Chapter 11
Formation and Characterization of Polyaromatic Hydrocarbons

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Abstract Issues concerning polycyclic aromatic hydrocarbons (PAH) carcinogenicity, and their important role in formation of dangerous pollutants, such as soot, have motivated their study under a wide range of laboratory conditions and for several kinds of thermochemical processes. Every experimental system, depending on the operating conditions, demands a specific protocol for PAH determination. This chapter aims to contribute to the knowledge of different procedures for PAH quantification both at the gas phase and when they are associated with soot particles. Different kinds of experimental set-ups for PAH formation together with the collection systems to capture them are explained here. Besides, some sample extraction techniques are reviewed, mainly focused on Soxhlet extraction because of its inexpensive equipment and overall simplicity to be applied by staff with limited analytical experience. Chromatographic techniques are also considered, paying special attention to gas chromatography coupled to mass spectrometry (GC–MS), popular in PAH analysis.

Abbreviations

PAH	Polycyclic aromatic hydrocarbons
GC–MS	Gas chromatography coupled to mass spectrometry
HACA	H-abstraction/C_2H_2 addition route
EPA	Environmental Protection Agency
EPA–PAH	Polycyclic aromatic hydrocarbons classified by EPA as priority pollutants
PUF	Polyurethane foam
PTFE	Polytetrafluoroethylene
DCM	Dichloromethane
ASE	Accelerated solvent extraction

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SFE	Supercritical fluid extraction
GPT	Thermochemical Processes Group
I3A	Aragón Institute of Engineering Research
HPLC–UV	Reversed-phase high performance liquid chromatograph with ultraviolet detection
FID	Flame ionization detection
SIM	Selected ion monitoring
SRM	Standard reference material

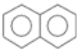
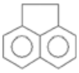
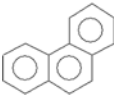
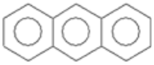
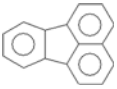
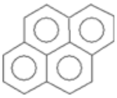
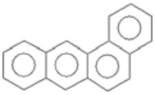
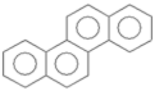
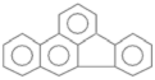
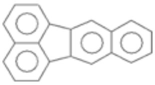
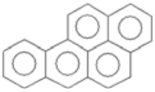
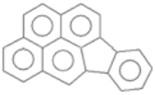
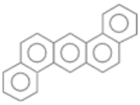
11.1 Introduction

Polycyclic aromatic hydrocarbons (PAH) are members of a class of air pollutants relevant to many scientific issues from a variety of aspects: chemical, toxicological, engineering, technological, public health, economic and regulatory (Finlayson-Pitts and Pitts 2000). They are a large number of compounds that consist of fused aromatic rings (Sander and Wise 1997). PAH are mainly formed in the combustion of fossil fuels and organic matter, and are ubiquitous in the atmosphere. Anthropogenic activities are the major sources of emission of PAH (WHO 2000; Lee 2001; Tang et al. 2005). It is well established that these aromatic compounds greatly contribute to the formation of primary soot particles, e.g. as explained by the H-abstraction/C_2H_2 addition (HACA) route (Frenklach 2002; Indarto et al. 2010), or they can appear adsorbed on the surface of soot. Thus, determination of PAH is, with no doubt, a necessary step for achieving a better understanding on the chemical details regarding the formation of nascent soot particles, which is still poorly understood (Faccinetto et al. 2011).

Different studies have shown that PAH can cause harmful effects on the human health and the environment (ATSDR 1996; Schneider et al. 2002; De Kok et al. 2006). This risk is increased because PAH exist as more or less pure particles, associated with particulate matter and dust, the latter capable of penetrating into the lower respiratory tract (Luch 2005). The Environmental Protection Agency of the USA (EPA) has given priority to 16 PAH (EPA–PAH) (EPA 1998a) detailed in Table 11.1, which are commonly called as “priority aromatic hydrocarbon pollutants”, because of their widespread presence and the fact that some of them are considered as probable human carcinogens. Unquestionably, some PAH from this list are important intermediates in the soot formation process, and they have been studied in different modelling and experimental investigations (Appel et al. 2000; Li et al. 2009; Norinaga et al. 2009).

