ISTISAN 94/5
(ISSN 0391-1675)

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ISTITUTO SUPERIORE DI SANITA'

Polycyclic aromatic hydrocarbons: identity, physical and chemical properties, analytical methods

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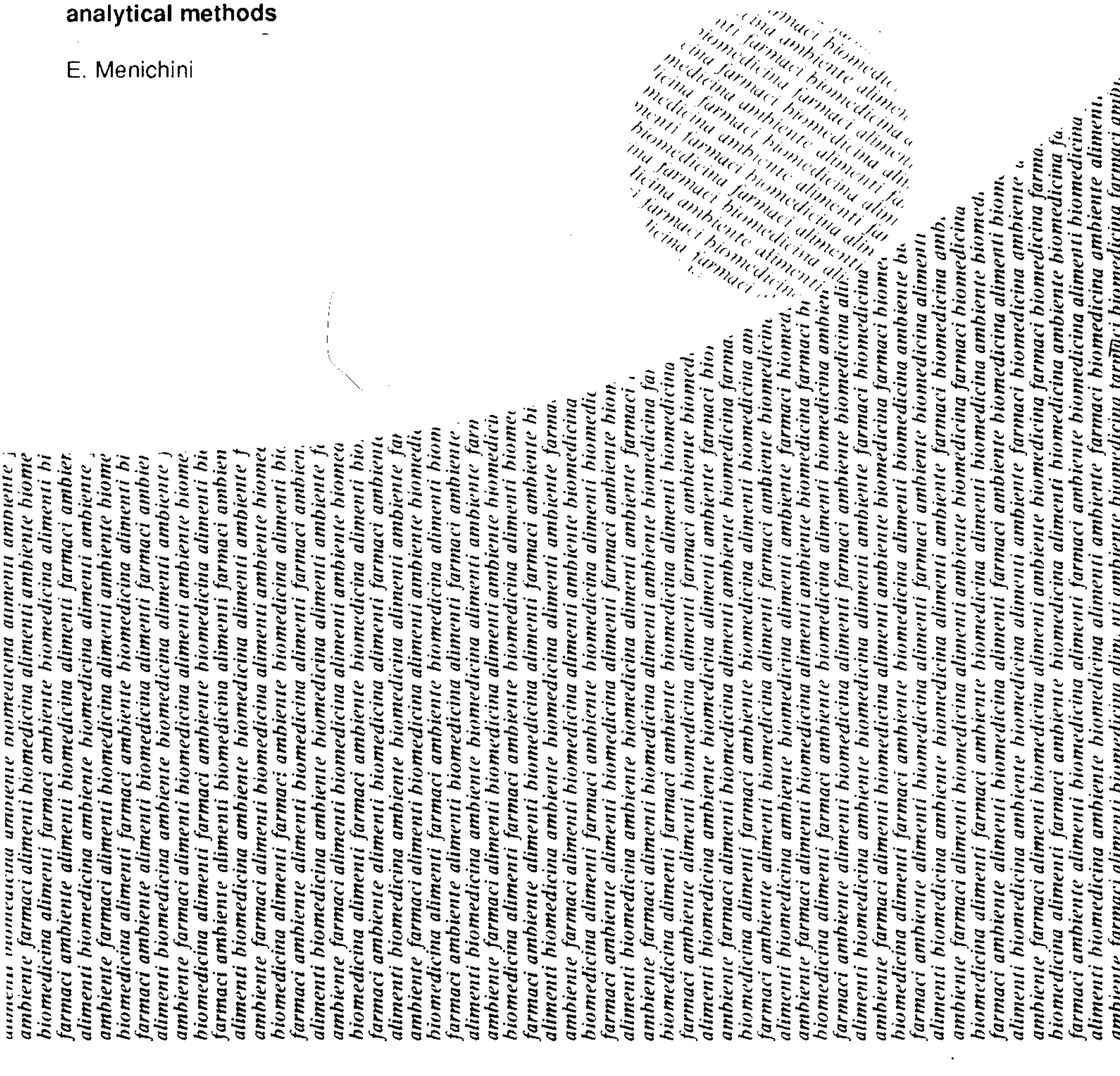

Rapporti ISTISAN

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Polycyclic aromatic hydrocarbons: identity, physical and chemical properties, analytical methods

Edoardo Menichini

Laboratorio di Igiene Ambientale

Roma
1994

Istituto Superiore di Sanità, Rome (Italy)
Polycyclic aromatic hydrocarbons: identity, physical and chemical properties, analytical methods
Edoardo Menichini
Jun 94, 48 p. Rapporti ISTISAN 94/5 (in English)

A basis for planning studies concerning the environmental fate and levels of polycyclic aromatic hydrocarbons (PAHs), as well as related human exposures is provided. Information on PAH chemical identity is given and chemical properties of the class are summarized. Afterwards, physical properties relevant to the toxicological and ecotoxicological evaluation are reported for 33 compounds: melting and boiling points, flash point and explosion limits, density, vapour pressure and vapour density, solubility in water, n-octanol/water partition coefficient and Henry's law constant. Analytical methods for PAH determination in different matrices (particularly, air and waters, working environment, soil, sediment, foodstuffs, waste, plants, biological fluids and tissues) are critically reviewed. Finally, some lists are reported of selected PAHs whose determination is required or recommended at national or international levels.

Key words: Chemical properties, PAH, Physical properties, Polycyclic aromatic hydrocarbons.

Istituto Superiore di Sanità, Roma
Idrocarburi policiclici aromatici: identità, proprietà fisiche e chimiche, metodi analitici
Edoardo Menichini
Giu 94, 48 p. Rapporti ISTISAN 94/5 (in inglese)

Sono fornite conoscenze di base per la programmazione di studi riguardanti il destino e i livelli ambientali degli idrocarburi policiclici aromatici (IPA), nonché l'esposizione dell'uomo associata a tali livelli. Vengono date informazioni sull'identità chimica degli IPA e riassunte le proprietà chimiche della classe. Per 33 sostanze, sono poi riportate le proprietà fisiche di interesse ai fini della loro valutazione tossicologica ed ecotossicologica: punti di fusione e di ebollizione, punto di infiammabilità e limiti di esplosione, densità, tensione di vapore e densità di vapore, solubilità in acqua, coefficiente di ripartizione n-ottanolo/acqua e costante di Henry. Segue una rassegna critica dei metodi analitici per la determinazione degli IPA in diverse matrici: in particolare, aria ed acque, ambienti di lavoro, suolo, sedimenti, alimenti, rifiuti, piante, fluidi e tessuti biologici. Infine, vengono riportate alcune liste di specifici IPA, la cui determinazione viene richiesta o raccomandata a livello nazionale o internazionale.

Parole chiave: Idrocarburi policiclici aromatici, IPA, Proprietà chimiche, Proprietà fisiche.

Acknowledgement. This document has been prepared for International Programme on Chemical Safety (UNEP-ILO-WHO) as part of its work on "Environmental Health Criteria for Polycyclic Aromatic Hydrocarbons".

CONTENTS

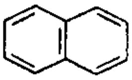
INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants. They are formed during incomplete combustion and pyrolysis of organic materials, from both natural and anthropogenic sources, the latter being by far the greatest contributors (Lee et al., 1981, Ch. 2). Hundreds of PAHs may be formed. For example, over one hundred PAHs have been identified in atmospheric particulate matter (Lao et al., 1973; Lee et al., 1976) and in emissions from coal-fired residential furnaces (Grimmer et al., 1985), about two hundred in tobacco smoke (reviewed by Lee et al., 1981, Ch. 2).

The experimental carcinogenicity and mutagenicity shown by many PAHs have resulted in a strong suspicion that they are also human carcinogens (IARC, 1983, 1987). In the light of such significance for human health, much interest has been shown in studying their environmental fate, as well as their environmental levels and human exposures.

With the aim of contributing to the development of such studies, this report presents a critical review of the important physical and chemical properties of PAHs, and of analytical methods for PAH determination in various matrices.

In particular, properties are presented for 33 compounds (31 parent PAHs and two alkyl derivatives, Figure 1 and Table 1): these PAHs have been selected as being those most commonly reported in literature, with regard to toxicological and/or exposure data. As to the analytical methods, PAHs are considered here as a class.



