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Recent Advances for Polycyclic Aromatic Analysis in Airborne Particulate Matter

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are formed in natural processes during combustion of biomass (e.g., forest fires) and by anthropogenic activities at high temperatures. In accordance with the suggestion the major sources of PAHs in the environment. The main sources of PAHs come basically from heat and power generation (e.g., coal, gas, wood, and oil), industrial processes (e.g., coke production), refuse burning and vehicle emissions. Human exposure to airborne PAHs can result from these processes, as well as from emissions from other sources, such as cooking, smoking, and materials containing PAHs (e.g., petroleum products and fuels). The potential serious health effects resulting from acute and chronic human exposure to PAHs are of concern. For this reason, the identification and quantification of PAHs in airborne particles have been a real challenge, given the multiple impacts that these substances represent for human health. In the last decade, multiple technological developments have been implemented, ranging from sampling systems, extraction and analysis of these compounds with the aim of obtaining more accurate and reliable results. This chapter was prepared to describe and to assess the state of the art about the evolution and application of sampling, extraction and analysis methodologies for the determination of PAHs in airborne particles.

Keywords: airborne particles, PAHs, cleanup, GC-MS/MS

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a large variety of organic compounds whose main characteristic is that they are formed by the fusion of benzene rings [1]. PAHs are originated mainly from incomplete pyrolysis of organic materials. Pyrolysis is the process in which organic compounds such as fuels undergo a change in the molecular structure at high temperature without sufficient oxygen concentration. These reactions are mainly dependent on temperature and concentration and are generally endothermic [2].

During combustion at high temperatures and relatively low amounts of oxygen, part of the combustible material is fragmented into small molecular masses, usually to free radicals by pyrolysis (approximately 500–800°C), which recombine to give




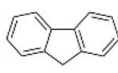
rise to the PAHs by pyrosynthesis by decreasing the temperature. Once PAH of low molecular weight is formed, (e.g., naphthalene, 128) the pyrosynthesis process continues with “zigzag additions,” which generates high molecular weight PAH [3].

PAHs are categorized as low molecular weight (LMW) and high molecular weight (HMW) based on molecular structure. The LMW PAHs include two and three rings structure while HMW PAHs comprise four and more rings structure. The carcinogenicity of PAHs increased with increasing molecular weight [4].

PAHs are ubiquitous pollutants in the atmosphere. The behavior of PAHs in the atmosphere depends on complex physicochemical reactions, interactions with other pollutants, photochemical transformations, and dry and wet deposition. PAHs in the ambient air exist in vapor phase or adsorb into airborne particulate matter depending on the atmospheric conditions (ambient temperature, relative humidity, etc.), the nature (i.e., origin and properties) of the aerosol, and the properties of the individual PAH [5]. The physicochemical properties of PAHs make them highly mobile in the environment, allowing them to distribute across air, soil, and water bodies where their presence is ubiquitous. PAHs are widely distributed in the atmosphere. The PAHs entering the atmosphere can be transported over long distances before deposition through atmospheric precipitation onto soils, vegetation or water [5].

The adsorption of PAHs onto particulate phases can also be affected by the humidity. Moreover, PAH adsorption also depends on the types of suspended particulates (e.g., soot, dust, fly ash, pyrogenic metal oxides, pollens, etc.) and the amounts of dust in the air influence PAH concentrations in the particulate phase [5].

PAHs are known to be toxic and carcinogenic [6]. They are metabolized in the body through oxidation by P450 enzymes and may produce carcinogenic metabolites. These metabolites have been shown to induce lung and skin tumors in animals [7]. People can be exposed through polluted air from urban or industrial environments, tobacco smoke, and diet [6]. The carcinogenicity of the PAHs usually increases with increased number of aromatic rings and higher molecular weight, while low molecular weight PAHs are more acute toxic [7]. Many hundreds of PAHs exist in the environment, but the US Environmental Protection Agency (USEPA) has listed 16 as “Consent Decree” priority pollutants chosen because, because of the likelier risk to be exposed to them, the high amount of information about them, and that they are believed to be more harmful [7] (**Table 1**).

PAH compound (s)	MW (g/mol)	CAS	Molecular formula	Carcinogenic classification	Agency	Structure
Naphthalene	128	91-20-3	C ₁₀ H ₈	Not classifiable as to human carcinogenicity	U.S. Environmental Protection Agency (EPA)	
Acenaphthylene	152	208-96-8	C ₁₂ H ₈	Not classifiable as to human carcinogenicity	U.S. Environmental Protection Agency (EPA)	
Acenaphthene	154	83-32-9	C ₁₂ H ₁₀	It has not been studied yet	U.S. Environmental Protection Agency (EPA)	
Fluorene	166	86-76-7	C ₁₃ H ₁₀	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	

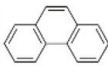
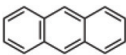
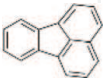

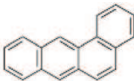
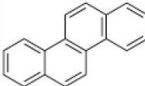
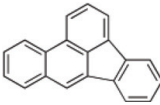
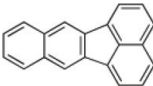
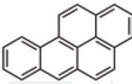
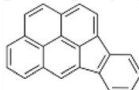
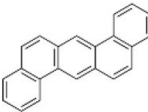

