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# Monitoring Method for Airborne Polycyclic Aromatic Hydrocarbons

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This paper describes a method for the determination of airborne polycyclic aromatic hydrocarbons (PAH), which has been employed in routine analysis of a large number of samples. The method is in principle based on well known techniques, but some improvements have been made in order to reduce the analysis time and the cost without lowering the quality of the analytical results. Recovery studies have been made for some important steps of the procedure, and the reproducibility of the sampler has been tested. The method has proved to be suitable for monitoring of PAH in highly polluted as well as pristine areas.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are, because of their adverse health effects, considered some of the most important organic air pollutants. They are produced by incomplete combustion of organic material, and are emitted into the air from many different mobile and stationary sources. Results from air pollution studies reported in the literature, show that PAH are present in ambient air, in industrialized and urban areas as well as in areas far away from the emission sources.<sup>1,2</sup> Studies are carried out in order to obtain a better understanding of the pathways of PAH in nature, and to learn about man's exposure to such compounds. Monitoring of PAH in

ambient air is, however, time consuming and a difficult task, and the cost of the analytical work is high. In many cases a very limited number of samples has been collected and analysed in order to keep the working time and the cost to a minimum. In this way important information, for example about the temporal variation of the concentrations, may be lost. One should also bear in mind that results based on few samples provide only a rough estimate of the concentration levels. The objectives of an air pollution study may vary from one investigation to another. In most cases they will include determination of pollution levels and studies of seasonal variations, as well as the influence of various emission sources and meteorological conditions. The purpose may also be to identify the main sources in an area, and to quantify their contribution on the basis of the monitoring data. These goals require that sampling is carried out during extended periods of time. However, to be able to distinguish between the changing weather conditions sampling time must be short. This means that a large number of samples should be analysed. It is also most important that the collected data are of high quality and that the effect of measurement noise is kept to a minimum. The methods for sampling and analysis should therefore be carefully selected.

In order to meet these requirements and to be able to carry out extensive monitoring programs on PAH, it was necessary to find methods that were less expensive and laborious than the existing ones. The principles of the methods described here and employed in our programs, are well known, but both the methods and the equipment for sampling, sample preparation and analysis have been simplified and improved. This paper describes the methods and the equipment in detail. Recovery and reliability of some important steps in the procedures have been investigated, and the results are discussed.

## EXPERIMENTAL

### Methods of sampling, sample preparation and analysis

#### *Sampling*

The sampling system for collection of PAH in ambient air, shown in

Figure 1, is very easy to use in the field and well suited in monitoring programs. Sampling is carried out according to the procedure given by Thrane and Mikalsen.<sup>1</sup> The particles are collected on a 142mm glass fibre filter, Gelman type AE or Whatman GF/A. The volatile part of the compounds is trapped by two cylindrical plugs of polyurethane (PUR<sup>3</sup>) foam located behind the filter, in a QVF glass drainline system (Corning Inc.) of 10cm diameter. A perforated plate supports the filter while no support is necessary for keeping the plugs in place. The density of the PUR foam is 25kg/m<sup>3</sup>. The thickness of the plugs is 5cm and the

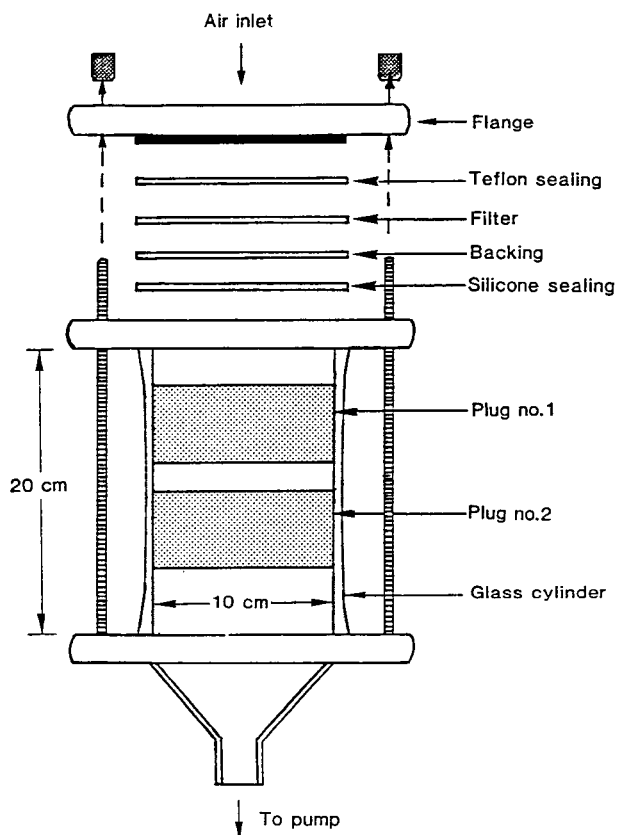


FIGURE 1 Sampling system for PAH in ambient air.

diameter 11 cm. A Siemens ELMO vacuum pump 2BH5 is used, and the flow rate is 20 m<sup>3</sup>/h. The air intake must be protected against precipitation.

#### *Cleaning procedures*

*Sampling equipment* The glass fibre filters, about 20 at the time, are heated at 400°C for 4 h, extracted in cyclohexane for 8 h and dried in a vacuum desiccator. Cleaning of the polyurethane plugs is a most important step because extracts from new or improperly purified plugs will contain compounds that interfere with the gas chromatographic analysis. The plugs are squeezed in toluene at 100°C, according to the procedure of Erickson *et al.*,<sup>4</sup> and then extracted in a Soxhlet apparatus in acetone for 24 h, and in cyclohexane for another period of 24 h. Soxhlet extractors that will hold up to eight PUR plugs are available and may be used in order to save time. After extraction the plugs are dried in a vacuum desiccator at 40°C for about 12 h. Used polyurethane plugs are cleaned by extraction for 8 h, first in acetone and then in cyclohexane. In order to avoid exposure to air before sampling, the filters and plugs are wrapped tightly in aluminum foil during storage.

*Laboratory equipment* All surfaces of the equipment that will come into contact with the samples must be thoroughly cleaned before use. The glass parts are soaked for 24 h in a synthetic detergent. Afterwards the parts are rinsed well in warm water, and finally in distilled acetone. If the equipment is stored before use, exposure to air must be avoided and all parts should be wrapped tightly in aluminum foil. Thimbles, used for Soxhlet extractions of exposed filters, are extracted in cyclohexane for 8 h and dried at 100°C in a vacuum desiccator.

