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Corresponding Author: Dr. A. Garrido Frenich,

Corresponding Author's Institution: University of Almeria, Dept. of Hydrogeology and

First Author: Patricia Plaza-Bolaños

Order of Authors: Patricia Plaza-Bolaños; A. Garrido Frenich; José Luis Martínez Vidal

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5 **Patricia Plaza-Bolaños[a,b], Antonia Garrido Frenich[a,]*, José Luis Martínez Vidal[a]**
6
7 [a]*Department of Analytical Chemistry, University of Almeria, E-04071 Almeria, Spain*
8 [b]*Department of Analytical Chemistry, University of Granada, E-18071, Granada, Spain*
9
10
11 * Corresponding author: Antonia Garrido Frenich, Department of Analytical Chemistry,
12 University of Almeria, E-04071 Almeria, Spain.
13 Tel: +34 950015985; fax: +34 950015483.
14 E-mail address: agarrido@ual.es (A. Garrido Frenich)
15
16
17

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are compounds widespread in the environment, many of them showing carcinogenic effects. These compounds can reach the food chain by different ways and, therefore, the analysis of PAHs in food is a matter of concern. This article reviews the extraction methodologies together with the separation and detection techniques which are currently applied in the determination of PAHs in food and beverages. Specific extraction conditions, performance characteristics, chromatographic and detection parameters are discussed. A review of the occurrence of these compounds in the matrixes under study is also provided.

***Keywords*:** polycyclic aromatic hydrocarbons (PAHs), analysis, food, beverages, gas chromatography (GC), liquid chromatography (LC), fluorescence detection (FLD), mass spectrometry (MS)

35 **Contents**

36

37 1. Introduction 4
38 2. Sample preparation: extraction and clean up....................6
39 2.1. Liquid matrices 7
40 2.1.1. Fatty matrices....................7
41 2.1.2. Non-fatty matrices 10
42 2.2. Solid matrices 13
43 2.2.1. Fatty matrices.................... 13
44 2.2.2. Non-fatty matrices 17
45 3. Chromatographic and detection techniques.................... 17
46 3.1. Liquid chromatography coupled to UV and FLD.................... 17
47 3.2. Gas chromatography coupled to MS 19
48 4. Determination of PAHs in real samples 22
49 5. Conclusions 26
50 6. Trends 27
51 References 28

52

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) or polyarenes constitute a large class of organic compounds (about 10,000 substances) characterized by a structure made up of carbon and hydrogen atoms ~~(Table 1)~~ forming two or more fused aromatic rings without any heteroatom or substituent (the most important compounds are shown in Table 1). The compounds containing five or more aromatic rings are know as “heavy” PAHs, whereas those containing less than five rings are named “light” PAHs. Both kinds of PAHs are non-polar compounds showing high lipophilic nature, although heavy PAHs are more stable and toxic than the other group.

PAHs are ubiquitous environmental contaminants which are widespread in the air bonded to particulate matter. In spite of PAHs show hydrophobic properties (especially heavy PAHs), they are also found in water. These compounds are produced during a variety of combustion and pyrolysis processes from anthropogenic and natural sources. A high amount of PAHs are emitted from processing coal, during incomplete combustion of organic matter (e.g. wood and fossil fuels), from motor vehicle exhaust and cigarettes [1,2]. Forest fires, volcanoes or hydrothermal processes are natural emission sources of PAHs [3].

A number of PAHs are considered as genotoxic carcinogens, and biological and mutagenic effects have also been reported [3]. Other PAHs not defined as carcinogens may act as synergists [2]. The occurrence of PAHs in the environment is therefore a cause of concern since humans are exposed to these compounds, for instance, by the air. However, one of the major routes of human exposure to PAHs in non-smoking people is food; for smokers, the contribution of cigarette smoke may be similar [4]. Food can be contaminated by PAHs present in the environment, i.e. PAHs can accumulate on the waxy surface of many vegetables and fruits [4]. Indeed, the presence of PAHs in uncooked food, such as vegetables, seeds and grains, has been demonstrated [5]. These products do not take up significant amounts of PAHs from the soil, but from air particles [2] throught deposition of contaminated matter. Nevertheless, other studies show contradictory results about the possibility of vegetables to take PAHs from soil and water and metabolize them [6]. Another example of possible PAH contamination in food is due to traffic, i.e. crops or livestock close to urban roads could be exposed to PAHs and nitro-PAHs (derivates from PAHs) [5]. Other food products, such as seafood and fish, can be exposed to PAHs present in water and sediments and the PAH content greatly depends on the ability of the aquatic organisms to metabolize them (e.g. bivalve

mollusks accumulate more PAHs than vertebrate fish, which metabolize these compounds very rapidly.

On the other hand, PAHs can be found in food products as a consequence of certain industrial processing methods, such as smoking, heating (grilling, roasting) and drying, which permit the direct contact between food and combustion products; these are important sources of PAH contamination for seeds, edible oils, and meat and dairy products [4]. In edible oils, the oilseed drying processes by direct combustion can be an important source of contamination in a variety of vegetable oils [7].

Furthermore, the use of smoke flavoring products (SFP), which are utilized to improve organoleptic characteristics, has increased in food industry~~ [8]~~. Since SFP are produced from smoke condensates, they are another significant source of PAHs in food. In food industry, materials as polyethylene are normally used. This material is effective in lowering PAH load from a contaminated food, but~~Besides,~~ an opposite effect can be observed when using~~the use of~~ recycled polyethylene film in oil packaging since it could contaminate vegetable oils with PAHs ~~in~~ by rediffusion, ~~-~~[8].

In general, PAHs are not present individually but in mixtures. PAHs that have been extensively monitored are the compounds included in the United States Environmental Protection Agency (US-EPA) list of priority organic pollutants (the so-called 16 EPA PAHs) [9]. ~~,~~Since 2005, ~~as well as~~ the European Union (EU) list of PAHs [10] (15 compounds) has also been included in the monitoring studies [2] (Table 1). Benzo[*a*]pyrene (BaP) is probably the most studied PAH. The International Agency for Research on Cancer (IARC) described BaP as probable human carcinogen in 1987 [11]. Thus, the determination of BaP has been widely used in environmental analysis as marker for the entire PAH content. Maximum permitted concentrations in foodstuffs for BaP have been established by the EU [12], as well as methods of sampling and analysis in order to perform official controls of this compound [13]. However, BaP contributes only with 1-20 % of the total content of PAH, and other aromatic compounds can be present as well [1]. In this sense, in 2002, the Scientific Committee on Food (SCF) of the European Commission considered that despite the use of BaP as a marker of occurrence and carcinogenic effect of the PAH content in food, it suggested that this evaluation should be accompanied by additional analysis of other PAHs in order to establish a PAH contamination profile in food commodities [14]. In 2007, the European Food Safety Authority (EFSA) pointed out that the supposition that BaP was a good indicator of any PAH contamination was uncertain [4]. The SCF noticed that a number

121 of derivatives of PAHs, such as nitro-PAHs and oxygenated PAHs, as well as
122 heterocyclic aromatic compounds (e.g. acridine, carbazole) can be generated by
123 incomplete combustion or reactions in air [14]. Consequently, the determination of all
124 these compounds in food is also an issue of concern.

125 The monitoring of other PAHs has been strongly recommended by the EU [10]. The
126 EFSA also remarked that food categories such as herbs and spices, food supplements,
127 coffee, tea and herbal infusions and other cereal and grain beverages are not
128 covered~~captured~~ by existing legislation [1,2,4,12]. Later, in 2008, the EFSA established
129 that BaP is not a suitable indicator for the occurrence of PAHs in food and that
130 occurrence data for benzo[*c*]fluorene (BcF) are needed [15]. It is important to notice
131 that this compound is not included in either the EPA or the EU list of PAHs.

132 Therefore, the need for reliable data about the concentration of PAHs in food is
133 increasing in order to establish new maximum permitted levels. In this sense, analytical
134 laboratories play an important role since they must have adequate methods for the
135 analysis of PAHs and their derivatives in food.

136 This review shows an overview of the analytical methodologies applied in the
137 determination of PAHs in food and beverages (e.g. edible oils, smoked foodstuffs, milk
138 or infusions), including recent approaches. The main techniques applied in the
139 extraction and clean up of the extracts and in the detection and quantification of the
140 analytes have been reviewed, focusing on liquid chromatography (LC) coupled to
141 fluorescence (FLD) and ultraviolet-visible (UV) detection and gas chromatography
142 (GC) coupled to mass spectrometry (MS). New trends based on instrumental analysis
143 and recent extraction techniques, some of them applied in other fields of food safety and
144 environmental analysis, have been pointed out.

145 The review covers the relevant literature published since the year 2000 and certain
146 previous references highly cited. The previous articles have already been revised and
147 discussed elsewhere [7,8,16].

148

149 **2. Sample preparation: extraction and clean up**

150 As general precautions to be considered when determining PAHs, it is important to
151 protect the solutions against light since these compounds are light sensitive and they can
152 decompose by photoirradiation and oxidation [17]. Thus, light exposure during the
153 sample pre-treatment has to be carefully controlled [17,18]. Besides, concentration to

dryness should be avoided in order to diminish possible losses due to evaporation of the lower molecular weight compounds [17].

2.1. Liquid matrices

2.1.1. Fatty matrices

It is well-known that one of the main difficulties in the analysis of fatty matrices is due to their high fat content (e.g. lipids, triglycerides, fatty acids) [19]. For this reason, the extraction of PAHs from these complex matrices is usually a laborious and time-consuming stage (Figure 1). The removal of lipidic material is important not only to minimize the maintenance of the chromatographic system (especially when using GC), but also to reach low detection limits (LODs). The need for high sensitivity is justified by the low concentrations of PAHs fixed as maximum levels permitted in current legislation [1,2,8,12,20].

Extraction of PAHs from foodstuffs has traditionally relied on a three-stage methodology including saponification, liquid-liquid extraction (LLE) and clean-up by column chromatography or, more recently, solid-phase extraction (SPE).

One of the most studied fatty commodities is edible oils since they can be exposed to PAHs by the use of heating processes (e.g. during solvent evaporation) [21] or solvent extraction during their production. Besides, the drying of the raw material (e.g. seeds) with combustion gases before oil extraction generates high amounts of PAHs [22]. The reported methods in bibliography described the use of two general strategies for the sample extraction and clean-up. The first strategy involves the dilution of the sample, LLE and a subsequent clean-up by SPE [17,23~~21~~,24~~22~~]; the other general methodology carries out a single SPE-stage after the sample dilution [22,23~~21,23~~,25,26~~ 25~~]. The dilution step is normally performed with *n*-hexane in order to modify the partition coefficients [8]. A variety of solvents are used in LLE, but the most common are dimethylsulfoxide (DMSO) and cyclohexane (Table 2). For the clean-up by SPE, very different cartridges have been utilized, such as C_{18}/C_8, aminopropyl, silica and polystyrene/divinylbenzene (PS-DVB) sorbents. For SPE (as extraction method), C_{18}/Florisil mixtures [21~~26~~] and PS-DVB [26~~25~~] have been used. Some authors have described PS-DVB sorbents as extremely selective to PAHs, considering this material as suitable to most of food matrices [27].

Recently, humic acid-bonded silica has been proposed as a new sorbent for the extraction of PAHs by SPE using BaP as example [25~~24~~]. The retention of PAHs in this

188 sorbent is based on charge-transfer and hydrophobic interactions. Nevertheless,
189 additional applications of this SPE material have not been found.
190 The performance of a saponification step prior to the LLE is also described in order to
191 reduce the lipidic content (e.g. triacylglicerols), for instance using mixtures of KOH or
192 NaOH solutions and ethanol or methanol~~containing an alcoholic percentage~~ [1,7,8,17].
193 However, losses of BaP have been reported by partial portioning to the alcoholic phase
194 when using this procedure [17], and other authors suggested that saponification could
195 negatively affect the most labile compounds [8].
196 The formation of caffeine complexes with PAHs prior to LLE has been also reported
197 by mixing the sample with a caffeine:formic acid solution, although it is not currently
198 applied. The complexes are then decomposed by extracting with an aqueous sodium
199 choride solution [7,8].
200 Column chromatography has also been applied as clean-up using alumina [28~~29~~] and
201 silica gel [29~~30~~]. The utilization of donor-acceptor complex chromatography (DACC)
202 for the clean-up of diluted oil samples is also described [28~~29~~,30~~31~~]. DACC is based on
203 a strong π-π interaction produced between the sorbent and the PAHs; then, certain
204 matrix components, such as neutral lipids and tocopherol, can be eluted by using a non-
205 π-electron containing solvents. After that, the PAHs are eluted with an appropriate
206 organic solvent that removes the interaction (e.g. *n*-hexane:tetrahydrofuran mixtures,
207 acetonitrile). However, some problems can be found. The lightest PAHs (namely
208 naphthalene (NPH), acenaphthylene (ACY), acenaphthene (ACP) and fluorene (FLR))
209 co-eluted with the fatty fraction and the use of more than 5 % of tetrahydrofuran caused
210 additional co-elution problems.
211 In general, the reported recoveries applying the methodologies commented above are
212 quite similar, showing good relative standard deviation (RSD)~~precision~~ values (< 10 %).
213 However, the application of the saponification stage prior to an LLE and SPE clean-up
214 can provide very high recovery (> 120 %) values for some compounds [17]. Despite the
215 problems reported for the application of DACC, the recoveries reported for edible oils
216 are slightly higher than the recoveries obtained using LLE and/or SPE (Table 2).
217 Gel permeation chromatography (GPC, also size exclusion chromatography, SEC) has
218 been utilized after LLE operating in the normal phase mode (e.g. mobile phase:
219 dichloromethane; stationary phase: styrene-divinylbenzene copolymer) [31~~32~~]. This
220 kind of chromatography has been extensively used for the purification of fatty extracts
221 separating lipids from the analytes. Despite GPC is broadly applied in food analysis,~~;~~

222 ~~although~~ its application in the reported methods for edible oils is scarce (Table 2). The
223 reported recoveries are higher than those using other methodologies, although this
224 procedure (LLE + GPC) was only carried out for the determination of medium
225 molecular weight PAHs. GPC is a semi-automatic clean-up, which is an obvious
226 advantage, but the solvent consumption is moderated, especially considering a typical
227 flow of 5 mL min^{-1} and 30-40-min running times. Thus, about 150-200 mL of solvent
228 per sample can be required, which could explain its low use.

229 Bogusz et al. [21~~26~~] carried out a comparison between the performance of SPE and
230 matrix-solid phase dispersion (MSPD) for the extraction of PAHs from olive oil. In the
231 MSPD technique, a small amount of sample (typically 0.5 g) is mixed with a solid
232 support (e.g. C_{18} material) in a mortar. Then, the mixture is transferred to an SPE
233 reservoir and eluted in the same way as in SPE. The main advantage of MSPD is the
234 low amount of solvent needed. Nevertheless, reproducibility problems are often
235 observed, with medium-high RSD~~precision~~ values. The extraction of PAHs with this
236 technique is not an exception: MSPD provided lower recoveries and worse repeatability
237 than the SPE procedure used. However, MSPD is simpler and faster than the LLE-based
238 methods.

239 Due to the volatile character of certain PAHs, they have been also determined by
240 head-space (HS) and solid-phase microextraction (SPME) techniques, namely, HS
241 [32~~33~~], HS-SPME [33~~34~~] and SPME [34~~35~~,35~~36~~], with or without a previous dilution
242 of the oil. HS-SPME has been applied for the analysis of PAHs showing a molecular
243 weight ≤ 202 using a DVB/carboxen/polydimethylsiloxane (DVB/Car/PDMS) fiber,
244 which was chosen on the basis of its affinity for low/medium molecular weight
245 compounds [33~~34~~]. The recovery values were adequate, even for NPH, which is a
246 problematic compound because of well-known losses during the evaporation stages in
247 the extraction. This can be explained since the HS-SPME does not involve any
248 evaporation or pre-concentration stage. However, the ~~precision~~ RSD values are higher
249 in comparison to other extraction techniques. The application of SPME with direct
250 immersion of the fiber in the oil has also been reported [34~~35~~,35~~36~~], using
251 Carbopack/PDMS fibers and dilution of the oil. In the analysis of fatty commodities,
252 one of the main problems when using SPME is matrix effect, causing a decrease in the
253 fiber efficiency. In order to decrease the possible matrix effect, the fiber needs to ~~can~~ be
254 rinsed with *n*-hexane prior to desorption and injection in order to remove triglycerides
255 residues on the surface of the fiber [34~~35~~,35~~36~~]. Purcaro et al. [35~~36~~] described the use

of an SPME method for the determination of the EU list of PAHs with low ~~relative standard deviation (~~RSD~~)~~ values (<11%, except for BcF (16%) and cyclopenta[*c*~~,~~*d*]pyrene (CPcdP) (35%)). It was observed that at high extraction times (>30 min), the extraction efficiency decreased for some compounds, due to a rising effect by the organic solvent used in the dilution. Desorption time was limited to 10 min to avoid broadening of the peaks of the later eluted compounds (heavy PAHs). As commented above, the SPME methodologies are limited with respect to precision~~can provide high precision values~~. This is one of its drawbacks, the lack of reproducibility, together with a short lifetime of the fibers and possible carry-over problems. On the contrary, the use of HS/SPME technique reduces sample handling and minimizes solvent consumption.

Another fatty liquid matrix that has been monitored for PAHs is milk, but to a lesser extent. Although the fat content of this matrix is much lower than the fat percentage of edible oils, the methodologies used in the revised literature are quite similar (Table 2). LLE-based methods are therefore applied, but the number of LLE stages is more reduced [36~~37~~-38~~39~~]. Lutz et al. [37~~38~~] described the analysis of PAHs and hydrox~~i~~y-PAHs using the same extraction procedure involving LLE, SPE as clean-up and subsequent LLE steps for clean-up (different for each group). It is important to notice that any SPE procedure has been found for the extraction of PAHs from milk (Table 2). The use of saponification is also reported; the alcohol percentage was found to influence the extractability of the compounds, increasing the extractability but also the intensity of interfering peaks when working at 100 % ethanol. HS-SPME [39~~40~~] and SPME have been also applied [40~~41~~]. In both studies, PDMS-DVB fibres were used; in the case of SPME, the sample was diluted with water prior to the extraction. The HS-SPME modality was also evaluated but it was not able to extract the high molecular weight PAHs [40~~41~~]. In a later study, the HS-SPME mode was used for the extraction of PAHs containing up to four aromatic rings [39~~40~~]. Similar recoveries were obtained, although better ~~precision~~ RSD values were found in the HS-SPME procedure. In comparison to the LLE-based methodologies, these two microextraction techniques provided an improvement in the recovery values.

More detailed information about extraction methods is shown in (Table 2).

2.1.2. Non-fatty matrices

289 The monitoring of PAHs has been carried out in a number of non-fatty liquid matrices,
290 namely coffee, tea, alcoholic beverages and juice. In general, the extraction of PAHs
291 from these commodities is performed by less laborious procedures less laborious than
292 the protocols used for fatty matrices since the amount of lipidic material, and thus the
293 possible matrix interferences, is much lower than in thate previous group of matrices
294 (Table 2).
295 The use of LLE with subsequent SPE clean-up (silica sorbent) has been reported in
296 coffee brew [4142]. The application of a single SPE stage was discarded because of
297 clogging problems when passing instant coffee solutions through the SPE cartridge
298 (C_{18}); the application of microwave-assisted extraction (MAE) was also ruled out due to
299 stability problems observed for some PAHs. LLE and subsequent clean-up using
300 column chromatography with silica gel has been recently applied forin cachaça
301 (Brazilian spirit) [4243].
302 In the extraction of PAHs by SPE using reversed-phase or polymeric sorbents, some
303 questions must be taken into account. Depending on the solvent used, adsorption
304 problems related to PAH solubility can be found (e.g. adsorption onto the glassware
305 walls). The addition of a small percentage (e.g. 10%) of an organic solvent (i.e.
306 methanol, acetonitrile or 2-propanol) to the sample can be used to increase solubility
307 and minimize this adsorption. However, the optimization of the solvent percentage is a
308 critical point since low percentages cannot improve the solubilization of the heavy
309 PAHs, whereas a high percentage can reduce the breakthrough volume for the light
310 PAHs [43].
311 SPE-based procedures have been used for the analysis of PAHs in coffee [44], but also
312 in tea [45] and spirits [46] using different cartridges, such as PS-DVB and C_{18}.
313 However, Houessou et al. [44] consider PS-DVB sorbents as the most suitable material
314 for the extraction of PAHs from liquid samples due to π-π interactions that can increase
315 the retention in comparison to C_{18} or silica sorbents, which do not show this type of
316 interaction. Moreover, slightly better reproducibility was found when using PS-DVB
317 cartridges instead of C_{18} sorbents for the analysis of coffee. The addition of methanol or
318 acetonitrile to the sample has been described in order to minimize the adsorption of
319 PAHs onto the glass and/or cartridge surfaces [44-46]. However, contradictory results
320 concerning the methanol percentage have been reported: about 1% (v/v) of methanol
321 has been described as the optimal amount in order to avoid competitive effects between
322 PAHs and the solvent on the stationary phase [44] for tea samples, whereas higher

323 percentages (10-20%, v/v) have been used in coffee samples and spirits [45,46].
324 Alternatively, SPE has been performed using molecularly imprinted polymers (MIP-
325 SPE) for the extraction of BaP in coffee with adequate performance characteristics; the
326 MIP-SPE sorbent was compared to C_{18}, obtaining better recovery values for the first
327 approach [47].

328 LLE [42~~43~~] and SPE [46] have been utilized for the analysis of spirits, obtaining
329 similar recovery values but better RSDs when using SPE, probably due to the high
330 number of LLE steps included in the first method. Moreover, the SPE-based
331 methodology was applied for the analysis of a higher number of PAHs (15) in
332 comparison with the LLE method (5).

333 HS-SPME has been applied for the analysis of PAHs in tea infusions; a variety of
334 fibres were evaluated, including polyacrilate (polar), PDMS (non-polar), and PDMS-
335 DVB (medium polarity). The optimal results were obtained using PDMS-DVB fibres
336 [48]. Nevertheless, some drawbacks have been reported, such as overloading problems
337 due to insufficient coating film of the fibres [49]. In this sense, two recent approaches
338 described the application of stir bar sorptive extraction (SBSE) for the analysis of mate
339 tea [49] and sugarcane juice [50]. In SBSE, the adsorption process occurs ~~i~~on bars and
340 so the amount of coating film is higher, increasing the adsorption capacity in
341 comparison with SPME and also minimizing the amount of co-extracted matrix material
342 (Figure 2). SBSE is currently considered as an environmentally friendly technique since
343 it permits the reduction of solvent consumption to the minimum (no solvent required).
344 SBSE with thermal desorption (SBSE-TD) is the solvent-free mode but it requires a
345 special device in the chromatographic system to carry out the desorption of the analytes.
346 As an alternative, the desorption process can be performed by using an appropriate
347 solvent; in this case, the volume needed is still reduced (from a few microliters up to 1-2
348 mL). This modality has been used in mate tea samples with results comparable to LLE
349 [49]; this study described the negative effect of the addition of NaCl to increase the
350 ionic strength since the presence of salt provokes the transfer of the PAHs to the surface
351 of the solution, minimizing the interaction with the sorbent on the bar: it is the "oil
352 effect". The addition of methanol or acetonitrile to reduce adsorption onto the walls was
353 discarded since any improvement was found. SBSE-TD was applied satisfactorily for
354 the determination of only BaP in sugarcane juice [50]. Bearing in mind that the matrices
355 were different, worse ~~precision~~ RSD values were obtained for BaP with this modality
356 (19 % by SBSE-TD and 4-6% by SBSE), which is an unexpected data since the SBSE-

357 TD involves an automated desorption that should improve this parameter. The
358 performance of SBSE-TD was compared to another environmentally friendly technique,
359 membrane-assisted solvent extraction (MASE) [50], concluding that MASE provided
360 better recovery and ~~precision~~ RSD values. MASE was also applied for the
361 determination of PAHs in several beverages [51]; in this case, a higher number of
362 compounds were monitored (16) and the addition of methanol was found adequate since
363 it improved the enrichment of the compounds in the membrane bag. It is important to
364 notice that the recovery of the more volatile PAHs (e.g. NPH) was more than
365 acceptable, probably due to the fact that any evaporation stage was needed in this
366 procedure.
367 More detailed information about extraction methods is shown in (Table 2).
368

369 ***2.2. Solid matrices***

370 *2.2.1. Fatty matrices*

371 There are two food commodities that have been extensively monitored for PAHs, meat
372 and fish (Table 2). The analysis of PAHs in meat, especially smoked meat, is due to the
373 occurrence of these compounds after traditional or industrial smoking processes.
374 Despite there are controversial results, many authors agree on the facts that vertebrate
375 fish did not accumulate PAHs in their tissue as they rapidly metabolize them. However,
376 PAHs~~, whereas fish~~ can bioaccumulate ~~PAHs~~ in ~~their~~ fatty tissues and fish is not free
377 from the exposure to these contaminants ~~PAHs~~ from~~in~~ the environment~~al compartment~~.
378 Despite this review aims to cover the most relevant literature after 2000, there are
379 previous studies widely referred which are related to the analysis of meat using solid-
380 liquid extraction (SLE), and SPE for clean up [52-54]. Chen et al. [52,53] proposed the
381 extraction of the sample, which was previously lyophilized, by SLE using ultrasounds
382 or ultrasound extraction (USE), and subsequent SPE clean-up with Florisil. This method
383 was then compared to a more laborious procedure involving saponification using a
384 Soxhlet extractor, and a number of LLE steps prior to a final SPE clean-up (Florisil).
385 Despite the recovery values were quite similar and USE reduced extraction time and
386 solvent consumption, the Soxhlet method was eventually selected due to the
387 saponification stage was described as necessary for a successful ~~the~~ determination of the
388 selected PAHs. Chiu et al. [54] also described the performance of a saponification stage
389 in a similar way as described in [52].

The utilization of supercritical fluid extraction (SFE) together with C_{18} sorbent inside the SFE chamber to perform a simultaneous extraction and clean up of the samples has been described. Although promising results were obtained, the application of SFE has not succeeded, as in other analytical fields [55-57].

Wang et al. [58~~55~~] first described the use of pressurized liquid extraction (PLE~~, also known as accelerated solvent extraction, ASE~~) for the analysis of PAHs in meat samples. A dichloromethane/acetonitrile mixture was used and C_{18} or C_8 bulk sorbent and sodium sulphate were used to prepare the extraction cell. Although the performance of the SLE process by using PLE allowed the semi-automation of the extraction stage, a laborious clean-up procedure was still applied since partitionings~~s~~ with sulphuric acid and column chromatography (Florisil) were also performed. More recent PLE-based methodologies have been published for this aim, but using in the clean-up stage GPC and column chromatography [59~~56~~] or GPC and SPE [60~~57~~]. These studies utilized *n*-hexane as extraction solvent and polymeric-based columns (styrene DVB) for the GPC process (normal phase). This stage permitted the removal of a high percentage of lipids from the matrix; however, this was insufficient and an additional clean-up step was needed, as described in both studies. Jira et al. [59~~56~~] pointed out the use of GPC as an effective way of removing lipidic material instead of saponification; for the remaining lipids and polar compounds, silica gel column chromatography was chosen. The use of sea sand and/or drying material to homogenize the sample was discarded because of certain PAHs (pyrene (PYR), benz~~o~~[*a*]anthracene (BaA), BaP, indeno[1,2,3-*cd*]-pyrene (IP), dibenzo[*a,h*]anthracene (DBahA) and benzo[*g*~~,~~*h*~~,~~*i*]perylene (BghiP)) could be adsorbed on these materials. The use of GPC and subsequent SPE by silica gel is a similar procedure also reported [60~~57~~,61~~58~~]. The use of GPC and column chromatography offered higher recoveries and lower RSD values in comparison with GPC plus SPE, although the number of monitored PAHs was superior in this last study.

In relation to the recovery rates, in general, the results obtained by LLE-based and PLE-based procedures are very similar; although it is obvious that PLE shows certain advantages, such as automation of the process and less solvent and time consumption.

Although SPME is normally used with liquid samples, Martin et al. [62~~59~~] described the application of this extraction technique to the analysis of PAHs in meat by using a direct extraction device (SPME-DED). This device contains a gelatine support for the SPME fiber that permits the interaction between the fiber and the solid sample (Figure

423 3). Although recovery values were not provided, the ~~precision~~ RSD values obtained
424 were consistent.
425 Fish (and seafood) is the second most studied fatty matrix in PAH analysis. Despite
426 the disadvantages of Soxhlet have been largely discussed (e.g. solvent consumption,
427 time-consuming, non-selective), its efficiency still makes it used and selected in PAH
428 analysis. In this type of commodity, the use of Soxhlet extraction (e.g. dichloromethane,
429 *n*-hexane) is widely reported [63~~60~~-67~~64~~]; lyophilization [63~~60~~] ~~-~~and homogenization
430 with sodium sulphate [64~~61~~,67~~64~~] have been applied prior to the SLE process. As in
431 previous matrices, a clean-up stage is mandatory after the Soxhlet extraction due to the
432 high amount of co-extracted material. The use of GPC is preferred for this aim
433 [63~~60~~,65~~62~~], although saponification plus subsequent LLE stages and column
434 chromatography [66~~63~~,67~~64~~] have also been described. The main disadvantage of the
435 application of GPC in this type of matrices is not only the moderate solvent
436 consumption but also the widespread utilization of chlorinated solvents such as
437 dichloromethane or chloroform as mobile phases (Table 2). In relation to the
438 performance characteristics, the procedures using~~se~~ Soxhlet~~-based procedures~~ provided
439 adequate recoveries but~~and~~ the reported RSD ~~ranges~~ were quite high for certain
440 compounds~~significantly wide~~ (e.g. 2-20%); these high~~est~~ RSD values could be due to
441 the application of such~~se~~ time-consuming protocols involving~~cluding~~ numerous steps.
442 Although the performance of a saponification and subsequent LLE stages is less time-
443 consuming than Soxhlet plus GPC or LLE, it provided low recoveries and similar
444 ~~precision~~ RSD values [68~~65~~].
445 PLE is applied as a suitable option to the aforementioned procedures
446 [58~~55~~,65~~62~~,69~~66~~]. The decrease in the extraction time against the Soxhlet methods is an
447 obvious advantage. However, PLE is also a non-selective extraction and further clean-
448 up is normally performed. Wang et al. [58~~55~~] described that the removal of the fatty
449 material in the PLE extracts was incomplete when applying saponification and an acid
450 treatment with sulphuric acid (18 M) was found to cause decomposition of several
451 PAHs (namely ACY, anthracene (ANT), and BaP) and losses of signal (e.g. ACP, IP,
452 DBahA and BghiP). Nevertheless, this effect was not observed when a less concentrated
453 solution was used (9 M). On the contrary, Martinez et al. [69~~66~~] utilized a
454 saponification stage for the clean-up of the raw PLE extracts with adequate recoveries,
455 although a different extraction solvent was used (*n*-hexane:dichloromethane (1:1)
456 instead of dichloromethane:acetonitrile (9:1)). In this study, Soxhlet extraction, USE

457 and PLE were compared; similar results were found when using PLE and USE,
458 although this last methodology was less repetitive. Surprisingly, the classical Soxhlet
459 extraction yielded worse recovery and ~~precision~~ RSD values than PLE and USE. In a
460 similar study, Janska et al. [65~~62~~] established that the results provided by PLE and USE
461 were not significantly different from those found by using the Soxhlet extraction, using
462 GPC for the clean-up of the extracts in all cases, but higher repeatability was observed
463 with PLE. The utilization of extraction mixtures containing a water-miscible solvent
464 was strongly recommended in PLE to enhance the penetration into wet fatty matrices,
465 such as fish [65].
466 The saponification stage has also been performed together with the extraction step by
467 MAE [70~~67~~], reducing the whole extraction time. However, further purification by SPE
468 (silica) was needed and the number of analyzed PAHs was reduced (7 compounds).
469 Additionally, direct SPE or GPC clean-up of MAE extracts has been applied; despite
470 any recovery or precision rates were provided, the results of the analysis of a certified
471 reference material were adequate [71-73~~68~~].
472 The use of HS-SPME has been described for the analysis of PAHs showing up to 4
473 rings in fish and seafood using polyacrylate [74~~69~~] and PDMS-DVB fibres ~~-~~[75~~70~~].
474 Two approaches can be used considering that these matrices are solid samples: first, the
475 sample can be put directly into the HS vial [74~~69~~]; a second option involves the
476 homogenization of the sample with a liquid solution [75~~70~~]. Any comparison could be
477 established between both procedures (with and without homogenization of the sample
478 with solvent) since performance characteristics were not provided in the method using
479 the raw sample.
480 MSPD was also evaluated for the determination of 6 PAHs in fish and seafood [76~~71~~].
481 For clean-up purposes, an acid treatment with sulphuric acid impregnated silica gel was
482 evaluated thanks to its compatibility with MSPD. However, the compounds were
483 retained in the sorbent, although the lipidic removal was effective. The recovery rates
484 were adequate and the ~~precision~~ RSD values were significantly low, which is
485 remarkable since one of the main drawbacks of MSPD is its moderately low
486 repeatability/reproducibility. As previously discussed, sulfuric acid can be used for the
487 removal of lipids.
488 Recently, Ramalhosa et al. [77~~72~~] evaluated the so-called QuEChERS method
489 (acronymic name from quick, easy, cheap, effective, rugged and safe) in fish. This
490 method is a procedure extensively applied and originally developed for the analysis of

pesticide residues in food samples. The described approach results very appropriate for the analysis of volatile PAHs, such as NPH, ACP or FLR, often lost during pre-concentration stages, since it does not involve any evaporation step. The results obtained for heavy PAHs were also consistent, as verified by the analysis of a certified reference material. Beside this, the QuEChERS method is much easier than the typical procedures described for the analysis of PAHs (e.g. Soxhlet, LLE, etc.), showing adequate performance characteristics.

Smoked cheese is another fatty matrix of interest for the monitoring of PAHs, although the number of related studies is very scarce. As in other fatty matrices, Soxhlet plus GPC [78~~73~~] and LLE-based methods [79~~74~~], sometimes including saponification [80~~75~~], are described in literature. SPE has been applied for clean-up purposes using silica sorbents. The recovery values for the revised references are adequate and comprise between~~lower than~~ 52 and 96~~100~~%. For the most volatile compounds, Suchanova et al. [78~~73~~] remarked the poor recoveries obtained (namely, NPH, ACP and FLR). This is a well-known fact that has been confirmed in many other studies; however, these authors do not consider important to improve the efforts in increasing the recovery rates for these PAHs since they are not health concerns in terms of carcinogenicity.

More detailed information about extraction methods is shown in (Table 2).

2.2.2. Non-fatty matrices

Besides the matrices discussed before, PAHs have been monitored in a variety of solid foodstuffs, i.e. tea leaves [81~~76,~~82~~77~~], vegetables [83~~78~~-85~~80~~], fruits [84~~79~~], bread [85~~80~~], cane sugar [86~~81~~], fatty food mixtures [27], ground coffee [87~~82~~] and palm dates [66~~63~~] (Table 2). The methodologies applied are not different from those applied in the main food groups. Soxhlet, LLE, PLE or USE have been utilized in the extraction step (involving in some cases a saponification stage), whereas GPC or SPE have been applied in the clean-up step. Borjadandi et al. [88~~83~~] reported the analysis of PAHs in a great variety of food samples, such as fish, seafood, meat products, vegetable oils, breads and pastries. For this aim, a generic methodology based on Soxhlet extraction was applied, concluding that this extraction technique is the most suitable for the determination of very different food commodities with adequate performance.

More detailed information about extraction methods is shown in (Table 2).

3. Chromatographic and detection techniques

In general, the determination of PAHs is carried out by liquid chromatography coupled to fluorescence (LC-FLD) or ultraviolet-visible detection (LC-UV), or gas chromatography coupled to mass spectrometry (GC-MS) detection, techniques which are discussed below.

3.1. Liquid chromatography coupled to UV and FLD

In the past, the determination of PAHs by LC was carried out by using UV detection [52,54]. However, it is well-known that UV detection shows a number of disadvantages, such as selectivity problems and sensitivity limitations, and it cannot discriminate matrix interferences, especially in complex matrices. On the contrary, FLD is more selective and sensitive than UV detection, and it is currently the detection system of choice in LC, normally with variable excitation and emission wavelengths. LC-FLD has been extensively applied for the determination of PAHs in very different matrices, including foodstuffs and beverages, since it is cheap and simple, in comparison to other detection systems. Indeed, LC-FLD has been the basis of different official methods for the analysis of PAHs in food [2,89~~84~~] (Table 3).

In this sense, LC-FLD has been largely used for the determination of the EPA priority list of PAHs [22,23~~21,23~~,46,49,52,65~~62~~,77~~72~~]. It has been reported that ANT and perylene (PER) are best measured by FLD due to their selective and sensitive fluorescence characteristics [3]. ~~BghiP cannot be properly determined due to its low fluorescence sensitivity [3], and~~ CPcdP does not give rise to fluorescence and can only be quantified by UV detection [1]. Despite there is an improvement in comparison to UV detection, FLD can still show a lack of selectivity, and then GC-MS is applied in order to confirm the positive results [17,54,84~~79~~,87~~82~~].

Moreover, some authors describe certain selectivity problems due to the presence of alkylated PAHs [16], which are considered the main impurities of PAH fractions. These compounds show similar fluorescence responses to the unsubstituted PAHs. Another disadvantage is the impossibility of using certain isotopically labeled compounds because of FLD cannot distinguish these ones from the native PAHs. As an alternative, benzo[*b*]chrysene or deuterated compounds, which can be chromatographically separated, have been used [1].

In relation to sensitivity, the reported limits of detection (LODs) are frequently found at the sub-ppb level (e.g. 0.01-1 μg L^{-1} or μg kg^{-1}), and in some applications in

beverages, LODs at the ppt level (e.g. 0.01-1 μg L^{-1} or μg kg^{-1}) have been achieved [44,48,49]. This fact can be justified since in this type of samples, pre-concentration techniques such as SPE or SBSE have been applied.

Despite the widespread use of columns with particle size ≤ 2 μm in trace analysis (i.e. pesticide or veterinary drug residues analysis [90~~85~~]), the utilization of ultra-high performance liquid chromatography (UHPLC) has not been reported in PAH analysis, up to our knowledge. The main advantages of UHPLC are well-known (e.g. reduction of running time or narrower peaks than conventional LC) and its application has rapidly increased. Thus, the coupling of UHPLC to FLD would provide an increase in chromatographic resolution that could improve the discrimination of co-eluted interferences, especially in complex matrices such as foodstuffs.

