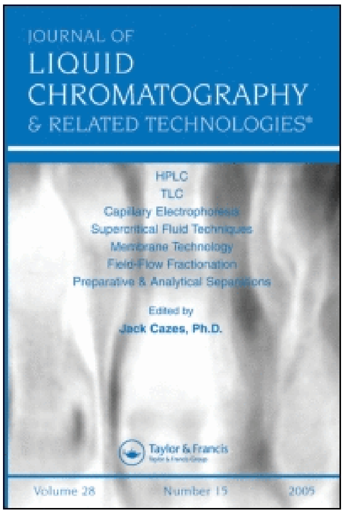

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN AIRBORNE DIESEL EXHAUST PARTICULATES BY HPLC WITH UV DETECTION AND WAVELENGTH PROGRAMMING

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ABSTRACT

HPLC with ultraviolet detection and wavelength programming was used to determine nineteen polycyclic aromatic hydrocarbons (PAH) in airborne diesel exhaust particulates. Eleven of these PAHs are included in the priority pollutants list of the US Environmental Protection Agency. Separation of PAHs is made with 5-µm polymeric C_{18} column. The possibility of selecting the optimum wavelengths for each PAH gives the advantages of improved selectivity and increased sensitivity. Detection limits ranging from 0.1 to 0.2 ng are reached for most PAHs. Samples were soxhlet extracted and different organic solvents were compared.

The best results were obtained by use of acetonitrile. The recoveries obtained were > 70%. Clean-up of diesel particulate extracts was not found necessary for accurate quantification of most of PAHs studied.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) form a large class of organic compounds, which is of great environmental concern. PAHs are toxic and many of them are known to be carcinogenic and/or mutagenic.[1-3] They are formed from the carbonization and the incomplete combustion of the fossil fuel and other organic materials.[4,5] Although many natural sources of PAHs are known to exist, anthropogenic sources are still the major contributors of PAHs to the environment, particularly soot and the diesel exhaust emissions.[6,7] Since the sources can be monitored and controlled, knowledge of the analytical chemistry of these compounds is imperative not only in characterizing individual components, but also in attempting to determine the sources or origins of the PAHs emitted so that steps can be taken to eliminate or minimize the discharge of these substances into the environment at the first place.

As a first step in an analytical procedure for PAHs in airborne particulates, extraction of target compounds retained on PTFE or glass-fiber filters is necessary. Soxhlet extraction and ultrasonication using a variety of organic solvents including acetone, benzene, toluene, dichloromethane, and acetonitrile are the most widely used processes.[8-10]

The analysis of the purified extract can be carried out using gas[11-13] and liquid[14,15] chromatographic methods with different detection devices to achieve simultaneously high resolution, sensitivity, and selectivity. High performance liquid chromatography with UV-Visible[16-20] or fluorometric[21,22] detectors has been the selected technique for PAH determination. However, UV detection yields a sensitivity and selectivity lower than that of fluorimetry. Nevertheless, its performances can be widely improved by selecting the wavelength of maximum absorbance for each compound to be determined.

The objectives of this study are to evaluate and improve upon methods used for the extraction of PAHs from airborne particulates by using Soxhlet extraction, followed by HPLC-UV analysis, as a part of fast and selective methods for monitoring some carcinogenic and /or mutagenic compounds in diesel exhaust particulates. For this purpose, HPLC separation of 19 PAHs with a 5-μm polymeric C_{18} column was checked and UV detection with constant-wavelength and variable-wavelength were compared. Different organic solvents for the Soxhlet extraction of PAHs retained in glass-fibers were also studied. Finally, to demonstrate the applicability of the method, PAHs were determined in ten diesel exhaust particulate samples.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of two Waters (Milford, MA) Model 6000A solvent delivery systems, a Waters Model 660 solvent programmer, a Hewlett-Packard (Palo Alto, CA) Model 1050 UV-Vis detector (a programmable absorbance detector), a Rheodyne (Cotati, CA) 7125 sample injector with 20 µL loop, a Hewlett-Packard Model 3395 integrator, a Supelcosil LC-PAH column (Supelco, Bellefonte, PA), 15 cm x 4.6 mm I.D., 5 µm particulate size, and a Supelguard LC-18 guard column. A Hitachi 150-20 spectrophotometer, was used for absorbance measurements.