*Chemicals* A Millipore Milli-Q system is used for purification of the water.<sup>5</sup> Cyclohexane (Merck 2832) is distilled once, in a distillation apparatus equipped with a 60 cm Vigreux column. Dimethylformamide (DMF) (Merck 3034 p.a.) is distilled twice. The 130 cm column used for the purification of DMF, is filled with steel chips. The drying agent, sodium sulphate (Merck 6649 p.a.) is purified by Soxhlet extraction for 8 h in cyclohexane, dried at 110°C and kept in an air-tight container.

### *Sample preparation*

After sampling the exposed filters and plugs are removed from the sampler by using forceps. Plastic gloves are recommended when handling the filters and the plugs before and after sampling. The filters and the plugs are wrapped separately in aluminum foil and sent to the laboratory. The transportation of filters and plugs causes no problem, but the samples must be protected against heat. Insulating bags may be used for this purpose.

The samples may be stored at  $-20^{\circ}\text{C}$ , but the length of storage should be kept to a minimum. The extraction, cleanup, enrichment and analysis of the samples are carried out according to the scheme in Figure 2. The PAH samples are extracted in cyclohexane for 8 h in a Soxhlet apparatus. The exposed filters are cut into small pieces and transferred to an extraction thimble (Schleicher & Schüll,  $28 \times 80$  mm). The two plugs from each sample are extracted separately. Filter samples are extracted in 100 ml of solvent, and the plugs in 300 ml. Before extraction internal standard solutions containing 3,6-dimethylphenanthrene (std. I) and  $\beta, \beta'$ -binaphthyl (std. II), are added to the samples. The solutions are injected either into the thimble or into the plug. The amount of internal standard added, varies and depends on the expected concentrations of PAH in the sample. If a large number of samples are being analysed and one finds that the extraction causes a delay, more Soxhlet apparatus should be used rather than reducing the extraction time. The Soxhlet extraction is followed by liquid/liquid separation of PAH from the complex mixture of other organic compounds in the solution.<sup>6,7</sup> The extract is transferred to a separatory funnel and shaken with 80 or 200 ml (the amount used for filters and plugs, respectively) of DMF containing 10% water. After 15 min the DMF/water solution is transferred to a 1000 ml separatory funnel and the extraction of the cyclohexane in the first funnel is repeated. The two DMF/water extracts are combined and shaken with 130 or 300 ml of water and then with 80 or 200 ml of cyclohexane. The extraction is repeated with 25 or 65 ml of cyclohexane. The cyclohexane solutions are combined, washed with 50 or 125 ml of water, and transferred to a 500 ml Erlenmeyer flask. The cyclohexane solution is dried by adding sodium sulphate.

As shown in Figure 2, the evaporation of the solvent is carried out in three steps. The first takes place in a rotary evaporator under

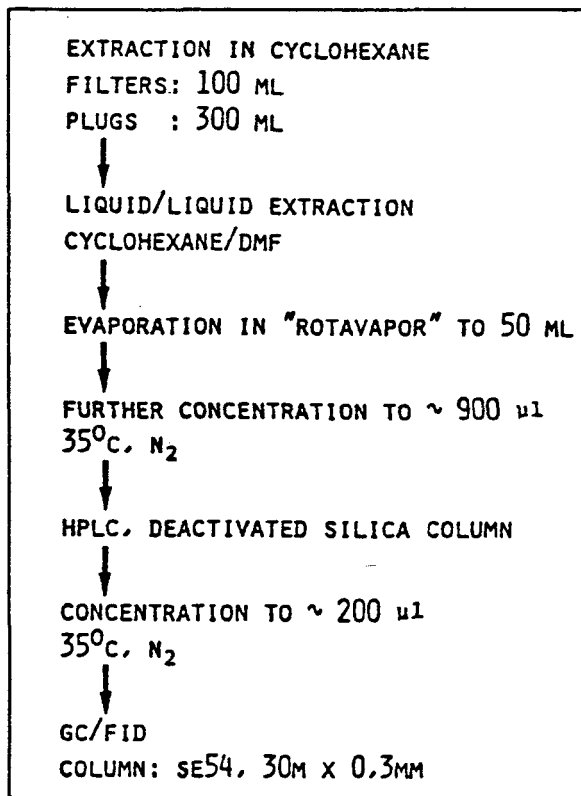


FIGURE 2 Scheme for extraction, enrichment, cleanup and analysis of PAH collected on glass fibre filters and PUR plugs.

reduced pressure (vacuum pump) at 40°C. When there is about 50 ml left, the cyclohexane solution is transferred to a flask with a tube melted into the bottom end. This flask is connected to a manifold, see Figure 3, where up to four sample solutions may be evaporated simultaneously. The evaporation is continued under reduced pressure at 35°C with a stream of nitrogen onto the surface of the solution, until the volume of the solution left in the flask is 900 µl. At this stage a further purification of PAH is carried out. The PAH are separated by column chromatography from the more polar organic compounds that are still present in the solution. This

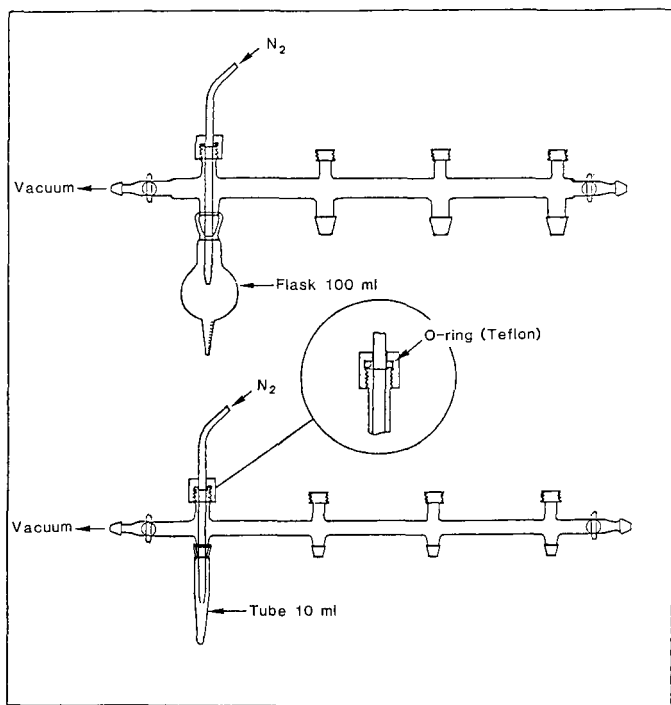


FIGURE 3 Apparatus for enrichment of PAH extracts.

purification is important. Substances that interfere with the PAH peaks in the gas chromatogram are efficiently removed. This means that the time of the gas chromatographic analysis may be shortened and that the identification and quantification of the compounds become more reliable.

