Translated from *Uspekhi Khimii*, **56**, 679-700 (1987) U.D.C. 543.544

Analysis of Polycyclic Aromatic Hydrocarbons by High Performance Liquid Chromatography

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The review gives a systematic account of a survey of data on the high performance liquid chromatography of polycyclic aromatic hydrocarbons using phases of normal polarity and reversed phases. The factors influencing the parameters of the chromatographic separation of the above compounds are examined and the conditions for the analysis of polycyclic aromatic hydrocarbons in objects within the environment are presented.
The bibliography includes 318 references.

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I. INTRODUCTION

The monitoring of the content of polycyclic aromatic hydrocarbons (PAH) in various objects in the environment is very important. Since it has been demonstrated that the carcinogenic and mutagenic action of certain PAH depends on their composition and structure, the exact knowledge of the structure of each component of the complex mixture of PAH is essential for the determination of the total carcinogenic (mutagenic) potential of the test specimen.[1,2]

With increase of the intensity of man's action on nature during the XXth century, the entry of PAH into the environment has become more pronounced at an increasing rate. The principal anthropogenic sources of PAH are[3] internal combustion engines, boiler engines operating on solid and liquid fuels, metal casting, chemical, coke, and shale industries, self-igniting coal bearing rock, etc. Thus the exhaust gas from internal combustion engines contains more than 200 different components of which 160 are carcinogenic. In city air with intense automobile traffic and metallurgical and coke-chemical industries, the content of PAH can reach 1.5–2.5 μg/100 m^3 of air.[4] It has been suggested that the contribution of tobacco smoking to the overall level of the accumulation of PAH is small but has a very dangerous effect on human health.[5,6] More than 170 carcinogenic substances have been detected in tobacco smoke.[4] At the same time the accumulation of PAH in the Planet's biosphere is expressed by the impressive overall figure of 5000 tonnes annually;[7,8] PAH have been detected also in the air and atmospheric dust of industrially developed cities, in drinking water, in industrial waste water, in various marine organisms and deposits, in the work places of certain industries, in food products, etc.

The content of 3,4-benzopyrene, which is comparatively easy to determine, can serve as a fairly reliable criterion for the estimation of the overall content of PAH in objects in the environment.[2,7] Approximately 80% of 3,4-benzopyrene released can be transported over a distance in excess of 100 km and can influence the state of the environment in non-industrial regions.[8] During winter, the content of PAH in the atmosphere is usually several times greater than in the summer.[9]

Analysis of PAH is important for the hygienic assessment of the quality of the environment for the determination of the source of contamination by carcinogenic substances.[10] The possibility of direct analysis of PAH in various objects of the environment is determined primarily by the sensitivity of the method[11] and in many cases preliminary concentration of the sample is necessary. The most promising analytical methods for PAH are capillary and gas–liquid chromatography (GLC) and high performance liquid chromatography (HPLC).[5] The possibilities of capillary GLC become increasingly limited with increase of the molecular weight of the PAH and the method is unsuitable for the analysis of samples containing six and more aromatic nuclei in the molecule. Similar limitations apply to a much lesser extent to the analysis of PAH by the HPLC method and in recent years there has been an increase in the number of publications on the HPLC of various PAH.[5,10,12–24]

The present review covers the literature on the analysis of PAH by the HPLC method published between 1973 and 1983 inclusive and partly the literature in 1984–1985; the analytical methods using normal-polarity and reversed phases, gradient elution, and highly sensitive detection systems are examined. The review does not include studies on the separation of PAH using exclusion or ion-exchange chromatography.

II. SEPARATION BY NORMAL-PHASE CHROMATOGRAPHY

During many years, alumina and silica gel were the commonest sorbents for the separation of PAH. Microdisperse[25] or surface-porous silica gels[26] are most often used nowadays. Thin-layer chromatographic data obtains using saturated hydrocarbons as the mobile phases (MP) are as a rule employed for the selection of conditions in the preparation of PAH on packed columns. In the analysis of PAH with high molecular weights, the MP are modified by activating additives in order to intensify their eluting properties.[27–31]

In one of the first studies on the HPLC of PAH,[32] it was shown that a mixture of substances ranging from naphthalene to 1,2-benzopyrene is effectively separated on a 300 × 3 mm column filled with Spherosil XOA 400 (MP = iso-octane and cyclohexane). The sensitivity of the determination of the individual components with UV detection (at wavelengths of 250 and 220 nm) is approximately to within 2 ng.

The earlier attempts to correlate the chromatographic parameters with the structure of the PAH molecules are presented in a monograph.[21] It was noted that the content of unsubstituted PAH increases with increase of the molecular

weight and of the number of carbon atoms in the molecule; with increase of the length of aliphatic side chains, the content of PA also increases as a rule.[33-37] The relation between the capacity factor of the test substance k', the adsorption energy S_a^0, and other parameters is:[21]

$$\lg k' = \lg V_a + \alpha(S_a^0 - A_S\varepsilon^0), \quad (1)$$

where V_a is the volume of the adsorbent in the column, α the adsorption activity of the adsorbent, A_S the size of the adsorbate molecule, and ε_0 the eluting power of the mobile phase. When pentane is used as the MP, $\varepsilon^0 = 0$ and the expression simplifies:

$$\lg k' = \lg V_a + \alpha S_a^0 . \quad (2)$$

The adsorption energy S^0 can be expressed by the equation[126]

$$S^0 = \sum_i Q_i^0 + \sum_i q_i^0 , \quad (3)$$

where Q_i^0 are the additive contributions of the individual groups of the molecule to the overall adsorption energy and q_i^0 are the contributions determined taking into account the possibility of the interaction between the groups indicated. The retention parameters of alkylnaphthalenes and alkylphenanthrenes are described satisfactorily by Eqn.(2) only for compounds with unbranched groups; the presence of secondary alkyl groups induces a significant discrepancy between the experimental and calculated data.[33]

A systematic study of the chromatographic behaviour of alkylnaphthalenes and alkylphenanthrenes has been undertaken by Popl et al.,[33,38] who established that Snyder's empirical formula

$$S^0 = 0.31\, nC_a , \quad (4)$$

where C_a is the number of aromatic carbon atoms in the molecule, holds vigorously in the alumina–pentane system only for arenes whose molecules contain 1–3 aromatic nuclei; on passing to PAH with four nuclei and non-planar PAH, the deviations become considerable. The relation expressed by Eqn.(4) breaks down on passing from straight-chain groups to branched groups owing to steric hindrance to the adsorption of such compounds.

