91:9, v/v) at a flow rate of 1 mL/min, respectively. An LOD, LOQ and recovery of 0.27–0.64 ng/g, 0.94–2.12 ng/g and 90.6–100.4% were reported for the former method, while 0.012 ng/g, 0.040 ng/g and 96–99% for the latter method. Obviously, the sensitivity variation can be attributed to the difference in sample preparation methods as the NaOH/urea/thiourea (8:8:6%) extraction at 10 °C for 20 min was used for bovine tissue and MSPD-SPE extraction with C18 sorbent used for fish tissue/shrimp.

Taghvaee et al. [60] developed an HPLC-FLD method for determination of 15 PAHs in olive oil and refined pomace olive oil by comparison of the extraction efficiency ultrasound-assisted liquid–liquid (UALL) extraction and modified low temperature (MLT) extraction. The former method with purification by 3 cartridges (C18, Florisil and NH_2) showed a LOD value of 0.16–0.97 ng/g and LOQ of 0.57–2.93 ng/g, while the latter method with purification by a NH_2 cartridge showed a lower LOD (0.09–1.97 ng/g) and LOQ (0.29–5.99 ng/g) by employing an Agilent Zorbax Eclipse PAH C18 column (150 × 4.6 mm, particle size 5 μm) and a gradient mobile phase of acetonitrile (A) and acetonitrile/water (50:50, v/v) with flow rate at 1.2 mL/min and column temperature at 30 °C. In addition, the PAH recovery was found to be 75–111% and 81.5–113.8% for HPLC-FLD analysis with the UALL and MLT methods, respectively. Comparatively, the MLT method was rapid and cost effective than the UALL method as the latter method involved more solvent volume and multiple purification steps.

3.2.3. With green extraction and FLD detection

The QuEChERS method is a green sample preparation approach that can effectively minimize solvent consumption, extraction time, energy and space for easy, cheap and rapid analysis of organic compounds. In a study dealing with the analysis of 16 EPA priority PAHs in charcoal-grilled chicken drumsticks by HPLC-FLD method, Chiang et al. [61] developed a QuEChERS extraction/purification method by using 10 mL of acetone as the extraction solvent, 4 g $MgSO_4$ plus 1 g sodium acetate as the extraction powder and 900 mg $MgSO_4$+300 mg primary secondary amine+300 mg ODS silica gel as the purification powder, followed by separation using a Pinnacle II PAH column (150 × 3 mm, particle size 4 μm) and a gradient mobile phase of water (A) and 4% THF in acetonitrile (B) with a gradient flow rate at 1.4–2 mL/min. The LOD, LOQ and recovery ranging from 0.004 to 0.25 ng/g, 0.01–0.75 ng/g and 67–114% were shown with the RSD of the intra-day and inter-day precision being 1–15% and 1–21%, respectively, and all these validation parameters complied with the EU and TFDA regulations. More recently, Onopiuk et al. [26] compared three different extraction methods including QuEChERS, saponification plus SPE, and lyophilizate extraction for HPLC-FLD determination of 6 PAHs (FLU, BbF, BaA, CHR, BaP and dBahA) in fish and meat (pork, beef) samples and demonstrated that saponification plus SPE was the most effective extraction method for subsequent analysis using an Agilent Zorbax Eclipse PAH column (150 × 4.6 mm, particle size 3.5 μm) and a gradient mobile phase of water (A) and acetonitrile (B) with flow rate at 1.3 mL/min and column temperature at 25 °C. With the exception of FLU (LOD, 0.05 ng/g), the LOD of the other 5 PAHs and LOQ of all 6 PAHs was 0.10 and 0.25 ng/g respectively, with the recovery being from 76.28 to 95.25 ng/g and the total PAH content higher in smoked meat products compared to the grilled ones.

The employment of green techniques such as supercritical fluid can provide high extraction efficiency, increased selectivity, decreased extraction time and smaller sample size with no use of toxic organic solvents. However, a solvent evaporation step required to attain a high preconcentration factor is time-consuming and volatile analytes are prone to degradation. To overcome this problem, Falsafi et al. [29] used a sequential supercritical fluid extraction (SCFE) method coupled with a reverse micelle-based supramolecular solvent microextraction (SSME) technique for HPLC-FLD analysis of 16 PAHs in apple peels. A Waters PAH C18 column (250 × 4.6 mm, particle size 5 μm) and a gradient mobile phase of acetonitrile/water (65:35, v/v) (A) and acetonitrile (B) could separate PAHs within 39 min with flow rate at 1 mL/min. By using the reversed micelles of decanoic acid in

tetrahydrofuran-water mixture as a supramolecular solvent, a high extraction efficiency with rapid preconcentration was achieved through high-binding capacity involving hydrophobic and hydrogen bond interactions. Consequently, a low LOD and LOQ ranging from 0.34 to 1.27 ng/g and 1.03–3.82 ng/g was shown respectively with the recovery and RSD of the intra-day and inter-day precision respectively ranging from 70.5 to 92.7%, 3.2–6.9% and 4.3–8.1%, implying that this SCFE-SSME-HPLC-FLD method can be successfully applied for comprehensive analysis of PAHs in fruit samples.

3.2.4. EU PAH4 marker analysis with FLD and MS/MS detection

Simultaneous determination of PAH4 markers (BaA, CHR, BbF and BaP) in different food matrices including 10 different Brazilian tea varieties [62], 26 dark chocolates [63] and 5 smoked bacons [30] respectively by HPLC-FLD, HPLC-dopant assisted-atmospheric pressure photoionization-high resolution mass spectrometry (HPLC-DA-APPI-HRMS) and HPLC-ESI-MS/MS were also recently reported (Table 3). Comparatively, the separation time of PAH4 by the latter two methods was shorter (6 and 8 min) than that by HPLC-FLD method (36 min), which may be due to the smaller columns, Pinnacle DB PAH (50 × 2.1 mm, particle size 1.9 μm) and Zorbax 300 SB-CN (150 × 4.6 mm, particle size 5 μm) used in HPLC-DA-APPI-HRMS and HPLC-ESI-MS/MS methods, respectively. Regardless of the method employed, the sensitivity of PAH4 analysis in terms of sample matrix followed the order: dark chocolate > tea > smoked bacon, with the LOD and LOQ ranging respectively from 0.016 to 0.024 and 0.054–0.081 ng/g, 0.03–0.30 and 0.1–0.5 ng/g as well as 0.10–0.25 and 0.50 ng/g. However, the PAH4 recovery for dark chocolate (86–102%) and smoked bacon (73.9–99.8%) was higher than that of tea samples (54–99%), which can be accounted for by a highly efficient detection method of mass spectrometry as well as the adoption of multiple extraction/purification steps involving DCM/hexane extraction followed by GPC and SPE purification for dark chocolate, and a novel PLE method based on hard cap espresso machine for smoked bacon, as opposed to a combination of extraction/purification by QuEChERS for tea samples. Furthermore, the PLE based on hard cap espresso machine method was also used recently to analyze 8 PAHs (BaA, BaP, BbF, BkF, CHR, DBahA, BghiP and IP) within 10 min in different seafoods including fish, shrimp, lobster, mussel, oyster and octopus by a HPLC-APCI-MS/MS method with a Zorbax Eclipse PAH column (100 × 2.1 mm, particle size 1.8 μm) and a mobile phase of water (A) and acetonitrile (B) with flow rate at 0.5 mL/min and column temperature at 25 °C [64]. The LOD and LOQ values were respectively ranged from 0.90 to 1.25 ng/g and 1.25–5.00 ng/g, while a high recovery (75–115%) was shown for 6 PAHs from the different seafoods.

3.3. Hyphenated HPLC and GC–MS method for PAH analysis

As most reported methods are capable of analyzing a total of only 16 PAHs, Ekner et al. [49] recently developed an online HPLC/GC–MS hyphenated method for analysis of 45 PAHs in 16 commercial olive oils. Prior to analysis, the samples were subjected to SPE using a Supelco LC-Florisil Z-Sep/C18-filled cartridge by conditioning and eluting with acetone and acetonitrile, respectively. The hyphenated HPLC/GC–MS technique enables sample purification automatically by removing interfering triglycerides by HPLC by using backflush fractionation on a Cosmosil pentabromobenzyloxypropyl-modified silica column (150 × 4.6 mm) with a mobile phase of 20% methyl t-butyl ether in hexane at a flow rate of 1 mL/min, followed by coupling with a GC–MS system using a fused silica capillary tube and the separation was performed in a DB-17MS capillary column (60 m × 0.25 mm ID, film thickness 0.15 μm) with helium as carrier gas (1 mL/min). With the temperature of the transfer line between GC and MS at 325 °C, MS detection was done in electron ionization and SIM mode. A total of 45 PAHs with ≥3-ring PAHs plus alkylated derivatives were separated within 93.1 min with the LOD and LOQ being from 1.77×10^{-4}-9.76×10^{-3} ng/g and 5.90×10^{-4}-32.50×10^{-3} ng/g, respectively, while the contents of 45 PAHs were in the range of 9.17–94.7 ng/g in different olive samples. Regardless of the olive oil type, an abundant amount of low MW PAHs and alkylated PAHs were found in tested olive oil samples, with diesel exhaust emission/biomass combustion/traffic emission being the possible sources of PAHs in olive oil. However, this hyphenated HPLC/GC–MS using a backflush fractionation technique failed to analyze PAHs ≤3-rings such as NAP, ACE, ACY and FLU, all of which are included in the 16 EPA priority PAHs.

3.4. Supercritical fluid chromatographic methods for PAH analysis

Table 4 summarizes the SFC methods recently developed for PAH determination in foods and environmental samples. Although GC and HPLC are the most commonly techniques to determine

Table 3. High performance liquid chromatographic (HPLC) methods developed recently for PAH determination in food and water.

Analytes	Chromatographic conditions/Detection	Performance characteristics	Analysis time (min)	Application sample	Reference
15 PAHs	Agilent Zorbax Eclipse PAH C18 column 150 × 4.6 mm, particle size 5 μm Mobile phase: ACN/ACN:H_2O (50:50) Flow rate: 1.2 mL/min Detection: FLD	Recovery (RSD): 81.5–113.9% (3–10%) LOD: 0.09–1.95 ng/g LOQ: 0.29–5.99 ng/g	38	Olive oil, refined pomace olive oil	[60]
6 PAHs	Nucleosil LC-PAH column 250 × 4.6 mm, particle size 5 μm Mobile phase: ACN/H_2O Flow rate: 1 mL/min Detection: FLD	Recovery: 96–99% Precision RSD: Intraday, 1–4% Interday, 1.3–10.0% LOD: 0.27–0.64 ng/g LOQ: 0.94–2.12 ng/g	26	Fish tissue/shrimp	[58]
4 PAHs	Spheri-5 ODS stainless steel column 250 × 4.6 mm, particle size 5 μm Mobile phase: MeOH/H_2O (91:9) Flow rate: 1 mL/min Detection: FLD	Recovery: 96–99% Precision RSD: Intraday 1.0–4.0% Interday 1.3–10.0% LOD: 0.012 ng/g LOQ: 0.04 ng/g	25	Bovine tissue	[59]
4 PAHs	TC-C18 column 250 × 4.6 mm, particle size 5 μm Mobile phase: ACN/H_2O (85:15) (isocratic) Flow rate: 1 mL/min Detection: DAD	Recovery (RSD): 93.6–102.8% (1.24–3.27%) LOD: 0.14–0.71 ng/mL LOQ: 0.4–1.8 ng/mL	15	Milk	[56]
15 PAHs	RP-18 column 150 × 4.6 mm, particle size 3 μm Mobile phase: 5% ACN-H_2O/ACN Flow rate: 1 mL/min Detection: DAD	Recovery: 84.4–104.3% Precision RSD: Intraday 1.7–3.7% Interday 2.5–4.3% LOD: 0.83–11.7 ng/L LOQ: 2.76–39.0 ng/L	40	Pork (smoked), wild fish, fish (grilled), bacon (smoked), coffee, water	[57]
4 PAHs	Vydac 201 TP54C18 column 250 × 4.6 mm, particle size 5 μm Mobile phase: ACN/H_2O Flow rate: 1 mL/min Detection: FLD	Recovery (RSD): 54–99% (1–21%) LOD: 0.03–0.3 ng/g LOQ: 0.1–0.5 ng/g	47	Tea	[62]
4 PAHs (EU marker)	Pinnacle DB PAH column 50 × 2.1 mm, particle sioze 1.9 μm Mobile phase: H_2O/ACN Flow rate: 0.4 mL/min Detection: DA-APPI-HRMS	Recovery (RSD): 86–102% (7–11%) LOD: 0.016–0.024 ng/g LOQ: 0.054–0.081 ng/g	6	26 dark chocolate (cocoa content 41–77%)	[63]
16 PAHs (15 + 1 EU)	Pinnacle II PAH column 150 × 3 mm, particle size 4 μm Mobile phase: H_2O/4% THF-ACN Flow rate: 1.4–2 mL/min Detection: FLD	Recovery: 67–114% Precision RSD: Intraday 1–15% Interday 1–21% LOD: 0.004–0.25 ng/g LOQ: 0.01–0.75 ng/g	20	Chicken drumsticks (charcoal-grilled, with and without skin, deskinned after processing)	[61]

