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Review

Recent applications of gas and high-performance liquid chromatographic techniques to the analysis of polycyclic aromatic hydrocarbons in airborne particulates

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Abstract

Advances in the development of analytical separation techniques can be said to have been significantly fueled by the ever-increasing demands of environmental analyses. Complex environmental matrices and sample mixtures have motivated chromatographers to improve their craft to the present level of excellence in terms of functionality and applicability. This paper reviews the most recent application of two of the most important chromatographic methods —gas chromatography and high-performance liquid chromatography— to the analysis of an important class of environmental pollutants, polycyclic aromatic hydrocarbons (PAHs) and their derivatives. The review focuses on the use of the two aforementioned techniques in the characterization of PAHs and related compounds present in airborne particulates, reported in the literature in the past three years.

Contents

1. Introduction

Man has had to contend with environmental pollution since he first appeared on earth. However, it has only been from the beginning of the industrial revolution (generally considered to be in the 1750s) to the present day that environmental problems have assumed a scale of such magnitude that it is incumbent upon the earth's inhabitants to do something about them. Currently, air pollution, water pollution and solid-waste disposal are considered the three most important environmental problems facing the human population [1]. Environmental analyses have therefore assumed a position of critical importance in analytical chemistry.

It is probably true to say that advances in environmental analyses have more or less occurred concomitantly with those in the separation sciences. The reason is not difficult to

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ascertain; environmental samples are extremely complex, and often contain many different classes of compounds in varying amounts. An appropriate chromatographic procedure is therefore necessary to fractionate initially the sample extract into various classes of pollutants. This is followed by a similar technique to resolve, identify and quantify individual components within the respective compound classes. In other words, chromatographic techniques have invariably been part and parcel of this important segment of analytical chemistry. The efficacy and capability of a novel or improved separation technique is usually evaluated in the environmental area, because the latter field arguably places the greatest demands on any particular analytical procedure.

A cursory examination of accepted and certified methods of analysis of many environmental pollutants indicates that chromatographic techniques play a significant role, and may well be the most widely used procedures in this area of application. More specifically, chromatography is a principal technique in the analysis of air pollutants; the continued advent of new or improved instrumentation and novel column technologies have meant that chromatography has remained at the forefront in this area of research, and its preeminent position appears unchallenged in the foreseeable future.

The present review discusses the applications of gas chromatographic and high-performance liquid chromatographic techniques to the analysis of an important class of pollutants present in the air, the polycyclic aromatic hydrocarbons and their derivatives.

2. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) may well be the most widely studied class of environmental pollutants. [PAHs, strictly speaking, comprise carbon and hydrogen atoms only, and are just one class of pollutants classified under the more generic term of polycyclic aromatic compounds (PACs). The term PAC is usually considered to also include substituted PAH containing alkyl, amino, chloro, cyano, hydroxy, carboxy, nitro or thio functionalities as ring substituents, as well as the hetero-PACs in which a nitrogen, oxygen or sulphur atom is part of the ring nucleus. Even polycyclic aromatic quinones may be classified under PACs [2]. Nevertheless, there is as yet no universal appellation, amenable to everyone, to describe all of these aromatic compounds collectively. Even the term PAH itself is often substituted by "PNAHs" (polynuclear aromatic hydrocarbons), and is popularly taken to encompass the heterocyclics. Historically, amongst this category of polycyclic compounds, PAHs were the first to garner attention, and consequently "PAH" has been the most familiar term. It will hence be used here, even though the discussion following may be on those compounds containing other than just carbon and hydrogen atoms.] Fig. 1 shows examples of PAHs and their various derivatives. Boldfaced numbers on the following pages refer to the corresponding structures in this figure.

The interest in PAHs began in earnest in the 18th century, when in 1775, Pott suggested a link between scrotal cancer suffered by chimney sweeps and the soot to which they were exposed [3]. (At that time, of course, these compounds were unknown.) More than 150 years were to pass before Cook et al. [4], in the 1930s, finally confirmed that the cancer-causing substances present in soot were PAHs (specifically, dibenz-[*a*,*h*]anthracene and benzo[*a*]pyrene (**12**)). The carcinogenic and mutagenic activities of many types of PAHs [5,6] as well as their widespread presence and persistence have provided the impetus for the subsequent and continuing study of these compounds in environmental samples, 220 years after Pott's initial investigations. The importance attached to PAHs is indicated by the substantial interest given them by analytical chemists today, and it is not uncommon for a novel or improved analytical technique to be evaluated using PAHs as test compounds,

PAHs are formed from the combustion of fossil fuels, and are ubiquitous to the environment, the major contributors to which are anthropogenic sources [7]. Since the sources can be monitored and controlled, knowledge of the

