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INVESTIGATION INTO THE FACTORS AFFECTING PERFORMANCE IN THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS USING CAPILLARY GAS CHROMATOGRAPHY–MASS SPECTROMETRY WITH SPLITLESS INJECTION

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SUMMARY

The importance of solvent choice and temperature program for the separation and quantification of sixteen polycyclic aromatic hydrocarbons (PAHs), considered as priority pollutants, was investigated. For the eight late-eluting PAHs, higher boiling solvents, such as toluene and the xylenes, gave enhanced signals that were between 1 and 100 times greater than those from splitless injections in solvents such as dichloromethane, hexane, acetonitrile, benzene and isooctane. The results indicate that the greatest enhancement can be found by choosing a proper solvent for a specific range of PAHs coupled with an appropriate initial column temperature. Further studies of other parameters were accomplished with toluene as solvent. Simplex optimization of the injection temperature and the initial column temperature gave 260 and 120°C, respectively, as the optima. These optimum conditions also improved the peak shape and resolution. The dependence of the initial column temperature on solvent is discussed with respect of sensitivity and resolution. Detection limits (signal-to-noise ratio = 3) range from 2.4 pg for naphthalene to 86 pg for benzo-[*ghi*]perylene. Relative standard deviations of seven replicate determinations of a 3-ng injection ranged from 2.2 to 10.5% when measured by peak area and from 3.9 to 11.0% when measured by peak height. The studies further illustrate that the sensitivity of late-eluting PAHs can be further improved when xylenes are used as solvents.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been shown to contain several potent carcinogens. One of them (benzo[*a*]pyrene) was identified as the causative agent of scrotal cancer among English chimney sweeps in the eighteenth century[1], the first reported case of occupational carcinogenesis. PAHs are emitted from a wide range of activities such as coal burning, coking operations, household fireplaces, automobiles and cigarette smoking[2]. These activities have resulted in the discovery of PAHs in natural waters, sediment, air and the fatty tissue of exposed animals. The occurrence and potential hazards of this class of compounds have stimulated developments in analytical methods for PAHs, their nitration products and their metabolites[3,4].

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High-performance liquid chromatography (HPLC) and gas chromatography (GC) have usually been considered as most sensitive techniques for the determination of PAHs. Reversed-phase HPLC on C_{18} columns with fluorescence detection has been developed over the last decade. This technique offers both low cost and high sensitivity, but usually requires the collection of fractions composed of isomers or small number of PAHs, before the PAHs can be separated[5–8]. Gas chromatography–mass spectrometry (GC–MS) has the advantage of providing comprehensive information that allows qualitative identification and quantification of the analyte of interest. It also separates a wide range of PAHs in a single run. However, it appears to give relatively poor signals for late-eluting PAH peaks[9].

One way to improve the sensitivity and separation of PAHs by GC is to search for the optimum conditions for the determination. One of the most important factors, the solvent effect, was described by Grob and Grob[10,11] when the analytes such as *n*-heptane, *n*-octane and *n*-nonane were introduced by splitless injection. Cold trapping was originally described as the mechanism operating in the splitless injection mode. Further work[11,12] led to a description of the solvent effect, which is now considered to be an important mechanism for both splitless injection and on-column injection. Grob and Grob's work[12] also suggested that the solvent effect was controlled by four independent factors: column temperature, volatility of the solvent, amount of solvent and injection time. Based on Grob and Grob's studies, Jennings *et al.*[13] described the theoretical basis of the solvent effect. Cold trapping and the solvent effect were described as the two functions that led to the reconcentration of eluates on the top of the column.

The effect of solvent on the response factors of PAHs was recently reported by Lee *et al.*[14]. Their work indicated that different solvents can change drastically the response of an analyte under the same GC conditions. Hence, they suggested that there should be consistency in the solvent used for standards and samples in capillary GC. They used the same conditions of analysis to show the effect so that the other factors, *e.g.*, the relationship between the boiling point of the solvent and the GC conditions, such as injector temperature and oven program, were not investigated.

To achieve the best separation and the highest sensitivity in the determination of PAHs, especially the late-eluting PAHs, by capillary GC, it was felt necessary to study the effect of solvent, the relationship between the boiling point of the solvent and the optimum initial temperature of the column and other factors that might affect the performance in the determination of PAHs by GC–MS.