PAH compound (s)	MW (g/mol)	CAS	Molecular formula	Carcinogenic classification	Agency	Structure
Phenanthrene	178	85-01-8	C ₁₄ H ₁₀	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	
Anthracene	178	120-12-7	C ₁₄ H ₁₀	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	
Fluoranthene	202	206-44-0	C ₁₆ H ₁₀	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	
Pyrene	202	129-00-0	C ₁₆ H ₁₀	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	
Benzo(a)anthracene	228	56-55-3	C ₁₈ H ₁₂	Probably carcinogenic to humans	International Agency for Research on Cancer (IARC)	
Chrysene	228	218-01-9	C ₁₈ H ₁₂	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	
Benzo(b)fluoranthene	252	205-99-2	C ₂₀ H ₁₂	Probable human carcinogens	U.S. Environmental Protection Agency (EPA)	
Benzo(k)fluoranthene	252	207-08-9	C ₂₀ H ₁₂	Probable human carcinogens	U.S. Environmental Protection Agency (EPA)	
Benzo(a)pyrene	252	50-32-8	C ₂₀ H ₁₂	Probable human carcinogens	U.S. Environmental Protection Agency (EPA)	
Indeno(1 2 3-cd)pyrene	276	193-39-5	C ₂₂ H ₁₂	Probable human carcinogens	U.S. Environmental Protection Agency (EPA)	
Dibenzo(a,h)anthracene	278	53-07-3	C ₂₂ H ₁₄	Probable human carcinogens	U.S. Environmental Protection Agency (EPA)	
Benzo(g,h,i)perylene	276	191-24-2	C ₂₂ H ₁₂	Not classifiable as to their carcinogenicity to humans	International Agency for Research on Cancer (IARC)	

Table 1.
Some characteristics and carcinogenic classification for PAHs.

2. Methodology and analysis of polycyclic aromatic compounds in airborne particles

2.1 Sampling

The partition of PAHs between gas and particulate phases in the atmosphere fundamentally depends on the vapor pressure, temperature, atmospheric pressure, and the concentration [8, 9]. PAHs having two rings exist in the gas phase, PAHs having three and four rings are in both phases and PAHs having five rings or more exist in the particle phase [10].

The standard methods to measure PAHs in ambient air are active samplers, and these equipment use a pump to draw the air into the sampler, through the filter and the following adsorbent.

The samplers have a sampling module which often consists of two compartments: a filter and a solid adsorbent to collect the particle associated and the gas phase pollutants, respectively. The filter, often teflon, glass or quartz fiber, is placed in the inlet of the sampler [11–15]. The solid adsorbent normally consists of a polyurethane foam (PUF) plug or a sorbent tube with XAD-2 or Tenax depending on the target pollutants and the capacity required; the adsorbent also retains pollutants that volatilize from the particles on the filter during sampling.

The other alternative is passive samplers, in contrast to active samplers, not in need of a pump and electricity to collect pollutants. Instead, the collection is based on a free flow of pollutants from the air to the collecting medium. Most of the existing passive samplers are designed for gas sampling of semi-volatile organic compounds and based on high capacity sampling against a linear sampling rate for long durations such as weeks or months. Polyurethane (SPMDs), XAD-resin based samplers and membrane samplers are such examples [16–18].

In conclusion, sampling equipment can be active or passive, must be compatible and consistent with the analysis method and the monitoring objectives.

2.2 Extraction and cleanup

Given the complexity of environmental matrices, specialized analytical procedures are required for the determination of PAHs. The analytical procedures must include different stages for extraction of compounds from complex samples, purification and detection techniques for multicomponent mixtures that consist of compounds with a wide range of molecular weights, volatilities and polarities.

The extraction of PAHs from airborne particulates is mainly done through methods based on the use of solvents [19]. Being soxleth and ultrasound techniques the most commonly used for extracting soluble organic matter [20]. Subsequently, other solvent-based methods have been developed, accelerated solvent extraction and microwave extraction, both methods have the characteristics that use less solvent and extraction time [21, 22]. Finally, solid phase microextraction (SPME) was adapted for the extraction of PAHs associated with airborne particles, specifically for those of low molecular weight (less than four rings). The main characteristic of this method is that it uses very small amounts of solvents compared to the other extraction techniques mentioned [23]. **Table 2** shows a summary of the main techniques for the extraction of organic compounds from environmental matrices, some characteristics and applications.

PAHs extracts from airborne particulate matter represent a very complex matrix in trace amounts, which contain saturated hydrocarbons, nitrogen, oxygen, and

