Polycyclic aromatic hydrocarbons in edible oils: an overview on sample preparation, determination strategies and relative abundance of prevalent compounds

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ABSTRACT:

Polycyclic aromatic hydrocarbons (PAHs) are food contaminants whose presence in foodstuffs is especially alarming due to their carcinogenic character. These substances are highly lipophilic and thus, unsafe levels of these compounds have been found in edible fats and oils. Efficient methodologies to determine such molecules in lipidic matrixes are therefore essential. In this review, a detailed description of the analytical methods for PAHs determination in vegetable oils from the last fifteen years has been conducted. Particular emphasis has been placed on innovative sample treatments, which facilitate and shorten the pretreatment of the oils. Finally, results from recent investigations have been reviewed and studied in depth, in order to elucidate which PAHs are most commonly found in vegetable oils. ~~To the best of our knowledge, this is the first time that individual occurrence of every HAP included in each investigation (of those examined herein) is considered and thoughfully studied.~~

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds containing several fused aromatic rings in their chemical structure (Mafra, Amaral, & Oliveira, 2010). They have attracted great interest because of their proven carcinogenity (Mafra et al., 2010; Rose, 2010). Once they enter the organism, PAHs undergo a metabolic activation through the cytochrome P450 and, as a result of that transformation, electrophilic species are produced. Those metabolites are able to covalently bind to DNA molecules, leading to mutations and potential genotoxicity (Mafra et al., 2010; Purcaro, Barp, & Moret, 2016). In fact, the molecule of benzo(a)pyrene (BaP) has been classified as a human carcinogen (Group 1 carcinogens) by the International Agency for Research on Cancer (IARC) (IARC, 2012).

There are different mechanisms in which human beings can be exposed to those compounds, but food has been pointed out as the major contributor to the contamination of non-occupationally exposed and non-smokers adults (Cirillo et al., 2006; Phillips, 1999; Plaza-Bolaños, Garrido-Frenich, & Martínez-Vidal, 2010). Therefore, PAHs occurrence in foodstuffs must be accurately and constantly controlled to avoid food poisoning (Bansal & Kim, 2015). Because of the lipophilic nature of the mentioned compounds, unsafe levels of PAHs can be easily found in fats and oils (Dennis et al., 1991; Guillén, Sopelana, & Palencia, 2004; Moret & Conte, 2000; Rose, 2010).

Vegetable oils, such as sunflower, corn, soybean, coconut oil, etc. are massively produced all over the world and preferably consumed and appreciated out of the Mediterranean basin, due to their lower price, among other reasons (Unites States Department of Agriculture, 2018). There is a considerable risk of PAHs incidence in these edible oils, as their production requires the drying of the vegetable seeds before the oil extraction; generated combustion gases may be rich in PAHs that would eventually reach the commercial oil (León-Camacho, Viera-Alcaide, & Ruiz-Méndez, 2003;

Mafra et al., 2010; Teixeira, Casal, & Oliveira, 2007). Meanwhile, virgin olive oil (VOO) is considered the principal fat source of the Mediterranean area and its excellent organoleptic properties and positive health effects are valued all over the world (Cerretani et al., 2007). It is exclusively obtained by mechanical operations. Thus, any contamination may be attributed to the contact of the olive fruit with polluted air, mineral oil residues from packaging or with any contaminated element present in the production line (mill, transport containers, etc.) (Bansal & Kim, 2015; Gharbi et al., 2017; Guillén et al., 2004; Rodríguez-Acuña, Pérez-Camino, Cert, & Moreda, 2008b).

As stated before, PAHs exposure may lead to several affections. The link between PAHs exposure and an increase in cancer risk and age-related affections has been extensively investigated (Bauer et al., 2018; Boström et al., 2002; W. Fu et al., 2018; Wohak et al., 2016). Scientific evidences have motivated the passage of some regulations regarding the maximum levels allowed in foods and, more specifically, in edible oils and fats. In 1970, the Environmental Protection Agency of the United States (EPA) pointed 16 PAHs as priority pollutants that have to be routinely monitored, according to their occurrence in daily-diet products (EPA, 1999). Those substances have been listed in Table 1. This table also contains the corresponding fluorescence program (including excitation and emission wavelengths) applied in some articles to detect them. No maximum levels of PAHs were established until 2001, when the discovery of a pomace olive oil (POO) with alarming levels of PAHs in Czech Republic prompted that many European countries internally authorized maximum permitted levels for different groups of PAHs in olive pomace (Purcaro et al., 2016; Purcaro, Moret, & Conte, 2013). In 2002, the Scientific Committee on Food (SCF), which belongs to the EU boards, identified another 15 PAHs (only eight of them were coincident with some of the EPA PAHs) as carcinogens/mutagens. They also recognized BaP as a suitable marker of the presence of the rest of PAHs in food (Scientific Committee on Food, 2002). In 2005, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) advised the addition of another PAH, BcFl, to the already existing list of the EU PAHs, finally

setting the 15+1 priority EU PAHs (JECFA, 2005). It was also that year, with the Regulation 208/2005 (European Union, 2005) (and later in 2006, with Regulation 1881/2006 (European Union, 2006)) when the EU first dictated maximum limits for BaP in foods, supporting its use as a PAHs-incidence marker.In 2008, the European Food Safety Authority (EFSA) concluded that BaP does not always work as an appropriate marker, as some PAHs, namely Chr and BcFl, were detected in samples even in the absence of BaP. As a result, they advised on the monitoring of a set of eight PAHs (PAH8) and a subgroup of four PAHs (PAH4) (EFSA, 2008). EU released in 2011 the most recent regulation to date (Regulation 835/2011 (European Union, 2011)). It covers maximum levels for the set of PAH4 and BaP in foods. Limits of 10 µg/kg for the sum of PAH4 and 2 µg/kg for BaP in vegetable oils were established, whereas 20 µg/kg of PAH4 were permitted in coconut oil (European Union, 2011). ~~An illustrative overview of the regulation process that has affected PAHs allowed levels in edible oils and fats is shown in Figure 1.~~

EPA and EU regulations incur significant differences. SCF considers heavier and more complex compounds, whereas EPA list includes the so-called “light PAHs” (with 2-4 rings), as well as the sets of PAH4 and PAH8 (EPA, 2014). The great majority of the scientific reports published to date focus on the determination of the 16 EPA PAHs, taking PAH8 or PAH4 as risk indicators. However, there is no assurance of avoiding any contamination if no PAH8 or PAH4 are detected, and neither is certain that the set of PAH8 or PAH4 are the most dangerous in terms of carcinogenity. Structural heterogeneity of this kind of analytes hinders the simultaneous determination of all PAHs of concern within a single analysis. Thus, further studies pointing out the most commonly found compounds in real samples would be of great interest. Ideally, those investigations should take into account the PAHs current occurrence as well as their potential risk. This aspect will be more deeply explored in Section 6, “PAHs incidence. Is there any reliable PAH as an indicator of their occurrence in edible oils?”.

To date, none of the previously mentioned regulatory authorities have published an official method for the determination of the priority PAHs in vegetable oils. Many reports have followed in some way the guidelines proposed in a reference methodology described by the ISO regulation; this standard has been revised through the years, and the current accepted procedure is reflected in ISO 15753:2016 (ISO 15753, 2016). According to this specification, PAHs are extracted with a mixture of acetonitrile/acetone (ACN/acetone) and purified first in a reverse-phase C18 cartridge and in a Florisil cartridge afterwards. Individual determination of each PAH is achieved by high performance liquid chromatography with fluorescence detection (HPLC-FLD). Due to possible interferences of matrix components, this method is not suitable for the quantitative determination of these substances in POO or palm oil.

The just enumerated recommendations have served as a basis for the studies aiming to determine PAHs in oil matrices. Indeed, for the last fifteen years, the most generally applied methodology has consisted on a liquid-liquid extraction (LLE) followed by a solid-phase extraction (SPE), and the subsequent individual separation and detection by LC-FLD or gas chromatography with mass spectrometry detection (GC-MS), respectively. Excellent reviews have been previously published giving an extensive overview about PAHs determination, covering food and beverages, in general (Plaza-Bolaños et al., 2010; Purcaro et al., 2016; Purcaro, Moret, et al., 2013; Y. Sun, Wu, & Gong, 2019), and fats and oils, in particular (Moret & Conte, 2000; Rose, 2010).

Besides the mentioned widespread workflow (LLE (plus SPE) followed by LC-FLD or GC-MS), other innovative and advanced strategies have been implemented for the determination of PAHs in edible oils and fats. In the coming sections, a general overview of the preferred techniques for PAHs analysis in edible oils will be presented, as well as a detailed explanation of the outstanding advances that have been accomplished over the last years in this field. A graphical summary of the methodologies employed so far can be found in ~~Figure 2~~Figure 1. Moreover, relevant results

obtained in the most recent investigations have been deeply studied and discussed within the current review. A summary of the primarily found PAHs has been given, aiming to identify which compounds are repeatedly present in vegetable oils and, therefore, should represent the actual target to ensure the safety of lipidic foodstuff.

2. Sample treatment

The isolation procedure is obviously an essential step for the determination of this kind of analytes in vegetable oils. Studies focusing on edible oils as a source of PAHs use variable sample amounts, usually ranging from 0.2 to 2.5 g of oil. As PAHs are present at very low levels in comparison with triacylglicerides (TAGs) (Purcaro, Moret, et al., 2013), it is necessary to isolate the compounds under study from the rest of the major components of the matrix. The latter is not a straightforward step, since PAHs great hydrophobicity rules a high affinity for the oily phase (Plaza-Bolaños et al., 2010; Q. Zhao et al., 2011). Howard and Fazio (Howard & Fazio, 1969), in 1969, and Chen (Chen, 1997), in 1997, both provided thoughtful overviews of the analysis of PAHs in foods (including vegetable oils, cereal products, water, fish, meat and smoked meat), but Moret et al. (Moret & Conte, 2000) were the first authors that focused in edible fats and oils and reviewed in 2000 the traditional and alternative methods (at that moment) for the sample preparation of these lipidic matrixes when the determination of PAHs was intended. After that, some other complete reviews have been published over the years (Plaza-Bolaños et al., 2010; Purcaro et al., 2016; Purcaro, Moret, et al., 2013; Y. Sun et al., 2019; Wu, Gong, Yan, Sun, & Zhang, 2020). According to these authors, extraction of PAHs traditionally relied on a several-stages methodology involving saponification, LLE and clean-up by thin-layer chromatography (TLC), column chromatography or, more recently, SPE. The direct use of LLE followed by SPE, TLC, packed columns, gel permeation chromatography (GPC), donor-acceptor complex chromatography (DACC), etc. has been also suggested. Lately, SPE (useful for carrying out both extraction and purification steps) as well as some other strategies are widely employed too.

149 The current section will try to give a general overview to the reader, taking into account both the
150 most extensively used procedures and those which can be considered as more innovative. Tables 2
151 and 3 contain in-depth information about the methodologies applied by the articles discussed in
152 this review and provide specific details that may be useful to fully understand the description
153 included within the text.

154 **2.1 Previous stage before the liquid-liquid extraction**

155 When a saponification step is included prior the LLE (Alomirah et al., 2010; Dost & Ideli, 2012;
156 Mohammadi et al., 2020), the authors generally have the aim of reducing the lipidic content
157 (considerably lessening the presence of TAGs); however, it does not allow the complete removal of
158 some interfering molecules (such as squalene) that are present in the unsaponifiable fraction and
159 could eventually reach the chromatographic column, making it necessary to conduct an additional
160 extraction step (Moret & Conte, 2000). In the past, some authors also described another strategy to
161 be applied before the LLE. It was based on the phenomenon of caffeine-PAH complex formation
162 (Kolarovič & Traitler, 1982; Sagredos & Sinha-Roy, 1979; Sagredos, Sinha-Roy, & Thomas, 1988), that
163 allows the extraction of the PAHs with cyclohexane after decomposing the complex with an aqueous
164 sodium chloride solution (Moreda, Pérez-Camino, & Cert, 2001).

165 **2.2 Liquid-liquid extraction**

166 LLE logically aims to gradually increase the presence of PAHs in a separated fraction. Usually, the
167 following solutions are preferred: ACN/acetone, dimethylformamide/water (DMF/water),
168 water/dimethylsulfoxide (water/DMSO) or ACN. This partition has been microwave assisted
169 (Alarcón, Báez, Bravo, Richter, & Fuentes, 2012) and, more commonly, ultrasound assisted
170 (Costopoulou et al., 2010; Ergönül & Sánchez, 2013; Hossain & Salehuddin, 2012; Ju, Kim, Kim, &
171 Baek, 2020; L. K. Shi, Zhang, & Liu, 2016; X. Shi et al., 2018; Taghvaee, Piravivanak, Rezaei, & Faraji,

2016; Teixeira et al., 2007; J.-H. Wang & Guo, 2010; Yousefi et al., 2018; W. Zhao, Chen, Fang, Li, & Zhao, 2013). Samples may be diluted in hexane (Barranco et al., 2003; Camargo, Antoniolli, & Vicente, 2011; Cassimiro Belo, Nunes, Vieira Dos Santos, Augusti, & Pissinatti, 2012; Farrokhzadeh & Razmi, 2018; Guillén et al., 2004; Molle, Abballe, Gomes, Furlani, & Tfouni, 2017; Rascón, Azzouz, & Ballesteros, 2018; Tfouni, Padovani, Reis, Furlani, & Camargo, 2014) or pentane (Diletti et al., 2005) prior to the extraction. Alternatively, samples may be directly applied to the partition, which has been the more common choice (Alves da Silva, Ferraz da Silva Torres, Palma de Almeida, & Rodrigues-Sampaio, 2018; Alves da Silva, Rodrigues-Sampaio, & Ferraz da Silva Torres, 2017; L. K. Shi et al., 2016; X. Shi et al., 2018; Taghvaee et al., 2016; Yousefi et al., 2018; Zhou, Jiang, Mao, Zhao, & Lu, 2016). The addition of hexane may facilitate the separation of the oily fraction and the aqueous phase, but special attention should be devoted to avoid analytes losses by dissolution in the hexane, considering their non-polar nature. In 2013, Payanan et al. introduced a freezing step in the extraction procedure, in order to reduce the fat content of the organic fraction by precipitation of the lipidic compounds (Payanan, Leepipatpiboon, & Varanusupakul, 2013). In contrast with other strategies of LLE based on centrifugation cycles, Payanan and co-workers performed a low-temperature clean up to separate both phases. They found that a long time of 24-36 h was needed to lower the fat percentage to a satisfactory level, but the number of interfering peaks in the chromatogram was positively reduced. 94% of the lipids in the edible oils were easily removed without any significant loss of the PAH analytes. To complete the clean-up, the authors also used an Alumina-N SPE cartridge afterwards.In the past, some alternatives to LLE were reported. Supercritical fluid extraction (SFE) drew attention because of the reduction of the analysis time and the achievement of very good recoveries. It has been successfully applied to extract PAHs from lipidic matrixes (Lage Yusty & Cortizo Daviña, 2005; Zougagh, Redigolo, Ríos, & Valcárcel, 2004),

even though it has not been so widely reported in recent literature. DACC has also been used for the sample preparation of edible oils (Hollosi & Wenzl, 2011).

2.3 Purification stage

As stated above, a purification step is commonly applied after LLE, in order to remove interfering constituents that might be present in the oil. Several techniques have been applied to that end. GPC has proved to be very efficient to remove fatty interferences (Ballesteros, García-Sánchez, & Ramos-Martos, 2006; Bordajandi, Dabrio, Ulberth, & Emons, 2008; Ciecierska & Obiedziński, 2013; Fromberg, Højgård, & Duedahl-Olesen, 2007; Gómez-Ruiz & Wenzl, 2009; Martinez-López, Morales-Noé, Pastor-Garcia, Morales-Rubio, & De La Guardia, 2005; J.-H. Wang & Guo, 2010), due to the substantial difference between TAGs and PAHs molecular size. This allows a first elution of lipidic substances and a successive elution of the analytes of interest. Despite the high volume of solvents that are required, the semi-automatic character of this technique and the good recoveries that are usually obtained are advantages to be considered.

In any case, PAHs purification has been mostly based in SPE procedures. This technique, as mentioned before, has been applied either for the purification of the extract containing the analytes or for the direct extraction of the PAHs from the matrix. The sorbents utilised in one or another approach may coincide, but the solvents employed to activate the column and elute the compounds are different depending on the specific objective of the process (purification or extraction).

