

Determination of Polycyclic Aromatic Hydrocarbons, Azaarenes, and Thiaarenes Emitted from Coal-Fired Residential Furnaces by Gas Chromatography/Mass Spectrometry

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Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen, Azaarenen und Thiaarenen in der Emission von Kohle-beheizten Haushaltöfen — Bestandsaufnahme durch GC/MS

Zusammenfassung. Da die krebserzeugende Wirkung von Emissionen aus Steinkohlebrikett-beheizten Zimmeröfen nahezu vollständig durch die im Kondensat enthaltene polycyclischen aromatischen Verbindungen (PAC) mit mehr als 3 Ringen verursacht wird, wurde die Zusammensetzung dieser PAC-Fraktion untersucht.

Mehr als 170 neutrale [111 polycyclische aromatische Kohlenwasserstoffe (PAH), 57 Thiaarene, 6 Oxaarene] sowie 70 basische Verbindungen (Azaarene) konnten mit der GC/MS-Kombination als PAC charakterisiert werden (Nachweisgrenze 0,1 mg/kg Brikett). Etwa 80 Verbindungen wurden durch den Vergleich mit Referenzsubstanzen identifiziert. Um in einigen zweifelhaften Fällen die Identität der isolierten mit der synthetischen Verbindung zu bestätigen, wurden bei 11 PAH mit einem Molgewicht von 302 zusätzlich auch UV- und Fluoreszenzspektren verglichen [Naphtho(1,2-k)fluoranthren, Dibenz(e,k)acephenanthrylen, Naphth(2,3-e)acephenanthrylen, Naphtho(2,3-k)fluoranthren, Dibenzo(de,qr)naphthacen, Coronen, Dibenzo(fg,op)naphthacen, Naphtho(1,2,3,4-def)chrysen, Benzo(b)perylene, Dibenzo(def,j)chrysen, Benzo(rst)pentaphen]. Diese Verbindungen sind von besonderem Interesse, da PAC mit 6 und mehr Ringen im Tierversuch etwa 50% der carcinogenen Wirkung des Steinkohlebrikett-Emissionskondensates verursachen.

Summary. Since the carcinogenic effect of emissions from hard coal briquet-fired furnaces is almost entirely caused by polycyclic aromatic compounds (PAC) with more than three rings, the composition of this fraction has been analyzed in detail.

More than 170 neutral [111 polycyclic aromatic hydrocarbons (PAH), 57 thiaarenes, 6 oxaarenes] and 70 basic (azaarenes) compounds were characterized as PAC by means of GC/MS (limit of detection 0.1 mg/kg briquet). About 80 compounds were identified by comparison with reference standards. In order to obtain unequivocal evidence for the identification of 11 PAH with a molecular weight of 302, the UV- and fluorescence spectra were compared with those of the synthesized reference compounds [naphtho(1,2-k)fluoranthene, dibenz(e,k)acephenanthrylene, naphth-(2,3-e)acephenanthrylene, naphtho(2,3-k)fluoranthene, dibenzo-

(de,qr)naphthacene, coronene, dibenzo(fg,op)naphthacene, naphtho(1,2,3,4-def)chrysen, benzo(b)perylene, dibenzo(-def,j)chrysen, benzo(rst)pentaphene]. In case of the emission condensate from hard coal briquets, PAC containing 6 and more rings cause about 50% of the carcinogenic effect in animal experiments.

Introduction

The condensate emitted from hard coal-fired residential furnaces provoke local tumors, exhibiting a clear dose-response relationship after repeated application to the dorsal skin of mice [1]. To identify the substances chiefly responsible for the carcinogenic effect of this emission, the condensate was separated into a fraction free of polycyclic aromatic compounds (PAC) and into various PAC-containing fractions. The carcinogenic potency of all these fractions have been compared with that of the unseparated sample of the emission condensate by testing them in different doses onto the dorsal skin of mice. It should be noted that the fraction of PAC consisting of more than 3 rings account for almost the total carcinogenicity [1]. Subfractions containing polycyclic aromatic hydrocarbons (PAH), thiaarenes (S-PAC) and oxaarenes (O-PAC) with 4 and 5 rings as well as 6 and more rings were almost equally active, each contributing by about 50% to the total carcinogenicity [2], whereas the subfraction containing azaarenes (N-PAC) and nitroarenes (NO₂-PAH) accounted for only 4–7% of the total carcinomas. In contrast to these carcinogenic fractions, the PAC-free fraction and that containing PAC with 2 and 3 rings (together about 77% by wt) were almost inactive.

Consequently, the objective of this investigation was to identify or to characterize PAH and their nitrogen-, sulfur-, and oxygen-containing heterocyclic analogues (N-PAC; S-PAC; O-PAC) occurring in hard coal briquets emission condensate which was used for the animal experiments [1, 2].

In Germany as well as in other countries, most of the air suspended PAC originate from coal-fired residential furnaces, coke plants or gasoline- and diesel-driven vehicles, whereas oil- and gas-fired heatings as well as coal-fired power plants contribute only very small amounts to the air pollution by PAC. A comparison of the benzo(a)pyrene emission from 5 sources (in total 18 t during 1981) shows that about 56% of the benzo(a)pyrene results from coal-fired residential

furnaces and minor consumers, whereas coke production and passenger cars contribute by about 31% and 13% to the total amount. In contrast to that, coal-fired power plants and residential oil heatings contribute by only 0.006 and 0.1%, respectively [3]. This confirms a previous investigation [4, 5] in which the PAC-mass concentrations were monitored during 50 weeks in various areas of a city (Essen, FRG). The areas characterized predominantly by domestic coal heatings, coke oven, or automobile traffic (tunnel) showed by far the highest PAC-concentrations, in contrast to the low concentration of the oil-heating area. The PAC-profile analysis from the oil-heating area exhibited a better correlation with coal emission sources than with oil, which indicates that less than one third of the PAC-concentration in this area originates from oil-heatings [4, 5].

