

## DETERMINATION OF POLYAROMATIC HYDROCARBONS IN THE GAS PHASE OF AIR

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Received January 26, 1995

Accepted April 8, 1995

Polyaromatic hydrocarbons (PAH) were isolated from the gas phase of air by sorption on the Separon CHN polymeric sorbent and quantitated by capillary gas chromatography using flame ionization detection. The conditions for PAH desorption from the sorbent were examined. Hexane, giving desorption recoveries of 90–100%, was the most efficient eluent. The recovery was found independent of the amount of PAH sorbed over a wide region. Analyte losses associated with the removal of eluent were investigated. Based on the experimental results, a procedure was developed for the determination of PAH in the gaseous phase of air and tested on field samples. When 5 m<sup>3</sup> volumes of air are sampled, the limits of determination of the individual PAH are from 10 to 20 ng/m<sup>3</sup>.

Polycyclic aromatic hydrocarbons (PAH) are among serious environmental pollutants; for 9 of them, their carcinogenesis has been proved. Their occurrence in the environment is mainly associated with imperfect combustion of fossil fuels.

PAH in air are present either in the gas phase or sorbed on particulate matter of aerosol droplets. Studies examining the distribution of PAH in air between particulate matter and the gas phase found that only PAH with 2–4 rings in a molecule and with molecular weights not exceeding 252 pass into the gas phase whereas PAH with more than four rings in a molecule are nearly completely bound to particulate matter<sup>1</sup>. With respect to their occurrence in air, PAH can be crudely divided into 3 categories: (i) volatile PAH occurring nearly completely in the gas phase, such as indene, naphthalene, biphenyl, acenaphthene, and fluorene; (ii) PAH occurring both in the gas phase and bound to particulate matter, such as phenanthrene, anthracene, fluoranthene, and pyrene; and (iii) PAH sorbed on particulate matter such as benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, and benzo[*g,h,i*]perylene. There are no sharp boundaries between the categories, the situation being affected by the total PAH concentration in air, temperature, season of the year, time and contact of PAH with particulate matter, etc.<sup>2</sup>.

Quantitation of PAH in air implies analysis of multicomponent mixtures in trace concentrations. Particulate matter is collected on microfilters containing silica or glass fibres, silver membrane filters, or teflon filters, and analyzed<sup>3–5</sup>. Air freed from

particulate matter is passed through sorbents on which the PAH are trapped. Polymeric sorbents, e.g. Amberlite XAD-2, Tenax GC, Porapak PS, and other materials such as polyurethane foam are most commonly used<sup>1,6-8</sup>. Subsequently, the PAH are desorbed with a suitable solvent (benzene, dichloromethane, acetone, methanol, cyclohexane) or solvent mixture, preconcentrated if desirable, and quantitated chromatographically. GC with MS detection is suitable for the determination of volatile PAH, whereas LC with fluorimetric detection is better suited to the analysis of higher PAH.

The present work was aimed at finding conditions for an efficient separation and preconcentration of PAH from the gas phase of air on Separon CHN polymeric sorbent, followed by their capillary gas chromatographic analysis.

## EXPERIMENTAL

### Materials

PAH in air were trapped on the Separon CHN sorbent (Tessek, Prague) 150–170  $\mu\text{m}$  grain size; this is an acrylonitrile–divinylbenzene copolymer 650  $\text{m}^2/\text{g}$  specific surface area.

The PAH included naphthalene (NF), acenaphthene (AC), fluorene (FL), phenanthrene (FE), fluoranthene (FN), and pyrene (PY), which were substances from the standards collection of the Department. The substances were used in methanolic solutions at concentrations of 0.5–100  $\mu\text{g}/\text{ml}$ . The standard solutions were kept in dark and cold to prevent any degradation.

The following distilled solvents were employed for sorbent purification and PAH desorption: methanol, acetone, hexane, and chloroform. Their purity was checked by gas chromatography.

### Apparatus

Air samples were taken by using apparatus consisting of a sampling probe, a membrane pump 5 l/min maximum throughput, and a wet gas meter.

