COMPARATIVE EVALUATION OF PROCEDURES FOR THE DETERMINATION OF PAH IN LOW-VOLUME SAMPLES

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(Received May 1990)

Abstract. The aim of this investigation was to evaluate a simplified version of an HPLC method for the determination of PAH in suspended particles collected from small air volumes indoors, outdoors or in personal exposure measurements. The simplification consisted in: (a) collecting PAH by low-volume samplers; (b) extracting PAH ultrasonically; and (c) omitting separation of interfering substances before analysis by HPLC. The results show that the introduction of these modifications affords a considerable reduction in analysis time and solvent expenditure, without affecting the quality of measurement.

1. Introduction

Airborne polycyclic aromatic hydrocarbons (PAH) are predominantly bound to particles of 1–3 μm MMD (Pierce and Katz 1975, Van Vaeck *et al.* 1980, De Wiest 1978). Therefore samples of suspended particulate matter (SPM) are used for PAH determination. In outdoor air samples collected from 1000 to 2000 m^3 of air during 24 hours were analysed for PAH. Glass fiber filters 20×25 cm placed in a filter holder of a high-volume (HV) sampler usually serve as a collection surface.

HV samplers, being unwieldy, noisy and having too high an air flow, cannot be used indoors. Therefore silent medium volume samplers (36 m^3/24 h) have been designed for stationary indoor PAH sampling (Bake and Laskus 1978). For personal monitoring, however, only low-volume personal samplers (2–4 m^3/24 h) can be used. Miguel and Friedlander (1978) used a low-volume impactor during 72 h to study the size distribution of benzo-*a*-pyrene and coronene associated with particles.

Since high sensitivity has been achieved in PAH analysis by means of a high performance liquid chromatograph (HPLC) coupled with a fluorescence detector (May and Wise 1984, Dong *et al.* 1976), the possibility of using daily low-volume samples was considered.

Preparation of HV samples for analysis comprises Soxhlet extraction, separation of interfering compounds (clean-up) and concentration. All these steps are time consuming and require large volumes of solvent. In place of the Soxhlet method, ultrasonic extraction has been applied successfully by Seifert and Steinbach (1977) in the determination of BaP in SPM by thin-layer chromatography. The efficiency was about 96%.

According to Lee (1981) the clean-up step may not be necessary if a selective analytical method is applied.

May and Wise (1984) have shown that the omission of the clean-up step should not

Environmental Monitoring and Assessment **18**: 235–241, 1991.

influence the results of analysis for selected PAH (but may shorten the life of the analytical column).

As we intended to analyse small samples (primarily for benzo-*a*-pyrene), the substitution of Soxhlet by ultrasonic extraction and the omission of a clean-up procedure were considered to be appropriate.

2. Comparative Evaluation of Procedures

2.1. SAMPLING

In order to establish whether low-volume, personal SPM samples may contain sufficient PAH for analysis, we inspected PAH concentrations previously measured in the Zagreb air using HV samples. Taking the benzo-*a*-pyrene concentration as an indicator of PAH levels we found that it varied from 3 to 50 ng m^{-3} in winter and down to 0.5 ng m^{-3} in summer. According to literature data indoor B*a*P concentrations vary from 0.1 to 8 ng m^{-3} (Moschandreas *et al.* 1982) depending on the fuel used for heating and cooking and on the presence of tobacco smokers.

Thus it had to be established whether about 0.2 ng BaP in a sample obtained from 2 m^3 of air may be determined with sufficient accuracy and precision. A mixture of standard PAH solutions containing 5.68 ng fluoranthene (Flu), 0.94 ng benzo-*b*-fluoranthene (BbF), 0.27 ng benzo-*k*-floranthene (B*k*F), 0.26 ng benzo-*a*-pyrene (B*a*P), 0.48 ng benzo-*b*-chrysene (B*b*Chr), 2.24 ng benzo-*ghi*-perylene (B*ghi*Per), 0.41 ng anthanthrene (Ant) and 4.60 ng coronene (Cor) in 10 μL of acetonitrile was injected nine times into the HPLC apparatus and analysed. The results of the analyses showed that there was no statistically significant difference between the expected and measured concentrations. The coefficient of variation (*V*%) for repeated measurements ranged from 2.6 to 3.8% for the eight compounds, proving that at the given concentration levels the repeatability of the method was acceptable for all compounds measured.

In order to check the repeatability of the whole procedure (extraction, clean-up, evaporation, dissolution and analysis) six equal parts were cut out from an HV sample and analysed, each corresponding in its SPM load to low-volume samples (area through which about 2 m^2 of air has passed). The results are shown in Table I.