In this context, the characterization and quantification of PAH appearing in combustion processes is needed for determining the possible toxicological effect of the emission sources, or when a deeper understanding of soot formation is

Table 11.1 Structures, common names, used abbreviations, molecular formulas and molecular weights (MW) for the 16 EPA–PAH

Structure	Common name	Abbreviations for PAH	Molecular formula	MW (g mol^{-1})
	Naphthalene	NAP	$C_{10}H_8$	128.18
	Acenaphthylene	ACY	$C_{12}H_8$	152.20
	Acenaphthene	ACE	$C_{12}H_{10}$	154.20
	Fluorene	FLO	$C_{13}H_{10}$	166.23
	Phenanthrene	PHE	$C_{14}H_{10}$	178.23
	Anthracene	ANT	$C_{14}H_{10}$	178.23
	Fluoranthene	FLA	$C_{16}H_{10}$	202.26
	Pyrene	PYR	$C_{16}H_{10}$	202.25
	Benzo(a)anthracene	BaA	$C_{18}H_{12}$	228.28
	Chrysene	CHR	$C_{18}H_{12}$	228.28
	Benzo(b)fluoranthene	BbF	$C_{20}H_{12}$	252.32
	Benzo(k)fluoranthene	BkF	$C_{20}H_{12}$	252.32
	Benzo(a)Pyrene	BaP	$C_{20}H_{12}$	252.31
	Indeno(1,2,3-cd)pyrene	IcdP	$C_{22}H_{12}$	276.34
	Dibenzo(a,h)anthracene	DahA	$C_{22}H_{14}$	278.35
	Benzo(g,h,i)perylene	BghiP	$C_{22}H_{12}$	276.34

required. This knowledge would allow the relevant authorities to develop strategies to reduce, if not eliminate, PAH emissions into our surrounding (Lee 2001).

Depending on the properties exhibited by PAH, mainly the vapour pressure, they exist in the gas phase or as solid particles. PAH at the outlet gas stream of combustion processes usually consist of compounds with few aromatic rings such as naphthalene (Finlayson-Pitts and Pitts 2000). The processes, where both PAH and particulate matter, such as soot, can be formed, require a specific method for collection and especially for PAH analysis, since their nature and the variety of organic matter need a particular technique capable to handle the complex mixture of products at the outlet (Lee 2001).

The aim of this chapter is to present a number of devices used to study the PAH formation in thermochemical processes. Different techniques for PAH determination/quantification are also considered, including PAH collection (taking into account the different places where PAH are found), sample treatment by solvent extraction techniques, and PAH analysis by chromatographic methodologies. An example on formation, collection and quantification of the 16 EPA–PAH in a specific tubular flow reactor in the pyrolysis of acetylene and ethylene will be also shown.

11.2 Characterization and Formation of Polycyclic Aromatic Hydrocarbons

Frequently for different processes, the concentration of PAH, such as the 16 EPA–PAH (Table 11.1), needs to be monitored in different places: the atmosphere (e.g. Mastral et al. 2003), soil (e.g. Ortiz et al. 2012), food (e.g. Viegas et al. 2012), water (e.g. Ardag et al. 2011) and exhaust gases (e.g. Ballesteros et al. 2010). In this latter case, PAH formation is evaluated for both pollution assessment and to achieve a better understanding of the effect of different variables on their formation and/or their role in soot formation. Several investigations on PAH and soot formation in flames have been carried out by using different devices: commercial burners, such as a McKenna burner (Apicella et al. 2003; Wu et al. 2006; Faccinetto et al. 2011), spray flames using spray burners (Allouis et al. 2003; Lemaire et al. 2010), or open diffusion flames by an stainless steel conical container and premixed flames by a flat-flame burner (Andrade-Eiroa et al. 2010a). Under pyrolysis conditions in shock tubes (Wang and Cadman 1998; Mathieu et al. 2007) (as it can be seen in Chaps. 6 and 24), tubular reactors (Mendiara et al. 2005; Norinaga et al. 2007; Ruiz et al. 2007a; Thomas and Wornat 2008; Sánchez et al. 2012a) and a well stirred reactor coupled to a plug flow reactor (Macadam et al. 1996, Manzello et al. 2007).

As an example, Fig. 11.1 shows the EPA–PAH formed from ethylene pyrolysis at 1,273 K at laboratory scale in a tubular reactor (Sánchez et al. 2012b). As it can be observed, under these specific conditions a higher concentration of lighter PAH (NAP and ACY, almost 60 % of the total) is formed. From Fig. 11.1, it is also

