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Large volatility range airborne polycyclic aromatic
hydrocarbons (PAHs) determination by isotope dilution
gas chromatography-mass spectrometry

S. Wybraniec¹, A.P.J.M. de Jong

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¹ Cracow University of Technology, Cracow, Poland

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ABSTRACT

A method was developed for the measurement for polycyclic aromatic hydrocarbons in ambient air by gas chromatography isotope dilution mass spectrometry. The method was designed to measure the largest possible volatility range of PAHs including the abundant naphthalenes. Sample volumes were approx. 500 m³ in size at a sampling rate of approx. 18 m³/h. The sampler contained three sorption stages for the simultaneous capturing of particle bound and low and high volatile gaseous PAHs, respectively. Recoveries of sampling spikes were on average 90%. The detection limit was approx. 5 pg/m³ for the high boiling range PAHs. Results obtained showed a quite steady profile for most PAHs in background air in The Netherlands. Comparison of abundance ratios with data in the literature indicate that traffic exhausts were the major source for the PAHs in the area.

SAMENVATTING

Een methode is ontwikkeld voor de meting van polycyclische aromatische koolwaterstoffen (PAK) in de buitenlucht m.b.v. gaschromatografie - isotoopverdunding massa spectrometrie. De methode was ontworpen voor de meting van de grootst mogelijke vluchtigheidstraject binnen de groep inclusief de meestvoorkomende en vluchtige naftalenen. Het monstervolume bedroeg circa 500 m³ bij een bemonsteringssnelheid van ca. 18 m³/h. Het monsternamen apparaat bevatte drie sortie trappen voor de simultane bemonstering van resp. de deeltjes gebonden fractie, de weinig vluchtige en de vluchtige PAK's.

De recoverie van de methode bedroeg gemiddeld ca. 90 %. De detectiegrens was circa 5 pg/ m³ voor de niet-vluchtig en deeltjes gebonden fractie.

Resultaten van toepassing van de methode in een woongebied (Bilthoven) toonden een vrij stabiel profiel van voorkomen van de belangrijkste PAK congenen in achtergrondlucht.

Vergelijking van specifieke verhoudingen van bepaalde PAK congenen met literatuur gegevens duidde op een belangrijke bijdrage van verkeer aan PAK's in lucht

INTRODUCTION

During the past few decades, polynuclear aromatic hydrocarbons (PAHs) have received increasing interest due to their possible harmful impact on human health [1]. This class of compounds belongs to the high priority pollutants, particularly the potentially mutagenic congeners like benzo[a]pyrene and others. PAHs in ambient air have considerable half lives and can be transported over long distances through the atmosphere. Well-known sources for airborne PAHs are traffic exhaust [2, 3], processes based on combustion of fossil fuels, [4] waste incineration [5] and aluminium production [6]. In order to get a better insight in human exposure levels to these compounds through inhalation, reliable sampling and analysis methods are required capable of measuring a large range of congeners of the PAH family.

One of the difficulties that may occur with air analysis is the great complexity of organic compounds and their large concentration ranges. PAHs of different volatility ranges in ambient air were measured in few studies [7-10]. Such methods employed glass fiber filters (GFF) and a variety of sorbents like polyurethane foam (PUF), XAD-2 resin, Tenax, Florisil, Chromosorb 102 and others [11].

The objectives of this work were (i) the development of a sampling method for a wide volatility and concentration range of airborne PAHs and (ii) the application of the method to establish baseline PAH profiles in an average urbanized area. The results will be used in the framework with ongoing studies in our laboratory concerning the assessment of exposure of individuals to naphthalene (personal monitoring) as a candidate marker compound for indoor air PAHs.

Because of the great complexity of airborne organic compounds, it is worthwhile to search for marker compounds representing a group or class of compounds which as such are difficult to determine.

Today, several methods have been published for the measurement of indoor air PAHs with special attention to volatile fraction such as naphthalene, fluorene, phenanthrene, anthracene, pyrene and fluoranthene and their relative ratios to the potential mutagenic and carcinogenic congeners which are normally present in much lower concentrations [12, 13, 14]. Such marker compounds should be readily measurable at low costs owing to their relatively high concentrations. Results may indicate the necessity to perform further and more complex examinations.

Until today, only few results have appeared in the literature on the large volatility range of airborne PAHs. The present method is based on the method of Mikalsen [9]. The sampling head comprised a glass fiber filter for the capturing of the particle bound fraction, a polyurethane foam plug (PUF) to trap the medium volatile fraction and XAD-2 resin for the volatile congeners [11, 15, 16]. In addition, use was made of deuterated PAH analogues that were added to the sampler sorbent (PUF) prior to sampling to control and correct for sample losses. Their use is particularly important for the volatile compounds which may be more easily lost during sampling and sample processing.

EXPERIMENTAL

Materials. Air samples were collected using a high volume sampler (HVS), type III, purchased from Stranovsky GmbH, Essen, Germany, previously used for sampling of ambient air PCDDs and PCDFs on glassfiber filters and polyurethane foam plugs (PUF) [17]. PUF plugs were obtained from Sunde & Co., Soesilfabrikk for Skumplastartkler, Gan, Norway, density 25 kg/m³. Amberlite XAD-2 resin was obtained from Supelco Inc., density 1.02 g/cm³, mesh size 20-60. Glassfiber filters (GFF) type A/E, 142 mm., were obtained from Gelman Sciences, Inc., Ann Arbor, MI, USA. Standard PAHs were obtained as a Standard Reference Material (SRM) 2260 of the National Institute of Standards and Technology through C.N. Schmidt B.V. , Amsterdam, The Netherlands. Deuterated PAHs were obtained from Cambridge Isotope Laboratories, Woburn, Massachusetts, USA. All solvents were of residue analysis grade (Merck, Darmstadt, Germany) and were used without prior cleaning. Solid phase extraction cartridges (500 mg, 6 ml) were obtained from J.T. Baker, Germany.

