

A Chromatographic Analysis for Polynuclear Aromatic Hydrocarbons in Small Quantities of Cigarette Smoke Condensate*

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INTRODUCTION

Recently, many laboratories have been concerned with the development of profile analysis methods for polynuclear aromatic hydrocarbons (PAH) of cigarette smoke condensate (CSC) (1-4). Generally, these methods have employed several partitioning steps to remove materials which would interfere in the gas chromatographic (GC) analysis for the PAH. However, solvent partitioning affects the quantitative recoveries of the individual and total PAH. Substantial differences in partition coefficients between various organic solvents have been reported for PAH, especially methylated PAH (5). Another disadvantage has been the increased possibility of oxidation of some of the PAH during extended partitioning times (5).

Recent work in this laboratory on the isolation and identification of PAH has resulted in a gel filtration method (6, 7), which, with improvements on previous techniques, has eliminated these solvent partitioning steps. The developed gel filtration-GC technique is described and its advantages for the quantitative analysis of PAH from various CSC are detailed. Various cigarette brands can now be compared on the basis of their smoke PAH contents in a manner similar to the established tar and nicotine analyses.

METHODS AND MATERIALS

Cigarette Smoke Condensate (CSC) Preparation

The University of Kentucky cigarettes, type 1R1 (8); commercial, 85 mm nonfilter; and commercial 85 mm filter cigarettes were smoked to a 30 mm butt length on a 30-port Borgwaldt** smoking machine. The cigarettes were preconditioned at 60% relative humidity for 48 h and smoked under standard conditions: 1 puff/min, 2-second duration, and a puff volume of 35 ml (9, 10). Condensate from 90-120 cigarettes was collected in two dry ice-cooled traps, the last one containing a glass

wool plug. The glass connecting lines in the trapping system were washed into the traps, alternately, with methanol (M) and benzene (B). The traps were warmed to room temperature and the CSC was quantitatively washed into a separatory funnel with 100, 200, and 100 ml of M, B, and ethyl ether (E), respectively. All solvents used were Burdick and Jackson Laboratories glass-distilled type.

CSC Fractionation and Chromatography

The total M-B-E mixture was washed in the separatory funnel with three 200 ml volumes of glass-distilled water. The aqueous portions were cross extracted with B:E (1:1, $\frac{v}{v}$, 3 \times 50 ml). After reduction of the organic solution to about 100 ml on a rotary evaporator (40° C), 20 g of silicic acid (100 mesh, Mallinckrodt, washed with nanograde M and dried in a forced air oven at 150° C for 18 h) and 50 ml of iso-octane were added to the organic solubles.

The residual B and E were removed on a rotary evaporator (40° C), being displaced from the silicic acid (SA) by the iso-octane. The iso-octane sample-SA slurry was added to the top of a 100 g SA column, 3 \times 35 cm, [prepared as a slurry in petroleum ether (PE)] with 200 ml of PE. The column was eluted with 1 l of PE. The flask that contained the sample-coated SA was rinsed with a 100 ml portion of a B:PE (1:3, $\frac{v}{v}$) solvent and the rinsings poured onto the column. The column was eluted with 1 l of B:PE (1:3, $\frac{v}{v}$) to give fraction B-PE. The SA column was operated at a pressure of 8-10 psi of nitrogen. The solvent from fraction B-PE was removed on a rotary evaporator, and the residue transferred quantitatively to a 1 ml volumetric flask.

Gel Filtration (GF) System

Samples of fraction B-PE were fractionated on a GF system consisting of four 1.25 \times 109 cm Chromatronix LC columns connected in series and packed with Bio-Beads SX-12 (a neutral, porous, styrene-divinylbenzene copolymer, M. exclusion 400, Bio-Rad Laboratories) in B. Total length of the wet gel bed was 400 cm (approximately 200 g of dry beads). Samples in B were

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** Reference to a company or product name does not imply approval or recommendation by the USDA.

placed on the column with a 0.9 ml injection loop. The eluting solvent, B, was pumped by a Chromatronix CMP-3 pump at a flow rate of 120 ml/h; 8 ml fractions were collected. Column effluent was monitored with an Isco Model UA5 detector (280 nm), equipped with an 8 μ l flow cell. Sixty 8 ml fractions were collected by an automatic fraction collector. Fractions that were collected beginning with the elution of 2-methylfluorene and ending after the methylbenzopyrenes (GF fractions 39-60) were combined to yield the PAH-enriched fraction. This fraction was reduced in volume to about 1 ml on a rotary evaporator and quantitatively transferred to a tapered test tube. The solvent was removed under a stream of nitrogen, and the residue immediately redissolved in 50 μ l of B, in preparation for gas chromatography.

Gas Chromatography (GC)

The PAH-enriched fraction (GF fractions 39-60) was analyzed on a 15 ft. \times 1/8 in. stainless steel column, containing 3% Dexsil 300 GC on 100/120 mesh Gas-Chrom P. The solid support was coated by the evaporative method and the column was filled by the gravity-vertical drop method and coiled after packing (11). The column was conditioned by programming from room temperature to 325°C at 2°/min, held at 325°C for 8 h, and finally at 350°C for 1 h. A molecular sieve filter, followed by an oxygen trap, was used on the carrier gas line to extend column life. Chromatographic conditions were: oven temperature at 90°C for 5 min, then programmed at 2°/min to 325°C, and held at 325°C for 30 min. Injection port and detector were at 290° and 350°C, respectively. Helium flow rate was 48 ml/min, measured at room temperature. GC analyses were obtained on a Hewlett-Packard Model 5750 flame ionization gas chromatograph. Peak areas were measured

by an Autolab Systems IV integrator. The PAH were identified by GC retention time, UV, and mass spectra (7).

