

Review

Recent advances in the analysis of polycyclic aromatic hydrocarbons and fullerenes

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ABSTRACT

This paper highlights advances which have occurred in the last three years related to the analysis of polycyclic aromatic hydrocarbons (PAHs) and fullerenes by chromatographic and related techniques. The techniques reviewed include sample preparation, supercritical fluid extraction (SFE), gas chromatography, liquid chromatography, supercritical fluid chromatography, thin-layer chromatography and micellar electrokinetic capillary chromatography. Some of the most significant advances have occurred in the area of sample preparation, including the increased adoption of solid-phase extraction, supercritical fluid extraction, hyphenated chromatographic methods (e.g. LC-LC, LC-GC, etc.) and the chromatographic separation of fullerenes which did not exist on a macroscopic scale three years ago.

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) comprise the largest class of known chemical carcinogens, produced during the combustion, pyrolysis and pyrosynthesis of organic matter. PAHs are ubiquitous in air, water and soil, and their identification and determination continues to be an impor-

tant analytical problem. No less than one hundred articles have appeared in each of the last three years relating to the analysis of PAHs, making it a formidable task to keep abreast of the current literature. In this review, we survey the recent literature relating to the chromatographic analysis of PAHs. We have attempted to highlight advances which have occurred in the last three years (*ca.* August, 1989–August, 1992) in chromatographic and related techniques and refer readers to more comprehen-

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sive reviews if more thorough background material is required [1,2]. We have also included analysis methods for the closely related family of carbon allotropes known collectively as fullerenes, which have only recently been isolated on a macroscopic scale. Due to their chemical similarities, PAHs (e.g. triphenylene) and fullerenes (e.g. C₆₀) can be analyzed by similar chromatographic methods as discussed later in this paper. To make this review more manageable, we have limited the scope to advancements in analytical methodologies related to chromatography and, therefore, studies focusing on the distribution, biotransformation, flux and spectroscopic properties of PAHs have been omitted.

2. ASTRONOMICAL ANALYSIS

PAHs are more ubiquitous than some readers may be aware of. In fact, it is now generally accepted that PAHs are present in interstellar medium and that they may significantly influence the chemistries and charge balance within interstellar environments. PAHs are believed to be responsible for so-called unidentified infrared emission features (UIRs) and possibly diffuse interstellar band (DIBs) observed in outer space. In fact, PAHs are probably more abundant than all other known interstellar polyatomic molecules combined [3]. Scores of articles have appeared recently, including studies of the possible origin of interstellar PAHs [4,5], their stability [6,7], their location [8], and some interesting chemical implications here on earth. For example, it has been suggested that interstellar PAHs on meteorites may represent the starting material for the synthesis of complex molecules including amino acids [9], and primitive pigments in the prebiotic environment [10]. A thorough discussion of this topic is beyond the scope of this paper and interested readers are referred to reviews of interstellar PAHs which have appeared recently such as ref. 11.

3. SAMPLE PREPARATION

The PAHs from solid environmental samples such as air particulates, soils and sediments are traditionally extracted by Soxhlet extraction or ultrasonication using a variety of organic solvents including acetone, benzene, toluene, methylene chloride, etc. These traditional methods are efficient for

many samples; however, they often require large volumes of solvents, are time consuming, and yield incomplete recovery of higher-molecular-mass PAHs from materials on which they are strongly adsorbed (i.e. carbon black or coal fly ash). For these reasons, supercritical fluid extraction (SFE) has received considerable attention as an alternative to these classical methods as discussed later in this paper and in other papers in this issue. The recovery of PAHs from aqueous solutions has traditionally involved liquid-liquid extraction (LLE) methods with organic solvents (i.e. hexane, dichloromethane, chloroform, etc.). Since environmental samples generally contain interferents and trace amounts of PAHs of interest, concentration and clean-up procedures are usually required prior to the final chromatographic analysis. In many cases, the sample pretreatment procedure is the critical step in achieving reliable quantitative results.

PAH concentration and clean-up is increasingly being performed by solid-phase extraction (SPE). For preconcentration of PAHs from drinking water samples, best results were obtained for combined octadecylsilane (C₁₈)/ammonia (NH₂) solid-phase cartridges, whereas the enrichment of PAHs from soil samples was best achieved with silica (Si)/cyano (CN) or C₁₈/CN combinations [12]. The choice of SPE sorbent type is often dictated by the chromatographic method to be subsequently used for PAH separation and identification. For example, a recent study showed that for the determination of PAHs in lake sediments, C₁₈ and silica columns could be used to satisfactorily clean up extracts for subsequent HPLC analysis with fluorescence detection; however, they could not be used for gas chromatography (GC)-mass spectrometry (MS) for PAHs greater than chrysene due to interferences from aliphatic waxes. Fully activated silicic acid and neutral alumina columns were recommended [13]. A standard leaching test employing SPE with C₁₈ packings has proven to be a fast reliable method for determining the PAH leachability from waste materials [14]. Florisil (SiO₂ and MgO) cartridges have yielded rapid and efficient recovery of PAHs for petroleum and sediment extracts [15]. Extraction and concentration of PAHs in oils was achieved by charge-transfer liquid chromatography on an improved tetrachlorophthalimidopropyl-bonded silica [16]. A quantitative procedure for the determina-