Filter and sorbent cleaning. Before use, glass fiber filters were cleaned by ultrasonic treatment with dichloromethane (150 ml) for 50 min. PUF plugs were cleaned, initially by soxhlet extraction with toluene (24 h), followed by soxhlet extraction with 10% diethyl ether in hexane (24 h). Later, cleaning was performed by soxhlet extraction with dichloromethane for 48 hours. After cleaning, plugs were dried for 24 h in a vacuum oven at 60°C. XAD-2 resin was cleaned by Soxhlet extraction with methanol (48 h), followed by refluxing with dichloromethane for 2 weeks. Next, the material was dried in a vacuum oven at 60°C. Cleaned resin was stored in a clean glass flask.

Filter and sorbent blanks. Sorbents were spiked with 500 ng d₈-naphthalene and 100 ng d₁₀-methyl-naphthalene (deuterated analogues) by injection in the middle of the sorbent material using a syringe with a stainless steel needle. Next, the filters were placed in a soxhlet apparatus and kept there for 3 days before starting extraction (incubation time). Next, sorbents were extracted with dichloromethane (initially 10% diethylether/hexane) during 24 hours. Blanks were processed and analyzed as unknowns.

Sampling. The sampling head consisted of an alumina cylinder (25 cm x 10 cm ID) in which were placed (top to bottom) a GFF filter, a PUF plug (5 cm x 11 cm O.D.), 100 g of XAD-2 resin (about 3 cm in height) and another PUF plug. The XAD resin was separated from the PUF plugs by stainless steel sieves on both sides. The sampling module was connected to the pump in vertical position with a protecting roof on top.

Before sampling, the front PUF plug was spiked with 1.5 ml of d-PAHs solution (1 µg/ml each) and 1 ml of d₈-naphthalene (100 µg/ml). Spiking solutions were prepared in isooctane.

After spiking, the sampling head was connected to the sampler and the pump switched on immediately. Samplings were performed during the end of August and September 1994, usually with a few day break between samplings. The sampling duration was 20 to 28 h at a flow rate of approx. 18 m³/h. The equipment is schematically depicted in Fig. 1.

Extraction. A scheme of the method for sample extraction and clean-up is shown in Fig. 2. After sampling, the PUF plug and the XAD resin were spiked with 1 ml of d₁₀-1-methyl-naphthalene (recovery standard, 100 µg/ml) and extracted separately using a Soxhlet apparatus with 250 ml of dichloromethane for 24 hours.

GFF filters were spiked with 500 µl of a mixture of deuterated PAHs (1 µg/ml) and extracted in an ultrasonic bath in 150 ml of dichloromethane for 50 min. All extracts obtained were evaporated in a Kuderna-Danish apparatus until approx. 1 ml. Then, hexane (20 ml) was added and reevaporated until 6 - 12 ml. For the PUF and XAD extracts, aliquots (500 µl) were taken for analysis of the high abundant PAHs without any further clean-up or concentration. A holder or keeper (isooctane, 400 µl) was then added to the remaining portion of the extract and evaporated to about 400 µl under gentle stream of nitrogen at room temperature.

Clean-up. Extracts of both the GFF and the front PUF plug were cleaned by solid phase extraction (SPE) according to a slightly modified method of Tan et al. [18]. Before use, SPE columns were activated by heating overnight at 85°C followed by rinsing with 6 ml of hexane. After loading with the sample, the column was wetted three times with 100 µL of hexane followed by rinsing with 5 ml of hexane. Subsequently, PAHs were eluted with 3 ml of dichloromethane/hexane (40/60, v/v). The solvent was evaporated until approx. 100 µl with a nitrogen stream at room temperature, followed by the addition of isooctane (500 µl) and reevaporated till 100 µl. Next, 100 µl of the syringe standard solution (3 µg/ml d₁₀-anthracene) was added just before analysis by GC/MS.

GC/MS analysis. Quantitative analyses were carried out on a Hewlett Packard gas chromatograph/Finnigan SSQ 710 (San Jose, CA, USA) quadrupole mass spectrometer combination. Aliquots of 1 µl were injected in the splitless mode. Samples were separated on an Ultra-2 (Hewlett Packard) fused silica capillary column (25 m x 0.20 mm I.D., df=0.11 µm) with helium as the carrier gas. The injector and interface temperature were 290 and 275°C, resp. The source temperature was 200°C.

The GC temperature program was: initial temperature, 70°C increased after 1min to 300°C at a rate of 5°C/min and maintained isothermal at the final temperature for 10 min. A lower initial temperature (60°C) was used for the analysis of the volatile PAHs. The mass spectrometer was operated in selected ion recording (SIR) mode for monitoring of the molecular ions for both native and deuterated PAHs (see Table 1). The dwell time was 50 ms/channel. The ionization mode was electron impact (EI) at 70 eV and a filament emission current of 200 μ A.

RESULTS AND DISCUSSION

Sampling. The sampling strategy in this study aimed at the quantitative recovery of the widest possible range for airborne PAHs, including the highly volatile fraction, in relatively large sample volumes. A main difficulty to fulfill is to prevent from losses of the volatile compounds due to migration through the sampling system or to evaporation during sample clean-up and concentration. Therefore, XAD-2, a known strong sorbent for PAHs, was placed at the back end of the sampling module to ensure the capturing of the less retained compounds. On the other hand, however, it should be avoided that heavier compounds reach this area as they might be absorbed irreversibly to this material. Therefore, the dimensions of the intermediate PUF plug should be selected carefully in relation to the sample size or sampling duration. Table 2 shows the estimated breakthrough volumes for representative PAH compounds for two to four membered ring PAH congeners. Calculations were based on the migration velocity as function of the vapor pressure as according to You and Bidleman [19]. The resulting breakthrough volumes for the PUF plug used (10 cm in height) ranges from 1 to over 700.000 m³ of air for naphthalene and benz[a]anthracene, respectively.