Techniques	Characteristics	Analytes	References
Soxhlet	It has been so far applied for organic compound extraction from solid matrices due to its high extraction efficiency	PAHs, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), among others	[29–31]
Ultrasound assisted extraction (UAE)	Ultrasound energy has also been widely used for the leaching of organic and inorganic compounds from solid matrices	Pharmaceutical Endocrine disruptor compounds (EDCs), perfluorochemicals (PFCs), antibiotics, tetrabromobisphenol-A (TBBPA) PAHs, phthalate esters (PEs), PCBs, nonylphenols (NPs), nonylphenol ethoxylates (NPEOs) and pharmaceuticals and personal care products	[32–35]
Pressurized liquid extraction (PLE)	Pressure is applied to allow the use of extraction solvents or mixtures at temperatures higher than their normal boiling point. The increase on the extraction temperature can promote higher analyte solubility by increasing both solubility and mass transfer rate	Perfluorinated acids (PFAs), perfluorosulfonates (PFSS) and perfluorooctanesulfonamide PAHs	[36, 37]
Microwave-assisted extraction (MAE)	Microwave-assisted extraction (MAE) uses microwave energy to heat the sample-solvent mixture. This technique reduces the extraction times and the extractant amount for the extraction of organic compounds from solid matrices	PAHs in airborne particles, 17-estradiol (E2), estriol (E3), 17-ethinyl estradiol (EE2)	[38, 39]
Supercritical fluid extraction (SFE)	Supercritical fluid extraction is an alternative extraction method with the advantages of reduced solvent consumption and extraction time compared with the classical extraction techniques. Carbon dioxide is commonly used as fluid and methanol is added as organic modifier when polar compounds are extracted	PAHs in marine sediment	[40, 41]
Solid Phase Microextraction (SPME)	It is used specifically for the extraction of low molecular weight organic compounds, from liquid, air and solid matrix	PAHs or polybrominated biphenyls (PBBs)	[42]

Table 2.
Classification of the main extraction techniques, characteristics and applications.

sulfur heterocompounds, among others, what difficult the identification of the PAHs identification in environmental samples [24–26]. After liquid extraction, a cleanup procedure is recommended to eliminate some interferences that can affect the PAHs detection in the chromatographic analysis. The most common cleanup procedures are as follows: liquid-liquid extraction (LLE) and solid phase extraction (SPE) with silica gel and/or C18 cartridges [27, 28].

2.3 Chromatographic analysis

2.3.1 Gas chromatography coupling to mass spectrometer (GC-MS)

Traditionally, the analysis of PAHs in environmental samples has been carried out by gas chromatography (GC), rather than liquid chromatography (LC), and this is due to its greater selectivity, resolution and sensitivity. GC-MS is one of the most powerful analytical tools available for the chemical analysis of complex mixtures. The use of mass spectrometry enhances the capabilities of gas chromatography; the specific information provided in the mass spectrum makes the mass spectrometer a highly selective detector that can be used for qualitative analysis and structural determination.

Mass spectrometry is undoubtedly one of the most widely used for the analysis and characterization of chemical compounds due to its high sensitivity and resolution capacity. Then, when it is coupled to the chromatographic techniques, it is particularly useful in the identification and quantification of organic substances of interest, which are in trace concentrations in environmental samples, it is highly valued mainly for its high sensitivity, that is, it is feasible to quantify those substances contained in a sample quantity of the order of mg.

One of the main disadvantages of mass spectrometry is the conditions used for the generation of stable ionized species and their adequate detection. This process can be a limitation to clearly observe the molecular ion and, therefore, perform a detailed analysis of the chemical structure. In the literature, a significant number of ionization methods have been reported, which depend on the physicochemical properties of the system in question. However, ionization is not the only limitation in mass technique; there are previous problems such as the distinction of different structures when analyzing complex mixtures. Therefore, the use of chromatography as a separation technique is essential for environmental samples such as those obtained in the ambient air, while after the ionization is the analyzer that is where the ionized species are separated and detected, they are also of great importance for analysis.

The criteria considered the most relevant in mass spectrometry are as follows: sensitivity, resolution, stability and selectivity; that depending on the level we need to reach each one of these, there are several types of coupled mass spectrometry equipment arrangements, so their choice depends mainly on the different chemical systems and the scope of the analysis. In the case of air samples such as gases and respirable suspended particles, the unambiguous quantification and identification of the analyte are the main objectives; therefore, the standardization and prior validation of the method used are essential, so it is necessary to carry out several preliminary tests with specific equipment arrangements in order to achieve reliable results.

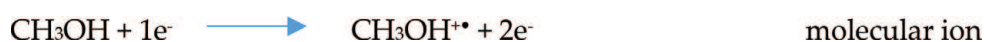
The mass spectrometer is among the most sensitive chromatographic detectors, having a detection limit below the picogram level, through the use of selected ion monitoring (SIM) mode. PAHs are easily resolved using standard GC columns without a requirement for derivatization. Most separations can be achieved in less than 30 min using capillary columns such as 30 m \times 0.25 mm i.d. and 0.25 μ m film thickness, 5% phenyl polysiloxane type phases. The use of a narrow bore, thin film column allows an increase in chromatographic resolving power, coupled with a reduction in analysis time.

GC-MS method has been used to all or some subset of the US Environmental Protection Agency (US-EPA) 16 priority PAHs. Single quadrupole GC-MS has offered the opportunity to increase selectivity for these analytes over that of classical detectors, such as UV and fluorescence detectors in high pressure liquid

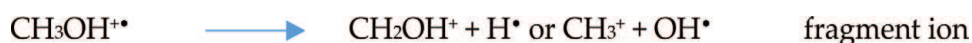
chromatography (HPLC) and electron capture detector (ECD) and flame ionization detector (FID) detectors in GC. This has allowed for limited optimization of sample preparation procedures to increase time to result [43, 44].