The variability coefficients for the PAH present in the sample in quantities equal to or larger than in the standard mixture were 1.5–2.0 times higher, which is still acceptable

Table I

Determination of PAH in six equal parts of the same filter (N=6).

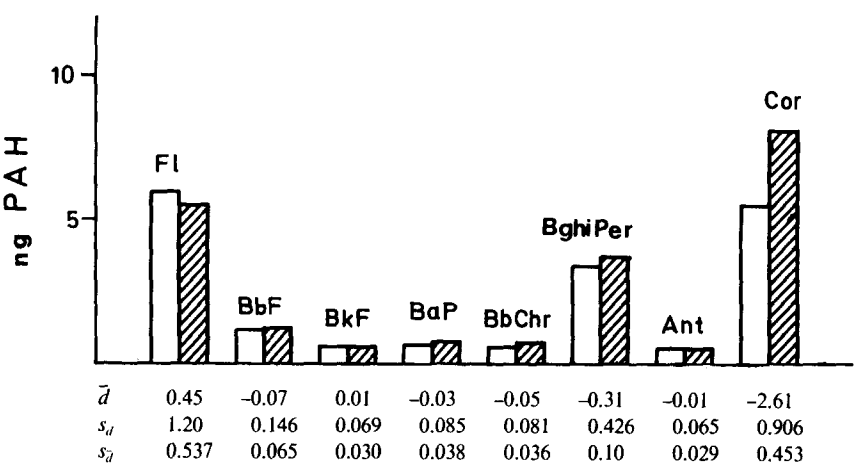
Parameter	Flu	B*b*F	B*k*F	B*a*P	B*b*Chr	B*ghi*Per	Ant	Cor
$\bar{x}$	0.8965	1.8001	0.4257	0.6255	0.1228	2.8294	0.1105	n.d.
s	0.1169	0.1213	0.0287	0.03518	0.0236	0.1332	0.0279	
$s_{\bar{x}}$	0.0477	0.0495	0.0117	0.01436	0.0096	0.0544	0.0114	
V%	13.04	6.740	6.753	5.625	19.2	4.71	25.29	

considering the complexity of the procedure and the error in dividing the sample. For the PAH present in much lower quantities (about 1/4) (Flu, B*b*Chr and Ant) than in the standard mixture the coefficient of variability was proportionally higher, but not the standard deviation.

2.2. EXTRACTION

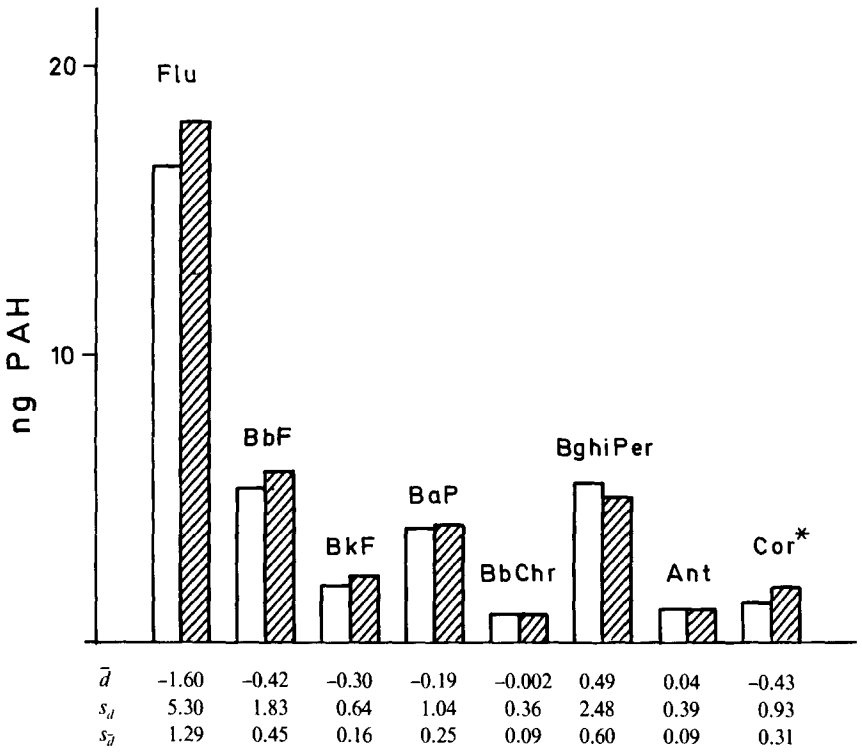
Various solvents have been used for PAH extraction. The most efficient was benzene, but it is no longer in use owing to its carcinogenicity. In these experiments cyclohexane was used, following Dong (1976) and Fechner and Seifert (1978).