PAH Recovery Study

The recovery of carbon-14 labeled benzo(a)pyrene (¹⁴C-BaP) and ¹⁴C-anthracene was monitored by standard liquid scintillation counting techniques. A 0.798 μ g sample of ¹⁴C-BaP (activity: 145,265 dpm) in B was added to the CSC solution (contained in a separatory funnel) from 90 1R1 cigarettes. The CSC was fractionated as described above, and recovery of ¹⁴C-BaP determined at various steps in the procedure. Similarly, a 11.17 mg sample of ¹⁴C-anthracene (activity: 97,648 dpm) was added to the CSC of 90 1R1 cigarettes and its recovery was determined.

RESULTS AND DISCUSSION

In developing a rapid, quantitative method for the analysis of PAH in smoke, our objectives were that: it should be quantitative, reproducible, applicable for rapid PAH screening from different sources of CSC, and applicable to both large and small amounts of CSC. The starting point was the general scheme that is employed for the preparation of bioassay fractions, an abbreviated version of which is shown in Fig. 1 (12). In this procedure, the neutrals from the CSC were placed on a silicic acid column, eluted with PE to remove the waxes (13), and then with B-PE, which eluted neutrals that also contained the PAH. The B-PE fraction (F-BPE) was then partitioned between dimethylsulfoxide (DMSO) and cyclohexane to yield the DMSO-soluble, PAH-containing fraction (F-20), which represented about 0.32% by weight of the crude condensate,

Figure 1. Abbreviated CSC bioassay fractionation scheme.

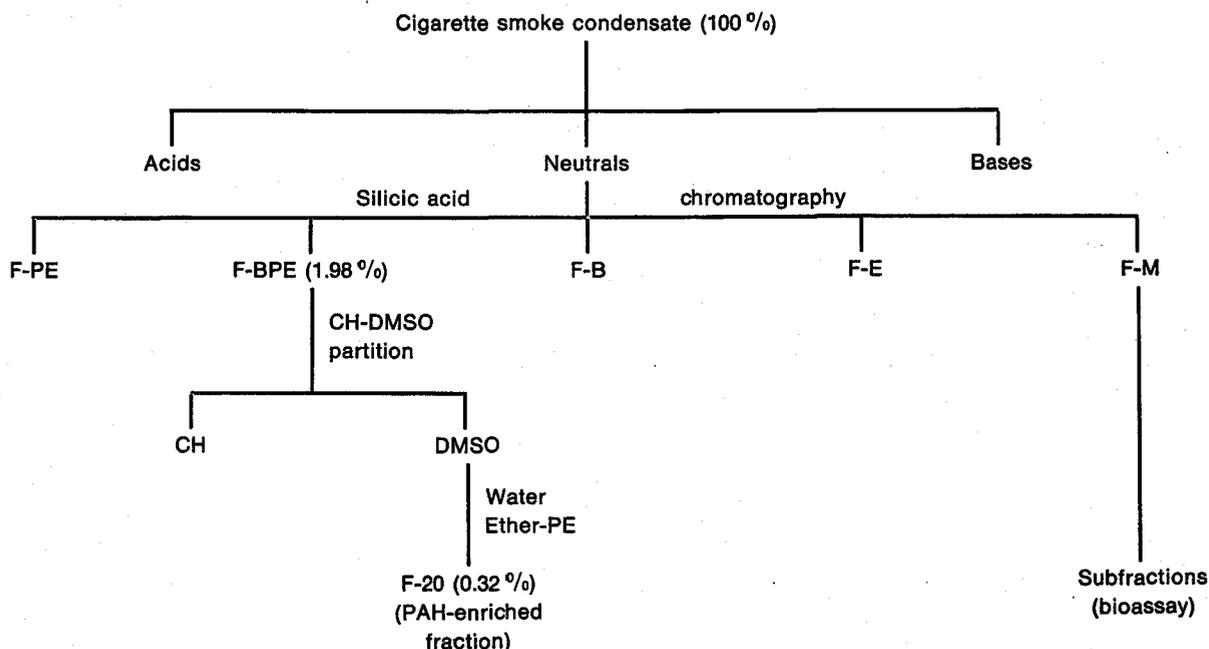
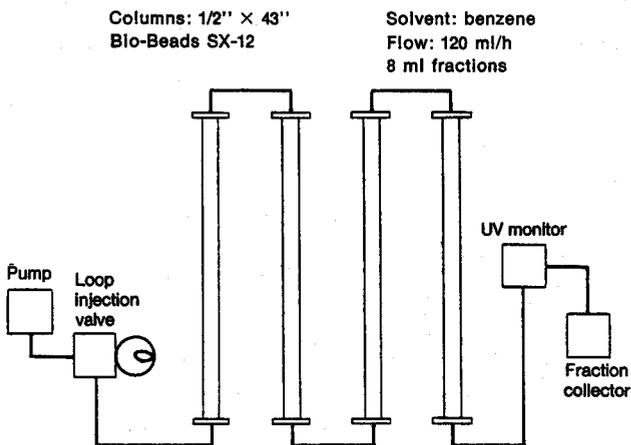


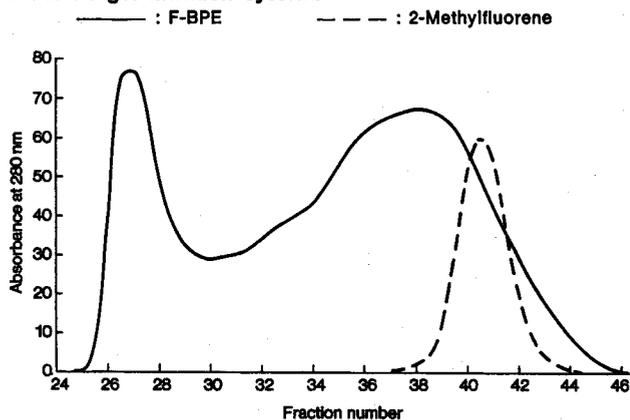
Figure 2. Gel filtration system.



and was suitable for bioassay. The one deterrent to development of this procedure for a quantitative method for PAH was the fact that unfavorable DMSO-partitioning coefficients have been reported for several methylated PAH (5). Consequently, DMSO-partitioning was eliminated and fraction F-BPE was, instead, directly chromatographed by gel filtration on SX-12 Bio-Beads. This resulted in a PAH-enriched fraction that was essentially similar to that obtained from F-20, but even more concentrated in PAH (7). More importantly, we observed that some components, assumed and later confirmed to be methylated-PAH, did increase in relative concentration.

