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1 **Environmental analysis of polar and non-polar Polycyclic Aromatic**
2 **Compounds in airborne particulate matter, settled dust and soot: Part I:**
3 **Sampling and sample preparation**

4

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22

23 **Abstract**

24

25 Interests in Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives (nitrated PAHs,
26 oxygenated PAHs, Azaarenes and Polycyclic Aromatic Sulfur Heterocycles) have been growing
27 because of their toxicity.

28 The first part of this review gathers information on sampling of Polycyclic Aromatic Compounds
29 (PACs) in airborne particulate matter (PM), dust and soot, on their extraction thanks to solvent
30 extraction methods, and on sample clean-up for further analysis.

31 Atmospheric PM is generally sampled on quartz-fiber filters. For settled dust as well as for PM,
32 active samplers are used in most cases.

33 After sampling, solid/liquid extraction is necessary. At this step, yields can be enhanced
34 depending on the device and solvent used, but also with optimization of solvent volume and
35 extraction time. Most up-to-date extraction devices are Pressurized Liquid Extraction (PLE),
36 Ultrasound Assisted Extraction (UAE) and Microwave Assisted Extraction (MAE).

37 After the extraction, sample purification (generally by SPE) and concentration is advised.

38

39 **Keywords**

40

41 PAHs, Nitrated PAHs, Oxygenated PAHs, Azaarenes, PASHs, Sampling, Extraction

42

1. Introduction

PAHs have been reported as major hazardous compounds in various environments for decades. From the 1970s, efforts have been made in the United States of America to define a list of priority pollutants, finally resulting in the well-known U.S. EPA's 16 PAH Priority Pollutants list [1].

The toxicity, carcinogenicity and mutagenicity of PAHs have been assessed and reported by the International Agency for Research on Cancer (IARC) since 1983 with regular updates [2–5], but due to the high number of compounds which can be classified as PAHs, it can be tough to assess with certainty the human health risks related to various individual PAHs in environmental samples. Indeed, about 500 PAHs have already been detected in ambient air, and PAHs exposure always happens with complex mixtures [5,6]. Therefore, relying only on individual PAHs or on the sum of the 16 EPA PAHs is not sufficient for a reliable evaluation [7].

Methods have been developed to characterize health and environmental risks based on a single reference compound : Benzo[a]Pyrene (B[a]P), the first PAH to have been thoroughly studied in terms of toxicology [6,8,9]. Toxic Equivalency Factor (TEF) and Potency Equivalency Factor (PEF) approaches with respect to B[a]P have been implemented by various authors to summarize the risks related to PAH occurrence in the environment [8,10–12]. However, even with such kinds of approaches, the PAHs-related carcinogenicity of a sample can be underestimated. Indeed, TEFs and PEFs should be handled with care as they are often approximations. Moreover, for too long, many toxic PAHs with potencies comparable to or higher than B[a]P have been neglected [7,12].

Furthermore, a lot of risk assessment studies are restricted to Polycyclic Aromatic Hydrocarbons in the narrow sense of the term. This can be a major shortcut, since there is growing evidence that polar Polycyclic Aromatic Compounds (PACs) are crucial compounds in terms of toxicity, carcinogenicity and mutagenicity. Indeed, some of them have a more significant toxicology than the non-polar PAHs, because unlike PAHs, they do not require a prior enzymatic activation to exert their toxicity [10,13,14]. Thus, nitrated PAHs for instance have been reported as accounting for over half of the total direct mutagenicity of ambient air [15]. Among polar PACs, nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs) are the most studied [16–18].

In addition to NPAHs and OPAHs, other polar PACs are of a growing interest: azaarenes (AZAs), sometimes alternatively referred to as Polycyclic Aromatic Nitrogen Heterocycles (PANHs), and Polycyclic Aromatic Sulfur Heterocycles (PASHs). While AZAs are quite similar to the above-mentioned PAHs, NPAHs and OPAHs in terms of sources and

80 toxicology [10,19,20], PASHs are particularly typical of petrogenic emissions and have been
81 studied sooner in the evolution of environmental analysis of PACs [21,22]. Both categories
82 have also been studied by the IARC and some of their compounds have been classified as
83 possible or probable carcinogens [23].

84 To illustrate chemical differences between these categories of PACs, Figure 1 gathers the
85 chemical structures of 3-ring oxygenated, nitrated, nitrogen heterocycle and sulfur
86 heterocycle variants of anthracene.

87

88 Airborne particulate matter, dusts and soots have been widely described as major sources of
89 exposure to PAHs for human beings in indoor [24–30] as well as in outdoor environments
90 [30–33]. Naturally, these matrices also play an important role in the exposure to polar PACs
91 and their content of polar PACs has been growingly reported in recent years [20,31,33–38].

92 For PACs occurrence studies, particular focuses have been made on atmospheric particulate
93 matter (PM_{10} , $PM_{2.5}$ and PM_1) because of its well-known negative health effects [18,39].

