Review

Air sampling and analysis of polycyclic aromatic hydrocarbons

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) occur in particles or in vapour phase. The size of the particles is affected by the season: in the winter there is a shift from large to small particles. PAHs, which are associated with particulate matter, are usually collected on filters and are then vaporized from the filter, or exist in the vapour phase and are trapped by a back-up solid sorbent. Many PAHs can react with other environmental pollutants. Benzo[a]pyrene deposited on a filter was reported to undergo chemical reactions with ozone and nitric acid. The loss of benzo[a]pyrene can be as high as 85%. The most common sampling method applied is integration of the sample by pumping the air stream through a sample device (active sampling). Passive sampling relies on the diffusion-controlled gradients towards a surface. Passive sampling is more often used for vapour-phase PAHs in occupational environments. Sample clean-up is increasingly performed by solid-phase extraction and is also applied to air samples. The samples are traditionally desorbed using Soxhlet apparatus, ultrasonication and various organic solvents, but supercritical fluid extraction is getting more popular. The analysis of PAH samples is usually carried out by high-performance liquid chromatography equipped with a fluorescence detector or gas chromatography–mass spectrometry with electron and negative chemical ionization methods. For quantitative analysis the correlation of these two methods have shown to be good. In qualitative analysis mass spectrometry lacks the ability to resolve the isomeric structures and high-performance liquid chromatography with time programming fluorescence seems to be the detection method of choice.

Contents

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which are formed in combustion processes of carbonaceous materials at high temperature. These combustion sources include emissions from automobiles, industrial processes, domestic heating systems, waste incineration facilities, tobacco smoking, and several natural sources including forest fires and volcanic eruptions [1]. Human exposure to polycyclic aromatic hydrocarbons may occur via food, water, air, and direct contact with materi-

als containing PAHs. PAHs have been measured in many matrices (air, water, sediment and tissue samples) because some of them are known to be mutagens and/or carcinogens [2].

Typically environmental samples contain an extremely complex mixture of various PAHs, including isomeric structures, and both alkylated and non-alkylated forms of PAHs. The structures of the 16 PAHs identified as priority pollutants by The U.S. EPA are shown in Fig. 1. In the atmosphere PAHs are known to be distributed between the gas and particle phases according to their volatility. In the particle phase PAHs are
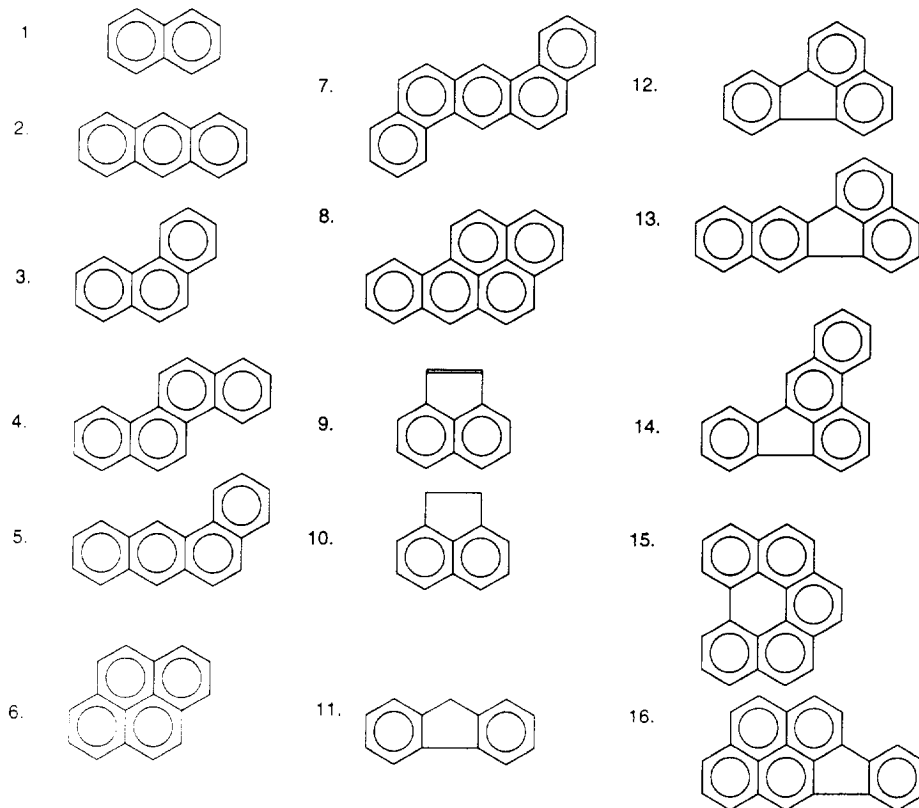

Fig. 1. Structures of the 16 PAHs as priority pollutants by the U.S. Environmental Protection Agency. The suspected carcinogens are marked with asterisk. 1 = naphthalene, 2 = anthracene, 3 = phenanthrene, 4 = chrysene, 5 = benz[a]anthracene*, 6 = pyrene, 7 = dibenz[a,h]anthracene*, 8 = benzo[a]pyrene* 9 = acenaphthylene, 10 = acenaphthene, 11 = fluorene, 12 = fluoranthene, 13 = benzo[k]fluoranthene*, 14 = benzo[b]fluoranthene*, 15 = benzo[ghi]perylene*, 16 = indeno[1,2,3-cd]pyrene*.

adsorbed mainly onto the respirable fraction (<5 μm) of suspended material. A seasonal variation in the size of the particles has also been observed [3]. Several techniques have been developed and used for sampling of PAH compounds from outdoor and indoor air. Environmental monitoring is conventionally performed by trapping the particulate bound fraction of PAHs onto filters using high-volume sampling techniques. In order to improve the determination of personal exposure integrative low-volume portable equipment is generally used for direct sampling of the breathing zone. In both approaches solid adsorbents which are known to effectively trap volatile organics have been used to collect low-molecular-mass PAHs. The most commonly used analytical methods are based either on liquid chromatographic separation and fluorescence detection or gas chromatographic separation together with mass spectrometry. These two analytical techniques have been reported to provide comparable results [4]. In addition to these conventional approaches some new techniques such as capillary electrophoresis have successfully been used to analyze PAH compounds. The intent of this review is to cover some basic factors, which affect air sampling of PAHs from occupational (low volume) and environmental (high volume) sources. Experiences about the different filters and adsorbents concerning sampling and recovery efficiencies of PAHs are given. Finally, a short discussion of the current analytical methods is presented.

2. Chemical reactivity of PAH compounds

Benzo[a]pyrene deposited on a filter was reported to undergo reactions with ozone and nitrogen dioxide. Benzo[a]pyrene, benzo[b]-fluoranthene or benzo[h]fluoranthene were exposed at sub-ppm levels of ozone both in the dark and sunlight for up to 12 h [5]. The decomposition rate was found to be linear and dependent on the ozone concentration. Half-lives for the decomposition in the dark on exposure to ozone were 52.7 to 29 h for benzo[a]pyrene, and 34.9 to 3.3 h for benzo[b]-

fluoranthene. Benzo[a]pyrene deposited on glass fibre filters, and exposed to ppm levels of ozone for 24 h, was shown to form benzo[a]pyrene quinones and 4,5-benzo[a]pyrene oxide [6,7]. When benzo[a]pyrene was exposed to 200 ppm of ozone for 1 and 4 h, losses of 50% and 80% were detected, respectively [7].

The reactions of ozone with PAHs, collected during previous ambient high-volume sampling, have been studied by some authors [8–11]. The losses of benz[a]anthracene, benzo[a]pyrene, benzo[k]fluoranthene, benzo[ghi]perylene from filters after exposure to an air stream with 0–200 ppb ozone for up to 24 h were studied and only benzo[a]pyrene had any significant loss attributable to ozone [10]. However, losses attributable to volatilization ranged from 25% for benzo[ghi]perylene to 85% for benzo[k]fluoranthene. The total loss for benzo[a]pyrene was about 45%.

