

Polycyclic aromatic hydrocarbons in the work atmosphere

I. Determination in an aluminum reduction plant

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BJØRSETH, A., BJØRSETH, O. and FJELDSTAD, P. E. Polycyclic aromatic hydrocarbons in the work atmosphere: I. Determination in an aluminum reduction plant. *Scand. j. work environ. & health* 4 (1978) 212—223. The content of polycyclic aromatic hydrocarbons (PAH) in a Søderberg prebaked aluminum reduction plant and an anode plant was studied. Both stationary and personal sampling were used, and the samples were analyzed by glass capillary gas chromatography. In many samples more than 30 PAH and heterocyclic compounds were identified. Comparison of the results from the different plants revealed that the atmospheric PAH content was significantly higher in the Søderberg plant than in the others. However, the relative distribution of PAH components (PAH profile) was relatively constant in the prebaked and the anode baking plant, and different in the Søderberg plant. As a consequence of the variation in the pollution level among the different job categories, personal sampling showed a broader range of PAH concentrations than the stationary method.

Key words: aluminum reduction plant, analysis, benzo(a)pyrene, determination, polycyclic aromatic hydrocarbons, sampling, work atmosphere.

It is well known that polycyclic aromatic hydrocarbons (PAH) may be formed by pyrolysis and incomplete combustion of coal, tar, oil, and other organic material (8). In an industrialized society there exists a large number of anthropogenic sources of PAH. Much interest has been focused on analyzing and characterizing these sources and the distribution of PAH, both in the outdoor environment and in

work atmospheres. The reason for this is basically that animal experiments have shown that some PAH have carcinogenic properties, and they are suspected to be human carcinogens as well (8). It has also been shown that smokers or persons breathing air containing PAH develop lung cancer more often than the general population (8). An epidemiologic investigation among employees in a coke plant revealed a 2.5 to 10 times higher cancer frequency than among the control group (7). Most analyses of PAH in the work environment have, however, been limited to the determination of "benzene soluble material" (9) or to the determination of one single component, such as benzo(a)pyrene, while complete information on the PAH content in atmospheres is more scarce.

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In parallel with the increasing concern for occupational exposure to hazardous compounds, there is also a need for more-detailed knowledge of the composition and pollution levels in various work atmospheres. The mixture of PAH formed by high temperature reactions may be of a very complex nature and may consist of a large number of carcinogens and non-carcinogens. Recent results have demonstrated that PAH compounds also exhibit synergistic effects (10). Detailed knowledge of the composition of the PAH compounds in a work atmosphere is therefore essential for an estimation of possible hazardous effects.

In connection with a research program on the occurrence and analysis of PAH in work atmospheres, we have previously reported on a method for analyzing PAH (2) and the PAH content of airborne particulate pollutants in a Söderberg paste plant (4). In this paper we present the results of an investigation of the PAH content both in air and in airborne particulate matter in a Norwegian primary aluminum smelting plant (3). The aluminum plant has both vertical pin Söderberg and closed prebaked anode cells. In addition there are an anode paste and an anode baking plant. The work atmospheres in these plants have been investigated, and the results are compared. As a means of comparison, the concept of PAH profiles has also been utilized.

MATERIAL AND METHODS

Sampling

In this work, both stationary and personal sampling were used. 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 the personal samples give a better estimate of the occupational exposure.

The stationary sampling equipment consisted basically of a filter (Acropore AN 800, 47 mm Ø) and two absorption bottles, each with 125 ml of ethanol. The bottles were cooled by dry ice to reduce the evap-

oration of ethanol. (Under normal conditions, about 20 ml of ethanol/h evaporate from the bottles.) An Edwards ECB 1 vacuum pump drew the air through the equipment with a flow rate of about 1 m³/h. The sampling volume was measured with a dry gas meter.

In personal sampling, two types of devices were used. The first one consisted of a 27 mm Ø Acropore AN 800 filter, connected to an Casella pump. The filter was placed in the breathing zone of the workers, and the sampling rate was about 2 l/min. With this method we collected only particulate matter.

The other type of personal sampling device is, in principle, equal to the stationary device. By means of a battery-driven pump (flow rate ~ 2 l/min), air was drawn through a 37 mm Ø Acropore AN 800 filter and then bubbled through two leakproof absorption bottles with 7 ml of ethanol in each. The bottles were cooled with dry ice. The sampling unit weighed 3 kg and was carried around in a little backpack. The sampling time varied between 2 and 6 h.

Sampling sites

Air samples were collected at a number of places in the anode plant (production and prebaking of anodes and production of anode parts), the vertical pin Söderberg plant, and the closed prebaked anode

Table 1. Chromatographic conditions.