In common sampling practice, a few hundreds of cubic meters of sample sizes are normally used, so that naphthalene (1 m³), acenaphthene (45 m³), fluorene (110 m³) and acenaphthylene (170 m³) will be entirely or partially lost. The value for phenanthrene exceeded already one thousand cubic meters. These findings were confirmed for the sampler used in this study by spiking experiments with deuterated PAHs.

Spiking was performed on the PUF plug for a sample volume of approximately 500 m³. Naphthalene and 1-methylnaphthalene were almost completely recovered from the XAD sorbent (84±12% and 86±15%, respectively). More volatile congeners than phenanthrene were almost quantitatively recovered from the PUF. Difficulties were encountered for acenaphthylene.

For this compound, only about half of the spiking quantity ($49\pm 10\%$) was recovered from XAD. The remaining half was lost. It remained unclear where these losses occurred.

Another difficulty concerned the spiking position of the sampler. The preferred position was the GFF filter. However, combined recoveries from GFF and PUF were essentially not quantitative. Part of these losses was found back on the metal support sieve that was placed underneath the glass fiber filter to protect it from damage during sampling. Therefore, spikes were applied on the PUF material. This procedure enables, in part, to differentiate between particle bound and vapor phase PAHs in air. Despite possible losses for airborne PAHs passing the GFF filter and the metal support sieve, the ratio between PAHs on the GFF and the PUF filter may represent the ratio occurring in air particles and as vapors. The result, however, must be interpreted with care because evaporation of particulate PAHs may occur during the sampling period, to an unknown extent depending on experimental and field conditions like the ambient temperature and sampling duration.

Recoveries and detection limits. Recoveries of high boiling congeners were quantitative during the clean-up procedure. No evaporation losses, like readily may occur for the volatile fraction, were found. In order to minimize such losses, low boiling solvents were used for extraction (dichloromethane and 10% diethylether in hexane). In addition, solvents were evaporated step wise using a Kuderna- Danish equipment. A holder or keeper liquid was always added at this stage prior to further reduction to the final volume for injection (100 μ l)

Recoveries after solvent evaporation exceeded on average 90%. Extraction yields were satisfactory for both solvents but always slightly better for DCM (table 3).

Blanks of Sampling Media. PUF and XAD-2 resin as received contained significant background values for PAH. Most effective cleaning was achieved by Soxhlet extraction with DCM compared to toluene and 10% diethyl ether in hexane. Using DCM, blank values were near the detection limit of the method (table 4). Blank values for XAD were difficult to remove. Prolonged extraction with DCM for more than 2 weeks resulted ultimately in a reduction to about 0.5% of the normal quantity in 500 m³ air samples. GFF filters were always clean and were used without any pretreatment. The detection limit of the method at a signal to noise ratio of 3 was approx. 5 pg/m³ at a sample size of 500 m³. The precision of the method varied from about 5% for the high abundant congeners to about 20% for the low abundant congeners (table 5).

Analysis. Determination of PAHs in air samples was performed in two separate analyses. After extraction and cleaning, extracts were concentrated to about 10 ml and a small fraction was analyzed directly for the highly abundant airborne congeners naphthalene, 1 and 2-methylnaphthalene, 2,6-dimethylnaphthalene, biphenyl, acenaphthene, 2,3,5-trimethyl-naphthalene, fluorene and phenanthrene. Subsequently, the remaining portion was further concentrated (100 µl) and analyzed for the minor components (acenaphthylene through benzo[ghi]perylene). This procedure reduces the risk for evaporation losses, as all the volatile congeners belong to the abundant fraction in air.

Application to air sampling. Results of PAH measurement in air are shown in table 6. An example of the GC/MS traces is shown in figure 3. The level of the most abundant compound, naphthalene, ranged between 80 and 180 ng/m³. The least abundant congener was always perylene with a level ranging between 0.01 - 0.04 ng/m³ (near detection limit). These concentrations were relatively low compared to levels found by Mikalsen et al who used a similar sampling technique [9]. In their analysis naphthalene peaked sometimes to levels up to a few µg per cubic meter.

The relative low concentrations found in this study could be explained, because of period of the year (September). In preliminary samplings in February of the same year (1994), levels for naphthalene were incidentally at the low μg per cubic meter range. Seasonal variations of PAH levels are well known [20] with highest levels in the winter period due to higher combustion rates of fossil fuels (house heating, energy production). Another factor may be the longer half life in air in the winter because of diminished degradation rates under the influence of UV.

Weather conditions may affect airborne PAH concentrations significantly. High temperatures, for instance, may cause increased dispersion volumes for pollutants in the atmosphere. Other conditions, like inversions may cause the opposite. The influence of rain is quite obvious as it will result in an increased precipitation rate for particles and the associated PAHs. The meteorological conditions during samplings are shown in table 7.

The profiles (relative abundances) of PAHs in air samples are shown in figure 4. In general, profiles were consistent, with naphthalene being the most abundant, followed by the various alkylnaphthalenes and fluoranthene. Of interest was the observation that the naphthalene to benzo[a]pyrene ratio was reasonably constant with an average of 1455 ± 270 ($n=7$; RSD, 18.6%). This result indicate that naphthalene may be considered as a good marker compound for airborne PAHs. However, more analyses are needed to confirm this conclusion. The relative standard deviation for naphthalene B[a]P ratio is within the precision range of the method for both compounds.

