2. Occurrence and Analysis

2.1 Occupational exposure

The occupational exposures to components of diesel engine exhaust of several groups of workers, including railroad workers, workers in mines with diesel-powered equipment, bus garage workers, truck drivers, fork-lift truck operators and fire-fighters, have been studied. The exposures of toll-booth attendants, border-station inspectors, traffic-control officers, professional drivers (truck, bus, taxi), car mechanics, car ferry workers, parking garage attendants and lumberjacks to components of gasoline engine exhaust have also been studied. Many workers are exposed to both diesel and gasoline engine exhausts. The extent of exposure to these specific exhausts in different occupational groups depends on many factors, such as country and time period considered; in addition, environmental exposure to exhausts (see section 2.2) influences the total exposure of workers.

A primary focus of this monograph is on human exposure to respirable particles emitted by diesel and gasoline engines. It is important in studying such exposures that the relative contributions from various types of engine exhaust be distinguished from each other and from those of other particulate sources. In source apportionment studies, chemical tracers are used which are unique to the combustion source, representative of the total particulate emissions, chemically stable, present in abundance, and easy to collect and analyse. Many compounds that may appear to be good tracers are not representative of the total sample, varying significantly with the fuel source, temperature of combustion and other factors.

Methods have been developed and used for apportioning the contribution of vehicle emissions from various sources. These are based upon the use of barium (a diesel fuel additive) and of lead for diesel and gasoline vehicles, respectively (Hampton *et al.*, 1983; Johnson, 1988). The method may not be suitable for characterizing certain occupational exposures (e.g., mining, train and heavy-equipment operations) because barium is not typically used as a fuel additive in these applications.

Several new methods have been developed to apportion sources of occupational exposure to engine exhaust. For example, Currie and Klouda (1982) used measurements of $^{14}C/^{12}C$ to distinguish between carbon compounds in particles derived from combustion of old carbon sources (e.g., petroleum) and of contemporary carbon sources (e.g., wood, tobacco). Johnson *et al.* (1981) developed a thermal-optical analytical technique which has been used to apportion samples containing cigarette smoke and diesel exhaust particles (Zaebst *et al.*, 1988). Cantrell *et al.* (1986) indicated that size selective sampling is a suitable method for distinguishing diesel particles from other particles in coal mines.

Unfortunately, for the studies of exposure reviewed in this section, the source apportionment techniques described above were not available. The data on components of engine exhausts, such as carbon monoxide, nitrogen oxides and sulfur dioxide, can be used to indicate the presence of engine exhaust but cannot be used to apportion exposures. Thus, information on single components reported in these studies cannot be used to rank relative exposures to total engine exhaust reliably, due to the variable relationships among the components resulting from factors such as engine speed, engine load and control techniques.

It should also be noted that occupational exposures to PAHs can be measured, but samples are typically not large enough to allow quantitative measurements to be made.

(*a*) *Workers whose predominant exhaust exposure is that from diesel engines*

(i) *Railroad workers*

Diesel locomotives were introduced on railroads in Canada and the USA in 1928 and in Germany in 1932. In the USA, the change-over to diesel engines was 95% complete by 1959 (Garshick *et al.*, 1988).

Hobbs *et al.* (1977) reviewed the earlier literature on air contaminants in the environment of train crews. In addition, measurements of air contaminants in locomotives and cabooses were made during their passage through tunnels and during freighting and switch-yard operations. These authors estimated 8-h time-weighted averages (TWAs) for combined tunnel and freight operations, and Heino *et al.* (1978) evaluated levels of diesel exhaust components in locomotive cabs and round-houses in Finland (Table 12).

As part of a large epidemiological study on railroad workers, Hammond *et al.* (1984) presented data on components of diesel exhaust. The respirable particles collected had a dichloromethane extractable fraction of 46% (liquid chromatography fractionation), which was found to be composed of 45% aliphatic hydrocarbons, 33% olefinic and aromatic hydrocarbons and 23% polar compounds. The aromatic fraction included phenanthrene and alkylated phenanthrenes.

Woskie *et al.* (1988a) conducted an industrial hygiene survey of the US railroad industry as a part of epidemiological studies reported by Garshick *et al.* (1987, 1988). Personal exposure to respirable particles was measured and then corrected for the estimated contribution of cigarette smoke particulates. These data are presented in Table 13. Corrections for cigarette smoke were made by analysing composited respirable particulate samples for nicotine content; an adjusted respirable particulate concentration was then calculated for each job group, and the applicable average fraction of cigarette smoke was subtracted from the average respirable particulate concentration.

(ii) *Mine workers*

The first diesel engine-powered vehicles in underground mines were used in Germany in 1927 (Kaplan, 1959), and they are now used widely throughout the world (Daniel, 1984).

Table 12. Levels of air contaminants to which railroad workers are exposed

Substance	Locomotive cabs					Caboose (8–h TWA in 1 tunnel trip)[b]	Roundhouses (mean; range)[a]
	Mean (range)[a]	Tunnels (8-h TWA)[b]		Freighting[b] (7.5-h TWA)	Switch-yard[b] (5-h TWA)		
		1 trip	5 trips				
Carbon monoxide (mg/m³)	–	8.9	40.2	1.43	0.3	1.43	–
Nitric oxide (mg/m³)	–	5.7	27	0.2	0.09	2.4	–
Nitrogen oxides (ppm)	0.35 (ND–2.0)						2.55 (ND–10)
Nitrogen dioxide (mg/m³)	–	0.04	0.06	0.04	0.06	0.02	0.26 (ND–0.4)
Total hydrocarbons (ppm)	–	4.55	4.94	2.89	3.12	3.69	–
Total aldehydes (as formaldehyde)	0.01 (ND–0.1) mg/m³	0.07 ppm	0.09 ppm	0.05 ppm	0.02 ppm	0.14 ppm	0.19 (ND–1.0) mg/m³
Acrolein (mg/m³)	0.02 (ND–0.2)	–	–	–	–	–	0.07 (ND–0.5)
Total particulate matter (mg/m³)	0.38 (0.1–0.8)	0.05	0.07	0.16	0.01	0.27	1.99 (0.07–8.7)

[a] From Heino *et al.* (1978)

[b] From Hobbs *et al.* (1977); TWA, time-weighted average (estimated)

ND, not detected

Table 13. Personal exposures to respirable particulate matter, and adjusted respirable particulate matter concentration[a], among railroad workers by job group[b]

Exposure group	Job group	No.	Arithmetic mean (SD) of respirable particulate matter ($\mu g/m^3$)	Arithmetic mean (SD) of adjusted respirable particulate matter ($\mu g/m^3$)
Clerks	Clerk/station agent	59	125 (75)	42 (36)
Signal maintainers	Signal maintainer	13	69 (39)	58 (33)
Engineers/firers	Freight worker	55	115 (67)	94 (55)
	Yard worker	50	108 (109)	69 (70)
	Passenger	23	75 (52)	51 (35)
Brakers/conductors	Freight conductor	62	126 (65)	69 (52)
	Freight braker	21	145 (80)	102 (62)
	Passenger	35	111 (62)	104 (58)
	Yard worker	32	180 (117)	114 (76)
	Hostler	8	231 (134)	224 (130)
Shop workers	Electrician	42	256 (332)	192 (248)
	Machinist	110	191 (146)	147 (120)
	Supervisor, labourer and other shop workers	24	244 (141)	155 (83)

[a] Cigarette smoke particulate matter subtracted from total respirable particulate matter (see text for explanation)

[b] From Woskie *et al.* (1988a); each sample was collected over a single work shift (7–12 h).

Other sources of exposure in mines include activities that produce large quantities of airborne particles, and blasting, which produces particles and gases such as methane and sulfur dioxide. In addition, these gases may be released spontaneously from the ore bed or from surrounding geological formations. Some exposures that may occur in mines, depending on the ores present, were evaluated by previous IARC working groups; these include radon (IARC, 1988), silica (IARC, 1987b), nickel (IARC, 1987a), chromium (IARC, 1987a) and asbestos (IARC, 1987a).

Lassiter and Milby (1978) gave examples of the levels of carbon monoxide and nitrogen dioxide that can be found at the diesel operator's position in an underground mine. On the basis of 2977 samples taken in 1963–72, the average concentration of carbon monoxide was 8.5 ppm (9.7 mg/m^3), 5% of the samples containing >50 ppm (>57 mg/m^3); 1504 samples contained an average concentration of 0.2 ppm (0.4 mg/m^3) nitrogen dioxide, with 0.75% above 3 ppm (>6 mg/m^3) and one sample >5 ppm (>10 mg/m^3).

A study conducted for the US Bureau of Mines on levels of diesel exhaust components in 24 mines included two coal mines (Holland, 1978); the results are shown in Table 14. Anthracene and phenanthrene were found at measurable levels, but five other PAHs (benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, chrysene and pyrene) were not.

Table 14. Levels of diesel exhaust components (mg/m^3) in 24 US mines[a]

Contaminant	Diesel exhaust source			Personal and area samples		
	No. of samples	Mean	Range	No. of samples	Mean	Range
Carbon monoxide	6	140	11.5–344	21	14.2	0–26.3
Nitric oxide	3	6.3	<0.1–16.5	10	12.7	0.5–70
Nitrogen dioxide	5	16.8	1–40	29	1.6	0–11
Sulfur dioxide	5	0.3	0–<1	6	2.1	0–13
Sulfuric acid	4	12.8	<0.2–46	9	0.3	<0.004–2
Formaldehyde	10	7	0–42	23	0.8	0–8
Acrolein	7	2.1	<0.1–3.2	16	<0.4	<0.02–<5
Total particulate matter	8	50.2	0.5–236	13	4.6	0.2–14
Anthracene	8	0.05	0.02–0.2	13	0.001	0.00005–0.004
Phenanthrene	8	0.001	0–0.008	13	0.01	0–0.17

[a] From Holland (1978)

Levels of air contaminants due to diesel emissions in other coal mines are summarized in Table 15.

The environment of six potash mines in New Mexico, USA, was investigated in 1976 (Attfield *et al.*, 1982). The use of diesel equipment in these mines had begun between 1950 and 1966, and seven to 57 diesel-powered units were used. Environmental concentrations in production jobs and other areas in the six mines (based on 25–34 samples) were 6–10 mg/m^3 carbon monoxide, 0.2–6.6 mg/m^3 nitrogen dioxide and 0.1–4.0 ppm aldehydes.

Cornwell (1982) evaluated employee exposure to diesel emissions at a molybdenum mine in Colorado, USA. Diesel-powered equipment used in the mine included drills, five-yard load haul-dumps and two-yard load haul-dumps. Personal and area sampling was conducted for oxides of carbon, nitrogen and sulfur, formaldehyde, respirable particulate matter, PAHs and cyclohexane-soluble material (sum of particulate and gaseous samples). The results are shown in Table 16.

