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Polycyclic aromatic hydrocarbons in the work atmosphere

II. Determination in a coke plant

by ALF BJØRSETH,¹ OLAV BJØRSETH² and PER E. FJELDSTAD³

BJØRSETH, A., BJØRSETH, O. and FJELDSTAD, P. E. Polycyclic aromatic hydrocarbons in the work atmosphere: II. Determination in a coke plant. *Scand. j. work environ. & health* 4 (1978) 224—236. The content of polycyclic aromatic hydrocarbons (PAH) in the work atmosphere of a coke plant was investigated on two occasions. Stationary, mobile, and personal sampling were used, and the samples were analyzed by glass capillary gas chromatography. Up to 39 PAH and heterocyclic compounds were identified in the samples. By personal sampling, the occupational exposure to PAH was determined to vary between 5 and 1,000 mg/m³. A study of the occurrence of PAH on particulate matter revealed that 98 % of the PAH was respirable. No significant variation in the relative distribution of the PAH components (PAH profile) was observed during the two sampling periods. The PAH profile for the coke plant was similar to that of a Söderberg aluminum plant, but different from that of a Söderberg paste plant.

Key words: analysis, benzo(a)pyrene, coke plant, determination, particle size distribution, polycyclic aromatic hydrocarbons, work atmosphere.

Occupational exposure to polycyclic aromatic hydrocarbons (PAH) is found in a number of industrial atmospheres. In particular this concerns work operations connected with tar, pitch or asphalt handling and production, coke oven operations, and petroleum distilling (13). In addition there might be occupational exposure to PAH in electrochemical industries such as aluminum smelters and fer-

roalloy plants. Of particular interest is the production of coke. Workers on coke oven batteries are exposed to coal tar pitch volatiles containing a large number of PAH, some of which are known to be carcinogenic (17). Lloyd (11) reported a 2.5-fold increase of respiratory cancer among coke oven employees and a 10-fold increase in lung cancer for battery top workers who had been employed five or more years. Exposure to coal tar pitch volatiles was thought to cause this increase. It is also generally accepted that exposure to soots, tars, and oils may cause occupational cancer (10). The mere presence of PAH in the work atmosphere must be regarded as a potential occupational hazard (5).

Several studies of PAH and coal tar pitch volatiles in and around coke manu-

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facturing facilities have been reported. These studies include both gravimetric determination of the benzene soluble fraction of air filter samples and analysis of one or a few components by gas, liquid or thin layer chromatography. A combined gas chromatographic/ultraviolet spectroscopic method for the determination of PAH in coke oven effluents has also been proposed (18). The benzene soluble method has been shown to be inaccurate (19) and does not correlate well with the analytical determination of PAH (17). Furthermore, most of the analytical techniques suffer from low resolution and incomplete separation efficiency for a complete characterization of PAH in the samples.

In connection with a research program on the determination of PAH in work atmospheres we have previously reported on a method utilizing glass capillary gas chromatography for analyzing PAH (1). Furthermore, the PAH content of airborne particulate pollutants in a Söderberg paste plant (4) and in an aluminum reduction plant (3) have been reported. In this paper we present the results of two investigations of the PAH content in the work atmosphere of a Norwegian coke plant. The sampling was carried out with six-month intervals (spring and fall 1976) so that the variation in the PAH concentrations with time could be studied and any effect of a reconstruction of the coke plant could be ascertained. The distribution of PAH as a function of particle size was also studied.

MATERIALS AND METHODS

Sampling

Stationary, mobile, and personal sampling were used in this work. Stationary sampling gave larger amounts of particulate and volatile matter and therefore made possible a more complete characterization of the PAH in the work atmosphere,

while personal sampling gave a better estimate of the occupational exposure to the individual worker. The methods for sampling and determining PAH have been described previously (3) and therefore are only be briefly outlined in this report.

Stationary sampling. In the stationary sampling air was pulled through an Acropore filter (AN-800) and through two subsequent absorption bottles with ethanol cooled with dry ice. The air then passed a gas tight pump and a dry gas meter, where the air volume was registered. The equipment had a capacity of approximately 1 m³/h.

The samples were collected on the top of the coke oven batteries approximately 0.3–0.5 m above the floor in an area frequently occupied by the operators. Four stationary units were used simultaneously, and a total of 13 samples were taken in the spring and 10 samples in the fall of 1976. A typical sampling time was 1 h.

Mobile sampling. The equipment used for mobile sampling was similar to that for stationary sampling, except for smaller absorption bottles and portable pumps. The air volume in this case was about 2 l/min. The air volume was determined by use of a rotameter prior to and after the sampling and by registration of the sampling time. The sampling took place,

Table 1. Chromatographic conditions.

