Flame ionization detection relative response factors of some polycyclic aromatic compounds

Determination of the main components of the coal tar pitch volatile fraction

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ABSTRACT

The flame ionization detection (FID) relative response factors of some commercially available polycyclic aromatic compounds using split injection were determined and compared with other published FID relative response factors obtained using splitless and cold on-column injection technique. From these data FID relative response factors of some non-available polycyclic aromatic compounds were calculated in an approximate way. These factors were used in a quantitative study of the main components of a coal tar pitch volatile fraction. For this quantification the internal standard method and the absolute calibration with separate standard method were employed. Good reproducibility of the determinations using both methods was found.

INTRODUCTION

Coal tar pitches are very complex mixtures of polycyclic aromatic compounds (PACs). The behaviour and properties of coal tar pitches should be governed by their composition, and in the study of relationships between composition, properties and behaviour of this carbonaceous material, gas chromatography (GC) and combined gas chromatography–mass spectrometry (MS), apart from other techniques, are very useful tools.

The chromatographic retention of several commercially available PACs has been studied on stationary phases of different polarity [1–3]. Likewise, relationships between the chromatographic retention of some polycyclic aromatic hydrocarbons (PAHs) and some of their structural and physico-chemical properties have also been studied [1,4,5]. On the other hand, the identification of the components of the volatile fraction of a coal tar pitch on stationary phases of different polarity has been carried out, using PAH retention indices and GC–MS [6,7].

However, the determination of different PACs in a sample is a difficult task. If the sampling being studied is not a very complex mixture and its components are volatile compounds, the cold on-column injection technique is recommended for quantitative purposes [8,9]. However, coal tar pitch extracts form a very complex mixture and are difficult to separate using splitless injection as they contain considerable amounts of non-volatile compounds, which cause problems in the column if the cold on-column injection technique is used.

For these reasons, in this work the split injection technique was used for the quantitative study of the various components of a coal tar pitch volatile fraction. In order to carry out a more rigorous study, the relative response factors of 47 commercially available PACs were determined using split injection. The relative response factors of non-available PACs were calculated by extrapolation. Owing to the almost complete absence of the relative response factors of PACs in the literature, the values obtained here were compared with others obtained using the splitless and on-column injection techniques. The influence of volatility and carbon content of the different compounds on their relative response factors is discussed. The determination of the components of the sample under study was carried out by making use of the relative response factors determined here.

EXPERIMENTAL

The chromatographic study was carried out using a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph with flame ionization detection (FID) and using a Hewlett-Packard Vectra ES/12 computer which allows chromatograms to be stored. A fused-silica capillary column coated with OV-1701 stationary phase (Quadrex, New Haven, CT, USA) was used. The operating conditions and column characteristics are given in Table I.

The standard compounds used are listed in Table II and were obtained from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Janssen (Beerse, Belgium). Their purities were tested and in most instances were greater than 98%.

The sample of coal tar pitch to be analysed was obtained by extraction using pyridine as solvent and a procedure described elsewhere [10]. All samples to be chromatographed were dissolved in pyridine and kept for a few minutes in an ultrasonic bath in order to effect total dissolution. This is very important because of the large difference in solubility between PACs.

RESULTS AND DISCUSSION

First, careful checks of the purity of the standard

compounds used in this study were carried out, in order to make the corresponding corrections. Then, the influence of the concentration of the compounds in the sample injected on their chromatographic responses was tested. The results show that, over the wide concentration range studied (250–4250 ng/μl), the response factor [peak-area counts/amount of compound injected (ng)] does not change with the amount of compound injected. The experimental data fitted the linear equation $y = 2195.61 + 69.55x$ [y = peak area counts and x = amount of compound injected (ng)] with a correlation coefficient of 0.9964.

