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CLEAN-UP OF POLYNUCLEAR AROMATIC HYDROCARBONS FROM AIR PARTICULATE MATTER ON XAD-2

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SUMMARY

A clean-up procedure is developed for polynuclear aromatic compounds. It is based on adsorption chromatography on XAD-2 and stepwise elution with ethanol, *n*-pentane and toluene. The polynuclear aromatic fraction of air particulate matter is isolated by this method and analyzed by glass capillary gas chromatography. Recoveries of nine polynuclear aromatic compounds are reported. The efficiency of group isolation is demonstrated with mixtures of polyaromatic compounds, phthalates and hydrocarbons.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are carcinogenic^{1,2} and appear in the environment at concentrations at parts per 10⁶ and 10⁹ levels. Their determination requires efficient separation from polar and non-polar substrates, which usually appear in the sample at much higher concentrations. This has been achieved by various methods, e.g., column chromatography on silica gel or Sephadex LH-20³ or thin-layer chromatography⁴. In order to obtain a clean PAH fraction, normally several methods have to be combined. The analysis of air particulate matter is usually carried out by solvent extraction, partition, chromatography on silica gel and Sephadex LH-20 and glass capillary gas chromatography (GC)⁵.

Considering the good solubility of PAHs in aromatic solvents, a polymer consisting of aromatic units should adsorb these compounds strongly. One such polymer is XAD-2, a resin consisting of copolymerized styrene and divinylbenzene⁶. This polymer is normally employed in trace enrichment of organic compounds from water^{7,8}. In this work, the applicability of XAD-2 to group separation of polyaromatic compounds from polar and non-polar contaminants in air particulate matter was investigated.

EXPERIMENTAL

Reagents and standards

A reference solution was prepared from phenanthrene, anthracene, pyrene

(Merck, Darmstadt, G.F.R.), benzo(a)pyrene, benzo(e)pyrene, perylene, coronene, benzo(ghi)perylene and chrysene (EGA-Chemie, Steinheim, G.F.R.) at concentrations of 40–300 ppm in toluene. Another stock solution was prepared from *n*-alkanes (C_{16} , C_{18} , C_{20} , C_{22} , C_{23} , C_{24} , C_{25} , C_{26} and C_{28}) (Supelco, Bellefonte, PA, U.S.A.) at concentrations from 180 to 850 ppm and from diethyl and dibutyl phthalate at a concentration of 15,000 ppm in *n*-hexane. Squalane, squalene, *n*-eicosane (Supelco) and nonyl phthalate (Merck) were dissolved in cyclohexane. Dilutions of the desired strength were prepared with cyclohexane, using a Hamilton digital dilutor.

Solvents were glass-distilled through a column 40 cm long. XAD-2 of particle size 150–200 μm was supplied by Serva (Heidelberg, G.F.R.). OV-1 was purchased from Phase Separations (Queensferry, Great Britain).

Sample preparation

Airborne particulates were precipitated on glass-fibre filters (Schleicher & Schüll, Dassel, G.F.R.) with a high-volume sampling system (HVS 100; Sartorius, Göttingen, G.F.R.). The loaded filters (257 mm in diameter) were extracted with toluene or cyclohexane in a Soxhlet extraction apparatus. The extracts were evaporated to dryness at 40°C (rotary evaporator).

A glass column of 1.4 cm I.D. was filled with XAD-2 resin to a height of 9 cm. A solvent reservoir was fitted to the top of the column and a stop-cock to the bottom. The extracts were dissolved in ethanol and transferred quantitatively to the top of the resin bed. The column was then eluted successively with 25 ml of ethanol (polar fraction), 10 ml of *n*-pentane, followed by 10 ml of ethanol (non-polar fraction) and 12 ml of toluene, followed by 10 ml of ethanol (PAH fraction). The solvent flow-rate was adjusted to 2 ml/min. Finally, a further 20 ml of toluene were passed through the column, followed by 25 ml of ethanol, and the column was then ready for the next sample.

The PAH fraction was evaporated to a small volume (0.5 ml). *n*-Dotriacontane was added as an internal standard if quantitative results were to be obtained.

Gas chromatography

Extracts were analysed on a Carlo Erba 4160 high-resolution gas chromatograph, equipped with a flame-ionization detector and a column of OV-1 (30 m \times 0.22 mm I.D., WCOT). The capillary was drawn from Pyrex tubing, high-temperature silanized and coated statically. Column bleed was low up to 300°C, and no deterioration occurred during operation.

RESULTS AND DISCUSSION

Desorption of organic compounds from the macroreticular XAD-2 resin is strongly influenced by the type of solvent. Table I lists the volumes of different solvents required for complete elution of *n*-alkanes (C_{16} – C_{28}), phthalates (diethyl and dibutyl) and PAHs at column loads of 40 μg per *n*-alkane, 5 μg per PAH and 1 mg per phthalate. The values were obtained by collecting 20–50-ml portions stepwise from the column eluate and analysis by GC.

n-Pentane is a strong eluent for *n*-alkanes and phthalates, but its drawback is the early elution of phenanthrene and anthracene, which start at 15 ml. On the other

TABLE I
 DESORPTION OF COMPOUND CLASSES FROM XAD-2
 Column: 9 cm × 1.4 cm I.D.