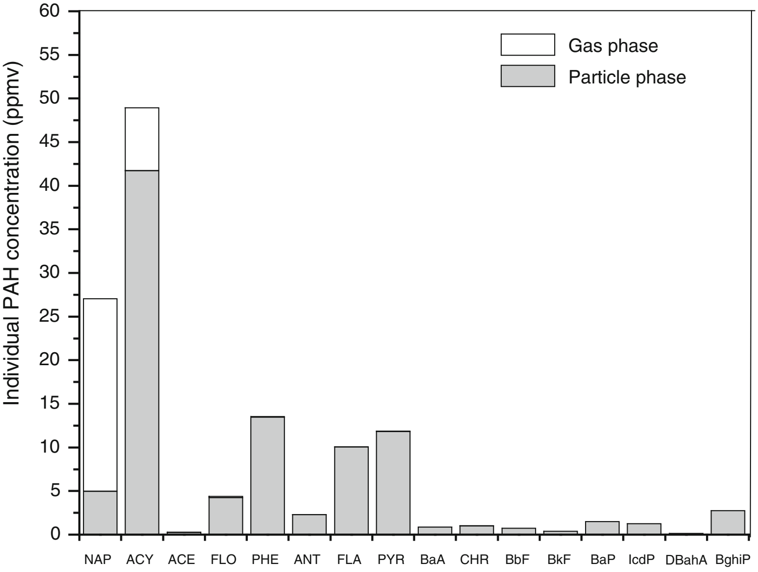


Fig. 11.1 PAH generated from ethylene pyrolysis at 1,273 K, with a fixed concentration of 30,000 ppmv in a tubular reactor (adapted with permission from Sánchez et al. 2012b. Copyright 2012 American Chemical Society)

deduced that the particle-gas phase PAH partitioning is an important issue to be considered in this kind of experiments, especially for lighter PAH preferably present at the gas phase, whereas the heavier ones are mainly found adsorbed on the particle.

11.3 PAH Collection

The collection technique should consider that PAH can appear on different surfaces (soot and reactor walls) as well as at the outlet gas stream. This distribution depends on their molecular weights, environment temperature, PAH concentration and soot characteristics (Christensen 2003; Sánchez et al. 2012a). It must also be taken into account that PAH cover a wide range of vapour pressures, e.g. approximately 10.6 Pa for naphthalene versus 2.0×10^{-10} Pa for coronene, at 298 K in both cases (Finlayson-Pitts and Pitts 2000). Figure 11.2 shows the PAH found in the particle phase and gas phase from biomass combustion in a cooking stove (Shen et al. 2011). In agreement with the data of Fig. 11.1, in both cases the lighter PAH remain preferentially at the gas phase, whereas the heavier ones show almost complete association with particles.

Several works (e.g. Shen et al. 2011; Kim et al. 2012) on PAH distribution in different conditions reveal the importance of considering their partitioning (particle-gas phase), especially when compounds involving only a few aromatic rings

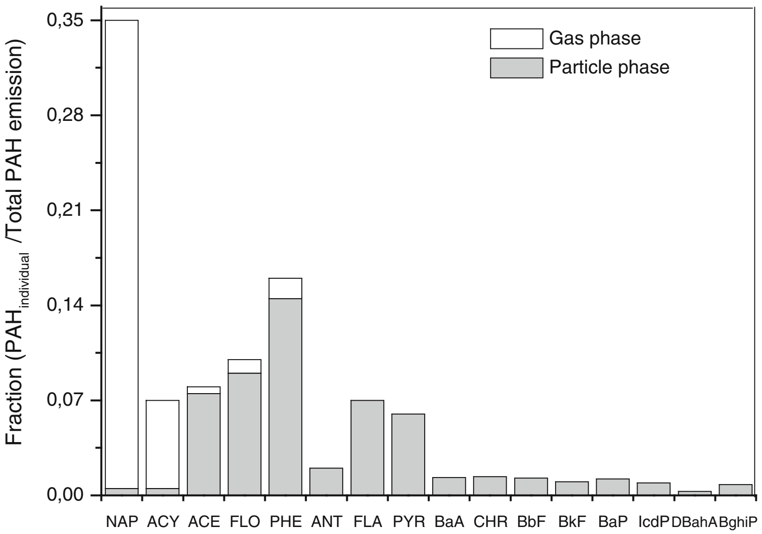


Fig. 11.2 Stacked bars show the PAH emission from crop residues burned in the cooking stove (combustion process) during a whole burning cycle (adapted with permission from Shen et al. 2011. Copyright 2012 American Chemical Society)

are evaluated, e.g. NAP and ACY. For airborne PAH both in gas and particle phases, large volumes of air must be sampled to achieve a high enough concentration factor. This is because their concentration in air at most locations is relatively low (of order ng m^{-3}) (Pandey et al. 2011), whereas in the laboratory, this depends on the specific operating conditions.

11.3.1 PAH in the Gas Phase

The method for PAH sampling can vary depending on their partitioning in the different phases. Beginning with the gas phase, NAP, ACY, methylnaphthalenes, and other abundant and highly volatile PAH are frequently trapped with sorbent materials. Polyurethane foam (PUF) and XAD resins are two of the adsorbents most commonly used for PAH sampling in gas phase (e.g. Lee et al. 2004). Different studies have proved that the XAD-2 resin exhibits a higher efficiency for PAH adsorption and retention than PUF. Additionally, the XAD-2 resin shows higher recovery of compounds with two and three aromatic rings, like NAP, which is abundant in the combustion processes outlet gases (Chuang et al. 1987). Other sorbent materials (e.g. XAD-4 and Tenax) have also been employed occasionally in air sampling or under controlled laboratory conditions (e.g. Liu et al. 2001; Font et al. 2003). Aromatic compounds can also be captured by other techniques, as those used by Wornat's group in their experiments (e.g. Somers et al. 2007).

