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POLYCYCLIC AROMATIC COMPOUNDS IN WOOD PRESERVATIVES DERIVED FROM COAL AND PETROLEUM

Five commercial coal tar oils (DB, B, GX, PO, MA) and an oil sample derived from petroleum (RPO) were investigated in this work. The contents of benzo[a]pyrene (B[a]P) and 13 other polycyclic aromatic compounds (PACs) were determined. According to today's legislation RPO, DB, B, and GX containing less than 500 mg/Kg B[a]P may be used as wood preservatives for railway sleepers and wood poles. By law it is prohibited to apply PO and MA for wood treatments in EU countries at all. The B[a]P content of creosotes and other aromatic oils could be decreased through distillation, but in that case the concentration of other PACs with lower boiling points and similar or even higher relative cancerogenic potencies compared to B[a]P could remain unchanged. For instance, RPO contains more B[a]P than DB, B, and GX, but reveals the lowest value of total B[a]P equivalents compared to other coal tar oils. Therefore, determination of total B[a]P equivalents, i. e. cancerogenic PACs in a given oil sample is much safer than that of B[a]P solely, as it has been regulated by legislation so far.

Coal tar oils, termed as "creosotes", have been employed over several hundreds years for the prevention of wood softening [1]. However, in recent years legislation concerning the protection of the environment has become more restrictive. Wood treatments with creosotes that contain more than 50 mg/Kg B[a]P are no longer permitted in the countries of the European Union, and wood treated with creosotes may not be placed on the market, except for the use of outdoor industrial installations. However, by the way of derogation creosotes with a B[a]P content up to 500 mg/Kg may be used as wood preservatives for railway sleepers and wood poles [2]. Recently, almost odourless creosotes containing no more than 50 mg/Kg B[a]P have been produced by correcting the boiling range and blending an aromatic extract derived from petroleum [3]. Taking all of that into account we investigated the B[a]P content of some commercial creosotes used for sleepers and poles in Southeast Europe, and compared these creosotes with an oil derived from petroleum. For that purpose we determined the content of fourteen individual polycyclic aromatic compounds (PACs), among them of course B[a]P, in five creosotes and in one oil derived from petroleum. We used the generally accepted and today already standardized method of HPLC-chromatography with a fluorescence detector [4, 5].

EXPERIMENTAL

Samples

DB, B, and GX represent creosotes produced in Germany by Ruetgers VFT AG.

PO and MA represent creosotes produced in Poland and Hungary, respectively.

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RPO represents an oil derived from petroleum produced in Serbia [6].

HPLC analysis

Column: Ultrasep ES PAK 6m (Fa. Sepserve) 250 mm x 3 mm, 30° C.

Detector: Shimadzu RF 551 (Fluorescence). The wavelengths of the excitation and emission of the fluorescence detector were 275 and 350 nm in the first 14 minutes; 260 and 420 nm between 14 and 22.5 minutes and 290 and 430 nm from 22.5 minutes till the end, i.e. 36 minutes, respectively.

Instrument: Gynkotek HPLC pump M480 with degaser; Autosampler Gynkotek Gina 50.

Solvents: Water (A) and Acetonitrile (B)