Chemicals and Reagents

Organic solvents (acetonitrile, methanol, dichloromethane, hexane, toluene, and isooctane) were of HPLC grade (Prolabo, Paris, France). Deionized water was distilled and further purified through a C_{18} cartridge. Silica gel, 230-400 mesh (Fluka, Buchs, Switzerland), was activated at 450°C over night and stored in a desiccator. Acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, chrysene, 1-methylphenanthrene, 2-methylanthracene, 2-methylnaphthalene, dibenzofurane, dibenz[*a,c*]anthracene, dibenz[*a,h*]anthracene, fluorene, 9-methylanthracene, and 9-phenyl-anthracene were supplied by Janssen Chimica (Geel, Belgium) and benzo[*ghi*]perylene by Supelco. Phenanthrene, pyrene, perylene, and fluoranthene were purchased from Merck (Darmstadt, Germany). These standards were dissolved in dichloromethane at 1mg/mL. Stock mixtures of PAH standards were made up from the individual solutions in methanol. The solutions were protected from light and stored in the cold (4°C).

Chromatographic Conditions

The mobile phase (acetonitrile- water) gradient was: 60% acetonitrile + 40% water for 5 min, increasing linearly up to 100% acetonitrile in 15 min; isocratic 100% acetonitrile up to 30 min. The flow rate was 1 mL/min and the temperature was 25°C. During chromatography the mobile phase was degassed by passage of a continuous flow of helium through the solvents. UV detection was performed both at the fixed wavelength of 254 nm and at the programmed wavelengths during the analysis: (time, value), 226 nm; 11.2 min, 254 nm; 15.8 min, 340 nm; 16.5 min, 239 nm; 18 min, 254 nm; 20.9 min, 285 nm; 21.99 min, 265 nm; 24.5 min, 254 nm; 28 min, 300 nm.

Diesel Exhaust Sampling

Airborne diesel exhaust particulates were collected with a pump on a weighted glass fiber filter (0,7 µm; Whatmann GF/B), at the engine exhaust of a diesel car.

After sampling, the filter was weighted again, covered with aluminium, and stored at 4°C until analysis.

Extraction and Clean-up Procedures

The filter was extracted with 300 mL of an organic solvent (recycled approximately every 15 min) in a glass Soxhlet apparatus. The choice of the solvent and the optimum of extraction have been determined using filters spiked with 10 µL of a solution of PAHs; these should be equivalent to 100 ng for each compound.

Four organic solvents with a wide range of polarity have been examined : acetonitrile, methanol, isooctane and dichloromethane. The organic extract was concentrated to 20 mL in a rotary evaporator, then under a gentle stream of nitrogen in a Kuderna-Danish (K-D) evaporator (at a temperature of 30-35°C on water bath) to 1 mL for the solvent that could be used in HPLC with reversed phase (methanol, acetonitrile) and until dryness in the reversed case. The residue was redissolved in 1 mL of methanol.

To clean up the extract before analysis, it was initially changed into 1 mL of n-hexane and the organic extract was transferred on top of a glass column (35 x 0.9 cm I.D.) packed with 2g of activated silica.

The sequences of eluents were as follows: 12 mL of n-hexane (aliphatic hydrocarbon). Then 12 mL of n-hexane/ toluene (aromatic hydrocarbons). The second fraction was evaporated to dryness in K-D and redissolved in methanol.