Solvent	Elution volume (ml)		
	<i>n</i> -Alkanes	Phthalates	PAHs
Ethanol	> 150	100	> 150
Isopropanol	100	60	> 150
Acetone	20	20	20
Toluene	20	20	20
Diethyl ether	20	20	40
<i>n</i> -Pentane	20	20	> 150

hand, heavy PAHs such as benzo(*ghi*)perylene require elution volumes in excess of 150 ml. Ethanol is a weak eluent for non-polar compounds and PAHs. Owing to these difficulties, a clean-up with three different solvents was developed, as outlined in Fig. 1. The procedure can remove 200 mg of diethyl phthalate from a sample. Filters can be impregnated with diethyl phthalate⁹ in order to improve the recovery of volatile PAHs (phenanthrene, fluoranthene) from air.

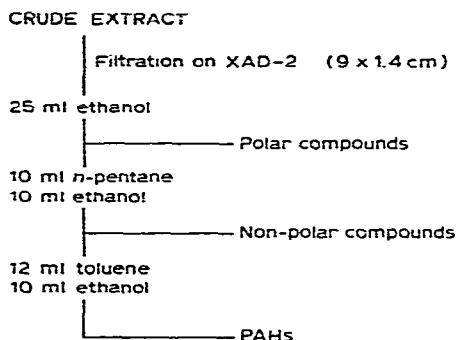


Fig. 1. Scheme for clean-up on XAD-2.

The solvents acetone, toluene and diethyl ether are strong eluents and do not achieve any group separation of alkanes and PAHs on XAD-2 if they are used alone.

Recoveries were determined by applying standard mixtures of PAHs to the column and elution according to the standard procedure outlined in Fig. 1. Values were obtained by capillary GC with an internal standard (*n*-dotriacontane) and are listed in Table II. Repeating the clean-up procedure with a sample did not cause losses of PAHs, apart from phenanthrene and anthracene. When fresh resin was used for the first time, recoveries of some PAHs [*e.g.*, benzo(*a*)pyrene] were low. Nevertheless, irreversible absorption does not occur after repeated use of the column.

The efficiency of clean-up was tested with artificial mixtures containing nine PAHs (amounts as given in Table II) and increasing amounts of six contaminants as listed in Table III.

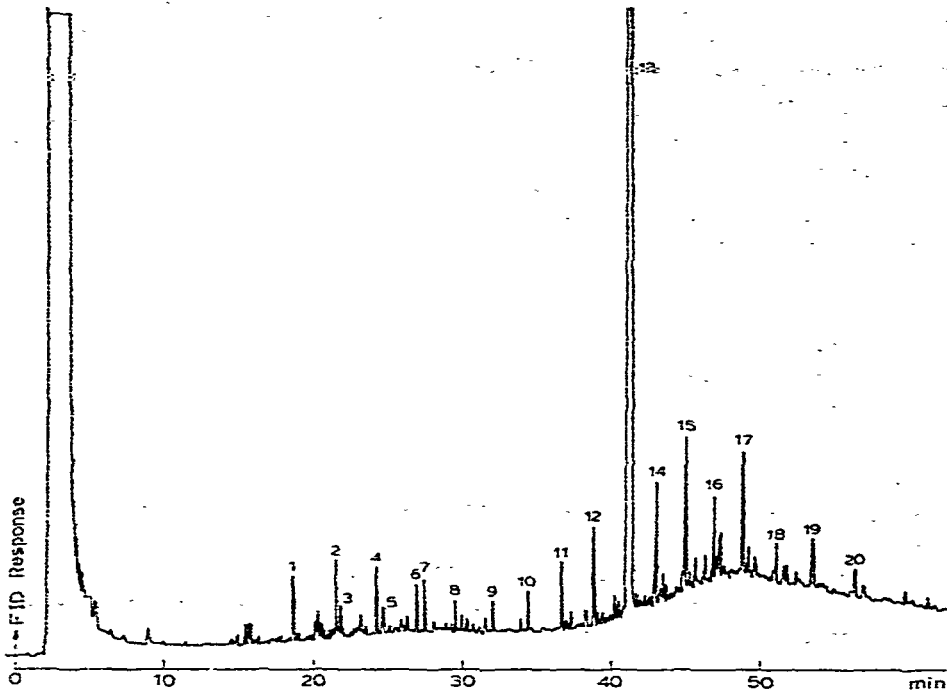


Fig. 2. Gas chromatogram obtained from the crude extract of air particulates. GC conditions: injection, 2 μ l splitless; injection port temperature, 290°C; column, 30 m \times 0.22 mm I.D.; stationary phase, OV-1; temperature programme, 110 to 300°C at 4°C/min. Peaks: 3 = pristane; 5 = phytane; 7 = unknown; 13 = *n*-pentacosane + phthalate; remaining peaks 1–20, C₁₆–C₃₂ *n*-alkanes.