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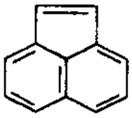

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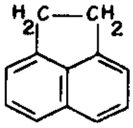

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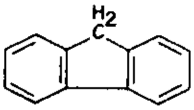

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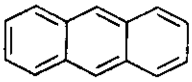

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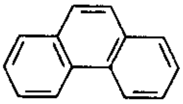

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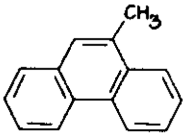

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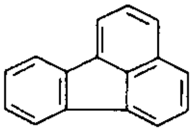

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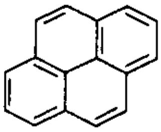

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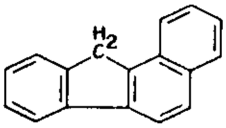

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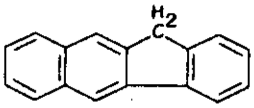

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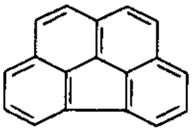

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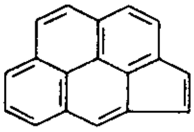

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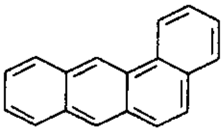

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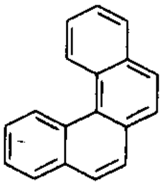

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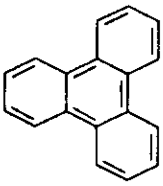

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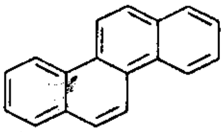

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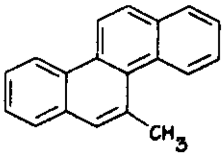
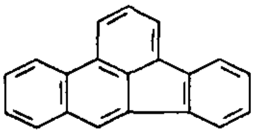


5-MCH

Fig. 1. Structural formulae of PAHs.



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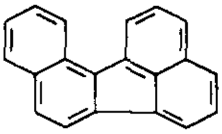

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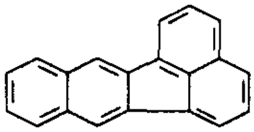

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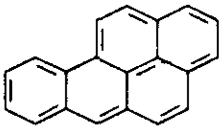

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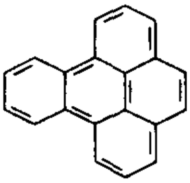

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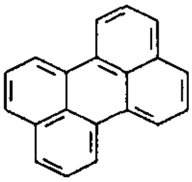

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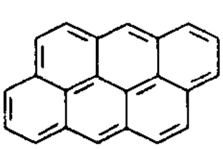

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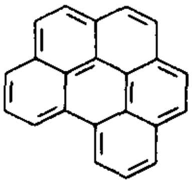

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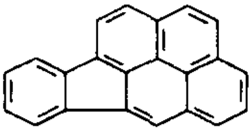

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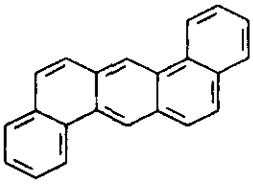

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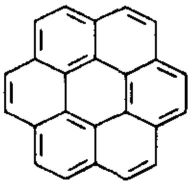

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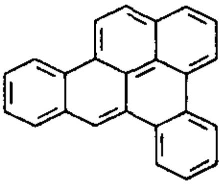

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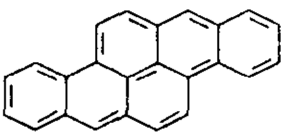

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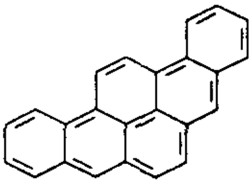

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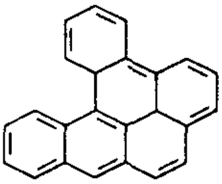

DBalP

Fig. 1 (continued)

Table 1. PAHs considered in this report

Common name[a]	Abbr.[b]	CAS name	Synonym[c]
Naphthalene	NA	Naphthalene	
Acenaphthylene	ACL	Acenaphthylene	
Acenaphthene	AC	Acenaphthylene, 1,2-dihydro-	
Fluorene	FL	9H-Fluorene	
Anthracene	AN	Anthracene	
Phenanthrene	PHE	Phenanthrene	
1-Methylphenanthrene	1-MPH	Phenanthrene, 1-methyl-	
Fluoranthene	FA	Fluoranthene	
Pyrene	PY	Pyrene	Benzo[def]phenanthrene
Benzo(a)fluorene	BaFL	11H-Benzo[a]fluorene	1,2-Benzofluorene
Benzo(b)fluorene	BbFL	11H-Benzo[b]fluorene	2,3-Benzofluorene
Benzo(ghi)fluoranthene	BghiF	Benzo[ghi]fluoranthene	2,13-Benzofluoranthene
Cyclopenta(cd)pyrene	CPP	Cyclopenta[cd]pyrene	Cyclopenteno[cd]pyrene
Benz(a)anthracene	BaA	Benz[a]anthracene	1,2-Benzanthracene
Benzo(c)phenanthrene	BcPH	Benzo[c]phenanthrene	3,4-Benzophenanthrene
Chrysene	CHR	Chrysene	1,2-Benzophenanthrene
Triphenylene	TRI	Triphenylene	9,10-Benzophenanthrene
5-Methylchrysene	5-MCH	Chrysene, 5-methyl-	
Benzo(b)fluoranthene	BbFA	Benz[e]acephenanthrylene	3,4-Benzofluoranthene
Benzo(j)fluoranthene	BjFA	Benzo[j]fluoranthene	10,11-Benzofluoranthene
Benzo(k)fluoranthene	BkFA	Benzo[k]fluoranthene	11,12-Benzofluoranthene
Benzo(a)pyrene	BaP	Benzo[a]pyrene	3,4-Benzopyrene
Benzo(e)pyrene	BeP	Benzo[e]pyrene	1,2-Benzopyrene
Perylene	PE	Perylene	peri-Dinaphthalene
Anthanthrene	ATR	Dibenzo[def,mno]chrysene	
Benzo(ghi)perylene	BghiP	Benzo[ghi]perylene	1,12-Benzoperylene
Indeno(1,2,3-cd)pyrene	IP	Indeno[1,2,3-cd]pyrene	2,3-o-phenylenpyrene
Dibenz(a,h)anthracene	DBahA	Dibenz[a,h]anthracene	1,2:5,6-Dibenzanthracene
Coronene	COR	Coronene	Hexabenzobenzene
Dibenzo(a,e)pyrene	DBaeP	Naphto[1,2,3,4-def]chrysene	1,2:4,5-Dibenzopyrene
Dibenzo(a,h)pyrene	DBahP	Dibenzo[b,def]chrysene	3,4:8,9-Dibenzopyrene
Dibenzo(a,i)pyrene	DBaiP	Benzo[rst]pentaphene	3,4:9,10-Dibenzopyrene
Dibenzo(a,l)pyrene	DBalP	Dibenzo[def,p]chrysene	1,2:3,4-Dibenzopyrene

[a] Ranked according to increasing molecular mass (see Table 2) and, for isomers, in alphabetical order.

[b] As used in this report.

[c] Common synonym which appeared in the literature.

1. IDENTITY

The name "polycyclic aromatic hydrocarbons" commonly refers to a large class of organic compounds containing two or more fused aromatic rings, even though, interpreted in a broad sense, non-fused ring systems should also be included. In particular, the term PAHs refers to compounds containing only carbon and hydrogen atoms (i.e., unsubstituted parent PAHs and their alkyl-substituted derivatives), whereas the more general term "polycyclic aromatic compounds" (PACs) also includes the functional derivatives (e.g., nitro- and hydroxy-PAHs) as well as the heterocyclic analogs, which contain one or more heteroatoms in the aromatic structure (aza-, oxa- and thia-arenes). A number of authors have also referred to PACs as "polycyclic organic matter" (POM). In addition, the term "polynuclear" is frequently used for "polycyclic", e.g., "polynuclear aromatic (PNA) compounds".