Regarding the clean-up process, ISO 15753:2016 recommends two steps; a first application of a C18 column and a subsequent SPE based on a Florisil cartridge. This procedure has been effectively reproduced by some authors (Costopoulou et al., 2010; Ergönül & Sánchez, 2013; Teixeira et al., 2007; Yousefi et al., 2018). In other cases, the single use of C18 cartridges (without any further SPE) for the purification has been reported, mainly following two diverse strategies. Some authors have

218 followed the indications of the ISO regulation for the C18 column (with slight modifications in some
219 cases), activating the cartridge with MeOH, ACN or a mixture of both solvents and eluting the PAHs
220 with mixtures of ACN/acetone (Rascón et al., 2018; W. Zhao et al., 2013). In other cases, C18
221 cartridges have been conditioned with MeOH and DMF/water (at different proportions) and PAHs
222 have been subsequently eluted with hexane (Alves da Silva et al., 2018; Barranco et al., 2003;
223 Camargo et al., 2011; Cassimiro Belo et al., 2012; Tfouni et al., 2014). Silica cartridges have been
224 also used during the purification stage. MeOH, water (Molle et al., 2017), hexane (L. K. Shi et al.,
225 2016), dichloromethane (CH_2Cl_2) (Hossain & Salehuddin, 2012) and cyclohexane (Fromberg et al.,
226 2007; Guillén et al., 2004) have been chosen for silica cartridges conditioning, whereas DMF/water
227 (Molle et al., 2017), hexane/CH_2Cl_2 (L. K. Shi et al., 2016), ACN/acetone (Hossain & Salehuddin, 2012)
228 and cyclohexane (Fromberg et al., 2007; Gómez-Ruiz & Wenzl, 2009; Guillén et al., 2004) have been
229 selected as eluents. Some other uncommon clean-up approaches involving the use of SPE can be
230 found in literature. Jiang et al. concatenated two SPE steps, selecting Oasis HLB and Florisil as the
231 solid phase of each of the cartridges, respectively (Jiang et al., 2015); Cassimiro-Belo and co-workers
232 conducted a similar strategy, carrying out the first SPE in a C18 cartridge and a subsequent silica-
233 based SPE (Cassimiro Belo et al., 2012). Finally, it is worth mentioning that Jung et al. (Jung et al.,
234 2013) and Veyrand and co-workers (Veyrand et al., 2007) employed a styrene-divinylbenzene solid
235 phase, eluting the analytes with hexane/CH_2Cl_2 (80:20, v/v) or cyclohexane/ethyl acetate (40:60,
236 v/v), respectively.

237 **2.4 SPE as extraction technique**

238 As explained above, many authors have reported a direct application of the samples to the SPE,
239 combining the extraction and cleaning step and avoiding the time and solvents consumed during
240 the LLE or any other preceding step. Samples have been applied to the cartridge without any dilution
241 (Bogusz, El Hajj, Ehaideb, Hassan, & Al-Tufail, 2004; Chung & Lau, 2015; Stenerson, Shimelis,

242 Halpenny, Espenschied, & Ye, 2015), or after carrying out a simple dilution with hexane (Gharbi et
243 al., 2017; Purcaro, Moret, & Conte, 2008; Purcaro, Morrison, Moret, Conte, & Marriott, 2007) or
244 isooctane/cyclohexane (1:2, v/v) (Cortesi & Fusari, 2006), but no previous steps (e.g. LLE,
245 saponification, etc.) have been conducted. Silica adsorbents have been preferably used, applying
246 CH_2Cl_2 and hexane (Gharbi et al., 2017; Purcaro et al., 2008) as activation solvents and mixtures of
247 hexane/CH_2Cl_2 (70:30, v/v) (Gharbi et al., 2017; Purcaro et al., 2008) or cyclohexane (Alomirah et al.,
248 2010) as elution solvents. In the past, some authors reported the use of tetrahydrofuran (THF) as
249 eluent solvent too (Weißhaar, 2002).

250 Moreover, Dost and Ideli prepared a mixed phase containing silica and alumina (1:1, w/w) to extract
251 the PAHs after a saponification step (Dost & Ideli, 2012). The column was activated and washed with
252 hexane, and the analytes were then eluted with hexane/CH_2Cl_2 (80:20, v/v). Bogusz et al. proposed
253 in 2004 the utilization of a dual-layer SPE cartridge, containing a bottom layer of C18 and an upper
254 layer of Florisil to directly extract BaP without any previous dilution or partition (Bogusz et al., 2004).
255 They compared the efficiency of such methodology with a dispersive SPE (dSPE) consisting in a
256 mixture of the oil with a C18 sorbent and a subsequent application to a Florisil cartridge. The dual-
257 layer SPE offered higher recoveries and was faster, simpler and more repeatable. Later on, other
258 investigations have exploited dual-layer cartridges, successfully achieving the extraction of four EU
259 PAHs (Chung & Lau, 2015) and the 16 EPA PAHs (Stenerson et al., 2015) after a proper elution with
260 ACN. Styrene-divinylbenzene cartridges have been employed too. For instance, Cortesi and co-
261 workers conditioned the cartridge with CH_2Cl_2 and isooctane/cyclohexane (1:2, v/v) to extract a
262 group of PAH (see Table 2) after a dilution with isooctane/cyclohexane (1:2, v/v) (as mentioned
263 above) (Cortesi & Fusari, 2006).

264 Moreda and co-workers combined the two strategies previously presented (SPE both to extract the
265 PAHs from the oil and also to purify the obtained extract) through the application of POO samples

to silica cartridges (extraction step) and the performance of an additional SPE to remove interferences and procure cleaner chromatograms (purification step) (Moreda, Rodríguez-Acuña, Pérez-Camino, & Cert, 2004). This approach has been reproduced afterwards by the teams of Rodríguez-Acuña (Rodríguez-Acuña, Pérez-Camino, Cert, & Moreda, 2008a) and Taghvaee (Taghvaee et al., 2016).

More references of works applying SPE as an extraction step will be provided in Section 2.6 "Innovative isolation procedures"; the innovative character of the employed adsorbents has motivated their inclusion in a specific category to deeply review these contributions.

After properly obtaining the extract, elution solvents are generally evaporated and the corresponding residue is usually redissolved in ACN prior to the injection into the separation instrument. Evaporation is not a trivial step during PAHs analysis. Some of the 16 EPA PAHs, namely Na, Ace and Fl are volatile, and may be lost if a complete dryness is carried out (Hossain & Salehuddin, 2012; Plaza-Bolaños et al., 2010; Teixeira et al., 2007; Veyrand et al., 2007). An accepted procedure to prevent PAHs losses is to avoid the complete dryness and to allow the residual solvent to spontaneously evaporate at room temperature (Gharbi et al., 2017). According to ISO 15753:2016, 50 µL of the solvent should be left in the vial (ISO 15753, 2016).

2.5 Alternative isolation procedures

Classical methodologies for sample preparation have proven to be efficient for the extraction of PAHs from vegetable oils. However, some of mentioned solvent-based methods imply arduous and time-consuming procedures that demand large volumes of solvents and substantial expenses regarding laboratory material. Most of them require a considerable number of steps that enlarge the possibilities of incurring in analytes losses throughout the process. Thus, in order to overcome these downsides, novel approaches have been developed in the field of advanced materials. As

289 reflected in the present section, the exploitation of π–π bonds, formed by the interaction of the
290 analytes of interest and several forefront adsorbents with advanced technological characteristics,
291 has represented a notable progress in the development of innovative alternatives for the extraction
292 of PAHs from oil samples. It is worth mentioning that most of the procedures reported in this section
293 are based on an SPE (either dispersive or on a cartridge) that combines both the extraction and
294 purification stages; some other works applying this strategy have been previously examined, but the
295 characteristics of the adsorbents included here definitely differentiate them from the already cited
296 investigations.

297 **2.5.1 Head-space extraction**

298 Arrebola and co-workers were pioneers in the development of a solvent-free PAHs extraction
299 procedure for olive oils analyses (Arrebola, Garrido-Frenich, González Rodríguez, Plaza-Bolaños, &
300 Martínez-Vidal, 2006). The methodology was based on the heating of the olive oil at a high
301 temperature (200ºC) and a subsequent automatic sampling of 100 µL from the head-space (HS), to
302 be injected in a GC-MS instrument. Excellent results were obtained in terms of LOD and recovery,
303 with values within the range of 0.02 – 0.06 µg/kg and 96 – 99%, respectively, as shown in Table 3.
304 Similar procedures are those described by Vichi et al., who applied a head-space solid phase
305 microextraction (HS-SPME) to isolate PAHs with up to four aromatic rings from extra virgin olive oils
306 (EVOOs) (Vichi, Pizzale, Conte, Buxaderas, & López-Tamames, 2005, 2007). To this end, the vial
307 containing the sample was placed in a 100ºC silicon bath during 2 min. After that, a
308 Divinylbenzene/Carboxen/Polydimethilsiloxane fibre was exposed to the sample HS during 60 min
309 and then the retained compounds were selectively injected into the GC-MS system. The authors
310 were able to determine several PAHs which had not been previously quantified in VOO.

311 **2.5.2 Solid-phase microextraction (SPME)**

SPME was studied by Purcaro et al. (Purcaro, Morrison, et al., 2007). They proposed a direct immersion of a Carbopack Z/polydimethylsiloxane fibre in an oil previously diluted in hexane. The fibre and the PAHs analytes would establish π–π interactions that allowed their collection from the oily matrix. This methodology was used for the determination of the 16 EPA PAHs by means of a GC x GC (it will be discussed in Section 4 "PAHs measurement by gas-chromatography"). A similar approach (applying SPME) was also used to determine BaP in vegetable oils by using GC-MS (Purcaro, Moret, & Conte, 2007). In this case, the high amount of TAGs reaching the column shortened its durability and limited the routine application of the procedure. Thus, a LLE was sagely introduced in advance (Purcaro, Picardo, Barp, Moret, & Conte, 2013).

2.5.3 Multiwalled Carbon Nanotubes

Zhao et al. developed an interesting methodology consisting on a magnetic solid phase extraction (MSPE) to isolate PAH8 (Q. Zhao et al., 2011). To this end, magnetic multiwalled carbon nanotubes (mMWCNTs) were prepared and exposed to the oil samples (previously diluted in hexane). π–π interactions were established between PAHs and the mentioned adsorbent, which was easily collected with a magnet afterwards. To desorb the compounds of interest, a toluene elution and ultrasonic agitation were employed. Finally, desorption solution was analysed by GC-MS. The obtained LODs and LOQs were satisfactory and the recoveries of the studied PAHs were also adequate (as can be observed in Table 3). Q. Wang et al. assessed a very similar PAHs pre-concentration strategy, but introducing hydrophobic octadecylphosphonic acid modified zirconia (ZrO_2-C18) nanoparticles to enhance the extraction capability (Q. Wang et al., 2018). The resulting hybrid material (mMWCNT–ZrO_2–C18), which was fabricated via solvothermal extraction, combined the lipophilic and hydrophobic properties of all of its components and rendered excellent LODs, within the range of 0.06–0.55 μg/kg. Zacs and co-workers reported a non-magnetic dSPE using MWCNTs as a sorbent to determine PAH8 in edible oil samples (Zacs, Rozentale, Reinholds, &

Bartkevics, 2018). They compared the obtained results with those achieved through a GPC on the same samples and proved that both extraction methods were equivalent and acceptable LODs were achieved. Even though the application of MWCNTs is effective and straightforward, this nanomaterial must be washed and dried prior to its usage to avoid any contamination, in a process lasting for 3 days, which largely slows down the whole procedure. Moreover, it is not clear that mMWCNTs are suitable for reusability; this aspect is certainly relevant, since the necessity of producing the nanotubes every time the experiment is launched would tremendously increase the costs, the total analysis and could even affect the reproducibility of the applied methodology.

2.5.4 Molecularly Imprinted Polymers (MIPs)

These sorbents are produced by polymerisation of monomers in presence of a specific molecule that acts as a template. The obtained polymer will have plenty of holes that perfectly match the compound used as a template, which usually is the same (or structurally similar) as the target molecule (Ncube, Madikizela, Cukrowska, & Chimuka, 2018). The extraction process could be considered as the equivalent to a SPE in a cartridge. When the matrix containing the analytes reach the MIP, the analytes will be selectively retained and separated from the rest of the sample. A subsequent elution from the polymer would provide the compounds of interest purified for the quantitative detection.

A commercial MIP was used in a study conducted by Drabova and co-workers, aiming to detect 15+1 EU PAHs (Drabova et al., 2013). The polymer was not able to retain PAHs formed by 2-3 rings, consequently not being applicable to the extraction of the 16 PAHs pointed out by the EPA. Samples of EVOO diluted in cyclohexane were loaded into a cartridge containing the MIP and eluted with ethyl acetate (EtOAc) after a washing step with cyclohexane. Suitable recoveries of 70-99% were obtained and a viable methodology for heavy PAHs purification was established. This MIP cartridge

359 was also employed by Xu et al. to carry out the simultaneous determination of 24 PAHs (attending
360 to both EPA and EU recommendations) (Xu, Tang, Chen, Dong, & Li, 2015). Their proposed sample
361 treatment included a tandem SPE based in the coupling of a MIP cartridge (to extract and purify
362 heavy PAHs) and a graphitised carbon black cartridge (intended for light PAHs purification). Final
363 extracts were analysed by GC-MS/MS, obtaining adequate LODs in the range of 0.03–0.6 μg/kg.

364 In 2014, Pschenitza and co-workers developed a MIP to be used in the isolation of BaP from
365 vegetable oils (olive oil among them) and provided a prime methodology to achieve its
366 determination (Pschenitza, Hackenberg, Niessner, & Knopp, 2014). In short, an aliquot of the oil was
367 diluted with hexane and extracted with ACN. This solvent was then evaporated and the residue was
368 redissolved in hexane. The resulting solution was subjected to a molecularly-imprinted SPE, and
369 PAHs were finally eluted with CH_2Cl_2. Again, the solvent was evaporated and the residue was
370 reconstituted in DMSO. The reason for this last substitution was the subsequent technique of
371 choice. An enzyme-linked immunosorbent assay (ELISA) was used to determine BaP concentration
372 in spiked oil samples, obtaining recoveries from 65 to 99% in olive oils. A further validation consisting
373 on the comparison between the results achieved by molecularly-imprinted SPE/ELISA and the data
374 acquired from a GC-MS analysis (taken as a reference) revealed an overestimation of the BaP
375 concentration, with a factor of 2.1. This was justified by the authors as a presumable competition of
376 other PAHs for the interaction with the antibodies used in the ELISA. In any case, promising results
377 were obtained in pursuit of the application of sophisticated analytical tools for the determination
378 of PAHs in edible oil matrixes.

379 Recently, another commercially-available MIP has been tested for the clean-up of PAHs in peanut
380 oil (Ying Sun et al., 2017). The authors compared the performance of such polymer with a GPC-based
381 sample treatment and they found that the MIP-alternative required a lower volume of organic

382 solvent. The extracts derived from both techniques were equivalent in terms of interference
383 removal and the reported MIP utilisation was set as a feasible approach.

384 **2.5.5 Graphene Oxide**

385 Zhang et al. have latterly evaluated the efficiency of a magnetic three-dimensions graphene oxide
386 (GO) nanocomposite, developed for the sample treatment of edible oils from China (Y. Zhang et al.,
387 2017). They compared its efficiency with that of a commercial MIP that allowed the determination
388 of the complete collection of 16 EPA PAHs. According to their findings, both strategies displayed
389 similar results, but the extraction with the GO phase offered better LODs and required half of the
390 time as well as lower solvents volume. According to Ji and co-workers, oil fat hydrophobicity may
391 interfere with GO dispersion in the matrix (Ji et al., 2017). For this reason, they developed a modified
392 material that incorporated Fe_3O_4 as a support, and GO and phytic acid to add opposite polarities,
393 obtaining a magnetic and amphiphilic GO-based nanomaterial suitable for PAHs extraction from
394 vegetable oils. Interestingly, the new material was available to be used for 20 times without
395 recovery losses. The HPLC analysis only took twenty minutes and the procedure resulted in very low
396 LODs (0.6-0.15 ng/g). However, the determined molecules did not allow any regulated
397 characterisation of the analysed oils, as neither PAH4 nor PAH8 EPA sets were monitored. As shown
398 in Table 2, a large amount of oil (20 g) was needed to achieve the extraction.

399 **2.5.6 Other sample preparation strategies**

400 Some other interesting reports addressing an innovative sample preparation were conducted by the
401 groups of Farrokhzadeh et al. (Farrokhzadeh & Razmi, 2018), Zheng and co-workers (Zheng et al.,
402 2016) and X. Shi et al. (X. Shi et al., 2018). Such reports make use of sorbent materials that have not
403 been applied in any of the mentioned studies of this review, hence not being included in the
404 previous classifications. Team of Farrokhzadeh et al. evaluated the chicken feet yellow membrane

405 (CFYM) resulting from chicken feet cleaning before cooking and consumption. They powdered such
406 bio-waste and used it as a bio-sorbent for miniaturized-SPE after a dilution of the oil sample
407 (hexane), extraction (DMSO) and dilution of the extract with deionized water (containing 2.5 g of
408 NaCl). Successful extractions were achieved, as the biological membrane contained proteins and
409 glycolipids with carboxyl and amine groups able to establish π-π and hydrophobic interactions with
410 PAHs. The resulting solution was analysed by HPLC coupled to an ultraviolet detector (UV), with
411 isocratic elution. The use of this natural adsorbent was a stimulating contribution, due its eco-
412 friendly and low-cost character, however, only five light PAHs were retained, and more research is
413 consequently needed in order to improve the potential of this procedure. Carbon nitride nanosheets
414 (CNNs) were used as sorbent for MSPE in the study conducted by Zheng et al. to determine PAH8 in
415 edible oils (Zheng et al., 2016). After eluting the retained PAHs with toluene, they were analysed by
416 GC-MS and satisfactory LODs were achieved (0.1-0.3 µg/kg), especially for the heavier compounds.
417 X. Shi et al. have recently developed a promising magnetic covalent organic framework
418 (Fe_3O_4@COF(TpDA)) material used as a sorbent for the 16 EPA PAHs (X. Shi et al., 2018). The
419 magnetic nanoparticles retained the PAHs through hydrophobic and π-π interactions after a ten
420 minutes incubation period. Then, analytes were eluted with ACN and analysed through HPLC
421 coupled to a diode-array detector (DAD) in forty minutes.

