

Selective clean-up for polynuclear aromatic compounds in airborne particles and soil

Torsten Spitzer

Environmental, Industrial and Food Analysis, Leipziger Strasse 68, 3330 Helmstedt (Germany)

ABSTRACT

Urban air particulate matter, internal combustion engine particulate emissions, gas turbine particulate emissions and soil were analysed for polynuclear aromatic compounds. Polynuclear aromatic compounds were isolated by adsorption chromatography on XAD-2. Polynuclear aromatic hydrocarbons (PAHs), polynuclear aromatic ketones and nitro-PAHs were obtained together in the aromatic fraction, while interfering compounds were absent. Glass capillary gas chromatography with the stationary phases OV-1, SE-54, Dexsil 300 and OV-25 was performed, and benzo[*a*]pyrene, 7-*H*-benz[*de*]anthracene-7-one and related compounds were identified. Differences between PAH profiles are discussed. It is concluded that cyclopenta[*cd*]pyrene and benzo[*ghi*]fluoranthene are rapidly decomposed in the atmosphere. 7-*H*-Benz[*de*]anthracene-7-one and 6-*H*-benzo[*cd*]pyrene-6-one are degraded during atmospheric exposure at a similar rate to benzo[*a*]pyrene, and nitro-derivatives are not formed in substantial amounts.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are lipophilic substances, and carcinogenic properties are attributed to many compounds of this class [1]. Determination of these compounds involves solvent partition, liquid chromatography or HPLC, and a large number of such methods have been reported and reviewed [2].

While PAHs are non-polar, derivatives of PAHs containing oxygen, sulphur or nitrogen atoms will have a higher polarity. PAHs and their derivatives or structurally related compounds thus form the larger group of polynuclear aromatic compounds (PACs). A method of determination should therefore deal with PACs as a group of compounds having one property in common: the polynuclear aromatic structure. Thus, an analytical method based on this common property was developed. It takes advantage of selective adsorption chromatography of PACs on XAD-2 followed directly by capillary GC or further fractionation by liquid chromatography [3,4].

7-*H*-Benz[*de*]anthracene-7-one (benzanthrone) and

other polynuclear aromatic ketones (PAKs) are present in particulate emissions of combustion sources at concentrations similar to PAHs. Furthermore, polar derivatives are found during exposure of particulate-adsorbed PAHs to an environment of air and light. All such compounds are not detected if standard isolation procedures of PAHs by clean-up on silica gel are employed [5–8].

Multistep procedures of isolation are required if PAHs are determined along with their carbonyl and nitro derivatives [9]. Research described in the present study ameliorates this situation. It is demonstrated that PAHs can be conveniently characterized along with PAKs in a one-step procedure that involves one uniform fraction of column eluate from the isolation procedure.

EXPERIMENTAL

Reagents and standards

Solvents were glass-distilled through a 40-cm-long column. XAD-2 of particle size 150–200 μm was supplied by Serva (Heidelberg, Germany). Stationary GC phases were purchased from Phase Separation

tions (Queensferry, UK). Chemicals and standards were obtained from Merck (Darmstadt, Germany), Wako (Tokyo, Japan) or Tokyo Kasei (Tokyo, Japan).

Particulate matter and soil

Air particulate matter was obtained by high-volume sampling at a sampling rate of 50–100 m³/h. Membrane filters (Type ST 69, 1.2 μm pore size, Schleicher & Schüll, Germany) were used. Total sampling time was 24 h for air particulate matter. Gas turbine particulates and internal combustion engine particulates were obtained by high-volume sampling for 60 min at a rate of 50–100 m³/h using glass fibre filters (Type 6, Schleicher & Schüll). The sampling apparatus was placed behind the turbine or exhaust ducts. Soil (Anjo soil, Japan, mineral soil, 1.8% carbon) was spiked with nitro derivatives of PAHs and subjected to analysis.

Extraction of PACs

Extraction of particulate matter was carried out in a Soxhlet apparatus. Pure toluene was used as a solvent, and total extraction time was 4 h, which corresponded to sixteen Soxhlet cycles. Soil samples were dried over silica gel for 48 h, and also extracted in a Soxhlet apparatus with 5% ethanol in toluene.

