



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



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## ABSTRACT

Interests in Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives (Nitrated PAHs, Oxygenated PAHs, Azaarenes and Polycyclic Aromatic Sulfur Heterocycles) have been growing because of their toxicity.

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

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

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

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

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## 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.

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

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

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

For PACs occurrence studies, particular focuses have been made on atmospheric particulate matter (PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>) because of its well-known negative health effects [18,39]. These effects are especially pronounced for the smallest of these particles, because of their higher surface area per unit mass, in addition to their deeper penetration into lungs [40,41]. According to the IARC, “there is sufficient evidence in humans for the carcinogenicity of particulate matter in outdoor air pollution” [42]. PACs account for an important part of this carcinogenicity. Other particulate matters such as settled dusts of indoor environments [24,25,27–29], “environmental” third-hand smoke (ETS) [43–46], urban road dust [32,47–49], particulate exhausts and soots from

vehicular emissions [32,50–52], are also of a great concern because of their ability to host toxic semi-volatile organic compounds (SVOCs) such as PACs.

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

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

## 2. Sampling

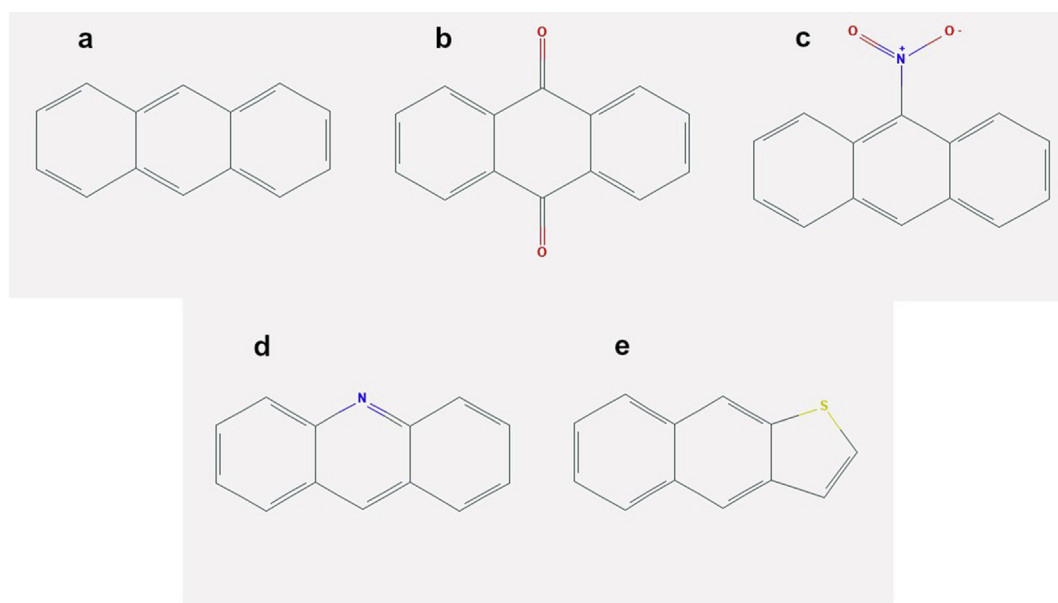
### 2.1. Atmospheric particulate matter

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. On 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 ( $\geq 350$  °C) for 6–24 h for their decontamination prior to



**Fig. 1.** Chemical structures of various 3-ring PACs: a) Anthracene (PAH); b) 9,10-Anthraquinone (OPAH); c) 9-Nitroanthracene (NPAH); d) Acridine (AZA); e) Naphtho[2,3-b]thiophene (PASH).

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 (20–25 °C) and humidity (40–50%) for 24–48 h [59,66]. This accounts for the absorption of water vapor [70].

For PM collection, sampling heads designed for PM<sub>10</sub> or PM<sub>2.5</sub> 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-0.1 µm range to particles larger than 10 µm. 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.

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

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

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

A table summarizing various recent works on PACs in airborne particulate matter, with regard to the PM collection system, the active sampler and the main sampling parameters (flow rate, time, total volume), is presented in the Supplemental Content of this article (Table S1).

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

Conversely, the study of Goriaux et al. highlighted the risk of over-estimation of polar PACs such as NPAHs and under-estimation of PAHs due to on-filter degradation reactions of the parent PAHs [76]. Consistently with the results of Schauer et al. and Tzapakis and Stephanou, they identified O<sub>3</sub> and OH radical as major oxidizing agents responsible for the on-filter degradation of PAHs during sampling, even if the role of NO<sub>x</sub> cannot be excluded [77,78]. Ozone levels and sampling time are therefore important parameters to take into account when assessing the risk of sampling artifacts for these compounds. Similarly, such kinds of reactions can lead to artifact formations of OPAHs. The main solution prescribed to reduce these artifacts is the use of a denuder able to trap or deactivate gas phase oxidants such as ozone. The reduction of the risk of artifact formation of polar PAHs derivatives induced by ozone denuders is a conclusion from the review of Cave et al. [79].