The PAH-emissions from hard coal- or hard coal briquet-fired residential furnaces were investigated by various authors [6–15]. The PAH-mass concentration in the flue gas varies widely, depending on the nature of coal e.g. anthracite nuts, bitumen- or pitch-pound hard coal briquets, broken coke and other special coals. The mass emission of benzo(a)pyrene and other PAH varies under comparable operation conditions and furnaces, the average values were found for anthracite nuts (0.04 mg/kg), for hard coal briquets (2.8–4.5 mg/kg), and for brown coal briquets (3.0–4.2 mg/kg) [3, 16]. It furthermore depends on the type of residential furnace, such as slow combustion stove (Durchbrandofen) and Universal slow combustion stove (Universaldauerbrenner) [3] as well as on the operating conditions (full, medium or low load) regulated by the air input [17].

Moreover, the kind of binder for the hard coal briquets significantly influences the PAC-mass emission. Using the most popular type of slow burning residential furnace in Germany (Durchbrandofen), the pitch-bound briquets produce about 200 mg benzo(a)pyrene (BaP) per kg in contrast to bitumen-bound briquets manufactured from the same hard coal, emitting only about 5 mg BaP/kg burned under the same operation conditions (DIN 18890) [15]. This confirms the results of Beine [6] who reported an emission of 380 mg BaP/kg for pitch-bound hard coal briquets. Since the federal regulation for prevention of emissions (Verordnung über Feuerungsanlagen, I. BImSchV) became effective in 1974, the production of pitch-bound briquets was stopped.

In contrast to brown coal-fired residential furnaces [17], no data on the total profile of the flue gas particle-bound PAC emitted by hard coal-fired residential stoves are available.

In the flue gas, the equilibrium between particle-bound and gaseous PAC depends on the temperature. At outdoor temperatures the PAH with more than 3 rings are predominantly bound to particles. Therefore, PAC with boiling points below 400°C (fluorene, phenanthrene, anthracene, fluoranthene, pyrene and their methyl derivatives) are incompletely collected on particulate filters such as silicone-bound glass fibre filters. On the other hand, these low boiling compounds re-evaporate readily from the filter, when trapping particulates by high volume air samplers operating with high-flow air stream velocities. Furthermore, the reactivity of various PAC, such as benz(a)anthracene, benzo(a)pyrene, anthanthrene, and cyclopenta(cd)pyrene already trapped on the filter, has to be taken into account, e.g. the destruction by UV-light, oxidation (SO_3 , O_3) and

nitration (NO_x). To perceive both effects, the chemical destruction of various PAC on the particle filter and the re-evaporation of already collected compounds, two criteria can be used:

- Reproducibility of the sampling process: with identical mass streams per hour or simultaneous sampling using two different filter systems at the same location, the collection of PAC must result in identical profiles and in the same masses.

- Invariability of the PAC profiles during various sampling periods: variability of the PAC profile is a criterion for destruction and/or blow-off of the PAC already trapped on the filter due to instability or volatility of certain individual compounds [16].

The collection arrangement applied for this investigation meets these requirements [15, 17].

Experimental Section

Collection System

The condensate of the emission during combustion of hard coal briquets (RA-briquets, 24 g, Sophia-Jacoba, in total 3.66 kg) was obtained from Bergbau-Forschung GmbH, Essen, FRG. The nominal operation output of the slow combustion furnace (Franck'sche Eisenwerke AG, Dillenburg, FRG; Durchbrandofen type Oranier 4312 DB) was 20.93 MJ/h, 5.8 kW, respectively. The furnace is connected with a smoke stack, 4.2 m in length and terminates in a change-over flap. The total testbench comprising furnace and the collection arrangement has been published previously [15]. The collecting system consisting of a glass cooler and a glass fibre filter (area ca. 1 m², Drägerwerk AG, Lübeck, FRG; type WB 50) separates all PAC with boiling points above 380°C (collection efficiency for particles of 0.3–0.5 µm was 99.998%). The repeatability of the trapping procedure was checked in separate experiments [15, 17]. The experimental conditions were in accordance with the regulation of DIN 18890. First, the basic glowing fire was prepared and continued for 2.5 h under full load operation conditions to standardize the state of the test-bench. During this time, the flue gas was directly released to the atmosphere.

For the main experiment the glowing fire was stoked, then the coal filled in (3.66 kg), and finally the flue gas led onto the collecting system by switching the change-over flap. The flue gas passed the glass cooler (25°C) and subsequently two parallel arranged filters (Micronfilter WB 50) followed by a control filter of the same type. The volume of the flue gas re-heated to 45°C was measured and the concentrations of O_2 , CO_2 , CO , NO_x , SO_2 and C_nC_m were determined. Furthermore, sub-atmospheric pressure was obtained by means of an automatic blower. Details on the concentration of the above flue gases have been reported elsewhere [15].

The condensate consisted of three parts: (a) particulate filter on the micron filter, (b) acetone glass cooler rinsing, and (c) condensed water originating from the combustion, which contains only very small amounts of PAC.

For the animal experiments [1, 2] the condensates of three operations 3 × 3.66 kg fuel) were used.

Methods

A small part of the condensate and the fractions (about 1%) used for the bioassay or alternatively, one thirtieth of the

glass fibre filter from a separate experiment were required for the analytical procedure.

Extraction. 1/30 of the filter (6 ribs out of 180) was extracted twice with boiling toluene (300 ml) for 30 min (with or without internal standard) and the extract separated from particles by filtration. The particles were extracted again with methanol and aqueous ammonia (pH 10) and then filtered again. The combined solutions were evaporated by a rotary evaporator under reduced pressure (bath temperature 35°C).