Variable	Condition
Carrier gas	H ₂ (0.8 kg/cm ²)
Column	50 m · 0.38 mm inner diameter, coated with SE 54 ^a
Injector temperature	275°C
Detector temperature	275°C
Temperature programming	100°C (held for 3 min) linearly programed with 3°/min to 250°C (held for 30 min)
Hydrogen (FID)	0.6 kg/cm ²
Oxygen (FID)	1.0 kg/cm ²

^a Purchased from H. and G. Jaeggi, 9043 Trogen, Switzerland.

Table 2. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, stationary sampling at the battery top, spring 1976. ($\mu\text{g}/\text{m}^3$)

PAH	Mean ^a		Range ^b	
	Particulate	Gaseous	Particulate	Gaseous
Naphtalene	1.2	653	0— 4.4	300—1,002
2-Methylnaphtalene	0.7	109	0— 3.0	61— 184
1-Methylnaphtalene	c	c	0— 0.08	0— 60
Biphenyl	c	c	0— 0.39	0— 23
Acenaphthylene	9.6	c	0— 30	0— 197
Acenaphthene	45	40	0— 17	13— 104
Dibenzofuran	20	41	4.0— 60	26— 56
Fluorene	26	58	14— 58	44— 90
9-Methylfluorene	24	6.3	0— 70	3.0— 11
2-Methylfluorene	8.2	5.7	4.6— 20	2.0— 8.6
1-Methylfluorene	15	0.5	0.7— 2.0	0— 10
Dipenzothiophene	41	2.9	15— 76	1.2— 49
Phenanthrene	420	35	164— 891	6.7— 67
Anthracene	133	12	52— 314	6.4— 15
Carbazole	7.4	3.8	3.0— 12	0— 11
Methylphenanthrene/ methylantracene ^d	63	7.5	30— 134	9— 30
Fluoranthene	282	c	153— 427	0— 3.0
Dihydrobenzo (a & b) fluorene	45	c	20— 115	0— 2.0
Pyrene	208	0.5	114— 319	0— 1.5
Benzo (a) fluorene	56	—	36— 90	—
Benzo (b) fluorene	30	—	15— 61	—
1-Methylpyrene	96	—	0— 24	—
Benzo (c) phanthrene	19	—	6.3— 49	—
Benz (a) anthracene	49	—	5.4— 156	—
Crysene/triphenylene	76	—	27— 189	—
Benzo (b, j & k) fluoranthene	40	—	13— 103	—
Benzo (e) pyrene	32	—	15— 73	—
Benzo (a) pyrene	55	—	24— 135	—
Perylene	11	—	5.8— 19	—
o-Phenylene-pyrene	25	—	9.8— 53	—
Bengo (ghi) perylene	15	—	8.7— 23	—
Anthanthrene	14	—	6.4— 33	—
Dibenzo (a, 1) pyrene	11	—	0— 21	—
Coronene	16	—	6.7— 24	—
Total PAH	1,733	1,072	817—3,423	560—1,499

^a Mean particle concentration 10.2 mg/m^3 .

^b Particle concentration range 5.7—20.8 mg/m^3 .

^c Less than three values observed; no mean value calculated.

^d The isomer not determined.

in the cabin of the larry car and on the catwalk outside the cabin. The equipment was also carried around on the battery top in a small backpack. Typical sampling time for this equipment was 4 h, approximately 0.5 m^3 of air being sampled.

Personal sampling. Personal sampling was performed by a Casella pump pulling air from the worker's breathing zone

through a 37 mm $\varnothing$ Acropore AN-800 filter. The pumping rate was about 2 l/min, and the air volume was determined as for the mobile sampling equipment.

Workers with different job types carried the sampling equipment for about 5 h. A total of 20 samples from 3 d in the spring and 10 samples from 1 d in the fall were collected.

Weather conditions

Weather conditions may influence the work conditions on the battery top. During the spring sampling there was a slight breeze from the west. During the fall sampling the wind was stronger from the southeast. The conditions on the coke batteries were therefore different for the

two samplings. However, such weather conditions are often found, and the results may therefore be regarded as typical.

Particle size distribution

A Lundgren impactor was used (12) for the determination of particle size distribu-

Table 3. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, stationary sampling at the battery top, fall 1976. ($\mu\text{g}/\text{m}^3$)