Isolation of PACs

XAD-2 of 150–200 μm particle size was slurry-packed into a glass column of 9 cm × 1.4 cm I.D. The column was washed with 20 ml of toluene, followed by 50 ml of ethanol. The concentrated (0.5 ml or less) crude sample solution was transferred to the top of the column. Elution was carried out with 25 ml of ethanol (fraction A), 10 ml of *n*-pentane and 10 ml of ethanol (fraction B), and 12 ml of toluene and 10 ml of ethanol (fraction C). The column was then eluted with an additional 20 ml of toluene, followed by 20 ml of ethanol, and could then be used for the next analysis. Fraction C was concentrated to 0.5 ml using a rotary evaporator, and aliquots of the concentrated solution were injected into the gas chromatograph.

Gas chromatography

GC was carried out with Hitachi or Carlo Erba instruments. They were modified for capillary column use and equipped with split-splitless injectors.

TABLE I

RECOVERIES OF SOME COMPOUNDS IN THE TOLUENE ELUATE FROM XAD-2

Substance	Recovery (%)
Benzo[<i>e</i>]pyrene	95
Benanthrone	98
1-Nitropyrene	98
1,2,7,8-Dibenzacridine	70
6-Nitroquinoline	0
Diethylphthalate	0
<i>n</i> -Eicosane	0

The temperature programmes were 110–260°C, and the heating rate was 4°C/min. Injector temperature was 280°C, and detector temperature was 300°C. Capillary columns were home-made Pyrex columns coated with SE-54, OV-25 and Dexsil 300, and one fused-silica column coated with OV-1.

RESULTS AND DISCUSSION

Table I lists recoveries of some components representing different classes of PACs and other substances. These data demonstrate that the suitability of clean-up on XAD-2 is not limited to parent PAHs. Oxygenated PAHs have been found together with PAHs in urban air particulate matter [10,11] and in particulate emissions of combustion sources [12,13]. Nitro derivatives of PAHs have also been found in particulate matter [14]. Nitro-PAHs can be determined conveniently with negative-ion chemical ionization MS coupled with GC, while PAHs can be present in a 10–100 fold excess in the sample [15,16]. Thus, capillary GC coupled with different detectors successfully provides qualitative and quantitative information on PAHs and their derivatives without prior separation.

Urban air particulate matter

Fig. 1 displays two chromatograms of PACs isolated from urban air particulate matter by adsorption chromatography on XAD-2. All major peaks are due to PAHs except two substances. These are 7-*H*-benz[*de*]anthracene-7-one (benanthrone, peak A) and 6-*H*-benzo[*cd*]pyrene-6-one (peak B, co-eluted with perylene). 6-*H*-Benzo[*cd*]pyrene-6-one