Table 8 shows the partition of PAHs between the GFF and PUF filter. The distribution was in good agreement with previously findings by others [21, 22]. Less volatile PAHs than benzo[e]pyrene were entirely recovered from the GFF filter. Congeners with liquid vapor pressure between 0.000024 Pa and 0.715 Pa (benzo[e]pyrene to fluorene) were recovered from the PUF and the more volatile congeners mainly from the XAD.

Results obtained were interpreted in terms of their origin. It is well known that different sources emit different profiles [23, 24, 25]. Indicative congener ratios specific for diesel car exhaust and other combustion sources were found for the pairs of indeno[1,2,3-cd]pyrene/benzo[g,h,i]perylene and benz[a]anthracene/chrysene [26]. The relatively high concentration ratio for chrysene and benzo[g,h,i]perylene (~1.7) found in this study points to a significant contribution of emissions from diesel fueled traffic to the airborne PAHs.

CONCLUSIONS

In summary, the method described here allowed the simultaneous sampling and analysis of a wide range of airborne PAHs in relatively large samples. Large sample sizes enabled the analysis of the low abundant fraction. The use of XAD-2 prevents from breakthrough losses of the volatile fraction. The PUF material prevents heavier PAH molecules reaching the XAD-2 where they may be adsorbed irreversibly. Parallel analysis of the abundant volatile congeners and the less abundant and less volatile fractions provided a large dynamic range of the method. Evaporation losses during sample work-up were small. Preliminary application of the method in field analysis showed the typical concentration pattern of PAHs, with the highest concentrations for naphthalene, alkylnaphthalenes, fluorene and phenanthrene. Results indicate that the abundant and readily measurable naphthalenes are candidate marker compounds for the mutagenic PAHs occurring at much lower levels in air.

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Table 1. M/z values used in the GC/MS analysis of PAHs and their deuterated analogues.

No	Compound	Quantifying Standard	Monitoring Ion (m/z)	Retention time [mm:ss]
1	Naphthalene	d ₈ -Naphthalene	128/136	6:29
2	2-methyl-naphthalene	d ₈ -Naphthalene	142/136	8:55
3	1-methyl-naphthalene	d ₈ -Naphthalene	142/136	9:18
4	Biphenyl	d ₈ -Acenaphthylene	156/160	10:56
5	2,6-dimethyl-naphthalene	d ₈ -Acenaphthylene	154/160	11:3
6	Acenaphthylene	d ₈ -Acenaphthylene	152/160	12:30
7	Acenaphthene	d ₈ -Acenaphthylene	154/160	13:21
8	2,3,5-trimethyl-naphthalene	d ₈ -Acenaphthylene	170/160	15:15
9	Fluorene	d ₁₀ -Phenanthrene	166/188	15:38
10	Phenanthrene	d ₁₀ -Phenanthrene	178/188	19:56
11	Anthracene	d ₁₀ -Phenanthrene	178/188	20:08
12	1-methyl-phenanthrene	d ₁₀ -Fluoranthene	192/212	22:55
13	Fluoranthene	d ₁₀ -Fluoranthene	202/212	25:30
14	Pyrene	d ₁₀ -Pyrene	202/212	26:26
15	Benz[a]anthracene	d ₁₂ -Benzo[a]pyrene	228/264	32:16
16	Chrysene	d ₁₂ -Benzo[a]pyrene	228/264	32:27
17	Benzo[b+j+k]fluoranthene	d ₁₂ -Benzo[a]pyrene	252/264	37:04
18	Benzo[e]pyrene	d ₁₂ -Benzo[a]pyrene	252/264	38:06
19	Benzo[a]pyrene	d ₁₂ -Benzo[a]pyrene	252/264	38:18
20	Perylene	d ₁₂ -Benzo[a]pyrene	252/264	38:38
21	Indeno[1,2,3-cd]pyrene	d ₁₂ -Benzo[g,h,i]perylene	276/288	42:29
22	Dibenzo[a,h]anthracene	d ₁₂ -Benzo[g,h,i]perylene	278/288	42:43
23	Benzo[g,h,i]perylene	d ₁₂ -Benzo[g,h,i]perylene	276/288	43:18

Table 2. Calculated breakthrough volumes for PAHs on PUF plug after You and Bidleman [19].

Compound	# Rings	Vapour pressure (20°C, torr)		Breakthrough Volume [m ³]
		Solid	Subcooled Liquid	
5 cm PUF				
Naphthalene	2	3.9x10 ⁻²	1.9x10 ⁻¹	1.2
Acenaphthene	3	1.2x10 ⁻³	6.9x10 ⁻³	45
Fluorene	3	3.2x10 ⁻⁴	3.0x10 ⁻³	110
Acenaphthylene	3	4.0x10 ⁻⁴	2.1x10 ⁻³	170
Phenanthrene	3	6.2x10 ⁻⁵	4.0x10 ⁻⁴	1040
Anthracene	3	3.2x10 ⁻⁶	1.0x10 ⁻⁴	1400
Fluoranthene	4	1.0x10 ⁻⁵	8.0x10 ⁻⁵	6100
Pyrene	4	2.4x10 ⁻⁶	5.6x10 ⁻⁵	9100
B[a]anthracene	4	1.2x10 ⁻⁷	9.8x10 ⁻⁷	792000

Table 3. Procedural recoveries for naphthalenes during evaporation of extracts in dichloromethane and diethylether/hexane.

Deuterated PAH	<u>PUF</u>		<u>XAD-2</u>		<u>GFF</u>	
	Rec	RSD	Rec %	RSD	Rec	RSD
Naphthalene	92.8	10.5	86.7	14.8	91.5	10.1
1-methyl-naphthalene	90.4	13.0	87.0	12.1	91.4	9.8
Acenaphthylene	82.8	14.8	56.3	13.8	92.5	10.4
Phenanthrene	99.4	4.9	78.7	12.0	98.0	9.1
Fluoranthene	96.1	10.7	83.7	13.6	97.0	4.9
Pyrene	95.4	9.1	95.7	9.1	94.3	6.3
Benzo[a]pyrene	86.0	10.9	83.7	18.4	86.5	12.3
Benzo[g,h,i]perylene	96.8	14.2	65.6	12.7	96.0	8.2

Table 4. Blank levels in PUF and XAD-2 resin recalculated to a sample size of 500 m³ of air.