In the past, the trivial names and different systems used to identify ring fusions by numbers or letters have often led to confusion, with respect to the nomenclature of PAHs (Loening & Merritt, 1990). Nowadays, the system codified by the International Union of Pure and Applied Chemistry (IUPAC, 1979) and used by the Chemical Abstracts Service (CAS, 1988, 1990) is generally accepted. However, a number of compounds are still commonly known and reported in the literature with the nonsystematic names. For each compound, Table 1 lists the common name and its abbreviation, as used throughout this report, together with the CAS name and any alternate name which most commonly appeared in the literature. Most of the alternate names use numbers to denote the sides where fusion occurs, but this type of nomenclature is definitely desappearing from publications. Extensive lists of synonyms are reported in IARC (1983) and Loening & Merritt (1990).

Molecular formulae, relative molecular masses, and CAS registry numbers (RN) are shown in Table 2.

Table 2. Identity

Compound	Molecular formula	Relative molecular mass	CAS RN[a]
NA	$C_{10}H_8$	128.2	91-20-3
ACL	$C_{12}H_8$	152.2	208-96-8
AC	$C_{12}H_{10}$	154.2	83-32-9
FL	$C_{13}H_{10}$	166.2	86-73-7
AN	$C_{14}H_{10}$	178.2	120-12-7
PHE	$C_{14}H_{10}$	178.2	85-01-8
1-MPH	$C_{15}H_{12}$	192.3	832-69-9
FA	$C_{16}H_{10}$	202.3	206-44-0
PY	$C_{16}H_{10}$	202.3	129-00-0
BaFL	$C_{17}H_{12}$	216.3	238-84-6
BbFL	$C_{17}H_{12}$	216.3	243-17-4
BghiF	$C_{18}H_{10}$	226.3	203-12-3
CPP	$C_{18}H_{10}$	226.3	27208-37-3
BaA	$C_{18}H_{12}$	228.3	56-55-3
BcPH	$C_{18}H_{12}$	228.3	195-19-7
CHR	$C_{18}H_{12}$	228.3	218-01-9
TRI	$C_{18}H_{12}$	228.3	217-59-4
5-MCH	$C_{19}H_{14}$	242.3	3697-24-3
BbFA	$C_{20}H_{12}$	252.3	205-99-2
BjFA	$C_{20}H_{12}$	252.3	205-82-3
BkFA	$C_{20}H_{12}$	252.3	207-08-9
BaP	$C_{20}H_{12}$	252.3	50-32-8
BeP	$C_{20}H_{12}$	252.3	192-97-2
PE	$C_{20}H_{12}$	252.3	198-55-0
ATR	$C_{22}H_{12}$	276.3	191-26-4
BghiP	$C_{22}H_{12}$	276.3	191-24-2
IP	$C_{22}H_{12}$	276.3	193-39-5
DBahA	$C_{22}H_{14}$	278.4	53-70-3
COR	$C_{24}H_{12}$	300.4	191-07-1
DBaeP	$C_{24}H_{14}$	302.4	192-65-4
DBahP	$C_{24}H_{14}$	302.4	189-64-0
DBaiP	$C_{24}H_{14}$	302.4	189-55-9
DBalP	$C_{24}H_{14}$	302.4	191-30-0

[a] Chemical Abstracts Service registry number.

2. PHYSICAL AND CHEMICAL PROPERTIES

Physical and chemical properties relevant to the toxicological and ecotoxicological evaluation of PAHs are summarized in Tables 3-5. It should be kept in mind that values of one parameter which are reported for various compounds, may derive from different sources and hence from different measurement - or calculation - methods. If this is so, individual values cannot be directly compared other than roughly, unless the original sources are consulted for the methods used. In particular, the vapour pressures reported in the literature for the same PAH vary even up to several orders of magnitude (Mackay and Shiu, 1981; Lane, 1989). Variations are also noticeable for water solubilities, although these are generally within one order of magnitude (NRCC, 1983, pp. 32-33).

Physical and chemical properties are dominated by the conjugated π-electron systems. They vary quite regularly with the number of rings and the molecular mass, giving rise to a more or less wide range of values for each parameter, within the whole class. Under ambient temperatures, all the PAHs are solids. The general characteristics common to the class are high melting and boiling points, low vapour pressures, and very low water solubilities. PAHs are soluble in many organic solvents (IARC, 1983; US DHHS, 1990; Lide, 1991) and are highly lipophilic.

Vapour pressures generally tend to decrease with increasing molecular mass, varying more than ten orders of magnitude from low- to high-molecular compounds. This affects the different percentages of individual PAHs that are adsorbed on particulate matter in the atmosphere and that are retained on the particulate matter during sampling on filters (Thrane & Mikalsen, 1981). Vapour pressures increase markedly with ambient temperatures (Murray et al., 1974), which then additionally affects the distribution coefficients between gas and particle phases (Lane, 1989). As a general trend, water solubility decreases with increasing molecular mass.

PAHs are chemically rather inert compounds. When they react, PAHs undergo two types of reactions characteristic of aromatic hydrocarbons: electrophilic substitution and addition. The former is

Table 3. Physical properties (1st part)

Compound	Colour	Melting point[i] (°C)	Boiling point (°C)	Flash point[t] (°C)	Explosion limits[v] (vol. %)
NA	white[a]	81	217.9[b]	78.9(OC)[u]	0.9-5.9
ACL		92-93	265-275[e]		
AC	white[a]	95	279[e]		
FL	white[b]	115-116	295[b]		
AN	colourless[c]	216.4	342[b]	121(CC)[a]	0.6
PHE	colourless[d]	100.5	340[e]	171(OC)[q]	
1-MPH		123	354-355[j]		
FA	pale yellow[e]	108.8	375[e]		
PY	colourless[b]	150.4	393[e]		
BaFL		189-190[e]	398-400[k]		
BbFL		213.5	401-402[k]		
BghiF	yellow[f]	128.4	432[l]		
CPP		170	439[m]		
BaA	colourless[a]	160.7	400[a]		
BcPH		66.1			
CHR	colourless[g]	253.8	448[e]		
TRI		199	425[f]		
5-MCH		117.1	458[n]		
BbFA	colourless[h]	168.3	481[o]		
BjFA	yellow[e]	165.4	480[m]		
BkFA	pale yellow[e]	215.7	480[e]		
BaP	yellowish[b]	178.1	496[o]		
BeP		178.7	493[o]		
PE	yellow to colourless[b]	277.5	503[p]		
ATR	golden yellow[f]	264	547[s]		
BghiP	pale yellow-green[f]	278.3	545[n]		
IP	yellow[h]	163.6	536[p]		
DBahA	colourless[h]	266.6	524[p]		
COR	yellow[e]	439	525[r]		
DBaeP	pale yellow[e]	244.4	592[s]		
DBahP	golden yellow[h]	317	596[s]		
DBaiP	greenish-yellow[h]	282	594[s]		
DBalP	pale yellow[h]	162.4	595[s]		

(notes on the following page)

Notes to Table 3

a From: Lewis (1992).

b From: Budavari (1989).

c When pure, colourless with violet fluorescence. From: Budavari (1989).

d From: Hawley (1987).

e From: Lide (1991).

f From: IARC (1983).

g With blue fluorescence. From: IARC (1973).

h From: IARC (1973).

i From: Karcher et al. (1985); Karcher (1988).

j From: Kruber & Marx (1938).

k From: Kruber (1937).

l From: Kruber & Grigoleit (1954).

m Reported in: Grimmer (1983).

n Calculated. From: White (1986).

o From the review of: Bjorseth (1983); the original references are cited in: White (1986).

p From: Verschueren (1983).

q From: HSDB (1993).

r From: Von Boente (1955).

s Estimated from the gas chromatographic retention time. From: Grimmer (1983).

t Open cup (OC) or closed cup (CC) method is indicated.

u 87.8°C by closed cup method. From: HSDB (1993).

v Lower-upper, for NA; lower, for AN. From: Lewis (1992).

