# Modern Analytical Methods for Environmental Polycyclic Aromatic Compounds

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## 1 Introduction

Polycyclic aromatic compounds (PAC) are ubiquitous environmental pollutants, and although they are formed from both natural and anthropogenic sources, the latter are by far the major contributors.[1] Natural sources include forest and prairie fires,[2] volcanoes,[3,4] and *in situ* synthesis from degraded biological material, which has led to the formation of these compounds in various sediments,[5–13] fossils,[14,15] and fossil fuels.[16–27] Several rare PAC minerals,

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pendletonite,[28,29] curtisite,[20,30] and idrialite,[29] have also been characterized.

Some reviews are available that cover in detail the anthropogenic sources of PAC.[31–34] Major sources include the burning of coal refuse banks, coke production, residential fireplaces, coal-fired residential furnaces, automobiles, commercial incinerators, oil-fired commercial boilers, and rubber tyre wear. A minor source in terms of total PAC production, but of considerable importance with respect to human health, is tobacco smoking. Until the beginning of this century there existed a natural balance between the production and natural degradation of PAC, which kept the background concentration low and fixed.[35] However, with increasing industrial development throughout the world, the natural balance has been disturbed and the production and accumulation rates of PAC are constantly rising.

During the last thirty years, many studies have been undertaken to characterize the polycyclic aromatic hydrocarbon (PAH) content in airborne particulate matter,[36–68] industrial effluents and work-place atmospheres,[63,64,68–78]

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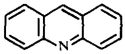
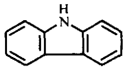
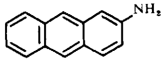
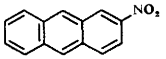
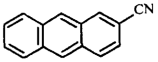
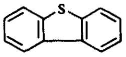
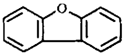
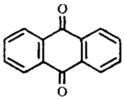
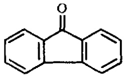
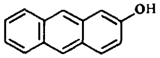
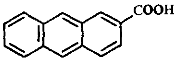
water,[35,79–82] sediments,[2,5–13,62,83–89] foods,[90–108] and tobacco smoke.[109–115] These efforts stem from the demonstrated carcinogenic and/or mutagenic activity of many PAC.[116] PAC are usually present in environmental samples as

**Table 1** *Classification of environmental PAC*

| *Structure* | *Name* | *Class* | *Refs.* |
|---|---|---|---|
|  | Acridine | Polycylic aromatic nitrogen heterocycles (PANH) | 56, 117—139 |
|  | Carbazole | | |
|  | 2-Aminoanthracene | Amino polycyclic aromatic hydrocarbons (APAH) | 139—141 |
|  | 2-Nitroanthracene | Nitro polycyclic aromatic hydrocarbons (NPAH) | 142—145 |
|  | 2-Cyanoanthracene | Cyano polycyclic aromatic hydrocarbons (CPAH) | 146, 147 |
|  | Dibenzothiophen | Polycyclic aromatic sulphur heterocycles (PASH) | 148—153 |
|  | Dibenzofuran | Polycyclic aromatic oxygen heterocycles (PAOH) | |
|  | Anthraquinone | Polycyclic aromatic quinones (PAQ) | 154—159 |
|  | 9-Fluorenone | | |
|  | 2-Hydroxyanthracene | Hydroxy polycyclic aromatic hydrocarbons (HPAH) | 160 |
|  | 2-Carboxyanthracene | Carboxy polycyclic aromatic hydrocarbons (CXPAH) | 56 |

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[157] R. C. Pierce and M. Katz, *Environ. Sci. Technol.*, 1976, **10**, 45.

[158] K. Winters, J. C. Batterton, and C. Van Baalen, *Environ. Sci. Technol.*, 1977, **11**, 270.

[159] I. Schmeltz, J. Tosk, G. Jacobs, and D. Hoffmann, *Anal. Chem.*, 1977, **49**, 1924.

complex mixtures that vary greatly in the relative concentrations of individual components. Table 1 gives structures of representative compounds in the main classes of PAC that have been found in environmental samples in addition to the PAH. Compound structure, position of substitution, and presence of heteroatoms in the ring have all been found to affect the carcinogenic and/or mutagenic properties of these aromatic compounds, and therefore exact structural elucidation of individual constituents of mixtures is necessary in order to determine the full carcinogenic potential of the sample.

As is evident from Table 1, PAC mixtures can be extremely complex, since they contain numerous isomeric compounds. The complexity increases for samples that contain alkylated, multi-substituted, and partially hydrogenated compounds in addition to the parent PAC. The success of the chemical analysis, whether it be quantitative or qualitative (of even a single-mixture component), hinges on the resolving power of the analytical method used.

In the following sections an attempt is made to review the most important analytical techniques for the analysis of PAC. It is virtually impossible to cite all papers that have been published on this subject. A bibliography of over 1000 references on the occurrence and analysis of PAC has recently been prepared,[161] several monographs covering various aspects of environmental PAC are available,[162–165] and the proceedings of the first four International Symposia on Polynuclear Aromatic Hydrocarbons have been published.[166–169] In this review, emphasis will be placed on more recent studies involving advanced analytical techniques.

## 2 Sample Preparation

PAH are soluble in many organic solvents and there have been several recommendations[170–172] for the best solvent for Soxhlet extraction of solid environmental samples, especially air particulates. Among these, acetone, benzene, and

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[160] W. S. Scholtzhauer, D. B. Walters, M. E. Snook, and H. C. Higman, *J. Agric. Food Chem.*, 1978, **26**, 1277.

[161] A. Martin and M. Blumer, 'Polycyclic Aromatic Hydrocarbons: Occurrence and Analysis – A Partial Bibliography', Woods Hole Oceanographic Institution, Woods Hole, MA, Rept. WHO1-75-22, 1975.

[162] 'Polycyclic Hydrocarbons and Cancer', ed. H. V. Gelboin and P. O. P. Ts'o, Academic Press, New York, 1978, Vols. 1 and 2.

[163] J. M. Neff, 'Polynuclear Aromatic Hydrocarbons in the Aquatic Environment', Applied Science, London, 1979.

[164] 'Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment', ed. B. K. Afghan and D. Mackay, Plenum Press, New York, 1980.

[165] M. L. Lee, M. Novotny, and K. D. Bartle, 'Analytical Chemistry of Polycyclic Aromatic Compounds', Academic Press, New York, 1981.

[166] 'Carcinogenesis – A Comprehensive Survey: Polynuclear Aromatic Hydrocarbons', ed. R. Freudenthal and P. W. Jones, Raven Press, New York, 1976, Vol. 1.

[167] 'Carcinogenesis – A Comprehensive Survey: Polynuclear Aromatic Hydrocarbons', ed. P. W. Jones and R. Freudenthal, Raven Press, New York, 1978, Vol. 3.

[168] 'Polynuclear Aromatic Hydrocarbons', ed. P. W. Jones and P. Leber, Ann Arbor Science, Ann Arbor, 1979.

[169] 'Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects', ed. A. Bjørseth and A. J. Dennis, Battelle Press, Columbus, Ohio, 1980.

[170] F. S. C. Lee, T. J. Prater, and F. Ferris, in ref. 168, p. 83.

cyclohexane are all said to be nearly 100% efficient in the extraction of benzo[*a*]pyrene.[171] Extraction curves for five PAH from glass-fibre filters showed that extraction with benzene was complete after 6 h.[51] Yields of major PAH were found to be >99% after only 2 h or 20 Soxhlet cycles with benzene in another study.[173] However, since cyclohexane extracts fewer uncharacterized materials than does benzene,[174,175] and is less hazardous, its use has been endorsed by official bodies such as the World Health Organisation (WHO).[176] Methanol has also been recommended as an efficient solvent for the extraction of PAH,[177] but has also been found to extract more inorganic material[178] and organic material[58,179] other than PAH.

Ultrasonic vibration at room temperature is an alternative to Soxhlet extraction. Benzo[*a*]pyrene and 'total PAH' were completely extracted after only 30 min.[172] The procedure has been refined by sonicating in the presence of silica powder to adsorb polar material.[180] Recovery of PAH between 95 and 98% was concluded, and both extraction efficiency and reproducibility were superior when compared with Soxhlet extraction, which may result in losses of volatile compounds;[180] this method has now been adopted by the National Institute of Occupational Safety and Health.[181]

Extraction of PAC may be difficult from materials on which they are strongly adsorbed, such as carbon black[182] or fly ash;[183] low (<30%) recoveries of [$^{14}$C]benzo[*a*]pyrene from spiked fly ash were found even by ultrasonic extraction.[183] Higher recoveries were found for two- and three-ring PAH, but larger PAH are likely to be incompletely extracted.[183]

Many solvents have been suggested for the liquid–liquid partition of PAC from water (*e.g.*, $C_5$—$C_8$ alkanes, chloroform, carbon tetrachloride, and dichloromethane);[81,184] while benzene is recommended by WHO, this may soon be replaced by cyclohexane.[185] An alternative to liquid extraction is preconcentra-

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[171] T. W. Stanley, J. E. Meeker, and M. J. Morgan, *Environ. Sci. Technol.*, 1967, **1**, 927.

[172] G. Chalot, M. Castegnaro, J. L. Roche, R. Fontagnons, and P. Obatan, *Anal. Chim. Acta*, 1971, **53**, 259.

[173] G. Broddin, L. Van Vaeck, and K. Van Cauwenberghe, *Atmos. Environ.*, 1977, **11**, 1061.

[174] B. S. Das and G. H. Thomas, *Anal. Chem.*, 1978, **50**, 967.

[175] M. Dong, D. C. Locke, and E. Ferrand, *Anal. Chem.*, 1976, **48**, 368.

[176] WHO – Working Group on Air Standardization of Sampling and Analytical Procedure for Estimation of Polynuclear Aromatic Hydrocarbons in the Environment, Geneva, December 1969.

[177] D. Grosjean, *Anal. Chem.*, 1975, **47**, 797.

[178] H. H. Hill, jun., K. W. Chan, and R. W. Karasek, *J. Chromatogr.*, 1977, **131**, 245.

[179] W. Cautreels and K. Van Cauwenberghe, *J. Chromatogr.*, 1977, **131**, 253.

[180] C. Golden and E. Sawicki, *Int. J. Environ. Anal. Chem.*, 1975, **4**, 9.

[181] National Institute of Occupational Safety and Health, in 'NIOSH Manual of Analytical Methods', HEW Publication No. (NIOSH 77-157), 1977.

[182] W. L. Fitch and D. H. Smith, *Environ. Sci. Technol.*, 1979, **13**, 341.

[183] W. H. Griest, J. E. Caton, M. R. Guerin, L. B. Yeatts, jun., and C. E. Higgins, in ref. 169, p. 819; *Anal. Chem.*, 1980, **52**, 199.

[184] R. A. Hites, *Adv. Chromatogr.*, 1977, **15**, 69.

[185] M. Fielding and B. Crathorne, *Proc. Anal. Div. Chem. Soc.*, 1978, **15**, 155.

tion on plugs of active carbon,[184] Amberlite XAD resin,[184,186] Tenax GC,[187] ion-exchange resins,[188] and open-pore polyurethane.[188,189] Removal of PAH is then accomplished by stripping with a solvent, or by thermal desorption. Preconcentration on HPLC columns is an attractive alternative[187,190] (see below).

Benzene/methanol mixtures are preferred for the extraction of PAC from soils and sediments;[85] for oils and fats that are themselves soluble in a non-polar solvent, cyclohexane is adequate.[104] For insoluble fats, and protein-rich foods and biotic samples such as meat and fish, extraction with saturated hydrocarbons is incomplete unless prior saponification is carried out, generally with alcoholic KOH.[104,191]

Extracts of environmental samples inevitably contain other materials in addition to PAC, and concentration and clean-up procedures usually must be applied to yield a PAC fraction sufficiently free from extraneous materials for analysis. A typical scheme is outlined in Figure 1, and is generally applicable, *e.g.*, to extracts of air-pollution filters,[48,55] cigarette-smoke condensates,[113] and synthetic fuels.[153] The organic material is dissolved in dichloromethane and washed successively with dilute alkali and acid to remove, respectively, acidic (*e.g.* phenols) and basic constituents. These steps may be omitted for air-particulate samples that contain predominantly neutral materials. Hydrophilic and polar compounds are next removed by partitioning between cyclohexane and either methanol/water[192] or acetone/water.[45] Further enrichment of the PAH is then possible by extraction from cylohexane into nitromethane,[192] dimethylsulphoxide (DMSO),[193] or dimethylformamide (DMF).[45,104] Five partitions with nitromethane are necessary to achieve >99% extraction because many of the partition coefficients are less than 2. The nitromethane is then evaporated to concentrate the PAH.

DMSO and DMF have often been preferred to nitromethane because the PAH may be recovered from these by dilution with water and back extraction into an alkane solvent, which may be evaporated at a lower temperature. High recoveries of PAH have been reported using DMSO,[194] and a simple scheme based on three extractions from n-pentane into DMSO followed by back extractions from DMSO/water into n-pentane has been shown to separate PAH from alkanes, alcohols, acids, and phenols.[195] Unfortunately, partition coefficients between DMSO and alkanes are less favourable for methyl derivatives of PAH,[193,195] and losses of such compounds may be significant. In a recent and detailed study of the

[186] G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder, *J. Chromatogr.*, 1974, **99**, 745.

[187] W. E. May, S. N. Chesler, S. P. Cram, B. H. Gump, H. S. Hertz, D. P. Enagonio, and S. M. Dyszel, *J. Chromatogr. Sci.*, 1975, **13**, 535.

[188] J. D. Navratil, R. E. Sievers, and H. F. Walton, *Anal. Chem.*, 1977, **49**, 2260.

[189] D. K. Dasu and J. Saxena, *Environ. Sci. Technol.*, 1978, **12**, 791.

[190] K. Ogan, E. Katz, and W. Slavin, *J. Chromatogr. Sci.*, 1978, **16**, 517.

[191] J. W. Howard, R. T. Teague, R. H. White, and B. E. Fry, jun., *J. Assoc. Off. Anal. Chem.*, 1966, **49**, 595.

[192] D. Hoffmann and E. Wynder, *Anal. Chem.*, 1960, **32**, 295.

[193] J. W. Howard and E. O. Haenni, *J. Assoc. Off. Agric. Chem.*, 1963, **46**, 933.

[194] M. A. Acheson, R. M. Harrison, R. Perry, and R. A. Wellings, *Water Res.*, 1976, **10**, 207.

[195] D. F. S. Natusch and B. A. Tomkins, *Anal. Chem.*, 1978, **50**, 1429.

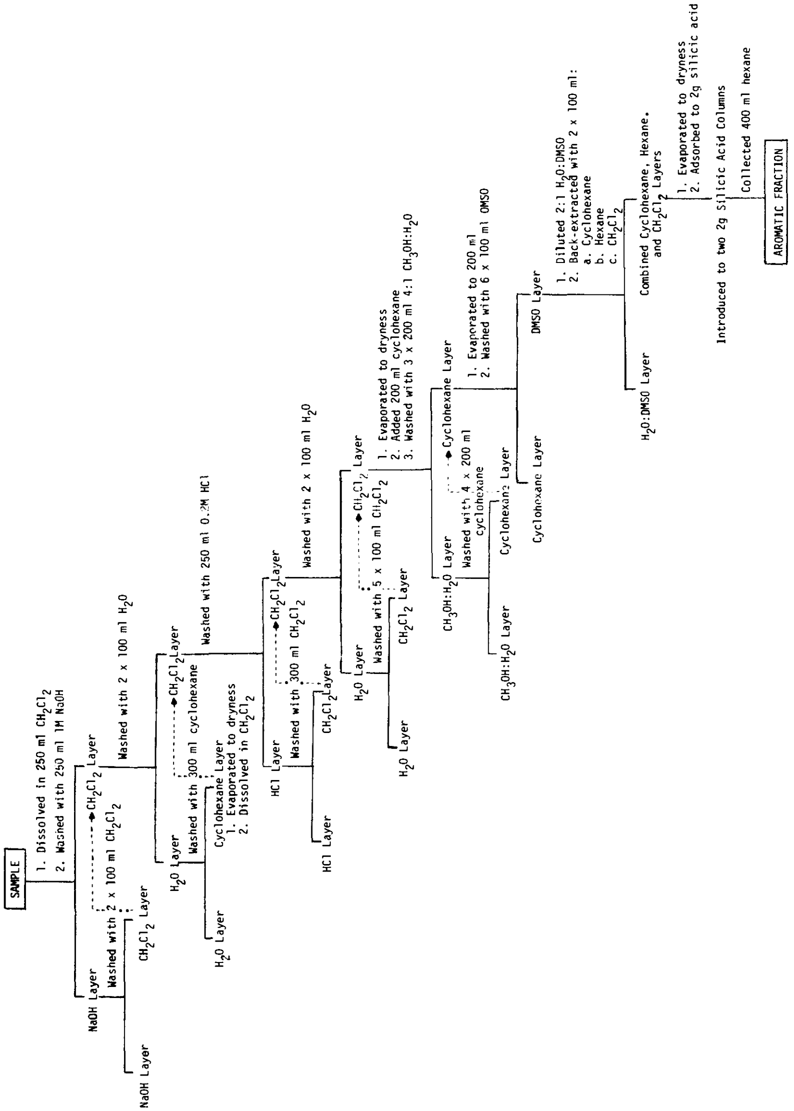

**Figure 1** *Fractionation scheme for concentration of PAH from environmental samples*

general extraction characteristics of PAH based on the variation of partition coefficients for a variety of solvents, it has been shown how the selectivity of extraction conditions may be tailored to the separation problem.[196]

Column chromatography is used in two ways in the preparation of PAC samples for analysis. First, clean-up on silica gel,[197] or latterly silicic acid or a lipophilic gel such as Sephadex LH-20,[83] can be used to remove any residual compounds that remain after the various partition steps. Secondly, the PAC fraction may be separated further into sub-fractions containing compounds of, for example, similar molecular weight. The latter is more readily achieved using alumina rather than silica, but other adsorbents such as Florisil[198] and cellulose acetate[199] have also been recommended.