An HPLC system equipped with a silica column (Zorbax-sil, 5  $\mu$ m, 250  $\times$  4.6 mm) is used. Prior to the sample purification, the column must be rinsed with chloroform (Merck 2445 p.a.) and deactivated by running methanol containing 5% water through the system for about 5 min at a flow rate of 2 ml/min. A high-pressure valve (Rheodyne 7125) with a 2 ml sampling loop is utilized for sample injection. The 900  $\mu$ l sample solution is transferred from the flask to the loop by means of a syringe. The PAH elute within about 5 min while the column adsorbs the polar compounds in the sample. The



eluent is cyclohexane saturated with water and the flow rate is 1 ml/min. The column is rinsed with chloroform after each sample injection. A Hamilton (86414) valve is used for switching from one solvent to the other. The pump is an LDC Constametric Model III and the detector is an LDC UV III monitor Model 1203. The detector wavelength is 254 nm. The starting and cut-off points of the PAH fraction are determined by injection of a solution containing 5  $\mu\text{g/ml}$  of naphthalene and 10  $\mu\text{g/ml}$  of coronene. Examples of the chromatograms are given in Figure 4.

In order to maintain a satisfactory separation, the system may be rinsed frequently, first with chloroform and for about 30 min with methanol-water (1:1). Then switch to methanol and back to chloroform. Finally, rinse with *n*-hexane containing 10% acetic acid and 2%

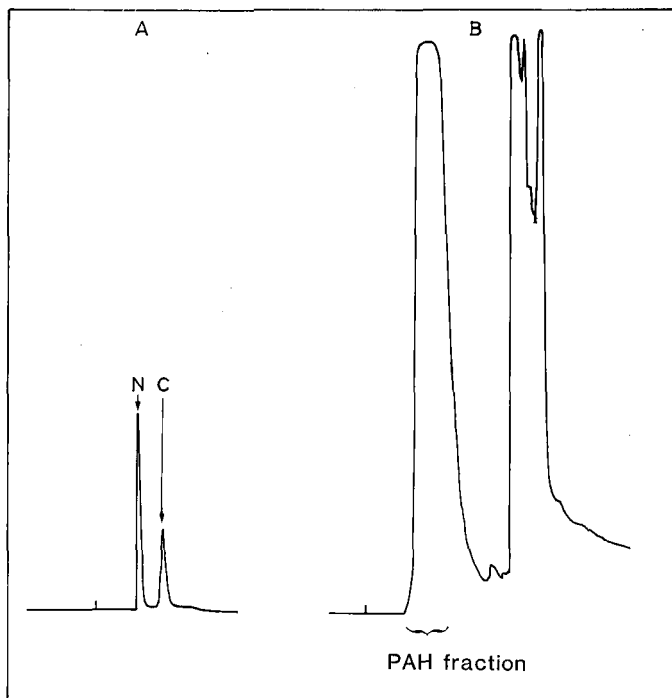


FIGURE 4 Examples of HPL chromatograms of A: Standard solution containing naphthalene (N) and coronene (C), and of B: Filter sample extract.

dimethoxypropane, for 20 min at a flow rate of 2 ml/min, and deactivate the column as described above.

The PAH fraction, about 5 ml, is collected in a graduated centrifuge tube with a conical end. The tube is connected to a manifold as shown in Figure 3, where four samples may be enriched simultaneously. The enrichment of the PAH solution is continued under the same conditions as before, until 200  $\mu$ l are left in the tube. It is most important to watch this evaporation carefully. Evaporation to dryness will cause severe losses of PAH. After evaporation the sample solution is transferred to a micro vial with PTFE-faced seals.

### *Analysis*

A Hewlett Packard 5880A gas chromatograph (GC) equipped with a splitless injection system and a flame ionization detector (FID) is suitable for the PAH analysis. This GC may be programmed by a desk computer, for example a Hewlett Packard 5880A series GC terminal-level four. This system has been used in our studies and the calibrations and the integrations are made automatically. The GC column is 25 m  $\times$  0.3 mm, and coated with SE 52 (0.1  $\mu$ m). The injection is made according to the hot needle principle, and the injected volume is 0.5  $\mu$ l. The GC conditions for the analysis are: Injection/detection block temperature; 300°C, oven temperature programming; 40–100°C at 30°C/min and 100–300°C at 12°C/min. Carrier gas is helium with a flow rate of 6 ml/min. The flow rate of the hydrogen is 20–25 ml/min and of the air, 400 ml/min. When this procedure is followed a satisfactory separation is obtained, and one sample may be injected every 30 min.

### *Calibration*

The reference PAH used for calibration and the recovery studies cover the range from the bicyclic compounds to coronene: Naphthalene (N), 2-methylnaphthalene (2-mN), 1-methylnaphthalene (1-mN), biphenyl (B), acenaphthene (Ac), fluorene (Fl), dibenzothiophene (dBt), dibenzofuran (dBf), phenanthrene (Ph), anthracene (A), 1-methylphenanthrene (1-mPh), fluoranthene (Fla), pyrene (P), benzo(a)fluorene (BaFl), benzo(b)fluorene (BbFl), benzo(a)anthracene (BaA), chrysene (Ch), triphenylene (Tr), benzo(j)fluoranthene (BjFla), benzo(b)fluoranthene (BbFla), benzo(k)fluoranthene (BkFla),

benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (Per), inden(1,2,3-cd)pyrene (Ind), dibenzo(a,c)anthracene (dBa,cA), dibenzo(a,h)anthracene (dBa,hA), benzo(ghi)perylene (BghiPer), anthanthrene (An) and coronene (C). The purity of the compounds should be better than 99%. The compounds are commercially available from Aldrich Chemical Company, Analabs., or the Commission of the European Communities, Community Bureau of Reference. The reference solutions prepared contain 5–10 ng/ $\mu$ l of PAH in cyclohexane. The relative concentrations should be similar to those expected in the air samples. The PAH standards may be dissolved ultrasonically in the cyclohexane.