422 The quoted studies suggest an inspiring line of action in order to improve the performance of the
423 so-called smart materials for PAHs extraction from edible oils. Solid supports with molecular
424 recognition properties and/or magnetic characteristics are uplifting tools that may offer great
425 selectivity; their implementation in sample treatment protocols could finally lead to rapid and
426 simple methodologies. However, the preceding attempts exhibit some aspects susceptible of
427 improvement. First, the cost of the adsorbent must be lowered as much as possible, in order to
428 promote the access and general use of such material, which would also contribute to an effective

optimisation of the related procedures. Secondly, the reduction in the number of steps conducted during the sample treatment and the elimination of preparatory stages for the adsorbent material would tremendously increase its interest, as it would contrast with some laborious and time-consuming methodologies that are currently in use. Thirdly, reproducibility is a key factor that should be thoughtfully considered, paying attention to the morphology of the materials, the consistent retention of the analytes and the achievement of a complete elution. Finally, the development of a sorbent which is able to retain the complete collection of priority PAHs would be desirable. This prospect implies a major challenge, but remarkable progress have been already made, and more effective and sophisticated methodologies are currently being developed.

3 PAHs determination by liquid chromatography

The 16 EPA PAHs have been extensively separated by reverse-phase LC, using columns specifically developed for their analysis. The most widely used columns are based on modified C18 stationary phases, with 4.6 mm x 250 mm as typical dimensions and 5 µm particle size. Nevertheless, columns with different lengths, diameter and particle sizes have been also employed (as can be observed in Table 2) (Alves da Silva et al., 2018, 2017; L. K. Shi, Liu, Liu, & Zhang, 2015; X. Shi et al., 2018; Taghvaee et al., 2016). The optimum separation conditions usually imply a solvent gradient with ACN and water. Gradients normally start with a 40-50% ACN, in most cases (Barranco et al., 2003; Costopoulou et al., 2010; Gharbi et al., 2017; Martinez-López et al., 2005; Payanan et al., 2013; L. K. Shi et al., 2015; X. Shi et al., 2018; Stenerson et al., 2015; Taghvaee et al., 2016; Teixeira et al., 2007; Yousefi et al., 2018; W. Zhao et al., 2013); then this concentration is linearly risen to 89-100% in an approximate time of 45 min, as so suggests ISO 15753:2016. Some reports have indicated the use of gradients with a higher proportion of ACN (70-85%) at the beginning of the run (Alves da Silva et al., 2017; Camargo et al., 2011; Ergönül & Sánchez, 2013; Ji et al., 2017; Molle et al., 2017; Moreda et al., 2004; Purcaro et al., 2008; Rodríguez-Acuña et al., 2008a; Tfouni et al., 2014). Some of those

453 methodologies required isocratic segments to separate molecules with very similar polarities. As a
454 consequence, analysis time was not reduced, but adequate analytical parameters were obtained
455 either way. Only three reports applying an isocratic elution have been found within the revised
456 literature from the last fifteen years. One of them is the investigation of Farrokhzadeh et al.
457 (Farrokhzadeh & Razmi, 2018), which has been previously mentioned. The second one is the work
458 of Dost and Ideli (Dost & Ideli, 2012), who performed an isocratic elution with ACN 80% (v/v) to
459 achieve the determination of 9 EPA PAHs (Fl, Phe, A, F, P, BbF, BaA, BkF, BaP) in olive, corn and
460 sunflower oil. The third one is the work of Lage-Yusty (Lage Yusty & Cortizo Daviña, 2005), who used
461 a mixture of ACN/Water (78/22, v/v) to isocratically separate BaA, BeP, BbF, BkF, BaP, DBaA and
462 BghiP from supercritical fluid extracts obtained from vegetable oils. Although ACN/water mixtures
463 have been predominantly used for PAHs separation, a couple of examples employing other solvents
464 can also be found. Jiang et al. combined water, ACN and MeOH in a gradient (see Table 2) to
465 determine 15 EPA PAHs (Acy was not included) in Chinese vegetable oils (Jiang et al., 2015). Q. Wang
466 et al. also made use of a mixture of MeOH and water as a mobile phase to separate six EPA PAHs
467 (Q. Wang et al., 2018). Hollosi and co-workers employed MeOH and EtOAc as mobile phases, since
468 ACN generated poor signal intensities when standards were detected by MS, using atmospheric
469 pressure photoionisation (APPI) as ionisation source. In comparison with the use of ACN, eluent
470 strength was lower and common eluent order of PAHs was altered, however better signal-to-noise
471 ratios were obtained. LC-MS will be further discussed in section 3.2. “Mass spectrometry detector
472 after LC separation”

473 As far as the flow rate is concerned, ISO 15753:2016 recommends a value of 1.2 mL/minute. Some
474 adjustments have been made with respect to this guidance, and flow has been also set at values of
475 1 mL/min (Barranco et al., 2003; Camargo et al., 2011; Costopoulou et al., 2010; Ergönül & Sánchez,
476 2013; Gharbi et al., 2017; Ji et al., 2017; Molle et al., 2017; Moreda et al., 2004; Rodríguez-Acuña et

al., 2008a; X. Shi et al., 2018; Tfouni et al., 2014), 1.4 mL/min (Alarcón et al., 2012; Stenerson et al., 2015) and 1.5 mL/min (Dost & Ideli, 2012; Payanan et al., 2013; Purcaro et al., 2008; Teixeira et al., 2007; Q. Wang et al., 2018; W. Zhao et al., 2013). Alves da Silva and co-workers focused on the determination of the set of PAH4 in some cold-pressed vegetable oils, applying a lower flow rate (0.4 mL/min) and a column with the following dimensions: 100 mm x 2.1 mm x 1.8 µm (Alves da Silva et al., 2018, 2017). Total analysis time was consequently reduced and satisfactory LODs (0.08-0.3 µg/kg) were obtained. A similarly low flow rate was applied by Ciercierska and Obiedzinski, for the determination of some light PAHs and the set of 15 EU PAHs (except BcFl) within the same analysis (Ciecierska & Obiedziński, 2013). This challenging objective required longer analysis time, but the results were satisfactory and a suitable methodology for the simultaneous determination of 19 analytes within a single run was achieved.

3.1 Fluorescence detector for LC

Fluorescence spectrometry is the most widely extended technique for the detection of PAHs after their separation by LC. The inherent fluorescence of PAHs and their characteristic excitation and emission wavelengths make the FLD a proper choice in terms of sensitivity (Moret & Conte, 2000). Nonetheless, the occurring overlapping of some fluorescent bands limits the selectivity of the technique to discriminate between the molecules of interest in a complex matrix. Besides, neither all the 16 EPA PAHs nor the whole set of 15+1 EU PAHs can be detected by fluorescence. The Acy molecule presents a too low fluorescence signal, which has precluded its quantitation in many works (Barranco et al., 2003; Cao, Ruan, Chen, Hong, & Cai, 2017; Ergönül & Sánchez, 2013; Payanan et al., 2013; Teixeira et al., 2007). Another option to achieve Acy detection when pursuing the quantitative measurement of the complete set of EPA PAHs is the combination of the fluorimeter with a DAD detector. For example, Zhao et al. has put into practice this alternative, determining this compound at 228 nm (W. Zhao et al., 2013). The same occurs with the EU PAH CPP , which has to be determined

by DAD at 222 nm (Costopoulou et al., 2010; Simon, Ruiz, Von Holst, Wenzl, & Anklam, 2008) or 254 nm (Ciecierska & Obiedziński, 2013).

~~Figure 3a~~Figure 2a illustrates a chromatogram of the 16 EPA PAHs obtained by LC-FLD. The results correspond to the work of Payanan et al. (Payanan et al., 2013). In this case, the peak corresponding to Acy is missing, probably due to its lack of fluorescent emission.

3.2 Mass spectrometry detector after LC separation

MS detection has not commonly been the detection technique of choice, since the ionisation efficiency of PAHs is very low (due to their non-polar character) when the most widespread ion sources (i.e. electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI)) are used (Chung & Lau, 2015; Veyrand et al., 2007). In 2011, Hollosi and co-workers (whose study has been previously mentioned with regard to the selected mobile phases) developed the first proper methodology for the determination of 15+1 EU priority PAHs by LC-MS in edible oils (Hollosi & Wenzl, 2011). They investigated three different ionisation alternatives, with APPI resulting the most appropriate. On the contrary, APCI and the combination mode of APCI and APPI did not lead to high enough signal intensities, as the ionisation efficiency was lower than that achieved with APPI operating in positive mode.

Furthermore, dopant assistance was also evaluated by these authors. Generally, the dopant molecule is an easily ionisable specie that absorbs the photons and transfers the energy to the sample molecules, thus avoiding energy losses and enhancing ionisation efficiency (Kauppila et al., 2002). In the mentioned study, acetone, toluene, 2,4-difluoroanisole, xylene and anisole were examined as dopant agents. Anisole reported the best values, because its higher proton affinity allowed its remaining for longer time in the ionisation source, hence facilitating PAHs ionisation. In this case, mobile phase of ACN was replaced by methanol, due to an ion suppression phenomenon

that led to reduced signals. This ion suppression effect could be due to the high proton affinity and high photoabsorption cross-section of ACN, which lowers the number of available photons for the ionisation.

The determination of the 16 EPA PAHs by LC-MS in edible oils was published for the first time in 2015, by L. K. Shi et al. (L. K. Shi et al., 2015). They also made use of a dopant assisted-APPI as interface, evaluating chlorobenzene and toluene as both capable dopants. Although chlorobenzene doping offered higher signals for PAHs with three and four rings, chromatogram noise was also enlarged, leading to a lower sensitivity. Therefore, toluene was pointed out as the substance of choice. Remarkably low LODs (0.006–0.156 µg/kg) were obtained with this procedure, as shown in Table 2.

4 PAHs measurement by gas chromatography

GC has been a commonly selected option for the analysis of PAHs in edible oils. This technique combines an efficient separation and the possibility to easily incorporate a MS detector, obtaining valuable and reliable information about the contamination of the samples and giving the possibility to resolve overlapping peaks with distinctive molecular mass. Moreover, MS gives the chance to the analyst of taking advantage of the isotope-dilution strategy, consisting on the addition of isotope-labelled or deuterated-labelled standards, which allows the achievement of accurate identification and quantification results (Purcaro et al., 2016; Rose, 2010; Wolska, Gdaniec-Pietryka, Konieczka, & Namieśnik, 2009). It has been successfully applied in many reports (Bogusz et al., 2004; Fromberg et al., 2007; Ju et al., 2020; L. K. Shi et al., 2016; Veyrand et al., 2007; J.-H. Wang & Guo, 2010; Wolska et al., 2009; Zelinkova & Wenzl, 2015). ~~Figure 3b~~Figure 2b shows a typical chromatogram obtained by GC-Q-MS, containing 16 peaks corresponding to the 16 EPA PAHs and four additional peaks of isotopically labelled standards.

Even though rigorous clean-up processes are required to avoid lipidic compounds to accumulate and alter the column, GC-MS may act as a solution for the determination of those PAH whose fluorescence is too low to be detected by the previously described HPLC-FLD methodologies (Poster, Schantz, Sander, & Wise, 2006).

Stationary phase of the GC columns is usually characterised by a low polarity. Capillary columns of (5%-Phenyl)-methylpolysiloxane or equivalent, with dimensions of about 30 m x 0.25 mm and 0.25 µm film thickness have been widely employed (Alomirah et al., 2010; Arrebola et al., 2006; Ballesteros et al., 2006; Drabova et al., 2013; Hossain & Salehuddin, 2012; Jung et al., 2013; Rascón et al., 2018; Vichi et al., 2007; J.-H. Wang & Guo, 2010; Y. Zhang et al., 2017; Q. Zhao et al., 2011) to separate the 16 EPA PAHs. Longer columns have also been used (Fromberg et al., 2007; Guillén et al., 2004; Mohammadi et al., 2020; L. K. Shi et al., 2016), with the consequent extension of the total analysis time. For instance, Guillén and co-workers used a 60 m x 0.25 mm x 0.25 µm column to achieve the separation of a numerous group of PAHs (including the 16 EPA PAHs and some of their methylated derivatives) in five samples of POO (Guillén et al., 2004). Shorter columns can be utilised as well; indeed, Chung et al. employed a 20 m x 0.18 mm x 0.15 µm column to analyse the EPA set of PAH4 (Chung & Lau, 2015).

The set of 15+1 EU PAHs have not been so extensively studied as the group of 16 EPA PAHs. The teams of Bordajandi and Gómez-Ruiz et al. reported in 2008 and 2009, respectively, GC-MS methods for the 15+1 EU PAHs determination in edible oils, paying attention to the column dimensions and polarity, injection mode, etc. (Bordajandi et al., 2008; Gómez-Ruiz & Wenzl, 2009). The compounds under study in the just quoted reports are heavier and more structurally similar molecules than EPA PAHs. As a result, the discrimination of some compounds may be arduous, as they are susceptible of coelution during the chromatographic separation (what is particularly important for PAHs isomers which cannot be resolved by extracting their corresponding *m/z* traces or common fragments). In

this regard, CPP-BaA-Chr, BbF-BjF-BkF and DBahA-IP are the most critical groups. Gómez-Ruiz et al. and Bordajandi´s team independently optimized such separation through the evaluation of the classic non-polar columns, mid-polar and mid-to-high polar phases (Bordajandi et al., 2008; Gómez-Ruiz & Wenzl, 2009). Finally, the mid-polar stationary phase, consisting on a (50%-Phenyl)-methylpolysiloxane, 60 m x 0.25 mm x 0.25 µm DB-17MS column provided the best isomers resolution in both studies. A similar, but shorter column (9 m x 0.10 mm x 0.10 µm BPX50) was employed later by Purcaro and co-workers to determine the set of PAH8 (plus BjF and BeP) in vegetable oils (Purcaro, Picardo, et al., 2013).

Specific details about the temperature gradients applied within each study can be found in Table 3. Generally, oven temperature starts at 70-80ºC, and it is progressively increased by applying diverse temperature gradient slopes. Only a few reports (Alomirah et al., 2010; Bogusz et al., 2004; Cassimiro Belo et al., 2012; Chung & Lau, 2015; Guillén et al., 2004; Hossain & Salehuddin, 2012; Purcaro, Morrison, et al., 2007; Vichi et al., 2005, 2007) stated a lower starting temperature (40-50ºC). In the case of Vichi and co-workers the lower temperature is justified considering the variety of target analytes to be encompassed within the same analysis (Vichi et al., 2005, 2007).

In some cases, the separation of the 15+1 EU PAHs required higher starting temperatures, as reported by Jung et al. (Jung et al., 2013), Veyrand and co-workers (Marchand et al., 2007) (who started the gradient at 150ºC and 110ºC, respectively), and the teams of Gomez and Wenzl (Gómez-Ruiz & Wenzl, 2009), Bordajandi (Bordajandi et al., 2008), Purcaro (Purcaro, Morrison, et al., 2007) and Drabova (Drabova et al., 2013). This fact is easy to understand considering that such temperatures are needed to elute heavier dibenzopyrenes (absent in the 16 EPA PAHs set). Generally, when the highest temperature of the run (around 280-360ºC) is reached, an isocratic elution is maintained during some minutes (oscillating from 9 to 20 minutes).

The mobile phase used in most of the studies is primarily helium. Due to the low PAHs concentration in edible oils, analytes are always injected in splitless mode. Only two studies reported a different kind of injection, applying a 20% (Hossain & Salehuddin, 2012) and 25% split mode (Mohammadi et al., 2020). The sample injection step must be thoughtfully optimized, because of the differences of molecular weights among the sets of PAHs. It is possible that not all the compounds behave equally during the transfer of the analytes to the column; heavier compounds might be discriminated and, correspondingly, underestimated in the determination (Gómez-Ruiz & Wenzl, 2009). To avoid this problem, programmable temperature vaporizing (PTV) injection has been applied by some authors (Ballesteros et al., 2006; Bordajandi et al., 2008; Zelinkova & Wenzl, 2015). The temperature gradient established in this injection mode allows to adjust the temperature of vaporization according to a specific group of compounds, normally starting with lower temperatures, around 55-70ºC (meant for the volatilization of lighter PAHs) and progressively increasing the temperature while heavier compounds are injected, reaching 300-400ºC.

Regarding the flow rate, the most recurrently used value is 1 mL/min. There are some studies reporting flow rate settings of 1.2 mL/min (Zacs et al., 2018; Q. Zhao et al., 2011; Zheng et al., 2016) or 1.3 mL/min (Drabova et al., 2013). Additionally, some papers dealing with EU PAHs applied higher fluxes, as 1.5 mL/min (Bordajandi et al., 2008; Gómez-Ruiz & Wenzl, 2009) and 1.7 mL/min (Chung & Lau, 2015). Xu et al. made use of a flow gradient during the simultaneous determination of EPA and EU PAHs, switching from 1 mL/min to 1.7 mL/min after 10 minutes of analysis (Xu et al., 2015).

The MS detection is normally carried out through a quadrupole analyser (Q), with electron impact (EI) ionization, operating in single ion monitoring (SIM) mode. However, it is possible to find applications where some authors determined their target PAHs by means of a triple-quadrupole (QQQ) (Arrebola et al., 2006; Hollosi & Wenzl, 2011; L. K. Shi et al., 2015; Veyrand et al., 2007; Xu et al., 2015). Among them, Xu and co-workers (Xu et al., 2015) applied a multiple reaction monitoring

618 (MRM) and Arrebola et al. (Arrebola et al., 2006) combined SIM and MS/MS modes, therefore being
619 able to identify each compound by means of their precursor ion and characteristic fragments.
620 Simultaneous scan/SIM acquisition mode has been used by Purcaro et al. (Purcaro, Picardo, et al.,
621 2013) to increase sensitivity without losing any structural information for further identification. A
622 similar strategy was applied by Guillén et al. (Guillén et al., 2004); in their research, scan mode was
623 used to determine the type of compounds present in the samples, whereas SIM was used to identify
624 and quantify the found PAHs. Full scan mode was applied by the teams of Diletti (Diletti et al., 2005)
625 and Sun (Ying Sun et al., 2017).