Table 4. Physical properties (2nd part)

Compound	Vapour pressure (Pa at 25°C)	Density[i]	Vapour density[s]
NA	10.4[a]	1.154^{25} [j]	4.42[t]
ACL	8.9×10^{-1} [a]	$0.899^{16/2}$ [j]	
AC	2.9×10^{-1} [a]	$1.024^{90/4}$ [j]	5.32[t]
FL	8.0×10^{-2} [a]	$1.203^{0/4}$ [j]	
AN	8.0×10^{-4} [a]	$1.283^{25/4}$ [j]	6.15[t]
PHE	1.6×10^{-2} [a]	0.980^{4} [j]	6.15[u]
1-MPH			
FA	1.2×10^{-3} [a]	$1.252^{0/4}$ [j]	
PY	6.0×10^{-4} [a]	$1.271^{23/4}$ [j]	
BaFL			
BbFL		1.226[k]	
BghiF		1.345^{23} [v]	
CPP			
BaA	2.8×10^{-5} [a]	1.226[k]	
BcPH		1.265[l]	
CHR	8.4×10^{-5} (20°C)[b]	$1.274^{20/4}$ [m]	
TRI		1.3[n]	
5-MCH			
BbFA	6.7×10^{-5} (20°C)[b]		
BjFA	2.0×10^{-6} [c]		
BkFA	1.3×10^{-8} (20°C)[d]		
BaP	7.3×10^{-7} [e]	1.351[o]	8.7[u]
BeP	7.4×10^{-7} [e]		
PE		1.35[p]	
ATR		1.39[p]	
BghiP	1.4×10^{-8} [f]	1.349^{20} [q]	
IP	1.3×10^{-8} (20°C)[b]		
DBahA	1.3×10^{-6} (20°C)[f]	1.282[r]	
COR	2.0×10^{-10} [e]	1.371[j]	
DBaeP			
DBahP			
DBaiP	3.2×10^{-12} [g,h]		
DBalP			

(notes on the following page)

Notes to Table 4

a From: Sonnefeld et al. (1983).
b Reported in: Sims & Overcash (1983).
c Calculated by Syracuse Research Center. From: HSDB (1993).
d From: US EPA (1980).
e From the review of: Santodonato et al. (1981).
f From: US DHHS (1990).
g Temperature not given.
h Calculated. From: HSDB (1993).
i When two temperatures are reported as superscripts, the datum indicates the specific gravity (the density of the substance at the first reported temperature relative to the density of water at the second reported temperature). When there is no value, or only one, for temperature, the datum is in grams per millilitre, at the indicated temperature (if any).
j From: Lide (1991).
k From: Schuyer et al. (1953).
l From: Beilstein (1993).
m From: Budavari (1989).
n Approximate value. From: Klug (1950).
o From: Kronberger & Weiss (1944).
p At ambient temperature. From: Inokuchi & Nakagaki (1959).
q From: White (1948).
r From: IARC (1973).
s Air=1.
t From: Lewis (1992).
u From: NIOSH/OSHA (1981).
v From: Ehrlich & Beevers (1956).

Table 5. Physical properties (3rd part)

Compound	n-Octanol/water partition coefficient (log K_{ow})	Solubility in water[m] at 25°C (µg/litre)	Henry's law constant at 25°C (kPa m^3/mol)
NA	3.4[a]	3.17×10^{4}	4.89×10^{-2} [u]
ACL	4.07[b]		1.14×10^{-3} [t]
AC	3.92[b]	3.93×10^{3}	1.48×10^{-2} [u]
FL	4.18[i]	1.98×10^{3}	1.01×10^{-2} [v]
AN	4.5[a]	73	7.3×10^{-2} [v]
PHE	4.6[a]	1.29×10^{3}	3.98×10^{-3} [u]
1-MPH	5.07[d]	255 (24°C)[n]	
FA	5.22[f]	260	6.5×10^{-4} (20°C)[h]
PY	5.18[a]	135	1.1×10^{-3} [v]
BaFL	5.32[e]	45	
BbFL	5.75[e]	2.0	
BghiF			
CPP			
BaA	5.61[b]	14	
BcPH			
CHR	5.91[f]	2.0	
TRI	5.45[g]	43	
5-MCH		62 (27°C)[o]	
BbFA	6.12[b]	1.2[p]	5.1×10^{-5} (20°C)[h]
BjFA	6.12[k]	2.5[q]	
BkFA	6.84[i]	0.76[b]	4.4×10^{-5} (20°C)[h]
BaP	6.50[f]	3.8	3.4×10^{-5} (20°C)[h]
BeP	6.44[j]	5.07 (23°C)[r]	
PE	5.3[c]	0.4	
ATR			
BghiP	7.10[f]	0.26	2.7×10^{-5} (20°C)[h]
IP	6.58[b]	62[b,s]	2.9×10^{-5} (20°C)[h]
DBahA	6.50[l]	0.5 (27°C)[o]	7×10^{-6} [t]
COR	5.4[c]	0.14	
DBaeP			
DBahP			
DBaiP	7.30[k]	0.17[s,t]	4.31×10^{-6} [t]
DBalP			

(notes on the following page)

Notes to Table 5

a From: Karickoff et al. (1979).
b From: HSDB (1993).
c From: Brooke et al. (1986).
d Calculated. From: Karcher et al. (1991).
e Calculated. From: Miller et al. (1985).
f From: Bruggeman et al. (1982).
g Calculated. From: Yalkowsky & Valvani (1979).
h From: Ten Hulscher et al. (1992).
i Calculated as per Leo et al. (1971). From: US EPA (1980).
j Calculated. From: Ruepert et al. (1985).
k Calculated. From: HSDB (1993).
l From: Means et al. (1980).
m From: Mackay & Shiu (1977), except where noted.
n From: May et al. (1978).
o From: Davis et al. (1942).
p Temperature not given. Reported in: Sims & Overcash (1983).
q Temperature not given. Unpublished result, cited in: Wise et al. (1981).
r From: Schwarz (1977).
s Temperature not given.
t Calculated by Syracuse Research Center. From: HSDB (1993).
u From: Mackay et al. (1979).
v From: Mackay & Shiu (1981).

preferred since it does not destroy the aromatic character of the benzene ring affected; addition is often followed by elimination resulting in a net substitution. Chemical and photochemical reactions of PAHs in the atmosphere have been reviewed (Valerio et al., 1984; Lane, 1989). Following photodecomposition, in the presence of air and sunlight, a number of oxidative products have been identified, particularly quinones and endoperoxides. Various experimental studies have revealed reactions of PAHs with nitrogen oxides and nitric acid to form the nitro-derivatives of PAHs, as well as with sulphur oxides and sulfuric acid (in solution) to form sulfinic and sulfonic acids. PAHs may also be attacked by ozone and hydroxyl radicals, which are present in the atmosphere.

The formation of nitro-PAHs is particularly important owing to their biological impact, and particularly to their well-documented mutagenic activity (Howard et al., 1990).

In general, the above-mentioned reactions are of interest with regard to the environmental fate of PAHs, but the results of experimental studies are still difficult to interpret because of the complexity of interactions occurring in environmental mixtures and the difficulty in eliminating artifacts during analytical determinations. These reactions are also considered responsible for possible PAH losses during ambient atmospheric sampling (see 3.1.1).

3. ANALYTICAL METHODS

Hundreds of publications have described analytical methods for PAHs. Tables 6 and 7 synthetically present a limited number of methods applied to 'real' samples of different matrices, taken as examples. The methods and sources were selected, as far as possible, according to the following criteria: accessibility of the bibliographic source, completeness of the procedure description (or including reference to other accessible sources), practicability with common equipment for this type of analysis (even if requiring experienced personnel), recency, status of official or validated or recommended method.

3.1 Sampling

3.1.1 Ambient air

When selecting the sampling apparatus, one must consider the physical state of PAHs in the atmosphere. Compounds with 5 or more rings are present almost exclusively adsorbed on suspended particulate matter, whereas lower-molecular mass PAHs are partially or totally present in the vapour phase (Coutant et al., 1988).

It is common that in investigations for monitoring purposes in ambient air (reviewed by Menichini, 1992a), only particle-bound PAHs are determined. This is likely due to the increased workload when volatile compounds must be trapped (both in assembling the sampling unit and in analysing samples), but also to the lesser toxicological interest for lighter compounds: among 'probable' and 'possible' carcinogenic PAHs (IARC, 1987), only BaA is found at significant levels in the vapour phase (Van Vaeck et al., 1984; Coutant et al., 1988).