(*continued on next page*)

Table 3. (continued)

Analytes	Chromatographic conditions/Detection	Performance characteristics	Analysis time (min)	Application sample	Reference
15 PAHs	PAH C18 column 250 × 4.6 mm, particle size 5 μm Mobile phase: H_2O-ACN (35:65)/ACN Flow rate: 1 mL/min Detection: FLD	Recovery: 60−78% Precision RSD: Intraday 3.15−6.94% Interday 4.25−8.13% LOD: 0.34−1.27 ng/g LOQ: 1.03−3.82 ng/g	39	Apple peels	[29]
4 PAHs (EU marker)	Agilent Zorbax 300 SB-CN column 150 × 4.6 mm, particle size 5 μm Mobile phase: 0.1% AcOH/0.1% AcOH-MeOH Flow rate: 0.5 mL/min Detection: MS/MS	Recovery (RSD): 73.9−99.8% (10.1−25.95%) LOD: 0.10−0.25 ng/g LOQ: 0.50 ng/g (for all 4 PAHs)	8	Bacon (smoked)	[30]
8 PAHs	Agilent Zorbax Eclipse PAH column 100 × 2.1 mm, particle size 1.8 μm Mobile phase: H_2O/ACN Flow rate: 0.5 mL/min Detection: APCI-MS/MS	Recovery (RSD): 75−115% (15−21%) LOD: 0.90−1.25 ng/g LOQ: 1.25−5.00 ng/g	10	Seafoods (fish, shrimp, lobster, mussels, oyster, octopus)	[64]
6 PAHs	Zorbax Eclipse PAH 150 × 4.6 mm, particle size 3.5 μm Mobile phase: H_2O/ACN Flow rate: 1.3 mL/min Detection: FLD	Recovery (RSD): 76.28−95.25% (0.6−0.9%) LOD: 0.05−0.10 ng/g LOQ: 0.25 ng/g	36.1	Fish (salmon, vendace and Atlantic perch/smoked); meat (smoked and grilled pork/beef)	[26]

PAHs, polycyclic aromatic hydrocarbons; ACN, acetonitrile; MeOH, methanol; AcOH, acetic acid; THF, tetrahydrofuran; LOD, limit of detection; LOQ, limit of quantitation; ODS, octadecyl-silica; FLD, fluorescence detection; DAD, diode array detection; EU, European Union; MS/MS, tandem mass spectrometry; APCI, atmospheric pressure chemical ionization; DA-APPI-HRMS, dopant assisted-atmospheric pressure photoionization-high resolution mass spectrometry; RSD, relative standard deviation.

Table 4. Supercritical fluid chromatography methods developed recently for determination of PAH in food and environmental samples.

Analytes	Chromatographic conditions/Detection	Performance characteristics	Analysis time (min)	Application sample	Reference
15 PAHs	Agilent Zorbax Eclipse column 250 × 4.6 mm, particle size 5 μm Mobile phase: CO_2/MeOH (2 mL/min) Detection: APLI-MS	LOD: 592 ng/L (mean for 16 PAHs) LOD: 20 ng/L for PHE, BaA and CHR	11	Deuterated Complex PAH mixture	[65]
16 PAHs	Inertsil ODS-P column 150 × 3 mm, particle size 3 μm Mobile phase: CO_2/0.5% FA in ACN (2.5 mL/min) Detection: APCI-MS	Recovery (RSD): 86–105% (6–13%) LOD: 0.1–0.3 ng/g LOQ: 0.4–1.0 ng/g Recoveries (RSD): 80–111% (4–15%) LOD: 0.1–0.3 ng/g LOQ: 0.4–1.0 ng/g	14	Coffee Dark beer	[67]
16 PAHs	Cosmosil Cholester column 250 × 4.6 mm, particle size 5 μm Mobile phase: ACN/H_2O (3 mL/min) Detection: APCI-MS	Recovery (RSD): clay: 58–124% (2–11%) sediment: 9–173% (1–12%) sand: 12–131% (4–137%) LOD: 0.001–5 ng/g LOQ: 5–15 ng/g	20	Soil (clay, sediment, sand)	[68]
16 PAHs	Acquity UPC column 100 × 3.0 mm, particle size 1.7 μm Mobile phase: CO_2/MeOH (1.6 mL/min) Detection: APPI-MS/MS	Recovery (RSD): 37.9–115.7% (0.1–6.0%) LOD: 10–200 ng/g LOQ: 50–300 ng/g	7	Tire rubber	[70]
16 PAHs	Supelcosil LC-PAH column 250 × 4.6 mm, particle size 5 μm Mobile phase: 90% CO_2/10% ACN (2 mL/min) Detection: APCI-MS	Recovery (RSD): 22–115% (4–15%) LOD: 0.16–3.33 ng/g LOQ: 0.54–11.09 ng/g	15	Urban dust and DPM	[69]

PAHs, polycyclic aromatic hydrocarbons; ACN, acetonitrile; MeOH, methanol; FA, formic acid; CO_2, carbon dioxide; LOD, limit of detection; LOQ, limit of quantitation; ODS, octadecyl-silica; APLI-MS, atmospheric pressure laser ionization-mass spectrometry; APCI-MS, atmospheric pressure chemical ionization-mass spectrometry; APPI-MS/MS, atmospheric pressure photoionization-tandem mass spectrometry; DPM, diesel particulate matter; RSD, relative standard deviation.

PAH in complex mixtures, SFC has gained attention in recent years as a hybrid-technique between GC and HPLC that utilizes supercritical carbon dioxide as the mobile phase to exert both gas-like and liquid-like density at an optimum temperature and pressure [65]. Also, supercritical fluids possessing low viscosity and high diffusion coefficient can facilitate fast separation of even thermally labile compounds with high efficiency due to its high elution power [66]. Some organic modifiers such as methanol and acetonitrile as well as polar additives including trifluoroacetic acid, ammonium acetate and water were also used in combination with supercritical carbon dioxide to increase the separation efficiency [65].

3.4.1. In food and deuterated USEPA complex mixture

A rapid and highly sensitive SFC method coupled with APCI-MS was developed for determination of 16 PAHs in 11 coffee beverages and 6 dark beers commercially available in Japan [67]. Following extraction and purification by QuEChERS and a Bond Elut Alumina-N SPE cartridge, all the 16 PAHs were successfully separated within 14 min by using an Inertsil ODS-P column (150 × 3.0 mm, particle size 3 μm) and a gradient mobile phase of supercritical CO_2 with 0.5% formic acid in acetonitrile with flow rate at 2.5 mL/min. By controlling the back-pressure in SFC, the sensitivity of APCI-MS detection in SIM mode was enhanced with the LOD and LOQ ranging from 0.1 to 0.3 ng/g and 0.4–1.0 ng/g respectively, as well as the recovery from 86 to 105% in coffee and 80–111% in dark beer. Also, the LOD and LOQ of PAH4 in coffee (0.2 and 0.5–0.6 ng/g) and beer (0.1–0.3 and 0.5–0.9 ng/g) are in accordance with the EU and TFDA regulations. Application of this SFC/APCI-MS method for analysis of commercial coffee and beer samples showed the total PAH levels to be < 1 ng/g, suggesting a low health risk of PAHs on consumption of these beverages by the Japanese [67].

In another study, Klink and Schmitz [65] developed a hyphenated SFC method by combining with atmospheric-pressure laser ionization mass spectrometry (APLI-MS) which can ionize PAH molecules selectively through resonance-enhanced multiphoton ionization for highly sensitive detection. A total of 15 PAHs in a deuterated USEPA complex mixture was separated within 11 min by employing an Agilent Zorbax Eclipse column (250 × 4.6 mm,

Table 5. Electrochemical sensors developed recently for detection of PAHs in food and water samples.

PAH	Sensor	Electrochemical method	Linear range	Limit of detection	Application	Reference
PHE	Au-G3PPT-co-P3HT	ACV, CV	0.50–6.71 μg/L	0.25 μg/L	Oil-polluted wastewater	[77]
BaP	SPGE SPGE-11MDA	ESI, CV	20–40 mg/L 40–60 mg/L	0.01 mg/L 0.04 mg/L	River water	[83]
ANT	Au-G3PPT-co-P3HT	Phase-selective ACV, ACV	0.62–10.05 μg/L	0.47 μg/L	Oil-polluted wastewater	[78]
PYR	ITO-SAM–NH_2–PYR	EIS, CV	1.75–7.00 ng/L	1.75 ng/L	Aqueous solution	[74]
BaP	GE-mAB GE-MIPs	Capacitance, CV	2.5–100 ng/L 3–20 μg/L	1 ng/L 1 μg/L	Mineral water Tap water River water	[84]
ANT	IDE-MIPs-PU	Conductometry	–	0.23 μg/L	Aqueous solution	[80]
16 EPA priority PAHs	ITO-SAM–NH_2–SWCNTs	EIS, CV	1.75–7.00 ng/L	1.75 ng/L	Aqueous solution	[76]
ANT	GCE-Cd/Al-LDH	EIS, CV	0.02–17.82 ng/L	0.09 pg/L	Cloud and rain samples	[87]
BaP	CPE-MIPs-VF-EDME	SWV	0–4.54 mg/L	0.24 mg/L	Electrolyte solution (Bu_4NClO_4/CH_3CN/H_2O)	[79]
NAP	DNA/Cu_2O-GR	Conductometry, FET	0.03–0.39 mg/L	0.03 mg/L	Aqueous solution	[85]
ANT, PHE	GCE-Ag/AuNPs-oPP	SWV, CV	ANT, 5.35–55.61 mg/L PHE, 5.35–49.90 mg/L	ANT, 4.11 mg/L PHE, 4.35 mg/L	Aqueous solution	[86]
ANT	GCE-MIPs-PP	SWV, CV	1.77–66.5 μg/L	2.12 μg/L	Mineral water	[81]
PYR	SPGE-MIPs-4VP	DPV, CV	1×10^{-4}–1 ng/L	0.001 ng/L	Ground and surface water	[82]
ANT	SPCE-ERGO/4TBC	DPV, CV	0.36–1.43 μg/L	2.85 ng/L	River and lake water	[88]
NAP, ANT, PYR, FLR	ITO-SAM–NH_2–NAP/ANT/PYR/FLR	EIS, CV	0.5–7.0 ng/L	NAP & FLR, 0.79 ng/L; ANT, 0.91 ng/L; PYR, 1.70 ng/L	Aqueous solution	[75]