Variable	Condition
Carrier gas	H ₂ (0.8 kg/cm ²)
Column	50 mm x 0.38 mm inner diameter, coated with OV1 ^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 anode plant, stationary sampling. ($\mu\text{g PAH}/\text{m}^3$)

PAH	Sample 1 ^a		Sample 2 ^b		Sample 3 ^c		Sample 4 ^d		Sample 5 ^e	
	Particulates	Gaseous	Particulates	Gaseous	Particulates	Gaseous	Particulates	Particulates	Gaseous	
Naphtalene	—	147.0	—	4.0	—	20.0	—	—	—	
Methylnaphtalene	—	14.0	—	0.60	—	2.7	—	—	—	
Biphenyl	0.05	29.0	0.06	2.6	—	9.9	0.03	—	—	20.6
Dibenzofurane	0.02	15.3	0.04	0.44	0.14	5.1	—	—	—	27.1
Fluorene	0.04	12.8	0.04	0.79	0.09	4.6	0.05	—	—	25.2
9-Methylfluorene	—	0.97	—	—	—	0.52	—	—	—	—
2-Methylfluorene	—	0.22	—	—	—	0.19	—	—	—	1.35
1-Methylfluorene	—	0.08	—	—	—	0.08	—	—	—	0.48
Dibenzothiophene	0.06	1.67	—	0.30	0.09	1.4	—	1.9	—	11.4
Phenanthrene	0.45	16.0	0.47	—	1.4	13.0	0.25	19.9	—	134.0
Anthracene	0.05	2.3	0.04	1.4	0.13	1.4	0.06	2.8	—	18.5
Carbazole	—	—	—	—	0.03	0.04	0.21	0.8	—	0.19
Methylphenanthrene †	0.05	0.72	0.04	—	0.11	0.45	0.07	2.1	3.19	
Methylanthracene †										
Fluoranthene	1.0	6.58	1.2	0.15	1.6	2.1	0.88	23.1	—	5.63
Dihydrobenzo(a&b)fluorene	0.02	0.09	—	—	0.03	0.04	0.12	0.5	—	—
Pyrene	0.73	3.69	0.73	0.04	1.1	0.98	1.2	15.7	—	—
Benzo(a)fluorene	0.14	0.09	0.16	—	0.22	0.06	0.07	1.2	—	—
Benzo(b)fluorene	0.07	—	0.09	—	0.18	0.02	0.04	1.5	—	—
1-Methylpyrene	0.02	—	0.09	—	0.06	—	0.10	0.5	—	—
Benzo(c)phenanthrene	0.10	—	0.05	—	0.07	—	0.02	0.4	—	—
Benz(a)anthracene	0.26	—	0.10	—	0.13	—	0.17	1.0	—	—
Chrysene/triphenylene	0.32	—	0.15	—	0.18	—	0.16	1.1	—	—
Benzo(b&k)fluoranthene	0.09	—	0.13	—	0.03	—	0.04	0.2	—	—
Benzo(e)pyrene	0.07	—	0.04	—	0.03	—	—	0.2	—	—
Benzo(a)pyrene	0.08	—	0.04	—	0.03	—	—	0.3	—	—
Perylene	—	—	—	—	—	—	—	—	—	—
o-Phenylenepyrene	—	—	—	—	—	—	—	—	—	—
Benzo(ghi)perylene	0.04	—	—	—	—	—	—	—	—	—
Anthanthrene	0.04	—	—	—	—	—	—	—	—	—
Coronene	—	—	—	—	—	—	—	—	—	—
Dibenzopyrene	—	—	—	—	—	—	—	—	—	—
Total PAH	3.7	260.0	3.4	10.5	5.6	63.0	3.5	73.3	262.0	

^a Air volume sampled 4.64 m³; weight particulates 7 mg.

^b Air volume sampled 4.92 m³; weight particulates 5 mg.

^c Air volume sampled 5.31 m³; weight particulates 6 mg.

^d Air volume sampled 7.80 m³; weight particulates 7 mg.

^e Air volume sampled 6.9 m³; weight particulates 6.6 mg.

† Methyl position not determined.

plant. The filter house was placed about 1 m above the floor and the sampling time varied between 3 and 5 h.

The personal samplers were carried by workers with different jobs, as described later.

Analytical procedure

The analytical method has been reported previously (2) and will only be described briefly now. The internal standards (β,β' -binaphtyl and m-quaterphenyl) were added to the air filter samples, which were subsequently extracted in a Soxhlet apparatus for 8 h with 50 ml of cyclohexane. The cyclohexane solutions were extracted with 50 ml of N,N-dimethylformamide (DMF) : water (9:1), which transfer PAH

and more polar compounds to the DMF phase. The extraction was repeated with 25 ml of the DMF/water solution. To the combined DMF/water phases were added 100 ml of water, and PAH was re-extracted with 50 ml of cyclohexane. The extraction was repeated with 25 ml of cyclohexane. The combined cyclohexane phases were dried by Na₂SO₄ and concentrated to about 10 ml in a modified Kuderna-Danish apparatus. Further concentration was achieved in a centrifuge tube on an aluminum heating block at 30°C and a gentle stream of highly purified nitrogen (> 99.999 %).