Quadrupole mass analyzers are widely used in many areas of environmental analysis. Although popularly referred to as quadrupole mass spectrometers, the mass-resolving properties of such devices are really much more similar to those of a tunable variable band pass mass filter. Only ions within a narrow mass region (generally <1 amu) are allowed to pass through the device.

Quadrupole mass analyzers have several advantages such as no requirement for very high vacuum ($>10^{-7}$ Torr) and their relatively fast and simple operation for high-throughput analysis. Disadvantages include low transmittance, a low m/z cutoff, and low (generally unit) resolution. Electron impact (EI) is well established and is the most common method of ionization in gas chromatography (GC) [45]. The molecules exiting the gas chromatograph are bombarded by an electron beam (70 eV), which removes an electron from the molecule resulting in a charged ion.



EI mode produces single charged molecular ions and fragment ions, which are used for structure elucidation.



The generated mass spectrum plots the signal intensity at a given m/z ratio (**Figure 1**).

Mass spectrometric methods are particularly suited for analysis of PAHs, because these compounds are semi-volatile and occur as complex mixtures; electron ionization (EI) and chemical ionization (CI) with quadrupole or magnetic sector mass spectrometers have been effectively used to determine PAHs. Although distinguishing between the isomeric forms of PAHs using EI is difficult because the isomers tend to produce common intermediates that give identical losses upon high-energy ionization or collisional activation [46].

For example, when trying to distinguish between compounds with the same or similar molecular weight, the GC-MS coupling is difficult, given its low resolution, **Figures 2** and **3** show the separation of chrysene and triphenylene and mass spectrum respectively. The quantification of chrysene is often biased due to its coelution with triphenylene (the compounds with m/z 228 also contain fragments of m/z 226). Another case is the separation of the isomers of benzo(b, k, j)fluoranthene (252 m/z).

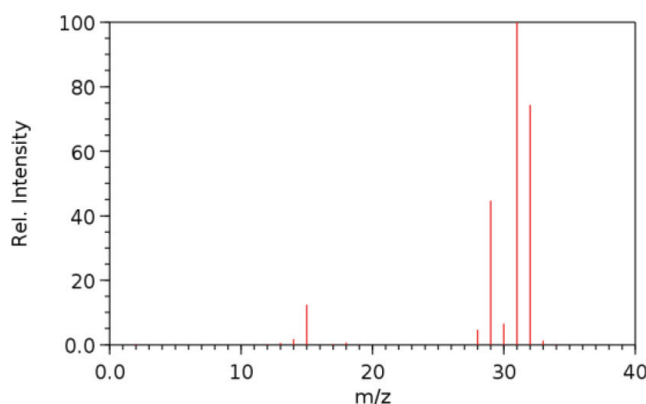


Figure 1.
 Mass spectrum for methanol obtained by electronic impact [47].

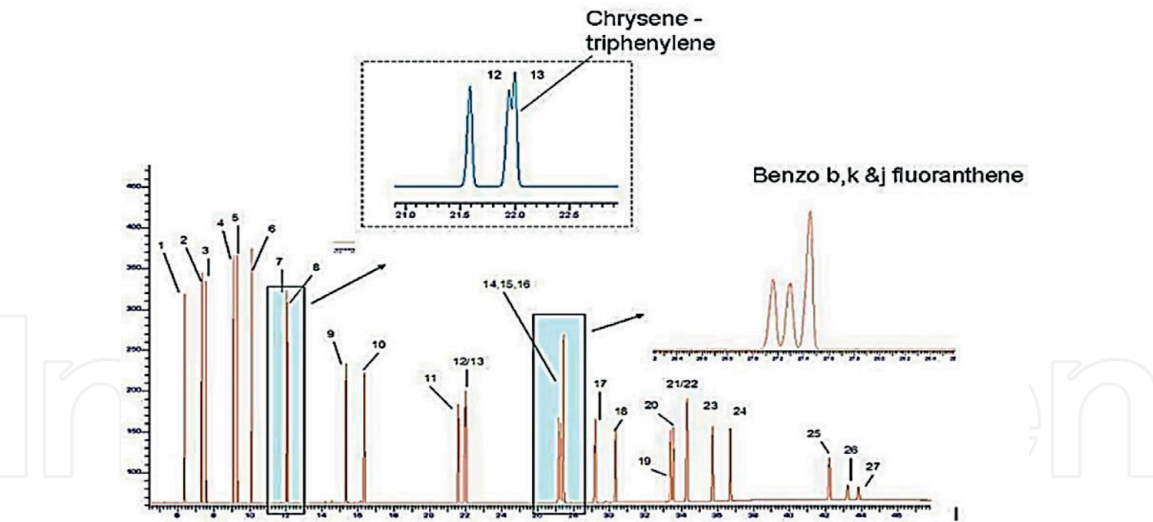


Figure 2.
Examples for PAHs separations with similar molecular weight [47].