Classical adsorbents suffer the disadvantages of high adsorptivity, which can result in losses and in peak tailing with consequent less sharp fractionation, and in poor reproducibility because of adsorption of traces of water. More recently the trend has been to use lipophilic gels, *e.g.*, Sephadex LH-20 or the Bio-Beads series in adsorption/partition mode. With benzene as eluent, Bio-Beads SX-12 (porous styrene divinylbenzene co-polymer) yields fractions containing compounds in sequence of increasing ring number[111] and also separates multi-alkylated PAH from parent plus mono-alkylated PAH.[200] Elution of PAH with isopropanol from Sephadex LH-20 is also in sequence of increasing ring number.[55,48,113]

Several approaches have been made to the isolation of the nitrogen heterocyclic fraction of PAC, and its separation into further fractions according to the nitrogen chemical type. Early methods depended on extraction with aqueous acid, but subsequently it was shown that neutral nitrogen compounds are important consituents of, for example, tobacco-smoke condensate.[136] Column chromatography on alumina of coal liquids yields a total-nitrogen fraction.[201] A fraction containing indoles and carbazoles, and another in which aza-arenes, aromatic amines, and nitriles were concentrated, were obtained by chromatography on silicic acid of tobacco-smoke condensate.[136] Purification of these materials was achieved by gel filtration on Bio-Beads SX-12. Chromatography on Sephadex LH-20 has also formed part of other schemes for the separation of nitrogen heterocycles.[132] Anion-exchange chromatography can be used to remove acidic compounds before separation of the nitrogen fraction.[128,202,203] A cation-exchange resin such as Amberlyst-15 then retains bases, and may yield fractions containing different nitrogen types.[128,203] Integrated schemes employing

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[196] W. K. Robbins, in ref. 169, p. 841.

[197] A. A. Rosen and F. M. Middleton, *Anal. Chem.*, 1955, **27**, 790.

[198] D. Hoffman and E. L. Wynder, in 'Identification and Measurement of Environmental Pollutants', ed. B. Westley, Symposium, Ottawa, Canada, June 1971, p. 9.

[199] W. H. Griest, H. Kubota, and M. R. Guerin, *Anal. Lett.*, 1975, **8**, 949.

[200] M. E. Snook, *Anal. Chim. Acta*, 1976, **81**, 423.

[201] J. E. Schiller and D. R. Mathiason, *Anal. Chem.*, 1977, **49**, 1225 and 2292.

[202] L. R. Snyder and B. E. Buell, *Anal. Chem.*, 1968, **40**, 1295.

[203] D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, *Anal. Chem.*, 1972, **44**, 1391.

combinations of ion-exchange and column chromatography have been described.[202]

The application to coal-derived products of a procedure for the isolation of a sulphur compound fraction from petroleum[148] involves oxidation of the PAC concentrate with $H_2O_2$ in acetic acid.[152,153] Sulphur heterocycles are oxidized to sulphones, which can be separated from PAH, *etc.*, by chromatography on silicic acid. Sulphones are then reduced back to sulphides with $LiAlH_4$.

## 3 Chromatographic Methods

**A. High-performance Liquid Chromatography.**—Since its inception in the early 1970's, high-performance liquid chromatography (HPLC) has been used for the separation of PAH. At present, HPLC does not approach the high separation efficiency of capillary gas chromatography (GC). However, HPLC does offer several advantages for the determination of PAH. First, HPLC offers a variety of stationary phases capable of providing unique selectivity for the separation of PAH isomers that are often difficult to separate by GC. Selectivity in HPLC is achieved because of interactions of the solute with both the stationary phase and the mobile phase rather than with only the stationary phase as in GC. Secondly, ultraviolet (u.v.) absorption and fluorescence spectroscopy provide extremely sensitive and, more important, selective detection for PAH in HPLC. Finally, HPLC provides a useful fractionation technique for the isolation of PAH for subsequent analysis by other chromatographic and spectroscopic techniques. Because of these characteristics, HPLC has been employed extensively for the determination of PAH in water,[187,190,204] sediments,[205,206] marine biota,[207] air particulates,[208–211] automobile exhaust,[212,213] and petroleum and related fuels.[214–217]

*Chemically-bonded Stationary Phases for PAH.* Reverse-phase HPLC on chemically-bonded $C_{18}$ (octadecyl) stationary phases is by far the most popular liquid

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[204] F. Eisenbeiss, H. Hein, R. Joester, and G. Naundorf, *Chem.-Tech.*, 1977, **6**, 227 (English translation in *Chromatogr. Newslett.*, 1978, 6, 8).

[205] S. A. Wise, S. N. Chesler, H. S. Hertz, L. R. Hilpert, and W. E. May, *Anal. Chem.*, 1977, **49**, 2306.

[206] J. J. Black, P. P. Dymerski, and W. F. Zapisek, *Bull. Environ. Contam. Toxicol.*, 1979, **22**, 278.

[207] B. Dunn, *Chromatogr. Newslett.*, 1980, **8**, 10.

[208] S. A. Wise, W. J. Bonnett, and W. E. May, in ref. 169, p. 791.

[209] E. P. Lankmayr and K. Müller, *J. Chromatogr.*, 1979, **170**, 139.

[210] A. M. Krstulovic, D. M. Rosie, and P. R. Brown, *Anal. Chem.*, 1976, **48**, 1383.

[211] D. Fechner and B. Seifert, *Fresenius' Z. Anal. Chem.*, 1978, **292**, 199.

[212] T. Nielsen, *J. Chromatogr.*, 1979, **170**, 147.

[213] P. Roumeliotis, K. K. Unger, G. Tesarek, and E. Mühlberg, *Fresenius' Z. Anal. Chem.*, 1979, **298**, 241.

[214] J. P. Durand and N. Petroff, *J. Chromatogr.*, 1980, **190**, 85.

[215] H. S. Hertz, J. M. Brown, S. N. Chesler, F. R. Guenther, L. R. Hilpert, W. E. May, R. M. Parris, and S. A. Wise, *Anal. Chem.*, 1980, **52**, 1650.

[216] J. M. Brown, S. A. Wise, and W. E. May, *J. Environ. Sci. Health*, 1980, **A15**, 613.

[217] W. A. Dark, W. H. McFadden, and D. L. Bradford, *J. Chromatogr. Sci.*, 1977, **15**, 454.

chromatographic mode for the separation of PAH. Reverse-phase HPLC provides unique selectivity for the separation of PAH isomers and particularly alkyl-substituted PAH. In addition, the compatibility of reverse-phase HPLC with gradient-elution techniques and the rapid equilibration of these columns to new mobile phase compositions make reverse-phase HPLC a convenient separation technique. The reverse-phase separations of some PAH on 10 $\mu$m $C_{18}$ columns are shown in Figure 2.

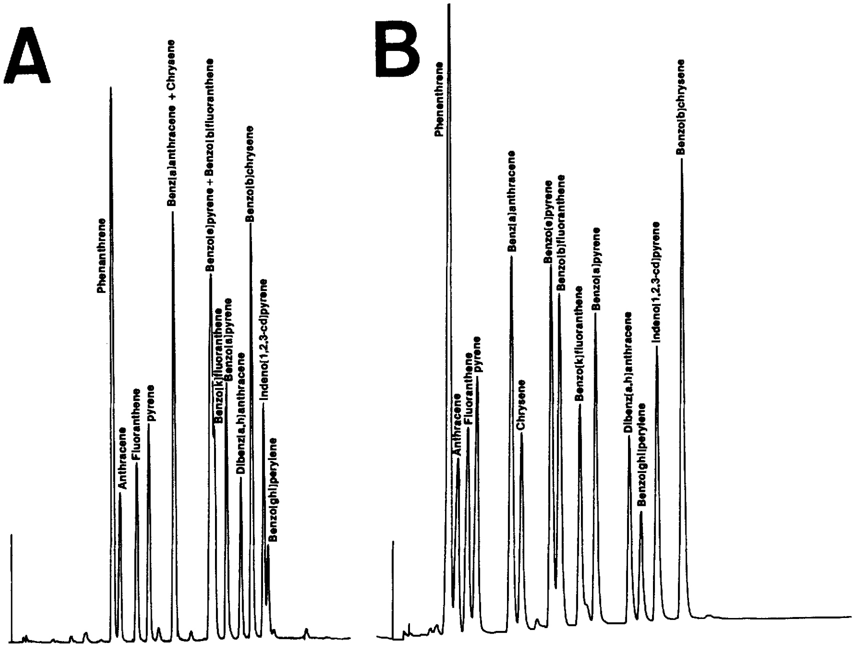

**Figure 2** *Comparison of reverse-phase HPLC separation of PAH on two different* $C_{18}$ *columns;* A, *Zorbax ODS, monomeric,* B, *Vydac* 201*TP, polymeric. Chromatographic conditions: mobile phase linear gradient* 80—100% *acetonitrile in water at* 1% min$^{-1}$ *and* 1 cm$^3$ min$^{-1}$; *u.v. detection at* 254 nm

Several recent reports[205,208,212,218,219] have included retention data for some PAH on specific $C_{18}$ columns. A comparison of these retention data and recent studies by Wise *et al.*,[208] Ogan and Katz,[220] and Colmsjö and MacDonald[221] indicate that $C_{18}$ columns from various manufacturers provide not only different separation efficiencies, but different selectivities and retention characteristics for PAH. The different selectivities for two $C_{18}$ columns, one with a polymeric and the other a monomeric $C_{18}$ layer, are illustrated in Figure 2. (Compare the separation of benz[*a*]anthracene and chrysene and the elution order reversals of

[218] G. P. Blumer and M. Zander, *Z. Anal. Chem.*, 1977, **288**, 277.
[219] J. Chmielowiec and A. E. George, *Anal. Chem.*, 1980, **52**, 1154.
[220] K. Ogan and E. Katz, *J. Chromatogr.*, 1980, **188**, 115.
[221] A. L. Colmsjö and J. C. MacDonald, *Chromatographia*, 1980, **13**, 350.

benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, and benzo[*b*]chrysene on the polymeric *vs.* the monomeric columns.) The retention characteristics of over 90 PAH on a monomeric and a polymeric $C_{18}$ column have been reported.[208] Polyphenyl arenes exhibit significantly different retention characteristics on monomeric *vs.* polymeric $C_{18}$ stationary phases. These compounds are generally retained longer, relative to the fused ring PAH, on the monomeric than on the polymeric phases.[208,222] Some of the selectivity differences observed on various $C_{18}$ columns can be attributed to the surface coverage of the $C_{18}$ layer.[223] Selectivity differences for columns from the same manufacturer, but from different production lots, have also been described.[220,224]

The mechanism of retention of PAH on chemically bonded $C_{18}$ phases has not been established and is a topic of much discussion and research.[225] Sleight,[226] and more recently Blumer and Zander,[218] correlated the retention of PAH on $C_{18}$ phases with the number of carbon atoms in the solute. Sleight[226] and Locke[227] suggested that the retention was dependent to some degree on their solubilities in the polar mobile phase. Recently, Wise *et al.*[222] described a relationship between the shape of PAH solutes, particularly the length-to-breadth ratio, and the reverse-phase retention. In this study the length-to-breadth ratios for 84 unsubstituted and methyl-substituted PAH were compared with the HPLC retention characteristics. In nearly all cases, this ratio was successful in predicting the elution order of isomeric PAH, *i.e.* the retention increases with increasing length-to-breadth ratio. These ratios were found to be particularly useful in predicting the unique selectivity of reverse-phase HPLC for methyl-substituted PAH. The linear correlation for retention data *vs.* length-to-breadth ratios for 23 methyl-substituted isomeric benzo[*c*]phenanthrenes, benz[*a*]anthracenes, and chrysenes is shown in Figure 3.

Parameters such as composition of mobile phase and temperature can be used to achieve changes in the elution order of PAH in reverse-phase HPLC. Katz and Ogan[228] studied the effect of the mobile-phase composition on the selectivity factors for PAH on different $C_{18}$ columns. The use of temperature to achieve changes in selectivity was demonstrated by Chmielowiec and Sawatzky.[229]

Polar chemically bonded stationary phases, used in conjunction with nonpolar mobile phases (normal phase HPLC), have also been employed for the separation of PAH. Several polar phases are available containing such functional groups as amine ($NH_2$), diamine [$R(NH_2)_2$], nitrile (CN), diol [$R(OH)_2$], ether (ROR), and nitrophenyl ($NO_2$) bonded to the silica particles. In the normal-phase mode on these polar columns, the PAH separations achieved are similar to those obtained on the classical adsorbents such as silica and alumina.

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[222] S. A. Wise, W. J. Bonnett, F. R. Guenther, and W. E. May, *J. Chromatogr. Sci.*, submitted for publication.

[223] S. A. Wise, unpublished data.

[224] K. Ogan and E. Katz, *J. Liq. Chromatogr.*, 1980, **3**, 1151.

[225] H. Colin and G. Guiochon, *J. Chromatogr.*, 1977, **141**, 289.

[226] R. B. Sleight, *J. Chromatogr.*, 1973, **83**, 31.

[227] D. C. Locke, *J. Chromatogr.*, 1974, **12**, 433.

[228] E. Katz and K. Ogan, *Chromatogr. Newslett.*, 1980, **8**, 20.

[229] J. Chmielowiec and H. Sawatzky, *J. Chromatogr. Sci.*, 1979, **17**, 245.

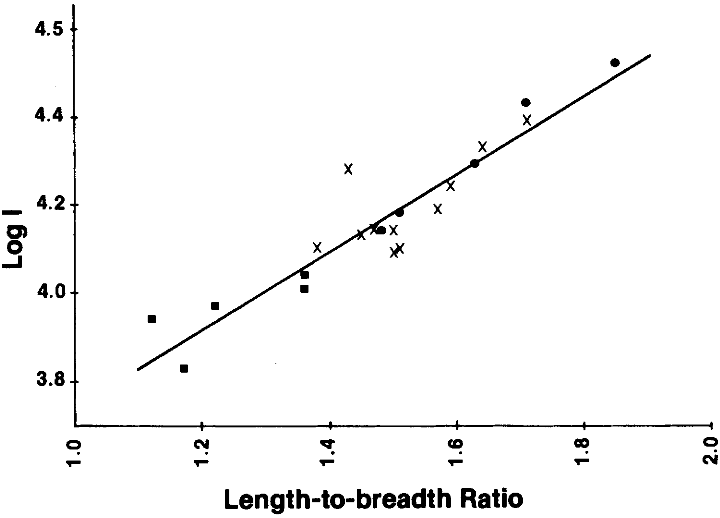

**Figure 3** *Linear correlation of reverse-phase LC retention* (log I) vs. *length-to-breadth ratio for methylbenzo*[c]*phenanthrenes* (■), *methylbenz*[a]*anthracenes* (×), *and methylchrysenes* (●)
(From ref. 222)

Wise *et al.*[208] have described the retention characteristics of over 90 unsubstituted and alkyl-substituted PAH on a polar amine phase. On this column the retention increases with increasing number of condensed aromatic rings (or number of aromatic carbon atoms). In contrast to reverse-phase HPLC, the presence of an alkyl group on the PAH has only a slight effect on retention on the amine phase. This characteristic is often advantageous in pre-fractionation techniques for the analysis of complex mixtures. The use of normal-phase HPLC on polar-bonded phases also eliminates one of the major difficulties encountered with classical adsorbents, *i.e.*, non-reproducible retention owing to small changes in the moisture content of the eluent. Finally, the use of volatile nonpolar mobile phases facilitates the concentration of collected fractions by evaporation.

Blumer and Zander[218] studied the retention of a number of PAH, biaryls, and PANH on silica modified with polar nitrophenyl groups. A linear relationship between log retention and carbon number was observed for these three groups of compounds. In addition, a class separation of the PAH and PANH could be achieved on this phase due to the more polar nature of the N-containing compounds. Blumer *et al.*[230] separated more than 100 components of coal tar using this polar stationary phase. Lankmayr and Müller[209] compared nitrophenyl, amine, and $C_{18}$ columns for the separation of 17 PAH commonly found in dust samples, and found that the nitrophenyl phase provided the best separation for those PAH evaluated. An extensive characterization and discussion of the

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[230] G.-P. Blumer, R. Thoms, and M. Zander, *Erdoel, Kohle, Erdgas, Petrochem. Brennst.-Chem.*, 1978, **31**, 197.

retention of PAH and alkyl-substituted PAH on the nitrophenyl phase has not yet appeared in the literature.

Chmielowiec and George[219] recently investigated the performance of several bonded phases (*i.e.* amine, nitrile, diol, ether, diamine, and quaternary ammonium) for normal-phase separations of 10 PAH and advocated the use of the diamine column. Several other polar-bonded phases have been described for PAH separations such as nitrofluorenimine,[231] phthalimidopropyl,[232] 3-(2,4-dinitroanilino)propyl,[233] and picramidopropyl.[234]

*Spectroscopic Detection in HPLC.* A major advantage of HPLC for the determination of PAH is the availability of extremely sensitive and selective detectors. U.v. absorption and fluorescence detectors are ideally suited for the detection of PAH. U.v. and fluorescence detectors are generally used in series; the u.v. detector is universal for PAH, whereas the fluorescence detector provides high sensitivity and specificity.