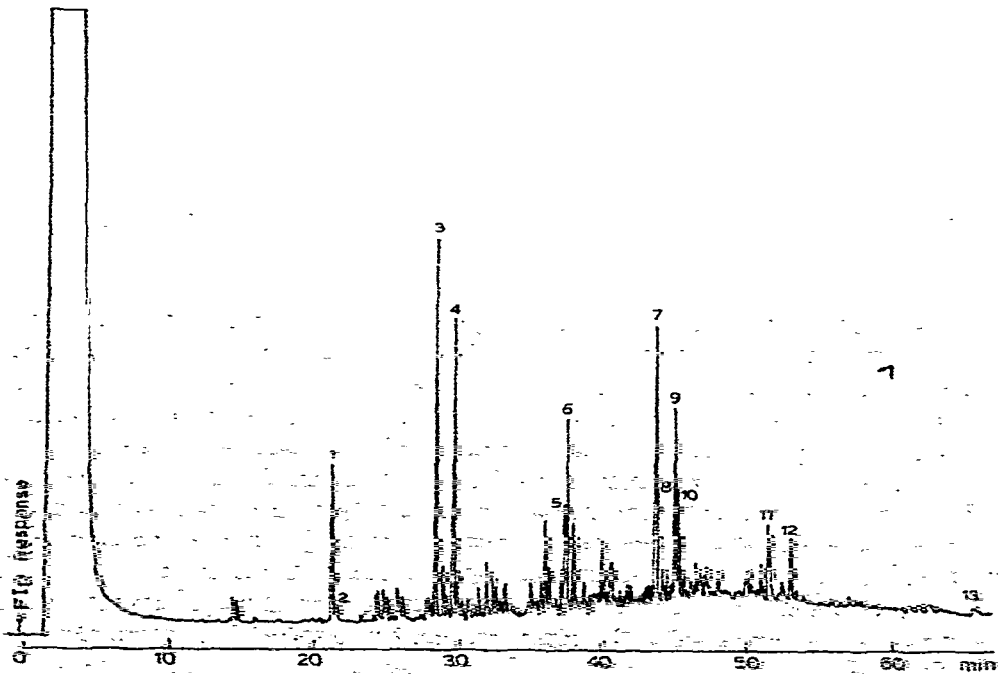


Fig. 3. PAH profile of air particulates after clean-up on XAD-2. Conditions as in Fig. 1. Peaks: 1 = phenanthrene; 2 = anthracene; 3 = fluoranthene; 4 = pyrene; 5 = benz(*a*)anthracene; 6 = chrysene + triphenylene; 7 = benzo(*b*)fluoranthene + benzo(*j*)fluoranthene; 8 = benzo(*k*)fluoranthene; 9 = benzo(*e*)pyrene; 10 = benzo(*a*)pyrene; 11 = indeno(1,2,3-*cd*)pyrene; 12 = benzo(*ghi*)perylene; 13 = coronene.

TABLE II
RECOVERIES OF POLYNUCLEAR AROMATIC HYDROCARBONS AFTER CLEAN-UP ON XAD-2

Compound	Amount (μg)	Recovery (%)	
		Cleaned-up once	Cleaned-up twice
Phenanthrene	14.1	81	69
Anthracene	9.8	81	65
Pyrene	2.8	85	90
Chrysene	5.6	88	87
Benzo(e)pyrene	3.5	93	91
Benzo(a)pyrene	2.0	85	86
Perylene	5.8	91	83
Benzo(ghi)perylene	9.8	95	70
Coronene	2.3	91	82

Contaminants are eluted with the polar or non-polar fraction. At higher column loads, however, they exhibit tailing behaviour on the XAD-2 resin, and less than 1% of their total amount is co-eluted with PAHs. Repeating the clean-up would purify the PAH fraction completely in such a case.

Fig. 2 shows the gas chromatogram of a cyclohexane extract from a glass-fibre filter after sampling 316 mg of urban particulates in the city of Hamburg. The extract was evaporated to 10 ml. All PAHs overlap with large amounts of co-extractants which are present in much higher concentrations.

Clean-up on XAD-2 removes polar and non-polar contaminants; Fig. 3 shows the PAH fraction from 228 mg of air particulates which had been extracted with toluene. The PAH fraction was evaporated to a volume of 0.5 ml.

TABLE III
AMOUNTS OF SIX COMPOUNDS ELUTED WITH THE PAH FRACTION FROM XAD-2 AFTER A SINGLE CLEAN-UP

Compound	Column load			
	10 μg	100 μg	1 mg	> 1 mg*
1-Eicosene	0	0.2 μg	0.8 μg	4.2 μg (9 mg)
n-Eicosane	0	0.2 μg	0.7 μg	3.9 μg (11 mg)
Squalane	0	1.1 μg	4.6 μg	35 μg (12.5 mg)
Dimonyl phthalate	0	0	4.9 μg	50 μg (15 mg)
n-Octacosane	0	0.7 μg	11.5 μg	46 μg (10 mg)
Squalene	0	0	0.7 μg	128 μg (28 mg)

* The actual column load is given in parentheses.

CONCLUSION

XAD-2 is a suitable adsorbent for group separation of PAHs from polar and non-polar compounds. It readily provides the PAH profile of airborne particulates.

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