PAH	Mean ^a		Range ^b	
	Particulates	Gaseous	Particulates	Gaseous
Naphtalene	—	646	—	278—1,151
2-Methylnaphtalene	—	104	—	43— 186
1-Methylnaphtalene	—	50	—	20— 86
Biphenyl	—	21	—	8.2— 34
Acenaphtylene	c	131	0— 2.2	63— 251
Acenaphtene	—	13	—	6.0— 24
Dibenzofuran	c	49	0— 1.6	19— 81
Fluorene	4.7	54	0— 15	23— 125
9-Methylfluorene	—	218	—	0.7—1,231
2-Methylfluorene	—	5.4	—	2.6— 10
1-Methylfluorene	—	2.1	—	0.8— 4.4
Dibenzothiophene	4.6	11	0— 13	5.2— 22
Phenanthrene	92	119	27— 217	55— 276
Anthracene	33	31	9.6— 73	6.0— 91
Carbazole	8.8	—	3.1— 19	—
2-Methylanthracene	11	4.7	2.8— 23	< 0.7— 16
1-Methylphenanthrene	10	2.3	2.7— 21	0— 7.0
9-Methylanthracene	9.6	4.2	3.2— 17	0.8— 16
Fluoranthene	135	9.5	45— 258	1.1— 24
Dihydrobenzo (a & b) fluorene	32	0.7	9.2— 68	0— 2.8
Pyrene	104	4.9	35— 200	0— 14
Benzo (a) fluorene	33	1.4	9.7— 64	0— 6.8
Benzo (b) fluorene	13	c	3.1— 26	0— 0.3
4-Methylpyrene	c	—	0— 3	—
1-Methylpyrene	7.0	c	2.5— 17	0— 0.2
Benzo (c) phenanthrene	6.6	—	2.6— 13	—
Benz (a) anthracene	60	0.8	23— 112	< 0.4— 1.6
Crysene/triphenylene	67	0.9	26— 124	0— 1.8
Benzo (b) fluoranthene	24	c	5.5— 67	0— 0.7
Benzo (j & k) fluoranthene	c	c	0— 35	0— 0.7
Benzo (e) pyrene	18	0.4	8— 36	0— 0.2
Benzo (a) pyrene	37	0.9	14— 69	0— 1.5
Perylene	8.2	c	3.3— 16	0— 0.1
o-Phenylenepyrene	23	c	6.3— 74	0— 1.2
Benzo (ghi) perylene	25	—	11— 45	—
Anthanthrene	15	—	2.6— 62	—
Dibenzo (a, l) pyrene	9.0	—	3.6— 14	—
Coronene	5.3	—	1.0— 19	—
Total PAH	1,002	1,694	270—2,423	645—3,670

^a Mean particulate concentration $6.4 \text{ mg}/\text{m}^3$.

^b Particulate concentration range $3.0\text{--}12.5 \text{ mg}/\text{m}^3$.

^c Less than three values observed; no mean value calculated.

Fig. 1. Gas chromatogram of polycyclic aromatic hydrocarbons in absorption bottles. The peak identities are (1) naphthalene, (2) 2-methylnaphthalene, (3) 1-methylnaphthalene, (4) biphenyl, (5) acenaphthylene, (6) acenaphthene, (7) dibenzofurane, (8) fluorene, (9) 9-methylfluorene, (10) 2-methylfluorene, (11) 1-methylfluorene, (12) dibenzothiophene, (13) phenanthrene, (14) anthracene, (15) carbazole, and (16) 2-methylantracene.

Fig. 2. Gas chromatogram of particulate polycyclic aromatic hydrocarbons. The peak identities are (13) phenanthrene, (14) anthracene, (15) carbazole, (16) 2-methylantracene, (17) 1-methylphenanthrene, (18) 9-methylantracene, (19) fluoranthene, (20) dihydrobenzo (a & b) fluorene, (21) pyrene, (22) benzo (a) fluorene, (23) benzo (b) fluorene, (24) 4-methylpyrene, (25) 1-methylpyrene, (26) benzo (c) phenanthrene, (27) benzo (a) anthracene, (28) chrysene/triphenylene, (29) benzo (b) fluoranthene, (30) benzo (k)-fluoranthene, (31) benzo (e) pyrene, (32) benzo (a) pyrene, (33) perylene, (34) o-phenylene-pyrene, (35) benzo (ghi) perylene, (36) anthanthrene, (37) 1,2-3,4 dibenzpyrene, and (38) coronene.

Table 4. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, mobile sampling, spring 1976.