Daniel (1984) reported 0.2–1.3 ppm (0.4–2.6 mg/m^3) nitrogen dioxide, 3.1–8.7 ppm (3.8–10.7 mg/m^3) nitric oxide and 0.5–2.1 ppm (0.6–2.4 mg/m^3) carbon monoxide in a South Dakota, USA, gold mine when samples were taken during the operation of a diesel mine vehicle. He found 0.3–0.6 ppm (0.8–1.6 mg/m^3) sulfur dioxide, 0.1–0.3 mg/m^3 sulfate, 0.4–1.7 mg/m^3 respirable combustible dust and 1.1–4.4 mg/m^3 total respirable dust.

(iii) *Bus garage and other bus workers*

Exposures of bus garage and other bus workers to diesel exhaust emissions are listed in Table 17. Few studies addressed other exposures that may occur in bus garages, such as to metal fumes from welding and similar operations and to asbestos during brake servicing.

Table 15. Levels of air contaminants (mg/m^3, unless otherwise specified) in coal mines

Contaminant	Concentration	Sampling	Reference
Carbon monoxide	8 (mean)	Personal	Lawter & Kendall (1977)
	0–2.3	Personal	Wheeler *et al.* (1981)
	3.9–26.7	Average of short-term area samples	Reger *et al.* (1982)
Nitrogen oxides	0–5.2 ppm	Average of short-term area samples	Reger *et al.* (1982)
Nitrogen dioxide	0.7 (mean)	Personal	Lawter & Kendall (1977)
	0.06–0.5	Personal	Wheeler *et al.* (1981)
	0–1.1	Average of short-term area samples	Reger *et al.* (1982)
	0.06–1.5	Range of full-shift area samples	Reger *et al.* (1982)
	0.3–0.5	Average of full-shift personal samples	Reger *et al.* (1982)
Nitric oxide	3.7 (mean)	Personal	Lawter & Kendall (1977)
Aldehydes	0.05 (mean)	Personal	Lawter & Kendall (1977)
	0–0.01	Personal	Wheeler *et al.* (1981)
Formaldehyde	0.04 (mean)	Personal	Lawter & Kendall (1977)
'Aromatics'	0.7 (mean)	Personal	Lawter & Kendall (1977)
Cyclohexane-extractable hydrocarbons	0.04–0.07	Personal	Wheeler *et al.* (1981)
Total dust	0–23.0	Average of full-shift area samples	Reger *et al.* (1982)
Respirable dust	0.6–1.7	Personal	Wheeler *et al.* (1981)
	0.9–2.7	Average of full-shift personal samples	Reger *et al.* (1982)
	0–16.1	Range of full-shift area samples	Reger *et al.* (1982)

Table 16. Air contaminant levels in a molybdenum mine[a]

Contaminant	Concentration	Sampling
Carbon monoxide	<1.1–6.1 mg/m^3	8–h TWA; area
Nitric oxide	ND–9.0 mg/m^3	Area
Nitrogen dioxide	ND–6.4	Area
	0.08–0.78 mg/m^3	8–h TWA; area
	0.06–4.32 mg/m^3	8–h TWA; personal
Sulfur dioxide	ND–0.05 mg/m^3	Area
Formaldehyde	ND	Instantaneous area
Respirable particulate matter	0.2–1.9 mg/m^3	8–h TWA; personal
Cyclohexane-soluble material	0.02–0.93 mg/m^3	8–h TWA; personal
	0.02–0.04 mg/m^3	8–h TWA; area
Benz[*a*]anthracene	30–40 ng/m^3	8–h TWA; personal; in 2/15 samples
Benzo[*a*]pyrene	40 ng/m^3	8–h TWA; personal; in 1/15 samples
Chrysene	320 ng/m^3	8–h TWA; personal; in 1/15 samples
Fluoranthene	60–340 ng/m^3	8–h TWA; personal; in 10/15 samples
	70 ng/m^3	8-h TWA; area; in 1/4 samples
Pyrene	80–480 ng/m^3	8–h TWA; personal; in 10/15 samples
	140 ng/m^3	8–h TWA; area; in 1/4 samples

[a] From Cornwell (1982); ND, not detected; TWA, time-weighted average

Table 17. Levels of air contaminants in bus garages (mg/m^3, unless otherwise specified)

Contaminant	Concentration	Sampling	Location	Time	Reference
Carbon monoxide	2–18	Diesel areas	Denver, CO, USA	March 1982	Apol (1983)
	7–11	Terminal (background)	Denver, CO, USA	July-Sept. 1982	Pryor (1983)
	22–46	Terminal (bus arrival/departure)	Denver, CO, USA	July-Sept. 1982	Pryor (1983)
	6–8	Package receiving area	Denver, CO, USA	July-Sept. 1982	Pryor (1983)
	8–40	Reservations room	Denver, CO, USA	July-Sept. 1982	Pryor (1983)
	8–401	Air inlet	Denver, CO, USA	July-Sept. 1982	Pryor (1983)
	<0.01–5.7	Unspecified	Italy	–	del Piano *et al.* (1986)
	1.7–24	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Nitric oxides as NO_2	0.8–1.4	Air analysis	Egypt	1965	El Batawi & Noweir (1966)
	2.6–2.8	Close to exhaust	Egypt	1965	El Batawi & Noweir (1966)
Nitric oxide	1.4–6.9	Peak morning period	Denver, CO, USA	March 1982	Apol (1983)
	0.5–2.8	Later morning period	Denver, CO, USA	March 1982	Apol (1983)
Nitrous oxide	0.3–1.0	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Nitrogen dioxide	0.8–3.2	Peak morning period	Denver, CO, USA	March 1982	Apol (1983)
	0.3–1.6	Later morning period	Denver, CO, USA	March 1982	Apol (1983)
	<0.07	Package receiving area	Denver, CO, USA	June 1982	Pryor (1983)
	0.1–0.8	Unspecified	Italy	–	del Piano *et al.* (1986)
	0.3–1.1	Personal, mean TWA	USA	–	Gamble *et al.* (1987)
	0.2–1.1	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Sulfur dioxide	0.14–0.86	Air analysis	Egypt	1965	El Batawi & Noweir (1966)
	1.8–2.1	Close to exhaust	Egypt	1965	El Batawi & Noweir (1966)
	≤0.13	Morning period	Denver, CO, USA	March 1982	Apol (1983)
	0.03–0.18	Unspecified	Denver, CO, USA	June 1982	Pryor (1983)
	0.03–1	Unspecified	Italy	–	del Piano *et al.* (1986)
	<1.8	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Aldehydes	0.7–1.8	Air analysis	Egypt	1965	El Batawi & Noweir (1966)
	42–52	Close to exhaust	Egypt	1965	El Batawi & Noweir (1966)
Aldehydes[a] as formaldehyde	<0.3 ppm	Morning period	Denver, CO, USA	March 1982	Apol (1983)
Formaldehyde	0.04–0.8	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Acetaldehyde	0.28–1.5	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
	2.3–9.5 ppm	Unspecified	Italy	–	del Piano *et al.* (1986)

Contaminant	Concentration	Sampling	Location	Time	Reference
PAH (ng/m^3)					
Anthanthrene	0.05	1.00–5.00 h (no bus moving)	London, UK	June 1979	Waller *et al.* (1985)
	4.5	5.00–9.00 h (buses starting)	London, UK	June 1979	Waller *et al.* (1985)
Benz[*a*]anthracene	<1–50	Unspecified	Italy	–	del Piano *et al.* (1986)
Benzo[*b*]fluoranthene	<1-50	Unspecified	Italy	–	del Piano *et al.* (1986)
Benzo[*k*]fluoranthene	<1–100	Unspecified	Italy	–	del Piano *et al.* (1986)
Benzo[*ghi*]perylene	1.1	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	27.2	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)
	<1–30	Unspecified	Italy	–	del Piano *et al.* (1986)
Benzo[*a*]pyrene	0.6	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	13.0	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)
	<1–20	Unspecified	Italy	–	del Piano *et al.* (1986)
	<10	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Benzo[*e*]pyrene	1.2	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	11.6	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)
	<1–3	Unspecified	Italy	-	del Piano *et al.* (1986)
Chrysene	<1–30	Unspecified	Italy	–	del Piano *et al.* (1986)
Coronene	0.8	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	13.6	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)
Fluoranthene	2–350	Unspecified	Italy	–	del Piano *et al.* (1986)
Indeno[1,2,3-*cd*]pyrene	<1–330	Unspecified	Italy	-	del Piano *et al.* (1986)
Pyrene	2.5	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	17.5	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)
	<1–460	Unspecified	Italy	–	del Piano *et al.* (1986)
Hydrocarbons					
Benzene	≤0.2	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Toluene	≤0.2	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
Total dust	<0.01–0.82	Unspecified	Italy	–	del Piano *et al.* (1986)
	0.46	Personal, during periods of high activity	Sweden	–	Ulfvarson *et al.* (1987)
	0.13–0.55	TWA, including dust stirred up by buses	Denver, CO, USA	March 1982	Apol (1983)
	0.15–0.81	Peak morning period	Denver, CO, USA	March 1982	Apol (1983)
	0.03–0.16	Cyclohexane-soluble	Denver, CO, USA	March 1982	Apol (1983)
	0.01–0.09	Unspecified	Denver, CO, USA	June 1982	Pryor (1983)
	0.17	1.00–5.00 h	London, UK	June 1979	Waller *et al.* (1985)
	0.58	5.00–9.00 h	London, UK	June 1979	Waller *et al.* (1985)

Table 17 (contd)

Contaminant	Concentration	Sampling	Location	Time	Reference
Respirable dust	<0.01–0.73	Unspecified	Italy	–	del Piano *et al.* (1986)
	0.12–0.61	Personal, mean TWA	USA	–	Gamble *et al.* (1987a)
Metals ($\mu g/m^3$)					
Cadmium	0.3–0.5	Unspecified	Italy	–	del Piano *et al.* (1986)
Chromium	<0.1–1.2	Unspecified	Italy	–	del Piano *et al.* (1986)
Copper	<0.1–6.4	Unspecified	Italy	–	del Piano *et al.* (1986)
Iron	2.8–455	Unspecified	Italy	–	del Piano *et al.* (1986)
Lead	<0.1–4.1	Unspecified	Italy	–	del Piano *et al.* (1986)
Manganese	<0.1–4	Unspecified	Italy	–	del Piano *et al.* (1986)
Nickel	<0.1–4.5	Unspecified	Italy	–	del Piano *et al.* (1986)
Zinc	<0.1–15	Unspecified	Italy	–	del Piano *et al.* (1986)

[a] Including acetaldehyde, butyraldehyde, formaldehyde, propionaldehyde

PAH, polycyclic aromatic hydrocarbons; TWA, time-weighted average

The table includes the results of analyses of air during operations in two diesel bus garages in Egypt (El Batawi & Noweir, 1966) and measurements of airborne concentrations of diesel exhaust components in three bus repair facilities in Denver, CO, USA (Apol, 1983). In the latter study, sampling took place in March 1982 at several locations within each facility during peak dispatch and return times. A carbon monoxide level of 195 mg/m^3 was recorded in one garage early in the morning near buses with gasoline engines that were starting up. The author stated that exposure of drivers to this and higher levels for 10–15 min is possible. Pryor (1983) also conducted an industrial hygiene survey of diesel exhaust at the garage of a bus company in Denver, CO, in 1982, where buses with gasoline engines parked nearby. Area samples were taken to measure carbon monoxide, sulfur dioxide, nitrogen dioxide, total particulate matter and formaldehyde in the terminal and in package-receiving areas (Table 17). The high concentrations of carbon monoxide in the terminal dropped to the background concentration within a few minutes of bus arrival or departure. The higher levels of carbon monoxide in the reservation room and at the inlet corresponded to peak car traffic in the parking area, and dropped to a background level within 10–15 min of the end of the peak traffic.