94 These effects are especially pronounced for the smallest of these particles, because of their
95 higher surface area per unit mass, in addition to their deeper penetration into lungs [40,41].

96 According to the IARC, “there is sufficient evidence in humans for the carcinogenicity of
97 particulate matter in outdoor air pollution” [42]. PACs account for an important part of this
98 carcinogenicity.

99 Other particulate matters such as settled dusts of indoor environments [24,25,27–29],
100 “environmental” third-hand smoke (ETS) [43–46], urban road dust [32,47–49], particulate
101 exhausts and soots from vehicular emissions [32,50–52], are also of a great concern
102 because of their ability to host toxic semi-volatile organic compounds (SVOCs) such as
103 PACs.

104

105 The purpose of this paper is to review the different options available to analytical scientists
106 willing to implement methods for the determination of polar and non-polar Polycyclic
107 Aromatic Compounds in airborne particulate matter, dust and soot, especially for
108 environmental evaluation of human exposure pathways to these pollutants.

109 In a first part, we will focus on the sampling methods applicable to airborne particulate matter
110 and settled dust, and on the preparation of such particulate samples for an optimal extraction
111 of the analytes and a good clean-up of the sample.

112

2. Sampling

2.1. Atmospheric particulate matter

In terms of sample collection techniques, only a few possibilities are currently implemented in the different studies about PACs analysis in atmospheric PM.

In the vast majority of cases, PM are collected on quartz-fiber filters (QFF) [20,36,53–60].

The main advantages of QFFs over glass-fiber filters (GFF), which can also be used for this kind of sampling [37,61,62], are the higher purity of the material, leading to lower blank levels [63], and its higher thermal stability, enabling the determination of organic and elemental carbon (OC/EC) by calcinating the filter at up to 850°C [36,64,65], a temperature range at which glass filters would be degraded. Therefore, QFF seem to be a better choice than GFF.

An alternative to siliceous materials is the use of organic filters such as PTFE membrane filters [45,66–68]. Generally speaking, these latter are less employed for organic pollutants analysis because of their higher content in organic compounds, increasing the risk of contamination in comparison to their inorganic counterparts. In the other hand, as a drawback, glass and quartz show a much higher physical fragility than PTFE.

Inorganic filters are generally baked out at very high temperatures ($\geq 350^\circ\text{C}$) for 6 to 24 hours for their decontamination prior to sampling [36,37,54–56,58,65]. The poor thermal stability of organic filters disables this treatment, which is why washing with organic solvents is preferable [69]. Such solvent washings are also applicable to inorganic filters [20]. Some authors rather proposed a “mild” conditioning of their PTFE filters at stable temperature (20 to 25°C) and humidity (40 to 50%) for 24 to 48 hours [59,66]. This accounts for the absorption of water vapor [70].

For PM collection, sampling heads designed for PM₁₀ or PM_{2.5} are generally adapted on active air samplers [36,45,56,59]. To get more accurate information about the PACs size-fractionation in atmospheric PM, it is possible to use devices differentiating various fractions of PM according to their size.

The most used is the cascade impactor [19,34,57,60,66,71–74]. This device is based on the progressive removal of particles of higher aerodynamic diameter, so that particles of various diameters can be separated into multiple (from 4 to 13) fractions, from the sub-0.1µm range to particles larger than 10µm. The theory of the cascade impactor has been described more precisely by Liaud et al. [61]. The only influence of the use of a cascade impactor instead of “classical” sampling heads on the design of the pumping system is that the selected air flow should meet the requirements prescribed by the impactor manufacturer.

149 However, a technical issue is likely to arise with cascade impactor: too low mass loadings.
150 Indeed, as the sampled particles are split up, sometimes in a dozen of fractions, the
151 quantities collected on each stage can be insufficient for further analysis. In such cases,
152 either the sampling time should be increased, or multiple fractions should be brought
153 together, but then the information on size fractionation is less precise.

154
155 Another possibility to study size distribution is the use of a light-scattering particle counter
156 [68,70]. However, as suggested by the term “counter”, it only gives information about the
157 number and mass concentration for each particle channel. It does not enable to collect the
158 PM fractions for further analyses.

159
160 All the PM collection systems introduced above rely on active air samplers. These ones can
161 be divided into three categories: high-volume, medium-volume, and low-volume.

162 A table summarizing various recent works on PACs in airborne particulate matter, with
163 regard to the PM collection system, the active sampler and the main sampling parameters
164 (flow rate, time, total volume) implemented, is presented in the Supplemental Content of this
165 article (Table S.1.).

166
167 When discussing the sampling of particulate matter, attention needs to be drawn on possible
168 analytical biases. The first one was highlighted by Albinet et al. for NPAHs, which could be
169 degraded at the sampling stage depending on the temperature inside the sampler [75]. This
170 is a parameter to take into account especially for outdoor sampling campaigns where
171 temperature variations can affect a lot more the results than when sampling is performed in
172 indoor environments.