EXPERIMENTAL

A Hewlett-Packard Model 5890 gas chromatograph equipped with a Model 5970 mass spectrometer, Model 7673A autosampler and Model 300 computer system was used for all determinations. A Hewlett-Packard Ultra 1 (25 m × 0.2 mm I.D., film thickness 0.33 μm) fused-silica capillary column coated with cross-linked methylsilicone gum as the stationary phase was used with splitless injection. Temperature program I in Table I was used to obtain the results in Table II and Fig. 1. With a number of optimization experiments temperature program II in Table I was used for the remainder of the experiments except that initial temperature was changed (see Results and Discussion). Helium (Linde "Zero gas") was used as the carrier gas at

TABLE I
TEMPERATURE PROGRAMS

Program No.[a]	*Level*	*Initial temperature (°C)*	*Initial time (min)*	*Rate (°C/min)*	*Final temperature (°C)*	*Final time (min)*
I	1	100	1	20.0	150	1.5
	2			30.0	200	4.0
	3			30.0	220	4.0
	4			30.0	250	0.2
	5			1.0	263	2.0
	6			50.0	270	0.0
	7			1.0	280	0.0
II	1	120	8	20.0	150	0.0
	2			5.0	187	0.0
	3			30.0	220	0.0
	4			20.0	260	25

[a] Injection port temperature, 250°C; transfer-line temperature, (I) 250°C; (II) 260°C.

a flow-rate of 0.8 ml min^{-1} at ambient temperature. Sample solution (3 μl) was injected onto the column by using the autosampler with a fast injection speed. Peak area and height were integrated by using the computer program.

A commercially available solution of a mixture of sixteen PAHs [2000 μg ml^{-1} of each PAH in dichloromethane–benzene (50:50)] was obtained from Supelco (Oakville, Canada). This standard was dissolved in benzene to give a stock solution containing 40 μg ml^{-1} of each PAH, and 2 μg ml^{-1} solutions of PAHs in different solvents were prepared by dilution of appropriate volumes of this stock solution. All the solvents were of HPLC grade.

RESULTS AND DISCUSSION

Effect of solvent

The sixteen PAHs available commercially represented a reasonably wide range of compounds from the list of priority pollutants. They are listed in Table II with their boiling points. The order of the list in Table II also corresponds to the order in which the PAHs are eluted from the capillary GC column.

Several solvents with different boiling points and different polarities were used to investigate the effect of solvent on the determination of PAHs by GC–MS. In an initial trial, the seven solvents with the lowest boiling points, listed in Table II, were chosen as solvents for the injection of the PAHs. Each of these solvents was used separately to prepare a standard solution containing 2 μg ml^{-1} of each of the sixteen PAHs. An aliquot of 3 μl of this solution was then introduced into the capillary GC column by splitless injection. Both the peak area and peak height of each PAH were determined from the total ion current (TIC) chromatogram with selected ion monitoring. For comparison, the peak areas and peak heights of all PAH peaks, with all seven solvents, were normalized, based on the results obtained with toluene as the solvent. The relative peak areas and peak heights are given in Table II. The peak areas generally increase with increasing boiling point of the solvent, except for the first five peaks in isooctane.

TABLE II

RELATIVE PEAK AREAS AND PEAK HEIGHTS (%) OF PAHs IN DIFFERENT SOLVENTS

Conditions: temperature program I (Table I) and injection volume 3 μl.

Component	*B.p. (°C).*	*Peak No.*	*Parameter*	*Solvent*[a]						
				Dichloromethane (9.080, 40°C)	*Hexane (1.890, 68°C)*	*Benzene (2.284, 80.1°C)*	*Cyclohexane (2.023, 80.7°C)*	*Acetonitrile (38.8, 81.6°C)*	*Isooctane (1.940, 99.2°C)*	*Toluene (2.379, 110.6°C)*
Naphthalene	218	1	Relative peak area	84	89	79	81	64	118	100
Acenaphthylene	270	2		77	84	75	78	63	118	100
Acenaphthene	274	3		77	83	75	76	63	115	100
Fluorene	294	4		69	77	71	72	61	111	100
Phenanthrene	338	5		55	67	62	63	53	112	100
Anthracene	340	6		61	78	73	72	61	99	100
Fluoranthene	383	7		44	63	59	63	54	97	100
Pyrene	393	8		42	61	57	60	53	94	100
Benzo[*a*]anthracene	431	9		15	30	33	35	33	60	100
Chrysene	414	10		24	65	50	52	49	69	100
Benzo[*b*]fluoranthene	481	11		6	17	20	21	25	37	100
Benzo[*k*]fluoranthene	481	12		11	26	31	32	36	47	100
Benzo[*a*]pyrene	496	13		5	17	21	21	27	35	100
Indeno[1,2,3-*cd*]pyrene	–	14		21	6	9	7	14	16	100