The internal standards, 3,6-dimethylphenanthrene and  $\beta,\beta'$ -binaphthyl are obtained from Aldrich Chemical Company. The concentration of the internal standard solution is in the range of 300–400 ng/ml for each compound. The amount added to the sample is adjusted according to the expected PAH concentration of the sample. Normally 5  $\mu$ l are added to filters and 20  $\mu$ l to the PUR plugs.

The response factors related to the internal standards were determined for each compound in the reference sample. The quantification of the individual PAH in the samples, is based upon this factor. Corrections should be made for the losses that have been observed in the recovery studies described below.

## RESULTS AND DISCUSSION

The determination of PAH is complicated and a full exploitation of the traceability of the methods will involve a considerable amount of work. The recovery of PAH and the reproducibility or repeatability have been investigated for some important steps of the procedure. The results are presented and discussed below.

### Sampling efficiency

Sampling of PAH in ambient air is a difficult task. The concentrations of PAH in air are low, usually in the range of ng/m<sup>3</sup> or even pg/m<sup>3</sup>, and large samples are needed in order to collect amounts of PAH above the detection limit of the analytical methods. Many of the compounds have high vapor pressures and will

evaporate during sampling. High volume samplers equipped with a glass fibre filter for collection of the particulate PAH and with traps of different kinds for the gaseous PAH, are commonly used. The collection efficiency will, however, depend on the sampling conditions such as ambient temperature, flow rate, concentrations of particles etc. It is most important that the collection efficiency of a sampler is known.

You and Bidleman<sup>8</sup> studied the influence of volatility on the collection efficiency of PAH for a sampling system similar to that described in this paper. They examined the frontal chromatographic movement of selected PAH through PUR plugs at high volume air flow, and found that the breakthrough of a compound could be estimated on the basis of the vapor pressure of the subcooled liquid. Keller and Bidleman<sup>9</sup> concluded that PUR plugs were effective collectors for the 3- and 4-ring PAH in their own sampling system when the air volume was limited to 600 m<sup>3</sup> at 20°C and to 317 m<sup>3</sup> at 25°C. The air flow was 30 m<sup>3</sup>/h. They used a 20 × 25 cm glass fibre filter in front of two PUR plugs 7.8 cm dia. × 7.6 cm thickness. The density of the foam was 22 kg/m<sup>3</sup>. Keller and Bidleman have also shown that the temperature is the most important factor to be considered in designing a collection system. Losses of bicyclic PAH have been observed from the sampler in Figure 1, especially in the summer when the temperature is high. The relationship between the average ambient temperature and the measured concentrations of two bicyclic PAH, naphthalene and biphenyl, and of phenanthrene is illustrated in Figure 5. All samples have been collected at one station. Due to the seasonal variation of the meteorological conditions, this station was exposed to PAH mostly in the summer. This means that higher PAH concentrations should be expected during the warm season, that is at elevated temperatures, than in the winter. The results of the bicyclic compounds in this figure indicate that the concentration increases with decreasing temperature. The concentration of phenanthrene, however, seems to be positively correlated with the temperature as expected. Positive correlations were also found between ambient temperature and other PAH with more than 3 rings in the molecule, measured at this station. The differences between the bicyclic PAH and those with more than 3 rings, illustrated in Figure 5, are caused by the loss of the bicyclic compounds during sampling at elevated temperature. In such cases

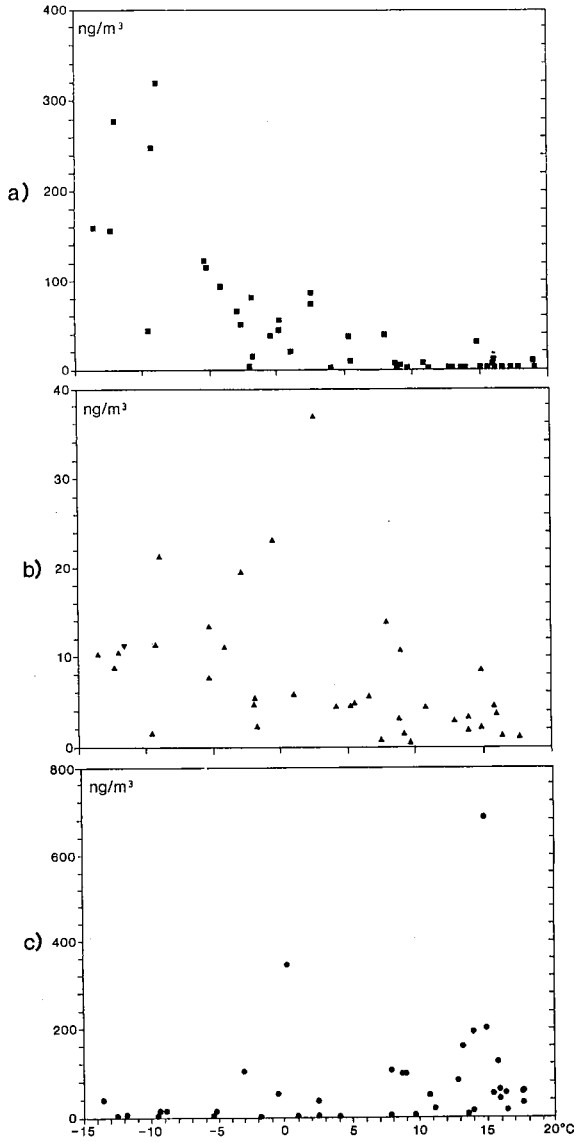


FIGURE 5 Relation between concentrations of (a) naphthalene, (b) biphenyl, (c) phenanthrene and the average ambient temperature during sampling.

the results of the bicyclic compounds should be discarded. This example shows the importance of testing the collection efficiency of a sampler before the evaluation of the analytical results.