tion of PAHs in biomass tar has been described using SPE with aminopropylsilane packings [17]. Chromosorb T and XAD-2 have been compared for the *in situ* extraction of PAHs from fresh water and seawater. Neither sorbent was useful for PAHs with molecular masses less than that of phenanthrene due to low recoveries or PAH contaminants, and were comparable for the study of three-ring and higher PAHs [18]. Structures for some common PAHs mentioned in this review are given in Fig. 1. A convenient method for the separation and pre-concentration of traces of PAHs in aqueous solutions has been achieved by adsorption on cobalt phthalocyanine and barium salts of sulphophthalocyanines followed by thermal desorption gas chromatography [19].

Numerous studies have dealt with the sampling procedure for airborne PAHs including the combination of a PTFE filter for particulates with polyurethane foam (PUF) for gaseous compounds [20]. A comparison of filter material used in high-volume sampling of PAHs revealed that glass-fibre filters yielded substantially higher concentrations of the lower-molecular-mass PAHs compared to PTFE

filters [21]. A new technique for controllable vapor-phase deposition of PAHs onto particulate matter was developed to provide particle-bound radiolabeled substrate for use in metabolism and toxicological studies [22]. The sorption and desorption properties of PAH-coated ultrafine particles was studied with a photoelectric sensor revealing the following ranking for desorption temperatures: Aerosil 200 > aluminum oxide > carbon > sodium chloride [23]. The concentrations of PAHs adsorbed onto air particulates was found to correlate negatively with temperature during the sampling, due to volatilization, photodegradation and seasonal modifications of emissions from urban traffic [24]. Storage stability tests revealed that PAHs (fluoranthene/pyrene to coronene) from ambient air collected on PTFE/PUF can be stored in the dark in closed vessels at room temperature for up to 118 days without observable losses [25].

Details of the preparation and analysis of a new National Institute of Science and Technology (NIST) Standard Reference Material (SRM) 1941 have been described. SRM 1941, Organics in Marine Sediment, has been certified for concentrations

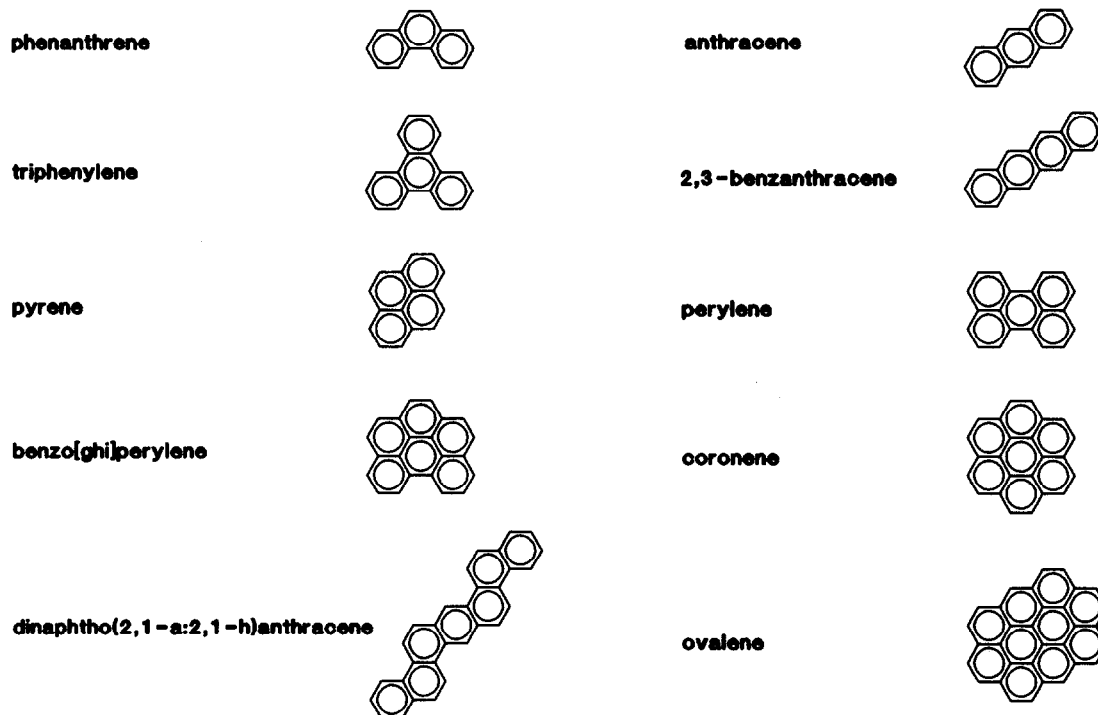


Fig. 1. Structures for some common PAHs mentioned in this review.