Waller *et al.* (1985) measured pollutant levels in two diesel bus garages in London, UK, in 1979. Sampling took place close to the buses in an area of only limited worker exposure, so the data are said by the authors to present extreme upper limits only. Table 17 gives data on levels of PAHs near the door of one garage during two different periods. del Piano *et al.* (1986), reporting in an abstract, found concentrations of several air contaminants in Italian bus garages surveyed over two years, as shown in the table. Gamble *et al.* (1987a) studied 232 workers in four diesel bus garages in the USA. Mean TWA concentrations of respirable particles and nitrogen dioxide in personal samples, combined over three shifts and for all four garages, were reported (Table 17). Ulfvarson *et al.* (1987) measured personal exposures of workers in a bus garage with both large and small diesel-powered vehicles as well as gasoline-powered ones. Storage, engine warm-up, refuelling, washing and repairs were all performed at the garage. Elevated concentrations, especially of diesel exhaust, accumulated in garage bays in the morning, afternoon and evening when most of the buses were coming or going. Specific exposures in the garage as measured by personal sampling during these periods of high activity are detailed in Table 17.

(iv) *Truck drivers*

Ziskind *et al.* (1978) measured the concentrations of several gases in the cabins of heavy-duty diesel trucks under a variety of conditions. Concentrations of carbon monoxide, nitric oxide and nitrogen dioxide in the air and in the cabins were measured continuously. The maximal total concentrations in cabins measured during idling and road testing were as follows: carbon monoxide, 30 ppm (34 mg/m^3); nitric oxide, 2 ppm (2.5 mg/m^3); nitrogen dioxide, 3 ppm (6 mg/m^3). The maximal self-contamination concentrations (total cabin concentration minus ambient concentration) were: carbon monoxide, 10.5 ppm (12 mg/m^3); nitric oxide, 1.55 ppm (1.9 mg/m^3); nitrogen dioxide, 0.7 ppm (1.4 mg/m^3). The authors found a correlation between vehicle-induced concentrations of specific gases in cabins and several testing parameters, including condition of windows, type of cabin configuration and the presence of exhaust leaks and underside cabin openings.

The results of a study of truck drivers on roll-on roll-off ships by personal sampling over an entire work shift (Ulfvarson *et al.*, 1987) are given in Table 18.

Table 18. Levels of airborne contaminants measured for truck drivers on Swedish roll-on roll-off ships (mg/m³)[a]

Contaminant	Study I	Study II
Carbon monoxide	1.4–2.7	1.1–5.1
Nitrogen dioxide	0.15–1.0	0.06–2.3
Nitrous acid	0.002–0.2	Not reported
[Nitric oxide]	0.1–0.8	0.2–0.7
[Total hydrocarbons]	12–14	Not reported
Benzene	⩽0.3	Not reported
Toluene	<0.8	Not reported
Formaldehyde	⩽ 0.03	0.1–0.5
Acetaldehyde	<1.6	Not reported
Dust	0.13–0.59	0.3–1.0

[a] From Ulfvarson *et al.* (1987)

(v) *Fork-lift truck operators*

Breathing zone exposures were measured in an army ammunition depot in the USA in the winter of 1983 during the use of diesel-powered fork-lift trucks. PAHs, sulfur dioxide and carbon monoxide levels were below the detection limits [not given], while the concentration of particulate matter ranged from <0.01 to 1.3 mg/m³, that of nitrogen dioxide from 0.1 to 3.2 ppm (<0.2–6.4 mg/m³) and that of total sulfates from <10 to 32 μg/m³. Area samples taken during the same test provided the following mean values: 1.1–2.6 ppm nitrogen oxides, 1.2–3.3 ppm (1.4–3.8 mg/m³) carbon monoxide, 0.2–0.4 ppm (0.4–0.7 mg/m³) sulfur dioxide and 7.4–8.5 ppm total hydrocarbons (Ungers, 1984). In a follow-up study in the summer of 1984 (Ungers, 1985), the level of PAHs was below the detection limit (3 ng/m³), while breathing zone values during warehouse operations were in the following ranges: particles, 0.5–5.0 mg/m³; sulfate, 0.02–0.6 mg/m³; sulfite, <0.02–0.09 mg/m³; nitric oxide, 1.6–13.6 mg/m³; and nitrogen dioxide, 0.7–2.5 mg/m³.

(vi) *Fire-fighters*

Fire-fighters are frequently and repeatedly exposed to diesel engine exhaust and other combustion products (Froines *et al.*, 1987). Exposure to diesel exhaust occurs during response to an incident and in the fire station. When personal sampling was used to determine the exposures of fire-fighters in fire stations in three US cities — Boston, New York and Los Angeles — in 1985, total airborne particle levels (TWA) ranged from <0.1 to 0.48 mg/m³. The authors predicted an average total particulate exposure of roughly 0.3 mg/m³ on a typical day in Boston or New York. With an estimated 0.075 mg/m³ contributed by background and smoking, exposure would be to approximately 0.225 mg/m³ diesel exhaust particles and 0.054 mg/m³ of dichloromethane extractable material. Sampling during simulated 'worst case' exposures in Los Angeles fire stations gave an upper bound concentration of 0.748 mg/m^3 particles.

(*b*) *Workers whose predominant exhaust exposure is that from gasoline engines*

(i) *Toll-booth workers*

Ayres *et al.* (1973) evaluated exposure to engine exhaust for perions who worked in both a tunnel and in an adjacent toll plaza in New York City, USA (Table 19). The authors reported a close correlation among the concentrations of various pollutants, such that the level of carbon monoxide could be considered to be indicative of total automotive pollution levels. Following the installation of ventilation systems in toll booths, carbon monoxide levels dropped to 16–18 mg/m^3.

Table 19. Levels of air contaminants (mg/m^3, unless otherwise specified) to which toll-booth operators are exposed

Contaminant	Concentration	Sampling	Reference
Carbon monoxide	72	30-day average	Ayres *et al.* (1973)
	249	Max hourly level	Ayres *et al.* (1973)
	26 ± 13	Ambient 8-h TWA	Johnson *et al.* (1974)
	17.6–38.5	Mean in booths	Burgess *et al.* (1977)
	150	Max 8-h TWA (summer, tunnel booth)	Burgess *et al.* (1977)
Nitrogen oxides	1.38 ppm	30-day average	Ayres *et al.* (1973)
	6.13 ppm	Max hourly level	Ayres *et al.* (1973)
Nitrogen dioxide	0.14	30-day average	Ayres *et al.* (1973)
	0.64	Max hourly level	Ayres *et al.* (1973)
	0.08–0.20	Mean in booths	Burgess *et al.* (1977)
Sulfur dioxide	0.04–0.07	Mean in booths	Burgess *et al.* (1977)
Aldehydes	0.05 ppm	30-day average	Ayres *et al.* (1973)
	0.16 ppm	Max hourly level	Ayres *et al.* (1973)
Acrolein	0.007	30-day average	Ayres *et al.* (1973)
	0.03	Max hourly level	Ayres *et al.* (1973)
Total hydrocarbons	7.9 ppm	30-day average	Ayres *et al.* (1973)
	29.6 ppm	Max hourly level	Ayres *et al.* (1973)
	5.7-19.8 ppm	Mean in booths	Burgess *et al.* (1977)
Lead	30.9 μg/m^3	30-day average	Ayres *et al.* (1973)
	98.0 μg/m^3	Max hourly level	Ayres *et al.* (1973)
	27.4 (5–87) μg/m^3	Ambient 8-h TWA	Johnson *et al.* (1974)
	7.7-16 μg/m^3	Mean respirable mass fraction	Burgess *et al.* (1977)
Manganese	<1 μg/m^3	Ambient 8-h TWA	Johnson *et al.* (1974)
Total suspended particulate matter	0.04–0.75		Burgess *et al.* (1977)
	0.2 (average)		Ayres *et al.* (1973)
Respirable mass fraction	0.10 (average)		Burgess *et al.* (1977)
Respirable particles	0.1 (average)		Ayres *et al.* (1973)

A study of exposure to carbon monoxide of toll collectors on an interstate highway near Louisville, KY, USA, was reported by Johnson *et al.* (1974). Testing was conducted over a 12-day period in April 1973, and ambient concentrations of carbon monoxide, lead and manganese at three booths were determined as an overall mean 8-h TWA (Table 19). Carboxyhaemoglobin (COHb) levels in the workers were measured before and after shifts; typical pre-shift levels were 0.8–1.5%; the post-shift mean was 3.9%, with a range of 1.6–11.7%.

Burgess *et al.* (1977) evaluated the exposure of toll-booth collectors in the Boston area, at a tunnel and at two interchanges during 1972–74 (Table 19). Airborne lead levels in the work environment were roughly four times ambient urban levels; correlated increases were found in the hair and blood of the workers.

(ii) *Border-station inspectors*

Cohen *et al.* (1971) studied a group of such workers at the San Ysidro, CA, USA, station in 1969. Ambient and expired carbon monoxide levels were measured over roughly a 24-h period encompassing three shifts. Average hourly carbon monoxide levels were 15 mg/m^3 (8.00 to 16.00 h), 75 mg/m^3 (16.00 to 0.00 h) and 131 mg/m^3 (0.00 to 8.00 h); hourly levels ranged from 6 to 195 mg/m^3. Taking data from all shifts combined, nonsmoking individuals had significantly higher expired carbon monoxide levels at the end of the shift than before the shift, corresponding to COHb levels of 3.6% after the shift and 1.5% before the shift. For smokers, the estimated pre- and post-shift COHb levels, estimated from carbon monoxide in expired air, were 4.8% and 6.4%, respectively.