Devices, like stainless steel probes or collectors equipped with a filter, for sampling combustion products along the flame axis are used in flame studies (e.g. Ciajolo et al. 2001; Bouvier et al. 2007; Andrade-Eiroa et al. 2010a). In conclusion, the collection of PAH depends on the kind of specific experimental set-up used.

11.3.2 PAH in the Particle Phase

Semivolatile compounds, like PAH associated to particles, can be collected on filters made of cellulose acetate, nylon or polytetrafluoroethylene (PTFE) (Mastral et al. 1996, 2003), quartz and glass fibre (Ballesteros et al. 2010; Sánchez et al. 2012a). Frequently, in thermochemical experiments, when the temperature of the outlet gas stream is high, glass or quartz fibre filters must be used. Therefore, it must be emphasized, the best filter to be chosen is that viable for the specific conditions used in the experiments (e.g. temperature, corrosion, high gas flow, size of solid particle generated).

11.3.3 Example of an Experimental Set-up for Formation and Collection of PAH

An experimental set-up used in the pyrolysis and oxidation of light hydrocarbons (e.g. C_2H_2, C_2H_4, CH_4), under well-controlled conditions, is shown in Fig. 11.3. It has been successfully used in several works (e.g. Ruiz et al. 2007a, b; Esarte et al. 2009; Sánchez et al. 2012a, b) and consists of different systems, namely: (1) gas feeding system, with mass flow meters and the gases to be fed; (2) reaction system, in which the reaction takes place in a quartz tube reactor of 45 mm internal diameter and 800 mm in length, since the reactor inlet and outlet are cooled by air flow; (3) soot and PAH collection system; (4) gas analysis system for volatile compounds. In the PAH-soot collection system of Fig. 11.3, the soot and their PAH associated are captured on a filter with fixed dimensions (30 mm external diameter, 100 mm length, and pore diameter lower than 1 mm). The PAH present at the gas phase are trapped when they pass through a tube packed with XAD-2 resin. The results showed in Fig. 11.1 were obtained by using this experimental system.

11.4 Sample Preparation and Extraction

Due to the high volatility of the lower molecular weight PAH, samples containing PAH must be preserved carefully (Li-bin et al. 2007). Filters with the particulate matter and their PAH adsorbed should be folded on the inner side, stored in glass bottles under refrigeration and analysed as quickly as possible.

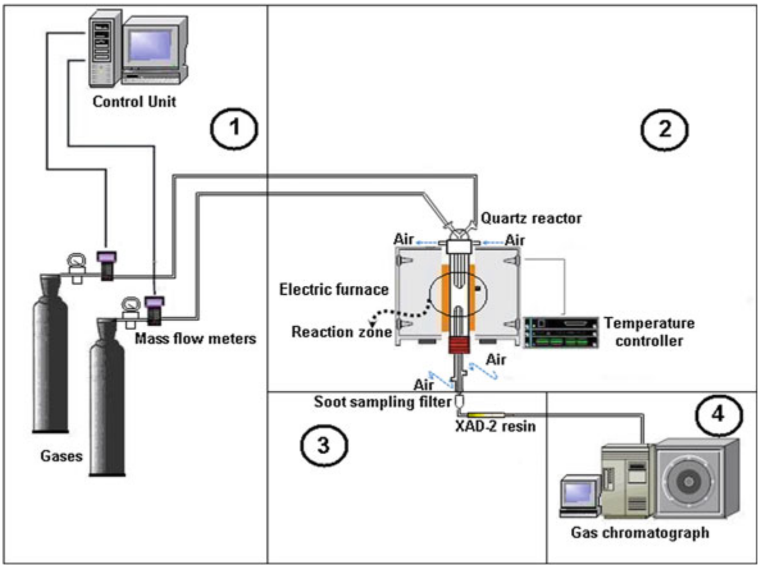


Fig. 11.3 Experimental set-up used for the light C_2 hydrocarbon pyrolysis and oxidation

The analysis of PAH commonly requires their trapping on a solid surface. This section will focus on the preparation of solid samples, which are to undergo elution with solvent. However, it is also worth mentioning that there are other solvent-free extraction techniques (not less important), such as the thermal extraction together with solid-phase micro-extraction (e.g. Ballesteros et al. 2009).

Sample preparation and extraction appear to be the most time-consuming stages in the analytical procedures (Luque de Castro and Luque de García 2002). The risk for analyte loss is also highest during this step. Hence, it is usually considered the bottleneck of PAH analytical methodologies. This represents one of the major problems associated with analysis of PAH in different samples. Other problems include: (1) most of PAH in environment samples are normally present in trace amounts (Lee 2001). On the contrary, some samples formed under laboratory controlled conditions contain high PAH amount, which can also become a serious problem due to saturation of the material used to collect them; (2) many organic compounds can be coextracted with PAH, which could interfere with their subsequent separation, identification and quantification; and (3) most of PAH are similar structurally and present isomeric forms, which makes difficult their separation and identification (Chen et al. 1996; Lee 2001). Hence, it is very important to choose an appropriate methodology for PAH determination, taking into account all these problems in any particular case.