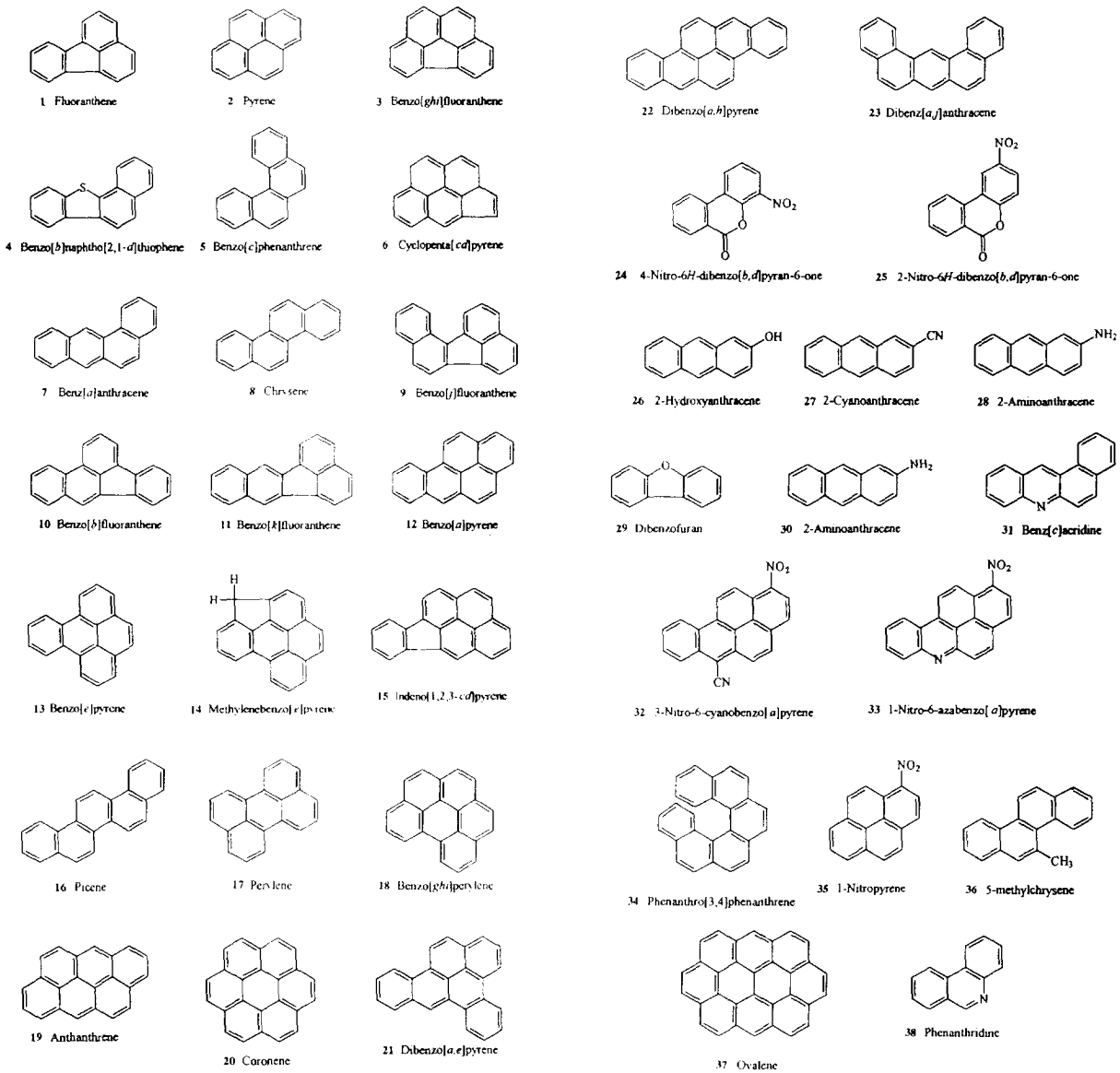

Fig. 1. Examples of some polycyclic aromatic hydrocarbons and derivatives.

analytical chemistry of these compounds is imperative not only in characterizing individual components, but also in attempting to determine the sources or origins of the PAHs emitted so that steps can be taken to eliminate or minimize the discharge of these substances into the environment. The main anthropogenic sources include coke production, motor vehicles (internal combustion engines), residential fireplaces, open fires (e.g. domestic or small-scale burning of refuse, and to a lesser extent, forest fires initiated accidentally or deliberately) and commercial incinerators. From these sources, a significant proportion of the PAH emissions enters the atmosphere directly, adsorbed on airborne particulate matter formed as a result of these combustion processes. Because of their biological properties, the dangers posed by the presence of PAHs in the atmosphere are obvious; their existence in the surrounding air has a direct

impact on the human population. The analysis of PAHs is thus a critical element in air pollution monitoring and control.

3. Gas chromatography

Amongst the various separation techniques, gas chromatography (GC) is still the most widely used in analytical chemistry. This in spite of the fact that, as an analytical tool, it can be considered to be somewhat old-fashioned, having been introduced more than forty years ago by James and Martin [8]. Improvements in GC instrumentation and ancillaries, especially the stationary phases, will, in all likelihood, extend the usefulness and applicability of the technique well into the future. The advantages of GC are many, the most important being the resolving power and the capability to detect low concentrations [9]. Speed of analysis is also a significant factor in its favour.

The fundamental characteristic for a compound to be analyzed by GC is its volatility within the temperature range used. By this measure, PAHs containing up to 24 carbon atoms may be analysed by GC [10], although structural differences may play a significant role in determining the volatilities of PAHs with the same carbon number; for example, the less condensed pyranthrene (which has thirty carbon atoms) can be easily analyzed by GC whereas its counterpart, naphtho[8,1,2-*abc*]coronene, requires special high-temperature GC [10], or supercritical fluid chromatography.