The dimensions of the sampler and the flow rate are important for the collection efficiency. This is illustrated by the following comparison of the results from two samplers of different sizes. Two samplers, the one shown in Figure 1, so-called sampler (a), and a sampler with a 5 cm diam. cylinder, sampler (b), were placed side by side in the field. The thickness of the plugs in the smaller sampler was 10 cm and the diameter 5.5 cm. The volume of each plug in samplers (a) and (b) was 475 and 237 cm<sup>3</sup>, respectively. The efficiency of the two samplers was compared by collecting four sets of samples in parallel. The air flow rate for both systems was 9 m<sup>3</sup>/h. The flow through the smaller sampler was four times the flow rate through the larger one. The results in Figure 6 show that the collection efficiency of the most volatile PAH is considerably lower in the smaller sampler, due to the much higher linear velocity and the smaller volume of the plugs. In this case satisfactory agreement between the collection efficiencies was obtained when the air flow rate for the smaller sampler was reduced to 5 m<sup>3</sup>/h. This example illustrates that it is necessary to test the collection efficiency of a sampling system in the field before it is used in a monitoring program.

### Sample storage

The exposed filters and plugs are tightly wrapped in aluminum foil and sent to the laboratory for analysis. Sometimes, for example when a large number of samples arrive at the same time, it is necessary to store some of the samples. The stability of selected PAH in field samples was therefore tested. Exposed filters were cut in two, one part was analysed immediately after sampling and the other one after six months of storage wrapped in aluminum foil, at -20°C. The results showed no concentration changes. For the stability test of PAH trapped in the PUR plugs four sets of samples were collected in parallel. For each set, one plug sample was analysed right after sampling while the other was wrapped and stored for six months at -20°C, and then analysed. A comparison of the results from the parallel sampling is given in Figure 7. Some analytical results had to be discarded due to interferences. Therefore, the ratio

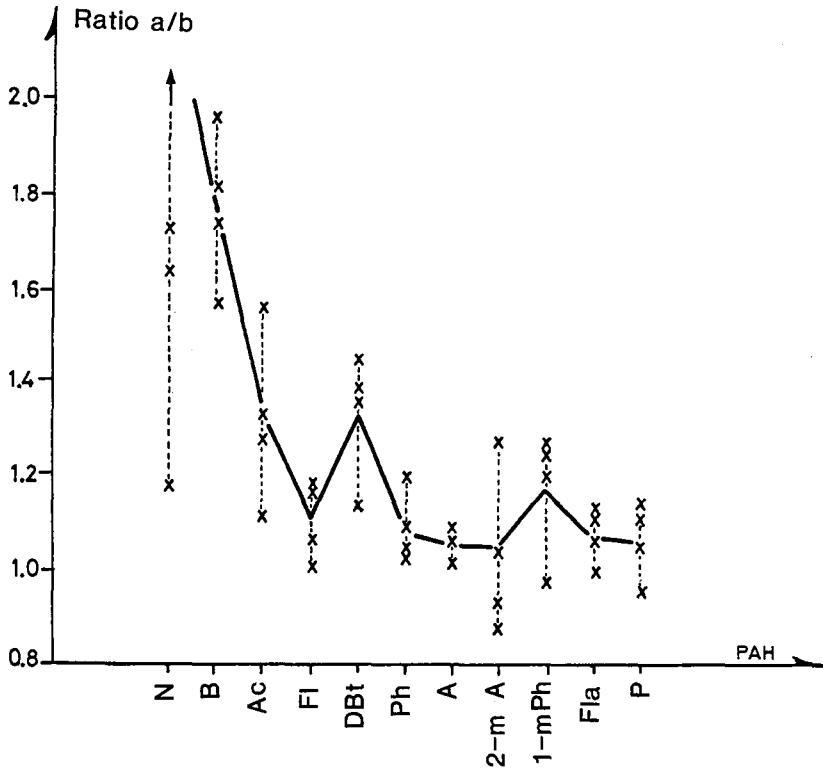


FIGURE 6 Comparison of the collection efficiency of two sampling systems for PAH. (a) Sampling system in Figure 1. (b) Sampling system with 5 cm diameter glass fibre filter and two plugs with 5.5 cm diameter and 10 cm thick.

for anthracene is presented for only one pair of samples. The results in the figure indicate that the samples have been contaminated by the most volatile compounds such as naphthalene, in spite of the tight wrapping and the low temperature during storage. Losses of compounds such as anthracene, fluoranthene and pyrene seem to occur when the samples are stored for as long as six months. It is, however, important to note that two separate samplers have been used for the stability study of the plug samples. Differences between the two samplers may have caused some of the discrepancies.

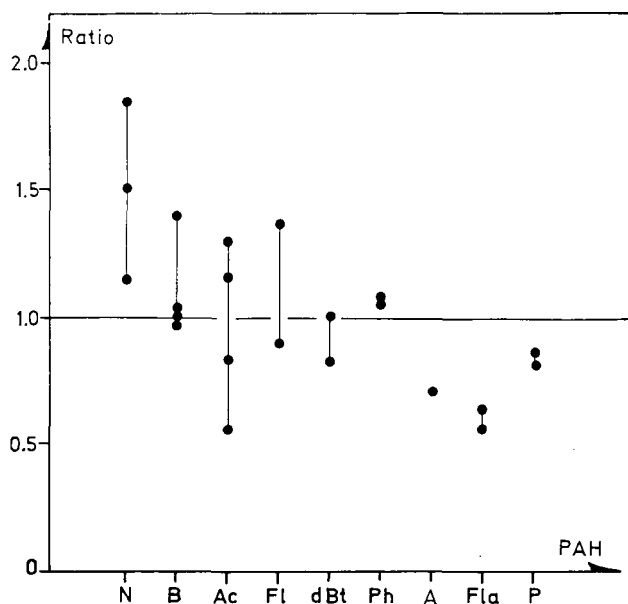


FIGURE 7 Ratios of the amount of PAH in PUR foam plugs stored for six months, to the amount in plugs analysed immediately after sampling.