Although FLD is the most utilized detection system for the analysis of PAHs in food and beverages by LC, MS has also been applied in other matrices such as environmental matrices [91~~86~~,92~~87~~] or biological matrices [93]. Up to our knowledge, only a study related to the determination of hydroxyl-PAHs describes the application of LC-MS using electrospray ionization (ESI) in negative mode [94]. Due to their non-polar character, atmospheric-pressure chemical ionization source (APCI) [91~~86~~] and atmospheric-pressure photoionization (APPI) [92~~87~~,~~–~~95~~88~~] have been applied as ionization techniques. However, the application of LC-MS using APCI or APPI as ionization modes for the determination of PAHs in food commodities has not been described yet.

More detailed information about determination methods and conditions is shown in (Table 3).

3.2. Gas chromatography coupled to MS

GC-MS is the main alternative to LC-FLD and it is applied in all kind of food samples. Besides, GC-MS-based methods are more frequently found in the more recent bibliography [27,34~~35~~,35~~36~~,39~~40~~,51~~51~~,60~~57~~,62~~59~~,75~~70~~,96~~89~~,97~~90~~]. As in the case of LC-FLD, there are official methods for the analysis of PAHs by GC-MS, such as the EPA method 8100 regarding the analysis of PAHs by GC [3,98~~91~~] (Table 3).

The utilization of GC-MS shows several advantages in comparison to LC-FLD, mainly in their resolution capability. GC offers high chromatographic resolving power and MS provides high mass selectivity and structural information. GC-MS permits the

determination of non-fluorescence PAHs, such as CPcdP, or PAHs showing poor fluorescence, such as NPH, ACY, ACP and FLR [99~~92~~].

For the separation stage, columns with a stationary phase based on 5 % phenyl-95 % methylpolysiloxane substitution are widely applied in the revised literature (e.g. typical HP-5 or HP-5ms). This type of column is also commonly utilized for the analysis of other organic contaminants and residues at trace level. However, obtaining an adequate resolution can become a critical point depending on the target PAHs since there are several groups of compounds which can co-elute (Figure 4). This issue is particularly important when these PAHs cannot be resolved mass spectrometrically by extracting their corresponding traces (e.g. isomers). If the overlapped compounds show isobaric ions, an accurate quantification is therefore difficult or impossible. Five groups of PAHs present this type of resolution problems: (i) chrysene (CHR) and triphenylene; (ii) CPcdP, BaA and CHR; (iii) benzo[*b*]fluoranthene (BbFA), benzo[*j*]fluoranthene (BjFA) and benzo[*k*]fluoranthene BkFA; (iv) dibenzo[*a,c*]anthracene and DBahA; and (v) DBahA and IP [3,97~~90~~].

The determination of heavy PAHs, such as dibenzopyrenes, by using typical 5ms columns is also problematic as~~due to~~ they show a strong interaction with the stationary phase provoking broadening peak and sensitivity problems. Some dibenzopyrenes are included in the EU-list (dibenzo[*a,e*]pyrene (DBaeP), dibenzo[*a,h*]pyrene (DBahP), dibenzo[*a,i*]pyrene (DBaiP), dibenzo[*a,l*]pyrene (DBalP)) and consequently, adequate analytical methods are needed for their monitoring. However, most of the revised literature is focused on the EPA list, and thus, DBahA (278 amu) is the heaviest compound which is normally determined, regardless the most heavy PAHs.

Although columns showing a more polar stationary phase have been pointed out as adequate for the determination of dibenzopyrenes (302 amu), their application in food analysis is not widespread [61~~58~~]. In relation to this, Gómez-Ruiz et al. [97~~90~~] evaluated thoroughly the performance of different stationary phases (Figure 5) for the analysis of the EU priority PAHs, including the typical 5%-phenyl columns and other more polar columns, such as 50 % phenyl-50 % methylpolysiloxane columns (e.g. DB-17ms) and a recently commercialized mid-polar to polar phase (Optima® δ-6) (Figure 5). The utilization of a 50 % phenyl-50 % methylpolysiloxane column (mid-polar phase) solved the resolution problems of three groups of co-eluted PAHs: DBahA-IP, BbFA-BjFA-BkFA and CPcdP-BaA-CHR, whereas a tailor-made DB-17ms column (20

625 m) showed the best results for the suitable determination of the four aforementioned
626 dibenzopyrenes, improving their peak shape and signal-to-noise (S/N) ratios.
627 Veyrand et al. [27] proposed the utilization of several mathematical formulae, which
628 are based on full scan spectra and relative abundances, in order to quantify separately
629 BaA and CDcdP. In relation to the quantification issue, Wolska et al. [100~~93~~] described
630 the different problems when using isotope-labeled standards, as recovery standards, in
631 PAH analysis. In this study, this strategy permitted the improvement of the accuracy
632 and precision in the determinations.
633 A few applications utilize fast chromatography modes, such as shorter columns (e.g.
634 10 m x 0.1 mm) [60~~57~~,61~~58~~]; or comprehensive or multidimensional GC (GC x GC)
635 [35~~36~~]. In this last modality, a first separation is performed with a non-polar column
636 (e.g. 5% phenyl polysilphenylene-siloxane, 30-m length, typical separation), and, then,
637 a second separation is carried out with a polar column (e.g. 50% phenyl
638 polysilphenylene-siloxane, 1-m length, separation based on polarity). The resolution
639 power is increased but the raw data and chromatograms are considerably complex and
640 powerful software tools are requested (Figure 6). Additionally, the use of columns with
641 >30-m length has been reported in specific applications in order to improve the
642 resolution of certain groups of isomers and some methyl derivatives [16].
643 In relation to the sample injection, the applied technique can be a key factor since
644 certain PAHs show very high boiling points (“heavy” PAHs). In literature, splitless
645 injection is preferred (e.g. [18,31~~32~~,34~~35~~]). Other techniques utilized are programmed-
646 temperature vaporization (PTV) (e.g. [31~~32~~,87~~82~~]), cold on-column injection, which is
647 also used since it improves peak shape in the early eluting PAHs (those with low
648 molecular mass) [3], and large-volume injection (LVI), which is rarely applied
649 [27,49,51] despite the fact that it can increase sensitivity. LVI and on-column injection
650 have been considered as a way of diminishing the discrimination of dibenzopyrenes
651 [97~~90~~]. In this sense, the combination of PTV and LVI has been successfully applied for
652 the analysis of both light and heavy PAHs in environmental analysis [101~~94~~], and more
653 recently in food [102~~95~~]. In this study, the optimized PTV in solvent mode (combined
654 with LVI) always provided higher sensitivity than the PTV process used in splitless
655 mode, and improved S/N ratios for the more heavy PAHs (especially important for
656 DBaeP, DBaiP and DBahP).
657 It is well-known that MS has become the most popular detection system in trace
658 analysis due to its intrinsic characteristics such as selectivity, sensitivity, different

659 available monitoring modes, etc. In the determination of PAHs in food and beverages,
660 GC-MS can offer an improvement in selectivity in comparison to LC-FLD; besides,
661 identification and confirmation can be carried out in a single step. Indeed, the re-
662 injection of samples by GC-MS for confirmation purposes when using LC-FLD is often
663 reported (Table 3).

664 Most of the studies use single quadrupole analyzers (Q) working in the single ion
665 monitoring mode (SIM) (Table 3), whereas other analyzers such as ion trap (IT)
666 [18,31~~32~~,63~~60~~,64~~61~~,66~~63~~] and triple quadrupole (QqQ) [32~~33~~,96~~89~~] are rarely used.
667 For these instruments, selected-ion storage or product ion scan mode (for IT), and
668 selected-reaction monitoring (for QqQ) are normally applied. High-resolution mass
669 spectrometry (HRMS) analyzers (e.g. time-of-flight [34~~35~~,35~~36~~,96~~89~~], magnetic sectors
670 [59~~56~~-61~~58~~]) have been also used (Figure 6), but because of its high cost, its application
671 is not common.

672 The application of tandem MS and other advanced analyzers would provide an
673 increase in selectivity. However, the use of single-stage MS and Q analyzers is
674 widespread, which could be explained as a consequence of the highly stable structure of
675 PAHs. Despite the use of a high-energy ionization mode, such as electronic ionization
676 (EI), the number of fragments produced is extremely low, mainly the $[M\text{-}H]^+$ or $[M\text{-}$
677 $2H]^+$ [27]. These ions are at the same time very stable and complicated to fragment by
678 MS/MS, providing product ions with a few *m/z* units less than the precursor ion.
679 Besides, the application of higher energy values does not change this pattern
680 significantly (e.g. 150 eV).

681 Finally, in relation to sensitivity, the majority of LODs reported are at the (sub)-/ppb
682 level (Table 3). Significant differences between the performance of Q and other
683 analyzers have not been found. The studies using Q or QqQ and IT analyzers reported
684 LODs (and LOQs when determined) at the sub-ppb level (e.g. [27,31~~32~~,96~~89~~]). It must
685 be noticed that similar results for lower limits have also been found when using LC-
686 FLD and GC-MS(/MS). However, the comparison between the LOQs obtained by GC-
687 MS(/MS) and LC-FLD was not possible due to the lack of reported LOQs in many of
688 the revised references.

689 More detailed information about determination methods and conditions is shown in
690 (Table 3).

691

692 **4. Determination of PAHs in real samples**

693 A summary of the reported concentrations of PAHs found in real food and beverage
694 samples is shown in Table 4.
695 A comparison between refined and unrefined oil showed that the levels of BaP in
696 most of refined oils were < 1.5 μg kg^{-1}, while for oil of unrefined or oils used for frying,
697 BaP concentrations were found to be > 2.0 μg kg^{-1} (above the maximum permitted level
698 in the Spanish legislation) [25~~24~~]. ~~In fried oil, BaP levels were higher than in fresh oil~~
699 ~~because of the high temperatures applied.~~ Besides, the use of activated carbon in the
700 refinement process, which produces an efficient removal of BaP, explained the lower
701 levels of this compound found in refined oil. In fried oil, BaP levels were higher than in
702 fresh oil; the authors justified this difference because of the high temperatures applied.
703 However, other authors state that the maximum temperature reached during oil frying is
704 not high enough as to generate PAHs [103].
705 Another comprehensive study (296 samples) [29~~30~~] revealed that 66.4% of the
706 analyzed edible oil samples exceeded the German Society of Fat Sciences limit (25 μg
707 kg^{-1}). Olive oil showed the maximum concentration (265 μg kg^{-1}) of heavy PAHs,
708 whereas rice brand oil showed the minimum values (4.6 μg kg^{-1}). Phenanthrene (PHE)
709 and ANT were found in more than half of the samples (58.3% and 53%, respectively),
710 whereas BaP was found only in 25.5% of them. One of its isomers, benzo[*e*]pyrene,
711 which is not normally monitored, was found in 31.2% of the studied oils. In total,
712 88.5% of samples showed PAH contamination, and only 11.5% of them were devoid of
713 any PAH.
714 Olive pomace oil has also been under study and a high number of PAHs (both light
715 and heavy) have been found in most of the analyzed samples [24~~22~~]. Besides, it is
716 important to point out that alkyl derivatives, which are rarely determined, were also
717 found and, in many cases, at higher concentrations than the ~~original~~ parent PAHs. The
718 high PAH concentration determined in refined olive and olive pomace oil in comparison
719 to virgin olive oil was explained as a consequence of the refining process, which can
720 partially remove these contaminants [31~~32~~].
721 Another study focused on the analysis of a variety of edible oils reported that CHR
722 was the most abundant PAH. This result can be related to the high concentrations of 5-
723 methylchr~~i~~ysene reported by the aforementioned study [24~~22~~]. In relation to olive
724 pomace oil, the authors remarked that the amount of BaP increased from 0.5 μg kg^{-1} in
725 olive pomace oil samples to 16.1 μg kg^{-1} in dried oil. Thus, drying stages in the
726 presence of combustion gases can increase PAH contamination [35~~36~~].

727 The concentrations of PAHs found in milk samples are, in general, lower than those
728 reported in edible oils (< 20 μg kg^{-1}) [36~~37~~,38~~39~~,39~~40~~], which can be due to different
729 reasons: there is not an evident carry over of PAHs along the food chain; milk is less
730 exposed to environmental contamination; and ~~the~~ different food processes that are
731 applied in each commodity (Table 4).

732 Grova et al. [36~~37~~] described the monitoring of milk samples obtained under different
733 possible sources of contamination, such as cement factories or motorways (Figure 7).
734 Not surprisingly, milk from farms nearby these sources showed maximum
735 concentrations higher than the concentrations determined in milk from control farms.
736 PAHs with more than four aromatic cycles were not detected and BaP (considered as
737 marker of exposure) was not detected either.

738 The monitoring of PAHs in infant formula revealed higher PAH concentrations than
739 in commercial and human milk [38~~39~~]. This important result was explained as a
740 consequence of drying processes which can provoke the formation of PAHs.

741 Since the manufacturing process in coffee industry also includes roasting stages,
742 coffee samples have been also analyzed in several studies. The results reported by
743 García Falcón et al. [41~~42~~] showed that PAHs were not found in instant coffee samples
744 but in highly roasted coffee without caffeine. In these samples, BbF, BkF and BaP were
745 found at very low levels: 0.03-0.1 μg kg^{-1} for BbF and 0.01-0.04 μg kg^{-1} for BkF and
746 BaP. Houessou et al. found significant differences in the PAH content of lots of coffee
747 from the same origin [44]. These results were potentially attributed to variations in the
748 roasting conditions, and the need for systematic analysis of coffee brews was pointed
749 out. Lai et al. [47] also observed variations in the BaP concentration found in different
750 coffee samples due to the same roasting process. However, Houessou et al. [87~~82~~]
751 determined in another study that PHE and PYR were mainly found regardless the coffee
752 lot considered. The absence of the highly toxic DBahA in the analyzed samples was
753 also remarked.

754 In mate infusions, BaP was found in the majority of samples. Considering the
755 European legislation for drinking water as reference, ~~showing~~ concentrations 5-11.2
756 times higher than the maximum limit for BaP (0.01 μg L^{-1}) were found~~allowed by the~~
757 ~~European guidelines (0.01 μg L^{-1})~~ [49~~50~~].

758 The determination of PAHs in tea leaves demonstrated that the PAH content in the
759 crude black tea and black tea were much higher than the levels found in tea leaves not

760 submitted to the drying stage, which is one of the manufacturing processes in black tea
761 industry [8176].
762 The monitoring of PAHs in spirits revealed that BaA and BbFA were detected in 96%
763 of the analyzed cachaça samples and only one sample did not contain any of the 5 target
764 PAHs [4243]. Different PAH profiles were found in different types of this spirit: BaP
765 showed higher concentrations when burned sugar cane was used in the production,
766 although always below the limit established by the EU for food products (2 μg L^{-1}) [46].
767 Meat samples have been extensively monitored for PAHs, especially those meat
768 products based on smoked meat. The concentrations found in these products are quite
769 lower than the concentrations found in other important food matrices, such as edible
770 oils. Mottier et al. [17] described that the levels of carcinogenic PAHs were below the
771 LOQ in almost all samples (Figure 8) and the compounds listed as carcinogenic by the
772 IARC (BaA, BbFA, BkFA, BaP, IP and DBahA were not the major PAHs present in the
773 samples). Beside this, samples containing higher fat content showed a higher PAH total
774 content, which was in accordance with previous studies describing the ratio between
775 PAH formation (during grilling) and fat content.
776 The smoking technology utilized in the production of smoked products was also found
777 a key factor in the PAH content of the final foodstuff [6057]. In a similar study [6158],
778 BcF showed the highest concentration in all types of samples. Besides, the total PAH
779 content increased during the different smoking steps.
780 In general, PAH content in fish (Figure 9) and seafood samples are considerably
781 higher than those found in meat and similar to the levels determined in edible oils
782 (Table 4). The use of BaP as a marker of the total PAH content was again discussed
783 since it was not detected in the analysis of 27 fish samples when other PAHs were
784 found [7772]. This fact was also confirmed in another study [6865] focused on the
785 analysis of fish and seafood. Despite several PAHs were found in all samples (ANT,
786 fluoranthene (FA), PYR, BaA, CHR, BbFA and BkFA), BaP was only detected in
787 Mediterranean mussels. In this kind of samples, a seasonal variation was found: 72% of
788 mussels collected in winter exceeded the EU MRL set for BaP, whereas the values
789 shown by mussels collected in summer were below this limit. Moreover, comparing the
790 PAH levels of the different organisms evaluated, mussels showed the maximum
791 amounts.
792 The evaluation of the PAH profiles in food from marine origin revealed that PYR was
793 the major PAH, representing more than 80% of the total content in all samples, except

794 in prawns, where NPH showed the maximum contribution (49%) [8883]. AnOother
795 compound often found was PHE, which is one of the main components of crude oil. In
796 this sense, the authors remarked that profiles showing high percentages of light PAHs
797 are typical of oil-polluted areas and intense oil activity.
798 A thorough study of the levels of BaP in cheese (96 samples) demonstrated that the
799 concentrations in cheese smoked with straw and cardboard were statistically higher than
800 the concentrations found in samples smoked and aromatized with wood shavings and
801 SFPs [8075]. However, samples treated with SFPs showed BaP concentrations
802 exceeding the limits set by the EU. BaP levels were dependent on the smoking process
803 (temperature, time, etc.), which was also observed in other smoked products. In another
804 study [7873], the PAH content found in home-made smoked cheese was up to ten timer
805 higher than in cheese smoked under industrial conditions (Figure 10). This trend was
806 also observed for BaP. Besides, significant differences were observed in the PAH
807 content when comparing the cheese surface and internal parts of the product.
808 The analysis of cane sugar showed PAH contamination in 57% of the samples; BaA
809 was found in 51% of the samples [8681]. The obtained results suggested that the PAH
810 content relied on the amount of burnt sugar cane utilized (if so), and in the number of
811 steps involving the refining process. Furthermore, PAHs were also detected in 33% of
812 the organic samples analyzed. The deposition of airborne particles containing PAHs on
813 the plant surface was proposed as a possible explanation, probably because of the
814 environmental pollution.
815 Danyi et al. [10496] determined that 50% of the food dietary supplement samples
816 submitted to analysis showed PAH concentrations above the limit established by the EU
817 (2 μg kg^{-1}) for one to seven PAHs. In general, light PAHs were mostly found and
818 several genotoxic PAHs were found at relatively high concentrations in certain food
819 supplements from plant origin.
820 A recent study involving the monitoring of parent PAHs and hydroxy-PAHs in infant
821 milk and cereals demonstrated the absence of PAH metabolites. However, parent PAHs
822 were found in two samples (total number of samples: 36), namely B[*k*]F at 0.1 and 0.3
823 μg kg^{-1} [94].
824 The study carried out by Rojo-Camargo et al. [8479], which was focused on the
825 analysis of a variety of vegetable and fruit samples, showed that BaA was detected in
826 89% of the samples. Vegetables, which are rarely monitored, also showed PAH
827 contamination at levels higher than those found in fruits (4.38–17.93 μg kg^{-1}, and 3.77–

4.05 µg kg^{-1}, respectively). Lettuce and grape were the matrixes showing higher PAH total content. Moreover, vegetable samples collected close to road traffic revealed higher PAH levels than in samples grown in rural areas. It is important to notice that organic samples also shown PAH contamination, probably due to the exposure to environmental pollution, as aforementioned in sugar cane samples.

5. Conclusions

The determination of PAHs in foodstuffs and beverages has focused attention for a long time, as it is demonstrated by existing publications in the early 90's. However, a high percentage of this literature has been devoted to the analysis of the PAHs included in the well-known EPA list, and especially BaP. It seems necessary to increase and improve the available information and data about the occurrence of other PAHs, such as those included in the EU list (e.g. dibenzopyrenes) or transformation products (e.g. alkyl derivatives or hydroxy-PAHs), in order to achieve a better knowledge about PAHs levels in foodstuffs. On the other hand, the revised literature shows that edible oils and animal products are the most analyzed matrices for PAHs, which was expected as many of the current legislation is established for them. Additional data about the levels of PAHs found in other food matrices, such as vegetables or livestock, which can be exposed to PAH contamination when roads or traffic are nearby, could be of interest.

In relation to the extraction techniques, conventional techniques such as Soxhlet (solid matrices), LLE and SPE (liquid matrices) are still widely used, although the application of less-solvent-consuming techniques, such as MSPD, and micro-extraction techniques, such as LPME, has been recently reported. The performance of clean-up stages is also requested for most of applications, but the utilization of techniques such as SPME or HS-SPME has permitted the reduction of the pre-treatment stage. The clean-up stage is still a time-consuming step, especially in fatty matrices. SPE and GPC are the most applied techniques for this aim.

It is important to notice, that the implementation of the most recent extraction techniques, such as LPME, MSPD or (HS)-SPME is still reduced in routine analysis, but they must be considered as new approaches that can be useful in the near future for this aim in terms of solvent consumption or sample throughput.

With respect to separation and detection issues, LC-FLD and GC-MS(/MS) are the outstanding techniques, although any of them is particularly preferred. The revised literature shows the utilization of both techniques without regarding the type of sample

862 or extraction methodology. Nevertheless, it must be noticed that GC-MS(/MS)
863 instruments have been used in the most recent studies. This trend is contrary to the so-
864 called GC-to-LC movement observed in the analysis of other organic compounds at
865 trace levels (e.g. veterinary drugs). This fact can be justified due to the need for a more
866 accurate confirmation of the identity of the compound, which is not possible only with
867 determinations by LC-FLD. Besides, the lack of native fluorescence of certain PAHs
868 does not permit the monitoring of such compounds, which is an obvious drawback in
869 comparison to GC-MS(/MS).

870

871 **6. Trends**

872 Bearing in mind the aforementioned considerations and conclusions and the current
873 challenges, more research and efforts should be focused on the specific issues such as:

874 • A more thorough evaluation of recent API sources for LC instruments, such as
875 APPI, which are designed for more non-polar compounds, in order to establish
876 their possible utilization for the determination of PAHs in LC-MS systems. The
877 comparison of these instruments with conventional LC-FLD would be also of
878 interest since simultaneous identification and confirmation would be possible.

879 • The feasibility of the APPI sources for the determination of PAHs, but
880 especially compounds not included in the EPA list (e.g. heavy PAHs such as
881 dibenzopyrenes) should be evaluated.

882 • UHPLC instruments, which are widely applied for the analysis of other organic
883 compounds at trace levels, have not been used for PAH analysis yet. The
884 increase in resolution provided by these systems may also allow an increase in
885 selectivity, especially in very complex matrices and when using FLD as
886 detection technique. Besides, the study of the suitability of UHPLC coupled to
887 MS and the aforementioned ionization sources in this field would be also
888 desirable.

889 • More data about the utilization of specific columns for PAH analysis in food
890 should be generated. Although the typical 5%-phenyl columns are widely used,
891 the separation of certain groups is not achievable and heavy PAHs, such as
892 dibenzopyrenes, do not show adequate peak shape and/or sensitivity. These
893 problems can be overcome employing other stationary phases, but their use is
894 very scarce.

895 • Extra efforts should be made in order to improve the data about PAH
896 concentrations in food products exposed to possible contamination, such as
897 agricultural areas near to road traffic.
898 • Data about PAHs out of the EPA and ~~U~~EU lists should be increased in order to
899 propose new maximum concentrations as well as extended lists of priority
900 PAHs.
901
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Figure Captions

Fig. 1.
Example of a scheme of a methodology employed for the extraction of PAHs in olive pomace oil samples, an example of fatty matrix. Reprinted from [22] copyright 2004, with permission from American Chemical Society.

Fig. 2.
HPLC–FLD chromatogram obtained by SBSE from Mate tea spiked with 500 ng L^{-1} (extraction time: 240 min). Peak identities are: (1) naphthalene (NPH); (2) acenaphthene (ACP); (3) fluorene (FLR); (4) phenanthrene (PHE); (5) anthracene (ANT); (6) fluoranthene (FA); (7) pyrene (PYR); (8) benz~~o~~[*a*]anthracene (BaA); (9) chrysene (CHR); (10) benzo[*b*]fluoranthene (BbFA); (11) benzo[*k*]fluoranthene (BkFA); (12) benzo[*a*]pyrene (BaP); (13) dibenzo[*a,h*]anthracene (DBahA); (14) benzo[*g*~~,~~*h*~~,~~*i*]perylene (BghiP) and (15) indeno[1,2,3-*c*~~,~~*d*]pyrene (IP). Reprinted from [49] copyright 2005, with permission from Elsevier.

Fig. 3.
Scheme of the use of SPME-DED in model systems of gelatine for the determination of the 16-EPA PAHs in smoked meat by GC-MS. The diffusion process of the analytes from the matrix to the headspace of the DED and the equilibriums implied in the process are shown. Reprinted from [59] copyright 2007, with permission from Elsevier.

Fig. 4.
GC-MS chromatogram of the 15 + 1 EU PAHs on a DB-17MS column 20 m length, 0.18 mm i.d. and 0.14 µm film thickness. Peak identities are: (1) benzo[*c*]fluorene (BbF); (2) benz~~o~~[*a*]anthracene (BaA); (3) cyclopenta[*c*~~,~~*d*]pyrene (CPcdP); (4) d12-chrysene (d12-CHR); (5) chrysene (CHR); (6) 5-methylchrysene (MCH); (7) 9-fluorobenzo[*k*]fluoranthene (FBkF); (8) benzo[*b*]fluoranthene (BbF); (9) benzo[*k*]fluoranthene (BkF); (10) benzo[*j*]fluoranthene (BjF); (11) d12-benzo[*a*]pyrene (d12-BaP); (12) benzo[*a*]pyrene (BaP); (13) indeno[1,2,3-*c*~~,~~*d*]pyrene (IP); (14) dibenzo[*a,h*]anthracene (DBahA); (15) d12-benzo[*g*~~,~~*h*~~,~~*i*]perylene (d12-BghiP); (16) benzo[*g*~~,~~*h*~~,~~*i*]perylene (BghiP); (17) dibenzo[*a,l*]pyrene (DBalP); (18) d12-coronene (d12-COR); (19) dibenzo[*a,e*]pyrene (DBaeP); (20) dibenzo[*a,i*]pyrene (DBaiP) and (21) dibenzo[*a,h*]pyrene (DBahP). Reprinted from [90] copyright 2009, with permission from Springer.

Fig. 5.
Chromatographic separation of critical pairs/triplets by GC-MS obtained on three different stationary phases: (a) DB-17MS column, 60 m length, 0.25 mm i.d., 0.25 µm film thickness; (b) DB-5MS column, 60 m length, 0.25 mm i.d., 0.25 µm; (c) Optima® δ-6 column, 30 m length, 0.25 mm i.d., 0.25 µm. Reprinted from [90] copyright 2009, with permission from Springer.

Fig. 6.
Example of SPME-GC x GC-TOF-MS analysis showing a contour plot of a vegetable oil sample spiked with a PAHs solution (others groups of compounds are also shown). Abbreviations: BaA: benz~~o~~[*a*]anthracene; BbF: benzo[*b*]fluoranthene; BghiP: benzo[*g*~~,~~*h*~~,~~*i*]perylene; BjF: benzo[*j*]fluoranthene; BkF: benzo[*k*]fluoranthene; BcF: benzo[c]fluorene; BaP: benzo[*a*]pyrene; CCP: cyclopenta[*c*~~,~~*d*]pyrene; Ch: chrysene;

DBahA: dibenzo[*a,h*]anthracene; IP: indeno[1,2,3-*c*~~,~~*d*]pyrene; 5MeCh: 5-methylchrysene; DBaeP: dibenzo[*a,e*]pyrene; DBahP: dibenzo[*a,h*]pyrene; DBaiP: dibenzo[*a,i*]pyrene; DBalP: dibenzo[*a,l*]pyrene. Reprinted from [36] copyright 2007, with permission from Elsevier.

Fig. 7.
Concentration of PAHs in milk samples collected close to various potential contamination sources. Abbreviations: NA: naphthalene; ACEY: acenaphthylene; ACEA: acenaphthene; FLUO: fluorene; ANT: anthracene; FLUT: fluoranthene; PYR: pyrene; B[a]A: benz~~o~~[*a*]anthracene. Reprinted from [37] copyright 2002, with permission from American Chemical Society.

Fig. 8.
GC-MS/MS chromatogram of a meat sausage sample containing endogenous PAHs and internal standards (1 µg kg^{-1}). Peak identities are: (1) naphthalene; (2) acenaphthylene; (3) acenaphthene; (4) fluorene; (5) phenanthrene; (6) anthracene; (7) fluoranthene; (8) pyrene; (9) benz~~o~~[*a*]anthracene; (10) chrysene; (11) benzo[*b*]fluoranthene; (12) benzo[*k*]fluoranthene; (13) benzo[*a*]pyrene; (14) indeno[1,2,3-*c*~~,~~*d*]pyrene; (15) dibenzo[*a,h*]anthracene; (16) benzo[*g*~~,~~*h*~~,~~*i*]~~-~~perylene. Reprinted from [17] copyright 2000, with permission from American Chemical Society.

Fig. 9.
GC-MS/MS chromatograms in the selected-reaction monitoring (SRM) mode of different fish samples: (a) non-spiked sample; (b) spiked sample (1.25 µg kg^{-1} for naphthalene and 0.125 µg kg^{-1} for dibenzo[*a,h*]anthracene); and (c) matrix-matched standard (10 ng mL^{-1}, equivalent to 1.25 µg kg^{-1} for naphthalene; and 1 ng mL^{-1}, equivalent to 0.125 µg kg^{-1} for dibenzo[*a,h*]anthracene). Reprinted from [89] copyright 2009, with permission from John Wiley and Sons.

Fig. 10.
HPLC-FLD chromatogram of a real smoked cheese sample with PAH concentrations in the range 0.03 to 60 µg kg^{-1}. Abbreviations: Naph: naphthalene; Ace: acenaphthene; Fln: fluorene; Phe: phenanthrene; Ant: anthracene; Flt: fluoranthene; Pyr: pyrene; B[a]A: benz~~o~~[*a*]anthracene; Chr: chrysene; B[b]F: benzo[*b*]fluoranthene; B[k]F: benzo[*k*]fluoranthene; B[a]P: benzo[*a*]pyrene; DB[ah]A: dibenzo[*a,h*]anthracene; B[ghi]P: benzo[*g*~~,~~*h*~~,~~*i*]perylene; I[1,2,3-cd]P: indeno[1,2,3-*c*~~,~~*d*]pyrene. Reprinted from [73] copyright 2008, with permission from John Wiley and Sons.

Table 1.

Summary of the most important PAHs analyzed in food

Compound	Abbreviation	Structure	Molecular weight (amu)	Boiling point (°C)	CAS No
Acenaphthene[a]	ACP		154	279	83-32-9
Acenaphthylene[a]	ACY		152	280	208-96-8
Anthracene[a]	ANT		178	340	120-12-7
Benzo[*a*]anthracene[a,b]	BaA		228	438	56-55-3
Benzo[*b*]fluoranthene[a,b]	BbFA		252	N.A.	205-99-2
Benzo[*k*]fluoranthene[a,b]	BkFA		252	N.A.	207-08-9
Benzo[*g,h,i*]perylene[a,b]	BghiP		276	>500	191-24-2
Benzo[*a*]pyrene[a,b]	BaP		252	495	50-32-8
Chrysene[a,b]	CHR		228	448	218-01-9
Dibenzo[*a,h*]anthracene[a,b]	DBahA		278	524	53-70-3
Fluoranthene[a]	FA		202	384	206-44-0
Fluorene[a]	FLR		166	298	86-73-7
Indeno[1,2,3-*c,d*]pyrene[a,b]	IP		276	N.A.	193-39-5
Naphthalene[a]	NPH		128	218	91-20-3
Phenanthrene[a]	PHE		178	340	85-01-8
Pyrene[a]	PYR		202	404	129-00-0
Benzo[*j*]fluoranthene[b]	BjFA		252	N.A.	205-82-3
Cyclopenta[*c,d*]pyrene[b]	CPcdP		226	N.A.	27208-37-3
Dibenzo[*a,e*]pyrene[b]	DBaeP		302	N.A.	192-65-4
Dibenzo[*a,h*]pyrene[b]	DBahP		302	N.A.	189-64-0
Dibenzo[*a,i*]pyrene[b]	DBaiP		302	N.A.	189-55-9
Dibenzo[*a,l*]pyrene[b]	DBalP		302	N.A.	191-30-0
5-Methylchrysene[b]	MCH		242	N.A.	3697-24-3

[a] 16 EPA priority PAHs [9]

[b] UE PAHs of concern in food [10]

N.A. Data not available

1189
1190
1191

Table 2
Summary of extraction and clean-up methods in the discussed matrices

Matrix	*Extraction*	*Clean-up*	*Separation/detection*	*Rec*
Liquid fatty matrices				
Edible oils	Dilution (*n*-hexane); LLE (2 x DMF/water, 9:1, v/v)	SPE (C_{18}/C_8)	LC-FLD	50-
Edible oils	Dilution (*n*-hexane)	(A) DACC column (Varian ChromSpher 5π, 80 x 3 mm i.d., 5 µm) (B) Column chromatography (alumina)	LC-FLD	(A) (B)
Edible oils	Dilution (*n*-hexane); SPE (silica)	-	LC-FLD	32-
Edible oils	Dilution *n*-hexane; SPE (Humic acid-bonded silica)	-	LC-FLD	79-
Edible oils	Dilution (*n*-heptane); LLE (4 x 20 mL DMSO); LLE (3 x 50 mL cyclohexane); LLE (2 x 100 mL water)	Column chromatography (silica gel + Na_2SO_4, 200 x 22 mm)	LC-FLD	58-
Edible oils, fat	Dilution (isohexane:butyldimethylether,)%:5, v/v); SPE (PS-DVB)	-	LC-FLD	60-
Edible oil, smoked meat	(A) Smoked meat: Saponification (10 mL KOH 2 M in EtOH:water, 9:1, v/v, 1 h); LLE (2 x 2 mL cyclohexane) (B) Oil: Addition 15 mL cyclohexane; LLE (15 mL DMF:water, 9:1, v/v); LLE (15 mL water); LLE (2 x 15 mL cyclohexane)	SPE (aminopropyl, C_{18})	GC-MS	(A)
Olive oil	(A) SPE (C_{18} Nucleoprep+Florisil) (B) MSPD (C_{18}+Florisil)	-	GC-MS, LP-GC-MS, LC-FLD	(A) (B)
Olive oil	Dilution (25 mL *n*-hexane); LLE (50 mL DMSO); addition 120 mL water + 6 g NaCl; LLE (3 x 150 mL cyclohexane); LLE (100 mL water)	-SPE (silica) -Optional: Soxhlet (100 mL MeOH:water, 8:2, v/v + KOH, 4 h); LLE (3 x 150 mL cyclohexane)	GC-MS	52-
Olive oil	HS-SPME (DVB/Car/PDMS 50/30 µm)	-	GC-MS	74-
Olive oil	HS	-	GC-MS(-MS)	96-
Oil, food mixture	PLE (celite + Florisil, *n*-hexane:acetone, 1:1, v/v)	SPE (PS-DVB)	GC-MS/MS	12- iso
Olive, olive-pomace oil	SLE or LLE (ACN/ *n*-hexane, 83:17, v/v)	GPC (styrene-divinylbenzene copolymer, 5 ml min^{-1} CH_2Cl_2)	GC-MS/MS	84-
Olive pomace oil	Dilution (25 mL *n*-pentane); LLE (15 mL, 2 x 10 mL DMSO); addition 70 mL water; LLE (3 x 50 mL cyclohexane); LLE (100 mL water)	TLC (silica gel)	GC-MS	69-
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 µm)	-	GC-MS	N.A
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 µm)	-	GC x GC-MS	N.A
Fish oil, fish	Homogenization (Na_2SO_4); saponification (10 mL methanolic KOH 1M, 3 h); LLE (2 x 8 mL *n*-hexane)	SPE (Florisil)	GC-MS(/MS)	64-
Fish oil, dried plants	(A) Fish oil: SLE with rotary agitator (3 x CH_2Cl_2/cyclohexane, 1:1, v/v); centrifugation (B) Dried plants: dilution (cyclohexane)	(A), (B) DACC column (Varian Chromspher π, 80 x 3 mm i.d., 5 µm)	LC-FLD	74-
Milk	HS-SPME (PDMS-DVB)	-	GC-MS	90-
Milk	Dilution (water), SPME (PDMS-DVB)	-	GC-MS	88-
Milk	Addition sodium oxalate; LLE (250 mL MeOH); LLE (250 mL diethyl ether); LLE (250 mL petroleum ether)	Column chromatography (silica gel)	GC-MS	40-
Milk	LLE (20 mL cyclohexane:ethyl acetate, 1:1, v/v); centrifugation	SPE (styrene-divinylbenzene copolymer Envi-Chrom); addition 2 mL cyclohexane + 2 mL MeOH:water (80:20, v/v); centrifugation; LLE (2 mL cyclohexane); centrifugation PAHs: Cyclohexane fraction; saponification (5 mL KOH 10%, 90ºC, 80 min); addition 3 mL water + 5 mL cyclohexane; centrifugation Hydroxi-PAHs: MeOH layer; LLE (4 mL water:ethyl acetate, 1:1, v/v); centrifugation	GC-MS (Derivatization)	N.A
Milk	Saponification (4 mL NaOH 0.4M in EtOH:water, 9:1, v/v, 60ºC, 30 min); LLE (2 x 2 mL *n*-hexane)	-	LC-FLD	90-
Liquid non-fatty matrices				
Coffee	LLE (*n*-hexane)	SPE (silica)	LC-FLD	87-
Coffee brew	SPE (BondElut PPL polystyrene-divinylbenzene)	-	LC-FLD	84-
Coffee	MIP-SPE	-	LC-FLD	Co
Tea	SPE (C_{18})	-	LC-FLD	44-

