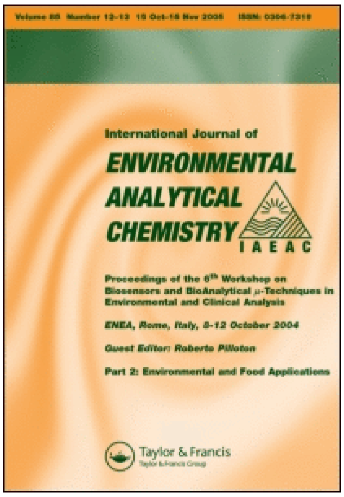

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A Routine Method for the Quantitative Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Air†

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We have developed a method for the quantitative determination of polycyclic aromatic hydrocarbons (PAHs) present in urban air, which can be performed rather quickly, and which uses a minimal amount of solvents.

Air samples were collected using a home-made low-volume air sampler equipped with glass fibre filter and polyurethane foam plugs. After Soxhlet extraction a liquid–liquid partition was carried out to isolate the PAH fraction. This liquid–liquid partition was performed in micro-scale, enabling us to use small quantities of the solvents and to separate the solution layers very rapidly using a centrifuge. Sample clean-up was accomplished on a high performance liquid chromatograph equipped with two normal phase silica columns. The losses of all investigated PAHs occurring during the various steps of sample clean-up have been determined. The qualitative and quantitative determination of the PAHs was carried out by capillary gas chromatography; the results were confirmed by GC/MS measurements.

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‡Dedicated to Professor Dr. Otto Hromatka on the occasion of his 80th birthday.

The analytical procedure described was applied over a period of one year to measure the concentrations of 21 PAHs in the city of Vienna at a site with high traffic density. The concentrations of the four more volatile PAHs were determined on a semi-quantitative basis. The ratio of two selected PAHs was used to estimate the respective contribution of traffic and domestic heating to the total PAH level at the sampling site.

KEY WORDS: Polycyclic aromatic hydrocarbons, airborne particulate matter, air sampling, air-sample preparation.

METHOD

Sampling

A home-made low-volume air sampler (Figure 1), consisting of a Gelman 1235 filterholder and a glass tube (18 mm inner dia., 200 mm high), was used for collecting the samples. The particles were collected on a 47 mm dia. glass fibre filter (Whatman GF/A) and the

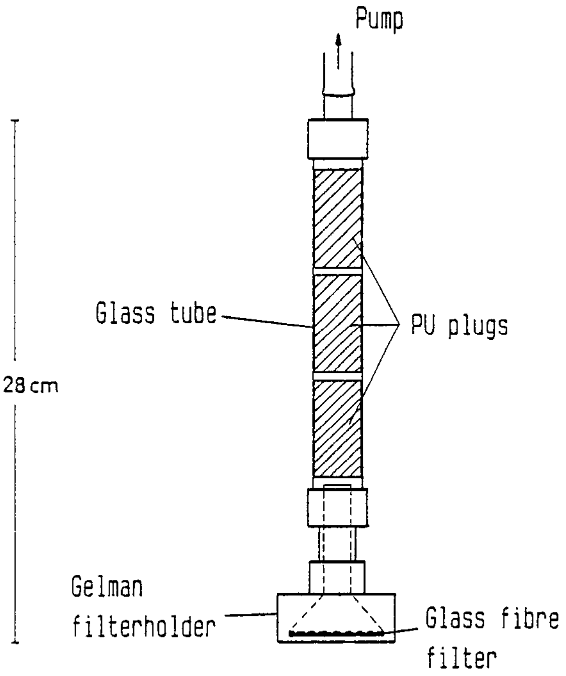

FIGURE 1 Schematic diagram of the low-volume air sampler.

volatile PAHs were trapped by three polyurethane foam plugs (23 mm dia., 50 mm high) located behind the filter in the glass tube.[1,2] A WERIE TLE 6DV vacuum pump and a ELSTER G6 flow control was used for sampling. The sampling time was 24 h and the volume of the air samples was 80–90 Nm^3.

When two sampling apparatus were used simultaneously, and the sampling time (24 h) was divided into shorter periods and the samples were separately analysed, higher amounts of the more volatile PAHs naphthalene, acenaphthylene, acenaphthene and fluorene were found. This result demonstrates a partial loss of these relatively more volatile PAHs during sampling. These compounds could therefore only be determined on a semi-quantitative basis. No sampling-loss was observed for the other 21 PAHs under consideration.