Liquid-Liquid Partition. The residue dissolved in cyclohexane was extracted by methanol and aqueous ammonia (0.1 N) (1 + 1) and washed with water. The cyclohexane phase was evaporated to about 10 ml, isopropanol (30 ml) added and evaporated again to about 5 ml.

Chromatography on Sephadex LH 20. The solution (5 ml) of the liquid-liquid partition was transferred to a Sephadex LH 20 column (50 g) and the non-aromatic compounds together with the PAC with 2 rings were eluted with isopropanol (175 ml). This fraction was discarded. PAC with more than two rings were eluted with acetone (500 ml). The solvent was evaporated to few milliliters and then a mixture of methanol and benzene (5 + 1, 20 ml) was added. Finally this solution was evaporated to 5 ml.

Separation by SP-Sephadex C 25. SP-Sephadex C 25 (8 g) was activated with aqueous hydrochloric acid (0.05 N, 400 ml) and subsequently washed with methanol/water (1 + 1, 500 ml) and methanol (500 ml).

The methanol/benzene concentrate from the chromatography on Sephadex LH 20 was transferred to the column and the neutral PAC (PAH, S-PAC, O-PAC) were eluted with methanol (400 ml). Basic compounds (azaarenes) were eluted with a solution of ammonium chloride (5 N), aqueous ammonia (2.5 N), and methanol (3 + 2 + 5, 300 ml) and this solution after dilution with water (300 ml) was extracted with cyclohexane (600 ml).

Chromatography on Silica Gel. The methanol residue from the separation by SP-Sephadex C 25 containing the neutral PAC was dissolved in cyclohexane (3 ml) and chromatographed on silica gel (10 g, 10% water content) by elution with cyclohexane (200 ml).

Fractionation of PAC with 3 and more Rings on Sephadex LH 20. To facilitate the interpretation of the capillary gas chromatographic and mass spectrometric results, the neutral PAC (PAH, S-PAC, O-PAC) were separated by Sephadex LH 20 (50 g) as described above, using isopropanol (190–385 ml for PAC with 3–5 rings; 385–1,000 ml for PAC with more than 5 rings) and acetone (500 ml, for high condensed PAC).

Isolation of S-PAC. To facilitate the interpretation of the gas chromatographic and mass spectrometric data of the S-PAC, one part of the neutral PAC fraction from the separation by SP-Sephadex C 25 was oxidized. The resulting thiaarenesulfones were then separated from the non-polar PAH and O-PAC. — To this end the neutral fraction was dissolved in benzene, pure acetic acid and H₂O₂ (30%) (5 + 5 + 1), refluxed for 5 h, and subsequently diluted with

water (1 + 1). The benzene phase was collected, the aqueous phase extracted twice with dichloromethane and both phases washed with water before evaporation.

Separation of the S-PAC from the PAC-Mixture. The combined residues of both phases, dissolved in cyclohexane were transferred to a silica gel column (5 g, 10% water content), the PAH were eluted with cyclohexane (80 ml) and the thiaarenesulfones with a methanol-benzene mixture (1 + 1, 80 ml). To the residue of the methanol-benzene mixture dissolved in ether-benzene (4 + 1), LiAlH₄ (500 mg) was added and the mixture refluxed for 3 h, avoiding contact to air. Thiaarenes were then extracted with benzene, evaporated, the residue dissolved in cyclohexane, and transferred to a silica gel column (5 g, 10% water content) and the S-PAC eluted with cyclohexane (80 ml).

Further purification of the N-PAC as well as the S-PAC for capillary gas chromatography was carried out by chromatography on Sephadex LH 20 (10 g) with isopropanol (0–38 ml discarded; 38–200 ml collected).

Conditions for Gas Chromatography. Apparatus: Perkin-Elmer, model Sigma 2B. Columns: fused silica column 25 m × 0.32 mm coated with methyl(94%)-phenyl(5%)-vinyl(1%)-polysiloxane (SE 54, Oribond). Carrier gas: Helium 2 ml/min. Splitless injected at 115°C, split opened after 5 min; 6 min at 115°C followed by a 115°C–180°C with 30°C/min, subsequently 180°C–270°C with 3°C/min temperature program (for S-PAC), then isothermally; 115°C–160°C with 30°C/min, subsequently 160°C–270°C with 3°C/min (for N-PAC). Integrator: SES GmbH, model Trilab 2002.

Conditions of Mass Spectrometry. Apparatus (PAH, S-PAC, O-PAC): Finnigan MAT GC/MS, model 5100 with fused