Solvent-based extraction techniques for PAH determination are an active area of research and many novel techniques have been developed, some of them described below.

Ultrasonic extraction of PAH is a popular method because of both time and solvent-saving (Li-bin et al. 2007). Nevertheless, due to the limited contact time between the solvent and the sample, ultrasonic extraction may not be as rigorous as other extraction methods (EPA 2000), especially when the target sample contains a high PAH concentration. However, this technique has been used with success in several works (Kado et al. 2000; Mastral et al. 2001; Christensen et al. 2005).

PAH extraction is also possible by means of microwaves, which are high frequency (usually 2.45 GHz) electromagnetic waves that can be strongly absorbed by polar molecules, whereas weak interaction occurs with non-polar solvents. This results in accelerated extraction (through elevated temperatures) of polar compounds from various matrices into non- or weak polar solvents. The efficiency of extraction with microwaves lies in the ability of the bulk material to transform electromagnetic radiation into heat, without the disadvantage of convection and conduction, thus preventing loss of analyte (Lee 2001). The solvents commonly used for PAH extraction with microwaves are hexane, acetone and dichloromethane (DCM), among others (Lee 2001). Some results on microwaves applied for PAH determination are reported by Portet-Koltalo et al. (2008), who have used this technique for extracting a complex mixture containing PAH, nitrated PAH and heavy n-alkanes from a particularly refractory carbonaceous material resulting from combustion in a diesel engine.

Accelerated solvent extraction (ASE) is a kind of pressurized-fluid extraction method. Its advantage over classical techniques is to provide faster extraction (5–15 min), and a relatively low consumption of organic solvents (Lee 2001). However, ASE equipment is very expensive and this factor has limited its use.

Supercritical fluid extraction (SFE) is another technique commonly used in PAH characterization, mainly in environment samples with low PAH concentration (e.g. Becnel and Dooley 1998; Librando et al. 2004). SFE uses supercritical fluids (used as solvent) to seep through the pores of the sample, thus extracting the analytes. CO_2, NH_3, C_2H_4, C_2H_6, N_2O, C_3H_8, C_3H_6 and H_2O are the most common substances used in SFE (Li-bin et al. 2007). The use of SFE avoids the necessity of a further extensive concentration and clean-up previous to analysis (Lee 2001). EPA 3561 is a method recommended for PAH extraction from different sources by using SFE (EPA 1996a). It suggests that the method performance demonstration should be based on the extraction of a certified sample and, alternatively, a comparison of SFE and Soxhlet extraction data using an environmentally contaminated PAH sample may be performed.

In this context, Soxhlet extraction is a reference extraction method for analysing the correct behaviour of emerging methods such as those above mentioned. Filtration of the extract from Soxhlet extraction is not required and several simultaneous extractions can be carried out by this inexpensive equipment (Luque de Castro and Priego-Capote 2010). Moreover, it is not necessary to employ highly qualified personnel for optimizing and carrying out extractions. In this way, the Soxhlet method is a good option for laboratories with limited experience on analytical chemistry or for researches not specifically devoted to the analytical procedures, or non-analytical research in general. Hence, the next section will be focused mainly on this technique.

11.4.1 Soxhlet Extraction

Soxhlet extraction is a classical method because of its high extraction efficiency (Li-bin et al. 2007). Nowadays, it represents the main method of reference to compare the recovery obtained with other extraction techniques (e.g. Song et al. 2002; Gfrerer et al. 2004). Soxhlet extraction has some attractive advantages, since the sample is repeatedly soaked in fresh portions of solvent, facilitating the displacement of the transfer equilibrium.

Due to amount of PAH generated in combustion experiments, mainly when light hydrocarbons (e.g. soot precursors such as C_2H_2, C_2H_4) are burned in fuel rich conditions, the Soxhlet extraction is a good option. Indeed, the high solvent volume used avoids the saturation of the extract, which may cause wrong results. The solvent from the Soxhlet extraction can be recovered by rota-evaporation and, after a distillation process, it could be used again.

The thermochemical processes group (GPT) of the Aragón Institute of Engineering Research (I3A) of the University of Zaragoza has developed and optimized an analytical method for PAH determination (Sánchez et al. 2013), which is shown as an example of an extraction procedure applied to samples obtained from pyrolysis processes. This method (GPT-I3A) includes the collection of PAH as explained in Sect. 11.3, followed by sample treatment using the Soxhlet extraction and subsequent extract analysis using gas chromatography coupled to mass spectrometry (GC–MS).