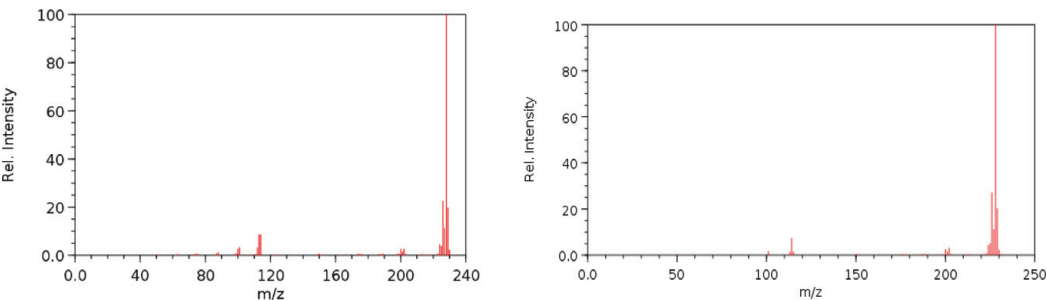


Figure 3.
Mass spectrum for chrysene and triphenylene [47].

2.3.2 Gas chromatography triple quadrupole

As seen in the previous examples, the mass spectrum with a single quadrupole is limited to distinguish among compounds that have structural isomers, since it only considers a single identification criterion, in fact they show a similar mass to charge fragmentation patterns (**Figure 4**). Recently, the coupling gas chromatography coupled to triple quadrupole mass spectrometry (GC-QqQ) was developed. Comparing triple quadrupole analyzer (QqQ) with single quadrupole analyzer, the product ion is more specific than the ion in the simple MS spectrum because the tandem configuration offers the only alternative of selecting the precursor ion of each compound by

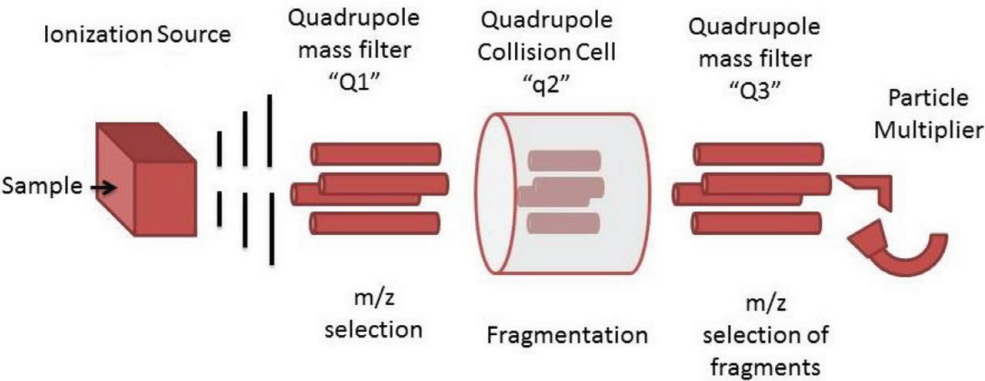


Figure 4.
Triple quadrupole mass analyzer (QqQ) [49].

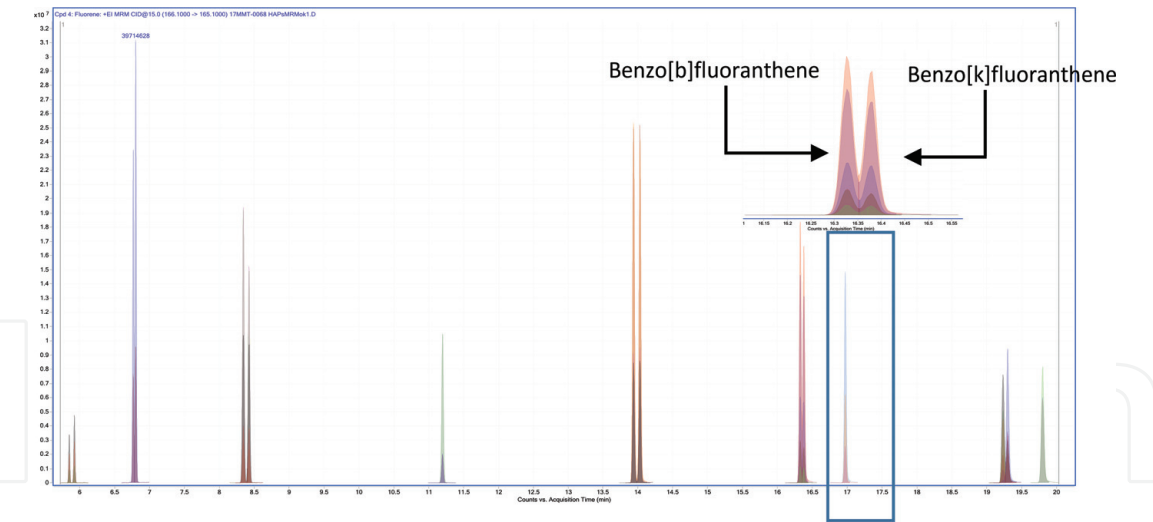


Figure 5.
Chromatogram 14 PAHs by GC-Qq (own authorship).

the first quadrupole and filtering it into the collision cell, with the consequent elimination of the remaining fragments and consequently the decrease in noise (**Figure 5**). Then that mass to charge pattern obtained by the second spectrometer, which is derived from the collision of the parent fragment, this usually has a unique pattern mass to charge daughter that provides invaluable structural information of the substance, which decreases the probability of false positives and facilitates the unequivocal identification of the target compound. It is clear that the coupling substantially solves the difficulties of simple couplings and can significantly improve the reliability of the determination by offering lower noise levels and additional identification criteria. Several reports show the utility of different arrays of mass spectrometers coupled to gas and liquid chromatographs used for the PAHs and their derivatives analysis. Among the most used is the triple quadrupole GC-MS/MS system, which provides detection and quantification levels equivalent to parts per trillion.