SERS, surface enhanced Raman spectroscopy; PAHs, polycyclic aromatic hydrocarbons; EPA, environmental protection agency; NAP, naphthalene; PHE, phenanthrene; PYR, pyrene; FLR, fluoranthene; ANT, anthracene; BaP, benzo[a]pyrene; CV, cyclic voltammetry; ACV, alternating current voltammetry; EIS, electrochemical impedance spectroscopy; SWV, square wave voltammetry; FET, field effect transistor; DPV, differential pulse voltammetry; Au-G3PPT-co-P3HT, electrochemically copolymerized generation 3 poly(propylene thiophenoimine) and poly(3-hexythiophene) on a gold electrode; SPGE-11MDA, 11-mercaptodecanoic acid modified screen printed gold electrode; ITO-SAM-NH_2, Self-assembled monolayer of 3-glycidoxypropyltrimethoxysilane and 1-aminopyrene fabricated on indium tin oxide; ITO-SAM–NH_2–SWCNTs, ITO fabricated with 3-aminopropyltrimethoxysilane-based SAM and single-walled carbon nanotubes; GE-mAB, natural monoclonal antibody modified gold electrode; GE-MIPs, molecularly imprinted polymer modified gold electrode, IDE-MIPs-PU, screen-printed interdigital gold electrodes on glass substrate coated with molecularly imprinted polyurethane layers; CPE-MIPs-VF-EDME, vinylferrocene integrated ethylene glycol dimethacrylate on molecularly imprinted carbon paste electrode; GCE-Cd/Al-LDH, cadmium/aluminum layered double hydroxide clay on glass carbon electrode; DNA/Cu_2O-GR, DNA immobilized on copper(I) oxide–graphene surface; GCE-Ag/AuNPs-oPP, glassy carbon electrode modified with over oxidized polypyrrole and bimetallic Ag/AuNPs; GCE-MIPs-PP, polypyrrole-based molecularly imprinted polymer coated on glass carbon electrode; SPGE-MIPs-4VP, electropolymerization of 4-vinylpyridine based MIP film on SPGE; ITO-SAM–NH_2–NAP/ANT/PYR/FLR, Self-assembled monolayer of 3-glycidoxypropyltrimethoxysilane and amino derivative of NAP/ANT/PYR/FLR fabricated on indium tin oxide; SPCE-ERGO/4TBC, electrochemically reduced GO and 4-tertbutylcalix[4]arene deposited on screen printed carbon electrode.

particle size 5 μm) and a gradient elution of CO_2 and methanol (100:0 to 60:40 in 11 min) with flow rate at 2 mL/min, column temperature at 60 °C and injection volume at 5 μL. A mean LOD of 592 ng/L was shown with the lowest value of 20 ng/L being attained for PHE, BaA and CHR.

3.4.2. In environmental samples

Several SFC methods were also reported for analysis of PAHs in some other environmental samples. In three different studies, the SFC method was optimized for determination of 16 PAHs in soil [68], dust/diesel particulate matter [69] and tire rubber [70] by respectively using Cosmosil (250 × 4.6 mm, particle size 5 μm), Supelcosil LC-PAH (250 × 4.6 mm, particle size 5 μm) and Acquity UPLC (100 × 3.0 mm, particle size 1.7 μm) columns, and gradient mobile phases of CO_2/ACN, CO_2/ACN and CO_2/MeOH at a flow rate of 3, 2 and 1.6 mL/min, with the LOD and LOQ ranging from 0.001 to 5

and 5–15 ng/g, 0.16–3.33 and 00.54–11.09 ng/g, as well as 10–200 and 50–300 ng/g. However, a broader range of the recovery values was shown in these studies, implying that a significant matrix effect occurred during PAH analysis of environmental samples. Apparently there is a lack of study dealing with application of SFC method for PAH analysis to food samples and more studies are necessary to further explore its application to complex food and environmental sample matrices in the future.

4. Electrochemical sensors for detection of PAHs

Electrochemical sensors (ECS) are a class of versatile sensors used for analysis of PAHs. They are easy to handle with low fabrication cost and simple electronic setup to overcome the limitation of conventional methods and enable designing of portable devices for onsite applications [71]. The ECS offer highly sensitive and selective determination of target analytes and the different detectable principles include potential difference (potentiometry), current intensity (voltammetry/amperometry), time and resistance for induction of electrode process (conductometry), resistance to electric current in a circuit (electrochemical impedance spectroscopy) and amount of electricity (coulometry) [72]. Of these detection methods, voltammetry is the most frequently used method for PAHs detection, which involves scanning over a range of potential and monitoring the current response originating from the redox process on the surface of working electrode [73]. This current response varies depending on the analyte concentrate and the different voltammetry techniques include differential pulse voltammetry (DPV), cyclic voltammetry (CV), linear sweep voltammetry (LSV) and square-wave voltammetry (SWV) [72]. However, the ECS methods has the limitation of peak overlapping caused by interference of coexisting compounds as well as electrode fouling and over-voltage problems associated with suppression of electron transfer kinetics [73]. Consequently, the working electrodes are subjected to different modification strategies by using polymer, porous material and/or nanomaterial to impart unique electrical and chemical properties to ECS for improved response, speed, sensitivity and selectivity for various analytes in different matrices. Moreover, electrochemical biosensors are also designed by modifying the electrodes with biological agents. Table 5 summarizes several electrochemical sensors developed recently for detection of PAHs in food and water samples.

4.1. Self-assembled monolayer platform based electrochemical sensors

Three different impedimetric ECS were developed by Munoz et al. [74–76] by modifying an indium tin oxide (ITO) electrode with appropriate recognition elements for analysis of PAHs. In the first study, a novel PYR-based self-assembled monolayer (SAM) platform was fabricated on ITO electrode for sensitive detection of PYR through synergistic π-π interactions [74]. The construction of SAM involved an initial treatment of ITO electrode with an oxidizing bath of NH_4OH:H_2O_2:H_2O (1:1:5, v/v/v), followed by sequential immersing in a toluene solution containing 1% of 3-glycidoxypropyltrimethoxysilane and 1 mM 1-aminopyrene at 80 °C for 36 h. By preparing 0.1 M KCl solution containing 10 mM $[Fe(CN)_6]^{3-/4-}$ as redox marker, Ag/AgCl as reference electrode and platinum wire as counter electrode, PYR was detected with a LOD as low as 1.75 ng/L in the linear range of 1.75–7.00 ng/L with high selectivity even in the presence of some other PAHs such as NAP, ANT, FLR, BaP and BghiP.

More recently, a similar strategy was employed for fabricating a SAM-based impedimetric ECS involving the unique π–stacking interactions between 4 analyte PAHs (NAP, ANT, PYR and FLR) and covalently grafting the same 4 PAHs on modified ITO electrode [75]. This ECS with PAH-based recognition unit on ITO electrode showed an excellent sensitivity toward 4 PAHs with the LOD being 0.79, 0.91, 1.70 and 0.79 ng/L for NAP, ANT, PYR and FLR respectively in the linear response ranging from 0.5 to 7.0 ng/L. A high selectivity with <10% signal interference for all the 4 PAHs as well as a high recovery ranging from 95.7 to 108.0% was shown for aqueous samples spiked with each PAH at 4 ng/L, implying that this ECS can be tailored with some other selected PAH targets by covalently anchoring them as recognition units on ITO electrode.

In another study, ITO electrode was functionalized with hydroxyl groups, followed by 3-aminopropyltrimethoxysilane-based SAM formation and grafting single-walled carbon nanotubes (SWCNTs) through amide bond formation [76]. Regardless of PAH type, this CNTs-rich recognition element on ITO electrode could provide a linear response in the concentration range of 1.75–7.00 ng/L with a LOD of 1.75 ng/L, implying a non-selective sensing of total PAHs among 16 EPA priority PAHs. Also, a high recovery ranging from 93.8 to 100.7% was shown for two spiked levels (2.0 and 5.5 ng/L) of each PAH in aqueous solution as well as 97.8 and 98.5% for 7

PAHs-spiked Milli-Q and tap water samples respectively with the total PAHs at 5.25 ng/L.

4.2. Polymer and molecularly-imprinted polymer based electrochemical sensors

Given the molecular uniformity, multifunctional surface architecture, high surface area, good solubility and presence of internal cavities, dendrimers are perfect templates for fabrication of ECS. Makelane et al. [77] prepared a novel dendritic star copolymer for determination of PHE in oil-polluted wastewater by in situ electrochemical co-polymerization of generation-3 poly (propylene thiophenoimine) and poly (3-hexythiophene) on a gold electrode (Au/G3PPT-co-P3HT). Based on alternating current voltammetry (ACV) in a supporting electrolyte of 0.1 M Bu_4NClO_4 in acetonitrile, the Au/G3PPT-co-P3HT electrode was characterized and evaluation of this sensor performance, a linear response in the PHE concentration ranging from 0.50 to 6.71 μg/L with a LOD at 0.25 μg/L was shown. This dendrite-based ECS was stable during storage for 30 days at 4 °C and a high recovery (93–107%), repeatability (RSD, 18.1%) and reproducibility (RSD, 6.10%) were reported for its application in oil polluted wastewater. In a later study, the same sensor was used for ANT analysis by using a phase-selective ACV in the linear range of 0.62–10.05 μg/L and LOD of 0.47 μg/L was shown [78]. Its application in oil polluted wastewater revealed a 95–105% recovery as well as 25.7% RSD for repeatability and 10.4% RSD for reproducibility.

Electrochemical MIPs are intensively investigated as stable recognition elements in the fabrication of electrochemical sensors involving copolymerization of a crosslinker and functional monomer. For example, Udomsap et al. [79] prepared electrochemical MIPs on carbon paste working electrodes by directly integrating vinylferrocene (redox tracer) into the binding cavities during copolymerization with ethylene glycol dimethacrylate (crosslinker) and used for detection of BaP by SWV, a LOD of 0.24 mg/L in the linear range of 0–4.54 mg/L with high selectivity in the presence of PHE, FLR and PYR was reported. In another study, a conductometric sensor based on screen-printed interdigital gold electrode on glass substrate coated with MIP-based polyurethane layers was used for detection of ANT [80]. Following a change in resistance of MIP layers upon exposure to ANT, a LOD value of 0.23 μg/L was reported with high selectivity in the presence of BaA, PYR, PER and BPER as well as high stability over a two-month storage period. An electrochemical polypyrrole-based MIP coated on glass carbon electrode was reported by Mathieu-Scheers et al. [81] for detection of ANT by SWV and a LOD and LOQ value of 2.12 and 7.07 μg/L respectively in the linear range of 1.77–66.25 μg/L was shown with high selectivity in the presence of isoproturon, BaP and NAP.

Interestingly, Munawar et al. [82] developed an electrochemical MIP sensor in the absence of a crosslinker/initiator by electropolymerization of 4-vinyl pyridine with KBr and coating the MIP film on screen printed gold electrode. Upon exposure to the target PAH compound PYR, a noncovalent π-π interaction with 4-vinyl pyridine resulted in PYR recognition for analysis by DPV in a linear response ranging from 1×10^{-4}–1 ng/L with the LOD at 0.001 ng/L. A high selectivity in the presence of CHR and BaP as well as a high recovery (83–110%) for ground and surface water samples were reported.