626 Some other mass analysers were employed in other three studies. Ballesteros et al. (Ballesteros et
627 al., 2006) evaluated the presence of different pesticides and four benzopyrenes (BaP, BkF, BghiP,
628 BeP) in olive and olive oil and POO using an ion trap (IT) mass spectrometer. IT has been utilised in
629 other cases, such as the studies conducted by Hossain and Salehuddin (Hossain & Salehuddin, 2012)
630 and Diletti and co-workers (Diletti et al., 2005). Regarding bidimensional approaches, only two
631 reports have been published to date (Drabova et al., 2013; Purcaro, Morrison, et al., 2007). Both
632 studies aimed to determine the group of 15+1 EU PAHs by performing a two dimensions GC coupled
633 to a time-of-flight (ToF) mass spectrometer (GC x GC-ToF), applying the conditions specified in Table
634 3; Drabova et al. (Drabova et al., 2013) were able to avoid coelutions within the separation, whereas
635 Purcaro and co-workers (Purcaro, Morrison, et al., 2007) smartly reported the quantitative data of
636 coeluting molecules (BbF, BjF and BkF) as the sum of these three benzopyrenes.

637 **5 Other analytical strategies not entailing chromatographic separation**

638 As stated above, the chromatographic analysis of PAHs (by LC or GC with different kind of detectors)
639 is very widely used and give to the analyst interesting information on the PAH-profiling of a
640 particular sample. Regarding separative techniques, capillary electrophoresis (CE) could be useful
641 too. The absence of electric charge in PAHs could suggest a difficult migration through the capillary,

642 which would affect the efficiency of the separation. Nevertheless, this can be solved by the addition
643 of ionic species to the buffer (Nolte & Andersson, 2011). These species (micelles, cyclodextrins, ionic
644 or polymeric surfactants, etc.) will establish different interactions with PAHs. The modulation of the
645 buffer composition to create individual interactions for each analyte can modify their relative
646 mobility and allow their separation. The application of cyclodextrin-modified CE to determine PAHs
647 in real samples of vegetable oils was performed by Ferey et al. (Ferey et al., 2014).

648 Separative strategies display multiple benefits, but it is also true that such analyses can be
649 considered in some cases as time and solvent consuming. Indeed, when the sample throughput is a
650 priority, approaches avoiding the need of the chromatographic (or electrophoretic) separation-
651 dimension (prior detection) can represent an appropriate option. Therefore, it would be desirable
652 to have screening methods to sift out the positive samples, which could be confirmed by a LC or GC
653 methodology in a subsequent stage. It is well-known that a screening must detect the presence of
654 a specific class of analytes at the concentration of interest, providing a low rate of false compliant
655 samples, and exhibiting high throughput and adequate analytical features (Alarcón et al., 2012).

656 Fluorescence spectroscopy (FLS) is considered an alternative, since most of the PAHs present a
657 strong native fluorescence; moreover, the measurements are rapid and inexpensive. Unfortunately,
658 their broad fluorescence bands can lead to serious spectral overlap. This fact, together with the
659 presence of other interfering compounds have greatly limited the application of traditional
660 fluorescence strategies in multi-component analysis of vegetable oils. In any case, several
661 applications can be found in literature regarding the determination of PAHs by using FLS, combining
662 the use of the just mentioned technique with advanced chemometric tools aiming at enhancing the
663 spectral resolution (Alarcoń et al., 2013; Alarcón et al., 2012; Liu et al., 2016; Vásquez, Báez, Bravo,
664 & Fuentes, 2013). For instance, Alarcón et al. evaluated the potential of microwave-assisted LLE and
665 SPE (silica, C18 and graphitized carbon black) coupled with FLS (employing one- to three-way

spectral data) for the rapid detection of heavy PAHs in olive and sunflower oils (Alarcón et al., 2012); the same team, one year later, developed another application where they compared the usefulness of unfolded partial least-squares with residual bilinearization (U-PLS/RBL) and parallel factor analysis (PARAFAC) to process the fluorescence excitation-emission data matrices (Alarcoń et al., 2013). Vásquez et al. determined 7 heavy PAHs in EVOOs based on the measurement of excitation-emission matrices on nylon membranes coupled to U-PLS/RBL, achieving detection limits from 0.29 to 1.0 ug/kg and reasonably good recoveries (between 64 and 78%) (Vásquez et al., 2013). In a more recent example, a second-derivative nonlinear variable-angle-matrix isopotential synchronous fluorescence spectroscopic approach has been proposed for the simultaneous determination of PAH4 in vegetable oils with ultrasonic-assisted extraction (Liu et al., 2016). In most of these instances, the authors compared the predicted data with those coming from LC-FLD, achieving good agreement.

Even though all the chosen examples are works of very high quality, most of them lead to predicted (not absolute) quantitative values and entail the use of intricate data treatment.

Another tool to be mentioned in this section is Raman spectroscopy (RS), which has an important role in oil safety, overcoming the disadvantages of other analytical techniques (Hu, Yang, Liu, He, & Zhang, 2018). BaP has been determined by applying RS. Fu et al. have synthesized inositol hexaphosphate (IP6) to stabilize gold nanoparticles (IP6-AuNPs) (S. Fu et al., 2015), describing a promising surface-enhanced RS (SERS) protocol with ppb-sensitivity. Interestingly, the authors avoided complicated pretreatment of oil samples (if compared with other applications) as well as complex hydrophobic surface modifications on AuNPs. The method was described as a very quick, direct, portable and reliable manner for on-site evaluation of BaP concentration in edible oils.

688 It is also worthy to include within this part of the review other illustrative examples where the
689 potential of matrix assisted laser desorption/ionization mass spectrometry (MALDI) has been
690 assessed. In a recent publication, the MALDI-ToF-based determination of BaP by using the metal-
691 organic framework (MOF) MIL-101(Fe) as a matrix has been described (J. Wang et al., 2018). After a
692 careful optimisation of sample preparation protocol, type of target plate, concentration of MIL-
693 101(Fe), dispersant for MIL-101(Fe) and laser energy, the developed method exhibited a detection
694 limit of 0.1 ug/L (1 min of analysis), a wide linearity range and adequate reproducibility. Its
695 applicability was checked by analysing sesame oil, linseed oil, camellia seed oil, and olive oil spiked
696 with BaP at three different levels. The authors compared the performance of their methodology
697 with other previously published ones using different types of matrix, such as graphene and
698 Fe_3O_4@SiO_2/OCNT for MALDI (Li et al., 2011; J. Zhang, Dong, Cheng, Li, & Wang, 2011) and MIL-
699 100(Fe) for surface-assisted laser desorption/ionization MS (Shih et al., 2013). In the last three
700 quoted papers, no “real” samples were tested.

701 In recent years, immunoassay methods have been applied in environmental and food analysis of
702 PAHs. These approaches have been defined by several authors as highly sensitive, selective and cost-
703 effective alternatives to complement traditional chromatographic analysis (Ma & Zhuang, 2018; Y.
704 F. Zhang & Gao, 2017). Although there have been quite a few antibodies and immunoassays for
705 PAHs available , there is room for improvement and more novel antibodies and immunoanalytical
706 methods are still welcome. Two applications focused on the determination on BaP residues by
707 applying immunoassays can be mentioned (Pschenitza et al., 2014; Xi, Shi, & Lu, 2016); in the latter,
708 the authors selected some vegetable oil samples.

709 We can conclude this part of the review standing out that no analytical strategy in this section can
710 compete with LC and GC (with FLD and MS as detection systems, respectively), in particular, when
711 the aim of the analyst is to reveal the complete PAH profile. Some of the downsides of the included

712 alternative analytical tools are: spectral overlapping, requirement of using advanced chemometric
713 approaches, or leading only to predicted quantitative values (not absolute). That does not mean
714 that LC-FLD and GC-MS methodologies are the perfect ones; LC-FLD could exhibit sensitivity
715 problems due to a too low fluorescence signals and in GC-MS, the baseline separation of several
716 PAHs is challenging. Having reliable and robust screening methods to be applied before the profiling
717 ones would be indisputably useful.

718 **6 PAHs incidence. Is there any reliable PAH as an indicator of their occurrence in edible**
719 **oils?**

720 The previous extraction and analysis methodologies have been applied to a large variety of
721 vegetable oils. As previously mentioned, the source and category of the oils determine, to some
722 extent, the final concentration of PAHs. However, rigorous comprehensive examinations of the
723 different edible oil classes and the PAHs incidence in each one of them are not abundant in
724 literature. Table 4 summarises all the studies aiming to determine PAHs in edible oils that have been
725 included in this review. The table presents the identity of all the molecules that were intended to
726 be detected and quantified by the authors, and which of them were found at higher levels within
727 the results of each study. The molecule of BeP, whose determination has been intended in many
728 reports, has been also included in the table, although it is not part of any of the contemplated
729 priority list (EPA or EU). This is the first time that individual occurrence of every analyte included in
730 each investigation is considered and thoughtfully studied. Prevalently found molecules are indicated
731 in Table 4, according to their relative abundance in respect to the rest of the compounds determined
732 in each report. No crossed comparison among separated reports has been conducted, as
733 concentration ranges were not equal between different investigations and also because PAHs
734 content of each type of oil strongly depends on the specific processing that the sample has suffered
735 and the cultivation area of the raw material (that can be affected by factors like proximity of

736 factories, fires, etc.). Thus, the table only gives information about the most prevalent compounds
737 that were found at the particular conditions (and selected samples) of each report. The following
738 criteria has been adopted to denote a compound as abundant in the table: the most concentrated
739 PAHs found in the study has been marked with an "X", followed by the second-largest analytes. In
740 some cases, some other compounds have been pointed too if their concentration were very similar
741 to the second-largest molecule/s. Exceptionally, additional compounds have been marked if a
742 considerable difference between their concentration and the lowest-level molecules occurred
743 within the study.

744 As it can be seen in the first page of Table 4, EVOO, VOO and olive oil samples usually contain light
745 PAHs, principally Na. In the case of POO, the molecules of Na and P, as well as Chr and BeP, have
746 been found as abundant compounds (in relation with the concentration of the rest of analytes). It
747 is worth highlighting the crude POO analysed by Ergönül and Sánchez (Ergönül & Sánchez, 2013);
748 this sample stood out not only because of the presence of light and heavy PAHs, but also due to the
749 remarkably high levels of those compounds, with concentrations of 3251.84 ± 32.48 μg/kg for the
750 total PAHs content, opposite to the much lower concentration values (28.29 ± 0.15 μg/kg) assigned
751 for refined pomace samples. Crude pomace oils are logically more contaminated, owing to the use
752 of potentially polluted solvents to extract the oil and thermal treatment to evaporate the solvent
753 (Bogusz et al., 2004; Ciecierska & Obiedziński, 2013; Mafra et al., 2010). Some PAHs are eliminated
754 during the refining process, but, as shown in Table 4, refined POO still contain significant relative
755 concentrations of several of these compounds.

756 Considering the sunflower oil, most of the reports (Dost & Ideli, 2012; Farrokhzadeh & Razmi, 2018;
757 Payanan et al., 2013; Rascón et al., 2018; L. K. Shi et al., 2016; Yousefi et al., 2018; Y. F. Zhang & Gao,
758 2017; Zheng et al., 2016) focused in the determination of EPA PAHs, encountering higher relative
759 levels of light PAH, from which Na, Phe, A and F are noteworthy. BeP was only determined in one

760 article (Moreda et al., 2004), but it was one of the most concentrated compound in the analysed
761 samples. Peanut oil has been investigated to determine EPA PAHs (Ji et al., 2017; Jiang et al., 2015;
762 L. K. Shi et al., 2015, 2016; Y. Zhang et al., 2017). As shown in the table, Na and Phe have been
763 labeled as prevalent by all of the studies. Following these compounds, other analytes with major
764 relative abundance are Fl, F and P. The molecules of Na and Phe also presented a considerable
765 occurrence in several studies addressing the analysis of soybean oil (Jiang et al., 2015; Payanan et
766 al., 2013; Rascón et al., 2018; L. K. Shi et al., 2015, 2016; Xu et al., 2015; Y. Zhang et al., 2017). Other
767 PAHs from this matrix exhibiting a noticeable presence are A, F, P and Chr.

768 The terms “colza”, “canola” and “rapeseed” all correspond to different cultivars from the same
769 species, and, therefore, they have been grouped within the same sub-table and will be compared
770 as an only one type of oil. The occurrence of light PAHs such as Na and Phe was noteworthy. Acy
771 and F were prevalent in half of the investigations addressing their determination. Other substances
772 -Chr, BaP and BkF- stood out as additional prevailing PAHs in three of the seven reviewed reports.

773 When F was determined in sesame oil (Ciecierska & Obiedziński, 2013; Rascón et al., 2018; L. K. Shi
774 et al., 2016), it was found in all the cases at high relative levels. The compounds Na, Ace, Acy and Fl
775 were only determined by the teams of Rascón (Rascón et al., 2018) and L. K. Shi (L. K. Shi et al.,
776 2016); the latter study found Na, Acy and Fl present at high concentrations (in comparison with the
777 rest of analytes). Besides, from the PAH8 group, Chr could also be designated as one of the most
778 prevalent contaminants considering the results of several of the examined studies. Concerning corn
779 oil, it prevalently contained Na, Ace (found as prevalent in one of the two studies addressing its
780 determination), Phe and P.

781 Four studies from the last fifteen years have analysed coconut oil as a source of PAHs (Alves da Silva
782 et al., 2018, 2017; Hossain & Salehuddin, 2012; Rascón et al., 2018). Three of those investigations

783 coincided in setting Chr and BaP as the most predominant PAHs in the samples. Other remarkable
784 molecules are Na, A and P. The complete set of analytes (PAH4) considered by Alves da Silva and co-
785 workers (Alves da Silva et al., 2018, 2017) has been marked as relatively significant in the table
786 because all of them presented similar concentrations. Thus, the selection of only a few prevalent
787 compounds derived from those studies would have interfered with the established criteria to
788 evaluate the PAHs occurrence in the rest of investigations included in Table 4.

789 Safflower oil was analysed solely by the group of Alves da Silva and co-workers, in two different
790 studies (Alves da Silva et al., 2018, 2017). Both reports coincided in the indication of BaA and Chr as
791 the most abundant in comparison with the rest of the determined PAH4. When cold-press evening
792 primrose oil was analysed, BaA and Chr were again the major found PAHs (Alves da Silva et al., 2018,
793 2017), whereas lighter PAHs, such as Phe, F and P were found at outstanding levels in another study
794 (Ciecierska & Obiedziński, 2013). A similar situation happened with cold-press linseed oil, as can
795 been seen in Table 4. In contrast, Zelinkova et al. did not detect any of the PAH4 compounds neither
796 in the studied linseed oil nor primrose oil supplements (Zelinkova & Wenzl, 2015). Regarding
797 pumpkin oil, Drabova and co-workers found high levels of the set of PAH4 (other notable PAHs were
798 BghiP, IP and CPP) (Drabova et al., 2013). From this PAH4 group, only BaA and BaP stood out in the
799 study of Ciecierska and Obiedzinski (Ciecierska & Obiedziński, 2013), but other light PAHs were
800 found at considerable relative concentrations.

801 From those PAHs that have been examined in both grapeseed oil (Ju et al., 2020; Purcaro, Picardo,
802 et al., 2013; L. K. Shi et al., 2016) and sea buckthorn oil (Drabova et al., 2013; Zelinkova & Wenzl,
803 2015), Na, Phe, Chr, BkF, Bghi and IP were predominant in the first oily matrix and BaA and Chr
804 (followed by BbF, BaP and CPP) in the second one. Perilla seed oil principally contained BaA, Chr and
805 CPP (Ju et al., 2020; Jung et al., 2013). Ju and co-workers examined rice bran oil and red pepper oil
806 (Ju et al., 2020). As in many other cases, Chr was found predominant, as well as BbF for the red

807 pepper oil. Camellia oil -analysed by Zheng et al. - was rich in Chr and BbF (Zheng et al., 2016). The
808 molecules of Na, A and Phe were found at a high occurrence in mustard oil when analysed by
809 Hossain and Salehuddin (Hossain & Salehuddin, 2012). According to L. K. Shi et al. (L. K. Shi et al.,
810 2016), wheat germ oil contained high relative levels of Na, Fl, Phe, A, F and P. In the case of palm oil
811 analysed by Payanan et al. (Payanan et al., 2013), numerous PAHs were found to highly contribute
812 to the overall contamination of this oil sample, with presence of light and heavy PAHs at rather
813 significant concentrations.

814 The rest of oils listed in Table 4 are a variety of non-conventional vegetable oils obtained only by
815 cold-pressing, in a process similar to that normally applied to obtain VOO. They were analysed by
816 Ciecierska and Obiedzinski; the authors intended the determination of the complete set of 15 EU
817 PAHs plus four compounds from the group of light PAHs listed by the US EPA; light PAHs were
818 predominant in all the cases, in particular Phe and F (substances which were detected in every
819 evaluated sample) (Ciecierska & Obiedziński, 2013).