Several workers[210,211,235] have described the use of variable-wavelength u.v. detection to achieve some degree of selectivity. Thoms and Zander[236] used complete u.v. absorption spectra of PAH for their identification in HPLC effluents. Others[210,237] have employed absorbance ratios at several wavelengths for qualitative analysis.

Fluorescence detection provides selectivity for individual PAH and the possibility of identification of specific compounds in complex mixtures. Several reports have described the application of both filter fluorimeters and spectrofluorimeters for the determination of PAH in diesel exhaust,[238] cigarette smoke,[239] shale oil,[215] oil,[214,216] and air particulates.[211] Recently, Ogan *et al.*[240] compared the use of a cut-off filter and a monochromator in the fluorescence detection of PAH in environmental samples. The cut-off filter provided an improvement of 3—5 times in sensitivity over the monochromator; however, these gains were often offset by spectral interferences from other compounds in the sample. Christensen and May[241] compared the sensitivities of several filter fluorimeters, a spectrofluorimeter, and u.v. detectors for PAH determinations.

Selective fluorescence quenching of certain PAH in the presence of nitromethane has been investigated as a selective detection system for HPLC.[242,243] Sawicki *et al.*[244] and later Dreeskamp *et al.*[245] reported that in the presence of

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[231] C. H. Lochmüller, R. R. Rydall, and C. W. Amoss, *J. Chromatogr.*, 1979, **178**, 298.
[232] D. C. Hunt, P. J. Wild, and N. T. Crosby, *J. Chromatogr.*, 1977, **130**, 320.
[233] L. Nondek, M. Minárik, and J. Málek, *J. Chromatogr.*, 1979, **178**, 427.
[234] S. A. Martin, W. J. Lough, and D. G. Bryan, *HRC & CC*, 1980, **3**, 33.
[235] R. D. Smillie, D. T. Wang, and O. Meresz, *J. Environ. Sci. Health*, 1978, **A13**, 47.
[236] R. Thoms and M. Zander, *Fresenius' Z. Anal. Chem.*, 1976, **282**, 443.
[237] R. K. Sorrell and R. Reding, *J. Chromatogr.*, 1979, **185**, 655.
[238] D. E. Seizinger, *Trends in Fluorescence*, 1978, **1**, 9.
[239] N. M. Sinclair and B. E. Frost, *Analyst (London)*, 1978, **103**, 1199.
[240] K. Ogan, E. Katz, and T. J. Porro, *J. Chromatogr. Sci.*, 1979, **17**, 597.
[241] R. G. Christensen and W. E. May, *J. Liq. Chromatogr.*, 1978, **1**, 385.
[242] G.-P. Blumer and M. Zander, *Fresenius' Z. Anal. Chem.*, 1979, **296**, 409.
[243] P. L. Konash, W. E. May, and S. A. Wise, submitted for publication in *J. Liq. Chromatogr.*
[244] E. Sawicki, T. W. Stanley, and W. C. Elbert, *Talanta*, 1964, **11**, 1433.
[245] H. Dreeskamp, E. Koch, and M. Zander, *Z. Naturforsh., Teil A*, 1975, **30**, 1311.

nitromethane, the fluorescence emission of six-membered ring PAH was quenched to a much greater degree than was that of those containing a fluoranthenic structure. Blumer and Zander[242] briefly described the application of this selective quenching as an HPLC detector. Recently, Konash *et al.*[243] investigated further the potential of this phenomenon for the selective detection of the benzofluoranthene isomers in the presence of the benzopyrene isomers and perylene. As illustrated in Figure 4, the addition of 0.5% nitromethane to the mobile phase significantly quenches all the non-fluoranthenic PAH (except a small percentage of anthracene) resulting in a selective chromatogram of only fluoranthenic PAH. This technique was found to be particularly useful using an inexpensive broad-

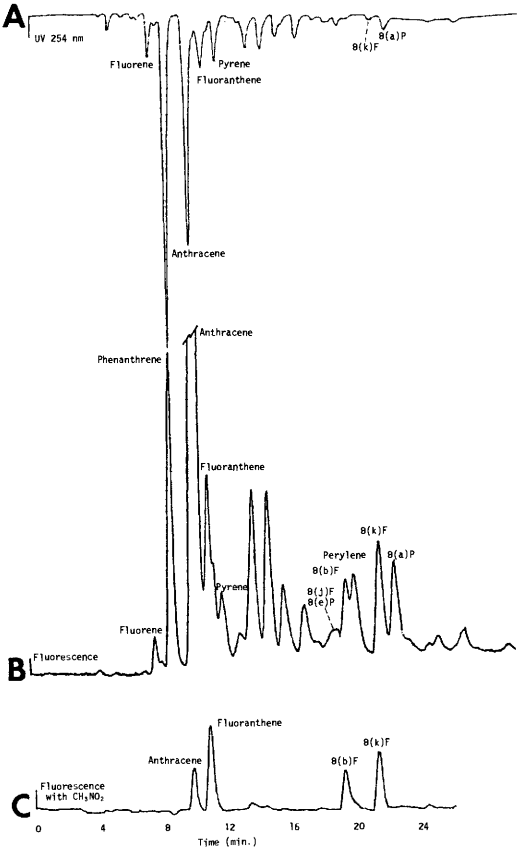

**Figure 4** *Reverse-phase HPLC separation of coal-tar extract with:* A, *detection at* 254 nm; B, *fluorescence detection with filter fluorimeter* ($\lambda_{ex}$ = 250—380 nm *and* $\lambda_{em}$ = >380 nm); C, *fluorescence detection with* 0.5% *nitromethane in the mobile phase. Chromatographic conditions: Vydac* 201*TP column; mobile phase linear gradient* 50—100% *acetonitrile in water at* 2% $min^{-1}$ *and* 2 $cm^3$ $min^{-1}$
(From ref. 243)

band filter fluorimeter to achieve selectivity for fluoranthenic PAH as a group. This procedure has been used for quantifying benzo[*k*]fluoranthene in a shale oil sample.[243]

A recent development in spectroscopic detection of PAH in chromatographic effluents is the use of multi-channel rapid scanning spectrometers. These detectors permit the recording of fluorescence spectra 'on-the-fly', thereby eliminating stop flow or valving to trap the chromatographic peak in the flow cell. Jadamec *et al.*[246] described the use of such a system for the characterization of petroleum fractions in the determination of the source of oil spills. More recently, Warner and co-workers[247] reported a two-dimensional 'video fluorimeter' as an LC detector. They recorded the fluorescence intensity as a function of emitting and exciting wavelengths every 25 s to produce an emission–excitation matrix for PAH standards as they eluted from the LC. These systems, when combined with computers and floppy disks for data storage, will allow the rapid acquisition of an enormous amount of data during one chromatographic run. These data can then be evaluated to identify and quantify the PAH in the complex chromatograms.

The potential of the combination of liquid chromatography–mass spectrometry (LC–MS) for the separation and identification of organic compounds has generated considerable research in the past few years. The inherent problems of introducing a liquid stream ($\sim 1$ cm$^3$ min$^{-1}$) into the high-vacuum system of the mass spectrometer have led to several approaches. Arpino and Guiochon[248] and Games[249] recently reviewed the various LC–MS interfaces and described the construction, operating principles, and performance of each approach. Another review of the LC–MS techniques by McFadden[250] emphasized the current applications of this technique.

At present, two LC–MS approaches are commercially available, *i.e.* direct liquid injection and depositing the effluent onto a moving belt from which the mobile phase is evaporated before introduction into the mass spectrometer. Both of these approaches transfer only a portion of the LC solute into the MS. Christensen *et al.*[251] recently described a new LC–MS interface that combines several of the advantages of both the direct liquid-injection and moving-belt techniques. The LC effluent is concentrated by evaporation as it flows down an electrically heated wire. The concentrated effluent then flows through a small needle valve and is sprayed into the MS ion source. The application of this approach to the analysis of PAH standards resulted in a 20-fold enrichment of the analyte in the mobile phase before it entered the MS.

Dark *et al.*[217] using the moving-belt method demonstrated the LC fractionation of coal liquid samples with structural characterization by LC–MS. From the LC retention data on two different columns and the molecular weight data, they

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[246] J. R. Jadamec, W. A. Saner, and Y. Talmi, *Anal. Chem.*, 1977, **49**, 316.

[247] D. C. Shelly, W. A. Ilger, M. P. Fogarty, and I. M. Warner, *Altex Chromatogram*, 1979, **3**, 4.

[248] P. J. Arpino and G. Guiochon, *Anal. Chem.*, 1979, **51**, 682A.

[249] D. E. Games, *Proc. Anal. Div. Chem. Soc.*, 1980, **17**, 110.

[250] W. H. McFadden, *J. Chromatogr. Sci.*, 1980, **18**, 97.

[251] R. G. Christensen, H. S. Hertz, S. Meiselman, and E. White V, *Anal. Chem.*, 1981, **53**, 171.

identified a number of aromatic compounds (molecular weight up to ~250) in the coal liquid. Other applications of LC–MS involving PAH have been reported.[252,253] In the future, LC–MS will find greater application in the determination of higher molecular weight PAH that are not amenable to GC analysis.

*Multi-dimensional HPLC Techniques.* As described earlier, both reverse-phase and normal-phase HPLC are useful for the separation of PAH. However, even the most selective and efficient HPLC columns available are unsuccessful in resolving all the PAH in complex mixtures. The determination of individual PAH in these mixtures generally requires the use of several chromatographic modes [*e.g.*, thin-layer chromatography (TLC), GC, and various LC modes] and/or selective detection for the determination of individual PAH. HPLC is extremely useful for both prefractionation/isolation techniques and for analytical determinations.

Traditionally in PAH analyses, sample preparation has consisted of separation on silica or alumina by column chromatography, TLC, or more recently HPLC. After isolation of the PAH fraction, GC or spectroscopic techniques have generally been employed for the final analytical measurement. However, multi-dimensional or sequential chromatographic analysis using two different HPLC modes has been found to be useful for the determination of PAH in complex mixtures.

In their early work with a chemically bonded $C_{18}$ phase, Schmit *et al.*[254] recognized the potential of reverse-phase LC separation of PAH after an initial separation step involving gel permeation chromatography for the analysis of automobile-exhaust condensate. More recently, Wise *et al.*[205,208] have advocated the use of normal-phase HPLC on a polar chemically bonded amine phase for the separation of PAH based on the number of condensed aromatic rings, followed by separation of the various PAH isomers and/or alkyl-substituted PAH by reverse-phase HPLC. This sequential combination of normal- and reverse-phase HPLC has been employed for the quantitation of benzo[*a*]pyrene in some virgin, waste, and recycled oils,[216] and for the quantitation of several PAH in shale oil.[215] In the sample of shale oil the amounts of pyrene, fluoranthene, benzo[*e*]pyrene, and benzo[*a*]pyrene determined using this technique were similar to the values obtained using either 'classical' extraction methods followed by GC–MS quantitation or direct sample injection GC–MS with single-ion monitoring for selectivity.[215] Dark *et al.*[217,255] have also used similar sequential techniques with silica or an amine column followed by reverse-phase separation with mass-spectrometric detection for the characterization of coal liquids.

*Unique Applications of HPLC for PAH Determinations.* The low levels of PAH normally found in water samples necessitates the use of a sample-enrichment step

[252] T. Takeuchi, Y. Hirata, and Y. Ohumura, *Anal. Chem.*, 1978, **50**, 660.
[253] W. H. McFadden, *J. Chromatogr. Sci.*, 1979, **17**, 2.
[254] J. A. Schmit, R. A. Henry, R. C. Williams, and J. F. Dieckman, *J. Chromatogr. Sci.*, 1971, **9**, 645.
[255] W. A. Dark and W. H. McFadden, *J. Chromatogr. Sci.*, 1978, **16**, 289.

and sensitive detection methods. HPLC satisfies both of these criteria. Traditional enrichment procedures involve concentration of an organic solvent extract by evaporation. However, PAH enrichment directly on a reverse-phase LC column has been described.[187,190,204]

In 1975, May *et al.*[187] described the use of a 'coupled column' procedure for the enrichment and separation of trace-level PAH in water. In this procedure a large water sample (1—2 dm$^3$) is passed through a short LC column containing 27—50 $\mu$m pellicular $C_{18}$ material to concentrate the nonpolar compounds. After the enrichment step, the short column is connected at the head of an analytical column containing 10 $\mu$m totally porous microparticulate $C_{18}$ material. A mobile-phase gradient of 30—100% methanol was used to desorb the PAH from the pre-column (enrichment column) and to separate them on the analytical column. At the initial mobile-phase composition of 30% methanol, the PAH are rapidly desorbed from the pellicular packing, but are retained as a narrow band at the inlet of the analytical column, thereby resulting in negligible peak broadening during the analytical separation. Recently, Eisenbeiss *et al.*[204] and Ogan *et al.*[190] described similar approaches for the concentration and determination of PAH in aqueous samples. In these two reports an LC injection valve was used to place the enrichment column in-line with the analytical column after the enrichment step.

Most environmental PAH mixtures can be analysed using capillary GC; however, low volatility limits the application of GC for the determination of high-molecular-weight PAH (molecular weight > 300). At present, HPLC is the most advantageous technique for the separation of these compounds. Coal-tar pitch contains a relatively high proportion of high-molecular-weight PAH and PANH, and recently, Blumer *et al.*[230] reported that approximately 70% of the pitch could be eluted from a nitrophenyl phase column compared to only 30% by GC.

Separations of high-molecular-weight PAH in both normal- and reverse-phase systems require stronger mobile-phase compositions than are generally employed in order to achieve sufficient solubility of the sample. Blumer and Zander[256] achieved normal-phase separation of PAH of molecular weight 400—600 on a nitrophenyl phase with 60—80% chloroform in hexane. In a reverse-phase system using a $C_8$ column, Felscher and Stein[257] used a gradient of 40—100% acetonitrile/DMF (75:25) in water to separate coal tar constituents. Numerous high-molecular-weight PAH (up to molecular weight 448) were separated and identified in a carbon-black extract using a $C_{18}$ column with a gradient from 50% water/acetonitrile to 100% ethyl acetate and finally to 100% methylene chloride (see Figure 5).[258]

*HPLC Separations of Polycyclic Aromatic Nitrogen-, Sulphur-, and Oxygen-heterocycles.* Normal- and reverse-phase HPLC are useful in the separation of

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[256] G.-P. Blumer and M. Zander, Compendium 78/79 Supplement to *Erdoel, Kohle, Erdgas, Petrochem.*, 1978, p. 1472.

[257] D. Felscher and J. Stein, *Z. Chem.*, 1979, **19**, 303.

[258] P. Peaden, M. L. Lee, Y. Hirata, and M. Novotny, *Anal. Chem.*, 1980, **52**, 2268.

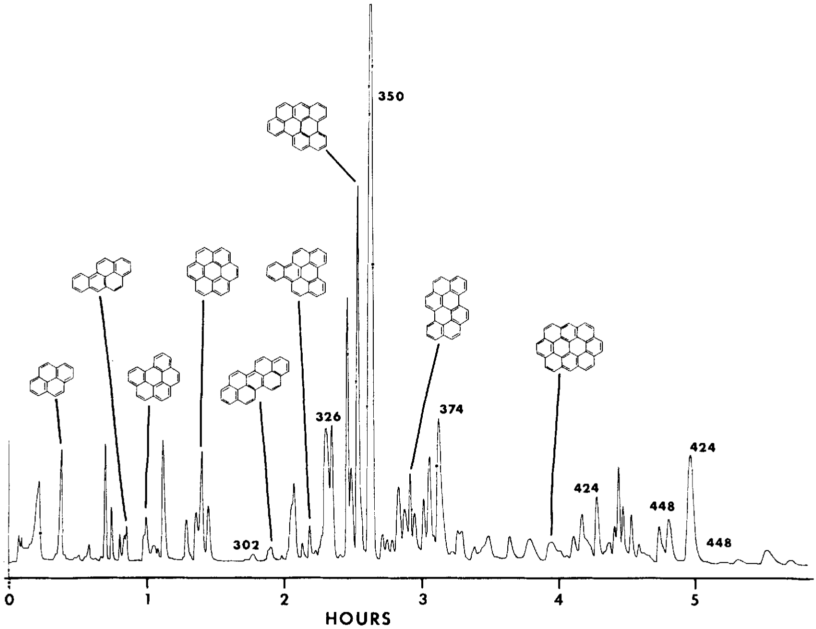

**Figure 5** *Non-aqueous reverse-phase HPLC separation of carbon-black extract. Chromatographic conditions: Vydac* 201*TP column; mobile phase flow rate* 0.7 $cm^3$ $min^{-1}$; *solvent programme isocratic for the first* 15 min *with* 50% *acetonitrile in water, non-linear programme (Programme* 5 *on Waters Model* 660 *solvent programmer) to* 100% *acetonitrile for the next* 70 min, *linear programme to* 100% *ethyl acetate for the next* 130 min, *and linear programme to* 100% *methylène chloride for the last* 60 min; *fluorescence detection with* $\lambda_{ex}$ = 335 nm *and* $\lambda_{em}$ = 480 nm *with* 20 nm *slit widths*

(Reproduced by permission from *Anal. Chem.*, 1980, **52,** 2268)

PANH, but only a few applications have been reported.[57,126,218,259–263] Dong *et al.*[57] described the retention characteristics of 16 PANH on both a $C_{18}$ phase and on $\mu$-silica. Blumer and Zander[218] studied the retention of 12 similar PANH on chemically bonded $C_{18}$ and nitrophenyl phases. On chemically bonded $C_{18}$ phases the retention characteristics of PANH are similar to that of PAH, *i.e.* retention is governed by the number of aromatic carbon atoms, but less organic solvent in the mobile phase is required owing to the increased polarity of the PANH. Isomeric PANH can often be resolved in reverse-phase HPLC, but retention data are available for only a few of these compounds.