173 Conversely, the study of Goriaux et al. highlighted the risk of over-estimation of polar PACs
174 such as NPAHs and under-estimation of PAHs due to on-filter degradation reactions of the
175 parent PAHs [76]. Consistently with the results of Schauer et al. and Tsapakis and
176 Stephanou, they identified O₃ and OH radical as major oxidizing agents responsible for the
177 on-filter degradation of PAHs during sampling, even if the role of NO_x cannot be excluded
178 [77,78]. Ozone levels and sampling time are therefore important parameters to take into
179 account when assessing the risk of sampling artifacts for these compounds.

180 Similarly, such kinds of reactions can lead to artifact formations of OPAHs. The main solution
181 prescribed to reduce these artifacts is the use of a denuder able to trap or deactivate gas
182 phase oxidants such as ozone. The reduction of the risk of artifact formation of polar PAHs
183 derivatives induced by ozone denuders is a conclusion from the review of Cave et al [79].

184 On the other hand, results obtained for more volatile PACs could indicate that they are likely
185 to be formed catalytically at the denuder surface, so that sampling biases can still exist with

186 the use of ozone denuders, as stated by Walgraeve et al. in their review [18]. Moreover, in
187 several of their works, Albinet et al. observed under-estimations of PAHs generally lower
188 than 10% when ozone denuders were not used [80]. Thus, the gain of precision with an
189 ozone denuder seems to be rather minor.

190 In addition to these artifacts characteristic to PACs, Turpin et al. have reviewed sampling
191 issues related to atmospheric particulate organics, noting risks of volatilization of particulate
192 organics, adsorption of gas phase organics on the filter, and bounce-off of particles, among
193 others [81].

194

195 **2.2 Settled dust**

196

197 For what regards settled dust, the easiest and most common sampling method is to collect it
198 in classical vacuum cleaner bags [29,82–84], which can be further fractionated depending on
199 the particles size thanks to sieves [25,48]. Depending on the type of analysis performed
200 afterwards, various other sampling techniques are available, such as simple manual wiping,
201 sweeping or scraping of surfaces [24,85,86] or passive techniques involving dust fall jars or
202 non-electrostatic plates [24]. Active sampling is generally considered as the ideal solution,
203 because it is more time-efficient and offers more control over the sampling procedure.

204 The most up-to-date and standardized sampling method has been defined by ASTM
205 International and is based on the use of the High Volume Small Surface Sampler (HVS3)
206 [87]. This standardization has had the benefits of reducing the biases between different
207 studies when different sampling devices were used, as well as the biases inside each study
208 due to differences in dust load and carpet type for instance. Some parameters characteristic
209 of each sampling site such as levels of carpet wear and ambient humidity during sampling
210 can still give birth to sampling variations with HVS3 [88].

211 However, due to the supplemental cost of the HVS3, household vacuum cleaner methods
212 can be preferred, knowing that studies such as the one of Colt et al. have shown an excellent
213 agreement in detection and good correlation coefficients between analyses of typical
214 household pollutants (PAHs, pesticides, PCBs ...) performed with both HVS3 and household
215 vacuum cleaner as samplers [89].

216 Even if most of the examples quoted in this section concern indoor dust sampling, it is
217 interesting to note that such kinds of sampling techniques (household vacuum cleaners for
218 instance) have also been used for urban road dust collection [48,90,91].

219

220 **2.3. Sample storage**

221

222 After sampling, it is necessary to store the samples in aluminium foil (or equivalent) to protect
223 them from light, which causes degradation of photosensitive PACs [16]. For the same
224 purpose of avoiding analyte degradation, storage of samples before their extraction should
225 take place either in a refrigerator (3 to 7°C) or in a freezer (-10 to -25°C). In the first case, it is
226 considered that filters can be extracted up to 2 months after sample collection, in the latter,
227 this delay can be extended up to 12 months [80].
228

3. Extraction

The most common extraction methods which have been implemented for PACs in particulate matters belong to the group of solid/liquid extractions. They can be listed as follows: Soxhlet extraction, Pressurized Liquid Extraction (PLE) or Accelerated Solvent Extraction (ASE), Ultrasonic Assisted Extraction (UAE) or sonication, Microwave Assisted Extraction (MAE), and Supercritical Fluid Extraction (SFE).

SFE is an exception to this list. Indeed, after some attempts to implement this technique for PACs in particulate samples in the 90s, some drawbacks have been quickly identified. First and foremost its strong matrix-dependence, precluding a satisfying variability when applied to different kinds of real solid samples, then big differences between various works in terms of ideal parameters and extraction yields, and finally the high expense of the technical investment [92–95]. Despite its well-known advantages such as time-efficiency and a greatly reduced use of organic solvents for instance [94,96,97], in the last decade, very few works have reported its use for particulate matter, a little more for soil matrices [97,98].