The stability during storage of purified and concentrated PAH-solutions has also been investigated. Aliquots of four extracts from exposed filter samples and of six extracts from exposed PUR-plugs were analysed immediately after preparation. The vials containing the rest of the solutions, were stored for six months at  $-20^{\circ}\text{C}$  and re-analysed. The results, shown in Figures 8 and 9, indicate some changes of the PAH profiles in the samples. Evaporation of the solvent, contamination and decomposition of PAH may be the reasons for these changes.

### Sample preparation

*Extraction* The efficiency of the PAH extraction has been tested by Bjørseth<sup>7</sup> and the results were satisfactory. Different extraction methods and solvents have been compared.<sup>10,11</sup> Soxhlet extraction and ultrasonic extractions seem to be the methods most frequently



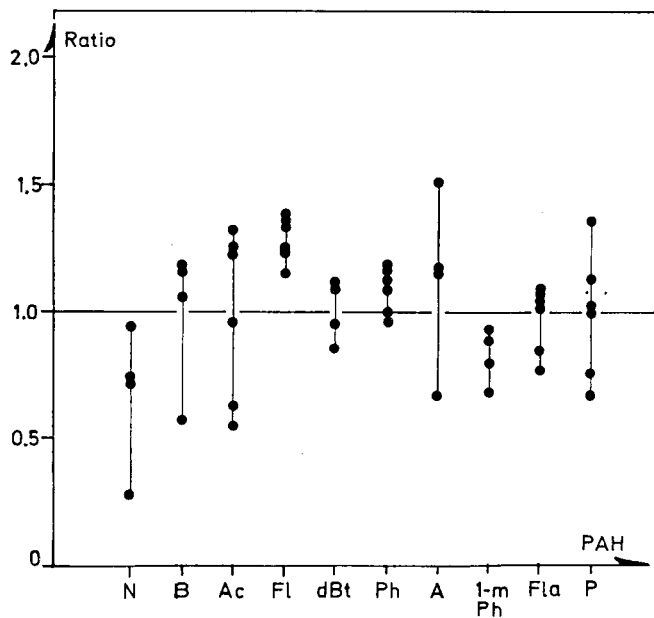


FIGURE 8 Ratios of the amount of PAH in enriched and purified cyclohexane extracts from PUR foam plugs stored for six months, to the amount in extracts analysed immediately after extraction.

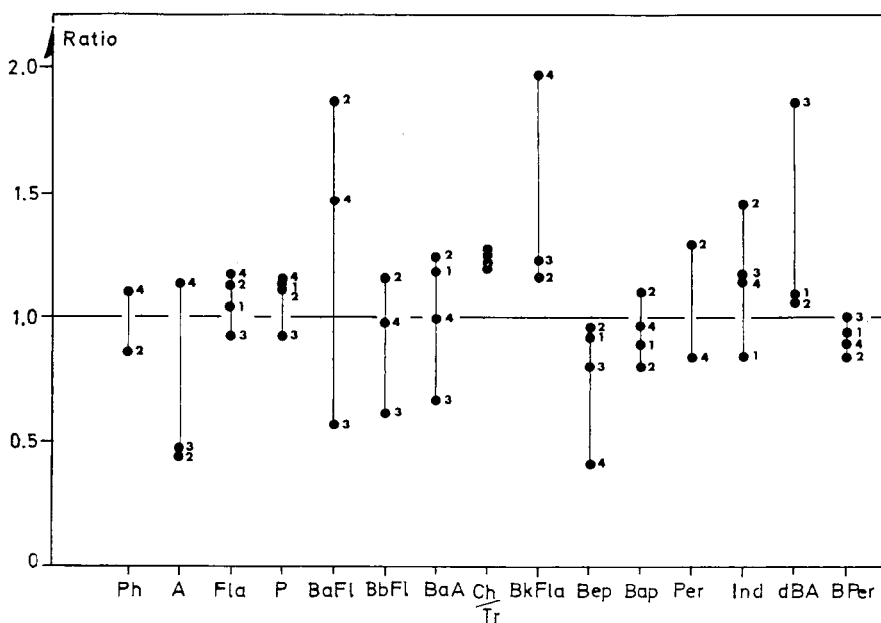


FIGURE 9 Ratios of the amount of PAH in extracts of filter samples stored for six months, to the amount in the extracts analysed immediately after sample preparation.

used. The ultrasonic extraction has some advantages. It is not as time-consuming as the Soxhlet extraction and allows higher recoveries of the two- and three-ring compounds,<sup>12</sup> but the method is not convenient for extraction of the PUR plugs. In order to keep the same extraction procedure for both the filters and the plugs, the Soxhlet extraction in cyclohexane was selected. The choice of solvent is based on the fact that cyclohexane is widely used for extraction of airborne PAH and it is considered less harmful compared to other recommended solvents such as benzene, chloroform or dichloromethane. The price is reasonable which is important in monitoring programs where large numbers of samples need to be extracted.

*Enrichment* The concentrations of PAH in the extracts from the filters and the plugs are too low to be detected by FID. It is therefore necessary to concentrate the PAH in the solutions. This is usually done by evaporation of the solvent. Losses of PAH during the evaporation have, however, been observed.<sup>13</sup> The more volatile PAH will to some extent evaporate with the solvent while others may decompose or react. In order to minimize the loss this step should be carried out under very gentle conditions.

Careful evaporation of a large number of samples requires high capacity in the laboratory. This is usually not the case, and it is therefore necessary to compromise. In order to find the most satisfactory procedure for the evaporation a study of the recovery under different conditions was carried out. Some selected PAH were dissolved in 100–300 ml of cyclohexane. The concentrations of the compounds were in the same order as the concentrations in extracts from field samples. Three concentration procedures were compared by evaporating cyclohexane solutions containing known amounts of PAH. The evaporations were carried out (1) in a rotary evaporator down to 200  $\mu$ l; (2) under a stream of nitrogen to 200  $\mu$ l; and (3) in a rotary evaporator to 50 ml and then under stream of nitrogen to 200  $\mu$ l. The temperature of the solutions during evaporation was 35–40°C, and all the tests were carried out under reduced pressure (vacuum pump). The tests were repeated four times. The results in Figure 10, show the average recovery for each compound. The best recovery is obtained when the solution is evaporated under a stream of nitrogen without rotation. This method is time-consuming and cannot be carried out in a routine program. The first method is the