The normal-phase HPLC separations of PANH on $\mu$-silica,[57] amine,[259] and nitrophenyl[218] columns appear to depend on the steric availability of the

[259] P. L. Konash and S. A. Wise, unpublished data.

[260] W. E. May, J. M. Brown, L. R. Hilpert, and S. A. Wise, 'Proceedings, 5th International Symposium on Polynuclear Aromatic Hydrocarbons', Columbus, Ohio, October, 1980.

[261] R. Vivilecchia, M. Thiébaud, and R. W. Frei, *J. Chromatogr. Sci.*, 1972, **10**, 411.

[262] S. Ray and R. W. Frei, *J. Chromatogr.*, 1972, **71**, 451.

[263] Chemex Scientific Ltd., Product Literature, Ottawa, Ontario, Canada.

nitrogen lone pair. Compounds such as benz[*c*]acridine, benzo[*h*]quinoline, and dibenz[*a,h*]acridine are only weakly retained on the silica or amine column, when compared to the isomers benz[*a*]acridine, benzo[*f*]quinoline, and dibenz[*a,j*]-acridine, owing to the steric hindrance of the lone pair. May *et al.*[260] quantified benzo[*f*]quinoline in shale oil using a multi-dimensional HPLC procedure on an amine column followed by analysis on a $C_{18}$ column.

Complex formation of PANH on silver-impregnated adsorbents has been described by Vivilecchia *et al.*[261] and Frei *et al.*[126,262] More recently, a similar column, based on chemically bonded mercury salts (phenylmercury acetate), has become commercially available.[263] These columns exhibit excellent thermal and chemical stability and may be used in either normal- or reverse-phase modes. Separations are insensitive to the degree of alkyl substitution and are therefore capable of giving class separations. Examples of separations on this organomercury phase have been illustrated for nitrogen-, sulphur-, and oxygen-heterocyclic compounds as well as PAH.[262] The use of HPLC for the determination of heterocyclic compounds will certainly increase in the future.

**B. Gas Chromatography.**—The extreme complexity of PAC mixtures demands the greatest resolution possible in their analysis, and in this respect gas chromatography (GC) with packed columns[264] even as long as 20 m has fallen short of the capabilities of glass-capillary column GC.[265] First used in 1964, for the analysis of PAH,[36] the latter technique was significantly refined[266,267] when it was found that acid-leaching of Lewis acids from the glass from which

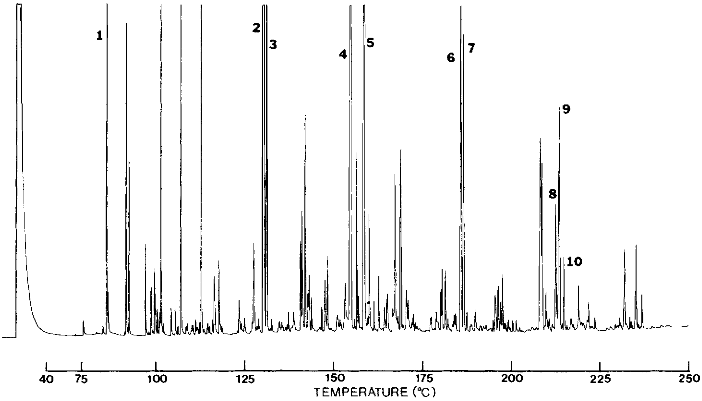

**Figure 6** *Capillary column gas chromatogram of coal-tar PAH. Chromatographic conditions:* 20 m × 0.30 mm i.d. *glass column coated with* 0.10 μm *film* SE-52; *temperature programmed from* 40 *to* 80 °C *at* 10 °C $min^{-1}$ *and then from* 80 *to* 250 °C at 2 °C $min^{-1}$; He *carrier gas velocity* 50 cm $s^{-1}$. *Peak* (1) *naphthalene*, (2) *phenanthrene*, (3) *anthracene*, (4) *fluoranthene*, (5) *pyrene*, (6) *benz*[a]*anthracene*, (7) *chrysene*, (8) *benzo*[e]*pyrene*, (9) *benzo*[a]*pyrene*, (10) *perylene*

[264] G. Grimmer, H. Böhnke, and A. Hildebrandt, *Fresenius' Z. Anal. Chem.*, 1976, **279**, 139.
[265] M. L. Lee and B. W. Wright, *J. Chromatogr. Sci.*, 1980, **18**, 345.
[266] M. L. Lee, Thesis, Indiana University, 1975.
[267] M. L. Lee, K. D. Bartle, and M. V. Novotny, *Anal. Chem.*, 1975, **47**, 540.

capillaries were made greatly improved the deactivation and efficiency of columns. Figure 6 shows a chromatogram of coal-tar PAH obtained with an acid-leached column, subsequently coated with SE-52. The performance of this column, as measured by the resolution between the isomer pairs phenanthrene–anthracene, benz[*a*]anthracene–chrysene, and benzo[*e*]pyrene–benzo[*a*]pyrene, represents the best resolution currently available.

Glass,[268] and most recently fused-silica,[269] columns are now used universally, and if surface activity is controlled by acid leaching and other treatments,[268] particularly silanization,[270] trace compounds that may be adsorbed on high-surface area supports are eluted as sharp peaks.[265]

A variety of stationary phases has been employed in capillary-column separations of PAH,[265] but because of their moderate selectivities and high temperature stabilities, SE-52 (methylsilicone gum with 5% phenyl groups) and SE-54 (methylsilicone gum with 1% vinyl and 5% phenyl groups) have gained wide acceptance; only minoı further selectivity effects are observed for more polar phases.[271–273] For capillary-column GC of the nitrogen heterocycles, more polar phases such as XE-60,[274] Versamid 900,[125] and SP 2340[138] have been used in addition to SE-52.[49]

The retention of a planar PAH on a non-polar or slightly polar phase is related only to the logarithm of vapour pressure, and therefore to the boiling point and molecular weight.[275] On a nematic liquid-crystal phase, however, a variation in activity coefficient, expressed in terms of a length-to-breadth ratio shape factor, also influences the retention of PAH.[276,277] Thus, liquid crystal phases such as the *NN*′-bis(*p*-alkoxybenzylidene)-$\alpha,\alpha'$-bi-*p*-toluidines show pronounced selectivity for PAH in packed column GC[277–279] and allow resolution of a variety of isomer pairs such as anthracene and phenanthrene, and benzo[*a*]- and benzo[*e*]pyrenes. Elution of $C_{24}$ hydrocarbons is possible on the most stable liquid-crystal phase and there have been applications to PAH analysis.[280–282] Aza-arenes may also be separated on a nematic liquid crystal.[283] Attempts to coat these phases onto glass capillaries have generally resulted in inefficient columns,

[268] M. L. Lee and B. W. Wright, *J. Chromatogr.*, 1980, **184**, 235.

[269] R. D. Dandereau and E. H. Zerenner, *HRC & CC*, 1979, **2**, 351.

[270] B. W. Wright, M. L. Lee, S. W. Graham, L. V. Phillips, and D. M. Hercules, *J. Chromatogr.*, 1980, **199**, 355.

[271] L. S. Lysyuk and A. N. Korol, *Chromatographia*, 1977, **10**, 712.

[272] H. Borwitzky and G. Schomburg, *J. Chromatogr.*, 1979, **170**, 99.

[273] M. P. Maskarinec and G. Olerich, *Anal. Chem.*, 1980, **52**, 588.

[274] G. Alberini, V. Cantuti, and G. P. Cartoni, in 'Gas Chromatography 1966', ed. A. B. Littlewood, Institute of Petroleum, London, 1967, p. 258.

[275] K. D. Bartle, M. L. Lee, and S. A. Wise, *Chromatographia*, 1981, **14**, 69.

[276] A. Radecki, H. Lamparczyk, and R. Kaliszan, *Chromatographia*, 1979, **12**, 595.

[277] M. Janini, K. Johnston, and W. L. Zielinski, *Anal. Chem.*, 1975, **47**, 670.

[278] W. L. Zielinski and G. M. Janini, *J. Chromatogr.*, 1979, **186**, 237.

[279] G. M. Janini, G. M. Muschik, and W. L. Zielinski, *Anal. Chem.*, 1976, **48**, 1879.

[280] G. M. Janini, B. Shaikh, and W. L. Zielinski, *J. Chromatogr.*, 1977, **132**, 136.

[281] S. Wasik and S. Chesler, *J. Chromatogr.*, 1976, **122**, 451.

[282] A. Radecki, H. Lamparczyk, J. Grzybowski, and J. Halkiewicz, *J. Chromatogr.*, 1978, **150**, 527.

[283] M. Pailer and V. Hlozek, *J. Chromatogr.*, 1976, **128**, 163.

but recent work has shown how mixed stationary phases composed of blends of a nematic liquid crystal with SE-52 result in retention of both efficiency and selectivity for PAH separation by capillary GC.[284]

For most PAC analytical work, columns need be no longer than 10—25 m with internal diameter 0.2—0.3 mm and film thicknesses near 0.3 μm.[265] A graph of column resolution (measured by the separation number) against square root of column length has shown that loss in resolution between 15 and 30 m is minimal.[285] Useful separations can even be achieved[285] on columns as short as 4 m. Smaller column internal diameters lead to increased retention and slightly greater efficiency, although larger i.d. columns have greater capacity, as do columns with thicker films.[265] There is however a decrease in efficiency with increase in film thickness because of greater resistance to mass transfer.[265] Analysis times can be shortened[286] by the use of hydrogen as carrier gas (which results in lower elution temperatures) at linear velocities up to 100 cm $s^{-1}$.[265,285]

Glass-capillary-column GC was used in many of the representative applications referred to in Section 1. Chromatograms generally extend up to coronene[265] (molecular weight 300). Some attempts have been made recently to extend the temperature range of capillary columns in order to chromatograph compounds of higher molecular weight. Grob[287] was able to chromatograph compounds from coronene ($C_{24}H_{12}$) to rubrene ($C_{42}H_{28}$) on a short (5.5 m × 0.32 mm i.d.) glass capillary coated with OV-101, with temperature programming from 200 to 260 °C. Figure 7 shows a chromatogram recently obtained of an extract of carbon black.[265] The column was a 15 m × 0.27 mm i.d. Pyrex capillary that was

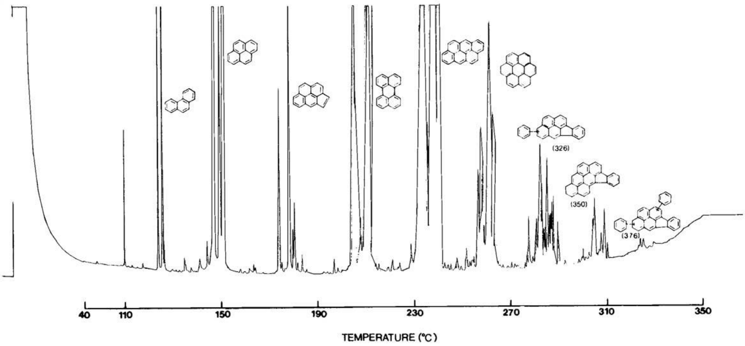

**Figure 7** *High-temperature capillary-column gas chromatogram of the PAH extracted from a carbon black. Chromatographic conditions:* 15 m × 0.27 mm i.d. *glass column coated with* SE-52; *temperature programmed from* 40 *to* 110 °C *at* 10 °C $min^{-1}$ *and then from* 110 *to* 350 °C *at* 2 °C $min^{-1}$

(Reproduced by permission from *J. Chromatogr. Sci.*, 1980, **18**, 345)

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[284] R. J. Laub, W. L. Roberts, and C. A. Smith, *HRC & CC*, 1980, **3**, 355.

[285] B. W. Wright and M. L. Lee *HRC & CC*, 1980, **3**, 352.

[286] G. Schomburg, R. Dielmann, H. Borwitzky, and H. Husmann, *J. Chromatogr.*, 1978, **167**, 337.

[287] K. Grob, *Chromatographia*, 1974, **7**, 94.

extremely well deactivated[270] before being coated with SE-52. The oven was programmed from 110 to 350 °C and hydrogen was used as the carrier gas.

The capillary gas chromatograph is an excellent separation tool, but is less effective for identification. Some information can be gained concerning the general composition of PAC mixtures by using selective detectors as discussed below. In addition, the chromatographic system can provide retention data that can yield complementary information for the positive identification of resolved components. Some studies have reported[104,288] Kovats retention indices for PAC, and it was found that the retention indices of the PAC are influenced by the stationary-phase film thickness, the length of the column, the temperature programming rate, the carrier-gas flow rate, and the injection system. For this reason, a new and more reliable index system was defined by Lee *et al.*[289] based on the set of standards – naphthalene, phenanthrene, chrysene, and picene – and the retention indices of over 200 PAC were determined. The average 95% confidence limits for four measurements on each PAC were ±0.25 index unit.

The performance of a sample-introduction device is critical when mixtures of compounds differing widely in volatility, such as PAC, are chromatographed. A comparison of the various sample-introduction techniques with regard to discrimination and decomposition effects has been published.[290] In general, the splitless techniques are much more desirable than those involving splitting. The development of the on-column injector[291] has essentially eliminated discrimination caused by differences in volatility, polarity, or concentration. The sample must, however, be relatively free of non-volatile material to avoid reduction of column life if on-column injection is used.

The most widely used gas-chromatographic detector for PAC is the flame ionization detector (FID). This is a result of its universally accepted characteristics of excellent response linearity, sensitivity, and reliability. Lao *et al.*[47] have reported response factors for a large number of PAC using an FID. As expected, response increases with molecular weight and response factors are similar for most structural isomers. Since discrimination can occur when chromatographing a wide range of PAC as a result of injection technique, degree of column deactivation, and detector design, it is advisable to measure response factors for each chromatographic system if accurate quantitative results are desired.

As early as 1965, Cantuti *et al.*[37,274] showed that the response of the electron capture detector (ECD) for PAH was dependent on the structure of the compound, and that the detector could be selective for PAH in hydrocarbon mixtures. Bjørseth and Eklund[67] measured the ECD/FID response ratios for 29 PAH and found that many isomers could be differentiated by measurements of these ratios. In a recent study, Grimsrud *et al.*[292] found that adding oxygen to the

[288] H. Beernaert, *J. Chromatogr.*, 1979, **173**, 109.

[289] M. L. Lee, D. L. Vassilaros, C. M. White, and M. Novotny, *Anal. Chem.*, 1979, **51**, 768.

[290] G. Schomburg, H. Behlau, R. Dielmann, H. Husmann, and F. Weeke, *J. Chromatogr.*, 1977, **142**, 87.

[291] K. Grob and K. Grob, jun., *J. Chromatogr.*, 1978, **151**, 311.

[292] E. P. Grimsrud, D. A. Miller, R. G. Stebbins, and S. H. Kim, *J. Chromatogr.*, 1980, **197**, 51.

carrier gas greatly enhanced the signal obtained from a constant-current ECD for certain PAH. This response enhancement was found to be dependent on the structural detail of the PAH. It was suggested that this structure-dependent response enhancement could assist in the identification of resolved PAH isomers.

A nitrogen-selective thermionic detector has been used for the selective detection of nitrogen heterocycles in air particulate matter[49] and in lake sediments.[137] The selectivity factor for nitrogen over hydrocarbons has been shown to be $10^4$:1. The selectivity and sensitivity of this detector for various nitrogen compounds has been described.[49]

Recent improvements in the Hall electrolytic conductivity detector (HECD) have provided some potential for the use of this detector for PAC. The HECD can selectively detect both nitrogen- and sulphur-containing PAC. The selectivity factor for nitrogen over hydrocarbons is $10^6$:1, and for sulphur over hydro-carbons is $10^5$:1.[293]

In recent studies, a flame photometric detector (FPD) has been employed for the analysis of sulphur heterocycles in petroleum,[151] various coal-derived products,[27,152,294] and shale oils.[294] Care must be taken when using this detector because of its often non-linear response and observed response quenching due to other co-eluting compounds.[151] The selectivity factor of sulphur over hydrocarbons can be as large as $10^4$:1.

The photoionization detector (PID) can be used selectively for PAC. The use of u.v. lamps with different wavelengths allows some selectivity in detection because only radiation with energy greater than or equal to the ionization potential of the species will produce a signal. By using both PID (with 10.2 eV lamp) and FID, one can differentiate between aromatic and aliphatic hydrocarbons.[295] The relative molar response for the PID increases with unsaturation, and when the PID and FID responses are normalized to any alkane and the normalized PID/FID ratios calculated, those with a ratio of 5—10 are due to aromatics, 2—4 to alkenes, and $<2$ to alkanes. Although this detector has been optimized for use with capillary columns, a slight loss in resolution is observed owing to the volume of the detector.[296]

Resonance enhanced two-photon photoionization has recently been applied to the detection of PAH in gas-chromatographic effluents.[297] A small-volume proportional counter cell and a low-power laser were used. This method has several advantages with respect to the conventional one-photon photoionization detection previously discussed. One can expect increased spectral selectivity, improved ionization efficiency, and decreased detection volume in applications involving capillary columns. Detection limits of the order of 10 pg were obtained for a number of PAH using this detector.[297]

Gas-phase spectroscopic detectors for PAC include both u.v. and fluorescence.