No.	Compound	PUF [ng/m ³]	XAD-2 [ng/m ³]
1	Naphthalene	0.19	0.53
2	2-methyl-naphthalene	0.06	0.32
3	1-methyl-naphthalene	0.02	0.14
4	2,6-dimethyl-naphthalene	0.02	0.009
5	Biphenyl	0.03	0.007
6	Acenaphthylene	0.07	n.d.
7	Acenaphthene	0.03	0.005
8	2,3,5-trimethyl-napht.	0.01	n.d.
9	Fluorene	0.01	0.006
10	Phenanthrene	0.04	0.007
11	Anthracene	n.d.	n.d.
12	1-methyl-phenanthrene	n.d.	n.d.
13	Fluoranthene	n.d.	0.007
14	Pyrene	n.d.	0.008
15	Benz[a]anthracene	n.d.	n.d.
16	Chrysene	n.d.	n.d.
17	Benzo[b+j+k]fluoranthene	n.d.	n.d.
18	Benzo[e]pyrene	n.d.	n.d.
19	Benzo[a]pyrene	n.d.	n.d.
20	Perylene	n.d.	n.d.
21	Indeno[1,2,3-cd]pyrene	n.d.	n.d.
22	Dibenzo[a,h]anthracene	n.d.	n.d.
23	Benzo[g,h,i]perylene	n.d.	n.d.

n.d.: not detected

Table 5. Recoveries of native PAHs from sorbents and filters after extraction with dichloromethane.

Compound	Sample						Mean	RSD [%]
	1	2	3	4	5	6		
	XAD-2							
d8-Naphthalene	76	95	69	76	91	95	84	14
d10-1-methyl-naphthalene	78	97	70	72	96	105	86	17
d8-Acenaphthylene	42	56	62	41	37	54	49	20
d10-Phenanthrene	1	3	0	1	1	3	2	-
d10-Fluoranthene	1	0	0	0	0	1	0	-
d10-Pyrene	2	0	0	0	0	1	0	-
	PUF (concentrated samples)							
d12-Benz[a]pyrene	119	101	103	102	109	94	105	8
d12-Benz[g,h,i]perylene	94	92	82	104	100	105	96	9
	PUF (diluted samples)							
d8-Naphthalene	1	1	0	0	0	0	1	-
d8-Acenaphthylene	1	1	1	1	1	2	1	-
d10-Phenanthrene	91	86	94	89	90	89	90	3
d10-Fluoranthene	97	99	97	92	93	95	96	3
d10-Pyrene	103	101	105	102	100	100	102	2
	Glass Fiber Filter							
d10-Phenanthrene	87	84	56	55	74	51	68	23
d10-Fluoranthene	107	107	87	75	86	73	89	17
d10-Pyrene	114	103	85	73	80	73	88	19
d12-Benz[a]pyrene	102	92	90	74	104	94	93	12
d12-Benz[g,h,i]perylene	93	99	93	97	106	91	96	6

Table 6. Level of airborne PAHs during the period of August-September 1994 in an urbanized area (Bilthoven, The Netherlands).

No Compound	Sample						Mean	%RSD
	1	2	3	4	5	6		
	ng/m ³							
1 Naphthalene	174.0	136.7	164.6	81.6	90.5	85.9	122.2	34.0
2 2-methyl-naphthalene	99.7	96.0	68.9	35.9	34.4	29.9	60.8	52.5
3 1-methyl-naphthalene	52.7	46.8	38.8	20.2	19.6	18.3	32.7	46.7
4 2,6-dimethyl-naphthalene	29.1	26.1	14.4	11.6	14.6	10.3	17.7	44.8
5 Biphenyl	38.7	46.6	20.7	14.9	21.6	12.9	25.9	52.6
6 Acenaphthylene	5.5	2.2	4.3	1.5	3.6	1.3	3.1	54.9
7 Acenaphthene	56.1	82.2	18.9	12.6	24.3	13.5	34.6	81.9
8 2,3,5-trimethyl-naphth	3.3	4.5	2.4	1.8	2.4	2.0	2.7	36.3
9 Fluorene	28.4	10.0	9.2	4.1	6.7	6.9	10.9	81.1
10 Phenanthrene	42.7	54.9	22.9	14.4	19.0	17.5	28.6	57.3
11 Anthracene	1.31	1.14	0.74	0.34	0.41	0.38	0.72	58.5
12 1-methyl-phenanthrene	0.91	0.96	0.73	0.47	0.49	0.53	0.68	31.9
13 Fluoranthene	5.71	7.82	3.62	2.78	3.03	2.89	4.31	47.3
14 Pyrene	2.52	3.28	1.72	1.21	1.23	1.28	1.87	45.4
15 Benz[a]anthracene	0.19	0.20	0.24	0.11	0.14	0.12	0.16	30.9
16 Chrysene	0.35	0.46	0.45	0.30	0.27	0.26	0.35	25.3
17 Benzo[b+j+k]fluoranthene	0.48	0.66	0.74	0.43	0.36	0.32	0.50	33.4
18 Benzo[e]pyrene	0.21	0.28	0.28	0.18	0.16	0.14	0.21	29.1
19 Benzo[a]pyrene	0.12	0.11	0.12	0.04	0.07	0.06	0.09	36.6
20 Perylene	0.04	0.03	0.04	0.01	0.02	0.02	0.03	38.2
21 Indeno[1,2,3-cd]pyrene	0.33	0.29	0.44	0.19	0.24	0.19	0.28	33.6
22 Dibenzo[a,h]anthracene	0.05	0.06	0.09	0.04	0.05	0.05	0.06	29.1
23 Benzo[g,h,i]perylene	0.29	0.23	0.27	0.14	0.17	0.15	0.21	31.8
Sum	542.6	521.5	374.6	204.9	243.4	205.0	348.7	44.5