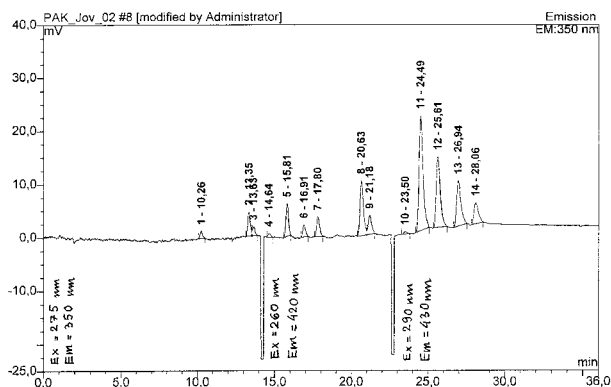
Flowrate: 0.8 mL/min

Gradient: Linear: 0', 40 % B; 25', 95 % B; 25-36', 95 % B

RESULTS

Fig. 1 shows the HPLC chromatogram of a mixture of fourteen PACs. The concentration of the individual PACs amounted to about 0.01 mg/L (except benzo[a,h]pyrene). The wavelengths of the excitation and emission of the fluorescence detector were 275 and 350 nm in the first 14 minutes, 260 and 420 nm between 14 and 22.5 minutes and 290 and 430 nm from 22.5 minutes till the end, i.e. 36 minutes, respectively. Of all PACs only acenaphthene, fluorene, benzo[a]anthracene and chrysene did not separate well. The intensities of peaks sufficed for a precise calculation of height and area. The area of the peaks was used for calibration. Benzo[a]pyrene and dibenzo[a,h]anthracene, known to have the highest cancerogenic potency, compared to other PACs, showed retention times of 25.61 and 26.94 minutes, respectively.

The calibration was accomplished with mixtures of PACs containing 0.01; 0.02; 0.05; and 0.2 mg/L of each of the fourteen PACs. Five parallel measurements were

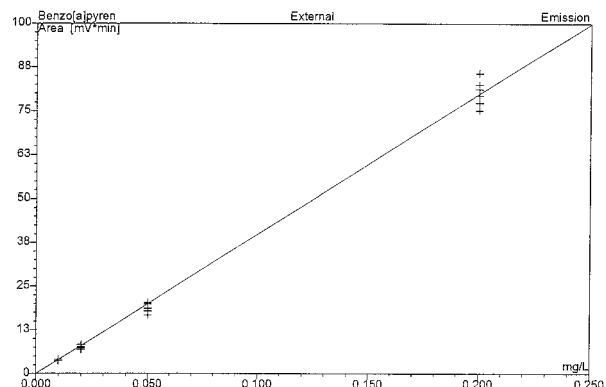


No	Ret. Time min	Peak Name	Height mV	Area mV·min	Rel. Area %	Amount mg/L
1	10.26	Naphthalene	1.437	0.260	1.16	0.009
2	13.35	Acenaphthene	4.491	0.854	3.82	0.010
3	13.63	Fluorene	1.587	0.292	1.31	0.011
4	14.64	Phenanthrene	0.761	0.153	0.68	0.014
5	15.81	Anthracene	6.089	1.139	5.10	0.009
6	16.91	Fluoranthene	2.264	0.480	2.15	0.010
7	17.80	Pyrene	3.729	0.853	3.82	0.011
8	20.63	Benzo[a]anthracene	10.358	2.708	12.12	0.011
9	21.18	Chrysene	3.504	0.903	4.04	0.010
10	23.50	Perylene	0.424	0.090	0.40	0.009
11	24.50	Benzo[k]fluoranthene	21.679	6.506	29.12	0.009
12	25.61	Benzo[a]pyrene	13.300	4.043	18.10	0.010
13	26.94	Dibenzo[a,h]-anthracene	8.531	2.766	12.38	0.021
14	28.06	Benzo[g,h,i]-perylene	3.943	1.298	5.81	0.008
Total:			82.098	22.344	100.00	0.154

Figure 1. HPLC–chromatogram of the PAC–mixture (0.01 mg/L) and table with corresponding results

performed for each mixture. Fig. 2 gives all data employed for the calibration. The relative standard deviation ranged between 5 and 8 % except for fluorene, phenanthrene and dibenzo[a,h]anthracene. The calibration curve given in Fig. 2 was used to determine the B[a]P content of investigated samples.

Figures 3 and 4 illustrate the HPLC chromatograms of DB and RPO. To determine the concentration of lower molecular weight PACs in DB with retention times up to 20 minutes, the sample had to be diluted 1:10 or 1:100 (Fig. 3). RPO derived from petroleum had to be diluted in order to determine the content of PACs with shorter retention times, i. e. lower than 14 minutes (Fig. 4). The height and area of the B[a]P peak of the RPO sample was comparable to those of the DB sample, as well as the concentrations of the samples in acetonitrile (443 and 475 mg/L, respectively). Therefore, the RPO and DB