The next step was the determination of the FID response factors of the available commercially compounds. To this end, mixtures of different groups of PACs with known concentrations were analysed using the previously mentioned operating conditions. Obviously the response factors determined here will be affected not only by the detector and injection technique used, but also by the human factor, technique, operating conditions and characteristics of the gas chromatograph and column used. Table II gives the FID relative response factors (*RRF*) obtained here for various compounds, using as reference compounds fluoranthene and 7,12-dimethylbenz[*a*]anthracene. To the best of our knowledge, the FID *RRF* values for many of the compounds in Table II have not been reported previously. The relative response factor of a compound *i* in relation to a reference compound r is defined as $RRF_i = A_r M_i / M_r A_i$, where A and M are peak-area counts and weight of the compounds, respectively. From this

TABLE I

CHROMATOGRAPHIC OPERATING CONDITIONS

Stationary phase	OV-1701
Film thickness (μm)	0.18
Column length (m)	25
Column inside diameter (mm)	0.22
Carrier gas (hydrogen) flow-rate (ml min^{-1})	2
Splitting ratio	1:87
Injector temperature (°C)	300
Detector temperature (°C)	350
Temperature programming rate from 50 to 300°C (°C min^{-1})	4
Volume of sample injected (μl)	1
Minimum number of sample injections	5

definition, it is clear that compounds with a response lower (higher) than that of the reference compound shows an *RRF* greater (less) than 1. The small values of the standard deviation, S.D., and of the relative standard deviation R.S.D., obtained in the determination of the *RRF* values are notable. These show the high reproducibility of the chromatographic run obtained under the conditions applied. Other workers have found R.S.D.s from 8 to 45% when they used split injection [11].

Response factors of PACs have not been frequently reported. Lao *et al.* [12] reported FID relative response factors using fluoranthene as a reference compound for 57 PACs (from compounds such as biphenyl with 12 carbon atoms to coronene or dibenzopyrene with 24 carbon atoms), obtained using the split injection technique. Table II also gives FID response factors relative to fluoranthene calculated from data obtained, using splitless (RRF_F') [13] and cold on-column injection techniques (RFF_F'') [14] for a smaller number of compounds (15 and 22, respectively). The carbon contents, defined as CC = mass of the total carbon atoms/molecular mass, and the boiling points (b.p.) [15,16] of the different compounds are also given in Table II.

It is generally accepted [17,18] that, if the entire amount of solute injected reaches the flame ionization detector, the response factor will theoretically only be a function of the carbon content of each

TABLE II

RELATIVE RESPONSE FACTORS OF SOME PACs OBTAINED IN THIS STUDY, AND OTHERS CALCULATED FROM THE LITERATURE [13,14], TOGETHER WITH THEIR CARBON CONTENTS AND BOILING POINTS

Compound	RRF_F	S.D.	R.S.D. (%)	RRF_{DMBA}	RRF_F' [13]	RRF_F'' [14]	CC	B.p. (°C)
Naphthalene	0.793	0.012	1.5	0.651	0.912	0.964	0.9375	218.00
Quinoline	0.915	0.027	3.0	0.751			0.8372	238.00
2-Methylnaphthalene	0.832	0.016	1.9	0.683	0.991	0.983	0.9296	241.00
8-Methylquinoline	0.996	0.039	3.9	0.818			0.8392	247.00
Diphenyl	0.837	0.024	2.9	0.687	1.037		0.9351	255.90
2-Ethylnaphthalene	0.824	0.005	0.6	0.677			0.9231	257.90
Diphenyl ether	0.956	0.029	3.0	0.785			0.8471	257.90
1,6-Dimethylnaphthalene	0.898	0.026	2.9	0.737			0.9231	264.00
2,6-Dimethylnaphthalene						0.992	0.9231	262.00
2,3-Dimethylnaphthalene						0.992	0.9231	268.00
Diphenylmethane	0.884	0.026	2.9	0.726			0.9286	264.30
Acenaphthylene	0.871	0.030	3.4	0.715			0.9474	265-75
Acenaphthene	0.804	0.007	0.9	0.660		0.954	0.9351	279.00
Dibenzofuran	1.096	0.022	2.0	0.900			0.8571	287.00
2,3,5-Trimethylnaphthalene	0.892	0.034	3.8	0.732			0.9176	
Fluorene	0.883	0.014	1.6	0.725	1.036	0.989	0.9397	293-95
4-Azafluorene	1.006	0.002	0.2	0.826			0.8612	306.00
9,10-Dihydrophenanthrene	0.838	0.019	2.3	0.688			0.9333	
9,10-Dihydroanthracene						0.993	0.9333	305.00
1-Methylfluorene	0.934	0.014	1.5	0.767			0.9333	
2-Methylfluorene					1.135		0.9333	
Dibenzothiophene	1.119	0.009	0.8	0.919			0.7826	332-33
Phenanthrene	0.901	0.023	2.6	0.740	1.107	0.981	0.9438	340.00
Anthracene	0.883	0.015	1.7	0.725		0.975	0.9438	340.00
Benzo[h]quinoline	1.130	0.013	1.2	0.928			0.8715	338.00
1-Phenylnaphthalene	0.868	0.006	0.7	0.713			0.9412	334.00
Acridine	1.127	0.012	1.1	0.925			0.8715	346.00
Phenanthridine	1.168	0.013	1.1	0.959			0.8715	349.00
1-Methylphenanthrene					1.041		0.9375	358.60
2-Methylphenanthrene	0.938	0.014	1.5	0.770			0.9375	354.80
2-Methylanthracene	0.956	0.009	0.9	0.785		1.007	0.9375	358.60
9-Methylanthracene						0.946	0.9375	