Tea infusion	(A) HS-SPME (PDMS-DVB 60 µm) (B) SPME (Confirmation GC-MS, PDMS-DVB 65 µm)	-	LC-FLD, GC-MS (Confirmation)	N.
Mate tea	SBSE: 10-mm bars coated with PDMS (0.5 mm), room temperature, 2 h, 160 µL ACN:water, 4:1, v/v (desorption)	-	LC-FLD	24-
Beverages	Addition 10% MeOH; MASE (polypropylene, ethyl acetate)	-	GC-MS	65-
Sugarcane juice	(A) SBSE-TD: Addition of NaCl; 10-mm bars coated with PDMS (0.5 mm), room temperature, 3 h (B) MASE: polypropylene, 800 µL cyclohexane	-	GC-MS	(A) (B)
Cachaça (spirit)	LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel 15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	70-
Spirits	SPE (C_{18})	-	LC-FLD	82-
Solid fatty matrices				
Meat	Freeze-drying; Soxhlet (25 mL KOH 25% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water), LLE (150 + 100 mL *n*-hexane); LLE (3 x 100 mL water)	SPE (Florisil)	GC-MS	62-
Meat	(A) Freeze-drying; USE (*n*-hexane) (B) Soxhlet (25 mL KOH 50% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water), LLE (150 + 100 mL *n*-hexane)	(A), (B) SPE (Florisil)	LC-UV, LC-FLD	(A) (B)
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	58-
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	N.
Smoked meat	Saponification (MeOH + KOH)	SPE (Florisil)	LC-UV, LC-FLD, GC-EI-MS	68-
Smoked meat	SPME-DED (PDMS 100 µm)	-	GC-MS	N.
Smoked meat	PLE (*n*-hexane, 100ºC, 100 bar)	-GPC (Bio-Beads S-X3, 420 mm x 25 mm; cyclohexane:ethyl acetate, 1:1, v/v) -Column chromatography (silica)	GC-MS	75-
Smoked meat	MAE (*n*-hexane, 115ºC)	SPE (silica)	LC-FLD	77-
Fish, smoked meat	(A) Pork: PLE (Supelclean LC-18 + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC) (B) Smoked meat and fish: PLE (C_{18} + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC)	LLE (2 x 1 mL H_2SO_4 9 M); LLE (water); column chromatography (Florisil, 6 g, 1 cm i.d.)	GC-MS	(A) (B)
Fish	Homogenization (Na_2SO_4), Soxhlet (CH_2Cl_2:*n*-hexane, 1:1, v/v, 16 h)	Addition water + K_2CO_3 + acetic anhydride; dilution water; LLE (3 x 100 ml CH_2Cl_2); LLE (2 x 2 ml K_2CO_3); column chromatography (silica gel + Na_2SO_4); GPC (2 ml min^{-1} CH_2Cl_2)	GC-MS	N.
Fish	(A) Soxhlet (170 ml *n*-hexane:acetone, 1:1, v/v, 6 h) (B) PLE (*n*-hexane:acetone, 1:1, v/v, 100ºC, 10 MPa)	GPC (Bio-Beads S-X3, 500 mm x 8 mm; $CHCl_3$)	LC-FLD	N.
Fish	HS-SPME (polyacrilate)	-	GC-MS	N.
Fish	MAE (4 mL saturated KOH in MeOH + 10 mL *n*-hexane, 129ºC); centrifugation	SPE (Silica)	LC-FLD	86-
Fish	Lyophilization; MSPD (C_{18} + Na_2SO_4)	Simultaneous SPE (Florisil + C_{18})	LC-FLD	80-
Fish	Homogenization (Na_2SO_4), Soxhlet (150 mL, CH_2Cl_2, 16 h)	Column chromatography (silica gel + Na_2SO_4, 1 cm i.d.)	GC-MS	Fis
Fish	QuEChERS method: SLE (ACN); vortex; induced partition ($MgSO_4$+sodium acetate); centrifugation	-	LC-FLD	64-
Fish, seafood	Saponification (10 mL ethanolic KOH 1M, 3 h, 80ºC); addition 10 mL water; LLE (2 x 20 mL cyclohexane)	-	LC-FLD	41-
Fish, seafood	MAE (15 mL acetone, 21 psi, 80 % microwave power)	(A) SPE (Florisil) (B) GPC (Envirosep ABC, 350 mm x 21.2 mm, 5 ml min^{-1} CH_2Cl_2)	GC-MS	N.
Fish, mussel	Dilution (NaCl solution 24 %), HS-SPME (PDMS-DVB)	-	GC-MS	8-1
Fish, palm dates	Soxhlet (150 mL, *n*-hexane, 8 h)	Column chromatography (silica gel + Florisil + Na_2SO_4)	GC-MS	59-
Shellfish	Freeze-drying; Soxhlet (CH_2Cl_2, 24 h)	-GPC (Bio-Beads S-X3; $CHCl_3$) -Column chromatography (aluminosilicate)	GC-MS	62-
Mussel	Lyophilization; PLE (*n*-hexane:CH_2Cl_2, 1:1, v/v, 150ºC, 150 psi)	Saponification (25 mL KOH 6 M, ambient temperature, 24 h)	GC-MS	64-
Cheese	Saponification (10 mL KOH ethanolic solution); addition water (10 mL); LLE (2 x 20 mL cyclohexane)	SPE (Isolute silica 500 mg)	LC-FLD	84-
Cheese	Soxhlet (Na_2SO_4 + 170 mL *n*-hexane: CH_2Cl_2, 1:1, v/v,	GPC (Bio-Beads S-X3, CH_3Cl)	LC-FLD	52-

	7 h)			
Cheese	(A) Cheese: lipid extraction (N.A.); addition 30 mL cyclohexane; LLE (DMF:water, 9:1, v/v); LLE 30 mL cyclohexane	(A), (B) SPE (Silica)	LC-FLD	75-
Infant milk, infant cereals	(A) Parent PAHs: USE (3 x 10 mL *n*-hexane); centrifugation (B) Hydroxy-PAHs: USE (3 x 9/6/5 mL ACN:ethyl acetate, 70:30, v/v, containing 0.8 g/L *tert*-butyl hydroquinone); centrifugation; hydrolysis of conjugated PAHs (β-glucuronidase/aryl sulphatase)	(A) SPE (Silica) (B) SPE (C_{18})	(A) LC-FLD (B) LC-MS	Inf 116 Inf 103
Solid non-fatty matrices				
Bread, potato	(A) Bread: Addition 1 mL water; USE (3 mL ethyl ether:CH_2Cl_2, 1:1, v/v) (B) Potato: USE (as explained in (A))	-	LC-FLD, GC-MS (Confirmation)	70-
Cane sugar	SLE (100 mL cyclohexane); LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	74-
Foodstuffs	Soxhlet (150 mL, CH_2Cl_2, 8 h)	Column chromatography (silica gel)	LC-FLD	70-
Food supplements	SLE with rotary agitator (3 x cyclohexane/CH_2Cl_2, 1:1, v/v + HF-M + alumina); centrifugation	Column chromatography (silica gel)	LC-FLD	63-
Fruits, vegetables	Saponification (100 mL KOH methanolic, 5 h); addition MeOH:water (100 mL, 9:1, v/v); LLE (2 x 150 mL cyclohexane); LLE (100 mL MeOH:water, 9:1, v/v; 100 water); LLE (N,N-dimethylformamide:water, 9:1, v/v)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD, GC-MS	74-
Ground coffee	PLE (*n*-hexane:acetone, 1:1, v/v; 150ºC)	-Saponification (EtOH+KOH, 30 min) -LLE (100 mL cyclohexane); LLE (3 x 100 mL water) - SPE (silica)	LC-FLD, GC-MS/MS, LC-UV	64-
Tea leaves	USE[e] (3 x 20 mL CH_2Cl_2:acetone, 1:1, v/v)	Column chromatography (silica)	LC-UV	>70
Tea leaves	Soxhlet (CH_2Cl_2:acetone, 1:1, v/v, 18 h)	SPE (Florisil)	GC-EI-MS	N.A
Vegetables	Soxhlet (300 mL *n*-hexane:acetone, 1:1, v/v, 24 h)	SPE (Acid treated silica, aromatic sulfonic acid)	GC-MS	69-

[a] N.A.: Data not available
[b] Values corresponding to isotope labeled compounds
[c] Coefficient of variation
Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; DMF: dimethylformamide; DMSO: dimethylsulfoxide; DVB: divinylbenzene; EtOH: ethanol; GC-MS: gas chromatography coupled to mass spectrometry; GCxGC-MS: multidimensional GC-MS; HF-M: modified diatomaceous earth; HS-SPME: headspace solid-phase microextraction; GPC: gel permeation chromatography; i.d.: internal diameter; LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LLE: liquid-liquid extraction; LP-GC-MS: low pressure GC-MS; MAE: microwave-assisted extraction; MASE: membrane-assisted solvent extraction; MeOH: methanol; MIP-SPE: molecularly imprinted polymers solid-phase extraction; MSPD: matrix solid-phase dispersion; PDMS: polydimethylsiloxane; PLE: pressurized-liquid extraction; PS-DVB: polystyrene /divinylbenzene; SBSE: stir bar sorptive extraction; SBSE-TD: SBSE-thermal desorption; SFE: supercritical fluid extraction; SLE solid-liquid extraction; SPE: solid-phase extraction; SPME: solid-phase microextraction; SPME-DED: SPME coupled to a direct extraction device; TLC: thin layer chromatography; USE: ultrasound extraction

1206
1207
1208

Table 3

Summary of separation and detection techniques in the discussed matrices

Matrix	*Separation/detection technique*	*Separation remarks*	*Detection remarks*	*LO*
Liquid fatty matrices				
Edible oils	LC-FLD	Vydac C_{18} (250 x 4.6 mm i.d., 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 330-500 nm	N.A
Edible oils	LC-FLD	Vydac C_{18} (250 x 4.6 mm i.d., 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.0
Edible oils	LC-FLD	Supelcosil LC-PAH (250 mm x 3 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=240-290 , λ_{em}= 330-484 nm	N.A
Edible oils	LC-FLD	Thermo Hypersil ODS (200 mm x 4.6 mm x 5 µm) Isocratic elution: MeOH:water, 9:1, v/v	λ_{ex}=255 , λ_{em}= 420 nm	0.0
Edible oils	LC-FLD	C-18 Lichrocart (125 mm x 4 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=242-350 , λ_{em}= 380-443 nm	0.1
Edible oils, fat	LC-FLD	(250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-300 , λ_{em}= 376-418 nm	0.2
Edible oil, smoked meat	GC-EI-MS	Injection : Pulsed splitless Supelco SPB-5 (25 m x 0.20 mm x 0.33 µm)	Q, SIM	0.0
Olive oil	(A) GC-EI-MS (B) LP-GC-EI-MS (C) LC-FLD (D) DACC	(A) Injection: N.A.; DB-5ms (30 m × 0.25 mm, 0.25 µm) (B) Injection: N.A.; Rapid MS FS CP-Sil 8 (10 m × 0.53 mm, 0.50 µm) + restrictor (0.6 m x 0.25 mm) (C) CP EcoSpher 4 PAH (150 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v) (D) CP ChromSpher π (20 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v)	(A),(B) SIM (C), (D) λ_{ex}=370 , λ_{em}= 470 nm	(A) (B) (C) (D)
Olive oil	GC-EI-MS	Injection: Pulsed splitless HP-5ms, (60 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A
Olive oil	GC-EI-MS	Injection: Splitless Supelcowax-10 and HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.0
Olive oil	GC-EI-MS(/MS)	Injection: Splitless VF-5ms, 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	QqQ, SIM, SRM	0.0
Oil, food mixture	GC-EI-MS/MS	Injection: N.A. Zebron ZB-5ms, (30 m x 0.25 mm x 0.25 µm)	QqQ, SRM	0.0 (dr
Olive, olive-pomace oil	GC-EI-MS/MS	Injection: LVI + PTV HP-5, crosslinked 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	IT, Product ion scan, Resonant mode	0.0
Olive pomace oil	GC-EI-MS	Injection: splitless DB-5ms (30 m x 0.25 mm x 0.20 µm)	IT, Full scan	0.1
Vegetable oils	GC-EI-MS	Injection: Splitless SPB-5, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.2
Vegetable oils	GCxGC-EI-MS	Injection: Splitless First dimension: SGE BPX5, (30 m x 0.25 mm x 0.25 µm) Second dimension: SGE BPX50, 50% phenyl polysilphenylenesiloxane (1 m x 0.1 mm x 0.1 µm)	TOF, Full scan	0.1
Fish oil, fish	(A) GC-EI-MS/MS (B) GC-EI-MS (Confirmation)	(A), (B) Injection: Splitless; HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	(A) QqQ, SRM (B) TOF, Full scan	0.0
Fish oil, dried plants	LC-FLD	Varian Pursuit 3 PAH (100 mm × 4.6 mm × 1/4'') Gradient elution: A: ACN; B: MeOH; C: water	λ program: λ_{ex}=222-380 , λ_{em}= 353-499 nm	0.0
Milk	GC-EI-MS	N.A.	Q, SIM	0.2
Milk	GC-EI-MS	Injection: Splitless HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.0
Milk	GC-EI-MS	Injection: N.A. DB-XLB, proprietary phase, (60 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A
Milk	GC-EI-MS	Injection: Splitless OV-1, (30 m x 0.25 mm x 0.25 µm)	Q, SIM Derivatization: (MSTFA)	0.0
Milk	LC-FLD	Wakosil-PAHs (250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: MeOH:water, 8:2, v/v	λ program: λ_{ex}=248-364 , λ_{em}= 360-500 nm	1.3
Liquid non-fatty matrices				
Coffee	LC-FLD	C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=274-300 , λ_{em}= 406-470 nm	0.0
Coffee	LC-FLD	C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=230-250 , λ_{em}= 410-420 nm	0.8
Coffee	LC-FLD	Isocratic elution: ACN:water, 4:6, v/v Phenomenex Envirosep PP (125 mm x 3.2 mm)	λ program: λ_{ex}=252-300 , λ_{em}= 322-500 nm	N.A
Tea	LC-FLD	Nova-Pak C_{18} (150 mm x 3.9 mm x 4 µm)	λ program:	0.0

		-Gradient elution: A: ACN; B: water	λ_{ex}=250-295 , λ_{em}= 365-465 nm	
Tea infusion	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) LiChrospher PAH, modified RP-18 silica gel (250 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: Splitless; HP-5ms, (30 m x 0.25 mm x 0.25 µm)	(A) λ program: λ_{ex}=250 , λ_{em}= 330-500 nm (B) Q, SIM	5-1
Mate tea	LC-FLD	-Vydac 201TP52 (250 x 2.1 mm i.d., 5 µm) -Gradient elution: A: ACN; B: water		0.1
Beverages	GC-EI-MS	-Injection: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	3-2
Sugarcane juice	GC-EI-MS	-Injection: (A) SBSE: Splitless; (B) MASE: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	(A) (B)
Cachaça (spirit)	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) Vydac 201TP54 (250 mm x 4.6 mm x 5 µm); isocratic elution: ACN/water (75:25, v/v) (B) Injection: Splitless + PTV; HP-5ms, (30 m x 0.25 mm x 0.25 µm)	(A) λ_{ex}=290 , λ_{em}=430 (B) Q, SIM	0.0
Spirits	LC-FLD	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=270-356 , λ_{em}= 330-500 nm	1.0 µg
Solid fatty matrices				
Meat	GC-EI-MS	-Injection: splitless -DB-5ms (30 m x 0.32 mm x 0.25 µm)	IT, Full scan	5-5
Meat	(A) LC-UV (B) LC-FLD	-ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	(A) λ = 254 nm (B) λ program: λ_{ex}=254-270 , λ_{em}= 340-420 nm	(A) (B)
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.0
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.0
Smoked meat	(A) LC-UV (B) LC-FLD (C) GC-EI-MS (Confirmation)	(A), (B) ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (C) Injection: splitless; DB-5ms (30 m x 0.32 mm x 0.25 µm)	(A) λ = 254 nm (B) λ program: λ_{ex}=254-320 , λ_{em}= 340-533 nm (C) IT, Full scan	(A) (B) (C)
Smoked meat	GC-EI-MS	-Injection: Splitless -HP-5, (50 m x 0.32 mm x 1.05 µm)	Q, SIM	0.0
Smoked meat	GC-EI-MS	-Injection: Splitless -DB-5ms, (60 m x 0.25 mm x 0.25 µm)	Magnetic sector, SIR	N.A
Smoked meat	LC-FLD	-Supelcosil LC-PAH (250 mm x 3 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program (detector A): λ_{ex}= 250-290, λ_{em}= 350-470 nm λ program (detector B): λ_{ex}= 240-290, λ_{em}= 330-484 nm	N.A
Fish, smoked meat	GC-EI-MS	-Injection: Splitless -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.0
Fish	GC-EI-MS	-Injection : Pulsed splitless -DB-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	2-7
Fish	LC-FLD	-LiChroCART (250 mm x 4.0) with LiChrospher PAHs sorbent -Gradient elution: A: ACN; B: water	λ program: λ_{ex}= 217- 295, λ_{em}= 341-484 nm	N.A
Fish	GC-EI-MS	-Injection: Splitless -HP-5ms, (60 m x 0.25 mm x 0.25 µm)	Q	N.A
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.1 we
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.0
Fish	GC-EI-MS	-Injection: Splitless -DB-5ms, 5% phenyl 95% dimethyl arylene siloxane(30 m x 0.25 mm x 0.25 µm)	IT, Full scan	0.0
Fish	LC-FLD	-CC 150/4 Nucleosil 100-5 C18 PAH (150 mm x 4.0 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=315-590 , λ_{em}= 260-290 nm	0.0
Fish, seafood	LC-FLD	-Phenomenex C18 Envirosep (125 mm x 4.6 mm x 3 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 380-450 nm	0.0
Fish, seafood	GC-EI-MS	-Injection: Splitless -HP-5, (30 m x 0.25 mm x 0.25 µm)	Q, Full scan	N.A
Fish, mussel	GC-EI-MS	-Injection: Splitless -HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	8-4
Fish, palm dates	GC-EI-MS	-Injection: Splitless -CP-SIL 8CB-MS arylene-modified 5% phenyl 95% methyl polydimethylsiloxane (30 m x 0.25 mm x 0.25 µm)	IT, SIS	0.1
Shellfish	GC-EI-MS	-Injection: Splitless -VF-5ms, (30 m x 0.25 mm x 0.25 µm)	IT, SIS	0.5
Mussel	GC-EI-MS	-Injection: Splitless -DB-5, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.5 ma

Cheese	LC-FLD	Envirosep-PP (125 x 4.6 mm i.d., 4.6 µm) Isocratic elution: ACN/water (88:12, v/v)	λ_{ex}=295 , λ_{em}= 404 nm	0.0
Cheese	LC-FLD	Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=216-295 , λ_{em}= 320-484 nm	0.0
Cheese	LC-FLD	Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) Gradient elution: A: ACN; B: water	λ program: λ_{ex}=224-268 , λ_{em}= 320-400 nm	N.A
Infant milk, infant cereals	(A) Parent and hydroxy-PAHs: LC-FLD (B) Hydroxy-PAHs: LC-MS (Confirmation)	(A) Luna C_8 Supelcosil (120 mm x 2.0 mm x 5 µm); gradient elution: A: ACN; B: water (B) Hypersil Green PAH (100 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water	(A) λ program: λ_{ex}=274-393 , λ_{em}= 406-470 nm (B) QqQ, SRM, ESI (-)	(A (B
Solid non-fatty matrices				
Bread, potato	(A) LC-FLD (B) GC-MS/MS (Confirmation)	(A) Hypersil Green PAH (100 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: Splitless; VA-5, (30 m x 0.25 mm x 0.25 µm)	(A) λ program: λ_{ex}=250-300 , λ_{em}= 325-465 nm (B) Q, full scan	0.0
Cane sugar	LC-FLD	Vydac 201TP54 (250 mm x 4.6 mm x 5 µm) Isocratic elution: ACN/water (75:25, v/v)	λ_{ex}=290 , λ_{em}=430	0.0
Foodstuffs	LC-FLD	Spherisorb ODS2-C_{18} (250 mm x 4.6 mm i.d., 5 µm) Gradient elution: A: ACN; B: water	λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.0 [b]
Food supplements	LC-FLD	Varian C_{18} Pursuit 3 PAH (100 mm x 4.6 mm i.d., 3 µm) Gradient elution: A: ACN; B: MeOH; C: water	N.A.	0.1
Fruits, vegetables	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) C18 Vydac 201 TP (250 mm x 4.6 mm i.d., 5 µm); isocratic elution: ACN:water (75:25, v/v) (B) Injection: Splitless; Supelco 5% diphenyl-95% dimethylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	(A) λ_{ex}=290 , λ_{em}= 430 nm (B) Q, SIM	(A [b]
Ground coffee	(A) LC-FLD (B) GC-MS/MS (Confirmation) (C) LC-UV (Confirmation)	(A) Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: programmed temperature vaporization; Rtx-5MS (30 m x 0.25 mm x 0.25 µm) (C) C18 Supelcosil LC-PAH (150 mm x 3.0 mm x 5 µm); gradient elution: A: ACN; B: water	(A) λ program: λ_{ex}=220-286 , λ_{em}= 340-420 nm (B) IT, Product ion scan	0.1
Tea leaves	LC-UV	Elution: N.A. Agilent C-18 (250 mm x 4.6 mm)	N.A.	0.1
Tea leaves	GC-EI-MS	Injection: N.A. HP-5ms (30 m x 0.25 mm x N.A.)	Q	N.A
Vegetables	GC-EI-MS	Injection: Splitless HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A

[a] N.A.: Data not available
[b] Method detection limit (MDL)
[c] Method quantification limit (MQL)
Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; ESI (-): electrospray ionization in negative mode; GC-EI-MS: gas chromatography coupled to mass spectrometry operating in electronic ionization; GC-EI-MS/MS: GC coupled to tandem MS; GCxGC-MS: multidimensional GC-EI-MS; IT: ion trap analyzer; LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LP-GC-EI-MS low pressure GC-MS in electronic ionization; LVI: large volume injection; MASE: membrane-assisted solvent extraction; MeOH: methanol; MSTFA: N-methyl-N-(trimethylsilyl)trifluoroacetamide; PTV: programmed-temperature vaporization; Q: single quadrupole analyzer; QqQ: triple quadrupole analyzer; SBSE: stir bar sorptive extraction; SIM: single-ion monitoring; SIR: selected ion recording; SIS: selected-ion storage; SRM: selected-reaction monitoring; TOF: time of flight analyzer; λ_{ex}: excitation wavelength; λ_{em}: emission wavelength

1222 Table 4
1223 Summary of analyzed PAHs and concentrations found in real samples
1224

Analytes	*Type of sample*	*Concentration*[a]	*Observations*	**Reference**
	Liquid fatty matrices			
16 EPA PAHs[b]	Edible oils	0.3 (BaA, IP)[c]–1145 (PHE)[d] ng g^{-1}	47 samples	[2321]
BaP	Edible oils	Refined oil: < 1.5 µg kg^{-1} Unrefined oil: > 2 µg kg^{-1}	8 samples (refined, unrefined oils)	[2524]
ACP, ANT, BaP, BeP, BghiP, CHR, COR, CPdefPHE, PHE, PYR	Edible oils	Refined vegetable oil: 40.2 µg kg^{-1} (total PAH content) Olive oil: 624 µg kg^{-1} (total PAH content)	296 samples	[2930]
BaP	Olive oil	84–89 ng g^{-1}	48 samples	[2126]
16 EPA PAHs + 4 EU PAHs[b] + (> 35)	Olive oil	0.30 – 320 (3-methylCHR) µg kg^{-1}	5 samples (olive pomace oil)	[2422]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR + 2 alkyl derivatives	Olive oil	0.4 (ACP, ACY) – 26 (PHE) µg kg^{-1}	10 samples (extra virgin olive oil)	[3334]
BkFA, BghiP, BeP, BaP	Olive, olive-pomace oil	0.3 (BghiP, BeP, BaP) – 88.7 (BkFA) µg kg^{-1}	25 samples (virgin olive oil, olive pomace oil)	[3132]
ACP, ACY, ANT, BaA, BbFA, BjFA, BkFA, BcF, BghiP, BaP, CHR, CPcdP, DBahA, DBaeP, DBahP, DBaiP, DBalP, FA, FLR, IP, MCH, NPH, PHE, PYR,	Vegetable oils	0.5 (BaP) – 133.2 (CHR) µg kg^{-1}	14 samples (olive oil, extra virgin olive oil, pomace olive oil, sunflower oil)	[3536]
16 EPA PAHs	Fish oil, fish	Fish: 0.06 (BaA) – 11.4 (PYR) µg kg^{-1} Fish feed: 0.2 (ACP, ACY) – 242 (NPH) µg kg^{-1} Fish oil: 0.3 (ACP, BbFA, BkFA) – 38.2 (PHE) µg kg^{-1} Linseed oil: 0.3 (BaP) –16.7 (FA) µg kg^{-1} Palm oil: 0.2 (ACY) –1.4 (BaP) µg kg^{-1} Rapeseed oil: 0.2 (ACY) –1.9 (NPH) µg kg^{-1}	31 samples (fish, fish feed, fish oil, linseed oil, palm oil, rapeseed oils) Fish exposed to long-term feed trials	[9689]
ACP, ACY, ANT, BaA, CHR, FA, FLR, NPH,	Milk	31.9 (PYR) – 160.5 (PHE) µg L^{-1}	10 samples	[3940]

PHE, PYR				
16 EPA PAHs	Milk	Only 8 PAHs found: ACP, ACY, ANT, BaA , FA, FLR, NPH, PYR Control: 0.3 (ACP) – 6.4 (NPH) ng g^{-1} (milk fat) Cementwork: 0.2 (ACP) –16.2 (FLR) ng g^{-1} (milk fat) Motorway: 0.5 (ACP) – 10.7 (FLR) ng g^{-1} (milk fat) Combined sources: 0.8 (ACP) – 15.2 (NPH) ng g^{-1} (milk fat)	-14 samples (control, cementwork, motorway, combined sources) -Average values	[3637]
ANT, BaP, BaA, BbFA, BkFA, BghiP, CHR, DBahA, FA, IP, PHE, PYR	Milk	Milk: 0.01 (ANT, IP) – 0.35 (BbFA) µg kg^{-1} Infant formula: 0.02 (ANT) – 0.40 (PHE) µg kg^{-1}	17 samples (commercial milk and infant formula)	[3839]
	Liquid non-fatty matrices			
BaA, BbFA, BkFA, BaP, BghiP, DBahA, IP	Coffee	0.01 (all except BbF) – 0.1 (BbFA) µg kg^{-1}	12 samples (with and without caffeine, natural roasting)	[4142]
BaP	Coffee	1.1 ng g^{-1}	1 sample (standard addition method)	[47]
ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, NPH, PHE, PYR	Tea infusion	4 PAHs found: 6.6 (PHE) – 82 (FLR) ng mL^{-1}	6 samples	[48]
16 EPA PAHs (except ACY)	Mate tea	1.4 (BaA) – 1156 (ACP) ng L^{-1}	11 samples	[49]
BaP	Sugarcane juice	0.05 – 0.11 µg L^{-1}		[50]
BaA, BbFA, BkFA, BaP, DBahA	Cachaça (spirit)	0.01 (BkFA) – 0.83 (BbFA) µg L^{-1}	25 samples	[4243]
16 EPA PAHs (except ACY)	Spirits	From burned sugar cane: 0.003 (BghiP) – 138 (BaA) µg L^{-1} From non-burned sugar cane: 0.002 (BaP) – 3.13 (PHE) µg L^{-1}	131 samples (from burned and non-burned sugar cane crops)	[46]
	Solid fatty matrices			
16 EPA PAHs	Smoked meat	< 0.20 (BaA, BbFA, BkFA, BaP, BghiP, CHR, FA, PY) –38.59 (PHE) µg kg^{-1}	7 samples (smoked meat)	[17]
15 EU PAHs + BcF	Smoked meat	Before processing: 0.003 (DBalP) – 0.101 (BcF) µg kg^{-1} Traditional smokehouse: 0.002 (DBahP, DBalP) – 2.134 (BcF) µg kg^{-1} Industrial smokehouse: 0.003 (DBahA, DBalP) – 1.539 (BcF) µg kg^{-1}	22 samples (before processing and traditional and industrial smokehouse)	[6057]
15 EU PAHs + BcF	Smoked meat	0.001 (DBaHP, DBalP) – 10.6 (BcF) µg kg^{-1}	32 samples	[6158]
BaA, BbFA, BkFA, BghiP,	Smoked meat	0.1 (DBahA, BbFA) – 26.22 (FA) µg kg^{-1}	18 samples	[5956]

BaP, CHR, DBahA, FA, IP, PYR				
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.2 (BaA) – 51.4 (BbFA) ng g^{-1}	10 samples	[7067]
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.37 (BaP) – 42.49 (BbFA) ng g^{-1}	10 samples	[7671]
16 EPA PAHs	Fish	0.42 (ACY) – 34.48 (BghiP) µg g^{-1}	Number of samples not defined	[6461]
16 EPA PAHs (except ACY) + DBalP	Fish	0.12 (PHE) – 4.99 (NPH) ng g^{-1}	27 samples	[7772]
ANT, BaA, BbFA, BkFA, BaP, BghiP, CHR, DBahA, FA, IP, PYR	Fish, seafood	Summer: 0.12 (ANT) – 23.23 (PYR) ng g^{-1} (average values) Winter: 0.35 (FA) – 46.01 (CHR) ng g^{-1} (average values)	Number of samples not defined	[6865]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR	Fish, mussel	0.52 (NPH) – 8.00 (PHE) ng g^{-1}	- 8 samples - PAHs showing up to 4 rings	[7570]
16 EPA PAHs	Shellfish	24.4 – 140.0 ng g^{-1} (total PAH content)	10 samples	[6360]
BaP	Cheese	Samples smoked with straw/cardboard: 0.38 – 2.40 µg kg^{-1} Samples smoked with wood shavings/ liquid smoke flavorings: 0.18 – 0.80 µg kg^{-1}	96 samples	[8075]
16 EPA PAHs	Cheese	0.01 (BkFA, BaP, DBahA) – 60.0 (NPH, PHE) µg kg^{-1}	36 samples	[7873]
16 EPA PAHs	Cheese	0.12 – 6.21 µg kg^{-1} (total PAH content)	- 16 samples - Analysis before and after smoking	[7974]
	Solid non-fatty matrices			
16 EPA PAHs (except ACY) + BeP	Bread, potato	Mashed potato: 9.35 – 17.10 µg kg^{-1} (total PAH content) Potato: 8.47 – 17.20 µg kg^{-1} (total PAH content) Toasted bread: 7.38 – 18.00 µg kg^{-1} (total PAH content)	5 samples	[8580]
BaA, BbFA, BkFA, BaP, DBahA	Cane sugar	Typical sugar: 0.015 (BaP) – 0.300 (BaA) µg kg^{-1} (average values) Organic sugar: 0.002 (BkFA) – 0.104 (BaA) µg kg^{-1} (average values)	57 samples (18 organic samples)	[8681]
16 EPA PAHs (except ACY)	Foodstuffs	0.08 (ANT) – 61.4 (PYR) ng g^{-1}	Number of samples not defined	[8883]
15 EU PAHs + BcF	Food supplements	0.02 (BaA, BkFA, BghiP, DAaeP) – 32.50 (BcF) µg kg^{-1}	20 samples	[10496]
BaA, BbFA, BkFA, BaP, BeP, BghiP, CHR, DBahA,	Fruits, vegetables	Lettuce: 0.08 (BaP) – 8.68 (FA) µg kg^{-1} (average values) Tomato: 0.08 (BaP) – 6.19 (FA) µg kg^{-1} (average values)	Number of samples not defined (combined samples of lettuce,	[8479]

FA, PYR		Cabbage: 0.06 (BkFA) – 5.53 (BkFA) µg kg^{-1} (average values) Fruits: 0.08 (BaP) – 6.22 (BghiP) µg kg^{-1} (average values)	tomato, cabbage, apple, grape and pear)	
16 EPA PAHs	Tea leaves	Leaves: 0.42 (ANT) – 83.40 (PYR) µg kg^{-1} (dry mass) Crude tea: 2.35 (DBahA) – 1120.00 (PHE) µg kg^{-1} (dry mass) Tea: 8.42 (DBahA) – 3930.00 (PHE) µg kg^{-1} (dry mass)	-6 samples -Leaves analyzed during the whole tea manufacturing process	[8176]
ACP, ACY, ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, IP, NPH, PHE, PYR	Vegetables	Potato: 0.23 (ACY) – 459 (IP) µg kg^{-1} (average values) Carrot: 0.40 (NPH) – 291 (IP) µg kg^{-1} (average values)	21 samples (organic agriculture)	[8378]

[a] Compounds showing the minimum and maximum values of the range are shown in parentheses
[b] For more details see Table 1
[c] Compound(s) showing the minimum concentration found
[d] Compound(s) showing the maximum concentration found
Abbreviations: COR: Coronene; BeP: Benzo[*e*]pyrene; CPdefPHE: Cyclopenta[*d,e,f*]phenanthrene; 3-methylCHR: 3-methylchrysene; BcF: Benzo[*c*]fluorene; BeP: Benzo[*e*]pyrene (For other abbreviations see Table 1)

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1 Polycyclic aromatic hydrocarbons in food and beverages. Analytical
2 methods and trends
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4
5 **Patricia Plaza-Bolaños[a,b], Antonia Garrido Frenich[a,*], José Luis Martínez Vidal[a]**
6
7 [a]*Department of Analytical Chemistry, University of Almeria, E-04071 Almeria, Spain*
8 [b]*Department of Analytical Chemistry, University of Granada, E-18071, Granada, Spain*
9
10
11 * Corresponding author: Antonia Garrido Frenich, Department of Analytical Chemistry,
12 University of Almeria, E-04071 Almeria, Spain.
13 Tel: +34 950015985; fax: +34 950015483.
14 E-mail address: agarrido@ual.es (A. Garrido Frenich)
15
16
17

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are compounds widespread in the environment, many of them showing carcinogenic effects. These compounds can reach the food chain by different ways and, therefore, the analysis of PAHs in food is a matter of concern. This article reviews the extraction methodologies together with the separation and detection techniques which are currently applied in the determination of PAHs in food and beverages. Specific extraction conditions, performance characteristics, chromatographic and detection parameters are discussed. A review of the occurrence of these compounds in the matrixes under study is also provided.

***Keywords*:** polycyclic aromatic hydrocarbons (PAHs), analysis, food, beverages, gas chromatography (GC), liquid chromatography (LC), fluorescence detection (FLD), mass spectrometry (MS)

35 **Contents**

36

37 1. Introduction 4
38 2. Sample preparation: extraction and clean up..6
39 2.1. Liquid matrices 6
40 2.1.1. Fatty matrices...6
41 2.1.2. Non-fatty matrices 10
42 2.2. Solid matrices 12
43 2.2.1. Fatty matrices.. 12
44 2.2.2. Non-fatty matrices 16
45 3. Chromatographic and detection techniques... 17
46 3.1. Liquid chromatography coupled to UV and FLD....................................... 17
47 3.2. Gas chromatography coupled to MS 18
48 4. Determination of PAHs in real samples 21
49 5. Conclusions 25
50 6. Trends 26
51 References 28

52

53 **1. Introduction**

54 Polycyclic aromatic hydrocarbons (PAHs) or polyarenes constitute a large class of
55 organic compounds (about 10,000 substances) characterized by a structure made up of
56 carbon and hydrogen atoms (Table 1) forming two or more fused aromatic rings without
57 any heteroatom or substituent. The compounds containing five or more aromatic rings
58 are know as "heavy" PAHs, whereas those containing less than five rings are named
59 "light" PAHs. Both kinds of PAHs are non-polar compounds showing high lipophilic
60 nature, although heavy PAHs are more stable and toxic than the other group.

61 PAHs are ubiquitous environmental contaminants which are widespread in the air
62 bonded to particulate matter. In spite of PAHs show hydrophobic properties (especially
63 heavy PAHs), they are also found in water. These compounds are produced during a
64 variety of combustion and pyrolysis processes from anthropogenic and natural sources.
65 A high amount of PAHs are emitted from processing coal, during incomplete
66 combustion of organic matter (e.g. wood and fossil fuels), from motor vehicle exhaust
67 and cigarettes [1,2]. Forest fires, volcanoes or hydrothermal processes are natural
68 emission sources of PAHs [3].

69 A number of PAHs are considered as genotoxic carcinogens, and biological and
70 mutagenic effects have also been reported [3]. Other PAHs not defined as carcinogens
71 may act as synergists [2]. The occurrence of PAHs in the environment is therefore a
72 cause of concern since humans are exposed to these compounds, for instance, by the air.
73 However, one of the major routes of human exposure to PAHs in non-smoking people is
74 food; for smokers, the contribution of cigarette smoke may be similar [4]. Food can be
75 contaminated by PAHs present in the environment, i.e. PAHs can accumulate on the
76 waxy surface of many vegetables and fruits [4]. Indeed, the presence of PAHs in
77 uncooked food, such as vegetables, seeds and grains, has been demonstrated [5]. These
78 products do not take up significant amounts of PAHs from the soil, but from air
79 particles [2] thought deposition of contaminated matter. Nevertheless, other studies
80 show contradictory results about the possibility of vegetables to take PAHs from soil
81 and water and metabolize them [6]. Another example of possible PAH contamination in
82 food is due to traffic, i.e. crops or livestock close to urban roads could be exposed to
83 PAHs and nitro-PAHs (derivates from PAHs) [5]. Other food products, such as seafood
84 and fish, can be exposed to PAHs present in water and sediments.

85 On the other hand, PAHs can be found in food products as a consequence of certain
86 industrial processing methods, such as smoking, heating (grilling, roasting) and drying,

87 which permit the direct contact between food and combustion products; these are
88 important sources of PAH contamination for seeds, edible oils, and meat and dairy
89 products [4]. In edible oils, the oilseed drying processes by direct combustion can be an
90 important source of contamination in a variety of vegetable oils [7].

91 Furthermore, the use of smoke flavoring products (SFP), which are utilized to
92 improve organoleptic characteristics, has increased in food industry [8]. Since SFP are
93 produced from smoke condensates, they are another significant source of PAHs in food.
94 Besides, the use of recycled polyethylene film in oil packaging could contaminate
95 vegetable oils with PAHs in by rediffusion [8].