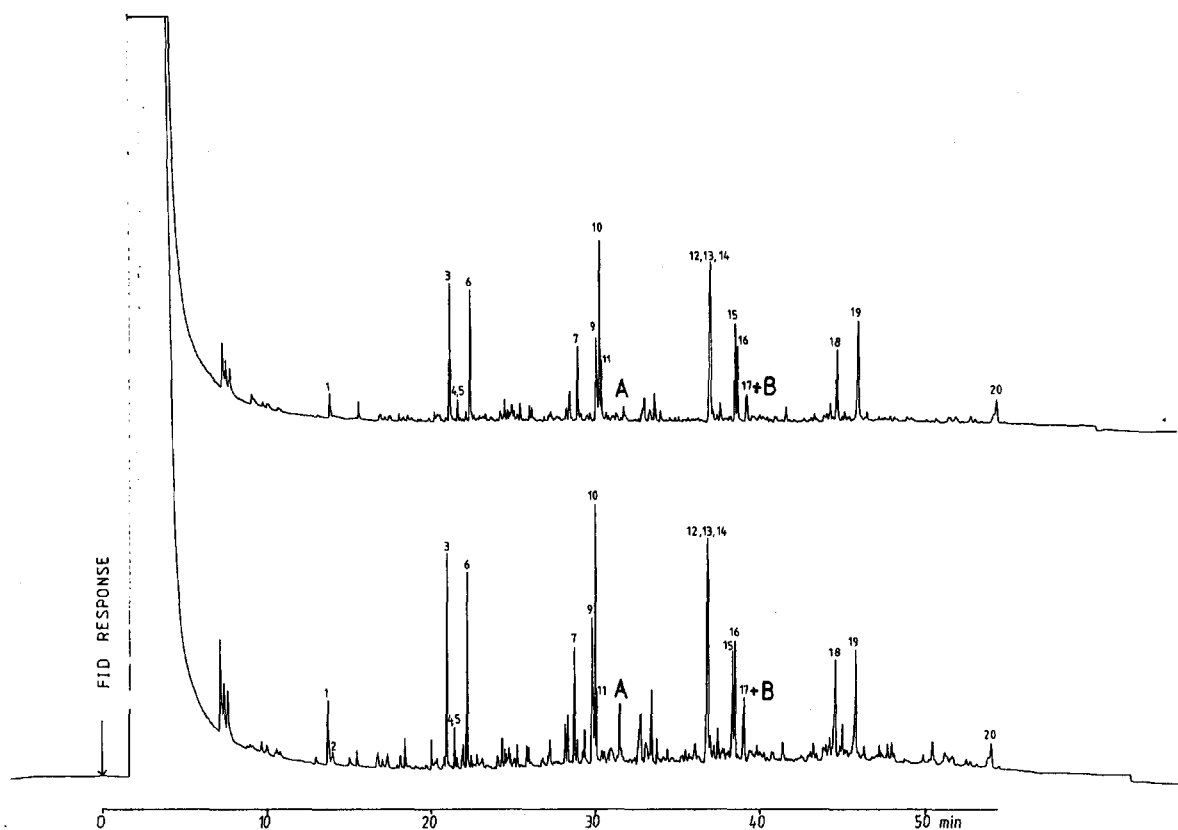


Fig. 1. Gas chromatograms of PACs from two samples of urban air particulate matter. Column: 40 m \times 0.3 mm I.D., Dexsil 300. Peaks: 1 = phenanthrene; 2 = anthracene; 3 = fluoranthene; 4 = acephenanthrylene; 5 = aceanthrylene; 6 = pyrene; 7 = benzo[ghi]fluoranthene; 9 = benz[a]anthracene; 10 = chrysene; 11 = triphenylene; 12 = benzo[b]fluoranthene; 13 = benzo[j]fluoranthene; 14 = benzo[k]fluoranthene; 15 = benzo[e]pyrene; 16 = benzo[a]pyrene; 17 = perylene; 18 = indeno[1,2,3cd]pyrene; 19 = benzo[ghi]perylene; 20 = coronene; A = benzanthrone; B = 6-*H*-benzo[cd]pyrene-6-one.

can be identified by additional GC analysis on SE-54 (co-elution with benzo[a]pyrene) or GC-MS (MW = 254).

The upper chromatogram in Fig. 1 reveals an excess of benzo[e]pyrene (peak 15) over benzo[a]pyrene (peak 16). Concentrations of benzo[ghi]fluoranthene and benz[a]anthracene are close to the level of triphenylene (peak 11). Benzanthrone (peak A) and 6-*H*-benzo[cd]pyrene-6-one (peak B) are minor components.

A slight excess of benzo[a]pyrene over benzo[e]pyrene is found in the lower chromatogram. The relative amounts of benzanthrone (peak B) and 6-*H*-benzo[cd]pyrene-6-one are higher, and benzo[ghi]-

fluoranthene (peak 7) and benz[a]anthracene (peak 9) are in a substantial excess over triphenylene.

PACs in the lower chromatogram have undergone less atmospheric change than PACs in the upper chromatogram. This can be deduced from the fact that the amounts of benzo[ghi]fluoranthene, benz[a]anthracene or benzo[a]pyrene relative to benzo[e]pyrene are lower than the amounts found in major sources [17] of PAC emission (e.g., combustion engines, gas turbines, residential heating). Other important indicators of atmospheric degradation are benzanthrone and 6-*H*-benzo[cd]pyrene-6-one. Both components disappear at a slightly higher rate than benzo[a]pyrene during exposure to light and

atmosphere. Thus, determination of these two compounds is important in providing information on the chemical fate PAHs have undergone in the atmosphere. Since atmospheric conditions in the summertime are more PAH-degrading than atmospheric conditions in the wintertime, a comparison of PAH profiles obtained in summer and winter can give some information on the stability of PAHs in the atmosphere [18].