820 Most of the samples reported in the table did not conflict with the current regulation regarding the
821 permitted limits in fats and oils, but they did contain considerable levels of some PAHs. As the
822 regulation only consider the group of PAH4 or PAH8, and BaP, some samples relatively rich in light
823 PAHs could escape from the applied food safety controls. This finding casts some doubts about the
824 number and identity of the molecules that should be monitored. It is very reasonable to
825 contemplate in the regulation those compounds for which oral carcinogenity is known, but the
826 synergic action of the rest of PAHs must be taken into account as well. Regarding the role of BaP,
827 some authors have investigated its suitability as indicator of the presence of PAHs in food samples.
828 Rodríguez-Acuña and co-workers found a good correlation between BaP concentration and the sum
829 of other nine PAHs determined in different categories of olive oils (Rodríguez-Acuña et al., 2008a).
830 In contrast, Alomirah et al. found that BaA and Chr, on a proportion of 37% and 45%, were

831 respectively present in the forty-four analysed oils, despite a negative result for BaP (Alomirah et
832 al., 2010). This scenario could have occurred in the report of Lv et al. (Lv, Yang, Pang, Xie, & Shen,
833 2019). BaP was the only PAH determined over a wide range of analysed oils (peanut, pepper,
834 rapeseed and soybean oil). However, BaP was not found in any of the real samples. In the current
835 review, Table 4 corroborates that a single determination of BaP is not a reliable approach to confirm
836 the presence (or absence) of PAH contamination, as EFSA already indicated in 2008. It was found
837 that many samples that did not contain considerable levels of BaP were in fact contaminated with
838 other PAHs, what set the detection of BaP as a mere indicator of a positive test for PAHs in food
839 samples.

840 At this point, it seems pertinent to stress that in 2008, Simon and co-workers reported the results
841 of an inter-laboratory study in which the participant laboratories had to determine (using the
842 methodology and platform of their election) as many of the 15+1 EU PAHs as possible in some
843 vegetable oils (Simon et al., 2008). Only a few of the participants (around 20%) reported the
844 concentration of the whole group of EU PAHs, whereas most of them had problems determining
845 some of the compounds, especially CPP, BcFl and BjF. Even in some cases, the eight EPA PAHs that
846 are included in the EU list could not be quantified, despite being so much familiar to the analytical
847 community. Ultimately, a minority of the reports included in the inter-laboratory initiative met the
848 EU recommendation that was in force at that moment (European Union, 2005). This situation can
849 be brought to the current moment. Excellent investigations have been conducted, providing useful
850 information about oils and fats contamination with PAHs. Nonetheless, diverse techniques are
851 applied in each report, and also very different subgroups of PAHs are analysed in each case. In this
852 context, a standardisation of the applied methodologies and the target analytes would be of great
853 interest. This would enable future comparisons between investigations and a better knowledge of
854 the studied matrices.

7 Conclusions and future perspectives

The importance of an accurate determination of PAHs in foods relies on their carcinogenic effects for the consumers. Edible oils constitute the principal food being analysed in search for PAHs. For that reason, numerous methodologies for the quantitative estimation of these compounds in lipidic matrixes have been proposed. Nevertheless, in many cases, they are based on long and tedious procedures. Studies from the last fifteen years have been reviewed in the current contribution. Most of them make use of a LLE and/or SPE step to extract and purify the PAHs from the samples, as recommended in ISO 15753:2016. Still, the tendency of reducing the time and solvent consumption has prompted the development of novel approaches that include MWCNTs, MIPs, GO and other sophisticated adsorbents that promise a future improvement on the efficiency of the process. Extracts derived from the sample treatment are usually determined by LC-FLD or GC-MS. The use of LC-MS and GC-MS/MS has also been reported and discussed in a few investigations. Regarding the PAHs content in real samples, a thoughtful examination of the studies from the last fifteen years have confirmed that the traditional marker of BaP is not always present in the contaminated samples. Also, it has been revealed that light PAHs, especially Na and Phe, are the most recurrent molecules in vegetable oils. Regarding heavier compounds, Chr could be pointed out as a recurrent molecule in the analysed matrices.

As discussed in different sections of the present paper, quantitative detection of PAHs has traditionally been conducted through multiple-step methodologies. One of the major drawbacks of those procedures is that reproducibility and recovery of compounds may be affected during the process. To overcome such shortcomings, it would be desirable to unify (if possible) the whole sample treatment in a single step which is able to satisfactory extract and purify the compounds of interest. SPE (and miniaturized-SPE) remains a promising isolation approach, although more research, including on-line coupling with chromatographic system, is needed. As reflected in this

879 review, some other approaches have been already carried out in this direction, through the
880 development and application of advanced adsorbents for the analysis of edible oils. In many cases,
881 the use of nanomaterials or modern smart materials only requires a dilution of the sample prior to
882 the clean-up and/or extraction steps. As a matter of fact, it would be very recommendable to focus
883 in those innovative strategies and continue to improve their performance to ensure a maximum
884 reproducibility and robustness for the determination of PAHs in food-related samples. New
885 stationary phases in LC and GC to reduce analysis time and enlarge the number of analytes to be
886 determined within a single run are desirable too. Apart from the traditional detectors, the
887 performance of MS in LC should be improved to fully exploit this powerful platform. ~~Figure 4~~
888 ~~presents a scheme of the just mentioned aspects regarding the future perspectives of PAHs~~
889 ~~determination in edible oils.~~

890 Besides, a better knowledge about the compounds that actually contaminate the oils and are found
891 at higher relative concentrations in the samples would contribute to an improved control of the
892 food safety. Harmonisation of analytical methodologies, inter-collaboratory studies and the use of
893 Certified Reference Materials (crucial in verifying the accuracy and in establishing traceability of
894 analytical measurements) are also imperative to enlarge the data about PAHs in vegetable oils. This
895 will allow for the corroboration of the established maximum levels (or the proposal of new ones, if
896 required) and the extension of the priority list.

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Table 1 Identity of PAHs generally determined in food.

Excitation wavelengths (nm)	Emission wavelengths (nm)	Compound		
275	322	Naphthalene (Na)	EPA	
270	322	Acenaphthene (Ace)		
DAD		Acenaphthylene (Acy)		
270	304	Fluorene (Fl)		
251	364	Phenanthrene (Phe)		
251	402	Anthracene (A)		
280	460	Fluoranthene (F)		
270	406	Pyrene (P)		
270	388	**Benzo(a)anthracene (BaA)**		EU
270	386	**Chrysene (Chr)**		
256	446	**Benzo(b)fluoranthene (BbF)**		
292	406	**Benzo(a)pyrene (BaP)**		
292	414	**Benzo(k)fluoranthene (BkF)**		
295	404	**Dibenz(a,h)anthracene (DBahA)**		
292	394	**Benzo(g,h,i)perylene (BghiP)**		
274	496	**Indeno(1,2,3-cd)pyrene (IP)**		
DAD		Cyclopenta(cd)pyrene (CPP)		
309	359	Benzo(c)fluorene (BcFl)		
270	420	5-methylchrysene (5MCh)		
270	500	Benzo(j)fluoranthene (BjF)		
270	420	Dibenzo(a,l)pyrene (DBalP)		
270	420	Dibenzo(a,e)pyrene (DBaeP)		
270	470	Dibenzo(a,i)pyrene (DBaiP)		
270	470	Dibenzo(a,h)pyrene (DBahP)		
264	410	Benzo(e)pyrene (BeP)		

-Data included within the table were obtained from the reports of Teixeira et al., 2007; Costopoulu et al., 2010 and Payanan et al., 2013 and may be subjected to slight variations. Emission and excitation wavelengths of BcFl were taken from Songsermsaku et al., 2018, who analysed spiked acetonitrile solutions.

-The regulatory organism that has recommended their monitorisation has been indicated in different columns (colouring the cells of the considered compounds by each organism). Groups of PAH4 (lighter shaded, in blue) and PAH8 (darker shaded, in blue) have been highlighted. The molecule of BcFl, pointed as mutagenic by the JEFCA, has been included in the EU priority PAHs. The program of excitation and emission wavelengths generally used for the detection of PAHs in acetonitrile/water are also provided. The molecule of benzo(e)pyrene (BeP), recurrently determined in the literature, has been included within the compounds of

interest of this review, even though its determination has not been advised by the EPA or the European Union (EU).

Table 2 Thorough description of the experimental parameters used in the research works discussed in the present review (regarding **liquid chromatography**), including the number (and identity) of determined compounds in each study, as well as parameters about sample preparation, liquid chromatography conditions, detection settings and analytical performance of the applied methodologies.

Ref.	Nº of determined compounds	Source	Sample treatment	Separation	Detection	Analytical performance[a]
(ISO 15753, 2016)	15 EPA PAHs (Acy n.d.)	Animal and vegetable fats and oils	- 2.5 g - LLE (10 mL ACN/Acetona 60:40, v/v) + Sonication - SPE C18; AS: MeOH, ACN; ES: ACN/Acetona 60:40, v/v - SPE Florisil; AS: CH_2Cl_2, hexane; ES: hexane/ CH_2Cl_2 (75:25, v/v)	- ZORBAX Eclipse (250 mm x 4.6 mm x 5 µm) + C18 guard column - A: ACN, B: ACN/Water (50:50) - 100% B (0-5'), 100%-40% B (5-27'), 40%-0% B (36-41') - 1.2 mL/min	FLD	LOD: 0.6 µg/kg (F and BghiP: 0.3 µg/kg; IP: 1 µg/kg) RSD < 5% Recov > 60-70%
(Lv et al., 2019)	BaP	Peanut, pepper, rapeseed and soybean oil	- 0.5 g - 5 mL hexane - dSPE: MIL-101(Cr); ES: acetone	- XSelect HSS C18 column (150 mm x 2.1 mm x 2.5 µm) - A: ACN, B:Water - Isocratic - 0.3 mL/min	FLD	LOD: 0.19 ng/mL RSD: 0.4-15% Recov: 79.6-117.1%
(Shi et al., 2018)	14 EPA PAHs (Acy and IP n.d.)	Edible oil (not specified)	- 2 g - LLE (10 mL ACN/acetone 60:40, v/v) + Sonication - MSPE: Fe_3O_4@COF(TpDA)	- Hypersil gold (150 mm x 4.6 mm x 3 µm) - A: ACN, B: ACN/Water - 50-65% B (0-30'), 65-70% B (30-35'), 70-100% B (35-40') - 1 mL/min	DAD (254 nm)	LOD: 0.03-0.73 µg/L RSD: 1.4-2.5% Recov: 82.5-102.5%
(Farrokhzadeh and Razmi, 2018)	Na, Phe, A, F and P	Olive and sunflower oil	- 2 mL - 4 mL hexane - 8 mL DMF - Diluted to 50 mL (Water + NaCl) - SPE (CFYM)	- Perfectsil target ODS-3 (250 x 4.6 mm x 5 µm) - ACN 80%, Water 20% - Isocratic - 1 mL/min	UV (254 nm)	LOD: 0.37-38.5 ng/L RSD: 2.7-5.3%; Recov: 60-103.1% Repro (µSPE): 4.9-6.4%

(Yousefi et al., 2018)	13 EPA PAHs (Na, Ace and F n.d.)	Sunflower, corn, canola, frying and blended oil	Same as ISO 15753:2016, starting from 2 g of oil.	- Vydac 201 TP54 (250 mm x 4.6 mm x 5 µm) - A: ACN, B: ACN/Water (50:50) - 100% B (0-5'), 60% A (5-27'), 100% A (27-41'), 100% B (41-45') - 1.2 mL/min	FLD	LOD: 0.1-0.38 µg/kg Recov: 81.5-107.1% RSD: 3.68-7.44%
(Alves da Silva et al., 2018)	PAH4 + fatty acids profile	Cold pressed oils: coconut, evening primrose, linseed and safflower oil.	Same as Da Silva, 2017	- Zorbax Eclipse PAH (100 mm x 2.1 mm x 1.8 µm) + guard column - ACN, Water - 50% ACN (0-0.9'), 50 - 75% ACN (0.9-7'), 75% ACN (7-17'), 75-100% ACN (17-20'), 100% ACN (20-24') - 0.4 mL/min	FLD	LOD: 0.08-0.3 µg/kg Recov: 90.46-96.78% RSD: 1.9-4.55%
(Wang et al., 2018)	Na, Ace, Phe, A, P, BbF	Peanut, soybean and sunflower oil	- 1 g - 10 mL hexane - MSPE: mMWCNTs	- Inertsil ODS-3 (250 mm x 4.6 mm x 5 µm) - MeOH/water (9:1, v/v) - Gradient n.a. - 1.5 mL/min	UV	LOD: 0.06-0.55 µg/kg Recov: 93.9-112.2% RSD: 6.29-9.42% intra-day; 7.94-11.23% inter-day
(Gharbi et al., 2017)	Fl, Phe, A, F, P + PAH8	EVOO	- 2.5 g - 10 mL hexane - SPE: same as Purcaro, 2008.	- C18 Supelcosil (250 mm x 3 mm x 5 µm) - ACN, Water - 40% ACN (0-5'), 40-100% (5-40') - 1 mL/min	FLD	LOD: n.a. Recov: 32-152% RSD: 5.34-21.01%;
(Molle et al., 2017)	13 EU PAHs (BghiP, CPP and BcFl n.d.)	Canola, sunflower and corn oil	- 0.5 g - 5 mL hexane - LLE (10 mL DMF-water 9:1, v/v) - SPE: C18; AS: MeOH, water; ES: DMF/water (9:1, v/v), water	- Vydac 201 TP54 (250 mm x 3 mm x 5 µm) - ACN, Water - 70-75% ACN (0-20'), 75-100% ACN (20-35'), 100% ACN (35-55') - 1 mL/min	FLD	LOD: 0.07-1.95 µg/kg Recov: 71-110% RSD: 4-20% intra-day; 3-12% inter-day

(Alves da Silva et al., 2017)	PAH4	Cold pressed oils: Coconut, safflower, linseed and evening primrose oil	- 0.5 g - LLE (5 mL DMF-water 9:1, v/v) - SPE: C18; AS: MeOH, DMF/water (1:2, v/v), water; WS: DMF/water (1:2, v/v), water; ES: hexane	- Zorbax Eclipse PAH (100 mm x 2.1 mm x 1.8 µm) + guard column - A: ACN, B: Water - 65% A (0-0.9'), 65-75% A (0.9-7), 75% A (7-17'), 75-100% A (17-20'), 100% A (20-24') - 0.4 mL/min	FLD	LOD: 0.08-0.30 µg/kg Recov: 80.13-100.04% RSD: 1.08-9.17%
(Ji et al., 2017)	A, F, P, Chr, BaP, DBahA, BghiP, IP	Olive and sunflower oil	- 20 g - MSPE: Modified GO	- Waters Symmetry C18 (250 mm x 4.6 mm x 5 µm) - ACN, Water - 65%-100 ACN (0-14'), 100% ACN (14-20'). - 1 mL/min	DAD (219 nm)	LOD: 0.06-0.15 µg/kg Recov: 80.13-100.04% RSD: 3.44-6.64% intra-day; 5.39-8.41% inter-day Repro: 3.2-6.45%
(Taghvaee et al., 2016)	15 EPA HAPs (Acy n.d.)	Olive oil and POO	- Same as ISO 15753:2016 - SPE: amino phase. AS: hexane; ES: hexane/toluene (70:30, v/v)	Same as ISO 15753:2016, but using a 250 mm x 4.6 mm x 5 µm Zorbax Eclipse PAH column		LOD: 0.16-0.97 µg/kg Recov: 75-111% RSD: 3-8%;
(Jiang et al., 2015)	15 EPA HAPs (Acy n.d.)	Corn, peanut, soybean oil and blend oils	- 2 g - LLE (5 mL ACN/acetone (1:1, v/v)) - SPE: Oasis HLB; AS: CH_2Cl_2, MeOH, ACN; ES: ACN/acetone (1:1, v:v), CH_2Cl_2 - SPE: Florisil; AS: CH_2Cl_2, hexane; ES: hexane/ CH_2Cl_2 (2:1, v/v)	- Waters PAH C18 (250 mm x 4.6 mm x 5 µm) - A: Water, B: ACN, C: MeOH - 70% C + 30% A (0-15'), 70% C + 30% B (15-23.33'), 100% B (23.33-24') - 0.9 mL/min	FLD	LOD < 0.3 µg/kg Recov: 79.8-127.2% RSD: 4.6-11.5% intra-day; 5.4-13.4 inter-day
(Stenerson et al., 2015)	15 EPA HAPs (Acy n.d.)	EVOO and EVOO + Refined olive oil blend	- 0.4 g - SPE: C18 (bottom layer) + Florisil (upper layer); AS: acetone; ES: ACN	- C18 Supelcosil (250 mm x 4.6 mm x 5 µm) - ACN, Water - 40% ACN (0-5'), 40-100% ACN (5-20'), 100% ACN (20-32') - 1.4 mL/min	FLD	LOD: 0.19-1.01 µg/kg Recov: 79-123% RSD: 5-16% intra-day; 10-68% inter-day