The sampling probe was made of Teflon. Particulate matter was trapped on a filter in the probe, consisting of glass microfibrils density Z5 (FILPAP, Steti). The probe contained spacer rings 14 mm i.d., defining the space available for PAH trapping. The height of the ring governs the sorbent column length, and if several rings are used, the sorbent space can be divided into sections with microfilters. The probe end was formed by a glass frit.

Gas chromatographic analyses were performed on a Varian 3600 instrument. The parameters were as follows: a DB-5 capillary column 30 m long, 0.518 mm i.d.; hydrogen as the carrier gas; a flame ionization detector (FID); temperature programme: 80  $^{\circ}\text{C}$  for 1 min, increase to 250  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C}/\text{min}$ , 8 min; injection: splitless; volume injected: 1  $\mu\text{l}$ .

### Sorbent Purification

Sorbent was purified prior to use. Two purification procedures were compared: extraction in a Soxhlet apparatus, and simple elution. In the former procedure, extraction was performed with methanol for 3 h and with acetone for another 3 h. In the latter procedure, about 1 g of sorbent was placed in a column and eluted at a flow rate of 1–2 ml/min, 10 ml of a solvent or a series of solvents were used. The solvents included hexane, chloroform, acetone, and methanol. After the treatment (by either procedure) the sorbent was dried in air at room temperature. The efficiency of the procedures was assessed based on the total impurity peak area in the chromatogram relative to the analyte peak area.

### Sampling

For each sampling, or each experiment, the probe was filled at underpressure with a new sorbent batch of a known weight of about 0.36–0.40 g, which gave a column 10 mm high, 14 mm in diameter. During the sampling the probe was attached to the pump, whose output was connected to the gas meter. Air volumes of 2 or 5 m<sup>3</sup> were aspirated at a flow rate of 3–5 l/min.

When examining the analyte passage through the probe, the sorbent layer was divided into 3 sections. A volume of 100 µl of a methanolic solution of the standard PAH mixture (1 µg each) was applied to the sorbent in section 1, and 2 or 5 m<sup>3</sup> of pure air were aspirated through the probe.

### PAH Desorption from the Sorbent

To investigate the desorption of PAH from Separon CHN, 100 µl of a standard methanolic solution of PAH at a desired concentration was injected on the sorbent in the sampling probe, methanol was removed with a stream of pure air, and the probe was allowed to rest in dark and cold for 24 h. Subsequently, the PAH were desorbed as follows. The sorbent was transferred into a glass column with a glass wool plug and washed with a solvent (hexane, acetone, methanol) at a flow rate of 1–2 ml/min. Eluate fractions 0.1 to 2 ml in volume were collected and analyzed by gas chromatography, either directly or after preconcentration.

The analytical procedure for field samples was similar. After sampling, the sorbent was transferred from the probe to a desorption column and eluted with hexane. Fractions of 1.5 ml were collected, preconcentrated, and analyzed by gas chromatography.

The reason for sorbent transfer from the probe to a column was as follows. With respect to the aspirated air flow rate the probe had to be so designed that the inner diameter to sorbent column height ratio was about 1.4 : 1. With such configuration, however, solvent desorption was impracticable. By transfer to glass column 6.6 mm i.d. a sorbent column height of 45 mm was obtained, which was well suited to solvent elution.

Sorbent loss during the transfer, arising from the sorbent sticking to the probe wall, was determined for each experiment by weighing the batch. The loss was typically 5–7%, and correction for it was invariably made.

### Desorbate Preconcentration

Several procedures for hexane removal from the desorbate were tested: nitrogen bubbling, solvent entrainment with a nitrogen stream, and partial or complete solvent evaporation in air or in a rotary vacuum evaporator. Losses were determined as follows: 1 ml of a standard PAH solution in hexane was added to a calibrated ground-in test tube, preconcentrated by the method of choice, and diluted to the initial volume of 1 ml, and the gas chromatograms of the initial and final solutions were compared.