Dibenz[*a*,*h*]anthracene	–	15		0(nd)[a]	6	11	8	14	16	100
Benzo[*ghi*]perylene	–	16		1	8	12	9	17	17	100
Naphthalene	218	1	Relative peak height	18	23	37	35	19	103	100
Acenaphthylene	270	2		56	75	79	79	54	84	100
Acenaphthene	274	3		65	82	86	87	61	87	100
Fluorene	294	4		85	106	108	107	84	107	100
Phenanthrene	338	5		92	115	107	110	92	119	100
Anthracene	340	6		85	107	109	108	91	113	100
Fluoranthene	383	7		65	95	89	96	82	111	100
Pyrene	393	8		61	91	85	87	78	106	100
Benzo[*a*]anthracene	431	9		20	42	45	48	45	69	100
Chrysene	414	10		23	50	52	55	50	73	100
Benzo[*b*]fluoranthene	481	11		7	23	26	27	33	45	100
Benzo[*k*]fluoranthene	481	12		8	23	27	29	32	44	100
Benzo[*a*]pyrene	496	13		5	17	27	21	27	37	100
Indeno[1,2,3-*cd*]pyrene	–	14		1	5	9	6	14	16	100
Dibenz[*ah*]anthracene	–	15		0	4	8	6	11	13	100
Benzo[*ghi*]perylene	–	16		1	7	11	8	16	17	100

[a] With dielectric constants and boiling points in parentheses.
[b] Not detected.

TABLE III
RELATIVE PEAK HEIGHTS (%) ON TIC CHROMATOGRAMS OF PAHs
Conditions: temperature program II (Table I) and injection volume 3 μl.

Peak No.[a]	*Solvent*[b]			
	Benzene (2.284, 80.1°C)	*Toluene (2.379, 110.6°C)*	*p-Xylene (2.270, 138°C)*	*o-Xylene (2.568, 144°C)*
1	37	100	94	109
2	60	100	142	167
3	40	100	138	157
4	45	100	92	61
5	38	100	52	65
6	54	100	50	45
7	55	100	49	49
8	55	100	59	53
9	45	100	91	92
10	46	100	71	70
11	70	100	117	109
12	66	100	99	96
13	41	100	112	107
14	24	100	147	120
15	21	100	162	134
16	27	100	143	118

[a] As in Table II.
[b] With dielectic constants and boiling points in parentheses.

The late-eluting peaks from the toluene solution are much larger than those from all the other solvents, which suggests that toluene is much more efficient in transferring the higher molecular weight PAHs onto the column. The peaks from fluorene, phenanthrene, anthracene, fluoranthene and pyrene in low-boiling solvents are more comparable in height with similar peaks from the toluene solutions.

In order to confirm the importance of the boiling point of the solvent on the determination of PAHs by GC–MS, benzene, toluene, *o*-xylene and *p*-xylene, which have similar polarities, with dielectric constants of 2.284, 2.379, 2.568 and 2.270, respectively, but different boiling points, were used as solvents. The TIC chromatograms of PAHs in these four solvents were obtained, under similar conditions, as discussed above, except that the initial temperature was increased from 100 to 120°C. The peak height of each PAH, relative to that of the same PAH in toluene as 100%, are given in Table III. Despite their similar polarities, these solvents caused significant differences in the signals from the PAHs, probably owing to the difference in their volatilities. Again, the greater the difference in boiling point between these solvents, the greater is the difference in relative peak height. Similar observations were made by Lee *et al.*[14], solvents with similar polarity, such as acetonitrile and methanol, giving significantly different responses. This also suggests that this difference in behaviour might be due to the difference in the boiling points of these two solvents.

Determinations of the same amount of PAHs in benzene and toluene as solvents gave the chromatograms shown in Fig. 1 when the initial temperature was 100°C. Comparing Fig. 1a and b, the enhancement of the chromatographic signals when the