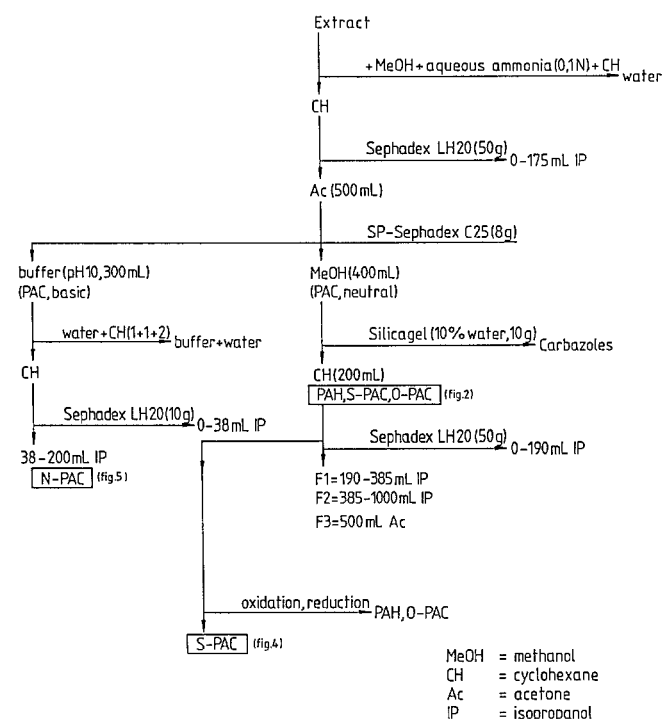


Fig. 1. Scheme of enrichment of PAH, S-PAC, O-PAC, and N-PAC

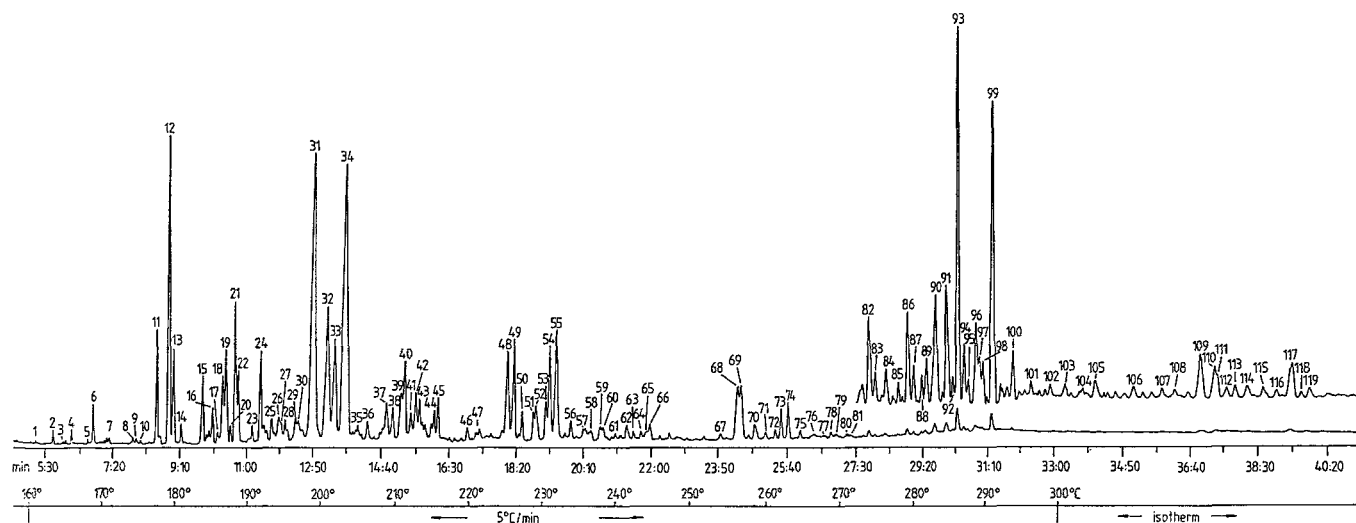


Fig. 2. Fraction of neutral PAC (PAH, S-PAC, O-PAC) of the emission from briquet-fired furnaces recorded as total ion current. Numbers correspond to those of Table 1. GC/MS conditions see "Methods"

Table 1. Identification and characterization of polycyclic aromatic compounds from coal emission condensate

No.	Mass	Compound	mg/kg fuel
1	154	Biphenyl	0.152
2	152	Acenaphthylene	0.427
3	153	n.i.	0.142
4	168	Dibenzofuran	0.475
5	166	Phenylene	0.190
6	166	Fluorene	1.045
7	182	Methyldibenzofuran	0.237
8	180	Methylfluorene	0.261
9	184	S-PAC	0.226
10	182	Methyldibenzofuran	0.190
11	184	Dibenzothiophene	2.778
12	178	Phenanthrene	3.984
13	178	Anthracene	2.113
	198	Methyldibenzothiophene(tr)	
14	184	Naphthothiophene	0.450
15	198	Methyldibenzothiophene	1.867
	192	O-PAC(tr)	
16	198	Methyldibenzothiophene	1.030
17	198	Methyldibenzothiophene	0.228
18	204	1-Phenyl-naphthalene	2.033
	198	Methyldibenzothiophene(tr)	
	210	n.i.(tr)	
19	192	2-Methylphenanthrene	2.767
20	192	2-Methylantracene	0.453
21	190	4,5-Methylenphenanthrene	4.146
	192	4-Methylphenanthrene	
	192	9-Methylphenanthrene	
22	192	1-Methylphenanthrene	2.217
23	212	Dimethyldibenzothiophene	0.633
24	204	2-Phenyl-naphthalene	2.735
	212	Dimethyldibenzothiophene	
25	212	Dimethyldibenzothiophene	1.060
26	212	Dimethyldibenzothiophene	0.398
27	212	Dimethyldibenzothiophene	0.331
28	206	2,7-Dimethylphenanthrene	0.370
	212	Dimethyldibenzothiophene	
29	204	n.i.	0.398
30	206	Dimethyl-178	0.345
31	202	Fluoranthene	28.357
	208	S-PAC(tr)	
32	202	Acphenanthrylene	9.612
	208	S-PAC	

Table 1 (continued)