It was also desirable to replace or eliminate the acid-base extractions of the original CSC. We found that a simple water extraction of the total CSC, dissolved in a B-M-E mixture, removed large quantities of material. Based on CSC from 90 1R1 cigarettes, about 52% by weight of CSC was removed by water. Also, the elimination of the acid-base extraction steps halved the extraction time. The organic solubles could then be chromatographed on silicic acid. The only complication was the presence of B in the fraction, as the B would

Figure 3. UV absorption curve for elution of fraction B-PE on gel filtration system.



cause the early elution of the PAH with the waxes on SA chromatography. This problem was overcome by the displacement of the B, upon solvent removal, by higher boiling iso-octane. The resulting CSC organic solubles-SA slurry was suitable for column chromatography. Elution of the SA column with B-PE yielded PAH-containing fraction B-PE, which was similar to that obtained from CSC neutrals. This fraction was then analyzed by analytical GF chromatography on the four-column system shown in Fig. 2. Fraction B-PE was dissolved in B, placed in the injection loop, and automatically pumped onto the gel columns. The eluate passed through a UV monitor and was collected in 8 ml fractions. Figure 3 shows a typical UV trace (the solid line) of the effluent from the gel column. The early eluting materials are the high-molecular weight components, which are not fractionated by the gel. The PAH elute at the end of the components being resolved by the gel. One of the earliest eluting major PAH was 2-methylfluorene (dashed line, Fig. 3), and its elution volume was used to define the beginning of the elution of the PAH-enriched fraction. The end of the PAH elution was determined by the use of a portable UV light. In

Figure 4. Developed PAH analysis procedure.

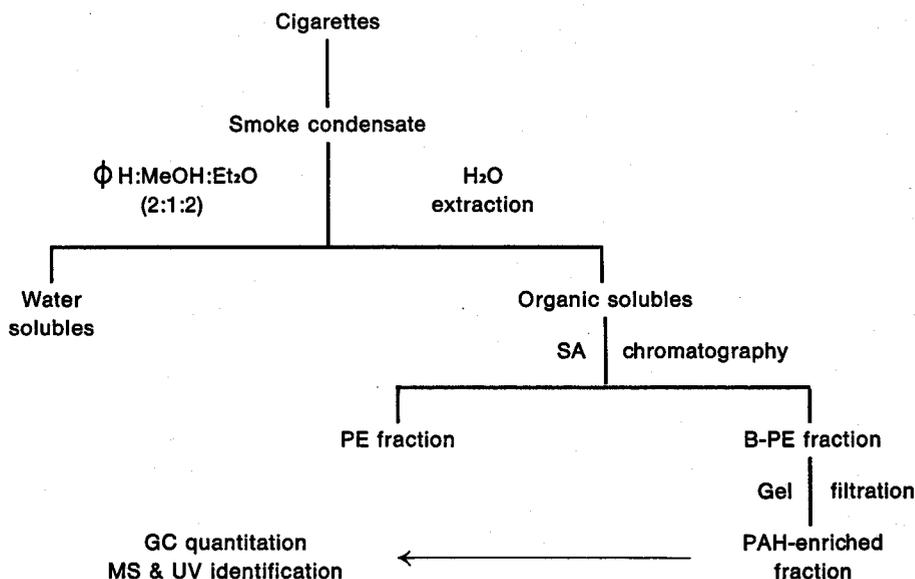


Figure 5. Gas chromatogram of PAH constituents in five 1R1 and eight commercial nonfilter cigarettes.