4.3. Electrochemical biosensors

Biosensors represent an important analytical technique for sensitive detection of PAHs at a faster speed especially for analytes with small amount [72]. In a study dealing with comparison of the bare and 11-mercaptodecanoic acid modified screen-printed gold electrode (SPGE) on immunosensing of BaP, Jusoh et al. [83] adopted an indirect competitive enzyme-linked immunosorbent assay (ELISA) with amperometric measurement (300 mV) and reported respectively a LOD and LOQ of 0.26 and 0.79 mg/L for bare SPGE as well as 0.01 and 0.04 mg/L for 11-mercaptodecanoic acid modified SPGE with the linear response ranging from 20 to 40 mg/L and 40–60 mg/L, implying that an improved sensitivity upon modification of SPGE was attained. Also, the application to analysis of river water samples showed a high recovery of BaP ranging from 97 to 114%. In addition, a much lower LOD (1 ng/L or 1 μg/L) was reported for the capacitive sensing system with a monoclonal antibody (mAB)- or BaP based MIP-immobilized gold electrode in the linear response ranging from 2.5 to 100 ng/L and 3–20 μg/L, respectively, with the former showing a higher sensitivity and the latter exhibiting a better reusable ability by using methanol/phosphate buffer (pH 7.2)/triethylamine (47.5/47.5/5, v/v/v) as a regeneration buffer [84]. The cross reactivity tests revealed that with the exception of PYR and FLR (23 and 18% interference), no significant interference was observed with NAP, PHE and ANT for the mAB-based sensor, whereas all the tested PAHs competed for binding sites with BaP for the MIP-based sensor. A high precision was also demonstrated for mAB-based and MIP-based sensors (RSD, 4.2 and 6.3%) for

Table 6. SERS based optical sensors developed recently for detection of PAHs in food and water samples.

PAH	Sensor	Affinity/aggregation agent	Linear range	Limit of detection	Matrix/real sample	Reference
16 EPA priority PAHs	Fe_3O_4@AuNPs	Fe_3O_4	–	1.01–16.62 μg/L	River water	[92]
BaP	5,5′-DSN@AuNPs	Raman label 5,5′-DSN + anti-BaP monoclonal antibodies	–	0.5 μg/L	Sea water	[99]
PYR	1-PT@AgNPs	Thiol functionalization	11.9–395 μg/L	0.5 μg/L	Lake, spring and drinking water	[98]
PHE, PYR, BbF, BaP and BghiP	DPQ@AuNPs	Amine functionalization + NaOH	PHE, 8.91–8.91 × 10^4 μg/L PYR, 10.11–10.13 × 10^4 μg/L BbF & BaP, 12.62–12.6 × 10^4 μg/L BgP, 13.82–13.82 × 10^4 μg/L	PHE, 89.12 μg/L PYR, 101.13 μg/L BbF & BaP, 12.62 μg/L BgP, 13.82 μg/L	River water	[97]
NAP, PHE, PYR	Colloidal AuNPs + NaCl	Chloride ions	NAP & PYR, 100–1000 μg/L PHE, 80–1000 μg/L	NAP, 1.38 μg/L PHE, 0.23 μg/L PYR, 0.45 μg/L	Mixture of 3 PAHs in aqueous ethanol	[93]
ANT, PYR, PER	MOFs@AgNPs	MOFs	ANT, 0.09–8.91 × 10^7 μg/L PYR, 0.10–1.01 × 10^8 μg/L PER, 0.12–1.26 × 10^8 μg/L	ANT, 3.56 μg/L PYR, 0.03 μg/L PER, 0.76 μg/L	Sewage, river and sea water	[107]
NAP, ACY, CHR, ANT, BaP, BbF and BkF	Colloidal AuNPs + NaCl	Chloride ions	NAP, 0.13–2.56 μg/L ACY, 0.15–3.04 μg/L CHR, 0.23–4.57 μg/L ANT, 0.18–3.56 μg/L BaP, BbF & BkF, 0.25–5.05 μg/L	NAP, 0.07 μg/L ACY, 0.09 μg/L CHR, 0.13 μg/L ANT, 0.01 μg/L BaP, BbF & BkF, 0.14 μg/L	Sea water	[94]
PHE, PYR, BaP, BkF	GMA-EDMA + pH 13 colloidal AuNPs	Porous co-polymer	PHE, 0.05–1.78 μg/L PYR, 0.06–2.02 μg/L BaP & BkF, 0.08–2.52 μg/L	PHE, 0.15 μg/L PYR & BkF, 0.04 μg/L BaP, 0.10 μg/L	Aqueous methanol	[105]
PYR, ANT	βCD-4MPBA@AuNPs	Host-guest interaction with βCD	PYR, 0.40–2.02 μg/L ANT, 1.78–17.82 μg/L	PYR, 0.08 μg/L ANT, 0.78 μg/L	Soil sample extract	[102]
PYR, FLU	MIPs@AuNPs	MIPs	PYR, 0.02–2.02 × 10^3 μg/L FLU, 0.02–1.66 × 10^3 μg/L	0.20 μg/L 0.17 μg/L	Stream & river water	[104]
ANT, PYR, CHR, TPL	βCD@AgNPs	Host-guest interaction with βCD	ANT, 1.78 × 10^2-1.78 × 10^4 μg/L PYR, 2.02 × 10^2-2.02 × 10^4 μg/L CHR & TPL, 2.28 × 10^2-2.28 × 10^4 μg/L	ANT, 1.7 × 10^3 μg/L PYR, 2.02 × 10^2 μg/L CHR & TPL, 2.28 × 10^2 μg/L	NaOH solution	[101]
PYR, ANT, PHE	GR@AgNPs	GR	PYR, 0.02–2.02 × 10^4 μg/L ANT & PHE, 0.02–1.78 × 10^4 μg/L	PYR, 0.73 μg/L PHE, 0.57 μg/L ANT, 1.10 μg/L	Mixture of 3 PAHs in acetone	[108]
16 EPA priority PAHs	GO@AuNPs	Doubly oxidized GO	1–1000 μg/L	0.2–2 μg/L	Chinese traditional fried food (youtiao)	[109]
BaP	n-DDT@AuNPs	Thiol functionalization	2.52–2.52 × 10^4 μg/L	0.09 μg/L	Aqueous methanol	[100]
NAP, ANT	tβCD@mAuNPs	Host-guest interaction with tβCD	NAP, 1–10000 μg/L ANT, 0.1–1000 μg/L	NAP, 10 μg/L ANT, 1 μg/L	Ethanol	[103]

mNAP1, ACE, PHE, FLU, FLR, TPL	GP-CS@AgNPs	Polymer and π-acceptor molecule	mNAP1, 1.42 × 10^2-4.27 × 10^3 μg/L ACE, 1.54 × 10^2-1.54 × 10^4 μg/L PHE, 8.9−8.9 × 10^3 μg/L FLU, 1.66 × 10^2-8.31 × 10^4 μg/L FLR, 2.02 × 10^2-2.02 × 10^4 μg/L TPL, 1.14 × 10^2-4.57 × 10^4 μg/L	mNAP1, 0.71 × 10^2 μg/L ACE, 0.77 × 10^2 μg/L PHE, 1.78 μg/L FLU, 0.49 × 10^2 μg/L FLR, 0.10 × 10^2 μg/L TPL, 0.23 × 10^2 μg/L	Oil fuel sample	[106]
BaP	Hydroxylamine enriched colloidal AuNPs	Bare plasmonic NPs	0.1−1x10^5 μg/L	0.1 μg/L	Snack fried oil and other oils	[95]
PYR	AgNPs film on Cr/Au bilayer	Activation of AgNPs film by ICP treatment and plasma treatment in argon.	0.10−10.11 μg/L	4.65 μg/L	Aqueous methanol	[96]

SERS, surface enhanced Raman spectroscopy; PAHs, polycyclic aromatic hydrocarbons; EPA, environmental protection agency; NAP, naphthalene; PHE, phenanthrene; PYR, pyrene; FLU, fluorene; FLR, fluoranthene; ACE, acenaphthene; ACY, acenaphthylene; CHR, chrysene; ANT, anthracene; BaP, benzo[a]pyrene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BghiP, benzo[g,h,i]perylene; TPL, triphenylene; mNAP1, 1-methylnaphthalene; PER, perylene; NaCl, sodium chloride; AuNPs, gold nanoparticles, AgNPs, silver nanoparticles; mAuNPs, mesoporous gold nanoparticles; Cr/Au bilayer, chromium/gold bilayer; DPQ, dopamine quinone; 1-PT, 1-propanethiol; 5,5′-DSN, 5,5′-dithiobis(succinimidyl-2-nitrobenzoate); n-DDT, n-dodecanethiol; βCD, β-cyclodextrin; tβCD, mono-6-thio-β-cyclodextrin; MIPs, molecularly imprinted polymers; MOFs, metal−organic frameworks; GR, graphene; GO, graphene oxide; Fe_3O_4, iron(III) oxide nanoparticles; GP-CS@AgNPs, chitosan deposited on AgNPs-sprayed glass plate; −, data not available.

20 measurements recorded over 5 days. Application of mAB-based sensor to mineral water, tap water and river water samples showed comparable BaP levels (nd-523 ng/L) with that determined by HPLC-FLD method (nd-516 ng/L).

In another study, Babolghani and Mohammadi-Manesh [85] simulated DNA/Cu_2O-graphene nanomaterial and experimentally studied its ability to detect benzene, toluene and NAP, a linear response in the range of 0.03–0.39 mg/L for NAP was reported. The working principle was based on measurement of change in electric current by a field effect transistor resulting from electrical charge transfer on DNA/Cu_2O-graphene surface caused by adsorption of PAH and DNA molecules. A glassy carbon electrode modified with oxidized polypyrrole and bimetallic Ag/AuNPs was also demonstrated to be effective in simultaneous detection of ANT and PHE by SWV exhibiting a linear response in the range of 30–312 μM for ANT and 30–280 μM for PHE as well as the LOD at 23.05 and 24.41 μM, respectively [86].

4.4. Other electrochemical sensors

Some other unique 2D-nanostructured anionic clays, 3D-macrocyclic oligomers and electrochemical reduced GO were also employed for fabrication of electrochemical sensor for detection of PAHs. Qiao et al. [87] synthesized a 2D-nanostructured anionic clay material composed of layered double hydroxides of cadmium/aluminum by one-step green method directly on a glass carbon electrode (GCE-Cd/Al-LDH) and used for voltammetric detection of ANT. The electrochemical response is greatly suppressed in the presence of ANT in a concentration-dependent manner, while showing a linear range from 0.02 to 17.82 ng/L with a LOD value at 0.09 pg/L. This sensor was also tested in cloud/rain water samples and a high recovery ranging from 98.7 to 99.1% was obtained. In a later study, Zainal et al. [88] evaluated the synergistic effects of electrochemically reduced GO (ERGO) and 4-tertbutylcalix [4]arene (4TBC) for sensitive detection of ANT by DPV following deposition on the surface of the screen printed carbon electrode (SPCE). Compared to SPCE-GO and SPCE-ERGO, a great enhancement in peak current was shown by SPCE-ERGO/4TBC due to enhanced π-π/hydrophobic interaction and strong non-covalent bond formation through π–π interaction. Ultimately, a high linear response for the ANT concentrations ranging from 0.36 to 1.43 μg/L was shown with a LOD value of 2.85 ng/L. The developed sensor not only showed a negligible interference from various organic compounds and heavy metals (Pb^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}, Cu^{2+}, and Ni^{2+}), but also a high stability during storage for 30 days at 25 °C and high reproducibility with the RSD at 2.6% was attained. Also, its application to water samples revealed a high recovery ranging from 96 to 97% in river and lake water samples.