No.	Mass	Compound	mg/kg fuel
33	208	Phenanthro(4,5-bcd)thiophene	5.466
34	202	Pyrene	26.589
35	218	Benzo(b)naphtho(2,1-d)furan	0.349
36	218	Benzo(b)naphtho(1,2-d)furan	0.413
37	216	2-Methylfluoranthene	0.731
38	222	S-PAC, methyl-208	0.635
39	222	S-PAC, methyl-208	0.858
40	216	Benzo(a)fluorene	1.366
41	216	Methyl-202	0.572
42	216	Benzo(b)fluorene	0.874
	216	Benzo(c)fluorene	
43	222	Methyl-208	0.762
44	216	4-Methylpyrene	1.487
45	216	1-Methylpyrene	2.065
46	240	S2-PAC	0.768
47	236	S-PAC, dimethyl-208	0.725
48	234	Benzo(b)naphtho(2,1-d)thiophene	6.744
49	226	Benzo(ghi)fluoranthene	3.323
	228	Benzo(c)phenanthrene	2.215
50	234	Benzo(b)naphtho(1,2-d)thiophene	2.291
51	240	S2-PAC	2.309
52	234	Benzo(b)naphtho(2,3-d)thiophene	2.694
53	226	Cyclopenta(cd)pyrene	3.590
54	228	Benz(a)anthracene	7.181
55	228	Chrysene	9.571
	228	Triphenylene	
56	248	S-PAC, methyl-234	1.674
57	248	S-PAC, methyl-234	2.383
58	248	S-PAC, methyl-234	0.993
59	242	Methyl-228	0.200
60	248	S-PAC, methyl-234	0.146
61	248	S-PAC, methyl-234	0.832
62	242	3-Methylchrysene	1.167
	240	Methyl-226	
	248	S-PAC, methyl-234	
63	242	6-Methylchrysene	0.826
64	242	5-Methylchrysene	1.047
	262	S-PAC, methyl-234 (tr)	
65	260	S-PAC	1.053
66	240	Methylen-228	1.880
	242	1-Methylchrysene	
67	258	S-PAC	0.782

Table 1 (continued)

No.	Mass	Compound	mg/kg fuel
68	252	Benzo(b)fluoranthene	6.102
69	252	Benzo(j)fluoranthene	6.782
	252	Benzo(k)fluoranthene	
	258	S-PAC	
70	252	Benzo(a)fluoranthene	1.878
71	258	Triphenyleno(4,5-bcd)thiophene	0.978
72	258	S-PAC	1.252
	252	Benz(e)aceanthrylene(tr)	
	252	Benz(j)aceanthrylene(tr)	
73	252	Benzo(e)pyrene	3.994
74	252	Benzo(a)pyrene	4.303
75	252	Perylene	1.134
	272	S-PAC, methyl-258 (tr)	
76	266	Methyl-252	0.743
	272	S-PAC, methyl-258 (tr)	
77	264	Methylen-252	0.430
	272	S-PAC, methyl-258 (tr)	
78	266	Methyl-252	0.900
79	266	Methyl-252	0.626
80	266	Methyl-252	0.704
	278	PAH (parent)	
81	266	Methyl-252	0.469
82	264	Methylene-252	1.090
	290	n.i.	
	266	Methyl-252(tr)	
83	278	n.i.	0.424
	266	Methyl-252	
84	264	Methylene-252	0.454
	290	S2-PAC	
85	290	S2-PAC	0.293
86	290	S2-PAC	1.137
	284	Dinaphthothiophene	
87	290	S2-PAC	0.492
	278	Naphth(1,2-a)anthracene	
88	276	Indeno(1,2,3-cd)fluoranthene	0.378
89	284	Dinaphthothiophene	0.581
	278	PAH (parent)	
90	276	PAH (parent)	0.341
	284	Dinaphthothiophene	
91	276	Dibenzo(k,mno)fluoranthene	1.451
92	284	Dinaphthothiophene	0.344
93	276	Indeno(1,2,3-cd)pyrene	4.600
	304	n.i.	
94	278	Dibenz(a,c)anthracene	0.738
	278	Dibenz(a,h)anthracene	
95	278	Pentaphene	0.306
96	278	Benzo(b)chrysene	0.997
97	282	S2-PAC	0.581
98	278	Picene	0.518
	278	Benzo(a)naphthacene	
99	276	Benzo(ghi)perylene	3.855
100	276	Anthanthrene	0.665
101	290	Methyl-276	0.288
	302	PAH (parent)	
102	290	Methyl-276	0.244
	304	n.i.	
103	290	Methyl-276	0.240
104	291	N-PAC	0.182
	296	S-PAC, methyl-282	
	304	n.i.	
	310	Tetrahydrodimethylpicene	
105	288	Methylene-276	0.279
	312	S-PAC	
	332	S-PAC	
106	308	S-PAC	0.208
	328	n.i.	
107	314	S-PAC (284)	0.175
	300	PAH (parent)	

Table 1 (continued)

No.	Mass	Compound	mg/kg fuel
108	314	S-PAC (284)	0.157
	308	S-PAC	
109	302	Naphtho(1,2-k)fluoranthene + 3 isomers	0.609
110	308	S-PAC	0.448
111	302	Dibenz(e,k)acephenanthrylene	0.349
	302	Naphth(2,3-e)acephenanthrylene	
112	302	PAH (parent)	0.179
	314	S-PAC	
113	300	PAH300A ^a	0.206
	302	Naphtho(2,3-k)fluoranthene	
114	300	PAH (parent)	0.220
	308	S-PAC	
115	306	PAH (parent)	0.179
	328	n.i.	
116	302	Dibenzo(de,qr)naphthacene	0.085
117	300	Coronene	1.898
	300	PAH (parent)	
118	302	Dibenzo(fg,op)naphthacene	0.103
	302	Naphtho(1,2,3,4-def)chrysene	
119	302	Benzo(b)perylene	0.143
	302	Dibenzo(def,j)chrysene	
	302	Benzo(rst)pentaphene	

^a Detected also in automobile exhaust [18]

As can be seen from the table, in various cases peaks listed under one number consist of more than one compound

silica column 30 m × 0.25 mm methyl(95%)-phenyl(5%)-polysiloxane (SE 54). The capillary column was connected directly with the electron-impact ion source (70 eV, 200°C). Apparatus (N-PAC): Varian MAT, model 112S. The gas chromatograph of this model is replaced by one from Perkin-Elmer, model F 22 with fused silica column 60 m × 0.32 mm coated with polydimethylsiloxane (SE 30).