The separation of the extract was performed on a Carlo Erba gas chromatograph model Fractovap 2100 A, equipped with a glass capillary column and flame ionization detector (FID). The sample was

introduced on the gas chromatographic column with the technique of splitless injection (5). The chromatographic conditions are given in table 1.

The PAH components were identified in a comparison of the retention times with those of a set of PAH standards and with chromatograms from previous studies in which mass spectrometric identification was used (4). The compounds were quantified by electronic integration of the peak areas (Minigrator, Spectra-physics) and by a comparison of these areas with the areas of the internal standards.

The precision of the method measured as one standard deviation has been reported to be better than 14 % (average of 15 compounds is 4.8 %), and the goodness of the method is 11.6 % (2).

RESULTS

In the course of this work, a number of air filter samples and absorption solutions were analyzed. In the following, the results for those analyzed by gas chromatography are presented separately for each

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

PAH	Sample 6 ^a (Particulates)	Sample 7 ^b (Particulates)	Sample 8 ^c (Particulates)	Sample 9 ^d (Particulates)
Naphtalene	0.09	—	—	—
Methylnaphtalene	—	—	—	—
Biphenyl	0.59	—	0.10	—
Dibenzofurane	—	—	—	—
Fluorene	0.21	—	—	—
9-Methylfluorene	—	—	—	—
2-Methylfluorene	—	—	—	—
1-Methylfluorene	—	—	—	—
Dibenzothiophene	—	3.0	—	—
Phenanthrene	1.70	22.7	0.35	—
Anthracene	0.32	1.9	0.03	—
Carbazole	0.12	—	—	—
Methylphenanthrene ^e	—	—	—	—
Methylanthracene ^e	—	3.1	—	—
Fluoranthene	7.28	59.2	2.47	2.04
Dihydrobenzo(a&b)fluorene	0.11	1.2	—	—
Pyrene	5.22	43.3	1.47	1.16
Benzo(a)fluorene	1.37	12.0	0.44	0.33
Benzo(b)fluorene	0.92	8.9	0.26	—
1-Methylpyrene	—	2.8	—	—
Benzo(c)phenanthrene	0.81	7.6	0.07	—
Benz(a)anthracene	2.46	18.8	0.57	0.39
Chrysene/triphenylene	3.11	28.6	0.89	0.75
Benzo(b&k)fluoranthene	2.22	34.4	0.77	2.26
Benzo(e)pyrene	2.26	25.6	0.72	0.84
Benzo(a)pyrene	2.97	27.9	0.80	0.89
Perylene	0.69	8.5	0.19	0.22
o-Phenylene pyrene	2.16	25.0	0.75	0.91
Benzo(ghi)perylene	2.24	22.2	0.68	1.03
Anthanthrene	—	—	—	—
Coronene	—	7.0	—	—
Dibenzopyrene	—	—	—	—
Total PAH	36.84	373.7	10.58	10.82

^a Air volume 0.23 m³; job type, coke packer.

^b Air volume 0.67 m³; job type, pitch bin worker.

^c Air volume 0.56 m³; job type, operator.

^d Air volume 0.58 m³; job type, pitch dust sweeper.

^e Methyl position not determined.

Table 4. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the prebaked plant, stationary sampling. ($\mu\text{g PAH}/\text{m}^3$)

PAH	Sample 10 ^a		Sample 11 ^b		Sample 12 ^c	
	Particu- lates	Gaseous	Particu- lates	Gaseous	Particu- lates	Gaseous
Naphtalene	—	8.2	—	12.04	—	6.35
Methylnaphtalene	—	2.15	—	4.07	—	1.59
Biphenyl	—	7.68	—	14.48	—	6.16
Dibenzofurane	—	1.2	—	3.0	—	1.96
Fluorene	—	3.32	—	8.85	—	3.5
9-Methylfluorene	—	—	—	0.28	—	0.28
2-Methylfluorene	—	—	—	0.86	—	0.12
1-Methylfluorene	—	—	—	1.1	—	0.20
Dibenzothiophene	—	0.85	—	5.2	—	0.88
Phenanthrene	—	12.19	0.16	49.0	0.16	7.66
Anthracene	—	—	—	3.7	—	0.31
Carbazole	—	—	—	0.20	—	—
Methylphenanthrene ^d }	—	—	—	1.5	—	0.07
Methylantracene ^d }	—	—	—	—	—	—
Fluoranthene	0.31	4.1	0.51	13.0	0.66	1.7
Dihydrobenzo(a&b)fluorene	—	—	—	0.20	—	—
Pyrene	0.19	2.3	0.25	5.7	0.37	0.99
Benzo(a)fluorene	—	—	—	0.70	—	—
Benzo(b)fluorene	—	—	—	0.15	—	—
1-Methylpyrene	—	—	—	—	—	—
Benzo(c)phenanthrene	—	—	—	—	—	—
Benz(a)anthracene	0.16	—	0.08	—	0.18	—
Chrysene/triphenylene	0.33	—	0.28	—	0.36	—
Benzo(b&k)fluoranthene	0.09	—	—	—	—	—
Benzo(e)pyrene	—	—	—	—	—	—
Benzo(a)pyrene	—	—	—	—	—	—
Perylene	—	—	—	—	—	—
o-Phenylene-pyrene	0.16	—	—	—	—	—
Benzo(ghi)perylene	0.32	—	—	—	—	—
Anthanthrene	—	—	—	—	—	—
Coronene	—	—	—	—	—	—
Dibenzopyrene	—	—	—	—	—	—
Total PAH	1.6	42.3	1.3	123.95	1.7	31.53