## RESULTS AND DISCUSSION

The use of a sorbent which traps all PAH from air and does not release them during the sampling is prerequisite for a successful analysis. Furthermore, a minimal volume of the desorbing agent must be sufficient to desorb the PAH from the sorbent. Since the amounts of PAH concerned are always very low, they must be preconcentrated, which is invariably associated with losses; these must be ascertained experimentally in advance.

The following sorbents were tested: Porapak Q, Tenax GC, Separon CHN, and Separon SE. The final choice was governed by criteria including toluene breakthrough volumes and PAH desorption efficiency. For Separon CHN, the toluene breakthrough volume was found to be 3.5-fold as compared to Porapak Q and Separon SE and 7.4-fold as compared to Tenax GC. The efficiency of PAH desorption from Separon CHN by using conventional solvents is high as well<sup>9</sup>. Toluene was employed as the test substance for determining the breakthrough volumes because defined toluene mixtures with air can be prepared, whereas gaseous mixtures of PAH with air cannot, and toluene as one of the first members of the aromatics series can be expected to behave similarly to PAH with respect to sorption on the sorbents tested.

The sorbent purity is an important factor that can affect the results of analyses. Long-run sorbent extraction in a Soxhlet apparatus using one or several solvents is usually recommended. The results achieved, as compared to simple solvent elution, are given in Table I, listing the methods sorted by efficiency in the ascending order. When ranking the procedures, the total impurity contents of desorbate after treatment as well as the presence of impurities with retention times very close to those of the PAH were taken into account. Table I demonstrates that the use of a single solvent is insufficient and the application of two or three solvents of different polarity is preferable. Furthermore, purification in a Soxhlet apparatus taking several hours was found unnecessary; in fact, a simple elution of impurities from the sorbent with acetone and methanol proved to be most efficient. All the subsequent measurements were made using sorbent so purified.

The next step in the determination of PAH in the gas phase of air consists in PAH desorption from the sorbent. Extraction in a Soxhlet apparatus is unsuitable because large volumes of solvent are required for this. Direct desorption with a solvent was therefore investigated. The desorption curves were measured for all the PAH using solvents of different polarity, viz. hexane, acetone, and methanol. The desorption curves of phenanthrene are shown in Fig. 1, the other desorption curves are similar.

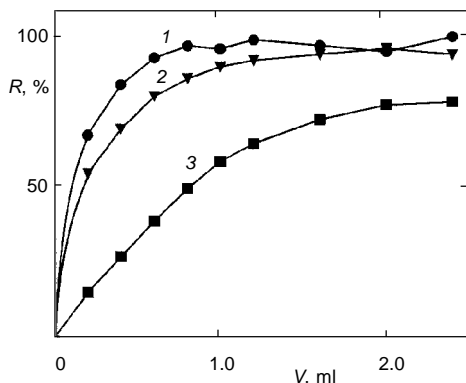


FIG. 1  
Curves of phenanthrene desorption from Separon CHN (sorbent weight 0.36 g). Eluent: 1 hexane, 2 acetone, 3 methanol

Hexane, exhibiting the highest desorption efficiency, was found to suit best as the desorbing agent for PAH: the recoveries of all PAH approached 100% when using 1.2 ml of hexane per 0.36 g of sorbent. Methanol is least suitable: desorption with 2.4 ml of this solvent led to a recovery of mere 80%. The effect of PAH molecular size on the desorption efficiency using hexane is documented by Fig. 2. While lower boiling PAH – naphthalene and acenaphthene – are more than 90% desorbed with 0.4 ml of hexane, a hexane volume of 0.8 ml is necessary to desorb more than 90% of fluoranthene or pyrene. A hexane volume of 1.2 ml is sufficient for achieving a recovery approaching 100% for PAH possessing 2–4 rings. Based on the results obtained, hexane was chosen as the desorbing agent for the subsequent experiments.