Collectively, of the various electrochemical sensors recently developed for PAHs, none of them were applied to food samples. Nevertheless, these sensors may be successful in applying to food samples following an appropriate sample pretreatment method. Two separate studies with self-assembled monolayers fabricated on indium tin oxide without and with SWCNTs showed multiplexing capability respectively for determination of 16 EPA priority PAHs [76] and 4 PAHs (ANT, NAP, PYR and FLR) [75] with low LOD values (1.75 ng/L and 0.79–1.70 ng/L). For electrochemical sensors with single PAH detection capability, the sensor developed with Cd/Al layered double hydroxide clay showed the lowest LOD (0.09 pg/L) for ANT detection [87], followed by those with GO/4-tert-butylcalix [4]arene (2.85 ng/L) [88] and MIPs (0.23 μg/L) [80], while for BaP and PHE, a monoclonal antibody based biosensor on gold electrode [84] and copolymers on gold electrode [77] showed the lowest LOD values (1 ng/L and 0.25 μg/L) among other sensors.

5. SERS based optical sensors for detection of PAHs

SERS is emerging as a popular analytical technique for quantitative determination of PAHs in different matrices. The mechanism of detection involves extremely high enhancement of weak intrinsic Raman signals by plasmonic nanostructures such as gold and silver through generation of surface plasmon resonance from localized electromagnetic fields [89]. Such unique characteristics makes the SERS technique suitable for sensor development to attain an ultra-high sensitivity with tailored synthesis of metal nanostructures for a specific purpose as well as modification with multiple anchoring of ligands/functional groups enabling detection of different analytes with multiplexing capability [71,90]. Furthermore, the SERS requires only simple sample preparation and the analysis is not affected by water which is important for its application to PAHs detection in food, environmental and biological samples.

Owing to the hydrophobicity of PAHs, significant challenges exist in bringing PAHs close to the SERS substrate. Consequently, several functionalized gold

or silver SERS substrates were investigated by conjugating with functional molecules such as humic acids, dicarbamates, thiols, calixarenes, viologen and cyclodextrin derivatives [71,91]. Moreover, some novel SERS substrates with high enhancement factors have been reported such as gold on nickel 3D foam, gold on TiO_2 nanotube arrays, gold coffee-ring, gold on alginate gel and gold on porous polymer [71,92]. Despite the development of several SERS substrates so far, some notable shortcomings still persist in PAHs detection by SERS which include restricted application to a specific class/number of PAHs, requirement of preconcentration step due to poor water solubility of PAHs, significant decrease in signal enhancement due to continuous laser irradiation and distortion of SERS signals of PAHs by those generated by functionalized molecules itself [89]. Table 6 summarizes the SERS-based optical sensors recently developed for detection of PAHs in food and water samples.

5.1. Non-functionalized SERS sensors

Simple SERS sensors without any functionalization of metal nanoparticles have been developed. For example, Gong et al. [93] prepared non-functionalized colloidal AuNPs for rapid detection of NAP, PHE and PYR using a portable Raman spectrometer. A 20-fold enhancement in SERS signals was shown by this colloidal AuNPs SERS substrate in the presence of chloride ions compared to that without chloride ions. Furthermore, with an optimum level of reducing agent (2.0 mL of 1% trisodium citrate) and 1 M NaCl (80 μL), an enhancement factor in the order of 10^3 was shown for all the three PAHs with the LOD values of 1.38 μg/L for NAP, 0.23 μg/L for PHE and 0.45 μg/L for PYR.

Similarly, Shi et al. [94] demonstrated that a total of 7 PAHs can be successfully detected in a linear range of 0.13–2.56 μg/L for NAP, 0.15–3.08 μg/L for ACY, 0.23–4.57 μg/L for CHR, 0.18–3.56 μg/L for ANT and 0.25–5.05 μg/L for BaP, BbF and BkF. Also, the LOD of NAP, ACY, CHR and ANT were 0.07, 0.09, 0.13 and 0.01 μg/L, respectively, while for BAP, BbF and BkF it was 0.14 μg/L in sea water by using colloidal AuNPs, PAH standard and NaCl (2.6 M) at a ratio in the volume ratio of 1.4:4.2:1 (v/v/v) as well as a laser power at 10 s and an integration time at 10 s. The mechanism of signal enhancement by chloride ions can be attributed to creation and stabilization of surface-active sites caused by a large charge transfer between metal nanoparticles and PAHs. In addition, the addition of chloride ions generates numerous SERS hotspots by promoting aggregation of colloidal AuNPs [93,94]. However, the incorporation of excess chloride ions can decrease the PAH/AuNPs surface ratio and/or cause precipitation of AuNPs resulting in weakening of the SERS signals.

More recently, AuNPs colloid prepared by a citrate-reduction method followed by hydroxylamine-enriched growth was used as a SERS substrate for sensitive detection of BaP within 3 min in oil [95]. A linear response ranging from 0.1 to 100000 μg/L with a LOD value at 0.1 μg/L was shown for BaP and this method was successfully applied to analysis of BaP in repeatedly-used frying oils for snacks preparation and gutter oil-adulterated soybean oil without sample pretreatment. In addition, by using this method, BaP could be determined in different oils including corn oil, corn germ oil, sunflower seed oil, rapeseed oil and linseed oil at a LOD of 0.1, 10, 10, 0.1 and 10 μg/L, respectively. Also, Capaccio et al. [96] fabricated a label-free and high porous 3D SERS substrate without any functionalization for detection of PYR (LOD, 4.65 μg/L; linear range, 0.10–10.11 μg/L) by depositing 30 nm AgNPs film on Cr/Au bilayer followed by sequential inductively-coupled plasma treatment and plasma treatment in argon atmosphere.

5.2. Amine or thiol functionalized SERS sensors

The SERS substrates were also prepared by functionalizing metal nanoparticles with amine or thiol molecules for PAH analysis. By using dopamine as a reducing agent, AuNPs were prepared by adopting a facile one pot method, followed by oxidizing dopamine to dopamine quinone (DQ), 5,6-dihydroxyindole and polydopamine (PDA) through Raper-Mason mechanism [97]. The PDA modified AuNPs surface could capture PAHs close to the AuNPs' hotspots for SERS detection, while the DQ modified AuNPs surface exhibited a selective binding capacity for Cd^{2+} ions in the presence of other metals ions. The linear range and LOD for detection in river water samples were respectively 8.91–8.91 × 10^4 μg/L and 89.12 μg/L for PHE, 10.11–10.13 × 10^4 μg/L and 101.13 μg/L for PYR, 12.62–12.62 × 10^4 μg/L and 12.62 μg/L for BbF and BaP as well as 13.82–13.82 × 10^4 μg/L and 13.82 μg/L for BgP.

In two different studies, AgNPs and AuNPs were respectively modified with 1-propanethiol and 5,5′-dithiobis (succinimidyl-2-nitrobenzoate) (gold–sulfur interaction) plus anti-BaP antibodies immobilization (cross linking reaction) for SERS detection of PYR in lake, spring and drinking water [98] and BaP in sea water [99] at the same LOD of 0.5 μg/L. More recently, Zhang et al. [100] functionalized AuNPs with n-dodecanethiol (DDT) and transferred the DDT-AuNPs thin-film by tilt-lifting onto the silicon wafer, the fabricated SERS substrate

was shown to enhance the Raman signal of BaP by 2.9×10^5 with the LOD and linear range being 0.09 μg/L and 2.52–2.52×10^4 μg/L, respectively, as well as the recovery being from 89.5 to 103.7%.

5.3. Cyclodextrins based SERS sensors

Among the various supramolecular host molecules, cyclodextrins (CDs) and their derivatives are often used for functionalization of metal nanoparticles. They are either used directly as a reducing and stabilizing agent for the synthesis of gold/silver nanoparticles [101] or conjugated on metal nanoparticles' surface through a linking agent [102]. As CDs possess an outer hydrophilic ring structure and hydrophobic inner cavity, hydrophobic PAHs can be easily bound by host-guest interaction through formation of inclusion complexes [103]. Moreover, CD molecules act as an internal standard to enhance the reliability of PAH sensing by SERS.

Two ratiometric SERS methods were developed by Yu et al. [102] and Zhang et al. [103], in which β-CD was conjugated to AuNPs through 4-mercaptophenylboronic acid (4-MPBA) for detection of PYR and ANT in the former study, while in the latter study, mono-6-thio-β-CD (tβ-CD) was functionalized on 3D mesoporous AuNPs (mAuNPs) for NAP and ANT detection. With a linear response from 2 to 10 nM and 10–100 nM, the β-CD/4-MPBA@AuNPs based SERS substrate could respectively detect PYR and ANT in soil sample extract with a LOD of 0.20 μg/L and 0.17 μg/L as well as a high recovery (102.2% for PYR and 104.1% for ANT) [102]. On the other hand, by using tβ-CD@mAuNPs as SERS substrate, NAP and ANT were detected with a LOD of 10 and 1 μg/L respectively, while a high reproducibility and a 50-fold signal enhancement compared to PVP-capped mAuNPs was shown. The high sensitivity of tβ-CD@mAuNPs can be attributed to the host-guest effect of tβ-CD as well as large surface area and high density of <10 nm mesoporous AuNPs network [103]. In another study, Li et al. [101] adopted a green synthesis strategy by using β-CD as a reducing and stabilizing agent for preparation of β-CD@AgNPs SERS substrate and a LOD of 1.7×10^3 μg/L, 2.02×10^2 μg/L and 2.28×10^2 μg/L for ANT, PYR and CHR/triphenylene (TPL) respectively, was shown in the linear ranges of 1.78×10^2-1.78×10^4 μg/L, 2.02×10^2-2.02×10^4 μg/L and 2.28×10^2-2.28×10^4 μg/L.

5.4. Polymers and MIPs based SERS sensors

Some polymers and 3D-supramolecular smart materials such as molecularly imprinted polymer (MIPs) with remarkable molecular recognition properties were also employed for fabrication of SERS substrates. The MIPs are tailor-made polymers usually prepared in the presence of a template entity such as ion, atom, molecule or ionic/molecular assembly [104]. Following the eventual removal of a template entity, the vacant spaces generated can act as recognition sites for analytes. However, some limitations still exist in the use of MIPs as SERS substrates which include difficulty in performing multiplex analysis and issues associated with conversion of the binding event into a quantifiable signal [71,91]. A 3D SERS substrate in a syringe filter composed of a porous glycidyl methacrylate-ethylene dimethacrylate (GMA-EDMA) and pH 13 colloidal AuNPs was developed for sensitive detection of 4 PAHs, while a LOD of 0.15 μg/L for PHE, 0.10 μg/L for BaP and 0.04 μg/L for both PYR and BkF was reported [105]. Interestingly, an 8-fold or 12-fold higher signal enhancement was shown compared to that using only pH 13 colloidal AuNPs or GMA-EDMA plus AuNPs without pH adjustment. More recently, a dual-purpose SERS sensor based on colored charge–transfer conjugates formed by trapping PAHs into an organic π-acceptor molecule 2,3-dichloro-5,6-dicyano-p-benzoquinone tagged on chitosan-coated AgNPs was developed by Eremina et al. [106], who reported a LOD of 0.71×10^2, 0.77×10^2, 1.78, 0.49×10^2, 0.10×10^2 and 0.23×10^2 μg/L for mNAP1, ACE, PHE, FLU, FLR and TPL, respectively and the method was successfully applied to real oil fuel samples.