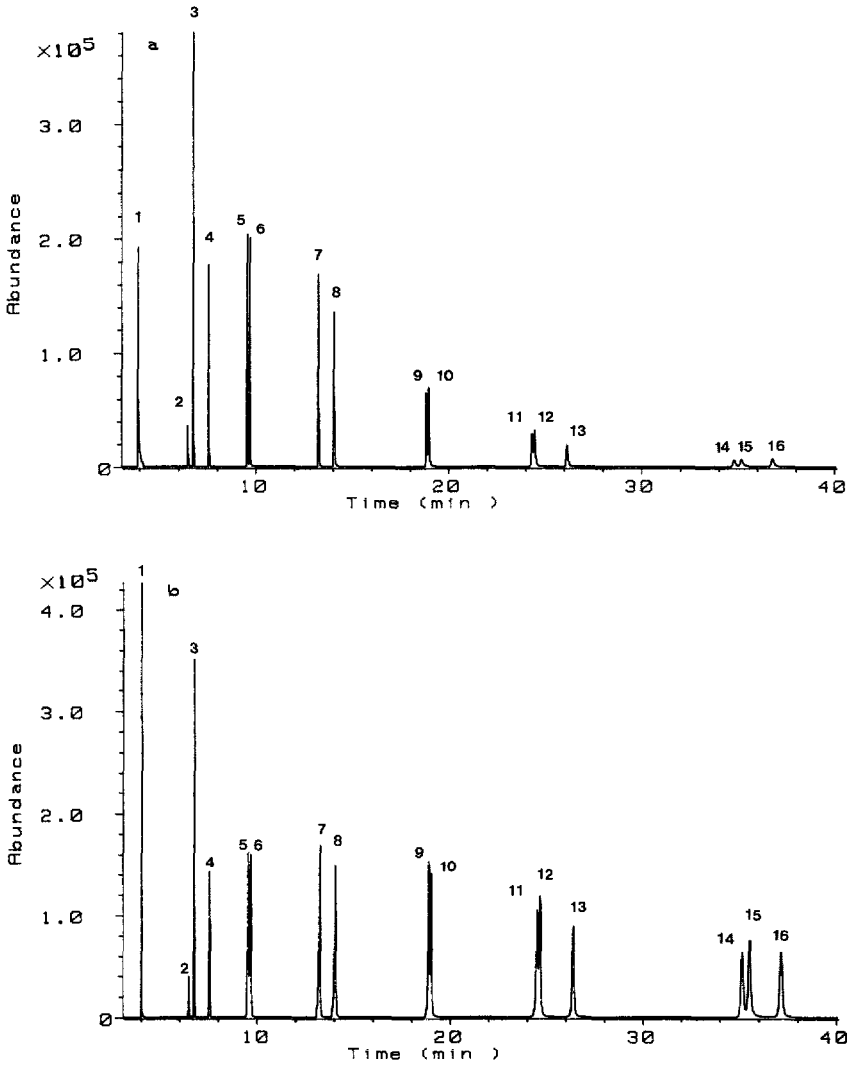

Fig. 1. Chromatograms of the sixteen PAHs: 3 μl of 2 μg ml^{-1} solutions in (a) benzene and (b) toluene. Peak numbering as in Table II.

solvent is toluene can be clearly seen, especially the dramatic enhancement of the late-eluting peaks. The enhancing effect of the higher boiling solvent on the TIC signal can be interpreted as reconcentration of PAHs by the solvent effect. In Grob and Grob's model of the solvent effect[12], the vaporized material is transferred onto the column essentially as a mixture. In the first stage of separation on the column, the solvent shifts away from the sample components and the relatively wider band of solvent blocks the expansion of the vapors of the solutes so that the solutes are reconcentrated in a narrow band. This effect appears to become more pronounced as

the boiling point of the solvent increases. Thus the responses of the solutes are greater from toluene than from benzene solutions.

The solvent itself would not be expected to change the ionization process in mass spectrometric detector as the solutes and solvent will be separated in time. This, was confirmed by the observations that the ratio $[M+1]^+/M^+$ for each PAH was independent of the solvent. If the solvent participated in the process of ionization of the PAH, the abundance of $[M+1]^+$ would be changed owing to chemical ionization in addition to electron-impact ionization.

Effect of initial temperature

Column temperature and temperature programming were found to affect the resolution and sensitivity of the mixture of PAHs. The temperature program mentioned under Experimental was found to be optimum for the determination of PAHs in toluene solution with regard to both resolution and sensitivity. This temperature program was also appropriate when PAHs were dissolved in other solvents, except that the initial temperature was changed. The effect of the initial temperature on the determination of PAHs was found to be more significant than the temperatures during the later stages. Therefore, studies on the effect of initial

