

Plane tree bark as a passive sampler of polycyclic aromatic hydrocarbons in an urban environment

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ABSTRACT

The use of plane tree bark as a natural and passive sampler allowed the detection of nineteen polycyclic aromatic hydrocarbons in the molecular mass range 128–202. The compounds extracted using a Soxtec system were separated by gas chromatography, characterized by mass spectrometry and confirmed by comparison with reference product data. The investigation emphasized the amount of pollution in the urban and rural environments, the kind of traffic and the concentrations of pollutants at various heights in the trunk of the plane trees. The accuracy and precision of the method were also studied.

INTRODUCTION

The sampling of air pollutants is a fundamental phase in the whole analytical process. In fact, the most efficient collection system applied for a suitable time ensures the accuracy of the measurements performed on the species under investigation [1–3].

The choice of the sampler may be difficult because its adsorption efficiency is not constant and uniform over a wide range of compounds, even though these may belong to the same family, because of the different physical characteristics of the substances to be collected [4]. Further, the monitoring of a large zone needs a large number of pumping systems, for a long time, so as to obtain data that correspond to an experimental integration of the pollutants in a particular period. Hence passive samplers are of interest because no power supply and operator presence are necessary [5,6]. The only limitation may be the vulnerability of the apparatus with reference to intentional damage if the collection time in the areas under investigation must be prolonged for runs of several days or weeks.

An index of the pollution level produced by vehicles is represented by the presence of the polycyclic aromatic hydrocarbons (PAHs) in the air [7–9]. Reduced monitoring, like sampling numbers, may be performed according to the NIOSH method using a PTFE filter followed, on-line, by an XAD-2 sorbent tube [10]. In this case, double or triple analytical runs with the three components of the adsorption system (filter and first and second load of sorbent tube) must be carried out.

On the basis of these considerations, the study of a wide zone for a number of days becomes complex and large numbers of samplings and partial analyses must be accurately managed. On the other hand, the sampling phase may be simple and immediate, reducing at least the events which occur outside laboratory if the bark of the trees is used. This paper shows that such a biological matrix is polluted by PAHs and that it represents a natural and passive sampler, constantly present in the investigated zone. The PAH concentration, compared with that detected in a reference zone, is of interest in order to establish not only how the traffic contributes to the level of pollution, but also which kind of traffic flow (slow, fast, queuing) is most responsible for polluting the passive sampler.

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EXPERIMENTAL

Chemicals

All the reference compounds and HPLC-grade solvents (dichloromethane, *n*-hexane and acetone) were purchased from Aldrich Chemie (Steinheim, Germany).

Collection of the samples

Bark was collected as chips in the form in which they left plane trees (*Platanus hybrida*) situated in urban and rural environments. Samples collected at three different heights (0.3–0.8, 0.8–1.2 and 1.2–2 m) up the trunk facing north-east were studied with the aim of identifying and determining the PAHs present. The trees skirted urban roads (2 m from car traffic) with normal traffic in a town of 300 000 inhabitants. The samplings in the urban area corresponded to two zones with different types of traffic flow. The data for each zone investigated were obtained by the averaged analyses of three trees.

Preparation of samples

Bark samples (100 cm², corresponding to about 12 g) were broken into small pieces and placed in a Soxtec system (Tecator, Höganäs, Sweden) for extraction with 70 ml of dichloromethane for 3 h in rinsing conditions [10,11]. The organic solution was dried and the residue was successively treated with five 2-ml portions of *n*-hexane so as to obtain a quantitative recovery of the pollutants. This organic phase was evaporated to dryness under a flow of nitrogen and the residue was dissolved in 1 ml of hexane–acetone (1:1, v/v). A 1- μ l volume of each sample was injected into a GC–MS instrument after the addition of 10 μ l of acetophenone solution (0.3 g l⁻¹) as an internal standard.

GC–MS apparatus and conditions

The measurements were performed using a Hewlett-Packard GC–MS system, consisting of a Model 5890 gas chromatograph equipped with a 25 m \times 0.31 mm I.D. fused-silica capillary column coated with Ultra-2 and a Model 5971 A quadrupole. An HP 59970 C data system was used for data acquisition and editing.

For GC separations the column temperature was programmed from 100°C (isothermal for 3 min) at 10°C min⁻¹ to 250°C (maintained for 10 min). The

injector and transfer line temperatures were 260 and 280°C, respectively.