(Shi et al., 2015)	16 EPA PAHs	Olive, peanut and soybean oil	- 1 g - LLE (8 mL ACN)	- Zorbax Eclipse PAH (100 mm x 2.1 mm x 3.5 µm) - ACN, Water - 45% ACN (0-5'), 45-100% ACN (5-15'), 100% ACN (15-21') - 0.4 mL/min	MS - APPI - QQQ - SIM	LOD: 0.006-0.156 µg/kg Recov: 77.8-106.4 % RSD: 2-7.5% intra-day; 2.5-8.9 inter-day
(Tfouni et al., 2014)	13 EU PAHs (BghiP, CPP and BcFl n.d.)	Vegetable oil blends	Same as Camargo, 2011	- Vydac 201 TP54 (250 mm x 4.6 mm x 5 µm) - ACN, Water - 70-75% ACN (0-20'), 75-100% ACN (20-35'), 100% ACN (35'-55') - 1 mL/min	FLD	LOD: 0.02-0.52 µg/kg Recov: 67-115% RSD: 2-18%
(Zhao et al., 2013)	16 EPA HAPs	Soybean, sunflower, sesame, groundnut, corn and olive oil (spiked samples)	- 1 g - LLE (10 mL ACN:Acetone 60:40) + Sonication - SPE: C18; AS: ACN; ES: ACN/acetone (60:40, v:v)	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) - ACN, Water - 40-87% ACN (0-30'), 87% ACN (30-40') - 1.5 mL/min	FLD (Acy: DAD 228 nm)	LOD: 0.01-2.35 µg/kg Recov: 59.5-94.6% RSD: 0.48-4.98%
(Payanan et al., 2013)	15 EPA HAPs (Acy n.d.) + BeP	Refined olive, soybean, sunflower, canola and palm oil	- 1 g - 8 mL ACN:Acetone (4:1 v/v) - Freezing step - SPE: Alumina-N; AS n.a.; ES: hexane/ CH_2Cl_2 (1:1, v/v)	- PAH C18 (250 mm x 4.6 mm x 5 µm) + C18 guard column - ACN, Water - 45-90% ACN (0-35'), 90% ACN (35-45') - 1.5 mL/min	FLD	LOD: 0.13-3.13 µg/kg Recov: 45.9-118.5% RSD: 2.73-19.9%
(Ciecierska and Obiedziński, 2013)	Phe, A, Ft, P + 15 EU PAHs (BcFl n.d.)	Cold pressed oils: Amaranth, linseed, common flax, camelina, pumpkin and sesame, poppy, mustard, safflower, blackseed, walnut, borage and evening primrose oil	- 0.5 g - 5 mL cyclohexane/ethyl acetate (50:50 v/v) - GPC	- Bakerbond PAH-16 (250 mm x 3 mm x 5 µm) - A: ACN, B: ACN/Water (50:50) - 30% B (0-25'), 30-100% B (25-50'), 100% B (50-68.5) - 0.5 mL/min	FLD (CPP: DAD 254 nm)	LOD: 0.05-0.47 µg/kg Recov: 79-108% RSD: 2.7-9.1%

(Ergönül and Sánchez, 2013)	15 EPA PAHs (Acy n.d.)	EVOO, VOO, second centrifugation olive oil, lampante, refined olive oil, crude POO, POO	Same as ISO 15753:2016	- ZORBAX Eclipse PAH (250 mm x 4.6 mm x 5 µm) - ACN, Water - 75% ACN (0-10'), 75-100% ACN (10-35'), 100% ACN (35-45') - 1 mL/min	FLD	n.a.
(Dost and Ideli, 2012)	Fl, Phe, A, F, P, BbF, BaA, BkF, BaP	Olive, corn and sunflower oil	- 50 mL - Saponification - SPE: silica-alumina; AS: hexane; WS: hexane; ES: hexane/ CH_2Cl_2 (80:20, v/v)	- ODS (250 mm x 4.6 mm x 5 µm) - ACN 80%, Water 20% - Isocratic - 1.5 mL/min	UV: 254 nm	LOD: 0.26-1.15 µg/L Recov: 80-127% RSD: 0.35-1.6% intra-day;
(Camargo et al., 2011)	13 EU PAHs (BghiP, CPP and BcFl n.d.)	Soybean oil	- 0.5 g - 5 mL hexane - LLE (5 mL DMF/water 9:1 v/v) - SPE: C18; AS: MeOH, water; WS: DMF/water (1:1, v/v); ES: hexane	- C18 Vydac TP54 (250 mm x 4.6 mm x 5 µm) - ACN, Water - 70-75% ACN (0-20'), 75-100% ACN (20-35'), 100% ACN (35-55') - 1mL/min	FLD	LOD: 0.02-0.76 µg/kg Recov: 61-115% RSD: 1.42-8.83% intra-day; 0.47-6.09% inter-day
(Hollosi and Wenzl, 2011)	15+1 EU PAHs	Spiked olive oil and spiked POO	- 1.05 mL oil - 0.45 mL iso-propanol - DACC	- ChromSpher (250 mm x 2.1 mm x 5 µm) - MeOH in Water; EtOAc in MeOH - 72% MeOH (0-1'), 72-100% MeOH (1-9'), 0-65% EtOAc (9-16'), 65% EtOAc (16-18') - 700 µL/min	MS - APPI - QQQ - SIM	LOD: 0.19-0.36 µg/kg Recov: n.a. RSD: < 5%;
(Costopoulou et al., 2010)	Na, F, P + 15 EU PAHs (BcFl n.d.)	Olive oil from fire-affected areas	Same as ISO 15753:2016	- Vydac 201 TP 54 (250 mm x 4.6 mm x 5 µm) - A: ACN, B: ACN/Water - 50-65% A (0-43'), 65-100% (43-44') - 1 mL/min	FLD (CPP: DAD 222 nm)	LOD: 0.005-2.155 µg/kg Recov: 30.3-120.7% RSD: 0.52-14.68%
(Purcaro et al., 2008)	16 PAHs + BeP	Olive oils	- 0.2 g - 1 mL hexane - SPE: silica; AS: CH_2Cl_2, hexane; ES: hexane/CH_2Cl_2 70:30, v/v	- C18 LC-PAH Supelcosil (250 mm x 3 mm x 5 µm) - ACN, Water	FLD	LOD: 0.003-0.43 µg/kg (CPP: 18.9 µg/kg)

				- 75% ACN (0-10'), 75-100% ACN (10-35'), 100% ACN (35-45') - 1.5 mL/min		Recov: 59.6-124.1 % RSD: 6.2-11.3% intra-day; 6.8-16.2% inter-day
(Rodríguez-Acuña et al., 2008)	PAH8 + BeP	EVOO, VOO, POO and crude pomace oil	Same as Moreda, 2004			
(Teixeira et al., 2007)	15 EPA PAHs (Acy n. d.)	Olive oil, soybean and sunflower oil	Same as ISO 15753:2016	- C18 LC-PAH Supelcosil (250 mm x 4.6 mm x 5 µm) - ACN, Water - 40% ACN (0-5'), 100% ACN (30-45') - 1.5mL/min	FLD	LOD: 0.004-0.092 µg/kg Recov: 29-65% RSD: 1.09-4.23%;
(Cortesi and Fusari, 2006)	BaA, BbF, BaP, DBahA, BkF, BghiP, IP, BeP	Olive oil, POO and palm oil	- 2 g - 10 mL isooctane/cyclohexane (1:2, v/v) - SPE: Styrene-divinyl benzene; AS: CH_2Cl_2, isooctane/cyclohexane (1:2, v/v); ES: CH_2Cl_2	- Lichrocart-Lichrospher PAH (250 × 3 mm x 5 µm) - ACN, Water - 81% ACN (0-15'), 95% ACN (30-32'), 100% ACN (32-40') - 0.9 mL/min	FLD	LOD: 0.2 µg/kg (IP: 0.5 µg/kg) Recov: 79-97% RSD: 2.3-11.2%;
(Lage Yusty and Cortizo Daviña, 2005)	BaA, BbF, BaP, DBahA, BkF, BghiP, BeP	Vegetable oils	- 1 g - SFE (CO_2 + MeOH)	- Hypersil Green PAH (100 mm x 4.6 mm x 5 µm) - ACN 78%, Water 22% - Isocratic - 0.5 mL/min	FLD	LOD: 0.075-10.1 µg/L Recov: 18.4-93.3% RSD: 0.73-8.6%;
(Martinez-López et al., 2005)	Phe, A, Ft, P, PAH8, BeP	POO	- 1 g - LLE (10 mL ACN) - GPC[b]	- C18 201TP52 (250 mm x 2.1 mm x 5 µm) + guard column - ACN, Water - 50% ACN (0-7'), 50-80% ACN (7-20%), 80% ACN (20-25'), 80-95% ACN (25-30') - 0.250 mL/min	FLD	LOD: 0.05-0.48 µg/kg Recov: 75-111% RSD: 1-5%

(Moreda et al., 2004)	PAH8 + BeP	VOO, olive oil, refined olive oil, POO and sunflower oil	- 0.25 g - 2.5 mL alkane mixture - SPE: C18; AS: alkene mixture; WS: hexane; ES: hexane - SPE: amino phase; AS: alkene mixture; WS: alkene mixture; ES: alkane mixture/toluene (70:30, v/v)	- Inertsil ODS-P (250 mm x 4.6 mm x 5 µm) + guard column - ACN, Water - 85% ACN (0-3'), 85-100% ACN (3-37'), 100% ACN (37-55'), 100-85% (65-66'), 85% (66-70') - 1 mL/min	FLD	LOD: 0.01-0.2 µg/kg Recov: 79.5-91.3% RSD: 7.6-26.6%
(Bogusz et al., 2004)	BaP	Spiked olive oil	- 5 g - SPE[b]: C18 (bottom layer) + Florisil (upper layer); AS (only for Florisil): ACN, hexane/ CH_2Cl_2 (4:1); ES: ACN	- CP ChromSpher π (20 mm x 3 mm). Particle size n.a. - ACN, water - Gradient n.a. - 1 mL/min	FLD	LOD: 0.3 µg/kg Recov: 84% RSD: 4.76%
(Barranco et al., 2003)	15 EPA PAHs (Acy n.d.)	Olive oil, residue olive oil, palm, palm kernel oil and crude and refined coconut oil	- 0.5 g - 5 mL hexane - LLE (5 mL DMF/water 9:1 v/v) - SPE: C18 or C8; AS: MeOH, DMF/water (1:1, v/v); ES: n.a.	- C18 Vydac (250 mm x 4.6 mm x 5 µm) + guard column - ACN, Water - 50% ACN (0-10'), 50-100% ACN (10-24'), 100% ACN (24-35') - 1 mL/min	FLD	LOD: 0.1-1.5 µg/kg Recov: 50-103% RSD: 2.5-6.1% intra-day; 1.7-5.5% inter-day; Na < 32%
(Zougagh et al., 2004)	A, P, BaA, BkF	Spiked EVOO	- 5 g - SFE (CO_2)	- Ultrabase C18 (250mm × 4.6mm x 5 µm) - ACN, MeOH, Water - 85% ACN, 1.8 % MeOH, 13.2% Water (0-5') -> 90% ACN, 1.8% MeOH, 8.2% Water (5-20') - 0.8 mL/min	FLD	LOD: 12-16 µg/kg Recov: 102-106% RSD: 2.8-4.5%

Explanatory note: Washing solvents have been indicated only in those cases in which the SPE column has been washed. Activating and elution solvents for the SPE of investigations included in Section 2.5 have not been mentioned in this table, because the characteristics of the employed adsorbents make the parameters of the technique not comparable with the rest of isolation SPEs and clean-up SPEs. Gradient schemes do not include the final phase of returning to initial conditions of the method. In those articles in which the recoveries have been calculated for different concentrations, the results for the lower level have been reported here.

Footnote:

Abbreviations (in alphabetical order): ACN: acetonitrile; AS: Activation solvent for the SPE adsorbent; DACC: donor-acceptor complex chromatography; EtOAc: ethyl acetate; EVOO: extra virgin olive oil; DAD: diode array detector; CFYM: chicken feet yellow membrane; DMF: dimethylformamide; FLD: fluorescence detector; GPC: gel permeation chromatography; LLE: liquid-liquid extraction; GO: graphene oxide; LOD: limit of detection; LOQ: limit of quantification; MeOH: methanol; MSPE: magnetic solid phase extraction; n.a.: not available; n.d.: not determined; POO: pomace olive oil; Recov: recovery; RSD: relative standard deviation; SFE: supercritical fluid extraction; SPE: solid phase extraction; WS: washing solvent for the SPE; ES: elution solvent for the SPE; UV: ultraviolet-vis; VOO: virgin olive oil.

[a]: LODs and LOQs are expressed either using µg/kg, µg/L or ng/L, considering the units utilized by the authors in the original paper.

[b]: Method of choice after the testing of other procedures and evaluation of the obtained results from all of them.

Table 3 Detailed information about the articles discussed in this review (regarding **gas chromatography**). Experimental details about sample preparation, gas chromatography separation conditions, detection parameters and analytical performance of the applied methodologies are listed in the table.

Ref.	Determined compounds	Source	Sample treatment	Separation	Detection	Analytical performance[a]
(Ju et al., 2020)	PAH4	EVOO, olive oil, grapeseed, red pepper, perilla, rice bran, soybean, sesame and sunflower oil	- 5 g - LLE (10 mL ACN/Acetone 60:40 v/v) + Sonication - SPE: C18 (bottom layer) + Florisil (upper layer); AS: acetone; ES: ACN - SPE: amino phase. AS: hexane; ES: hexane/toluene (70:30, v/v)	- DB-EUPAH (60 m x 0.25 mm x 0.25 µm) - 50º (10') -> 280 at 40ºC/min -> 320ºC at 2ºC/min (10') - 1.5 mL/min	- EI - Q - SIM	LOD: 0.08-0.1 µg/kg Recov: 97.5-102% REU: 1-5%
(Mohammadi et al., 2020)	Na, Acy, Fl, Phe, A, F, P, BbF, BaA, BaP, DBahA, Bghi, IP	Edible oil (not specified)	- 1 mL - LLE (1 mL acetone + 1 mL ACN) - Microwave-assited Saponification - LLME	- HP-5MS (60 m x 0.25 mm x 0.25 µm) - 150º (2') -> 180º at 8ºC/min (2') -> 230ºC at 10ºC/min (6') -> 250º at 5ºC/min (1') -> 300ºC at 30ºC/min (30') - 1 mL/min	- EI - Q - SIM	LOD: 0.2-2.7 ng/mL Recov: 82.9-102.4% RSD: < 9.1%
(Rascón et al., 2018)	16 EPA PAHs	EVOO, VOO, olive oil, POO sunflower, sesame, coconut and soybean oil	- 0.5 g - 5 mL hexane - LLE (10 mL DMF/Water (9:1 v/v)) - SPE: C18[b]; AS: ACN, MeOH, water; ES: ACN	- DB-5-MS (30 m x 0.25 mm x 0.15 µm) - 70º (2') -> 240 at 10ºC/min -> 290ºC at 15ºC/min (12') - 1 mL/min	- EI - Q - SIM	LOD: 0.004-0.11 µg/kg Recov: 87-104% RSD: < 5.9% intra-day; < 7.2% inter-day
(Zacs et al., 2018)	PAH4	15 Edible oils (not specified)	- 1 g - 10 mL hexane - dSPE: MWCNTs[b]	- (Brand n.a.) 30 m x 0.25 mm x 0.15 µm - 80º (2') -> 265 at 15ºC/min -> 290ºC at 5ºC/min -> 320ºC at 20ºC/min (20') - 1.2 mL/min	- EI - Q - SIM	LOD: 0.06-0.21 µg/kg Recov: 98-108% RSD: 2-5% intra-day; 4-6% inter-day
(Zhang et al., 2017)	16 EPA PAHs	Colza, peanut, soybean, sunflower oil	- 5 g - 20 mL hexaneMSPE: magnetic 3-D GOb	- DB-5MS (30 m x 0.25 mm x 0.25 µm)	- EI - Q - SIM	LOD: 0.05-0.30 µg/kg Recov: 81.9-111 %