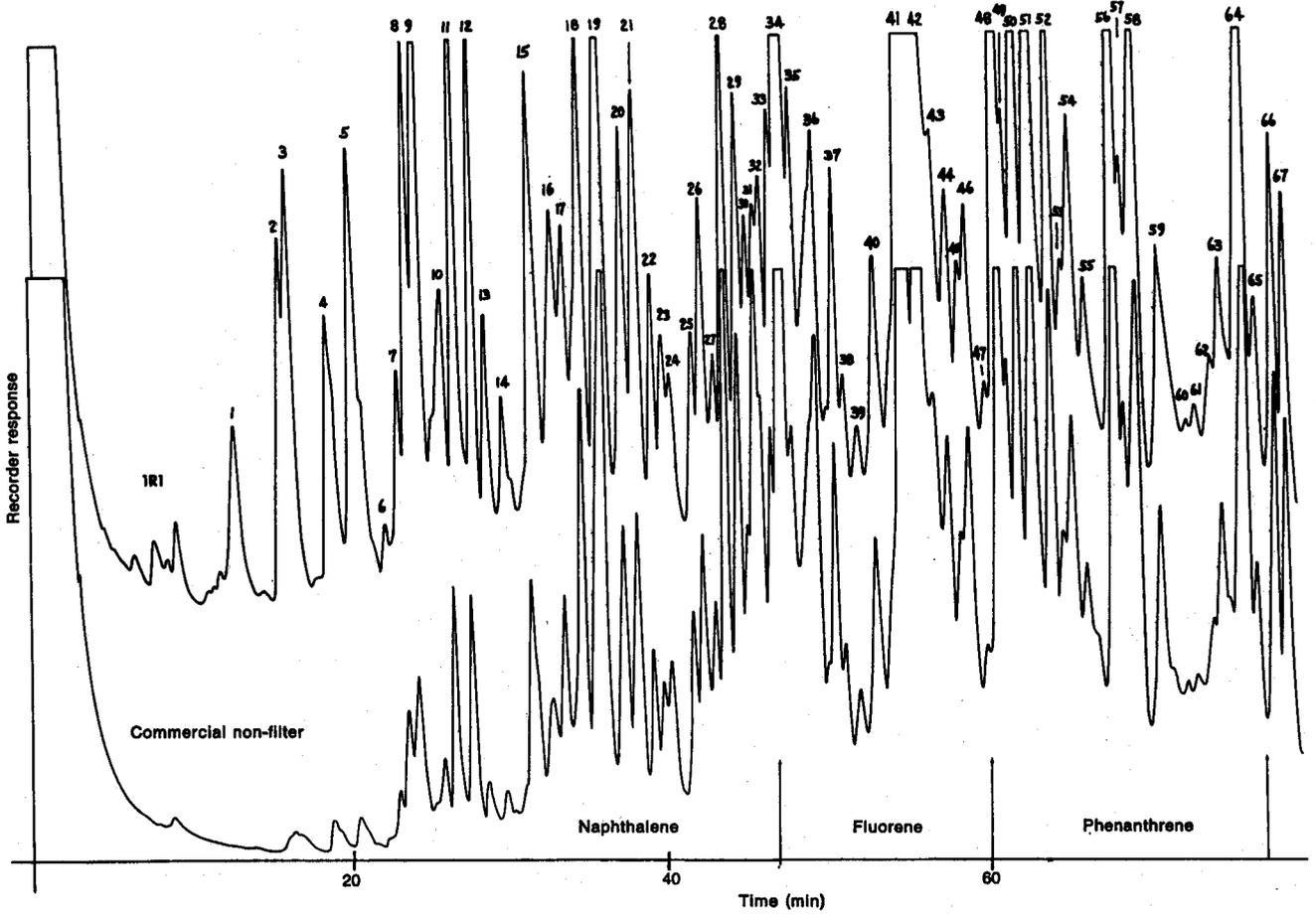


Figure 6. Continuation of gas chromatogram of PAH constituents in five 1R1, eight commercial nonfilter, and eleven commercial filter cigarettes.

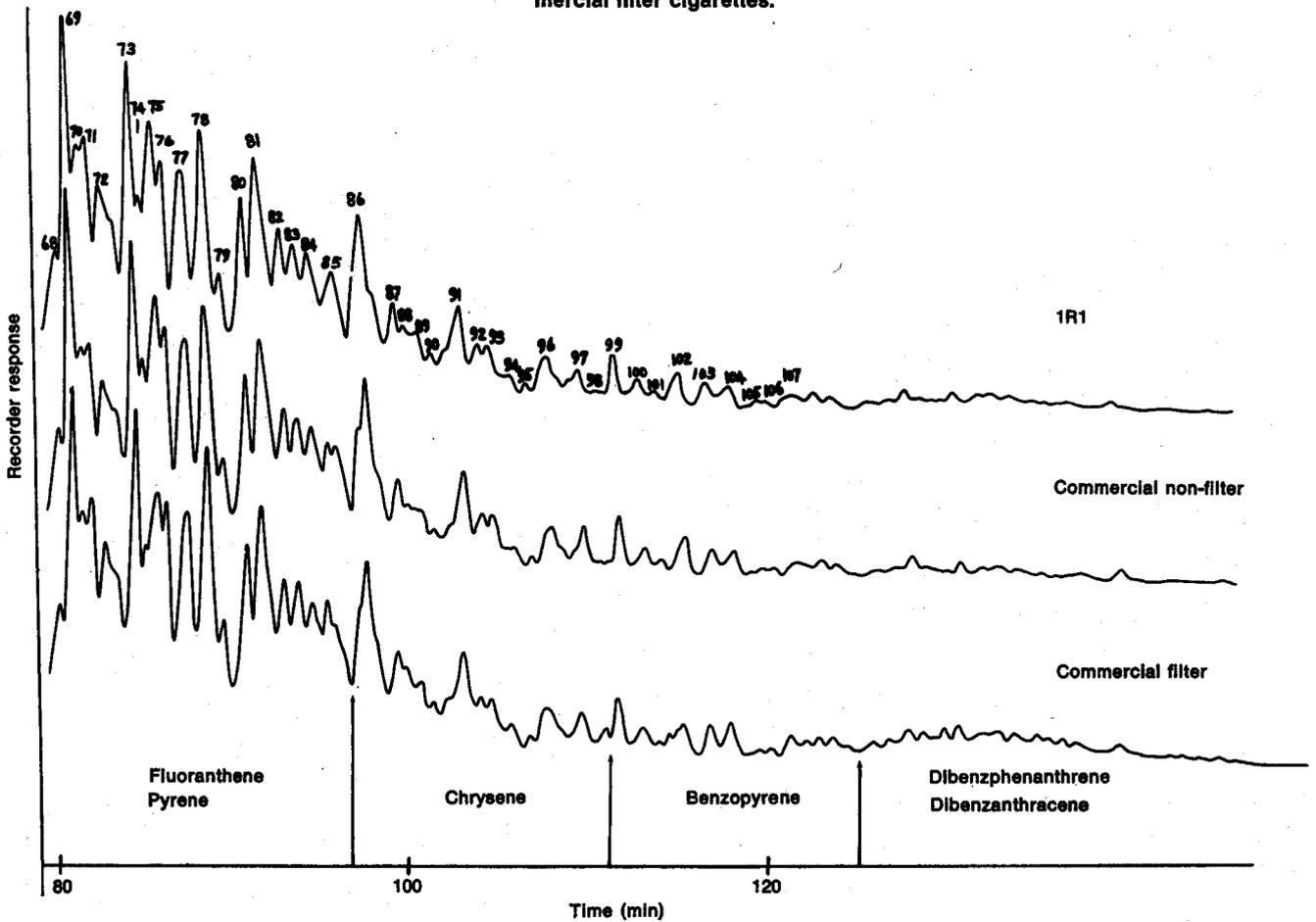


Table 1. Recovery of ¹⁴C-labeled PAH.

Fraction	Recovery ^a (%)	
	BaP	Anthracene
CSC	100	100
Organic soluble	96.5	—
B-PE	94.5	95.0
PAH isolate	92.0	95.0

a: Based on ¹⁴C levels added to original CSC.

the presence of long-wave length UV light, the GF fractions containing PAH fluoresced brightly. Thus, GF fractions 39-60 were defined as the "PAH-enriched fraction", which contained only 0.02% by weight of the original CSC. This concentrated fraction was now suitable for GC and further identification and quantitation of individual PAH. The total PAH analytical procedure is briefly summarized in Fig. 4.