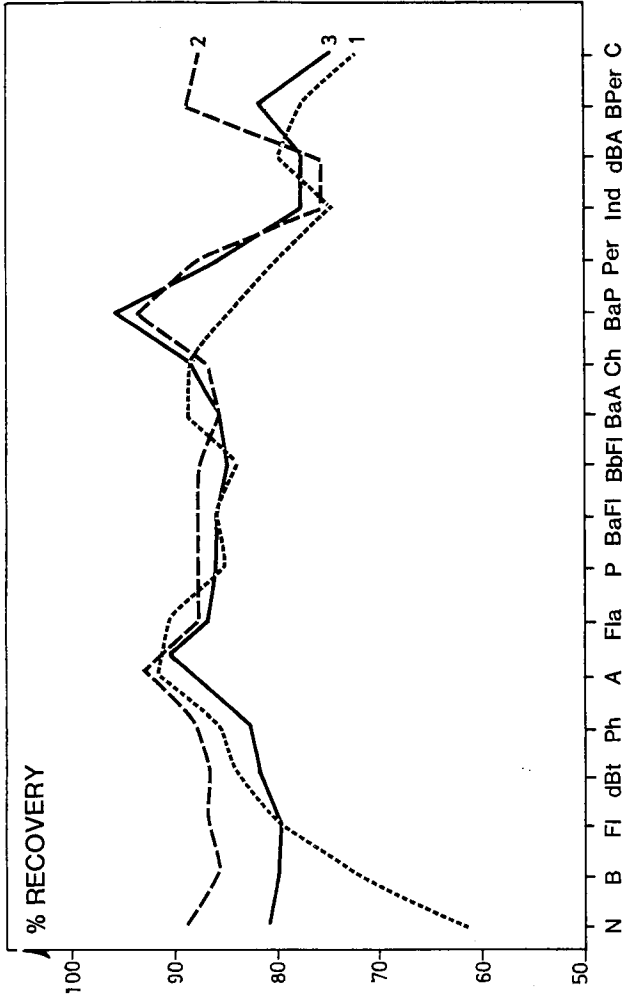


FIGURE 10 Recovery of PAH after evaporation. (1) in rotary evaporator, (2) under a stream of nitrogen, (3) 1+2 combined.

faster, but as shown in Figure 10, the recovery is low. The third method is a compromise: it gives a somewhat better recovery than the first method and is faster than the second method. The results show that about 10–20% of the PAH was lost during evaporation and that the recovery varied from one compound to another. The best result has been obtained for anthracene and benzo(a)pyrene. The low recovery for the two- and three-ring PAH can be explained by their volatility. It is, however, more difficult to give an explanation for the low recovery of the high-molecular-weight PAH.

*Clean-up* The cyclohexane extracts of the exposed samples contain a mixture of pollutants that will interfere with the GC analysis of PAH. Some of the interfering substances are removed by the liquid/liquid extraction with the DMF and water solution and the back-extraction with cyclohexane. The recovery of PAH from these extractions have been reported as satisfactory.<sup>6,7</sup> A further isolation of PAH is, however, necessary in most air samples, that contain interfering organic substances after the liquid/liquid extraction. Column chromatography is often used for this clean-up. The HPLC technique described in this paper yielded good results, and no loss of PAH could be detected. The importance and the efficiency of this clean-up are illustrated in Figure 11 which shows two chromatograms of a PUR sample, before and after the HPLC separation.

### Reproducibility

Monitoring of PAH in ambient air comprises several steps from sampling to analysis and data evaluation. So far very little has been done to determine the reliability of the whole procedure. However, efforts have been made in order to determine the precision of the work carried out in the laboratory. Standard reference materials of PAH in particulates are available,<sup>14</sup> and such samples are very useful for checking the quality of the laboratory techniques, but unfortunately no information is obtained about the quality of the field work. In general too little attention is given to the sampling part, mainly because such tests are difficult to carry out, and they are also very laborious. The reproducibility of the sampling system in Figure 1 was tested by collecting samples in parallel. Two samplers were placed side by side in the field and samples were collected for 24 h. The analyses of all samples were carried out in the

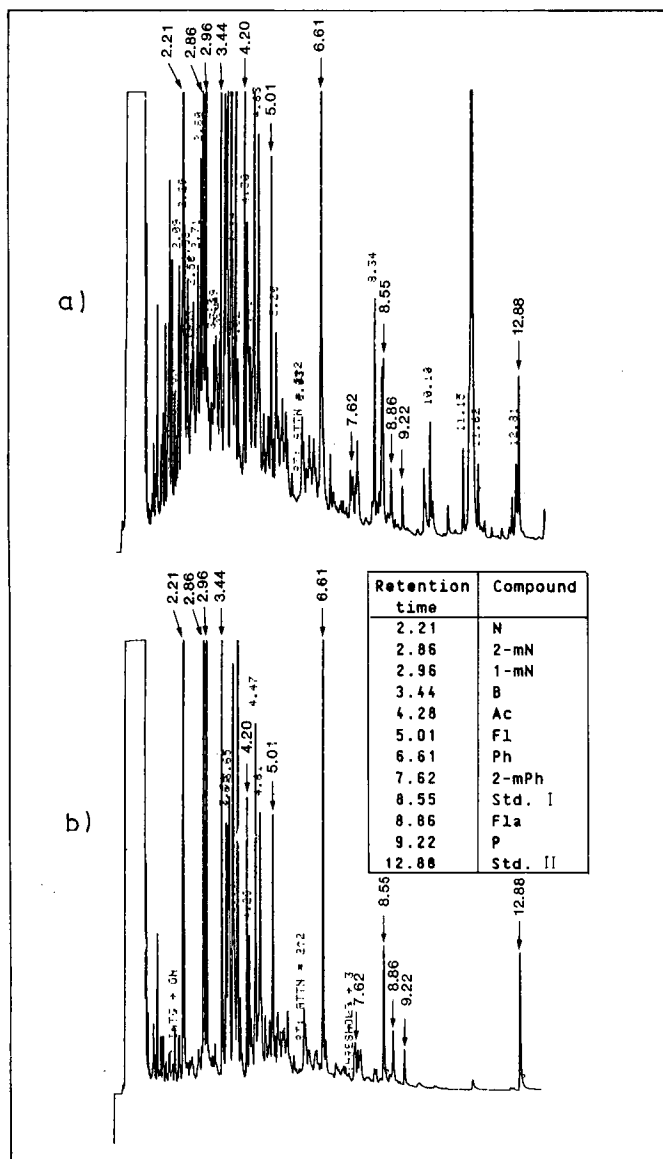


FIGURE 11 Examples of gas chromatograms of PUR-extracts: (a) before and (b) after the HPLC clean-up.

same laboratory. The personnel were not informed about the test and the samples were analysed on a routine basis. The analytical results, shown in Table I, indicate a satisfactory agreement between two separate samplers. The best agreement is obtained for compounds in the range from phenanthrene to coronene.