Acid–base interactions influence significantly the sorption process. The adsorption energies on sorbents of the type Al_2O_3 increase appreciably for PA with acidic hydrogen atoms (indene, fluorene, and benzofluorenes) and low ionisation potentials (anthracene, naphthacene, and pentacene).[38] The acidity of the Al_2O_3 surface influences significantly the retention sequence of the components and, when the standardisation of the sorbent is adequately reliable, this phenomenon can be used successfully for both group[39] and individual analyses.[40]

Alumina and silica gel differ significantly in their sorption characteristics owing to the different acidities and structures of their surfaces.[22,43-46] These differences are fairly clearly manifested in relation to the separation of the anthracene–fluoroanthene pair.[41,42] It is believed that the sorption of PAH on Al_2O_3 is determined by electrostatic interactions and that on SiO_2 by hydrogen bonds. Detailed investigation of the characteristics of the separation of PAH on different brands of silica gel has shown that the capacity coefficient depends on the difference between the changes in free energies,[47] partition coefficients, specific surfaces, packing densities of the sorbent, and the proportions of its particles of different size.[48,49] The alkyl groups in naphthalenes and phenanthrenes influence differently their sorption on Al_2O_3 and SiO_2.[33,50,51] It is noteworthy that certain cyclic aromatic compounds have retention parameters close to those of aromatic polymethyl-substituted hydrocarbons containing identical numbers of carbon atoms. This phenomenon has not so far been convincingly explained.

Isomers of PAH with substituents in different positions have significantly different Kovac indices.[38] For the same number of carbon atoms in a series of aromatic hydrocarbons, the retention indices either differ significantly, as, for example, in 1,4- and 2,3-dimethylnaphthalenes and 1- and 2-phenylnaphthalenes, or are approximately the same as in 1,7- and 1,3-dimethylnaphthalenes and 1- and 9-methylphenanthrenes. In the latter case liquid chromatography on reversed phases with a careful selection of the eluent can be usefully employed for separation.

Other sorbents are also used in the analysis of PAH. Thus isomeric benzopyrenes and coronene have been separated[52,53] on columns with cellulose acetate and polyamide. Cellulose[54] and macroporous polystyrene[55] are also employed to separate PAH. One must assume that mixed partition and adsorption processes occur for these and similar sorbents.[56] A significant disadvantage of these fillers is their low mechanical strength and it is therefore useful to deposit them on strong carriers. The deposition of picric acid,[57] melamine polymerisate,[58] Bentone,[34,59] and carbon black[60,315] on silica gel and the use of such deposits for the separation of aromatic hydrocarbons by the HPLC method have been described in a number of studies. A new packing material, namely porous carbon glass, has been proposed recently.[61] Using methylene chloride with the addition of 0.1% of 1,3-terphenyl as the MP, it has been possible to separate successfully into individual components a mixture consisting of five PAH. The modification of hexane by more polar solvents has been examined on Silasorb 600 silica gel.[301]

III. THE USE OF CHEMICALLY MODIFIED SORBENTS

One of the main criteria of the reliability of chromatographic determination is the reproducibility of the retention parameters. Classical adsorbents are modified even in the presence of a very small water content in the MP. The retention times of the components vary within wide limits because the chromatographic column is in a non-equilibrium state.[62] Difficulties therefore arise in the use of gradient elution, for example, in the analysis of high-molecular-weight PAH.[63]

The deficiencies of liquid–liquid partition chromatography are frequently more significant than its advantages. The stationary phases fixed on the carrier become unstable when MP with similar polarities are used; the instability is manifested to an even greater extent when a gradient MP with highly polar eluents is employed.[64] The separation of PAH exclusively on chemically bound stationary phases will be considered below because ~80% of all the separations by the HPLC method are carried out on such sorbents.[65]

1. Separation on Reversed Phases

In separation on reversed phases (RP) a non-polar adsorbent and a polar eluent are used. This system is universal for PAH, their reaction products, and their heterocyclic analogues. In this variant of liquid chromatography, the retention of the components is inversely proportional to their polarity and is determined both by the non-polar non-specific sorbate–sorbent interaction and by the polar specific sorbate–eluent interaction.[14] In the analysis of PAH on RP, the relations between such interactions are frequently fairly complex. With increase of the chain length of the MP, the capacity factors rapidly fall (Fig.1) which significantly complicates the analysis of multicomponent PAH mixtures.[66]

As a consequence of the unique properties and the wide availability of octadecylsilane (ODS) reversed phases, the majority of the analyses of PAH have been carried out on

such phases. Sorbents with RP are also used for the determination of vapour pressures of various PAH by the HPLC method under dynamic conditions.[67] When silica gel is treated with octadecylsilanes, its specific surface diminishes; it has been suggested that the silica gel pores are then not only narrowed but are also frequently blocked by the RP groups.[68]

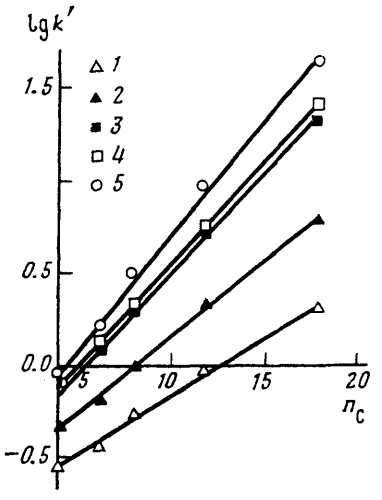


Figure 1. Dependence of the capacity factors of various aromatic hydrocarbons on the length of the chain grafted to the surface of the Spherosil silica gel in an amount of 2.1 μmol m^2 [55] (70:30 methanol–water mobile phase): *1*) benzene; *2*) naphthalene; *3*) phenanthrene; *4*) anthracene; *5*) pyrene.[55]

Under identical conditions (identical RP composition, eluent flow rate, temperature, and column size), the retention times of PAH on a column with Nucleosil C_{18} are approximately twice as great as on Nucleosil C_8.[21] It is believed that PAH molecules are retained on the bound RP by van der Waals forces and that the bond strength increases with increase of the length of the side chain.