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[293] V. F. Cox and R. J. Anderson, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Abstract No. 208, Atlantic City, N.J., March, 1980.

[294] C. Willey, M. Iwao, R. N. Castle, and M. L. Lee, *Anal. Chem.*, 1981, **53**, 400.

[295] J. N. Driscoll, J. Ford, L. F. Jaramillo, and E. T. Gruber, *J. Chromatogr.*, 1978, **158**, 171.

[296] L. F. Jaramillo and J. N. Driscoll, *HRC & CC*, 1979, **2**, 536.

[297] C. M. Klimcak and J. E. Wessel, *Anal. Chem.*, 1980, **52**, 1233.

While earlier studies[298,299] of u.v. detection were limited by rather poor sensitivities ($\mu$g levels), Novotny *et al.*[300] have successfully coupled glass-capillary columns to a variable-wavelength u.v. detector with a 50 $\mu$l cell volume. Detection limits similar to those obtained with an FID were observed.

Spectrofluorimetric detectors offer more promise than do u.v. detectors because of their inherent higher sensitivity and greater selectivity. Some studies involving the use of gas-phase fluorescence detection of gas-chromatographic effluents have been reported,[301–307] and many PAC have been detected in sub-nanogram amounts.[304,307]

The most powerful approach available today for the analysis of complex PAC mixtures is capillary column gas chromatography/mass spectrometry (GC–MS). The maximum resolution of mixture components before mass-spectral analysis is of the utmost importance in providing unambiguous identifications of individual compounds. This is especially true in the case of PAC because the conventional mass spectra of many isomers are identical (see below).

The gas-chromatographic peaks obtained from capillary columns are often extremely narrow, sometimes only a few seconds. This means that the scan times of the mass spectrometer must be short in order to obtain several spectra per peak and without having too much distortion of the mass spectra as a result of the changing concentrations along the peak elution profile. Modern GC–MS–computer systems have been built that easily handle four mass spectra per second.

With the short cycle times for obtaining the mass spectra, the number of spectra taken during the gas-chromatographic run can easily run into thousands. At four mass spectra per second, the number of mass spectra in 45 min is already more than $10^4$. These figures emphasize the need for computerized data acquisition and reduction. The power of the combined GC–MS system for the analysis of PAC is demonstrated by the numerous applications found in the literature. Most of the identifications of PAC in the applications listed in Section 1 were made using GC–MS techniques.

## 4 Mass Spectrometry

In the last decade, mass spectrometry (MS) has gained wide acceptance for the analysis of PAC. New rapid-scan techniques coupled with high-resolution chromatography as discussed in the previous section have greatly surpassed any

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[298] W. Kaye, *Anal. Chem.*, 1962, **34**, 287.

[299] J. Merritt, F. Comendant, S. T. Agrams, and V. N. Smith, *Anal. Chem.*, 1963, **35**, 1461.

[300] M. Novotny, F. J. Schwende, M. J. Hartigan, and J. E. Purcell, *Anal. Chem.*, 1980, **52**, 736.

[301] M. C. Bowman and M. Beroza, *Anal. Chem.*, 1968, **40**, 535.

[302] H. P. Burchfield, R. J. Wheeler, and J. B. Bernos, *Anal. Chem.*, 1971, **43**, 1976.

[303] H. P. Burchfield, E. E. Green, R. J. Wheeler, and S. M. Billedeau, *J. Chromatogr.*, 1974, **99**, 697.

[304] D. J. Freed and L. R. Faulkner, *Anal. Chem.*, 1972, **44**, 1194.

[305] J. W. Robinson and J. P. Goodbread, *Anal. Chim. Acta*, 1973, **66**, 239.

[306] R. P. Cooney, T. Vo-Dinh, and J. D. Winefordner, *Anal. Chim. Acta*, 1977, **89**, 9.

[307] R. P. Cooney and J. D. Winefordner, *Anal. Chem.*, 1977, **49**, 1057.

other method or combination of methods used for PAC analysis. Furthermore, new ionization methods that differentiate between isomeric PAC promise increased diagnostic power in the future.

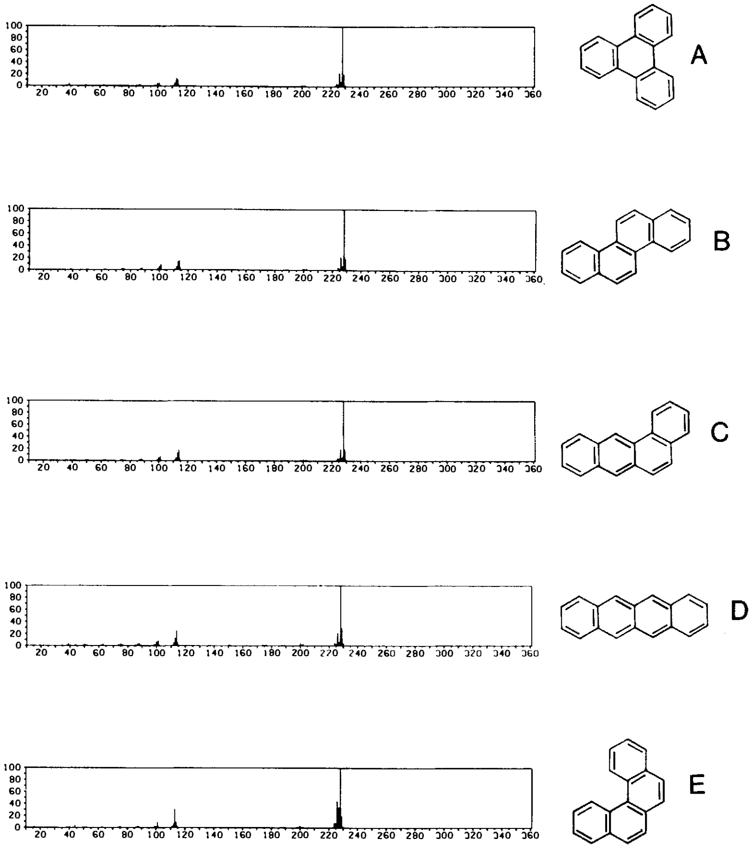
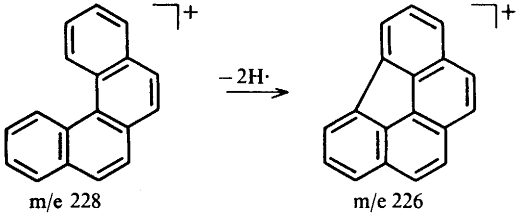


**Figure 8** *Electron-impact mass spectra of:* A, *triphenylene;* B, *chrysene;* C, *benz*[a]*anthracene;* D, *naphthacene;* E, *benzo*[c]*phenanthrene*



(1)

**A. Electron Impact.**—The electron-impact mass spectra of PAC are well characterized as being quite simple, mainly consisting of an intense molecular ion and lower intensity ions due to the loss of one to four hydrogen atoms. The $(M + 1)^+$ ion is always present and is due mainly to the $^{13}C$ isotope. Doubly charged molecular ions are quite common and are usually near 20% of the abundance of the molecular ion. Ions due to the expulsion of $C_2H_2$ are present, but at very low intensities. Alkylated PAH demonstrate the normal $(M - 15)^+$, $(M - 29)^+$, *etc.*, fragmentation pattern for alkyl chains even in the case of methyl-substituted compounds. The $(M - 15)^+$ ion is lower in abundance for methyl-substituted compounds than it is for PAH with longer alkyl side chains because of the favourable loss of a proton followed by ring expansion to form the tropylium ion.

In most cases, differentiation of PAH isomers by electron-impact mass spectra alone cannot be achieved. Even in the cases of isomers with very different structures, such as fluoranthene and pyrene, the mass spectra are most often indistinguishable. Figure 8 compares the mass spectra of the four-ring isomers, triphenylene, chrysene, benz[*a*]anthracene, naphthacene, and benzo[*c*]phenanthrene. All the mass spectra are essentially identical except for benzo[*c*]phenanthrene. In this case, steric interaction between the protons on the 1 and 12 carbons facilitates the loss of these two protons with the subsequent formation of the benzo[*ghi*]fluoranthene ion [equation (1)]. Similarly, steric interactions are probably responsible for the increased intensities of the $(M - 1)^+$, $(M - 2)^+$, and $(M - 3)^+$ ions for 4-methylphenanthrene, 1-methyltriphenylene, 12-methylbenz[*a*]anthracene, 4-methylchrysene, and 5-methylchrysene as compared with their respective isomers.

The mass spectra for hydro-aromatic compounds such as fluorene and acenaphthene show the ease of removal of protons from saturated carbons under electron impact to give abundant $(M - 1)^+$ ions for both compounds and an abundant $(M - 2)^+$ ion for acenaphthene. The substitution of a heteroatom in the ring makes little difference to the appearance of the mass spectra. The position of nitrogen substitution in the ring makes essentially no difference to the observed spectra. The same results are found in the mass spectra of sulphur-containing PAH except for the presence of the $^{34}S$ isotope peaks. In comparing the mass spectra for dinaphtho[2,1-*b*:1′,2′-*d*]thiophen and dinaphtho[1,2-*b*:1′,2′-*d*]thiophen (Figure 9) large abundances of the $(M - 1)^+$ and $(M - 2)^+$ ions are seen in the former. This is due probably to the formation of the perylo[1,12-*bcd*]thiophen ion by the same mechanism that was observed previously for benzo[*c*]phenanthrene [equation (2)].

A large number of electron-impact mass spectra for PAC have been compiled and can be found in several reference books.[308–311]

[308] S. Safe and O. Hutzinger, 'Mass Spectrometry of Pesticides and Pollutants', CRC Press, Cleveland, 1973, p. 77.

[309] E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, 'Registry of Mass Spectral Data', John Wiley and Sons, New York, 1974, Vol. 1—4.

[310] S. R. Heller and G. W. A. Milne, 'EPA/NIH Mass Spectral Data Base', U.S. Government Printing Office, Washington, D.C. 1978, Vol. 1—4.

[311] 'Eight Peak Index of Mass Spectra', Mass Spectrometry Data Centre, Aldermaston, Reading, United Kingdom, 1974, Vol. 1—4.

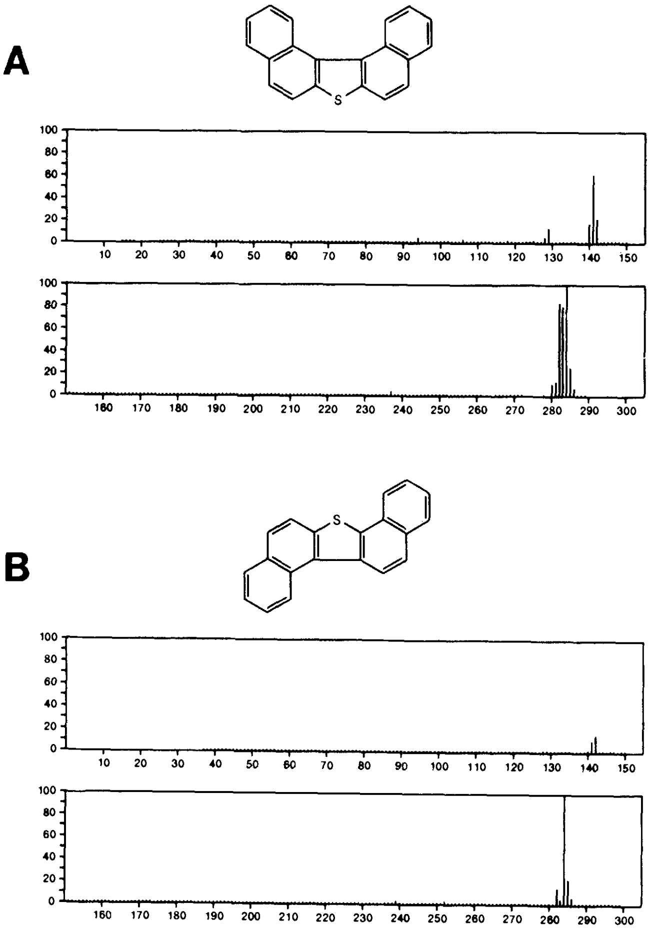
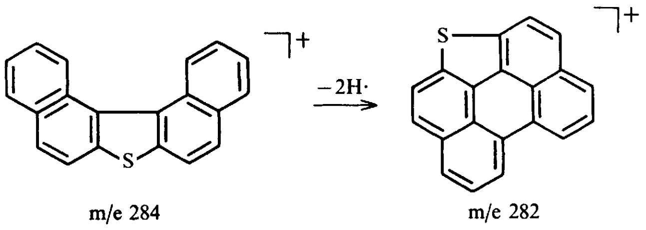


**Figure 9** *Electron-impact mass spectra of:* A, *dinaphtho*[2,1-b:1′,2′-d]*thiophen;* B, *dinaphtho*[1,2-b:1′,2′-d]*thiophen*



(2)

**B. Chemical Ionization.**—Conventional chemical ionization (CI) mass spectrometry, using methane as the reagent gas, produces mass spectra of PAC that also appear quite simple. The most abundant ion is the $(M + 1)^+$ or protonated molecular ion, and the second most abundant ion is the $(M + 29)^+$ ion. Because of the proton affinities of PAC, the major ionization process is protonation of the aromatic compound by the reagent gas, which produces the $(M + 1)^+$ ion. Of second importance is the addition of an ethyl group to the aromatic system to produce the $(M + 29)^+$ ion. Munson and Field[312] have discussed the CI of some alkylbenzenes and two alkylnaphthalenes, but little has been published on larger ring systems. Recent studies,[65,106,313] however, do indicate that the mass spectra of different isomers appear in most cases to be identical.

The use of a mixed charge exchange–chemical ionization reagent gas for MS of PAH that differentiates between isomers has recently been reported.[65,313,314] The theory behind the use of the mixed reagent gas was discussed by Arsenault[315] and later by Beggs.[316] The relative rates of the charge-exchange and proton-exchange reactions, and hence the ratio of the abundance of the $(M + 1)^+$ ion to the abundance of the $M^+$ ion will vary according to the proton affinity and/or ionization potential of each PAH. Since the ionization potentials of PAH isomers are dependent on the specific structure of the molecule, the argon–methane reagent can produce quite different spectra for different isomers. This is seen by comparison of the argon–methane CI spectra for anthracene and phenanthrene (Figure 10).

Hunt *et al.*[317–320] have recently described the use of oxygen as reagent in both positive and negative CI mass spectrometry of PAH. Electron bombardment of oxygen at 1 mm Hg pressure yields $O_2^+$ and $O^+$ in the positive ion mode, and $O_2^-$ and $O^-$ in the negative ion mode. The reaction of $O_2^+$ with aromatic systems

[312] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, 1967, **89**, 1047.

[313] M. L. Lee and R. A. Hites, *J. Am. Chem. Soc.*, 1977, **99**, 2008.

[314] R. A. Hites and G. R. Dubay, in ref. 63, p. 85.

[315] G. P. Arsenault, *J. Am. Chem. Soc.*, 1972, **94**, 8241.

[316] D. P. Beggs, Hewlett-Packard Applications Note No. 176-19.

[317] D. F. Hunt, C. N. McEwen, and T. M. Harvey, *Anal. Chem.*, 1975, **47**, 1730.

[318] D. F. Hunt, G. C. Stafford, jun., F. W. Crow, and J. W. Russell, *Anal. Chem.*, 1976, **48**, 2098.

[319] D. F. Hunt and S. K. Sethi, in 'High Performance Mass Spectrometry: Chemical Applications', ed. M. L. Gross, *Am. Chem. Soc. Symp. Ser.*, **70**, American Chemical Society, Washington, D.C., 1978, p. 150.

[320] D. F. Hunt, P. J. Gale, and S. K. Sethi, 26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Missouri, May, 1978.

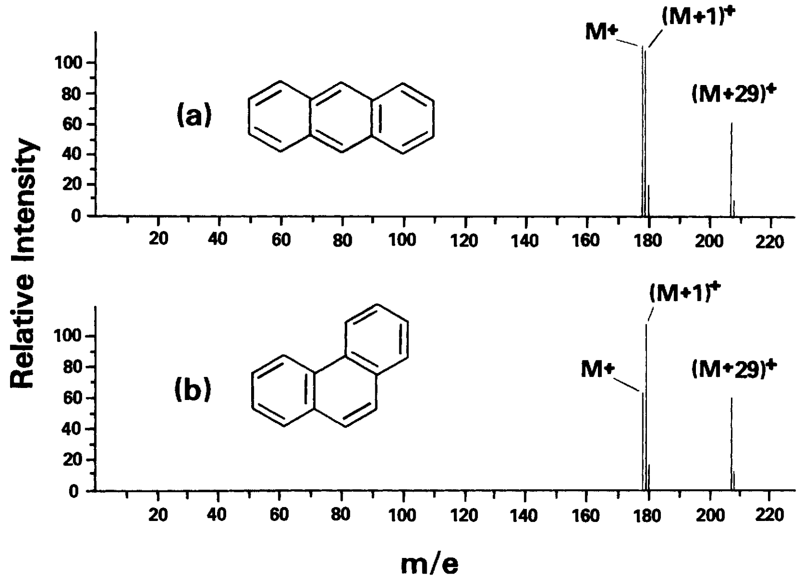


**Figure 10** *Argon–methane chemical ionization mass spectra of:* A, *anthracene;* B, *phenanthrene*

such as pyrene yields spectra containing a single ion, $M^+$. In the negative ion mode, CI ($O_2/H_2$) spectra show an abundant $(M + 15)^-$ ion formed by either capture of a thermal electron followed by reaction with neutral oxygen, or by direct reaction with $O_2^-$.