TABLE II *(continued)*

Compound	RRF_F	S.D.	R.S.D. (%)	RRF_{DMBA}	RRF_F^r [13]	RRF_F'' [14]	CC	B.p. (°C)
Carbazole	1.069	0.008	0.7	0.878			0.8623	355.00
1,2,3,6,7,8-Hexahydropyrene	0.980	0.020	2.0	0.805			0.9231	
3,6-Dimethylphenanthrene	0.977	0.032	3.3	0.802			0.9320	363.20
1,2,6,7-Tetrahydropyrene						1.139	0.9320	
Fluoranthene	1.000	0.000	0.0	0.821	1.000	1.000	0.9505	383.00
9-Phenylfluorene	0.995	0.015	1.5	0.817			0.9421	
9,10-Dimethylanthracene	0.982	0.008	0.8	0.806			0.9320	
Pyrene	0.992	0.008	0.8	0.814	1.092	0.985	0.9505	393.00
2-Phenylindole	1.192	0.016	1.3	0.979			0.8705	
Benzo[*a*]fluorene	1.149	0.009	0.8	0.943		1.072	0.9444	407.00
Benzo[*b*]fluorene	1.137	0.027	2.4	0.933	1.158		0.9444	401.00
1,1-Binaphthyl						0.971	0.9449	
Benz[*a*]anthracene	1.177	0.035	3.0	0.966			0.9473	437.50
Chrysene	1.117	0.076	6.8	0.917	1.260	1.049	0.9473	441.00
Triphenylene	1.161	0.012	1.0	0.953		0.959	0.9473	385.00
7,12-Dimethylbenz[*a*]anthracene	1.218	0.019	1.6	1.000		1.051	0.9375	
Benzo[*b*]fluoranthene	1.250	0.020	1.6	1.026			0.9524	
Benzo[*e*]pyrene	1.242	0.022	1.8	1.020	1.216	1.055	0.9524	492.90
Benzo[*a*]pyrene	1.251	0.041	3.3	1.027		0.912	0.9524	495.50
o-Phenylenepyrene					1.539		0.9565	
Perylene	1.253	0.061	4.9	1.029			0.9524	
Dibenz[*a*,*h*]anthracene	1.256	0.081	6.4	1.031		1.171	0.9496	
Benzo[*ghi*]perylene	1.269	0.036	2.8	1.042			0.9565	500.00
Anthanthrene					1.997		0.9103	
Coronene					2.134		0.9600	525.00

compound. Obviously, of the three above-mentioned injection methods, taking into account the great difference in volatility between the various PACs studied, those closest to and furthest from this ideal case are the cold on-column and split injection methods, respectively.

However, the unsubstituted PAHs, regardless of their carbon content and the injection technique used, show a decreasing response (and for that reason the *RRF* increases) as the boiling point increases. This variation is small in the cold on-column injection method (RRF_F dibenzo[*a*,*h*]anthracene $- RRF_F$ naphthalene $= 0.207$) and greater for the other methods (split injection, RRF_F dibenzo[*a*,*h*]anthracene $- RRF_F$ naphthalene $= 0.463$). In splitless injection, there is a sharp decrease in the response of the compounds of very high molecular mass (see anthanthrene and coronene in Table II). In Table II it can also be observed with cold on-column injection that the response is not the same for PAH isomers with the same carbon content. The difference in response between isomers increases as the carbon content and boiling point of these PAHs

increase. The isomer that elutes later has a higher response (and a smaller *RRF*) than the isomer that elutes first [see Table II; RRF_F''(phenanthrene) $- RRF_F''$(anthracene) $= 0.006$, RRF_F''(fluoranthene) $- RRF_F''$(pyrene) $= 0.015$, RRF_F''(chrysene) $- RRF_F''$(triphenylene) $= 0.090$ and RRF_F''(benzo[*e*]pyrene) $- RRF_F''$(benzo[*a*]pyrene) $= 0.143$]. This effect is also observed in split injection but only with some isomers and is smaller than in the cold on-column injection technique. All these results show that even using the cold on-column injection method, the carbon content alone does not determine the response of the compounds in a flame ionization detector.