Environmental sampling was conducted by the National Institute for Occupational Safety and Health at a number of US border crossing facilities in 1973–74, to investigate the exposure of Federal border inspectors (Kronoveter, 1976). Inspectors are rotated between different work locations through a shift, and the facilities are operated three shifts per day, seven days per week. Mean 8-h average carbon monoxide levels ranged from 2 to 54 ppm (2.3–62 mg/m^3) with maximal 8-h average levels of 3–73 ppm (3.4–83.6 mg/m^3). Sampling for total particulate matter revealed concentrations from <1.0 to 4.3 mg/m^3. Ozone levels ranged from <0.01–0.08 ppm (<0.02–0.16 mg/m^3), and concentrations of lead ranged from <10 to 20 μg/m^3.

deBruin (1967) measured COHb levels in 13 nonsmoking Dutch customs officers stationed at four remote sites in 1965. The mean concentrations at the four locations studied ranged from 0.8 to 1.5% before work and 1.1 to 3.0% after work.

(iii) *Traffic-control officers*

deBruin (1967) measured COHb levels in nonsmoking and smoking traffic policemen in Rotterdam and Amsterdam, the Netherlands. Results are shown in Table 20. Ambient carbon monoxide levels in Rotterdam at the time of that study averaged 5–15 ppm (6–17 mg/m^3) at crossings and crowded streets, ranging up to 50 ppm (60 mg/m^3).

Göthe *et al.* (1969) measured COHb levels in 76 traffic policemen in three Swedish towns. Ambient carbon monoxide levels were not given, but in Stockholm nonsmoking officers who had controlled traffic in either the morning or afternoon rush hours had an

Table 20. Carboxyhaemoglobin (COHb) levels in traffic control officers[a]

Group	No. of subjects	% COHb (mean ± SD)	
		Before work	After work
Rotterdam			
Exposed nonsmokers (1-4-h average)	36	0.92 ± 0.07	1.11 ± 0.07
Control nonsmokers (office)	16	0.85 ± 0.13	0.83 ± 0.17
Amsterdam			
Exposed nonsmokers (4.5-h average)	10	1.43 ± 0.26	1.66 ± 0.27
Exposed smokers (4.5-h average)	14	4.62 ± 0.97	5.16 ± 0.81
Control nonsmokers (office)	9	1.45 ± 0.22	1.40 ± 0.18

[a] From deBruin (1967)

average COHb of 1.2% ± 0.39; smokers had a level of 3.5% ± 1.17. In Malmö and Örebro, the levels were 0.8% ± 0.14 and 0.6% ± 0.38 for nonsmokers and 5.0% ± 2.44 and 2.4% ± 1.10 for smokers. The authors noted that unexposed persons in Sweden have an average COHb of 0.5%.

(iv) *Professional drivers*

deBruin (1967) determined COHb levels before and after work in nonsmoking taxi, delivery van and motor hearse drivers in Amsterdam, the Netherlands, in 1965. The mean COHb levels before and after work were 2.0 and 2.15 for 13 taxi drivers exposed for 7 h; 1.5 and 1.65 for six delivery men exposed for 8 h; and 2.0 and 2.45 for four drivers of motor hearses exposed for 6.5 h. The average difference was 0.25%, which was significant ($p < 0.01$).

Maruna and Maruna (1975) investigated δ-aminolaevulinic acid elimination in the urine of 200 taxi drivers in Vienna, Austria, as a means of measuring lead burden. The authors found that 26.5% of the taxi drivers had normal levels (<5.0 mg/l urine), 27% had borderline levels (5.1–7.0 mg/l) and 46.5% had elevated levels (>7.1 mg/l). The authors concluded that the source of the lead was the atmosphere polluted by automobile engine emissions.

del Piano *et al.* (1986), reporting in an abstract, measured hydrocarbons in the breathing zone of the drivers of an Italian bus company. The concentration of aliphatic hydrocarbons ranged from below 0.01 to 51.8 ppm and that of aromatic hydrocarbons, including benzene (<0.01–9.6 ppm; <0.03–31 mg/m^3), from below 0.01 to 36.7 ppm. [The Working Group was unable to determine if these workers were exposed mainly to gasoline or to diesel exhausts.]

(v) *Ferry workers*

Purdham *et al.* (1987) studied the potential exposure of stevedores employed in ferry operations to diesel and gasoline exhaust emissions. The constituents considered were total particles, PAHs, aldehydes, nitrogen oxides, sulfur dioxide and carbon monoxide. Exposures to particles averaged 0.50 mg/m^3 (range, 0.06–1.72 mg/m^3); carbon monoxide levels were detected, in the range of 20–100 ppm (23–115 mg/m^3), only when gasoline-powered vehicles were being loaded onto the ferries. The levels of the other constituents did not differ from the background.

Ulfvarson *et al.* (1987) measured personal exposures to airborne contaminants on two types of car ferries during loading and unloading. On the first one, a 2-h route, loading and unloading of vehicles took an average of 20 min; on the second, a 20-min crossing, loading and unloading times were not specified. The results are shown in Table 21.

Table 21. Levels of airborne contaminants measured on Swedish car ferries (mg/m^3, unless otherwise specified)[a]

Contaminant	Car ferry (2-h run)[b]	Car ferry (20-min run)
Carbon monoxide	13–100	5–190
Nitrogen dioxide	<0.6	0.2–0.8
Sulfur dioxide	<1.8	Not measured
Benzene	⩽0.2	Not measured
Toluene	<0.2	Not measured
Formaldehyde	0.03–0.31	0.1–0.3
Acetaldehyde	0.49–1.5	1.02–2.1
Dust	Not measured	0.1–0.3
Benzo[*a*]pyrene (ng/m^3)	<10	⩽30

[a] From Ulfvarson *et al.* (1987)

[b] Loading and unloading of vehicles took an average of 20 min

(vi) *Exhaust system mechanics*

Chambers *et al.* (1984) measured the lead levels in airborne particles and deposited dusts in three centres for the replacement of passenger car exhaust systems. Airborne concentrations of lead collected with environmental and personal samplers ranged from 8.8 to 55.4 μg/m^3, with peak concentrations ranging from 20.2 to 92.7 μg/m^3 when floors were being swept during sampling. Dust concentrations in samples from floors and shelves ranged from 0.14 to 3.02% lead by weight. Dust in samples collected from inside exhaust systems ranged from 0.20 to 58.7% lead by weight, according to site.

(vii) *Motor vehicle inspectors*

An industrial hygiene survey of 38 motor vehicle inspection stations in New Jersey, USA, in 1973–74 indicated that inspectors were exposed to carbon monoxide at a TWA average of 10–24 ppm (11–28 mg/m^3); measurements in semi-open and enclosed stations were 11–40 ppm (13–46 mg/m^3) and those in outdoor stations, 4–21 ppm (5–24 mg/m^3). Average COHb levels in nonsmokers were 2.1% before a shift and 3.7% after a shift ($p < 0.01$) (Stern *et al.*, 1981).

(viii) *Parking garage attendants*

Ramsey (1967) determined both airborne carbon monoxide levels and blood COHb levels for 38 parking attendants in six garages in Dayton, OH, USA. These garages typically had four floors and a capacity of 300–500 cars. Hourly air sampling revealed a carbon monoxide concentration in the range of 8–275 mg/m^3, with a mean of 67.4 ± 28.5 mg/m^3 for 18 daily averages. COHb levels were determined in employees prior to and after the work day on Monday; a group of control students was also monitored. The 8:00 and 17.00 h levels were 1.5 ± 0.83 (SD) and 7.3 ± 3.46 for 14 nonsmokers; and 2.9 ± 1.88 and 9.3 ± 3.16 for 24 smokers. In controls, the levels were 0.81 ± 0.54 for ten nonsmokers and 3.9 ± 1.48 for 17 smokers. The differences between 8.00 and 17.00 h levels in garage workers, and between garage workers at 17.00 h and controls are highly significant ($p < 0.0001$).

(ix) *Lumberjacks*

Nilsson *et al.* (1987) studied the composition of exhaust emissions from two-stroke chain-saw engines run on gasoline and estimated operator exposure to chain-saw exhaust under snow-free conditions and with snow on the ground (Table 22). The presence of snow affects techniques used in cutting.

Table 22. Estimated exposure of lumberjacks using chain saws during loggng under snow-free conditions and in the winter with snow on the ground (mg/m^3)^a

Compound	Snow-free		With snow	
	Time-weighted average	Range	Time-weighted average	Range
Total hydrocarbons	15.0	7–40	19.0	3–74
Benzene	0.7	0.3–1.8	0.6	0.1–2.4
Formaldehyde	0.08	0.04–0.2	0.08	0.02–0.1
Tetramethyllead	0.0008	0.0005–0.001	0.002	0.0004–0.004
1,2-Dibromoethane	0.0008	0.0004–0.001	0.002	0.0001–0.005
PAHs	0.02	0.01–0.04	0.03	0.02–0.04
Carbon monoxide	34.0	24–44	20.0	10–23

^{a}From Nilsson *et al.* (1987)

2.2 Environmental exposure

In many studies, levels have been reported of combustion products of fossil fuels (including gasoline and diesel fuel) in ambient air. The most frequently determined combustion products have been particles, carbon monoxide, nitrogen oxides, hydrocarbons and lead. These data are difficult to use in assessing the adverse health effects of engine exhausts, for several reasons: (i) the occurrence of these combustion products in ambient air may arise from sources other than engine exhausts; (ii) primary engine emissions may undergo further reactions in the environment at variable rates; and (iii) exposed populations tend to be transient, with variable and poorly characterized exposures (for review, see Holmberg & Ahlborg, 1983). Thus, the occurrence in the environment of the components of engine exhausts has only limited relevance to this monograph and the data have not been reviewed in detail.

Environmental emissions of fossil fuel combustion products from various sources, including engine exhausts, have been estimated for the major categories of pollutants (National Air Pollution Control Administration, 1970; National Research Council, 1972a,b; Howard & Durkin, 1974; National Research Council, 1977a,b; US Environmental Protection Agency, 1979; Bradow, 1980; Cuddihy *et al.*, 1980; Morandi & Eisenbud, 1980; Cuddihy *et al.*, 1981; US Environmental Protection Agency, 1982; Cuddihy *et al.*, 1984; The Motor Vehicle Manufacturers Association of the United States, Inc. and the Engine Manufacturers Association, 1986; US Environmental Protection Agency, 1986).

On the basis of estimates made by the National Research Council (1972a,b, 1977a,b), Hinkle (1980) estimated the environmental contribution of motor vehicle emissions for four categories of air pollutants, as a percentage of total emissions from all sources (and, in parentheses, from man-made sources): carbon monoxide, 7.7% (70%); nitrogen oxides, 2.3% (51%); particles, $1 \times 10^{-6}\%$ (1.8%); and lead, 98% (98%). It has been estimated that motor vehicle emissions contribute 80% or more of the polynuclear organic matter in the air of some cities (IARC, 1983).