In order to verify whether ultrasonic extraction can successfully substitute for the Soxhlet extraction two sets of five glass fiber (GF) filters were spiked with 100, 200, 300, 400 and 500 μL of the above mixture of standard solutions. One set was extracted in a Soxhlet apparatus and the other in an ultrasonic bath. The extracts were evaporated to dryness, dissolved in 200 μL of acetonitrile and 10 μL was injected into the chromatograph. Summarized results are shown in Figure 1. Soxhlet and ultrasonic extractions were also compared using equal parts of real samples (Figure 2). The difference in the extraction efficiency by the two techniques was not statistically significant ($P>0.05$) either in spiked or in real samples (except for coronene in spiked samples, which seems to be an artefact since the difference was not significant for real samples). Therefore it was decided to extract samples ultrasonically in the future, since the following advantages are observed: (a) shorter extraction time (1.5 against 8h), (b) less solvent required (5 mL against 50), (c) more samples can be extracted simultaneously, (d) considerable energy saving.



$\bar{d}$	0.45	-0.07	0.01	-0.03	-0.05	-0.31	-0.01	-2.61
s_d	1.20	0.146	0.069	0.085	0.081	0.426	0.065	0.906
$s_{\bar{d}}$	0.537	0.065	0.030	0.038	0.036	0.10	0.029	0.453

Fig. 1. Means for filter pairs spiked with 5 different quantities of standard PAH mixture extracted in Soxhlet apparatus □ and ultrasonic bath ▨. $\bar{d}$ = mean difference, s_d = standard deviation, $s_{\bar{d}}$ = standard error of mean difference.

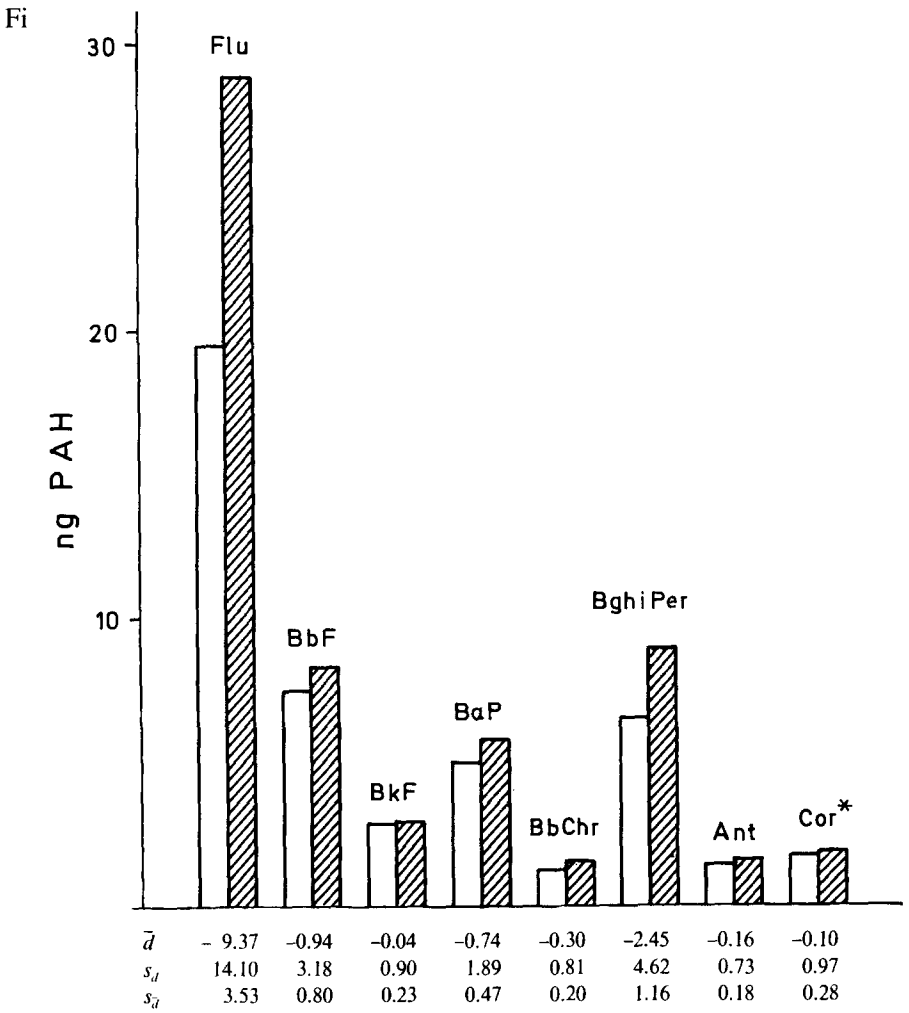


$\bar{d}$	-1.60	-0.42	-0.30	-0.19	-0.002	0.49	0.04	-0.43
s_d	5.30	1.83	0.64	1.04	0.36	2.48	0.39	0.93
$s_{\bar{d}}$	1.29	0.45	0.16	0.25	0.09	0.60	0.09	0.31