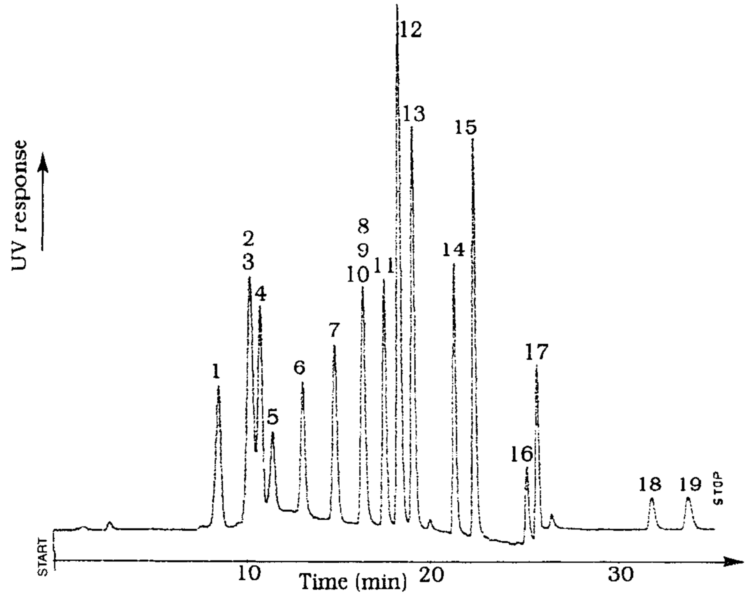

Figure 1. HPLC-UV chromatogram of standard PAH mixture. Peak identification are listed in Table 1. For experimental conditions see text.

RESULTS AND DISCUSSION

Separation and Detection

The nineteen PAHs studied contain from two to five rings. Eleven of those PAHs are on the US EPA Priority List. Figure 1 shows the chromatographic separation on a C_{18} polymeric column of the studied hydrocarbons when using the conditions already detailed above. The bibliography data suggest that this kind of stationary phase yields to the PAHs best selectivity in LC. Thus, the 16 PAHs' Priority List are totally separated on a LC-PAH Supelcosil column with an acetonitrile-water elution gradient.[23,24]

However, for the studied compounds, two coelutions are observed as it can be seen from the retention times of Table 1. The 2-methylnaphthalene and dibenzofurane peaks overlap as those of 2-methylanthracene and fluroranthene do.

Table 1

Peak Identification (Figures 1 and 3) and Retention Times (RT) of Studied PAHs

Compound	No.	Rings	TR(min)
Acenaphthylene	1	3	8.69
Dibenzofurane	2	3	10.39
2-Methylnaphthalene	3	2	10.39
Acenaphthlene	4	3	10.93
Fluorene	5	3	11.59
Phenanthrene	6	3	13.22
Anthracene	7	3	14.91
1-Methylphenanthrene	8	3	16.46
2-Methylanthracene	9	3	16.46
Fluoranthene	10	4	16.46
Pyrene	11	4	17.61
9-Phenylanthracene	12	4	18.41
9-Methylanthracene	13	3	19.16
Benz[a]anthracene	14	4	21.39
Chrysene	15	4	22.44
Perylene	16	4	25.19
Dibenzo[a,c]anthracene	17	5	25.72
Dibenzo[a,h]anthracene	18	5	31.72
Benzo[ghi]perylene	19	5	33.62

Nevertheless, despite many chromatographic condition changes such as the mobile phase flow rate and the elution gradient rate, it was not possible to improve the resolution. Other investigators have reported difficulties in separating these two PAHs groups.[25,26]

The UV absorption spectra of the studied PAHs obtained in the range 200 and 400 nm show that these compounds have no maximum absorbance at the same wavelength (λ_{max}). Table 2 gives the λ_{max} of the studied hydrocarbons. It is to be noted that one PAH λ_{max} increases when its aromaticity increases. Most of the obtained λ_{max} lay in three ranges: from 208 to 230 nm; from 252 to 258 nm and from 280 to 300 nm. Thus, using a single detection wavelength, such as λ= 254 nm which is often called upon for PAH analysis[16-18] does not permit the best sensitivities. The detection limits at λ=254 nm vary along a wide

Table 2

Maximum Absorbance and Detection Wavelengths and Limit of Detection (LOD) at Constant and Variable Wavelength

Compound	λ Max (nm)	λ Det (nm)	LOD (ng)	
			λ=254	λ Var.
Acenaphthylene	228	226	10	0.1
Dibenzofurane	229	226	N.E.	N.E.
2-Methylnaphthalene	223	226	N.E.	N.E.
Acenaphthene	226	226	10	0.05
Fluorene	208	226	0.4	0.4
Phenanthrene	252	254	0.2	0.2
Anthracene	254	254	0.2	0.2
1-Methylphenanthrene	258	340	N.E.	N.E.
2-Methylanthracene	257	340	N.E.	N.E.
Fluoranthracene	237	340	N.E.	4
Pyrene	239	239	4	0.1
9-Phenylanthracene	257	254	0.1	0.1
9-Methylanthracene	254	254	0.1	0.1
Benz[a]anthracene	285	285	0.2	0.1
Chrysene	265	265	0.2	0.1
Perylene	254	254	0.2	0.2
Dibenzo[a,c]anthracene	288	254	0.2	0.2
Dibenzo[a,h]anthracene	299	300	4	0.1
Benzo[ghi]perylene	301	300	4	0.1