The general amenability of PAHs to GC analysis has caused this technique to be the principal analytical technique for these compounds in environmental samples for more than thirty years. The nature and variability of combustion processes cause the PAH mixtures formed and subsequently emitted into the atmosphere to be extremely complex. Thus, the high resolution furnished by capillary GC, first used for separating PAHs in 1964 [11], is tailor-made for the analysis of these otherwise recalcitrant mixtures. The fact that the analysis of PAHs by GC is well-established and extensively documented has also been instrumental in maintaining its status as the method of choice. A slight modification of an existing GC procedure is usually all that is required to satisfy a particular analyst's requirements.

The enormous improvements in the quality of the chromatography of PAHs can be traced back to the mid-1970s when Lee [12,13] discovered that acid-leaching of Lewis acids (present in the glass used to make capillary columns) resulted in much greater efficiencies and deactivation of the columns. Subsequent improvements in the GC columns used for PAH analysis have primarily been in the development of stationary phases with increased thermal stability. In the early eighties, crosslinked polymeric phases as well as chemically-bonded phases were introduced [14,15]. With these, analyses at temperatures ca. 100°C above those previously used were now possible. Because of the high stability afforded by these phases, in contrast to the older types which were statically coated onto the capillary walls, and which were therefore prone to decomposition and volatilization, more consistent and reproducible chromatographic data could be obtained. This is an important consideration because the proper use of such data for the identification of PAH components in extremely complex samples depends heavily on the reliability and consistency of these data. An important factor that also accelerated the development of these newer phases was the problem of wettability; modern phases have better glass-wetting properties which ensure that as the temperature is varied, the coated film maintains its homogeneity and does not form droplets.

The advent of liquid crystalline phases was another development beneficial to the GC analysis of PAHs [16,17], although in the end these phases were not as successful for routine applications as the more conventional phases. Examples of liquid crystals which were used for separating PAHs include N,N′-bis(*p*-x-benzylidene)-α,α'-bi-*p*-toluidine in which x denotes a butoxy, hexyloxy or phenyl group [16,17]. The interest in liquid crystalline phases was raised because for some isomeric PAH pairs separation is critical

since their carcinogenic or mutagenic properties differ significantly, and it may be difficult to resolve them with conventional phases. For example, the five-ringed PAH, benzo[*a*]pyrene (**12**), is considered to be one of the most potent carcinogens; on the other hand, benzo[*e*]pyrene (**13**) has lower activity [18], and separating them was one of the early challenges faced by chromatographers interested in PAHs, as was resolving important sets of isomers such as the benz[*j*]-, [*b*]- and [*k*]-fluoranthenes (**9**,**10**,**11**), all of which have different carcinogenic activities.

Chromatographers in the mid-eighties [19,20] began developing liquid crystalline stationary phases to exploit the slight structural differences in PAH isomers which translate into variations in their chemical affinities for the stationary phase, which in turn depend on the surface area of interaction [21]. A particular isomer may exhibit a higher retention because its shape and size permit greater interaction with the liquid crystalline surface. Its isomeric counterpart, on the other hand, may lack the structural entity to interact with equivalent facility with the same surface; its retention is therefore different, thus enabling separation. In a study of the retention behaviour of dibenzothiophene derivatives on a smectic liquid crystalline polysiloxane stationary phase [22], it was found that retention, vapour pressure and polarity were influenced by the molecular geometry of the compounds, especially the length-to-width ratio. An earlier study also investigated liquid crystalline phases that were sensitive to the latter parameter of eleven PAHs (each containing five benzene rings) with a molecular mass of 278 [23]. Despite this interesting foray into liquid crystals, however, many PAH analyses that formerly necessitated the use of these or other unconventional phases can now be carried out by capillary GC with commercially available columns packed with more traditional stationary phases; however, there is still an occasional interest in these unorthodox phases [24]. Generally, the popularity of these phases has waned mainly because long equilibrium times are needed between runs, and their properties tend to change with prolonged use, giving rise to irreproducible separations.

In recent years, further improvements in PAH analysis by GC have extended to the development of the more conventional stationary phases specifically for these compounds. For example, Klasson–Wehler et al. [25] and Sinkkoken et al. [26] described the use of improved stationary phases for chromatography of PAHs, while Bemgard et al. [27] compared several high-temperature stationary phases for their separation.

Over the past two to three years, there have been numerous papers on the application of GC to the determination of PAHs extracted from atmospheric samples. Some of these are highlighted in the following paragraphs.

The PAH content in diesel vehicle exhaust particulates received special attention in several of these recent publications, a timely development since diesel-fueled private automobiles appear to be making a comeback, especially in Europe. A short review on the sampling and gas chromatographic analysis of PAHs present in diesel exhaust emissions is available [28]. The US National Institute of Standards and Technology has also been developing or re-certifying diesel particulate extracts as standard reference materials [29].