of 11 PAHs and provides non-certified values for 24 additional PAHs using results from GC with flame ionization detection, GC-MS and liquid chromatography with fluorescence detection [26]. Improvement in the precision and accuracy of the analytical procedures used by fourteen European laboratories should now permit the certification of coconut oil reference materials for low concentrations of PAHs [27]. A simplified version of an HPLC method has been described for the determination of PAH in suspended particles collected from small air volumes collected indoors, outdoors and in personal exposure measurements. A comparison of procedures for the determination of PAHs in low-volume samples has recently appeared [28]. A simple low-pressure liquid chromatography procedure has been developed for the isolation of PAHs from shale oil followed by GC analysis [29].

4. SUPERCRITICAL FLUID EXTRACTION AND CHROMATOGRAPHY

Supercritical fluid extraction (SFE) has proven to be a powerful alternative to conventional liquid extraction methods used in environmental analysis [30,21]. PAHs have been extracted directly from endogenous solid and liquid matrices, as well as trapped onto solid adsorbents with subsequent recovery by SFE [32,33]. One major advantage of SFE is the relative ease with which it can be coupled to chromatographic techniques, particularly GC and supercritical fluid chromatography (SFC). Hyphenated SFE-GC [34] and SFE-SFC techniques have recently been applied for the determination of PAHs from environmental samples [35,36].

Carbon dioxide is the primary fluid used in most SFE applications because it has low critical points (critical temperature 31.3°C, critical pressure 1070 p.s.i., 1 p.s.i. = 6894.76 Pa), is non-toxic, non-flammable, odorless, readily available in high purity, inexpensive, and eliminates solvent waste disposal problems. Unfortunately, the non-polar nature of carbon dioxide has hindered its application for the recovery of higher molecular PAHs or those strongly adsorbed to (or trapped in) the environmental matrix. Workers have strived to overcome this limitation in recent years. Alternative fluids such as N₂O and CHClF₂ (Freon-22) yield higher recovery

of PAHs from petroleum waste sludge and railroad bed soil, compared to CO₂ [37]. Alternatively, the use of organic solvent modifiers (*i.e.* methanol) or *in situ* chemical derivitization has been shown to improve the recovery of PAHs while still employing the preferred supercritical fluid, carbon dioxide [38]. Other studies have focused on optimizing the major controllable SFE variables and minimizing problems including restrictor plugging, particularly when extracting high-molecular-mass PAHs or employing samples with a high sulfur content. One approach to minimizing restrictor blocking employed a copper scavenger column placed after the sample cell. By this technique, SFE of PAHs was accomplished for high-sulfur-content samples without restrictor blocking [39]. Restrictor plugging while extracting PAHs has also been minimized by nebulizing an organic solvent with the restrictor effluent or by simply heating the restrictor from 50 to 200°C, depending on the analyte and sample matrix [40].

A model for dynamic SFE has been proposed and applied to the SFE of the PAH, phenanthrene, from railroad-bed soil with generally good agreement [41]. Models such as this are useful as they provide an extrapolation method for obtaining quantitative analytical extractions in the shortest analysis time. A dynamic tracer response technique has been applied for simultaneous measurement of equilibrium and rate parameters for the dynamic extraction of analytes from solid matrices. The technique has allowed adsorption equilibrium constants, effective diffusivities and axial dispersion coefficients to be determined for the system naphthalene-alumina-supercritical CO₂ [42]. We have reported the measurable effect of the extraction vessel dimensions (length × I.D.) on the elution of PAHs from octadecylsilane SPE sorbents [43], and the relative effect compare to the two major controllable variables; namely, temperature and density [44]. These results from SPE sorbents differ from those seen for the SFE of PAHs directly from environmental solids where no effect has been observed [45]. More thorough discussions of the effect of SFE variables and comparisons for different SPE matrix/analyte types have recently been published [46,47].