^a Air volume sampled 3.51 m³; weight particulates 2.0 mg.

^b Air volume sampled 4.24 m³; weight particulates 7.0 mg.

^c Air volume sampled 3.96 m³; weight particulates 7 mg.

^d Methyl position not determined.

of the three plants. In addition, a few results from a high-pressure liquid chromatographic (HPLC) analysis are also given for comparison.

Anode plant

Air samples were collected by stationary sampling at different sites in the plant. Four of these sites were located above the baking ovens (samples 1—4), while the fifth was above the anode compressor (sample 5). The results are given in table 2, both for the particular matter and for

the absorption solutions. In addition, a number of air filter samples from personal samplers have been analyzed. The results of four of these are given in table 3. All the samples represent different work operations, such as coke packer (sample 6), pitch bin worker (sample 7), hydraulic press operator (sample 8) and pitch dust sweeper (sample 9).

Prebaked plant

Stationary sampling was also used in the prebaked plant. Results from analyses of

Table 4. (continued)

PAH	Sample 13 ^a		Sample 14 ^b		Sample 15 ^c	
	Particu- lates	Gaseous	Particu- lates	Gaseous	Particu- lates	Gaseous
Naphtalene	—	10.2	—	—	—	—
Methylnaphtalene	—	22.3	—	—	—	—
Biphenyl	—	13.0	—	—	—	0.50
Dibenzofurane	—	3.57	—	—	—	0.23
Fluorene	—	7.39	—	—	—	0.40
9-Methylfluorene	—	—	—	—	—	—
2-Methylfluorene	—	—	—	—	—	—
1-Methylfluorene	—	—	—	—	—	—
Dibenzothiophene	—	2.40	—	0.19	—	0.15
Phenanthrene	—	26.7	—	7.79	—	1.91
Anthracene	—	1.07	—	5.27	—	0.06
Carbazole	—	—	—	—	—	—
Methylphenanthrene ^d	—	0.44	—	0.42	—	0.02
Methylanthracene ^d						
Fluoranthene	0.39	12.6	0.15	13.4	0.14	0.88
Dihydrobenzo(a&b)fluorene	—	—	—	0.14	—	—
Pyrene	0.26	7.55	0.08	7.84	0.08	0.40
Benzo(a)fluorene	—	—	—	0.65	—	—
Benzo(b)fluorene	—	—	—	0.14	—	—
1-Methylpyrene	—	—	—	—	—	—
Benzo(c)phenanthrene	—	—	—	—	—	—
Benz(a)anthracene	0.26	—	0.10	—	0.05	—
Chrysene/triphenylene	0.29	—	0.07	—	0.14	—
Benzo(b&k)fluoranthene	0.28	—	0.16	—	0.15	—
Benzo(e)pyrene	0.09	—	0.05	—	—	—
Benzo(a)pyrene	0.05	—	0.02	—	—	—
Perylene	—	—	—	—	—	—
o-Phenylenepyrene	—	—	0.01	—	—	—
Benzo(ghi)perylene	—	—	0.01	—	—	—
Anthanthrene	—	—	—	—	—	—
Coronene	—	—	—	—	—	—
Dibenzopyrene	—	—	—	—	—	—
Total PAH	1.61	107.2	0.65	31.1	0.56	4.56

^a Air volume sampled 5.0 m³; weight particulates 9.6 mg.^b Air volume sampled 6.4 m³; weight particulates 13.0 mg.^c Air volume sampled 10.0 m³; weight particulates 37.1 mg.^d Methyl position not determined.

six of the filters and adsorption solutions (samples 10–15) are given in table 4. Personal sampling was done by workers performing different operations. Due to the rather low concentrations of PAH in these samples, they could not be analyzed by gas chromatography. The samples were, however, analyzed by HPLC for determination of the total amount of PAH. Some typical values are given in table 5. The documentation of this method will be reported in another communication.