PAH	Sampling site							
	Battery top ^a		Battery top ^b		Battery top ^c		Battery top ^d	
	Particu- lates	Gaseous	Particu- lates	Gaseous	Particu- lates	Gaseous	Particu- lates	Gaseous
Naphtalene	—	203.22	—	11.35	—	1,119.37	—	192.71
2-Methylnaphtalene	—	14.23	—	1.66	—	64.72	—	23.97
1-Methylnaphtalene	—	—	—	—	—	—	—	—
Biphenyl	—	—	—	—	—	—	—	—
Acenaphthylene	—	—	—	—	—	—	—	—
Acenaphthene	—	3.38	—	0.98	—	11.52	—	6.15
Dibenzofuran	—	0.55	—	1.45	—	20.57	—	6.70
Fluorene	—	2.91	—	1.41	—	18.57	—	5.79
9-Methylfluorene	—	—	—	—	—	—	—	1.06
2-Methylfluorene	—	—	—	—	—	—	—	0.62
1-Methylfluorene	—	—	—	—	—	—	—	0.59
Dibenzothiophene	—	—	—	—	—	—	—	6.93
Phenanthrene	—	—	1.32	3.95	13.98	—	3.55	6.16
Anthracene	—	—	0.92	—	13.92	—	1.59	—
Carbazole	—	—	—	—	0.94	2.97	—	—
Methylanthracene/ methylphenan- threne ^e	—	—	1.59	—	12.97	—	3.65	—
Fluoranthene	21.70	—	14.01	—	120.67	—	30.40	—
Dihydrobenzo (a & b) fluorene	3.89	—	2.64	—	32.51	—	6.87	—
Pyrene	18.84	—	12.51	—	123.87	—	31.20	—
Benzo (a) fluorene	10.59	—	6.01	—	53.25	—	13.33	—
Benzo (b) fluorene	10.02	—	5.59	—	52.93	—	11.01	—
1-Methylpyrene	2.66	—	1.70	—	9.65	—	3.61	—
Benzo (c) phenanthrene	4.79	—	2.84	—	13.81	10.76	3.08	—
Benzo (a) anthracene	17.69	—	7.28	—	47.70	—	12.35	—
Chrysene/ triphenylene	24.11	—	10.19	—	62.09	—	16.81	—
Benzo (b, j & k) fluoranthene	11.04	—	5.58	—	28.72	—	9.40	—
Benzo (e) pyrene	9.86	0.84	4.53	—	29.77	—	7.50	—
Benzo (a) pyrene	14.55	1.28	8.00	—	57.14	—	11.44	—
Perylene	2.97	1.45	1.86	—	13.64	—	3.34	—
o-Phenylenepyrene	8.23	—	4.28	—	30.64	—	6.08	—
Benzo (ghi) perylene	4.78	—	2.32	—	18.77	—	3.75	—
Anthanthrene	5.94	—	2.33	—	17.96	—	3.13	—
Dibenzopyrene ^d	6.86	—	6.01	—	9.56	—	9.30	—
Coronene	8.30	—	4.31	—	23.74	—	5.69	—
Total PAH	186.81	227.86	105.82	20.80	788.23	1,248.48	197.08	250.68

^a Carried by one person for 4 h; particle concentration 4.81 mg/m³.

^b Outside larry car; particle concentration 4.0 mg/m³.

^c In the larry car cabin; particle concentration 11.87 mg/m³.

^d Particle concentration 11.70 mg/m³.

^e The isomer not determined.

tion. The impactor had the following particle size range: > 16 μ m, 16–7 μ m, 7–3 μ m, 3–0.9 μ m, and > 0.9 μ m. The four largest fractions of particles were

collected on drums, while the smallest particles were collected on a membrane filter.

Table 5. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, mobile sampling, fall 1976.

PAH	Sampling site			
	Battery top ^a		Battery top ^b	
	Particulates	Gaseous	Particulates	Gaseous
Naphtalene	—	294.46	—	459.91
2-Methylnaphtalene	—	41.03	—	126.34
1-Methylnaphtalene	—	20.78	—	68.35
Biphenyl	—	7.62	—	17.93
Acenaphtylene	—	47.55	—	113.14
Acenaphtene	—	10.86	—	25.19
Dibenzofuran	—	17.33	—	35.24
Fluorene	—	24.92	—	37.14
Dibenzothiophene	0.77	5.35	4.07	8.43
Phenanthrene	11.24	71.39	59.40	71.82
Anthracene	1.76	16.85	25.83	18.66
Carbazole	1.89	—	4.22	0.46
2-Methylanthracene	0.76	—	9.12	—
1-Methylphenanthrene	1.15	1.00	7.54	1.02
Fluoranthene	32.38	7.60	71.29	1.62
Dihydrobenzo (a & b) fluorene	3.25	—	16.30	—
Pyrene	24.87	3.98	51.56	0.77
Benzo (a) fluorene	6.40	—	21.10	—
Benzo (b) fluorene	0.92	—	28.27	—
4-Methylpyrene	0.68	—	—	—
1-Methylpyrene	1.27	—	5.81	—
Benzo (c) phenanthrene	5.47	—	5.21	0.38
Benzo (a) anthracene	11.32	—	31.09	—
Chrysene/triphenylene	14.49	—	35.55	—
Benzo (b, j & k) fluoranthene	4.70	—	7.20	—
Benzo (e) pyrene	3.88	—	6.41	—
Benzo (a) pyrene	8.02	—	14.51	—
Perylene	1.80	—	3.15	—
o-Phenylene pyrene	3.83	—	3.14	—
Benzo (ghi) perylene	4.20	—	7.53	—
Anthanthrene	1.70	—	1.48	—
Total PAH	146.75	569.72	419.78	986.40

^a Particle concentration 5.76 mg/m³.