Sampling is generally performed by collecting total suspended particulate matter for 24 h on glass fiber (GF) filters by means of high-volume samplers. Other filter media have been used: teflon membrane (Benner et al., 1989; Baek et al., 1992), teflon-coated GF, and quartz fiber.

All these filters have been evaluated comparatively, with respect to the effect of the filter material on the PAH decomposition during sampling (see chapter 2). Some studies have shown that higher PAH recoveries are obtained from teflon or teflon-coated filters (Lee et al., 1980; Grosjean, 1983). However, successive investigations did not confirm this finding (Lindskog et al., 1987; Ligocki & Pankow, 1989; De Raat et al., 1990), so that the importance of this effect is still difficult to assess, and a conclusion cannot be drawn. More rarely, cellulose acetate membranes have been used (Baek et al., 1992); when compared with GF filters, they yielded similar collection efficiencies for heavier PAHs, and better efficiencies for 3- and 4-ring compounds (Spitzer & Dannecker, 1983).

The method most used to trap vapour-phase PAHs is adsorption on plugs of polyurethane foam (PUF) located behind the GF filter (Keller & Bidleman, 1984; Chuang et al., 1987; De Raat et al., 1987; Benner et al., 1989; Hawthorne et al., 1992). The success of PUF probably results from the low pressure drop, low blanks, low cost, and ease of handling. Among the various other sorbents tested (reviewed by: Leinster & Evans, 1986; Davis et al., 1987), two polymeric materials have received particular attention: the Amberlite XAD-2 resin, which is a valid alternative to PUF (Chuang et al., 1987), and Tenax (Baek et al., 1992). Trapped vapours include both PAHs initially present in the vapour phase, and those already collected on the filter and volatilized during sampling (the 'blowing-off' effect) (Van Vaeck et al., 1984; Coutant et al., 1988). The amounts of PAHs which are found in the vapour phase increase with ambient temperatures (Yamasaki et al., 1982).

A useful method has been proposed to control chemical degradation and volatilization losses from filters, based on the invariability of PAH-profiles (i.e., the ratio of all PAHs to one another) during the collection time (Grimmer et al., 1982).

Elutriators and cascade impactors have been used to perform a particle size-selective sampling of PAHs (measurements reviewed in Menichini, 1992a). Instruments designed as additions to high-volume samplers are available, including 'PM_{10}' inlets (enabling collection of particulate matter below a 10 µm cut size; US EPA, 1987) (Lioy et al., 1988; Hawthorne et al., 1992) and cascade impactors (Van Vaeck et al., 1984; Catoggio et al., 1989).

In atmospheric PAH determination, the sampling step is by far the most important source of variability in the results. Generally speaking, different investigations are poorly comparable owing to differences in factors such as season, meteorological conditions, time of day, number and characteristics of sampling sites, and sampling parameters (Menichini, 1992a).

3.1.2 Workplace air

General considerations expressed for ambient air are valid also for the working environment.

The amounts of volatile PAHs which are not retained by filter may be higher than in ambient air, because of the elevated temperatures often present at the workplace. In a pot-room of a Soderberg aluminium plant, 42% of BaA was found in the vapour phase (Andersson et al., 1983); in an iron foundry, at a site where the temperature of PAH source was about 600–700°C, 4- to 7-ring PAHs were determined in the vapour phase at concentrations corresponding to, on an average, about 70% of the total (Knecht et al., 1986).

GF- or teflon-filters are usually used to collect particle-bound PAHs. A number of back-up systems efficiently trap volatile PAHs: in particular, liquid impingers, and solid sorbents such as Tenax-GC, Chromosorb, and XAD-2 (reviewed by: Bjorseth & Becher, 1986; Davis et al., 1987). The latter seems to be the most practicable.

The NIOSH (1985) recommends the use of a teflon-laminated membrane followed by a tube containing two sections of XAD-2.

The worker's actual exposure is best estimated by 'personal sampling': portable battery-operated air pumps are used at low flow rates (ca. 2 litres/min), with the filter holder placed in the 'breathing-zone', i.e., clipped to the shirt collar of the worker.

3.1.3 *Combustion effluents*

The validity of the collected sample, i.e., its capability to reflect the *'true'* composition of the emission, is a crucial factor in the determination of PAH emissions.

The problems associated with collection efficiency for volatile PAHs are enhanced when sampling for combustion effluents, such as stack gases and vehicle exhausts, because of the elevated temperatures at sampling positions.

A sampling device for stack gases is constituted by a glass- or quartz-fiber filter, followed by a special unit generally consisting in a cooler for collecting condensable matter and an adsorbent cartridge (Colmsjo et al., 1986; Funcke et al., 1988). Tenax-GC has been used as an adsorbent (Jones et al., 1976), but XAD-2 seems to be more suitable (Warman, 1985) and is generally preferred.

Two sampling procedures have been described in detail by the US EPA (1986c). In the first one ('Modified method 5 sampling train'), the train basically includes a GF or quartz-fiber filter kept at ca. 120°C, a condenser coil conditioning the gas at max. 20°C, and a bed of XAD-2 jacketed to mantain the internal gas temperature at ca. 17°C. The second procedure ('Source assessment sampling system') is often used in stationary investigations (Warman, 1985). The apparatus consists of a stainless steel probe which enters a thermostated oven: this contains the filter preceded by three cyclone separators in series (the cutoff diameters are 10, 3, and 1 µm, respectively); the volatile organics are cooled and trapped by XAD-2. The sorbent is followed by a condensate collection trap and an impinger train.

Sampling of vehicle exhausts is made under laboratory conditions, using chassis or engine dynamometer testing. Standard driving cycles are employed to simulate on-road conditions: usually, the US 'Federal Test Procedure' (FTP) (CONCAWE, 1991) and the 'Europa Test' (or ECE-15 Test) (Off J Eur Comm, 1983). The choice of the cycle does not seem to play an important role in levels of PAH emissions (Stenberg, 1985).

Basically, two techniques have been used for exhaust collection (sampling and analytical methods reviewed by: Levsen, 1988; IARC, 1989). In the first one ('raw gas sampling'), the exhaust pipe is directly connected to the sampling apparatus: undiluted emissions are cooled in a condenser and then allowed to pass through a filter for particulate collection (Grimmer et al., 1979,1988; VDI, 1989). Nowadays, a second technique ('dilution tube sampling') is often adopted: hot exhaust is diluted with filtered cold air in a tunnel, from which samples are collected isokinetically. This technique simulates the process of dilution occurring under real road conditions. Dilution apparatus and related sampling systems were described by the US EPA (1992).

Particles are almost always collected by filters: GF, GF with teflon binder, and quartz-fiber filters, as well as teflon membranes; the latter have been reported to be particularly adequate in terms of efficiency and chemical inertness (Lee & Schuetzle, 1983). GF filters impregnated with liquid paraffin are also used (Grimmer et al., 1979; VDI, 1989). Collection of vapour-phase PAHs (reviewed by Stenberg, 1985) may be performed by cryo-condensation (Stenberg et al., 1983) or by an adsorbent trap with a polymeric material such as XAD-2 (Lee & Schuetzle, 1983).

Artifacts during filter collection may result from chemical conversion of PAHs, particularly into nitro-PAHs and oxidation products (reviewed by: Lee & Schuetzle, 1983; Schuetzle, 1983; IARC, 1989); such effects still need to be fully evaluated.

3.1.4 Water

PAH concentrations are generally very small, at 0.1 and 1 ng/litre levels in uncontaminated groundwater supplies and in drinking waters. This implies: (a) the possibility, during collection and storage of samples, of serious errors arising from adsorption losses and contamination; (b) the need, in some cases, for a preconcentration step to enrich the sample. Sampling is recommended to be performed on-site, directly in the extraction vessel (Smith et al., 1981).

Various solid sorbents have been successfully used for the preconcentration (reviewed by Smith et al., 1981): Tenax-GC, prefiltered if necessary (Leoni et al., 1975); XAD resins (reviewed by Griest & Caton, 1983); open-pore PUF (Basu et al., 1987); and prepacked disposable cartridges of bonded-phase silica gel (Chladek & Marano, 1984; Van Noort & Wondergem, 1985). Solid sorbents have limitations when the sample contains suspended material, since adsorbed PAHs may be lost by filtration (Van Noort & Wondergem, 1985).