N.E.: not evaluated (peaks overlap)

range between 0.2 and 10 ng (Table 2). However, the wavelength variation during the chromatographic elution improves both sensitivity and selectivity. For the former quality, the best is to select for each compound the detection wavelength (λ_{det}) which corresponds to its maximum absorbance through the detector programming in terms of retention times. But, for the sake of reaching accurate quantitative results, the chromatographic resolutions must equal 1.5 or better. These resolutions can only be obtained when few PAHs are analysed, and in the absence of interfering compounds. When the analysis of samples extracted from complex matrices is carried out, it is only possible to change the detector parameters a few times during the elution of the chromatogram. Various PAHs are therefore detected at the same wavelength. Table 2 gives the seven λ_{det} chosen for this work. Under such conditions, the λ_{det} for each of the

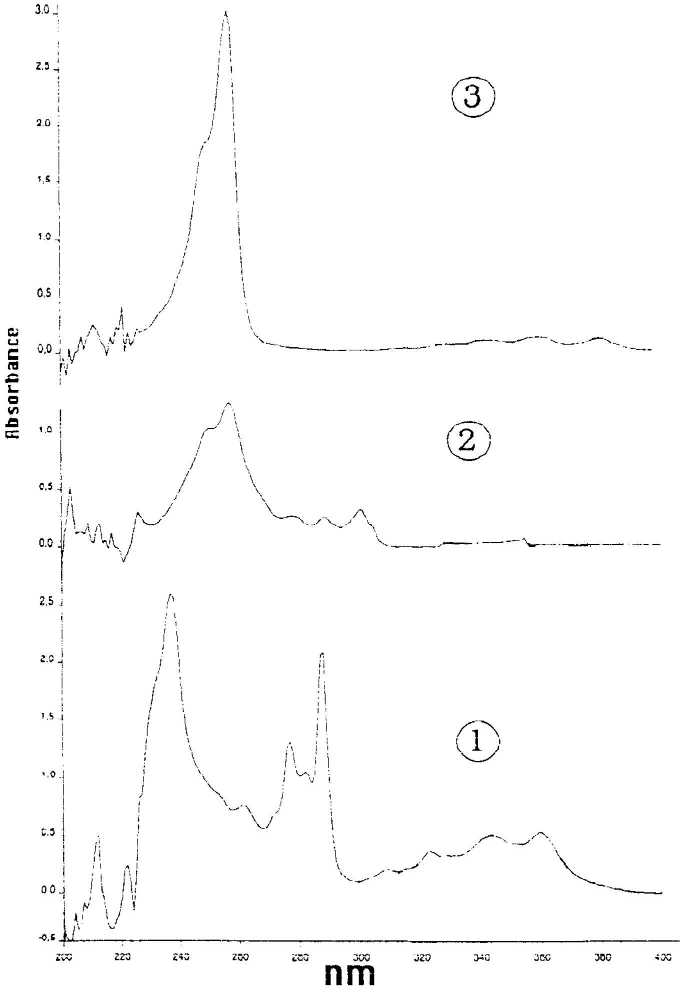

Figure 2. UV spectra of (1) fluoranthene, (2) 2-methylanthracene and (3) 1-methylanthracene

fourteen separated PAHs is equal to its λ_{max} or differs from it by 2 to 4 nm. For all these PAHs, the detection limits estimated, thanks to the signal-noise ratio, (S/N =3) lay between 0.1 to 0.2 ng (Table 2). For the coeluted PAHs, the determination become impossible when the UV absorption spectra are similar as in the dibenzofurane and 2- methylnaphthalene case. For the three other coeluted PAHs (viz. 1-methylphenanthrene, 2- methylanthracene and fluoranthene). Figure 2 shows that the two alkyl PAHs display very different UV absorption spectra compared to the fluoranthene one. Moreover, the former compounds do not practically absorb at 340 nm and that is why this wavelength was selected in this study. It is thus clear that this wavelength is suitable for the fluoranthene determination even when the two other hydrocarbons are present.