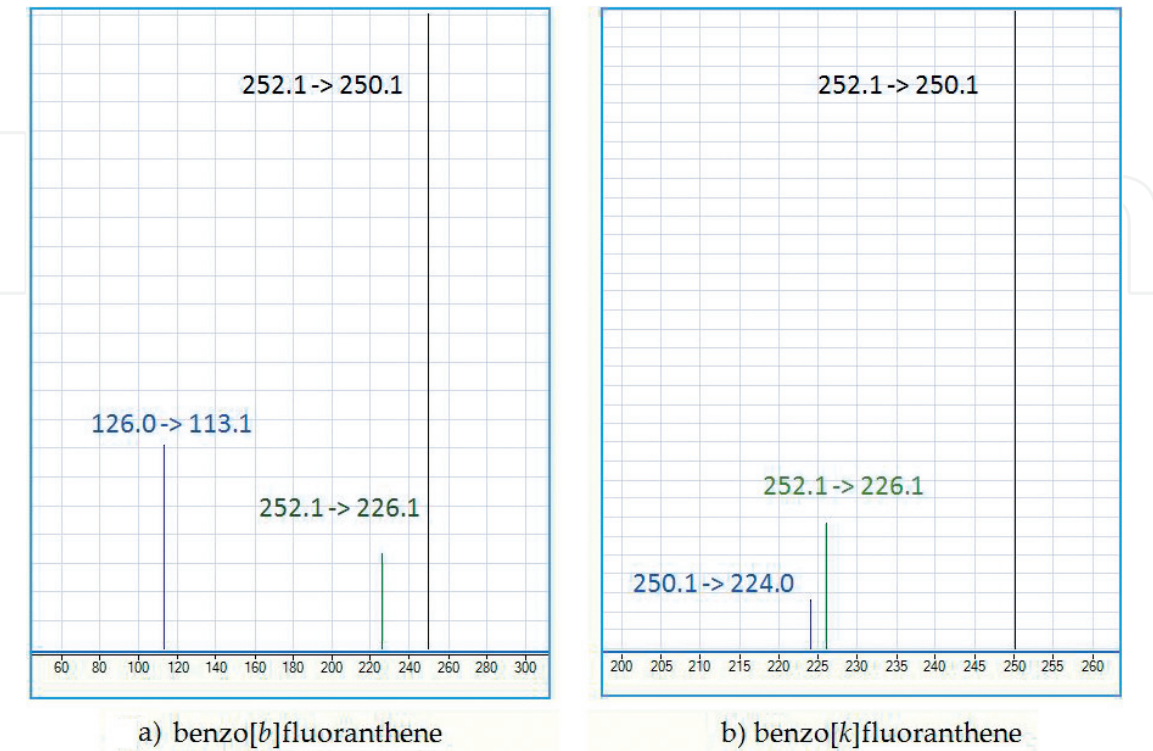


Figure 6.
Mass to charge (m/z) transitions (a) and (b).

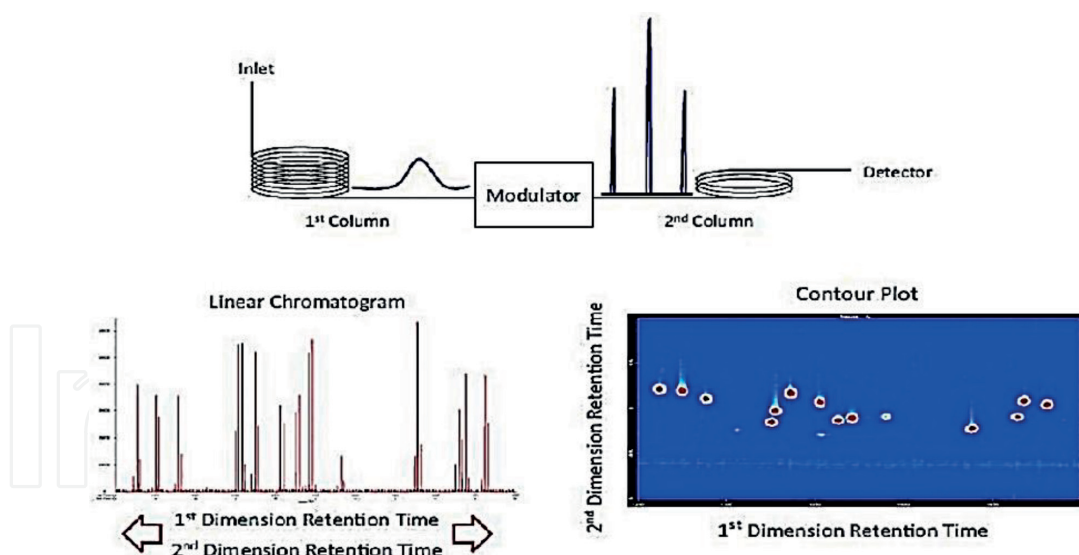


Figure 7.

Scheme of the gas chromatography bidimensional (GC × GC): peaks eluting from the first dimension column enter the second dimension column through the modulator [60].

