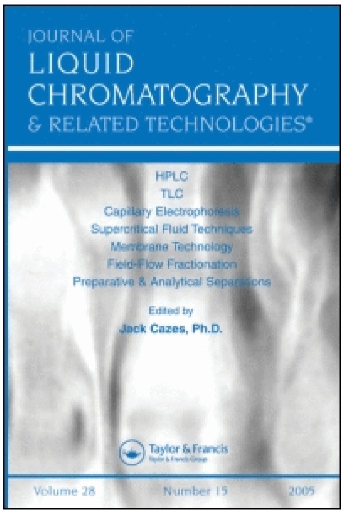

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DETERMINATION OF POLYPHENYLARENES AND POLYNUCLEAR AROMATIC HYDROCARBONS BY REVERSED PHASE HPLC

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ABSTRACT

Standard mixtures of polycyclic compounds are analyzed by reversed phase microcapillary liquid chromatography. Acetonitrile/water and acetonitrile/THF/water are employed as stationary phases, and capacity ratios are reported. Polyphenylarenes can be distinguished from polynuclear aromatic hydrocarbons by a large shift in capacity ratios when changing the mobile phase. The shift in capacity ratios is most significant for 1,3,5-triphenylbenzene, which is demonstrated by a gradient elution. The influence of THF and water on retention behaviour of solutes is described.

INTRODUCTION

Although polynuclear aromatic hydrocarbons (PAHs) can be determined efficiently by glass capillary gas chromatography (1,2,

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3), the importance of HPLC for the determination of these compounds is increasing. This is due to the fact that PAHs with more than 6 fused benzene rings and their derivatives are involatile, which makes their determination by GC difficult. Furthermore, some isomeric PAHs can be separated easily by liquid chromatography, whereas their separation by gas chromatography is difficult to achieve.

Hydrophobic ODS-silica is widely employed in HPLC of PAHs (4). Differences in selectivity of ODS-silica from different manufacturers and different batches have been noted when analyzing mixtures of polycyclic compounds (5,6,7). Acetonitrile with varying water content is used almost exclusively as a mobile phase.

When analyzing mixtures of PAHs and polyphenylarenes by reversed phase HPLC with acetonitrile as a mobile phase, members of both compound classes show similar capacity ratios. PAHs and polyphenylarenes will then be eluted from the column at random when analyzing samples containing both PAHs and polyphenylarenes. In order to avoid the difficulties arising from this situation, the applicability of a different solvent system to such mixtures is investigated in this work.

MATERIALS AND METHODS

Reagents

Pure reference compounds of polyphenylarenes and polynuclear aromatic hydrocarbons were purchased from Aldrich (Milwaukee, Wis., USA) and from Tokyo Kasei Chemicals (TCI, Japan). Solvents were supplied by Wako Pure Chemical Industries Ltd. (Japan). All standard compounds and solvents were of analytical grade and were used without further purification.

Equipment

A micro-HPLC apparatus consisting of a Micro-Feeder (Azumaden Kikogyo Co. Ltd. Japan), an Uvidec 100-II UV-spectrophotometer (Jasco, Japan), a Jasco Micro-Loop Injector ML-422 with a cell volume of 0.08 µl and YEW Typ 3056 Pen Recorder were used. The microfeeder was fitted with a Terumo microsyringe of 100, 250 or 500 µl volume.

Columns

Columns were prepared from fused silica tubing (Scientific glass Engineering, Australia) of 0.30 mm ID. They were packed with a slurry of ODS-silica (particle size 5 µm, type SC 101, Jasco) in acetonitrile after one end had been plugged with glass wool. The column length was 10 cm.

Procedure

Columns were rinsed with 1 ml of acetonitrile at a flow rate of 2 µl/min after packing. They were then fitted to the micro-HPLC apparatus. Injections of samples were done with the loop injector or by the stopped-flow method. Standard solutions of PAHs and polyphenylarenes in ethanol or acetonitrile at concentrations of 200 ppm were used. They were prepared from stock solutions of these compounds in toluene by evaporation of the toluene and addition of the appropriate solvent. Mobile phases were acetonitrile/water or a mixture of 50 vol% water, 25 vol% tetrahydrofuran and 25 vol% acetonitrile. A gradient elution starting with 60% acetonitrile in water, and progressing to the aforementioned mixture containing THF was also performed. The UV-adsorption of both mobile phases was brought to the same level by addition of potassium phthalate to the solvent of higher UV-transmission.