It was also desirable to determine the PAH-recovery in the new procedure. For this purpose, ¹⁴C-BaP and ¹⁴C-anthracene were added to the CSC, from 90 1R1 cigarettes, which was then fractionated. The results of this study are given in Table 1. For BaP and anthracene, 92% and 95% of the radioactivity was recovered in the PAH-enriched fraction. Considering the small amount of material and experimental errors in counting, the recovery was assumed to be quantitative.

The PAH were finally separated and identified by GC on the high temperature-stable phase, Dexsil 300 GC. Identifications were established or confirmed by UV and mass spectra (7). Thus, the next objective was to evaluate the reproducibility of the GC techniques. An example of the reproducibility of the GC analyses of the still complicated PAH-fraction of 1R1 CSC is shown in Table 2. The numbers are based on peak areas relative to pyrene. The first two columns show the data from duplicate GC analyses of the same sample of 1R1 PAH isolate. For this sample, the GC data were very reproducible and consistent. However, from sample to sample, variation in the low molecular weight PAH, i.e., naphthalene through fluorene, was observed. This variation in areas ratios of these components was due to the fact that these materials are volatile and are readily lost during evaporation of the PAH-enriched fraction to volumes suitable for GC analysis. Thus, for small amounts of condensate, quantitative results for PAH smaller than phenanthrene can only be obtained by applying special techniques and precautions to minimize losses. From the examples in Table 2, some typical problems with GC analyses of PAH, using packed columns, became apparent. The inability to separate 1,2-benzanthracene from chrysene and triphenylene and benzo(e)pyrene (BeP) from BaP is evident.

The method was subsequently used to determine the PAH profiles of commercial filter and nonfilter cigarettes. Data on some of the major PAH in the 1R1 and commercial cigarettes are presented in Table 3. Consider-

Table 2. Reproducibility data on PAH profiles of CSC from 90 1R1 cigarettes.

PAH	Relative areas ^a				
	Run 1	Run 1	Run 2	Run 3	Average
Naphthalene	1.03	1.02	2.15	1.33	1.50
2-Methylnaphthalene	1.59	1.62	2.76	1.78	2.05
Acenaphthylene/ 2,7-dimethylnaphthalene	1.38	1.42	2.13	1.39	1.64
Acenaphthene	0.68	0.70	0.89	0.68	0.75
Fluorene	3.99	4.09	4.86	3.82	4.24
Phenanthrene	2.68	3.00	2.96	2.96	2.92
Anthracene	0.79	0.84	0.93	0.84	0.86
Fluoranthene	1.14	1.15	1.10	1.10	1.11
Pyrene	1.00	1.00	1.00	1.00	1.00
2-Methylfluoranthene	1.00	1.01	0.97	1.00	0.99
1,2-Benzanthracene/ chrysene/triphenylene	1.15	1.13	1.09	1.14	1.12
BeP/BaP	0.09	0.10	0.08	0.10	0.09

a: Relative to pyrene; assuming unitary detector response;

$$\text{relative areas} = \frac{\text{GC peak area of individual PAH}}{\text{GC peak area of pyrene}}$$

ing phenanthrene and the higher molecular weight members, the PAH in the condensates occurred in the same relative amounts. Figures 5 and 6 illustrate representative GC chromatograms from which the data were obtained. The chromatograms in Fig. 5 represent the amount of PAH calculated to be present in five 1R1 and in eight commercial nonfilter cigarettes. As indicated, the chromatograms have been subdivided into several sections: i.e., the naphthalene fraction, all components eluting before fluorene; the fluorene fraction, containing fluorene and methylfluorenes; the phenanthrene frac-

Table 3. Comparison of PAH profiles of CSC from 1R1, commercial nonfilter and filter cigarettes.

PAH	Relative areas ^a		
	1R1	Commercial nonfilter	Commercial filter
Naphthalene	1.50	0.88	0.81
2-Methylnaphthalene	2.05	1.58	1.15
Acenaphthylene/ 2,7-dimethylnaphthalene	0.75	0.74	0.50
Fluorene	3.99	3.75	2.14
Phenanthrene	2.79	2.95	2.91
Anthracene	0.79	0.94	0.66
Fluoranthene	1.11	1.22	1.21
Pyrene	1.00	1.00	1.00
2-Methylfluoranthene	0.99	1.00	1.04
1,2-Benzanthracene/ chrysene/triphenylene	1.12	1.06	1.12
BeP/BaP	0.09	0.10	0.07

a: Relative to pyrene; assuming unitary detector response;

$$\text{relative areas} = \frac{\text{GC peak area of individual PAH}}{\text{GC peak area of pyrene}}$$

tion, containing phenanthrene, methyl-, dimethyl-, and trimethylphenanthrenes and anthracenes, and fluoranthene. The chromatogram for the nonfilter CSC illustrates the possible losses of the lower PAH that occurred due to differences in solvent evaporation methods, i.e., before special care was taken in solvent reductions. Essentially the same pattern for both types of cigarettes was observed in the phenanthrene fraction. The remainder of the profile chromatogram is shown in Fig. 6. The PAH contents equivalent to five 1R1, eight commercial nonfilter, and eleven commercial filter cigarettes are compared. The first segment, the pyrene fraction, consisted of pyrene, the trimethylphenanthrenes and anthracenes, the benzofluorenes, the methyl- and dimethylfluoranthenes and pyrenes. The chrysene fraction contained the unresolved 1,2-benzanthracene, chrysene and triphenylene peak, the trimethylpyrenes, the methyl- and dimethylchrysenes, methylbenzanthracene, and other compounds. The benzofluoranthenes and the unresolved BeP and BaP and their methyl derivatives were the major PAH in the benzopyrene fraction. The last group, containing the very high molecular weight PAH, was the dibenzphenanthrene-dibenzanthracene fraction. A complete listing of the relative peak areas and component identification is given in Table 4.