Simultaneous recording of positive and negative ion CI mass spectra can be accomplished by pulsing the polarity of the ion source potential and the focusing lens potential.[318] An example of the differentiation between isomeric PAH using pulsed positive ion negative ion CI can be seen by comparing the spectra obtained for benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene[319] (Figure 11). Both isomers exhibit a single ion corresponding to $M^+$ in the positive ion mode, but in the negative mode, benzo[*ghi*]perylene shows ions corresponding to $M^-$ and $(M + 15)^-$ in a 1/1 ratio while indeno[1,2,3-*cd*]pyrene has a much more abundant $M^-$ ion. The presence of the five-membered ring in the indenopyrene facilitates formation of the stable negative ion.

Hunt *et al.*[320] have also shown that careful selection of reagent gases based on proton affinities can provide a means for differentiating PAH isomers. For example, the use of $C_2H_5OD$ as a reagent gas can produce different spectra for phenanthrene and anthracene.

**C. Other Ionization Techniques.**—Field-ionization (FI) and field-desorption (FD) mass spectrometry produce virtually fragment-ion-free mass spectra and should be ideally suited to the group-type quantitative analysis of PAH mixtures.

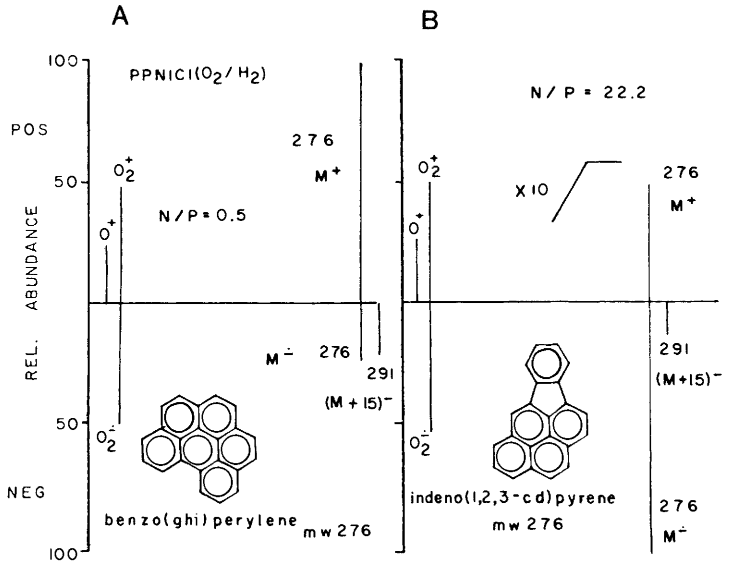


**Figure 11** *Pulsed positive ion/negative ion chemical ionization* ($O_2/H_2$) *mass spectra of:* A, *benzo*[ghi]*perylene;* B, *indeno*[1,2,3-cd]*pyrene. The intensities of reagent ions are* 50—100 *times greater than as shown*

[Reproduced by permission from *High Performance Mass Spectrometry: Chemical Applications*, ed. M. L. Gross, *Am. Chem. Soc. Symp. Ser.*, No. 70, 1978, p. 150 (ref. 319)]

Both techniques provide virtually single molecular-ion spectra for compounds like PAH, which makes them attractive techniques for the determination of molecular-weight distributions in mixtures. Although these techniques have not enjoyed very widespread use, the recent determination of FI relative sensitivities for a number of PAH[321] and improvements in quantitative aspects of FD[322,323] have helped. The applications of FI and FD mass spectrometry in the analysis of the aromatic fractions of fossil fuels have been described in several recent studies.[321–327]

Photoionization (PI) techniques yield pure molecular-ion spectra for aromatics, but the low-voltage FI technique is preferable because of the experimental difficulties of PI. A description of the method for analysis of mixtures including the analysis of aromatic hydrocarbons is given by Severin.[328]

[321] S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, *Anal. Chem.*, 1976, **48**, 2105.

[322] D. F. Barofsky, E. Barofsky, and R. Held-Aigner, *Adv. Mass Spectrom.*, 1978, **7**, 109.

[323] S. Pfeifer, H. D. Beckey, and H.-R. Schulten, *Fresenius' Z. Anal. Chem.*, 1977, **284**, 193.

[324] A. M. Hogg and J. D. Payzant, *Int. J. Mass Spectrom. Ion Phys.*, 1978, **27**, 291.

[325] S. E. Scheppele, G. J. Greenwood, P. L. Grizzle, T. D. Marriott, C. S. Hsu, N. B. Perreira, P. A. Benzon, K. N. Detwiler, and G. M. Stewart, *Prepr. Div. Pet. Chem., Am. Chem. Soc.*, 1977, **22**, 665.

[326] M. Anbar and G. A. St. John, *Fuel*, 1978, **57**, 105.

[327] G. A. St. John, S. E. Buttrill, and M. Anbar, *Am. Chem. Soc. Symp. Ser.*, **71**, 1978, p. 223.

[328] D. Severin, *Compend. - Dtsch. Ges. Mineraloelwiss. Kohlechem.*, 1976, **76—77**, 949.

**D. Group-type Analysis.**—In as early as 1951, Brown[329] showed that compound types could be reliably determined in complex mixtures by selecting the appropriate masses that are characteristic of the compound type, calculating response factors, and formulating a series of linear simultaneous equations for taking into consideration the contributions of different components in the mixture to the analytical mass-spectral peaks.

Although the early group type analyses were made using conventional 70 eV electron-impact mass spectrometry, the use of low-ionizing-voltage mass spectrometry has become widespread for the analysis of complex samples. The original description of the method and many of its advantages and difficulties was given by Field and Hastings[330] and later by Lumpkin.[331]

Although group-type mass-spectral analysis has been used most extensively in the analysis of petroleum,[124,128,329–345] the techniques have recently been extended to the study of coal and coal-derived products[346–352] and the analysis of environmental pollutants.[1,2,60,83–85,132,353–359] The typical analytical approach is to introduce a portion of the PAC sample into the mass spectrometer through the direct introduction probe system and to vaporize the sample slowly with

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[329] R. A. Brown, *Anal. Chem.*, 1951, **23**, 430.

[330] F. H. Field and S. H. Hastings, *Anal. Chem.*, 1956, **28**, 1248.

[331] H. E. Lumpkin, *Anal. Chem.*, 1958, **30**, 321.

[332] H. E. Lumpkin and B. H. Johnson, *Anal. Chem.*, 1954, **26**, 1719.

[333] S. H. Hastings, B. H. Johnson, and H. E. Lumpkin, *Anal. Chem.*, 1956, **28**, 1243.

[334] K. S. Quisenberry, T. T. Scolman, and A. O. Nier, *Phys. Rev.*, 1956, **102**, 1071.

[335] H. E. Lumpkin and T. Aczel, *Anal. Chem.*, 1964, **36**, 181.

[336] H. E. Lumpkin, *Anal. Chem.*, 1964, **36**, 2399.

[337] E. J. Gallegos, J. W. Green, L. P. Lindeman, R. L. LeTourneau, and R. M. Teeter, *Anal. Chem.*, 1967, **39**, 1833.

[338] B. H. Johnson and T. Aczel, *Anal. Chem.*, 1967, **39**, 682.

[339] L. R. Snyder, B. E. Buell, and H. E. Howard, *Anal. Chem.*, 1968, **40**, 1303.

[340] L. R. Snyder, *Anal. Chem.*, 1969, **41**, 1084.

[341] C. J. Robinson and G. L. Cook, *Anal. Chem.*, 1969, **41**, 1548.

[342] T. Aczel, D. E. Allan, J. H. Harding, and E. A. Knipp, *Anal. Chem.*, 1970, **42**, 341.

[343] C. J. Robinson, *Anal. Chem.*, 1971, **43**, 1425.

[344] J. L. Schultz, A. G. Sharkey, jun., and R. A. Brown, *Anal. Chem.*, 1972, **44**, 1486.

[345] J. E. Schiller, *Anal. Chem.*, 1977, **49**, 1260.

[346] H. W. Holden and J. C. Robb, *Fuel*, 1960, **39**, 39.

[347] A. G. Sharkey, jun., J. L. Shultz, and R. A. Friedel, *Fuel*, 1962, **41**, 359.

[348] J. L. Shultz, R. A. Friedel, and A. G. Sharkey, jun., 'Mass Spectrometric Analyses of Coal-Tar Distillates and Residues', Washington, U.S. Dept. of the Interior, Bureau of Mines, 1967.

[349] T. Kessler, R. Raymond, and A G Sharkey, jun., *Fuel*, 1969, **48**, 179.

[350] J. T. Swansiger, F. E. Dickson, and H. T. Best, *Anal. Chem.*, 1974, **46**, 730.

[351] A. G. Sharkey, jun., in ref. 112, p. 341.

[352] H. E. Lumpkin and T. Aczel, in ref. 319, p. 261.

[353] A. G. Sharkey, jun., J. L. Shultz, T. Kessler, and R. A. Friedel, *Res. Dev.*, 1969, **20**, 30.

[354] A. G. Sharkey, jun., J. L. Shultz, T. Kessler, and R. A. Friedel, in 'Proceedings of the Second International Clean Air Congress', ed. H. M. England and W. T. Berry, Academic Press, New York, 1971, p. 539.

[355] D. Schuetzle, A. L. Crittenden, and R. J. Charlson, *J. Air Pollut. Control Assoc.*, 1973, **23**, 704.

[356] J. L. Shultz, A. G. Sharkey, jun., and R. A. Friedel, *Biomed. Mass Spectrom.*, 1974, **1**, 137.

[357] D. Schuetzle, *Biomed. Mass Spectrom.*, 1975, **2**, 288.

[358] A. Hase and R. A. Hites, *Geochim. Cosmochim. Acta*, 1976, **40**, 1141.

[359] J. L. Stauffer, P. L. Levins, and J. E. Oberholtzer, in ref. 63, p. 89.

increasing temperature while mass-spectral data are being collected. Plots can then be constructed that display the relative abundance of each parent compound and its alkyl-derivatives as a function of carbon number. These are referred to as 'alkyl homologue' plots.

**E. Metastable Ions and Collision Spectroscopy.**—A relatively new technique that is growing rapidly and is related to the processes involved in the formation of metastable ions is collision spectroscopy.[360] By introducing a collision gas in the field-free region, intermolecular processes such as charge-exchange and collision-induced fragmentations can be studied.

One reported study of the fragmentation processes of aromatic hydrocarbons in the first field-free region employed a mass spectrometer with fields arranged in the order accelerating voltage (V)/electric sector voltage (E)/and magnetic field (B), and used a detector located behind the energy-resolving slit located between the sectors.[361] Scanning of the electric sector voltage gave a fingerprint of all fragmentations without prior mass separation. This is called an ion-kinetic-energy (IKE) scan because the ions are separated on the basis of their kinetic energies. Subsequent mass analysis of selected peaks in the IKE spectrum can be made. Both the IKE spectra and mass spectra can be used to give detailed fingerprints of organic compounds. PAH that have been studied using this technique include naphthalene, 2-methylnaphthalene, biphenyl, anthracene, dimethylnaphthalene, benzo[*a*]pyrene, and benzo[*k*]fluoranthene isomers.[362,363]

Shushan *et al.*[364] recently described a method in which both B and E are scanned so that (B/E) is held at the constant value required to transmit stable parent ions of pre-selected (m/e) ratio; in this way fragment ions formed in the first field-free region, from the pre-selected parent ions, are successively transmitted. The daughter-ion spectra of the four isomers, chrysene, triphenylene, benz[*a*]anthracene, and naphthacene, showed considerable differences in the relative abundances of the $M^+$, $(M - H)^+$, and $(M - 2H)^+$ ions, the latter two being the products of fragmentation of $M^+$ ions in the first field-free region. Plots of the $(M/M - H)$ and $(M - H/M - 2H)$ intensity ratios against the number of benzo interactions per molecule facilitated the structural assignments of these isomers.

Another widely used configuration is that in which the second stage of the instrument is an energy rather than a mass analyser. With the arrangement of fields V/B/E, fragmentations between the sectors can be observed. The initial magnetic field is set to select the $m_1^+$ ions, and the fragmentation products of these ions can then be plotted in a single spectrum by varying the electric sector voltage. This is called a MIKE scan for 'mass-analysed ion kinetic energy'. An example of the use of MIKE for the analysis of coal liquids was reported by

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[360] 'Collision Spectroscopy', ed. R. G. Cooks, Plenum Press, New York, 1978.
[361] J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, 1970, **3**, 455.
[362] T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, 1972, **6**, 749.
[363] R. C. Lao, R. S. Thomas, and J. L. Monkman, *Adv. Mass Spectrom.*, 1974, **6**, 129.
[364] B. Shushan, S. H. Safe, and R. K. Boyd, *Anal. Chem.*, 1979, **51**, 156.

Zakett *et al.*[365] Identifications of specific nitrogen heterocycles were made without prior treatment or fractionation of the sample.

The mass spectroscopic method chosen for the analysis of PAH is dependent on the type of results desired. For group-type analysis, low- and high-voltage electron impact, field ionization, field desorption, photoionization and sometimes chemical ionization may be used. By far the most universal approach is low-voltage electron impact. The availability of instrumentation, sensitivity data, and reproducibility are the main reasons for this. On the other hand, if structural identification of individual components of mixtures is desired, GC–MS is the method of choice as discussed earlier. The relatively new techniques of chemical ionization, metastable ion, and collision-induced mass spectrometry have the potential of being able to solve many of these problems without prior sample fractionation.

## 5 Spectroscopic Methods

**A. Luminescence.**—The limitations of relatively low sensitivity and the poor specificity of spectra containing broad lines (although derivative spectroscopy and computer resolution can increase the information available)[366] now severely restrict the applications of u.v. absorption spectroscopy in the analysis of PAC. Luminescence methods frequently afford 10—$10^3$ times the sensitivity of absorption methods and are much more specific. Thus, while benzo[*a*]pyrene and benzo[*ghi*]perylene have similar u.v. absorption spectra, and therefore similar fluorescence excitation spectra, they are readily distinguished by their fluorescence emission spectra.[367]

Many methods for the determination by fluorescence techniques of single compounds in mixtures containing interfering components are available,[368] and many of these refer to benzo[*a*]pyrene.[369] Commonly used analytical procedures for 'marker' PAH, such as those specified for drinking water by the WHO,[370] employ fluorimetry preceded either by column chromatography on alumina or by two-dimensional TLC. In the latter method, each PAC is identified on the plate from its position and fluorescence colour under u.v. light. Quantitation is then by densitometry, with either visual comparison with reference plates, or by use of a chromatogram scanner.[371] Alternatively, the spots may be microsublimed from the plate, or more usually scraped off and extracted,[51] before recording of the fluorescence excitation and emission spectra. Care may be necessary in interpreting the results of combined TLC/fluorimetric procedures, since tests with

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[365] D. Zakett, V. M. Shaddok, and R. G. Cooks, *Anal. Chem.*, 1979, **51**, 1849.

[366] G. E. Barker and M. F. Fox, *Chem. Soc. Rev.*, 1980, **9**, 143.

[367] T. J. Porro, *J. Assoc. Off. Anal. Chem.*, 1973, **56**, 607.

[368] O. Hutzinger, S. Safe, and M. Zander, *Analabs Res. Notes*, 1973, **13**(3), 13.

[369] L. Dubois, A. Zdrojewski, and J. L. Monkman, *Mikrochim. Acta*, 1967, 903.

[370] J. Borneff, 'Fate of Pollutants in the Air and Water Environment', ed. I. H. Suffet, Wiley, New York, 1977, Part 2, p. 393.

[371] R. Tomingas, G. Voltmer, and R. Bednarik, *Sci. Total Environ.*, 1977, **7**, 267.

$^{14}C$-labelled compounds have shown poor reproducibility for quantities below 1 $\mu g$.[372]

The selectivity of phosphorimetry is greater than that of fluorimetry, although its range of application is not as great; fewer compounds have measurable phosphorescence than fluorescence, but the spectra, especially of PAC, may be more characteristic.[373] The limits of detection of PAC in phosphorimetry and fluorimetry are of the same order of magnitude. Because of non-radiative interactions in solution, phosphorescence was, up until recently, generally observed at low temperature in frozen-solution glasses; the technique is usually less sensitive than is fluorimetry. However, if concentrations are available at which both techniques give analytically useful signals, it is convenient to measure both fluorescence and phosphorescence: by combining the two techniques, an analytical range over four decades results.[374]

Phosphorimetry is most applicable where the mixture contains strongly fluorescent but weakly phosphorescent interfering species. For example, perylene interferes with the determination of benzo[*rst*]pentaphene by fluorimetry but gives negligible interference in phosphorimetry.[374] Applications of phosphorimetry in air pollution studies were pioneered by Sawicki,[375] who detected PAH on thin-layer chromatograms by their phosphorescence in liquid nitrogen. Phosphorescence emission may also be observed at room temperature from salts of ionic compounds adsorbed on silica gel, alumina, and even filter paper.[376] The effect, ascribed to increased molecular rigidity through adsorption, which is presumed to reduce collisional deactivation, has been developed as a sensitive spectroscopic method of analysis.[377–379] Winefordner[378] showed that sodium iodide and silver nitrate induce room-temperature phosphorescence (RTP) from a number of PAH and allow detection at the ng level for phenanthrene and pyrene. Strong RTP emission can be induced from nitrogen heterocycles adsorbed on silica gel chromatoplates containing a polymeric binder.[379] These approaches may increase the application of phosphorescence in the analysis of PAC.