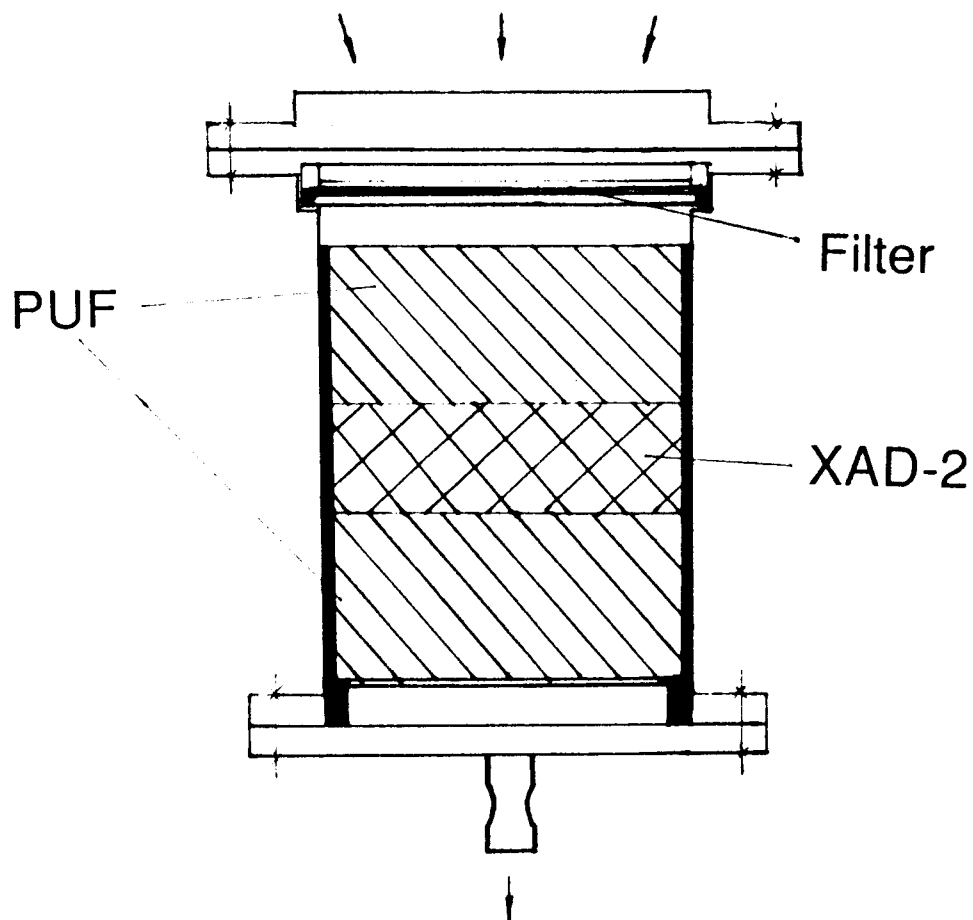
Table 7. Meteorological conditions during samplings.

Sample No	Temp [°C]	<u>Rain</u>		<u>Wind</u>	
		Intensity [mm]	Duration [h]	Main Trajectory ¹ (°)	Velocity [m/s]
1	17.2	0.8	0.7	WNW (294)	2.1
2	17.8	0.5	0.6	SE (137)	4.2
3	14.2	0.2	0.3	WSW (248)	3.2
4	13.7	0.5	0.5	SW (215)	7.0
5	12.6	1.5	0.8	WSW (235)	3.7
6	12.8	1.8	1.0	NNW (324)	3.9

¹N =North (0°); E = East (90°); S = South (180°); W = West (270°).

Table 8. Average airborne PAH levels found on glass fiber filters (GFF) and polyurethane foam (PUF).

No.	Compound	GFF		PUF		GFF/Total x100%
		ng/m ³	RSD (%)	ng/m ³	RSD(%)	
9	Fluorene	0.013	53	10.9	81	0
10	Phenanthrene	0.14	37	28.4	58	0
11	Anthracene	0.008	27	0.7	59	1
12	1-methyl-phenanthrene	0.011	36	0.7	32	2
13	Fluoranthene	0.17	44	4.1	48	4
14	Pyrene	0.10	41	1.8	46	5
15	Benz[a]anthracene	0.10	39	0.063	52	62
16	Chrysene	0.18	40	0.16	27	53
17	Benzo[b+j+k]fluoranthene	0.49	34	0.02	79	97
18	Benzo[e]pyrene	0.21	30	0.003	83	98
19	Benzo[a]pyrene	0.086	37	nd	-	100
20	Perylene	0.027	39	nd	-	100
21	Indeno[1,2,3-cd]pyrene	0.28	34	nd	-	100
22	Dibenz[a,h]anthracene	0.05	29	nd	-	100
23	Benzo[g,h,i]perylene	0.21	32	nd	-	100



SAMPLING MODULE

Figure 1. Sampling module for PAHs.