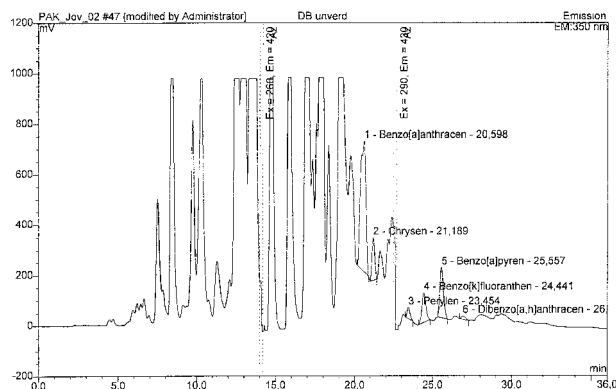


No	Ret. Time min	Peak Name	Cal. Time	Points	Corr. Coeff. %	Slope	Rel. Std. Dev. %
1	10.17	Naphthalene	Lin	21	99.89	27.75	4.90
2	13.29	Acenaphthene	Lin	21	99.88	84.37	5.33
3	13.58	Fluorene	Lin	21	99.66	26.05	8.81
4	14.61	Phenanthrene	Lin	19	99.62	11.30	9.47
5	15.77	Anthracene	Lin	21	99.88	124.60	5.36
6	16.86	Fluoranthene	Lin	21	99.77	46.43	7.99
7	17.76	Pyrene	Lin	21	99.81	80.19	6.65
8	20.61	Benzo[a]anthracene	Lin	21	99.86	244.58	5.77
9	21.18	Chrysene	Lin	21	99.91	91.47	4.94
10	23.51	Perylene	Lin	21	99.84	9.98	6.33
11	24.50	Benzo[k]fluoranthene	Lin	21	99.83	690.71	6.52
12	25.62	Benzo[a]pyrene	Lin	21	99.80	399.62	7.07
13	26.95	Dibenzo[a,h]anthracene	Lin	21	99.80	130.42	10.71
14	28.08	Benzo[g,h,i]perylene	Lin	21	99.88	152.90	6.23
Average:					99.82	151.45	6.8625

Figure 2. Calibration curve of benzo[a]pyrene and table with corresponding results of the calibration of 14 PACs

samples analyzed in the present study contained similar quantities of B[a]P.

The concentrations of the fourteen PACs of investigated samples are given in Table 1. The concentrations of B[a]P, the only by legislation limited PAC, are printed in "bold". B[a]P concentrations of oils used for wood treatments must be lower than 50 mg/Kg. Only creosotes employed for railway sleepers and wood poles may contain up to 500 mg B[a]P mg/Kg. Therefore, PO and MA are not allowed for wood treatments, but RPO as well as DB, B and GX may be used for sleepers and poles. Only B and GX are allowed for the unlimited treatment of wood, if the wood is used in outdoor industrial installations, as they contain less than 50 mg/Kg of B[a]P. Values giving the cancerogenic potency relative to B[a]P are presented in the right end column of Table 1 [7]. The relative cancerogenic potency of dibenzo[a,h]anthracene is higher than one

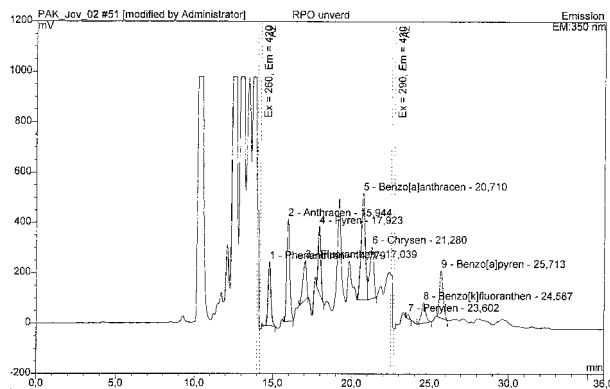


No	Ret. Time min	Peak Name	Height mV	Area mV·min	Rel. Area %	Amount mg/L
1	20.60	Benzo[a]anthracene	518.4	209.6	60.65	0.857
2	21.19	Chrysene	167.6	34.8	10.06	0.380
3	23.45	Perylene	43.3	9.3	2.68	0.929
4	24.44	Benzo[k]fluoranthene	117.1	34.8	10.08	0.050
5	25.56	Benzo[a]pyrene	199.6	52.9	15.31	0.132
6	26.91	Dibenzo[a,h]anthracene	13.1	4.2	1.22	0.032
Total:			1059.0	345.6	100.0	2.381