The luminescence characteristics of PAC are markedly dependent on the environment. Thus, reduction of luminescence intensity, or quenching, occurs if an electronically excited molecule gives up its energy to a solvent or other molecule. This property may be used to increase the selectivity of luminescence in various ways, collectively known as 'quenchofluorimetry'.

A commonly applied approach uses the property of a substituted atom or group such as chlorine, bromine, or nitro in the solvent to enhance phosphor-

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[372] F. deWiest, D. Rondia, and H. Della Fiorentina, *J. Chromatogr.*, 1975, **104**, 399.

[373] M. Zander, 'Phosphorimetry', Academic Press, New York, 1968.

[374] L. V. S. Hood and J. D. Winefordner, *Anal. Chim. Acta*, 1968, **42**, 199.

[375] E. Sawicki and J. D. Pfaff, *Anal. Chim. Acta*, 1964, **32**, 521.

[376] E. M. Schulman and C. Walling, *Science*, 1972, **178**, 53.

[377] S. L. Wellons, R. A. Paynter, and J. D. Winefordner, *Spectrochim. Acta, Part A*, 1974, **30**, 2133; *Anal. Chem.*, 1974, **46**, 736.

[378] T. Vo-Dinh, F. Lue Yen, and J. D. Winefordner, *Anal. Chem.*, 1976, **48**, 1186; *Talanta*, 1977, **24**, 146.

[379] O. D. Ford and R. J. Hurtubise, *Anal. Chem.*, 1980, **52**, 656.

escence at the expense of fluorescence; intersystem crossing from excited-singlet to phosphorescent-triplet states is made easier through an increase in spin-orbit coupling (the 'heavy-atom' effect).[380] Zander [381] found that the addition of 10% by volume of iodomethane to a standard solvent system of diethyl ether, isopentane, and ethanol (5:5:2 by volume) gave significantly improved detection limits, *e.g.*, from $2 \times 10^{-6}$ to $5 \times 10^{-7}$ g cm$^{-3}$ for the determination of fluoranthene by phosphorescence. The fluorescence of this compound is correspondingly quenched, as is that of numerous other PAH, *e.g.*, anthracene, chrysene, naphthacene, and benzo[*a*]pyrene.[381]

However, certain PAH are exceptions; dibenzo[*b,def*]chrysene shows only slight quenching in the presence of iodomethane,[381] and perylene, 2-methylperylene, and dibenzo[*a,f*]perylene are not quenched.[382] It is thus possible to determine small concentrations (0.1—2%) of perylene in the presence of large excesses of benzo[*e*]pyrene and naphthacene by fluorimetry. This application may be important in view of the suggested use of perylene as a geochemical marker.[1,9]

Other heavy-atom perturbers of fluorescence that have been investigated include iodoethane in ethanol solutions of PAH, for which two kinds of behaviour are observed:[383,384] (*a*) fluorescence is quenched and phosphorescence enhanced relative to ethanol alone; (*b*) fluorescence is enhanced and phosphorescence quenched according to perturber concentration. The first effect is typical of benzo[*a*]- and benzo[*b*]fluorene, benz[*a*]anthracene, benzo[*a*]pyrene, and dibenz[*a,c*]anthracene, and increases with increasing iodoethane concentration. However, the limits of detection of these compounds decrease accordingly. Naphthalene, anthracene, phenanthrene, and triphenylene exhibit the second effect.

Zander has shown how silver nitrate selectively enhances the phosphorescence of aza-aromatics relative to that of PAH because of the strong electron-donor properties of the former compounds.[385] Another useful application of the heavy-atom effect in the observation of RTP of PAC in presence of silver and sodium nitrates has already been noted.

Selective quenching of the fluorescence of PAH containing only six-membered rings by electron acceptors such as nitromethane was noted by Sawicki;[244] the fluorescence of PAH containing the fluoranthene skeleton was found not to be quenched. Dreeskamp *et al.*[245] have shown a few exceptions to this 'rule'; benzo[*b*]- and benzo[*k*]fluoranthene showed significant quenching. However, this phenomenon is still general enough[386] to allow the identification of *non-*

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[380] W. J. McCarthy, in 'Spectrochemical Methods of Analysis', ed. J. D. Winefordner, Wiley-Interscience, New York, 1971, Chapter 8.

[381] M. Zander, *Fresenius' Z. Anal. Chem.*, 1967, **226**, 251; 1973, **263**, 19; *Erdoel. Kohle*, 1969, **22**, 81.

[382] M. Zander, *Fresenius' Z. Anal. Chem.*, 1967, **229**, 352.

[383] L. V. S. Hood and J. D. Winefordner, *Anal. Chem.*, 1968, **38**, 1922.

[384] M. Zander, *Int. J. Environ. Anal. Chem.*, 1973, **3**, 29.

[385] M. Zander, *Z. Naturforsch., Teil A*, 1978, **33**, 998.

[386] M. Zander, U. Breymann, H. Dreeskamp, and E. Koch, *Z. Naturforsch., Teil A*, 1977, **32**, 1561.

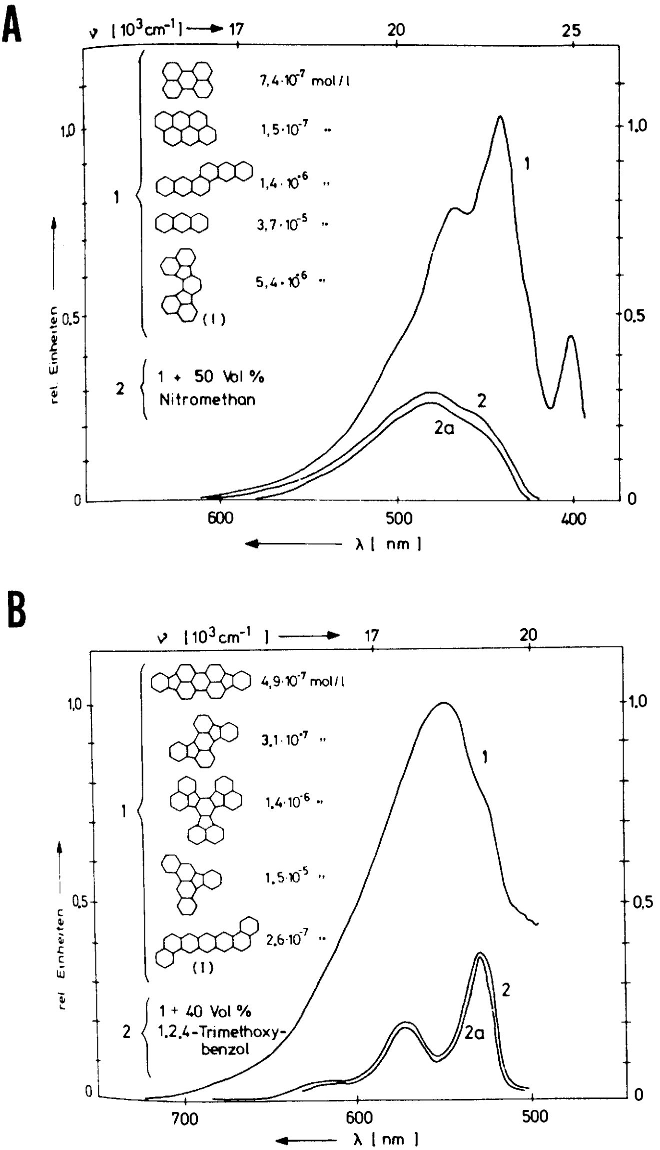

**Figure 12** A, *Fluorescence spectra in acetonitrile with excitation at* 383 nm *of:* (1) *a mixture of mainly alternant PAH;* (2) *same mixture in acetonitrile containing* 50% v/v *nitromethane;* (2a) *pure acenaphtho*[1,2-j]*fluoranthene.* B, *Fluoresence spectra in acetonitrile with excitation at* 430 nm *of:* (1) *a mixture of mainly non-alternant PAH;* (2) *same mixture in acetonitrile containing* 40% v/v 1,2,4-*trimethoxybenzene;* (2a) *pure dibenzo*[a, l]*pentacene*

(Reproduced by permission from *Fresenius' Z. Anal. Chem.*, 1978, **293,** 208) alternant PAH after separation, *e.g.*, on thin-layer plates, in HPLC elutes (as reported above), and in mixtures with alternant PAH [Figure 12(A)]. Complementary quenchofluorimetry with electron donors such as 1,2,4-trimethoxybenzene, moreoever, suppresses the fluorescence of non-alternants and allows recognition of alternants in mixtures[387] [Figure 12(B)].

The broadened peaks of the fluorescence spectra of PAC recorded in liquid solution may inhibit analysis, and the usefulness of low-temperature luminescence is well known, particularly in the enhancement of sensitivity that results from the increase in fluorescent intensity and the narrowing of lines from PAH in frozen-solution glasses.[374,388] For example, laser excitation of PAH in glycerol/water glasses at 4 K yields sharp-line spectra, and the problems of solubility, concentration gradients, and light scattering are minimized.[389,390] Sub part-per-trillion ($1 \times 10^{-12}$ g $cm^{-3}$) detection of contaminant PAC in water is then possible with a tunable dye-laser source.[390]

However, exceedingly line-rich Shpol'skii spectra are produced if PAC molecules are separated by large distances and embedded in a crystalline solvent lattice like an oriented gas molecule.[391] Vibrational and rotational energy are reduced, interaction between the solute molecules is prevented, and compounds having liquid-solution spectra with half-bandwidths of several nm have frozen-solution half-bandwidths of one or two nm, further split by the Shpol'skii effect to extremely sharp lines with half-bandwidths of the order of a few hundredths of a nm. Further sharpening of lines is then possible with laser excitation.

For Shpol'skii luminescence to be observed, the dimensions of the solute molecules must be approximately equal to those of the solvent; n-alkanes of suitable molecular dimensions are the most commonly used solvents, although spectra are also observed in tetrahydrofuran.[392–394] The sharpness of the Shpol'skii spectra also depends on the temperature; at 77 K, the spectrum of pyrene in n-hexane contains about 60 lines, whereas at 4 K the same solution shows approximately 220 lines.[395] Although the majority of the many quasilinear luminescence emission spectra of PAH so far reported have been obtained near 77 K, even a temperature reduction to 63 K with a cell cooled by nitrogen at its freezing temperature allows a marked improvement in resolution[396] (Figure 13).

Causey *et al.*[397] have compared some excitation sources (including a helium–cadmium laser), sample cells, and various detection systems and concluded that a

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[387] U. Breymann, H. Dreeskamp, E. Koch, and M. Zander, *Fresenius' Z. Anal. Chem.*, 1978, **293**, 208.

[388] S. P. McGlyn, B. T. Neely, and C. Neely, *Anal. Chim. Acta*, 1963, **28**, 472.

[389] J. C. Brown, M. Edelson, and G. J. Small, *Anal. Chem.*, 1978, **50**, 1394.

[390] J. C. Brown, J. A. Duncanson, jun., and G. J. Small, *Anal. Chem.*, 1980, **52**, 1711.

[391] E. V. Shpol'skii, *Soviet Phys. Usp.*, 1959, **2**, 378; 1960, **3**, 372; 1962, **5**, 522; 1963, **6**, 252, 411.

[392] G. F. Kirkbright and C. G. deLima, *Analyst* (*London*), 1974, **99**, 338.

[393] G. F. Kirkbright and C. G. deLima, *Chem. Phys. Lett.*, 1976, **37**, 165.

[394] E. V. Shpol'skii and T. N. Bolotnikova, *Pure Appl. Chem.*, 1974, **37**, 183.

[395] L. A. Klimova, *Opt. Spectrosc.*, 1963, **15**, 185.

[396] A. Colmsjö and U. Stenberg, *Chem. Scr.*, 1977, **11**, 220.

[397] B. S. Causey, G. F. Kirkbright, and C. G. deLima, *Analyst* (*London*), 1976, **101**, 367.

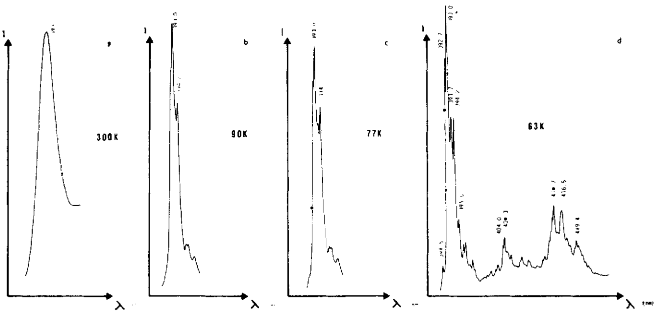

**Figure 13** *Fluorescence spectra of dibenz*[a,h]*anthracene in n-heptane at different temperatures*
(Reproduced by permission from *Chem. Scr.*, 1977, **11**, 220)

xenon arc or mercury lamp with a specially designed copper cryostat containing a Dewar tube as cell and d.c. integration of the luminescence signals constitute a simple and reliable system. Detection limits between 0.1 ng $cm^{-3}$ (benzo[*a*]pyrene) and 300 ng $cm^{-3}$ (indeno[1,2,3-*cd*]pyrene) have been quoted.[392]

Shpol'skii spectra can provide very useful fingerprints of individual compounds, and a variety of qualitative analyses have been reported. Thus, line-rich spectra were obtained by Colmsjö and Stenberg[398] for PAH from a number of environmental sources such as automobile-exhaust gas. Drake *et al.*[399] showed how such spectra allowed twelve PAC containing between three and ten rings to be identified in extracts of coal and coal-tar pitch, including ovalene, previously only postulated as a constituent of coal. In these mixtures only species resistant to deactivation and quenching are detected because of the formation of inhomogeneous micellar aggregates. This effect favours the detection of benzo[*a*]pyrene at levels down to 0.1 p.p.m., and many applications of the quasi-linear luminescence method have been reported for this compound. However, benzo[*a*]pyrene quenches the spectrum of benzo[*e*]pyrene,[398] so they must be separated before Shpol'skii analysis.

Thus, benzo[*a*]pyrene has been determined in atmospheric particulates by direct measurement of the intensity of the emission at 79 K.[400] Dikun[401] used luminescence to determine benzo[*a*]pyrene *via* the Shpol'skii effect using benzo[*ghi*]perylene as internal standard, and a similar method was reported by Personov,[402] using coronene for the same purpose. The standard addition procedure to minimize the effect of quenching was preferred by Muel and

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[398] A. Colmsjö and U. Stenberg, *Anal. Chem.* 1979, **51**, 145 and in 'Polynuclear Aromatic Hydrocarbons', ed. P. W. Jones and P. Leber, Ann Arbor Science, Ann Arbor, 1979, p. 121.

[399] J. A. G. Drake, D. W. Jones, B. S. Causey, and G. F. Kirkbright, *Fuel*, 1978, **57**, 663.

[400] M. J. Eichhoff and N. Köhler, *Fresenius' Z. Anal. Chem.*, 1963, **197**, 272.

[401] P. O. Dikun, *Vop. Onkol.*, 1961, 7, 42 (*Chem. Abstr.*, 1961, **57**, 658).

[402] R. I. Personov, *Zh. Anal. Khim.*, 1962, **17**, 506.

Lacroix[403] for the determination of benzo[*a*]pyrene in cigarette smoke, water, and various alcoholic drinks from the 403.0 nm emission line in n-octane at 83 K; a relative precision of 10% was claimed.

In spite of numerous applications of the Shpol'skii effect to the analysis of PAC in a variety of mixtures, the practical utility of the method may be limited and few examples have quoted reproducibility, accuracy, or precision. For these reasons, two detailed studies have been made of the applicability of Shpol'skii luminescence in the analysis of PAH. Gaevaya and Khesina[404] investigated the conditions necessary for the determination of fifteen PAH in multi-component solutions by using the effect. A combination of addition and internal-standard methods was necessary, and standard deviations of 2—10% were found for sensitivities of $10^{-8}$—$10^{-10}$ g cm$^{-3}$. Kirkbright and deLima[392] first demonstrated that unambiguous qualitative identification of PAH at very low concentration is possible. A careful investigation of the conditions necessary for the quantitative analysis of a mixture of dibenzopyrenes also showed that a combined standard addition plus internal-standard calibration procedure was necessary. Although internal standardization improves precision by decreasing random errors, an 'inner filter' effect may occur because of overlap of the excitation spectrum with that of the analyte so that there is a reduction in emission intensity and increase in detection limit.[392]

The limitations of Shpol'skii luminescence led Wehry *et al.*[405] to investigate matrix-isolation (MI) fluorescence for the analysis of PAH. Hydrocarbon vapours from a Knudsen cell are mixed in an evacuable cryostat head with a large excess of nitrogen and condensed on a cold (11—15 K) sapphire surface. Detection limits of the order of $10^{-11}$ g and linear quantitative working curves over five decades were observed for the resulting matrices. MI fluorimetry is substantially free from interference by intramolecular energy transfer or inner-filter effects even for samples containing high (*i.e.* $\mu$g) concentrations of several closely related PAH.[405] Thus, the working curve for chrysene in a four-component mixture is virtually the same as that of pure chrysene, while linear calibration curves were also obtained for 4-methylchrysene in the presence of a fifty-fold excess of three of its isomers.[406] Band-widths in nitrogen and argon matrices were generally greater than in Shpol'skii matrices, although MI experiments with n-alkanes as the matrix gave quasilinear spectra similar to those in conventional Shpol'skii fluorescence.[407] Selective dye-laser excitation of individual compounds in complex mixtures is then possible both for vapour-deposited[408] and conventional[409] Shpol'skii n-alkane matrices.