96 In general, PAHs are not present individually but in mixtures. PAHs that have been
97 extensively monitored are the compounds included in the United States Environmental
98 Protection Agency (US-EPA) list of priority organic pollutants (the so-called 16 EPA
99 PAHs) [9], as well as the European Union (EU) list of PAHs [10] (15 compounds) [2]
100 (Table 1). Benzo[*a*]pyrene (BaP) is probably the most studied PAH. The International
101 Agency for Research on Cancer (IARC) described BaP as probable human carcinogen
102 in 1987 [11]. Thus, the determination of BaP has been widely used in environmental
103 analysis as marker for the entire PAH content. Maximum permitted concentrations in
104 foodstuffs for BaP have been established by the EU [12], as well as methods of
105 sampling and analysis in order to perform official controls of this compound [13].
106 However, BaP contributes only with 1-20 % of the total content of PAH, and other
107 aromatic compounds can be present as well [1]. In this sense, in 2002, the Scientific
108 Committee on Food (SCF) of the European Commission considered that despite the use
109 of BaP as a marker of occurrence and carcinogenic effect of the PAH content in food, it
110 suggested that this evaluation should be accompanied by additional analysis of other
111 PAHs in order to establish a PAH contamination profile in food commodities [14]. In
112 2007, the European Food Safety Authority (EFSA) pointed out that the supposition that
113 BaP was a good indicator of any PAH contamination was uncertain [4]. The SCF
114 noticed that a number of derivatives of PAHs, such as nitro-PAHs and oxygenated
115 PAHs, as well as heterocyclic aromatic compounds (e.g. acridine, carbazole) can be
116 generated by incomplete combustion or reactions in air [14]. Consequently, the
117 determination of all these compounds in food is also an issue of concern.

118 The monitoring of other PAHs has been strongly recommended by the EU [10]. The
119 EFSA also remarked that food categories such as herbs and spices, food supplements,
120 coffee, tea and herbal infusions and other cereal and grain beverages are not captured by

121 existing legislation [1,2,4,12]. Later, in 2008, the EFSA established that BaP is not a
122 suitable indicator for the occurrence of PAHs in food and that occurrence data for
123 benzo[*c*]fluorene (BcF) are needed [15]. It is important to notice that this compound is
124 not included in either the EPA or the EU list of PAHs.
125 Therefore, the need for reliable data about the concentration of PAHs in food is
126 increasing in order to establish new maximum permitted levels. In this sense, analytical
127 laboratories play an important role since they must have adequate methods for the
128 analysis of PAHs and their derivatives in food.
129 This review shows an overview of the analytical methodologies applied in the
130 determination of PAHs in food and beverages (e.g. edible oils, smoked foodstuffs, milk
131 or infusions), including recent approaches. The main techniques applied in the
132 extraction and clean up of the extracts and in the detection and quantification of the
133 analytes have been reviewed, focusing on liquid chromatography (LC) coupled to
134 fluorescence (FLD) and ultraviolet-visible (UV) detection and gas chromatography
135 (GC) coupled to mass spectrometry (MS). New trends based on instrumental analysis
136 and recent extraction techniques, some of them applied in other fields of food safety and
137 environmental analysis, have been pointed out.
138 The review covers the relevant literature published since the year 2000 and certain
139 previous references highly cited. The previous articles have already been revised and
140 discussed elsewhere [7,8,16].
141
142 **2. Sample preparation: extraction and clean up**
143 As general precautions to be considered when determining PAHs, it is important to
144 protect the solutions against light since these compounds are light sensitive and they can
145 decompose by photoirradiation and oxidation [17]. Thus, light exposure during the
146 sample pre-treatment has to be carefully controlled [17,18]. Besides, concentration to
147 dryness should be avoided in order to diminish possible losses due to evaporation of the
148 lower molecular weight compounds [17].
149
150 ***2.1. Liquid matrices***
151 *2.1.1. Fatty matrices*
152 It is well-known that one of the main difficulties in the analysis of fatty matrices is due
153 to their high fat content (e.g. lipids, triglycerides, fatty acids) [19]. For this reason, the
154 extraction of PAHs from these complex matrices is usually a laborious and time-

155 consuming stage (Figure 1). The removal of lipidic material is important not only to
156 minimize the maintenance of the chromatographic system (especially when using GC),
157 but also to reach low detection limits (LODs). The need for high sensitivity is justified
158 by the low concentrations of PAHs fixed as maximum levels permitted in current
159 legislation [1,2,8,12,20].

160 Extraction of PAHs from foodstuffs has traditionally relied on a three-stage
161 methodology including saponification, liquid-liquid extraction (LLE) and clean-up by
162 solid-phase extraction (SPE).

163 One of the most studied fatty commodities is edible oils since they can be exposed to
164 PAHs by heating processes or solvent extraction during the production. The reported
165 methods in bibliography described the use of two general strategies for the sample
166 extraction and clean-up. The first strategy involves the dilution of the sample, LLE and
167 a subsequent clean-up by SPE [17,21,22]; the other general methodology carries out a
168 single SPE-stage after the sample dilution [21,23-25]. The dilution step is normally
169 performed with *n*-hexane in order to modify the partition coefficients [8]. A variety of
170 solvents are used in LLE, but the most common are dimethylsulfoxide (DMSO) and
171 cyclohexane (Table 2). For the clean-up by SPE, very different cartridges have been
172 utilized, such as C_{18}/C_8, aminopropyl, silica and polystyrene/divinylbenzene (PS-DVB)
173 sorbents. For SPE (as extraction method), C_{18}/Florisil mixtures [26] PS-DVB [25] have
174 been used. Some authors have described PS-DVB sorbents as extremely selective to
175 PAHs, considering this material as suitable to most of food matrices [27].

176 In the extraction of PAHs by SPE using reversed-phase or polymeric sorbents, some
177 questions must be taken into account. Due to the low solubility of these compounds,
178 adsorption problems can be found (e.g. glass walls). The addition of a small percentage
179 of an organic solvent (i.e. methanol, acetonitrile or 2-propanol) can be used to minimize
180 this adsorption. However, the optimization of the solvent percentage is a critical point
181 since low percentages cannot improve the solubilization of the heavy PAHs, whereas a
182 high percentage can reduce the breakthrough volume for the light PAHs [28]. Recently,
183 humic acid-bonded silica has been proposed as a new sorbent for the extraction of
184 PAHs by SPE using BaP as example [24]. The retention of PAHs in this sorbent is
185 based on charge-transfer and hydrophobic interactions. Nevertheless, additional
186 applications of this SPE material have not been found.

187 The performance of a saponification step prior to the LLE is also described in order to
188 reduce the lipidic content (e.g. triacylglicerols), for instance using KOH or NaOH

189 solutions containing an alcoholic percentage [1,7,8,17]. However, losses of BaP have
190 been reported by partial portioning to the alcoholic phase when using this procedure
191 [17], and other authors suggested that saponification could negatively affect the most
192 labile compounds [8].

193 The formation of caffeine complexes with PAHs prior to LLE has been also reported
194 by mixing the sample with a caffeine:formic acid solution, although it is not currently
195 applied. The complexes are then decomposed by extracting with an aqueous sodium
196 choride solution [7,8].

197 Column chromatography has also been applied as clean-up using alumina [29] and
198 silica gel [30]. The utilization of donor-acceptor complex chromatography (DACC) for
199 the clean-up of diluted oil samples is also described [29,31]. DACC is based on a strong
200 π-π interaction produced between the sorbent and the PAHs; then, certain matrix
201 components, such as neutral lipids and tocopherol, can be eluted by using a non-electron
202 containing solvent. After that, the PAHs are eluted with an appropriate organic solvent
203 that removes the interaction (e.g. *n*-hexane:tetrahydrofuran mixtures). However, some
204 problems can be found. The lightest PAHs (namely naphthalene (NPH), acenaphthylene
205 (ACY), acenaphthene (ACP) and fluorene (FLR)) co-eluted with the fatty fraction and
206 the use of more than 5 % of tetrahydrofuran caused additional co-elution problems.

207 In general, the reported recoveries applying the methodologies commented above are
208 quite similar, showing good precision values (< 10 %). However, the application of the
209 saponification stage prior to an LLE and SPE clean-up can provide very high recovery
210 (> 120 %) values for some compounds [17]. Despite the problems reported for the
211 application of DACC, the recoveries reported for edible oils are slightly higher than the
212 recoveries obtained using LLE and/or SPE.

213 Gel permeation chromatography (GPC, also size exclusion chromatography, SEC) has
214 been utilized after LLE operating in the normal phase mode (e.g. mobile phase:
215 dichloromethane; stationary phase: styrene-divinylbenzene copolymer) [32]. This kind
216 of chromatography has been extensively used for the purification of fatty extracts
217 separating lipids from the analytes; although its application in edible oils is scarce
218 (Table 2). The reported recoveries are higher than those using other methodologies,
219 although this procedure (LLE + GPC) was only carried out for the determination of
220 medium molecular weight PAHs. GPC is a semi-automatic clean-up, which is an
221 obvious advantage, but the solvent consumption is moderated, especially considering a

222 typical flow of 5 mL min^{-1} and 30-40-min running times. Thus, about 150-200 mL of
223 solvent per sample can be required, which could explain its low use.
224 Bogusz et al. [26] carried out a comparison between the performance of SPE and
225 matrix-solid phase dispersion (MSPD) for the extraction of PAHs from olive oil. In the
226 MSPD technique, a small amount of sample (typically 0.5 g) is mixed with a solid
227 support (e.g. C_{18} material) in a mortar. Then, the mixture is transferred to an SPE
228 reservoir and eluted in the same way as in SPE. The main advantage of MSPD is the
229 low amount of solvent needed. Nevertheless, reproducibility problems are often
230 observed, with medium-high precision values. The extraction of PAHs with this
231 technique is not an exception: MSPD provided lower recoveries and worse repeatability
232 than the SPE procedure used. However, MSPD is simpler and faster than the LLE-based
233 methods.
234 Due to the volatile character of PAHs, they have been also determined by head-space
235 (HS) and solid-phase microextraction (SPME) techniques, namely, HS [33], HS-SPME
236 [34] and SPME [35,36], with or without a previous dilution of the oil. HS-SPME has
237 been applied for the analysis of PAHs showing a molecular weight $\leq$ 202 using a
238 DVB/carboxen/polydimethylsiloxane (DVB/Car/PDMS) fiber, which was chosen on the
239 basis of its affinity for low/medium molecular weight compounds [34]. The recovery
240 values were adequate, even for NPH, which is a problematic compound because of
241 well-known losses during the evaporation stages in the extraction. This can be explained
242 since the HS-SPME does not involve any evaporation or pre-concentration stage.
243 However, the precision values are higher in comparison to other extraction techniques.
244 The application of SPME with direct immersion of the fiber in the oil has also been
245 reported [35,36], using Carbopack/PDMS fibers and dilution of the oil. In the analysis
246 of fatty commodities, one of the main problems when using SPME is matrix effect,
247 causing a decrease in the fiber efficiency. In order to decrease the possible matrix effect,
248 the fiber can be rinsed with *n*-hexane prior to desorption and injection in order to
249 remove triglycerides residues on the surface of the fiber [35,36]. Purcaro et al. [36]
250 described the use of an SPME method for the determination of the EU list of PAHs with
251 low relative standard deviation (RSD) values (<11%, except for BcF (16%) and
252 cyclopenta[*c,d*]pyrene (CPcdP) (35%)). It was observed that at high extraction times
253 (>30 min), the extraction efficiency decreased for some compounds, due to a rising
254 effect by the organic solvent used in the dilution. Desorption time was limited to 10 min
255 to avoid broadening of the peaks of the later eluted compounds (heavy PAHs). As

256 commented above, the SPME methodologies can provide high precision values. This is
257 one of its drawbacks, the lack of reproducibility, together with a short lifetime of the
258 fibers and possible carry-over problems. On the contrary, the use of HS/SPME
259 technique reduces sample handling and minimizes solvent consumption.
260 Another fatty liquid matrix that has been monitored for PAHs is milk, but to a lesser
261 extent. Although the fat content of this matrix is much lower than the fat percentage of
262 edible oils, the methodologies used in the revised literature are quite similar (Table 2).
263 LLE-based methods are therefore applied, but the number of LLE stages is more
264 reduced [37-39]. Lutz et al. [38] described the analysis of PAHs and hydroxi-PAHs
265 using the same extraction procedure involving LLE, SPE as clean-up and subsequent
266 LLE steps for clean-up (different for each group). It is important to notice that any SPE
267 procedure has been found for the extraction of PAHs from milk (Table 2). The use of
268 saponification is also reported; the alcohol percentage was found to influence the
269 extractability of the compounds, increasing the extractability but also the intensity of
270 interfering peaks when working at 100 % ethanol. HS-SPME [40] and SPME have been
271 also applied [41]. In both studies, PDMS-DVB fibres were used; in the case of SPME,
272 the sample was diluted with water prior to the extraction. The HS-SPME modality was
273 also evaluated but it was not able to extract the high molecular weight PAHs [41]. In a
274 later study, the HS-SPME mode was used for the extraction of PAHs containing up to
275 four aromatic rings [40]. Similar recoveries were obtained, although better precision
276 values were found in the HS-SPME procedure. In comparison to the LLE-based
277 methodologies, these two microextraction techniques provided an improvement in the
278 recovery values.
279 More detailed information about extraction methods is shown in (Table 2).
280
281 *2.1.2. Non-fatty matrices*
282 The monitoring of PAHs has been carried out in a number of non-fatty liquid matrices,
283 namely coffee, tea, alcoholic beverages and juice. In general, the extraction of PAHs
284 from these commodities is performed by less laborious procedures since the amount of
285 lipidic material, and thus the possible matrix interferences, is much lower than in the
286 previous group of matrices (Table 2).
287 The use of LLE with subsequent SPE clean-up (silica sorbent) has been reported in
288 coffee brew [42]. The application of a single SPE stage was discarded because of
289 clogging problems when passing instant coffee solutions through the SPE cartridge

290 (C_{18}); the application of microwave-assisted extraction (MAE) was also ruled out due to
291 stability problems observed for some PAHs. LLE and subsequent clean-up using
292 column chromatography with silica gel has been recently applied in cachaça (Brazilian
293 spirit) [43].
294 SPE-based procedures have been used for the analysis of PAHs in coffee [44], but
295 also in tea [45] and spirits [46] using different cartridges, such as PS-DVB and C_{18}.
296 However, Houessou et al. [44] consider PS-DVB sorbents as the most suitable material
297 for the extraction of PAHs from liquid samples due to π-π interactions that can increase
298 the retention in comparison to C_{18} or silica sorbents, which do not show this type of
299 interaction. Moreover, slightly better reproducibility was found when using PS-DVB
300 cartridges instead of C_{18} sorbents for the analysis of coffee. The addition of methanol or
301 acetonitrile to the sample has been described in order to minimize the adsorption of
302 PAHs onto the glass and/or cartridge surfaces [44-46]. However, contradictory results
303 concerning the methanol percentage have been reported: about 1% (v/v) of methanol
304 has been described as the optimal amount in order to avoid competitive effects between
305 PAHs and the solvent on the stationary phase [44] for tea samples, whereas higher
306 percentages (10-20%, v/v) have been used in coffee samples and spirits [45,46].
307 Alternatively, SPE has been performed using molecularly imprinted polymers (MIP-
308 SPE) for the extraction of BaP in coffee with adequate performance characteristics; the
309 MIP-SPE sorbent was compared to C_{18}, obtaining better recovery values for the first
310 approach [47].
311 LLE [43] and SPE [46] have been utilized for the analysis of spirits, obtaining similar
312 recovery values but better RSDs when using SPE, probably due to the high number of
313 LLE steps included in the first method. Moreover, the SPE-based methodology was
314 applied for the analysis of a higher number of PAHs (15) in comparison with the LLE
315 method (5).
316 HS-SPME has been applied for the analysis of PAHs in tea infusions; a variety of
317 fibres were evaluated, including polyacrilate (polar), PDMS (non-polar), and PDMS-
318 DVB (medium polarity). The optimal results were obtained using PDMS-DVB fibres
319 [48]. Nevertheless, some drawbacks have been reported, such as overloading problems
320 due to insufficient coating film of the fibres [49]. In this sense, two recent approaches
321 described the application of stir bar sorptive extraction (SBSE) for the analysis of mate
322 tea [49] and sugarcane juice [50]. In SBSE, the adsorption process occurs in bars and so
323 the coating film is higher, increasing the adsorption capacity in comparison with SPME

324 and also minimizing the amount of co-extracted matrix material (Figure 2). SBSE is
325 currently considered as an environmentally friendly technique since it permits the
326 reduction of solvent consumption to the minimum (no solvent required). SBSE with
327 thermal desorption (SBSE-TD) is the solvent-free mode but it requires a special device
328 in the chromatographic system to carry out the desorption of the analytes. As an
329 alternative, the desorption process can be performed by using an appropriate solvent; in
330 this case, the volume needed is still reduced (from a few microliters up to 1-2 mL). This
331 modality has been used in mate tea samples with results comparable to LLE [49]; this
332 study described the negative effect of the addition of NaCl to increase the ionic strength
333 since the presence of salt provokes the transfer of the PAHs to the surface of the
334 solution, minimizing the interaction with the sorbent on the bar: it is the “oil effect”.
335 The addition of methanol or acetonitrile to reduce adsorption onto the walls was
336 discarded since any improvement was found. SBSE-TD was applied satisfactorily for
337 the determination of only BaP in sugarcane juice [50]. Bearing in mind that the matrices
338 were different, worse precision values were obtained for BaP with this modality (19 %
339 by SBSE-TD and 4-6% by SBSE), which is an unexpected data since the SBSE-TD
340 involves an automated desorption that should improve this parameter. The performance
341 of SBSE-TD was compared to another environmentally friendly technique, membrane-
342 assisted solvent extraction (MASE) [50], concluding that MASE provided better
343 recovery and precision values. MASE was also applied for the determination of PAHs
344 in several beverages [51]; in this case, a higher number of compounds were monitored
345 (16) and the addition of methanol was found adequate since it improved the enrichment
346 of the compounds in the membrane bag. It is important to notice that the recovery of the
347 more volatile PAHs (e.g. NPH) was more than acceptable, probably due to the fact that
348 any evaporation stage was needed in this procedure.
349 More detailed information about extraction methods is shown in (Table 2).
350

351 ***2.2. Solid matrices***

352 *2.2.1. Fatty matrices*

353 There are two food commodities that have been extensively monitored for PAHs, meat
354 and fish (Table 2). The analysis of PAHs in meat, especially smoked meat, is due to the
355 occurrence of these compounds after traditional or industrial smoking processes,
356 whereas fish can bioaccumulate PAHs in their fatty tissues in the environmental
357 compartment.

358 Despite this review aims to cover the most relevant literature after 2000, there are
359 previous studies widely referred which are related to the analysis of meat using solid-
360 liquid extraction (SLE), and SPE for clean up [52-54]. Chen et al. [52,53] proposed the
361 extraction of the sample, which was previously lyophilized, by SLE using ultrasounds
362 or ultrasound extraction (USE), and subsequent SPE clean-up with Florisil. This method
363 was then compared to a more laborious procedure involving saponification using a
364 Soxhlet extractor, and a number of LLE steps prior to a final SPE clean-up (Florisil).
365 Despite the recovery values were quite similar and USE reduced extraction time and
366 solvent consumption, the Soxhlet method was eventually selected due to the
367 saponification stage was described as necessary for the determination. Chiu et al. [54]
368 also described the performance of a saponification stage in a similar way as described in
369 [52].
370 Wang et al. [55] first described the use of pressurized liquid extraction (PLE, also
371 known as accelerated solvent extraction, ASE) for the analysis of PAHs in meat
372 samples. A dichloromethane/acetonitrile mixture was used and C_{18} or C_8 bulk sorbent
373 and sodium sulphate were used to prepare the extraction cell. Although the performance
374 of the SLE process by using PLE allowed the semi-automation of the extraction stage, a
375 laborious clean-up procedure was still applied since partitions with sulphuric acid and
376 column chromatography (Florisil) were also performed. More recent PLE-based
377 methodologies have been published for this aim, but using in the clean-up stage GPC
378 and column chromatography [56] or GPC and SPE [57]. These studies utilized *n*-
379 hexane as extraction solvent and polymeric-based columns (styrene DVB) for the GPC
380 process (normal phase). This stage permitted the removal of a high percentage of lipids
381 from the matrix; however, this was insufficient and an additional clean-up step was
382 needed, as described in both studies. Jira et al. [56] pointed out the use of GPC as an
383 effective way of removing lipidic material instead of saponification; for the remaining
384 lipids and polar compounds, silica gel column chromatography was chosen. The use of
385 sea sand and/or drying material to homogenize the sample was discarded because of
386 certain PAHs (pyrene (PYR), benzo[*a*]anthracene (BaA), BaP, indeno[1,2,3-*cd*]-pyrene
387 (IP), dibenzo[*a,h*]anthracene (DBahA) and benzo[*g,h,i*]perylene (BghiP)) could be
388 adsorbed on these materials. The use of GPC and subsequent SPE by silica gel is a
389 similar procedure also reported [57,58]. The use of GPC and column chromatography
390 offered higher recoveries and lower RSD values in comparison with GPC plus SPE,
391 although the number of monitored PAHs was superior in this last study.

392 In relation to the recovery rates, in general, the results obtained by LLE-based and
393 PLE-based procedures are very similar; although it is obvious that PLE shows certain
394 advantages, such as automation of the process and less solvent and time consumption.
395 Although SPME is normally used with liquid samples, Martin et al. [59] described the
396 application of this extraction technique to the analysis of PAHs in meat by using a direct
397 extraction device (SPME-DED). This device contains a gelatine support for the SPME
398 fiber that permits the interaction between the fiber and the solid sample (Figure 3).
399 Although recovery values were not provided, the precision values obtained were
400 consistent.
401 Fish (and seafood) is the second most studied fatty matrix in PAH analysis. Despite
402 the disadvantages of Soxhlet have been largely discussed (e.g. solvent consumption,
403 time-consuming, non-selective), its efficiency still makes it used and selected in PAH
404 analysis. In this type of commodity, the use of Soxhlet extraction (e.g. dichloromethane,
405 *n*-hexane) is widely reported [60-64]; lyophilization [60] and homogenization with
406 sodium sulphate [61,64] have been applied prior to the SLE process. As in previous
407 matrices, a clean-up stage is mandatory after the Soxhlet extraction due to the high
408 amount of co-extracted material. The use of GPC is preferred for this aim [60,62],
409 although saponification plus subsequent LLE stages and column chromatography
410 [63,64] have also been described. The main disadvantage of the application of GPC in
411 this type of matrices is not only the moderate solvent consumption but also the
412 widespread utilization of chlorinated solvents such as dichloromethane or chloroform as
413 mobile phases (Table 2). In relation to the performance characteristics, these Soxhlet-
414 based procedures provided adequate recoveries and the reported RSD ranges were
415 significantly wide (e.g. 2-20%); the highest values could be due to these time-
416 consuming protocols including numerous steps.
417 Although the performance of a saponification and subsequent LLE stages is less time-
418 consuming than Soxhlet plus GPC or LLE, it provided low recoveries and similar
419 precision values [65].
420 PLE is applied as a suitable option to the aforementioned procedures [55,62,66]. The
421 decrease in the extraction time against the Soxhlet methods is an obvious advantage.
422 However, PLE is also a non-selective extraction and further clean-up is normally
423 performed. Wang et al. [55] described that the removal of the fatty material in the PLE
424 extracts was incomplete when applying saponification and an acid treatment with
425 sulphuric acid (18 M) was found to cause decomposition of several PAHs (namely

426 ACY, anthracene (ANT), and BaP) and losses of signal (e.g. ACP, IP, DBahA and
427 BghiP). Nevertheless, this effect was not observed when a less concentrated solution
428 was used (9 M). On the contrary, Martinez et al. [66] utilized a saponification stage for
429 the clean-up of the raw PLE extracts with adequate recoveries, although a different
430 extraction solvent was used (*n*-hexane:dichloromethane (1:1) instead of
431 dichloromethane:acetonitrile (9:1)). In this study, Soxhlet extraction, USE and PLE
432 were compared; similar results were found when using PLE and USE, although this last
433 methodology was less repetitive. Surprisingly, the classical Soxhlet extraction yielded
434 worse recovery and precision values than PLE and USE. In a similar study, Janska et
435 al. [62] established that the results provided by PLE and USE were not significantly
436 different from those found by using the Soxhlet extraction, using GPC for the clean-up
437 of the extracts in all cases, but higher repeatability was observed with PLE. The
438 utilization of extraction mixtures containing a water-miscible solvent was strongly
439 recommended in PLE to enhance the penetration into wet fatty matrices, such as fish.
440 The saponification stage has also been performed together with the extraction step by
441 MAE [67], reducing the whole extraction time. However, further purification by SPE
442 (silica) was needed and the number of analyzed PAHs was reduced (7 compounds).
443 Additionally, direct SPE or GPC clean-up of MAE extracts has been applied; despite
444 any recovery or precision rates were provided, the results of the analysis of a certified
445 reference material were adequate [68].
446 The use of HS-SPME has been described for the analysis of PAHs showing up to 4
447 rings in fish and seafood using polyacrylate [69] and PDMS-DVB fibres [70]. Two
448 approaches can be used considering that these matrices are solid samples: first, the
449 sample can be put directly into the HS vial [69]; a second option involves the
450 homogenization of the sample with a liquid solution [70]. Any comparison could be
451 established between both procedures (with and without homogenization of the sample
452 with solvent) since performance characteristics were not provided in the method using
453 the raw sample.
454 MSPD was also evaluated for the determination of 6 PAHs in fish and seafood [71].
455 For clean-up purposes, an acid treatment with sulphuric acid impregnated silica gel was
456 evaluated thanks to its compatibility with MSPD. However, the compounds were
457 retained in the sorbent, although the lipidic removal was effective. The recovery rates
458 were adequate and the precision values were significantly low, which is remarkable
459 since one of the main drawbacks of MSPD is its moderately low

460 repeatability/reproducibility. As previously discussed, sulfuric acid can be used for the
461 removal of lipids.
462 Recently, Ramalhosa et al. [72] evaluated the so-called QuEChERS method
463 (acronymic name from quick, easy, cheap, effective, rugged and safe) in fish. This
464 method is a procedure extensively applied and originally developed for the analysis of
465 pesticide residues in food samples. The described approach results very appropriate for
466 the analysis of volatile PAHs, such as NPH, ACP or FLR, often lost during pre-
467 concentration stages, since it does not involve any evaporation step. Beside this, the
468 QuEChERS method is much easier than the typical procedures described for the
469 analysis of PAHs (e.g. Soxhlet, LLE, etc.), showing adequate performance
470 characteristics.
471 Smoked cheese is another fatty matrix of interest for the monitoring of PAHs,
472 although the number of related studies is very scarce. As in other fatty matrices, Soxhlet
473 plus GPC [73] and LLE-based methods [74], sometimes including saponification [75],
474 are described in literature. SPE has been applied for clean-up purposes using silica
475 sorbents. The recovery values for the revised references are adequate and lower than
476 100%. For the most volatile compounds, Suchanova et al. [73] remarked the poor
477 recoveries obtained (namely, NPH, ACP and FLR). This is a well-known fact that has
478 been confirmed in many other studies; however, these authors do not consider important
479 to improve the efforts in increasing the recovery rates for these PAHs since they are not
480 health concerns in terms of carcinogenicity.
481 More detailed information about extraction methods is shown in (Table 2).
482
483 *2.2.2. Non-fatty matrices*
484 Besides the matrices discussed before, PAHs have been monitored in a variety of solid
485 foodstuffs, i.e. tea leaves [76,77], vegetables [78-80], fruits [79], bread [80], cane sugar
486 [81], fatty food mixtures [27], ground coffee [82] and palm dates [63] (Table 2). The
487 methodologies applied are not different from those applied in the main food groups.
488 Soxhlet, LLE, PLE or USE have been utilized in the extraction step (involving in some
489 cases a saponification stage), whereas GPC or SPE have been applied in the clean-up
490 step. Borjadandi et al. [83] reported the analysis of PAHs in a great variety of food
491 samples, such as fish, seafood, meat products, vegetable oils, breads and pastries. For
492 this aim, a generic methodology based on Soxhlet extraction was applied, concluding

493 that this extraction technique is the most suitable for the determination of very different
494 food commodities with adequate performance.
495 More detailed information about extraction methods is shown in (Table 2).
496
497 **3. Chromatographic and detection techniques**
498 In general, the determination of PAHs is carried out by liquid chromatography coupled
499 to fluorescence (LC-FLD) or ultraviolet-visible detection (LC-UV), or gas
500 chromatography coupled to mass spectrometry (GC-MS) detection, techniques which
501 are discussed below.
502
503 ***3.1. Liquid chromatography coupled to UV and FLD***
504 In the past, the determination of PAHs by LC was carried out by using UV detection
505 [52,54]. However, it is well-known that UV detection shows a number of disadvantages,
506 such as selectivity problems and sensitivity limitations, and it cannot discriminate
507 matrix interferences, especially in complex matrices. On the contrary, FLD is more
508 selective and sensitive than UV detection, and it is currently the detection system of
509 choice in LC, normally with variable excitation and emission wavelengths. LC-FLD
510 has been extensively applied for the determination of PAHs in very different matrices,
511 including foodstuffs and beverages, since it is cheap and simple, in comparison to other
512 detection systems. Indeed, LC-FLD has been the basis of different official methods for
513 the analysis of PAHs in food [2,84] (Table 3).
514 In this sense, LC-FLD has been largely used for the determination of the EPA priority
515 list of PAHs [21,23,46,49,52,62,72]. It has been reported that ANT and perylene (PER)
516 are best measured by FLD due to their selective and sensitive fluorescence
517 characteristics [3]. BghiP cannot be properly determined due to its low fluorescence
518 sensitivity [3], and CPcdP does not give rise to fluorescence and can only be quantified
519 by UV detection [1]. Despite there is an improvement in comparison to UV detection,
520 FLD can still show a lack of selectivity, and then GC-MS is applied in order to confirm
521 the positive results [17,54,79,82].
522 Moreover, some authors describe certain selectivity problems due to the presence of
523 alkylated PAHs [16], which are considered the main impurities of PAH fractions. These
524 compounds show similar fluorescence responses to the unsubstituted PAHs. Another
525 disadvantage is the impossibility of using certain isotopically labeled compounds
526 because of FLD cannot distinguish these ones from the native PAHs. As an alternative,

527 benzo[*b*]chrysene or deuterated compounds, which can be chromatographically
528 separated, have been used [1].
529 In relation to sensitivity, the reported limits of detection (LODs) are frequently found
530 at the sub-ppb level (e.g. 0.01-1 μg L^{-1} or μg kg^{-1}), and in some applications in
531 beverages, LODs at the ppt level (e.g. 0.01-1 μg L^{-1} or μg kg^{-1}) have been achieved
532 [44,48,49]. This fact can be justified since in this type of samples, pre-concentration
533 techniques such as SPE or SBSE have been applied.
534 Despite the widespread use of columns with particle size ≤ 2 μm in trace analysis (i.e.
535 pesticide or veterinary drug residues analysis [85]), the utilization of ultra-high
536 performance liquid chromatography (UHPLC) has not been reported in PAH analysis,
537 up to our knowledge. The main advantages of UHPLC are well-known (e.g. reduction
538 of running time or narrower peaks than conventional LC) and its application has rapidly
539 increased. Thus, the coupling of UHPLC to FLD would provide an increase in
540 chromatographic resolution that could improve the discrimination of co-eluted
541 interferences, especially in complex matrices such as foodstuffs.
542 Although FLD is the most utilized detection system for the analysis of PAHs in food
543 and beverages by LC, MS has also been applied in other matrices such as environmental
544 matrices [86,87]. Due to their non-polar character, atmospheric-pressure chemical
545 ionization source (APCI) [86] and atmospheric-pressure photoionization (APPI) [87,
546 88] have been applied as ionization techniques. However, the application of LC-MS
547 using APCI or APPI as ionization modes for the determination of PAHs in food
548 commodities has not been described yet.
549 More detailed information about determination methods and conditions is shown in
550 (Table 3).
551

552 ***3.2. Gas chromatography coupled to MS***

553 GC-MS is the main alternative to LC-FLD and it is applied in all kind of food samples.
554 Besides, GC-MS-based methods are more frequently found in the more recent
555 bibliography [27,35,36,40,51,57,59,70,89,90]. As in the case of LC-FLD, there are
556 official methods for the analysis of PAHs by GC-MS, such as the EPA method 8100
557 regarding the analysis of PAHs by GC [3,91] (Table 3).
558 The utilization of GC-MS shows several advantages in comparison to LC-FLD,
559 mainly in their resolution capability. GC offers high chromatographic resolving power
560 and MS provides high mass selectivity and structural information. GC-MS permits the

561 determination of non-fluorescence PAHs, such as CPcdP, or PAHs showing poor
562 fluorescence, such as NPH, ACY, ACP and FLR [92].
563 For the separation stage, columns with a stationary phase based on 5 % phenyl-95 %
564 methylpolysiloxane substitution are widely applied in the revised literature (e.g. typical
565 HP-5 or HP-5ms). This type of column is also commonly utilized for the analysis of
566 other organic contaminants and residues at trace level. However, obtaining an adequate
567 resolution can become a critical point depending on the target PAHs since there are
568 several groups of compounds which can co-elute (Figure 4). This issue is particularly
569 important when these PAHs cannot be resolved mass spectrometrically by extracting
570 their corresponding traces (e.g. isomers). If the overlapped compounds show isobaric
571 ions, an accurate quantification is therefore difficult or impossible. Five groups of PAHs
572 present this type of resolution problems: (i) chrysene (CHR) and triphenylene; (ii)
573 CPcdP, BaA and CHR; (iii) benzo[*b*]fluoranthene (BbFA), benzo[*j*]fluoranthene (BjFA)
574 and benzo[*k*]fluoranthene BkFA; (iv) dibenzo[*a,c*]anthracene and DBahA; and (v)
575 DBahA and IP [3,90].
576 The determination of heavy PAHs, such as dibenzopyrenes, by using typical 5ms
577 columns is also problematic due to they show a strong interaction with the stationary
578 phase provoking broadening peak and sensitivity problems. Some dibenzopyrenes are
579 included in the EU-list (dibenzo[*a,e*]pyrene (DBaeP), dibenzo[*a,h*]pyrene (DBahP),
580 dibenzo[*a,i*]pyrene (DBaiP), dibenzo[*a,l*]pyrene (DBalP)) and consequently, adequate
581 analytical methods are needed for their monitoring. However, most of the revised
582 literature is focused on the EPA list, and thus, DBahA (278 amu) is the heaviest
583 compound which is normally determined, regardless the most heavy PAHs.
584 Although columns showing a more polar stationary phase have been pointed out as
585 adequate for the determination of dibenzopyrenes (302 amu), their application in food
586 analysis is not widespread [58]. In relation to this, Gómez-Ruiz et al. [90] evaluated
587 thoroughly the performance of different stationary phases (Figure 5) for the analysis of
588 the EU priority PAHs, including the typical 5%-phenyl columns and other more polar
589 columns, such as 50 % phenyl-50 % methylpolysiloxane columns (e.g. DB-17ms) and
590 a recently commercialized mid-polar to polar phase (Optima® δ-6) (Figure 5). The
591 utilization of a 50 % phenyl-50 % methylpolysiloxane column (mid-polar phase) solved
592 the resolution problems of three groups of co-eluted PAHs: DBahA-IP, BbFA-BjFA-
593 BkFA and CPcdP-BaA-CHR, whereas a tailor-made DB-17ms column (20 m) showed

594 the best results for the suitable determination of the four aforementioned
595 dibenzopyrenes, improving their peak shape and signal-to-noise (S/N) ratios.
596 Veyrand et al. [27] proposed the utilization of several mathematical formulae, which
597 are based on full scan spectra and relative abundances, in order to quantify separately
598 BaA and CDcdP. In relation to the quantification issue, Wolska et al. [93] described the
599 different problems when using isotope-labeled standards, as recovery standards, in PAH
600 analysis. In this study, this strategy permitted the improvement of the accuracy and
601 precision in the determinations.
602 A few applications utilize fast chromatography modes, such as shorter columns (e.g.
603 10 m x 0.1 mm) [57,58]; or comprehensive or multidimensional GC (GC x GC) [36]. In
604 this last modality, a first separation is performed with a non-polar column (e.g. 5%
605 phenyl polysilphenylene-siloxane, 30-m length, typical separation), and, then, a second
606 separation is carried out with a polar column (e.g. 50% phenyl polysilphenylene-
607 siloxane, 1-m length, separation based on polarity). The resolution power is increased
608 but the raw data and chromatograms are considerably complex and powerful software
609 tools are requested (Figure 6). Additionally, the use of columns with >30-m length has
610 been reported in specific applications in order to improve the resolution of certain
611 groups of isomers and some methyl derivatives [16].
612 In relation to the sample injection, the applied technique can be a key factor since
613 certain PAHs show very high boiling points ("heavy" PAHs). In literature, splitless
614 injection is preferred (e.g. [18,32,35]). Other techniques utilized are programmed-
615 temperature vaporization (PTV) (e.g. [32,82]), cold on-column injection, which is also
616 used since it improves peak shape in the early eluting PAHs (those with low molecular
617 mass) [3], and large-volume injection (LVI), which is rarely applied [27,49,51] despite
618 the fact that it can increase sensitivity. LVI and on-column injection have been
619 considered as a way of diminishing the discrimination of dibenzopyrenes [90]. In this
620 sense, the combination of PTV and LVI has been successfully applied for the analysis
621 of both light and heavy PAHs in environmental analysis [94], and more recently in food
622 [95]. In this study, the optimized PTV in solvent mode (combined with LVI) always
623 provided higher sensitivity than the PTV process used in splitless mode, and improved
624 S/N ratios for the more heavy PAHs (especially important for DBaeP, DBaiP and
625 DBahP).
626 It is well-known that MS has become the most popular detection system in trace
627 analysis due to its intrinsic characteristics such as selectivity, sensitivity, different

628 available monitoring modes, etc. In the determination of PAHs in food and beverages,
629 GC-MS can offer an improvement in selectivity in comparison to LC-FLD; besides,
630 identification and confirmation can be carried out in a single step. Indeed, the re-
631 injection of samples by GC-MS for confirmation purposes when using LC-FLD is often
632 reported (Table 3).

633 Most of the studies use single quadrupole analyzers (Q) working in the single ion
634 monitoring mode (SIM) (Table 3), whereas other analyzers such as ion trap (IT)
635 [18,32,60,61,63] and triple quadrupole (QqQ) [33,89] are rarely used. For these
636 instruments, selected-ion storage or product ion scan mode (for IT), and selected-
637 reaction monitoring (for QqQ) are normally applied. High-resolution mass spectrometry
638 (HRMS) analyzers (e.g. time-of-flight [35,36,89], magnetic sectors [56-58]) have been
639 also used (Figure 6), but because of its high cost, its application is not common.