3.1.5 Solid samples

A homogenization of the material (e.g., some foodstuffs, soil, sediment, tissues, plants) is normally required before a sample is extracted. Pretreatment of food products has been reviewed (together with techniques for their analysis) by Liem et al. (1992).

3.2 Preparation

Most environmental samples contain small amounts of PAHs, requiring sophisticated techniques for detection and quantification. Therefore, it is essential to perform an efficient extraction from the sample matrix, followed by one or more purification steps enabling the sample to be analysed as much as possible free from impurities and interferences. A vary large number of extraction and purification techniques, as well as of their combinations ('isolation schemes'), are described in the literature. Also considering one specific matrix, there is no single scheme commonly recognized as 'the best', although various methods have been validated and recommended. A classification of isolation schemes, according to specific groups of matrices, has been made (Jacob & Grimmer, 1979; Grimmer, 1983), which basically is still widely used and is briefly summarized here.

The available techniques have been reviewed (Lee et al., 1981; Santodonato et al., 1981; Grimmer, 1983), particularly the extraction methods (Griest & Caton, 1983): in very general terms, depending on the matrix, PAHs are extracted from the sample by a Soxhlet apparatus (e.g., filters loaded with particulate matter or vehicle exhausts, sediments), or directly by liquid-liquid partition (water samples), or - after complete sample dissolution (e.g., fats, vegetable and mineral oils) or alkaline digestion (e.g., meat products) - by a selective solvent such as N,N-dimethylformamide or (Natusch & Tomkins, 1978) dimethylsulfoxide. The complete PAH extraction from samples such as soot emitted by diesel engines, carbon blacks, and other carbonaceous materials is particularly difficult.

As an alternative to Soxhlet extraction, particularly from solid samples and filters loaded with particulate matter, ultrasonic extraction (review by Griest & Caton, 1983) is becoming more and more successful for the advantages in terms of reduced time of extraction (minutes versus hours), with recovery efficiencies and reproducibilities which may also be superior. There is not a generally valid conclusion regarding which technique is most favourable since the results of a comparison depend on matrix, solvent and experimental conditions.

Recently, supercritical fluid extraction (SFE) (Langenfeld et al., 1993) has gained attention as a rapid alternative to conventional liquid extraction from PUF sorbents (Hawthorne et al., 1989a), soil (Wenclawiak et al., 1992), and other environmental solids such as urban dust, fly ash, and sediment (Hawthorne & Miller, 1987). SFE may also be directly coupled with on-column GC (see 3.3.1): the extract is quantitatively transferred into the GC column, yielding rapid (less than 1 h) analysis with maximum sensitivity. This technique has been applied to urban dust samples (Hawthorn et al., 1989b).

Purification of extracted samples from other classes of interfering substances is most commonly accomplished by adsorption column chromatography. The classical sorbents, alumina and especially silica gel, are widely used. In addition, the hydrophobic Sephadex LH-20 has been found to be suitable to isolate PAHs from nonaromatic, nonpolar compounds (which is important if the sample is analysed by GC) (Grimmer & Bonke, 1979b), and - in partition chromatography, as a carrier of the stationary phase - to separate PAHs from alkyl derivatives (Grimmer & Bonke, 1979a). Chromatographies on silica gel and Sephadex are often combined (Jacob & Grimmer, 1979; Grimmer, 1983). Clean-up has been performed also by eluting extracted samples through XAD-2 (soil samples: Spitzer & Kuwatsuka, 1986), or XAD-2 and Sephadex LH-20 in series (foods: Vaessen et al., 1988), or Florisil columns (food, water and sediment samples: ref. in Table 7).

Conventional chromatographic columns may be substituted with prepacked commercial cartridges, with advantages in terms of time and solvents consumed, and of reproducibility performance. For example, silica cartridges have been used in purification of foodstuffs (Dennis et al., 1983), urine (Becher & Bjorseth, 1983), vehicle emissions (Benner et al., 1989), mineral oil mist (Menichini et al., 1990), and atmospheric samples (Baek et al., 1992); soil samples have been cleaned up through Florisil cartridges (Jones et al., 1989).

Alternatively to chromatography on silica gel columns, preparative thin-layer chromatography is also used, e.g., with air particulates (see Table 6) and vegetable oils (Menichini et al., 1991).

To avoid photodecomposition of PAHs, sample handling in the absence of UV light is recommended at any stage, and particularly during adsorption on chromatographic media. To avoid significant losses of more volatile PAHs, samples do not have to be evaporated to dryness. Other generally recommended precautions are: to control possible sources of contamination (particularly, from solvents), to store samples - at all stages - refrigerated and in the dark, to keep the water bath temperature of the rotary evaporator under about 35-40°C.

3.3 Analysis

At present, identification and quantification of PAHs are routinely performed by gas chromatography (GC) or high-performance liquid chromatography (HPLC). Each technique presents a number of advantages over the other one. Both of them are rather expensive, particularly HPLC, and require qualified operating personnel. Nevertheless, they are deemed necessary to analyse 'real' samples for a large number of PAHs with accuracy and precision.

Reference materials of certified higher than 99% purity are available for 22 of the PAHs considered (BCR, 1992); the remaining compounds are commercially available as chemical standards, with purities of 99% or higher.

3.3.1 Gas chromatography

Excellent separation capacities (about 3000 and more plates per meter) are obtained by fused silica capillary columns which are commercially available. This makes it possible to analyse very complex mixtures containing over one hundred PAHs.

The most widely used stationary phases are the methylpolylsiloxanes: especially SE-54 (5% phenyl, 1% vinyl-substituted) and SE-52 (5% phenyl-), but also SE-30 and OV-101 (unsubstituted), OV-17 (50% phenyl-), Dexsil 300 (carborane-), as well as their equivalent phases. The use of chemically-bonded phases is increasing because of the advantages in terms of rinsability to restore column performance and lower bleeding at the high temperatures of analysis (about 300°C) that are required for determining high-boiling compounds.

Splitless or on-column injections are necessary to gain sensitivity in trace analysis, the latter being preferred as it allows better reproducibility. A flame ionization detector (FID) is almost universally employed because of its excellent response linearity, sensitivity and reliability. Since the FID signal is related linearly to the carbon mass of the compound, PAHs are recorded in proportion to their quantities and the chromatogram directly represents the quantitative composition of the sample. Because of the non-selectivity of FID, samples for GC need to be highly purified from interferences. Peak identification, which is routinely performed by means of retention data, has to be confirmed by analysing the sample with a different GC column or by an independent technique, such as HPLC, or by a mass spectrometric (MS) detector directly coupled to the gas chromatograph (GC-MS).

MS detectors have gained wide acceptance. They are powerful tools in identifying compounds, especially when the commercially available libraries of reference spectra are used to match the spectra obtained and control the compound purity. However, isomeric compounds often exhibit indistinguishable spectra, so that the final assignment must also rely upon retention data.

For applications of GC and MS to PAHs, reference is made to published reviews (Lee et al., 1981; Sortland Olufsen & Bjorseth, 1983; Bartle, 1985; Hites, 1989)

An on-line coupling of liquid chromatography (LC), capillary GC and quadrupole MS has been performed in determining PAHs in vegetable oils (Vreuls et al., 1991).

3.3.2 High-performance liquid chromatography

The packing material considered the most suitable for PAH separation consists of silica particles chemically bonded to linear C18 hydrocarbon chains. Typically, 25-cm columns packed with 5-µm particles are used with the gradient elution technique, and the mobile phase consists of mixtures of acetonitrile/water or methanol/water ('reversed-phase HPLC'). The separation efficiency which can be achieved with HPLC columns is quite lower than in capillary GC, which makes HPLC generally less suitable for samples containing complex PAH mixtures.

On the other hand, relevant advantages of HPLC derive from the capabilities of the detectors. Those most widely used for PAHs are ultraviolet (UV) and fluorescence detectors, generally arranged in series, employing flow-cell photometers or spectrophotometers. Both of them, and especially the latter, are high specific and sensitive (the detection limits in fluorescence are at least one order of magnitude lower than in UV). Specificity of fluorescence detector allows for the determination of individual PAHs in the presence of other non-fluorescing substances. In addition, since different PAHs have different absorptivities or different fluorescence spectral characteristics at given wavelengths, the detectors can be optimised for maximum response for specific compounds; in particular, this may prove advantageous in the identification of unresolved components. HPLC is not suitable for lower-molecular mass compounds (namely, NA, AC, and ACL), which have relatively high detection limits (US EPA, 1984).