The peaks quantification was performed by the external standard method using peak heights and the calibration curve of each PAH. The accuracy and the linearity of the detector response were checked for each solute at the corresponding $\lambda_{det.}$ The relative standard deviations of the peak heights for five 20 μL consecutive injections originating from a standard solution lay between 1.5% for acenaphthylene and 2.5% for benzo [*ghi*]perylene. This standard solution has a concentration of 10 μg/L for each PAH. Inside a domain of injected quantity comprised between 2 and 40 ng (5 points), a good linearity is observed for all the solutes. The regression coefficients obtained vary from 0.999 for acenaphthylene and 0.995 for 9- methylanthracene.

Analyzing Diesel Particulate Samples.

Sample handling

PAH analysis in airborne particulates collected on filters must go through two steps: extraction then clean-up. The last step is specially useful in the case of heavily contaminated samples. The clean-up level depends mainly on the selectivity of the detection step. Since the programming of the UV wavelength detection improves the selectivity, the necessity of the clean-up step for the samples studied was assessed. Figure 3 gives the chromatograms of the analytical blank without cleaning and those of a raw extract, as well as of a purified extract sample.

Two points must be stressed: (i) The blank chromatogram (Figure 3 A) shows no interfering peaks with the PAHs under study. (ii) The chromatograms of the purified extract and of the raw sample (Figure 3 B & C) are qualitatively similar. However, smaller recoveries were experienced for the more volatile PAHs at the purification stage. These losses are due to the fact that the solvents employed for the cleaning by silica gel adsorption chromatography are not suitable with the C_{18} analytical column and must be evaporated to dryness. That is why it was decided to ignore the purification step in the course of this work.

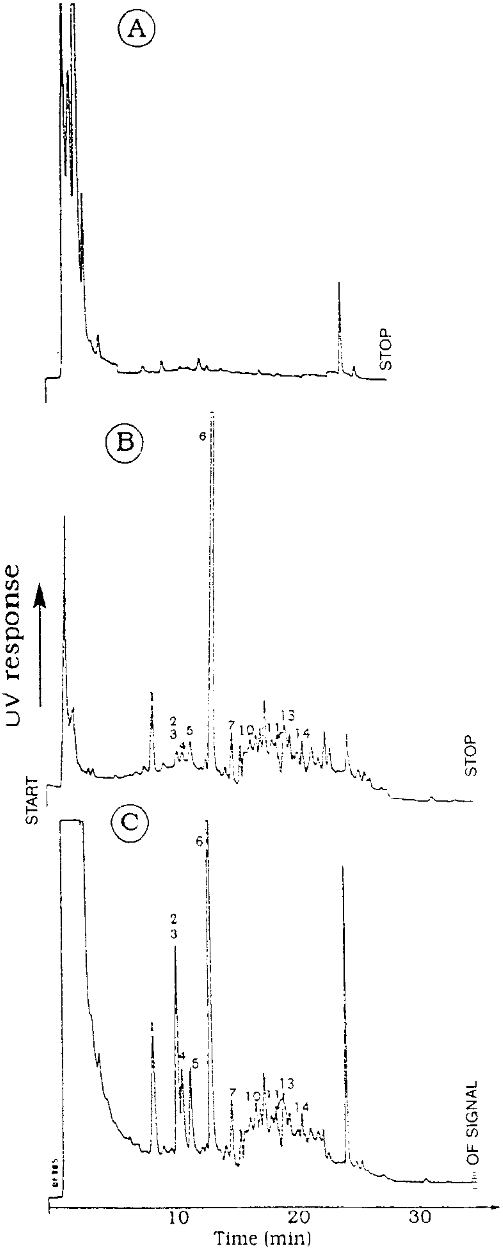

Figure 3. HPLC-UV chromatograms of A: blank and B&C: with clean-up and without clean-up extracts respectively.