640 The application of tandem MS and other advanced analyzers would provide an
641 increase in selectivity. However, the use of single-stage MS and Q analyzers is
642 widespread, which could be explained as a consequence of the highly stable structure of
643 PAHs. Despite the use of a high-energy ionization mode, such as electronic ionization
644 (EI), the number of fragments produced is extremely low, mainly the $[M-H]^+$ or $[M-$
645 $2H]^+$ [27]. These ions are at the same time very stable and complicated to fragment by
646 MS/MS, providing product ions with a few *m/z* units less than the precursor ion.
647 Besides, the application of higher energy values does not change this pattern
648 significantly (e.g. 150 eV).

649 Finally, in relation to sensitivity, the majority of LODs reported are at the (sub)-/ppb
650 level (Table 3). Significant differences between the performance of Q and other
651 analyzers have not been found. The studies using Q or QqQ and IT analyzers reported
652 LODs (and LOQs when determined) at the sub-ppb level (e.g. [27,32,89]). It must be
653 noticed that similar results for lower limits have also been found when using LC-FLD
654 and GC-MS(/MS). However, the comparison between the LOQs obtained by GC-
655 MS(/MS) and LC-FLD was not possible due to the lack of reported LOQs in many of
656 the revised references.

657 More detailed information about determination methods and conditions is shown in
658 (Table 3).

659

660 **4. Determination of PAHs in real samples**

661 A summary of the reported concentrations of PAHs found in real food and beverage
662 samples is shown in Table 4.
663 A comparison between refined and unrefined oil showed that the levels of BaP in
664 most of refined oils were < 1.5 µg kg^{-1}, while for oil of unrefined or oils used for frying,
665 BaP concentrations were found to be > 2.0 µg kg^{-1} (above the maximum permitted level
666 in the Spanish legislation) [24]. In fried oil, BaP levels were higher than in fresh oil
667 because of the high temperatures applied. Besides, the use of activated carbon in the
668 refinement process, which produces an efficient removal of BaP, explained the lower
669 levels of this compound found in refined oil.
670 Another comprehensive study (296 samples) [30] revealed that 66.4% of the analyzed
671 edible oil samples exceeded the German Society of Fat Sciences limit (25 µg kg^{-1}).
672 Olive oil showed the maximum concentration (265 µg kg^{-1}) of heavy PAHs, whereas
673 rice brand oil showed the minimum values (4.6 µg kg^{-1}). Phenanthrene (PHE) and ANT
674 were found in more than half of the samples (58.3% and 53%, respectively), whereas
675 BaP was found only in 25.5% of them. One of its isomers, benzo[*e*]pyrene, which is not
676 normally monitored, was found in 31.2% of the studied oils. In total, 88.5% of samples
677 showed PAH contamination, and only 11.5% of them were devoid of any PAH.
678 Olive pomace oil has also been under study and a high number of PAHs (both light
679 and heavy) have been found in most of the analyzed samples [22]. Besides, it is
680 important to point out that alkyl derivatives, which are rarely determined, were also
681 found and, in many cases, at higher concentrations than the original PAHs. The high
682 PAH concentration determined in refined olive and olive pomace oil in comparison to
683 virgin olive oil was explained as a consequence of the refining process, which can
684 partially remove these contaminants [32].
685 Another study focused on the analysis of a variety of edible oils reported that CHR
686 was the most abundant PAH. This result can be related to the high concentrations of 5-
687 methylchrisene reported by the aforementioned study [22]. In relation to olive pomace
688 oil, the authors remarked that the amount of BaP increased from 0.5 µg kg^{-1} in olive
689 pomace oil samples to 16.1 µg kg^{-1} in dried oil. Thus, drying stages in the presence of
690 combustion gases can increase PAH contamination [36].
691 The concentrations of PAHs found in milk samples are, in general, lower than those
692 reported in edible oils (< 20 µg kg^{-1}) [37,39,40], which can be due to the different food
693 processes that are applied in each commodity (Table 4).

694 Grova et al. [37] described the monitoring of milk samples obtained under different
695 possible sources of contamination, such as cement factories or motorways (Figure 7).
696 Not surprisingly, milk from farms nearby these sources showed maximum
697 concentrations higher than the concentrations determined in milk from control farms.
698 PAHs with more than four aromatic cycles were not detected and BaP (considered as
699 marker of exposure) was not detected either.
700 The monitoring of PAHs in infant formula revealed higher PAH concentrations than
701 in commercial and human milk [39]. This important result was explained as a
702 consequence of drying processes which can provoke the formation of PAHs.
703 Since the manufacturing process in coffee industry also includes roasting stages,
704 coffee samples have been also analyzed in several studies. The results reported by
705 García Falcón et al. [42] showed that PAHs were not found in instant coffee samples
706 but in highly roasted coffee without caffeine. In these samples, BbF, BkF and BaP were
707 found at very low levels: 0.03-0.1 μg kg^{-1} for BbF and 0.01-0.04 μg kg^{-1} for BkF and
708 BaP. Houessou et al. found significant differences in the PAH content of lots of coffee
709 from the same origin [44]. These results were potentially attributed to variations in the
710 roasting conditions, and the need for systematic analysis of coffee brews was pointed
711 out. Lai et al. [47] also observed variations in the BaP concentration found in different
712 coffee samples due to the same roasting process. However, Houessou et al. [82]
713 determined in another study that PHE and PYR were mainly found regardless the coffee
714 lot considered. The absence of the highly toxic DBahA in the analyzed samples was
715 also remarked.
716 In mate infusions, BaP was found in the majority of samples showing concentrations
717 5-11.2 times higher than the maximum limit allowed by the European guidelines (0.01
718 μg L^{-1}) [50].
719 The determination of PAHs in tea leaves demonstrated that the PAH content in the
720 crude black tea and black tea were much higher than the levels found in tea leaves not
721 submitted to the drying stage, which is one of the manufacturing processes in black tea
722 industry [76].
723 The monitoring of PAHs in spirits revealed that BaA and BbFA were detected in 96%
724 of the analyzed cachaça samples and only one sample did not contain any of the 5 target
725 PAHs [43]. Different PAH profiles were found in different types of this spirit: BaP
726 showed higher concentrations when burned sugar cane was used in the production,
727 although always below the limit established by the EU for food products (2 μg L^{-1}) [46].

728 Meat samples have been extensively monitored for PAHs, especially those meat
729 products based on smoked meat. The concentrations found in these products are quite
730 lower than the concentrations found in other important food matrices, such as edible
731 oils. Mottier et al. [17] described that the levels of carcinogenic PAHs were below the
732 LOQ in almost all samples (Figure 8) and the compounds listed as carcinogenic by the
733 IARC (BaA, BbFA, BkFA, BaP, IP and DBahA were not the major PAHs present in the
734 samples). Beside this, samples containing higher fat content showed a higher PAH total
735 content, which was in accordance with previous studies describing the ratio between
736 PAH formation (during grilling) and fat content.
737 The smoking technology utilized in the production of smoked products was also found
738 a key factor in the PAH content of the final foodstuff [57]. In a similar study [58], BcF
739 showed the highest concentration in all types of samples. Besides, the total PAH content
740 increased during the different smoking steps.
741 In general, PAH content in fish (Figure 9) and seafood samples are considerably
742 higher than those found in meat and similar to the levels determined in edible oils
743 (Table 4). The use of BaP as a marker of the total PAH content was again discussed
744 since it was not detected in the analysis of 27 fish samples when other PAHs were
745 found [72]. This fact was also confirmed in another study [65] focused on the analysis
746 of fish and seafood. Despite several PAHs were found in all samples (ANT,
747 fluoranthene (FA), PYR, BaA, CHR, BbFA and BkFA), BaP was only detected in
748 Mediterranean mussels. In this kind of samples, a seasonal variation was found: 72% of
749 mussels collected in winter exceeded the EU MRL set for BaP, whereas the values
750 shown by mussels collected in summer were below this limit. Moreover, comparing the
751 PAH levels of the different organisms evaluated, mussels showed the maximum
752 amounts.
753 The evaluation of the PAH profiles in food from marine origin revealed that PYR was
754 the major PAH, representing more than 80% of the total content in all samples, except
755 in prawns, where NPH showed the maximum contribution (49%) [83]. Other compound
756 often found was PHE, which is one of the main components of crude oil. In this sense,
757 the authors remarked that profiles showing high percentages of light PAHs are typical
758 of oil-polluted areas and intense oil activity.
759 A thorough study of the levels of BaP in cheese (96 samples) demonstrated that the
760 concentrations in cheese smoked with straw and cardboard were statistically higher than
761 the concentrations found in samples smoked and aromatized with wood shavings and

762 SFPs [75]. However, samples treated with SFPs showed BaP concentrations exceeding
763 the limits set by the EU. BaP levels were dependent on the smoking process
764 (temperature, time, etc.), which was also observed in other smoked products. In another
765 study [73], the PAH content found in home-made smoked cheese was up to ten timer
766 higher than in cheese smoked under industrial conditions (Figure 10). This trend was
767 also observed for BaP. Besides, significant differences were observed in the PAH
768 content when comparing the cheese surface and internal parts of the product.
769 The analysis of cane sugar showed PAH contamination in 57% of the samples; BaA
770 was found in 51% of the samples [81]. The obtained results suggested that the PAH
771 content relied on the amount of burnt sugar cane utilized (if so), and in the number of
772 steps involving the refining process. Furthermore, PAHs were also detected in 33% of
773 the organic samples analyzed. The deposition of airborne particles containing PAHs on
774 the plant surface was proposed as a possible explanation, probably because of the
775 environmental pollution.
776 Danyi et al. [96] determined that 50% of the food dietary samples submitted to
777 analysis showed PAH concentrations above the limit established by the EU (2 μg kg^{-1})
778 for one to seven PAHs. In general, light PAHs were mostly found and several genotoxic
779 PAHs were found at relatively high concentrations in certain food supplements from
780 plant origin.
781 The study carried out by Rojo-Camargo et al. [79], which was focused on the analysis
782 of a variety of vegetable and fruit samples, showed that BaA was detected in 89% of the
783 samples. Vegetables, which are rarely monitored, also showed PAH contamination at
784 levels higher than those found in fruits (4.38–17.93 μg kg^{-1}, and 3.77–4.05 μg kg^{-1},
785 respectively). Lettuce and grape were the matrixes showing higher PAH total content.
786 Moreover, vegetable samples collected close to road traffic revealed higher PAH levels
787 than in samples grown in rural areas. It is important to notice that organic samples also
788 shown PAH contamination, probably due to the exposure to environmental pollution, as
789 aforementioned in sugar cane samples.
790
791 **5. Conclusions**
792 The determination of PAHs in foodstuffs and beverages has focused attention for a
793 long time, as it is demonstrated by existing publications in the early 90's. However, a
794 high percentage of this literature has been devoted to the analysis of the PAHs included
795 in the well-known EPA list, and especially BaP. It seems necessary to increase and

796 improve the available information and data about the occurrence of other PAHs, such as
797 those included in the EU list (e.g. dibenzopyrenes) or transformation products (e.g.
798 alkyl derivatives or hydroxi-PAHs), in order to achieve a better knowledge about PAHs
799 levels in foodstuffs. On the other hand, the revised literature shows that edible oils and
800 animal products are the most analyzed matrices for PAHs, which was expected as many
801 of the current legislation is established for them. Additional data about the levels of
802 PAHs found in other food matrices, such as vegetables or livestock, which can be
803 exposed to PAH contamination when roads or traffic are nearby, could be of interest.
804 In relation to the extraction techniques, conventional techniques such as Soxhlet (solid
805 matrices), LLE and SPE (liquid matrices) are still widely used, although the application
806 of less-solvent-consuming techniques, such as MSPD, and micro-extraction techniques,
807 such as LPME, has been recently reported. The performance of clean-up stages is also
808 requested for most of applications, but the utilization of techniques such as SPME or
809 HS-SPME has permitted the reduction of the pre-treatment stage.
810 With respect to separation and detection issues, LC-FLD and GC-MS(/MS) are the
811 outstanding techniques, although any of them is particularly preferred. The revised
812 literature shows the utilization of both techniques without regarding the type of sample
813 or extraction methodology. Nevertheless, it must be noticed that GC-MS(/MS)
814 instruments have been used in the most recent studies. This trend is contrary to the so-
815 called GC-to-LC movement observed in the analysis of other organic compounds at
816 trace levels (e.g. veterinary drugs). This fact can be justified due to the need for a more
817 accurate confirmation of the identity of the compound, which is not possible only with
818 determinations by LC-FLD. Besides, the lack of native fluorescence of certain PAHs
819 does not permit the monitoring of such compounds, which is an obvious drawback in
820 comparison to GC-MS(/MS).
821
822 **6. Trends**
823 Bearing in mind the aforementioned considerations and conclusions and the current
824 challenges, more research and efforts should be focused on the specific issues such as:
825 • A more thorough evaluation of recent API sources for LC instruments, such as
826 APPI, which are designed for more non-polar compounds, in order to establish
827 their possible utilization for the determination of PAHs in LC-MS systems. The
828 comparison of these instruments with conventional LC-FLD would be also of
829 interest since simultaneous identification and confirmation would be possible.

830 • The feasibility of the APPI sources for the determination of PAHs, but
831 especially compounds not included in the EPA list (e.g. heavy PAHs such as
832 dibenzopyrenes) should be evaluated.
833 • UHPLC instruments, which are widely applied for the analysis of other organic
834 compounds at trace levels, have not been used for PAH analysis yet. The
835 increase in resolution provided by these systems may also allow an increase in
836 selectivity, especially in very complex matrices and when using FLD as
837 detection technique. Besides, the study of the suitability of UHPLC coupled to
838 MS and the aforementioned ionization sources in this field would be also
839 desirable.
840 • More data about the utilization of specific columns for PAH analysis in food
841 should be generated. Although the typical 5%-phenyl columns are widely used,
842 the separation of certain groups is not achievable and heavy PAHs, such as
843 dibenzopyrenes, do not show adequate peak shape and/or sensitivity. These
844 problems can be overcome employing other stationary phases, but their use is
845 very scarce.
846 • Extra efforts should be made in order to improve the data about PAH
847 concentrations in food products exposed to possible contamination, such as
848 agricultural areas near to road traffic.
849 • Data about PAHs out of the EPA and UE lists should be increased in order to
850 propose new maximum concentrations as well as extended lists of priority
851 PAHs.
852
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1028 **Figure Captions**
1029
1030 **Fig. 1**.
1031 Example of a scheme of a methodology employed for the extraction of PAHs in olive
1032 pomace oil samples, an example of fatty matrix. Reprinted from [22] copyright 2004,
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1034
1035 **Fig. 2.**
1036 HPLC–FLD chromatogram obtained by SBSE from Mate tea spiked with 500 ng L^{-1}
1037 (extraction time: 240 min). Peak identities are: (1) naphthalene (NPH); (2) acenaphthene
1038 (ACP); (3) fluorene (FLR); (4) phenanthrene (PHE); (5) anthracene (ANT); (6)
1039 fluoranthene (FA); (7) pyrene (PYR); (8) benzo[*a*]anthracene (BaA); (9) chrysene
1040 (CHR); (10) benzo[*b*]fluoranthene (BbFA); (11) benzo[*k*]fluoranthene (BkFA); (12)
1041 benzo[*a*]pyrene (BaP); (13) dibenzo[*a,h*]anthracene (DBahA); (14) benzo[*g,h,i*]perylene
1042 (BghiP) and (15) indeno[1,2,3-*c,d*]pyrene (IP). Reprinted from [49] copyright 2005,
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1045 **Fig. 3.**
1046 Scheme of the use of SPME-DED in model systems of gelatine for the determination of
1047 the 16-EPA PAHs in smoked meat by GC-MS. The diffusion process of the analytes
1048 from the matrix to the headspace of the DED and the equilibriums implied in the
1049 process are shown. Reprinted from [59] copyright 2007, with permission from Elsevier.
1050
1051 **Fig. 4.**
1052 GC-MS chromatogram of the 15 + 1 EU PAHs on a DB-17MS column 20 m length,
1053 0.18 mm i.d. and 0.14 μm film thickness. Peak identities are: (1) benzo[*c*]fluorene
1054 (BbF); (2) benzo[*a*]anthracene (BaA); (3) cyclopenta[*c,d*]pyrene (CPcdP); (4) d12-
1055 chrysene (d12-CHR); (5) chrysene (CHR); (6) 5-methylchrysene (MCH); (7) 9-
1056 fluorobenzo[*k*]fluoranthene (FBkF); (8) benzo[*b*]fluoranthene (BbF); (9)
1057 benzo[*k*]fluoranthene (BkF); (10) benzo[*j*]fluoranthene (BjF); (11) d12-benzo[*a*]pyrene
1058 (d12-BaP); (12) benzo[*a*]pyrene (BaP); (13) indeno[1,2,3-*c,d*]pyrene (IP); (14)
1059 dibenzo[*a,h*]anthracene (DBahA); (15) d12-benzo[*g,h,i*]perylene (d12-BghiP); (16)
1060 benzo[*g,h,i*]perylene (BghiP); (17) dibenzo[*a,l*]pyrene (DBalP); (18) d12-coronene
1061 (d12-COR); (19) dibenzo[*a,e*]pyrene (DBaeP); (20) dibenzo[*a,i*]pyrene (DBaiP) and
1062 (21) dibenzo[*a,h*]pyrene (DBahP). Reprinted from [90] copyright 2009, with permission
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1064
1065 **Fig. 5.**
1066 Chromatographic separation of critical pairs/triplets by GC-MS obtained on three
1067 different stationary phases: (a) DB-17MS column, 60 m length, 0.25 mm i.d., 0.25 μm
1068 film thickness; (b) DB-5MS column, 60 m length, 0.25 mm i.d., 0.25 μm; (c) Optima®
1069 δ-6 column, 30 m length, 0.25 mm i.d., 0.25 μm. Reprinted from [90] copyright 2009,
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1071
1072 **Fig. 6**.
1073 Example of SPME-GC x GC-TOF-MS analysis showing a contour plot of a vegetable
1074 oil sample spiked with a PAHs solution (others groups of compounds are also shown).
1075 Abbreviations: BaA: benzo[*a*]anthracene; BbF: benzo[*b*]fluoranthene; BghiP:
1076 benzo[*g,h,i*]perylene; BjF: benzo[*j*]fluoranthene; BkF: benzo[*k*]fluoranthene; BcF:
1077 benzo[c]fluorene; BaP: benzo[*a*]pyrene; CCP: cyclopenta[*c,d*]pyrene; Ch: chrysene;

1078 DBahA: dibenzo[*a,h*]anthracene; IP: indeno[1,2,3-*c,d*]pyrene; 5MeCh: 5-
1079 methylchrysene; DBaeP: dibenzo[*a,e*]pyrene; DBahP: dibenzo[*a,h*]pyrene; DBaiP:
1080 dibenzo[*a,i*]pyrene; DBalP: dibenzo[*a,l*]pyrene. Reprinted from [36] copyright 2007,
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1082
1083 **Fig. 7**.
1084 Concentration of PAHs in milk samples collected close to various potential
1085 contamination sources. Abbreviations: NA: naphthalene; ACEY: acenaphthylene;
1086 ACEA: acenaphthene; FLUO: fluorene; ANT: anthracene; FLUT: fluoranthene; PYR:
1087 pyrene; B[a]A: benzo[*a*]anthracene. Reprinted from [37] copyright 2002, with
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1089
1090 **Fig. 8**.
1091 GC-MS/MS chromatogram of a meat sausage sample containing endogenous PAHs and
1092 internal standards (1 µg kg^{-1}). Peak identities are: (1) naphthalene; (2) acenaphthylene;
1093 (3) acenaphthene; (4) fluorene; (5) phenanthrene; (6) anthracene; (7) fluoranthene; (8)
1094 pyrene; (9) benzo[*a*]anthracene; (10) chrysene; (11) benzo[*b*]fluoranthene; (12)
1095 benzo[*k*]fluoranthene; (13) benzo[*a*]pyrene; (14) indeno[1,2,3-*c,d*]pyrene; (15)
1096 dibenzo[*a,h*]anthracene; (16) benzo[*g,h,i*] perylene. Reprinted from [17] copyright
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1098
1099 **Fig. 9**.
1100 GC-MS/MS chromatograms in the selected-reaction monitoring (SRM) mode of
1101 different fish samples: (a) non-spiked sample; (b) spiked sample (1.25 µg kg^{-1} for
1102 naphthalene and 0.125 µg kg^{-1} for dibenzo[*a,h*]anthracene); and (c) matrix-matched
1103 standard (10 ng mL^{-1}, equivalent to 1.25 µg kg^{-1} for naphthalene; and 1 ng mL^{-1},
1104 equivalent to 0.125 µg kg^{-1} for dibenzo[*a,h*]anthracene). Reprinted from [89] copyright
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1106
1107 **Fig. 10**.
1108 HPLC-FLD chromatogram of a real smoked cheese sample with PAH concentrations in
1109 the range 0.03 to 60 µg kg^{-1}. Abbreviations: Naph: naphthalene; Ace: acenaphthene;
1110 Fln: fluorene; Phe: phenanthrene; Ant: anthracene; Flt: fluoranthene; Pyr: pyrene;
1111 B[a]A: benzo[*a*]anthracene; Chr: chrysene; B[b]F: benzo[*b*]fluoranthene; B[k]F:
1112 benzo[*k*]fluoranthene; B[a]P: benzo[*a*]pyrene; DB[ah]A: dibenzo[*a,h*]anthracene;
1113 B[ghi]P: benzo[*g,h,i*]perylene; I[1,2,3-cd]P: indeno[1,2,3-*c,d*]pyrene. Reprinted from
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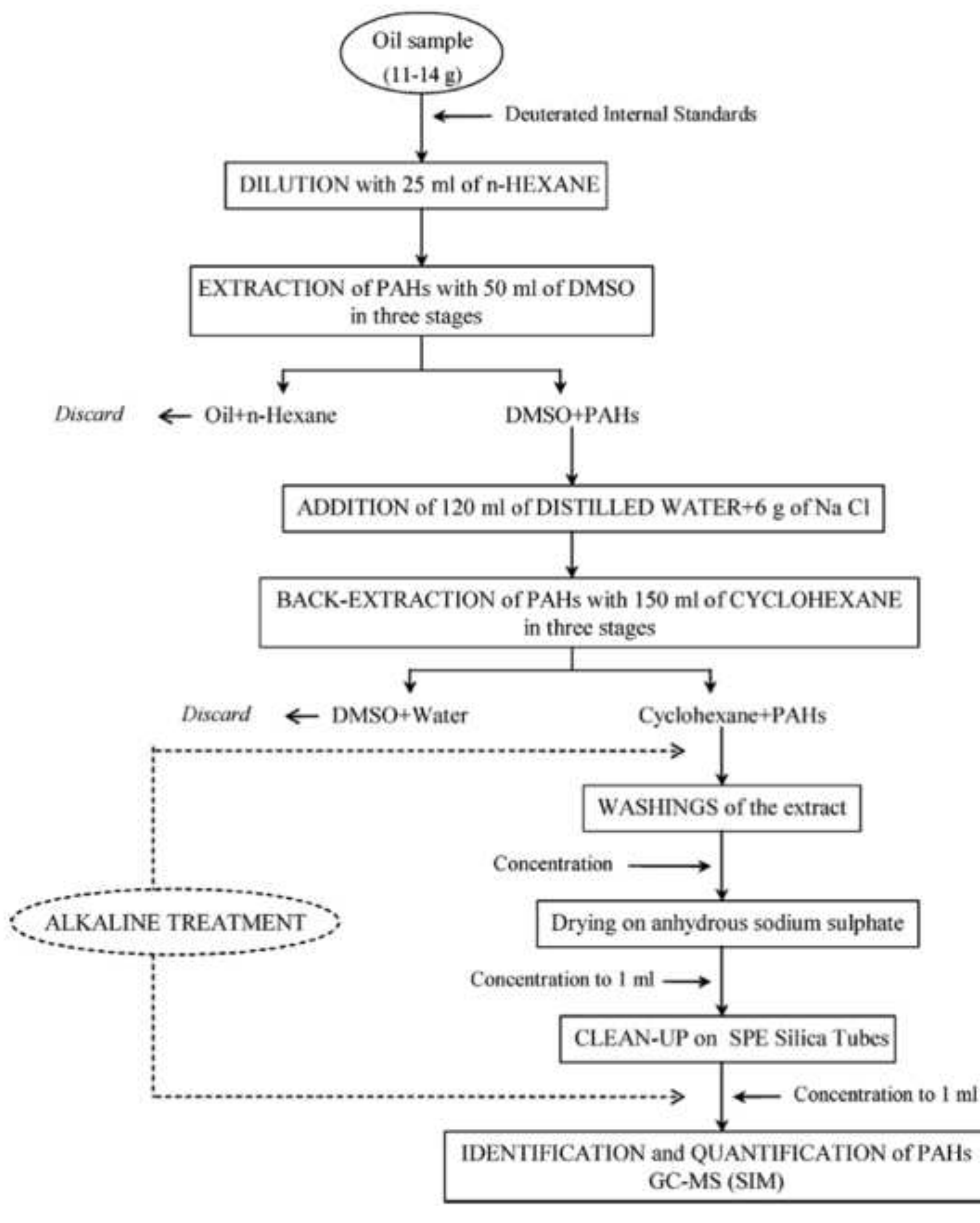

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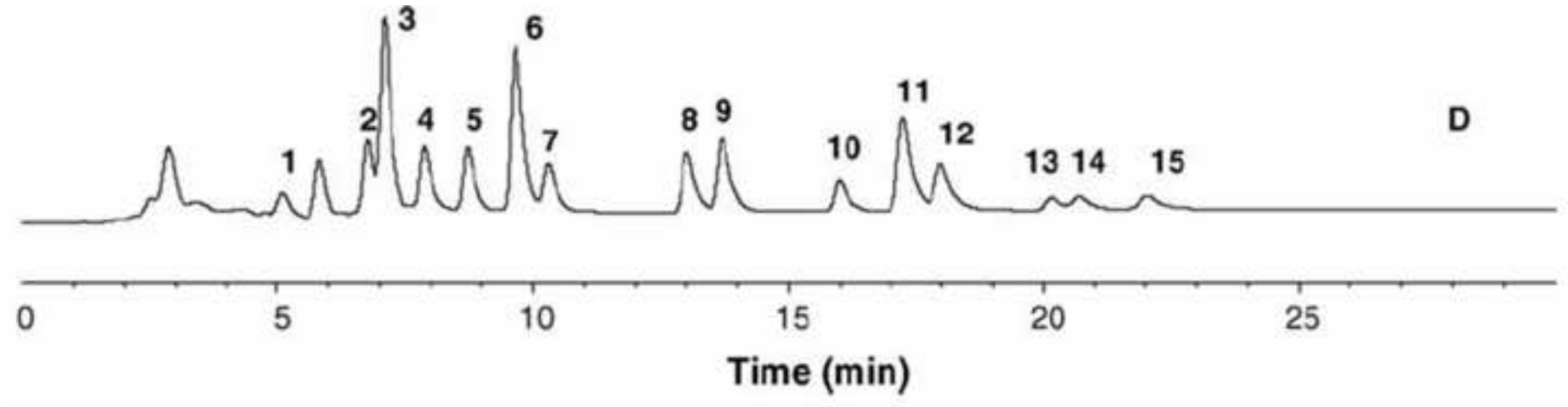

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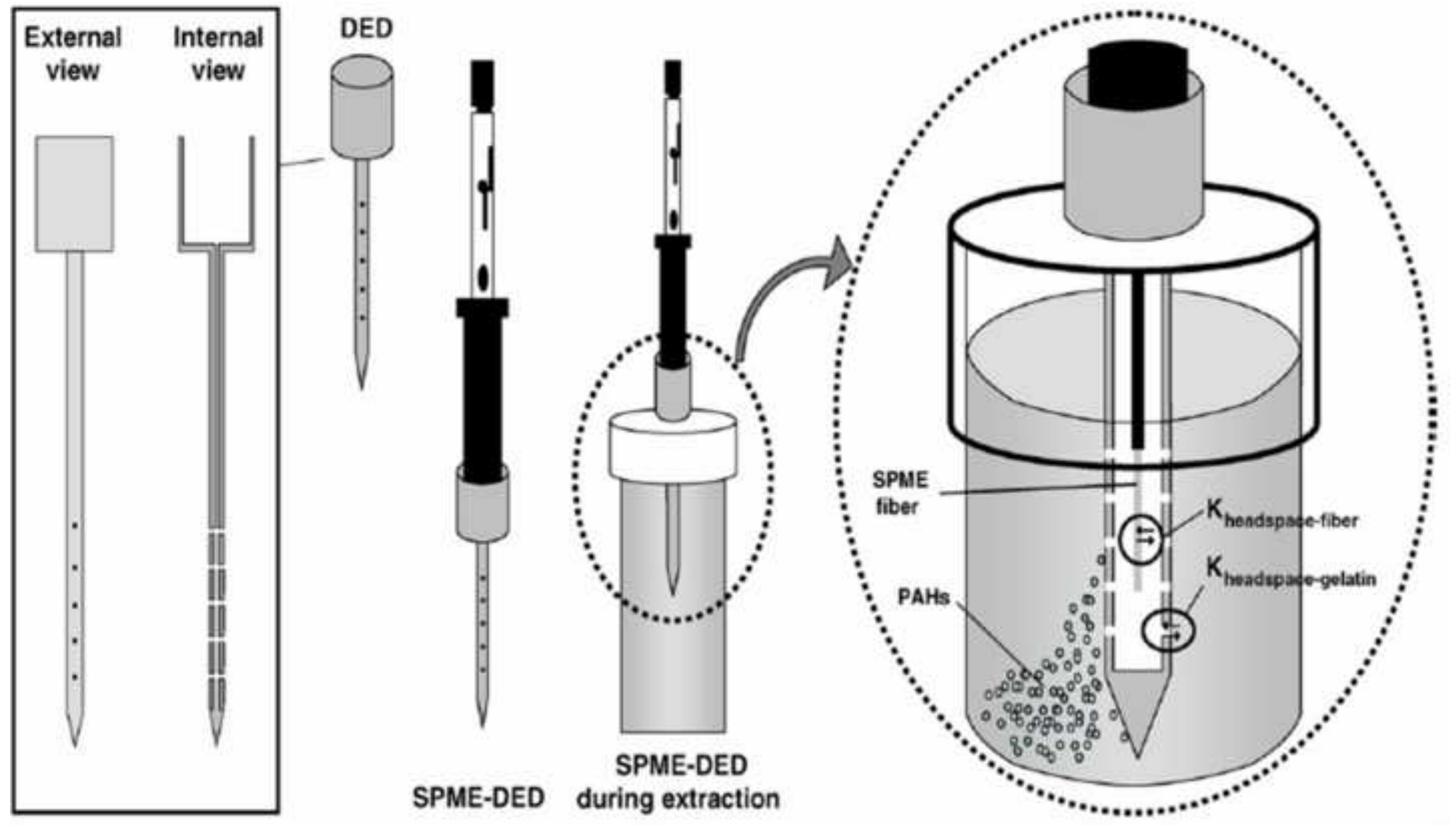

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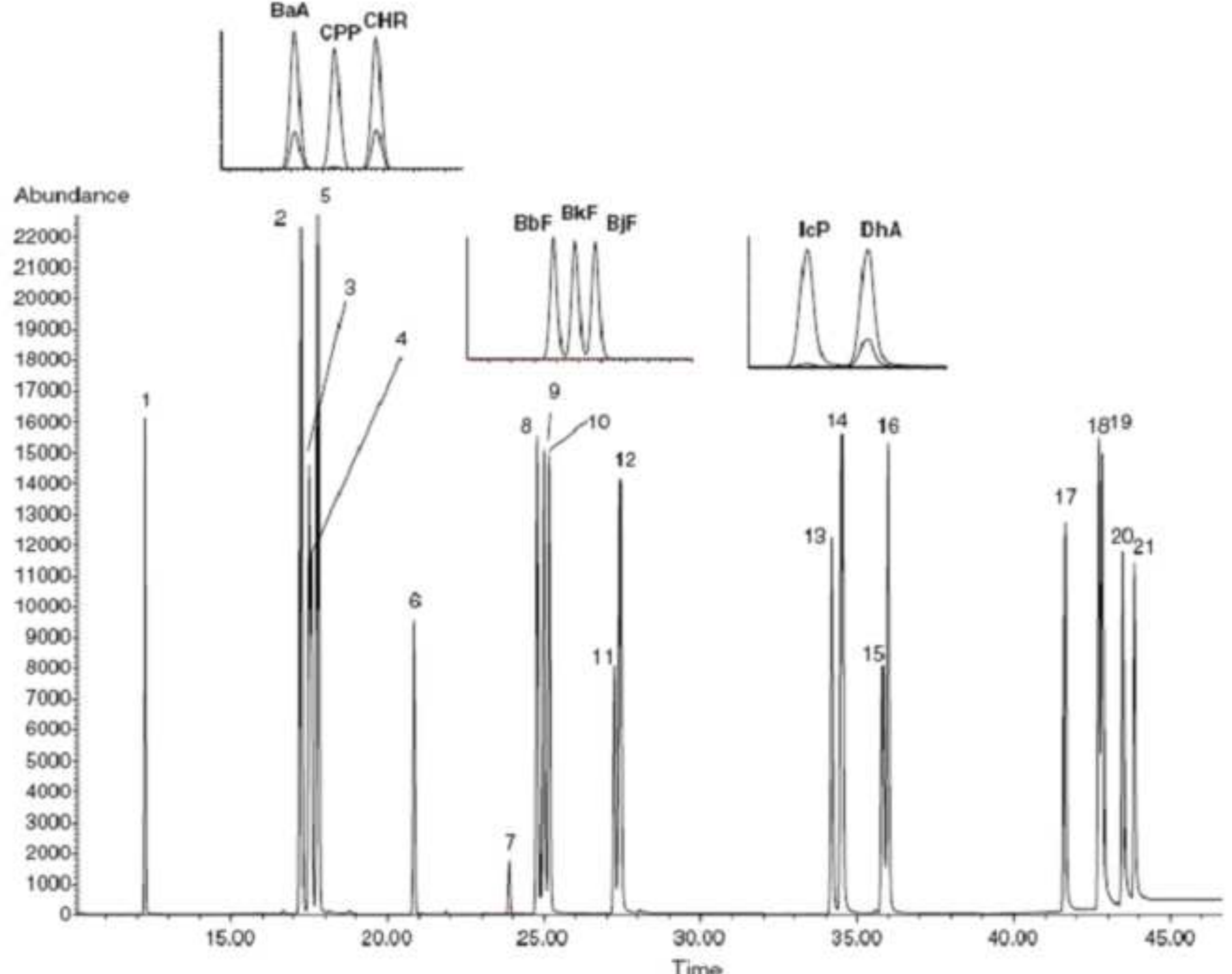

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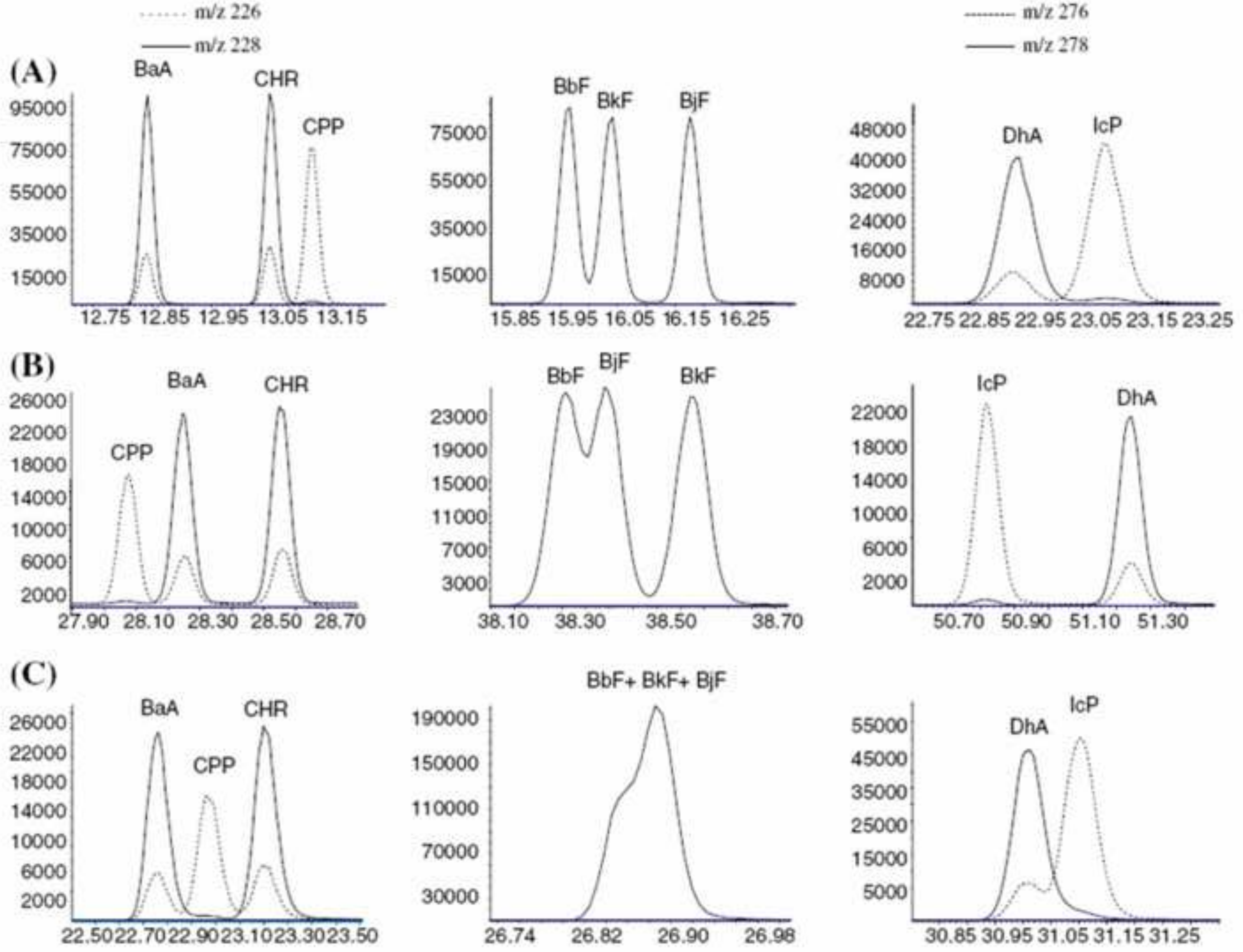