As early as 1973, Sleight[69] derived equations relating the capacity factor and the number of carbon atoms in both unsubstituted and substituted PAH; the methanol–water system was used as the MP. For unsubstituted PAH, the relation is linear along the section from benzene to benzopyrene isomers and is described by the equation

$$\lg k' = a + bC_N \quad (5)$$

where k' is the capacity factor, C_N is the number of carbon atoms in the molecule, and a and b are constants. The introduction of alkyl substituents into the PAH molecule entails an appreciable increase in the retention of the component. This relation is characteristic not only of alkylbenzenes but also of alkylnaphthalenes and alkylphenanthrenes and is likewise described by a linear equation.[69]

Attempts to find correlations between the retention parameters of PAH on ODS phases and the composition and structure of the adsorbate have been made.[70–73,99] Thus a relation has been found[73] between the retention parameter and the geometry of the sorbed molecules for 84 alkylated and nonalkylated PAH. The ratio L/B, where L is the length and B width of the rectangle into which the PAH molecule can be "inscribed" taking into account the bond lengths and the covalent radii of the atoms, served as the criterion for the estimation of sorbability. In almost all cases the elution sequence of the isomeric PAH could be predicted with the aid of this relation: the retention increases with increase of the ratio L/B.

In order to estimate the retention of PAH on RP, the relation between the capacity factors k' and molecular binding χ, taking into account the steric structure of the PAH molecule and the bond orders, has also been employed.[75] The correlation factor F,[74,75] which takes into account the number of double bonds and the number of primary and secondary carbon atoms, has likewise been used to predict the chromatographic properties of the PAH determined. The factors F and χ have been calculated for 34 alkyl-substituted and partly reduced PAH.[75] It has been shown that the retention indices calculated on a computer taking into account these and other parameters can be used to predict the chromatographic behaviour of unknown PAH.[76]

A definite relation has been observed[77] between the retention and the physical properties of PAH. For columns containing different RP, the type of molecules, their structure, and their hydrophobic properties are of the main importance.

Table 1. Thermodynamic characteristics of the sorption of various PAH.

No.	Substance	$-\Delta H^0$, kJ mol^{-1}	$-\Delta S^{0*}$, J $mol^{-1}K^{-1}$
	Group A		
1	*o*-Terphenyl	8.3	17
2	Anthracene	16.0	43
3	*m*-Terphenyl	11.3	25
4	Fluoranthene	16.9	44
5	1,1-Binaphthyl	13.3	30
6	Triphenylene	18.9	48
7	Chrysene	23.5	62
8	1,3,5-Triphenylbenzene	12.5	23
9	4-Methylpyrene	21.8	55
10	9,10-Dimethyl-1,2-benzoanthracene	21.6	52
11	3,4-Benzofluoranthene	26.6	68
12	9,10-Diphenylanthracene	16.6	32
13	1,2,5,6-Dibenzoanthracene	30.7	79
	Group B		
14	*p*-Terphenyl	18.3	47
15	2,3-Benzofluorene	18.5	47
16	Bifluorenyl	18.0	45
17	1-Phenylnaphthalene	13.1	33
18	3-Methylphenanthrene	14.2	35
9	4-Methylpyrene	21.8	55
19	3-Methylpyrene	21.6	55
20	1,2-Benzoanthracene	22.4	59
	Group C		
21	2-Phenylanthracene	25.4	66
22	2,2′-Binaphthyl	21.9	55
23	9-Phenylanthracene	15.2	35
24	4,4′-Dimethylbiphenyl	14.4	36
25	2-Phenylnaphthalene	15.5	40
26	1-Benzylnaphthalene	10.8	27
27	Phenanthrene	13.3	35
28	Biphenyl	9.1	25
29	Naphthalene	13.3	40

*The entropy changes have been calculated under conditions such that V_S is equivalent to the volume of the sorbent in the column.

The elucidation of the mechanism of the retention of PAH on ODS phases has been prevented by the fact that until recently it was fairly difficult to follow the degree of surface coverage of the sorbent by the reversed phase; as a result, together with the RP monolayers, polymolecular layers appeared, which actually led to the reversal of the elution

sequence of PAH from the column.[78-80] Sorbents with identical types of grafted phases can differ appreciably in their selectivity even if they have been manufactured in the same factory.[81,82] New generation sorbents, namely ODS-3, are almost free from the above disadvantages.[83] The influence of the degree of coverage of the sorbent by the reversed phase on the separation of the PAH can be seen in relation to the retention of the isomeric 1,2-benzoanthracene–1,2-benzophenanthrene pair. On monolayer reversed phases, 1,2-benzophenanthrene is eluted before 1,2-benzoanthracene, while on polymolecular layers the reverse order obtains. For pairs such as anthracene–phenanthrene, pyrene–fluoroanthene, and 1,2-benzopyrene–1,2-benzoanthracene, the separation factors α increase on passing from monolayer to polymolecular layer RP.[68]

The characteristics of the retention of PAH on columns with different degrees of coverage of the sorbent by ODS groups differ significantly. Thus, on a monolayer column with an ODS phase, polyphenylarenes are retained more strongly than condensed PAH.[73,78] It has been shown[84] that two series-connected columns filled with sorbents having different ODS group contents on the surface exhibit the same selectivity in relation to PAH as columns filled with mixed ODS sorbents at different concentrations. Data on the retention of PAH on C_{13} RP, grafted to silica gel,[85-90] surface-porous materials,[85,91,92] porous glass,[86] etc.[93-95] are available in the literature.

The retention of unsubstituted PAH and their homologues is influenced significantly by the composition of the MP,[96] which actually makes it possible to alter the elution sequence of the components (Table 1).[69] In studies with reversed phases, the methanol–water and acetonitrile–water systems are usually employed.[97] In certain cases the separation of complex PAH mixtures and individual pairs, for example, 1,5-naphthalenophanes,[103] is improved by modifying the mobile phase by additives containing sodium sulphonates and perchlorates[98,100] or silver ions (0.001–0.02 M);[101,102] the silica gel surface is treated with cetyltrimethylammonium bromide.[104]

With the increase of temperature, not only are the peaks narrowed but the duration of analysis is reduced. The use of a temperature gradient also makes it possible to separate substances eluted under isothermal conditions in the form of one peak and for certain pairs of compounds the reverse elution order is observed. With increase of the separation temperature, the retention of more condensed PAH diminishes at a higher rate compared with less condensed PAH.[105] The use of plots of the relation $\ln K = f(1/T)$ and of the Gibbs equation permits the calculation of the entropy and enthalpy factors and the estimation of their contributions to the overall retention and the sorption mechanism:

$$\Delta G^0 = -RT\ln K = -RT\ln\frac{c_s^x}{c_m^x} = -RT\ln\frac{V_r - V_m}{V_s}, \qquad (6)$$

where ΔG^0 is the free energy of the transfer of the sorbate between the phases, K the partition coefficient assumed equal to the equilibrium distribution constant, c_s^x the concentration of the sorbate X in the adsorbent, c_m^x the concentration of the sorbate X in the MP, V_r the retention volume, V_m the "dead" volume, and V_s the overall volume of the stationary phase or the overall surface area of the sorbent.