Table 3

Mean Recovery (%) (n=5) of Selected PAHs Extracted from Spiked Filters with Different Solvents

Compound	**Solvents**			
	ACN	**Methanol**	**DCM**	**Isooct.**
Acenaphthene	70.63	63.23	ND	ND
Phenanthrene	73.65	55.56	63.33	78
Anthracene	78.42	69.69	66.66	80
2-Methylanthracene	75.57	68.75	49.52	79
Fluoranthene	78.04	67.75	69.74	83.42
Pyrene	75.18	68	62.96	87
9-Phenylanthracene	76.92	68.78	6.85	82.53
Benz[a]anthracene	75.45	61.66	69.91	83.84
Dibenzo[a,c]anthracene	76.71	68.33	65.45	79.34
Dibenzo[a,h]anthracene	79.33	68.42	63.63	72.72
Benzo[ghi]perylene	78.21	65.36	66.59	73

ND: not detected

In order to optimise the extraction procedure performed by using a Soxhlet apparatus, two parameters were studied, namely the organic solvent nature and the extraction time. Table 3 gives the recoveries of the ten selected PAHs for four solvents: acetonitrile (ACN), methanol, dichloromethane (DCM), and isooctane. These data pertain to filters initially spiked by 100 ng of each PAH. All the chosen PAHs but acenaphthene are recovered at more than 70% using either ACN or isooctane. These recoveries are however less than 70% when DCM or methanol are the extraction medias. For acenaphthene, which is somehow volatile, the recovery is 70.63% with ACN and 63.23% with methanol but it is practically nil with DCM and isooctane. The extracts originating from the latter solvents are in fact evaporated to dryness prior to the chromatographic analysis for compatibility reasons. ACN is thus finally retained as the extraction solvent during this work.

In order to define the extraction time, the recoveries of the selected PAHs are performed for various durations viz. 8, 10, 12 and 24 hours. The observed extraction yields gain 12 and 5 % when the extraction times increase from 8 to 10 hours and from 10 to 12 hours respectively. Beyond 12 hours, the increase is of the order of 1 to 2% only.

Table 4

Values of PAHs (ng/g) in Diesel Exhaust Particulate Samples

	"Hot" Engine*		"Cold" Engine**	
Compound	Average	Range	Average	Range
Acenaphthylene	535	1034-304	222	497-20
Acenaphthene	125	179-81	103	216-19
Fluorene	941	1410-356	323	652-95
Phenanthrene	2416	5464-859	554	891-232
Anthracene	116	200-3	65	91-35
Fluoranthene	361	1038-89	84	129-49
Pyrene	182	494-48	62	85-36
9-Methylanthracene	121	121-54	72	125-38
Benz[a]anthracene	60	110-9	50	89-25

*Sample collected after an hour travel at mean speed of 60 Km/h.
**Sample collected at starting.

Finally, the reproducibility of the whole analytical procedure is checked. The RSD of the recoveries for five consecutive trials lay between 8.77% for acenaphthene and 3.8% for 9-phenylanthracene. These trials were performed with filters spiked by 100ng for each PAH.

Application

For this work, a standard 1800 cm^3 diesel car engine (direct injection) was used. Its exhaust airborne particulates trapped on filters were analysed by this optimised procedure. The exhaust particulates were obtained for two normal runnings of the engine: first, at starting, when the engine is "cold" and after an hour travel at a mean speed of 60 km/h ("Hot" engine).

Table 4 shows the concentrations of the nine PAH detected in ten samples; five of which are collected at the engine starting and the other after an hour - long travel. The analysis of these ten samples show that acenaphthylene, fluorene, and phenanthrene are the most abundant hydrocarbons in the exhaust particulates.

It is worthy to note that these three compounds are among the aromatic hydrocarbons usually found in the diesel motor fuel and that they survive the combustion processes at it is reported by many workers.[25,27-32] Moreover, the concentrations of the detected compounds are higher when the engine is "hot". This result is in accordance with the literature reports which say that many PAHs could be produced in flames or by high-temperature pyrolysis of various hydrocarbons.[27]

REFERENCES

1. R. G. Harvey, Ed., **Polycyclic Hydrocarbons and Carcinogenesis**, American Chemical Society, New york, 1985.

2. M. L. Lee, M. Novotny, K. D. Bartle, **Analytical Chemistry of Polycyclic Aromatic Compounds**, Academic Press, New York, NY, 1981.