RESULTS AND DISCUSSION

Mixtures of PAHs isolated from coal, airparticulate matter or automobile exhaust (8,9) are extremely complex. The separation efficiency of columns employed in liquid chromatography is much less than what is the minimum requirement for a resolution of such mixtures unless very long columns and analysis times are employed

(10). It was not intended to achieve maximum separation efficiency in this work, but to investigate the influence of the mobile phase on the chromatographic separation. Microcapillary LC columns employed in this investigation were packed with 10 µm ODS-silica and separation efficiencies of 4000 - 5000 theoretical plates/m were obtained. Standard mixtures with up to 10 polycyclic solutes were submitted to analysis, and since the number of standard compounds was limited, chromatograms could be interpreted easily.

Acetonitrile/water is the most common solvent system used in determination of PAHs by reversed phase HPLC. This solvent system was also used in the chromatogram displayed in Figure 1a. 1,3,5-Triphenylbenzene, which does not contain any fused benzene rings and can thus be distinguished from PAHs, is eluted along with PAHs. The solvent system methanol/water also elutes PAHs and 1,3,5-triphenylbenzene at similar retention times. Tetrahydrofuran, however, has a different selectivity towards PAHs and 1,3,5-triphenylbenzene. When employing a mixture of 25% THF, 25% acetonitrile and 50% H_2O, the capacity ratio of 1,3,5-triphenylbenzene shows a large shift, and the compound is clearly separated from PAHs. (Fig. 1b)

This remarkable effect is also observed when a gradient elution is carried out (Fig. 2). A shift of the baseline of the UV-detector during mixing of the starting solvent and the gradient forming solvent was not observed, since their UV-absorbance was adjusted to the same value by addition of potassium phthalate.

The shift in the elution volume of 1,3,5-triphenylbenzene is remarkable. The shift of capacity ratios of 1,4-diphenylbenzene and 9-phenylanthracene is larger than the shift of capacity ratios of polynuclear aromatic hydrocarbons (Table 1, Figure 1), and the elution order of some PAHs is reversed. These results indicate that the effect can contribute to a characterization of these polyphenylarenes in mixtures of PAHs, if two or three chromatograms obtained under different chromatographic conditions are available.

Furthermore, it was investigated what caused this remarkably different retention behaviour of such structurally closely related

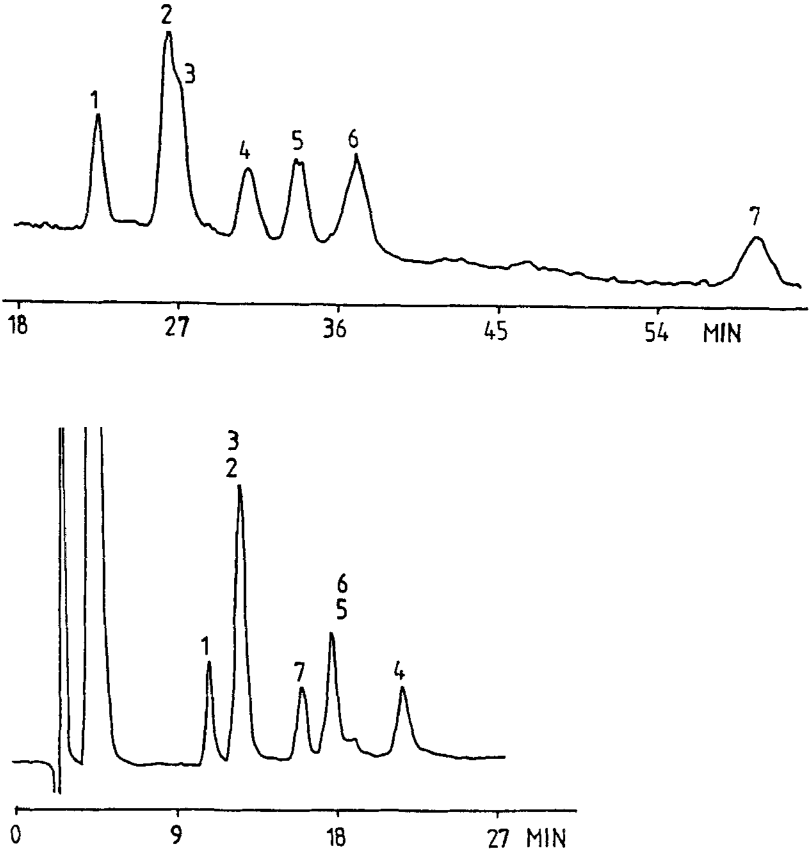

Figure 1. Liquid Chromatograms of a standard mixture of polycyclic compounds, column: 0.3 mm x 10 cm packed with ODS 10 µm, flow rate: 2.0 µl/min.