^b Particle concentration 7.21 mg/m³.

Analytical procedure

The analytical methods used in this work have been reported previously (1), and only a brief description follows. The filters were extracted with cyclohexane in a Soxhlet apparatus. An equal volume of distilled water was added to the ethanol from the absorption bottles, and the mixture was extracted twice with cyclohexane. The cyclohexane phase was cleaned by liquid/liquid extraction with N, N-dimethyl formamide (DMF)/water (9:1). By subsequent addition of distilled water and cyclohexane to the DMF phase, PAH was

re-extracted into the cyclohexane. The cyclohexane extract was then concentrated to about 5–10 ml under nitrogen atmosphere, and further concentration took place in a small centrifuge tube on an aluminum heating block at 30°C under a gentle stream of highly purified nitrogen (99.999 %).

For personal samples the method was modified. The filters were extracted with 7 ml of ethanol in an ultrasonic bath. The extracts were concentrated to about 0.6 ml, added to cyclohexane and water, and cleaned by liquid/liquid extraction with DMF/water (30:1). After re-extrac-

tion into cyclohexane the samples were concentrated to about 1 ml prior to the gas chromatographic analysis.

The gas chromatographic analysis was performed on a Carlo Erba gas chromatograph model Fractovap 2100 A equipped with a glass capillary column and flame ionization detector. The sample was introduced on the gas chromatographic column with the technique of splitless injection (7). The chromatographic conditions are given in table 1. The PAH components were identified through a comparison of their retention times with those of a set of PAH standards and with chromatograms from previous studies, where mass spectrometric identification had been used (4). The compounds were quantified by electronic integration of the peak areas (Minigrator, Spectra Physics) and through a comparison of

these areas with those of the internal standard.

The precision of the methods for sampling and analysis was tested both with prepared standards and real samples. The precision measured as the relative standard deviation was better than 20 % for the sampling and about 5 % for clean-up and analysis, expressed as an average of five replicate samples containing 15 PAH compounds (1).

RESULTS

Stationary sampling

A total of 23 samples were collected by stationary sampling (2). In tables 2 and

Table 6. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, personal sampling, spring 1976. ($\mu\text{g}/\text{m}^3$)

PAH	Larry car operator ^a					Coke car operator ^b		Jamb cleaner ^c		Door cleaner ^d		Push car operator ^e		Wharf man ^f
	1	2	3	4	5	1	2	1	2	1	2	1	2	
Fluorene	—	—	—	—	5.83	—	—	—	—	—	—	—	—	—
9-Methylfluorene	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2-Methylfluorene	—	—	—	—	6.17	—	—	—	—	—	—	—	—	—
1-Methylfluorene	—	—	—	—	2.98	—	—	—	—	—	—	—	—	—
Dibenzothiophene	—	—	—	—	7.11	—	—	—	—	—	—	—	—	—
Phenanthrene	1.41	2.29	14.62	3.31	90.61	—	0.81	0.79	4.60	0.22	—	—	0.59	4.50
Anthracene	0.59	1.09	6.16	1.48	32.07	—	0.36	0.47	1.82	0.17	—	—	0.44	2.80
Carbazole	—	—	—	0.33	—	—	—	—	—	0.07	0.10	—	—	—
Methylphenanthrene/ methylantracene ^g	2.12	2.88	10.59	3.15	39.72	—	0.72	0.70	4.06	0.22	0.17	—	—	4.94
Fluoranthene	23.27	24.32	73.16	27.36	133.79	0.22	3.23	5.61	33.10	1.45	1.09	0.56	7.98	55.65
Dihydrobenzo (a & b) fluorene	5.30	7.73	18.48	7.80	40.63	0.18	0.61	1.27	7.58	0.27	0.03	0.10	0.98	13.41
Pyrene	20.30	22.35	65.27	26.02	104.46	0.27	3.17	5.14	27.10	1.43	1.15	0.60	8.02	47.50
Benzo (a) fluorene	11.25	12.77	23.32	9.55	68.28	—	1.59	3.09	14.82	0.60	0.75	0.38	3.72	24.94
Benzo (b) fluorene	9.77	10.33	23.77	9.02	56.81	—	1.66	2.99	13.27	0.69	0.71	0.46	3.49	21.94
1-Methylpyrene	2.77	2.91	5.85	2.49	18.10	—	0.47	0.73	3.59	0.14	0.26	0.13	0.96	5.97
Benzo (c) phenanthrene	2.62	2.83	6.21	3.07	12.40	—	0.46	1.17	4.50	0.27	0.23	0.14	1.18	6.03
Benzo (a) anthracene	12.44	12.80	22.16	10.72	50.87	0.43	2.77	5.79	18.06	1.79	1.24	1.03	6.11	30.76
Chrysene/triphenylene	16.42	16.63	28.46	14.15	67.14	0.60	3.83	8.11	22.37	2.53	1.77	1.42	7.90	39.21
Benzo (b, j & k) fluoranthene	8.50	10.00	13.53	8.33	32.68	0.40	1.91	3.84	12.01	1.28	0.89	0.79	3.40	16.49
Benzo (e) pyrene	7.17	7.69	13.59	6.02	27.03	0.39	1.96	3.59	10.23	1.15	0.83	0.71	3.04	14.47
Benzo (a) pyrene	12.98	15.26	25.12	12.12	43.18	0.50	3.00	6.13	18.67	1.95	1.32	0.96	4.42	21.49
Perylene	2.72	3.20	5.49	2.64	12.25	—	0.60	1.13	3.55	0.39	0.30	0.22	0.98	4.66
o-Phenylene pyrene	6.38	7.54	9.79	5.75	23.90	0.28	1.49	2.98	9.41	0.99	0.69	0.61	2.02	11.87
Benzo (ghi) perylene	3.18	4.40	5.36	3.11	17.73	0.28	1.08	1.74	4.99	0.61	0.44	0.41	1.15	6.33
Anthanthrene	3.89	4.94	5.53	1.98	14.78	0.15	0.79	1.58	5.74	0.45	0.33	0.28	1.04	6.63
Coronene	9.10	10.54	7.96	4.62	57.79	—	1.68	2.85	13.38	0.60	0.92	0.61	2.56	13.36
Dibenzopyrene	10.00	10.96	8.90	5.18	78.61	1.12	2.40	2.36	10.90	—	1.26	—	2.46	10.02
Total PAH	172.18	193.46	393.32	168.20	1044.92	4.82	34.59	62.06	243.75	17.27	14.48	9.41	62.44	362.97