In a study dealing with evaluation of hybrid MIPs@AuNPs as SERS substrate, Castro-Grijalba et al. [104] used templates of PYR or FLU for fabrication of respective MIPs@AuNPs and the SERS performance was enhanced by 100-fold for both templates when compared to non-MIP AuNPs sensor with the LOD at 0.20 μg/L or 0.17 μg/L, respectively. This MIPs@AuNPs substrate possessed high selectivity towards PYR/FLU and PYR/FLU/BaP mixtures with its application to stream and river water samples showing a linear response in the range of 0.02–2.02×10^3 μg/L for PYR and 0.02–1.66×10^3 μg/L for FLU.

5.5. Metal organic frameworks-based SERS sensors

The 3D substrates in the form of metal–organic frameworks (MOFs) have attracted attention recently as a porous organic-inorganic material for encapsulation of metal nanoparticles to impart unique characteristics of high surface area, tunable pore size, easy functionalization and stability for

attachment of an abundant amount of SERS active metal nanoparticles in the unique 3D configuration of MOFs [89,107]. Also, the MOFs can adsorb analytes making them in close proximity to hotspots created by metal nanoparticles, thereby facilitating the MOFs-based sensors to function without requiring a preconcentration step. Li et al. [107] fabricated a core–shell MOFs@AgNPs nanocomposite (MOFs, Cu_3(1,3,5-benzenetricarboxylic acid)$_2$) on a screen-printed carbon electrode by in situ electrodeposition for onsite SERS detection of ANT, PYR and perylene (PER). With an enhancement factor of 5×10^4 shown for the model molecule 4-aminothiophenol, the MOFs@AgNPs exhibited high SERS activity for detection of 3 PAHs at a LOD of 3.56 μg/L for ANT, 0.03 μg/L for PYR and 0.76 μg/L for PER, and a high recovery (80.62–118.20%) was shown in water samples.

5.6. Graphene/graphene oxide based SERS sensors

Graphene and graphene oxide materials composed of sp2-bonded carbon atoms have been extensively explored in various fields. Due to the presence of aromatic domains, they can act as an adsorbent to bring the analytes with benzene rings close to hot spots generated by metal nanoparticles through π-π stacking interaction [71]. Moreover, the nanocomposites formed between metal nanoparticles and graphene/graphene oxide can synergistically enhance the SERS performance for organic compounds especially PAHs. In an attempt to develop a SERS method for simultaneous determination of 3 PAHs including PYR, ANT and PHE, Wang et al. [108] prepared hybrid AgNPs decorated graphene as SERS substrate and reported a linear response in the concentration ranging from 0.02–2.02 $\times 10^4$ μg/L for PYR and 0.02–1.78 $\times 10^4$ μg/L for both PHE and ANT, with the LOD at 0.73, 0.57 and 1.10 μg/L, respectively. In another study, a versatile SERS sensor with AuNPs decorated on doubly-oxidized graphene oxide was developed for simultaneous analysis of 16 EPA priority PAHs [109]. The typical peaks for all the 16 PAHs were identified in the SERS spectra of both standard mixture and Chinese traditional fried food (youtiao) with a LOD value ranging from 0.2 to 2.0 ng/mL, while the latter showed no significant background interference.

5.7. Magnetic nanoparticles based SERS sensors

Incorporation of magnetic nanoparticles into SERS sensors for detection PAHs has been particularly attractive as MNPs can offer synergistic signal enhancement with plasmonic nanoparticles, improved sensitivity by enrichment of analytes and reuse by their adsorptive and magnetic properties as well as enabling conjugation with receptors including antibodies and aptamers for biosensing application [71,89]. Du et al. [92] developed a versatile Fe_3O_4@Au SERS substrate for detection of 16 EPA priority PAHs by homogenously grafting AuNPs on Fe_3O_4 microspheres. This label-free SERS sensor containing magnetic structure was shown to efficiently adsorb PAHs from river water for signal enhancement by plasmonic AuNPs with the LOD ranging from 1.01 to 16.62 μg/L.

Taken together, compared to electrochemical sensors, a high number of SERS-based optical sensors developed recently showed a multiplexing capability to simultaneously detect 2–16 PAHs. For analysis of 16 PAHs, the SERS sensor with AuNPs deposited on GO showed a lower LOD (0.2–2 μg/L) [109] compared to that deposited on Fe_3O_4 nanoparticles (1.01–16.62 μg/L) [99]. Among the various SERS sensors with multiplexing capability of detecting 2–7 PAHs, the lowest LOD was shown for 7 PAHs (0.01–0.14 μg/L) with SERS-active colloidal AuNPs/NaCl [94], followed by 4 PAHs (0.04–0.15 μg/L) with porous copolymer-based colloid AuNPs [105], 3 PAHs (0.03–3.56 μg/L) with MOFs-based AgNPs [107] and 2 PAHs (0.08–0.78 μg/L) with β-cyclodextrin-based AuNPs [102]. For the SERS sensors for single PAH detection, both n-dodecanethiol-functionalized AuNPs [100] and hydroxylamine enriched colloidal AuNPs [95] showed the lowest LOD (0.09 and 0.1 μg/L) for BaP detection, while 1-propanethiol-functionalized AgNPs provided the lowest LOD (0.5 μg/L) for PYR [98], implying that the thiol-functionalized AuNPs or AgNPs were efficient in enhancing the SERS signals with enriched hot spots through increased PAH capture in the vicinity of SERS-active Au/Ag nanoparticles. Nevertheless, besides LOD, several other factors such as stability, recovery and reproducibility should also be taken into account during selection of an appropriate method for specific PAHs for practical application.

6. Conclusion and future perspective

In conclusion, recent advances in PAH analysis by various chromatographic methods including GC, HPLC and SFC as well as electrochemical and SERS-based optical sensing methods were overviewed. There is an urgent need for replacing the conventional sample preparation methods with advanced extraction/purification techniques for enhanced recovery of PAHs from food samples. While most GC methods use a flame ionization

detector for PAH analysis, the number of studies employing a highly sensitive MS/MS detection is inadequate. Critical optimization of column type and length, stationary phase and film thickness as well as temperature programming is necessary for improving PAH resolution and reducing analysis time by GC methods. Also, the HPLC methods reported recently adopt a fluorescence detection method, while the employment of advanced MS/MS detection methods is still lacking. The existing challenges in using UPLC-MS/MS methods with short and small particle-sized columns should be overcome. Although the emerging SFC methods are mostly used for PAH analysis in water samples, its application to food samples are insufficient to meet demands of PAH monitoring in food and water.

On the other hand, the increased sensitivity through incorporating nanomaterials, cost effectiveness, reduced analysis time and miniaturization for onsite determination capability has attracted a great attention towards electrochemical and optical sensing methods for PAH analysis. The electrochemical methods are able to attain very high sensitivity due to the synergistic effect of nanomaterials on catalytic activity of working electrodes as well as through appropriate modification of electrode surface. Also, the SERS based optical methods provide a remarkable enhancement in Raman signals by the use of a variety of nanomaterials attaining high sensitivity. However, the application of sensing methods is mostly limited to analysis of single PAH or a small number of PAHs necessitating the development of sensors for simultaneous analysis of multiple PAHs. In addition, a large number of sensing methods reported are restricted to only water samples, which should be inadequate. Other frequently encountered problems include electrode fouling, peak overlapping due to interfering compounds and over voltage-associated suppression of electron transfer kinetics for electrochemical sensors, while the reduction in signal enhancement due to continuous laser irradiation and distortion of SERS signals by those generated by functionalized molecules for SERS-based sensors have to be solved.

Conflict of interest

The authors have no conflicts of interest to declare.

References

[1] Chen BH, Wang CY, Chiu CP. Evaluation of analysis of polycyclic aromatic hydrocarbons in meat products by liquid chromatography. J Agric Food Chem 1996;44: 2244–51.

[2] Patel AB, Shaikh S, Jain KR, Desai C, Madamwar D. Polycyclic aromatic hydrocarbons: sources, toxicity and remediation approaches. Front Microbiol 2020;11:562813.

[3] Chen BH. Analysis, formation and inhibition of polycyclic aromatic hydrocarbons in foods: an overview. J Food Drug Anal 1997;5:25–42.

[4] Singh L, Varshney JG, Agarwal T. Polycyclic aromatic hydrocarbons formation and occurrence in processed food. Food Chem 2016;199:768–81.

[5] Chen BH, Chen YC. Formation of polycyclic aromatic hydrocarbons in the smoke from heated model lipids and food lipids. J Agric Food Chem 2001;49:5238–43.

[6] Alomirah H, Al-Zenki S, Al-Hooti S, Zaghloul S, Sawaya W, Ahmed N, et al. Concentration and dietary exposure to polycyclic aromatic hydrocarbons (PAHs) from grilled and smoked foods. Food Control 2011;22:2028–35.

[7] Chen YC, Chen BH. Determination of polycyclic aromatic hydrocarbons in fumes from fried chicken legs. J Agric Food Chem 2003;51:4162–7.

[8] Farhadian A, Jinap S, Abas F, Sakar IS. Determination of polycyclic aromatic hydrocarbons in grilled meat. Food Control 2010;21:606–10.

[9] Kao TH, Chen S, Chen CJ, Huang CW, Chen BH. Evaluation of analysis of polycyclic aromatic hydrocarbons by the QuEChERS method and gas chromatography-mass spectrometry and their formation in poultry meat as affected by marinating and frying. J Agric Food Chem 2012;60:1380–9.

[10] Chen S, Kao TH, Chen CJ, Huang CW, Chen BH. Reduction of carcinogenic polycyclic aromatic hydrocarbons in meat by sugar-smoking and dietary exposure assessment in Taiwan. J Agric Food Chem 2013;61:7645–53.

[11] Bansal V, Kumar P, Kwon EE, Kim KH. Review of the quantification techniques for polycyclic aromatic hydrocarbons (PAHs) in food products. Crit Rev Food Sci Nutr 2017;57:3297–312.

[12] Tfouni SAV, Vitorino SHP, Toledo MCF. Effect of the process on the contamination of sugar cane and its by-products by polycyclic aromatic hydrocarbons. Food Sci Technol 2007;27:76–82.

[13] Chinnici F, Natali N, Spinabelli U, Riponi C. Presence of polycyclic aromatic hydrocarbons in woody chips used as adjuvant in wines, vinegars and distillates. LWT–Food Sci Technol 2007;40:1587–92.

[14] Kao TH, Chen S, Huang CW, Chen CJ, Chen BH. Occurrence and exposure to polycyclic aromatic hydrocarbons in kindling-free-charcoal meat products in Taiwan. Food Chem Toxicol 2014;71:149–58.

[15] Hung YT, Lee YT, Inbaraj BS, Sridhar K, Chen BH. Analysis and formation of polycyclic aromatic hydrocarbons and cholesterol oxidation products in thin slices of dried pork during processing. Food Chem 2021;353:129474.

[16] Onopiuk A, Kolodziejczak K, Szpicer A, Wojtasik-Kalinowska I, Wierzbicka A, Poltorak A. Analysis of factors that influence the PAH profile and amount in meat products to thermal processing. Trends Food Sci Technol 2021; 115:366–79.

[17] Inbaraj BS, Sridhar K, Chen BH. Removal of polycyclic aromatic hydrocarbons from water by magnetic activated carbon nanocomposite from green tea waste. J Hazard Mater 2021;415:125701.