Prior to Soxhlet extraction, each sample is placed in a cellulose cartridge, whose packaging consists of quartz wool at the bottom, followed by 3 g of sodium sulphate anhydrous to absorb sample moisture. The target sample with 10 µL of a solution of the five deuterated internal standards is added after the drying compound. Then, the cartridge is covered with quartz wool to prevent sample loss during extraction cycles. Finally, the cartridge, as a whole, is situated inside the thimble of the Soxhlet extractor.

Internal standards are used for correcting the possible losses of analytes during sample preparation, since the chromatographic signal of both the target compound and its internal standard have a similar response. Thus, if target compounds are lost during sample treatment, a proportional amount of their internal standard is lost as well. This ratio of signals, which is independent on the sampling history, is used to obtain the calibration curves and subsequently, the analyte concentration (Ferreira 2007).

Once the cartridge with the sample is placed within the thimble of the Soxhlet extractor, it is gradually filled with solvent from a distillation flask. The assembly extractor is operated as a batch system, since vapours of solvent move up to a condenser and flood over the thimble. When the liquid reaches the overflow level, a siphon aspirates the solvent from the thimble-holder and unloads it back into the distillation flask (Luque de Castro and Priego-Capote 2010). This process is repeated until complete extraction is achieved. The extraction time for the optimized method is fixed at 24 h using a total amount of 200 mL of dichloromethane (DCM) and 4 extraction cycles per hour, in accordance with the EPA method 3540C (EPA 1996b). Other solvents can also be used, such as acetone, ethanol and hexane. Similar conditions have been used by other authors (Levendis et al. 2001; Moltó et al. 2005, 2011). Xue et al. (2007) showed that using Soxhlet extraction 24 h is suitable for PAH extraction from different coal samples, with DCM more effective than hexane.

Sometimes, PAH are present at low concentration, and thus further concentration of the extract is needed because of the large amount of solvent present. The most common solvent concentration process is done by rota-evaporation followed by a micro-concentration under gentle nitrogen stream. This is especially valid for relatively clean samples, since an additional careful concentration is required to achieve the detection limits. The aromatic compounds may be lost during the evaporation process of the solvent. For this reason, the sample concentration is another critical step during the sample treatment. In this way, compounds such as DCM offer an advantage due to their low boiling point, far below of those at which target compounds are evaporated, thus avoiding significant losses of analytes.

11.5 Identification and Quantification of PAH

The complex characterization of the PAH extract requires that analytical procedures must be able to detect relevant substances in a mixture of compounds with a wide range of volatilities, sizes and polarities. In case very little amount of material is available, PAH can be advantageously desorbed from material (soot) and then identified by using laser desorption/laser ionisation/mass spectrometry technique as detailed in Chap. 12. Additional studies using laser diagnostic techniques for determining the PAH-soot distribution and for their characterization are reported in Wartel et al. (2010) and Furuhata et al. (2012).

Others use chromatographic methods such as reversed-phase high performance liquid chromatograph with ultraviolet detection (HPLC-UV) or GC–MS, combined with extraction processes (Poster et al. 2006; Borrás and Tortajada-Genaro 2007; Andrade-Eiroa et al. 2010a, b). Nevertheless, other techniques have been used (e.g. supercritical fluid chromatography and capillary electrophoresis) but are not generally acceptable (Lee 2001).

The capillary column technique in GC, used to separate PAH, has progressed since the sixties and has now become the standard method for the determination of these compounds. The main advantage of using GC for PAH analysis is that a slight modification of an existing GC protocol is usually enough to meet the requirements of a particular application. Further, by adjusting the carrier gas flow rate, temperature programming, and switching to a similar stationary phase, different types of matrices can be effectively analysed using GC with detectors such as flame ionisation detection (FID). However, GC–MS coupling is nowadays preferred for the analysis of complex matrices. Mainly, the application of selected ion monitoring (SIM) represents an integrated tool for separation, identification, and quantification of PAH, because generally it affords greater selectivity, resolution and sensitivity than other techniques (Lee 1995; Poster et al. 2006).

Determinations of PAH from combustion in flow reactors by using GC–MS have been carried out over the past twenty years. Howard et al. (1995) studied the concentration ratios of the isomer pairs of some PAH in ethylene combustion with naphthalene injection using a plug flow reactor. The main objective of this work was to evaluate the mutagenic effect of the combustion products. Durlak et al. (1998) used GC–MS for determining PAH from polystyrene combustion in order to evaluate the feasibility of incineration for this material. Another point of view was considered by Wornat's group (Ledesma et al. 2002) who analysed PAH by means of GC–MS to obtain kinetic parameters on PAH formation relevant to the combustion of solid fuels. Other works (Thomas et al. 2007; Thomas and Wornat 2008, 2009) using GC–MS have been developed throughout this decade with different purposes, such as those developed by connecting a laminar flow muffle furnace to a laminar flow reactor for the combustion of different polymers, and using GC–MS to determine PAH (Wang et al. 2002, 2003).