In addition, owing to the selectivity of packing materials, various isomers which cannot be separated, or only partially so, by usual capillary GC columns, are baseline resolved and identified by HPLC: for example, the pairs CHR-TRI, and BbFA-BkFA (Wise et al., 1980).

The coupling of an MS detector to HPLC has been developed and also applied to PAH detection (e.g., Quilliam & Sim, 1988).

Much information on the isomeric structure may be obtained from spectra acquired during the elution of chromatographic peaks. For this purpose, the UV diode-array detector (DAD) is gaining acceptance in PAH analysis for confirmation of peaks (Dong & Greenberg, 1988; Kicinski et al., 1989).

For applications of HPLC to PAHs, reference is made to published reviews (Lee et al., 1981; Wise 1983,1985).

3.3.3 Thin-layer chromatography

Nowadays, thin-layer chromatography (TLC) is commonly limited to the identification of individual compounds (namely, BaP), particularly for screening purposes (IUPAC, 1987), or of selected PAHs such as the six PAHs (Borneff & Kunte, 1979) whose determination was recommended by the WHO (1971) in drinking water. Indeed, it is an inexpensive and quick analytical technique, but with low separation efficiency. This last parameter is improved by two-dimensional processes (e.g., Borneff & Kunte, 1979).

Quantification may be performed by spectrophotometric or spectrofluorimetric methods in solution after extracting the scrubbed substance spot (Howard, 1979; also reported in AOAC, 1990), or <u>in situ</u> by scanning spectrofluorimetry (Borneff & Kunte, 1979).

As an adsorbent, acetylated cellulose has been mostly used for one-step separation of the PAH fraction, and mixed aluminum oxide and acetylated cellulose for two-dimensional development (reviewed by Daisey, 1983)

3.3.4 Other techniques

A number of non-conventional instruments and techniques, based on spectroscopic principles, have been - and still are being - developed as possible alternatives to the chromatographic methods for PAHs. However, most of them are quite expensive, require skilled personnel, and are not yet considered useful for the practicing analyst. For details on such techniques and their applications to PAHs, reference is made to published reviews (Wehry, 1983; Vo-Dinh, 1989, various chapters). Low-temperature luminescence in frozen solutions ("Shpol'skii effect") has been applied to various environmental samples, particularly to identify methylated PAH isomers (Garrigues &

Ewald, 1987; Saber et al., 1987). Synchronous luminescence and room temperature phosphorimetry have been reported as simple and cost-effective screening techniques for PAHs (Vo-Dinh et al., 1984; Abbott et al., 1986).

Infrared analysis - and particularly Fourier transform infrared (FTIR) spectroscopy coupled to GC (Stout & Mamantov, 1989) -, and capillary supercritical fluid chromatography (SFC) (Wright & Smith, 1989) have also been applied to PAHs.

3.4 Choice of PAHs to be determined

The choice depends on the purpose of measurement. For example, carcinogenic PAHs are of interest in human health studies; other, more abundant compounds may be of interest in ecotoxicological studies. In addition, a multitude of compounds are advantageous when PAH profiles have to be correlated to sources and/or effects.

Table 8 (p. 32) shows some lists of compounds whose determination has been required or recommended at national or international levels.

According to an EEC Directive (Off J Eur Comm, 1980), which followed a WHO (1971) recommendation, the concentrations of six reference compounds (also known as 'Borneff PAHs') must be measured in drinking waters in order to check their compliance with the cumulative limit value of 0.2 µg/litre for the PAH class. The original WHO choice of these six PAHs was not based on any toxicological considerations, but on the fact that analytical investigations were then largely confined to these (relatively easily detected) compounds (WHO, 1984).

The method required by the US EPA (1984) for the analysis of municipal and industrial wastewater covers the determination of 16 PAHs ('priority pollutant PAHs') considered representative of the class. Even outside the USA, this list of compounds is often taken as a reference list for the analysis of various environmental matrices.

The European Aluminium Association (EAA-EHS, 1990) has recommended a list of 19 PAHs to be determined in any kind of samples related to operations in that specific industry. The list is based on the PAH composition of emissions from aluminium smelters, the IARC classification of carcinogenicity, and the existing official lists.

The Italian National Advisory Toxicological Committee (Menichini, 1992b) has recommended including the determination of seven PAHs in health-related investigations, based on their carcinogenicity ('probably' or 'possibly' carcinogenic to humans; IARC, 1987) and their occurrence in the environment.

As a conclusion of an international Workshop on PAHs (SFT-SNT, 1992), it was recommended to determine 15 carcinogenic PAHs in health-related studies and to include another six abundant PAHs for environment-related studies.

Table 6. Analytical methods (matrix: air)

Matrix	Sampling, extraction	Clean-up	Analysis	Limit of detection[a]	Reference
ambient air	sampling on GF+PUF, at 45 m^3/h; soxhlet extr. (c-hexane)	liq.-liq. partition (c-hexane:H_2O:DMSO); then CC (SiO_2)	GC/MS		Yamasaki et al. (1982)
	sampling on GF+PUF, at 30 m^3/h; soxhlet extr. with petr. ether (GF) and DCM (PUF)	CC (Al_2O_3 + SiO_2)	HPLC/Fl	0.01-0.7 ng/m^3	Keller & Bidleman (1984)
	sampling on GF (particle d < 15 µm), at 68 m^3/h; soxhlet extr. with c-hexane + DCM + acetone	TLC (SiO_2)	HPLC/UV+Fl	0.01-0.4 ng/m^3	Greenberg et al. (1985)
	sampling on GF, at 83 m^3/h; sonication (c-hexane)	TLC (SiO_2)	GC		Valerio et al. (1992)
emissions (municipal incenerator)	sampling by glass wool + condenser + XAD-2; extr. with acetone (glass wool and XAD-2: by soxhlet)	liq.-liq. partition with DMF	GC	10 ng/m^3	Colmsjo et al. (1986)
vehicle exhaust	sampling by GF + condenser; liq.-liq. partition with acetone:H_2O:c-hexane and DMF:H_2O:c-hexane	CC (SiO_2 + Sephadex LH-20)	GC	2.5-20 ng per 'Europa test'	Grimmer et al. (1979)
	sampling in dilution tunnel by teflon-coated GF + condenser; soxhlet extr. of filter (DCM) and condensate (acetone); remaining aqueous phase extr. with DCM	liq.-liq. partition (c-hexane:H_2O:DMF)	GC		Westerholm et al. (1988)

Table 6 (contd.)

indoor air	sampling on GF (particle d < 10 μm) at 10 litres/min; sonication (c-hexane)	TLC (acetyloxylated cellulose)	spectrofluor. (BaP only)		Lioy et al. (1988)
	sampling on quartz fiber filter + XAD-4, at 226 litres/min; soxhlet extr. with DCM		GC/MS		Chuang et al. (1991)
	sampling on teflon-coated GF, at 20 litres/min for 24 h; soxhlet extr. with DCM	filtration; then CC (SiO_2 cartridge), optional	HPLC/Fl	0.02-0.12 ng/m^3 [b]	Daisey & Gundel (1993)
	sampling on quartz fiber filter + PUF or XAD-2, at 20 litres/min for 24 h; soxhlet extr. with DCM (filter and XAD-2) or ether:n-hexane (PUF)	CC (SiO_2 or amino-silane), if needed	GC or GC/MS or HPLC/UV+Fl	ca. 0.1 ng/m^3 (BaP)	Winberry et al. (1990)
workplace air	sampling on teflon filter + XAD-2, at 2 litres/min; sonication or soxhlet extr. of filter[c], extr. of XAD-2 with toluene (for GC) or acetonitrile (for HPLC)		a) GC b) HPLC/UV+Fl	a) 0.3-0.5 μg per sample b) 0.05-0.8 μg per sample	NIOSH (1985)
	sampling on filter (GF or quartz fiber or teflon or silver membrane) at 2 litres/min; sonication or soxhlet extr. with c-hexane or toluene	CC (XAD-2)	GC	ca. 0.5 μg/m^3	DFG (1991)
tobacco smoke	sampling by acetone trap; solvent partition scheme (acids/bases/neutrals/PAHs)	CC (SiO_2 + Sephadex LH-20); then HPLC/UV	GC/MS + NMR	ng/cigarette level	Lee et al. (1976)

CC: column chromatography; c-hexane: cyclohexane; DCM: dichloromethane; DMF: N,N-dimethylformamide; DMSO: dimethylsulfoxide; Fl: fluorescence; NMR: nuclear magnetic resonance; other abbreviations: see text.