The development of SFE for extending the molecular mass range of PAHs normally separated by

GC continues. The modification of a GC–MS to SFC–MS mode has been described and used to separate PAHs with molecular masses up to 532 [48]. The retention behavior of PAHs in SFC for various stationary phases has been shown to be controlled by molecular size as in liquid chromatography, but also influenced by additional parameters including solute dipole moments, solubilities and volatility [49]. A molecular theory of chromatography based on mean-field statistical thermodynamics has been developed to describe the partitioning of blocklike molecules, such as PAHs, between an isotropic mobile phase and an anisotropic stationary phase. The theory was qualitatively applied to the interpretation and analysis of experimental data in gas, liquid and supercritical fluid chromatography [50]. The supercritical fluid retention of PAHs on a polymeric smectic phase has been compared to theoretical predictions using this molecular theory of chromatography with encouraging results [51]. The potential for predicting the utility of SFE from existing SFC retention data has recently been addressed [52]. In addition, we have found that of numerous physical and molecular descriptors studied, the molecular connectivity correlates best with SFC retention data for normal- and reversed-phase systems. Table 1 lists various physical parameters and the molecular connectivity calculated for some common PAHs. The excellent correlation between molecular connectivity and the logarithm of the capacity factor for three different SFC systems is illustrated in Fig. 2. The correlation is linear for the reversed-phase

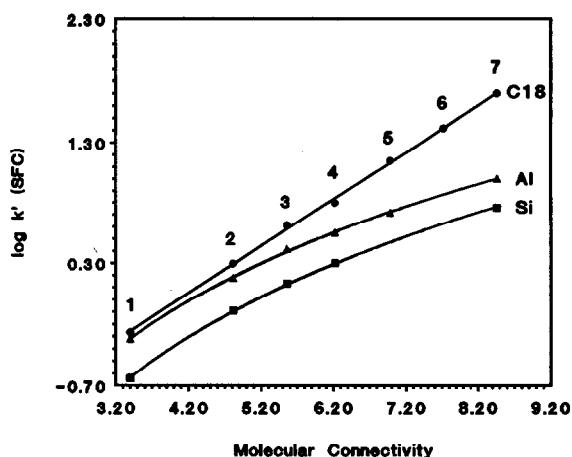


Fig. 2. Plot of $\log k'$ versus the molecular connectivity for PAHs. C18 = octadecyl column, 100°C, 300 atm, supercritical carbon dioxide mobile phase; Al = alumina column, 245°C, 47 atm, supercritical isopropanol mobile phase; Si = silica gel column, 260°C, 40 atm, supercritical ethanol–hexane (10:90) mobile phase. PAH identities given in Table 1.

octadecylsilane column and logarithmic for the normal-phase alumina and silica columns.

5. GAS CHROMATOGRAPHY

GC is the method of choice for high-resolution separation of complex PAH mixtures with moderate to low molecular masses. GC analysis of high-molecular mass PAHs (molecular mass exceeding 500) has been performed; however, these analyses

TABLE 1
PHYSICAL PARAMETERS FOR SOME COMMON POLYCYCLIC AROMATIC HYDROCARBONS

No.	Name	Molecular mass	Fused ring number	Melting point (°C)	Boiling point (°C)	van der Waals volume (Å ³)	Average molecular polarizability	Molecular connectivity (χ)
1	Naphthalene	128.17	2	81	218	127.1	17.48	3.40
2	Anthracene	178.23	3	217	340	170.0	25.93	4.81
3	Pyrene	202.26	4	150	404 (S) ^a	185.5	29.34	5.56
4	2,3-Benzanthracene	228.29	4	347	380 (S)	213.9	32.86	6.22
5	Perylene	252.32	5	274	340 (S)	229.0	38.84	6.98
6	Benzo[ghi]perylene	276.34	6	278	510 (S)	243.8	41.31	7.72
7	Coronene	300.36	7	427	525	259.2	42.50	8.46

^a S = sublimes.

have traditionally involved very short columns with correspondingly low resolution. Improved phases for high-temperature use continue their development and will allow even higher-molecular-mass PAHs to be separated while maintaining high resolution. A recent comparison of four high-temperature GC columns illustrated their utility for the high-resolution separation of PAHs with a molecular mass of 328 with seven-ring PAHs including dinaphtho(2,1-*a*:2.1-*h*)anthracene eluting in less than 35 min [53]. The utility of selective liquid crystalline phases has been demonstrated for the determination of bioconcentration factors of PAHs in polychaete worms [54]. Another recent study praised the long column lifetime (more than six years) and short analysis time (*ca.* 15 min) of a liquid-crystalline stationary phase for the analysis of PAHs in carbochemical products [55]. A double internal standard procedure has been described to increase the precision and accuracy of PAH determinations by GC [56].

Several recent studies have focused on relationships between GC retention of PAHs and molecular properties. Regularities of GC retention behavior have been described by structural models containing Van der Waals volume and molecular connectivity indices of different levels depending on the class of PAHs [57]. The heats of adsorption for PAHs on macroporous silicas has been studied by GC in the range 80–200°C [58]. Investigation of the relationship between GC retention indexes and computer-calculated physical properties of PAHs revealed that molecular polarizability was the most important property [59]. A study of the relationship between GC retention and thermal reactivity for PAHs in coal tar pitch indicates that, generally, those retained on OV-1701 more strongly than on SE-54 stationary phase are more thermally stable [60].

