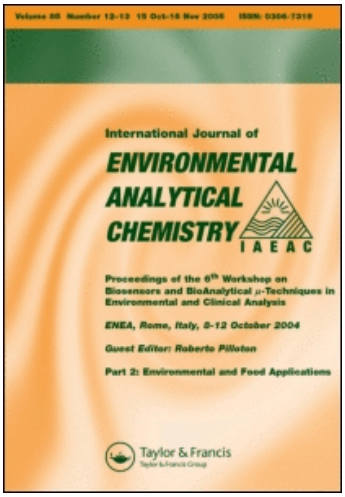

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Robert Alexander[a]; Kimberley m. Cumbers[a]; Robert I. Kagi[a]
[a] Petroleum Geochemistry Group, School of Applied Chemistry, Western Australian Institute of Technology, BENTLEY, Western, Australia

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Analysis of Multiring Aromatic Hydrocarbons by HPLC Using a Reverse-Phase Radial Compression Column System†

ROBERT ALEXANDER, KIMBERLEY M. CUMBERS and ROBERT I. KAGI

Petroleum Geochemistry Group, School of Applied Chemistry, Western Australian Institute of Technology, Kent Street, BENTLEY 6102, Western Australia

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The performance of a radially-compressed C_{18} reverse-phase column system for analysis of multiring aromatics has been assessed in terms of efficiency, resolution and analysis time, and these parameters are compared with those reported for other column systems. The optimum conditions for analysis were established using nine standard aromatic compounds. These conditions are aslo shown to be suitable for analysis of complex mixtures of aromatic compounds obtained from petroleum refinery effluent waters, marine biota and combustion residues (soot).

INTRODUCTION

Analysis of aromatic compounds in samples of effluent waters and marine biota is of continuing interest.[1,2] HPLC techniques have proven particularly useful for the analysis of polynuclear aromatics (PNA's) because of the speed, sensitivity and specificity which can be achieved, particularly when used in conjunction with UV fluorescence detectors.[3,4]

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Separations using normal-phase column packing materials have been widely used,[5,6] however the more recently-developed bonded-phase packings offer significant practical advantages to the analyst in terms of reduced activation cycles and speed of analysis. In this paper we report the use of a radially-compressed non-polar column for the simultaneous, rapid analysis of aromatics ranging from dinuclear compounds through to six-ring PNA's.

EXPERIMENTAL

HPLC analysis

All measurements were performed using a Varian 8500 dual pump LC system equipped with a VARISCAN variable wavelength UV detector. The column system consisted of a WATERS ASSOCIATES Radial Compression Module equipped with a RADIAL PAK C_{18} Cartridge.

Sample volumes were usually 1.5 μl, and the optimum flow rate was 1.5 ml min^{-1}. The initial composition of the solvent was 62% acetonitrile in water. This was continued for ten minutes, then the acetonitrile content was increased at 4% per minute for four minutes, followed by constant composition for five minutes, and a final increase to 100% acetonitrile at the initial rate of 5% per minute for four minutes and finally at a rate of 2% per minute.

GC-MS analysis

All measurements were made using a Hewlett-Packard 5985B system equipped with a 25 m × 0.25 mm ID, fused-silica capillary column coated with SP2100 liquid phase. The column was programmed from an initial temperature of 60°C, to a final temperature of 270°C at 4°C/min. Hydrogen was used as carrier gas at a flow velocity of 30 cm sec^{-1}.

Standards

All compounds used as standards were of analytical grade and were purchased from Unilab (naphthalene), BDH (phenanthrene), KOCH-LIGHT (pyrene, fluoranthrene, chrysene, benzo(α)pyrene, benzo(g,h,i)perylene), SIGMA (perylene, dibenz(a,h)anthracene).

Sample preparation

Samples of oil refinery effluent water, marine biota and soot were extracted with dichloromethane using established procedures.[7,8] The concentrated organic extract was then subjected to column chromatography using silicic acid and the fraction eluting from the

column with pentane-ether (20:1) was retained. This fraction was further purified by medium pressure liquid chromatography using a SILICA 60 MERCK column. The compounds which had retention times between those of naphthalene and perylene eluted from the column with hexane-dichloromethane (7:1) solvent were retained for further HPLC analysis.

RESULTS AND DISCUSSION

In order to provide a direct comparison of the performance of the RADIAL PAK C_{18} radial compression system with that reported recently for other column systems,[9] performance parameters were measured under isocratic conditions with perylene and benzo(α)pyrene as substrates. Table I contains the retention time (tr), plate number (N) and HETP (H) data for the two substrates, together with resolution values (Rs) determined using acetonitrile-water (70:30) as solvent. Comparison of the performance of the radial compression system with that reported by Amos for two other reverse-phase columns[9] shows that its performance is intermediate between that of the other two. The radial compression system does however meet the minimum requirements specified by this author for analysis of PNA's, in that resolution is greater than 1.5 and the longer retention time is less than thirty minutes.