Losses from 68 to 84% for fluoranthene, pyrene, benzo[a]pyrene, 3-methylcholanthrene and 1,2,4,5-dibenzanthracene were observed in the presence of 140 ppb ozone for 24 h. These, however, include volatilization losses. The losses in the presence of the denuder were from 41 to 59% for the same PAH compounds [12]. The use of a denuder to remove ozone from the ambient air stream during high-volume sampling showed promising results in reducing reactions of collected PAHs with ozone.

Diesel exhaust particles, <0.5 μm aerodynamic diameter, collected on glass fibre filters and subsequently exposed to 1.5 ppm ozone for up to 4 h showed losses of PAHs (such as phenanthrene/anthracene, methylated fluorenes and pyrenes) due to volatilization. However, these as well as less volatile compounds such as benzo[a]pyrene, benzo[e]pyrene, and perylene showed considerable reactivity to ozone. The conversions ranged from 47 to 100% in 4 h under the experimental conditions applied [13].

Fitz et al. reported that the exposure of filters loaded with ambient airborne particles to ozone concentrations of up to 290 ppb resulted in no changes in mutagenic activity, relative to ozone concentrations [11].

Exposure of pyrene on filter paper to NO$_2$ (10 ppm) resulted in formation of nitropyrene [14]. Up to 2.8% of the pyrene was converted to nitropyrene. The presence of nitric acid impurity in NO$_2$ streams has been suggested as the prime cause of the formation of nitro-PAH derivatives [6,15]. No nitro-PAHs were found when a nylon filter was used to remove HNO$_3$ from a 100 ppb NO$_2$ stream passing through PTFE and glass fibre filters with PAH-loaded coal fly ash, diesel exhaust or ambient particles [15]. An experiment using benzo[a]pyrene spiked onto similar filters and exposed to ppb level of NO$_2$, also indicated no loss of benzo[a]pyrene [6].

Benzo[a]pyrene was added to PTFE filters with and without diesel exhaust particles. These were exposed to an equilibrium concentration of nitric acid vapour over nitric acid, resulting in complete degradation of benzo[a]pyrene. Mono-nitro- and dinitro-benzo[a]pyrene products were identified [15]. The addition of ppb levels of HNO$_3$ to the air stream during sampling resulted in losses of benzo[a]pyrene (95%), benz[a]anthracene and perylene (55%) and benzo-[ghi]perylene (20%). The mutagenicity of filter extracts also increased [16]. The addition of 200 ppb NO$_2$ during high-volume sampling in the winter resulted in degradation of pyrene, benzo[a]pyrene and benz[a]anthracene, however, several benzofluoranthenes, and chrysene were not degraded [16,17]. The mutagenicity of extracts was enhanced compared to sampling without addition of NO$_2$.

The age and origin of the aerosol sampled seemed to affect the extent of degradation. Considerable uncertainty still exists about the effect of co-pollutants present (O$_3$, NO, NO$_2$, HNO$_3$) in PAH samples on filters.

3. Air sampling of PAHs

The monitoring methods for airborne PAHs may be classified into those concerned with either direct occupational exposures or with ambient exposures. PAH concentrations in the former class are usually higher. The PAHs occur in particles of respirable size and reported me-

dian diameters are typically 0.5 μm or less. Diameters of 0.7 μm for benzo[a]pyrene and 0.32 μm for pyrene were reported [18]. The season has an impact on the size of the aerosols; in the winter, there was a shift from large to small particles and the size distribution of the more volatile low-molecular-mass PAHs is more uniform in the small particle size range. More than 95% of the PAHs in winter aerosols are in the size fraction 3 μm. The fraction below 1 μm contained 70–80% of PAHs in the winter but only 10% or less in other seasons [3]. Aerosols from a coke oven emission source had maximum amounts of PAHs in the 1.86 to 0.85 μm size fraction range and 94% of the PAHs measured were in the 2.9 μm or smaller fraction [19].

PAHs have been associated with particulate matter, but three- to five-ring PAHs have been shown to occur in the vapour-phase as well [20–26]. It has also been shown in several publications that volatilization of particulate PAHs collected on filters represents a considerable loss, especially of PAHs containing less than five rings. Vapour-phase PAHs and those volatilized during sampling have been captured by using backup sorbents. The distribution of PAHs between particle-sorbed and vapour-phase fractions has also been estimated with such sampling systems. Several studies have been undertaken to determine the vapour–particle distribution in high-volume as well as in low-volume sampling [12,21,27–32].

The distribution ratios of particulate to gas phase concentration of several PAHs as well as other classes of organics were reported by Cautreels and Van Cauwenberghe [21]. For phenanthrene, anthracene, methylpyrene and methylanthracene, the distribution factors ranged from 0.027 to 0.088. Fluoranthene, pyrene and benzofluorenes had intermediate values 0.26, 0.49 and 1.25, respectively, while benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]-fluoranthene, benzo[a]pyrene, benzo[e]pyrene and perylene were primarily in the particle phase with distribution factors ranging from 3.15 to 11.5. It should be noted that losses of particle-bound material due to blow off from the filter and gains on the cartridge due to material

volatilized during sampling may have introduced errors in the distribution ratios.

The amounts of PAHs retained on filters and sorbents collected by low-volume techniques in aluminum reduction plants, coke plants, iron and steel works, foundries and ferroalloy plants were summarized by Bjørseth [30]. Quantitative data for aluminum and coke plants revealed similar distributions between the particle and vapour phase. Fluorene, methylfluorenes, phenanthrene, methylanthracenes, fluoranthene, dihydrobenzo[a]- and benzo[b]fluorene and pyrene were found in both phases with percentages in the vapour-phase ranging from 100 to 35%. For heavier PAHs, the filter catch contained nearly all the PAHs measured.

In a study at a coke plant, two aluminum plants and a creosote plant silver membrane/glass fibre filters with XAD-2 backup sorbents were used [31]. More than 99% of benzo[a]pyrene, benzo[k]fluoranthene, benzo[b]fluoranthene and chrysene were retained on the filter. For naphthalene, phenanthrene, anthracene and fluoranthene, the amounts retained on the filter ranged from 0 to 35%.

It is clear that current sampling methods (i.e. cascade impactors, high- and low-volume samplers using filters and/or back-up sorbent traps) are inadequate for the determination of accurate concentrations of PAHs in air or bound on airborne particles. The sampling process using available techniques can produce redistribution of the PAHs both between the vapour and particle phase and among different particle sizes. Methods to overcome these deficiencies are not yet available.

3.1. Active sampling

Active sampling methods that rely on integration of the sample, require pumping the air stream through a medium (e.g., filter, sorbent, impinger, cryogenic trap) which will retain the target compounds. In environmental monitoring, sampling rates in the range of 300 to 1500 l/min^{-1} are used and much lower flow-rates are used in occupational exposure monitoring.

For particle size measurement in which par-

ticles are fractionated into specific size ranges, based on aerodynamic particle diameters, cascade impactors designed to complement high-volume samplers or as separate units are commercially available. The separate units typically employ flow-rates in the range of 30 to 90 l min^{-1}. Other particle size measuring devices, such as dichotomous samplers or optical particle counters have not been used extensively in sampling for PAHs [33].

Impregnated filters, impingers, solid sorbents and cryogenic traps are used to collect vapour-phase PAHs. Studies using multiple filters, some of which were impregnated, simply used filters placed on top of each other or in specially fabricated multiple filter holders [8,20,34]. Cartridges for housing solid sorbents are often used. Modifications to standard high-volume samplers have been provided for partial flow diversion through the sorbent cartridge [12,18,21,27–29,35–37].

Low-volume samplers used in occupational environments often have battery operated personal sampling pumps. In addition, readily available vacuum pumps are also used. The usual flow-rates in these samplers are 1–3 l min^{-1} through filter holders or cassettes housing 37 or 47 mm filters.