Data obtained using silica gel for grafted ODS groups and the 80:20 acetonitrile–water MP are presented in Table 1.[105] The negative enthalpy changes indicate a high probability of the transition of the sample from the MP to the sorbed state. The absolute entropy change increases with increase of adsorbability. For more condensed PAH, a more rigorous elution sequence on the column is observed. With increase of temperature, the entropy differences become dominant, which alters significantly the partition coefficients of the PAH.

Thus the components of the pairs separated with appreciably different entropies (Table 1, group A) are eluted in the reverse sequence, while for components in group B with similar or identical entropies, the usual elution sequence is obtained. We may note that, in order to separate components 18, 23, and 27 (Table 1), characterised by identical ΔS^0 but different ΔH^0, the "enthalpy" factor assumes a decisive role. On the other hand, for components 5, 27, and 29 with identical ΔH^0, one may postulate the "entropy" mechanism of the separation process. The separation of a mixture of components with different thermodynamic parameters is determined by the relative contributions of the factors indicated. In this case it is extremely difficult to predict beforehand the results of the chromatographic separation.

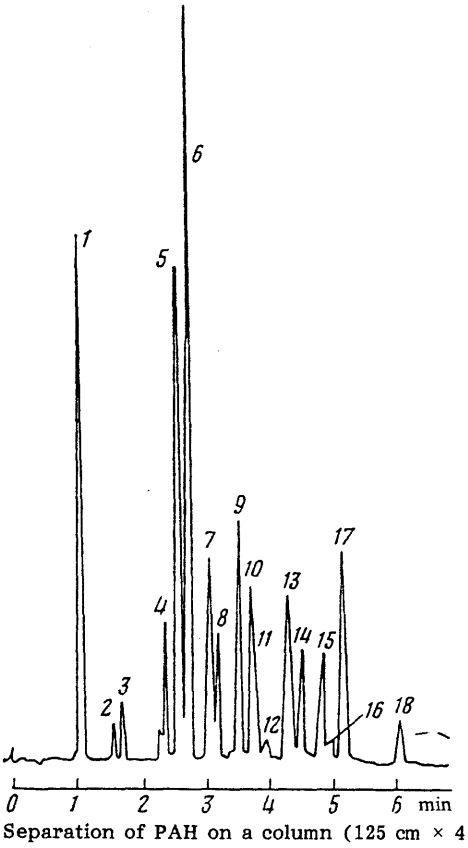


Figure 2. Separation of PAH on a column (125 cm × 4.6 mm) filled with the μ-Bondapak C_{18} sorbent (5 μm) (acetonitrile–water mobile phase; linear concentration gradient of 60–100% of acetonitrile in water over a period of 5 min; eluent flow rate 4 ml min^{-1}; UV detector, 254 mm):[121] *1*) benzene; *2*) admixture; *3*) naphthalene; *4*) fluorene + acenaphthene; *5*) phenanthrene; *6*) anthracene; *7*) fluoranthene; *8*) pyrene; *9*) 3,4-benzofluoranthene; *10*) chrysene; *11*) 1,2-benzanthracene; *12*) admixture; *13*) 1,2-benzopyrene + perylene; *14*) 3,4-benzopyrene; *15*) 1,2,5,6-dibenzoanthracene; *16*) 1,2,3,4-dibenzoanthracene; *17*) 1,12-benzoperylene + 2,3-o-phenylenepyrene; *18*) coronene.

The selection of the composition of the mobile phase and temperature plays an important role in the optimisation of the PAH separation process.[126] By virtue of their exceptional

stability, columns with bound RP are widely used in the analysis of PAH by HPLC. The PAH present in carbon black, with molecular weights up to 448, have been successfully separated on such columns.[106] It has been shown that alkylnaphthalenes can be analysed on carbon black.[107] Examples of the gradient elution of PAH mixtures have been fairly widely described in the literature. By altering the composition of their MP, it is possible to achieve not only an acceptable separation and retention but also a change in the elution sequence. With increase of the content of the organic component in the MP, PAH having increasingly higher molecular weights are eluted.[108,109] Both linear and non-linear gradients have been used. The advantages of the employment of the gradient technique in the analysis of PAC have been demonstrated in a number of studies.[110,111,112] For the effective separation of heavy PAH with a molecular weight up to 450, the tetrahydrofuran–acetonitrile–methanol–water four-component gradient system has been proposed.[113]

The separation of PAC on the high performance Vydac 201 TP, C_{18} column (linear gradient; acetonitrile–water MP) has been carried out.[78] The same composition of the MP under gradient conditions has been used for the separation of a model mixture of PAH ranging from coronene to bicoronyl on a column containing Nucleosil 5 C_{18} [114] and also for other PAH mixtures.[115–119] A gradient anhydrous MP, for example a methylene chloride–acetonitrile mixture, can sometimes be usefully employed for the analysis of PAH.[120] The gradient elution of a mixture containing 18 different PAH is illustrated in Fig. 2.[121]

A programmed variation of the flow rate or temperature is sometimes used to improve separation.[21] However, the latter exerts a significantly smaller influence on the retention parameters in liquid chromatography than in gas chromatography.

High resolution chromatography on RP can be readily achieved with gradient elution and the rapid return of such columns to the initial equilibrium and the rapid change to the new composition of the MP makes them very convenient to operate.

The separation of high-molecular-weight PAH in both the normal and reversed phase variants requires a careful selection of the MP. In many studies using isocratic and gradient elution, it has been possible to separate PAH with molecular weights of 400–600.[122–124]

2. Separation on Sorbents with Grafted Polar Groups

Sorbents with grafted polar groups (SGPG) are being increasingly used for the separation of PAH. The groups in alkyl(aryl)silanes, used to modify the surfaces of classical sorbents, contain one or several polar groups (NH_2, NO_2, OH, CN, etc.). The bound organic layer of polar stationary phases is monomeric because the mass transfer across the layer proceeds at a high rate and the mass transfer along the layer becomes minimal. By selecting SGPG with different functional groups, it is possible to vary widely the sorption characteristics.[125] In other words, the separation on SGPG combines the advantages of partition and sorption chromatography. The concentration of functional groups on the silica gel surface is as a rule 3–4 group on 100 Å.[126] The properties of various polar phases suitable for the separation of PAH have been compared.[127]

The mechanism of the retention of PAH on SGPG is fairly complex. Here one must take into account the interaction between the π-electron systems of the sample components and various structures on the polar surface.[128] Unsubstituted PAH are eluted in order of increasing molecular weight[129] and ponents which cannot be separated on a non-polar RP.[130]

The characteristics of the retention of more than 90 unsubstituted and alkyl-substituted PAH on a polar phase containing amino-groups have been described.[78] It was noted that the retention of the PAH increases with increasing number of aromatic nuclei in the molecule. In contrast to the usual columns with RP, the presence of alkyl groups in the PAH molecules influences only insignificantly the retention sequence, which makes it possible to use the above phase for preliminary fractionation in the analysis of complex mixtures. Furthermore, the use of volatile non-polar MP facilitates the concentration of the collected fractions.