## CONCLUSION

The methods and the equipment described here have proved to be well suited for monitoring of PAH. The quality of the analytical results obtained is good and the time needed for the analysis has been significantly reduced as several samples may be prepared at the same time. For example, one of the most time consuming steps in the procedure is the concentration of the extracts. Time is saved by concentrating four samples at the time. The procedure also allows samples to be injected every half hour while a frequency of 50–60 min is more common.

The methods have been applied for monitoring of PAH in highly polluted areas as well as in non-urban areas,<sup>2,15</sup> and in monitoring programs in the surroundings of six different aluminum production plants in Norway. The objectives of the investigations in the neighbourhood of the aluminum factories, were to determine the ambient air concentrations and the frequency distributions of PAH, and to study the seasonal variations as well as the influence of various emission sources. The contributions of PAH to ambient air from the aluminum production were estimated by a cluster analysis of the monitoring data.<sup>16</sup> The procedures described above have proved to be very successful.

The sampling system is easy to handle in the field, and the reproducibility is satisfactory for the relevant components. Tests have shown that two-ring PAH are lost when the sampling is carried out according to the methods described here. The system is, however, efficient for PAH with more than three rings in the molecule. Losses of PAH in a sampling system depends on the ambient conditions such as temperature, and it is illustrated that a satisfactory collection efficiency can be obtained by adjusting the dimensions of the sampler and the air flow. Therefore, it is recommended that the efficiency of a sampling system is tested and optimized in the field before it is used in a monitoring program.

TABLE I  
Data on the reproducibility of the sampling system. Unit: ng/m<sup>3</sup>. Part: particulate phase. Gas: gaseous phase.

Set no.:	1		2		a		b	
	Part	Gas	Total	Part	Gas	Total	Part	Gas
Sampler:	a		b		a		b	
	Part	Gas	Total	Part	Gas	Total	Part	Gas
Naphthalene	10.1	10.1	6.6	6.1	6.1	6.1	4.4	4.4
2-Methylnaphthalene	7.3	7.3	4.7	4.4	4.4	4.4	2.8	2.8
1-Methylnaphthalene	4.6	4.6	3.1	2.5	2.5	2.5	1.7	1.7
Biphenyl	4.2	4.2	2.8	1.9	1.9	1.9	1.4	1.4
1,8-Dimethyl naphthalene	3.6	3.6	4.2	0.8	0.8	0.8	0.8	0.8
Acenaphthene	29.5	29.5	19.8	3.1	3.1	3.1	2.1	2.1
Fluorene	80.0	80.0	68.9	15.5	15.5	15.5	13.8	13.8
Dibenzothiophene	30.7	30.7	32.8	4.3	4.3	4.3	3.4	3.4
Phenanthrene	1.8	244.0	246.0	<0.1	34.3	34.3	<0.1	39.0
Anthracene	0.2	20.5	20.7	0.4	21.7	22.1	3.0	3.7
1-Methylphenanthrene	0.1	20.2	20.3	0.4	32.8	33.2	3.0	3.7
Fluoranthene	4.5	112.0	117.0	4.8	106.0	111.0	0.2	14.1
Pyrene	4.0	72.9	76.9	4.2	70.1	74.3	0.3	8.9
Benzo(a)fluorene	2.8	16.5	19.3	2.8	17.5	20.3	0.1	0.8
Benzo(b)fluorene	2.2	10.7	12.9	2.2	10.5	12.7	<0.1	0.8
Benzo(a)anthracene	13.0	19.7	32.7	12.8	22.4	35.2	0.1	0.4
Chrysene/triphenylene	26.1	26.3	50.4	25.6	26.6	52.5	0.5	1.0
Benzo(b)/k/fluoranthene	60.9	4.7	65.6	58.1	6.5	64.6	1.2	1.5
Benzo(e)pyrene	26.6	26.6	25.5	0.6	25.5	25.5	0.6	0.7
Benzo(a)pyrene	13.0	13.0	12.9	0.3	12.9	12.9	0.3	0.4
Perylene	2.5	2.5	2.6	0.3	2.6	2.6	0.3	0.2
o-Phenylene pyrene	13.2	13.2	13.1	0.8	13.1	13.1	1.0	1.0
Dibenzo(ac/ah)anthracene	4.7	4.7	4.9	0.5	4.9	4.9	0.3	0.3
Benzo(ghi)perylene	15.7	15.7	15.8	1.5	15.8	15.8	1.4	1.4
Anthanthrene	0.5	0.5	1.6	1.8	1.6	1.6	1.4	1.4
Coronene	4.2	4.2	4.3	1.8	4.3	4.3	1.4	1.4
Sum:	196	716	912	195	695	890	8.2	105
				8.3	113	113	8.3	105
								113

The stability of the samples during storage at  $-20^{\circ}\text{C}$  has been tested. The results showed that filter samples wrapped in aluminum foil may be stored for as long as six months. Both losses and contaminations occurred when exposed PUR plugs were stored in the same way. The PAH profiles in extracts from exposed filters and plugs did also change during storage. The most reliable results are obtained when the samples are prepared and analysed as soon as possible after sampling.

Losses were observed in some important steps of the sample preparation. The enrichment of PAH in the extracts is carried out by evaporating the solvent. If this is not done in a gentle way, the most volatile PAH will evaporate with the solvent and be lost. On the other hand a gentle evaporation is time consuming, and difficult to carry out when a large number of samples is being analysed. This problem was solved by using a manifold where four samples can be enriched at the same time. It is, however, important that the last part of the evaporation is watched carefully and stopped before complete dryness in order to avoid severe losses of PAH. The results of our tests showed that 10–20% of the PAH were lost during the evaporation.

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