Other authors have placed the contribution of motor vehicle emissions to carbon monoxide and nitrogen oxides in the environment at higher levels, the principal basis for uncertainty being the global input of these oxides from natural sources. In the USA, vehicle engine exhausts were estimated to produce 83% of the carbon monoxide and 44% of the nitrogen oxides from man-made sources in 1976 (US Environmental Protection Agency, 1979, 1982). Very similar estimates were reported for carbon monoxide (86%) and nitrogen oxides (42%) in the UK in 1984, with vehicle exhausts accounting for much higher percentages (up to 85%) of nitrogen oxides at street level in urban environments (Williams, 1987).

Concentrations of a number of engine exhaust components have been measured in ambient air in urban and rural environments. Representative data for particles, hydrocarbons, lead and oxides of nitrogen are given in Table 23. Concentrations of particle-associated PAHs in ambient air have also been reported by others (Sawicki, 1976; Egan *et al.*, 1979; Edwards, 1983; Chuang & Petersen, 1985). Benzo[*a*]pyrene concentrations in the air of over 200 cities in 25 countries worldwide were summarized by Sawicki (1976).

Table 23. Measured concentrations in ambient air of selected pollutants associated with engine exhausts

Pollutant	Site	Time period	Type of engine exhaust[a]	Concentrations (μg/m³)	Reference
Particulate matter					
Suspended	London, UK: Blackwall Tunnel, daytime average	Summers, 1958 and 1959	Approximately 70% gasoline, 30% diesel	2250 (daytime)	Waller *et al.* (1961)
Total suspended	Boston, MA, USA: Sumner Tunnel	September 1961	NS	588[b]	Larsen & Konopinski (1962)
Respirable	Boston, MA: street-level traffic stations, average	Spring, 1971	NS	47	Burgess *et al.* (1973)
Total suspended	Central London, UK: top of County Hall (30 m)	1975–76	NS	Summer: 77 Winter: 108	Ball & Hume (1977)
	St Louis, MO, USA: annual average for various sectors	1977	Mixed	60–130[c]	Bradow (1980)
Inhalable	Watertown, MA, USA (suburb of Boston): high-school athletic field	1979–81	NS	Total: 25.9 (3.2)[d] Fine: 17.4 (2.5) Coarse: 8.6 (0.6)	Thurston & Spengler (1985)
Inhalable (primarily <15 μm diameter)	Camden, Elizabeth and Newark, NJ, USA	1981–83	NS	45–53[e]	Lioy & Daisey (1986)
Nitrogen dioxide	Four major US cities	1962–71	NS	Mean, 1962–66: 68 Mean, 1967–71: 72	US Environmental Protection Agency (1982)
	Boston, MA, USA: 16 street-level traffic stations	1970–71	NS	Summer: 115 (<10–570)[f] Autumn: 115 (50–340) Winter: 85 (<10–270) Spring: 105 (40–285)	Burgess *et al.* (1973)

Table 23 (contd)

Pollutant	Site	Time period	Type of engine exhaust[a]	Concentrations ($\mu g/m^3$)	Reference
Nitrogen dioxide (contd)	St Louis, MO, USA: 18 regional air monitoring sites within 20 km of the city	1976	NS	Annual 1976 means for the 18 sites: 21–62; highest hourly concentrations in 1976 for the 18 sites: 149–676	US Environmental Protection Agency (1982)
	Central London, UK: 40 locations	1985	87% gasoline, 13% diesel	'Background' sites: 54-75; weekly average values, 90–95; heavy traffic: 140 max	Laxen & Noordally (1987)
Nitrogen oxides	Several remote sites in the USA and Australia	1956-77	NS	0.1–3 ppb (background)	Data from several authors summarized by Ritter *et al.* (1979)
Lead	Berlin-Steglitz, FRG	1966–67	NS		Lahmann (1969)
	At town hall near major traffic intersection			>10	
	Low traffic areas			0.5	
	New York, NY, USA 1969–73[g] – 40 roof-top sampling stations; 1978 — 27 roof-top stations	1969–73, 1978	NS	Annual averages declined from 1.9 in 1970 to 1.1	Nathanson & Nudelman (1980) in 1978
	Boston, MA, USA: 16 street-level traffic stations	1970–71	NS	Summer: 5.4 (1.5–18)[f] Autumn: 6.9 (2.0–19.5) Winter: 6.5 (3.2–11.7) Spring: 4.5 (1.5–15.4)	Burgess *et al.* (1973)
	Central London, UK: top of County Hall (30 m)	1975–76	NS	Summer: 0.5 Winter: 1.06	Ball & Hume (1977)

Table 23 (contd)

Pollutant	Site	Time period	Type of engine exhaust[a]	Concentrations ($\mu g/m^3$)	Reference
Lead (contd)	Jeddah, Saudia Arabia: 2 road traffic areas	1985	Gasoline engine (leaded gasoline)	0.70 (low traffic) 2.38 (high traffic)	Al-Mutaz (1987)
	Riyadh, Saudi Arabia	1985	Gasoline engine (leaded gasoline)		El-Shobokshy (1985)
	Top of a one-storey building in centre of city			5.5	
	Top of a building in a new area 12 km from centre of city			2.5	
Polycyclic aromatic hydrocarbons (PAHs)					
Benzo[*a*]pyrene	Central London, UK: County Hall and St Bartholomews' Hospital	1949–73	NS	0.004–0.046	Waller (1981)
	122 urban and rural sites in the USA	1958–59	NS	Urban: 0.0001–0.061 Rural: 0.00001–0.0019	Sawicki *et al.* (1960)
	Toronto, Canada: 5 sites ranging from urban to rural	1972–73	NS	0.00011–0.00085	Pierce & Katz (1975)
	FRG industrial city	1978–79	NS	Means:	Grimmer *et al.* (1981)
	Area with mainly domestic coal heating			0.015	
	Area with mainly central oil heating			0.006	
	Tunnel with automobile traffic			0.031	
	Area around a coke plant			0.040	

Table 23 (contd)

Pollutant	Site	Time period	Type of engine exhaust[a]	Concentrations ($\mu g/m^3$)	Reference
15 PAHs	Los Angeles County, CA, USA: 13 sites	1974–75	NS	Geometric means: 0.0001–0.003 (benzo[*a*]pyrene, 0.0005)	Gordon (1976)
Cyclopenta[*cd*]pyrene	FRG industrial city	1978–79	NS	Means:	Grimmer *et al.* (1981)
	Area with mainly domestic coal heating			0.003	
	Area with mainly central oil heating			0.002	
	Tunnel with automobile traffic			0.088	
	Area around a coke plant			0.011	

[a] NS, not stated

[b] Mean concentration at outlet of tunnel ventilation system

[c] Vehicle contribution (mainly diesel) estimated to be 15% of total fine particles

[d] Numbers in parentheses, estimated contributions from motor vehicles in $\mu g/m^3$

[e] Vehicle contribution (mainly gasoline) estimated to be 5–10%

[f] Mean (minimum-maximum)

[g] 1969–73 data may be underestimated because cellulose filters were used which are less efficient than glass fibre (used in 1978).

Apportionment studies using receptor modelling methods have been used to estimate that the contribution of motor vehicle emissions to inhalable airborne particulate matter (<2.5 μm diameter) is 5–10% (Lioy & Daisey, 1986) or 15% of total fine particles (Bradow, 1980); mutagenicity was 50–74%. These studies were conducted in winter when domestic heating is the other major source of the pollutants in cities (Lewtas & Williams, 1986). Therefore, motor vehicles would be expected to make an even larger contribution to these pollutants during the rest of the year or on an annual average.

In the 1960s and early 1970s, typical average levels of lead in air in the USA ranged from 11.3 μg/m^3 or higher near busy motorways, to 1–4 μg/m^3 in the central areas of many cities, 0.1–0.5 μg/m^3 in suburban and rural areas, and as low as 0.02 μg/m^3 in remote areas (National Research Council, 1972b). These ranges appear to be typical for other industrialized nations where leaded gasoline is used in motor vehicles (Lahmann, 1969; Maziarka *et al.*, 1971; Bini, 1973; Fisher & LeRoy, 1975; Ball & Hume, 1977; El-Shoboksh y, 1985; Al-Mutaz, 1987). With the increasing use of lead-free gasoline and increasing restrictions on use of leaded gasoline, these levels are declining (Fishbein, 1976; Falk, 1977; US Environmental Protection Agency, 1986).

Motor vehicles have been identified as significant sources of ambient air concentrations of a number of specific volatile hydrocarbons, such as benzene, toluene, xylenes and acetylene (Seifert & Ullrich, 1978; Whitby & Altwicker, 1978; Häsänen *et al.*, 1981; Tsani-Bazaca *et al.*, 1981). The inventory of the Japanese Environmental Agency for total hydrocarbon emissions in 1978 indicates that 39% of hydrocarbon emissions in Japan were from mobile sources (Wadden *et al.*, 1986). In the UK, vehicle emissions were estimated to account for approximately 33% of the volatile organic compounds (mainly hydrocarbons) released to the environment in 1984 (Williams, 1987).

1,2-Dichloroethane and 1,2-dibromoethane are also present in engine exhausts, and the time-dependent concentrations of benzene and 1,2-dibromoethane near roads are reported to be closely correlated (Tsani-Bazaca *et al.*, 1981). Formaldehyde, the principal aldehyde component of engine exhausts, is generally found in ambient air at 12–18 μg/m^3, but concentrations of 107–180 μg/m^3 have been reported in heavy traffic or photochemical smog (National Research Council, 1981; Grosjean, 1982; Anon., 1984).

Limits have been set on motor vehicle emissions in many parts of the world. The Council of the European Communities (Commission of the European Communities, 1988) has, for example, adopted a phased programme for the implementation of emission standards for carbon monoxide, hydrocarbons and oxides of nitrogen from gasoline- and diesel-powered vehicles. The US Environmental Protection Agency is also proceeding with the phased implementation of standards for gasoline- and diesel-powered vehicles specifying decreasing limits for exhaust emissions of carbon monoxide, hydrocarbons, oxides of nitrogen and particles (diesel only); evaporative hydrocarbon emissions are regulated for gasoline-powered vehicles only (US Environmental Protection Agency, 1987).