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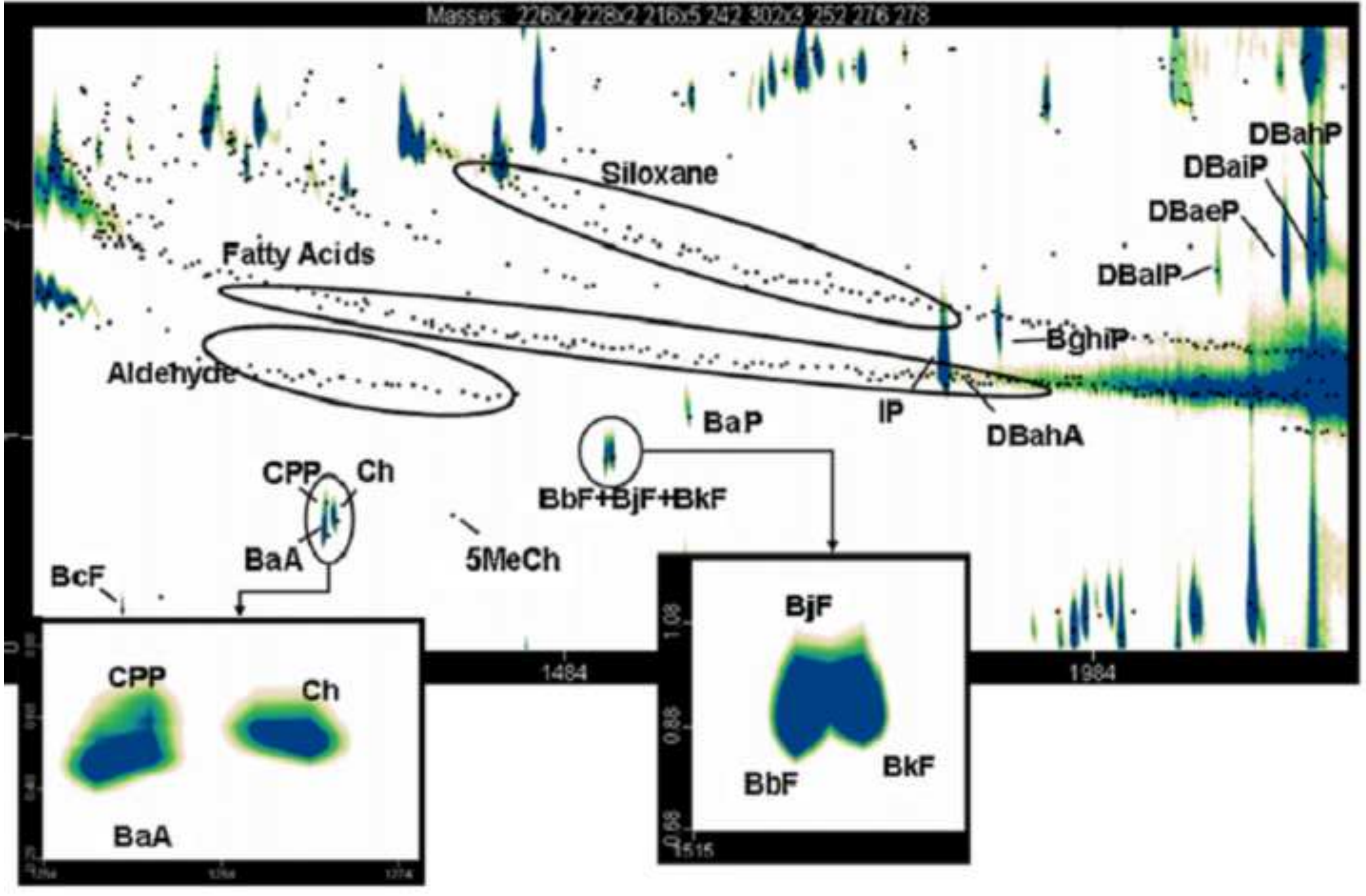

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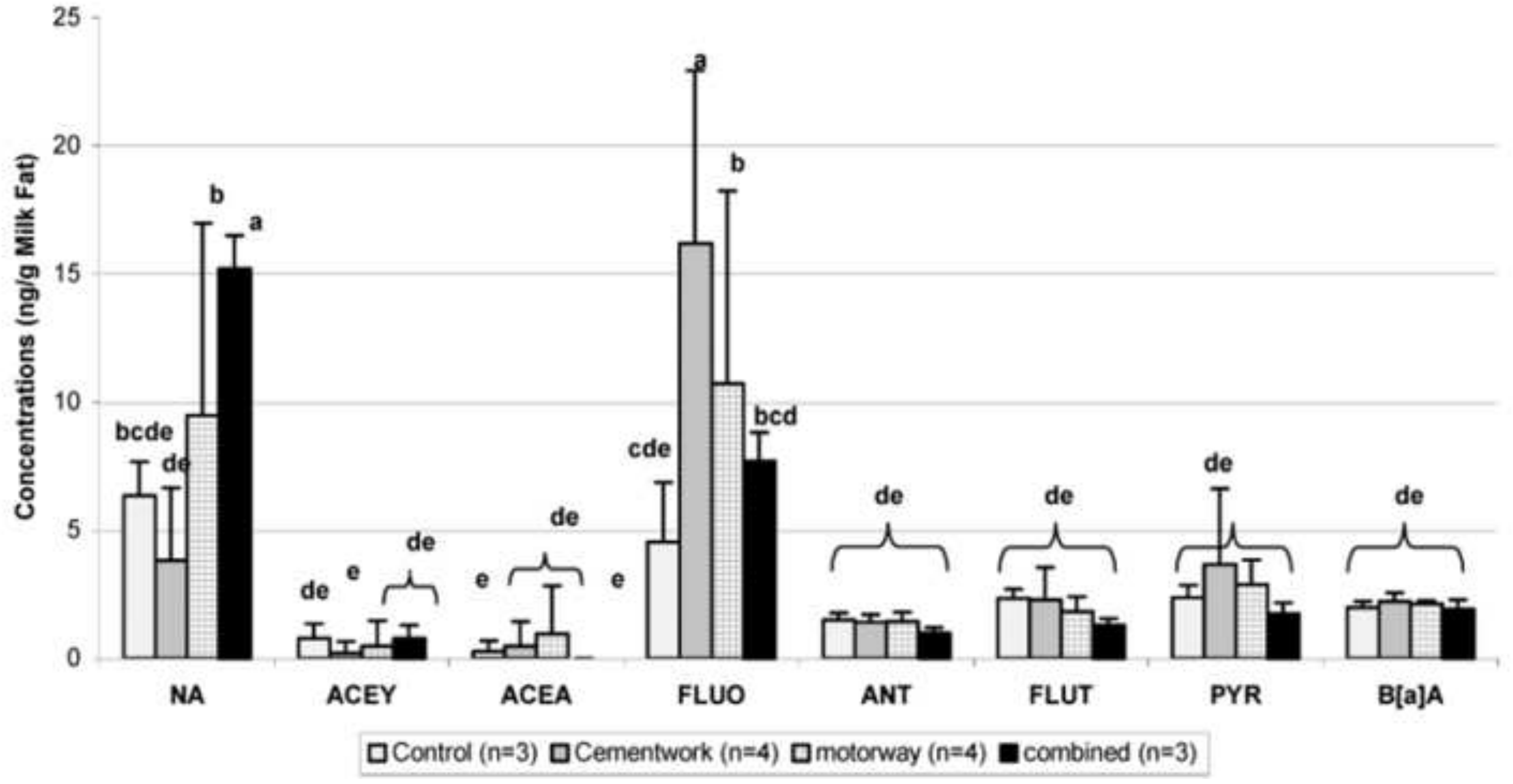

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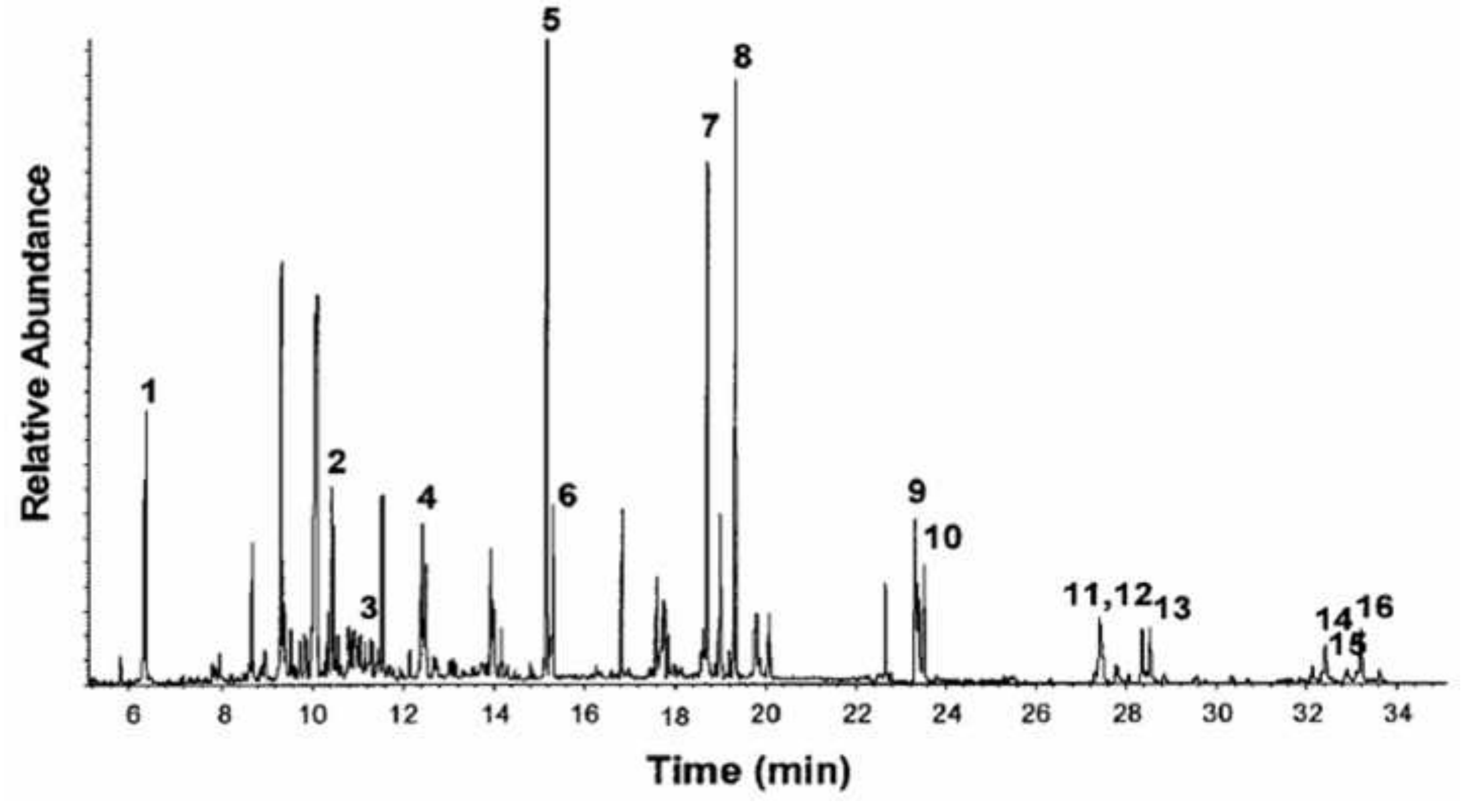

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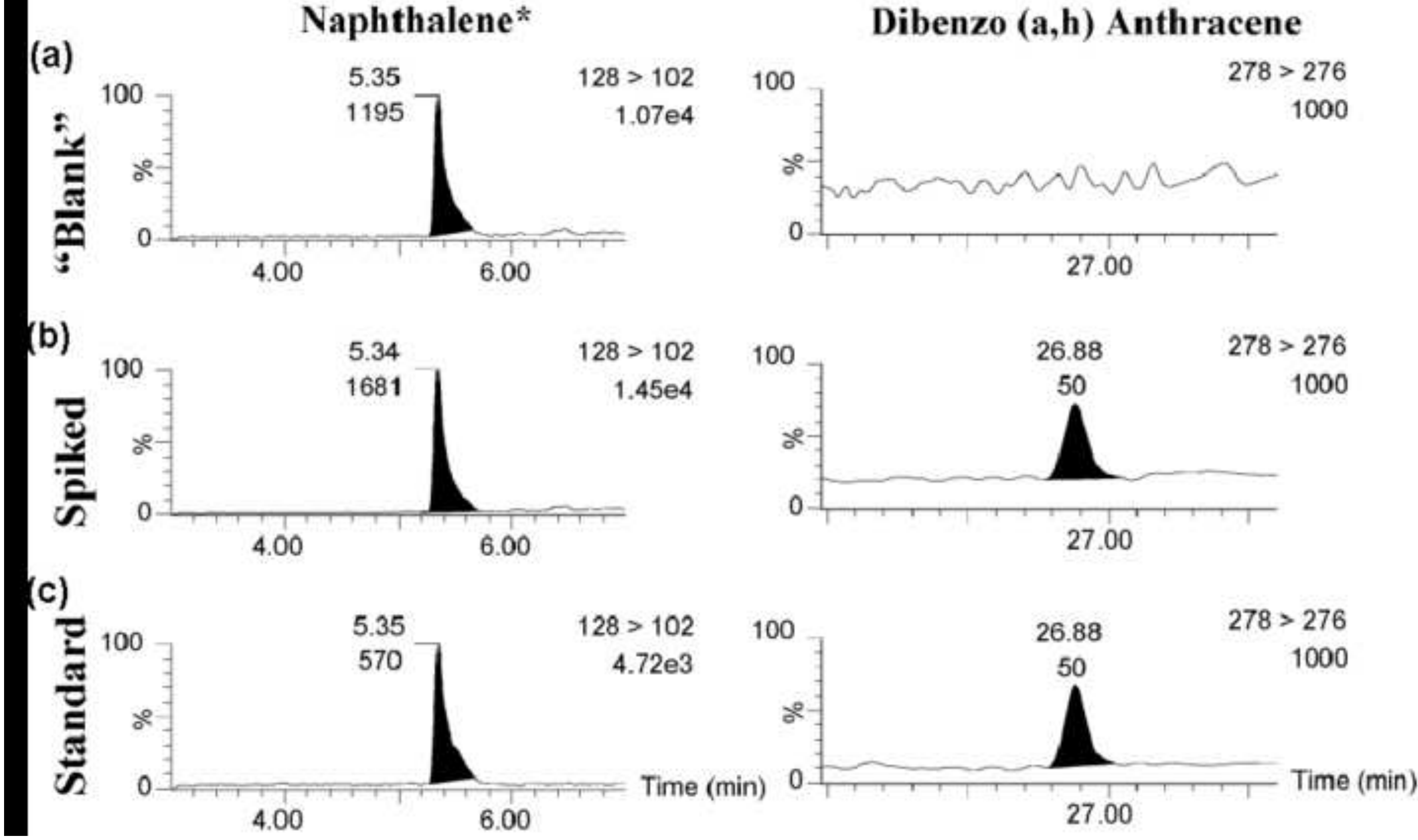

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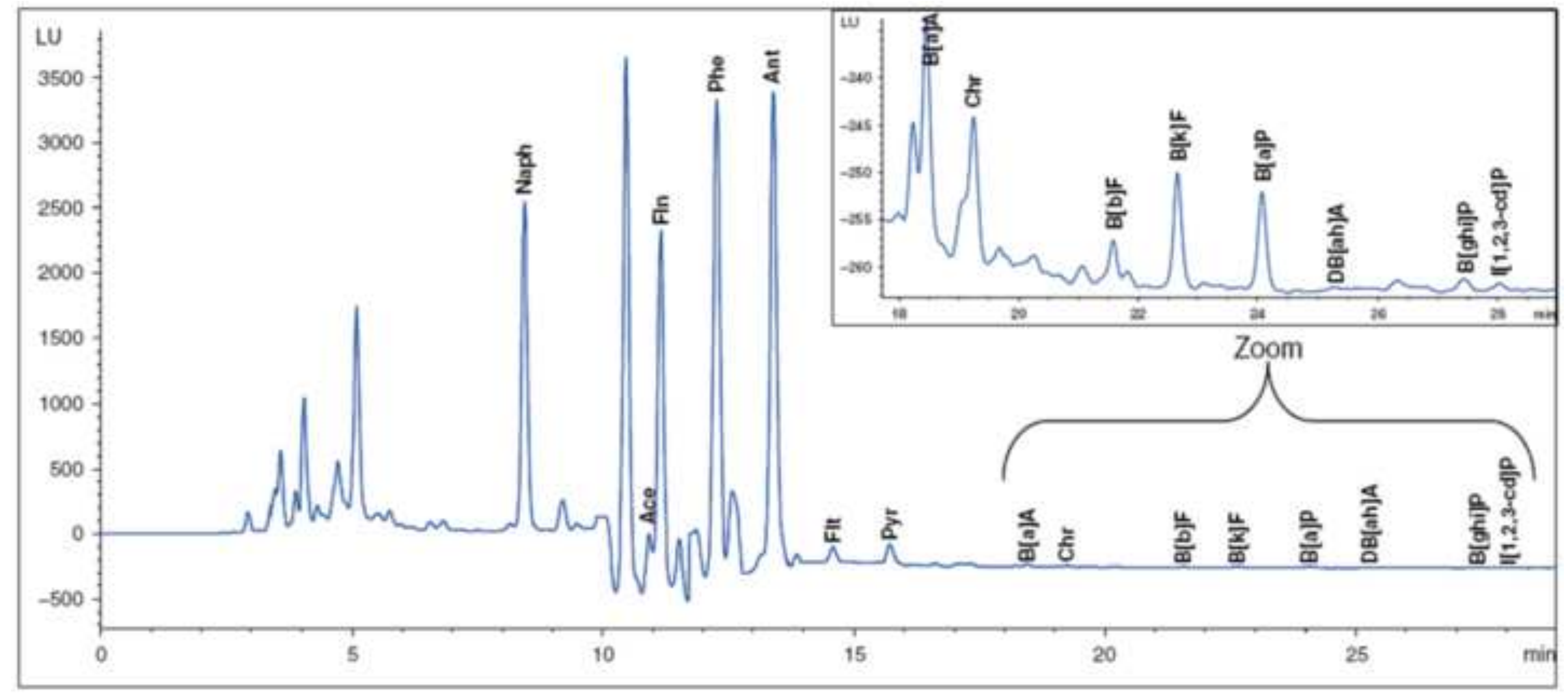

Table 1.
Summary of the most important PAHs analyzed in food

Compound	Abbreviation	Structure	Molecular weight (amu)	Boiling point (ºC)	CAS No
Acenaphthene[a]	ACP		154	279	83-32-9
Acenaphthylene[a]	ACY		152	280	208-96-8
Anthracene[a]	ANT		178	340	120-12-7
Benz[*a*]anthracene[a,b]	BaA		228	438	56-55-3
Benzo[*b*]fluoranthene[a,b]	BbFA		252	N.A.	205-99-2
Benzo[*k*]fluoranthene[a,b]	BkFA		252	N.A.	207-08-9
Benzo[*ghi*]perylene[a,b]	BghiP		276	>500	191-24-2
Benzo[*a*]pyrene[a,b]	BaP		252	495	50-32-8
Chrysene[a,b]	CHR		228	448	218-01-9
Dibenzo[*a,h*]anthracene[a,b]	DBahA		278	524	53-70-3
Fluoranthene[a]	FA		202	384	206-44-0
Fluorene[a]	FLR		166	298	86-73-7
Indeno[1,2,3-*cd*]pyrene[a,b]	IP		276	N.A.	193-39-5
Naphthalene[a]	NPH		128	218	91-20-3
Phenanthrene[a]	PHE		178	340	85-01-8
Pyrene[a]	PYR		202	404	129-00-0
Benzo[*j*]fluoranthene[b]	BjFA		252	N.A.	205-82-3
Cyclopenta[*cd*]pyrene[b]	CPcdP		226	N.A.	27208-37-3
Dibenzo[*a,e*]pyrene[b]	DBaeP		302	N.A.	192-65-4
Dibenzo[*a,h*]pyrene[b]	DBahP		302	N.A.	189-64-0
Dibenzo[*a,i*]pyrene[b]	DBaiP		302	N.A.	189-55-9
Dibenzo[*a,l*]pyrene[b]	DBalP		302	N.A.	191-30-0
5-Methylchrysene[b]	MCH		242	N.A.	3697-24-3

[a]16 EPA priority PAHs [9]
[b]UE PAHs of concern in food [10]
N.A. Data not available

Tables

Table 2

Summary of extraction and clean-up methods in the discussed matrices

Matrix	*Extraction*	*Clean-up*	*Separation/detection*	*Recovery (%)*	*RSD (%)*	*Ref.*
Liquid fatty matrices						
Edible oils	Dilution (*n*-hexane); LLE (2 x DMF/water, 9:1, v/v)	SPE (C_{18}/C_8)	LC-FLD	50-103	Intra-day: 3-6 Inter-day: 5-2	[23]
Edible oils	Dilution (*n*-hexane)	(A) DACC column (Varian ChromSpher 5π, 80 x 3 mm i.d., 5 μm) (B) Column chromatography (alumina)	LC-FLD	(A) 88-105 (B) 67-103	(A) 3-8 (B) 3-8	[28]
Edible oils	Dilution (*n*-hexane); SPE (silica)	-	LC-FLD	32-151	1-17	[22]
Edible oils	Dilution *n*-hexane; SPE (Humic acid-bonded silica)	-	LC-FLD	79-103	Intra-day: 1-9 Inter-day: 3-9	[25]
Edible oils	Dilution (*n*-heptane); LLE (4 x 20 mL DMSO); LLE (3 x 50 mL cyclohexane); LLE (2 x 100 mL water)	Column chromatography (silica gel + Na_2SO_4, 200 x 22 mm)	LC-FLD	58-99	N.A.[a]	[29]
Edible oils, fat	Dilution (isohexane:butyldimethylether,)%:5, v/v); SPE (PS-DVB)	-	LC-FLD	60-95	N.A.	[26]
Edible oil, smoked meat	(A) Smoked meat: Saponification (10 mL KOH 2 M in EtOH:water, 9:1, v/v, 1 h); LLE (2 x 2 mL cyclohexane) (B) Oil: Addition 15 mL cyclohexane; LLE (15 mL DMF:water, 9:1, v/v); LLE (15 mL water); LLE (2 x 15 mL cyclohexane)	SPE (aminopropyl, C_{18})	GC-MS	(A) 60-134	N.A.	[17]
Olive oil	(A) SPE (C_{18} Nucleoprep+Florisil) (B) MSPD (C_{18}+Florisil)	-	GC-MS, LP-GC-MS, LC-FLD	(A) 77-79 (B) 55-66	(A) 4-6 (B) 8-11	[21]
Olive oil	Dilution (25 mL *n*-hexane); LLE (50 mL DMSO); addition 120 mL water + 6 g NaCl; LLE (3 x 150 mL cyclohexane); LLE (100 mL water)	-SPE (silica) -Optional: Soxhlet (100 mL MeOH:water, 8:2, v/v + KOH, 4 h); LLE (3 x 150 mL cyclohexane)	GC-MS	52-80[b]	N.A	[24]
Olive oil	HS-SPME (DVB/Car/PDMS 50/30 μm)	-	GC-MS	74-28	Intra-day: 3-16 Inter-day: 1-14	[33]
Olive oil	HS	-	GC-MS(-MS)	96-99	3-9	[32]
Oil, food mixture	PLE (celite + Florisil, *n*-hexane:acetone, 1:1, v/v)	SPE (PS-DVB)	GC-MS/MS	12-70 (in food by isotopic dilution)	3-21 (in food)	[27]
Olive, olive-pomace oil	SLE or LLE (ACN/ *n*-hexane, 83:17, v/v)	GPC (styrene-divinylbenzene copolymer, 5 ml min^{-1} CH_2Cl_2)	GC-MS/MS	84-110	3-8	[31]
Olive pomace oil	Dilution (25 mL *n*-pentane); LLE (15 mL, 2 x 10 mL DMSO); addition 70 mL water; LLE (3 x 50 mL cyclohexane); LLE (100 mL water)	TLC (silica gel)	GC-MS	69-98	4-13	[18]
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 μm)	-	GC-MS	N.A.	Intra-day: 2-5 Inter-day: 2-6	[34]
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 μm)	-	GC x GC-MS	N.A.	3-35	[35]

Fish oil, fish	Homogenization (Na_2SO_4); saponification (10 mL methanolic KOH 1M, 3 h); LLE (2 x 8 mL *n*-hexane)	SPE (Florisil)	GC-MS(/MS)	64-124	1-37	[95]
Fish oil, dried plants	(A) Fish oil: SLE with rotary agitator (3 x CH_2Cl_2/cyclohexane, 1:1, v/v); centrifugation (B) Dried plants: dilution (cyclohexane)	(A), (B) DACC column (Varian Chromspher π, 80 x 3 mm i.d., 5 µm)	LC-FLD	74-120	Intra-day: 2-4 Inter-day: 4-11	[30]
Milk	HS-SPME (PDMS-DVB)	-	GC-MS	90-113	5-15	[39]
Milk	Dilution (water), SPME (PDMS-DVB)	-	GC-MS	88-112	< 20	[40]
Milk	Addition sodium oxalate; LLE (250 mL MeOH); LLE (250 mL diethyl ether); LLE (250 mL petroleum ether)	Column chromatography (silica gel)	GC-MS	40-125	N.A	[36]
Milk	LLE (20 mL cyclohexane:ethyl acetate, 1:1, v/v); centrifugation	SPE (styrene-divinylbenzene copolymer Envi Chrom); addition 2 mL cyclohexane + 2 mL MeOH:water (80:20, v/v); centrifugation; LLE (2 mL cyclohexane); centrifugation PAHs: Cyclohexane fraction; saponification (5 mL KOH 10%, 90ºC, 80 min); addition 3 mL water + 5 mL cyclohexane; centrifugation Hydroxi-PAHs: MeOH layer; LLE (4 mL water:ethyl acetate, 1:1, v/v); centrifugation	GC-MS (Derivatization)	N.A.	N.A.	[37]
Milk	Saponification (4 mL NaOH 0.4M in EtOH:water, 9:1, v/v, 60ºC, 30 min); LLE (2 x 2 mL *n*-hexane)	-	LC-FLD	90-105	Intra-day: 4-10 Inter-day: 7-10	[38]
Liquid non-fatty matrices						
Coffee	LLE (*n*-hexane)	SPE (silica)	LC-FLD	87-103	5-8	[41]
Coffee brew	SPE (BondElut PPL polystyrene-divinylbenzene)	-	LC-FLD	84-89	1-6	[44]
Coffee	MIP-SPE	-	LC-FLD	Coffee: 73	Coffee: 5	[47]
Tea	SPE (C_{18})	-	LC-FLD	44-103	3-17	[45]
Tea infusion	(A) HS-SPME (PDMS-DVB 60 µm) (B) SPME (Confirmation GC-MS, PDMS-DVB 65 µm)	-	LC-FLD, GC-MS (Confirmation)	N.A.	4-16	[48]
Mate tea	SBSE: 10-mm bars coated with PDMS (0.5 mm), room temperature, 2 h, 160 µL ACN:water, 4:1, v/v (desorption)	-	LC-FLD	24-87	1-11	[49]
Beverages	Addition 10% MeOH; MASE (polypropylene, ethyl acetate)	-	GC-MS	65-92	Intra-day: 6-18 Inter-day: 10-18	[51]
Sugarcane juice	(A) SBSE-TD: Addition of NaCl; 10-mm bars coated with PDMS (0.5 mm), room temperature, 3 h (B) MASE: polypropylene, 800 µL cyclohexane	-	GC-MS	(A) 2 (B) 14	(A) 19 (B) 4	[50]
Cachaça (spirit)	LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	70-97	12-21[c]	[42]
Spirits	SPE (C_{18})	-	LC-FLD	82-113	1-9	[46]

Solid fatty matrices						
Meat	Freeze-drying; Soxhlet (25 mL KOH 25% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water)¸ LLE (150 + 100 mL *n*-hexane); LLE (3 x 100 mL water)	SPE (Florisil)	GC-MS	62-91	4-16	[53]
Meat	(A) Freeze-drying; USE (*n*-hexane) (B) Soxhlet (25 mL KOH 50% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water)¸ LLE (150 + 100 mL *n*-hexane)	(A), (B) SPE (Florisil)	LC-UV, LC-FLD	(A) 74-111 (B) 72-102	N.A.	[52]
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	58-75	< 20	[60]
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	N.A.	N.A.	[61]
Smoked meat	Saponification (MeOH + KOH)	SPE (Florisil)	LC-UV, LC-FLD, GC-EI-MS	68-99	N.A.	[54]
Smoked meat	SPME-DED (PDMS 100 µm)	-	GC-MS	N.A.	5-18	[62]
Smoked meat	PLE (*n*-hexane, 100ºC, 100 bar)	-GPC (Bio-Beads S-X3, 420 mm x 25 mm; cyclohexane:ethyl acetate, 1:1, v/v) -Column chromatography (silica)	GC-MS	75-110	3-12	[59]
Smoked meat	MAE (*n*-hexane, 115ºC)	SPE (silica)	LC-FLD	77-103	1-10	[71]
Fish, smoked meat	(A) Pork: PLE (Supelclean LC-18 + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC) (B) Smoked meat and fish: PLE (C_{18} + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC)	LLE (2 x 1 mL H_2SO_4 9 M); LLE (water); column chromatography (Florisil, 6 g, 1 cm i.d.)	GC-MS	(A) 54-102 (B) 35-93	(A) 4-12 (B) 2-18	[58]
Fish	Homogenization (Na_2SO_4), Soxhlet (CH_2Cl_2:*n*-hexane, 1:1, v/v, 16 h)	Addition water + K_2CO_3 + acetic anhydride; dilution water; LLE (3 x 100 ml CH_2Cl_2); LLE (2 x 2 ml K_2CO_3); column chromatography (silica gel + Na_2SO_4); GPC (2 ml min^{-1} CH_2Cl_2)	GC-MS	N.A.	2.2-20.0	[67]
Fish	(A) Soxhlet (170 ml *n*-hexane:acetone, 1:1, v/v, 6 h) (B) PLE (*n*-hexane:acetone, 1:1, v/v, 100ºC, 10 MPa)	GPC (Bio-Beads S-X3, 500 mm x 8 mm; $CHCl_3$)	LC-FLD	N.A.	N.A.	[65]
Fish	HS-SPME (polyacrilate)	-	GC-MS	N.A	N.A	[74]
Fish	MAE (4 mL saturated KOH in MeOH + 10 mL *n*-hexane, 129ºC); centrifugation	SPE (Silica)	LC-FLD	86-98	1-5	[70]
Fish	Lyophilization; MSPD (C_{18} + Na_2SO_4)	Simultaneous SPE (Florisil + C_{18})	LC-FLD	80-105	2-6	[76]
Fish	Homogenization (Na_2SO_4), Soxhlet (150 mL, CH_2Cl_2, 16 h)	Column chromatography (silica gel + Na_2SO_4, 1 cm i.d.)	GC-MS	Fish: 70-118	< 10	[64]
Fish	QuEChERS method: SLE (ACN); vortex; induced partition ($MgSO_4$+sodium acetate); centrifugation	-	LC-FLD	64-110	< 8	[77]
Fish, seafood	Saponification (10 mL ethanolic KOH 1M, 3 h, 80ºC); addition 10 mL water; LLE (2 x 20 mL cyclohexane)	-	LC-FLD	41-67	3-18	[68]
Fish, seafood	MAE (15 mL acetone, 21 psi, 80 % microwave power)	(A) SPE (Florisil) (B) GPC (Envirosep ABC, 350 mm x 21.2	GC-MS	N.A.	N.A.	[73]

		mm, 5 ml min^{-1} CH_2Cl_2)				
Fish, mussel	Dilution (NaCl solution 24 %), HS-SPME (PDMS-DVB)	-	GC-MS	8-111	7-15	[75]
Fish, palm dates	Soxhlet (150 mL, *n*-hexane, 8 h)	Column chromatography (silica gel + Florisil + Na_2SO_4)	GC-MS	59-112	1-24	[66]
Shellfish	Freeze-drying; Soxhlet (CH_2Cl_2, 24 h)	-GPC (Bio-Beads S-X3; $CHCl_3$) -Column chromatography (aluminosilicate)	GC-MS	62-123	9-21	[63]
Mussel	Lyophilization; PLE (*n*-hexane:CH_2Cl_2, 1:1, v/v, 150ºC, 150 psi)	Saponification (25 mL KOH 6 M, ambient temperature, 24 h)	GC-MS	64-121	3-30	[69]
Cheese	Saponification (10 mL KOH ethanolic solution); addition water (10 mL); LLE (2 x 20 mL cyclohexane)	SPE (Isolute silica 500 mg)	LC-FLD	84-89	N.A.	[80]
Cheese	Soxhlet (Na_2SO_4 + 170 mL *n*-hexane: CH_2Cl_2, 1:1, v/v, 7 h)	GPC (Bio-Beads S-X3, CH_3Cl)	LC-FLD	52-94	9-34	[78]
Cheese	(A) Cheese: lipid extraction (N.A.); addition 30 mL cyclohexane; LLE (DMF:water, 9:1, v/v); LLE 30 mL cyclohexane	(A), (B) SPE (Silica)	LC-FLD	75-96	N.A.	[79]
Infant milk, infant cereals	(A) Parent PAHs: USE (3 x 10 mL *n*-hexane); centrifugation (B) Hydroxy-PAHs: USE (3 x 9/6/5 mL ACN:ethyl acetate, 70:30, v/v, containing 0.8 g/L *tert*-butyl hydroquinone); centrifugation; hydrolysis of conjugated PAHs (β-glucuronidase/aryl sulphatase)	(A) SPE (Silica) (B) SPE (C_{18})	(A) LC-FLD (B) LC-MS	Infant milk: 70-116 Infant cereals: 82-103	Infant milk: 4-9 Infant cereals: 2-7	[94]
Solid non-fatty matrices						
Bread, potato	(A) Bread: Addition 1 mL water; USE (3 mL ethyl ether:CH_2Cl_2, 1:1, v/v) (B) Potato: USE (as explained in (A))	-	LC-FLD, GC-MS (Confirmation)	70-86	4-11	[85]
Cane sugar	SLE (100 mL cyclohexane); LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	74-86	3-22[c]	[86]
Foodstuffs	Soxhlet (150 mL, CH_2Cl_2, 8 h)	Column chromatography (silica gel)	LC-FLD	70-110	Repeatability: < 7 Reproducibility: < 6	[88]
Food supplements	SLE with rotary agitator (3 x cyclohexane/CH_2Cl_2, 1:1, v/v + HF-M + alumina); centrifugation	Column chromatography (silica gel)	LC-FLD	63-116	N.A.	[100]
Fruits, vegetables	Saponification (100 mL KOH methanolic, 5 h); addition MeOH:water (100 mL, 9:1, v/v); LLE (2 x 150 mL cyclohexane); LLE (100 mL MeOH:water, 9:1, v/v; 100 water); LLE (N,N-dimethylformamide:water, 9:1, v/v)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD, GC-MS	74-99	3-21	[84]
Ground coffee	PLE (*n*-hexane:acetone, 1:1, v/v; 150ºC)	-Saponification (EtOH+KOH, 30 min) -LLE (100 mL cyclohexane); LLE (3 x 100 mL water) - SPE (silica)	LC-FLD, GC-MS/MS, LC-UV	64-106	1-12	[87]
Tea leaves	USE (3 x 20 mL CH_2Cl_2:acetone, 1:1, v/v)	Column chromatography (silica)	LC-UV	>70	>20	[81]
Tea leaves	Soxhlet (CH_2Cl_2:acetone, 1:1, v/v, 18 h)	SPE (Florisil)	GC-EI-MS	N.A	N.A	[82]

Vegetables	Soxhlet (300 mL *n*-hexane:acetone, 1:1, v/v, 24 h)	SPE (Acid treated silica, aromatic sulfonic acid)	GC-MS	69-111	3-12	[83]

[a] N.A.: Data not available

[b] Values corresponding to isotope labeled compounds

[c] Coefficient of variation

Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; DMF: dimethylformamide; DMSO: dimethylsulfoxide; DVB: divinylbenzene; EtOH: ethanol; GC-MS: gas chromatography coupled to mass spectrometry; GCxGC-MS: multidimensional GC-MS; HF-M: modified diatomaceous earth; HS-SPME: headspace solid-phase microextraction; GPC: gel permeation chromatography; i.d.: internal diameter; LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LLE: liquid-liquid extraction; LP-GC-MS: low pressure GC-MS; MAE: microwave-assisted extraction; MASE: membrane-assisted solvent extraction; MeOH: methanol; MIP-SPE: molecularly imprinted polymers solid-phase extraction; MSPD: matrix solid-phase dispersion; PDMS: polydimethylsiloxane; PLE: pressurized-liquid extraction; PS-DVB: polystyrene /divinylbenzene; SBSE: stir bar sorptive extraction; SBSE-TD: SBSE-thermal desorption; SFE: supercritical fluid extraction; SLE solid-liquid extraction; SPE: solid-phase extraction; SPME: solid-phase microextraction; SPME-DED: SPME coupled to a direct extraction device; TLC: thin layer chromatography; USE: ultrasound extraction