Sample preparation

The exposed filters and polyurethane plugs were Soxhlet-extracted with purified cyclohexane (200 ml) and the volume of this solution was then reduced to about 10 ml in a modified rotation evaporator under a slow stream of nitrogen. Before extraction, the internal standard β,β'-binaphthyl was added to the samples.

In order to isolate the PAH fraction a liquid–liquid partition in micro-scale was performed. A portion (1–5 ml) of the extract was transferred to a centrifuge vial and the volume was reduced to 1 ml. This solution was shaken with 0.8 ml of dimethylformamid (DMF). All aromatic and strongly polar species moved from the cyclohexane phase into the DMF phase, all aliphatic hydrocarbons remained in the cyclohexane phase. The two layers were separated using a centrifuge (3,800 rpm). The DMF phase was transferred with a Pasteur pipette to another centrifuge vial. It was then mixed with 1.3 ml of water and shaken out with 0.8 ml of cyclohexane. This process reduced the solubility of the PAHs in the DMF phase; the PAHs moved into the cyclohexane phase, whereas strongly polar compounds, such as alcohols, acids and phenols, remained in the DMF-water phase.[3,4] An emulsion was formed by shaking this mixture, but after using the centrifuge for only 5 minutes the phases separated. The cyclohexane phase was washed with 0.5 ml of water.

Sample clean-up was accomplished by high performance liquid chromatography (HPLC). The HPLC instrument (pump: LDC Constametric III; UV detector: LDC Spectromonitor 1204A, 254 nm) was equipped with a precolumn (120 × 4.6 mm, Merck Kieselgel 60, 70–230 mesh) and an analytical column (250 × 4 mm, Merck Lichrosorb Si 100, 10 μm); the mobile phase (solvent flow rate: 1 ml/min) was water saturated cyclohexane. The HPLC system is shown schematically in Figure 2. The PAH solution (0.4 ml) was injected directly on the precolumn, where very polar constituents and any suspended particles present were retained. When the PAHs had passed through the precolumn, this column was disconnected from the chromatographic system by switching the injection valve. The analytical column performed the separation of the PAHs from the other sample components, such as aza-arenes, oxygenated polycyclic aromatics and other heterocyclics. These compounds were retained by the stationary phase. All PAHs were eluted together without noticeable fractionation in an elution volume of 2–3 ml. After sample

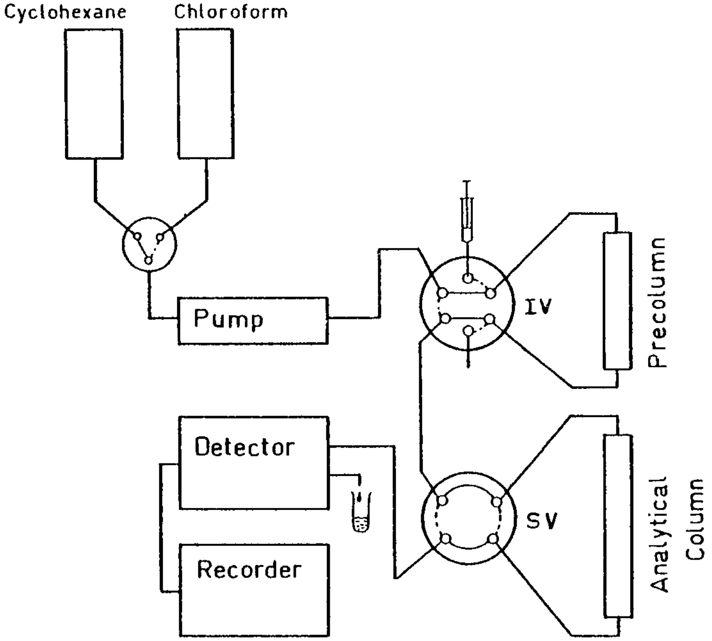

FIGURE 2 Schematic diagram of the HPLC system.

clean-up the mobile phase was changed to chloroform to purge the analytical column from the polar substances. It was possible to purge the precolumn without passing these substances through the analytical column, by changing the position of the switching valve (SV) and then the position of the injection valve (IV) (see Figure 2).

After reducing the volume of the PAH solution obtained to 0.4–0.1 ml, 50 μl of a standard solution (containing CW14, CW23 and CW32; abbreviations see Table I) were added.