Table 5. Total polycyclic aromatic hydrocarbons in the atmosphere of the prebaked Söderberg plant, determined by high-pressure liquid chromatography, personal sampling.

Job type	Concentration ($\mu\text{g}/\text{m}^3$) ^a
Tapper	0.87
Coke puller	2.0
Coke puller	0.87
Crust breaker	0.52

^a Particulates only.

The results of the analysis of stationary samples are given in table 6 (samples 16–25). Personal sampling was used in this plant as well, and the results are given in table 7. These samples include operations such as tapper (sample 26) and pin setter (samples 27 and 28). In fig. 1 a chromatogram of PAH from particulate matter in the atmosphere in this plant is given. Fig. 2 shows a chromatogram of the volatile PAH fraction from the same sampling. As revealed by this chromatogram, PAH up to pyrene is likely to pass through the filter.

As shown in the tables, more than 30 different PAH compounds were identified in the samples from the work atmospheres. Carcinogenic activities as revealed in animal experiments (8) have been assigned to a few of these, i.e., benz(a)anthracene, benzo(c)phenanthrene, benzo(b&k)fluoranthene, benzo(a)pyrene and dibenzopyrene. Previously, the main attention to potential carcinogenic compounds in work atmospheres has been focused on the occurrence of benzo(a)pyrene (BaP). BaP has also been suggested as an indicator of the PAH level in work atmospheres containing tar and

Table 6. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the vertical pin Søderberg plant. ($\mu\text{g PAH}/\text{m}^3$)

PAH	Sample 16 ^a		Sample 17 ^b		Sample 18 ^c		Sample 19 ^d		Sample 20 ^e	
	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous
Naphtalene	—	145.0	—	165.1	—	218.0	—	83.3	—	311.3
Methylnaphtalene	—	54.0	—	89.1	—	79.6	—	40.74	—	123.53
Biphenyl	0.20	168.0	0.15	294.2	0.19	238.4	0.12	141.9	0.12	381.0
Dibenzofurane	—	43.0	—	33.22	0.11	47.42	—	18.0	0.06	61.0
Fluorene	0.20	89.0	0.22	88.53	0.24	108.2	0.14	48.29	0.29	135.20
9-Methylfluorene	—	1.4	—	8.8	0.10	2.2	—	11.0	—	6.6
2-Methylfluorene	0.25	7.8	—	8.9	0.34	9.8	—	4.4	0.10	11.0
1-Methylfluorene	—	7.3	—	9.3	—	8.6	—	4.9	0.16	11.0
Dibenzothiophene	0.49	31.0	0.39	48.0	0.90	5.6	0.24	25.9	0.59	56.0
Phenanthrene	4.8	297.0	4.2	164.10	4.5	221.97	3.5	131.0	8.1	333.0
Anthracene	0.57	21.0	0.27	9.60	0.74	20.0	0.16	7.7	1.3	20.0
Carbazole	2.0	1.4	1.6	0.78	2.8	0.73	—	0.45	2.0	0.60
Methylphenanthrene ^f	0.45	9.2	3.2	4.1	3.2	8.1	0.44	3.4	0.87	8.7
Methylanthracene ^f										
Fluoranthene	10.3	70.0	11.1	26.11	12.0	51.0	14.0	24.0	20.0	65.0
Dihydrobenzo(a&b)fluorene	0.21	1.1	0.13	0.31	0.74	0.94	0.12	0.28	0.38	0.94
Pyrene	8.5	36.0	7.3	15.0	8.8	27.0	9.6	13.0	16.0	36.0
Benzo(a)fluorene	2.8	4.2	2.3	0.62	3.6	2.8	4.2	—	6.6	1.1
Benzo(b)fluorene	1.7	1.4	1.3	1.1	2.4	1.1	1.2	—	2.9	2.1
1-Methylpyrene	0.50	0.16	0.68	—	1.6	0.09	0.99	—	0.87	—
Benzo(c)phenanthrene	1.6	0.36	1.2	—	2.4	0.14	1.1	—	2.2	—
Benz(a)anthracene	6.3	0.21	4.9	—	6.3	0.06	3.6	—	5.6	—
Chrysene/triphenylene	12.3	0.44	10.2	—	12.0	0.10	8.1	—	13.0	—
Benzo(b&k)fluoranthene	7.1	—	5.5	—	11.0	—	3.8	—	6.6	—
Benzo(e)pyrene	4.9	—	3.6	—	4.8	—	2.5	—	5.8	—
Benzo(a)pyrene	3.4	—	2.2	—	3.5	—	1.7	—	4.5	—
Perylene	0.91	—	0.56	—	1.8	—	0.37	—	1.2	—
o-Phenylene-pyrene	1.8	—	1.2	—	1.1	—	0.96	—	2.4	—
Benzo(ghi)perylene	1.9	—	1.4	—	1.5	—	1.1	—	2.5	—
Anthanthrene	0.09	—	—	—	0.13	—	0.15	—	0.17	—
Coronene	0.26	—	0.14	—	0.48	—	—	—	0.40	—
Dibenzopyrene	0.09	—	—	—	—	—	—	—	0.18	—
Total PAH	74.0	990.0	61.0	969.3	87.0	1053.0	58.0	560.2	104.0	1564.1

^a Air volume sampled 5.53 m³; weight particulates 31.0 mg.