[a] Range refers to the various PAHs.

[b] The following PAHs can be determined: FA, PY, CHR, BeP, BbFA, BkFA, BaP, BghiP, IP.

[c] Appropriate solvent has to be determined through recovery tests on the specific sample.

Table 7. Analytical methods (matrices other than air)

Matrix	Extraction	Clean-up	Analysis	Limit of detection[a]	Reference
tap water	preconcentration on PUF; extr. (acetone + c-hexane)	liq.-liq. partition with c-hexane:H_2O:MeOH and c-hexane:H_2O:DMSO; then CC (Florisil)	GC or TLC (Al_2O_3: acetyl. cellul.) with Fl detector	0.1 ng/litre	Basu & Saxena (1978)
ground water	liq.-liq. partition with DCM	CC (SiO_2), if needed	a) GC b) GC/MS c) HPLC/UV+Fl	a) µg/litre level b) 10 µg/litre c) 0.01-2 µg/litre	US EPA (1986a)
waste water	liq.-liq. partition with DCM	CC (SiO_2), if needed	GC or HPLC/UV+Fl	0.01-0.2 µg/litre (by HPLC)	US EPA (1984)
sea water	liq.-liq. partition with n-hexane or CCl_4	CC (SiO_2 + Al_2O_3)	GC or HPLC/UV		Desideri et al. (1984)
soil	sonication with DCM	CC (Al_2O_3); then liq.-liq. partition (n-hexane:H_2O:DMSO)	GC/MS	1 µg/kg	Vogt et al. (1987)
	soxhlet extr. with DCM	CC (Florisil cartridge)	HPLC/UV+Fl	1 µg/kg	Jones et al. (1989)
sediment	soxhlet extr. with DCM	CC (SiO_2 + Sephadex LH-20)	HPLC/DAD/MS		Quilliam & Sim (1988)
	sonication with acetone:n-hexane	CC (Florisil)	HPLC/UV+Fl	1-160 µg/kg	Marcus et al. (1988)
meat and fish products (I), vegetable oils (II), and sewage sludge (III)	I) digestion (alc. KOH), then liq.-liq. partition (MeOH:H_2O:c-hexane) II) dissolution in c-hexane III) refluxing with acetone	liq.-liq. partition (c-hexane:H_2O:DMF); then CC (SiO_2 + Sephadex LH-20)	GC	2.5-20 ng/sample	Grimmer & Bohnke (1979)
food (total diet)	refluxing with alc. KOH, extr. with isooctane	liq.-liq. partition (isooctane:H_2O:DMF); then CC (SiO_2 cartridge)	HPLC/Fl	0.002-0.7 µg/kg	Dennis et al. (1983)
	saponification (alc. KOH), extr. with c-hexane	CC (SiO_2)	HPLC/Fl	0.03-2 µg/kg	De Vos et al. (1990)
	saponification (alc. KOH), extr. with isooctane	CC (Florisil); then liq.-liq. partition (isooctane:H_2O:DMSO)	TLC/UV+Fl	0.02 µg/kg (BaP)	Howard (1979); AOAC (1990)

Table 7 (contd.)

seafood	digestion with alc. KOH, extr. with TCTFE	CC (Al_2O_3 + SiO_2 + C18 cartridge)	HPLC/Fl	0.01-0.6 µg/kg	Perfetti et al. (1992)
smoked food	digestion with alc. KOH, extr. with TCTFE	CC (Al_2O_3 + SiO_2); liq.-liq. partition (c-hexane:H_2O:DMSO)	TLC/UV+Fl	0.03-0.4 µg/kg	Joe et al. (1984)
	refluxing with c-hexane or TCTFE, extr. with MeOH:H_2O	liq.-liq. partition (c-hexane:H_2O:DMF); then CC (SiO_2)	TLC/Fl[b] (only BaP)	0.5 ng/kg	IUPAC (1987)
solid waste	soxhlet extr. with DCM or sonication with DCM:acetone	CC (SiO_2), if needed	a) GC b) GC/MS c) HPLC/UV+Fl	a,c) µg/kg level b) 1-200 mg/kg	US EPA (1986b)
mineral oil and fuel	liq.-liq. partition (c-hexane:H_2O:DMF)	CC (SiO_2 + Sephadex LH-20)	GC	100 ng/kg	Grimmer & Bohnke (1971)
medicinal oil	liq.-liq. partition (c-hexane:H_2O:DMF)	CC (SiO_2 + Sephadex LH-20)	HPLC/Fl + GC	0.2-200 ng/kg	Geahchan et al. (1991)
plants	sonication (acetonitrile), extr. with pentane	CC (SiO_2)	GC		Coates et al. (1986)
urine	adjusted to pH3, extr. by C_{18} cartridge, reduction of metabolites with HI	CC (SiO_2 cartridge)	HPLC[c]		Becher & Bjorseth (1983)
urine and faeces	addition of HCl, refluxing with toluene, addition of MeOH + diazomethane in ether (faeces are saponificated before acidification)	CC (SiO_2 + Sephadex LH-20)	GC and GC/MS[d]		Jacob et al. (1989)
tissue	homogenization (*bezene:n-hexane*)	CC (Florisil)	GC/MS	5-50 µg/kg	Liao et al. (1988)
skin[e]	sonication of exposure pads with DCM, centrifugation		HPLC/Fl	6 ng/cm²	Jogenselen et al. (1988)

TCTFE: 1,1,2-trichlorotrifluoroethane; other abbreviations: see Table 6.

[a] Range refers to the various PAHs.

[b] The BaP content is estimated to be > or < 0.6 µg/kg (*screening method*).

[c] Determination of unmetabolized and metabolized PAHs.

[d] Determination of PY and 1-hydroxypyrene.

[e] Measurement of skin contamination with soft polypropylene exposure pads mounted on skin sites.

Table 8. Some existing lists of PAHs to be determined

Compound	WHO/EEC[a] drinking water	US EPA[b] wastewater	EAA[c] aluminium industry	CCTN[d] air	SFT-SNT[e] health	SFT-SNT[e] environ.
NA		X				X
ACL		X				
AC		X				
FL		X				
AN		X	X			X
PHE		X	X			X
FA	X	X	X			X
PY		X	X			X
BaFL			X			
BbFL			X			
CPP					X	X
BaA		X	X	X	X	X
BcPH					X	X
CHR		X	X		X	X
TRI			X			
BbFA	X	X	X	X	X	X
BjFA				X	X	X
BkFA	X	X	X	X	X	X
BaP	X	X	X	X	X	X
BeP			X			
ATR					X	X
BghiP	X	X	X			X
IP	X	X	X	X	X	X
DBahA		X	X	X	X	X
DBaeP			X		X	X
DBahP			X		X	X
DBaiP			X		X	X
DBalP					X	X

[a] Recommended by WHO (1971) and required by an EEC Directive (Off J Eur Comm, 1980).

[b] Required by US EPA (1984) for the analysis of municipal and industrial wastewater.

[c] Recommended by the European Aluminium Association (EAA-EHS, 1990).

[d] Recommended by the Italian National Advisory Toxicological Committee (CCTN) in health-related studies (Menichini, 1992b).

[e] Recommended at the International Workshop on PAHs (SFT-SNT, 1992) in health-related studies (left column) and in environment-related studies (right).

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Stampato dal Servizio per le attività editoriali
dell'Istituto Superiore di Sanità, Viale Regina Elena, 299 - 00161 ROMA

Reg. Stampa - Tribunale di Roma n. 131/88 del 1° marzo 1988

Roma, giugno 1994 (n. 2) 1^{e} Suppl.