Although flame ionization detection and MS remain the methods of choice for PAH detection, other methods continue to show promise. GC–matrix isolation infrared spectrometry (MI-IR) can identify PAHs difficult to distinguish by electron impact MS [61]. The GC–Fourier transform IR spectra of 33 PAHs have been measured and interpreted [62]. A highly sensitive method for determining PAHs using GC–electron-capture detection after derivatization with bromine has been presented [63]. Other

selective detectors, including the photoionization detector, continue to find application particularly when attempting to eliminate interferences such as aliphatic hydrocarbons [64]. Analysis techniques for PAHs by GC and GC/MS continue their development. A complete method for the determination of PAHs in soil by GC has been described [65]. Thermal desorption GC–MS has been applied to the analysis of PAHs in contaminated soils [66,67]. The importance of solvent choice and initial column temperature has been investigated for PAH determination by GC–MS with splitless injection [68]. The use of toluene and xylenes gave enhanced signals up to 100 times greater compared to other solvents for the higher-molecular-mass PAHs through benzo[*ghi*]perylene. Complete analytical methodologies including GC–MS analysis have recently been described for the determination of PAHs in sediments [69], in glass manufacturing oils [70], in soils [71], and in soot produced by combustion of plastics and wood [72]. A recent method for the analysis of PAHs in vegetable oils and fish includes a gel permeation chromatography clean-up step prior to final analysis by GC–MS [73].

6. LIQUID CHROMATOGRAPHY

Since its inception more than twenty years ago, high-performance liquid chromatography (HPLC) has been applied to the separation of PAHs. Although HPLC still cannot compete with GC in terms of high efficiency and short analysis times, it does offer numerous advantages, including very sensitive and selective detectors and the ability to be used as a fractionation method for other chromatographic or spectroscopic techniques. The application of HPLC for PAH fractionation has become very popular due to its high efficiency, ease of automation and potential for column switching techniques and on-line coupling with other techniques including gas chromatography. The recoveries of PAHs from a soot sample were compared for ultrasonic ether, Soxhlet toluene and Soxhlet extraction with liquid CO₂ followed by HPLC fractionation [74]. The results showed liquid CO₂ Soxhlet extraction to be superior for lower-molecular-mass PAHs (to chrysene). A routine method for the analysis of mononitro-PAHs in environmental samples has been developed based on micro-scale liquid–liquid

partition (dimethylformamide–cyclohexane) and silica column HPLC fractionation prior to GC–electron-capture detection and GC–MS [75].

Techniques incorporating HPLC fractionation have gained in popularity in recent years. HPLC fractionation followed by GC analysis has been applied to the determination of PAHs in urban street dusts with primary components found to range from phenanthrene (three aromatic rings) to benzo[ghi]perylene (six aromatic rings) [76]. A column-switching technique utilizing a silica gel and an aminosilane-bonded silica gel column has been used to separate PAHs in lubricating oil base stocks into compound class fractions followed by GC–MS analysis [77]. A similar HPLC column-switching technique with silica gel and aminosilane-bonded silica gel columns has been used to fractionate monomethylated PAHs from heavy oil followed by GC analysis [78]. Column-switching HPLC techniques have also been developed for the analysis of PAHs in petroleum products [79] and the group separation of PAHs and nitrogen-containing PAHs [80]. A fully automated column switching HPLC method has been developed for the determination of 1-hydroxypyrene in urine of subjects exposed to PAHs [81]. A new on-line concentrator has been developed and applied to the analysis of PAHs in soot by on-line HPLC–GC [82]. On-line HPLC fractionation–GC analysis has also been applied to the separation and identification of PAHs in heavy oil [83]. On-line LC–GC–MS has been demonstrated for the analysis of PAHs in vegetable oils with detection limits down to 1 pg with selective ion monitoring [84].

The most popular method of PAH separation is reversed-phase HPLC with octadecylsilica phases dominating. Notable exceptions include anthryl-modified silica phases used to separate PAHs and nitro-PAHs [85], and phenyl-modified silica gel column used for improved separation of ³²P-labelled nucleoside 3',5'-bisphosphate adducts of PAHs [86]. Multidentate phenyl-bonded phases have been shown to provide higher non-planarity recognition of PAHs than that typically seen for octadecylsilica phases [87]. Reversed-phase HPLC provides unique selectivity for the separation of PAH isomers and particularly alkyl-substituted PAHs. Anomalous retention behavior of methyl-substituted PAHs on polymeric C₁₈ phases was found to be related to the

non-planarity of the PAHs due to the presence of the methyl group in the so-called "bay-region" of the PAH structure [88]. Microcolumn C₁₈ HPLC with 200 000 theoretical plates was used to separate a standard mixture containing 16 PAHs employing selective fluorescence quenching [89].