On the other hand, results obtained for more volatile PACs could indicate that they are likely to be formed catalytically at the denuder surface, so that sampling biases can still exist with the use of ozone denuders, as stated by Walgraeve et al. in their review [18]. Moreover, in several of their works, Albinet et al. observed under-estimations of PAHs generally lower than 10% when ozone denuders were not used [80]. Thus, the gain of precision with an ozone denuder seems to be rather minor.

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

## 2.2. Settled dust

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

The most up-to-date and standardized sampling method has been defined by ASTM International and is based on the use of the High Volume Small Surface Sampler (HVS3) [87]. This standardization has had the benefits of reducing the biases between different studies when different sampling devices were used, as well as the biases inside each study due to differences in dust load and carpet type for instance. Some parameters characteristic of each sampling site such as levels of carpet wear and ambient humidity during sampling can still give birth to sampling variations with HVS3 [88]. However, due to the supplemental cost of the HVS3, household vacuum cleaner methods can be preferred, knowing that studies such as the one of Colt et al. have shown an excellent agreement in detection and good correlation coefficients between analyses of typical household pollutants (PAHs, pesticides, PCBs ...) performed with both HVS3 and household vacuum cleaner as samplers [89].

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

## 2.3. Sample storage

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

## 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 particulates. 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.

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 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].

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

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

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

### 3.3. Pressurized Liquid Extraction

Starting from the consideration that extractions were favored at higher temperatures, Richter et al. developed the Accelerated Solvent Extraction system around the year 1995 [113]. ASE has become a trademark from the brand Dionex, which is now widely used to characterize Pressurized Liquid Extraction (PLE). It enables to perform solid/liquid extractions based on a principle similar to Soxhlet extractions, but with higher efficiency in terms of time, solvent consumption, and recoveries. The system is designed to flush a solid or semi-solid sample with extracting solvents under high temperatures (50–200 °C) and high pressures (500–3000 psi, i.e. 35–205 bar), during short times (around 10 min) [113].

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

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

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

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

Another risk to take into account with PLE is the possibility of losing analytes during the evaporation steps afterwards,

**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

\*n.d.: not disclosed.

especially if high amounts of solvent are used, as sometimes required with PLE (see Section 3.6.). This analytical bias was reported by Delgado-Saborit et al. who compared various extraction solvents without reaching more than 76% of recovery on the whole extraction procedure, and who finally selected a much simpler method to extract PAHs from their filters, by shaking them in dichloromethane, a strategy that brought higher recoveries [63].

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

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

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

### 3.4. Ultrasound Assisted Extraction

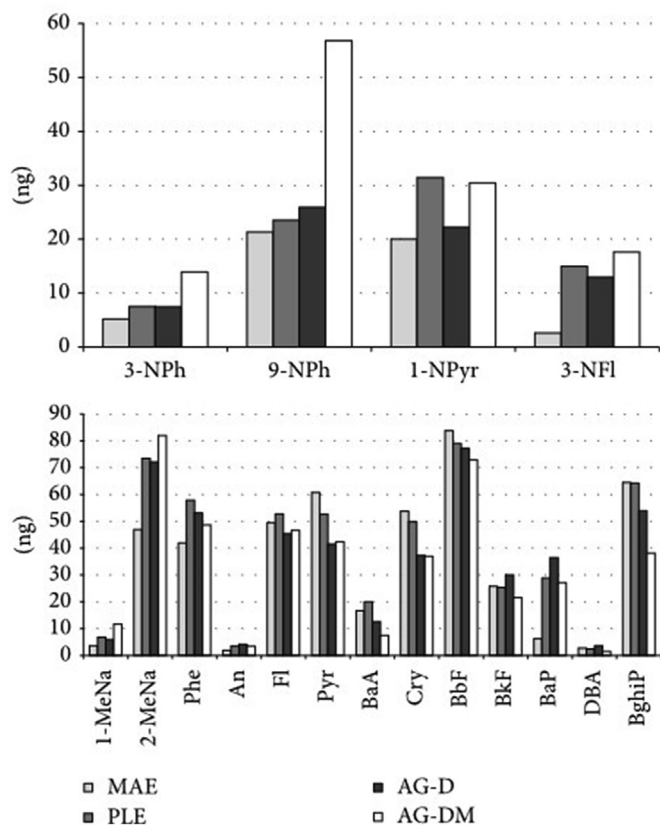
Ultrasound Assisted Extraction, frequently called “sonication”, has been widely employed for PACs extraction from particulates, thanks to its low cost, easy implementation in a lot of labs, and time-efficiency. Indeed, the only material requirements are an ultrasound-producing device and adapted vessels.