The alkylated PAHs, regardless of the injection technique, show an FID response lower (and for that reason a higher RRF_F) than the parent PAH compounds. In this group of compounds both the carbon content and the volatility are smaller than those of the corresponding PAHs. However, the hydro-PAH derivatives with split and cold on-column injection show a higher and lower response, respectively, than the parent PAHs. These compounds

show a higher volatility and a smaller carbon content than the parent PAHs. Finally, the hetero-PAH derivatives show in the split injection method a lower response (and a higher RRF_F) than the corresponding parent PAHs. FID response factors of hetero-PAH derivatives obtained using splitless or cold on-column injection techniques are not available in the literature. The carbon content and volatility of all these compounds is lower than those in the parent PAHs.

In general, from the data in Table II it can be concluded that, regardless of the nature of the PAC, the volatility is the factor that has the most influence on their response factors when the split and splitless injection techniques are used. When the cold on-column injection technique is used, the carbon content and volatility of the compound have an effect on their response factors, besides other factors not determined for isomers. However, the relative response factors obtained using the cold on-column injection technique are close to unity for the compounds studied.

The RRF values of some compounds not commercially available but present in the volatile fraction of coal tar pitch were calculated in an approximate way by taking the RRF values of the standard compounds as a basis. Table III gives these RRF_F and RRF_{DMBA} calculated values. The RRF values of compounds 5, 12, 13b, 14, 15, 16, 25, 26, 27, 36, 37 and 39a (peak numbers, see Fig. 1) were calculated by adding to the RRF values of the first of their series (namely dibenzofuran, dibenzo[b,d]thiophene, phenanthrene, benzo[h]quinoline, carbazole,

TABLE III

RELATIVE RESPONSE FACTORS CALCULATED FOR SOME COMPOUNDS

Peak No.[a]	Compound	RRF_F	RRF_{DMBA}
2	4H-Cyclopenta[def]phenanthrene	0.947	0.777
5	Benzonaphthofuran	1.367	1.122
10	Methylbenzonaphthofuran	1.409	1.157
11	Methylpyrene	1.034	0.849
12	Benzo[b]naphtho[2,1-d]thiophene	1.389	1.140
13b	Benzo[c]phenanthrene	1.172	0.962
14	Benzo[ghi]fluoranthene	1.091	0.896
15	Dibenzoquinoline	1.401	1.150
16	Benzo[a]naphtho[2,3-d]thiophene	1.389	1.140
20	Methylbenz[a]anthracene	1.219	1.001
22a	11H-Benz[b,c]aceantrylene	1.223	1.004
23a	4H-Cyclopenta[def]chrysene	1.223	1.004
24a	4H-Cyclopenta[def]triphenylene	1.207	0.991
25	11H-Benzo[a]carbazole	1.339	1.099
26	7H-Benzo[c]carbazole	1.339	1.099
27	5H-Benzo[b]carbazole	1.339	1.099
36	Benzo[b]chrysene	1.261	1.035
37	Picene	1.261	1.035
39a	Anthanthrene	1.326	1.089

[a] See Fig. 1.