Figure 1 demonstrates the scheme of enrichment for PAH, S-PAC, O-PAC, and N-PAC.

Results and Discussion

On the basis of a detection limit of 0.1 mg/kg burned hard coal briquets, more than 170 neutral PAC were detected by GC/MS. Figure 2 shows the gas chromatogram of this fraction which consists of PAH, S-PAC, and O-PAC recorded as total ion current.

The identification and quantitative composition of this PAC-mixture is presented in Table 1. 74 Compounds named in Table 1 were identified by comparing their GC-retention times and their mass spectrometric fragmentation with those of reference standards.

To confirm the identification in some cases eleven out of these compounds with molecular weights of 300/302 were characterized also by UV and fluorescence spectrometry [19]. To isolate these compounds from the condensate, the fraction containing PAC with more than 3 rings was separated by vacuum sublimation (short distance distillation) under reduced pressure (10^{-8} bar) at 105°C during 6 h into volatile PAC of less than 5 rings (mass < 300), and into a non-volatile residue (mass ≥ 300). The latter, containing PAC with 6 and more rings, was separated by repeated high-

performance TLC on RP-18 plates using various solvents. This procedure resulted in 20 compounds. Subsequent chromatography by Sephadex LH 20 using isopropanol for elution, in some cases led to PAC in almost pure state as

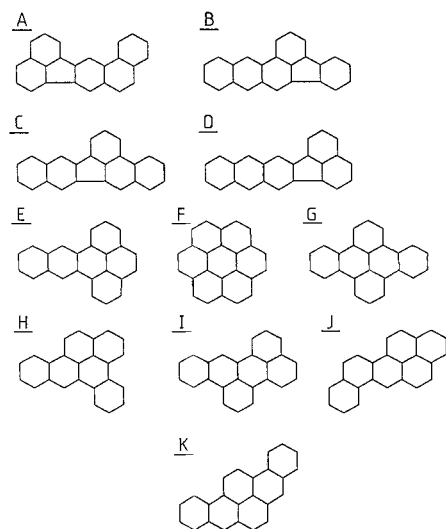


Fig. 3. **A** Naphtho(1,2-k)fluoranthene (No. 109, Table 1); **B** Dibenz(e,k)acephenanthrylene (naphtho(2,3-b)fluoranthene) (No. 111); **C** Naphth(2,3-e)acephenanthrylene (dibenzo(b,k)fluoranthene) (No. 111); **D** Naphtho(2,3-k)fluoranthene (No. 113); **E** Dibenzo(de,qr)naphthacene (naphtho(2,3-e)pyrene) (No. 116); **F** Coronene (No. 117); **G** Dibenzo(fg,op)naphthacene (dibenzo(e,1)-pyrene) (No. 118); **H** Naphtho(1,2,3,4-def)chrysene (dibenzo(a,e)-pyrene) (No. 118); **I** Benzo(b)perylene (dibenzo(fg,qr)naphthacene) (No. 119); **J** Dibenzo(def,j)chrysene (naphtho(2,1-a)pyrene) (No. 119); **K** Benzo(rst)pentaphene (dibenzo(a,i)pyrene) (No. 119)

indicated by GC, HPLC and UV analysis. Based on the GC retention times, mass-, UV-, and fluorescence spectra [19] in total eleven of these isolated PAH were found to be identical with reference PAH synthesized for this purpose. Their structures are presented in Fig. 3.

Five compounds with the mass of 300/302, although characterized by their UV- and fluorescence spectra, could not be positively identified due to the lack of reference materials.

To facilitate the interpretation of the gas chromatographic data, a part of the neutral PAC-containing fraction was oxidized and the resulting thiaarenesulfones were separated from the non-polar PAH and O-PAC. Subsequent

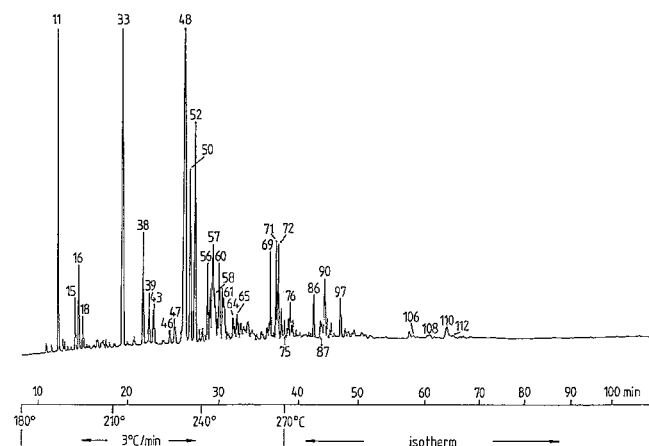


Fig. 4. Fraction of thiaarenes (S-PAC) separated from the neutral PAC (see Fig. 2). Numbers correspond to those of Table 1. GC-conditions see "Methods"