In their work, Paschke et al. [30] evaluated supercritical fluid extraction with a variety of fluids (carbon dioxide, chlorodifluoromethane and a mixture of the two) to remove the PAHs and nitro-PAHs from diesel particulates, and then used GC for the analysis. Nitro-PAHs were also studied by GC–MS in workplace atmospheres contaminated by diesel exhausts [31]. These workers focused on the 1- (**35**) and 2-nitropyrenes which were reduced and derivatized prior to GC separation and detection. Oxy- as well as unsubstituted PAHs were extracted from air and diesel particulates sampled on glass fibre filters by Kelly et al. [32] with supercritical CO_2 and fractionated by HPLC before analysis by GC. Normal-phase HPLC was used with two different mobile phases to fractionate the PAHs and the oxygenated derivatives before transfer to the GC system via an on-column interface.

In a study of 28 PAHs present in diesel exhaust particulates [33], classical LC with silica gel was used, after initial extraction on a Soxhlet

apparatus to fractionate the extract on the basis of polarity. PAH analysis was performed by GC–MS. The ability of the various fractions to bind to the dioxin (aH) receptor site on cytochrome P450-IA1 was then determined. It is this binding that, in general, initiates the series of events leading to genotoxicity and carcinogenicity. The fraction exhibiting the greatest binding activity was the one containing PAHs and nitro-PAHs, although the authors stated it was not possible to identify the specific components to which the strong dioxin-receptor binding was attributed.

The nitro-PAHs in diesel particulates such as nitropyrenes, nitrofluoranthenes, dinitropyrenes, hydroxynitropyrenes and acetoxynitropyrenes are generally considered to be responsible for the direct-acting mutagenicity of these particles [34]. Thus, these species have been of more interest than the parent PAHs themselves in such samples. Recently, however, Ball and Young [35] claimed to have discovered a new class of mutagens other than the mono- and dinitropyrenes in the dichloromethane extracts of diesel exhaust particulates. They obtained fractions of the mutagenic material with normal-phase HPLC and used GC–MS to determine the concentrations of selected nitro-PAHs; only 1 percent of the total mutagenicity as indicated in the Ames assay with strain TA102 could be attributed to the known nitrated compounds. According to the authors, this is evidence that a new class of mutagens, as yet uncharacterized, is present in diesel exhaust particles.

Sera et al. [36] collected airborne particulate matter and particles discharged from petrol- and diesel-powered vehicles on Teflon-coated filter paper or XAD-4 resin using high-volume samplers in Fukuoka city in Japan, and used GC–MS after HPLC purification to detect and identify nitro-azabenzo[*a*]pyrene derivatives. Some of these mutagens were previously unknown: 1-nitro-6-azabenzo[*a*]pyrene (**33**), 3-nitro-6-azabenzo[*a*]pyrene, 1-nitro-6-azabenzo[*a*]pyrene-N-oxide and 3-nitro-6-azabenzo[*a*]pyrene-N-oxide. These compounds contributed for 34.9, 9.8 and 4.3%, to the total semivolatile extracts from airborne, diesel and petrol vehicular particulates, respectively. The authors believe that diesel emissions may be the primary source of these mutagens.

In another vehicle-related study, Rogge et al. [37] analysed airborne particulates emanating from road dust, tyre debris and brake linings, for their organic composition by using GC–MS. PAHs and oxy-PAHs, including polycyclic aromatic ketones (PAKs) and polycyclic aromatic quinones (PAQs), were identified in all three types of samples. The same authors have also looked at the PAH and oxy-PAH emissions discharged by (i) catalyst-equipped trucks, (ii) non-catalyst-equipped automobiles, and (iii) heavy-duty diesel-fueled trucks, again by GC–MS, after extraction of the sampled particulates by hexane and benzene–2-propanol [38]. For non-catalyst automobiles, the bulk of the identifiable fraction consisted of PAHs and oxy-PAHs, including PAKs and PAQs. These classes of compounds, on the other hand, formed a smaller proportion of the total identifiable organic mass for catalyst-equipped automobiles; most of the PAHs detected were of the higher-molecular-mass species such as benzo[*ghi*]perylene (**18**) and coronene (**20**). The diesel trucks, which were reasonably new, exhibited total PAH emission rates very much lower than those recorded by the automobiles. The PAHs emitted by these diesel trucks were mainly the low-molecular-mass species.

Westerholm and Li [39] investigated the relationship between diesel-fuel parameters and the PAH content in these fuels by using principal component analysis. They used a combination of classical column chromatography (sample clean-up), HPLC (class fractionation), and GC–MS for analyzing the purified PAH fraction. Most abundant of the PAHs in the fuels were alkylated three-ring compounds (phenanthrenes and anthracenes). These comprised uncombusted PAHs as well as those formed from the combustion process. The authors concluded that PAH emissions to the atmosphere by diesel-powered vehicles may be minimized by reducing the PAH contents in commercial diesel fuel to ca. 4 mg/l.