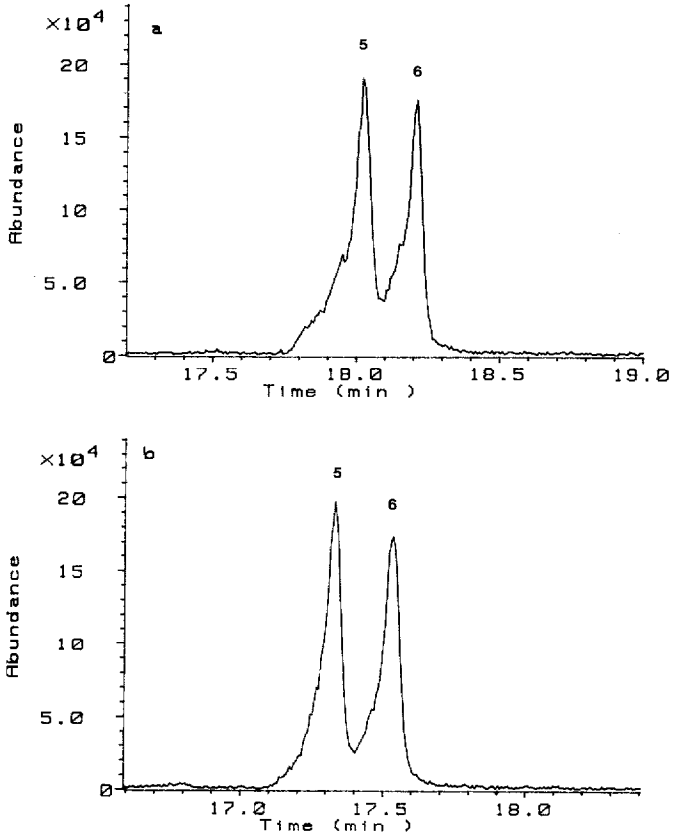

Fig. 2.

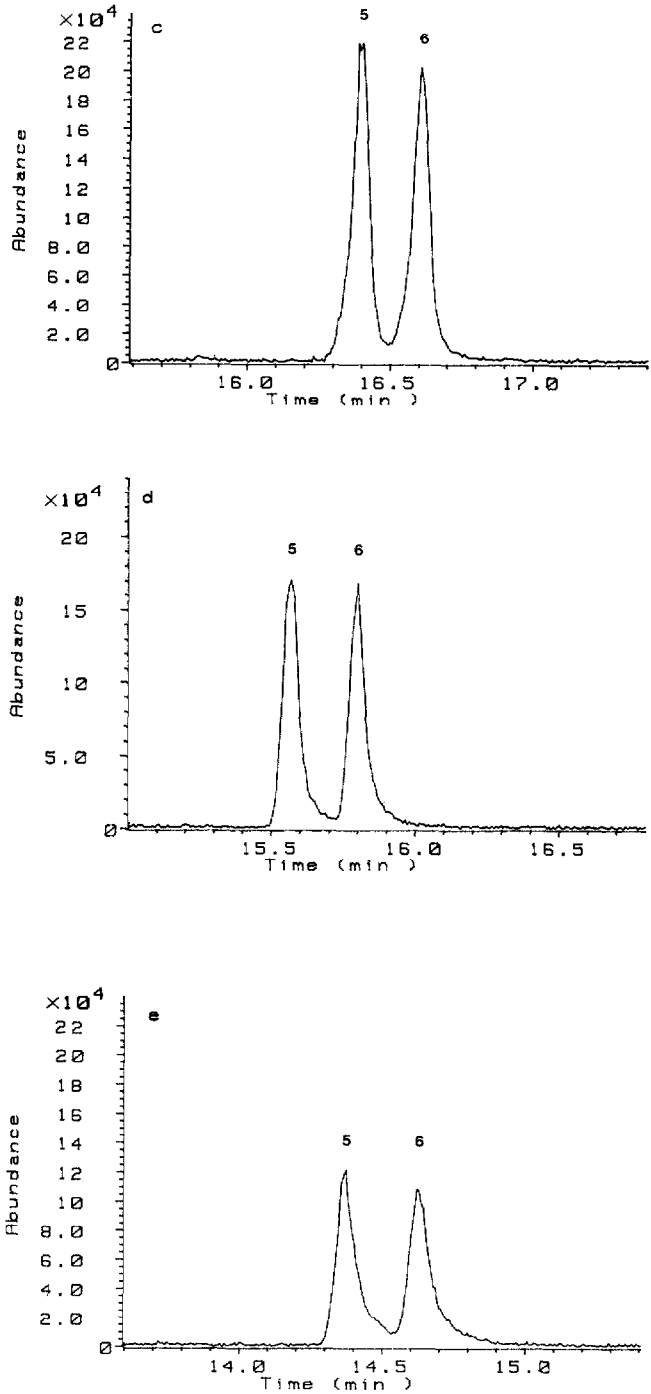

Fig. 2. Effect of initial temperature on peak shape of (5) phenanthrene and (6) anthracene: (a) 100; (b) 110; (c) 120; (d) 130; (e) 140°C.

temperature were carried out while the remainder of the temperature program was kept unchanged.