2.3 Analysis

(*a*) *Sampling*

Vehicle exhaust cannot be sampled correctly at temperatures that occur in or just behind the exhaust pipe because (i) the adsorption/desorption ratio on filter materials is disadvantageous at elevated temperatures and (ii) various exhaust constituents may be converted into artefacts on the filter, depending upon conditions, such as conversion of PAHs into nitroarenes (Pitts *et al.*, 1978; Lee, F.S.-C. *et al.*, 1980; Gibson *et al.*, 1981; Schuetzle & Perez, 1983; Grimmer *et al.*, 1988). Furthermore, exhaust is a heterogeneous material consisting of a gaseous phase and a particulate phase, and different techniques have been used for their collection, which can be classified into dilution tube sampling and raw gas sampling.

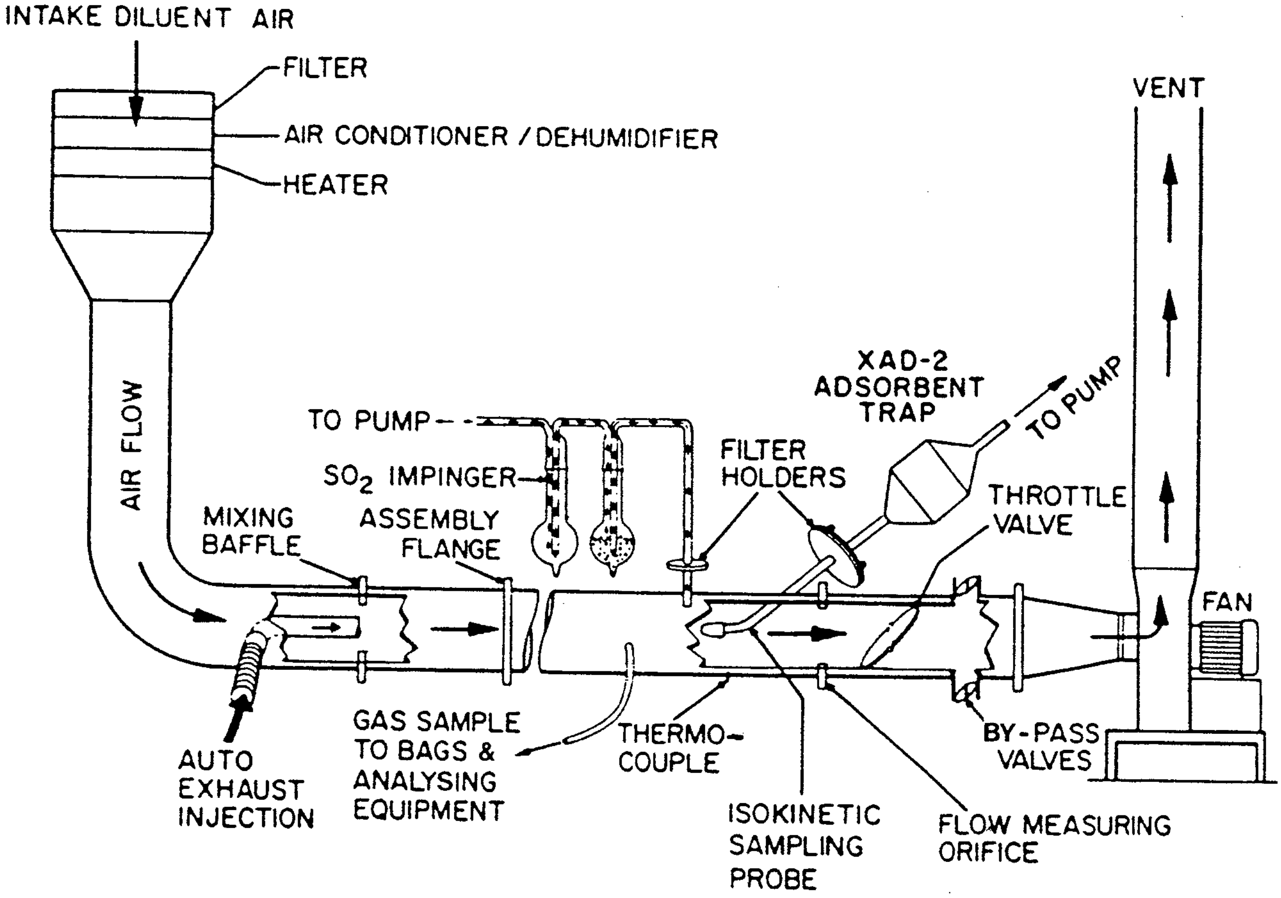
Measurements of vehicle emissions are typically made under laboratory conditions using chassis or engine dynamometer testing. Specified driving cycles are used to simulate on-road conditions. The Federal Test Procedure (FTP — also referred to as the LA-4, US-72 and the Urban Cycle; National Research Council, 1982) is the primary cycle used in the USA to approximate urban driving conditions (US Environmental Protection Agency, 1977). A similar test cycle is used in Europe (EEC Regulation 15/04; Commission of the European Communities, 1970).

Emissions collected for the purpose of chemical analysis and bioassays are typically referred to as particulate-phase emissions, gas-phase emissions and condensate emissions. 'Particulate emissions' are defined as all materials collected on a filter from a dilution tube at a dilution ratio of $\simeq$15:1 and at $\simeq$35°C (see below; Hare *et al.*, 1979). 'Gas-phase emissions' are defined as all materials which pass through a filter from the dilution tube under the conditions specified above. 'Condensate/extract' comprises: (i) material extractable by organic solvents (toluene, acetone) from particles collected on filters; (ii) residue obtained by evaporation of condensed water; and (iii) the evaporation residue after washing the condenser with organic solvents. Therefore, 'condensate extract' refers to organic compounds collected from exhaust by this procedure. In general, these compounds are less volatile than naphthalene and do not include nitrogen oxides, sulfur dioxide, C_1-C_9 hydrocarbons, benzene, most alkylbenzenes or inorganic substances such as elemental carbon and lead.

(i) *Dilution tube sampling*

Vehicle exhaust generated by driving schedules under standard conditions on a chassis dynamometer is diluted with a well-defined quantity of filtered air in a dilution tunnel, from which samples can be taken isokinetically after they have been cooled to about 50°C (Hare & Barnes, 1979). It has been shown that this device (presented schematically in Figure 3) closely simulates the process of dilution (Lee & Schuetzle, 1983; Schuetzle, 1983) under actual atmospheric conditions. The residence time of exhaust in the tunnel before being trapped on filters has been estimated to be less than 5 sec. Particles may be collected on filters, such as Teflon, or by electrostatic precipitators (Lee & Schuetzle, 1983). Hallock *et al.* (1987) recommended a liquid electrostatic aerosol precipitator which preserves

Fig. 3. Dilution tube used for monitoring and collecting gas- and particulate-phase vehicle emissions[a]



[a] From Schuetzle (1983)

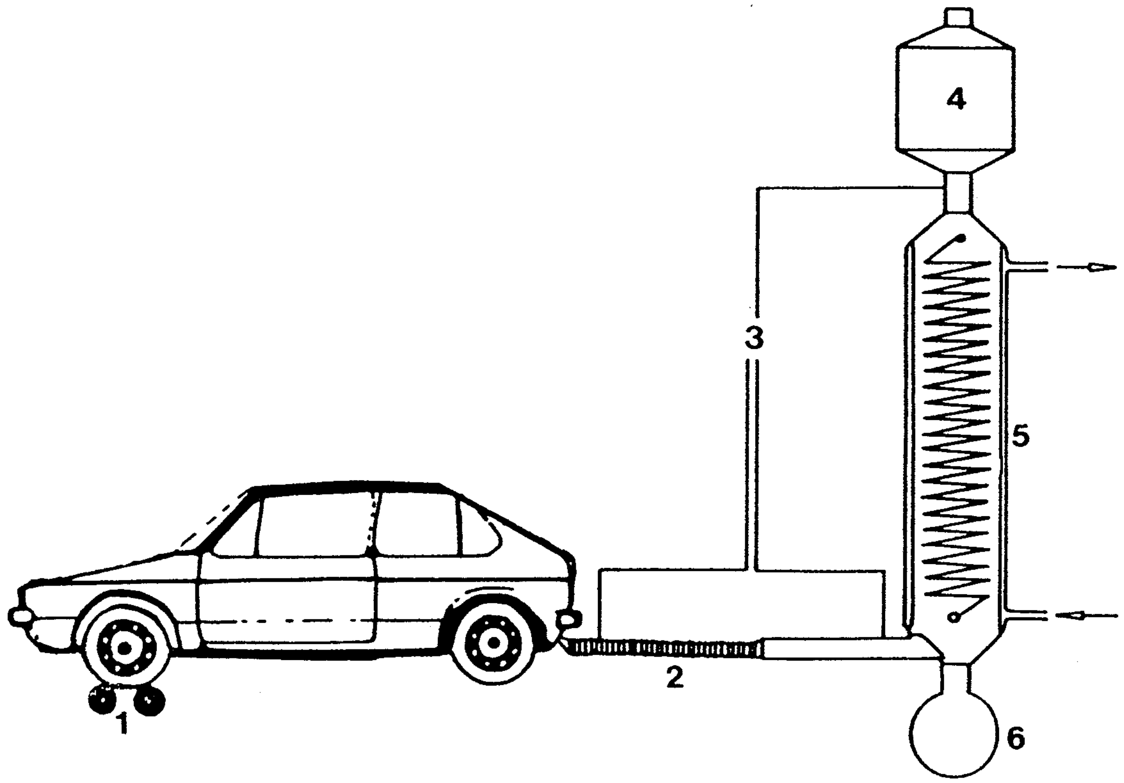
submicronic particle size. Semivolatile compounds in the gaseous phase can be trapped by adsorption filter systems containing inorganic silica or, more satisfactorily, organic materials (e.g., XAD-2, Tenax, Chromosorb 102, Porapak; Jones *et al.*, 1976; Lee *et al.*, 1979; Lee & Schuetzle, 1983; Schuetzle, 1983). Schuetzle (1983) recommended XAD-2, since this material, in contrast to Tenax, does not react with nitrogen oxides.

Gases are sampled in bags either before entering the filter system or after having passed the adsorbent trap (see Figure 3). Stenberg *et al.* (1983) described a cryogradient technique which allows the separation of NO by cooling with a liquid nitrogen condenser.

(ii) *Raw gas sampling*

In most of these devices, the exhaust is partially condensed before separation by filter combinations. Initially, steel condensers were used (Stenburg *et al.*, 1961); since that time, a collecting device consisting of a vertical glass cooler and a micron filter of impregnated glass fibre with a separation degree of over 99.9% for particle sizes of 0.3–0.5 μm has been described (Grimmer *et al.*, 1973a; Kraft & Lies, 1981; VDI-Kommision, 1987; see Figure 4).