TABLE I

Performance parameters for reverse-phase columns using isocratic conditions, (a) $Rs = 2\ (tr_2 - tr_1)/w_2 + w_1$ where tr_1 and tr_2 represent the retention times and w_1 and w_2 the base peak width of the two compounds and (b) data from reference 9.

Column	Perylene			Benzo(α)pyrene			Rs[a]
	t_r(min)	N (plates)	H(mm)	t_r(min)	N (plates)	H(mm)	
Radial Pac C_{18}	16.0	2200	0.054	18.3	2400	0.050	1.7
μ Bondapack C_{18}[b]	22.7	4303	0.058	25.0	4303	0.058	1.6
HC-ODS-Sil-x-1[b]	9.3	1697	0.15	13.7	1764	0.14	4.0

Samples often contain PNA's because of contamination by material of petrogenic origin. Such samples usually contain di- and trinuclear aromatic compounds in addition to the higher ring homologues. To analyse the complete range of aromatic compounds, the analysis conditions were optimised using a solvent gradient. Figure 1 shows the traces obtained from chromatographs of a set of standard aromatic compounds ranging from two to six aromatic rings using a UV detector at three different wavelengths. From these traces it is apparent that efficiency

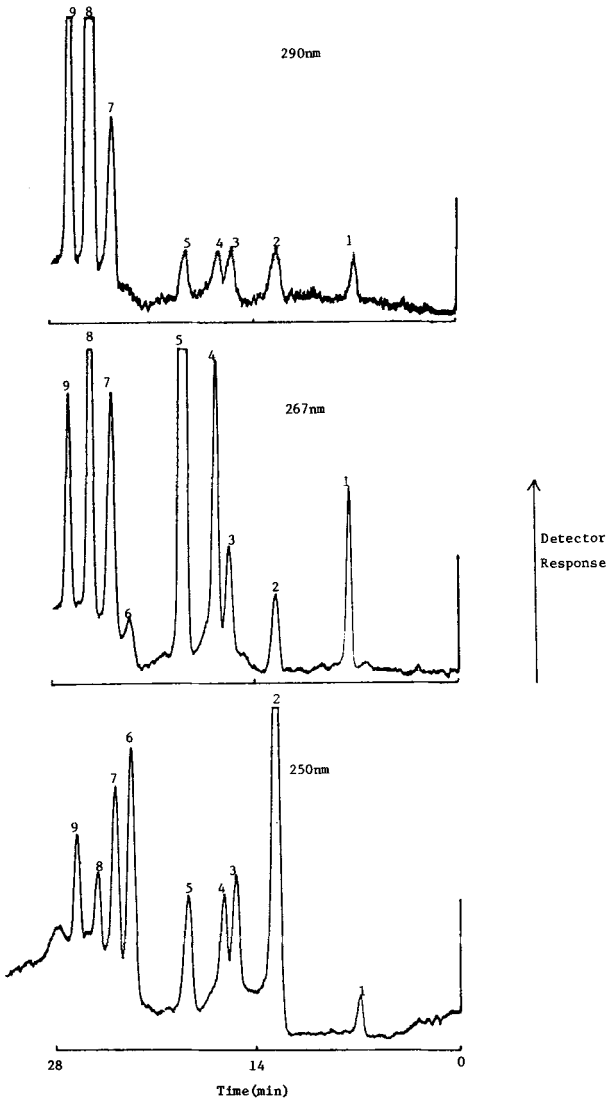

FIGURE 1 HPLC traces showing separation of aromatic standards using gradient elution and the detector response at three wavelengths. Numbers represent naphthalene (1), phenanthrene (2), fluoranthrene (3), pyrene (4), chrysene (5), perylene (6), benzo(α) pyrene (7), dibenz(a, h)anthracene (8) and benzo(g, h, i)perylene (9).

and resolution are maintained at suitable levels throughout the analysis, that the analysis can be completed in under thirty minutes, and that the most suitable wavelength for detection of these compounds is 267 nm.