The effect of initial temperature on peak resolution and peak shape is clearly demonstrated in Fig. 2, which compares chromatograms of phenanthrene and anthracene in toluene at initial temperatures of (a) 100, (b) 110, (c) 120 (d) 130 and (e) 140°C. At the lowest initial temperature, fronting of the peak appeared (Fig. 2a). With increase in the initial temperature from 100 to 120°C, the fronting of the peaks gradually disappeared, and a symmetrical peak was obtained when the initial temperature was 120°C (Fig. 2c). With a further increase in initial temperature from 120 to 140°C, tailing of the peaks occurred, leaving asymmetric peaks (Fig. 2e). Similar results were obtained using other solvents. Fronting appeared at initial temperatures lower than the boiling point of the solvent; tailing appeared at initial temperatures higher than 20°C above the boiling point of the solvent. This effect is more significant for the eight early-eluting peaks than for the late-eluting peaks.

In order to determine the effect of initial temperature on peak height and area, aliquots of 3 μl of 2 μg ml^{-1} PAH solutions in benzene, toluene, *o*-xylene and *p*-xylene were injected sequentially. At different initial temperatures varying within 10–20°C above and below the boiling point of the solvent, TIC chromatograms of the sixteen PAHs were obtained. Peak heights and peak areas were determined, and the relative peak height and area of each PAH were then calculated and compared with those determined at 10°C above the boiling point of the solvent. The results are summarized in Table IV. The optimum initial temperature depends on the solvent used; at an initial temperature between the boiling point of the solvent and 10–20°C higher than the boiling point, the highest response, measured by peak area and peak height, was achieved. The results in Table IV indicate that the solvent with the lowest boiling point (*i.e.*, benzene, 80°C) showed the smallest range of optimum initial temperature. If a higher boiling (*e.g.*, xylene) was used, the changes in response of the PAHs were small within a relatively wider initial temperature range. Hence the most symmetrical peaks with the highest responses were achieved by using an initial temperature 10–20°C above the boiling point of the solvent used. The data in Table V are based on these conditions. Initial temperatures of 90 and 120°C are optimum for benzene and toluene as solvents, respectively. The peak area and peak height of the PAHs in Table V show that toluene gives a higher sensitivity than benzene.

While other parameters were kept constant and the initial time was varied from 2 to 10 min, a series of determinations of the PAHs in toluene and *p*-xylene were carried out. The effect of the length of time at the initial column temperature is not as significant as the initial temperature itself. Resolutions of peaks 5 and 6, 9 and 10, 11 and 12, and 14 and 15, at different initial times, were not obviously changed. The relatively better resolution between the closest pairs of peaks and sensitivity for the sixteen PAHs were achieved with an initial time of 8 min for toluene and 4 min for *p*-xylene. When a higher boiling solvent was used, a different initial temperature was necessary for optimum sensitivity and resolution. Thus, for *p*-xylene the initial temperature was 148°C and the initial time was kept at 4 min.

Other factors

The injection port temperature directly affects the efficiency of sample vaporization, and therefore also affects the sensitivity of determination. As the

TABLE IV

RELATIVE PEAK AREAS AND HEIGHTS (%) OF PAHs IN AROMATIC SOLVENTS AT DIFFERENT INITIAL COLUMN TEMPERATURES

Conditions: temperature program II (Table I) and injection volume 3 μl.