Fig. 4. System for collecting undiluted vehicle exhaust[a]



[a]From Grimmer *et al.* (1988); 1, chassis dynamometer; 2, flexible pipe; 3, thermocouple; 4, glass-fibre filter (silicon bounded, 1 m^2); 5, glass cooler; 6, condensate

Proportional raw gas sampling, resulting in samples of more manageable size, has been described (Stenberg *et al.*, 1981; Johnson, 1988). Various filter materials, as such or in combination, have been used to separate particles and semivolatile compounds from exhausts. Quartz and glass fibre, cellulose acetate (Millipore), polyvinylidene fluoride (Duropore), polytetrafluoroethylene (Teflon, Zefluor, Fluoropore), polyvinyl chloride, polyethylene and polycarbonate (Nucleopore) can separate >99.9% of submicrometer particulates (John & Reischl, 1978; Lee, F.S.-C. *et al.*, 1980; Lee & Schuetzle, 1983). Teflon has been cited as being superior to other materials in terms of separation efficiency and chemical inertness (Lee & Schuetzle, 1983; Schuetzle, 1983).

Semivolatile compounds in the gaseous phase can be separated out using polymer materials, such as Tenax, XAD-2 and Porapak, or with Chromosorb. Purification of these materials may be time-consuming since repeated washing (or Soxhlet extraction) with various solvents is required to remove organic impurities which interfere with analysis. Trapping of the gaseous phase can be carried out as in the case of dilution tube sampling, by (i) the cryogradient technique or (ii) gas bag collection.

One of the main problems described in the literature regarding the correct sampling of exhaust is avoidance of chemical conversion of sensitive compounds (e.g., PAHs) to artefacts (e.g., ketones, quinones, phenols, halides and nitroarenes). Losses of pyrene and perylene were studied after direct injection into exhaust near the end of the exhaust pipe, with recoveries of only 20–60% by gas chromatography and high-performance liquid chromatography (Lee *et al.*, 1979). Schuetzle (1983) found that more than 90% of pyrene and benzo[*a*]pyrene was lost through oxidation under the same conditions.

PAHs can react with nitrogen oxides, ozone or sulfuric acid under sampling conditions. Photooxidation during sample analysis may result in the formation of endoperoxides which then undergo rearrangement to yield hydroquinones and subsequently quinones, or in the formation of exoperoxides which yield ketones (Schuetzle, 1983). In the presence of nitric acid, nitrogen dioxide reacts with PAHs to yield nitroarenes (Pitts *et al.*, 1978; Brorström *et al.*, 1983). On the assumption that nitroarene formation is acid-catalysed, diesel exhaust was collected with and without injection of ammonia during sampling; significantly higher amounts of 1-nitropyrene were found without ammonia injection at a sampling temperature of 100°C. When passed through an exhaust-loaded filter, the particle-free gaseous phase enhanced the concentration of 1-nitropyrene. No such effect was observed when collecting filters were maintained at below 35°C (Grimmer *et al.*, 1988).

The artificial formation of nitroarenes during sampling procedures is still a matter of controversy (Gaddo *et al.*, 1984) and has been critically reviewed (Lee & Schuetzle, 1983).

It should be noted that the invariance of the PAH profile over the collection period is the essential precondition for correct sampling, since certain individual compounds are more sensitive to chemical reactions and/or evaporation effects.

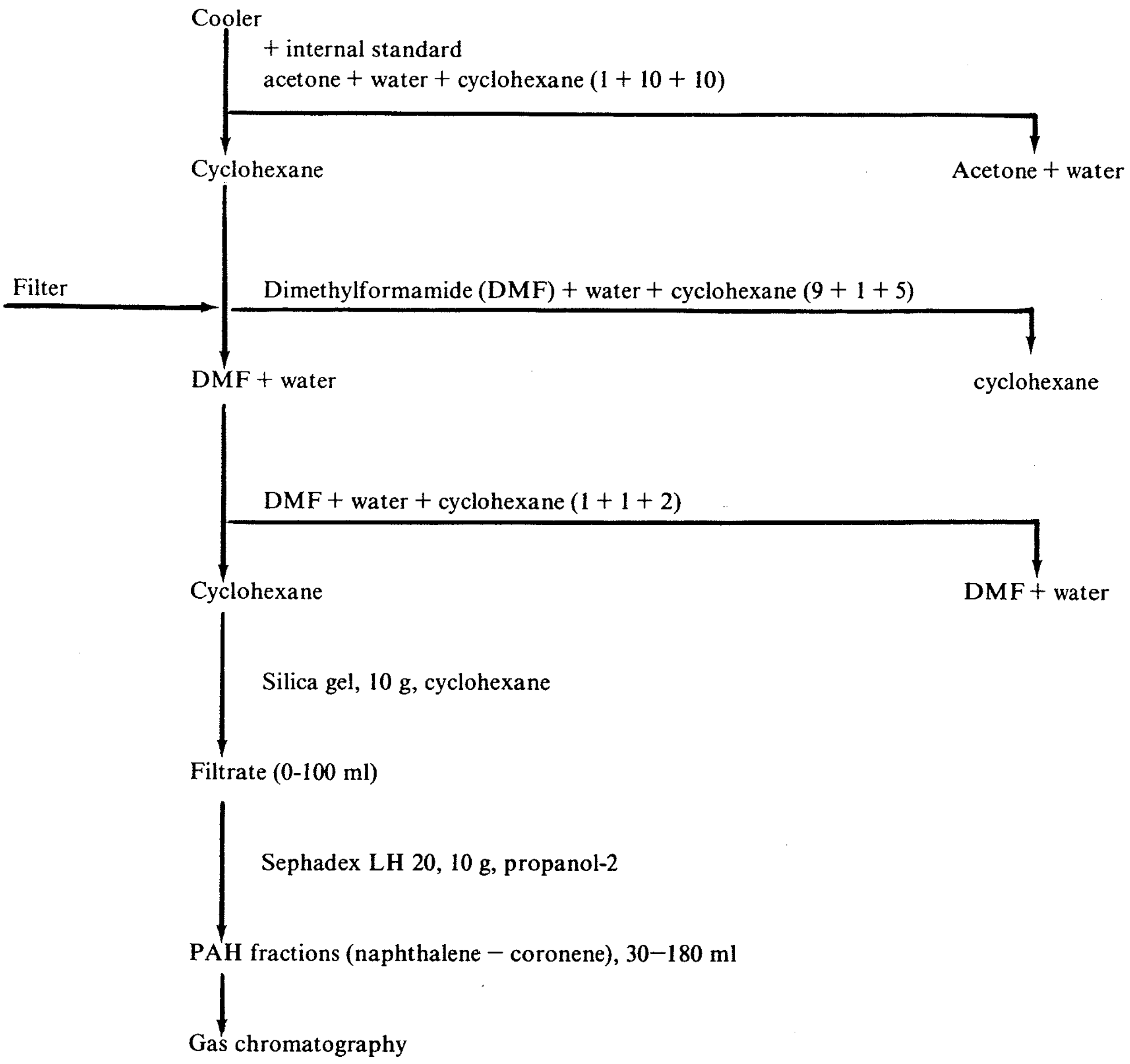
(*b*) *Extraction*

Extraction of organic material from exhaust collected on filters is often incomplete owing to an inadequate choice of solvent or extraction time (Köhler & Eichhoff, 1967; Stanley *et al.*, 1967; for reviews see Jacob & Grimmer, 1979; Griest & Caton, 1983; Lee & Schuetzle, 1983). The recommended extraction procedure is on a Soxhlet apparatus or hot-solvent extraction with toluene, benzene, xylene (Köhler & Eichhoff, 1967; Grimmer *et al.*, 1982), benzene/ethanol (methanol, propanol; Swarin & Williams, 1980), dichloromethane/methanol (Schuetzle *et al.*, 1985), toluene/ethanol (Schuetzle & Perez, 1981) or toluene/2-propanol (Lee & Schuetzle, 1983). Under these conditions, not only PAHs but also their more polar derivatives exhibit optimal extractability. This method also obviates the artefact formation that can occur with chloroform, dimethyl sulfoxide and other solvents used for extraction. In addition, Soxhlet solvent extraction results in higher recoveries of various PAHs than with cold ultrasonic extraction. If not analysed immediately after collection, the extract should be stored under nitrogen in the dark at 0°C or below.

(*c*) *Clean-up and fractionation*

After extraction, a small amount of organic material is obtained in a large volume of solvent. In order not to lose low-boiling constituents, the solution must be evaporated carefully. Vacuum rotatory evaporators with vacuum controller or specially designed devices are recommended (Dünges, 1979).

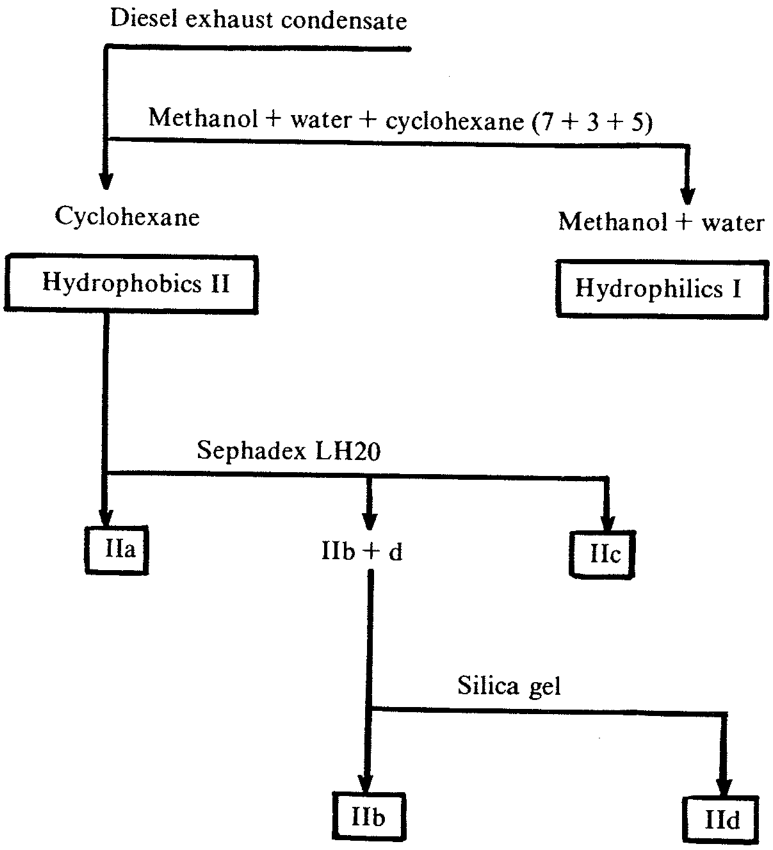
Fig. 5. One scheme for fractionating automotive exhaust[a]



[a] From Grimmer *et al.* (1977)