The separation of PAH on a polar phase containing aminopropyl groups has been investigated.[131,132] The non-polar MP were cyclohexane and the polar phases were methanol–water or acetonitrile–water mixtures. In the former cases the separation was attributed to the interaction of the unshared electron pair of the N atom and the π-electrons of the PAH and in the latter to the partition effect due to the employment of MP of high polarity and the mixed adsorption-partition effects in MP with a lower polarity.

A complex mixture of aromatic hydrocarbons and alcohols, which included also naphthalene and anthracene, has been successfully separated[133] on a column with aminated Lichrosorb.

The retention parameters of 32 PAH on the usual columns with silica gel and on columns with SGPG have been compared[134] and considerable differences in the retention volumes and capacity coefficients have been detected. According to the authors, the cyclic amide SGPG phase interacts with the PAH via both the normal-phase and reversed-phase mechanisms, exhibiting at the same time specific features in the separation process. This results in a significant change in the separation factors for the individual pairs and in the elution sequence of the components. Thus, on a normal-phase sorbent, 9,10-diphenylanthracene and phenanthrene emerge as a single peak, while on SGPG these compounds are separated (the selectivity was 3), phenanthrene emerging first.

PAH have been analysed on grafted phases containing nitrile, diol, ethyl, quaternary ammonium, and amino- and diamino-groups.[135,136,296] The phase with diamino-groups proved to be the most selective. The use of a system comprising two columns—one with a polar phase and another with a non-polar phase—is even more promising for the study of complex PAH mixtures.[137] The characteristics of the separation of a number of PAH, their nitrogen-containing analogues, and biaryls have been investigated[71] on silica gel modified with polar nitrophenyl groups. For each of these groups of compounds analysed, a linear relation was observed between the logarithm of the retention of the components and the number of carbon atoms in the molecule. Furthermore, the PAH were readily separated from their nitrogen-containing analogues owing to the greater polarity of the latter. In a number of studies Nucleosil 100-5 NO_2 has been used successfully for the analysis of heavy PAH.[138–140]

Blumer et al.[141] separated coal tar on a nitrophenyl phase into more than 100 components. In contrast to capillary gas chromatography, where only 30% of the composition of the resin can be determined, on the nitrophenyl phase up to 70% of the composition has been isolated by the HPLC method. Using the nitrophenyl phase, it has been possible to separate PAH of complex composition with molecular weights up to 600.[122] It has been found[142] that, under HPLC conditions, the nitrophenyl phase is preferable for the analysis of PAH present in dust to the amine phase and RP C_{18}. The characteristics of the retention of PAC on the nitrophenyl phase have not so far been investigated in detail.

Phases with other polar groups, for example, nitrofluoreneimine,[143,144] picramidopropyl,[145] 3-(2,4-dinitroanilino)-propyl,[146] and phthalimidopropyl[147] groups, are also suitable

for the separation of PAH. With the aid of the last phase, 1,12-benzofluoranthene and perylene were separated and the reverse elution sequence of the components of the binary 3,4-benzopyrene–1,2-benzopyrene mixture was noted compared with the C_{18} phase. Stationary SGPG phases, forming charge-transfer complexes with PAH, are entirely suitable for the separation of complex PAC mixtures into di-, tri-, and poly-aromatic compounds.[148]

Studies of the relation between the capacity factor k' and the molecular structure of PAH have been published.[149,313,318] A sufficiently distinct regularity in the deviation of the k' (Table 2) on passing from different silica gels with grafted phases to pure silica gel has not been observed on phases of different polarity in the separation of a number of PAH. Examination of the selectivity in relation to pairs of compounds difficult to separate has also revealed a scatter of the relevant values. For example, in the separation of the anthracene–phenanthrene pair the selectivity assumes values from 0.94 to 1.46, while for the anthracene–fluorene pair it ranges from 1.09 to 2.30, etc. The use of other factors (F and L/B) for the calculation of the capacity factor is fruitful when these are present simultaneously in an equation of the type

$$k' = aF + b(L/B) + c \,, \qquad (7)$$

where F = number of double bonds + number of primary and secondary carbon atoms—0.5 (for a non-aromatic nucleus) and a, b, and c are column constants.

Table 2. Characteristics of the retention of PAH on various stationary phases.[149]

Substance	F	L/B	Capacity factor, k'						
			C_2	C_p	C_8	C_{18}	S_{N_1}	S_{N_2}	S
Benzene	3.0	1.10	1.89	2.00	1.48	1.05	0.48	0.19	0.48
Naphthalene	5.0	1.24	3.01	3.55	2.22	1.67	1.42	0.50	1.06
Fluorene	6.5	1.57	4.40	5.29	2.89	2.44	2.68	0.76	1.92
Acenaphthylene	5.5	1.08	3.35	4.24	2.49	2.03	2.58	0.93	1.48
Anthracene	7.0	1.57	4.81	6.27	3.36	3.20	3.47	1.75	2.16
Phenanthrene	7.0	1.46	4.49	5.86	3.14	2.99	3.68	1.20	1.70
Pyrene	8.0	1.27	5.56	7.47	3.80	3.97	5.55	1.68	2.40
Fluoranthene	8.0	1.27	5.59	7.42	3.80	3.97	5.55	1.68	2.40
Chrysene	9.0	1.72	7.13	10.4	4.88	5.93	9.03	2.50	3.44
Naphthacene	9.0	1.89	8.28	11.4	5.27	7.18	8.71	2.54	3.31
Triphenylene	9.0	1.12	6.45	9.34	4.67	5.48	9.19	2.63	3.11
3,4-Benzopyrene	10.0	1.50	9.06	13.8	6.75	9.86	11.8	3.70	3.98

Notation: C_2 = dimethylsilica gel, C_p = phenylsilica gel, C_8 = octylsilica gel, C_{18} = octadecylsilica gel, S_{N_1} = Fine SIL-NH_2, S_{N_2} = Lichrosorb-NH_2, and S = pure silica gel.