Numerous standard methods for the analysis of PAHs employing C₁₈ columns have recently appeared including the determination of PAHs in air particulate samples [90], diesel soot [91], biomass emissions [92], mineral waters [93], sea mussels [94] and anthracene cake [95]. A variety of applications have involved the separation and detection of PAH metabolites. The determination of 1-hydroxypyrene in human urine has been developed as an indicator of exposure to PAHs [96,97]. Similarly, hydroxyphenanthrene has been detected after intake of PAHs [98]. Details of the metabolism [99], as well as the HPLC separation of nitro-PAHs, has been described [100]. A combination of both reversed- and normal-phase HPLC was used to provide efficient separation of the ring-oxidized derivatives of nitro-PAHs. A method using three C₁₈ columns in tandem has been described for the separation of fish biliary PAH metabolites [101]. Numerous additional methods employing C₁₈ HPLC separation have been developed for use in a variety of applications, including the study of PAHs originating from pan fry cooking of meat [102], woodburning [103] and sewage sludge-amended agricultural soil [104]. A method for derivatizing PAHs to quinones for C₁₈ HPLC with selective electrochemical detection has been applied to the detection of selective PAHs in tap water and motor oil [105].

The retention mechanism in reversed-phase liquid chromatography for large PAHs has been investigated by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy and differential scanning calorimetry. The results indicate that a change in mobile phase from methanol to dichloromethane induces further non-planarity in non-planar solutes; whereas, increases in column temperature drastically change the structure of the stationary phase from solid-like to liquid-like, with subsequent losses in planarity recognition [106]. The use of subambient temperatures (*ie.* 0 to –20°C) can significantly enhance shape selectivity of PAHs for polymeric C₁₈ phases resulting in a phase with liquid crystal-like retention properties

[107]. Retention characteristics of nitrated PAHs on C_{18} columns demonstrated a linear dependence of logarithm of the capacity factor *versus* both the organic modifier concentration and the reciprocal of the absolute column temperature, allowing thermodynamic variables to be evaluated [108]. The retention in non-aqueous reversed-phase HPLC has been studied with the use of large PAHs and correlated to the amount of red shift in the fluorescence spectra for 11 common HPLC solvents [109]. The elution order of 10 PAHs up to coronene on C_{18} columns could not be satisfactorily explained with retention models based on molecular weight and length to breadth ratio alone, but improvement was made by taking into account the effects of intramolecular steric strain and the resulting degree of non-planarity [110]. The separation of large PAHs (benzo[ghi]perylene to ovalene) from a diesel particulate extract by reversed-phase HPLC with photodiode array detection revealed that all of the PAHs of six or more rings were highly fused, and no linear or non-alternate types were seen [111].

Although reversed-phase HPLC has dominated PAH separations, numerous normal-phase and specialty columns have been investigated to improve the selectivity of PAH separations. The separation of amino- and acetylamino-PAHs using six different reversed- and normal-phase columns has been compared with a Pirkle-type chiral phase exhibiting the best separation [112]. Derivatization of dihydrols of PAHs to O-methyl ethers has been shown to improve enantiomeric separation on Pirkle-type chiral stationary phases [113]. A liquid-crystal bonded phase has been shown to possess a planarity recognition power higher than that seen for typical polymeric C_{18} phases [114]. A comparison of several normal-phase packings demonstrated the advantage of a cyanopropyl-dimethyl-bonded silica gel packings for the group separation of chloro-added and chloro-substituted PAHs [115]. The effect of polar mobile phase modifiers on the retention of various classes of PAHs and the selectivity of their separation by normal-phase (silica gel) HPLC has been studied. The linear dependence of logarithm of capacity factor *versus* number of carbon atoms of the sorbate has been studied for unsubstituted PAHs monoalkylbenzene, and monoalkylnaphthalenes with different mobile phases [116]. The effect of the column material and mobile phase sol-

vents on retention of PAHs in size-exclusion chromatography has been investigated. The use of sulfonated poly(divinylbenzene) packings has been shown to improve the performance of this technique whose application to PAH analysis has been problematic [117].

The incorporation of cyclodextrins has received attention recently as a way of improving the selectivity of PAH separations. The unique shape selectivity of a cyclodextrin phase towards eleven five-ring PAHs has been compared to C_{18} columns. Although the polymeric C_{18} demonstrated the highest overall selectivity for the PAHs isomers, it was suggested that the lack of retention dependence on molecular mass could be advantageous for the separation of PAHs of different molecular masses [118]. Bonded β - and γ -cyclodextrin phases showed relatively low efficiency but high selectivity, allowing the separation of different classes of isomeric compounds, including PAHs, which were difficult to separate on conventional LC stationary phases [119]. β -Cyclodextrin has also been used as a selective inclusion reagent in reverse-phase HPLC separation of PAHs. Molecular interaction of PAHs was determined to be mostly electrostatic and retention order strongly influenced by PAH molecular shape [120,121].