It is known that cigarette smoke is a significant source of PAHs and other compounds in urban atmospheres. Over the last thirty years many

studies have been published on the risks posed by cigarette smoke (see e.g., Ref. [40]). One recent study on this subject has been contributed by Rogge et al. [41] who measured several classes of compounds present in cigarette smoke by GC–MS. The authors focused on three- and four-ring PAHs in an attempt to identify a suitable marker for determining the contribution of this kind of smoke to the overall urban atmospheric particulate load. Because of contributions from other sources of PAHs to the urban atmosphere, these species were deemed unsuitable as tracers. Nevertheless, the use of other tracers by the same authors does indicate the urban pollution load attributable to cigarette smoke, and with it the accompanying risks assumed for the PAHs present in this type of smoke.

Indoor air has an important impact on a person's well-being. Indeed, working adults are exposed more to workplace air pollution than to outdoor pollution. Similarly, non-working adults and very young children may be exposed to air pollution at home. Several recent studies address this significant contribution to the pollution burden borne by the human population. Rogge et al. [42] have looked at the emissions from natural-gas home appliances, including a space heater and a water heater which were both evaluated to be in good condition. Apart from PAHs and oxy-PAHs, azaarenes and thiaarenes were identified by GC–MS in the exhausts of the appliances. The authors calculated that these mutagens formed 22% of the particle mass emitted, prompting them to suggest that exhausts from natural-gas combustion should be given more attention than hitherto by air pollution monitoring authorities.

The characterization of the mutagenic fractions in particulates resulting from indoor coal combustion was the subject of a study by Chuang et al. [43]. The work focused on a rural commune in China in which lung cancer mortality rates for women were the highest in that country even though most of the sufferers were non-smokers. High-volume samplers were used to collect particulates during cooking periods from one household. Soxhlet extraction followed by normal-phase HPLC was used to fractionate the extract. The fraction most active in the bioassay contained mainly PAHs and alkylated-PAHs, which were determined by GC–MS. The authors concluded that alkylated three- and four-ring PAHs produced from smoky coal combustion were probably significant factors linked to the high lung cancer mortalities in the commune. The authors believed that the more polar fractions containing nitrogen heterocyclic compounds could also contribute to the mutagenicity of the smoke extracts.

A preliminary study on the potential risks represented by the burning of plastics has been carried out [44]. With limited land available for landfill, an alternative method to handle the disposal of solid waste including plastics is incineration. However, there is concern over the toxic emissions, including PAHs, resulting from the incineration of solid waste, especially plastics. To address this issue, Wheatly et al. [44] conducted an exploratory laboratory-level investigation on PAH emissions originating from the combustion of common plastics. By using GC, the authors identified a whole series of PAHs produced during the combustion processes. The study sought to identify various incineration parameters which might be adopted to minimize the emission of toxic components, including PAHs, produced by the burning of waste plastics.

There have been several publications describing the use of biological markers to indicate atmospheric PAH pollution. PAHs characterized and measured in kale by GC was used to study the effect of climatic factors on PAH emissions [45]; the identities of these PAHs provided information on the combustion sources contributing to the PAH load. In a similar study, tree bark was used as a "passive sampler" for PAHs in the urban and rural environment [46]. The authors measured the concentrations of PAHs by GC in these materials and found a correlation with the extent of pollution, type of traffic conditions and the height from the ground of the bark sampled.

Nitrated fluorenes have also been the subject of interest amongst environmental chemists. Hel-

mig and Arey [23] used a GC column packed with a smectic liquid crystal phase to separate various isomeric nitrofluorenes present in the air. They also compared the retention characteristics of these species on this phase with other conventional GC packings.

Mention was made above of some studies which considered the carcinogenic and mutagenic potential of airborne particulates in urban atmospheres attributable to the PAHs present in diesel emissions. In a similar way, cancer risks due to exposure to PAHs faced by commuters in busy streets were evaluated by Chan et al. [47]. They used GC–MS to determine the PAHs collected on Tenax adsorbents. They claimed that motor cyclists faced two times the cancer risk encountered by bus commuters. The latter, in turn, were three times more at risk than non-commuters.

A recent study on PAHs focused on determining the particle size fraction associated with these compounds [48], the rationale being that controls on emission sources can be better effected by establishing the link between particulate sizes with emission processes producing the particulates. The ramifications of this are that the health effects posed by various size fractions of particulate matter can then be better understood and investigated. In the work in question, GC–MS was the principal technique used to identify the PAHs detected in the airborne particulates.

Other recent studies involving the use of GC or GC–MS as the primary technique for airborne PAHs include those by the following workers: Beard et al. [49] looked at the formation of polychlorinated dibenzofurans and other PAHs in petroleum refining processes; Luijk et al. [50] also studied the formation of dibenzofurans (**29**), but from the catalysed combustion of fly ash residual carbon; Rogge et al. [51] investigated the contribution of biogenic sources (leaf surface abrasion products) of trace amounts of PAHs to urban atmospheres; Hippelein et al. [52] used separate particle and gaseous samplers for collecting particulate and gas-phase PAHs respectively in ambient air; Fernandez et al. [53] identified and quantified 15 PAHs in urban and semi-urban atmospheres; Östman and co-workers used automated clean-up systems consisting of a coupled LC–negative-ion GC–MS setup [54], and an on-line LC–GC [55] to detect, respectively, chlorinated PAHs and ordinary PAHs in urban air; Roussel et al. [56] used both HPLC and GC–MS to establish the point source of atmospheric PAH emissions; Escrivó et al. [57] compared the analysis of PAHs in airborne particulates by GC with flame ionization detection and MS, with that by reversed-phase HPLC with UV and fluorescence detection; and Odum et al. [58] carried out a study on the photodegradation of benz[*a*]anthracene (**7**), one of the known carcinogenic PAHs commonly present in atmospheric samples, in the presence of methoxyphenols, which form a large proportion of the organic material associated with wood smoke.