^b Air volume sampled 3.80 m³; weight particulates 12 mg.

^c Air volume sampled 4.45 m³; weight particulates 20.0 mg.

^d Air volume sampled 2.78 m³; weight particulates 4.0 mg.

^e Air volume sampled 2.96 m³; weight particulates 14.0 mg.

^f Methyl position not determined.

pitch volatiles (11). The present study demonstrates the existence of other potentially hazardous materials as well.

The total concentration of PAH also varied within the three plants. The results from the stationary sampling in the Söderberg plant showed an average value of 0.1 mg/m³ for PAH on particulates and 1 mg/m³ for volatile PAH. The personal sampling filters showed values for PAH on particulate matter from 0.003 to 2.8 mg/m³.

For the prebaked plant, the values obtained from the gas chromatographic analysis were quite low. On the average the stationary sampling gave values of parti-

culate PAH of the order of 0.001 mg/m³ and volatile PAH of about 0.07 mg/m³, which is in the region of 1–10 % of the amount in the Söderberg plant. The personal sampling filters also showed quite low values. For PAH in particulate material it was determined to be about 0.001 mg/m³. It is, however, necessary to point out that these results are not representative of the PAH concentration in the atmosphere of the prebaked plant, since only those filters with high amounts of PAH have been analyzed by gas chromatography. The results from a HPLC analysis of filters with less PAH should also be taken into consideration when the occupational

Table 6. (continued)

PAH	Sample 21 ^a		Sample 22 ^b		Sample 23 ^c		Sample 24 ^d		Sample 25 ^e	
	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous	Particulates	Gas-eous
Naphtalene	4.0	207.6	—	23.6	—	294.0	—	184.0	—	0.72
Methylnaphtalene	0.12	100.42	—	12.8	—	92.7	—	70.8	—	1.22
Biphenyl	0.42	333.6	—	34.3	—	198.0	—	170.0	—	5.38
Dibenzofurane	0.46	50.0	—	13.0	—	53.8	—	53.0	—	2.09
Fluorene	0.53	128.59	—	24.2	—	111.0	—	101.0	—	6.31
9-Methylfluorene	—	7.9	—	0.6	—	—	—	2.4	—	0.12
2-Methylfluorene	0.18	13.0	—	2.3	—	9.0	—	7.5	—	0.85
1-Methylfluorene	0.23	13.0	—	2.1	—	6.8	—	6.5	—	0.27
Dibenzothiophene	0.69	58.0	0.3	10.7	0.2	46.1	0.5	41.7	1.2	3.46
Phenanthrene	12.0	337.0	4.0	125.0	3.6	295.0	8.1	446.0	—	39.9
Anthracene	1.8	26.0	0.2	11.1	0.5	32.6	1.7	27.7	—	2.98
Carbazole	2.6	0.77	0.8	—	1.3	—	2.4	—	—	—
Methylphenanthrene ^f	1.5	10.0	0.6	4.4	0.5	15.3	1.2	12.1	—	0.17
Methylanthracene ^f	—	—	—	—	—	—	—	—	—	—
Fluoranthene	30.0	63.0	20.8	51.1	23.0	144.0	29.9	162.0	5.5	14.1
Dihydrobenzo(a&b)fluorene	0.91	0.94	0.3	0.6	0.3	1.8	1.0	—	—	0.48
Pyrene	22.0	34.0	15.6	29.0	16.7	77.2	24.8	91.1	3.7	8.03
Benzo(a)fluorene	7.8	2.5	4.1	1.1	4.7	5.6	9.1	7.5	1.4	—
Benzo(b)fluorene	4.8	1.8	2.2	2.3	2.6	—	5.7	—	0.9	—
1-Methylpyrene	1.6	—	1.7	—	1.6	—	3.0	—	0.3	—
Benzo(c)phenanthrene	3.2	—	3.8	—	4.3	—	7.9	—	0.4	—
Benz(a)anthracene	10.0	—	7.5	—	8.8	—	15.0	—	1.0	—
Chrysene/triphenylene	19.0	—	14.7	—	17.7	—	30.1	—	2.1	—
Benzo(b&k)fluoranthene	15.0	—	8.2	—	11.7	—	26.9	—	1.1	—
Benzo(e)pyrene	6.1	—	6.3	—	10.8	—	12.2	—	0.8	—
Benzo(a)pyrene	5.0	—	4.7	—	8.7	—	9.0	—	0.7	—
Perylene	1.2	—	1.2	—	2.3	—	2.4	—	—	—
o-Phenylene-pyrene	2.6	—	2.8	—	5.3	—	4.7	—	0.4	—
Benzo(ghi)perylene	2.7	—	3.1	—	5.8	—	5.5	—	0.4	—
Anthanthrene	0.32	—	—	—	—	—	—	—	—	—
Coronene	0.26	—	0.9	—	1.2	—	—	—	—	—
Dibenzopyrene	0.12	—	—	—	—	—	1.2	—	—	—
Total PAH	157.0	1386.2	103.9	349.0	131.9	1333.0	202.0	1383.0	19.7	86.0