For low-volume sampling, in which sorbents in combination with single or multiple filters are used, commercial devices specifically designed for PAH sampling are not widely available but are generally assembled from commercially available components [38–40].

3.2. Passive sampling

Passive sampling techniques rely on the controlled transport of the analyte material along a concentration gradient towards a surface which acts as a sink for the target compound. If the surface adsorbs the compound completely, the concentration at the surface is zero and this serves to establish the concentration gradient. It should be noted that because there is an order of magnitude difference between the diffusion coefficients of gases and fine particles (if turbulent diffusion is ignored), the diffusion of particles in

the tube is therefore negligible. These and close-ly related devices may involve diffusion through a membrane or filter before reaching the sink [35,41].

Passive sampling techniques have been applied infrequently to ambient (outdoor) monitoring of PAHs, mainly because of the long sampling times required due to the low PAH levels and limited analytical sensitivity.

The PAH dosimeter utilizes a filter paper disc or a solid substrate treated with sorbent material such as a heavy-atom doped chemical reagent [42]. The heavy-atom doped sorbent allows detection and analysis by room temperature phosphorescence. This technique is convenient and sensitive but does not allow resolution of many components in mixtures [43]. Detection limits of several homocyclic and heterocyclic PAHs have been reported in the picogram range [44]. Laboratory and field tests of the dosimeter demonstrated the capability of measuring vapour-phase levels of azarenes such as quinoline, phenanthridine and acridine and PAHs such as fluoranthene, naphthalene, methylnaphthalene, phenanthrene and pyrene [41,43,45–49].

Passive sampling methods have also been successfully employed in monitoring occupational levels. This technique has been applied only relatively recently to specific vapour-phase PAH compounds but has been commonly used for monitoring other low-molecular-mass organics in occupational environments. The low cost and reasonably good sensitivity of this technique for specific compounds, are very useful for sampling surveys requiring the collection of large numbers of samples.

The passive monitor has several highly desirable features. It is sensitive, light-weight, inexpensive, amenable to large sampling volumes, analytical costs are low, and turn-around times are short. Currently, it is the only device that allows the true vapour-phase measurement of PAHs.

3.3. Sampling of particulate PAHs

Several types of filter materials have been used to collect PAHs. Two types of filters — glass

fibre and silver membrane — have been utilized most often in the sampling of airborne PAHs with high- and low-volume samplers.

The high-volume sampler has been used in most cases where ambient monitoring has been required and 25 × 20 cm glass fibre filters have been used most frequently in the USA and a 12.5 cm diameter filter in Germany. For occupational sampling, filter cassettes employing 37 mm diameter silver-membrane filters have been most widely used. The choice of the glass fibre filter is based on the ability to obtain consistently low organic blank levels on filters. Pretreatment of glass fibre filters most often involves firing at 400–500°C, but pre-extraction of filters with a variety of solvents is used as well. PTFE-coated glass fibre filters, are enjoying increased use as a collection medium for sampling of organics. A comparison of the regular glass fibre filter and the PTFE-coated filter showed no differences in the high-volume sampling of PAHs of diesel exhausts [50].

The PAH collection on glass fibre, quartz and PTFE were compared in sampling ambient air at varying flow-rates to give similar face velocities [51]. The quartz and glass fibre filters collected lesser amounts of PAHs (85 and 83%, respectively) than the PTFE filters, and it was suggested that reported ambient PAH levels are underestimated as a result of the use of glass fibre filters [52]. This assumes that the PTFE filters are not absorbing PAH vapour. It was not possible to determine whether or not the smaller amount of PAHs from quartz or glass fibre filters could be attributed to chemical reaction with other air pollutants [15].

Five filter types, namely glass fibre, silica quartz, microglass fibre with PTFE binder on fibres, PTFE membrane bonded to polyethylene net, and PTFE membrane supported by PTFE fibres, were compared for blank levels, amount of PAHs retained and losses from filters [53]. PTFE gave the lowest levels of background impurities in methylene chloride extracts. The polar fraction of the extract from PTFE/polyethylene was clean but there were non-polar impurities, probably from the polymeric backing material, that are potential interferents in fluo-

rescence determinations. The PTFE membrane type filter retained most of the PAHs based on recovery of ^{14}C-labeled benzo[a]pyrene spiked on filters prior to sampling. The order of recovery was PTFE membrane > TA60A20 > glass fibre or silica fibre. The superior performance of PTFE filters was attributed to less degradation of collected PAHs on PTFE filters compared to the other filters. This degradation was monitored for benzo[a]pyrene during storage in the dark. It was postulated that an active surface such as quartz or silica is necessary for reaction of collected material during and/or after sampling. The extent of degradation was dependent on the filter loading, i.e., lightly loaded filters were more susceptible to degradation due to the greater percentage of particles contacting the filter surface [53]. The loss of benzo[a]pyrene in stored samples of diesel exhaust particulates collected on glass fibre filters amounted to 67% after 150 days [54].

In a recent evaluation of membrane filters for PAH sampling, cellulose acetate filters collected more of the PAHs with three or four rings than glass fibre filters [8]. The amounts of phenanthrene, fluoranthene and pyrene on the glass fibre filter ranged from 7 to 42% of that collected on a single membrane filter. For benzo[b]-fluoranthene, benzo[j]fluoranthene, benzo[e]-pyrene, benzo[a]pyrene and benzo[ghi]-perylene, similar amounts were collected on the glass fibre and membrane filters [8]. However, even the use of membrane filters led to losses of small amounts of anthracene and pyrene; up to 20% of anthracene and pyrene were lost from upstream membrane filters indicating that the capacity of membrane filter for low-molecular-mass PAHs is low.

The use of silver membrane filters in sampling for PAHs in occupational environments was initially suggested in view of the difficulty of obtaining a suitable low blank from glass fibre filters on extraction with benzene and the better weight stability of silver membrane filters. Because the silver membrane filter tends to be easily plugged by particulate matter, the use of the glass fibre filter preceding the silver membrane filter has been a standard NIOSH pro-

cedure for sampling in occupational environments [55]. The high resistance of the silver membrane filter to air flow limits the sampling rate [56]. The NIOSH method and other applications in which silver membrane filters are used typically have sampling rates of 1–5 l min^{-1}.

3.4. Sampling of volatile PAHs

Improvements in sampling methods designed to minimize the losses of PAHs volatilized during sampling, have relied on impregnated filters, reduction in sampling duration, addition of solid sorbent back-up cartridges and cryogenic traps.

Several solid sorbents or liquids coated on supports acting as stationary phases have been used to trap vapour-phase air pollutants. The choice of sorbent is determined by several factors such as collection efficiency, capacity of sorbent (breakthrough volume), chemical stability of sorbent during sampling, storage and extraction, low blank levels, low affinity for water vapour and high and facile recovery of sorbed vapours. For the sampling of PAHs the sorbents used include Tenax, XAD-2, polyurethane foam (PUF), Florisil, Chromosorb 102 and SepPak-C_{18} on Porasil [36,38]. The use of charcoal tubes for the collection of organic vapours was widespread and these tubes have been used to collect three-ring PAHs, but the release of PAHs from charcoal is usually difficult [57]. Tenax GC was utilized as a sorbent in source sampling of combustion sources [58,59].

Glass fibre filters impregnated with glycerotricaprylate captured larger amounts of volatile PAHs than untreated filters, but impregnated filters also lost volatile PAHs when sampling periods were extended to 4–12 weeks. For example, 78% less fluoranthene was found in a sample using a 12-week period compared to sampling carried out with three filters for the concurrent three 4-week periods. Less volatile PAHs were not found on back-up impregnated filters, but losses of these compounds were attributed to reaction with other air pollutants [20]. Filters impregnated with tricaprylate or liquid paraffin retained similar amounts of PAHs [60]. Although the impregnated filters trapped vaporized PAHs,

losses were observed during prolonged sampling periods. As a curiosity, the treatment of filters with a 3:1 mixture of methanol and glycerine was used successfully for sampling in coke oven plants [55].