Tables

Table 3
Summary of separation and detection techniques in the discussed matrices

Matrix	*Separation/detection technique*	*Separation remarks*	*Detection remarks*	*LOD (units)*	*LOQ (units)*	*Ref.*
Liquid fatty matrices						
Edible oils	LC-FLD	-Vydac C_{18} (250 x 4.6 mm i.d., 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 330-500 nm	N.A.[a]	0.3-6.0 ng g^{-1}	[23]
Edible oils	LC-FLD	-Vydac C_{18} (250 x 4.6 mm i.d., 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.03-0.2 ng g^{-1}	0.1-8.0 ng g^{-1}	[28]
Edible oils	LC-FLD	-Supelcosil LC-PAH (250 mm x 3 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=240-290 , λ_{em}= 330-484 nm	N.A.	N.A.	[22]
Edible oils	LC-FLD	-Thermo Hypersil ODS (200 mm x 4.6 mm x 5 µm) -Isocratic elution: MeOH:water, 9:1, v/v	λ_{ex}=255 , λ_{em}= 420 nm	0.06 µg kg^{-1}	0.2 µg kg^{-1}	[25]
Edible oils	LC-FLD	-C-18 Lichrocart (125 mm x 4 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=242-350 , λ_{em}= 380-443 nm	0.1-4.0 ng	N.A.	[29]
Edible oils, fat	LC-FLD	- (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-300 , λ_{em}= 376-418 nm	0.2-0.8 µg kg^{-1}	N.A.	[26]
Edible oil, smoked meat	GC-EI-MS	-Injection : Pulsed splitless -Supelco SPB-5 (25 m x 0.20 mm x 0.33 µm)	Q, SIM	0.06 µg kg^{-1}	0.20 µg kg^{-1}	[17]
Olive oil	(A) GC-EI-MS (B) LP-GC-EI-MS (C) LC-FLD (D) DACC	(A) Injection: N.A.; DB-5ms (30 m × 0.25 mm, 0.25 µm) (B) Injection: N.A.; Rapid MS FS CP-Sil 8 (10 m × 0.53 mm, 0.50 µm) + restrictor (0.6 m x 0.25 mm) (C) CP EcoSpher 4 PAH (150 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v) (D) CP ChromSpher π (20 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v)	(A),(B) SIM (C), (D) λ_{ex}=370 , λ_{em}= 470 nm	(A) 1 ng g^{-1} (B) 1.6 ng g^{-1} (C) 0.5 ng g^{-1} (D) 0.3 ng g^{-1}	(A) 3.4 ng g^{-1} (B) 5.5 ng g^{-1} (C) 1.7 ng g^{-1} (D) 1.1 ng g^{-1}	[21]
Olive oil	GC-EI-MS	-Injection: Pulsed splitless -HP-5ms, (60 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A	N.A	[24]
Olive oil	GC-EI-MS	-Injection: Splitless -Supelcowax-10 and HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.05-1.60 µg kg^{-1}	0.20-5.20 µg kg^{-1}	[33]
Olive oil	GC-EI-MS(/MS)	-Injection: Splitless -VF-5ms, 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	QqQ, SIM, SRM	0.02-0.06 µg kg^{-1}	0.07-0.26 µg kg^{-1}	[32]
Oil, food mixture	GC-EI-MS/MS	-Injection: N.A. -Zebron ZB-5ms, (30 m x 0.25 mm x 0.25 µm)	QqQ, SRM	0.008-0.150 µg kg^{-1} (dry weight)	0.024-0.920 µg kg^{-1} (dry weight)	[27]
Olive, olive-pomace oil	GC-EI-MS/MS	-Injection: LVI + PTV -HP-5, crosslinked 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	IT, Product-ion scan, Resonant mode	0.05-0.07 µg kg^{-1}	0.1-0.2 µg kg^{-1}	[31]
Olive pomace oil	GC-EI-MS	-Injection: splitless -DB-5ms (30 m x 0.25 mm x 0.20 µm)	IT, Full scan	0.1-0.4 µg kg^{-1}	N.A	[18]
Vegetable oils	GC-EI-MS	-Injection: Splitless -SPB-5, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.2 µg kg^{-1}	0.5 µg kg^{-1}	[34]

Vegetable oils	GCxGC-EI-MS	-Injection: Splitless -First dimension: SGE BPX5, (30 m x 0.25 mm x 0.25 μm) -Second dimension: SGE BPX50, 50% phenyl polysilphenylenesiloxane (1 m x 0.1 mm x 0.1 μm)	TOF, Full scan	0.1-1.4 μg kg^{-1}	0.4-4.6 μg kg^{-1}	[35]
Fish oil, fish	(A) GC-EI-MS/MS (B) GC-EI-MS (Confirmation)	(A), (B) Injection: Splitless; HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 μm)	(A) QqQ, SRM (B) TOF, Full scan	0.02-1.25 μg kg^{-1}	0.125-1.250 μg kg^{-1}	[95]
Fish oil, dried plants	LC-FLD	-Varian Pursuit 3 PAH (100 mm × 4.6 mm × 1/4'') -Gradient elution: A: ACN; B: MeOH; C: water	λ program: λ_{ex}=222-380 , λ_{em}= 353-499 nm	0.07-7.80 μg kg^{-1}	0.13-16 μg kg^{-1}	[30]
Milk	GC-EI-MS	N.A.	Q, SIM	0.2-5.0 ng l^{-1}	0.7-16.6 ng l^{-1}	[39]
Milk	GC-EI-MS	-Injection: Splitless -HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	0.003-1.56 μg l^{-1}	N.A.	[40]
Milk	GC-EI-MS	-Injection: N.A. -DB-XLB, proprietary phase, (60 m x 0.25 mm x 0.25 μm)	Q, SIM	N.A	N.A	[36]
Milk	GC-EI-MS	-Injection: Splitless -OV-1, (30 m x 0.25 mm x 0.25 μm)	-Q, SIM -Derivatization: (MSTFA)	0.04-0.39 ng mL^{-1}	N.A.	[37]
Milk	LC-FLD	-Wakosil-PAHs (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: MeOH:water, 8:2, v/v	λ program: λ_{ex}=248-364 , λ_{em}= 360-500 nm	1.3-76.0 ng kg^{-1}	N.A.	[38]
Liquid non-fatty matrices						
Coffee	LC-FLD	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=274-300 , λ_{em}= 406-470 nm	0.01-0.05 μg L^{-1}	0.04-0.20 μg L^{-1}	[41]
Coffee	LC-FLD	-C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=230-250 , λ_{em}= 410-420 nm	0.8-10.0 ng L^{-1} [b]	2.5-33.2 ng L^{-1} [c]	[44]
Coffee	LC-FLD	-Isocratic elution: ACN:water, 4:6, v/v -Phenomenex Envirosep PP (125 mm x 3.2 mm)	λ program: λ_{ex}=252-300 , λ_{em}= 322-500 nm	N.A.	N.A.	[47]
Tea	LC-FLD	-Nova-Pak C_{18} (150 mm x 3.9 mm x 4 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-295 , λ_{em}= 365-465 nm	0.016-0.140 ng mL^{-1}	N.A.	[45]
Tea infusion	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) LiChrospher PAH, modified RP-18 silica gel (250 mm x 4.6 mm x 5 μm); gradient elution: A: ACN; B: water (B) Injection: Splitless; HP-5ms, (30 m x 0.25 mm x 0.25 μm)	(A) λ program: λ_{ex}=250 , λ_{em}= 330-500 nm (B) Q, SIM	5-145 ng L^{-1}	N.A.	[48]
Mate tea	LC-FLD	-Vydac 201TP52 (250 x 2.1 mm i.d., 5 μm) -Gradient elution: A: ACN; B: water		0.1-8.9 ng L^{-1}	0.3-30 ng L^{-1}	[49]
Beverages	GC-EI-MS	-Injection: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	3-27 ng L^{1}	30-133 ng L^{-1}	[51]
Sugarcane juice	GC-EI-MS	-Injection: (A) SBSE: Splitless; (B) MASE: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	(A) 0.04 μg L^{-1} (B) 0.06 μg L^{-1}	N.A.	[50]
Cachaça (spirit)	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) Vydac 201TP54 (250 mm x 4.6 mm x 5 μm); isocratic elution: ACN/water (75:25, v/v) (B) Injection: Splitless + PTV; HP-5ms, (30 m x 0.25 mm x 0.25 μm)	(A) λ_{ex}=290 , λ_{em}=430 (B) Q, SIM	0.006-0.090 μg L^{-1}	N.A.	[42]
Spirits	LC-FLD	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=270-356 , λ_{em}= 330-500 nm	$1.08 \cdot 10^{-3}$-$1.28 \cdot 10^{-2}$ μg L^{-1}	0.11-0.93 μg L^{-1}	[46]

Solid fatty matrices						
Meat	GC-EI-MS	-Injection: splitless -DB-5ms (30 m x 0.32 mm x 0.25 µm)	IT, Full scan	5-50 pg	N.A.	[53]
Meat	(A) LC-UV (B) LC-FLD	-ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	(A) λ = 254 nm (B) λ program: λ_{ex}=254-270 , λ_{em}= 340-420 nm	(A) 0.03-1.54 ng (B) Not detected-6 pg	N.A.	[52]
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.001-0.049 µg kg^{-1}	N.A	[60]
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.001-0.045 µg kg^{-1}	N.A	[61]
Smoked meat	(A) LC-UV (B) LC-FLD (C) GC-EI-MS (Confirmation)	(A), (B) ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (C) Injection: splitless; DB-5ms (30 m x 0.32 mm x 0.25 µm)	(A) λ = 254 nm (B) λ program: λ_{ex}=254-320 , λ_{em}= 340-533 nm (C) IT, Full scan	(A) 0.03-1.54 ng (B) $2 \cdot 10^{7}$ -6 pg (C) 5-50 pg	N.A.	[54]
Smoked meat	GC-EI-MS	-Injection: Splitless -HP-5, (50 m x 0.32 mm x 1.05 µm)	Q, SIM	0.008-0.102 ng mL^{-1}	N.A.	[62]
Smoked meat	GC-EI-MS	-Injection: Splitless -DB-5ms, (60 m x 0.25 mm x 0.25 µm)	Magnetic sector, SIR	N.A.	N.A.	[59]
Smoked meat	LC-FLD	-Supelcosil LC-PAH (250 mm x 3 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program (detector A): λ_{ex}= 250-290, λ_{em}= 350-470 nm λ program (detector B): λ_{ex}= 240-290, λ_{em}= 330-484 nm	N.A.	< 0.2-0.6 µg kg^{-1}	[71]
Fish, smoked meat	GC-EI-MS	-Injection: Splitless -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.002-0.100 µg mL^{-1}	N.A.	[58]
Fish	GC-EI-MS	-Injection : Pulsed splitless -DB-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	2-7 ng g^{-1} [b]	N.A.	[67]
Fish	LC-FLD	-LiChroCART (250 mm x 4.0) with LiChrospher PAHs sorbent -Gradient elution: A: ACN; B: water	λ program: λ_{ex}= 217- 295, λ_{em}= 341-484 nm	N.A.	N.A.	[65]
Fish	GC-EI-MS	-Injection: Splitless -HP-5ms, (60 m x 0.25 mm x 0.25 µm)	Q	N.A	N.A	[74]
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.1-0.5 ng g^{-1} (dry weight)	0.2-1.8 ng g^{-1} (dry weight)	[70]
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.04-0.32 ng g^{-1}	0.13-1.07 ng g^{-1}	[76]
Fish	GC-EI-MS	-Injection: Splitless -DB-5ms, 5% phenyl 95% dimethyl arylene siloxane(30 m x 0.25 mm x 0.25 µm)	IT, Full scan	0.02-1.70 µg ml^{-1}	0.06-5.00 µg ml^{-1}	[64]
Fish	LC-FLD	-CC 150/4 Nucleosil 100-5 C18 PAH (150 mm x 4.0 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=315-590 , λ_{em}= 260-290 nm	0.04-0.56 ng g^{-1}	0.12-1.90 ng g^{-1}	[77]
Fish, seafood	LC-FLD	-Phenomenex C18 Envirosep (125 mm x 4.6 mm x 3 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 380-450 nm	0.01-0.49 ng g^{-1}	0.02-0.62 ng g^{-1}	[68]

Fish, seafood	GC-EI-MS	-Injection: Splitless -HP-5, (30 m x 0.25 mm x 0.25 µm)	Q, Full scan	N.A.	N.A.	[73]
Fish, mussel	GC-EI-MS	-Injection: Splitless -HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	8-450 pg g^{-1}	50-1500 pg g^{-1}	[75]
Fish, palm dates	GC-EI-MS	-Injection: Splitless -CP-SIL 8CB-MS arylene-modified 5% phenyl-95% methyl polydimethylsiloxane (30 m x 0.25 mm x 0.25 µm)	IT, SIS	0.13-4.29 µg l^{-1}	0.43-14.29 µg l^{-1}	[66]
Shellfish	GC-EI-MS	-Injection: Splitless -VF-5ms, (30 m x 0.25 mm x 0.25 µm)	IT, SIS	0.52-0.81 ng g^{-1} [b]	N.A.	[63]
Mussel	GC-EI-MS	-Injection: Splitless -DB-5, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.5-8.0 µg kg^{-1} (dry mass)	N.A.	[69]
Cheese	LC-FLD	-Envirosep-PP (125 x 4.6 mm i.d., 4.6 µm) -Isocratic elution: ACN/water (88:12, v/v)	λ_{ex}=295 , λ_{em}= 404 nm	0.006 µg kg^{-1}	0.021 µg kg^{-1}	[80]
Cheese	LC-FLD	-Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=216-295 , λ_{em}= 320-484 nm	0.01-0.25 µg kg^{-1}	N.A.	[78]
Cheese	LC-FLD	-Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=224-268 , λ_{em}= 320-400 nm	N.A.	0.01-0.90 µg kg^{-1}	[79]
Infant milk, infant cereals	(A) Parent and hydroxy-PAHs: LC-FLD (B) Hydroxy-PAHs: LC-MS (Confirmation)	(A) Luna C_8 Supelcosil (120 mm x 2.0 mm x 5 µm); gradient elution: A: ACN; B: water (B) Hypersil Green PAH (100 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water	(A) λ program: λ_{ex}=274-393 , λ_{em}= 406-470 nm (B) QqQ, SRM, ESI (-)	(A) 0.01-0.70 µg kg^{-1} (B) 0.10-0.15 µg kg^{-1}	(A) 0.03-1.70 µg kg^{-1} (B) 0.25-0.50 µg kg^{-1}	[94]
Solid non-fatty matrices						
Bread, potato	(A) LC-FLD (B) GC-MS/MS (Confirmation)	(A) Hypersil Green PAH (100 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: Splitless; VA-5, (30 m x 0.25 mm x 0.25 µm)	(A) λ program: λ_{ex}=250-300 , λ_{em}= 325-465 nm (B) Q, full scan	0.007-6.400 µg L^{-1}	0.023-21.300 µg L^{-1}	[85]
Cane sugar	LC-FLD	-Vydac 201TP54 (250 mm x 4.6 mm x 5 µm) -Isocratic elution: ACN/water (75:25, v/v)	λ_{ex}=290 , λ_{em}=430	0.01-0.17 µg kg^{-1}	N.A.	[86]
Foodstuffs	LC-FLD	-Spherisorb ODS2-C_{18} (250 mm x 4.6 mm i.d., 5 µm) -Gradient elution: A: ACN; B: water	λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.0007-0.013 ng µL^{-1} [b]	N.A.	[88]
Food supplements	LC-FLD	-Varian C_{18} Pursuit 3 PAH (100 mm x 4.6 mm i.d., 3 µm) -Gradient elution: A: ACN; B: MeOH; C: water	N.A.	0.1-29.8 µg kg^{-1}	0.2-59.7 µg kg^{-1}	[100]
Fruits, vegetables	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) C18 Vydac 201 TP (250 mm x 4.6 mm i.d., 5 µm); isocratic elution: ACN:water (75:25, v/v) (B) Injection: Splitless; Supelco 5% diphenyl-95% dimethylpolysiloxane, (30 m x 0.25 mm x 0.25 µm)	(A) λ_{ex}=290 , λ_{em}= 430 nm (B) Q, SIM	(A) 0.07-1.29 µg kg^{-1} [b]	N.A.	[84]
Ground coffee	(A) LC-FLD (B) GC-MS/MS (Confirmation) (C) LC-UV (Confirmation)	(A) Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: programmed temperature vaporization; Rtx-5MS (30 m x 0.25 mm x 0.25 µm) (C) C18 Supelcosil LC-PAH (150 mm x 3.0 mm x 5 µm); gradient elution: A: ACN; B: water	(A) λ program: λ_{ex}=220-286 , λ_{em}= 340-420 nm (B) IT, Product ion scan	0.11-0.18 µg kg^{-1} [b]	N.A	[87]
Tea leaves	LC-UV	-Elution: N.A. -Agilent C-18 (250 mm x 4.6 mm)	N.A.	0.16-1.27 µg kg^{-1}	N.A.	[81]

Tea leaves	GC-EI-MS	-Injection: N.A. -HP-5ms (30 m x 0.25 mm x N.A.)	Q	N.A	N.A	[82]
Vegetables	GC-EI-MS	-Injection: Splitless -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A.	N.A.	[83]

[a] N.A.: Data not available
[b] Method detection limit (MDL)
[c] Method quantification limit (MQL)

Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; ESI (-): electrospray ionization in negative mode; GC-EI-MS: gas chromatography coupled to mass spectrometry operating in electronic ionization; GC-EI-MS/MS: GC coupled to tandem MS; GCxGC-MS: multidimensional GC-EI-MS; IT: ion trap analyzer; LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LP-GC-EI-MS low pressure GC-MS in electronic ionization; LVI: large-volume injection; MASE: membrane-assisted solvent extraction; MeOH: methanol; MSTFA: N-methyl-N-(trimethylsilyl)trifluoroacetamide; PTV: programmed-temperature vaporization; Q: single quadrupole analyzer; QqQ: triple quadrupole analyzer; SBSE: stir bar sorptive extraction; SIM: single-ion monitoring; SIR: selected ion recording; SIS: selected-ion storage; SRM: selected-reaction monitoring; TOF: time of flight analyzer; λ_{ex}: excitation wavelength; λ_{em}: emission wavelength

Tables

Table 4
Summary of analyzed PAHs and concentrations found in real samples

Analytes	*Type of sample*	*Concentration*[a]	*Observations*	Reference
	Liquid fatty matrices			
16 EPA PAHs[b]	Edible oils	0.3 (BaA, IP)[c]−1145 (PHE)[d] ng g^{-1}	47 samples	[23]
BaP	Edible oils	Refined oil: < 1.5 μg kg^{-1} Unrefined oil: > 2 μg kg^{-1}	8 samples (refined, unrefined oils)	[25]
ACP, ANT, BaP, BeP, BghiP, CHR, COR, CPdefPHE, PHE, PYR	Edible oils	Refined vegetable oil: 40.2 μg kg^{-1} (total PAH content) Olive oil: 624 μg kg^{-1} (total PAH content)	296 samples	[29]
BaP	Olive oil	84−89 ng g^{-1}	48 samples	[21]
16 EPA PAHs + 4 EU PAHs[b] + (> 35)	Olive oil	0.30 − 320 (3-methylCHR) μg kg^{-1}	5 samples (olive pomace oil)	[24]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR + 2 alkyl derivatives	Olive oil	0.4 (ACP, ACY) − 26 (PHE) μg kg^{-1}	10 samples (extra virgin olive oil)	[33]
BkFA, BghiP, BeP, BaP	Olive, olive-pomace oil	0.3 (BghiP, BeP, BaP) − 88.7 (BkFA) μg kg^{-1}	25 samples (virgin olive oil, olive pomace oil)	[31]
ACP, ACY, ANT, BaA, BbFA, BjFA, BkFA, BcF, BghiP, BaP, CHR, CPcdP, DBahA, DBaeP, DBahP, DBaiP, DBalP, FA, FLR, IP, MCH, NPH, PHE, PYR,	Vegetable oils	0.5 (BaP) − 133.2 (CHR) μg kg^{-1}	14 samples (olive oil, extra virgin olive oil, pomace olive oil, sunflower oil)	[35]
16 EPA PAHs	Fish oil, fish	Fish: 0.06 (BaA) − 11.4 (PYR) μg kg^{-1} Fish feed: 0.2 (ACP, ACY) − 242 (NPH) μg kg^{-1} Fish oil: 0.3 (ACP, BbFA, BkFA) − 38.2 (PHE) μg kg^{-1} Linseed oil: 0.3 (BaP) −16.7 (FA) μg kg^{-1} Palm oil: 0.2 (ACY) −1.4 (BaP) μg kg^{-1} Rapeseed oil: 0.2 (ACY) −1.9 (NPH) μg kg^{-1}	-31 samples (fish, fish feed, fish oil, linseed oil, palm oil, rapeseed oils) -Fish exposed to long-term feed trials	[96]
ACP, ACY, ANT, BaA, CHR, FA, FLR,	Milk	31.9 (PYR) − 160.5 (PHE) μg L^{-1}	10 samples	[39]

NPH, PHE, PYR				
16 EPA PAHs	Milk	Only 8 PAHs found: ACP, ACY, ANT, BaA , FA, FLR, NPH, PYR Control: 0.3 (ACP) − 6.4 (NPH) ng g^{-1} (milk fat) Cementwork: 0.2 (ACP) −16.2 (FLR) ng g^{-1} (milk fat) Motorway: 0.5 (ACP) − 10.7 (FLR) ng g^{-1} (milk fat) Combined sources: 0.8 (ACP) − 15.2 (NPH) ng g^{-1} (milk fat)	-14 samples (control, cementwork, motorway, combined sources) -Average values	[36]
ANT, BaP, BaA, BbFA, BkFA, BghiP, CHR, DBahA, FA, IP, PHE, PYR	Milk	Milk: 0.01 (ANT, IP) − 0.35 (BbFA) μg kg^{-1} Infant formula: 0.02 (ANT) − 0.40 (PHE) μg kg^{-1}	17 samples (commercial milk and infant formula)	[38]
	Liquid non-fatty matrices			
BaA, BbFA, BkFA, BaP, BghiP, DBahA, IP	Coffee	0.01 (all except BbF) – 0.1 (BbFA) μg kg^{-1}	12 samples (with and without caffeine, natural roasting)	[41]
BaP	Coffee	1.1 ng g^{-1}	1 sample (standard addition method)	[47]
ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, NPH, PHE, PYR	Tea infusion	4 PAHs found: 6.6 (PHE) – 82 (FLR) ng mL^{-1}	6 samples	[48]
16 EPA PAHs (except ACY)	Mate tea	1.4 (BaA) – 1156 (ACP) ng L^{-1}	11 samples	[49]
BaP	Sugarcane juice	0.05 – 0.11 μg L^{-1}		[50]
BaA, BbFA, BkFA, BaP, DBahA	Cachaça (spirit)	0.01 (BkFA) – 0.83 (BbFA) μg L^{-1}	25 samples	[42]
16 EPA PAHs (except ACY)	Spirits	From burned sugar cane: 0.003 (BghiP) – 138 (BaA) μg L^{-1} From non-burned sugar cane: 0.002 (BaP) – 3.13 (PHE) μg L^{-1}	131 samples (from burned and non-burned sugar cane crops)	[46]
	Solid fatty matrices			
16 EPA PAHs	Smoked meat	< 0.20 (BaA, BbFA, BkFA, BaP, BghiP, CHR, FA, PY) −38.59 (PHE) μg kg^{-1}	7 samples (smoked meat)	[17]
15 EU PAHs + BcF	Smoked meat	Before processing: 0.003 (DBalP) – 0.101 (BcF) μg kg^{-1} Traditional smokehouse: 0.002 (DBahP, DBalP) – 2.134 (BcF) μg kg^{-1} Industrial smokehouse: 0.003 (DBahA, DBalP) – 1.539 (BcF) μg kg^{-1}	22 samples (before processing and traditional and industrial smokehouse)	[60]
15 EU PAHs + BcF	Smoked meat	0.001 (DBaHP, DBalP) – 10.6 (BcF) μg kg^{-1}	32 samples	[61]

BaA, BbFA, BkFA, BghiP, BaP, CHR, DBahA, FA, IP, PYR	Smoked meat	0.1 (DBahA, BbFA) – 26.22 (FA) µg kg^{-1}	18 samples	[59]
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.2 (BaA) – 51.4 (BbFA) ng g^{-1}	10 samples	[70]
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.37 (BaP) – 42.49 (BbFA) ng g^{-1}	10 samples	[76]
16 EPA PAHs	Fish	0.42 (ACY) – 34.48 (BghiP) µg g^{-1}	Number of samples not defined	[64]
16 EPA PAHs (except ACY) + DBalP	Fish	0.12 (PHE) – 4.99 (NPH) ng g^{-1}	27 samples	[77]
ANT, BaA, BbFA, BkFA, BaP, BghiP, CHR, DBahA, FA, IP, PYR	Fish, seafood	Summer: 0.12 (ANT) – 23.23 (PYR) ng g^{-1} (average values) Winter: 0.35 (FA) – 46.01 (CHR) ng g^{-1}(average values)	Number of samples not defined	[68]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR	Fish, mussel	0.52 (NPH) – 8.00 (PHE) ng g^{-1}	-8 samples -PAHs showing up to 4 rings	[75]
16 EPA PAHs	Shellfish	24.4 – 140.0 ng g^{-1} (total PAH content)	10 samples	[63]
BaP	Cheese	Samples smoked with straw/cardboard: 0.38 – 2.40 µg kg^{-1} Samples smoked with wood shavings/ liquid smoke flavorings: 0.18 – 0.80 µg kg^{-1}	96 samples	[80]
16 EPA PAHs	Cheese	0.01 (BkFA, BaP, DBahA) – 60.0 (NPH, PHE) µg kg^{-1}	36 samples	[78]
16 EPA PAHs	Cheese	0.12 – 6.21 µg kg^{-1} (total PAH content)	-16 samples -Analysis before and after smoking	[79]
	Solid non-fatty matrices			
16 EPA PAHs (except ACY) + BeP	Bread, potato	Mashed potato: 9.35 – 17.10 µg kg^{-1} (total PAH content) Potato: 8.47 – 17.20 µg kg^{-1} (total PAH content) Toasted bread: 7.38 – 18.00 µg kg^{-1} (total PAH content)	5 samples	[85]
BaA, BbFA, BkFA, BaP, DBahA	Cane sugar	Typical sugar: 0.015 (BaP) – 0.300 (BaA) µg kg^{-1}(average values) Organic sugar: 0.002 (BkFA) – 0.104 (BaA) µg kg^{-1}(average values)	57 samples (18 organic samples)	[86]
16 EPA PAHs (except ACY)	Foodstuffs	0.08 (ANT) – 61.4 (PYR) ng g^{-1}	Number of samples not defined	[88]
15 EU PAHs + BcF	Food supplements	0.02 (BaA, BkFA, BghiP, DAaeP) – 32.50 (BcF) µg kg^{-1}	20 samples	[104]
BaA, BbFA, BkFA,	Fruits, vegetables	Lettuce: 0.08 (BaP) – 8.68 (FA) µg kg^{-1} (average values)	Number of samples not	[84]

BaP, BeP, BghiP, CHR, DBahA, FA, PYR		Tomato: 0.08 (BaP) – 6.19 (FA) μg kg^{-1}(average values) Cabbage: 0.06 (BkFA) – 5.53 (BkFA) μg kg^{-1}(average values) Fruits: 0.08 (BaP) – 6.22 (BghiP) μg kg^{-1}(average values)	defined (combined samples of lettuce, tomato, cabbage, apple, grape and pear)	
16 EPA PAHs	Tea leaves	Leaves: 0.42 (ANT) – 83.40 (PYR) μg kg^{-1}(dry mass) Crude tea: 2.35 (DBahA) – 1120.00 (PHE) μg kg^{-1}(dry mass) Tea: 8.42 (DBahA) – 3930.00 (PHE) μg kg^{-1}(dry mass)	-6 samples -Leaves analyzed during the whole tea manufacturing process	[81]
ACP, ACY, ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, IP, NPH, PHE, PYR	Vegetables	Potato: 0.23 (ACY) – 459 (IP) μg kg^{-1}(average values) Carrot: 0.40 (NPH) – 291 (IP) μg kg^{-1}(average values)	21 samples (organic agriculture)	[83]

[a] Compounds showing the minimum and maximum values of the range are shown in parentheses
[b] For more details see Table 1
[c] Compound(s) showing the minimum concentration found
[d] Compound(s) showing the maximum concentration found
Abbreviations: COR: Coronene; BeP: Benzo[*e*]pyrene; CPdefPHE: Cyclopenta[*d,e,f*]phenanthrene; 3-methylCHR: 3-methylchrysene; BcF: Benzo[*c*]fluorene; BeP: Benzo[*e*]pyrene (For other abbreviations see Table 1)

Tables

Table 1.
Summary of the most important PAHs analyzed in food

Compound	Abbreviation	Structure	Molecular weight (amu)	Boiling point (ºC)	CAS No
Acenaphthene[a]	ACP		154	279	83-32-9
Acenaphthylene[a]	ACY		152	280	208-96-8
Anthracene[a]	ANT		178	340	120-12-7
Benzo[*a*]anthracene[a,b]	BaA		228	438	56-55-3
Benzo[*b*]fluoranthene[a,b]	BbFA		252	N.A.	205-99-2
Benzo[*k*]fluoranthene[a,b]	BkFA		252	N.A.	207-08-9
Benzo[*g,h,i*]perylene[a,b]	BghiP		276	>500	191-24-2
Benzo[*a*]pyrene[a,b]	BaP		252	495	50-32-8
Chrysene[a,b]	CHR		228	448	218-01-9
Dibenzo[*a,h*]anthracene[a,b]	DBahA		278	524	53-70-3
Fluoranthene[a]	FA		202	384	206-44-0
Fluorene[a]	FLR		166	298	86-73-7
Indeno[1,2,3-*c,d*]pyrene[a,b]	IP		276	N.A.	193-39-5
Naphthalene[a]	NPH		128	218	91-20-3
Phenanthrene[a]	PHE		178	340	85-01-8
Pyrene[a]	PYR		202	404	129-00-0
Benzo[*j*]fluoranthene[b]	BjFA		252	N.A.	205-82-3
Cyclopenta[*c,d*]pyrene[b]	CPcdP		226	N.A.	27208-37-3
Dibenzo[*a,e*]pyrene[b]	DBaeP		302	N.A.	192-65-4
Dibenzo[*a,h*]pyrene[b]	DBahP		302	N.A.	189-64-0
Dibenzo[*a,i*]pyrene[b]	DBaiP		302	N.A.	189-55-9
Dibenzo[*a,l*]pyrene[b]	DBalP		302	N.A.	191-30-0
5-Methylchrysene[b]	MCH		242	N.A.	3697-24-3

[a]16 EPA priority PAHs [9]
[b]UE PAHs of concern in food [10]
N.A. Data not available

Tables

Table 2

Summary of extraction and clean-up methods in the discussed matrices

Matrix	*Extraction*	*Clean-up*	*Separation/detection*	*Recovery (%)*	*RSD (%)*	*Ref.*
Liquid fatty matrices						
Edible oils	Dilution (*n*-hexane); LLE (2 x DMF/water, 9:1, v/v)	SPE (C_{18}/C_8)	LC-FLD	50-103	Intra-day: 3-6 Inter-day: 5-2	[21]
Edible oils	Dilution (*n*-hexane)	(A) DACC column (Varian ChromSpher 5π, 80 x 3 mm i.d., 5 μm) (B) Column chromatography (alumina)	LC-FLD	(A) 88-105 (B) 67-103	(A) 3-8 (B) 3-8	[29]
Edible oils	Dilution (*n*-hexane); SPE (silica)	-	LC-FLD	32-151	1-17	[23]
Edible oils	Dilution *n*-hexane; SPE (Humic acid-bonded silica)	-	LC-FLD	79-103	Intra-day: 1-9 Inter-day: 3-9	[24]
Edible oils	Dilution (*n*-heptane); LLE (4 x 20 mL DMSO); LLE (3 x 50 mL cyclohexane); LLE (2 x 100 mL water)	Column chromatography (silica gel + Na_2SO_4, 200 x 22 mm)	LC-FLD	58-99	N.A.[a]	[30]
Edible oils, fat	Dilution (isohexane:butyldimethylether,)%:5, v/v); SPE (PS-DVB)	-	LC-FLD	60-95	N.A.	[25]
Edible oil, smoked meat	(A) Smoked meat: Saponification (10 mL KOH 2 M in EtOH:water, 9:1, v/v, 1 h); LLE (2 x 2 mL cyclohexane) (B) Oil: Addition 15 mL cyclohexane; LLE (15 mL DMF:water, 9:1, v/v); LLE (15 mL water); LLE (2 x 15 mL cyclohexane)	SPE (aminopropyl, C_{18})	GC-MS	(A) 60-134	N.A.	[17]
Olive oil	(A) SPE (C_{18} Nucleoprep+Florisil) (B) MSPD (C_{18}+Florisil)	-	GC-MS, LP-GC-MS, LC-FLD	(A) 77-79 (B) 55-66	(A) 4-6 (B) 8-11	[26]
Olive oil	Dilution (25 mL *n*-hexane); LLE (50 mL DMSO); addition 120 mL water + 6 g NaCl; LLE (3 x 150 mL cyclohexane); LLE (100 mL water)	-SPE (silica) -Optional: Soxhlet (100 mL MeOH:water, 8:2, v/v + KOH, 4 h); LLE (3 x 150 mL cyclohexane)	GC-MS	52-80[b]	N.A	[22]
Olive oil	HS-SPME (DVB/Car/PDMS 50/30 μm)	-	GC-MS	74-28	Intra-day: 3-16 Inter-day: 1-14	[34]
Olive oil	HS	-	GC-MS(-MS)	96-99	3-9	[33]
Oil, food mixture	PLE (celite + Florisil, *n*-hexane:acetone, 1:1, v/v)	SPE (PS-DVB)	GC-MS/MS	12-70 (in food by isotopic dilution)	3-21 (in food)	[27]
Olive, olive-pomace oil	SLE or LLE (ACN/ *n*-hexane, 83:17, v/v)	GPC (styrene-divinylbenzene copolymer, 5 ml min^{-1} CH_2Cl_2)	GC-MS/MS	84-110	3-8	[32]
Olive pomace oil	Dilution (25 mL *n*-pentane); LLE (15 mL, 2 x 10 mL DMSO); addition 70 mL water; LLE (3 x 50 mL cyclohexane); LLE (100 mL water)	TLC (silica gel)	GC-MS	69-98	4-13	[18]
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 μm)	-	GC-MS	N.A.	Intra-day: 2-5 Inter-day: 2-6	[35]
Vegetable oils	Dilution (*n*-hexane); SPME (Carbopack Z/PDMS, 15 μm)	-	GC x GC-MS	N.A.	3-35	[36]

Fish oil, fish	Homogenization (Na_2SO_4); saponification (10 mL methanolic KOH 1M, 3 h); LLE (2 x 8 mL *n*-hexane)	SPE (Florisil)	GC-MS(/MS)	64-124	1-37	[88]
Fish oil, dried plants	(A) Fish oil: SLE with rotary agitator (3 x CH_2Cl_2/cyclohexane, 1:1, v/v); centrifugation (B) Dried plants: dilution (cyclohexane)	(A), (B) DACC column (Varian Chromspher π, 80 x 3 mm i.d., 5 µm)	LC-FLD	74-120	Intra-day: 2-4 Inter-day: 4-11	[31]
Milk	HS-SPME (PDMS-DVB)	-	GC-MS	90-113	5-15	[40]
Milk	Dilution (water), SPME (PDMS-DVB)	-	GC-MS	88-112	< 20	[41]
Milk	Addition sodium oxalate; LLE (250 mL MeOH); LLE (250 mL diethyl ether); LLE (250 mL petroleum ether)	Column chromatography (silica gel)	GC-MS	40-125	N.A	[37]
Milk	LLE (20 mL cyclohexane:ethyl acetate, 1:1, v/v); centrifugation	SPE (styrene-divinylbenzene copolymer Envi Chrom); addition 2 mL cyclohexane + 2 mL MeOH:water (80:20, v/v); centrifugation; LLE (2 mL cyclohexane); centrifugation PAHs: Cyclohexane fraction; saponification (5 mL KOH 10%, 90ºC, 80 min); addition 3 mL water + 5 mL cyclohexane; centrifugation Hydroxi-PAHs: MeOH layer; LLE (4 mL water:ethyl acetate, 1:1, v/v); centrifugation	GC-MS (Derivatization)	N.A.	N.A.	[38]
Milk	Saponification (4 mL NaOH 0.4M in EtOH:water, 9:1, v/v, 60ºC, 30 min); LLE (2 x 2 mL *n*-hexane)	-	LC-FLD	90-105	Intra-day: 4-10 Inter-day: 7-10	[39]
Liquid non-fatty matrices						
Coffee	LLE (*n*-hexane)	SPE (silica)	LC-FLD	87-103	5-8	[42]
Coffee brew	SPE (BondElut PPL polystyrene-divinylbenzene)	-	LC-FLD	84-89	1-6	[44]
Coffee	MIP-SPE	-	LC-FLD	Coffee: 73	Coffee: 5	[47]
Tea	SPE (C_{18})	-	LC-FLD	44-103	3-17	[45]
Tea infusion	(A) HS-SPME (PDMS-DVB 60 µm) (B) SPME (Confirmation GC-MS, PDMS-DVB 65 µm)	-	LC-FLD, GC-MS (Confirmation)	N.A.	4-16	[48]
Mate tea	SBSE: 10-mm bars coated with PDMS (0.5 mm), room temperature, 2 h, 160 µL ACN:water, 4:1, v/v (desorption)	-	LC-FLD	24-87	1-11	[49]
Beverages	Addition 10% MeOH; MASE (polypropylene, ethyl acetate)	-	GC-MS	65-92	Intra-day: 6-18 Inter-day: 10-18	[51]
Sugarcane juice	(A) SBSE-TD: Addition of NaCl; 10-mm bars coated with PDMS (0.5 mm), room temperature, 3 h (B) MASE: polypropylene, 800 µL cyclohexane	-	GC-MS	(A) 2 (B) 14	(A) 19 (B) 4	[50]
Cachaça (spirit)	LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	70-97	12-21[c]	[43]
Spirits	SPE (C_{18})	-	LC-FLD	82-113	1-9	[46]