^a Particle concentration: sample 1, 5.71 mg/m^3 ; sample 2, 7.93 mg/m^3 ; sample 3, 13.94 mg/m^3 ; sample 4, 8.57 mg/m^3 ; sample 5, 73.13 mg/m^3 .

^b Particle concentration: sample 1, 5.38 mg/m^3 ; sample 2, 39.39 mg/m^3 .

^c Particle concentration: sample 1, 5.91 mg/m^3 ; sample 2, 8.15 mg/m^3 .

^d Particle concentration: sample 1, 1.8 mg/m^3 ; sample 2, 2.03 mg/m^3 .

^e Particle concentration: sample 1, 3.04 mg/m^3 ; sample 2, 5.42 mg/m^3 .

^f Particle concentration 13.13 mg/m^3 .

^g The isomer not determined.

Table 7. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the coke plant, personal sampling, fall 1976. ($\mu\text{g}/\text{m}^3$)

PAH	Larry car operator ^a		Coke car operator ^b	Jamb cleaner ^c	Door cleaner ^d		Push car operator ^e		Sweeper ^f	Quench car operator ^g
	1	2			1	2	1	2		
Dibenzothiophene	0.71	4.90	0.35	—	0.09	—	0.24	—	—	—
Phenanthrene	8.92	2.50	1.20	8.20	0.47	0.55	0.58	0.75	4.06	0.18
Anthracene	4.00	—	0.18	2.19	—	—	—	—	1.40	—
Carbazole	2.64	—	0.98	2.39	0.55	0.44	0.34	0.57	1.20	0.17
2-Methylanthracene	2.45	2.13	0.26	1.31	—	—	—	—	—	—
1-Methylphenanthrene	2.19	1.90	—	1.60	—	—	—	—	—	—
Fluoranthene	46.76	60.12	7.29	42.52	0.67	0.72	1.49	3.24	17.02	0.38
Dihydrobenzo (a & b) fluorene	8.70	13.33	0.50	6.07	—	—	0.12	0.46	1.65	—
Pyrene	38.10	60.44	6.83	36.11	0.72	0.77	1.42	3.03	14.60	0.41
Benzo (a) fluorene	16.39	16.67	4.89	11.43	0.27	0.24	2.80	2.06	5.74	0.29
Benzo (b) fluorene	19.75	21.67	0.47	2.28	0.15	—	0.18	0.31	1.33	—
4-Methylpyrene	—	—	0.43	1.49	—	—	0.10	0.22	—	—
1-Methylpyrene	4.03	4.21	0.66	3.19	0.10	—	0.17	0.47	1.14	—
Benzo (c) phenanthrene	7.75	3.57	10.07	2.41	0.59	0.46	6.25	0.23	4.00	0.28
Benzo (a) anthracene	29.24	35.54	7.24	23.92	1.20	1.11	2.47	3.86	12.21	0.81
Chrysene/triphenylene	33.72	39.99	9.49	29.13	1.44	1.47	3.06	4.81	15.98	1.01
Benzo (b) fluoranthene	1.00	1.43	1.50	2.71	0.35	0.37	0.51	0.75	1.90	0.26
Benzo (j & k) fluoranthene	7.84	9.77	2.22	6.45	—	—	0.88	1.45	3.91	—
Benzo (e) pyrene	7.78	10.09	3.43	8.00	0.44	0.47	1.73	1.67	4.31	0.32
Benzo (a) pyrene	18.96	25.71	5.82	20.18	1.20	1.42	2.75	3.40	8.81	0.79
Perylene	3.80	5.02	1.74	5.08	0.25	0.21	0.54	0.96	1.98	0.16
o-Phenylene pyrene	4.22	8.51	2.70	9.64	0.44	0.34	1.01	1.73	3.83	0.21
Benzo (ghi) perylene	3.82	17.28	3.54	5.49	0.55	0.54	1.38	2.53	4.53	0.48
Anthanthrene	2.97	3.47	1.04	3.59	0.07	—	0.51	0.78	1.26	—
Total PAH	275.80	348.25	72.83	235.38	9.55	9.11	28.48	33.28	110.92	5.75