The following section will give more details about the choice of the solvent and the solid/liquid extraction methods available for the analysis of polar and non-polar PACs in particulate matter matrices. The need of concentration and purification procedures will also be discussed. We will not differentiate atmospheric PM and settled dusts as extraction methods are the same for both kinds of matrices.

On the other hand, we will not discuss thermal desorption methods, which are relevant but less frequent than solvent extraction. These methods, applied to PAHs and derivatives, are the focus of the review of Liu et al. [99].

We will not discuss miniaturized extraction and micro-extraction techniques either. These are novel and promising for some of them, but to this day they have not been sufficiently implemented to represent an accurate overview of the state of the art. Besides, they have been presented in detail in the review of Manousi and Zachariadis [100].

3.1. Choice of solvent

The solvent selection is one of the most crucial parameters for any extraction method. Its extraction efficiency, its cost, its health and environmental toxicity, and its volatility (for further evaporation, see Section 3.6.) are the main characteristics to take into account when choosing the ideal solvent for a certain application. These criteria are equally applied when implementing Soxhlet, ASE, UAE or MAE methods.

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As a general rule, the most frequently used solvents for PACs extractions from particulates are, in increasing order of polarity: n-hexane, cyclohexane, toluene, dichloromethane, acetone, acetonitrile, ethanol and methanol. It is worth noting that benzene has also been used in some works [33,50,86], but because of its huge toxicity, it should be avoided. It may occur that in some cases, other less common solvents give better extraction recoveries and reproducibility, as highlighted by Lintelmann et al. who selected ethyl acetate for the extraction of OPAHs in particulate matter samples [101].

If attempts with different pure solvents do not yield satisfying results, they can be used in mixtures as it is often the case, or sequentially, for instance when several PAC categories are targeted [33,37,49,102,103]. In the case of PM extraction, Jonker and Koelmans hypothesized that the combination of an aromatic solvent (such as toluene) with methanol was particularly interesting because it associates the displacement capacity of the solvent which has the highest chemical similarity to PACs and the swelling capacity of methanol which has the lowest molar volume and therefore increases the accessibility to the sample for the second solvent [104]. This hypothesis was later validated by Masala et al. [105].

In their review, Bandowe and Meusel have reported dichloromethane alone as being a good extraction solvent for NPAHs, dichloromethane / methanol mixtures appropriate for OPAHs, and n-hexane / dichloromethane mixtures more adapted to non-polar PAHs [16]. Nonetheless, it is important to keep in mind that the choice of the “ideal solvent” is not only analyte-dependent, but also matrix-dependent. Anyway, no single solvent can be defined as optimal and comparative studies of solvents should be performed for each application.

3.2. Soxhlet extraction

Soxhlet is the “historical” system for solid samples solvent extraction. It has marked the beginning of environmental analyses of particulate matters, soils, etc. Therefore, it has been widely used in studies of the 90s [93,106,107]. It has especially been implemented by the National Institute of Standards and Technology (NIST) for the certification of air particulate matter and diesel particulate matter Standard Reference Materials (e.g. SRMs 1648, 1649 and 1650) [108,109].

As it earned a status of reliable extraction method, Soxhlet has remained the method of choice for a lot of analytical scientists around the world in more recent times [25,32,55,103,110].

303 The main drawbacks of Soxhlet are obvious and well-known to all in the environmental field:
 304 its time consumption, the high amounts of solvents required and the impossibility of
 305 automation. Indeed, Soxhlet extractions are generally from 8 to 48 hours long, in contrast
 306 with the other typical extractions whose durations are around 30 minutes.

307 Even if big technical investments, as would require ASE, MAE or SFE, want to be avoided,
 308 the Soxhlet drawbacks tend to orient the selection of the extraction method towards
 309 sonication for example [18,32,107].

310 Table 1 regroups the extraction conditions reported by various studies where Soxhlet was
 311 used.

312

313 **Table 1:** Typical parameters implemented for solvent extraction with a Soxhlet device

	Authors	Year	Compounds of interest	Solvent	Volume	Time
[108]	Wise et al.	1996	PAHs	Dichloromethane	n.d.	20 h
[106]	Chen and Preston	1997	AZAs	Dichloromethane	n.d.	Overnight / ~ 18 h
[78]	Tsapakis and Stephanou	2003	PAHs	n-Hexane	n.d.	24 h
[111]	Bamford and Baker	2003	NPAHs	Dichloromethane	n.d.	24 h
[32]	Christensen et al.	2005	PAHs	Dichloromethane	170 mL	18 h
[103]	Lalah and Kaigwara	2005	PAHs + PASHs + NPAHs + AZAs	Toluene / Methanol (4:1)	200 mL	8 h
[110]	Delhomme and Millet	2008	AZAs	n-Hexane / Dichloromethane (1:1)	n.d.	20 h
[112]	Lin et al.	2015	PAHs + NPAHs	n-Hexane / Acetone (1:1)	200 mL	22 h
[55]	Gao et al.	2018	NPAHs + OPAHs	Dichloromethane	150 mL	8 h
[25]	Cao et al.	2019	PAHs	n-Hexane / Acetone (1:1)	20 mL	36 h