Figure 2 shows traces obtained from the aromatic fraction of extracts

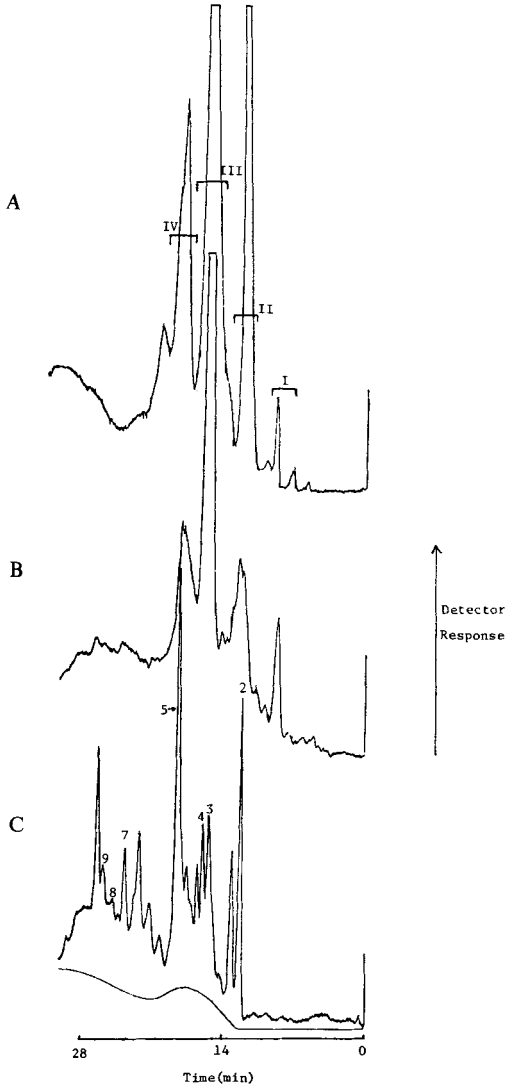

FIGURE 2 HPLC traces for the analysis of aromatic components of extracts of (A) mullet; (B) effluent water; (C) chimney soot using gradient elution and a detection wavelength of 267 nm. Peaks are numbered as described for Figure 1.

from fish (A), refinery effluent water (B) and chimney soot (C). The refinery effluent waters originate from a petroleum refinery and are discharged into a semi-enclosed bay. The fish sample was obtained from a specimen of mullet (*Aldrichetta foresteri*) captured within the effluent mixing zone adjacent to the effluent outfall. Traces A and B both show characteristics of petrogenic aromatic hydrocarbons. Peaks with retention times indicated by I coincide with those of naphthalene and methylnaphthalenes while peak II retention times coincide with dimethynaphthalenes and phenanthrene. These assignments were verified by collecting the fractions eluting over these time intervals and subjecting them to further analysis by capillary GC-MS. This technique provided further evidence that peak III represents both trimethylnaphthalenes and methylphenanthrenes, and peak IV dimethylphenanthrenes. This order of elution is also consistent with that reported by other workers.[10] Such a distribution of aromatic compounds is typical of crude oil[11] and suggests that the mullet has been contaminated by petroleum contained in the effluent waters. Trace C shows the results obtained from analysis of a sample obtained from chimney soot. Assignment of peaks was carried out by by coinjection with an authentic standard: the numbers on this trace represent the same compounds as those in Figure 1. One major difference between Trace C and Trace A and Trace B is that Trace C contains much sharper peaks. This is the result of the differences in composition of aromatic hydrocarbons derived from combustion sources from those of petrogenic origin.

Usually, the petrogenic compounds contain a greater variety of alkylsubstituted aromatic rings than do typical combustion-derived aromatics which contain predominantly unsubstituted aromatic compounds.[12,13] The resultant narrower retention time intervals in the HPLC trace for the combustion-derived sample may prove to be of value in deciding between possible sources of contamination by aromatic compounds.

References

1. B. K. Afghan and A. W. Wolkoff, *J. Liq. Chromatogr.* **4,** 99 (1981).
2. D. W. Grant and R. B. Meiris, *J. Chromatogr.* **203,** 293 (1981).
3. K. Ogan, E. Katz and W. Slavin, *Anal. Chem.* **51,** 1315 (1979).
4. R. C. Lao and R. S. Thomas, Analytical Techniques in Environmental Chemistry, Ed. J. Albaiges, p. 97, Pergamon, Oxford (1978).
5. R. K. Sorrell and R. Reding, *J. Chromatogr.* **185,** 655 (1979).
6. J. P. Durane and N. Petroff, *J. Chromatogr.* **190,** 85 (1980).
7. R. J. Law, Oily Water Discharges. Eds., C. S. Johnston and R. J. Morris, p. 167, Applied Science, London (1980).

8. D. G. Shaw and B. A. Baker, *Environ. Sci. Technol.* **12,** 1200 (1978).
9. R. Amos, *J. Chromatogr.* **204,** 469 (1981).
10. J. Chmiclowiec, J. E. Beshai and A. E. George, *Fuel,* **59,** 838 (1980).
11. B. P. Tissot and D. H. Welte, *Petroleum Formation and Occurrence* p. 351, Springer-Verlag, Berlin (1978).
12. J. L. Lake, C. Norwood, C. Dimock and R. Bowen, *Geochim. Cosmochim. Acta.* **43,** 1847 (1979).
13. R. E. Laflamme and R. A. Hites, *Geochim. Cosmochim. Acta.* **42,** 289 (1978).