Scheme of the analysis of PAHs in air

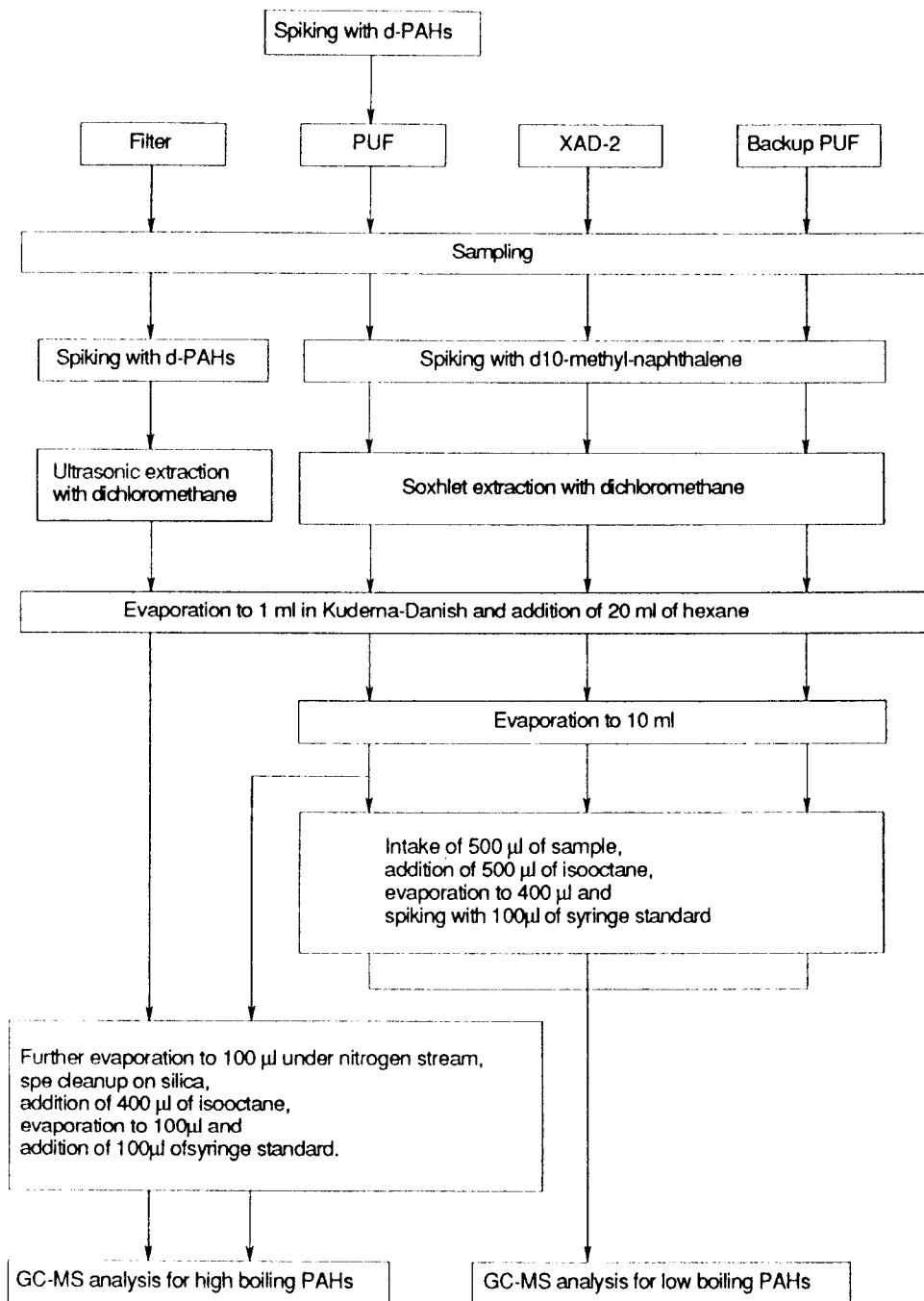


Figure 2. Scheme of the analytical method for analysis for airborne PAHs.