In order to obtain a clearer insight into the method, the losses of all investigated PAHs occurring during the various steps of sample clean-up (extraction, reduction of volume, liquid–liquid partition, HPLC separation) have been determined. The result was that the largest PAH-losses occur during liquid–liquid partition. These losses increase with decreasing molar mass, and vary from 10% for coronene to 43% for naphthalene (21% for the internal standard). This trend can be explained by the increasing solubility in water with decreasing molar mass of the PAHs. The losses for the complete sample clean-up range from 29% for coronene to 55% for naphthalene (34% for the internal standard).

GC and GC/MS

The gas chromatographic analyses, both qualitative and quantitative, were carried out on a Carlo Erba Fractovap 2350 instrument equipped with a fused silica capillary column (25 m, 0.32 mm i.d., coated with a cross-linked methylphenylsilicone stationary phase SE 52, 0.15 μm film thickness), a splitless injection system and a flame ionisation detector (FID). The carrier gas was helium. Temperature programming from 130°C to 300°C at 5°C min^{-1} was employed. PAH concentrations were determined by the internal standard method using a SPECTRA PHYSICS SP4270 integrator. Figure 3 shows a typical chromatogram of PAHs in airborne particulate matter collected at the sampling station Getreidemarkt.

Identification of the separated PAHs was confirmed by gas chromatography/mass spectrometry measurements (GC-instrument: Carlo Erba Fractovap 4160; capillary column: J & W, fused silica, 15 m, 0.25 mm i.d., DB5, 0.25 μm film thickness; carrier gas: helium; MS-instrument: Finnigan MAT 8230, EI, 70 eV, scanspeed: 0.5 s/decade).

TABLE I
List of PAHs determined at Getreidemarkt.

		PAH concentration (ng/Nm^3)		
Compound	Abbreviation	Winter half-year	Summer half-year	Annual average value
Naphthalene[a]	NAPH	(68)	(24)	(46)
Acenaphthylene[a]	ACNYLEN	(78)	(18)	(48)
Acenaphthene[a]	ACNEN	(21)	(6)	(14)
Fluorene[a]	FLUO	(92)	(23)	(58)
Phenanthrene	PHEN	197	112	153
Anthracene	ANTH	47	23	34
2-methylanthracene	2MEANTH	18	11	14
Fluoranthene	FLUA	94	52	72
Pyrene	PYR	95	55	74
Benzo(b)naphtho(2,1-d) thiophene	BNT	4.4	2.3	3.3
Benzo(ghi)fluoranthene	BGHIFLUA	17	8.1	12
Benzo(c)phenanthrene	BCPHEN	6.3	1.8	4.0
Cyclopenta(cd)pyrene	CPCDPYR	19	3.3	11
Benz(a)anthracene	BAANTH	16	5.1	10
Chrysene + triphenylene	CHRYTRI	22	8.7	15
β,β'-binaphthyl		Internal standard		
Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(k)fluoranthene	BBJKFLUA	30	9.5	19
Benzo(a)fluoranthene	BAFLUA	6.8	1.3	3.9
Benzo(e)pyrene	BEPYR	13	4.6	8.4
Benzo(a)pyrene	BAPYR	15	3.9	9.3
Perylene	PER	3.8	1.0	2.3
Indeno(1,2,3-cd)pyrene	INDPYR	13	4.5	8.6
Dibenz(a,c)anthracene Dibenz(a,h)anthracene	DBACAHANTH	2.2	0.6	1.4
Benzo(ghi)perylene	BGHIPER	20	8.5	14
Anthanthrene	ANTHAN	4.0	1.0	2.5
Coronene	CORO	15	6.3	10
Tetradecane	CW14	Standards		
Tricosane	CW23			
Dotriacontane	CW32			

[a] PAH concentrations determined on a semi-quantitative basis.