Figure 3. HPLC-chromatogram of DB and table with corresponding results

Table 1. Relative cancerogenic potency of PACs and their content (mg/Kg) in five commercial oils and in one oil derived from petroleum (RPO)

	DB	B	GX	PO	MA	RPO	Relative Potency
1 Naphthalene	19570	32380	16290	169030	104240	136560	0.001
2 Acenaphthene	14210	19360	18530	30080	48030	2054	0.001
3 Fluorene	21360	19910	30750	97990	46580	33060	0.001
4 Phenanthrene	96737	216190	139610	93320	62520	10270	0.001
5 Anthracene	7680	1892	2138	12580	12420	1625	0.320
6 Fluoranthene	32940	52840	70360	43540	34980	2042	0.010
7 Pyrene	15780	27130	36450	27460	21320	1467	0.081
8 Benzo[a]anthracene	1463	908	1456	7000	9830	1162	0.145
9 Chrysene	747	350	488	5360	7550	1455	0.026
10 Perylene	2021	312	707	31290	63560	700	0.001
11 Benzo[k]fluoranthene	107	2	18	1991	3322	88	0.100
12 Benzo[a]pyrene	279	0	19	2811	3830	292	1.000
13 Dibenzo[a,h]anthracene	65	14	30	0	672	0	1.110
14 Benzo[g,h,i]perylene	0	0	0	995	1677		0.022



No	Ret. Time min	Peak Name	Height mV	Area mV·min	Rel. Area %	Amount mg/L
1	14.78	Phenanthrene	253.7	50.7	10.11	4.493
2	15.94	Anthracene	407.6	92.3	18.38	0.741
3	17.04	Fluoranthene	156.4	40.9	8.15	0.881
4	17.92	Pyrene	261.1	50.6	10.08	0.631
5	20.71	Benzo[a]anthracene	424.0	125.4	24.98	0.513
6	21.28	Chrysene	206.3	62.2	12.40	0.680
7	23.60	Perylene	18.1	3.1	0.62	0.310
8	24.59	Benzo[k]fluoranthene	82.5	26.6	5.29	0.038
9	25.71	Benzo[a]pyrene	189.2	50.1	9.99	0.125
Total:			1998.8	501.9	100.00	8.412

Figure 4. HPLC-chromatogram of RPO and table with corresponding results

Table 2. Total B[a]P equivalents (relative potency multiplied by the content of PAC (mg/Kg) of the investigated samples

	DB	B	GX	PO	MA	RPO
Total	4812	3776	4824	11293	12943	1349
Fraction of B[a]P in the total	279 (5.8 %)	0	19 (0.4 %)	2811 (24.9 %)	3830 (29.6 %)	292 (21.6 %)

(1.110). DB, B and GX contain more dibenzo[a,h]anthracene than RPO, which, compared to other oils, also contains the least quantity of anthracene and pyrene, two PACs with relative cancerogenic potencies of 0.3 and 0.1, respectively. Therefore, it would be much safer for the comparison of the relative cancerogenic potency to take into account the content of other PACs and not of B[a]P per se.

Table 2 shows the total B[a]P equivalents obtained by multiplying the relative cancerogenic potency by the content of the corresponding PAC [7]. RPO revealed the lowest value, i. e. had the lowest total cancerogenic potency. The fraction of B[a]P potency in RPO amounted to 21.6 per cent. The relatively low B[a]P concentration of DB, B and GX shows that B[a]P must be eliminated by distillation. This potential is also present for RPO as well as for PO and MA. Therefore, the sum of B[a]P equivalents of RPO, PO and MA could

be lowered by about 20, 25, and 30 percent, compared to about 6.0, 0.0, and 0.4 percent in the case of the DB, B, and GX, respectively.

Woods treated with RPO passed standardized tests for mechanical and electrical properties and fungicidal activity [8].

CONCLUSION

The limitation of only the B[a]P concentration of creosotes and other aromatic oils as an indicator for their cancerogenic potency may result in false estimates. According to the present study, it would be much safer to use the sum of the B[a]P equivalents obtained by multiplying the content of the cancerogenic PAC and their relative cancerogenic potency. Once the calibration has been performed with an usual PAC mixture of known contents, there is practically no additional experimental work involved in the determination of the sum of B[a]P equivalents compared to the B[a]P content.