Shorter sampling times has been recommended to minimize losses of PAHs during sampling [61]. The PAHs and total extractable organic matter retained on filters have been shown to decrease if the sampling duration is extended [20,60,61]. Shorter duration time was recommended to minimize these losses and it was found that the PAH concentrations determined from 6-h sampling were up to 6.5 times larger than those obtained using 24-h sampling periods [50].

In high-volume samplers, sorbents such as Porapak Q and S, Chromosorb, Tenax and polyurethane foam have been used in the sampling of vapour-phase organics [42,62–65]. The use of Tenax GC as a sorbent for PAHs, however, was found to be prone to contamination and exhibited poor flow characteristics [66].

Polyurethane foam (PUF) has gained in popularity, particularly for the use in high-volume samplers because of the low pressure drop caused by PUF, low blanks, low cost and ease of handling. Flow-rates of 225–416 l min^{-1} were reported in PAH sampling using glass fibre filter PUF sorbent samplers [32,95]. Several studies have reported on the use high-volume samplers with a PUF plug as a back-up sorbent for sampling of ambient PAHs [36].

Jackson and Cupps used a personal monitor consisting of a 37-mm glass fibre–silver membrane filter combination before a solid sorbent cartridge of Chromosorb 102. Flow-rates of 2 or 10 l min^{-1} were used in different samplers [38]. Andersson et al. while sampling in occupational environments with coal tar sources, used a standard filter cassette without a silver membrane filter and with Amberlite XAD-2 [31].

The collection efficiencies of sorbents have not been systematically investigated in order to define and quantify relationships between parameters such as flow-rates, linear face velocities, retention volume, effects of temperature and nature of target compound.

4. Sample desorption and clean-up

The PAHs from solid environmental samples such as air particulates, soils and sediments are traditionally extracted by Soxhlet extraction or ultrasonication using a variety of organic solvents including acetone, benzene, toluene, methylene chloride, etc. These traditional methods are efficient for many samples; however, they often require large volumes of solvents, are time consuming, and yield incomplete recovery of higher-molecular-mass PAHs from materials on which they are strongly adsorbed (i.e., carbon black or coal fly ash). For these reasons, supercritical fluid extraction (SFE) has received considerable attention as an alternative to these classical methods. Since environmental samples generally contain interferents and trace amounts of PAHs of interest, concentration and clean-up procedures are usually required prior to the final chromatographic analysis. In many cases, the sample pretreatment procedure is the critical step in achieving reliable quantitative results.

PAH concentration and clean-up is increasingly being performed by solid-phase extraction (SPE). For preconcentration of PAHs from drinking water samples, best results were obtained for combined octadecylsilane (C_{18})–ammonia (NH_2) solid-phase cartridges, whereas the enrichment of PAHs from soil samples was best achieved with silica (Si)–cyano (CN) or C_{18}–CN combinations [67]. The choice of SPE sorbent type is often dictated by the chromatographic method used for PAH separation and identification. For example, a recent study showed that for the determination of PAHs in lake sediments, C_{18} and silica columns could be used satisfactorily to clean up extracts for subsequent HPLC analysis with fluorescence detection; however, they could not be used for gas chromatography (GC)–mass spectrometry (MS) for PAHs greater than chrysene due to interferences from aliphatic waxes. Fully activated silicic acid and neutral alumina columns were recommended [68]. A standard leaching test employing SPE with C_{18} packings has proven to be a fast reliable method for determining the PAH leachability from waste materials [69]. Florisil (SiO_2 and MgO) car-

tridges have yielded rapid and efficient recovery of PAHs for petroleum and sediment extracts [70]. Extraction and concentration of PAHs in oils was achieved by charge-transfer liquid chromatography on improved tetrachlorophthalimidopropyl-bonded silica [71]. A quantitative procedure for the determination of PAHs in biomass tar has been described using SPE with aminopropylsilane packings [72]. Chromosorb T and XAD-2 have been compared for in situ extraction of PAHs from fresh water and seawater. Neither sorbent was useful for PAHs with molecular masses less than that of phenanthrene due to low recoveries or PAH contaminants, and were comparable for the study of three-ring and higher PAHs [73].

Most of the air samples collected do not need purification prior to analysis. However, some laboratories uses normal-phase LC clean up and isolation of the total PAH fraction prior the analysis, especially when performed with GC–FID [74].

SFE has proven to be a powerful alternative to conventional liquid extraction methods used in environmental analysis [75,76]. PAHs have been extracted directly from endogenous solid and liquid matrices, as well as trapped onto solid adsorbents with subsequent recovery by SFE [77,78]. One major advantage of SFE is the relative ease with which it can be coupled to chromatographic techniques, particularly GC and supercritical fluid chromatography (SFC). Hyphenated SFE–GC and SFE–SFC techniques have recently been applied for the determination of PAHs from environmental samples [79–81].

Carbon dioxide is the primary fluid used in most SFE applications, because it has low critical points, it is non-toxic, non-flammable, odourless, readily available in high purity, inexpensive, and eliminates solvent waste disposal problems. Unfortunately, the non-polar nature of carbon dioxide has hindered its application for the recovery of higher-molecular-mass PAHs or those strongly adsorbed to (or trapped in) the environmental matrix. Alternative fluids such as N_2O and $CHClF_2$ (Freon-22) yield higher recovery of PAHs from petroleum waste sludge and railroad bed soil, compared to CO_2 [82]. Alternatively,

the use of organic solvent modifiers (i.e., methanol) or in situ chemical derivatization has been shown to improve the recovery of PAHs while still employing the preferred supercritical fluid, carbon dioxide [83]. Other studies have focused on optimizing the major controllable SFE variables and minimizing problems including restrictor plugging, particularly when extracting high-molecular-mass PAHs or employing samples with a high sulfur content [84,85].

A model for dynamic SFE has been proposed and applied to the SFE of the PAH, phenanthrene, from railroad-bed soil with good agreement [86]. Models such as this are useful as they provide an extrapolation method for obtaining quantitative analytical extractions in the shortest analysis time. A dynamic tracer response technique has been applied for simultaneous measurement of equilibrium and rate parameters for the dynamic extraction of analytes from solid matrices. The technique allows the determination of adsorption equilibrium constants, effective diffusivities and axial dispersion coefficients for the system naphthalene–alumina–supercritical CO_2 [87–90]. More thorough discussions of the effect of SFE variables and comparisons for different SPE matrix–analyte types have recently been published [91–93].

5. Chromatographic analysis of PAHs

5.1. HPLC analysis

For about two decades high-performance liquid chromatography (HPLC) has been successfully used for the separation of individual PAHs from complex mixtures. Since Schmit et al. first reported [94] the separation of PAHs with a chemically bonded octadecylsilane (C_{18}) stationary phase in 1971, Reversed-phase HPLC (RP-LC) on chemically bonded C_{18} phases have been widely used in PAH analyses of environmental samples. The popularity of this technique is based on several factors: its good selectivity in separating individual PAH compounds and their isomers, sensitive and selective detection by fluorescence spectroscopy, and its use as a frac-

tionation technique before analysis by other chromatographic and spectroscopic techniques [74].

Although it may be concluded that HPLC on C_{18} stationary phases is excellent in separating PAHs in complex mixtures, considerable differences in selectivity (i.e., relative separation) have been shown between different commercial columns. Intensive investigations have been conducted at NIST to get more detailed knowledge about numerous factors affecting selectivity in PAH separation by RP-LC. Studies by Sander and Wise have been summarized in the recent reviews [95,96].