Fig. 2. Equal parts of the same sample analysed for PAH after extraction in Soxhlet apparatus □ and ultrasonic bath ▨ ($N = 17$). *Coronene was not detected in 8 samples. $\bar{d}$ = mean difference, s_d = standard deviation, $s_{\bar{d}}$ = standard error of mean difference

2.3. SEPARATION OF IMPURITIES (CLEAN-UP)

In the procedure used so far for HV samples the impurities which may interfere with the analysis are removed by passing the extract through a silica gel column before analysis. As the preparation of column and the concentration of the extract take time and increase solvent consumption – i.e. the cost of analysis – paired parts of the same HV samples were analysed, corresponding in SPM load to the low-volume samples: one with the separation step and the other without it. Insoluble fractions of sample and filter residue were removed from the second set of sample (not cleaned up) by centrifugation. The results are presented in Figure 3. With the exception of Flu, which has a short retention time (and therefore is partly masked by the impurities), there is no statistically significant difference ($P>0.05$) between the results obtained when using or omitting the clean-up procedure. Thus if small samples have to be analysed, collected from general urban atmosphere (without large quantities of other organic (especially greasy) pollutants), if potentially carcinogenic pollutants are of prime interest (Flu is not considered carcinogenic (Lee 1981)) and if duration and cost of analysis are critical, the clean-up step may be omitted.



$\bar{d}$	- 9.37	-0.94	-0.04	-0.74	-0.30	-2.45	-0.16	-0.10
s_d	14.10	3.18	0.90	1.89	0.81	4.62	0.73	0.97
$s_{\bar{d}}$	3.53	0.80	0.23	0.47	0.20	1.16	0.18	0.28

Fig. 3. Equal parts of the same sample analysed with □ and without ▨ separation step ($N = 16$). *Coronene was not detected in 4 samples. $\bar{d}$ = mean difference, s_d standard deviation, $s_{\bar{d}}$ standard error of mean difference.

3. Conclusions

Comparative evaluation of procedures for the determination of PAH in air shows that:

- the sensitivity of HPLC/spectrofluorometric method permits application of low-volume SPM samples for PAH determination.
- The ultrasonic extraction of SPM samples with cyclohexane is comparable in efficiency to Soxhlet extraction but requires less time and solvent.
- Separation of interfering substances before analysis can be omitted for low-volume samples unless PAH with short retention time are of interest.

With the above modifications the procedure becomes suitable for large scale monitoring of selected PAH indoors, outdoors and in personal exposure assessment.

Acknowledgement

This research was commenced under Agreement A6/181/12 with WHO, which provided the analytical equipment, and was completed as a cooperative YU–US research activity under the joint funding project No. 869.

Appendix. Procedure Adopted

1. Sampling
   (a) stationary: low-volume sampler, e.g. 'Volumetric' apparatus (OECD, 1964)
   (b) personal: personal sampler, e.g. Casella F 13350 or similar
   sampling surface: glass fiber filter 2.5 – 5 cm open face diameter
   air flow 1.5 – 3.0 L/min
   sampling time $\geqslant$ 24 h
2. Preparation of samples for analysis
   Samples should be stored in refrigerator
   Extraction in ultrasonic bath with 5 mL of cyclohexane at 50 °C for 1 hour
   Separation of undissolved parts by centrifugation (~10 min)
   Evaporation to dryness in rotoevaporator (5–15 min)
   Redissolution of residue in 200 μL of acetonitrile
3. Analysis (40 min per sample)
   Injection of 10-20 μL of extract prepared under 2. into HPLC
   PAH are separated on a column e.g. Lychrosorb 5 RP-18 with a mixture of acetonitrile and water (80:20) as a mobile phase at a rate of 1.2 mL/min (Fechner and Seifert 1978).

The concentrations of divided PAH components are measured by a spectrofluorimetric detector at selected excitation and emission wavelengths ($\lambda_{ex}/\lambda_{em}$). In this study samples were analysed at λ_{ex}:300 and λ_{em}: 434 μm.

The retention times for the PAH measured in this study were:

PAH	Flu	BbF	BkF	BaP	BbChr	BghiPer	Ant	Cor
Retention time min	5.9	11.5	12.0	13.7	18.1	20.1	25.0	37.3

Total time for preparation and analysis is about 2 h for one sample, but 6–8 samples can be analysed during one day's working time.

If PAH which appear at different wavelengths are measured, more than one injection has to be made which prolongs the analysis time correspondingly.

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