^a Air volume sampled 2.70 m³; weight particulates 13.9 mg.

^b Air volume sampled 4.6 m³; weight particulates 13.9 mg.

^c Air volume sampled 4.1 m³; weight particulates 16.0 mg.

^d Air volume sampled 4.1 m³; weight particulates 35.1 mg.

^e Air volume sampled 3.4 m³; weight particulates 4.2 mg.

^f Methyl position not determined.

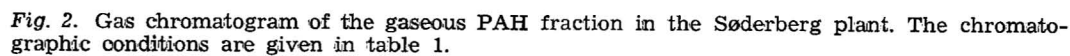
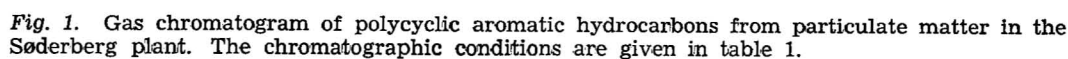


Table 7. Polycyclic aromatic hydrocarbons (PAH) in the atmosphere of the vertical pin Söderberg plant, personal sampling. ($\mu\text{g PAH}/\text{m}^3$)

PAH	Sample 26 ^a (Particulates)	Sample 27 ^b (Particulates)	Sample 28 ^c (Particulates)
Naphtalene	—	—	—
Methylnaphtalene	—	—	—
Biphenyl	—	—	—
Dibenzofurane	—	—	—
Fluorene	—	—	—
9-Methylfluorene	—	—	—
2-Methylfluorene	—	—	—
1-Methylfluorene	—	—	—
Dibenzothiophene	—	258.8	—
Phenantrene	—	36.2	60.4
Anthracene	—	—	—
Carbazole	—	29.7	—
Methylphenanthrene	—	—	—
Methylanthracene	—	12.9	—
Fluoranthene	1.5	648.7	188.3
Dihydrobenzo(a&b)fluorene	—	—	—
Pyrene	1.4	550.7	163.0
Benzo(a)fluorene	—	160.2	39.0
Benzo(b)fluorene	—	78.2	8.3
1-Methylpyrene	—	47.7	10.9
Benzo(c)phenanthrene	—	77.3	45.2
Benz(a)anthracene	2.5	125.2	64.2
Chrysene/triphenylene	7.1	251.3	96.9
Benzo(b&k)fluoranthene	12.1	122.5	68.0
Benzo(e)pyrene	4.6	116.7	50.2
Benzo(a)pyrene	3.4	116.3	53.7
Perylene	—	34.1	16.5
o-Phenylene pyrene	2.3	56.7	32.7
Benzo(ghi)perylene	2.8	54.0	29.5
Anthanthrene	—	—	—
Coronene	—	13.3	—
Dibenzopyrene	—	—	—
Total PAH	37.7	2790.5	926.8

a Air volume 0.33 m³; job type, tapper.

b Air volume 0.50 m³; job type, pin puller.

c Air volume approx. 0.78 m³; job type, pin puller.

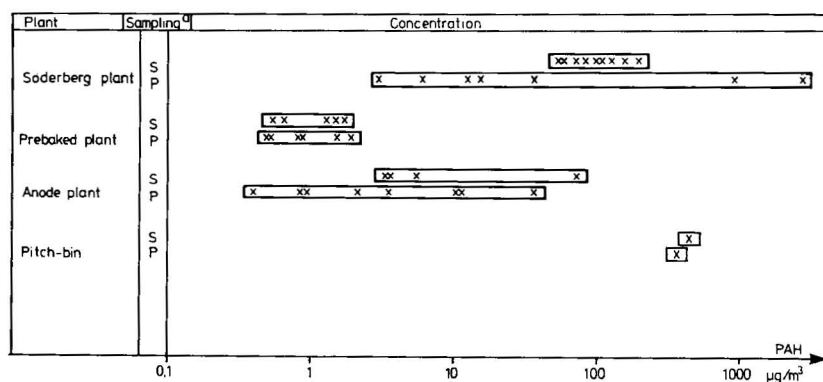


Fig. 3. Polycyclic aromatic hydrocarbons in particulate matter collected by personal and stationary sampling as a function of the sampling sites.