C_{18} bonded phases are classified as 'monomeric' or 'polymeric' depending on the nature of silane reagents and the conditions of the bonded phase synthesis. As a summary of several studies it has been concluded that this monomeric–polymeric character of C_{18} has a great influence on the separation of PAHs (Fig. 2) [74]. The elu-

tion order of the three-component mixture of phenanthro[3,4-c]phenanthrene (PhPh), 1,2:3,4:5,6:7,8-tetrabenzonaphthalene (TBN), and benzo[a]pyrene (BaP) has been shown to gauge the nature of a phase [97]. On a monomeric phase the order is BaP, PhPh, TBN, and on a polymeric phase PhPh, TBN, BaP. On the basis of this test column selectivity toward more complex PAH mixtures can be predicted. Sander and Wise [97] also stated that the effect of endcapping on PAH selectivity is negligible. Commercial C_{18} columns have also been classified according to the selectivity factor $\alpha_{TNB/BaP}$ (Table 1) [74]. $\alpha_{TNB/BaP}$ values of 1 indicate polymeric phases, which have been shown to separate PAHs more selectively. Some other characteristics to be mentioned are: surface coverage [98], alkyl chain length [99], and temperature [100] which have been shown to have an influence on PAH retention behaviour. On polymeric C_{18} phases planar PAHs have longer
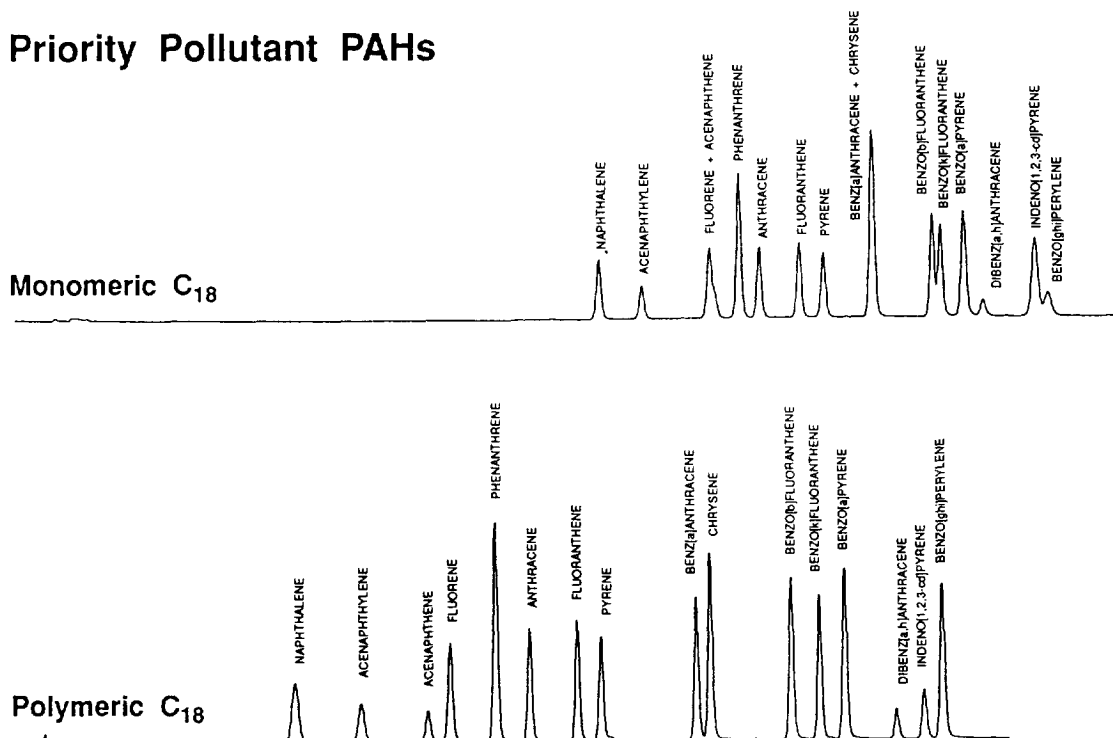

Fig. 2. Comparison of the separation of the 16 PAHs on a monomeric and a polymeric C_{18} stationary phase (reproduced with permission from Ref. [74]).

Table 1
Selectivity classification ($\alpha_{TBN/BaP}$) for various commercial C_{18} columns (reproduced with the permission from Ref. [74])

Column	$\alpha_{TBN/BaP}$
Polymeric phases	
Bakerbond C_{18} Wide-Pore	0.56
Hypersil Green PAH	0.8
Phenomenex Envirosep PP	0.58
Chromspher PAH	0.59
BioRad RP 318	0.59
Supelcosil LC-PAH	0.63
Vydac 201TP	0.74
Spherisorb PAH	0.82
Erbasil C_{18} H	0.91
Intermediate phases	
ES Industries BF-C_{18}	1.04
LiChrospher 100 RP-18	1.11
Bakerbond C_{18}	1.27
Erbasil C_{18} M	1.28
LiChrospher 60 RP-select B	1.36
Partisil 5 ODS-2	1.40
Partisil 5 ODS	1.48
Spherisorb ODS-1	1.50
Zorbax RX C_{18}	1.50
Brownlee ODS 5A	1.51
Sepralyte C_{18}	1.61
Spherisorb ODS-2	1.68
Monomeric phases	
Erbasil C_{18} L	1.76
Pecospher 5 Cr C_{18}	1.76
Partisphere C_{18}	1.79
Zorbax ODS	1.80
Serva C_{18}	1.84
Partisil 5 ODS-3	1.93
Hypersil ODS (HP)	1.94
Microsorb C_{18}	1.95
J and W Accuphase ODS 2	1.96
Novapak C_{18}	1.97
Ultrasphere ODS	1.98
Capcell C_{18} SG120 Å	1.99
Supelcosil LC-18	2.00
IBM ODS	2.00
Brownlee Spheri 5 RP-18	2.02
ODS Hypersil	2.04
Cosmosil C_{18}-P	2.04
Ultracarb 5 C_{18} (20%)	2.05
J and W Accuphase ODS	2.07
YMC 120 Å "A"	2.08
Ultracarb 5 C_{18} (30%)	2.10
Adsorbosphere C_{18} HS	2.10
Supelcosil LC-18-DB	2.18

retention times relative to non-planar ones [101,102].

Traditional PAH separations by RP-HPLC are made by gradient elution. The most widely used detectors with HPLC are the UV absorption and fluorescence detectors. In environmental analyses the far better sensitivity of the latter is usually needed. The selectivity of fluorescence detection is also essential for the sensitivity of LC in PAH analyses. Optimum excitation and emission wavelengths in detection do not necessarily correspond to the maxima in spectra of each compound, but best separation wavelengths depend on the interfering compounds in the sample matrix. Quantitation in HPLC is made by external or internal standards. As internal standards perdeuterated PAHs have at least two advantages: elution immediately prior to the non-deuterated PAHs, and fluorescence characteristics near the corresponding non-deuterated compound [103].

One advantage of selective fluorescence detection is the need for less sample clean-up than in GC analysis. Recently Sisovic and Fugas [104] evaluated the suitability of low-volume samples (2–4 m^3/24 h) for PAH analysis from suspended particles without any clean-up or separation steps. The conclusion was that the sensitivity of the HPLC–fluorescence method permits the application of low-volume suspended particulate matter (SPM) samples for PAH determination, and separation of interfering substances before analysis is not necessary unless PAHs with short retention time are of interest [104].

Multidimensional liquid chromatographic techniques have also been routinely used in PAH analyses. Normal-phase HPLC has been used as a prefractionation technique to analyze environmental samples (e.g., atmospheric particles) which contain a complex matrix of adsorbed organic compounds. This chromatographic technique overcomes many of the disadvantages of liquid–liquid extraction [105].

In a very recent paper a new application of a RP-HPLC column switching technique is presented in which a 20-component PAH mixture is rapidly and efficiently separated under isocratic conditions by use of two Superspher-100 ('mono-

meric') cartridges thermostatted at different temperatures [106]. The authors expect that this time and material saving method will become an attractive alternative to conventional gradient elution in HPLC.