314 * n.d.: not disclosed

315

316 **3.3. Pressurized Liquid Extraction**

317

318 Starting from the consideration that extractions were favored at higher temperatures, Richter
 319 et al. developed the Accelerated Solvent Extraction system around the year 1995 [113]. ASE
 320 has become a trademark from the brand Dionex, which is now widely used to characterize
 321 Pressurized Liquid Extraction (PLE). It enables to perform solid/liquid extractions based on a
 322 principle similar to Soxhlet extractions, but with higher efficiency in terms of time, solvent
 323 consumption, and recoveries. The system is designed to flush a solid or semi-solid sample

324 with extracting solvents under high temperatures (50 to 200°C) and high pressures (500 to 3
325 000 psi, i.e. 35 to 205 bar), during short times (around 10 minutes) [113].

326

327 This PLE system also gives the possibility to automate the sample preparation, so that a lot
328 of samples can be extracted sequentially, something which is not possible with Soxhlet.

329 Works focusing on the analysis of Standard Reference Materials (SRM) have studied the
330 efficiency of PLE in comparison with Soxhlet extraction. The results have shown satisfying
331 extraction yields, similar to those of Soxhlet for a majority of compounds, and even higher for
332 high molecular weight (HMW) PAHs, in a far shorter time [95].

333 After the promising early days of PLE, its extraction efficiency for PACs in particulates has
334 been confirmed [105], which is why the method has been implemented by a lot of labs in the
335 21st century, and is nowadays the major extraction technique reported in the literature for
336 organic pollutants such as PACs in particulates [36,47,49,58,61,114–116].

337

338 Because of the extreme conditions of PLE, there is a possibility of chemical degradation of
339 the analytes during extraction, as showed the example of Lintelmann et al. who observed
340 degradation of PAH quinones (OPAHs) during their PLE protocol [117].

341 Another risk to take into account with PLE is the possibility of losing analytes during the
342 evaporation steps afterwards, especially if high amounts of solvent are used, as sometimes
343 required with PLE (see Section 3.6.). This analytical bias was reported by Delgado-Saborit et
344 al. who compared various extraction solvents without reaching more than 76% of recovery on
345 the whole extraction procedure, and who finally selected a much simpler method to extract
346 PAHs from their filters, by shaking them in dichloromethane, a strategy that brought higher
347 recoveries [63].

348

349 The main parameters to study in the course of a method development with PLE are the
350 solvent, the temperature, the pressure, the heating time, and the number and duration of
351 static cycles (extraction cycle at constant temperature and pressure).

352 The optimization of these parameters is crucial, as shown by Masala et al. in their study of
353 the enhancement of PAHs extraction from a SRM of Diesel Particulate Matter [105]. In this
354 work, they chose to apply extreme pressures and temperatures during longer static cycles
355 than in the general rule, and they compared carefully different solvents and different
356 proportions of solvent mixtures, to obtain the most efficient extraction possible.

357 The PLE parameters reported in studies focusing on PACs in dusts and PM are reviewed in
358 Table 2.

359

360 **Table 2:** Typical parameters implemented for solvent extraction with a PLE device

	Authors	Year	Compounds of interest	Solvent	Temp.	Pressure	Heat time	Static time
[95]	Schantz et al.	1997	PAHs	- Dichloromethane - Toluene	100°C	138 bar	5 min	3 x 5 min
[117]	Lintelmann et al.	2005	PAHs + OPAHs	- Toluene / Methanol (1:1) Hexane / Acetone (7:3)	100°C	107 bar	7 min	3 x 5 min
[47]	Albinet et al.	2006	OPAHs + NPAHs	Dichloromethane	120°C	140 bar	6 min	6 min
[118]	Di Filippo et al.	2007	PAHs + NPAHs	Dichloromethane / Acetone (4:1)	100°C	110 bar	5 min	4 x 5 min
[119]	Bandowe and Wilcke	2010	PAHs + OPAHs	1. Dichloromethane 2. Acetone / Dichloromethane / TFA (250:125:1)	120°C	140 bar	6 min	5 min
[58]	Lintelmann et al.	2010	AZAs	Dichloromethane / Methanol (1:1)	100°C	100 bar	5 min	3 x 5 min
[105]	Masala et al.	2011	PAHs	Toluene / Methanol (9:1)	200°C	207 bar	9 min	5 x 30 min
[116]	Nocun and Schantz	2013	OPAHs	Dichloromethane	100°C	100 bar	5 min	4 x 5 min
[61]	Liaud et al.	2015	PAHs	Acetonitrile	120°C	104 bar	6 min	3 x 5 min
[34]	Alves et al.	2016	PAHs + OPAHs	1. Dichloromethane	n.d.	n.d.	n.d.	n.d.
[120]	Vicente et al.		+ NPAHs + AZAs	2. Acetone / Dichloromethane (2:1)				
[115]	Madruga et al.	2019	PAHs	Dichloromethane	120°C	140 bar	n.d.	n.d.
[49]	Gbeddy et al.	2020	PAHs + OPAHs + NPAHs	1. Dichloromethane 2. Dichloromethane / Methanol / Acetone (1:1:1)	120°C	170 bar	6 min	2 x 5 min