A reliable method for predicting the parameters of the chromatographic retention of various PAH has been proposed;[256] a high correlation coefficient (0.97–0.99) was obtained in all cases. The authors began with the fact that the logarithm of the capacity factor of the molecule can be represented as the sum of the logarithms of the capacity factor of its constituent fragments. The method is suitable for any type of chromatographic separation (adsorption, partition, or a mixed type). For the majority of PAH, the calculated capacity factors are satisfactorily correlated with experimental data over a wide range of polarities of the mobile and stationary phases. The isomeric 2,7- and 2,6-dimethylnaphthalenes are exceptions, but this in no way reduces the advantages of the new method, which can be extended to PAH derivatives after the appropriate correction of the calculated data.

IV. THE APPLICATION OF MICROPACKED AND CAPILLARY COLUMNS FOR THE ANALYSIS OF PAH

The increase of the molecular weight of PAH leads to a rapid increase of the number of isomers, which requires the application of high performance columns and a more careful selection of the MP. The efficiency of the system can be increased by connecting several columns in series.[151] However, this entails an increase of the pressure drop and of the duration of the analysis. Furthermore, a large pressure drop entails the heating of the silica gel particles owing to friction, which leads to additional spreading of the peak.[150]

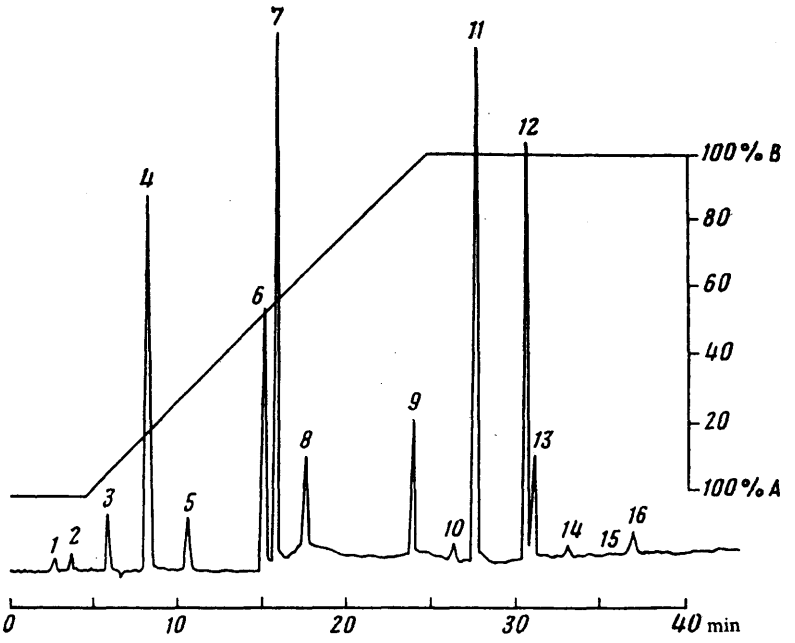
Micropacked, capillary, and microcapillary columns are being increasingly used nowadays for the analysis of complex PAH mixtures. These columns have a number of advantages, which include (1) the possibility of employing a combination of a chromatograph with a mass-spectrometer or a flame-ionisation detector, (2) high efficiency (more than 10^5 theoretical plates), which permits the separation of extremely complex mixtures, (3) a decrease of the consumption of the MP by a factor greater than 20, which permits a much wider use of expensive and toxic solvents, (4) an increase of the sensitivity of the determination of the components by a factor greater than 20, and (5) the need for very small amounts of the specimen in the analysis (less than 1 μl). Microcolumn liquid chromatographs, with the aid of which it is possible to solve a wide variety of research and technical problems, have received wide recognition in our country and abroad. Soviet investigators have used successfully the Ob'-4 and Milikhrom chromatographs for the analysis of PAC.[152]

Packed microcolumns are quite efficient. For example, a 1 m × 1 mm column filled with Partisil ODS/10 μm has an efficiency up to 30 000 theoretical plates (t.p.). A complex mixture of PAH extracted from coal has been separated on this column.[312] A battery of 14 series-connected columns of this kind has an efficiency of 650 000 t.p.[153] A multicomponent mixture of PAH has been separated on 100 × 0.12 mm and 100 × 0.340 mm ultramicrocolumns filled with ODS SC-01 silica gel.[154,155]

Capillary packed columns have an even greater efficiency,[156] which is calculated from the relation $H \leq 3d_p$ (d_p is the particle diameter). Thus the efficiency of a 1 m× 320 μm column filled with ODS silica gel (particle size 3 μm) is 110 000 t.p.; a 2 m × 300 μm column with the same filler has an even greater efficiency—144 000 t.p. (with respect to pyrene for $k' = 10$). Both columns have been used successfully for the identification of PAC contaminating the environment.[153,157]

A capillary column whose inner surface has been treated with silicone SE-30 proved to be highly efficient for the analysis of a model mixture of PAH.[158,308] The heavy aromatic fraction of coal tar has been separated[159–161] on a 55 m × 70 μm column filled with alumina (particle size 30 μm) having grafted ODS groups. The use of a glass capillary column on the inner surface of which a layer of silica gel modified by cetyltrimethylammonium bromide has been deposited[162,310] is also promising. The separation of PAH on such a column proceeds similarly to the separation on a capillary column with grafted ODS groups.

In order to reduce the duration of analysis, it is useful to employ gradient elution for the separation of PAH having a complex composition.[163,164,311] An example of such separation on a packed capillary column is illustrated in Fig. 3.



3. Gradient separation of PAH on a 66 cm × 250 μm column filled with Vydoc 201 TP silica gel (5 μm).[163] The variation of the composition of the MP during analysis is shown above: *A*) 65% acetonitrile + 35% water; *B*) 80% acetonitrile + 20% dimethoxyethane. Sample composition (the amount in ng is given in brackets): *1*) naphthalene (20); *2*) acenaphthylene (4); *3*) acenaphthene (20); *4*) fluorene (4); *5*) phenanthrene (2); *6*) anthracene (2); *7*) fluoranthene (4); *8*) pyrene (2); *9*) 1,2-benzoanthracene (2); *10*) chrysene (2); *11*) 3,4-benzofluoranthene (4); *12*) 1,12-benzofluoranthene (2); *13*) 3,4-benzopyrene (2, detectable minimum amount 50 pg); *14*) 1,2,5,6-dibenzoanthracene (4); *15*) 1,12-benzoperylene (4); *16*) 2,3-*o*-phenylenepyrene.

Microcolumns and capillary columns with MP of different polarity have been used to separate PAH in supercritical (fluid) chromatography. Hydrocarbons (pentane, butane, and isobutane), dimethyl ether, carbon dioxide, nitrous oxide, etc. have been used as the MP. Multicomponent PAH mixtures[166–168] as well as the PAC present in soot,[306] in the exhaust gases of automobiles,[169] and in coal tar[170] have been successfully separated with the aid of microcolumn liquid chromatography.