The quantitative amounts of the PAH in μg per 100 cigarettes could be calculated from the GC data. This has been done for several of the representative PAH in the cigarettes (Table 5). (The values were obtained by applying detector response corrections, based on standard detector response per μg data.) In all cases, the 1R1 cigarettes contained the largest amount of PAH in the CSC per 100 cigarettes. For example, the BeP/BaP content per 100 cigarettes decreased from 2 μg in the 1R1 to the 0.5 level in the commercial filter cigarette. Similar decreases were found for the other compounds.

Table 5. Comparison of the contents of selected PAH in CSC from 1R1, commercial nonfilter and filter cigarettes.

PAH	Amount ($\mu\text{g}/100$ cigarettes) ^a		
	1R1	Commercial nonfilter	Commercial filter
Phenanthrene	52.4	44.1	16.1
Fluoranthene	21.2	18.5	7.0
Pyrene	18.6	14.8	5.7
1,2-Benzanthracene/ chrysene/triphenylene	22.8	17.2	7.0
BeP/BaP	2.0	1.8	0.5

a: Data corrected for differences in GC detector response.

In order to determine if this decrease in PAH formation was due to a decrease in CSC per cigarette, the yields of condensate from the three types of cigarettes were determined. Table 6 lists the yields of CSC based on the recovery of condensate from the dry ice traps with acetone and solvent removal on a rotary evaporator to

Table 6. Yields of CSC of cigarettes.

	CSC/90 cig. (g)	CSC/cig. (mg)
1R1	2.74	30.4
Commercial nonfilter	2.18	23.8
Commercial filter	1.08	11.9

Table 7. Percent PAH content of CSC of cigarettes.

PAH	% of CSC $\times 10^5$		
	1R1	Commercial nonfilter	Commercial filter
Phenanthrene	170.0	180.0	140.0
Fluoranthene	70.0	78.0	59.0
Pyrene	6.1	6.2	4.8
1,2-Benzanthracene/ chrysene/triphenylene	7.5	7.2	5.9
BeP/BaP	0.7	0.8	0.4

constant weight. The 1R1 cigarettes yielded 30.4 mg, the commercial nonfilter a little less, and the commercial filter cigarettes 11.9 mg CSC per cigarette. From these yields, the percentages of the various PAH in the original CSC could be calculated (Table 7). For the 1R1 and the commercial nonfilter cigarettes, approximately the same percentage for each of the selected PAH was obtained. However, for the commercial filter cigarettes, there was a reduction in the overall percent content of the PAH. The filter may have reduced the amount of the condensate and the overall content of the PAH in the CSC; or else, the tobacco composition of the cigarettes was different from the nonfilter cigarettes.

In conclusion, a method for the successful analysis of PAH in CSC has been developed that possesses the following advantages: [1] it is quantitative for PAH above phenanthrene in small quantities of CSC and for all PAH in large quantities of CSC, [2] it is reproducible, [3] it can be used for rapid PAH screening of various sources of condensate, and [4] it can be used with condensate fractions obtained by the acid-base fractionation or by the water-extraction procedure.

SUMMARY

A four-step method has been described for the quantitative analysis of polynuclear aromatic hydrocarbons (PAH) in smoke condensate from 90 or more cigarettes. It involves the extraction of condensate solution with water, silicic acid and gel filtration chromatography, then separation and quantitation by gas chromatography. Individual PAH or total PAH profiles of condensates from different cigarettes can now be compared. The method was applied to reference, commercial nonfilter, and commercial filter cigarettes. The details and advantages of the method are elaborated.

ZUSAMMENFASSUNG

Es wird ein vierstufiges Verfahren für die quantitative Analyse der polycyclischen aromatischen Kohlenwasserstoffe (PAH) des Rauchkondensates von 90 und mehr Cigaretten beschrieben. Es besteht aus folgenden Schritten: Extraktion der Kondensatlösung mit Wasser, Kiesel säure- und Gel-Chromatographie, danach Trennung und quantitative Bestimmung durch Gaschromatographie. Auf diese Weise können die Kohlenwasserstoffe einzeln und in ihrer Gesamtheit anhand der Profile der Kondensate verschiedener Cigaretten miteinander verglichen werden. Die Methode wurde bei Versuchscigaretten, bei handelsüblichen filterlosen Cigaretten und bei handelsüblichen Filtercigaretten angewendet. Sie wird mit ihren Einzelheiten und Vorzügen ausführlich dargelegt.

RESUME

On a décrit une méthode en quatre étapes permettant l'analyse quantitative d'hydrocarbures aromatiques polynucléaires (PAH) dans le condensat de fumée produit par 90 cigarettes minimum. Cette méthode implique extraction à l'eau du condensat en solution, chromatographie à l'acide silicique et à perméation de gel, ensuite séparation et évaluation quantitative par chromatographie en phase gazeuse. Les profils des PAH individuels ou globaux de condensats de différentes cigarettes peuvent ainsi être comparés. On a appliqué cette méthode à des cigarettes référence, commerciales sans filtre et commerciales avec filtre. Enfin, les détails et les avantages de la méthode sont discutés.

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Table 4. Comparison of relative abundance of components in PAH profile of 1R1, commercial nonfilter, and commercial filter cigarettes.

Peak No.	Relative retention time ^b	Relative intensities ^a			Compound ^c
		1R1	Commercial non-filter	Commercial filter	
1	0.165	0.70	0.61	0.22	methylbenzo(b)furan
2	0.198	1.20	1.07	0.71	1- and 2-methylindene
3	0.206	2.00	1.92	1.21	methylindene
4	0.238	1.43	0.85	0.81	naphthalene
5	0.256	1.84	0.18	—	dimethylbenzo(b)furan
6	0.285	0.19	0.19	—	dimethylbenzo(b)furan(s), dimethylindene(s)
7	0.292	0.67	0.52	0.54	dimethylindene
8	0.300	1.59	1.09	0.74	dimethylindene
9	0.308	2.40	1.73	1.11	dimethylindene
10	0.327	1.58	0.67	0.40	dimethylindenes

Table 4. Comparison of relative abundance of components in PAH profile of 1R1, commercial nonfilter, and commercial filter cigarettes (contd.).