Different column package materials can also be utilized in column switching techniques for sample clean-up, depending on the nature of the matrix. For example silica–dinitro-aryl silica columns for the determination of benzo[a]pyrene in oil fractions have been used [107].

A sample fractioning technique, low-volume liquid chromatography, also called 'dry' column chromatography, suitable for air particulate matter has been presented in which the sample is eluted sequentially from an Al_2O_3 cartridge. Final analysis was made by gas chromatography [108].

5.2. Gas chromatography and gas chromatography–mass spectrometry

Gas chromatography is the method with a high resolution power in PAH mixture analysis. A recent comparison of some high temperature GC columns also illustrated their applicability to the analysis of moderately high-molecular-mass PAHs (seven ring) with a reasonable retention time [109]. Recent studies have focused on relationships between GC retention data and molecular properties of PAHs and some regularities between the molecular shape of PAHs and retention behaviour have been observed [110–112]. The temperature-programmed retention indices of volatile fractions of PAHs were studied using moderate and non-polar phases [113,114].

For the detectors used in GC analysis of PAH compounds the most utilized detectors are flame ionization (FID) and mass spectrometric (MS) detectors, but also FTIR has been applied [105,115,116]. The electron impact (EI) ionization technique is widely used and characteristic fragmentations allow identification of the PAHs. Another technique is based on chemical ionization and registration of negative ions (NCI). Thermal electrons are captured competitively by sample molecules with high electron affinity.

Compared to the EI technique little fragmentation is seen in the NCI mass spectra due to the low energy of the electrons [117]. Hilpert studied the usefulness of NCI to the quantitative determination of PAHs [118]. Benzo[a]pyrene was shown to be a good analyte for the NCI method due to its high sensitivity and the fact that benzo[e]pyrene is insensitive under NCI. Benzo[e]pyrene can cause impreciseness in the analysis if EI is used, and an SD of 25% was observed when the standard samples were analyzed. If the NCI method is used a good SD of 3.3% was observed. GC matrix isolation infrared spectrometry has been used to identify isomeric PAHs and 33 PAHs have been quantitatively measured and identified [119].

Electron-capture detection after derivatization with bromine and selective detection using photoionization detection have been also presented [120,121]. The optimal analytical conditions and solvent of choice in splitless injection has been investigated [122]. The use of toluene and xylene gave enhanced signals up to 100 times greater than other solvents tested, especially with high-molecular-mass PAHs.

5.3 Miscellaneous techniques

Thin-layer chromatography (TLC) was used especially in earlier works to analyze complex PAH extracts before the development of gas and liquid chromatographic methods which are nowadays usually preferred. However, TLC has proved to be a convenient technique if complete separation is not required. Individual PAHs on TLC plates are generally quantitated with fluorimetry, either directly on the plate or in solution after elution from the plate. Today TLC is still used as a sample preparation method in special applications with GC, which has been recently reviewed by Furton et al. [123]. A technique combining TLC with laser mass spectrometry (LMS) was demonstrated to effectively distinguish and determine even partly overlapping PAH compounds directly from the plate [124]. A high-performance thin-layer chromatography (HPTLC) method was described as a low-cost screening method for PAHs in crude en-

vironmental samples. In this application separation is made on octadecylsilanized silica gel plates and individual compounds are determined by fluorescence scanning densitometer [125].

SFC has recently been applied to the determination of PAHs from environmental samples [80,81]. Carbon dioxide is the primary fluid used in most SFC applications, and the detection is carried out by FID and MS [126]. The retention behaviour of PAHs in SFC for different stationary phases has been shown to be controlled by molecular size, but was also influenced by additional parameters such as dipole–dipole interactions and solubilities [127,128]. Furton et al. have found that of numerous physical and molecular descriptors studied, the molecular connectivity correlates best with SFC retention data for normal- and reversed-phase systems [124].

Capillary electrophoresis (CE) is a powerful technique and well suited for analysing complex microsamples because of its high separation efficiency. The CE analysis of PAHs is not straightforward since the electrophoretic separation of these neutral and highly hydrophobic compounds is difficult. However, methods were developed for electrophoretic separation of PAHs using solvophobic interaction of the analyte [129,130] and the use of organic additives in micellar electrokinetic chromatography [131]. In a recent paper Nie et al. reported on the use of CE with UV-laser-excited native fluorescence for ultra sensitive determination of polycyclic aromatic hydrocarbons [130]. The separation is based on solvophobic association of the analytes with tetraalkylammonium ions in acetonitrile–water solution. The reported mass detection limits were in the range 10^{-20} mol, with linear fluorescence response spanning over 4 orders of magnitude.

6. Conclusions

The most critical point in the evaluation of PAH compounds in air samples is the choice of sampling strategy. A different approach is needed if particulate or volatile PAHs are measured. In high-volume sampling the glass fibre

filters are most often used and PUF is used as a back-up 'sorbent'. The sampling volumes which are recommended are 10 000 to 25 000 liters with a flow of 10 l/min. In the occupational environment the choice of the filter is PTFE with XAD-2 as a back-up section. The sampling volume is normally 400 to 1000 l at a flow-rate of 1.5 l/min. The instrumentation in the analysis is not that critical, and most of the analysis can be carried out with HPLC and GC.

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References

[1] K. Nikolaou, P. Masclet and G. Mouvier, Sci. Total Environ., 32 (1984) 103.
[2] IARC Monograph Vol. 32, International Agency for Research on Cancer, Lyon, 1983.
[3] M. Katz and C. Chan, Environ. Sci. Technol., 14 (1980) 838.
[4] S.A. Wise, L.R. Hilpert, G.D. Byrd and W.E. May, Polycyclic Aromat. Comp., 1(1-2) (1990) 81.
[5] D.A. Lane, M. Katz, in I.M. Suffet (Editor), Fate of Pollutants in the Air and Water Environment, Part II, Wiley, New York, 1977, p. 137.
[6] J.N. Pitts, Jr., K.A. Van Cauwenberghe, D. Grosjean, J.P. Schmid, D.R. Fritz, W.L. Belser, Jr., G.B. Knudson and H. Hynds, Science, 202 (1978) 515.
[7] J.N. Pitts, Jr., D.M. Likensgard, P.S. Ripley, K.A. Van Cauwenberghe, L. Van Vaeck, S.D. Shaffer, A.J. Thill and W.L. Belser, Jr., Science, 210 (1980) 1347.
[8] T. Spitzer and W. Dannecker, Anal. Chem., 55 (1983) 2226.
[9] C. Kaiser, A. Kerr, D.R. McCalla, J.N. Lockington and E.S. Gibson, in A. Bjørseth and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, OH, 1980, p. 579.
[10] S.C. Barton, N.D. Johnson and B.S. Das, Final Report: A Feasibility Study of Alternatives to High-Volume Sampling for Labile Constituents of Atmospheric Particulates. Phase 1: Definition of Problem, Ontario Research Foundation Sheridan Research Park, Mississauga, Ontario Report No. P-2923/G, 1979.
[11] D.R. Fitz, D.M. Lokensgard and G.J. Doyle, Atmos. Environ., 18 (1984) 205.

[12] J.F. Galasyn, J.F. Hornig and R.H. Soderbergh, J. Air Pollut. Control Assoc., 34 (1984) 57.

[13] L. Van Vaeck and K. Van Cauwenberghe, Atmos. Environ., 18 (1984) 323.

[14] H. Tokiwa, R. Nakagawa, K. Morita and Y. Ohnishi, Mutat. Res., 85 (1981) 195.

[15] D. Grosjean, K. Fung and J. Harrison, Environ. Sci. Technol., 17 (1983) 673.

[16] E. Brorström, P. Greenfelt and A. Lindskog, Atmos. Environ., 17 (1983) 601.