Furthermore, the dependence of the desorption recovery on the amount of PAH applied to the sorbent was examined. The hexane volume was invariably 1.5 ml. The

TABLE I  
Separon CHN sorbent purification procedures arranged by increasing efficiency

Order	Purification procedure <sup>a</sup>	Order	Purification procedure <sup>a</sup>
1	elution A	8	Soxhlet M, A
2	elution CH	9	elution A, H
3	elution H	10	elution A, CH
4	elution M	11	elution CH, M
5	elution M, CH	12	elution CH, M
6	elution M, H	13	elution M, A, CH
7	elution M, A	14	elution A, M

<sup>a</sup> A acetone, CH chloroform, H hexane, M methanol.

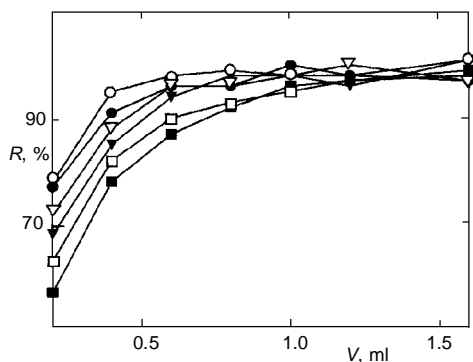


FIG. 2  
Relation between PAH molecular size and its desorption from Separon CHN (sorbent weight: 0.36 g, eluent: hexane). Substance: ○ naphthalene, ● acenaphthene, ∇ fluorene, ▼ phenanthrene, □ fluoranthene, ■ pyrene

average recoveries along with the standard deviations ( $s_r$ ) are given in Table II. The results give evidence that the desorption recovery is virtually independent of the PAH quantity within the region measured. The standard deviations also document that the high desorption efficiencies are not casual.

In some instances, the PAH concentrations in desorbate are insufficient for subsequent chromatographic quantitation. In such cases the desorbate has to be evaporated. This can be associated with analyte losses, as documented by Table III

TABLE II  
Recovery<sup>a</sup> of PAH desorbed from Separon CHN with hexane (sorbent weight 0.36 g)

Substance	Weight, $\mu\text{g}$					
	100		2		0.5	
	$\bar{x}$	$s_r$	$\bar{x}$	$s_r$	$\bar{x}$	$s_r$
NF	100.7	3.2	98.4	4.2	96.4	4.4
AC	98.8	3.4	106.1	5.9	97.1	4.4
FL	97.5	3.0	105.5	1.2	95.6	4.6
FE	96.1	1.1	94.5	6.0	94.5	4.8
FN	95.0	1.8	95.4	5.7	93.9	3.2
PY	93.5	1.4	92.2	2.2	99.8	6.2

<sup>a</sup> Average of 5 measurements with estimated standard deviation.

TABLE III  
PAH losses during evaporation of hexane desorbate

Procedure	Preconcentration degree	Loss, %						$s_r$ , %
		NF	AC	FL	FE	FN	PY	
N <sub>2</sub> bubbling	10 ×	32	28	25	24	25	27	5
Entrainment with N <sub>2</sub> stream	10 ×	17	19	14	14	15	15	4
Free evaporation	10 ×	20	17	12	15	16	14	5
Free evaporation	to dryness	54	31	28	26	29	26	4
Rotary vacuum evaporator	10 ×	49	32	25	29	23	20	8
Rotary vacuum evaporator	to dryness	70	40	40	35	33	40	10

comparing the various hexane removal procedures. The analyte losses are highest when evaporating the solvent in a rotary vacuum evaporator, for low boiling PAH in particular. Incomplete free solvent evaporation in air and entrainment with a nitrogen stream appear to be most gentle; the analyte losses in the two procedures are comparable and the repeatability, in relative standard deviation terms, is 3–7%. With respect to the time consumption, however, only the use of a nitrogen stream appears to be feasible: the time required to remove 90% from 1 ml of solvent is from 5 to 25 min, in dependence on the nitrogen stream flow rate and experimental arrangement; removing this volume by free evaporation is substantially more time consuming. Sorbate evaporation to dryness is unsuitable. At any rate, a 10–20% reduction in PAH recovery must be expected if the desorbate is evaporated.