7. MISCELLANEOUS TECHNIQUES/APPLICATIONS

Thin-layer chromatography (TLC) is often used as a sample preparation method in PAH analysis, particularly when oil samples are involved. Standardized GC methods employing TLC separation have been developed for the determination of PAHs in petrochemical plants and oil refineries [122] and in olive oil [123]. The utility of urea-solubilized β -cyclodextrin TLC mobile phases was demonstrated by the resolution of a variety of compounds, including four PAHs, on a polyamide stationary phase [124]. The analysis of PAHs in spa waters has been accomplished by two-dimensional TLC using plates containing a mixture of aluminum oxide, silica gel and acetylated cellulose with detection by spectrofluorometry [125]. Laser mass spectrometry has been used to detect separated PAHs directly from polyamide TLC plates [126]. On-line coupled HPLC–TLC allowed for the successful separation of PAHs in marine sediment using a simple isocratic

microbore HPLC system and a conventional fluorescence spectrometer for detection [127].

The effectiveness of the anionic surfactant dodecylsulfate in solubilizing various PAHs has been studied for several different sediment and soil solid phases and aqueous phases [128]. The solubilization and partitioning of PAHs between micelle phase and aqueous phase has also been determined for non-ionic polyoxyethylene surfactants [129]. These data can be combined with additional information on surfactant and PAH sorption on soil/sediment to understand mechanisms affecting the behavior of PAHs in soil/sediment–water systems in which surfactants play a role in contaminant remediation or facilitated transport. The effect of varying sodium dodecylsulfate concentration and the introduction of γ -cyclodextrin in the micellar electrokinetic capillary chromatographic separation of PAHs investigated with an average theoretical plate number of more than 160 000 [130,131].

Direct experimental determinations of Henry's law constants for nine PAHs using a wetted-wall column technique and GC analysis compared favorably to other calculated and measured values [132]. Molecular topology has been used to model *n*-octanol–water partition coefficients of PAHs and their alkyl derivatives [133]. PAH partitioning mechanisms with activated sludge have been studied and an equation developed from thermodynamic principles to estimate lipid–waste water distribution coefficients [134]. PAH–chlorobutane and PAH–dichlorobutane equilibrium constants have been calculated from solubility data [135]. The potential health hazard from water chlorination due to formation of chlorinated PAH has been investigated. Chlorination of PAH contaminated humus poor lake water was found to result in formation of chlorinated derivative for some PAHs. However, in the presence of high concentrations of humic substances, no chlorinated PAHs were detected [136]. The extent of reaction of PAHs with hypochlorite has been shown to depend on the chlorine dose, the solution pH, the concentration of both compounds (high values studied) and the structures [137].

8. FULLERENES

Although PAHs are customarily regarded as planar structures, there are well known exceptions

such as corannulene which has a bowl-shaped structure and forms one of the faces of C_{60} , buckminsterfullerene, named after Buckminster Fuller, the architect widely known for his invention and advocacy of the geodesic dome. The approximate structure of buckminsterfullerene is shown in Fig. 3 along with several PAHs (triphenylene, coronene and corannulene) for comparison. The motivation for the experiments which led to the hypothesis of the soccer ball-shaped C_{60} molecule [138] was an attempt to understand the mechanisms by which long-chain carbon molecules are formed in interstellar space and to explain spectral features of interstellar matter, including UIRs discussed earlier for PAHs [139–141]. In 1990, preparation of the first macroscopic quantities of C_{60} , the third allotropic and first molecular form of carbon, were reported [142]. Although not considered an environmental concern, fullerenes have recently been found in the geological environment [143] and may require the revision of our ideas about carbon structures, including graphite [144]. The first and most studied fullerenes, C_{60} and C_{70} , were extracted with benzene, toluene or carbon tetrachloride followed by column chromatography on alumina columns [145–

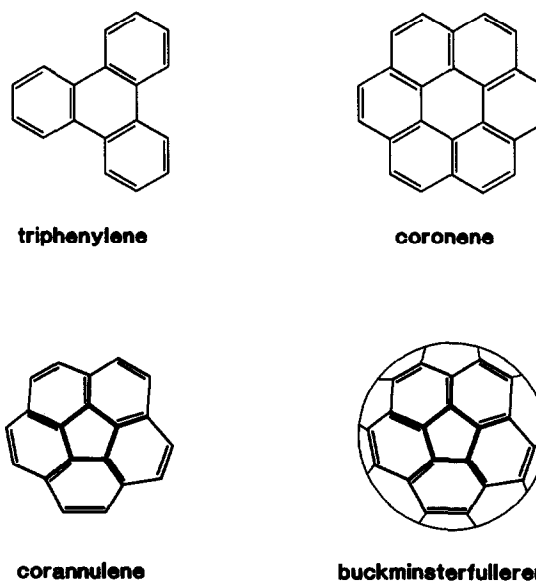


Fig. 3. The structures of the PAHs triphenylene, coronene and corannulene as well as an approximate structure for buckminsterfullerene (C_{60}).