361

362 * When several solvents are associated in a cell, the formatting “ / “ designates a mixture of solvents,
363 the list “1. 2. ...” expresses sequential extractions with different solvents, and the list “-“ is used when
364 in a study, various solvents have been tested and compared without a definite choice of a unique ideal
365 solvent.

366 * n.d.: not disclosed

367

368 3.4. Ultrasound Assisted Extraction

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370 Ultrasound Assisted Extraction, frequently called “sonication”, has been widely employed for
371 PACs extraction from particulates, thanks to its low cost, easy implementation in a lot of labs,
372 and time-efficiency. Indeed, the only material requirements are an ultrasound-producing
373 device and adapted vessels.

374 Even if the interesting possibilities offered by PLE, particularly in terms of automation, have
375 increased its use over Soxhlet and sonication in recent years, sonication remains one of the

376 most frequent extraction methods. With the “classical solvents” cited in Section 3.1,
 377 quantitative extractions of PACs from particulate matters are achieved in less than an hour,
 378 even sometimes in less than 20 minutes [32,101,121–123]. According to several works, the
 379 extraction recoveries obtained with UAE are similar to those obtained with Soxhlet extraction,
 380 but in a far shorter time [32,107,124].

381
 382 García-Alonso et al. compared multiple extraction techniques for PAHs and NPAHs in PM
 383 samples. When keeping the same solvent (dichloromethane), PLE and UAE gave
 384 comparable extraction yields. Even if they were slightly favorable to PLE, the authors
 385 reported the differences between both extractions as insignificant [121]. These results are
 386 presented in Figure 2, where the grey bars represent the quantities of analytes extracted by
 387 PLE with dichloromethane, and the darkest bars represent the quantities of analytes
 388 extracted by UAE with dichloromethane (abbreviated “AG-D”).

389 Thus, sonication can still be considered as a reliable extraction method for PACs in solid
 390 samples.

391
 392 Nonetheless, it is important to keep in mind that UAE is “less rigorous” than automated
 393 methods such as PLE or MAE. Therefore, it can cause higher uncertainties when applied to
 394 strongly sorptive matrices such as soots [104].

395 Moreover, the sonication completely destroys the particulate matter sampling filters, causing
 396 the release of a lot of particles, which need to be removed later by appropriate sample
 397 filtration and clean-up.

398
 399 The parameters reported by studies using UAE as extraction method are regrouped in Table
 400 3.

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 402 **Table 3:** Typical parameters implemented for solvent extraction with an UAE device

	Authors	Year	Compounds of interest	Solvent	Volume	Time
[72]	Allen et al.	1997	OPAHs	Dichloromethane	n.d.	30 min
[77]	Schauer et al.	2003	PAHs	Dichloromethane / Methanol / Toluene (1:1:1)	n.d.	30 min
[32]	Christensen et al.	2005	PAHs	Acetone	n.d.	10 min
[101]	Lintelmann et al.	2006	OPAHs	Ethyl acetate	20 mL	15 min
[125]	Delhomme et al.	2008	OPAHs	Dichloromethane	20 mL	20 min

[48]	Dong and Lee	2009	PAHs	n-Hexane / Dichloromethane (1:1)	30 mL	30 min
[126]	Kojima et al.	2010	PAHs + OPAHs + NPAHs	Dichloromethane	n.d.	2 x 20 min
[68]	Wingfors et al.	2011	PAHs + OPAHs	Dichloromethane	5 mL	3 x 10 min
[127]	Barrado et al.	2012	OPAHs	Methanol	10 mL	30 min
[123]	Sangiorgi et al.	2013	PAHs	Acetonitrile	2 mL	20 min
[60]	Wang et al.	2014	PAHs + OPAHs + PASHs	Dichloromethane	n.d.	3 x 10 min
[102]	Große- Brinkhaus et al.	2017	PAHs	1. Dichloromethane 2. Toluene / Methanol (6:1)	1. 7 mL 2. 3 x 7 mL	4 x 20 min
[121]	García-Alonso et al.	2017	PAHs + NPAHs	- Dichloromethane - Dichloromethane / Methanol (2:1)	5 mL	15 min
[122]	Niu et al.	2017	PAHs + OPAHs	Dichloromethane / Methanol (2:1)	n.d.	15 min
[128]	Ali	2019	PAHs	n-Hexane / Acetone (1:1)	n.d.	2 x 20 min

403 * When several solvents are associated in a cell, the formatting “ / “ designates a mixture of solvents,
404 the list “1. 2. ...” expresses sequential extractions with different solvents, and the list “-“ is used when
405 in a study, various solvents have been tested and compared without a definite choice of a unique ideal
406 solvent.