HPLC has also been applied for several years ago in PAH separation. This technique is the method of choice for analysing moderate to high molecular weight PAH (Furton and Pentzke 1998; Ledesma et al. 2002). It also offers advantages, such as selectivity and use of sensitive detectors, as well as the possibility to be used as a PAH fractionation to other chromatography techniques, even though, it also provides high efficiency and short analysis time (Ferreira 2007).

The analytical method optimised by the GPT-I3A of the University of Zaragoza allows the determination and quantification of PAH by means of GC–MS, and it is presented here as an example of technique for determination of PAH in thermochemical processes. Chromatographic conditions used are shown in Table 11.2. The different parameters were chosen following the EPA recommendations (EPA 1998b, 1999). All analyses are performed in the SIM mode of the MS in order to enhance the selectivity and sensitivity of the method. Table 11.3 shows the SIM profile programmed in the MS for PAH quantification; values in bold refer to the ion used for quantification and the MS window time in which each ion is monitored. The GC-MS system consisted of a 7890A gas chromatograph with a 7683B autosampler coupled to a MSD 5975C mass selective detector from Agilent Technologies. The capillary column was a DB-17 ms 60 m × 0.25 mm ID × 0.25 μm film thickness also supplied by Agilent.

It is important to highlight that prior to the application of any method, an appropriated calibration of every compound together with validation of the method must be carried out in order to ensure the quality of results. It is common to use standard reference materials (SRM) with similar matrices to those which will be analysed to ensure that the method provides good agreement with the values of certified materials. The GPT-I3A method was validated using SRM 1650b, a fully

Table 11.2 GC-MS operating conditions

Parameter	Value
Carrier gas	Helium at 1 mL min^{-1}
Injection mode	Splitless
Injection volume	1 μL
Injector temperature	300 °C
Temperature program	
Initial temperature	80 °C
Initial hold time	15 min
Ramp rate 1	5 °C min^{-1}
Final temperature 1	110 °C
Hold time 1	5 min
Ramp rate 2	5 °C min^{-1}
Final temperature 2	290 °C
Hold time 2	35 min
Ramp rate 3	1.5 °C min^{-1}
Final temperature 3	320 °C
Final hold time 3	5 min
Transfer line temperature	280 °C

Table 11.3 Monitoring ion profile (SIM)

Compounds	Monitored ions	MS window time (min)
Naphthalene	**128**–129	31.00–36.00
Naphthalene-d_8	**136**–108	
Acenaphthylene	**152**–153	43.00–47.00
Acenaphthene	**154**–153	
Acenaphthene-d_{10}	**164**–162	
Fluorene	**166**–165	47.01–56.00
Phenanthrene	**178**–179	
Anthracene	**178**–179	
Phenanthrene-d_{10}	**188**–189	
Fluoranthene	**202**–203	58.00–63.00
Pyrene	**202**–203	
Benzo(a)anthracene	**228**–226	67.00–72.00
Chrysene	**228**–226	
Chrysene-d_{12}	**240**–236	
Benzo(b)fluoranthene	**252**–253	81.00–84.00
Benzo(k)fluoranthene	**252**–253	
Benzo(a)pyrene	**252**–253	88.00–93.00
Perylene-d_{12}	**264**–260	
Indeno(1,2,3-cd)pyrene	**276**–277	110.00–114.00
Dibenz(a,h)anthracene	**278**–279	
Benzo(g,h,i)perylene	**276**–277	116.00–120.00

characterized soot from a diesel engine (NIST 2006), and a commercial soot used as diesel soot surrogate called Printex-U. The recoveries of the EPA–PAH for SRM 1650b were higher than 80 % in most of the cases and the PAH analysis using the Printex-U showed good method repeatability with a standard deviation for individual PAH as low as 0.5 ppmv (Sánchez et al. 2013). This fact proves its effectiveness to be applied in samples containing PAH formed in pyrolysis processes.

Figure 11.4 shows some results of individual PAH concentration obtained by using the analytical method developed by the GPT-I3A. These outcomes were obtained from ethylene and acetylene pyrolysis operating under different reaction temperatures ranging between 1,073 and 1,323 K. Extended details can be found elsewhere (Sánchez et al. 2010, 2012a, b).

11.6 Summary

The aim of this chapter is to provide practical information about different procedures to be used in the determination and quantification of PAH, mainly coming from thermochemical processes.

The methodology for quantifying the PAH usually consists of: (a) an efficient sample collection, (b) the sample treatment, and (c) the quantification of target compounds. During step (a), the different surfaces where the PAH can be adsorbed should be taken into consideration. PAH associated with particulate matter or/and at the gas phase are typically found in thermochemical processes. Frequently, this latter fraction is collected by sorbent materials (e.g. XAD resins and/or polyurethane foam, PUF). At the gas phase in flames, PAH can be collected by using apparatus like stainless steel probes or collectors, equipped with a filter for sampling combustion products along the flame axis. Thus, in general, the suitable collection depends on the facility where PAH are formed. PAH adsorbed on soot are often collected on filters. In the second stage, (b), the collection of samples is normally followed by an extraction process. Finally, in the (c) stage, the obtained extract is usually characterized by chromatographic techniques. Other approaches for PAH characterization, not requiring the extraction step, include laser diagnostic techniques which are commonly used in flames.