The MS conditions were electron energy 70 eV, emission current 300 μ A and ion source temperature 176°C. Mass spectra were recorded by cyclically scanning from 50 to 250 mass units with a total cycle time of 0.49 s and a solvent delay of 2.5 min. The injection volume was 1 μ l in splitless conditions (0.2 min). Quantitative analysis was performed by integration of the chromatographic peaks corresponding only to the current of the molecular ions of the compounds examined.

RESULTS AND DISCUSSION

The bark of fast-growing trees such as plane trees constitutes a superficial layer which is, on average, replaced within 2 years (half-life *ca.* 1.5 years) owing to the annual development of the trunk. The permanence of the bark in the same environment for a sufficiently long time as dead biological material allows the cumulative deposition and adsorption of the pollutants without their transformation during contact. Therefore, suitable extraction and subsequent analysis may indicate the compounds which characterize some particular kinds of environmental pollution. In this work, the use of the Soxtec system with dichloromethane as an extraction solvent allowed the recovery of the PAHs from the bark. These compounds are known as pyrolysis compounds and are present in vehicle particulate emissions [10–12].

The Soxtec thermal treatment and the evaporation to dryness were verified on two target compounds, acenaphthene and pyrene (2.0 μ g of each in injectable solution) of different molecular masses, 154 and 202, added to the thimble, to have no destructive or loss effect on the analytes, leading to their quantitative recovery.

GC–MS analysis of the bark extract, obtained according to the experimental conditions, led to the unequivocal detection of nineteen PAHs, some of which were methyl and dimethyl isomers of naphthalene and methyl derivatives of phenanthrene, as reported in Table I and Fig. 1. Such structures were confirmed by verifying the complete correspondence with the GC and MS data for standards under the same experimental conditions.

The average data obtained in duplicate analyses

TABLE I

AVERAGE CONCENTRATIONS ($\mu\text{g PER } 100 \text{ cm}^2$) OF PAH COMPOUNDS DETECTED ON PLANE TREE BARKS AT THREE DIFFERENT HEIGHTS

Sample height: A = 0.3-0.8, B = 0.8-1.2 and C = 1.2-2 m. Columns D show the average concentrations calculated in the 0.3-2 m range.

Peak No.	Compound	M_r	Urban 1 samples				Urban 2 samples				Rural sample
			A	B	C	D	A	B	C	D	
1	Naphthalene	128	2.76	2.44	1.56	2.25	1.40	1.47	1.50	1.45	0.33
2	1-Methylnaphthalene	142	3.35	2.92	2.19	2.82	1.87	1.59	1.44	1.63	0.28
3	2-Methylnaphthalene	142	1.61	1.35	1.08	1.34	0.85	0.70	0.70	0.75	0.10
4	Biphenyl	154	0.99	0.63	0.48	0.70	0.27	0.26	0.30	0.27	0.15
5	Dimethylnaphthalene (five isomers)	156	4.91	3.74	4.14	4.26	2.85	2.29	2.04	2.39	N.D.
6	Acenaphthylene	152	0.75	0.58	0.56	0.63	0.32	0.28	0.33	0.31	0.20
7	Fluorene	166	2.03	1.30	1.30	1.54	1.27	1.05	0.99	1.10	0.27
8	Phenanthrene	178	3.74	2.36	2.46	2.85	5.35	3.60	3.87	4.27	0.71
9	Anthracene	178	0.52	0.40	0.33	0.41	0.66	0.42	0.44	0.50	N.D.
10	Methylphenanthrene (four isomers)	192	3.17	1.84	1.84	2.28	7.34	3.75	4.32	5.13	0.25
11	Fluoranthene	202	1.14	0.77	0.61	0.84	5.48	2.51	3.14	3.71	N.D.
12	Pyrene	202	0.79	0.57	0.42	0.59	4.47	1.96	2.43	2.95	N.D.
Mean						20.51				24.46	2.29

for each compound of samples from the same tree ($\mu\text{g per } 100 \text{ cm}^2$) are given in Table I. It was interesting that the data seemed to be influenced by three variables, the height of the bark from to the ground, rural or urban environment and the type of urban area investigated.

With the reference to the first parameter, the results demonstrated that the maximum concentration of each compound was found in the lowest

band, 0.3-0.8 m from the ground, and decreased as the sampling height increased (Table I, columns A, B and C). This behaviour may be explained by the direct contamination from any vehicle exhaust gases.