For instance, the unequivocal identification of B(b)F and B(k)F isomers (**Figure 6**) was successfully achieved by distinct transitions mass to charge obtained with triple quadrupolar mass spectrometer arrange (**Figure 7**). It means QqQ may provide more accurate quantification and confirmation in trace analysis with complex matrix [48].

For these characteristics, recently the GC-QqQ has been proposed for the quantification of the PAHs and its derivatives. Its characteristics have proved to be useful for example in the determination of nitro-PAHs in PM₁₀ particles obtained with low sample volume (16.7 lpm). This implies a lower mass of the compound per gram of particle collected per day, and without an exhaustive treatment and sample purification need as those that are followed for particles obtained from high volume samplers (1.3 m³/h). An analytical method was recently developed for the simultaneous determination of 14 nitro-PAHs (2-nitrofluorene, 9-nitroanthracene, 9-nitrophenanthrene, 3-nitrophenanthrene, 2-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 2,7-dinitrofluorene, 7-nitrobenzo [a]anthracene, 6-nitrochrysene, 1,3-dinitropyrene, 1,8-dinitropyrene, 1,6-dinitropyrene, and 6-nitrobenzo[a]pyrene) in PM₁₀ by GC-QqQ in multiple reaction monitoring (MRM) mode. The method performance evaluation showed that the technique is quite reliable, since it provides high repeatability with relative standard deviation <10% and with detection limits between 0.25 and 10 ng/mL. This was also facilitated its application to only half of the filter containing the sample, in this way the remaining part served to complement the chemical characterization of the sample [50]. In the MRM mode, as the name implies, in the first quadrupole (Q1) one or multiple precursor ions of the analyzed substance were are filtered, which react by fragmenting in the collision cell (Q2), until arriving at the second quadrupole (Q3), where the ions product of the quantification and qualification are filtered. The results of this type of analysis are highly specific and sensitive because they provide unique structural information of the molecule that leads to its identification and unambiguous distinction between other substances contained in the sample [50].

Gas chromatography with tandem mass spectrometry has also been successfully applied for the determination of precursor PAHs. Although they are found in environmental levels between one and two orders of magnitude higher than their derivatives, they are trace concentrations substances, which are similarly affected by the different interferences that may come in the samples and by the matrix effect

in the extracts. Therefore, the organic extract must be purified before its analysis by GC-MS [51]. However, it was shown that when samples obtained with high volume equipment are analyzed, the extraction is sufficient, and the purification of the extract can be dispensed with before its analysis by GC-MS/MS [52].

Another coupling proposed for the analysis of the nitro-PAHs and oxy-PAHs derivatives is the ultrahigh pressure liquid chromatography-atmospheric pressure chemical ionization-tandem mass spectrometer (UHPLC-(+)-APCI-MS/MS). In addition to the stated advantage of the tandem arrangement, this alternative technique aims to contribute to reducing the thermal degradation that has been consistently reported for those oxy-PAHs classified as quinones in the injection port of the GC. Thus, facilitating their simultaneous analysis with the nitro-PAHs, and taking advantage of the improvements in the sensitivity and selectivity in the determination in organic and aqueous extracts obtained from PM_{2.5} and PM₁₀ particles. It has also been found that chemical ionization at atmospheric pressure (APCI), and photoionization at atmospheric pressure provides high ionization efficiency for oxy-PAHs, while electrospray ionization efficiency is usually lower [53]. In a pioneering study, it was shown that liquid chromatography atmospheric pressure chemical ionization-tandem mass spectrometer (LC-APCI-MS/MS) is feasible for the determination of oxy-PAHs and can contribute to the simplification of sample preparation by reducing it to an extraction and evaporation step [54]. Consistently, in a study of the simultaneous analysis of 5 nitro-PAHs—1-nitropyrene (1-NPYR), 2-nitrofluorene (2-NFLU), 3-nitrofluoranthene (3-NFLUANTH), 9-nitroanthracene (9-NANTH), 1,5-dinitronaphthalene (1,5-DNNAPHT)—, 3 oxy-PAHs-2-fluorencarboxaldehyde (2-FLUCHO), and 5,12-naphthacenequinone (5,12-NAPHTONA), it showed that the LC/MS arrangement provides a high degree of sensitivity and selectivity for the determination of these substances. In fact, it was demonstrated that it allowed the feasibility of its application to real samples. However, it was only possible to reliably report environmental levels of four of eight of these substances, at atmospheric concentrations between 0.01 and 240.62 ng/m³, equivalent to 0.3 and 30 mg/g, respectively [56] (Table 3).

2.3.3 Two-dimensional gas chromatography (GC × GC)

The widespread use of capillary columns in the 1980s improved significantly the separation power of complex mixtures. This positioned gas chromatography as the technique of choice whenever analyzing volatile substances. However, it soon became clear that in some fields, the separation capacity offered by a single chromatographic column was not sufficient. For example, in the case of the oil industry, environmental applications or aroma analysis, whose separations are highly

Location	Compounds	Equipment	Ionization mode	References
Industrial area of Taranto, Italy	Nitro-PAHs in airborne, PM ₁₀	GC/MS triple quadrupole	EI+	[48]
Seoul, Korea	PAHs in PM _{2.5} airborne particles	GC-GC-TOFMS	ESI+, APPI+	[55]
Buenos Aires, Argentina	Oxy-PAHs and nitro-PAHs airborne, PM _{2.5} and PM ₁₀	UHPL-MS/MS triple quadrupole	APCI+	[53]
Zaragoza, Spain	PAH associated to the airborne particulate matter, PM ₁₀	GC/MS triple quadrupole	EI+	[51]

Table 3.
Application of the GC/MS coupling for the analysis of PAH and its derivatives.