Despite of the fact that solvent-free techniques such as solid-phase microextraction (SPME) can be successfully used for PAH analysis, those based on solvents are normally preferred for extraction of samples from thermochemical processes. Some examples of solvent-based techniques include: ultrasonic extraction, extraction by microwaves, supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and Soxhlet extraction.

The high performance liquid chromatography with ultraviolet detection (HPLC–UV) and the gas chromatography-mass spectrometry (GC–MS) are the techniques mainly used for the identification and quantification of PAH.

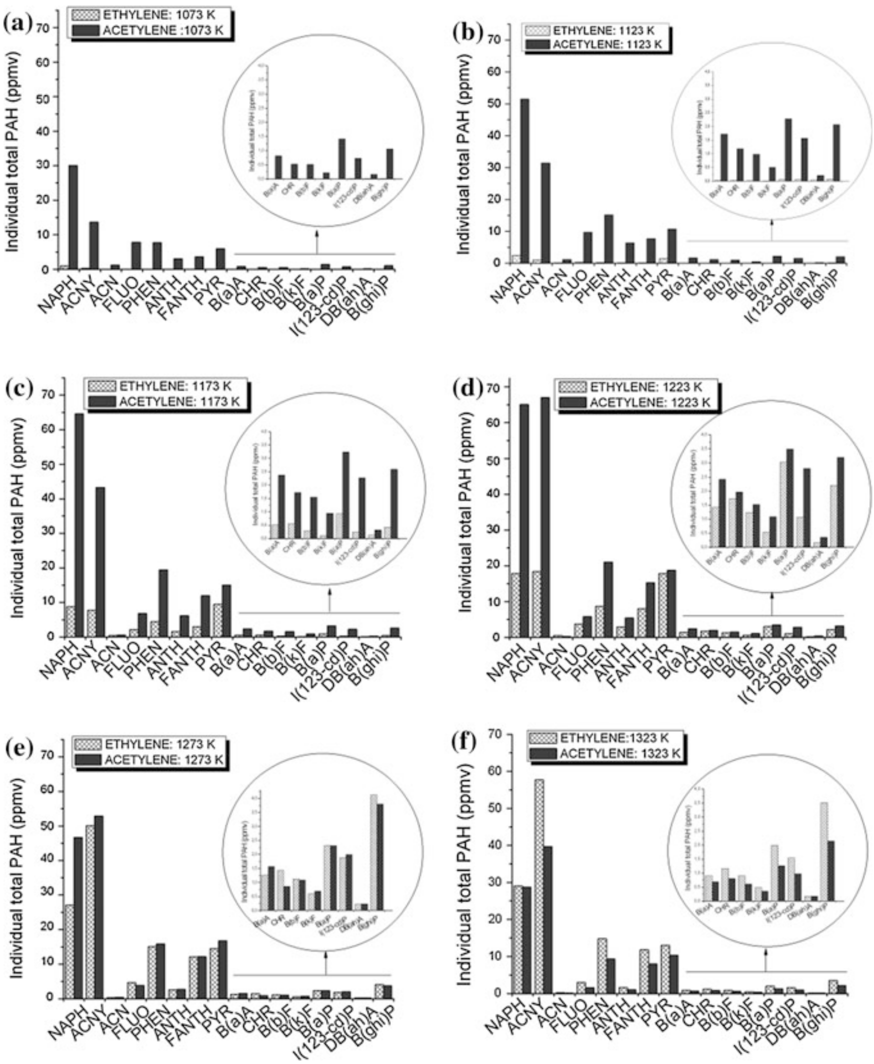


Fig. 11.4 Experimental results of PAH concentration obtained by GPT-I3A method, in the pyrolysis of acetylene and ethylene at different reaction temperatures: **a** 1073 K, **b** 1123 K, **c** 1173 K, **d** 1223 K, **e** 1273 K and **f** 1323 K (reprinted with permission from Sánchez et al. 2012b. Copyright 2012 American Chemical Society)

Nowadays, successful combinations of these techniques have been used for attaining the best results during the PAH speciation from thermochemical processes. Our experience suggests that the mentioned method (GPT-I3A), including the collection of PAH by using XAD-2 resin and quartz filters, followed by Soxhlet extraction of the samples and PAH quantification by means of GC–MS, would be a good procedure for application to thermochemical processes. The main reasons include its proved effectiveness, as well as the fact that it does not require expensive equipment and its simplicity to be applied by limited analytical experience staff.

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