The density of the traffic and the pollution sources differed between urban and rural areas. This difference was evident also from the analysis of the bark sampled in the country. The heaviest com-

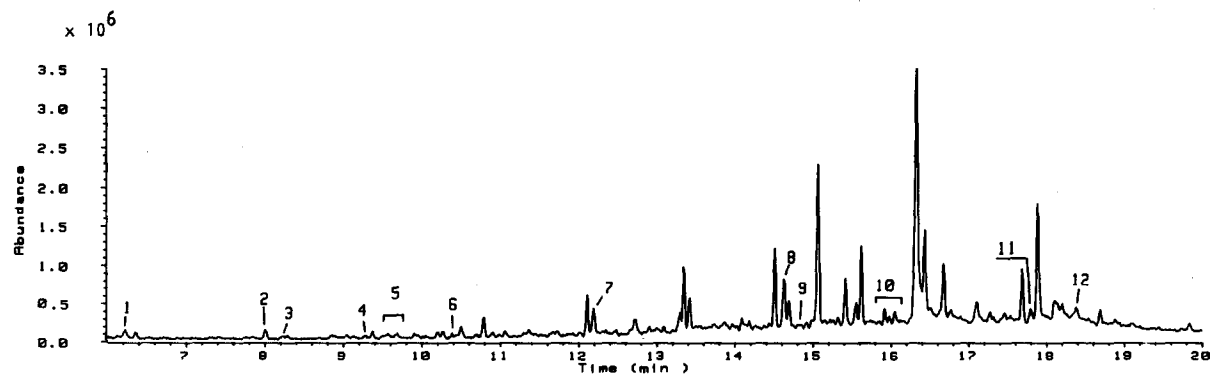


Fig. 1. GC-MS of a typical extract of plane tree bark. For peak identification, see Table I.

pounds such as fluoranthene and pyrene were not detected, whereas other compounds were present, on average, at a total concentration of 2.29 vs. 20.51 and 24.46 μg per 100 cm^2 in the two urban areas (Table I). The ratio of the PAH concentrations in urban and rural environments was thus about 10 [13]. In the country, the presence of the species responsible for pollution could also be due to the atmospheric precipitation, which might transfer the PAHs from polluted areas [8].

This investigation also emphasized a quantitative difference in PAHs within the same urban area. Table I, column D, shows an inversion of the concentration of the lighter with respect to the heavier PAHs. This phenomenon may be attributed to different kinds of traffic. In fact, the sample defined as urban 1 corresponded to bark near to a road with steady traffic whereas the second sample, urban 2, represented a road with slow and irregular traffic, often with queuing. Probably the different working conditions of the car engines might influence the distribution of molecular masses of the PAHs given out. The total concentration of PAHs was, on average, of the same order of magnitude in the two cases studied.

The accuracy of the method was verified by determining the percentage recovery of the examined compounds. Some rural bark samples were spiked with 100 μl of a solution containing 20.0 and 23.4 $\mu\text{g ml}^{-1}$ of acenaphthene and pyrene and extracted successively for periods of 1, 2 or 3 h, according to the usual procedure. These tests on aromatics were chosen because the former compound had never been detected in real samples whereas the latter was present only in urban samples, so the behaviour of the two meant that valid information about the efficiency of the overall Soxtec extraction process could be obtained. The recoveries of the two compounds after 1, 2 and 3 h were acenaphthene 35, 64 and 88% and pyrene 36, 67 and 91%, respectively. The explanation for this behaviour might be attributed to the difficulty in extracting the compounds because of the sample volume and its granulometry. Repeated measurements gave very similar values (relative standard deviation = 3%), demonstrating the good precision of the method used.

Tests carried out on pulverized bark demonstrated better PAH recoveries (almost 100%), but also the excessive presence of species of vegetable origin which interfered with the recovery from the dried organic phase and with the GC–MS analysis. On the basis of these results, it was more convenient to consider the use of bark broken into small pieces because the extraction of the matrix compounds was reduced, but about 90% of the PAHs distributed on the external surface of bark were recovered.

The efficiency of the Soxtec process allowed the detection of low levels of pollution and minor pollutants, as the GC–MS instrument reached equivalent determination limits of 0.02 μg per 100 cm^2 for naphthalene, 0.03 μg per 100 cm^2 for phenanthrene, anthracene and fluoranthene, 0.04 μg per 100 cm^2 for methylnaphthalenes, acenaphthylene and pyrene, and 0.05 μg per 100 cm^2 for biphenyl, dimethylnaphthalenes, fluorene and methylphenanthrenes.

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