148]. Larger fullerenes are not soluble in these solvents and alternative solvents, including quinoline and pyridine, have been used to extract very large fullerenes as large as C_{300} [149], and giant fullerenes as large as C_{500} [150].

Currently, column liquid chromatography using alumina columns is the method of choice for the separation C_{60} and C_{70} . Unfortunately, this classical technique is tedious, time consuming, and requires relatively large volumes of high-purity solvents, particularly when isolating C_{70} . Additionally, the reported yields of C_{60} by this method are currently limited to *ca.* 250 mg per column per day, or *ca.* 600 mg per column per day using improved procedures such as pre-adsorption onto alumina [151], and continuous column chromatography employing Kauffman columns [152]. The pace at which fullerene research can proceed will rely, in part, on the development of improved chromatographic methods for more rapid and efficient separation of fullerenes, as well as HPLC methods for testing the purity of fullerene extracts. HPLC techniques will also play an integral role in the separation and isolation of the higher fullerenes (*i.e.* C_{70} , C_{76} , C_{78} , C_{82} , C_{84} , C_{86} , C_{90} , C_{94} , etc.).

Due to the similarities between PAHs and fullerenes, many HPLC methods developed for PAH separation can be successfully adapted to the purification and analysis of fullerene mixtures. Good separation of C_{60} and C_{70} has been achieved on a dinitroanilinopropyl (DNAP) silica column with gradient elution from *n*-hexane–dichloromethane (50:50) over 35 min. The chromatographic characteristics of lower fullerenes on DNAP closely resembled PAHs with the retention of C_{60} nearly identical to that of triphenylene [153]. This early elution of C_{60} can be considered an extreme example of the effect of non-planarity on retention time in reversed-phase HPLC which is well documented with smaller molecules [154]. Although they have vastly different molecular masses, triphenylene (molecular mass 228.29) and buckminsterfullerene (molecular mass 720.67) have comparable diameters, as seen in Fig. 3. The relatively low solubility of the fullerenes in many of the HPLC solvent systems studied has limited column loadings and, therefore, the amount of material purified. The use of pure toluene, a solvent in which the fullerenes have good solubility, as a mobile phase has been

used to isolate 23 mg of 93% pure C_{60} in less than 20 min [155]. The rapid isolation of C_{60} by HPLC methods should provide for higher overall daily yields (*i.e.* > 1 g/day) than that currently available by column liquid chromatography. Undoubtedly, techniques for the isolation of fullerenes higher than C_{60} will increasingly rely on HPLC.

A commercially available Pirkle-type phenylglycine-based semipreparative HPLC column was used to very selectively ($\alpha = 2.25$) separate C_{60} and C_{70} in less than 25 min using hexane as the mobile phase [156]. C_{60} and C_{70} were separated by reversed-phase HPLC with a C_{18} column using toluene–isopropanol (40:60) as eluent [157]. The separation of fullerenes has been studied on new multi-legged phenyl group bonded silica phases in capillary HPLC using *n*-hexane as the mobile phase. Two-legged biphenyl bonded silica phases provided the best separation of C_{60} and C_{70} [158]. Preparative-scale non-aqueous, reversed-phase separation of C_{60} , C_{70} and higher fullerenes has been accomplished using up to 68% dichloromethane in acetonitrile with C_{60} and C_{70} eluting in less than 10 min [159]. Fractions isolated by this method have identified by MS to include C_{76} , C_{78} , C_{82} , C_{84} , C_{86} .

Another interesting application of HPLC in fullerene research is in the isolation and identification of fullerene isomers [160]. HPLC with on-line MS has been used to separate and positively identify isomers of the C_{60} and C_{70} fullerenes. HPLC with UV detection was used to monitor the thermal conversion of these isomers to stable fullerenes. The conversion of the newly reported C_{60} isomer to stable C_{60} occurred with a half-life of *ca.* 1 h in de-aerated boiling toluene (111°C) in an argon atmosphere [160]. Reversed-phase HPLC has been used to isolate pure C_{76} , C_{2v} - C_{78} , D_3 - C_{78} (C_{78} isomers), and a mixture of at least two C_{84} isomers [161]. Preliminary data on these higher fullerenes indicates that the chemistry of the higher fullerenes is diverse and distinctively different than that thus far reported for buckminsterfullerene and C_{70} . Advancement in the chemistry and physics of the higher fullerenes will rely, in part, on the optimization of the conditions for their formation as well as improved chromatographic methods for their isolation and characterization. Unfortunately, due to the current fervor of fullerene research, the present review of fullerene separations will likely be dated by the time it appears in print.

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