In addition to these studies, there is available a recent review on the use of chromatographic techniques for the analysis of benz[*c*]acridines (**31**) [59] in atmospheric samples.

4. High-performance liquid chromatography

The development and progress of high-performance liquid chromatography (HPLC) can be considered to have suffered from the explosive success of GC which began in the fifties, and continued, especially with the advent of capillary GC, from the late seventies onwards. Scott [60] has remarked that due to the remarkable successes of GC during this period, developments in HPLC were held up and it was not until the major advances in the former were completed that HPLC development became a priority with scientists. In a sense, however, HPLC has caught up to be an established separation technique, even though "its progress has been slow and arduous relative to that of GC" [60]. It is probably safe to say without fear of contradiction that it is today the most popular chromatographic technique, with 100 000 systems in current use [61]. HPLC has also been claimed to be the most important analytical technique [61]. As judged by the number of papers on HPLC that are currently being published in the major journals specializing in chromatography in particular and

the analytical sciences in general, it is difficult to dispute this statement. Thus, from a promising conception, HPLC went through a difficult childhood, but having reached maturity has attained a respectable status today. It has yet to exhibit any signs of senescence and the large amount of work currently devoted to it suggests that significant advances can still be expected in the future.

The majority of PAH compounds, including the sixteen listed by the US EPA, can be conveniently analysed by GC. Indeed, the biologically active PAHs are usually also the more volatile ones, so GC is, intuitively, the appropriate method for their analysis. Conversely, the larger or less volatile compounds must be separated by another techniques; HPLC is the most popular of these alternative techniques. Apart from being well-suited to handle less- or non-volatile species, HPLC has several other advantages over GC, including the fact that it is a milder technique that, in most cases, is conducted at ambient temperatures, and is thus more acceptable for thermally-unstable PAHs. The literature, however, abounds with HPLC analyses of even the smaller and more volatile PAHs, including those designated by the US EPA. Thus, the use of this technique is not confined to the larger PAHs only–this is obviously another advantage that HPLC has over GC in that it can be used for a much wider range of PAHs (based on number of rings) of which volatility is not a problem. For instance, Jinno et al. [62] have reported the reversed-phase HPLC of a ten-ring system, ovalene (**37**). Indeed, the US EPA specifies HPLC as the technique to use for PAHs present in aqueous effluents [63].

In HPLC, UV- and fluorescence detection are the most popular for PAHs. Fluorescence detection has two obvious advantages over UV detection: greater selectivity and higher sensitivity. These are crucial considerations since genuine environmental samples usually contain very low levels of PAHs, and because of the presence of many interfering compounds that may cause problems with the analysis.

Since both normal- and reversed-phase HPLC may be used with equal facility for these compounds, about the only requirement necessary for a PAH to be analyzed by HPLC is its solubility in the common solvents used for either of these HPLC modes. Reversed-phase HPLC has tended to be more popular for PAH separation than normal-phase HPLC [64]. Based on the foregoing, it is no wonder that in many situations, HPLC is preferred over GC for PAH analyses. In fact, already in the early eighties, it was shown that PAHs could be separated very rapidly by HPLC [65,66].

The versatility of HPLC in terms of the development of an optimum set of analytical conditions cannot be matched by GC. In the latter, apart from a judicious choice of stationary phases, only single- or multi-step temperature-programming and the rate of temperature increase provide a degree of control over the establishment of optimum separation conditions. With HPLC, the use of suitable solvents for the mobile phase and subsequent manipulation of their composition, and appropriate selection of a bewildering array of normal- and reversed-phase stationary phases all offer more flexible method developmental strategies. In addition, although separations are usually performed isothermally, temperature-programming may be used, if desired, as has been done for PAH analysis [67,68]. However, this does not always mean that it is easier to develop a method for HPLC since the greater number of parameters that may be exploited to effect a more satisfactory separation can also be a disadvantage. Specifically, the optimization of a particular combination of several possible parameters for satisfactory analysis (which encompasses not only favourable separation efficiency, but also analysis time, resolution, etc.) can be carried out by trial-and-error, but this is time-consuming, and may not always lead to the best results. More efficient would be a systematic, possibly computer-assisted, optimization procedure. Examples of such systematic procedures which have been used for optimizing the separation of PAHs have been published [69–71]. Nitroaromatics have also been the subject of such a study [72]. Although these studies did not particularly concern the analysis of PAHs or their derivatives as air pollutants, the optimized HPLC conditions determined by these

systematic procedures may be applied to the routine analyses of these compounds extracted from atmospheric samples.