407 * n.d.: not disclosed

408

3.5. Microwave Assisted Extraction

409

411 Only a few works have reported the application of MAE to particulate samples up to now.
412 The developments of this technique are relatively recent, so that in the review of Walgraeve
413 et al. published in 2010, only one research group had published data on microwave
414 extraction of OPAHs [18].

415 Nevertheless, in 1998, Colmsjö already reported the use of MAE as a possibility to extract
416 PAHs from solid environmental samples such as soil, with extraction recoveries comparable
417 to those obtained with Soxhlet. He mentioned acetone or acetone/hexane mixtures as ideal
418 extraction solvents for PAHs in soil matrices with this technique [124].

419

420 Recently, more and more groups studying polar and non-polar PACs in particulates have
421 utilized MAE [37,45,59,121,127,129]. Similarly to PFE, this technique enables the heating of
422 an organic solvent above its boiling point to enhance the extraction, thanks to specially
423 adapted vessels placed in a microwave oven. The microwave extraction can be performed

424 under constant magnetic agitation to ensure homogeneous mixing and uniform temperature
425 [59].

426
427 In their study, García-Alonso also compared MAE with UAE and PLE. The results obtained
428 proved to be very heterogeneous. Indeed, as shown in Figure 2, whereas MAE gave the
429 highest extraction recoveries for pyrene and benzo[b]fluoranthene, it was totally ineffective
430 for benzo[a]pyrene and 3-nitrofluoranthene [121]. Barrado et al. reported higher extraction
431 yields of PAHs in dichloromethane with the use of a microwave device than with ultrasound
432 or Soxhlet extractors [127].

433

434 Previously published MAE conditions are presented in Table 4.

435

436 **Table 4:** Typical parameters implemented for solvent extraction with a MAE device

	Authors	Year	Compounds of interest	Solvent	Volume	Temp.	Power	Time
[32]	Christensen et al.	2005	PAHs	Acetone / Cyclohexane (1:1)	35 mL	120 °C	n.d.	20 min
[45]	Slezakova et al.	2014	PAHs	Acetonitrile	30 mL	110 °C	n.d.	20 min
[59]	Tutino et al.	2016	PAHs + NPAHs	Acetone / n-Hexane (1:1)	10 mL	110 °C	200 W	25 min
[121]	García-Alonso et al.	2017	PAHs + NPAHs	Dichloromethane	15 mL	120 °C	900 W	40 min
[37]	Du et al.	2018	OPAHs + NPAHs	Acetone / n-Hexane (1:1)	25 mL	110 °C	1 200 W	2 x 10 min

437 * n.d.: not disclosed

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439 3.6. Extract concentration and purification

440

441 Atmospheric particulate matter, dusts and soots are generally very complex matrices.
442 Therefore, a sample clean-up is required before the instrumental analysis. Moreover, when
443 solvent extraction is performed, the extract is often obtained in a relatively large volume (see
444 Sections 3.2. to 3.5.), which should be reduced to optimize the detection limits of the
445 analytical method.

446

447 Generally, immediately after the extraction, it can be preferable to filter the extract through
448 syringe filters with Nylon or PTFE membranes (0.45 µm or less) to get rid of the residual
449 particles [32,45,68,116,123].

450 In some cases, authors also want to ensure the removal of residual water in their extracts,
451 especially to facilitate the solvent removal afterwards. For this purpose, filtration through
452 sodium sulfate can be considered [119].

453

454 Then, a major step is the solvent removal. In a lot of works, it is performed by rotary
455 evaporation [19,45,78,86,110,117,119]. This evaporation should take place at a low
456 temperature ($\leq 40^{\circ}\text{C}$) under low pressures in order to avoid analyte degradation. Other
457 techniques have been implemented for solvent removal, in particular the circulation of a
458 nitrogen stream over the extract to shift the liquid/vapor equilibrium towards vaporization of
459 the solvent [47,68,102,114,126,128,130]. This solution has the advantage of being easily
460 automatable and applicable to lots of extracts similarly thanks to specially designed devices.
461 Before the evaporation, it can be interesting to add small quantities of a less volatile solvent
462 which will act as a “keeper”, so that the sample doesn’t reach complete dryness when its
463 solvent is evaporated, and that the more volatile analytes are not evaporated with the
464 solvent. Toluene, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are good
465 examples of keepers [32,34,36,117,130].

466 If the kinds of instruments used for solvent removal cited above are not available, it is
467 conceivable to let the solvent evaporate under a lab extractor hood. This process takes a
468 longer time but has the benefit of reducing the risks of analyte losses under such mild
469 conditions, even if light-sensitivity of the compounds should be taken into account. This
470 evaporation procedure is naturally more appropriate if volatile solvents such as
471 dichloromethane, hexane, acetone or methanol are used, in decent quantities.