[18] Zheng H, Xing X, Hu T, Zhang Y, Zhang J, Zhu G. Biomass burning contributed most to the human cancer risk exposed to the soil-bound PAHs from Chengdu Economic Region, Western China. Ecotoxicol Environ Saf 2018;159:63–70.
[19] Yebra-Pimentel I, Fernandez-Gonzalez R, Martinez-Carballo E, Simal-Gandara J. A critical review about the health risk assessment of PAHs and their metabolites in foods. Crit Rev Food Sci Nutr 2015;55:1383–405.
[20] Hamidi EN, Hajeb P, Selamat J, Razis AFA. Polycyclic aromatic hydrocarbons (PAHs) and their bioaccessbility in meat: a tool for assessing human cancer risk. Asian Pac J Cancer Prev APJCP 2016;17:15–23.
[21] Wang F, Zhang H, Geng N, Ren X, Zhang B, Gong Y, et al. A metabolomics strategy to assess the combined toxicity of polycyclic aromatic hydrocarbons (PAHs) and short-chain chlorinated paraffins (SCCPs). Environ Pollut 2018;234:572–80.
[22] USEPA (United States Environmental Protection Agency). Appendix A to 40 CFR Par 423, Washington DC. 2010 (Accessed on May 20, 2022), http://www.epa.gov/waterscience/methods/pollutants.htm.
[23] EU (European Union). The Annexure to Regulation (EC) No. 1881/2006) of August 20, 2011, Section 6: maximum allowable levels of Benzo[a]pyrene and 4 polycyclic aromatic hydrocarbons combined. Retrieved from Off J Eur Union 2011;2011(215):1–5. Accessed May 20, 2022, https://eur-lex.europa.eu/.
[24] IARC (International Agency for Research on Cancer). Agents classified by the IARC Monographs, volumes 1-121. 2018. accessed on 20 May, 2022, http://monographs.iarc.fr/ENG/Classification.
[25] EFSA (European Food Safety Authority). Polycyclic aromatic hydrocarbons in foodscientific opinion of the panel on contaminants in the food chain. EFSA J 2008;2008(724):1–114.
[26] Onopiuk A, Kołodziejczak K, Marcinkowska-Lesiak M, Poltorak A. Determination of polycyclic aromatic hydrocarbons using different extraction methods and HPLC-FLD detection in smoked and grilled meat products. Food Chem 2022;373:131506.
[27] Masuda M, Wang Q, Tokumura M, Miyake Y, Amagai T. Simultaneous determination of polycyclic aromatic hydrocarbons and their chlorinated derivatives in grilled foods. Ecotoxicol Environ Saf 2019;178:188–94.
[28] Tan J, Lu X, Fu L, Yang G, Chen J. Quantification of Cl-PAHs and their parent compounds in fish by improved ASE method and stable isotope dilution GC-MS. Ecotoxicol Environ Saf 2019;186:109775.
[29] Falsafi E, Raofie F, Ariya PA. Supercritical fluid extraction followed by supramolecular solvent microextraction as a fast and efficient preconcentration method for determination of polycyclic aromatic hydrocarbons in apple peels. J Separ Sci 2020;43:1154–63.
[30] Merlo TC, Molognoni L, Hoff RB, Daguer H, Patinho I, Contreras-Castillo CJ. Alternative pressurized liquid extraction using a hard cap espresso machine for determination of polycyclic aromatic hydrocarbons in smoked bacon. Food Control 2021;120:107565.
[31] Jinadasa BKKK, Monteau F, Morais S. Critical review of microextraction techniques used in the determination of polycyclic aromatic hydrocarbons in biological, environmental and food samples. Food Addit Contam 2020;37:1004–26.
[32] Rascón AJ, Azzouz A, Ballesteros E. Trace level determination of polycyclic aromatic hydrocarbons in raw and processed meat and fish products from European markets by GC-MS. Food Control 2019;101:198–208.
[33] Passarella S, Guerriero E, Quici L, Ianiri G, Cerasa M, Notardonato I, et al. PAHs presence and source apportionment in honey samples: fingerprint identification of rural and urban contamination by means of chemometric approach. Food Chem 2022;382:132361.
[34] Jalili V, Barkhordari A, Ghiasvand A. Solid-phase microextraction technique for sampling and preconcentration of polycyclic aromatic hydrocarbons: a review. Microchem J 2020;157:104967.
[35] Manousi N, Zachariadis GA. Recent advances in the extraction of polycyclic aromatic hydrocarbons from environmental samples. Molecules 2020;25:2182.
[36] Camara JS, Perestrelo R, Berenguer CV, Andrade CFP, Gomes TM, Olayanju B, et al. Green extraction techniques as advanced sample preparation approaches in biological, food, and environmental matrices: a review. Molecules 2022;27:2953.
[37] Ncube S, Madikizela L, Cukrowska E, Chimuka L. Recent advances in the adsorbents for isolation of polycyclic aromatic hydrocarbons (PAHs) from environmental sample solutions. Trends Anal Chem 2018;99:101–16.
[38] Sajid M, Nazal MK, Ihsanullah I. Novel materials for dispersive (micro) solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples: a review. Anal Chim Acta 2021;1141:246–62.
[39] Peng PL, Lim LH. Polycyclic aromatic hydrocarbons (PAHs) sample preparation and analysis in beverages: a review. Food Anal Methods 2022;15:1042–61.
[40] Colón LP, Rascón AJ, Ballesteros E. Trace-level determination of polycyclic aromatic hydrocarbons in dairy products available in Spanish supermarkets by semi-automated solid-phase extraction and gas chromatography-mass spectrometry detection. Foods 2022;11:713.
[41] Moazzen M, Shariatifar N, Arabameri M, Hosseini H, Ahmadloo M. Measurement of polycyclic aromatic hydrocarbons in baby food samples in Tehran, Iran with magnetic-solid-phase-extraction and gas-chromatography/mass-spectrometry method: a health risk assessment. Front Nutr 2022;9:833158.
[42] Kiani A, Ahmadlo M, Moazzen M, Shariatifar N, Shahsavari S, Arabameri M, et al. Monitoring of polycyclic aromatic hydrocarbons and probabilistic health risk assessment in yogurt and butter in Iran. Food Sci Nutr 2021;9:2114–28.
[43] Shariatifar N, Moazzen M, Arabameri M, Moazzen M, Khaniki GJ, Sadighara P. Measurement of polycyclic aromatic hydrocarbons (PAHs) in edible mushrooms (raw, grilled and fried) using MSPE-GC/MS method: a risk assessment study. Appl Biol Chem 2021;64:61.
[44] Tran-Lam TT, Dao YH, Nguyen LKT, Ma HK, Tran HN, Le GT. Simultaneous determination of 18 polycyclic aromatic hydrocarbons in daily foods (Hanoi metropolitan area) by gas chromatography-tandem mass spectrometry. Foods 2018;7:201.
[45] Sun Y, Wu S. Analysis of PAHs in oily systems using modified QuEChERS with EMR-lipid clean-up followed by GC-QqQ-MS. Food Control 2020;109:106950.
[46] Akdogan A, Gursoy O. Determination of four priority polycyclic aromatic hydrocarbons (4PAHs) by GC-MS in traditional Turkish yoghurts. Food Addit Contam Chem Anal Control Expo Risk Assess 2020;37:391–400.
[47] Givechev I, Tanev D, Danalev D. Development and validation of GC/MS method for simultaneous determination of 16 polycyclic aromatic hydrocarbons (PAHs) in pork meat matrix. Acta Chromatogr 2021;33:57–63.
[48] Chiesa LM, Nobile M, Malandra R, Pessina D, Panseri S, Labella GF, et al. Food safety traits of mussels and clams: distribution of PCBs, PBDEs, OCPs, PAHs and PFASs in sample from different areas using HRMS-Orbitrap® and modified QuEChERS extraction followed by GC-MS/MS. Food Addit Contam-Chem Anal Control Expo Risk Assess 2018;35:959–71.
[49] Ekner H, Dreij K, Sadiktsis I. Determination of polycyclic aromatic hydrocarbons in commercial olive oils by HPLC/GC/MS-occurrence, composition and sources. Food Control 2022;132:108528.
[50] Al-Thaiban H, AL-Tamimi N, Helaleh M. Development of QuEChERS method for the determination of polycyclic