				- 80º (2') -> 150ºC (1') at 25ºC/min -> 280ºC at 8ºC/min (9') - 1 mL/min		RSD: 2.3-7.9% intra-day; 4.2-8.7 inter-day
(Zheng et al., 2016)	PAH8	Sunflower, corn and camellia oil	- 20 g - 100 mL hexane - MSPE: Magnetic Carbon nitride	- Rtx-5ms (30 m x 0.25mm x 0.25 µm) - 70º (2') -> 190º at 15ºC/min (1') -> 260º at 10ºC/min -> 320º at 5ºC/min (10') - 1.2 mL/min	- EI - Q - SIM	LOD: 0.1-0.3 µg/kg Recov: 91-124.1% RSD: 5.1-11.6% intra-day; 8.3-15% inter-day
(Shi et al., 2016)	16 EPA PAHs	Olive oil, corn, grapeseed, peanut, rapeseed, sesame, soybean, sunflower and wheat germ oil	- 1 g - LLE (5 mL ACN) + Sonication - SPE: silica; AS: hexane; WS: hexane; ES: hexane; hexane/ CH_4Cl_2 (9:1, v/v)	- DB-5MS (60 m × 0.25 mm × 0.25 µm) - 80º (1') -> 180ºC at 20ºC/min -> 200º at 3ºC/min -> 250ºC at 6ºC/min (3') - 1 mL/min	- EI - Q - SIM	LOD: 0.06-0.17 µg/kg Recov: 84.3-115.3 % RSD: 0.1-10.4% intra-day; 0.1-9.0% inter-day
(Sun et al., 2017)	16 EPA PAHs	Spiked peanut oil	- 0.1 g - 1 mL hexane - SPE: MIP[b]	- HP-5-MS (30 m x 0.25 mm x 0.25 µm) - 80º (1') -> 270º at 5ºC/min (2') -> 290º at 3ºC/min (1') -> 305º at 10ºC/min (10') - Flow rate n.a.	- EI - Q - Scan	LOD: n.a. Recov: ≈58-102% (values taken from a figure) RSD: n.a.
(Zhou et al., 2016)	All EPA and EU PAHs (except BcFl)	Corn, olive, peanut and soybean oil	- 0.5 g - LLE (150 mL hexane + 600 mL ACN)	- HP-5-MS (30 m x 0.25 mm x 0.25 µm) - 70º (2') -> 150º at 25ºC/min -> 200º at 3ºC/min -> 280º at 8ºC/min -> 320º at 20ºC/min (6') - Flow rate n.a.	- EI - Q - MRM	LOD: 0.1-1 µg/kg Recov: 71.5-109.9% RSD: 4.8-9.8%
(Chung and Lau, 2015)	PAH4	Olive oil, corn, grapeseed, peanut, rapeseed,	- 0.4 g - SPE: C18 (bottom layer) + Florisil (upper layer); AS: acetone; ES: ACN	- DB-EUPAH (20 m x 0.18 mm x 0.14 µm) - 45º -> 200 at 45ºC/min -> 225ºC at 2.5ºC/min -> 266 at 3ºC/min) -> 300	- EI - Q - SIM	LOD: 0.1 µg/kg Recov: 86-114% RSD: 5.2-7%

		sesame, soybean and sunflower oil		at 5ºC/min -> 320 at 10ºC/min - 1 mL/min (0.2'), 1.7 mL/min		
(Xu et al., 2015)	16 EPA and 15 + 1 EU PAHs	Olive, peanut, rapeseed and soybean oil	- 1.5 mL - 0.5 mL cyclohexane - SPE: MIP - SPE: GCB	- DB-EUPAH (20 m x 0.18 mm x 0.14 µm) - 70º (1') -> 200º at 30ºC/min -> 225º at 3ºC/min -> 266º at 4ºC/min -> 300º at 5ºC/min -> 320º at 10ºC/min (10') - 1 mL/min (0-10') -> 1.7 mL/min at 5 mL/min	- EI - QQQ - MRM	LOD: 0.03-0.6 µg/kg Recov: 56.8-117.7% RSD: 0.3-12.7%
(Zelinkova and Wenzl, 2015)	PAH4	Evening primrose, linseed, primrose and sea buckthorn oil (food supplements)	- 1 g - 5 mL cyclohexane:ethyl acetate (1:1, v/v) - GPC - SPE: silica; AS: cyclohexane; ES: cyclohexane	- 60º (1') -> 180º at 60ºC/min -> 240º at 4ºC/min -> 280º at 28ºC/min (3') -> 325º at 14ºC/min (10') - 1 mL/min	- EI - Q - SIM	LOD: 0.25 µg/kg Recov: 91.4-101% Combined RSU: 9.7-18.3%
(Drabova et al., 2013)	15 + 1 EU PAHs	EVOO, pumpkin, rapseed, sea buckthorn, sesame, soybean and sunflower oil (cold-pressed oils)	- 0.5 g - 0.5 mL cyclohexane - SPE: SupelMIP[b]	- GC x GC - 1st column: 30 m x 0.25 mm, 0.25 µm BPX-50. Gradient: 80º (4.3') -> 240º at 30ºC/min -> 270º at 2ºC/min -> 320º at 5ºC/min -> 360º at 40ºC/min (12'); 2nd column: 1 m x 0.1 mm, 0.1 µm BPX-50. Gradient: 90º (4.3') -> 250º at 30ºC/min -> 280º at 2ºC/min -> 330º at 5ºC/min -> 360º at 40ºC/min (12'); - 1.3 mL/min	- EI - ToF	LOD: 0.03-0.09 µg/kg Recov: 70-99% RSD: 2-11%

(Purcaro et al., 2013)	PAH8 + BjF + BeP	EVOO, POO, grapeseed and cereal oil	- 0.5 g - LLE (3 mL ACN) - SPME: Same as Purcaro, 2007	- BPX50 (9 m x 0.10 mm x 0.10 µm.) - 80º (2) -> 170ºC at 70ºC/min -> 350º at 15ºC/min - Flow rate n.a.	- EI - Q - SIM and full scan	LOQ: 0.1-0.32 µg/kg Recov: 35-85% RSD: 3.1-9.7%
(Jung et al., 2013)	15 EU PAHs (BcFl n.d.)	Sesame oil, perilla seed oil	- 2 g - LLE (10 mL isooctane/cyclohexane 1:1) - SPE: styrene-divinyl benzene copolymer; AS: ACN; WS: isooctane/cyclohexane (1:1, v/v); ES: hexane/ CH_2Cl_2 (80:20, v/v)	- VF-5ms (30 m x 0.25 mm x 0.25 µm) - 150º (2') -> 250º at 10ºC/min (10') -> 280º at 10ºC/min (30') - 1 mL/min	- EI - Q - SIM	LOD: 0.01-0.06 µg/kg Recov: 55.1-105% RSD: 0.8-7.5%
(Cassimiro Belo et al., 2012)	PAH8	Olive, soybean and sunflower oil	- 2 g - 8 mL hexane - LLE (8 mL DMF/Water 90:10 v/v) - SPE: C18; AS: MeOH, DMF/water (50:50 v,v); WS: DMF/water (50:50 v,v); ES: hexane - SPE: silica; AS: hexane; ES: hexane	- DB-5 (30 m x 0.25 mm x 0.25 µm) - 50º (1') -> 160º at 40ºC/min -> 300º at 6ºC/min (10') - 1 mL/min	- EI - Q - SIM	LOD: 0.04-0.23 µg/kg Recov: 54.01-114.69% RSD: 7.36-54.6%
(Hossain and Salehuddin, 2012)	8 EPA PAHs	Coconut, mustard, soybean oil	- 2.5 g - LLE (10 mL ACN/Acetone 60:40 v/v) + Sonication - SPE: silica; AS: CH_2Cl_2; ES: ACN/acetone (proportion n.a.)	- VF-5 (30 m x 0.25 mm x 0.25 µm) - 50ºC (1') -> 200º at 8ºC/min -> 300º at 10ºC/min - 1 mL/min	- EI - IT - TIM	LOD: 1.9-3.1 ng Recov: 56-84% RSD: 0.29-0.74 % intra-day; 0.63-2.34% inter-day
(Zhao et al., 2011)	PAH8	Olive, peanut, maize, rapeseed, sunflower, soybean and blend oil	- 1 g - dSPE: mMWCNTs	- Rxi-5 (30 m x 0.25 mm x 0.25 µm) - 70º (2') -> 190° at 15 °C/min (1') -> 260 °C at 10 °C/min -> 320º at 5 °C/min (10') - 1.2 mL/min	- n.a. - n.a. - SIM	LOD: 0.1-0.88 µg/kg Recov: 87.8-114.4% RSD: 1.7-6.2% intra-day; 0.7-6.6% inter-day
(Wang and Guo, 2010)	16 EPA PAHs	Cocoa, corn, olive, peanut and pepper oil	- 4 g - 10 mL ACN + Sonication - GPC	- HP-5MS (30 m x 0.25 mm, 0.25 µm) - 70º (2') -> 150º at 25ºC/min -> 200º at 3ºC/min -> 280º at 8ºC/min (10') - Flow rate n.a.	- EI - Q - SIM	LOQ: 0.3-0.6 µg/kg Recov: 84.5-96% RSD: 4-10.8%

(Alomirah et al., 2010)	16 EPA PAHs	EVOO, VOO, olive oil, POO, canola, corn, mustard, palm, peanut, sesame, soya, sunflower	- 5 g - Saponification - SPE: silica; AS: n.a.; ES: cyclohexane	- DB-5 (30 m x 0.25mm x 0.25 µm) - 45º (2') -> 290º at 10ºC/min (8') - Flow rate n.a.	- EI - Q - SIM	LOD: 0.1 µg/kg Recov: ≥85% RSD < 20%
(Gómez-Ruiz and Wenzl, 2009)	15+1 EU PAHs	Sunflower oil	- Solution (oil + cyclohexane/ethyl acetate 1:1, v/v) at 0.18 g/mL - GPC - SPE: silica; AS: n.a.; ES: cyclohexane	- DB-17MS (60 m x 0.25 mm x 0.25 µm)[b] - 80º (1') -> 250º at 40ºC/min -> 305º at 25ºC/min -> 315º at 2ºC/min -> 330º at 40ºC/min (35') - 1.5 mL/min	- EI - Q - SIM	n.a.
(Bordajandi et al., 2008)	15 EU PAHs (BcFl n.d.)	Sunflower oil	- Same as ISO 15753:2006 - GPC - SPE: silica; AS and ES: n.a.	- DB-17MS (60 m x 0.25 mm x 0.25 µm)[b] - 60º (1') -> 250º at 25ºC/min -> 310º - 1.5 mL/min	- EI - Q - SIM	n.a.
(Fromberg et al., 2007)	Ace, Acy, F, Phe, A, Ft, P, PAH8, BjF, BeP	EVOO, olive, grape seed, rapeseed, sesame and sunflower oil	- 1.5 g - cyclohexane–ethyl acetate 1:1 (v/v) (volume n.a.) - GPC - SPE: silica; AS: cyclohexane; ES: cyclohexane	- DB-5MS (50 m x 0.25 mm x 0.25 µm) - 90º (1') -> 270º at 7ºC/min -> 280º at 1ºC/min -> 320º at 1ºC/min -> 320º at 5ºC/min - 1 mL/min	- EI - Analyser n.a.	LOD: 0.2-1.5 µg/kg Recov: 14-120% RSD: 1-24%
(Purcaro et al., 2007)	15 + 1 EU PAHs	EVOO, olive oil, crude POO, POO, sunflower oil and vegetable oil	- 200 µL - 1.5 mL hexane - SPME: Carbopack Z/polydimethylsiloxane fibre; AS: hexane; ES: hexane	- GC x GC - 1st column: BPX5 (30 m x 0.25 mm x 0.25 µm) + guard column - 2nd column: BPX50 (1 m x 0.1 mm x 0.1 µm) - 40º (2') -> 210º at 30ºC/min -> 360º at 5ºC/min (15') - Flow rate n.a.	- EI - ToF	LOD: 0.1-1.1 µg/kg Recov: n.a. RSD: 2.8-34.5%
(Veyrand et al., 2007)	15 EU PAHs (BcFl n.d.)	Oil not specified	- 1 g - 10 mL cyclohexane	- Zebron ZB-5MS (30 m x 0.25 mm x 0.25 µm)	- EI - QQQ	LOD: 0.008-0.15 µg/kg

			- Pressurised liquid extraction (celite/florisil combined to hexane/acetone) - SPE: styrene-divinyl benzene; AS: n.a.; WS: cyclohexane/ethanol (70:30, v/v); ES: cyclohexane/ethyl acetate (40:60, v/v)	- 110º (1') -> 240º at 20ºC/min -> 320º at 5ºC/min (10') - 1 mL/min	- SIM	Recov: 12-70% RSD: 2.9-20.5%
(Vichi et al., 2007)	N, Ace, Acy, F, Phe, A, Ft, P	VOO	Same as Vichi, 2005			LOD: 0.1-1.6 µg/kg Recov: 74-128% RSD: 2.9-15.8%
(Ballesteros et al., 2006)	Some pesticides + BaP, BkF, BghiP, BeP	VOO, refined olive oil and POO	- 2 g - LLE (2 mL hexane, 10 mL ACN) - GPC	- PTV injection - HP-5 (30 m x 0.25 mm x 0.25 µm) - 70º (3.5') -> 180º at 25ºC/min (10') -> 300º at 4ºC/min (12') - 1mL/min	- EI and CI (MeOH) - IT - MS/MS	LOD: 0.05-1.7 µg/kg Recov: 84-109% RSD: 3-7.8%
(Arrebola et al., 2006)	PAH4 + (Ft + P), BkF, BghiP, IP	Olive oil	- 5 g - HS procedure	- VF-5ms (30 m x 0.25 mm x 0.25 µm) - 70º (2') -> 300º at 20ºC/min (10') - 1 mL/min	- EI - QQQ - SIM and MS/MS	LOD: 0.02-0.06 µg/kg Recov: 96-99% RSD: 3-9%
(Diletti et al., 2005)	BaP, BbF, BaP, BkF, DAahA, IP, BghiP, BeP	POO	- 10 g - 10 mL pentane - LLE (15 mL DMSO, 50 mL cyclohexane) - TLC	- DB-5MS (30 m x 0.25 mm x 0.25 µm) - 98º (1') -> 265º at 20ºC/min (0.1') -> 310º at 1ºC/min (1') -> 320º at 5ºC/min (5')	- Ionisation source n.a. - Ion trap - Full scan	LOD: 0.1-0.4 µg/kg Recov: 69-97.5% RSD: 11-21%
(Vichi et al., 2005)	N, Ace, Acy, F, Phe, A, Ft, P	Spiked VOO	- 2 g - HS-SPME: Divinylbenzene/Carboxen/Poly(dimethylsiloxane)	- Supelcowax-10 (30 m x 0.25mm x 0.25 µm) - 40º (3') -> 75º at 4ºC/min -> 250º at 8ºC/min (10') - 38 cm/s	- EI - Quadrupole - SIM and Scan	LOD: 0.05-1.6 µg/kg Recov: 74-128% RSD: 2.9-15.8% intra-day; 1.1-14.8% inter-day
(Guillén et al., 2004)	16 EPA PAHs + BjF, BkF, BcF, BeP	POO	- 11-14 g - 25 mL hexane - LLE (50 mL Water/DMSO 2.4:1)	- HP-5MS (60 m x 0.25 mm x 0.25 µm)	- EI - Q	LOD: 0.06-0.25 µg/kg Recov: >80

			- 2 x SPE: silica; AS: cyclohexane; ES: cyclohexane	- 50°C (0.50') -> 130°C at 8°C/min -> 290° at 5°C/min (50') - 1 mL/min	- SIM and Scan	RSD: n.a.
(Bogusz et al., 2004)	BaP	Olive oil	- 5 g - SPE[b]: C18 (bottom layer) + Florisil (upper layer) AS: n.a.; ES: ACN	- DB-5MS (30m x 0.25 mm x 0.25 µm) - 50º (1') -> 310º at 7.5ºC/min (6') - Flow rate n.a.	- EI - Analyser and MS mode n.a.	LOD: 1.6 µg/kg Recov: 79% RSD: 8.1%

Explanatory note: Washing solvents have been indicated only in those cases in which the SPE column has been washed. Activating and elution solvents for the SPE of investigations included in Section 2.5 have not been mentioned in this table, because the characteristics of the employed adsorbents make the parameters of the technique not comparable with the rest of isolation SPEs and clean-up SPEs. Gradient schemes do not include the final phase of returning to initial conditions. In those reports in which the recoveries have been calculated for different concentrations, the results for the lower level has been reported herewith.

Footnote:

Abbreviations (in alphabetical order): ACN: acetonitrile. AS: Activation solvent for the SPE adsorbent; CI: chemical ionisation; DMF: dimethylformamide; EI: electron impact; EVOO: extra virgin olive oil; GCB: graphitised carbon black; GC x GC: bi-dimensional gas chromatography; GPC: gel permeation chromatography; GO: graphene oxide; HS: head space; HS-SPME: head-space solid -phase microextraction; IT: ion trap; LOD: limit of detection; LLE: liquid-liquid extraction; LLME: liquid-liquid microextraction; LOQ: limit of quantitation; MeOH: methanol; MIP: molecularly imprinted polymer; MRM: multiple reaction monitoring; MSPE: magnetic solid phase extraction; MWCNTs: multiwalled carbon nanotubes; n.a.: not available; n.d.: not determined; POO: pomace olive oil; Q: quadrupole; QQQ: triple quadrupole; Recov: recovery; REU: relative expanded uncertainty; RSD: relative standard deviation; RSU: relative standard uncertainty; SIM: single ion monitoring; SPE: solid phase extraction; TIM: total ion monitoring; ToF: time of flight; WS: washing solvent for the SPE; ES: elution solvent for the SPE; UV: ultraviolet-vis; VOO: virgin olive oil.

[a]: LODs and LOQs are expressed either using µg/kg, µg/L or ng/L, considering the units utilized by the authors in the original paper.

[b]: Method of choice after the testing of other procedures and evaluation of the obtained results from all of them.

Table 4 Prevalent PAHs found in edible oils in the research works reviewed herein. Shaded yellow-orange cells indicate the analytes that were intended to be determined in the edible oil samples analysed by each study. Prevalent compounds, according to the criteria detailed in Section 6, have been marked with an "x".