peak numbers:

1 triphenylene, 2 chrysene, 3 benz(a)anthracene,
4 benzo(a)pyrene, 5 perylene+benzo(b)fluoranthene,
6 benzo(e)pyrene+benzo(k)fluoranthene,
7 1,3,5-triphenylbenzene

a) upper chromatogram: mobile phase THF/CH_3CN/H_2O 1:1:2
b) lower chromatogram: mobile phase CH_3CN/H_2O 7:3

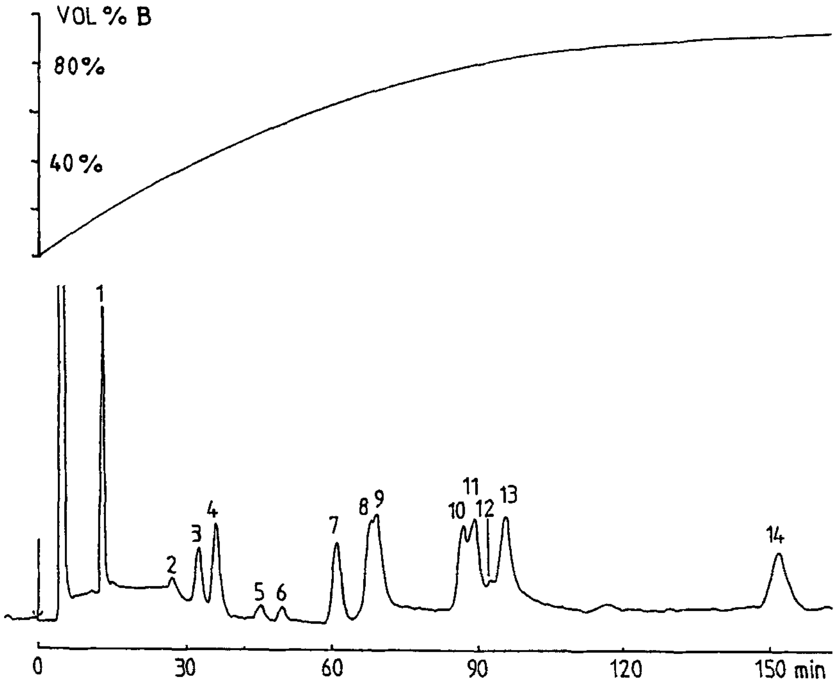

Figure 2. Liquid Chromatogram of 15 standard polycyclic compounds, column 0.3 mm x 10 cm, stationary phase: Jasco SC 101RP18 silica, 10 µm, flow rate: 2 µl/min.
Gradient: from acetonitrile/water 4+6 to THF/acetonitrile/H_2O 1+1+2 (B)
Detection: UV at 254 nm
peak numbers: 1 toluene, 2 fluorene, 3 phenanthrene, 4 anthracene, 5 fluoranthene, 6 pyrene, 7 triphenylene, 8 benz(a)anthracene, 9 chrysene, 10 benzo(a)pyrene, 11 perylene + benzo(b)fluoranthene, 12 benzo(k)fluoranthene, 13 benzo(e)pyrene, 14 1,3,5-triphenylbenzene.