As pointed out earlier, reversed-phase HPLC is the most popular mode for the analysis of PAHs. The universal appellation "C_{18}" or "ODS" is applied to most, if not all, commercially available columns packed with the octadecylsilane stationary phase. Despite this, it is well known that in reality, there are significant differences in the selectivities of phases produced by different manufacturers for PAH separations. Previous investigations have established that several factors can influence the separation of PAHs on these C_{18} materials; Wise et al. [64] have stated that the most important of these factors is the way the C_{18} stationary phase was prepared. Specifically, monomeric phases (synthesized by reacting monofunctional silanes with silica) exhibit different selectivities for PAHs than their polymeric counterparts (prepared by the reaction of trifunctional silanes with silica in the presence of water) [64]. Thus, under gradient elution conditions with acetonitrile and water, all the sixteen EPA-listed PAHs could be resolved on the latter phase, but with the monomeric phase, which was manufactured by a different company, some critical ring-isomeric pairs [for example, chrysene (**8**) and benz[*a*]anthracene (**7**); and benzo[*ghi*]perylene (**18**) and indeno-[1,2,3-*cd*]pyrene (**15**)] could not be separated from each other [64]. These authors reported a general scheme which could be used to determine the selectivity of monomeric and polymeric C_{18} phases for separating PAHs. The scheme [73] is based on investigating the relative order of elution of three specially selected PAHs on these two types of phases. The selectivity, which is based on the planarity or otherwise of the three PAHs (benzo[*a*]pyrene (**12**), phenanthro-[3,4-*c*]phenanthrene (**34**) and 1,2:3,4:5,6:7,8-tetrabenzonaphthalene) can be defined quantitatively, which subsequently allows the classification of various commercially available C_{18} stationary phases into monomeric, polymeric or intermediate types. By this yardstick, only the first-named phase can be used to separate all sixteen EPA-listed PAHs; some of these are currently being advertised by their manufacturers as being specially produced for the complete separation of these priority PAHs. It should be noted, however, that in the majority, if not in all cases, gradient elution must still be used to resolve the sixteen components. (Although the capital cost of acquiring a gradient elution HPLC system is becoming lower, most laboratories with isocratic systems would nevertheless use GC for the actual PAH analysis, and employ HPLC as a clean-up or fractionation procedure. In many of the applications mentioned above in which GC or GC–MS was used as the primary technique for PAH characterization, HPLC was used to isolate compound classes.)

The selectivity of stationary phases for PAHs can also be exploited in a manner similar to that in GC described above. To distinguish ring isomers, the shape-recognition capabilities of some stationary phases can be employed. Specifically, the length–width ratios of PAHs, which effectively determine the shape of the respective molecules, are the basis of such chromatographic discrimination. The more "rod-like" the PAHs are (i.e. the greater the length–width ratio), the greater is the retention [74]. In an extension of this type of selectivity studies, the use of a liquid crystalline bonded phase for reversed-phase HPLC has been reported [75] for several PAHs. The [4-(allyloxy)benzoyl]biphenyl phase was claimed [75] to have greater planarity recognition power than the polymeric C_{18} phases described earlier. This greater ability was attributed to the greater structural orderliness of the liquid crystal in comparison to the polymeric C_{18} phases.

Fu et al. [76] have also investigated the HPLC retention characteristics of PAHs. They studied a large group of structurally-related nitro-PAHs and their corresponding parent PAHs using reversed-phase HPLC. It was observed that the larger the molecule, the greater its retention time. Saturation of the rings led to shorter retention times. Nitro-groups which are perpendicular to the ring eluted earlier, whereas those that are parallel to the ring had longer retention times. The addition of a nitro group resulted in a decrease in the retention time relative to the

parent PAHs. These observations led the authors to conclude that the polarity of these molecules was the determining factor in their retention behaviour.

Recent papers focusing on the analysis of PAHs present in atmospheric samples include those by Nilsson and Östman [77], McDow et al. [78], Gundel et al. [79] and Halsall et al. [80]. In their paper [77], Nilsson and Östman described the sensitive and selective analysis of chlorinated PAHs by first isolating the PAH and chlorinated-PAH fraction by two-dimensional HPLC, then using GC–MS with negative-ion chemical ionization and selective-ion monitoring to detect and quantify the chlorinated PAHs. Urban particulates were collected on glass fibre filters and polyurethane foam plugs, and the compounds of interest isolated by Soxhlet extraction.

As a follow-up to an earlier work (Ref. [58]) on the photodegradation of PAHs, McDow et al. [78] investigated six of these compounds in atmospheric aerosols and reported that the organic composition (methoxyphenols which are found in wood smoke, and hexadecane, present in diesel and automobile exhaust) of atmospheric particulates can influence PAH decay. The authors used reversed-phase gradient elution HPLC with fluorescence detection to determine the PAHs.

Gundel et al. [79] collected inhalable particulates from the air and analysed the acetone extracts on a reversed-phase HPLC system with UV and fluorescence detection. Mutagenic studies were carried out, and although they did not identify any compounds, based on the results, the authors suspected that nitro-containing compounds, such as oxygenated nitro-PAHs and azaarenes, were present in the extracts.