Finally, both chromatograms in Fig. 1 prove that nitro derivatives of PAHs are not present as major components.

Internal combustion engine particulate emissions

Fig. 2 displays a profile of PACs isolated from internal combustion engine exhaust by clean-up on XAD-2.

OV-25 was chosen as a stationary phase in order to separate isomeric benzofluoranthenes (peaks 12-14). On SE-54, benzofluoranthenes are also separated,

but resolution on OV-25 is better [19,20]. Cyclopenta[*cd*]pyrene is revealed as a major compound among PAHs emitted. However, this compound rapidly decays during exposure to the atmosphere. Benzanthrone (peak A) and 6-*H*-benzo[*cd*]pyrene-6-one (peak B) are also released. Nitroderivatives of PAHs would also appear in this chromatogram if they are present. These compounds appear at much lower concentrations than PAHs [9] and are not visible as major peaks in this chromatogram. Benzo[*ghi*]perylene (peak 19) has a substantial excess over indeno[1,2,3*cd*]pyrene (peak 18). These data are in accordance with results published elsewhere [21], but additional information on PAKs is provided here.

Aircraft turbine particulate emissions

Fig. 3 displays a profile of PACs obtained from aircraft turbine particulate emissions after clean-up on XAD-2.

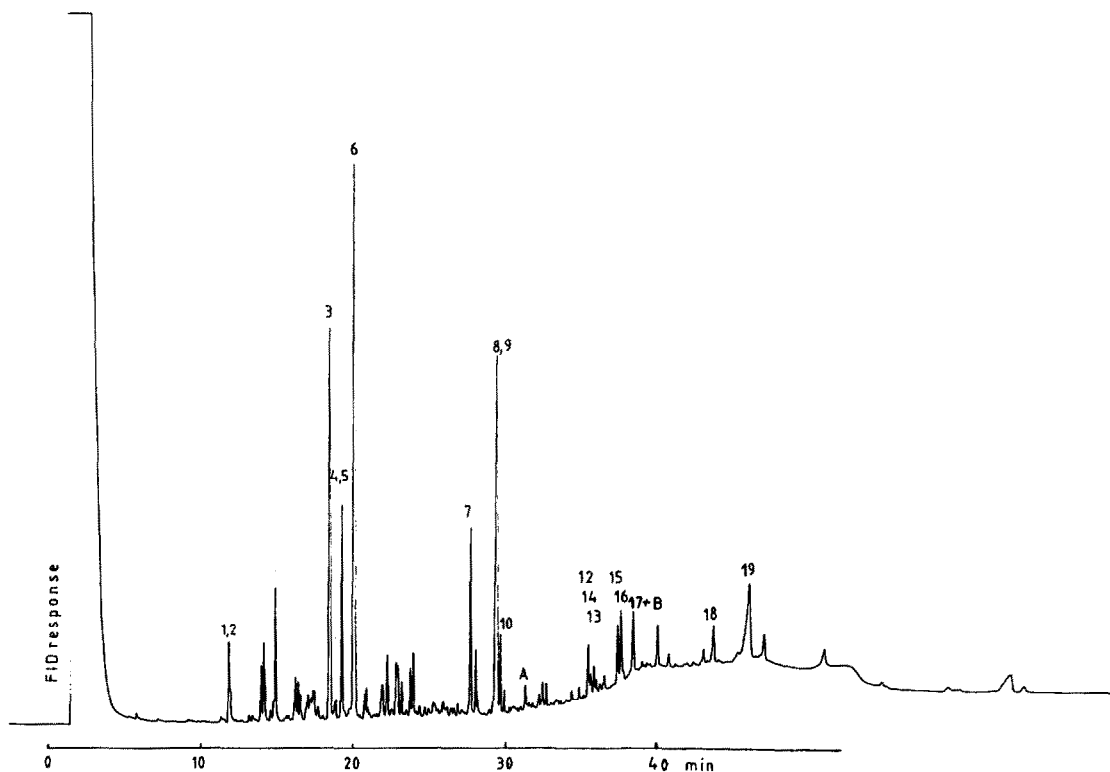


Fig. 2. Gas chromatogram of PACs from internal combustion engine particulate emissions. Engine: 1200 cm³ air cooled (VW motor works, Wolfsburg, Germany). Column: 25 m × 0.3 mm I.D., OV-25. Peak: 8 = cyclopenta[*cd*]pyrene; other peaks as in Fig. 1.