Despite their evident advantages, capillary columns are being fairly slowly introduced into chromatographic practice. The reasons are failure to develop as yet a reproducible method for the preparation of these columns, the absolute need for a new system for the introduction of the sample, inadequately improved pumps working at very high pressures, and, in addition, the need for very small flow cells in the detection of the components, for which one can usefully employ the "tail" section of a glass column. Micropacked columns are extremely promising.[171,172]

V. DETECTION SYSTEMS

The principal advantages of the analysis of PAH by the HPLC method are due to the possibility of employing highly sensitive and selective detectors. The molecules of aromatic compounds are known to be capable of absorbing ultraviolet light and certain PAH exhibit an intense fluorescence. Detectors working in accordance with the above principles have come to be widely used in the analysis of PAH by liquid chromatography.[173] Aromatic solvents cannot be used as MP, but this does not create difficulties in the selection of the eluent. There are fairly numerous different solvents which exhibit a minimal absorption at the wavelength employed for detection.

1. Ultraviolet Detectors

Although various PAH and their analogues differ somewhat in the absorption of UV light at fixed wavelengths, the detection of substances in amounts not exceeding several nanogrammes is quite feasible. The use of UV spectrophotometers permits the selection of the optimum wavelength for the detection of specific components of PAH.[174] A UV detector with a variable wavelength is quite often used to increase the selectivity.[175–177] The complete UV spectra have been used[114] to identify PAH after separation by HPLC. For analysis, it is useful to measure the relative absorption of PAH at several wavelengths.[178,179] The advantages of UV scanning with stopped flow for identification of PAH peaks have been demonstrated.[180,181] By altering the wavelength in the UV region it is possible to control successfully the content of, for example, 3,4-benzopyrene in the presence of perylene at 290 nm or of pyrene in the presence of fluoranthene at 360 nm.[175] Detection with a variable wavelength under the

conditions of reversed phase separation[182] make it possible to detect fairly readily 3,4-benzopyrene in coal tar.

In order to determine the maximum number of components, it is useful to employ rapid scanning and multi-wavelength detectors[183–185] with Fourier transformation.[186] The sensitivity of the determination of PAH can be increased by using weakly pulsating pumps. Pumps of the syringe type which do not give rise to pulsations in the flow are best for this purpose.[187]

Definite information can be obtained by using two combined detectors tuned to different wavelengths[188,189] and also by combining UV detectors with a fluorimetric detector.[190–192] The sensitivity of the determination of PAH can be increased with the aid of a detector based on the use of the Cherenkov effect,[193] etc,[194–197]

2. Fluorimetric Detectors

The rapid growth of the manufacture of fluorimetric detectors for HPLC is due to their selectivity with respect to condensed PAH[198,199] and high sensitivity.[173,200,201] The analysis of admixtures whose amount does not exceed 10–100 pg then becomes entirely realistic. It is believed[202–204] that PAH detection limits below 10^{-12} M are entirely attainable when laser-excited fluorescence is employed. At the same time the use of fluorescence detection can sometimes lead to inaccurate estimates of mixture compositions, because the signal intensities at different wavelengths are not the same. Under these conditions, the signals of a series of PAH components can diminish appreciably and can even disappear.[205]

Fluorimetric filters and spectrofluorimeters are used to determine PAH in air-borne dust,[176] in the exhaust gases from diesel engines,[204] in cigarette smoke,[206] and in various petroleums and oils.[207–209] The fluorescence peak intensity rations under different conditions of the excitation of the fluorescence have been used to identify 17 different PAH present in food, water, and tobacco smoke.[210]

In certain studies attempts have been made to improve the technique of the fluorimetric detection of PAH in systems in the environment.[211–214] In particular, the use of a narrow-band filter greatly improved the sensitivity of the determinations of the readily separated PAH; however, for poorly separated peaks, the best results are given by a monochromator.[211] A two-photon laser fluorescence detector[215–217] and a detector based on β-induced fluorescence[218] have been used successfully to analyse various asphaltenes.

The sensitivity of a fluorescence detector increased significantly when an MP with added dodecyl sulphate was used.[219] The selective extinction of the fluorescence of certain PAH in the presence of nitromethane has been investigated.[198,220,221] The addition of 0.5% of nitromethane to the MP significantly extinguishes the fluorescence of non-fluoranthene PAH (the fluorescence of anthracene is not fully extinguished).[220]

Table 3. Conditions in the analysis of PAH contained in various objects within the environment.

Object of analysis	Sorbent	Composition of mobile phase	Detector	References
Petroleum	Bio-Sil ODS-10	methanol – water, G	UV	[257]
Petroleum	Spherisorb C_{18}	methanol – water (80 : 20)	F	[258] ([230, 259, 260])
Petroleum, shale, coal liquefaction products	Chromegabond $(NH_2)_2$	hexane – methylene chloride, G	UV	[261]
Ditto	Woelm alumina	hexane – methylene chloride, G	UV	[261]
"	2,4-dinitroanilinopropylsilica gel	hexane – methylene chloride, G	UV	[261]
Bitumens, motor oils	Partisil 5	hexane	UV	[262] ([263])
Ditto	Corasil C_{18}	methanol – water (75 : 25)	UV, F	[264] ([265])
Heavy petroleum fractions, coal tar	Nucleosil NO_2, NH_2, CN, SA, Lichrosorb Si 60, Alox T; Spherisorb A5U	hexane; hexane – methylene chloride, G	UV	[266] ([304])
Coal tar, pitch	Lichrosorb, μPorasil	cyclohexane	UV	[182]
Ditto	μBondapak, C_{18}	acetonitrile – water (60 : 40)	UV	[182]
Coal tar	alumina C_{18}	acetonitrile, acetonitrile – dichloroethane, G	F	[160] ([307])
Coal pitch	Lichrosorb RP-8	water – acetonitrile – dimethylformamide, G	UV	[123]
Ditto	Nucleosil 100-5NO_2	hexane – chloroform, G	UV	[140] ([267])
Coal tar and petroleum processing products	HC-ODS	tetrahydrofuran-acetonitrile (70 : 30)	UV, F	[268]
Ditto	PAH/10	acetonitrile – water, G	F	[268] ([31, 191])
Coal liquefaction products	μBondapak, C_{18}	methanol – water (65 : 35)	UV	[74, 269]
Ditto	Partisil PXS 10/25 ODS	acetonitrile – water (70 : 30)	F	[203] ([239, 240, 270, 271, 317])
PAC hydrogenation products	Lichrosorb RP-18	methanol – water, G	UV	[272]
Tobacco smoke	Micropak C-H "Varian"	methanol – water, G	UV	[6]
Air contaminants	Vydac 201 TP	acetonitrile – water (70 : 30)	F	[273]
Ditto	Fine SIL C18-10	acetonitrile – water (70 : 30)	F	[274]
"	Lichrosorb NH_2	iso-octane	UV	[142]
"	Nucleosil 5 NO_2	iso-octane – methylene chloride (9 : 1)	UV	[142]
"	Lichrosorb RP-18	acetonitrile – water (85 : 15)	UV	[142] ([9, 81, 118, 119, 176, 187, 192, 205–281])
Water contaminants	Lichrosorb RP-18	methanol – water (85 : 15)	F	[282]
Ditto	PAC 254-400 "Contron"	methanol, acetonitrile	UV	[283]
"	Perkin-Elmer HC-ODS	acetonitrile – water, G	UV	[201]
"	Perkin-Elmer HC-ODS	aqueous solution of acetonitrile (38%) and methanol (15%)	F	[284]
"	μBondapak C_{18}	acetonitrile – water (80 : 20)	F	[285] ([286–290, 309])
Deposits on sea bottom, marine organisms	Lichrosorb RP-18	acetonitrile – water, G	UV	[291] ([292–295])
Exhaust gases from engines	Lichrosorb RP-18	acetonitrile – water (80 : 20)	UV	[296]
Ditto	Zorbax TM ODS	methanol – water (8 : 1)	F	[85]
"	Spherisorb ODS	methanol – water, G	UV	[297] ([250, 298–300, 316])
Automobile fuel	Fine SIL C_{18}-10	acetonitrile – water (80 : 20)	F	[302]
Barley malt	Zorbax ODS	methanol – acetonitrile – water, G	UV, F	[303]