RPO, i.e. the oil sample derived from petroleum, could be considered as a successful substitute for oils derived from coal tar, i.e. creosotes.

IZVOD

POLICIKLIČNI AROMATSKI UGLJOVODONICI U SREDSTVIMA ZA ZAŠTITU DRVETA NA BAZI UGLJA I NAFTE

(Naučni rad)

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U ovom radu ispitivano je pet trgovačkih uzoraka ulja dobivenih iz katrana uglja (kreozotna ulja) (DB, B, GX, PO, MA) i jedan uzorak ulja dobiven iz nafte (RPO). Određeni su, pri tome, sadržaji benzo[a]pirena (B[a]P) i 13 drugih policikličnih aromatskih ugljovodonika (PACs). U skladu sa današnjim zakonima Evropske Unije uzorci RPO, DB, B i GX, koji su sadržali manje od 500 mg/Kg B[a]P, smeju se koristiti kao sredstva za zaštitu drvenih željezničkih pragova i telegrafskih i električnih stubova. Zakon Evropske Unije zabranjuje upotrebu PO i MA za zaštitu drveta u svim slučajevima. Prema tome zakonu ukoliko sredstvo za zaštitu drveta sadrži manje od 50 mg/Kg B[a]P ono se sme koristiti u svim slučajevima kada se impregnisano drvo upotrebljava u industrijske svrhe van zatvorenih prostora, odnosno ne samo za pragove i stubove (B[a]P). Koncentracija B[a]P u kreozotnim i drugim aromatskim uljima može se smanjiti pomoću destilacije. U tom slučaju, međutim, koncentracija PACs koji imaju niže tačke ključanja, a slične ili čak veće relativne kancerogene potencije, mogu ostati nepromenjene. Na primer, RPO sadrži više B[a]P od DB, B i GX, ali ima najmanji zbir ukupnih B[a]P ekvivalenata. Zato današnje zakonsko ograničenje samo sadržaja B[a]P u kreozotnim i drugim aromatskim uljima može dovesti do pogrešnih procena njihove kancerogene potencije. Saglasno ovom radu mnogo je sigurnije koristiti zbir B[a]P ekvivalenata dobivenih množenjem sadržaja svakog kancerogenog PAC sa njegovom relativnom kancerogenom potencijom. Ovo tim pre, pošto posle jednom učinjene kalibracije sa smešom PACs poznatog sastava, praktično nema dodatnog eksperimentalnog rada u određivanju zbira B[a]P ekvivalenata u poređenju sa određivanjem sadržaja B[a]P.

Na osnovu rezultata ovoga rada RPO, tj. uzorak ulja dobiven iz nafte, može se smatrati uspešnom zamenom za ulja dobivena iz katrana uglja, tj. kreozotnih ulja.

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REFERENCES

- [1] E. Sandell, J. Tuiminen, Polycyclic Aromatic Compounds, **11** (1996) 83.
- [2] Official Journal of the European Communities, L 365 (31.12.1994).
- [3] W. Boenigk, H. Behr, F. Komora, Holz-Zentralblatt, 122, Nr. 23 (1996) 357.
- [4] Determination of the benzo[a]pyrene content of creosote, EN 1014-3,1, November 1997.
- [5] Determination of 15 polycyclic aromatic hydrocarbons (PAH) DIN 38407-18, May 1999.
- [6] M. Spitteller, J. Jovanovic, FUEL, **78** (1999) 1263.
- [7] K. Schneider, U.S. Schuhmacher, J. Oltmanns, F. Kalberlach, M. Hassauer, M. Roller, Toxikologische Bewertung von PAK, F+E-Vorhaben 29873771, Umweltbundesamt, July 1999.
- [8] D. Atanasovska, O. Djoković, R. Ilić, Report – Saobraćajni Institut, Belgrade, June 1996.

Key words: wood preservatives • creosates • PAC • B[a]P-equivalents.

Ključne reči: konzervatori za drvo • kreozotna ulja • PAC • B[a]P – ekvivalenti.