Peak No.[a]	*Parameter*	*Benzene (80°C)*[b]			*Toluene (110.6°C)*[b]					*p-Xylene (138°C)*[b]			*o-Xylene (144°C)*[b]			
		80°C	*90°C*	*100°C*	*100°C*	*110°C*	*120°C*	*130°C*	*140°C*	*128°C*	*138°C*	*148°C*	*158°C*	*144°C*	*154°C*	*164°C*
1	Relative	167	100	54	92	113	100	88	75	–	–	–	–	–	–	–
2	peak area	142	100	72	81	108	100	89	81	113	120	100	89	18	100	–
3		147	100	73	83	114	100	114	83	106	112	100	85	113	100	–
4		135	100	78	88	111	100	121	84	108	111	100	85	116	100	87
5		138	100	71	90	111	100	113	72	104	113	100	97	109	100	80
6		134	100	74	78	106	100	108	75	105	111	100	94	108	100	78
7		136	100	74	85	106	100	114	75	107	108	100	98	104	100	86
8		126	100	72	87	107	100	112	75	102	105	100	96	102	100	85
9		127	100	70	104	112	100	113	73	120	115	100	140	98	100	77
10		121	100	70	85	103	100	109	78	91	96	100	101	123	100	96
11		126	100	65	100	104	100	115	87	110	112	100	97	106	100	78
12		120	100	70	95	101	100	101	86	96	94	100	100	125	100	93
13		111	100	71	100	112	100	111	70	101	101	100	99	112	100	84
14		118	100	71	94	101	100	120	63	104	105	100	108	118	100	75
15		122	100	67	92	102	100	120	54	101	109	100	106	118	100	78
16		114	100	50	111	126	100	120	92	98	105	100	102	125	100	84
1	Relative	114	100	68	64	88	100	48	15	–	–	–	–	–	–	–
2	peak height	106	100	76	98	109	100	50	32	86	98	100	68	77	100	–
3		108	100	80	94	98	100	71	33	113	90	100	73	86	100	–
4		104	100	74	90	95	100	80	42	138	125	100	83	101	100	99
5		109	100	67	89	93	100	79	56	67	88	100	67	161	100	98
6		106	100	68	90	91	100	85	56	67	88	100	67	113	100	100
7		108	100	75	81	96	100	83	59	73	84	100	82	136	100	111
8		110	100	78	76	90	100	79	63	64	76	100	82	129	100	114
9		113	100	71	87	104	100	79	70	96	95	100	99	115	100	96
10		116	100	71	79	97	100	82	71	85	87	100	100	156	100	100
11		121	100	70	95	103	100	88	83	102	101	100	100	114	100	86
12		118	100	66	86	96	100	88	79	91	100	100	97	128	100	94
13		113	100	60	91	109	100	81	75	99	95	100	95	122	100	92
14		117	100	51	100	108	100	74	66	101	102	100	107	126	100	88
15		115	100	54	88	100	100	74	66	100	103	100	100	116	100	77
16		116	100	60	94	104	100	80	96	98	97	100	100	78	100	90

[a] As in Table II.

[b] Boiling point.

TABLE V
RELATIVE PEAK AREAS AND HEIGHTS (%)
Conditions: temperature program II (Table I) and injection volume 3 μl.

Peak No.[a]	*Relative peak area*		*Relative peak height*	
	Benzene (90°C)[b]	*Toluene (120°C)*[b]	*Benzene (90°C)*	*Toluene (120°C)*
1	76	100	59	100
2	66	100	107	100
3	67	100	120	100
4	65	100	125	100
5	67	100	111	100
6	63	100	99	100
7	61	100	71	100
8	60	100	73	100
9	45	100	48	100
10	49	100	51	100
11	37	100	39	100
12	37	100	37	100
13	33	100	34	100
14	24	100	25	100
15	22	100	22	100
16	24	100	24	100

[a] As in Table II.
[b] Initial column temperature.

injection port temperature was increased from 200 to 250°C, the peak areas of most of the sixteen PAHs gradually increased, reaching a maximum at 250°C and remaining similar between 250 and 260°C. When the injection port temperature was increased further to 270 and 280°C, a decrease in peak area was observed. A similar effect was also obtained for peak heights.

To obtain optimum conditions for both injection port temperature and initial temperature in the determination of PAHs, a simplex optimization method was applied to optimize these two factors. The mean value of the heights of all sixteen individual PAH peaks on the TIC chromatogram was used as the response as all the peaks changed in a similar fashion. Toluene was used to prepare standard solutions. Both factors were varied at the same time, regulated by the simplex optimization method. A full simplex optimization was accomplished with nine experimental units. The results indicate that the highest response for the sixteen PAHs was obtained under the optimum conditions of an injection port temperature of 260°C and an initial column temperature of 120°C.

The temperature of the interface (*i.e.*, transfer line) between the GC column and the mass spectrometer is also a factor that could influence sensitivity. It was found that a relatively high temperature of the interface is needed in order to achieve the highest sensitivity. An interface temperature of 260°C was chosen as it gave sufficient sensitivity and was the highest temperature in the temperature program and reasonably below the limiting temperature (300°C, suggested by the manufacturer). Although the sensitivity of PAHs depended on the interface temperature, the

TABLE VI
DETECTION LIMITS OF PAHs IN TOLUENE AND *p*-XYLENE
Conditions: temperature program II (Table I) and injection volume 3 μl.