aromatic hydrocarbons in smoked meat products using GC-MS from Qatar. J Anal Methods Chem 2018;2018: 9206237.
[51] Zhou RZ, Jiang J, Mao T, Zhao TM, Zhao YS, Lu Y. Multi-residue analysis of environmental pollutants in edible vegetable oils by gas chromatography–tandem mass spectrometry. Food Chem 2016;207:43–50.
[52] Petrović J, Kartalović B, Ratajac R, Spirić D, Djurdjević B, Polaček V, et al. PAHs in different honeys from Serbia. Food Addit Contam B Surveill 2019;12:116–23.
[53] Belo RFC, Figueiredo JP, Nunes CM, Pissinatti R, de Souza SVC, Junqueira RG. Accelerated solvent extraction method for the quantification of polycyclic aromatic hydrocarbons in cocoa beans by gas chromatography–mass spectrometry. J Chromatogr B 2017;1053:87–100.
[54] Hui BY, Zain NNM, Mohamad S, Varanusupakul P, Osman H, Raoov M. Poly(cyclodextrin-ionic liquid) based ferrofluid: a new class of magnetic colloid for dispersive liquid phase microextraction of polycyclic aromatic hydrocarbons from food samples prior to GC-FID analysis. Food Chem 2020;314:126214.
[55] Nazir NAM, Raoov M, Mohamad S. Spent tea leaves as an adsorbent for micro-solid-phase extraction of polycyclic aromatic hydrocarbons (PAHs) from water and food samples prior to GC-FID analysis. Microchem J 2020;159:105581.
[56] Wang M, Cheng C, Liu C, Yang Y. Hollow fiber supported ionic liquids liquid-phase micro-extraction followed by high-performance liquid chromatography for the determination of polycyclic aromatic hydrocarbons in milk samples. J Chromatogr Sci 2017;56:74–80.
[57] Li N, Wu D, Hu N, Fan G, Li X, Sun J, et al. Effective enrichment and detection of trace polycyclic aromatic hydrocarbons in food samples based on magnetic covalent organic framework hybrid microspheres. J Agric Food Chem 2018;66:3572–80.
[58] Mohammad SA, Ghanemi K, Larki A. Simultaneous extraction of polycyclic aromatic hydrocarbons through the complete dissolution of solid biological samples in sodium hydroxide/urea/thiourea aqueous solution. J Chromatogr A 2016;1476:9–18.
[59] Gutiérrez-Valencia TM, García de Llasera MP. On-line MSPD-SPE-HPLC/FLD analysis of polycyclic aromatic hydrocarbons in bovine tissues. Food Chem 2017;223:82–8.
[60] Taghvaee Z, Piravivanak Z, Rezaei K, Faraji M. Determination of polycyclic aromatic hydrocarbons (PAHs) in olive and refined pomace olive oils with modified low temperature and ultrasound-assisted liquid–liquid extraction method followed by the HPLC/FLD. Food Anal Methods 2016;9:1220–7.
[61] Chiang CF, Hsu KC, Cho CY, Tsai TY, Hsu CH, Yang DJ. Comparison and establishment of appropriate methods to determine EU priority PAHs in charcoal-grilled chicken drumsticks with different treatments and their dietary risk assessments. Food Chem Toxicol 2020;142:111400.
[62] Tfouni SAV, Reis RM, Kamikata K, Gomes FML, Morgano MA, Furiani RP. Polycyclic aromatic hydrocarbons in teas using QuEChERS and HPLC-FLD. Food Addit Contam Part B Surveill 2018;11(2):1440638.
[63] Rozentale I, Zacs D, Bartkevics V. Application of dopant-assisted atmospheric pressure photoionization HPLC-MS method for the sensitive determination of polycyclic aromatic hydrocarbons in dark chocolate. J Chromatogr Sci 2019;57:220–9.
[64] de Melo APZ, Hoff RB, Molognoni L, Kleemann CR, de Oliveira T, de Oliveira LVA, et al. Determination of polycyclic aromatic hydrocarbons in seafood by PLE-APCI-MS/MS and preliminary risk assessment of the Northeast Brazil oil spill. Food Anal Methods 2022;15:1826–42.
[65] Klink D, Schmitz OJ. SFC-APLI-(TOF)MS: hyphenation of supercritical fluid chromatography to atmospheric pressure laser ionization mass spectrometry. Anal Chem 2016;88: 1058–64.
[66] Lesellier E. Retention mechanisms in super/subcritical fluid chromatography on packed columns. J Chromatogr A 2009; 1216:1881–90.
[67] Yoshioka T, Nagatomi Y, Harayama K, Bamba T. Development of an analytical method for polycyclic aromatic hydrocarbons in coffee beverages and dark beer using novel high-sensitivity technique of supercritical fluid chromatography/mass spectrometry. J Biosci Bioeng 2018; 126:126–30.
[68] Wicker AP, Carlton Jr DD, Tanaka K, Nishimura M, Chen V, Ogura T, et al. On-line supercritical fluid extraction-supercritical fluid chromatography-mass spectrometry of polycyclic aromatic hydrocarbons in soil. J Chromatogr B 2018;1086:82–8.
[69] Tang S, Liu S, Frank BP. Feasibility of supercritical fluid extraction-supercritical fluid chromatography mass spectrometry for the determination of polycyclic aromatic hydrocarbons in particulate matter samples. J Separ Sci 2021; 44:3717–26.
[70] Tang Y, Sun S, Zhang L, Du Z, Zhuang J, Pan J. Determination of 16 polycyclic aromatic hydrocarbons in tire rubber by ultra-high performance supercritical fluid chromatography combined with atmospheric pressure photoionization-tandem mass spectrometry. Anal Methods 2018;10: 4902.
[71] Nsibande SA, Montaseri H, Forbes PBC. Advances in the application of nanomaterial-based sensors for detection of polycyclic aromatic hydrocarbons in aquatic systems. Trends Anal Chem 2019;115:52–69.
[72] Comnea-Stancu IR, van Staden JF, Stefan-van Staden. Review – trends in recent developments in electrochemical sensors for the determination of polycyclic aromatic hydrocarbons from water resources and catchment areas. J Electrochem Soc 2021;168:047504.
[73] Zainal PNS, Ahmad SAA, Aziz SFNA, Rosly NZ. Polycyclic aromatic hydrocarbons: occurrence, electroanalysis, challenges, and future outlooks. Crit Rev Anal Chem 2020;52: 878–96.
[74] Munoz J, Crivillers N, Mas-Torrent M. Carbon-rich monolayers on ITO as highly sensitive platforms for detecting polycyclic aromatic hydrocarbons in water: the case of pyrene. Chem Eur J 2017;23:15289.
[75] Munoz J, Campos-Lendinez A, Crivillers N, Mas-Torrent M. Selective discrimination of toxic polycyclic aromatic hydrocarbons in water by targeting π-stacking interactions. ACS Appl Mater Interfaces 2020;12: 26688–93.
[76] Munoz J, Navarro-Senent C, Crivillers N, Mas-Torrent M. Study of carbon nanotube-rich impedimetric recognition electrode for ultra-low determination of polycyclic aromatic hydrocarbons in water. Microchim Acta 2018;185:255.
[77] Makelane HR, John SV, Waryo TT, Baleg A, Mayedwa N, Rassie C, et al. AC voltammetric transductions and sensor application of a novel dendritic poly(propylene thiophenoimine)-co-poly(3-hexythiophene) star co-polymer. Sensor Actuator B Chem 2016;227:320–7.
[78] Makelane H, John SV, Yonkeu ALD, Waryo T, Tovide O, Iwuoha E. Phase selective alternating current voltammetric signaling protocol: application in dendritic co-polymer sensor for anthracene. Electroanalysis 2017;29:1887–93.
[79] Udomsap D, Brisseta H, Culioli G, Dollet P, Laatikainen K, Siren H, et al. Mater Today Commun 2018;17:458.
[80] Latif U, Ping L, Dickert FL. Conductometric sensor for PAH detection with molecular imprinted polymer as recognition layer. Sensors 2018;18:767.
[81] Mathieu-Scheers E, Bouden S, Grillot C, Nicolle J, Warmont F, Bertagna V, et al. Trace anthracene electrochemical detection based on electropolymerized-molecularly imprinted polypyrrole modified glassy carbon electrode. J Electroanal Chem 2019;848:113253.
[82] Munawar H, Mankar JS, Sharma MD, Garcia-Cruz A, Fernandes LAL, Peacock M, et al. Highly selective

electrochemical nanofilm sensor for detection of carcinogenic PAHs in environmental samples. Talanta 2020;219:121273.
[83] Jusoh NS, Azmi AAAR, Ahmad A. Enzyme-linked immunosorbent assay (ELISA)-based-sensor for determination of benzo[a]pyrene in river water using screen-printed gold electrode. Malay J Anal Sci 2017;21:518–26.
[84] Beloglazova NV, Lenain P, Rycke ED, Goryacheva IY, Knopp D, Saeger SD. Capacitive sensor for detection of benzo(a)pyrene in water. Talanta 2018;190:219.
[85] Babolghani FM, Mohammadi-Manesh E. Simulation and experimental study of FET biosensor to detect polycyclic aromatic hydrocarbons. Appl Surf Sci 2019;488:662–70.
[86] Mailu SN. Simultaneous detection of anthracene and phenanthrene on AgAu alloy nanoparticles/overoxidized-polypyrrole composite modified carbon. IOSR J Appl Chem 2019;12:65–80.
[87] Qiao X, Wei M, Tian D, Xia F, Chen P, Zhou C. One-step electrosynthesis of cadmium/aluminum layered double hydroxides composite as electrochemical probe for voltammetric detection of anthracene. J Electrochem Chem 2018;808:35–40.
[88] Zainal PNS, Ahmad SAA, Ngee LH. Surface modification of screen-printed carbon electrode (SPCE) with calixarene-functionalized electrochemically reduced graphene oxide (ERGO/C4) in the electrochemical detection of anthracene. J Electochem Soc 2019;166:B110–6.
[89] Caroleo RM, Magna G, Naitana ML, Di Zazzo L, Martini R, Pizzoli F, et al. Advances in optical Sensors for persistent organic pollutant environmental monitoring. Sensors 2022;22:2649.
[90] Kandi S, Inbaraj BS, Chen BH. An improved surface enhanced Raman spectroscopic method using a paper-based grape skin-gold nanoparticles/graphene oxide substrate for detection of rhodamine 6G in water and food. Chemosphere 2022;301:134702.
[91] Wang L, Pang S, Zhou G. Recent advances in spectroscopy technology for trace analysis of persistent organic pollutants. Appl Sci 2019;9:3439.
[92] Du J, Xu J, Sun Z, Jing C. Au nanoparticles grafted on Fe_3O_4 as effective SERS substrates for label-free detection of the 16 EPA priority polycyclic aromatic hydrocarbons. Anal Chim Acta 2016;915:81–9.
[93] Gong X, Liao X, Li Y, Cao H, Zhao Y, Li H, et al. Sensitive detection of polycyclic aromatic hydrocarbons with gold colloid coupled chloride ion SERS sensor. Analyst 2019;144:6698.
[94] Shi X, Zhang D, Jia W, Yang J, Wang C, Ma J. Portable surface-enhanced Raman scattering sensor for the rapid detection of polycyclic aromatic hydrocarbons in coastal seawater. Mar Technol 2019;53:46–55.
[95] Su M, Jiang Q, Guo J, Zhu Y, Cheng S, Yu T, et al. Quality alert from direct discrimination of polycyclic aromatic hydrocarbons in edible oil by liquid-interfacial surface-enhanced Raman spectroscopy. LWT–Food Sci Technol 2021;143:111143.
[96] Capaccio A, Sasso A, Rusciano G. Feasibility of SERS-active porous Ag substrates for the effective detection of pyrene in water. Sensors 2022;22:2764.
[97] Du J, Jing C. One-step fabrication of dopamine-inspired Au for SERS sensing of Cd^{2+} and polycyclic aromatic hydrocarbons. Anal Chim Acta 2019;1062:131–9.
[98] Zhang M, Zhang X, Qu B, Zhan J. Portable kit for high-throughput analysis of polycyclic aromatic hydrocarbons using surface enhanced Raman scattering after dispersive liquid-liquid microextraction. Talanta 2017;175:495–500.
[99] Dribek M, Rinnert E, Colas F, Crassous MP, Thioune N, David C, et al. Organometallic nanoprobe to enhance optical response on the polycyclic aromatic hydrocarbon benzo[a]pyrene immunoassay using SERS technology. Environ Sci Pollut Res 2017;24:27070–6.
[100] Zhang Q, Guo W, He L, He L, Chen Y, Shen X, et al. A new SERS substrate of self-assembled monolayer film of gold nanoparticles on silicon wafer for the rapid detection of polycyclic aromatic hydrocarbons. Mater Chem Phys 2020;250:122994.
[101] Li M, Yu H, Cheng Y, Guo Y, Yao W, Xie Y. Simultaneous and rapid determination of polycyclic aromatic hydrocarbons by facile and green synthesis of silver nanoparticles as effective SERS substrate. Ecotoxicol Environ Saf 2020;200:110780.
[102] Yu Z, Grasso MF, Sorensen HH, Zhang P. Ratiometric SERS detection of polycyclic aromatic hydrocarbons assisted by β-cyclodextrin-modified gold nanoparticles. Microchim Acta 2019;186:391.
[103] Zhang D, Hao R, Zhang L, You H, Fang J. Ratiometric sensing of polycyclic aromatic hydrocarbons using capturing ligand functionalized mesoporous Au nanoparticles as a surface-enhanced Raman scattering substrate. Langmuir 2020b;36:11366–73.
[104] Castro-Grijalba A, Montes-Garcia V, Cordero-Ferradas MJ, Coronado E, Perez-Juste J, Pastoriza-Santos I. SERS-based molecularly imprinted plasmonic sensor for highly sensitive PAH detection. ACS Sens 2020;5:693–702.
[105] Shi X, Yan X, Zhang X, Ma L, Zhang X, Wang C, et al. Ultrasensitive detection of polycyclic aromatic hydrocarbons (PAHs) in water using three-dimensional SERS substrate based on porous material and pH 13 gold nanoparticles. J Ocean Univ China 2019b;18:1523–31.
[106] Eremina OE, Sergeeva EA, Ferree MV, Shekhovtsova TN, Goodilin EA, Vaselova IA. Dual-purpose SERS sensor for selective determination of polycyclic aromatic compounds via electron donor-acceptor traps. ACS Sens 2021;6:1057–66.
[107] Li D, Cao X, Zhang Q, Ren X, Jiang L, Li D, et al. Facile in situ synthesis of core-shell MOF@Ag nanoparticle composites on screen-printed electrodes for ultrasensitive SERS detection of polycyclic aromatic hydrocarbons. J Mater Chem 2019;7:14108.
[108] Wang X, Xu Q, Hu X, Han F, Zhu C. Silver-nanoparticles/graphene hybrids for effective enrichment and sensitive SERS detection of polycyclic aromatic hydrocarbons. Spectrochim Acta Mol Biomol Spectrosc 2020;228:117783.
[109] Wang S, Cheng J, Han C, Xie J. A versatile SERS sensor for multiple determinations of polycyclic aromatic hydrocarbons and its application potential in analysis of fried foods. Int J Anal Chem 2020;2020:4248029.