A fractionation scheme for vehicle exhaust combining condensed water, cooler washing (acetone) and filter extract (see Figure 5) has been described, which is based on liquid/liquid partition and chromatography on silica gel and Sephadex LH 20 (Grimmer & Böhnke, 1972; Grimmer *et al.*, 1973b, 1977; Lee & Schuetzle, 1983). An additional fractionation step using Sephadex LH 20 partition chromatography may be used. This method has also been used to characterize biologically active fractions; in some cases, the silica gel chromatography step has been deleted (Brune *et al.*, 1978; Grimmer *et al.*, 1984, 1987). A fractionation scheme for the preparation of biologically active fractions from diesel exhaust is given in Figure 6; nitroarenes are also separated by this method. A more complex fractionation

Fig. 6. One scheme for fractionating diesel exhaust condensate[a]

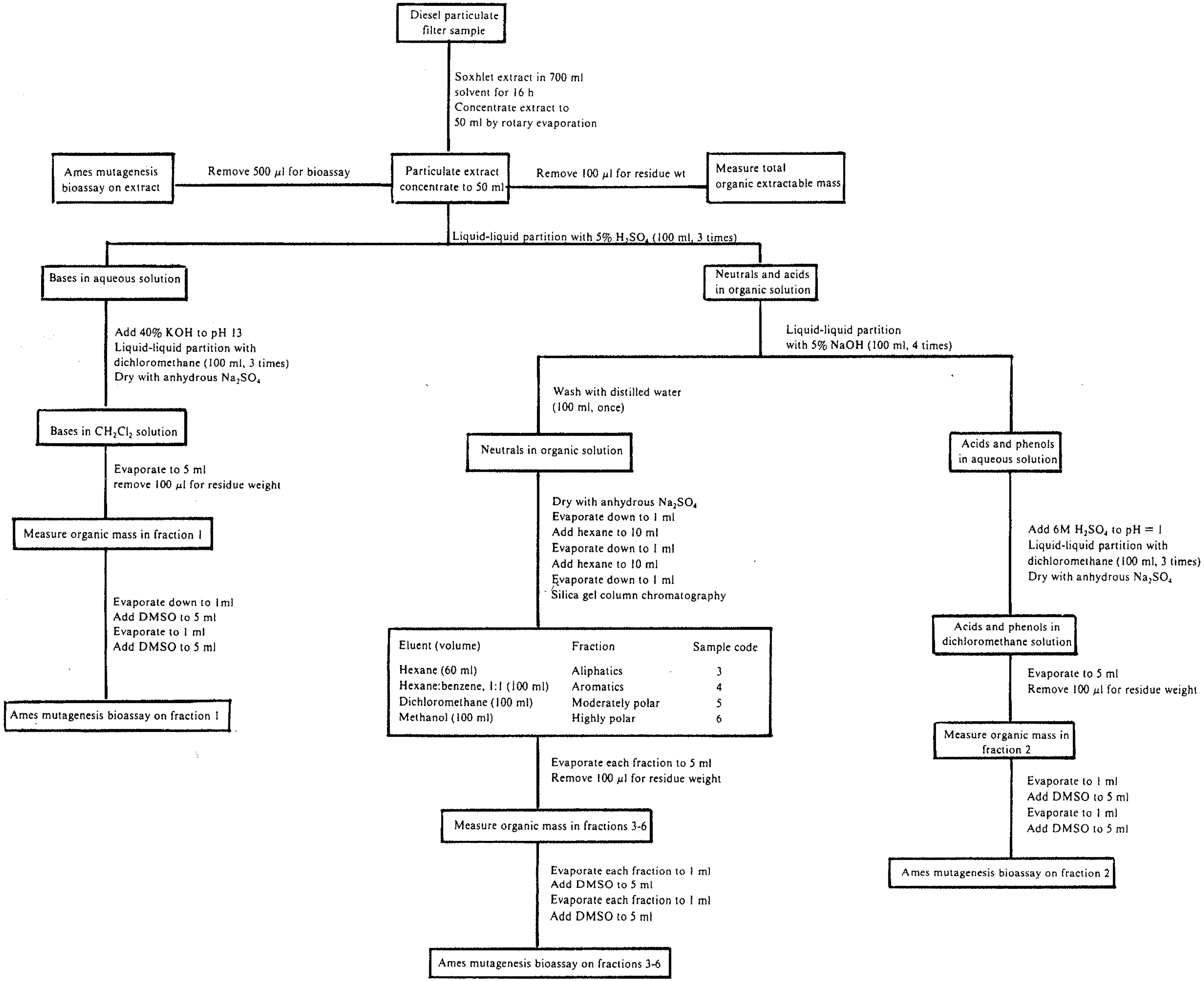


[a] From Grimmer *et al.* (1987); I, hydrophilic fraction; II, hydrophobic fraction; IIa, nonaromatic compounds and two- and three-ring polycyclic aromatic compounds (PAC); IIb, four- to seven-ring PACs; IIc, polar PACs; IId, nitro-polycyclic aromatic hydrocarbons (PAH)

scheme (Figure 7) can be used to separate the original exhaust extract into aliphatic compounds, aromatic compounds and moderately and highly-polar fractions after the removal of acidic and basic fractions (Petersen & Chuang, 1982). A similar scheme was used by Lee and Schuetzle (1983; see Fig. 1).

Methods for the separation and identification of nitroarenes are given in the monograph on 1-nitropyrene. Organic halides, such as methyl bromide, chloroform, carbon tetrachloride, trichloroethane, tetrachloroethane and various brominated PAHs, have also been analysed in the exhaust of gasoline- and diesel-fueled vehicles (Harsch & Rasmussen, 1977; Alsberg *et al.*, 1985).

Fig. 7. One scheme for extraction and fractionation of organic material in diesel particulate[a]



[a] From Petersen & Chuang (1982); DMSO, dimethyl sulfoxide

(*d*) *Chemical analysis*

In order to separate further the various fractions obtained by clean-up methods and to characterize and/or identify individual compounds simultaneously, thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC) and gas chromatography (GC) have been used in combination with ultra-violet, visible and fluorescence spectrophotometry, mass spectrometry (MS) and more or less specific detection methods, such as flame ionization, nitrogen flame ionization and sulfur-specific and electron-capture detectors (Kunte, 1979; Lee & Schuetzle, 1983; Nielsen, 1983; White, 1985).

(i) *Thin-layer chromatography (TLC)*

Two-dimensional cellulose TLC with fluorescence detection is the recommended TLC method for PAH fractions from vehicle exhaust and has given results in good agreement with those obtained by GC (Kraft & Lies, 1981). A simple TLC screening method for the determination of benzo[*a*]pyrene, which is also applicable to vehicle exhaust, has recently been recommended by the International Union of Pure and Applied Chemistry (Grimmer & Jacob, 1987). The use of TLC for the analysis of PAHs has been reviewed (Daisey, 1983).

(ii) *High-performance liquid chromatography (HPLC)*

The basic advantages and disadvantages of HPLC in comparison to other techniques such as GC have been reviewed (Wise *et al.*, 1980; Wise, 1983). The method has been widely used for the detection and identification of organic constituents of vehicle exhaust, and results of determinations of PAHs in automotive exhaust condensate using HPLC have been compared with those obtained using capillary GC (Doran & McTaggart, 1974). A comparative study of different HPLC methods for the analysis of PAHs in diesel emissions has been carried out (Eisenberg & Cunningham, 1984). Using HPLC/GC-MS, 74 polycyclic aromatic compounds were identified or tentatively identified in diesel particulate extracts (Tong & Karasek, 1984). A normal-phase HPLC method using silica gel columns and *n*-hexane:benzene (3:1) as eluent has been developed to isolate PAHs and their nitro derivatives (Nielsen, 1983). A very precise, routine, on-line reverse-phase HPLC/fluorescence method has been reported for the analysis of nitroarenes in the picogram range by their reduction to highly fluorescent amines (Tejada *et al.*, 1983). A 'pyrenebutyric acid amide phase' has been applied to a multidimensional HPLC method with on-line peak identification by ultra-violet-visible spectrometry, which allows the detection of 1-nitropyrene in the range of 3–100 ng per mg of soot collected on a filter (Lindner *et al.*, 1985). HPLC has been used to compare the concentrations of some PAHs and their nitro derivatives in exhausts from four diesel cars (Gibson *et al.*, 1981). A semipreparative HPLC analysis of a soluble organic fraction of diesel engine exhaust particulates has been reported, together with unsatisfactory results using HPLC/MS coupling (Levine *et al.*, 1982).

(iii) *Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS)*

GC methods for the determination of PAHs from exhaust condensates have been reviewed (Olufsen & Björseth, 1983), as have GC and GC/MS analyses of nitroarenes (White, 1985). Collaborative studies have been carried out to analyse PAHs in vehicle exhaust (Janssen, 1976; Metz *et al.*, 1984) in which GC methods were compared with those of HPLC (Metz *et al.*, 1984).

Packed-column GC has been largely replaced by high-resolution glass capillary column GC using fused silica columns and careful sample injection procedures (on-column injection at low temperatures of 50–80°C or thermal desorption cold trap injection procedure). Detection limits down to the picogram level have been reached with GC when single-ion monitoring mass spectrometry is used as the detection system (Ramdahl & Urdal, 1982).

Various classes of organic compounds from vehicle exhausts have been analysed by GC and GC/MS, including paraffins, olefins, PAHs, thia-arenes, aza-arenes, oxo-arenes and aldehyde, phenol, quinone and nitro derivatives of PAHs and their acid anhydrides (Hites *et al.*, 1981; Schuetzle *et al.*, 1981; Lee & Schuetzle, 1983; Alsberg *et al.*, 1984; Ramdahl, 1984; White, 1985). More than 70 individual nitroarenes were found in diesel particulate extracts by means of fused-silica capillary column GC and a nitrogen-specific detector, with detection limits of 0.2–0.5 mg/kg (Paputa-Peck *et al.*, 1983). The emission of PAHs and nitroarenes by diesel engines from PAH-containing and other well defined fuels (hexadecane) were studied using GC/MS and tandem triple-quadrupole MS (Fulford *et al.*, 1982; Henderson *et al.*, 1983, 1984).

The rapid analysis of gaseous and other combustion-related compounds in hot gas streams by atmospheric-pressure chemical ionization/MS has been reported (Sakuma *et al.*, 1981).

(iv) *Other methods*

Photometric, infra-red, colorimetric, electrochemical and chemiluminescence techniques have been used for the analysis of gases such as sulfur dioxide, carbon monoxide, carbon dioxide, nitrogen oxides and formaldehyde (Hare & Baines, 1979; Deutsche Forschungsgemeinschaft, 1985). Test tubes in which various colour reactions are seen are available for the analysis of various constituents of vehicle exhaust such as carbon monoxide, carbon dioxide, sulfur dioxide and nitrogen dioxide (Leichnitz, 1986).