3. I. Alfheim, G. Becher, J. K. Hougslo, T. Ramdahal, Environ. Mutagenesis, **6**, 91-103 (1984).

4. G. Grimmer, **Handbook of Polycyclic Aromatic Hydrocarbons**, A. Björseth, eds. Marcel Dekker, New York, 1983.

5. W. Auer, H. Malissa, Anal. Chim. Acta, **237**, 451-457 (1990).

6. D. H. Lowenthal, B. Zielinska, J. C. Chow, J. G. Watson, M. Gautam, D. H. Ferguson, G. R. Neuroth, K. D. Stevens, Atmos. Environ., **28**, 731-743 (1994).

7. P. F. Nelson, S. M. Quigley, Atmos. Environ., **18**, 79-87 (1984).

8. K. G. Furton, E. Jolly, G. Pentzke, J. Chromatogr., **642**, 33-45 (1993).

9. C. Escrivá, E. Viana, J. C. Moló, Y. Picó, J. Mañes, J. Chromatogr. A, **676**, 375-388 (1994).

10. S. Wybraniec, A. P. de Jong, Fresenius J. Anal. Chem., **356**, 396-402 (1996).

11. I. Eskinja, Z. Soljc, S. Svel-Cerovecki, M. Eskinja, V. Sojat, Intern. J. Environ. Anal. Chem., **63**, 251-268 (1996).

12. M. Aceves, J . O. Grimalt, Environ. Sci. Technol., **27**, 2896-2908 (1993).

13. P. T. J. Scheepers, D. D. Velders, M. H. J. Martens, J. Noordhoek, R. P. Bos, J. Chromatogr. A, **677**, 107-121 (1994).

14. H. Li, R. Westerholm, J. Chromatogr. A, **664**, 177-182 (1994).

15. K. Peltonen, T. Kuljukka, J. Chromatogr. A, **710**, 93-108 (1995).

16. G. Kowalewska, B. Toma, Chem. Anal. (Warsaw), **41**, 771-779 (1996).

17. G. Kiss, Z. V. Puchony, J. Hlavay, J. Chromatogr. A, **725**, 261-272 (1996).

18. A. Alebic-Juretic, Fresenius Environ. Bull., **3**, 89-94 (1994).

19. N. C. Fladung, J. Chromatogr. A, **692**, 21-26 (1995).

20. M. W. Dong, A. Greenberg, J. Liq. Chromatogr., **11**, 1887-1905 (1988).

21. J. L. Beltrán, R. Ferrer, J. Guiteras, J. Liq. Chromatogr. Relat. Technol., **19**, 477-488 (1996).

22. R. Williams, J. Meares, L. Brooks, R. Watts, P. Lemieux, Intern. J. Environ. Anal. Chem., **54**, 299-134 (1994).

23. L. C. Sander, S. A. Wise, Anal. Chem., **67**, 3284-3292 (1995).

24. S. A. Wise, L. C. Sander, W. E. May, J. Chromatogr., **642**, 329 (1993).

25. W. E. May, S. A. Wise, Anal. Chem., **56**, 225-232 (1984).

26. S. A. Wise, L. C. Sander, R. Lapouyade, P. Garrigues, J. Chromatogr., **514**, 193 (1990).

27. P. Degobert, Automobile et Pollution, Ed. Technip, Paris, 1992.

28. M. Yu, R. A. Hites, Anal. Chem., **53**, 951-954 (1981).

29. J. A. Yergey, T. H. Risby, S. S. Lestz, Anal. Chem., **54**, 354-357 (1982).

30. I. L. Davies, K. D. Bartle, P. T. Williams, G. E. Andrews, Anal. Chem., **60**, 204-209 (1988).

31. P. J. Tancell, M. M. Rhead, C. J. Trier, M. A. Bell, D. E. Fussey, Sci. Total Environ., **162**, 179-186 (1995).

32. R. Westerholm, H. Li, Environ. Sci. Technol., **28**, 965 (1994).

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