**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 - Toluene/Methanol (1:1)	100 °C	138 bar	5 min	3 × 5 min
[117]	Lintelmann et al.	2005	PAHs + OPAHs	Hexane/Acetone (7:3)	100 °C	107 bar	7 min	3 × 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 × 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 × 5 min
[105]	Masala et al.	2011	PAHs	Toluene/Methanol (9:1)	200 °C	207 bar	9 min	5 × 30 min
[116]	Nocun and Schantz	2013	OPAHs	Dichloromethane	100 °C	100 bar	5 min	4 × 5 min
[61]	Liaud et al.	2015	PAHs	Acetonitrile	120 °C	104 bar	6 min	3 × 5 min
[34]	Alves et al.	2016	PAHs + OPAHs + NPAHs + AZAs	1. Dichloromethane 2. Acetone/Dichloromethane (2:1)	n.d.	n.d.	n.d.	n.d.
[120]	Vicente et al.							
[115]	Madrugea 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 × 5 min

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

\*n.d.: not disclosed.



**Fig. 2.** Mean extracted values (ng per subsample) of selected PAHs and NPAHs with different extraction methods: MAE, PLE and UAE (written as AG). Dichloromethane (D) was the extracting solvent. For UAE, dichloromethane was compared with a dichloromethane / methanol mixture (DM). Reproduced from García-Alonso et al. [121].

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

### 3.5. Microwave Assisted Extraction

Only a few works have reported the application of MAE to particulate samples up to now. The developments of this technique

**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 × 20 min
[68]	Wingfors et al.	2011	PAHs + OPAHs	Dichloromethane	5 mL	3 × 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 × 10 min
[102]	Große-Brinkhaus et al.	2017	PAHs	1. Dichloromethane 2. Toluene/Methanol (6:1)	1. 7 mL 2. 3 × 7 mL	4 × 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 × 20 min

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

\*n.d.: not disclosed.

are relatively recent, so that in the review of Walgraeve et al. published in 2010, only one research group had published data on microwave extraction of OPAHs [18].

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

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

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

Previously published MAE conditions are presented in Table 4.

### 3.6. Extract concentration and purification

Atmospheric particulate matter, dusts and soots are generally very complex matrices. Therefore, a sample clean-up is required before the instrumental analysis. Moreover, when solvent extraction is performed, the extract is often obtained in a relatively large volume (see Sections 3.2, 3.3, 3.4, 3.5), which should be reduced to optimize the detection limits of the analytical method.

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

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

**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	1200 W	2 × 10 min

\*n.d.: not disclosed.

Then, a major step is the solvent removal. In a lot of works, it is performed by rotary evaporation [19,45,78,86,110,117,119]. This evaporation should take place at a low temperature ( $\leq 40$  °C) under low pressures in order to avoid analyte degradation. Other techniques have been implemented for solvent removal, in particular the circulation of a nitrogen stream over the extract to shift the liquid/vapor equilibrium towards vaporization of the solvent [47,68,102,114,126,128,130]. This solution has the advantage of being easily automatable and applicable to lots of extracts similarly thanks to specially designed devices.

Before the evaporation, it can be interesting to add small quantities of a less volatile solvent which will act as a “keeper”, so that the sample doesn't reach complete dryness when its solvent is evaporated, and that the more volatile analytes are not evaporated with the solvent. Toluene, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are good examples of keepers [32,34,36,117,130].

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

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

For the particular case of PLE, it is possible to perform “in-cell” clean-up similarly to the extraction. To this purpose, Bandowe et al. used a bulk sorbent containing a modified form of diatomaceous earth to fill in the void in the extraction cells [36]. Gbeddy et al. compared five different materials composed of either activated or deactivated silica gel, pure or mixed with alumina at various proportions, placed on top of the outlet filter. Besides these clean-up materials, they filled the cells with diatomaceous earth and anhydrous  $\text{Na}_2\text{SO}_4$  to remove potential excess of water [49]. Such clean-up methods enable to get rid of additional off-line purification steps.

In the vast majority of cases, the clean-up step is done by Solid Phase Extraction (SPE). The main SPE supports used are silica and alumina [32,47,57,60,68,126]. Aminopropylsilyl columns have also been proposed for SPE purification of extracts from particulates [108,131,132]. The choice of the SPE cartridge can have a major influence on the recovery of this purification step, therefore it can be beneficial to compare several commercially available stationary phases [133]. Further details on SPE conditions can be found in the supplemental content of this article (Table S2.).

SPE experiments in the course of the analytical procedure can also offer the possibility of isolating different fractions of PACs depending on their polarity. Such fractionation steps are useful for assessment of various classes of PACs in the same sample, but using

different analytical instruments to enhance the sensitivity for each fraction [52,120].

Apart from SPE, some authors have reported the use of different clean-up methods, more labor-intensive, such as glass column chromatography [25,55,77,119,129] and high performance liquid chromatography (HPLC) [72,114,131]. Sauvain et al. have even described a clean-up procedure composed of successive purification steps through SPE, semi-preparative normal phase liquid chromatography, open column chromatography, liquid-liquid partition and back extraction for diesel particulate, a particularly complex matrix [52].

We would like to highlight that these alternatives are generally found in older works and that nowadays, SPE is by far the most used purification technique.

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

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

#### 4. Conclusion

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 [134], 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.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.trac.2020.116099>.

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