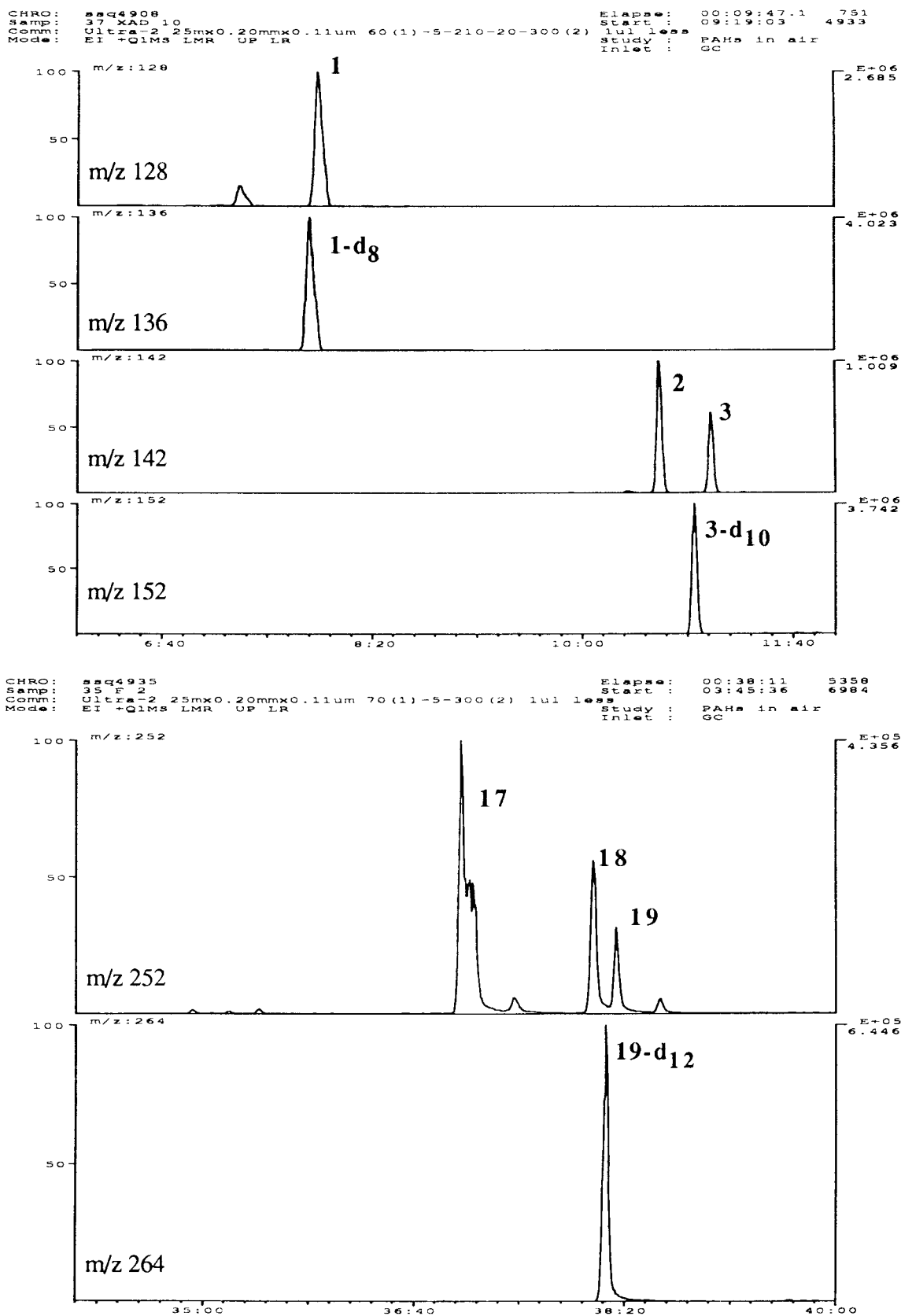


Figure 3. Example of GC/MS traces during analysis of an air sample. Shown are the traces for naphthalene and the elution region of benzo[a]pyrene and their corresponding deuterated internal standards.

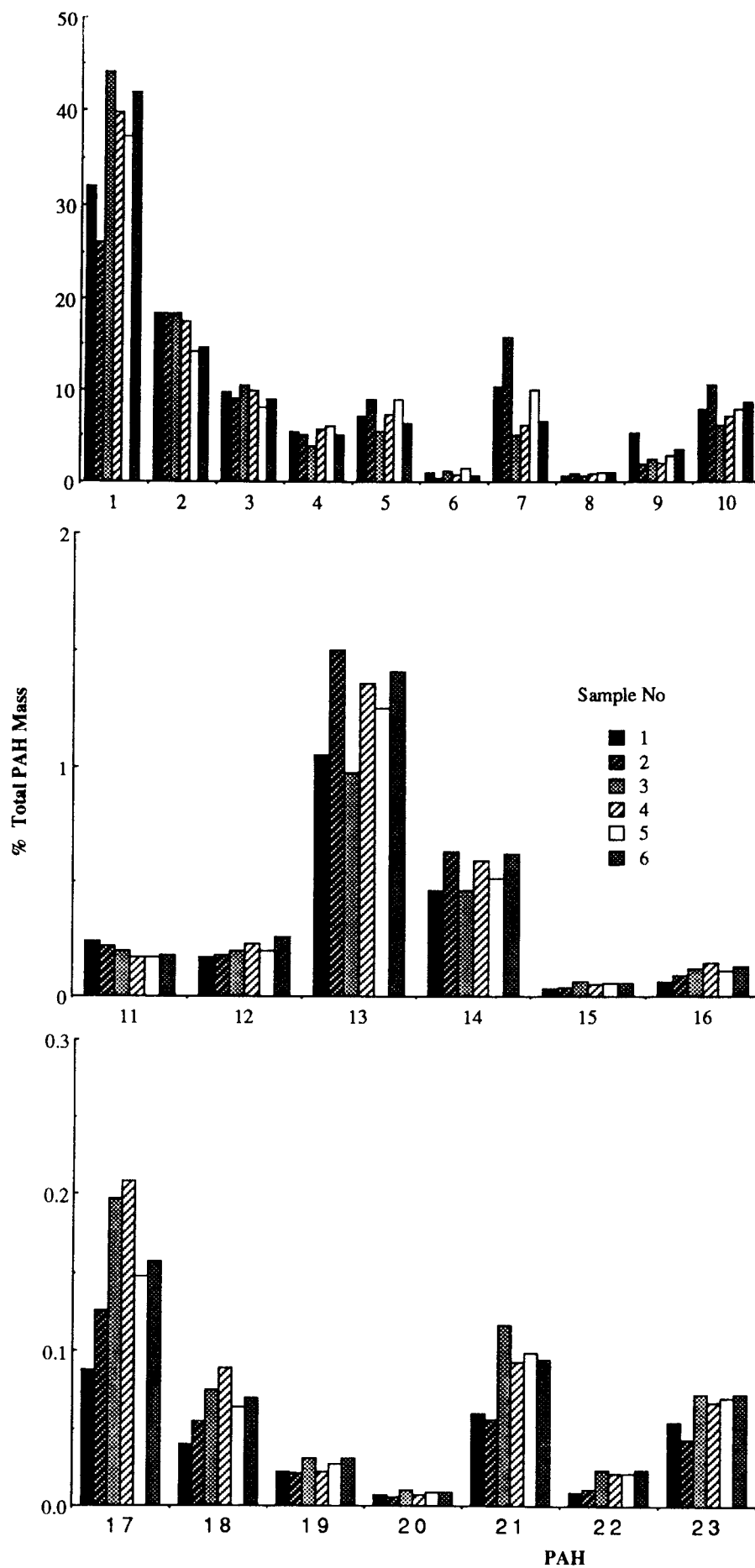


Figure 4. Relative abundance of airborne PAHs found in a residential area.