Analyte loss may also occur during air sampling, viz. by breakthrough. The probe was tested in this respect by dividing it into 3 sections. The PAH contents trapped in sections 1 and 2 were determined by analysis, whereas the PAH contents in section 3 were invariably below the detection limits and therefore were calculated by balance. Table IV demonstrates that no analyte breakthrough occurs in the conditions applied (sample volume up to 5 m<sup>3</sup>, air flow rate up to 300 l/h, sorbent amount in the probe about 0.36 g). A travel of the analyte zone through the sorbent layer, however, was demonstrated, occurring in an inverse dependence on the molecular weight of analyte.

Based on the experimental study, the following procedure was developed for the determination of PAH in the gas phase of air. Aspirate a volume of 2–5 m<sup>3</sup> of the air through a sampling probe containing 0.36–0.40 g of pure Separon CHN sorbent. Transfer the sorbent to a glass column with a silica wool plug purified with hexane.

TABLE IV  
PAH distribution (%) among the sorbent sections in the sampling probe<sup>a</sup> in dependence on sample volume

Substance	2 m <sup>3</sup>			5 m <sup>3</sup>		
	section 1	section 2	section 3	section 1	section 2	section 3
NF	88.1	11.7	0.2	69.0	27.9	3.1
AC	89.9	9.9	0.2	73.4	24.4	2.3
FL	91.3	8.6	0.1	75.3	22.9	1.8
FE	93.3	6.6	0.1	74.8	21.0	1.2
FN	93.9	6.0	0.1	81.1	18.0	1.0
PY	94.7	5.8	0.1	81.6	17.5	1.0

<sup>a</sup> Total Separon CHN sorbent weight 0.36 g.

Desorb PAH from the sorbent with 1.5 ml of hexane, and collect the desorbate in a calibrated test tube. Preconcentrate the desorbate 10–20 fold by using a nitrogen stream, and analyze it by capillary gas chromatography with an FID by injecting a volume of 1  $\mu\text{g}$ . You can omit the preconcentration step if a mass spectrometric detector is available. The recovery from the whole procedure is 85–95% if preconcentration is omitted, and 70–85% for the various PAH if preconcentration step is included. The limit of detection when 5  $\text{m}^3$  of air is aspirated is 10–20  $\text{ng}/\text{m}^3$  for the various PAH; these values also depend on the presence of other substances in air. The limit of determination is roughly one order of magnitude lower if GC-MS is employed. The relative standard deviation of the method, encompassing PAH desorption, 10-fold preconcentration by solvent removal with a nitrogen stream, and chromatographic analysis, lies within the region of  $\pm 7.8$  to  $\pm 8.5\%$  for the various PAH. The relative standard deviations were calculated for PAH applied to the sorbent in a standard solution because preparation of a gaseous mixture of PAH in air at a constant defined concentration is impractical by conventional methods.

The method developed was applied to the analysis of real air samples. We repeatedly sampled air from six selected sites in the Cheb, Sokolov and Tachov districts in 1993 (ref.<sup>10</sup>). The results of some analyses of air sampled in the capital Prague are given in Table V, using the probe and desorption column parameters as described earlier. Since the air sampling was a long-run process and the air composition was variable, the

TABLE V  
Mass concentrations of PAH in air in Prague

Sampling site <sup>a</sup>	Sampling date and time	Sample volume	$\rho$ , $\text{ng}/\text{m}^3$					
			NF	AC	FL	FE	FN	PY
1	10.3.1993 7.45–12.00	0.89	1 130	93	148	463	82	51
1	31.3.1993 8.00–14.30	1.64	1 625	101	136	512	65	30
2	30.3.1994 7.30–16.15	2.05	139	10	10	57	22	10
2	20.4.1994 7.15–17.00	2.28	174	10	15	44	18	10
3	27.4.1994 8.30–16.15	1.78	304	19	20	86	38	14

<sup>a</sup> 1 Pavlov square (Legerova and Jugoslavska streets junction); 2 Studentska street; 3 Vitezne Namesti circus.



results could not be evaluated statistically, i.e., the sampling could not be repeated with a view to comparing the results. Parallel multiple air sampling from a site would require a complex instrumentation.

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