^a Particle concentration: sample 1, 8.84 mg/m^3 ; sample 2, 7.35 mg/m^3 .

^b Particle concentration 10.53 mg/m^3 .

^c Particle concentration 9.23 mg/m^3 .

^d Particle concentration: sample 1, 3.33 mg/m^3 ; sample 2, 3.00 mg/m^3 .

^e Particle concentration: sample 1, 4.00 mg/m^3 ; sample 2, 6.94 mg/m^3 .

^f Particle concentration 5.43 mg/m^3 .

^g Particle concentration 1.13 mg/m^3 .

3 the mean values and the concentration ranges for particulate matter, PAH on particulate matter, and gaseous PAH are given for the spring and fall sampling. The tables show that the PAH concentration in the work atmospheres may vary within wide ranges. There was, however, no significant difference between the spring and the fall concentrations, and therefore the actual variations in the work atmospheres during sampling were larger than the long-term variation.

As revealed in tables 2 and 3, PAH components up to pyrene usually pass the filter. In extreme cases, we have observed that up to 5% of benzo(a)-pyrene also passes the filter. In most cases, the concentration of gaseous PAH is of the same order as the particulate PAH, the concentration ratio varying from 1:1 to 1:3.

In figs. 1 and 2 typical gas chromato-

grams of particulate and gaseous PAH are shown. The chromatograms show that the capillary columns are capable of separating critical isomers like benzo(a)-pyrene from benzo(e)-pyrene and benz(a)-anthracene from chrysene and triphenylene. This separation is essential for a characterization of PAH in the work atmosphere.

As many as 39 PAH compounds were identified in the samples from the work atmosphere in the coke plant. Several of these compounds, including benzo(a)-pyrene (BaP), have been reported to exhibit carcinogenic properties (5, 13). Little is known, however, about the synergistic or antagonistic effects of a mixture of PAH or PAH mixed with other compounds, although synergistic effects have been demonstrated for BaP and dibenzo(a, h) anthracene (14).

Mobile sampling

Tables 4 and 5 give the mean values and the concentration ranges of particulates and gaseous and particulate PAH by mobile sampling from the spring and fall. The results are in accordance with the results from the stationary sampling and show that phenanthrene is usually the most volatile PAH adsorbed on particulate material, while PAH compounds up to pyrene pass the filter.

Personal sampling

By the use of the personal sampling method only particulate matter was collected. In tables 6 and 7 the analytical results of these samples are presented according to job type. As revealed by the tables, the personal exposure varied with occupation. The larry car operators seemed to have

the highest exposure (168—1,044 μg PAH/ m^3). Jamb cleaners and the wharf man (one measurement) also showed high values (62—362 μg PAH/ m^3). The other job types usually involved lower exposure.

Particle size distribution

In one case the size distribution of the particles collected at the battery top was determined after the particles were divided into five diameter ranges. The particulates belonging to each of these ranges were analyzed separately by gas chromatography, and the results are given in table 8. The largest amounts of PAH were found for particles in the diameter ranges of 7—3 μm and 3—0.9 μm . Only about 1 % of the total PAH identified was connected to particles classified as not respirable (particle diameter larger than 7 μm).