472

473 Finally, the extract should be cleaned up before the analysis to get rid of as many
474 interferences as possible, and to preserve the instrumentation used for the analysis (injector,
475 chromatographic column, mass spectrometer, etc.).

476 For the particular case of PLE, it is possible to perform “in-cell” clean-up similarly to the
477 extraction. To this purpose, Bandowe et al. used a bulk sorbent containing a modified form of
478 diatomaceous earth to fill in the void in the extraction cells [36]. Gbeddy et al. compared five
479 different materials composed of either activated or deactivated silica gel, pure or mixed with
480 alumina at various proportions, placed on top of the outlet filter. Besides these clean-up
481 materials, they filled the cells with diatomaceous earth and anhydrous Na_2SO_4 to remove
482 potential excess of water [49]. Such clean-up methods enable to get rid of additional off-line
483 purification steps.

484 In the vast majority of cases, the clean-up step is done by Solid Phase Extraction (SPE). The
485 main SPE supports used are silica and alumina [32,47,57,60,68,126]. Aminopropylsilyl
486 columns have also been proposed for SPE purification of extracts from particulates

487 [108,131,132]. The choice of the SPE cartridge can have a major influence on the recovery
488 of this purification step, therefore it can be beneficial to compare several commercially
489 available stationary phases [133]. Further details on SPE conditions can be found in the
490 supplemental content of this article (Table S.2.).

491
492 SPE experiments in the course of the analytical procedure can also offer the possibility of
493 isolating different fractions of PACs depending on their polarity. Such fractionation steps are
494 useful for assessment of various classes of PACs in the same sample, but using different
495 analytical instruments to enhance the sensitivity for each fraction [52,120].

496
497 Apart from SPE, some authors have reported the use of different clean-up methods, more
498 labor-intensive, such as glass column chromatography [25,55,77,119,129] and high
499 performance liquid chromatography (HPLC) [72,114,131]. Sauvain et al. have even
500 described a clean-up procedure composed of successive purification steps through SPE,
501 semi-preparative normal phase liquid chromatography, open column chromatography, liquid-
502 liquid partition and back extraction for diesel particulate, a particularly complex matrix [52].
503 We would like to highlight that these alternatives are generally found in older works and that
504 nowadays, SPE is by far the most used purification technique.

505
506 However, we do not report SPE as a mandatory step for PACs determination. Indeed,
507 important losses of compounds can be expected for PACs with classical SPE phases,
508 especially when the goal is to analyse polar and non-polar simultaneously. Besides, many
509 studies regarding PACs analysis are based on analytical methods without any purification
510 step and still match quality criteria.

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512 After the purification of the extract, important volumes are once more obtained, they can be
513 concentrated as described above.

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4. Conclusion

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The objective of this first part of our review was to discuss the collection, extraction and purification of particulate samples for the determination of their PAC content.

It is important to note that even before the instrumental analysis of the extract, which will be the topic of the second part of this article, major analytical errors can be made.

The sampling step is crucial. One wants to collect a sufficient amount of sample, which should still be representative of a relatively short period of time if daily or hourly variations are studied, and representative of a relevant sampling place, i.e. not affected by airstream artifacts for instance.

Besides the possible contaminations due to the sampling filter which can easily be avoided, the major issue related to PM sampling is the risk of on-filter reactions causing artificial variations of PACs concentrations such as degradation of PAHs into their oxygenated or nitrated derivatives. To avoid such reactions, the use of ozone denuders has been reported, but gains associated to it can be considered as marginal.

The risk of such biases during the sampling is far lower in the case of settled dust which is less exposed to daylight and atmospheric oxidative conditions. Still, for settled dust as well as for PM, samples need to be completely protected from light and heat between their collection and their extraction, to avoid degradation of PACs.

The most common extraction techniques for PACs in particulates are solvent extractions. Among those, Soxhlet can be considered as obsolete because it is time-consuming, solvent-consuming and offers a poorer reproducibility compared to the others. Issues of reproducibility also arise with UAE. We would rather advise for the use of PLE and MAE, but their high expense should be taken into account.

In future years, as a result of technical evolutions, economic and environmental constraints, we expect non-solvent extraction methods to be increasingly implemented for this application. In this category, thermal desorption (TD) and Solid Phase Micro Extraction (SPME) are the most developed, but other novel sorptive micro-extraction techniques are promising. It is necessary that an extensive assessment of their advantages and drawbacks over solvent extractions be performed, including a comparison of a high amount of methods developed by various labs in various conditions. Depending on these results, they could be applied in routine analysis laboratories, but not before several years. To illustrate this delay between research stage and routine applications of extraction techniques, we can notice that Soxhlet is still applied in some of these quality control labs nowadays.

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553

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556

557 **Appendix**

558

559 Supplementary Material of this article can be found in the online version, at ...

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