*X*-Ray excited optical luminescence of PAC in frozen solutions may result in

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[403] B. Muel and G. Lacroix, *Bull. Soc. Chim. Fr.*, 1960, 2139.

[404] T. Ya. Gaevaya and A. Ya. Khesina, *Zh. Anal. Khim.*, 1974, **29**, 2225.

[405] E. L. Wehry and G. Mamantov, *Anal. Chem.*, 1979, **51**, 643A.

[406] P. Tokousbalides, E. R. Hinton, R. B. Dickinson, jun., P. V. Bilotta, E. R. Wehry, and G. Mamantov, *Anal. Chem.*, 1978, **50**, 1189.

[407] P. Tokousbalides, E. L. Wehry, and G. Mamantov, *J. Phys. Chem.*, 1977, **81**, 1769.

[408] J. R. Maple, E. L. Wehry, and G. Mamantov, *Anal. Chem.*, 1980, **52**, 920.

[409] Y. Yang, A. P. D'Silva, V. A. Fassel, and M. Iles, *Anal. Chem.*, 1980, **52**, 1350.

the population of electronic levels not accessible to u.v. excitation and thus eliminate optical interaction between exciting and emitted radiation.[410–412] This method also results in the observation of substantial phosphorescence,[410] and may augment analyses for PAC already made by Shpol'skii phosphorimetry.[404,413]

Recent approaches to the luminescence analysis of PAC have been aimed at increasing the sensitivity and selectivity of the methods through the use of new excitation sources and dispersive systems, more sophisticated detectors, and data-handling systems based on computer methods.[414–416] Laser light sources allow selective and sensitive detection in luminescence (*e.g.*, allowing detection limits in the sub part-per-trillion range and a linear dependence of fluorescence intensity on concentration extending over six decades)[417] and, if pulsed, yield time resolution.[417] For example, while benzo[*a*]pyrene and benzo[*k*]fluoranthene cannot easily be distinguished from each other by steady-state MI fluorimetry, their fluorescence decay times in $N_2$ matrices are sufficiently different (78 ns for BaP and 13 ns for BkF) to produce excellent temporal resolution of emission spectra for these compounds.[418] Correspondingly, pulsed-source time-resolved phosphorimetry shows improved sensitivity and selectivity compared with continuously operated source methods and can be applied to PAC.[419] Time resolution is also possible by computer methods,[419] and computation also allows the first- or second-derivative luminescence spectrum to be obtained, which contains much more information than the 'zeroth' order spectrum.[420,421]

If the spectra of two fluorophors overlap, selective modulation fluorescence excitation and/or emission spectra can be recorded for either component; the procedure involves wavelength modulating one monochromator, scanning the other, and detecting with a lock-in amplifier.[422] Modulation fluorescence has been used in a demonstration that the compound eluted with benzo[*e*]pyrene in the HPLC of air-particulate PAH is benzo[*k*]fluoranthene.[423]

In synchronous luminescence spectroscopy, both excitation and emission wavelength are scanned while keeping a constant interval between them, usually selected to be close to the Stokes shift.[424,425] The synchronous spectrum of each

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[410] A. P. D'Silva, G. J. Oestreich, and V. E. Fassel, *Anal. Chem.*, 1976, **48**, 915.

[411] C. P. Woo, A. P. D'Silva, V. E. Fassel, and G. Oestreich, *Environ. Sci. Technol.*, 1978, **12**, 173.

[412] C. S. Woo, A. P. D'Silva, and V. E. Fassel, *Anal. Chem.*, 1980, **52**, 159.

[413] V. D. Tuan and U. P. Wild, *J. Lumin.*, 1973, **6**, 296.

[414] K. R. Naqvi, A. R. Holzwarth, and U. P. Wild, *Appl. Spectrosc. Rev.*, 1977, **12**, 131.

[415] M. Soutif, *Pure Appl. Chem.*, 1976, **48**, 99.

[416] 'Modern Fluorescence Spectroscopy', ed. E. L. Wehry, Plenum Press, New York, 1976, Vol. 1 and 2.

[417] J. H. Richardson and M. E. Ando, *Anal. Chem.*, 1977, **49**, 955; Proceedings Ninth Materials Research Symposium on Trace Organic Analysis, Gaithersburg, Maryland, April, 1978, *Natl. Bur. Stand.* (*U.S.*) *Spec. Publ.*, **519**, 1979, p. 723.

[418] R. B. Dickinson, jun., and E. L. Wehry, *Anal. Chem.*, 1979, **51**, 776.

[419] G. D. Boutillier and J. D. Winefordner, *Anal. Chem.*, 1979, **51**, 1384.

[420] G. L. Green and T. C. O'Haver, *Anal. Chem.*, 1974, **46**, 2191.

[421] G. Talsky, L. Mayring, and H. Kreuzer, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 785.

[422] T. C. O'Haver and W. M. Parks, *Anal. Chem.*, 1974, **46**, 1886.

[423] M. A. Fox and S. W. Staley, *Anal. Chem.*, 1976, **48**, 992.

[424] T. Vo-Dinh, *Anal. Chem.*, 1978, **50**, 396.

[425] J. B. F. Lloyd, *Nature* (*London*), 1971, **231**, 64.

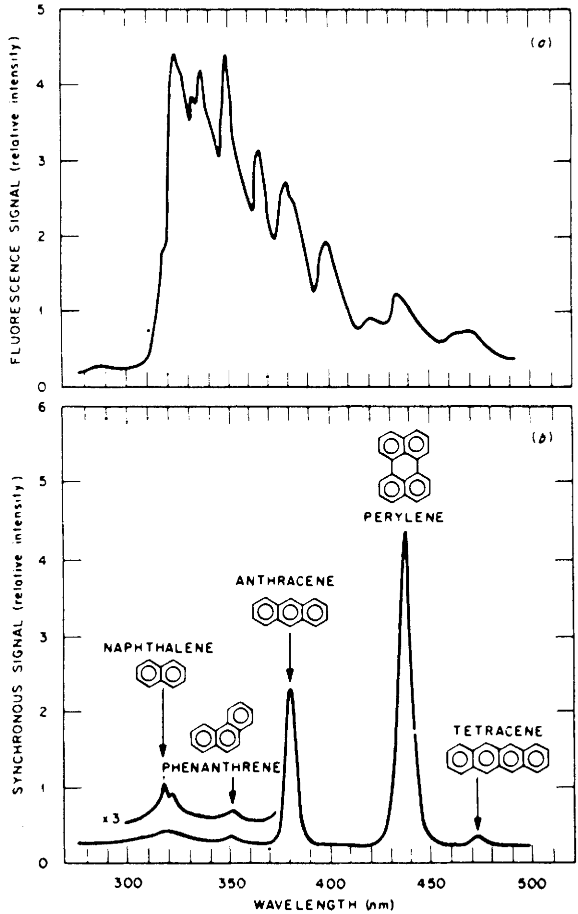

**Figure 14** A, *Conventional fluorescence spectrum of a mixture of naphthalene, phenanthrene, anthracene, perylene, and naphthacene.* B, *Synchronous spectrum of the mixture* (Reproduced by permission from *Anal. Chem.*, 1978, **50**, 396)

PAH now consists of a single peak (Figure 14). Caution may be necessary in applying the method to the quantitative analysis of multi-component mixtures, since the relative concentrations of species present would need to be fortuitous if errors from spectral overlap are to be avoided.[426] However, in spite of these reservations, there have been valuable applications such as the characterization of naphthalene derivatives in waste water,[427] the determination of perylene in

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[426] H. W. Latz, A. H. Ullman, and J. D. Winefordner, *Anal. Chem.*, 1978, **50**, 2149; 1980, **52**, 191.

[427] T. Vo-Dinh, R. B. Gammage, A. R. Hawthorne, and J. H. Thorngate, *Environ. Sci. Technol.*, 1978, **12**, 1297.

environmental samples,[9] and, in a development of RTP, the analysis of complex mixtures such as Synthoil on filter paper.[428] Lloyd has also shown how synchronous luminescence can provide 'fingerprints' in forensic science,[429–431] and can be used simultaneously with heavy-atom quenching.[430]

Video fluorimetry[432] involves the gathering of the emission–excitation matrix, M, the elements of which, $M_{ij}$, represent the fluorescence intensity measured at wavelength $\lambda_j$ for excitation at $\lambda_i$. A row of M represents the fluorescence-emission spectrum, and a column an excitation spectrum. The matrix is rapidly compiled by a computer-controlled fluorimeter,[433] and computational procedures may be applied to derive the individual spectra of up to six components in a mixture. Spectra may be displayed either as contours or as isometric projections[434] (Figure 15).

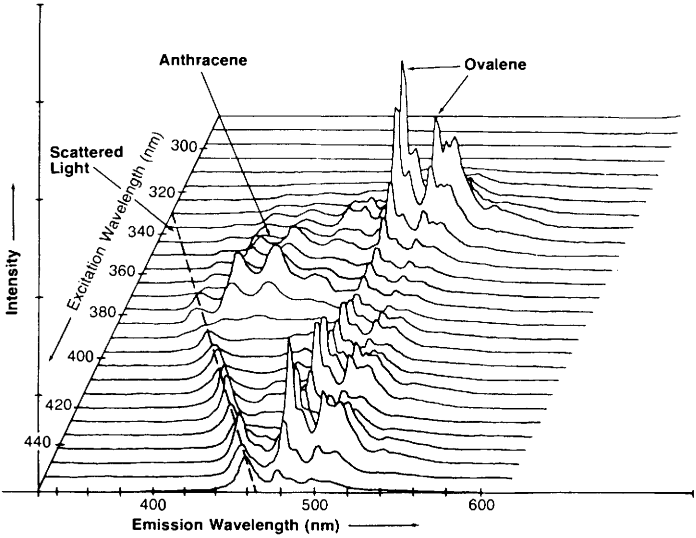

**Figure 15** *Total luminescence spectrum of anthracene and ovalene*
(Reproduced by permission from *Anal. Chem.*, 1978, **50**, 936A)

The use of parallel optoelectronic image detectors[435] (OID) allows the spectral matrix to be rapidly acquired so that transient spectrofluorimetry of photochemically labile compounds, and HPLC and GC detection are possible.

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[428] T. Vo-Dinh, R. B. Gammage, and A. R. Hawthorne, in ref. 168, p. 111.

[429] J. B. F. Lloyd, *J. Forensic Sci. Soc.*, 1971, **11**, 153 and 235.

[430] J. B. F. Lloyd, *Analyst (London)*, 1974, **99**, 729.

[431] J. B. F. Lloyd, *Anal. Chem.*, 1980, **52**, 189.

[432] I. M. Warner, G. D. Christian, E. R. Davidson, and J. B. Callis, *Anal. Chem.*, 1977, **49**, 564.

[433] I. M. Warner, J. B. Callis, E. R. Davidson, M. Gouterman, and G. D. Christian, *Anal. Lett.*, 1975, **9**, 665.

[434] C.-N. Ho, G. D. Christian, and E. R. Davidson, *Anal. Chem.*, 1980, **52**, 1071.

[435] Y. Talmi, D. C. Baker, J. R. Jadamec, and W. A. Saner, *Anal. Chem.*, 1978, **50**, 936A.

Spectra obtained with OID may be smoothed, source compensated, differentiated, *etc.*, in a computer. Laser-induced phosphorescence decay times may also be measured, and OID with diagonal scans across the spectral matrix, can yield information identical to that obtained by synchronous luminescence.

**B. Nuclear Magnetic Resonance.**—Conventional single-scan n.m.r. may confirm the presence of a given class of compounds, *e.g.*, alkyl-substituted derivatives, and may also be applied to the identification of specific individual compounds. Thus, Keefer *et al.*[436] carefully investigated the methods of identification of methyl-substituted PAH from environmental samples by continuous-wave $^1H$ n.m.r. The use of the chemical shifts of $CH_3$ (and their different concentration dependences), and of the benzylic coupling between $CH_3$ and ring protons were studied. The identities of 4-methylpyrene (1.1 Hz doublet) and 2-methylpyrene (0.7 Hz triplet) in the monomethyl pyrene fraction of petrolatum were confirmed from their chemical shifts; the dimethylpyrene fraction from the same material showed no resonances in regions characteristic of $—CH_2CH_3$ groups so that ethyl derivatives could be excluded, a conclusion not possible from mass-spectrometric data. A time-averaging method and use of a microcell as sample tube also allowed Keefer *et al.*[436] to analyse quantitatively mixtures with only 30—40 $\mu$g of individual components.

Pulse Fourier-transform (FT) $^1H$ n.m.r. can be applied with much more facility to small samples. Thus, Bartle *et al.*[437] were able to identify by FT $^1H$ n.m.r. as little as 20 $\mu$g of single PAH in mixtures generally totalling less than 1 mg separated from atmospheric dust and from the condensates of tobacco and marijuana smoke; pulse FT spectra at 90 MHz allowed identification of both parent PAH and their methyl derivatives. For example, the spectra of all the fluoranthene–pyrene fractions showed a number of other peaks near 2.5—3.0 p.p.m., in addition to those of $CH_3$ of the three methylpyrenes, indicating the presence of all five methylfluoranthenes (Figure 16). $^{13}C$ n.m.r. spectroscopy is a promising technique when sufficient sample is available. Signals from two sets of four-proton-bearing carbons and three quaternary carbons in the spectrum of a sulphur-containing PAC with molecular formula $C_{14}H_8S$ isolated from commercial pyrene suggested it to be phenanthro[4,5-*bcd*]thiophen.[438]

**C. Infrared.**—The chief disadvantages in the conventional infrared (i.r.) spectroscopy of PAC from the environment are the absence of unique features in the spectra and the lack of proportionality between band strengths and concentration, and until the introduction of matrix isolation FT–i.r. there had been few applications. Because the interactions of solute molecules with each other and with the solvent are minimized, the i.r. spectra of matrix-isolated species at cryogenic temperatures consist of very sharp vibrational lines.[439] It is hence

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[436] L. K. Keefer, L. Wallcave, J. Loo, and R. S. Peterson, *Anal. Chem.*, 1971, **43**, 1411.

[437] K. D. Bartle, M. L. Lee, and M. Novotny, *Analyst* (*London*), 1977, **102**, 731.

[438] W. Karcher, R. Depaus, J. van Eijk, and J. Jacob, in ref. 168, p. 341.

[439] I. R. Dunkin, *Chem. Soc. Rev.*, 1980, **9**, 1.

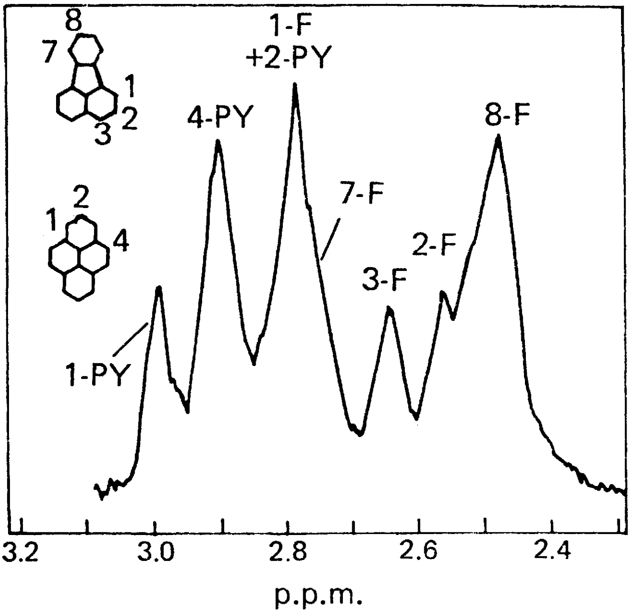

**Figure 16** *Methyl region of FT* $^1$H *n.m.r.* 90 MHz *spectrum of fluoranthene/pyrene fraction* (0.9 mg) *of tobacco-smoke condensate*
(Reproduced by permission from *Analyst* (*London*), 1977, **102,** 731)

possible to record highly resolved fingerprint spectra of PAC and to construct Beer's law plots as long as FT–i.r. is used to overcome the sensitivity limitations that apply for the now dilute analyte.

Wehry *et al.*[405,406,440,441] have conducted detailed investigations of the applicability of MI FT–i.r. in the qualitative and quantitative analysis of PAH. Samples in nitrogen matrices on a CsI surface at 15 K were produced by mixing the vapours of PAH effusing from a Knudsen cell with a large excess of nitrogen gas. Analyses of moderately complex mixtures (*e.g.*, the methylchrysenes[406]) are made possible by the line-rich spectra obtainable at 2 cm$^{-1}$ resolution.

The recording of FT–i.r. spectra in the gas phase of compounds eluted from a GC column allows a 'chemigram' to be determined by plotting absorbance in different i.r. spectral windows, corresponding to different functional group frequences, against time.[442]

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