fluoranthene, chrysene and benzo[a]pyrene) an increase corresponding to four or two carbon atoms, forming a new ring. In the phenanthrene–chrysene isomer interval the increase due to four or two carbon atoms was calculated from the difference in the RRF values of the average of the chrysene isomers or pyrene, respectively, and phenanthrene. In the
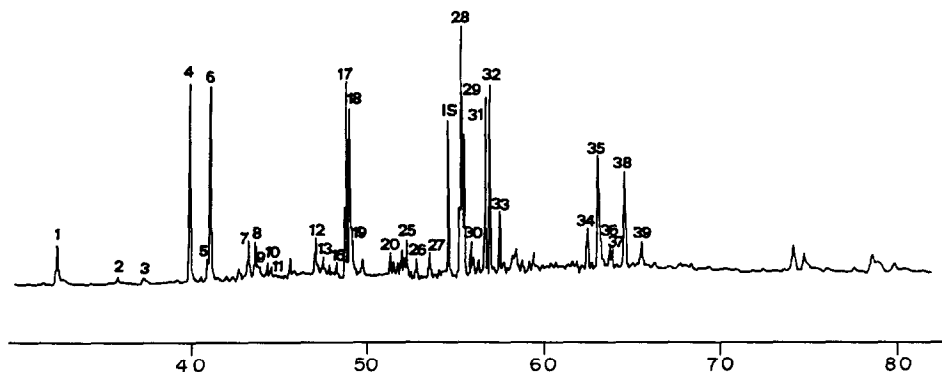

Fig. 1. Capillary gas chromatogram of the volatile fraction of a coal tar pitch on OV-1701 stationary phase. For peak identification, see Table IV. Internal standard (IS) = 7,12-dimethylbenz[a]anthracene.

TABLE IV

PAC CONCENTRATION IN THE COAL TAR PITCH EXTRACT, OBTAINED USING THE INTERNAL STANDARD METHOD (1) AND THE SEPARATE STANDARD METHOD (2)

Peak No.[a]	Compound	Method 1				Method 2			
		A_i/A_r^b	S.D.[c]	R.S.D. (%)	mg/g of extract	A_i^b	S.D.[c]	R.S.D. (%)	mg/g of extract
1	Phenanthrene	0.2025	0.0110	5.35	4.00	5785.33	203.99	3.53	3.52
2	4H-Cyclopenta[def]phenanthrene	0.0243	0.0006	2.56	0.50	783.67	20.27	2.59	0.50
3	Carbazole	0.0281	0.0016	5.69	0.65	997.33	39.47	3.95	0.72
4	Fluoranthene	0.5712	0.0160	2.74	12.53	17466.00	848.65	4.89	11.79
5	Benzonaphthofuran	0.0730	0.0022	3.04	2.19	2767.33	65.34	2.36	2.55
6	Pyrene	0.4900	0.0140	2.80	10.66	15783.00	302.08	1.91	10.55
7	Benzo[a]fluorene	0.1271	0.0045	3.59	3.20	4100.67	138.45	3.38	3.19
8	Benzo[b]fluorene	0.1221	0.0048	3.97	3.07	4291.00	78.79	1.84	3.32
9	Benzo[c]fluorene	0.0351	0.0023	6.06	0.89	848.00	4.97	0.59	0.65
10	Methylbenzonaphthofuran	0.0258	0.0017	6.81	0.80	951.00	23.04	2.42	0.90
11	Methylpyrene	0.0203	0.0010	4.94	0.46	825.67	18.45	2.23	0.58
12	Benzo[b]naphtho[2,1-d]thiophene	0.0981	0.0015	1.59	2.99	3341.33	145.51	4.35	3.13
13a	Tetrahydrochrysene	0.0489	0.0009	1.88	1.26	1401.00	89.71	6.40	1.11
13b	Benzo[c]phenanthrene								
14	Benzo[ghi]fluoranthene	0.0226	0.0009	4.18	0.54	955.00	58.67	6.14	0.71
15	Dibenzoquinoline	0.0259	0.0009	3.64	0.80	1020.00	59.60	5.84	0.96
16	Benzo[a]naphtho[2,3-d]thiophene	0.0379	0.0015	4.16	1.15	1114.33	33.31	2.99	1.04
17	Benz[a]anthracene	0.3808	0.0050	1.33	9.83	12337.67	387.92	3.14	9.81
18	Chrysene	0.5207	0.0083	1.60	13.45	16687.67	677.80	4.06	13.25
19	Triphenylene	0.1494	0.0054	3.60	3.81	3906.33	51.14	1.32	3.06
20	Methylbenz[a]anthracene	0.0676	0.0030	4.46	1.80	2058.67	24.53	1.19	1.69