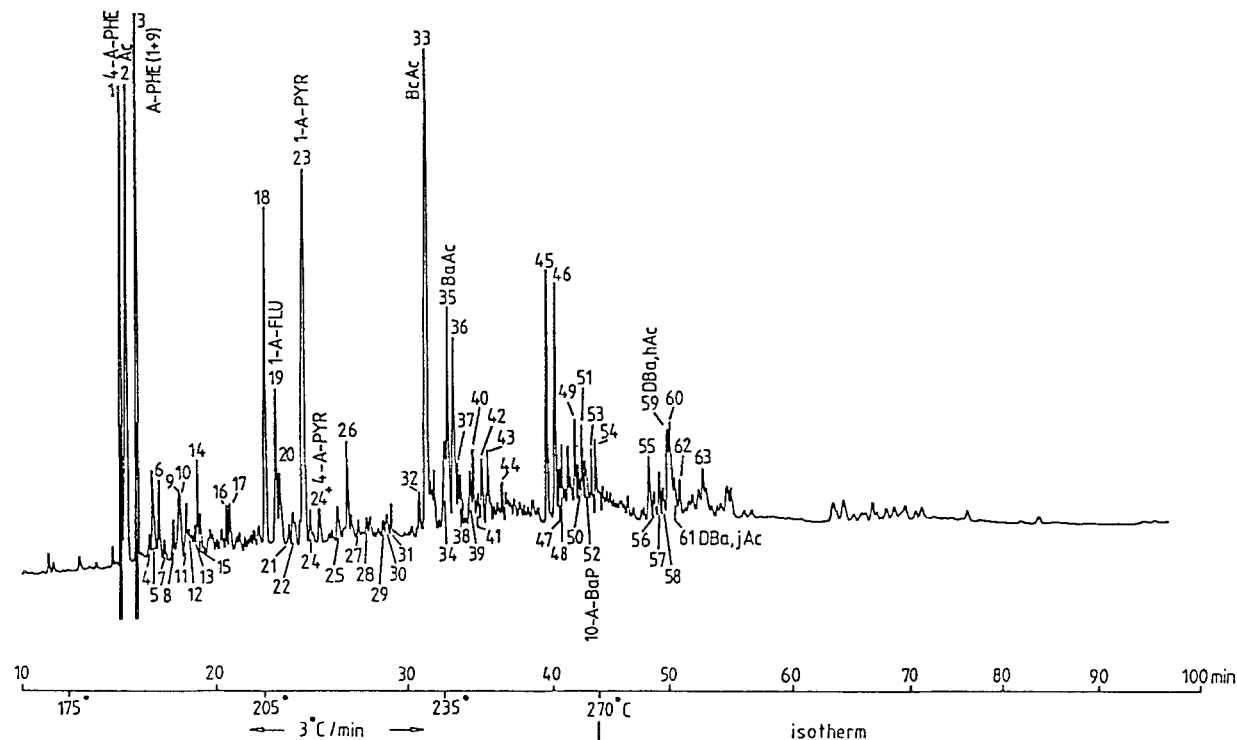


Fig. 5. Fraction of azaarenes (N-PAC) recorded by FID. Numbers correspond to those of Table 2. GC-conditions see "Methods"

Table 2. Identification and characterization of basic nitrogen containing polycyclic aromatic compounds from coal emission

No.	RT-min	Mass	Compound
1	15.23	179	4-Azaphenanthrene (Benzo(h)quinoline)
2	15.47	179	Acridine
3	16.10	179	1-Azaphenanthrene (Benzo(f)quinoline)
	16.10	179	9-Azaphenanthrene (Phenanthridine)
4	16.70	193	Methyl-179
5	16.87	179	Aza-178
6	17.23	193	Methyl-179
	17.23	199	n.i.
7	17.50	199	n.i.
8	17.93	193	Methyl-179
9	18.17	193	Methyl-179
10	18.33	193	Methyl-179
11	18.63	193	Methyl-179
12	18.83	193	Methyl-179
13	19.07	193	Methyl-179
14	19.20	193	Methyl-179
15	19.37	213	Methyl-199
16	20.77	213	Methyl-199
17	20.93	205	Aza-204
	20.93	207	Dimethyl-179
18	22.83	203	Aza-202
19	23.37	203	1-Azafluoranthene
20	23.57	203	Aza-202
21	24.03	219	Methyl-205
22	24.30	219	Methyl-205
23	24.93	203	1-Azapyrene
	24.93	219	Methyl-205
24	25.27	203	Aza-202
	25.27	217	Methyl-203
24A	25.73	203	4-Azapyrene
25	26.70	217	Methyl-203
26	27.20	217	Methyl-203
27	27.77	217	Methyl-203
28	28.20	217	Methyl-203
29	29.10	217	Methyl-203
30	29.30	217	Methyl-203
31	29.57	221	Dimethyl-203
32	31.13	235	n.i.
	31.13	221	Dimethyl-203
33	31.60	229	Benz(c)acridine
34	32.57	229	Azabenz(c)phenanthrene
35	32.77	229	Benz(a)acridine
36	33.10	229	Aza-228
37	33.27	229	Aza-228
38	33.47	229	Aza-228
39	33.93	227	Aza-226
40	34.13	229	Aza-228
41	34.40	229	Aza-228
42	34.60	243	Methyl-229
	34.60	249	n.i.
	34.60	255	n.i.
43	34.97	243	Methyl-229
44	36.15	243	Methyl-229
45	39.80	253	Aza-252
46	40.45	253	Aza-252
47	40.80	269	Methyl-255
48	41.00	253	Aza-252
49	42.05	269	Methyl-255
50	42.30	253	Aza-252
51	42.60	253	Aza-252
52	42.85	253	10-Azabenz(a)pyrene
53	43.35	267	Methyl-253
54	43.70	253	Aza-252
55	48.20	281	Dimethyl-253
56	48.65	285	n.i.
57	49.00	281	Dimethyl-253

Table 2. (continued)

No.	RT-min	Mass	Compound
58	49.30	277	Aza-276
59	49.70	279	Dibenz(a,h)acridine
60	49.90	277	Aza-276
61	50.25	279	Dibenz(a,j)acridine
62	50.75	279	Aza-278
63	52.60	279	Aza-278

AS can be seen from the table, in various cases peaks listed under one number consist of more than one compound

reduction resulted in the original S-PAC as presented in Fig. 4 (the numbering corresponds to that of Table 1).