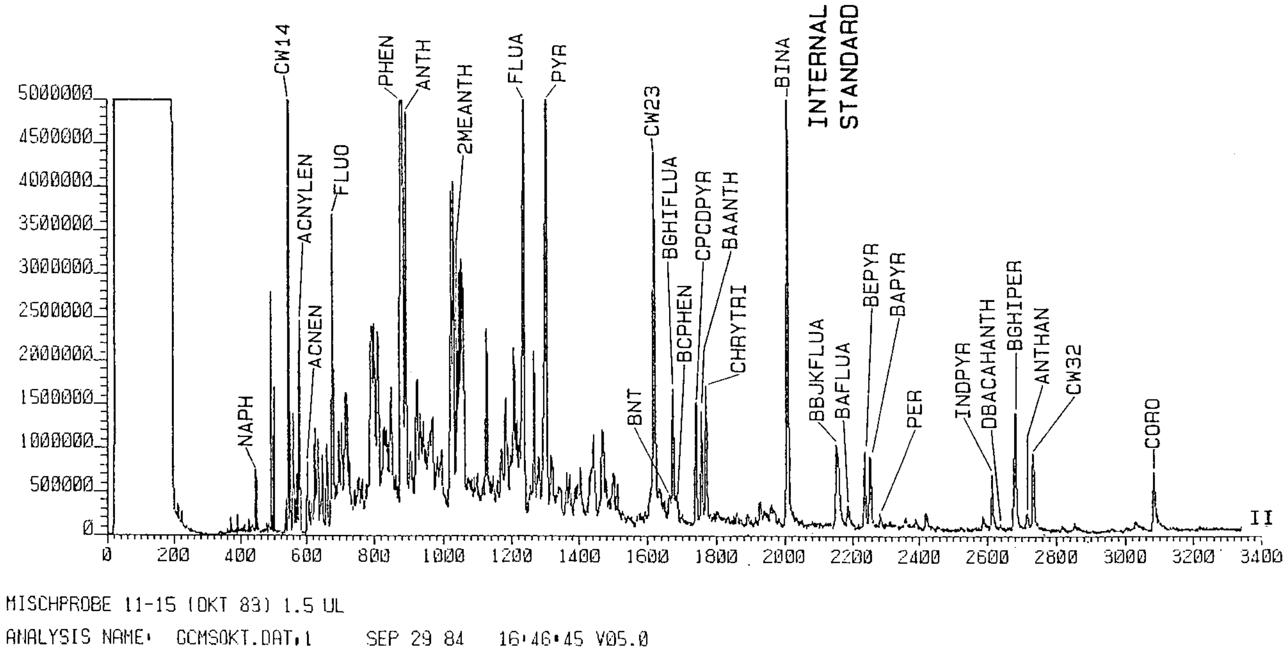

FIGURE 3 Gas chromatogram of PAH fraction (abbr. of PAHs see Table I).

APPLICATION

The sampling station was situated near the centre of Vienna, at the intersection of two busy roads (Getreidemarkt and Gumpendorferstraße; mean traffic density in the order of 50,000 vehicles per 24 hours). Over a period of one year (from August 1983 to August 1984) an air sample (80–90 Nm^3) was taken every week. The samples were collected at head-level, at a distance of 6 m from the kerb. Twenty-one PAHs were determined quantitatively, and 4 PAHs semi-quantitatively (see above).

The PAH profiles obtained correspond to a high degree with the profiles of other large European cities (Berlin and Essen[5,6]). The mean PAH concentrations for the winter half-year are about twice as large as the mean concentrations for the summer half-year (Table I). Figure 4 shows the profiles of the average concentrations of all the