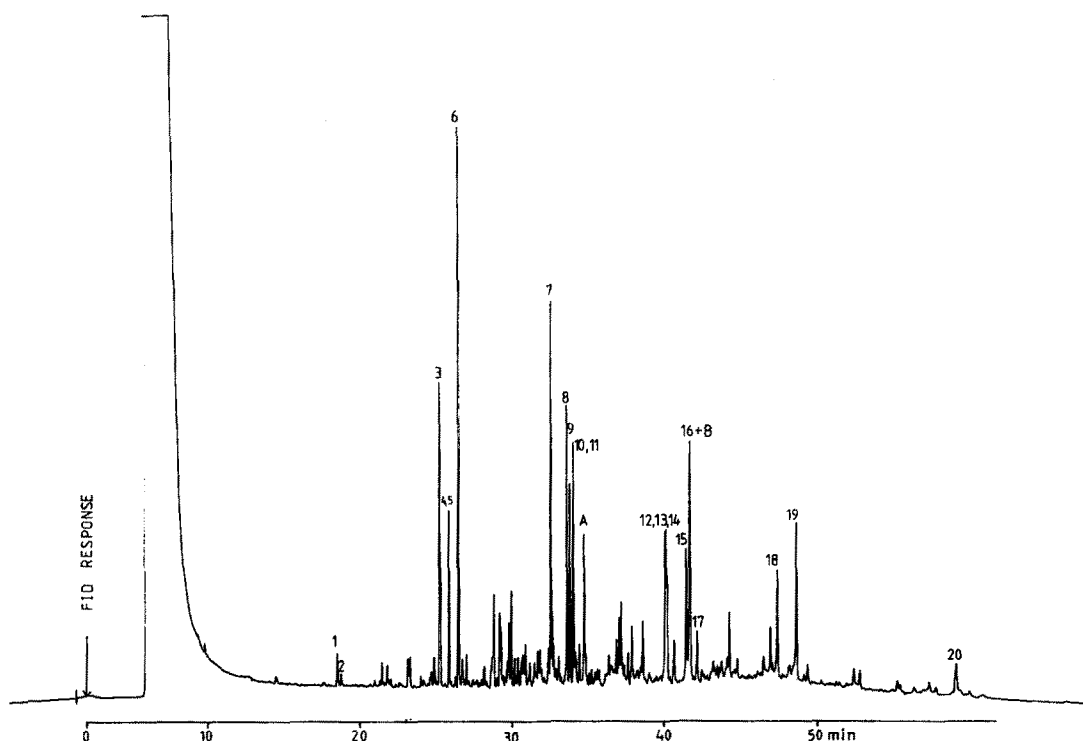


Fig. 3. Gas chromatogram of PACs from aircraft turbine particulate emissions. Engine: Pratt & Whitney JT3D3 gas turbine. Column: 70 m \times 0.3 mm I.D., SE-54. Peaks as in Figs. 1 and 2.

SE-54 was chosen as a stationary phase for GC separation of PAHs. There is a partial separation of benzofluoranthenes (peaks 12-14) because of the high efficiency of the capillary column. 6-*H*-Benzo[*cd*]pyrene-6-one is co-eluted with benzo[*a*]pyrene (peak 16 + B). Identification of this compound can be achieved by additional chromatography on OV-1 (co-elution with benzo[*e*]pyrene occurs) or by GC-MS. Benzanthrone is also present as a major component. The relative amount of cyclopenta[*cd*]pyrene is lower than encountered in internal combustion engine particulate emissions. Indeno[1,2,3*cd*]pyrene and benzo[*ghi*]perylene are present in similar amounts.

Soil

1-Nitronaphthalene, 2-nitronaphthalene, 2-nitrofluorene, 3-nitrofluoranthene, 1-nitropyrene and 6-nitrochrysene were added to soil, and the soil was

then analysed by Soxhlet extraction with toluene and isolation of PACs by clean-up on XAD-2. The column eluate containing the aromatic fraction was further analysed by capillary GC with electron-capture detection.