Halsall et al. [80] reported PAH data from the first two years (1991–1992) of a long-term study of a nationwide urban air monitoring scheme covering four cities in the UK. HPLC with fluorescence detection and GC with mass-selective detection were the techniques used in the study in which it was found that common sources were responsible for the PAHs at each sampling site. The PAH data for London indicated that air quality (at least as far as benzo[*a*]pyrene is concerned) has improved by two orders of magnitude over the previous 45 years.

Oxy- and nitro-substituted PAHs were also the subject of a study by Galceran and Moyano [81] who detected these substances in atmospheric aerosols by HPLC with electrochemical detection at sub-nanogram levels.

Hayakawa and co-workers have described the analysis of 1-nitropyrene (**35**) and dinitropyrenes extracted from airborne particulates, and petrol and diesel engine exhausts [82–84]. They used HPLC with pre-column or post-column conversion of the nitropyrenes to chemiluminescent derivatives before detection. They claimed that the analytes could be determined to femtomole levels by chemiluminescence detection which was 30–60 times more sensitive than fluorescence detection. Li and Westerholm [85] have also developed an HPLC–chemiluminescence detection technique for mono- and 1,3-, 1,6- and 1,8-dinitropyrenes in which reduction to the chemiluminescent derivatives was performed on-line. They applied their method to the determination of dinitropyrenes in diesel exhaust particulates. A study on 1- and other nitropyrenes present in diesel exhaust particulates was reported by Veigl et al. [86] who performed multi-column HPLC with post-column on-line reduction of the species of interest to aminopyrenes which were detected by fluorescence. The HPLC system consisted of three columns. The first column was packed with pyrenebutyric acid amide stationary phase and was used to isolate the nitropyrene fraction. This fraction was eluted into the second reversed-phase (C_{18}) column for separation. A third column was used for the reduction of the nitropyrenes to fluorescent derivatives to improve the detectability.

Heterocyclic aromatic amines are a class of carcinogenic compounds that are currently the subject of widespread interest [87,88]. While they are usually found in foods (cooked fish and meats) and beverages (wines and beers), some work has been conducted on their presence in cigarette smoke [89], airborne particulates, diesel exhaust particles and incineration ash from garbage-burning plants [90]. HPLC is the method most commonly applied for the determination

of these compounds [87–90], often with UV and/or fluorescence detection, and sometimes MS detection [91,92], since it is not necessary to derivatize the compounds for the chromatography. However, the use of GC–MS for the analysis of these amines (converted to their 1,3-bis-trifluoromethylbenzyl derivatives before chromatography) in cooking fumes generated in the workplace has recently been reported [93]. The method of collecting the fumes used in this work resembled that for airborne particulate matter, i.e. filtration of the fume aerosols through glass fibre filters and XAD-2 sorbent tubes.

The availability of pure reference standards is essential in environmental analysis, for qualitative and quantitative purposes. In this respect, Auger et al. [94] have improved the methods to synthesize polychlorinated naphthalenes and carried out the complete characterization (including X-ray crystallographic analysis) of these widespread pollutants. Hitherto, the physico-chemical data on these compounds were not sufficient to enable analytical studies. The authors used both GC–MS and HPLC for their purity analyses.

Other recently reported investigations on the use of HPLC as the primary analytical technique for PAHs and related compounds in airborne pollution studies include work by the following authors: Weisweiler et al. [95] collected particle-based and gaseous PAHs with glass fibre filters and tandem polyurethane foam plugs, respectively, and used reversed-phase HPLC with fluorescence detection to determine 15 PAHs in German cities in the late winter to spring period; Ignesti et al. [96] used olive fruits as a measure of air pollution by measuring several low-molecular-mass carcinogenic PAHs using reversed-phase HPLC with fluorescence detection; Librando and Fazzino [97] quantified PAHs and nitro-PAHs in airborne particulate matter in Augusta city in Italy using primarily HPLC; Dumont et al. [98] used HPLC with fluorescence detection to quantify PAHs present in cigarette smoke, which, as previously mentioned, can contribute to the overall air pollution load; Venkataraman et al. [99] also used HPLC with fluorescence detection to determine PAHs in particulate samples to characterize and compare vehicular and ambient aerosols as well as to study the effects of atmospheric processes on PAH size distributions; DeMarini et al. [100] evaluated the mutagenic potential of emissions resulting from the open burning of scrap rubber tyres by using the *Salmonella* mutagenicity test on fractions of the emission extracts isolated by HPLC; and Garcia Pinto et al. [101] used a micellar solution of Triton X114 for the extraction and preconcentration of PAHs from airborne particulates and wood ash, and subsequent centrifugation, before injection of the surfactant-rich phase into an HPLC–fluorescence system for analysis.

A paper published recently [102], while not specifically focusing on airborne PAHs, reviewed recent advances, including GC and HPLC in the analysis of PAHs and related compounds. Similarly, the following studies are relevant for the novelties in the analysis of PAHs: Doerge et al. [103], and Singh et al. [104] reported the use of HPLC–particle beam MS for the analysis of PAHs and their oxygenated metabolites; Galceran and Moyano [105] used HPLC–pneumatically-assisted electrospray ionization MS to characterize hydroxy-PAHs; and finally, Garcia et al. [106] used micellar HPLC to investigate the retention behaviour of benzene derivatives and PAHs.

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