Peak No.	Relative retention time ^b	Relative intensities ^a			Compound ^c
		1R1	Commercial non-filter	Commercial filter	
11	0.335	2.05	1.58	1.15	2-methylnaphthalene
12	0.350	1.50	1.37	1.04	1-methylnaphthalene
13	0.360	0.62	0.52	0.19	trimethylindene
14	0.372	0.78	0.32	0.10	trimethylindenes
15	0.396	1.98	1.84	0.97	biphenyl, trimethylindenes, trimethylbenzo(b)furan
16	0.412	1.43	0.84	0.46	trimethylbenzo(b)furan, trimethylindene
17	0.422	1.17	1.16	0.86	1- and 2-ethylnaphthalene
18	0.434	2.16	2.07	1.85	2,6- and 2,7-dimethylnaphthalene, 1-vinylnaphthalene
19	0.450	3.70	3.70	2.63	1,3- and 1,6-dimethylnaphthalene, 2-vinylnaphthalene
20	0.467	1.59	1.26	0.72	2,3-, 1,4- and 1,5-dimethylnaphthalene
21	0.476	1.34	1.36	0.78	acenaphthylene, 1,7-dimethylnaphthalene
22	0.489	0.71	0.62	0.40	3-methylbiphenyl
23	0.497	0.53	0.46	0.30	4-methylbiphenyl
24	0.503	0.75	0.74	0.50	acenaphthene, 1,8-dimethylnaphthalene, trimethylnaphthalene
25	0.520	0.63	0.75	0.58	trimethylnaphthalene(s)
26	0.526	1.09	1.00	0.58	dibenzofuran, trimethylnaphthalene
27	0.537	0.55	0.61	0.46	trimethylnaphthalene
28	0.545	1.64	1.72	1.33	naphthofuran, trimethylnaphthalene
29	0.555	1.38	1.46	1.19	trimethylnaphthalene, 2,3-naphtho-1,2-furan
30	0.562	0.77	0.63	0.47	trimethylnaphthalene
31	0.568	0.81	0.90	0.90	trimethylnaphthalenes
32	0.573	0.90	1.10	0.60	trimethylnaphthalene
33	0.581	1.01	1.06	0.56	1-methylacenaphthylene, trimethylnaphthalene
34	0.588	4.24	3.75	2.30	fluorene, methylacenaphthylene, trimethylnaphthalene
35	0.596	1.37	1.28	1.00	9-methylfluorene, methylacenaphthylene, trimethylnaphthalenes
36	0.612	2.52	2.84	2.20	methylacenaphthene, methylacenaphthylene, trimethylnaphthalene
37	0.629	1.33	1.40	0.75	methyl dibenzofuran
38	0.636	0.51	0.52	0.32	benz(f)indene
39	0.647	0.55	0.53	0.30	methylnaphthofuran, dimethylacenaphthene
40	0.660	1.26	1.30	0.85	methylnaphthofuran, dimethylacenaphthene
41	0.682	5.43	5.16	4.30	2- and 3-methylfluorene, dimethylacenaphthylene, methylnaphthofuran
42	0.694	4.49	4.01	3.58	1- and 4-methylfluorene, dimethylacenaphthylene, dimethylacenaphthene
43	0.704	1.27	1.45	1.24	dimethylacenaphthylene, dimethylacenaphthene, dimethyl dibenzofuran
44	0.716	1.22	1.35	1.08	dimethylacenaphthene, dimethyldibenzofuran
45	0.725	0.67	0.68	0.59	dimethylacenaphthene, methylbenz(f)furan
46	0.731	1.38	1.51	1.22	methyl dibenzofuran, dimethylacenaphthene, methylbenz(f)-indene
47	0.745	0.47	0.47	0.36	trimethylacenaphthene, trimethylacenaphthylene, methylbenz(f)-indene, methylnaphthofuran
48	0.754	2.92	2.95	2.91	phenanthrene, trimethylacenaphthene
49	0.760	0.79	0.83	0.71	anthracene
50	0.769	1.85	1.74	1.83	dimethylfluorenes, trimethylacenaphthylenes

Table 4 (contd.)