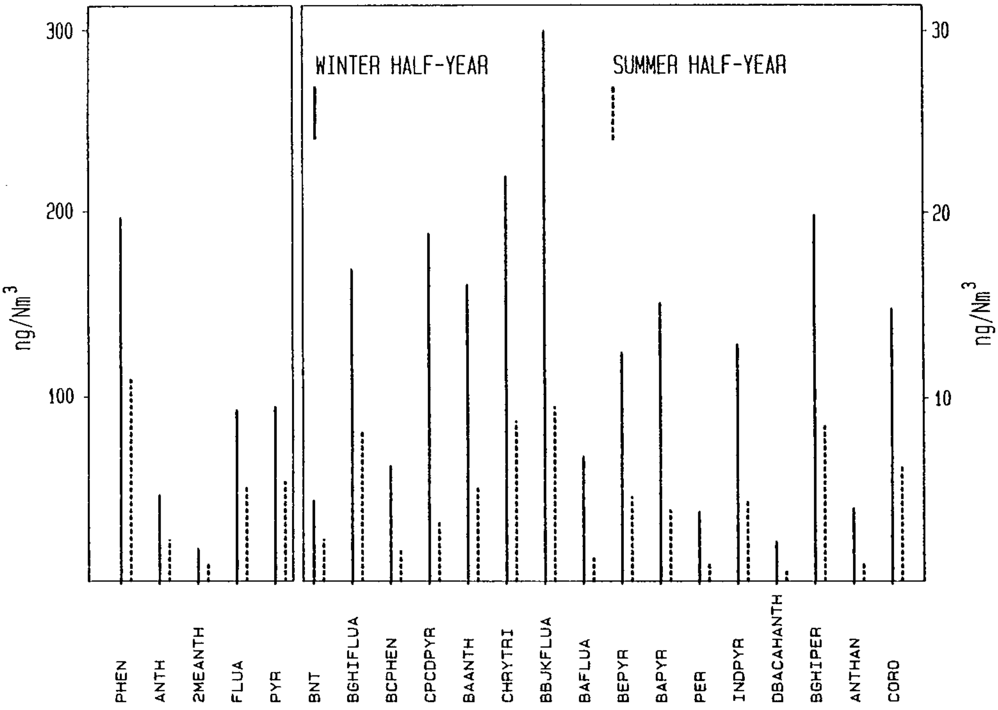

FIGURE 4 Profiles of the average concentrations of the PAHs determined quantitatively (abbr. of PAHs see Table I).

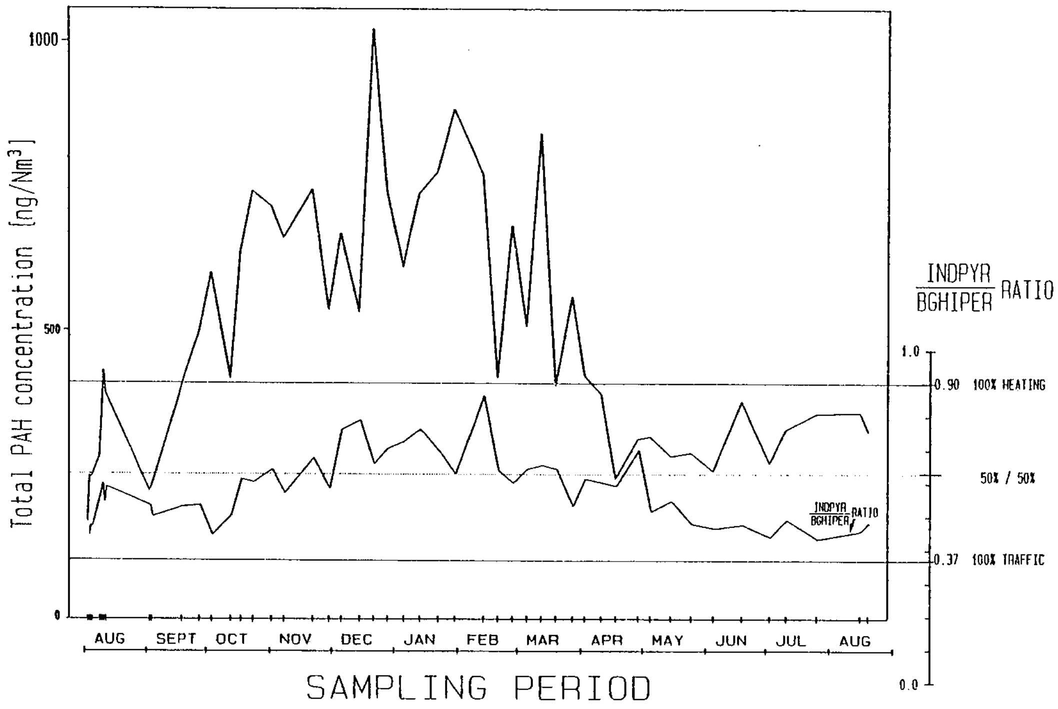

FIGURE 5 Total PAH concentration (upper curve) and indeno(1,2,3-cd)pyrene/benzo(ghi)perylene ratio (lower curve) during the sampling period.

PAHs which we have determined quantitatively. The annual average concentration for benzo(a)pyrene (9.3 ng/Nm^3) nearly reaches the "orientation mark" of 10 ng/Nm^3 proposed by the Federal Environmental Agency of Germany as a standard value.[7] (One Nm^3 is roughly the volume of air inhaled by one person in an hour.)

The ratio of the concentrations of indeno(1,2,3-cd)pyrene/benzo(ghi)perylene (henceforth: I/B) has been calculated in order to assess the contribution of motor vehicle emissions and domestic heating emissions to the PAH immission on Getreidemarkt.[5] According to the relevant literature,[6] the value of I/B should be respectively 0.37 and 0.90 for the PAH profiles from traffic exhaust and domestic heating exhaust. A comparison of these values with those which we obtained by calculation from the measurements made in Getreidemarkt shows that traffic exhaust accounts for about three-quarters of the PAH level in the summertime, while in the wintertime traffic exhaust and domestic heating exhaust contribute approximately equally to the PAH immission (cf. Figure 5).

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