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ENTROPY DOMINATED HIGH PRESSURE LIQUID CHROMATOGRAPHIC SEPARATIONS
OF POLYNUCLEAR AROMATIC COMPOUNDS. TEMPERATURE AS A SEPARATION
PARAMETER

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ABSTRACT

The elution sequences of some polynuclear aromatic hydrocarbons from a Chromegabond-C₁₈ column with aqueous acetonitrile have been found to be influenced by temperature changes. These influences are ascribed to domination by entropy effects.

INTRODUCTION

Polynuclear aromatic compounds in synthetic fuels have much significance. They must be partially hydrogenated to produce fuels with acceptable combustion characteristics. Some of them become involved in reactor fouling during upgrading processes and some are highly carcinogenic.

High pressure liquid chromatographic systems are used in many methods for analyses of polynuclear aromatic hydrocarbons and there is much development work in this field (1,2). In our preliminary work with chromatographic system consisting of a silica-C₁₈ column with aqueous solutions of acetonitrile as the mobile phase, poor reproducibility was found to be due to changes in ambient temperatures. Temperature effects on the separations of polynuclear aromatic hydrocarbons were therefore investigated to find optimum separation temperatures.

Although temperature changes during liquid chromatography have been utilized to some extent (4,5,6), the effect of temperature has received little attention with the exception of chromatographic systems employing small amounts of modifiers (7,8,9).

EXPERIMENTAL

- Column: - Chromegabond-C₁₈ (300 x 4.6 mm) (ES Industries)
- Mobile Phase: - Water-acetonitrile (20:80) and pure acetonitrile
- Pump: - Waters Associates Model 6000
- Flow Rate: - 2 ml/min with pressure drop of 1000 psi
- Injection: - Valco valve with 28 ml loop
- Dectors: - UV spectroflow monitor (Schoeffel SF 870) and UV spectrofluorometer (Varian SF-330) in series. Cell volumes were 8 μ l and 16 μ l respectively.
- Sample Solutions: - In acetonitrile (ca. $1 \cdot 10^{-4}$ - $5 \cdot 10^{-3}$ M)
- Temperature Control: - Water from a controlled temperature bath was circulated through the jacket of the column. Fixed temperatures controlled to $\pm 0.1^{\circ}\text{C}$ were used. When the gradient temperature was employed, control was $\pm 0.2^{\circ}\text{C}$.

RESULTS AND DISCUSSION

For most of the compounds, the mobile phase consisted of water-acetonitrile solution in the ratio 20:80 by volume. For 6-8 ring aromatic compounds, pure acetonitrile was needed. Retention values obtained using the aqueous solution at 25°C are shown in Table 1. Water-acetonitrile mobile phases with silica-C₁₈ columns have been used by other workers for the separation of aromatic compounds (2). They used gradients of 50 to 30% water in acetonitrile as the mobile phase to separate di- and trinuclear aromatic hydrocarbons, but gradients of 15 to 0% water were used to separate hydrocarbons with larger aromatic systems. Prather and co-workers (3) used a 55:45 water-acetonitrile mobile phase for studying aromatics and heteroatom compounds in creosote oils for coal liquefaction studies.

The effect of temperature gradient upon the resolution of the compounds shown in Figure 1 may be seen by comparing Figure 1, at constant temperature, with Figure 2, in which the temperature gradient of 2.6°C/min up to 50°C was employed. The temperature gradient resulted not only in compressing of the peaks but also in better separations. In Figure 1 compounds 13 and 14 are unresolved at 25°C, but were separated with the temperature gradient as shown in Figure 2. Compound 19 eluted after compound 20 at the higher temperature.

These temperature effects on the separation of polynuclear aromatic hydrocarbons have been studied in more detail with pairs of compounds selected from Table 1 whose retention values are similar. In a number of cases (Figure 3) the sequence of elution was reversed by changing the column temperature. All cases in Figure 3 involved the 20:80 water-acetonitrile mobile phase. The reversal was also found in the separation of o-phenylenepyrene and picene when the mobile phase was pure acetonitrile with temperature changes from 15 to 55°C. These effects were found to be independent of sample concentration when it was varied from 5×10^{-3} to 1×10^{-4} M. It appears that with increase in temperature, retention of more compactly condensed aromatic compounds decreases at a greater rate than retention of less compact compounds.

Generally, temperature increases cause decreases in the time required for separation and are detrimental to resolution with the exception of systems involving small amounts of modifiers in adsorption chromatography. This is described by Snyder (8) and Scott and Lawrence (9).