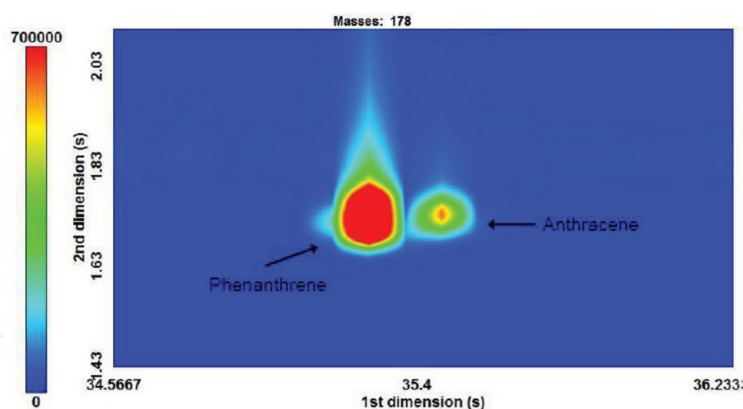


Figure 8.
Example of the application of the $GC \times GC$ for the separation and identification of structural isomers [61].

complex, often result in a chromatogram with a large portion of unresolved components [57]. Mass spectrometry can be used to resolve some of the complexity, but large concentration differences and structural isomers can complicate the spectral interpretation and data analysis. Some chromatographic resolution can be improved with an efficient, long, narrow bore, thin-film capillary column, but increased analysis time and decreased sample loading. This situation has been improved with the implementation of multidimensional gas chromatography ($GC \times GC$). Multidimensional gas chromatography increases resolution by using two separate columns with two different stationary phases. One form of $GC \times GC$ is heart-cutting. After a preliminary evaluation of the sample, a portion of the unresolved GC effluent is reoriented to a different column before detection. Heart-cutting is a simple way to obtain a better separation of a complex mixture but just a portion of the one-dimensional separation can be improved with the second-dimension column. A high-frequency modulator is utilized by the comprehensive two-dimensional gas chromatography ($GC \times GC$) for diverting the whole one-dimensional effluent onto a second-dimension column [58, 59] (**Figure 7**).

For instance, phenanthrene and anthracene are two important PAHs that can be used in order to assess whether material is petrogenic or pyrogenic in origin. Selecting mass 178 which is the molecular mass of the PAHs in question using the software allows isolated assessment (**Figure 8**).

As seen in the $GC \times GC$, saving time in sample preparation, instrumental analysis, has the ability to analyze an extensive range of complex samples with the simultaneous target and nontarget detection, which makes it a powerful technique for the elucidation of complex matrices; however, it is expensive.

3. Conclusions

PAHs are one of the families of organic compounds associated with the airborne particles that have generated the most concern. Currently, there is evidence of the multiple impacts that these compounds have on human health and the environment. The exposure time to which humans are exposed, the concentration levels of PAHs in the air, as well as the phase in which they occur; that is to say gas or particle, and the size of the particles with which they are associated. All these parameters must be measured and determined by the appropriate methods of sampling, extraction, and analysis. In the last 20 years, analytical methodologies and equipment development have experienced significant advances; all this has allowed the advance of more selective and less destructive extraction procedures; in the

same way, the purification methods of complex samples have been improved, but perhaps where greater progress has been made, has been in the instrumental analysis by coupling online extraction procedures, use of different detectors and the implementation of specialized software.

The main feature in the evolution of sampling systems has been the reduction of artifacts, through the use of adequate adsorption materials, as well as the mechanisms of PAHs uptake for both the gaseous and particulate phases. Regarding the extraction process, the greatest progress has been made in the reduction in the amount of solvents, compared with the traditional system (Soxhlet). To reduce the multiple interferences of the extracts obtained from the airborne particles and to increase the sensitivity in the detection of the PAHs, several purification schemes have been implemented based mainly on the use of solid phase extraction cartridges. Finally, the chromatographic techniques are those that have experienced the greatest advances, starting with the GC–MS coupling. However, this configuration does not allow to distinguish between compounds that have structural isomers. What caused the coupling of several quadrupoles (QqQ) in the same equipment, thus increasing the resolution. Finally, the inclusion of two-dimensional chromatography GC \times GC has allowed the simultaneous identification of compounds of different polarities, placing it as a powerful technique in the characterization of complex samples such as environmental samples.

There is no doubt the advance in the technology used for the analysis of PAHs in airborne particle matter in recent years. However, these new technologies require a high initial investment, in addition to highly qualified personnel, for this reason, before making the decision to acquire any of these new technologies, many aspects must be analyzed, for example if the equipment is going to be used for routine analysis, if the analytes to be studied can be extracted and detected with a simpler system, etc.

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Conflict of interest

The authors declare no conflict of interest.

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