No.	Compound								
21	Methylbenz[a]anthracene	0.0245	0.0005	0.02	0.65	770.00	55.76	7.24	0.64
22a 22b	11H-Benz[bc]aceanthrylene Binaphthalene	0.0227	0.0009	3.96	0.61	896.67	65.45	7.30	0.75
23a 23b	4H-Cyclopenta[def]chrysene Binaphthalene	0.0499	0.0024	4.84	1.33	1756.00	22.46	1.28	1.45
24a 24b	4H-Cyclopenta[def]triphenylene Dimethylbenz[a]anthracene	0.0483	0.0026	5.52	1.27	2095.33	43.21	2.06	1.70
25	11H-Benzo[a]carbazole	0.0930	0.0012	1.27	2.73	3188.67	84.95	2.66	2.88
26	7H-Benzo[c]carbazole	0.0578	0.0019	3.26	1.69	1790.33	106.91	5.97	1.62
27	5H-Benzo[b]carbazole	0.0417	0.0038	9.09	1.22	1743.33	43.41	2.49	1.58
28	Benzo[j]fluoranthene	0.5190	0.0032	0.61	14.42	16017.33	211.40	1.32	13.68
29	Benzo[b]fluoranthene	0.5068	0.0045	0.90	14.07	14438.00	123.79	0.86	12.34
30	Benzo[k]fluoranthene	0.0776	0.0014	1.87	2.16	2298.33	62.78	2.73	1.97
31	Benzo[e]pyrene	0.4273	0.0036	0.83	11.73	12730.00	123.81	0.97	10.75
32	Benzo[a]pyrene	0.4928	0.0019	0.38	13.53	14627.00	370.58	2.53	12.35
33	Perylene	0.1215	0.0021	1.70	3.34	3909.00	88.23	2.26	3.31
34	Dibenz[a,j]anthracene	0.1241	0.0031	2.48	3.42	3670.33	117.01	3.19	3.12
35a 35b	Indenopyrene Dibenz[a,c]anthracene	0.4335	0.0220	4.96	11.95	12622.33	135.14	1.07	10.69
36	Benzo[b]chrysene	0.0723	0.0077	10.68	1.99	1924.67	90.87	4.72	1.63
37	Picene	0.0691	0.0031	4.43	1.91	1911.67	74.84	3.92	1.62
38	Benzo[ghi]perylene	0.3404	0.0150	4.39	9.42	10709.67	43.52	0.41	9.11
39a 39b	Anthanthrene Methyl derivative of indenopyrene	0.0953	0.0028	2.99	2.63	3892.67	435.97	11.20	2.52

[a] See Fig. 1.
[b] A_i and A_r are peak-area counts of the particular compound i and the reference compound, respectively.
[c] Standard deviation obtained in five determinations.

chrysene–anthanthrene interval, the increase due to four or two carbon atoms was calculated from the difference in the RRF values of dibenzo[a,h]-anthracene or average of benzo[a]- and benzo[e]pyrene, respectively, and the average of the chrysene isomers. The RRF values of methyl derivatives [compounds (peaks) 10, 11 and 20] were calculated by adding to each parent compound (namely benzonaphthofuran, pyrene and benzo[a]anthracene) an increase for the methyl group. This increase is an average value obtained from different methyl derivative compounds in Table II. Finally, the RRF values of compounds (peaks) 2, 22a, 23a and 24a were calculated adding to the RRF of phenanthrene, benz[a]anthracene, chrysene and triphenylene an increase corresponding to a ring-forming methylene group. This increase was calculated from the difference between the RRF_F values of fluorene and diphenyl.

Taking into account the relative response factors in Tables II and III, the determination of the main components of the coal tar pitch volatile fraction was carried out. Fig. 1 shows the capillary gas chromatogram of the sample to be quantified. For quantification the internal standard method (method 1) was used. The standard compound to be used must satisfy certain requirements [19,20] and for this mixture 7,12-dimethylbenz[a]anthracene was selected. The absolute calibration method with a separate standard (method 2) was also used [8,21]. In this instance, fluoranthene was the separate standard compound. Table IV shows the results of quantification with both methods. The reproducibility of the determinations in both methods represented by the S.D. and R.S.D. can be considered to be satisfactory. Only in a small number of cases is the R.S.D. value higher than 5%. The PAC concentrations found in the coal tar pitch extract are also fairly similar using both methods. However, it should be pointed out that from benzo[j]fluoranthene to the end, a slightly higher concentration is obtained with the internal standard method. This could be due to the use of fluoranthene as a separate standard, because this compound elutes at the beginning of the chromatogram. In spite of this, either of the two methods can be used to determine the main components of the coal tar pitch volatile fraction.

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