[17] E. Brorström, P. Greenfelt, A. Lindskog, T. Nielsen and A. Sjodin, in Proceedings of the Seventh International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Press, Columbus, OH, October 1983.

[18] T. Handa, Y. Kato, T. Yamamura, T. Ishii and K. Suda, Environ. Sci. Technol., 14 (1980) 416.

[19] G. Broddin, L. Van Vaeck and K. Van Cauwenberghe, Atmos. Environ., 11 (1977) 1061.

[20] J. König, W. Funcke, E. Balfanz, B. Grosch and F. Pott, Atmos. Environ., 14 (1980) 609.

[21] W. Cautreels and K. Van Cauwenberghe, Atmos. Environ., 12 (1978) 1133.

[22] R. Tommingas, Fresenis Z. Anal. Chem., 297 (1979) 97.

[23] J. Peters and B. Seifert, Atmos. Environ., 14 (1980) 117.

[24] H. Yamasaki, K. Kuwata and H. Miyamoto, Bunseki Kagaku, 27 (1978) 317.

[25] R.C. Lao, R.S. Thomas, in A. Bjørseth and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, OH, 1980, p. 829.

[26] S.C. Barton, N.D. Johnson, B.S. Das, R.B. Caton, in Proceedings of the International Technical Conference of Toxic Air Contaminants, Niagara Falls, NY, 1980, p. 120.

[27] C.S. Davis, R.B. Caton, S.G. Guerin, W.C. Tam, in Abstracts: International Symposium on Polynuclear Aromatic Hydrocarbons, October 26–28, Battelle Columbus Laboratories, Columbus, OH, 1983, pp. 61.

[28] H. Yamasaki, K. Kuwata and H. Miyamoto, Environ. Sci. Technol., 16(1982) 189.

[29] K.E. Thrane and A. Mikalsen, Atmos. Environ., 15 (1981) 909.

[30] A. Bjørseth, VDI-Berichte, 358 (1980) 81.

[31] K. Andersson, J.O. Levin and C.-A. Nilsson, Chemosphere, 12 (1983) 197.

[32] R. Otson and I.-F. Hung, in M. Coode and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods and Metabolism, Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, OH, 1983, p. 999.

[33] T. Handa, K. Suda, Y. Kato, T. Yamamura, T. Ishii and A. Shintani, J. Dispersion Sci. Technol., 1 (1980) 209.

[34] J. König, E. Balfanz, W. Funcke and T. Romanowski, in M. Cooke and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons, Seventh International Symposium, Battelle Press, Columbus, OH, 1983, p. 711.

[35] R.G. Lewis and M.D. Jackson, Anal. Chem., 54 (1982) 592.

[36] J.L. Lindgren, H.J. Krauss and M.A. Fox, J. Air Pollut. Control Assoc., 30 (1980) 166.

[37] G.M. Russwurm, J.A. Stikeleather, P.M. Killough and J.G. Windsor, Jr., Atmos. Environ., 15 (1981) 929.

[38] J.O. Jackson and J.A. Cupps, in P.W. Jones and R.I. Freudenthal (Editors), Polynuclear Aromatic Hydrocarbons (Carcinogenesis, Vol. 3), Raven Press, New York, 1978, p. 183.

[39] K. Andersson, A. Gudehn, J.O. Levin and C.-A. Nilsson, Am. Ind. Hyg. Assoc. J., 44 (1983) 802.

[40] D.S. West, F.N. Hodgson, J.J. Brooks, D.G. DeAngelis, A.G. Desai and C.R. McMillin, Potential Atmospheric Carcinogens, Phase 2/3: Analytical Technique and Field Evaluation, U.S. EPA, Report No. EPA-600/2-81-106, 1981.

[41] T. Vo-Dinh, G.H. Miller, in Abstracts of the Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, OH, 1984, p. 1357.

[42] T.F. Bidleman and C.E. Olney, Bull. Environ. Contam. Toxicol., 11 (1974) 442.

[43] T. Vo-Dinh and R.B. Gammage, in A. Bjørseth and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, OH, 1980, p. 139.

[44] T. Vo-Dinh, in L.H. Keith (Editor), Identification and Analysis of Organic Pollutants in Air, Butterworth, London, 1983, p. 257.

[45] A.M. Krstulovic, D.M. Rosie and P.R. Brown, Anal. Chem., 48 (1976) 1383.

[46] F. You and T.F. Bidleman, Environ. Sci. Technol., 18 (1984) 330.

[47] T. Vo-Dinh and G.H. Miller, in M. Cooke and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods and Metabolism, Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, OH, 1983, p. 1357.

[48] T. Vo-Dinh, A.R. Hawthorne and R.B. Gammage, in M. Cooke and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods and Metabolism, Eighth International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, OH, 1983, p. 1343.

[49] C. Davis, P. Fellin and R. Otson, J. Air Pollut. Control Assoc., 37 (1987) 1397.

[50] K.C. Westaway, A.J. Faulds, A Quantitative Assessment of the Mutagens and Polynuclear Aromatic Hydrocarbons in Dieselized Underground Mines, Chemistry Dept., Laurentian University, Sudbury, Ontario, 1982.

[51] H.L. Falk, P. Kotin and A. Miller, Int. J. Air Poll., 2 (1960) 201.

[52] D. Grosjean, Atmos. Environ., 17 (1983) 2565.

[53] F.S.-C. Lee, W.R. Pierson and J. Ezike, in A. Bjørseth and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, Oh, 1980, p. 543.

[54] S.J. Swarin and R.L. Williams, in A. Bjørseth and A.J. Dennis (Editors), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, OH, 1980, p. 771.

[55] K.A. Schulte, D.J. Larsen, R.W. Hornung and J.V. Crable, Am. Ind. Hyg. Assoc. J., 36 (1975) 131.

[56] S.P. Tucker, in C. Karr, Jr. (Editor), Analytical Methods for Coal and Coal Products, Vol. III, Academic Press, New York, 1979, p. 163.

[57] A. Greenberg and R. Yokoyama, in P. Cheremisinoff (Editor), Air/Particulate Instrumentation and Analysis, Ann Arbor Science, Ann Arbor, MI, 1981, p. 275.

[58] P.W. Jones, R.D. Giammar, P.E. Strup and T.B. Stanford, Environ. Data Technol., 10 (1976) 806.

[59] C.M. White, A.G. Sharkey, Jr., M.L. Lee and D.L. Vassilaros, in P.W. Jones and P. Leber (Editors), Polynuclear Aromatic Hydrocarbons, Ann Arbor Science, Ann Arbor, MI, 1979, p. 261.

[60] R. Tomingas, Fresenius Z. Anal. Chem., 297 (1979) 97.

[61] G.P. Schwartz, J.M. Daisey and P.J. Lioy, Am. Ind. Hyg. Assoc. J., 42 (1981) 258.

[62] F.W. Williams and H.E. Umstead, Anal. Chem., 40 (1968) 2223.

[63] A. Dravnieks, B.K. Krotoszynski, J. Whitfield, A. O'Donnell and T. Burgwald, Environ. Sci. Technol., 5 (1971) 1220.

[64] A. Zlatkis, H.A. Lichtenstein and A. Tishbee, Chromatographia, 6 (1973) 67.

[65] W. Bertsch, R.C. Chang and A. Zlatkis, J. Chromatogr. Sci., 12 (1974) 175.

[66] L. Van Vaeck, G. Broddin and K. Van Cauwenberghe, Biomed. Mass Spectrom., 7 (1980) 473.

[67] J. Hicks and D. Corr, Comparison of Samplers to Measure Inhalable Particulate, Ontario Ministry of the Environment, Report No. ARB-40-83-ARSP, 1983.

[68] R. Leeming and W. Maher, Org. Geochem., 15 (1990) 469.

[69] D.H. Bauw, P.G.M. de Wilde, G.A. Rood and Th.G. Aalbers, Chemosphere, 22 (1991) 713.