TABLE 1

Table 1 Capacity ratios of several Polycyclic Compounds on ODS-silica, 10 µm Particle Size

A: mobile phase acetonitrile/water 70 vol% + 30 vol%
B: mobile phase water/acetonitrile/THF 50 + 25 + 25 vol%

	A	B
1,4-Diphenylbenzene	4.5	8.8
1,3,5-Triphenylbenzene	6.8	17.3
9-Phenylanthracene	6.2	9.7
Chrysene	5.1	7
Benzo(e)pyrene	7.4	9.2

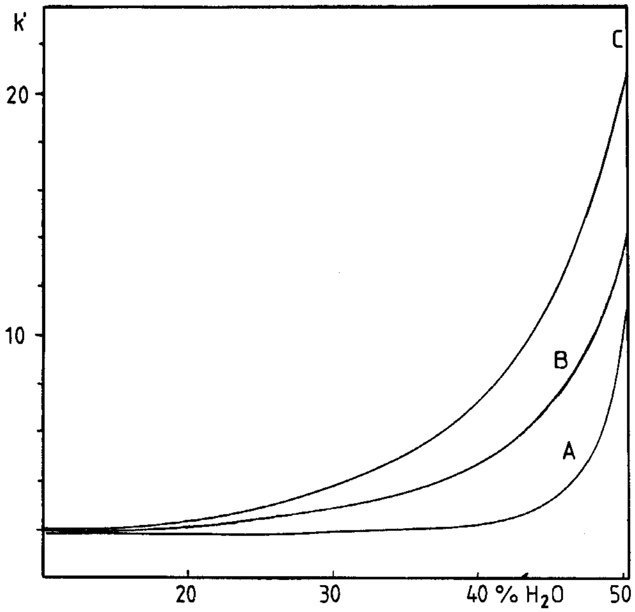

Figure 3. Capacity ratios of 3 polycyclic compounds on ODS-silica at varying water contents of the mobile phase (Tetrahydrofuran/Acetonitrile 1+1). A=Chrysene, B=1,3,5-Triphenylbenzene, C=Benzo(a)pyrene.

compounds. Fig. 3. shows the dependence of capacity ratios of 1,3,5-triphenylbenzene, chrysene and benzo(a)-pyrene on the water content in a mixture of acetonitrile/THF 1+1. Increasing the water content in the mobile phase doesn't change it's selectivity, but delays the elution of all components.

Fig. 4 displays the dependence of capacity ratios on the content of THF in the solvent system acetonitrile/water, while the water content is kept constant at 30%. It is obvious from these data that the addition of THF to the mobile phase alters its selectivity towards polycyclic compounds. At a high THF-content, 1,3,5-triphenylbenzene is eluted from the column after benzo(a)pyrene. The delayed retention of 1,3,5-triphenylbenzene

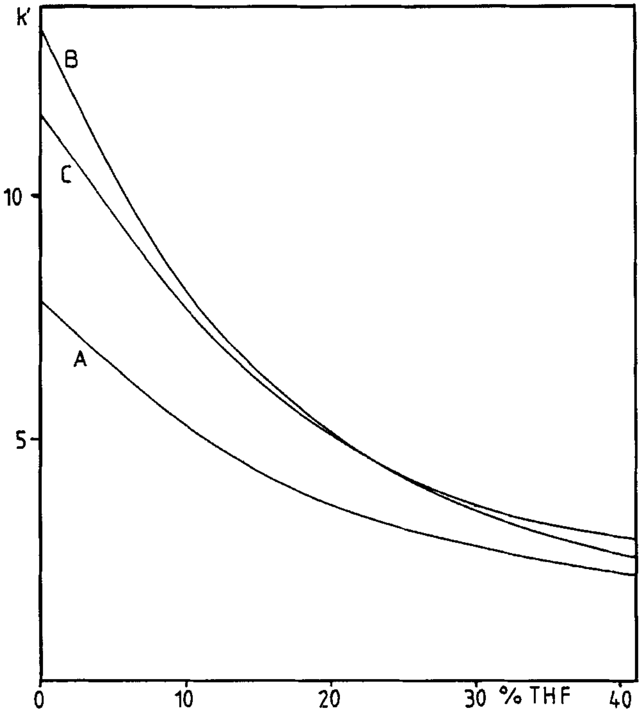

Figure 4. Capacity ratios of 3 polycyclic compounds on ODS-silica at increasing THF-content of the mobile phase (30% H_2O, 70%-30% Acetonitrile). A=Chrysene, B=1,3,5-Triphenylbenzene, C=Benzo(a)pyrene.

is most remarkable, if the water content of the stationary phase is more than 30%.

These experiments demonstrate how an appropriate change of the mobile phase improves the determination of polycyclic hydrocarbons by liquid chromatography. The microcapillary LC-system used in these investigations facilitated a rapid change of the mobile phase and was thus well suited for these investigations.

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