Notation: G = gradient elution, UV = ultraviolet detector, F = fluorimetric detector. The additional literature relevant to the object of analysis is indicated in round brackets.

Only the peaks of PAH of the fluoranthene series, namely fluoranthene, 3,4-benzofluoranthene, and 11,12-benzofluoranthene, remain on the chromatogram (Fig.4). The addition of a fluorophor, for example, aniline, to the MP makes it possible to detect both fluorescent and non-fluorescent PAH.[222]

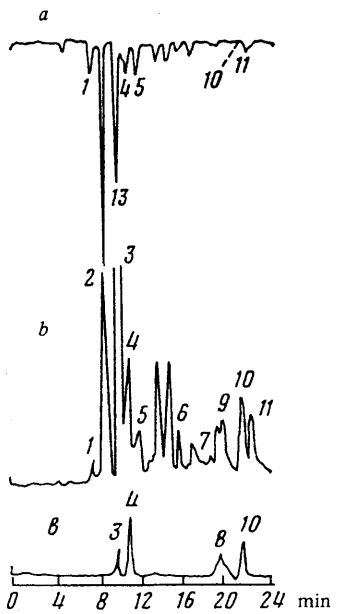


Figure 4. Separation of an extract from coal tar on a reversed phase: *a*) detection at 254 nm; *b*) fluorescence detection; *c*) detection with fluorimetric quenching (0.5% of nitromethane in the MP).[200] Column filled with Vydoc 201 TP silica gel (10 μm); mobile phase–linear gradient of 50–100% of acetonitrile in water over a period of 25 min; eluent flow rate 2 ml min^{-1}. Sample composition: *1*) fluorene; *2*) phenanthrene; *3*) anthracene; *4*) fluoranthene; *5*) pyrene; *6*) 10,11-benzofluoranthene; *7*) 1,2-benzopyrene; *8*) 3,4-benzofluoranthene; *9*) perylene; *10*) 11,12-benzofluoranthene; *11*) 3,4-benzopyrene.

Multichannel rapidly scanning spectrometers have been employed[223] for the detection of eluates containing PAH, for example, for the determination of the origin of oil slicks.[223] A fluorimetric detector combined with computer techniques and a data bank has been used successfully for the analysis of complex PAH mixtures.[224] The employment of a rapidly scanning device with a photodiode detector and a computer is promising for the optimisation of the composition of the MP.[314]

3. Other Detection Methods

The HPLC and mass-spectrometric methods have been combined successfully in recent years for the separation and identification of complex PAH mixtures.[225–231] This approach proved to be fruitful for the analysis of both model mixtures[154,232–236] and coal liquefaction products containing heavy aromatic hydrocarbons.[237–240]

Various ionisation procedures which make it possible to differentiate isomeric PAH are used to detect mass-spectrometrically the PAH eluted from the column, namely electron impact, chemical ionisation, and, much more rarely, field ionisation and field desorption. The reliability of the method is determined both by the selection of the ionisation procedure and of suitable masses, which are characteristic for the substances to be determined.[5,241] Detectors employing proton magnetic resonance,[242] IR spectroscopy,[243] and other spectroscopic methods combined with computer techniques[244] and Fourier transformation[186] have also been described.

It is noteworthy that even the use of the most selective and effective columns in the analysis by the HPLC method does not permit the complete separation of isomeric PAH in complex mixtures. For a greater reliability of the data obtained, it is useful to combine HPLC with gas chromatography and mass spectrometry[160,245–251] and also various spectroscopic methods,[6,252–255] which makes it possible to increase significantly the amount of information derivable from the analytical results.[256]

VI. ANALYSIS OF PAH IN VARIOUS OBJECTS WITHIN THE ENVIRONMENT

Table 3 presents the conditions for the analysis of PAH contained in various objects within the environment. It is seen that the use of adsorption chromatography permits the solution of a very limited range of problems. Furthermore, the long duration of the analytical cycle is a significant disadvantage in routine analyses of complex mixtures.

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It follows from the data described that the separation of PAH on reversed phases grafted to the spherical particles of wide-pore silica gel having a small diameter (3–5 μm) is much more effective (when both non-polar and polar grafted groups and appropriate eluents are employed). Gradient elution can be usefully applied in the study of PAH forming part of the composition of petroleum, coal tar, the products of their processing, and contaminated water and air. Good results have been obtained following the combined application of UV and fluorescence detectors. Computer techniques make it possible to detect, in particular, the UV spectra of individual PAH in the course of chromatographic separation and to compare them with the available information. Methods in which HPLC is used in combination with mass spectrometry, ^{1}H NMR, ^{13}C NMR, and other methods have been developed for the identification of unknown PAH. Computer techniques can then make it possible to reduce to a minimum the time consumed in comparing the data obtained and to increase the accuracy of the analytical determination.

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