[70] Ph. Garrigues and J. Bellocq, J. High Resolut. Chromatogr., 12 (1989) 400.

[71] J. Jadaud, M. Caude, R. Rosset, X. Dutertre and J. Henoux, J. Chromatogr., 464 (1989) 33.

[72] C. Brage and K. Sjöström, J. Chromatogr., 538 (1991) 303.

[73] M.B. Yunker, F.A. McLaughlin, R.W. Macdonald, W.J. Cretney, B.R. Fowler and T.A. Smyth, Anal. Chem., 61 (1989) 1333.

[74] S.A. Wise, L.C. Sander and W.E. May, J. Chromatogr., 642 (1993) 329.

[75] W.K. Raat, G.L. Bakker and F.A. Meijere, Atmos. Environ., 24A (1990) 2875.

[76] S.B. Hawthorne, Anal. Chem., 62 (1990) 663A.

[77] S.B. Hawthorne, M.S. Krieger and D.J. Miller, Anal. Chem., 61 (1989) 736.

[78] J.M. Wong, N.Y. Kado, P.A. Kuzmicky, H.-S. Ning, J.E. Woodrow, D.P.H. Hsieh and J.N. Seiber, Anal. Chem., 63 (1991) 1644.

[79] S.B. Hawthorne, D.J. Miller and J.J. Langenfeld, J. Chromatogr. Sci., 28 (1990) 2.

[80] J.M. Levy, R.A. Cavalier, T.N. Bosch, A.F. Rynaski and W.E. Huhak, J. Chromatogr. Sci., 27 (1989) 341.

[81] C.P. Ong, H.K. Lee and S.F.Y. Li, Environ. Monit. Assess., 19 (1991) 63.

[82] S.B. Hawthorne, J.J. Langenfeld, D.J. Miller and M.D. Burford, Anal. Chem., 64 (1992) 1614.

[83] S.B. Hawthorne, D.J. Miller, D.E. Nivens and D.C. White, Anal. Chem., 64 (1992) 405.

[84] S.M. Pyle and M.S. Setty, Talanta, 38 (1991) 1125.

[85] M.D. Burford, S.B. Hawthorne and D.J. Miller, J. Chromatogr., 609 (1992) 321.

[86] K.D. Bartle, A.A. Clifford, S.B. Hawthorne, J.J. Langenfeld, D.J. Miller and R. Robinson, J. Supercritical Fluids, 3 (1990) 143.

[87] C. Erkey and A. Akgerman, Am. Inst. Chem. Eng. J., 36 (1990) 1715.

[88] K.G. Furton and J. Rein, Chromatographia, 31 (1991) 297.

[89] K.G. Furton and J. Rein, in F.V. Bright and M.E.P. McNally (Editors), Supercritical Fluid Technology (ACS Symposium Series, No. 488), American Chemical Society, Washington, DC, 1992, p. 237.

[90] J.J. Langenfeld, M.D. Burford, S.N. Hawthorne and D.J. Miller, J. Chromatogr., 594 (1992) 297.

[91] K.G. Furton and Q. Lin, Chromatographia, 34 (1992) 185.

[92] K.G. Furton, E. Jolly and J. Rein, J. Chromatogr., 629 (1993) 3.

[93] S. Reindl and F. Höfler, Anal. Chem., 66 (1994) 1808.

[94] J.A. Schmit, R.A. Henry, R.C. Williams and J.F. Dieckman, J. Chromatogr. Sci., 9 (1971) 645.

[95] C. Sander and S.A. Wise, Adv. Chromatogr., 25 (1986) 139.

[96] C. Sander and S.A. Wise, CRC Crit. Rev. Anal. Chem., 18 (1988) 299.

[97] L.C. Sander and S.A. Wise, Anal. Chem., 56 (1984) 504.

[98] S.A. Wise and W.E. May, Anal. Chem., 55 (1983) 1479.

[99] L.C. Sander and S.A. Wise, Anal. Chem., 59 (1987) 2309.

[100] L.C. Sander and S.A. Wise, Anal. Chem., 61 (1989) 1749.

[101] S.A. Wise, W.J. Bonett, F.R. Guenther and W.E. May, J. Chromatogr. Sci., 19 (1981) 457.

[102] S.A. Wise, L.C. Sander, R. Lapouyade and P. Garrigues, J. Chromatogr., 514 (1990) 111.

[103] W.E. May and S.A. Wise, Anal. Chem., 56 (1984) 225.

[104] A. Sisovic and M. Fugas, Env. Monit. Assess., 18 (1991) 235.

[105] T. Ramdahl, G. Becher and A. Bjorseth, Identif. Anal. Org. Pollut. Air, (1984) 339.

[106] A. Kurganov and K.K. Unger, Chromatographia, 39 (1994) 175.

[107] G. Lamprecht and J.F.K. Huber, Chromatographia, 34 (1992) 376.

[108] S.-W. Zhou, G.-Y. Ren and S.-Y. Yu, Atmos. Environ., 23 (1989) 863.

[109] A. Bemgard, A. Colmsjo and B.-O. Lundmark, J. Chromatogr., 595 (1992) 247.

[110] V.M. Pozhidaev and K.A. Pozhidaeva, J. Anal. Chem. USSR, 44 (1989) 1716.

[111] V.A. Gerasimenko and V.M. Nabivach, J. Chromatogr., 498 (1990) 357.

[112] V.S. Ong and R.A. Hites, Anal. Chem., 63 (1991) 2829.

[113] C.G. Blanco, J. Blanco, P. Bernad and M.D. Guillen, J. Chromatogr., 539 (1991) 157.

[114] M.D. Guillen, M.J. Iglesias, A. Dominguez and C.G. Blanco, J. Chromatogr., 591 (1992) 287.

[115] J.W. Childers, N.K. Wilson and R.K. Barbour, Appl. Spectrosc., 43 (1989) 1344.

[116] J.R. Cretney, H.K. Lee, W.J. Graeme, W.H. Swallow and M.C. Taylor, Environ. Sci. Technol., 19 (1985) 397.

[117] G. Castello and T.C. Gerbino, J. Chromatogr., 642 (1993) 351.

[118] L.R. Hilpert, Biomed. Environ. Mass Spec., 14 (1987) 383.

[119] J. Semmler, P.W. Yang and G.E. Crawford, Vibrational Spectrosc., 2 (1991) 189.

[120] M. Seym and H. Parlar, Toxicol. Environ. Chem., 31/32 (1991) 227.

[121] J.A. Lebo, J.L. Zajicek, T.R. Schwartz, L.M. Smith and M.P. Beasly, J. Assoc. Off. Anal. Chem., 74 (1991) 538.

[122] I.D. Brindle and X.-F. Li, J. Chromatogr., 498 (1990) 11.

[123] K.G. Furton, E. Jolly and G. Pentzek, J. Chromatogr., 642 (1993) 33.

[124] A.J. Kubis, K.V. Somayajula, A.G. Sharkey and D.M. Hercules, Anal. Chem., 61 (1989) 2516.

[125] H.T. Butler, M.E. Coddens, S. Khatib and C.F. Poole, J. Chromatogr. Sci., 23 (1985) 200.

[126] K. Jinno and S. Niimi, J. Chromatogr., 455 (1988) 29.

[127] C. Yan and D.E. Martire, J. Phys. Chem., 96 (1992) 3489.

[128] C. Yan and D.E. Martire, J. Phys. Chem., 96 (1992) 3505.

[129] Y. Walbroehl and J.W. Jorgenson, Anal. Chem., 58 (1986) 479.

[130] S. Nie, R. Dadoo and R.N. Zare, Anal. Chem., 65 (1993) 3571.

[131] R.O. Cole, M. Sepaniak, W.L. Hinze, J. Gorse and K. Oldiges, J. Chromatogr., 557 (1991) 113.