The resulting gas chromatogram is shown in Fig. 4. This time a fused-silica capillary column coated with OV-1 was used in analysis. There are almost no interfering compounds giving rise to signals in the electron-capture detector. The concentration of 6-nitrochrysene added to the soil was 110 $\mu\text{g}/\text{kg}$.

CONCLUSION

Isolation of PACs by adsorption chromatography on XAD-2 is a simple chromatographic separation based on selectivity and not high efficiency of the separation column. Isolation of PACs is achieved

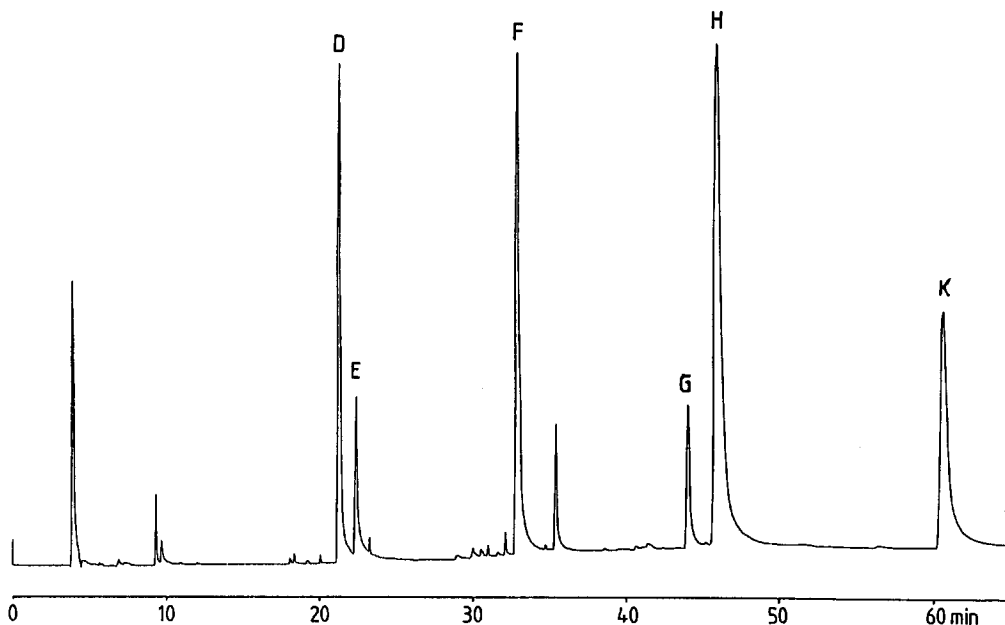


Fig. 4. Gas chromatogram of nitroarenes recovered from soil. Column: 25 m × 0.3 mm I.D., OV-1. Peaks: D = 1-nitronaphthalene; E = 2-nitronaphthalene; F = 2-nitrofluorene; G = 3-nitrofluoranthene; H = 1-nitropyrene; K = 6-nitrochrysene.

within 30 min, and solvent consumption is 70 ml for one sample. A simple glass column is used instead of an HPLC apparatus. Direct capillary column GC with the aromatic fraction reveals the qualitative nature of PAHs, nitro derivatives, PAKs and other PAH derivatives, and their quantitative ratios. The presence of PACs other than PAHs in the aromatic eluate from the XAD-2 column provides an additional information about decomposition reactions that might have occurred during exposure of PACs to the environment.

Comparing the profiles of PACs in the emission samples (Figs. 2 and 3) to the profiles of PACs in urban air particulate matter (Fig. 1), cyclopenta[*cd*]pyrene can be seen to have disappeared completely. Benzo[*ghi*]fluoranthene also decreased in concentration. Important indicators of degradation are 7-*H*-benz[*de*]anthracene-7-one and 6-*H*-benzo[*cd*]pyrene-6-one, which disappear at similar rates to benzo[*a*]pyrene during atmospheric exposure.

The choice of stationary phases for analysis of PAHs was Dextsil 300, OV-25, SE-54 and OV-1 in this work. Different stationary phases including liquid crystal phases can also be applied successfully

[22,23]. However, because of the large number of components present among PACs, a stationary phase able to separate all compounds is unlikely to exist. Instead of only one purpose-designed phase, at least two or three stationary phases of different polarity should be applied in order to recognize random overlap of components [24].

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