Table 8. Polycyclic aromatic hydrocarbons (PAH) on particles as a function of particle size, battery top, spring 1976. (μg)

PAH	Particle size				
	> 15 μm	7—15 μm	3—7 μm	0.9—3 μm	< 0.9 μm
Phenanthrene	0.5	0.5	0.8	2.0	a
Anthracene	0.3	0.2	0.6	0.7	a
Methylphenanthrene/ methylanthracene ^b	—	—	0.4	1.3	—
Fluoranthene	—	—	4.2	10.7	2.0
Dihydrobenzo (a & b) fluorene	—	—	0.6	2.1	—
Pyrene	—	—	4.3	12.3	1.3
Benzo (a) fluorene	—	—	3.5	9.1	0.5
Benzo (b) fluorene	—	—	2.6	7.2	0.3
Benzo (c) phenanthrene	—	—	2.0	5.2	0.8
Benz (a) anthracene	0.03	0.08	3.3	9.0	4.0
Chrysene/triphenylene	0.06	0.10	5.8	13.2	1.8
Benzo (b, j & k) fluoranthene	0.05	0.40	4.8	10.6	7.2
Benzo (e) pyrene	0.03	0.14	3.4	8.9	0.5
Benzo (a) pyrene	0.02	0.12	5.2	12.1	1.4
Perylene	—	—	1.3	2.9	—
o-Phenylene pyrene	—	—	3.8	7.2	0.5
Benzo (ghi) perylene	—	—	5.2	7.8	1.3
Anthanthrene	—	—	1.2	3.2	0.3
Coronene	—	—	5.9	6.3	0.5
Dibenzopyrene	—	—	0.9	1.5	0.3
Total PAH	0.69	1.54	59.8	133.3	22.7

a Detectable

b The isomer not determined.

DISCUSSION

In a number of cases, workers employed in industries connected with PAH exposure have been reported to have an increased lung cancer mortality. Kennaway and Kennaway (9) reported an approximately threefold excess of lung cancer mortality for gas production men, chimney sweeps, and several categories of gas workers from 1921 to 1938. The excess of lung cancer among gas workers was later confirmed by Doll et al. (6). Furthermore, it has been reported that topside coke oven workers employed five or more years had about a tenfold increase in lung cancer risk (11), and these findings were confirmed by a study of coke oven workers at ten steel plants in different geographic areas of the United States and Canada (15). The cancer experience among coke by-product workers has recently been summarized (16). Bearing this in mind, we feel that it is an important task in environmental chemistry to characterize the PAH level in work atmospheres as far as possible and to relate the concentrations to other data concerning occupational health.

The concentrations of total PAH in particulate matter measured by stationary, mobile, and personal sampling in both the spring and fall are summarized in fig. 3. Personal sampling gave somewhat lower values than stationary sampling because it also operated during rest periods. As revealed by the figure, the personal samples show that occupational

exposure to PAH is largest at the battery top. This finding is in accordance with previous findings that topside coke oven workers have the highest lung cancer risk among coke plant employees (11). The PAH concentration in the larry car cabin was of the same order of magnitude as for the battery top, while the other jobs had lower PAH exposure.

In a recent paper, Jackson et al. (8) reported the BaP concentration at a coke oven battery top to be 1.2–15.9 $\mu\text{g}/\text{m}^3$. Investigations in steel and iron works give values of 0.04–6 μg BaP/ m^3 (20). In this work we determined the BaP concentration for different job types to vary from 0.5 to 43.2 $\mu\text{g}/\text{m}^3$ for personal sampling and 14–134 $\mu\text{g}/\text{m}^3$ for stationary sampling. This result clearly demonstrates that PAH exposure varies strongly with job type and that some work operations in a coke plant may result in very high exposure to PAH. These values are also higher than the ones we recently reported from an aluminum plant (3). By stationary sampling, the BaP concentrations were determined to be 0.02–0.05 $\mu\text{g}/\text{m}^3$, 0.03–0.3 $\mu\text{g}/\text{m}^3$, and 0.7–9.0 $\mu\text{g}/\text{m}^3$ in the prebaked potroom, the anode plant and the Söderberg potroom, respectively, while personal sampling gave the values 0.8–27.9 $\mu\text{g}/\text{m}^3$ and 3.4–116.3 $\mu\text{g}/\text{m}^3$ in the anode plant and the Söderberg potroom, respectively (3).

The relative distribution of PAH in the spring and fall sampling was quite similar. Fig. 4 shows the PAH profiles (4) for this plant. As revealed by the figure the pro-

Fig. 3. Concentration of polycyclic aromatic hydrocarbons (PAH) measured by stationary (S), mobile (M) and personal (P) sampling in the spring (S) and fall (F).

Fig. 4. Polycyclic aromatic hydrocarbon (PAH) profiles in the spring and fall sampling.

files were not significantly affected by the battery top reconstruction. The profiles are also quite similar to the one found in an aluminum vertical pin smelter (3). They are, however, significantly different from the one observed in a Söderberg paste plant (4), which has a much lower operating temperature.

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