Peak No.	Relative retention time ^b	Relative intensities ^a			Compound ^c
		1R1	Commercial non-filter	Commercial filter	
51	0.780	2.70	2.58	2.61	dimethylfluorenes, trimethylacenaphthylene, dimethylnaphthofuran
52	0.794	1.69	1.54	1.70	dimethylfluorene, trimethylacenaphthylene
53	0.804	0.68	0.59	0.61	dimethylfluorene, trimethylacenaphthylene
54	0.810	1.48	1.46	2.08	dimethylfluorene, trimethylacenaphthylene
55	0.821	1.38	1.44	1.39	dimethylbenz(f)indene, trimethylacenaphthylene
56	0.843	2.49	2.54	2.52	2- and 3-methylphenanthrene, dimethylfluorene, trimethylacenaphthylene
57	0.849	0.78	0.80	0.79	2-methylanthracene
58	0.859	2.24	2.22	2.14	9-methylphenanthrene, 1-methylphenanthrene, 1-methylanthracene
59	0.877	1.72	1.53	1.68	9-methylanthracene, 4-methylphenanthrene, dimethylphenanthrene, tetramethylacenaphthene, tetramethylacenaphthylene
60	0.897	0.37	0.40	0.39	dimethylphenanthrene, tetramethylacenaphthene, tetramethylacenaphthylene
61	0.905	0.63	0.56	0.36	dimethylphenanthrene, dimethylanthracene
62	0.917	0.64	0.68	0.68	dimethylphenanthrene
63	0.924	1.22	1.33	1.31	dimethylphenanthrene, dimethylanthracene, tetramethylacenaphthylene
64	0.941	2.53	2.49	2.48	dimethylphenanthrene, dimethylanthracene
65	0.951	0.74	0.76	0.72	dimethylphenanthrene
66	0.964	1.11	1.22	1.21	fluoranthene, dimethylphenanthrene, dimethylanthracene
67	0.973	1.07	1.19	1.11	di- and trimethylphenanthrenes, aceanthrylene and/or acephenanthrylene
68	0.993	0.50	0.58	0.45	di- and trimethylphenanthrene
69	1.000	1.00	1.00	1.00	pyrene, dimethylphenanthrenes
70	1.008	0.46	0.52	0.44	trimethylphenanthrene, cyclopentenophenanthrene
71	1.013	0.64	0.68	0.65	di- and trimethylphenanthrene(s), cyclopentenophenanthrene
72	1.023	1.08	1.18	1.02	trimethylphenanthrenes, trimethylanthracene
73	1.044	0.99	1.00	1.04	8-methylfluoranthene, trimethylphenanthrene
74	1.051	0.33	0.41	0.35	1,2-benzofluorene, trimethylphenanthrene
75	1.060	0.93	0.97	0.88	1- and 2-methylfluoranthene, trimethylphenanthrene
76	1.067	0.53	0.56	0.53	2,3- and 3,4-benzofluorene, trimethylphenanthrene
77	1.080	1.00	1.16	1.01	2-methylpyrene, trimethylphenanthrene, methylcyclopentenophenanthrene, cyclopentenophenanthrene
78	1.095	1.05	1.10	1.06	4- and 1-methylpyrene, dimethylfluoranthene, trimethylphenanthrene, cyclopentenophenanthrene, methylcyclopentenophenanthrene
79	1.107	0.37	0.38	0.32	dimethylfluoranthene, cyclopentenophenanthrene, methylcyclopentenophenanthrene
80	1.124	0.73	0.79	0.75	dimethylfluoranthene(s), methyl-1,2-benzofluorene, methylcyclopentenophenanthrene
81	1.133	1.01	1.08	1.04	dimethylfluoranthene(s), methyl-1,2- and -2,3- and -3,4-benzofluorenes
82	1.150	0.50	0.57	0.50	dimethylfluoranthene, dimethylpyrene, methyl-1,2- and -3,4-benzofluorene

Table 4. Comparison of relative abundance of components in PAH profile of 1R1, commercial nonfilter, and commercial filter cigarettes (contd.).

Peak No.	Relative retention time ^b	Relative intensities ^a			Compound ^c
		1R1	Commercial non-filter	Commercial filter	
83	1.160	0.50	0.57	0.50	dimethylpyrene, dimethylfluoranthenes, methylbenzofluorene
84	1.169	0.57	0.60	0.51	dimethylpyrenes, benzo(g,h,i)fluoranthene, methylbenzofluorene, dimethylfluoranthene
85	1.186	0.73	0.93	0.78	dimethylpyrenes, methylbenzofluorene, trimethylfluoranthenes
86	1.207	1.12	1.06	1.12	1,2-benzanthracene, chrysene, triphenylene, trimethylpyrene, trimethylfluoranthene
87	1.230	0.33	0.38	0.31	trimethylpyrene, trimethylfluoranthene, trimethylbenzofluorene, 3,4-dimethylenepylene
88	1.236	0.29	0.25	0.26	trimethylpyrene, trimethylfluoranthene
89	1.246	0.18	0.14	0.15	trimethylpyrenes
90	1.255	0.16	0.19	0.18	trimethylpyrenes, methyl-1,2-benzanthracene, methyl(g,h,i)-fluoranthene
91	1.276	0.53	0.62	0.66	2- and 3-methylchrysene, methyl-1,2-benzanthracene, trimethylpyrene, methyltriphenylene, methylbenzo(g,h,i)fluoranthene
92	1.288	0.17	0.20	0.17	4-methylchrysene, trimethylpyrene, tetramethylpyrene, methyl-1,2-benzanthracenes
93	1.294	0.19	0.23	0.16	1- and 6-methylchrysene, methyl-1,2-benzanthracenes, trimethylpyrene, tetramethylpyrene, methyltriphenylene
94	1.310	0.10	0.13	0.06	3,4-trimethylenepylene, dimethylchrysene, trimethylpyrene, tetramethylpyrene
95	1.322	0.07	0.07	0.03	dimethylchrysene, dimethyl-1,2-benzanthracene, tetramethylpyrene
96	1.336	0.25	0.30	0.23	dimethylchrysenes, dimethyl-1,2-benzanthracenes, dimethyltriphenylene, tetramethylpyrene
97	1.359	0.13	0.19	0.11	dimethylchrysene(s), dimethyltriphenylene, dimethyl-1,2-benzanthracene
98	1.371	0.05	0.04	0.03	di- and trimethylchrysene, trimethyltriphenylene, di- and trimethyl-1,2-benzanthracene
99	1.384	0.12	0.16	0.12	benzo(b,j, and k)fluoranthene, di- and trimethylchrysene
100	1.401	0.05	0.04	0.03	benzo(a)fluoranthene, trimethylchrysene
101	1.413	0.01	0.01	0.02	trimethylchrysene, trimethyl-1,2-benzanthracene, trimethyltriphenylene
102	1.429	0.09	0.10	0.07	benzo(e)pyrene, benzo(a)pyrene, trimethylchrysene, trimethyltriphenylene
103	1.449	0.06	0.06	0.05	methyl(b,j, and k)benzofluoranthene(s), perylene, trimethylchrysene
104	1.464	0.04	0.08	0.05	methyl(b,j, and k)benzofluoranthene(s)
105	1.484	0.02	0.02	0.01	methylbenzo(e)pyrene
106	1.492	0.01	0.02	0.01	methylbenzo(a)pyrene
107	1.508	0.03	0.02	0.02	methylbenzo(e)pyrenes, methylbenzo(a)pyrenes

a: Area count ratios relative to pyrene (peak No. 69), based on unitary detector response.

b: Relative to pyrene; a factor of 80.5 converts this number to retention time in minutes from point of injection.

c: Methods of compound identification are described in detail in reference No. 7.