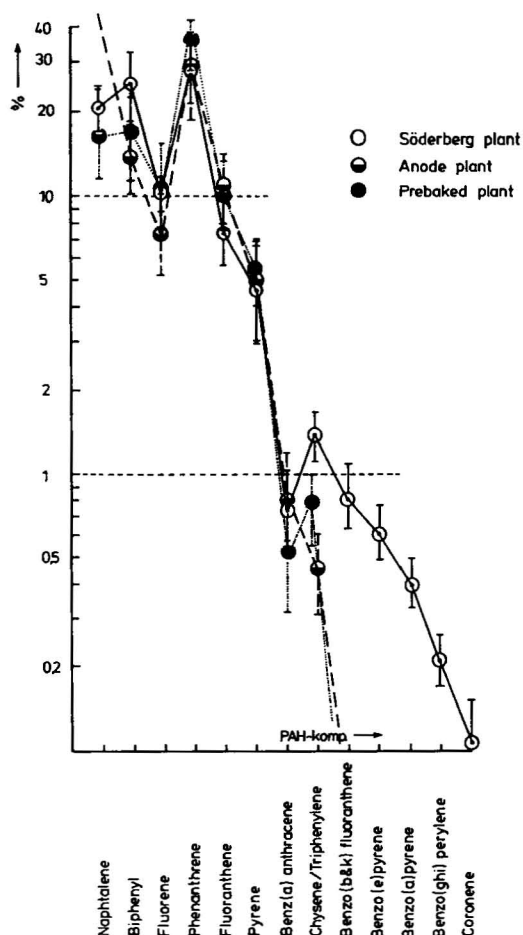


Fig. 4. Profiles of polycyclic aromatic hydrocarbons in the anode baking, prebaked, and Søderberg plants.

hazard of PAH in this environment is evaluated.

In the anode baking plant (samples 1 to 4), the average concentrations of PAH (stationary sampling) were determined to be 0.004 mg/m^3 in particulate materials. A maximum value of 0.07 mg/m^3 was determined in a sample from the atmosphere above the anode press (sample 5). The personal samplers in this plant gave concentrations of $0.01\text{--}0.4 \text{ mg/m}^3$.

In the anode paste plant there are two jobs with particularly high exposure risk, i.e., coke packing and working in the pitch bin. The coke packer had a concentration of 0.037 mg/m^3 PAH. In the pitch bin, both

stationary and personal sampling gave PAH concentrations on the order of 0.4 mg/m^3 in the particulate matter.

A recent paper by Jackson et al. (6) reported on BaP levels in a coke oven plant of $1.8 \text{ } \mu\text{g/m}^3$. In our study we observed values of $0.02\text{--}0.05 \text{ } \mu\text{g/m}^3$ in the prebaked potroom, $0.7\text{--}9.0 \text{ } \mu\text{g/m}^3$ in the Søderberg potroom, and $0.03\text{--}0.3 \text{ } \mu\text{g/m}^3$ in the anode plant, all values for stationary sampling. As expected, a lower PAH content was found in the potroom atmosphere of a prebaked plant in comparison to that of the vertical pin Søderberg plant.

A schematic listing of all the samples of PAH in particulate matter in the personal and stationary sampling as a function of sites is given in fig. 3. As expected, the personal samples show more scattered values than do the stationary ones, probably due to the fact that the oven control is performed only occasionally, and hence the exposure varies, and in addition different job situations involve different levels of exposure.

In order to compare the analytical results from the different work atmospheres, we utilized the concept of PAH profiles (4). We constructed the PAH profile by plotting the relative distribution of selected PAH components in the order of elution from the gas chromatographs. It has previously been postulated that the PAH profile is a characteristic of the process involved, i.e., the basic composition of the organic material, redox conditions, and reaction temperature. In fig. 4, the PAH profiles of the particulate matter in the work atmospheres in the three plants are depicted. As revealed in the figure the PAH profiles of the prebaked and anode baking plants are relatively parallel. Since these processes essentially use the same carbon material to approximately the same temperature, the results support the idea that the profile is a characteristic of the PAH source. The Søderberg plant, which has a different process, also gave a different PAH profile (fig. 4). In this case, a significant higher fraction of the PAH belonged to the high-boiling compounds than was shown for the anode prebaked plants.

The PAH profile is important for several reasons. If the profile is fairly constant

with time, the monitoring of PAH can be simplified, since indicator substances [like benzo(a)pyrene] can be used. Determination of the total amount of PAH is also more meaningful when the profile is known. Finally, there are some indications that the carcinogenic activity is a function of molecular size (1) and that the PAH profile may be used for the evaluation of potential PAH hazards in work atmospheres.

Additional studies of PAH in different branches of the electrochemical and other industries are in progress.

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