Peak No.[a]	*Detection limit (3σ) (pg)*	
	Toluene (120°C)[b]	*p-Xylene (148°C)*[b]
1	2.4	4.4
2	10.5	7.5
3	8.7	8.0
4	24.6	8.8
5	27.0	3.0
6	49.2	3.0
7	16.8	2.7
8	13.5	2.8
9	34.5	4.4
10	17.4	4.1
11	33.3	11.7
12	28.2	10.7
13	94.7	17.1
14	69.0	43.6
15	85.8	43.6
16	62.1	30.8

[a] As in Table II.
[b] Initial column temperature.

resolution of peaks was not affected appreciably by this factor within the range of temperatures used. Also, the length of the interface (20 cm) is very short compared with the 25-m length of the capillary column, and would not be expected to have a significant effect on resolution.

Analytical figures

Calibrations for the sixteen PAHs in toluene were carried out under the optimum conditions, as discussed above, for PAH concentrations in the range 0.02–6 μg ml^{-1}. Both peak area and peak height were used as response. The correlation coefficients of the calibration graphs in the concentration range 0.20–6.0 μg ml^{-1} were better than 0.97 for all sixteen PAHs.

Seven replicate determinations of 3 ng (3 μl of 1 μg ml^{-1} solution) of each of the sixteen PAHs in toluene were carried out under the optimum conditions in order to determine the precision. Relative standard deviations (R.S.D.s) in the range 3.9–11.0% based on peak height, and 2.2–10.5% based on peak area were obtained for the sixteen PAHs. Nine replicate determinations of 3 ng of the sixteen PAHs gave R.S.D.s for the retention time of 0.45% for naphthalene and less than 0.1% for the other fifteen PAHs.

The detection limits (signal-to-noise ratio = 3) for the determination of the sixteen PAHs by GC–MS were at low picogram levels, as shown in Table VI, ranging from 2.4 pg for naphthalene to 94.7 pg for benzo[*a*]pyrene when determinations were made in toluene and from 4.4 pg for naphthalene to 30.8 pg for benzo[*a*]pyrene for determinations in *p*-xylene.

CONCLUSIONS

When toluene and xylenes are used as solvents to prepare solutions of PAHs for injection into the GC–MS column, enhancement of signals can be obtained. The optimum initial temperature is based on the boiling point of the solvent. The results could be applied to the determination of PAHs in environmental samples.

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REFERENCES

1 P. Pott, 1775, quoted by A. Bjørseth and T. Ramdahl, in A. Bjørseth and T. Ramdahl (Editors), *Handbook of Polycyclic Aromatic Hydrocarbons, Vol. 2, Emission Sources and Recent Progress in Analytical Chemistry*, Marcel Dekker, New York, 1985, p. 1.
2 K. D. Bartle, M. L. Lee and S. A. Wise, *Chem. Soc. Rev.*, 10 (1981) 113.
3 M. L. Lee, M. V. Novotny and K. D. Bartle, *Analytical Chemistry of Polycyclic Aromatic Compounds*, Academic Press, New York, 1981, pp. 50–73.
4 K. D. Bartle, in A. Bjørseth and T. Ramdahl (Editors), *Handbook of Polycyclic Aromatic Hydrocarbons, Vol. 2, Emission Sources and Recent Progress in Analytical Chemistry*, Marcel Dekker, New York, 1985, p. 193.
5 M. V. Novotny, L. Lee and K. D. Bartle, *J. Chromatogr. Sci.*, 12 (1974) 606–607.
6 M. J. Dennis, R. C. Massey and D. J. McWeeny, *J. Chromatogr.*, 285 (1984) 127–133.
7 P. G. Sim, R. K. Boyd, R. M. Gershey, R. Guevremeont, W. D. Jamieson, M. A. Quilliam and R. J. Gergely, *Biomed. Environ. Mass Spectrom.*, 14 (1987) 357–381.
8 S. A. Wise, B. A. Benner, G. D. Byrd, S. N. Chesler, R. E. Rebbert and M. M. Schantz, *Anal. Chem.*, 60 (1988) 887–894.
9 H. G. Nowicki, C. A. Kieda and D. O. Bassett, in A. Bjørseth and A. J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons: Chemical and Biological Effects*, Battelle Press, Columbus, OH, 1980, pp. 75–87.
10 K. Grob and K. Grob, Jr., *J. Chromatogr. Sci.*, 7 (1969) 584–591.
11 K. Grob and K. Grob, Jr., *J. Chromatogr.*, 94 (1974) 53–64.
12 K. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 57–64.
13 W. G. Jennings, R. R. Freemann and T. A. Rooney, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 275–276.
14 H.-B. Lee, R. Szawiola and A. S. Y. Chau, *J. Assoc. Off. Anal. Chem.*, 70 (1987) 929–930.