Sample	4.1. Olive oil: PAHs found at highest levels																	Ref.
	Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
EVOO, VOO	x					x				x	x						-	(Rascón et al., 2018)
EVOO	x				x		x	x									-	(Stenerson et al., 2015)
EVOO, VOO	x	x				x									x		-	(Ergönül and Sánchez, 2013)
EVOO					x		x	x									-	(Gharbi et al., 2017)
EVOO										x	x						BeP	(Moreda et al., 2004)
EVOO										x							BjF, BeP	(Purcaro et al., 2013)
EVOO										x		x	x				CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)
EVOO										x							-	(Ju et al., 2020)
VOO										x							-	(Ju et al., 2020)
VOO									x	x							BeP	(Moreda et al., 2004)
VOO												x	x				BeP (abundant)	(Ballesteros et al., 2006)
VOO	x				x			x									-	(Vichi et al., 2007)
Olive oil	x	x			x												CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Xu et al., 2015)
Olive oil	x						x	x									-	(Shi et al., 2015)
Olive oil	x				x												-	(Shi et al., 2016)
Olive oil				x		x				x	x	x					-	(Rascón et al., 2018)
Olive oil	x						x										BeP	(Payanan et al., 2013)
Olive oil	x	x			x												-	(Taghvaee et al., 2016)
Olive oil	x	x											x		x		-	(Ergönül and Sánchez, 2013)
Olive oil				x				x									-	(Farrokhzadeh and Razmi, 2018)
Olive oil					x		x										BeP	(Barranco et al., 2003)
Olive oil							x	x									CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Costopoulou et al., 2010)
Olive oil										x	x				x		BeP (abundant)	(Moreda et al., 2004)

Olive oil																	-	(Ji et al., 2017)
Olive oil					x		x	x									-	(Dost and Ideli, 2012)
2nd centrifugation	x	x											x		x		-	(Ergönül and Sánchez, 2013)
EVOO + Refined olive oil	x			x	x												-	(Stenerson et al., 2015)
Lampante	x	x											x		x	x	-	(Ergönül and Sánchez, 2013)
POO					x		x	x	x		x						BjF + BkF, BcF, BeP (abundant)	(Guillén et al., 2004)
POO	x	x		x				x									-	(Taghvaee et al., 2016)
POO	x												x		x		-	(Ergönül and Sánchez, 2013)
POO										x			x				-	(Rascón et al., 2018)
POO										x					x		BeP (abundant)	(Moreda et al., 2004)
POO									x	x	x	x					-	(Purcaro et al., 2013)
POO (factory)									x	x							CPP, 5MChr (abundant), BjF+BkP+BbF (abundant), BcF, DBalP, DBaeP, DBaiP, DBahP	(Purcaro et al., 2007)
Crude Pomace	x	x				x		x					x		x		BjF, BeP (abundant)	(Ergönül and Sánchez, 2013)

4.2. Sunflower oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
									x		x					-	(Ju et al., 2020)
										x	x					-	(Zhao et al., 2011)
								x	x	x		x				-	(Zheng et al., 2016)
								x	x	x	x					5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Molle et al., 2017)
								x		x		x				BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)
								x	x	x						BeP (abundant)	(Moreda et al., 2004)
			x	x	x											-	(Dost and Ideli, 2012)
						x			x							-	(Rascón et al., 2018)
			x	x	x	x	x	x	x	x						-	(Shi et al., 2016)
x	x	x	x	x	x	x	x									-	(Zhang et al., 2017)
x				x		x	x									-	(Payanan et al., 2013)
x			x				x									-	(Farrokhzadeh and Razmi, 2018)
			x					x								-	(Yousefi et al., 2018)

4.3. Peanut oil: PAHs found at highest levels																Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
x				x		x	x									-	(Shi et al., 2015)
x			x	x		x	x									-	(Shi et al., 2016)
x	x	x	x	x		x	x	x	x							-	(Zhang et al., 2017)
x	x		x	x												-	(Jiang et al., 2015)
						x								x		-	(Ji et al., 2017)

4.4. Soybean oil: PAHs found at highest levels																Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
x							x									CPP, BcFl, 5MChr, BjF, DBalP, DBaeP, DBajP, DBahP	(Xu et al., 2015)
x					x				x		x					-	(Rascón et al., 2018)
x	x		x	x	x	x										-	(Shi et al., 2015)
x	x	x	x	x	x	x	x	x	x	x			x	x	x	-	(Zhang et al., 2017)
			x	x		x										-	(Shi et al., 2016)
x	x			x			x									BeP	(Jiang et al., 2015)
x				x		x	x									BeP	(Payanan et al., 2013)
					x				x							-	(Ji et al., 2017)
					x			x								-	(Hossain and Salehuddin, 2012)
									x							-	(Ju et al., 2020)
								x	x	x		x				CPP (abundant), BcFl, 5MChr, BjF (abundant), DBalP, DBaeP, DBajP, DBahP	(Drabova et al., 2013)
								x	x						x	5MChr, BjF, DBalP, BBaeP, DBaiP, DBahP	(Camargo et al., 2011)

4.5. Colza, canola and rapeseed oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
x	x	x	x	x		x	x		x							-	(Zhang et al., 2017)
x				x								x				-	(Payanan et al., 2013)
		x								x		x				-	(Yousefi et al., 2018)
								x	x		x					5MChr (abundant), BjF, DBalP, DBaeP, DBaiP, DBahP	(Molle et al., 2017)
x			x	x												CPP, BcFl, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Xu et al., 2015)
x				x		x	x				x					-	(Shi et al., 2016)
								x	x	x	x	x				CPP (abundant), BcFl, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)

	4.6. Sesame oil: PAHs found at highest levels															Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
					x	x			x							-	(Rascón et al., 2018)
		x	x	x		x	x									-	(Shi et al., 2016)
				x		x										CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Ciecierska and Obiedziński, 2013)
								x	x							CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Jung et al., 2013)
									x	x		x				CPP, BcFl, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)
									x							-	(Ju et al., 2020)

4.7. Corn oil: PAHs found at highest levels																Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
x				x												-	(Shi et al., 2016)
x	x			x			x									-	(Jiang et al., 2015)
								x	x	x	x					5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Molle et al., 2017)
			x					x								-	(Yousefi et al., 2018)
						x						x				-	(Dost and Ideli, 2012)
							x								x	-	(Ji et al., 2017)

4.8. Coconut oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
x					x				x		x			x		-	(Rascón et al., 2018)
					x		x									-	(Hossain and Salehuddin, 2012)
								x	x	x	x					-	(Alves da Silva et al., 2018)
								x	x	x	x					-	(Alves da Silva et al., 2017)

4.9. Safflower oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
								x	x							-	(Alves da Silva et al., 2018)
								x	x							-	(Alves da Silva et al., 2017)

4.10. Cold-press evening primrose oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
																-	(Zelinkova and Wenzl, 2015)
								x	x							-	(Alves da Silva et al., 2018)
								x	x							-	(Alves da Silva et al., 2017)
				x		x	x									CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Ciecierska and Obiedziński, 2013)

4.11. Cold-press linseed oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
																-	(Zelinkova and Wenzl, 2015)
								x	x							-	(Alves da Silva et al., 2018)
								x	x							-	(Alves da Silva et al., 2017)
			x		x	x										CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Ciecierska and Obiedziński,

																	2013)

4.12. Pumpkin oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
				x	x	x	x	x			x					CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Ciecierska and Obiedziński, 2013)
								x	x	x	x			x	x	CPP (abundant), BcF, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)

4.13. Grapeseed oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
									x							-	(Ju et al., 2020)
												x		x	x	BjF, BeP	(Purcaro et al., 2013)
x				x												-	(Shi et al., 2016)

4.14. Sea buckthorn oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
								x	x							-	(Zelinkova and Wenzl, 2015)
								x	x	x	x					CPP (abundant), BcFl, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)
4.15. Perilla oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
								x	x							-	(Ju et al., 2020)
									x							CPP (abundant), 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Jung et al., 2013)

4.14. Sea buckthorn oil: PAHs found at highest levels																	Ref.
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	

								x	x							-	(Zelinkova and Wenzl, 2015)
								x	x	x	x					CPP (abundant), BcFl, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Drabova et al., 2013)
4.15. Perilla oil: PAHs found at highest levels																	**Ref.**
Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
								x	x							-	(Ju et al., 2020)
									x							CPP (abundant), 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Jung et al., 2013)

Oil	4.16. Other kinds of oils: PAHs found at highest levels																	**Ref.**
	Na	Ace	Acy	Fl	Phe	A	F	P	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
Rice bran										x							-	(Ju et al., 2020)
Red pepper										x	x						--	(Ju et al., 2020)
Camellia										x	x						-	(Zheng et al., 2016)
Mustard	x				x	x											-	(Hossain and Salehuddin, 2012)
Wheat germ	x			x	x	x	x	x									-	(Shi et al., 2016)
Palm	x				x		x	x							x	x	BeP (abundant)	(Payanan et al., 2013)

Cold-pressed oil	4.17. Other kinds of cold-pressed oils: PAHs found at highest levels																	Ref.
	Na	Ace	Acy	Fl	Phe	A	F	P	BaA	BaA	Chr	BbF	BaP	BkF	DBahA	BghiP	IP	Other determined compounds	
Amaranth					x	x	x	x	x									CPP, 5MChr, BjF, DBalP, DBaeP, DBaiP, DBahP	(Ciecierska and Obiedziński, 2013)
Common flax					x		x												
Camelina					x	x	x												
Poppy					x	x	x												
Mustard					x		x												
Blackseed					x		x	x											
Walnut					x		x												
Borage					x		x												

Explanatory note: PAHs have been listed according to their molecular mass (from the lighter compound to the heaviest), except in the case of BaP and BkF. BaP has been set before BkF (despite its higher molecular mass) in order to group the four molecules belonging to the PAH4 list. Blue shaded cells correspond to PAH4 (lighter shaded) and PAH8 (darker shaded) lists. PAHs have been placed in individual cells until IP has been reached (according to elution order). The rest of molecules (when considered in the reports) have been placed in the "Other determined compounds" column, in order to facilitate the visual examination of the Table.

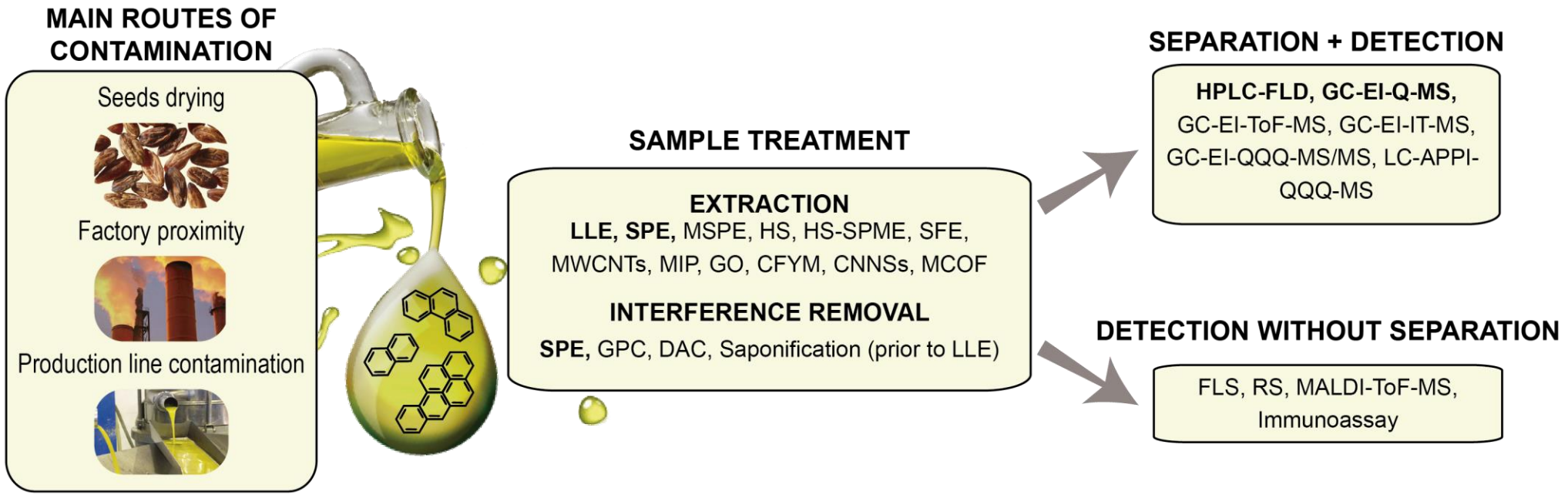

Figure 1 Graphical scheme of the techniques employed for the sample treatment and determination of PAHs in edible oils.

Abbreviations (in alphabetical order): APPI: atmospheric pressure photoionisation; CFYM: chicken feet yellow membrane; CNNS: carbon nitride nanosheets; DACC: donor-acceptor complex chromatography; EI: electron impact; FLD: fluorescence detector; FLS: fluorescence spectroscopy; GC: gas chromatography; GPC: gel permeation chromatography; GO: graphene oxide; HPLC: high performance liquid chromatography; HS: Head-space extraction; HS-SPME: Head-space-solid-phase microextraction; IT: ion trap; LLE: liquid-liquid extraction; MCOF: magnetic covalent organic frame; MALDI:Matrix-assisted laser desorption/ionisation; MIP: molecularly imprinted polymer; MS: mass detector; MSPE: magnetic solid-phase extraction; MWCNTs: multiwalled carbon nanotubes; Q: quadrupole; QQQ: triple quadrupole; RS: raman spectroscopy; SFE: supercritical fluid extraction; SPE: solid-phase extraction; ToF: time-of-flight.

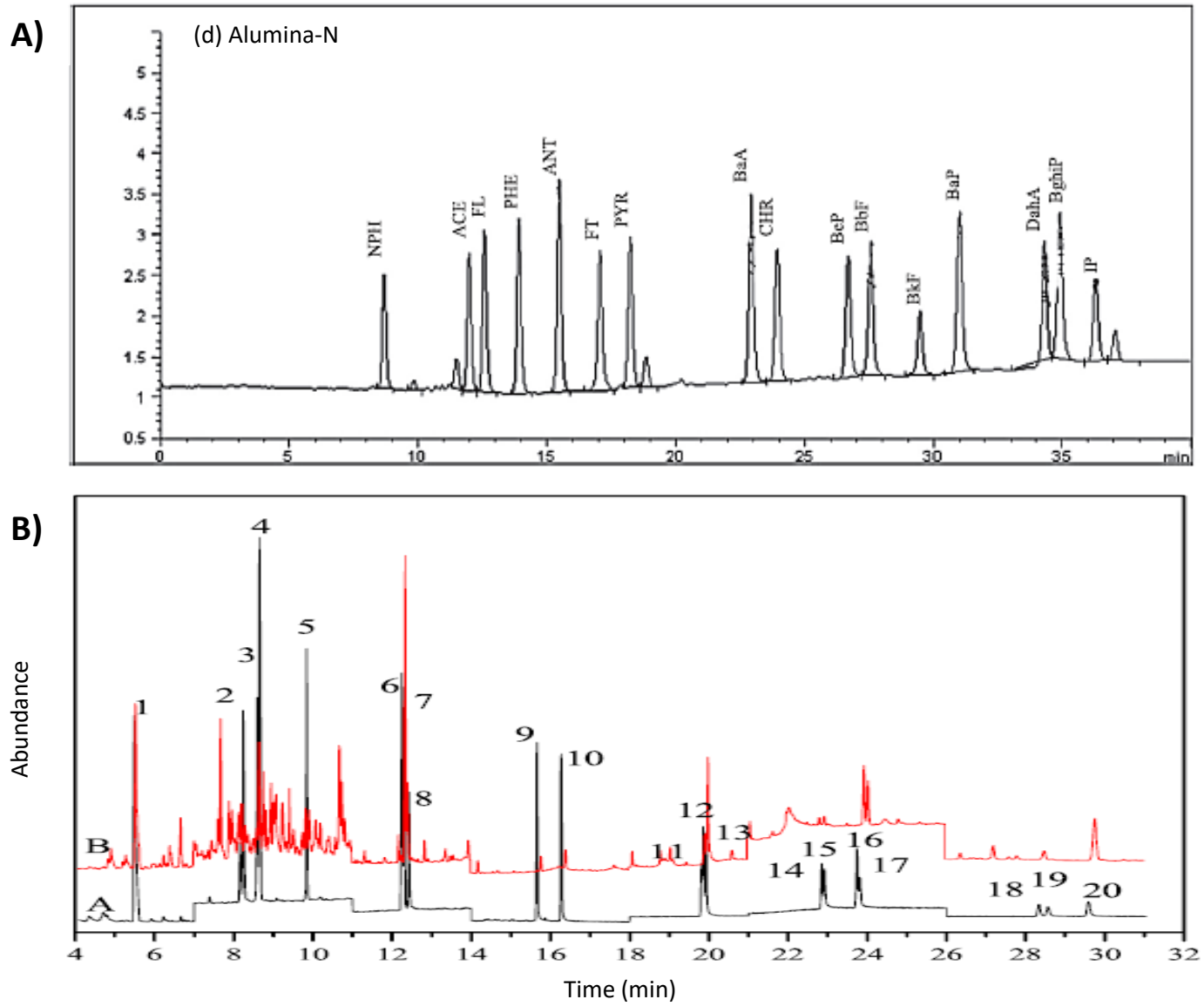

Figure 2 A) LC-FLD chromatogram obtained during the analysis of some PAHs. The corresponding extract was obtained by submitting a vegetable oil to a low temperature clean-up and a SPE (with Alumina-N as a sorbent). **B)** Profiles of PAHs standards at 10 µg/L (black line) and an edible oil sample extracted by a MSPE (magnetic 3D GO) (red line), analysed by GC-MS. See Tables 2 and 3 for more details.

Denotation of each analyte has been indicated as reflected in the original paper from Payanan et al., 2013 and Zhang et al., 2017 (**illustrations reproduced with permission**).

Abbreviations in 2A (in alphabetical order): ACE: acenaphthene; ANT: anthracene; BaA: benzo(a)anthracene; BaP: benzo(a)pyrene; BbF: benzo(b)fluranthene; BeP: benzo(e)pyrene; BghiP: benzo(g,h,i)perylene; BkF: benzo(k)fluranthene; CHR: chrysene; DBahA: dibenzo(a,h)anthracene; FL: fluorene; FT: fluoranthene; IP: Indeno(1,2,3-cd)pyrene; NPH: naphthalene; PHE: phenanthrene; PYR: pyrene

Numbers in 2B: 1: naphthalene; 2: acenaphthylene; 3: acenaphthene-d_{10}; 4: acenaphthene; 5: fluorene; 6: phenanthrene-d_{10}; 7: phenanthrene; 8: anthracene; 9: fluranthene; 10: pyrene; 11: bezo(a)anthracene; 12: chrysene-d_{12}; 13: chrysene; 14: benzo(b)fluoranthene; 15: benzo(k)fluoranthene; 16: benzo(a)pyrene-d_{12}; 17: benzo(a)pyrene; 18: indeno(1,2,3-cd)pyrene; 19: dibenzo(a,h)anthracene; 20: benzo(g,h,i)perylene.