As mentioned above, the subfraction containing PAH, S-PAC and O-PAC with 4 and 5 rings and that containing 6 and more rings were almost equally active, each contributing by about 50% to the total carcinogenicity of the emission condensate from coal briquet-fired furnaces [2]. All 4 ring-containing PAC as the majority of 5 ring compounds listed in Table 1, are volatile under the sublimation conditions (10^{-8} bar, 105°C , 6 h). Only 7% of the benzo(a)pyrene and 15% of the benzo(e)pyrene were found in the non-volatile residue. Overlapping appears in the range of indeno(1,2,3-cd)pyrene (No. 93, Table 1) and benzo(ghi)perylene (No. 99), which remain to 50% and 80% in the non-volatile part, respectively. The higher boiling PAC, such as dibenzofluoranthenes, dibenzopyrenes, coronene and their thiaarene-analogues remain entirely in this non-volatile fraction, and caused about half of the carcinogenicity of the total condensate when applied to the skin of mice.

The basic N-PAC (azaarenes) account for about 4–7% of the total carcinogenic activity of the emission condensate [1]. After separation by ion-exchange chromatography they were further analyzed by gas chromatography (Fig. 5) and mass spectrometry (Table 2).

The main constituents were structural analogues of PAH as found in the neutral fractions, namely azaphenanthrenes, azafluoranthenes, azapyrenes, benz(a)acridine, dibenz(a,h)acridine and others.

Under the sublimation conditions used most of the azaarenes were found in the volatile fraction and only very small amounts of them occur in the sublimation residue. Concentration of azaarenes consisting of more than 5 rings were below the detection limit.

Mass Spectrometry

The mass spectrometric identification (recorded at 70 eV) of the compounds listed in Table 1 is based on the following key fragments for PAH and hetero atoms containing PAC. A general discussion and a tabular presentation of the key-ions for characterization of unsubstituted and monomethyl-substituted PAH, thiophene- or furan-containing compounds has been published previously [20].

PAH and Methyl Derivatives. Both PAH and their methyl derivatives exhibit intense molecular ions (M^{+}) and the corresponding double-charged ions (M^{2+}). The parent PAH show intense $(M-2)^{+}$ - and $(M-26)^{+}$ -ions, whereas in monomethyl derivatives intense $(M-1)^{+}$, moderately intense

(M-3)⁺, but small (M-2)⁺-fragments are observed. The (M-26)⁺-ion is also shifted to (M-27)⁺ in methyl-PAH. Accordingly, the same intensity ratios are found for the double-charged ions with intense (M-1)²⁺ and (M-27)²⁺ in methyl-PAH. Under mass-spectrometric conditions compounds possessing 'fjord'-structures such as naphth(1,2-a)anthracene (No. 87a, Table 1) undergo further aromatisation giving rise to (M-2)⁺ which may exceed M⁺. Methylene-bridged structures such as fluorene (No. 6, Table 1), cyclopenta(def)phenanthrene (4,5-methylenephenanthrene, No. 21, Table 1), and the compounds deriving from base structures with masses 228, 252, and 276 (Nos. 66, 82, 84, and 105, Table 1) may be recognized from the ratio M⁺/(M-1)⁺ ≈ 1 and the corresponding intense (M-27)⁺ fragment.

S-PAC. According to the natural isotope ratio ³²S/³⁴S which is about 25:1, especially those with more than one S-atom (found among the higher mass S-PAC such as 282 (No. 97), 290 (Nos. 84a, 85, 86, 87, Table 1), 312 (No. 105a, Table 1), 314 (Nos. 107, 108, 112a, Table 1), and 332 (No. 105b, Table 1) may be recognized from the comparatively intense (M+2)⁺ ion. Highly indicative are the (M-32)- and (M-45)-fragments resulting from sulfur- and CHS-elimination. Double-charged ions M²⁺ and (M-45)²⁺ are also observed. As in the spectra of PAH, shifts by less one masses are found in the spectra of methyl derivatives of S-PAC: (M-1)⁺ becomes larger than (M-2)⁺, (M-33)⁺, and (M-46)⁺ are observed instead of (M-32)⁺ and (M-45)⁺.

Dimethyl-substitution results in an intense (M-15)-fragment the intensity of which increases with the number of methyl groups present in the molecule.

O-PAC. In Table 1 also some O-PAC are listed (Nos. 4, 7, 10, 15a, 35, 36) which were identified as dibenzofuran, benzonaphthofurans as well as their methyl derivatives on the basis of the (M-16)-, (M-29)- and (M-55)-fragments formed by elimination of oxygen, a CHO- and a $\square\text{CH}=\text{CH}-\text{O}-\text{CH}\square$ -group, respectively. Methyl substitution may be recognized from the ratio (M-1)⁺ > (M-2)⁺ and the occurrence of (M-17)- and (M-30)-fragments.

N-PAC. Odd-numbered parent peaks indicate the presence of nitrogen in the molecule. Elimination of nitrogen (M-14) is rarely observed; however, the elimination of CH=N or CH=NH resulting in intense (M-27)⁺ and (M-28)⁺ ions are common in N-PAC, often accompanied by a (M-29)-fragment. In addition, a (M-53)-fragment which result from the elimination of $\square\text{CH}=\text{N}-\text{CH}=\text{CH}\square$ is observed and which is analogous to the (M-55)-fragment in case of O-PAC. In methyl derivatives of O-PAC again the ratio (M-1)⁺ > (M-2)⁺ is found and (M-27)-, (M-29)- and (M-53)-fragments are shifted to (M-28), (M-30) and (M-54), respectively. A more detailed discussion of the mass spectra of azarenes has been published previously [21].

Apart from 70eV activation, for a preliminary characterization, mass spectra were also recorded at 15 eV in order to obtain the molecular ions exclusively.

In summary, it may be concluded that PAH, S-PAC, O-PAC, and N-PAC consisting of 4 and 5 rings as well as those of 6 and more rings, listed in Tables 1 and 2 each

contribute to about half of the total carcinogenicity found for the emission condensate of hard coal briquet-fired residential furnaces.

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