Solid fatty matrices						
Meat	Freeze-drying; Soxhlet (25 mL KOH 25% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water)¸ LLE (150 + 100 mL *n*-hexane); LLE (3 x 100 mL water)	SPE (Florisil)	GC-MS	62-91	4-16	[53]
Meat	(A) Freeze-drying; USE (*n*-hexane) (B) Soxhlet (25 mL KOH 50% + MeOH 200 mL, 3 h); addition *n*-hexane (150 mL); LLE (100 mL water)¸ LLE (150 + 100 mL *n*-hexane)	(A), (B) SPE (Florisil)	LC-UV, LC-FLD	(A) 74-111 (B) 72-102	N.A.	[52]
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	58-75	< 20	[57]
Smoked meat	PLE (*n*-hexane, 100ºC, 10 MPa)	-GPC (Bio-Beads S-X3, Cyclohexane:ethyl acetate, 1:1, v/v) -SPE (silica)	GC-EI-MS	N.A.	N.A.	[58]
Smoked meat	Saponification (MeOH + KOH)	SPE (Florisil)	LC-UV, LC-FLD, GC-EI-MS	68-99	N.A.	[54]
Smoked meat	SPME-DED (PDMS 100 µm)	-	GC-MS	N.A.	5-18	[59]
Smoked meat	PLE (*n*-hexane, 100ºC, 100 bar)	-GPC (Bio-Beads S-X3, 420 mm x 25 mm; cyclohexane:ethyl acetate, 1:1, v/v) -Column chromatography (silica)	GC-MS	75-110	3-12	[56]
Fish, smoked meat	(A) Pork: PLE (Supelclean LC-18 + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC) (B) Smoked meat and fish: PLE (C_{18} + Na_2SO_4, CH_2Cl_2:ACN, 90:10, v/v, 1500 psi, 100ºC)	LLE (2 x 1 mL H_2SO_4 9 M); LLE (water); column chromatography (Florisil, 6 g, 1 cm i.d.)	GC-MS	(A) 54-102 (B) 35-93	(A) 4-12 (B) 2-18	[55]
Fish	Homogenization (Na_2SO_4), Soxhlet (CH_2Cl_2:*n*-hexane, 1:1, v/v, 16 h)	Addition water + K_2CO_3 + acetic anhydride; dilution water; LLE (3 x 100 ml CH_2Cl_2); LLE (2 x 2 ml K_2CO_3); column chromatography (silica gel + Na_2SO_4); GPC (2 ml min^{-1} CH_2Cl_2)	GC-MS	N.A.	2.2-20.0	[64]
Fish	(A) Soxhlet (170 ml *n*-hexane:acetone, 1:1, v/v, 6 h) (B) PLE (*n*-hexane:acetone, 1:1, v/v, 100ºC, 10 MPa)	GPC (Bio-Beads S-X3, 500 mm x 8 mm; $CHCl_3$)	LC-FLD	N.A.	N.A.	[62]
Fish	HS-SPME (polyacrilate)	-	GC-MS	N.A	N.A	[69]
Fish	MAE (4 mL saturated KOH in MeOH + 10 mL *n*-hexane, 129ºC); centrifugation	SPE (Silica)	LC-FLD	86-98	1-5	[67]
Fish	Lyophilization; MSPD (C_{18} + Na_2SO_4)	Simultaneous SPE (Florisil + C_{18})	LC-FLD	80-105	2-6	[71]
Fish	Homogenization (Na_2SO_4), Soxhlet (150 mL, CH_2Cl_2, 16 h)	Column chromatography (silica gel + Na_2SO_4, 1 cm i.d.)	GC-MS	Fish: 70-118	< 10	[61]
Fish	QuEChERS method: SLE (ACN); vortex; induced partition ($MgSO_4$+sodium acetate); centrifugation	-	LC-FLD	64-110	< 8	[72]
Fish, seafood	Saponification (10 mL ethanolic KOH 1M, 3 h, 80ºC); addition 10 mL water; LLE (2 x 20 mL cyclohexane)	-	LC-FLD	41-67	3-18	[65]
Fish, seafood	MAE (15 mL acetone, 21 psi, 80 % microwave power)	(A) SPE (Florisil) (B) GPC (Envirosep ABC, 350 mm x 21.2 mm, 5 ml min^{-1} CH_2Cl_2)	GC-MS	N.A.	N.A.	[68]

Fish, mussel	Dilution (NaCl solution 24 %), HS-SPME (PDMS-DVB)	-	GC-MS	8-111	7-15	[70]
Fish, palm dates	Soxhlet (150 mL, *n*-hexane, 8 h)	Column chromatography (silica gel + Florisil + Na_2SO_4)	GC-MS	59-112	1-24	[63]
Shellfish	Freeze-drying; Soxhlet (CH_2Cl_2, 24 h)	-GPC (Bio-Beads S-X3; $CHCl_3$) -Column chromatography (aluminosilicate)	GC-MS	62-123	9-21	[60]
Mussel	Lyophilization; PLE (*n*-hexane:CH_2Cl_2, 1:1, v/v, 150ºC, 150 psi)	Saponification (25 mL KOH 6 M, ambient temperature, 24 h)	GC-MS	64-121	3-30	[66]
Cheese	Saponification (10 mL KOH ethanolic solution); addition water (10 mL); LLE (2 x 20 mL cyclohexane)	SPE (Isolute silica 500 mg)	LC-FLD	84-89	N.A.	[75]
Cheese	Soxhlet (Na_2SO_4 + 170 mL *n*-hexane: CH_2Cl_2, 1:1, v/v, 7 h)	GPC (Bio-Beads S-X3, CH_3Cl)	LC-FLD	52-94	9-34	[73]
Cheese	(A) Cheese: lipid extraction (N.A.); addition 30 mL cyclohexane; LLE (DMF:water, 9:1, v/v); LLE 30 mL cyclohexane	(A), (B) SPE (Silica)	LC-FLD	75-96	N.A.	[74]
Solid non-fatty matrices						
Bread, potato	(A) Bread: Addition 1 mL water; USE (3 mL ethyl ether:CH_2Cl_2, 1:1, v/v) (B) Potato: USE (as explained in (A))	-	LC-FLD, GC-MS (Confirmation)	70-86	4-11	[80]
Cane sugar	SLE (100 mL cyclohexane); LLE (50 mL, 2 x 25 mL DMF:water, 9:1, v/v); addition 100 mL Na_2SO_4 1 %; LLE (50 mL, 2 x 35 mL cyclohexane)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD	74-86	3-22[c]	[81]
Foodstuffs	Soxhlet (150 mL, CH_2Cl_2, 8 h)	Column chromatography (silica gel)	LC-FLD	70-110	Repeatability: < 7 Reproducibility: < 6	[83]
Food supplements	SLE with rotary agitator (3 x cyclohexane/CH_2Cl_2, 1:1, v/v + HF-M + alumina); centrifugation	Column chromatography (silica gel)	LC-FLD	63-116	N.A.	[93]
Fruits, vegetables	Saponification (100 mL KOH methanolic, 5 h); addition MeOH:water (100 mL, 9:1, v/v); LLE (2 x 150 mL cyclohexane); LLE (100 mL MeOH:water, 9:1, v/v; 100 water); LLE (N,N-dimethylformamide:water, 9:1, v/v)	Column chromatography (silica gel-15% water + Na_2SO_4, 200 x 10 mm)	LC-FLD, GC-MS	74-99	3-21	[79]
Ground coffee	PLE (*n*-hexane:acetone, 1:1, v/v; 150ºC)	-Saponification (EtOH+KOH, 30 min) -LLE (100 mL cyclohexane); LLE (3 x 100 mL water) - SPE (silica)	LC-FLD, GC-MS/MS, LC-UV	64-106	1-12	[82]
Tea leaves	USE[c] (3 x 20 mL CH_2Cl_2:acetone, 1:1, v/v)	Column chromatography (silica)	LC-UV	>70	>20	[76]
Tea leaves	Soxhlet (CH_2Cl_2:acetone, 1:1, v/v, 18 h)	SPE (Florisil)	GC-EI-MS	N.A	N.A	[77]
Vegetables	Soxhlet (300 mL *n*-hexane:acetone, 1:1, v/v, 24 h)	SPE (Acid treated silica, aromatic sulfonic acid)	GC-MS	69-111	3-12	[78]

[a] N.A.: Data not available
[b] Values corresponding to isotope labeled compounds
[c] Coefficient of variation
Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; DMF: dimethylformamide; DMSO: dimethylsulfoxide; DVB: divinylbenzene; EtOH: ethanol; GC-MS: gas chromatography coupled to mass spectrometry; GCxGC-MS: multidimensional GC-MS; HF-M: modified diatomaceous earth; HS-SPME: headspace solid-phase microextraction; GPC: gel permeation chromatography; i.d.: internal diameter;

LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LLE: liquid-liquid extraction; LP-GC-MS: low pressure GC-MS; MAE: microwave-assisted extraction; MASE: membrane-assisted solvent extraction; MeOH: methanol; MIP-SPE: molecularly imprinted polymers solid-phase extraction; MSPD: matrix solid-phase dispersion; PDMS: polydimethylsiloxane; PLE: pressurized-liquid extraction; PS-DVB: polystyrene /divinylbenzene; SBSE: stir bar sorptive extraction; SBSE-TD: SBSE-thermal desorption; SFE: supercritical fluid extraction; SLE solid-liquid extraction; SPE: solid-phase extraction; SPME: solid-phase microextraction; SPME-DED: SPME coupled to a direct extraction device; TLC: thin layer chromatography; USE: ultrasound extraction

Table 3
Summary of separation and detection techniques in the discussed matrices

Matrix	*Separation/detection technique*	*Separation remarks*	*Detection remarks*	*LOD (units)*	*LOQ (units)*	*Ref.*
Liquid fatty matrices						
Edible oils	LC-FLD	-Vydac C_{18} (250 x 4.6 mm i.d., 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 330-500 nm	N.A.[a]	0.3-6.0 ng g^{-1}	[21]
Edible oils	LC-FLD	-Vydac C_{18} (250 x 4.6 mm i.d., 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.03-0.2 ng g^{-1}	0.1-8.0 ng g^{-1}	[29]
Edible oils	LC-FLD	-Supelcosil LC-PAH (250 mm x 3 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=240-290 , λ_{em}= 330-484 nm	N.A.	N.A.	[23]
Edible oils	LC-FLD	-Thermo Hypersil ODS (200 mm x 4.6 mm x 5 μm) -Isocratic elution: MeOH:water, 9:1, v/v	λ_{ex}=255 , λ_{em}= 420 nm	0.06 μg kg^{-1}	0.2 μg kg^{-1}	[24]
Edible oils	LC-FLD	-C-18 Lichrocart (125 mm x 4 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=242-350 , λ_{em}= 380-443 nm	0.1-4.0 ng	N.A.	[30]
Edible oils, fat	LC-FLD	- (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-300 , λ_{em}= 376-418 nm	0.2-0.8 μg kg^{-1}	N.A.	[25]
Edible oil, smoked meat	GC-EI-MS	-Injection : Pulsed splitless -Supelco SPB-5 (25 m x 0.20 mm x 0.33 μm)	Q, SIM	0.06 μg kg^{-1}	0.20 μg kg^{-1}	[17]
Olive oil	(A) GC-EI-MS (B) LP-GC-EI-MS (C) LC-FLD (D) DACC	(A) Injection: N.A.; DB-5ms (30 m × 0.25 mm, 0.25 μm) (B) Injection: N.A.; Rapid MS FS CP-Sil 8 (10 m × 0.53 mm, 0.50 μm) + restrictor (0.6 m x 0.25 mm) (C) CP EcoSpher 4 PAH (150 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v) (D) CP ChromSpher π (20 mm × 3 mm); isocratic elution: ACN:water (85:15, v/v)	(A),(B) SIM (C), (D) λ_{ex}=370 , λ_{em}= 470 nm	(A) 1 ng g^{-1} (B) 1.6 ng g^{-1} (C) 0.5 ng g^{-1} (D) 0.3 ng g^{-1}	(A) 3.4 ng g^{-1} (B) 5.5 ng g^{-1} (C) 1.7 ng g^{-1} (D) 1.1 ng g^{-1}	[26]
Olive oil	GC-EI-MS	-Injection: Pulsed splitless -HP-5ms, (60 m x 0.25 mm x 0.25 μm)	Q, SIM	N.A	N.A	[22]
Olive oil	GC-EI-MS	-Injection: Splitless -Supelcowax-10 and HP-5ms, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	0.05-1.60 μg kg^{-1}	0.20-5.20 μg kg^{-1}	[34]
Olive oil	GC-EI-MS(/MS)	-Injection: Splitless -VF-5ms, 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 μm)	QqQ, SIM, SRM	0.02-0.06 μg kg^{-1}	0.07-0.26 μg kg^{-1}	[33]
Oil, food mixture	GC-EI-MS/MS	-Injection: N.A. -Zebron ZB-5ms, (30 m x 0.25 mm x 0.25 μm)	QqQ, SRM	0.008-0.150 μg kg^{-1} (dry weight)	0.024-0.920 μg kg^{-1} (dry weight)	[27]
Olive, olive-pomace oil	GC-EI-MS/MS	-Injection: LVI + PTV -HP-5, crosslinked 5% phenyl-95% methylpolysiloxane, (30 m x 0.25 mm x 0.25 μm)	IT, Product-ion scan, Resonant mode	0.05-0.07 μg kg^{-1}	0.1-0.2 μg kg^{-1}	[32]
Olive pomace oil	GC-EI-MS	-Injection: splitless -DB-5ms (30 m x 0.25 mm x 0.20 μm)	IT, Full scan	0.1-0.4 μg kg^{-1}	N.A	[18]
Vegetable oils	GC-EI-MS	-Injection: Splitless -SPB-5, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	0.2 μg kg^{-1}	0.5 μg kg^{-1}	[35]

Vegetable oils	GCxGC-EI-MS	-Injection: Splitless -First dimension: SGE BPX5, (30 m x 0.25 mm x 0.25 µm) -Second dimension: SGE BPX50, 50% phenyl polysilphenylenesiloxane (1 m x 0.1 mm x 0.1 µm)	TOF, Full scan	0.1-1.4 µg kg^{-1}	0.4-4.6 µg kg^{-1}	[36]
Fish oil, fish	(A) GC-EI-MS/MS (B) GC-EI-MS (Confirmation)	(A), (B) Injection: Splitless; HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	(A) QqQ, SRM (B) TOF, Full scan	0.02-1.25 µg kg^{-1}	0.125-1.250 µg kg^{-1}	[88]
Fish oil, dried plants	LC-FLD	-Varian Pursuit 3 PAH (100 mm × 4.6 mm × 1/4'') -Gradient elution: A: ACN; B: MeOH; C: water	λ program: λ_{ex}=222-380 , λ_{em}= 353-499 nm	0.07-7.80 µg kg^{-1}	0.13-16 µg kg^{-1}	[31]
Milk	GC-EI-MS	N.A.	Q, SIM	0.2-5.0 ng l^{-1}	0.7-16.6 ng l^{-1}	[40]
Milk	GC-EI-MS	-Injection: Splitless -HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.003-1.56 µg l^{-1}	N.A.	[41]
Milk	GC-EI-MS	-Injection: N.A. -DB-XLB, proprietary phase, (60 m x 0.25 mm x 0.25 µm)	Q, SIM	N.A	N.A	[37]
Milk	GC-EI-MS	-Injection: Splitless -OV-1, (30 m x 0.25 mm x 0.25 µm)	-Q, SIM -Derivatization: (MSTFA)	0.04-0.39 ng mL^{-1}	N.A.	[38]
Milk	LC-FLD	-Wakosil-PAHs (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: MeOH:water, 8:2, v/v	λ program: λ_{ex}=248-364 , λ_{em}= 360-500 nm	1.3-76.0 ng kg^{-1}	N.A.	[39]
Liquid non-fatty matrices						
Coffee	LC-FLD	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=274-300 , λ_{em}= 406-470 nm	0.01-0.05 µg L^{-1}	0.04-0.20 µg L^{-1}	[42]
Coffee	LC-FLD	-C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=230-250 , λ_{em}= 410-420 nm	0.8-10.0 ng L^{-1} [b]	2.5-33.2 ng L^{-1} [c]	[44]
Coffee	LC-FLD	-Isocratic elution: ACN:water, 4:6, v/v -Phenomenex Envirosep PP (125 mm x 3.2 mm)	λ program: λ_{ex}=252-300 , λ_{em}= 322-500 nm	N.A.	N.A.	[47]
Tea	LC-FLD	-Nova-Pak C_{18} (150 mm x 3.9 mm x 4 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-295 , λ_{em}= 365-465 nm	0.016-0.140 ng mL^{-1}	N.A.	[45]
Tea infusion	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) LiChrospher PAH, modified RP-18 silica gel (250 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (B) Injection: Splitless; HP-5ms, (30 m x 0.25 mm x 0.25 µm)	(A) λ program: λ_{ex}=250 , λ_{em}= 330-500 nm (B) Q, SIM	5-145 ng L^{-1}	N.A.	[48]
Mate tea	LC-FLD	-Vydac 201TP52 (250 x 2.1 mm i.d., 5 µm) -Gradient elution: A: ACN; B: water		0.1-8.9 ng L^{-1}	0.3-30 ng L^{-1}	[49]
Beverages	GC-EI-MS	-Injection: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	3-27 ng L^{1}	30-133 ng L^{-1}	[51]
Sugarcane juice	GC-EI-MS	-Injection: (A) SBSE: Splitless; (B) MASE: LVI + PTV -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	(A) 0.04 µg L^{-1} (B) 0.06 µg L^{-1}	N.A.	[50]
Cachaça (spirit)	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) Vydac 201TP54 (250 mm x 4.6 mm x 5 µm); isocratic elution: ACN/water (75:25, v/v) (B) Injection: Splitless + PTV; HP-5ms, (30 m x 0.25 mm x 0.25 µm)	(A) λ_{ex}=290 , λ_{em}=430 (B) Q, SIM	0.006-0.090 µg L^{-1}	N.A.	[43]
Spirits	LC-FLD	- C18 Supelcosil LC-PAH (250 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=270-356 , λ_{em}= 330-500 nm	$1.08 \cdot 10^{-3}$-$1.28 \cdot 10^{-2}$ µg L^{-1}	0.11-0.93 µg L^{-1}	[46]

Solid fatty matrices						
Meat	GC-EI-MS	-Injection: splitless -DB-5ms (30 m x 0.32 mm x 0.25 µm)	IT, Full scan	5-50 pg	N.A.	[53]
Meat	(A) LC-UV (B) LC-FLD	-ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm) -Gradient elution: A: ACN; B: water	(A) λ = 254 nm (B) λ program: λ_{ex}=254-270 , λ_{em}= 340-420 nm	(A) 0.03-1.54 ng (B) Not detected-6 pg	N.A.	[52]
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.001-0.049 µg kg^{-1}	N.A	[57]
Smoked meat	GC-EI-MS	-Injection: splitless -TR-50MS, 50% phenyl polysilphenylene-siloxane (10 m x 0.1 mm x 0.1 µm)	Magnetic sector, Full scan	0.001-0.045 µg kg^{-1}	N.A	[58]
Smoked meat	(A) LC-UV (B) LC-FLD (C) GC-EI-MS (Confirmation)	(A), (B) ED Envirosep-pp C18 column (125 mm x 4.6 mm x 5 µm); gradient elution: A: ACN; B: water (C) Injection: splitless; DB-5ms (30 m x 0.32 mm x 0.25 µm)	(A) λ = 254 nm (B) λ program: λ_{ex}=254-320 , λ_{em}= 340-533 nm (C) IT, Full scan	(A) 0.03-1.54 ng (B) $2\cdot10^{7}$ -6 pg (C) 5-50 pg	N.A.	[54]
Smoked meat	GC-EI-MS	-Injection: Splitless -HP-5, (50 m x 0.32 mm x 1.05 µm)	Q, SIM	0.008-0.102 ng mL^{-1}	N.A.	[59]
Smoked meat	GC-EI-MS	-Injection: Splitless -DB-5ms, (60 m x 0.25 mm x 0.25 µm)	Magnetic sector, SIR	N.A.	N.A.	[56]
Fish, smoked meat	GC-EI-MS	-Injection: Splitless -HP-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	0.002-0.100 µg mL^{-1}	N.A.	[55]
Fish	GC-EI-MS	-Injection : Pulsed splitless -DB-5ms, (30 m x 0.25 mm x 0.25 µm)	Q, SIM	2-7 ng g^{-1} [b]	N.A.	[64]
Fish	LC-FLD	-LiChroCART (250 mm x 4.0) with LiChrospher PAHs sorbent -Gradient elution: A: ACN; B: water	λ program: λ_{ex}= 217- 295, λ_{em}= 341-484 nm	N.A.	N.A.	[62]
Fish	GC-EI-MS	-Injection: Splitless -HP-5ms, (60 m x 0.25 mm x 0.25 µm)	Q	N.A	N.A	[69]
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.1-0.5 ng g^{-1} (dry weight)	0.2-1.8 ng g^{-1} (dry weight)	[67]
Fish	LC-FLD	-Vydac 201TP52 (250 mm x 2.1 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=245-294 , λ_{em}= 410-500 nm	0.04-0.32 ng g^{-1}	0.13-1.07 ng g^{-1}	[71]
Fish	GC-EI-MS	-Injection: Splitless -DB-5ms, 5% phenyl 95% dimethyl arylene siloxane(30 m x 0.25 mm x 0.25 µm)	IT, Full scan	0.02-1.70 µg ml^{-1}	0.06-5.00 µg ml^{-1}	[61]
Fish	LC-FLD	-CC 150/4 Nucleosil 100-5 C18 PAH (150 mm x 4.0 mm x 5 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=315-590 , λ_{em}= 260-290 nm	0.04-0.56 ng g^{-1}	0.12-1.90 ng g^{-1}	[72]
Fish, seafood	LC-FLD	-Phenomenex C18 Envirosep (125 mm x 4.6 mm x 3 µm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=250-290 , λ_{em}= 380-450 nm	0.01-0.49 ng g^{-1}	0.02-0.62 ng g^{-1}	[65]
Fish, seafood	GC-EI-MS	-Injection: Splitless -HP-5, (30 m x 0.25 mm x 0.25 µm)	Q, Full scan	N.A.	N.A.	[68]
Fish, mussel	GC-EI-MS	-Injection: Splitless -HP-5ms, 5% diphenyl-95% dimethyl polysiloxane, (30 m x 0.25	Q, SIM	8-450 pg g^{-1}	50-1500 pg g^{-1}	[70]

		mm x 0.25 μm)				
Fish, palm dates	GC-EI-MS	-Injection: Splitless -CP-SIL 8CB-MS arylene-modified 5% phenyl-95% methyl polydimethylsiloxane (30 m x 0.25 mm x 0.25 μm)	IT, SIS	0.13-4.29 μg l^{-1}	0.43-14.29 μg l^{-1}	[63]
Shellfish	GC-EI-MS	-Injection: Splitless -VF-5ms, (30 m x 0.25 mm x 0.25 μm)	IT, SIS	0.52-0.81 ng g^{-1} [b]	N.A.	[60]
Mussel	GC-EI-MS	-Injection: Splitless -DB-5, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	0.5-8.0 μg kg^{-1} (dry mass)	N.A.	[66]
Cheese	LC-FLD	-Envirosep-PP (125 x 4.6 mm i.d., 4.6 μm) -Isocratic elution: ACN/water (88:12, v/v)	λ_{ex}=295 , λ_{em}= 404 nm	0.006 μg kg^{-1}	0.021 μg kg^{-1}	[75]
Cheese	LC-FLD	-Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=216-295 , λ_{em}= 320-484 nm	0.01-0.25 μg kg^{-1}	N.A.	[73]
Cheese	LC-FLD	-Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm) -Gradient elution: A: ACN; B: water	λ program: λ_{ex}=224-268 , λ_{em}= 320-400 nm	N.A.	0.01-0.90 μg kg^{-1}	[74]
Solid non-fatty matrices						
Bread, potato	(A) LC-FLD (B) GC-MS/MS (Confirmation)	(A) Hypersil Green PAH (100 mm x 4.6 mm x 5 μm); gradient elution: A: ACN; B: water (B) Injection: Splitless; VA-5, (30 m x 0.25 mm x 0.25 μm)	(A) λ program: λ_{ex}=250-300 , λ_{em}= 325-465 nm (B) Q, full scan	0.007-6.400 μg L^{-1}	0.023-21.300 μg L^{-1}	[80]
Cane sugar	LC-FLD	-Vydac 201TP54 (250 mm x 4.6 mm x 5 μm) -Isocratic elution: ACN/water (75:25, v/v)	λ_{ex}=290 , λ_{em}=430	0.01-0.17 μg kg^{-1}	N.A.	[81]
Foodstuffs	LC-FLD	-Spherisorb ODS2-C_{18} (250 mm x 4.6 mm i.d., 5 μm) -Gradient elution: A: ACN; B: water	λ_{ex}=250-300 , λ_{em}= 330-500 nm	0.0007-0.013 ng μL^{-1} [b]	N.A.	[83]
Food supplements	LC-FLD	-Varian C_{18} Pursuit 3 PAH (100 mm x 4.6 mm i.d., 3 μm) -Gradient elution: A: ACN; B: MeOH; C: water	N.A.	0.1-29.8 μg kg^{-1}	0.2-59.7 μg kg^{-1}	[93]
Fruits, vegetables	(A) LC-FLD (B) GC-EI-MS (Confirmation)	(A) C18 Vydac 201 TP (250 mm x 4.6 mm i.d., 5 μm); isocratic elution: ACN:water (75:25, v/v) (B) Injection: Splitless; Supelco 5% diphenyl-95% dimethylpolysiloxane, (30 m x 0.25 mm x 0.25 μm)	(A) λ_{ex}=290 , λ_{em}= 430 nm (B) Q, SIM	(A) 0.07-1.29 μg kg^{-1} [b]	N.A.	[79]
Ground coffee	(A) LC-FLD (B) GC-MS/MS (Confirmation) (C) LC-UV (Confirmation)	(A) Supelcosil LC-PAH (250 mm x 4.6 mm x 5 μm); gradient elution: A: ACN; B: water (B) Injection: programmed temperature vaporization; Rtx-5MS (30 m x 0.25 mm x 0.25 μm) (C) C18 Supelcosil LC-PAH (150 mm x 3.0 mm x 5 μm); gradient elution: A: ACN; B: water	(A) λ program: λ_{ex}=220-286 , λ_{em}= 340-420 nm (B) IT, Product ion scan	0.11-0.18 μg kg^{-1} [b]	N.A	[82]
Tea leaves	LC-UV	-Elution: N.A. -Agilent C-18 (250 mm x 4.6 mm)	N.A.	0.16-1.27 μg kg^{-1}	N.A.	[76]
Tea leaves	GC-EI-MS	-Injection: N.A. -HP-5ms (30 m x 0.25 mm x N.A.)	Q	N.A	N.A	[77]
Vegetables	GC-EI-MS	-Injection: Splitless -HP-5ms, (30 m x 0.25 mm x 0.25 μm)	Q, SIM	N.A.	N.A.	[78]

[a] N.A.: Data not available
[b] Method detection limit (MDL)
[c] Method quantification limit (MQL)

Abbreviations: ACN: acetonitrile; DACC: donor-acceptor complex chromatography; GC-EI-MS: gas chromatography coupled to mass spectrometry operating in electronic ionization; GC-EI-MS/MS: GC coupled to tandem MS; GCxGC-MS: multidimensional GC-EI-MS; IT: ion trap analyzer; LC-FLD: liquid chromatography coupled to fluorescence detection; LC-UV: LC coupled to ultraviolet-Vis detection; LP-GC-EI-MS low pressure GC-MS in electronic ionization; LVI: large-volume injection; MASE: membrane-assisted solvent extraction; MeOH: methanol; MSTFA: N-methyl-N-(trimethylsilyl)trifluoroacetamide; PTV: programmed-temperature vaporization; Q: single quadrupole analyzer; QqQ: triple quadrupole analyzer; SBSE: stir bar sorptive extraction; SIM: single-ion monitoring; SIR: selected ion recording; SIS: selected-ion storage; SRM: selected-reaction monitoring; TOF: time of flight analyzer; λ_{ex}: excitation wavelength; λ_{em}: emission wavelength

Table 4
Summary of analyzed PAHs and concentrations found in real samples

Analytes	*Type of sample*	*Concentration*[a]	*Observations*	Reference
	Liquid fatty matrices			
16 EPA PAHs[b]	Edible oils	0.3 (BaA, IP)[c]−1145 (PHE)[d] ng g^{-1}	47 samples	[21]
BaP	Edible oils	Refined oil: < 1.5 μg kg^{-1} Unrefined oil: > 2 μg kg^{-1}	8 samples (refined, unrefined oils)	[24]
ACP, ANT, BaP, BeP, BghiP, CHR, COR, CPdefPHE, PHE, PYR	Edible oils	Refined vegetable oil: 40.2 μg kg^{-1} (total PAH content) Olive oil: 624 μg kg^{-1} (total PAH content)	296 samples	[30]
BaP	Olive oil	84−89 ng g^{-1}	48 samples	[26]
16 EPA PAHs + 4 EU PAHs[b] + (> 35)	Olive oil	0.30 − 320 (3-methylCHR) μg kg^{-1}	5 samples (olive pomace oil)	[22]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR + 2 alkyl derivatives	Olive oil	0.4 (ACP, ACY) − 26 (PHE) μg kg^{-1}	10 samples (extra virgin olive oil)	[34]
BkFA, BghiP, BeP, BaP	Olive, olive-pomace oil	0.3 (BghiP, BeP, BaP) − 88.7 (BkFA) μg kg^{-1}	25 samples (virgin olive oil, olive pomace oil)	[32]
ACP, ACY, ANT, BaA, BbFA, BjFA, BkFA, BcF, BghiP, BaP, CHR, CPcdP, DBahA, DBaeP, DBahP, DBaiP, DBalP, FA, FLR, IP, MCH, NPH, PHE, PYR,	Vegetable oils	0.5 (BaP) − 133.2 (CHR) μg kg^{-1}	14 samples (olive oil, extra virgin olive oil, pomace olive oil, sunflower oil)	[36]
16 EPA PAHs	Fish oil, fish	Fish: 0.06 (BaA) − 11.4 (PYR) μg kg^{-1} Fish feed: 0.2 (ACP, ACY) − 242 (NPH) μg kg^{-1} Fish oil: 0.3 (ACP, BbFA, BkFA) − 38.2 (PHE) μg kg^{-1} Linseed oil: 0.3 (BaP) −16.7 (FA) μg kg^{-1} Palm oil: 0.2 (ACY) −1.4 (BaP) μg kg^{-1} Rapeseed oil: 0.2 (ACY) −1.9 (NPH) μg kg^{-1}	-31 samples (fish, fish feed, fish oil, linseed oil, palm oil, rapeseed oils) -Fish exposed to long-term feed trials	[89]
ACP, ACY, ANT, BaA, CHR, FA, FLR,	Milk	31.9 (PYR) − 160.5 (PHE) μg L^{-1}	10 samples	[40]

NPH, PHE, PYR				
16 EPA PAHs	Milk	Only 8 PAHs found: ACP, ACY, ANT, BaA , FA, FLR, NPH, PYR Control: 0.3 (ACP) − 6.4 (NPH) ng g^{-1} (milk fat) Cementwork: 0.2 (ACP) −16.2 (FLR) ng g^{-1} (milk fat) Motorway: 0.5 (ACP) − 10.7 (FLR) ng g^{-1} (milk fat) Combined sources: 0.8 (ACP) − 15.2 (NPH) ng g^{-1} (milk fat)	-14 samples (control, cementwork, motorway, combined sources) -Average values	[37]
ANT, BaP, BaA, BbFA, BkFA, BghiP, CHR, DBahA, FA, IP, PHE, PYR	Milk	Milk: 0.01 (ANT, IP) − 0.35 (BbFA) µg kg^{-1} Infant formula: 0.02 (ANT) − 0.40 (PHE) µg kg^{-1}	17 samples (commercial milk and infant formula)	[39]
	Liquid non-fatty matrices			
BaA, BbFA, BkFA, BaP, BghiP, DBahA, IP	Coffee	0.01 (all except BbF) – 0.1 (BbFA) µg kg^{-1}	12 samples (with and without caffeine, natural roasting)	[42]
BaP	Coffee	1.1 ng g^{-1}	1 sample (standard addition method)	[47]
ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, NPH, PHE, PYR	Tea infusion	4 PAHs found: 6.6 (PHE) – 82 (FLR) ng mL^{-1}	6 samples	[48]
16 EPA PAHs (except ACY)	Mate tea	1.4 (BaA) – 1156 (ACP) ng L^{-1}	11 samples	[49]
BaP	Sugarcane juice	0.05 – 0.11 µg L^{-1}		[50]
BaA, BbFA, BkFA, BaP, DBahA	Cachaça (spirit)	0.01 (BkFA) – 0.83 (BbFA) µg L^{-1}	25 samples	[43]
16 EPA PAHs (except ACY)	Spirits	From burned sugar cane: 0.003 (BghiP) – 138 (BaA) µg L^{-1} From non-burned sugar cane: 0.002 (BaP) – 3.13 (PHE) µg L^{-1}	131 samples (from burned and non-burned sugar cane crops)	[46]
	Solid fatty matrices			
16 EPA PAHs	Smoked meat	< 0.20 (BaA, BbFA, BkFA, BaP, BghiP, CHR, FA, PY) −38.59 (PHE) µg kg^{-1}	7 samples (smoked meat)	[17]
15 EU PAHs + BcF	Smoked meat	Before processing: 0.003 (DBalP) – 0.101 (BcF) µg kg^{-1} Traditional smokehouse: 0.002 (DBahP, DBalP) – 2.134 (BcF) µg kg^{-1} Industrial smokehouse: 0.003 (DBahA, DBalP) – 1.539 (BcF) µg kg^{-1}	22 samples (before processing and traditional and industrial smokehouse)	[57]
15 EU PAHs + BcF	Smoked meat	0.001 (DBaHP, DBalP) – 10.6 (BcF) µg kg^{-1}	32 samples	[58]

BaA, BbFA, BkFA, BghiP, BaP, CHR, DBahA, FA, IP, PYR	Smoked meat	0.1 (DBahA, BbFA) – 26.22 (FA) µg kg^{-1}	18 samples	[56]
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.2 (BaA) – 51.4 (BbFA) ng g^{-1}	10 samples	[67]
BaA, BbFA, BkFA, BaP, DBahA, IP	Fish	14.37 (BaP) – 42.49 (BbFA) ng g^{-1}	10 samples	[71]
16 EPA PAHs	Fish	0.42 (ACY) – 34.48 (BghiP) µg g^{-1}	Number of samples not defined	[61]
16 EPA PAHs (except ACY) + DBalP	Fish	0.12 (PHE) – 4.99 (NPH) ng g^{-1}	27 samples	[72]
ANT, BaA, BbFA, BkFA, BaP, BghiP, CHR, DBahA, FA, IP, PYR	Fish, seafood	Summer: 0.12 (ANT) – 23.23 (PYR) ng g^{-1} (average values) Winter: 0.35 (FA) – 46.01 (CHR) ng g^{-1}(average values)	Number of samples not defined	[65]
ACP, ACY, ANT, FA, FLR, NPH, PHE, PYR	Fish, mussel	0.52 (NPH) – 8.00 (PHE) ng g^{-1}	-8 samples -PAHs showing up to 4 rings	[70]
16 EPA PAHs	Shellfish	24.4 – 140.0 ng g^{-1} (total PAH content)	10 samples	[60]
BaP	Cheese	Samples smoked with straw/cardboard: 0.38 – 2.40 µg kg^{-1} Samples smoked with wood shavings/ liquid smoke flavorings: 0.18 – 0.80 µg kg^{-1}	96 samples	[75]
16 EPA PAHs	Cheese	0.01 (BkFA, BaP, DBahA) – 60.0 (NPH, PHE) µg kg^{-1}	36 samples	[73]
16 EPA PAHs	Cheese	0.12 – 6.21 µg kg^{-1} (total PAH content)	-16 samples -Analysis before and after smoking	[74]
	Solid non-fatty matrices			
16 EPA PAHs (except ACY) + BeP	Bread, potato	Mashed potato: 9.35 – 17.10 µg kg^{-1} (total PAH content) Potato: 8.47 – 17.20 µg kg^{-1} (total PAH content) Toasted bread: 7.38 – 18.00 µg kg^{-1} (total PAH content)	5 samples	[80]
BaA, BbFA, BkFA, BaP, DBahA	Cane sugar	Typical sugar: 0.015 (BaP) – 0.300 (BaA) µg kg^{-1}(average values) Organic sugar: 0.002 (BkFA) – 0.104 (BaA) µg kg^{-1}(average values)	57 samples (18 organic samples)	[81]
16 EPA PAHs (except ACY)	Foodstuffs	0.08 (ANT) – 61.4 (PYR) ng g^{-1}	Number of samples not defined	[83]
15 EU PAHs + BcF	Food supplements	0.02 (BaA, BkFA, BghiP, DAaeP) – 32.50 (BcF) µg kg^{-1}	20 samples	[96]
BaA, BbFA, BkFA,	Fruits, vegetables	Lettuce: 0.08 (BaP) – 8.68 (FA) µg kg^{-1} (average values)	Number of samples not	[79]

BaP, BeP, BghiP, CHR, DBahA, FA, PYR		Tomato: 0.08 (BaP) – 6.19 (FA) $\mu g\ kg^{-1}$(average values) Cabbage: 0.06 (BkFA) – 5.53 (BkFA) $\mu g\ kg^{-1}$(average values) Fruits: 0.08 (BaP) – 6.22 (BghiP) $\mu g\ kg^{-1}$(average values)	defined (combined samples of lettuce, tomato, cabbage, apple, grape and pear)	
16 EPA PAHs	Tea leaves	Leaves: 0.42 (ANT) – 83.40 (PYR) $\mu g\ kg^{-1}$(dry mass) Crude tea: 2.35 (DBahA) – 1120.00 (PHE) $\mu g\ kg^{-1}$(dry mass) Tea: 8.42 (DBahA) – 3930.00 (PHE) $\mu g\ kg^{-1}$(dry mass)	-6 samples -Leaves analyzed during the whole tea manufacturing process	[76]
ACP, ACY, ANT, BaA, BbFA, BkFA, BaP, CHR, FA, FLR, IP, NPH, PHE, PYR	Vegetables	Potato: 0.23 (ACY) – 459 (IP) $\mu g\ kg^{-1}$(average values) Carrot: 0.40 (NPH) – 291 (IP) $\mu g\ kg^{-1}$(average values)	21 samples (organic agriculture)	[78]

[a] Compounds showing the minimum and maximum values of the range are shown in parentheses
[b] For more details see Table 1
[c] Compound(s) showing the minimum concentration found
[d] Compound(s) showing the maximum concentration found
Abbreviations: COR: Coronene; BeP: Benzo[*e*]pyrene; CPdefPHE: Cyclopenta[*d,e,f*]phenanthrene; 3-methylCHR: 3-methylchrysene; BcF: Benzo[*c*]fluorene; BeP: Benzo[*e*]pyrene (For other abbreviations see Table 1)

Miscellaneous

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