The changes in elution sequences obtained when different temperatures are used for chromatography of the polynuclear aromatic hydrocarbons can be ascribed to domination by entropy effects as discussed by Giddings (10). Successful separations depend on the magnitude of the difference " ΔK " between the distribution coefficients " K " of two species transferred between the mobile and stationary phases. The magnitude of ΔK can be expressed in thermodynamic terms by the equation

$$\Delta K/K = - \Delta(\Delta H^{\circ})/RT + \Delta(\Delta S^{\circ})/R$$

Changes in ΔH° and ΔS° are considered negligible and it can be seen from the above equation that only the term involving enthalpy differences is affected by changes in temperature. In most cases the enthalpy term is larger than the entropy term and thus temperature increases lead to decreases in ΔK and thus to poorer separation. However, when the enthalpy term is smaller than the entropy term, temperature increases are beneficial for separation because ΔK increases although of opposite sign.

Separation of the polynuclear aromatic hydrocarbons as shown in Figure 3 involves situations in which the enthalpy differences at the lower temperatures are larger than the entropy differences. Then as the temperatures are increased, enthalpy and entropy differences become equal and the entropy differences become the dominating factors, with further temperature increases causing desirable increased differences in the distribution coefficients.

Thus controlled temperature variations and the influences of entropy can have much significance during the liquid chromatography of polynuclear aromatic compounds and have much potential for improving the resolution of difficult-to-separate compounds. The effect of temperature changes on separations might be compared to changes in the compositions of mobile phases. Thus temperature changes might substitute for changes in mobile phase composition or might be complimentary to them.

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TABLE I

Elution Volumes (ml) of Polynuclear Aromatic Hydrocarbons with
Aqueous 80% Acetonitrile from Silica-C₁₈ Column at 25°C

| | | | |
|----------------------------|------|----------------------------------|-------|
| Indene | 5.8 | p-Terphenyl | 17.7 |
| Naphthalene | 7.0 | Triphenylene | 17.7 |
| Acenaphthylene | 7.6 | 1,1'-Dinaphthyl | 17.8 |
| Diphenyl | 8.1 | 2,3-Benzofluorene | 18.4 |
| Acenaphthylene | 8.7 | 1,2-Benzofluorene | 18.4 |
| 2-Methylnaphthene | 9.0 | Difluorenyl | 19.0 |
| Vinylnaphthalene | 9.2 | 1,2-Benzanthracene | 20.8 |
| Fluorene | 9.4 | Chrysene | 20.8 |
| 9,10-Dihydroanthracene | 9.5 | 9-Phenylanthracene | 21.8 |
| 2-Methyldiphenyl | 9.9 | 1-Methylpyrene | 23.4 |
| Phenanthrene | 10.3 | 3-Methylpyrene | 23.4 |
| 2,3-Dimethylnaphthalene | 10.5 | 1,3,5-Triphenylbenzene | 24.9 |
| 1,5-Dimethylnaphthalene | 10.8 | 2,2'-Dinaphthyl | 24.9 |
| Ethyl naphthalene | 11.1 | 4-Methylpyrene | 25.0 |
| 1-Benzyl naphthalene | 11.1 | 2-Phenylanthracene | 28.5 |
| 2,7-Dimethylnaphthalene | 11.3 | 3,4-Benzofluorene | 30.8 |
| 1,6-Dimethylnaphthalene | 11.7 | Tetracene | 30.8 |
| 2,6-Dimethylnaphthalene | 11.7 | 9,10-Dimethyl-1,2-benzanthracene | 30.8 |
| Anthracene | 11.8 | Perylene | 31.7 |
| o-Terphenyl | 11.8 | 11,12-Benzofluoranthene | 33.7 |
| 1-Phenylnaphthalene | 12.1 | 3,4-Benzopyrene | 38.8 |
| 2-Phenylnaphthalene | 13.1 | 9,10-Diphenylanthracene | 42.6 |
| 3-Methylphenanthrene | 13.3 | 1,2-5,6-Dibenzanthracene | 46.4 |
| Fluoranthene | 13.8 | 1,12-Benzoperylene | 57.2 |
| m-Terphenyl | 13.8 | p-Quaterphenyl | > 57 |
| 4,4'-Dimethyldiphenyl | 13.9 | o-Phenylene-pyrene | > 57 |
| 5,12-Dihydrotetracene | 14.3 | 3-Methylcholanthrene | > 57 |
| 4-Benzoyldiphenyl | 14.6 | 3,4-Benzotetraphene | > 57 |
| 9-Methylanthracene | 14.6 | 1,2-3,4-Dibenzopyrene | > 57 |
| 1,3,7-Trimethylnaphthalene | 14.9 | Picene | > 57 |
| Pyrene | 15.9 | Anthanthrene | > 57 |
| 3,4-Benzofluorene | 17.6 | Coronene* | >> 57 |
| | | Rubrene* | >> 57 |
| | | 1,2-8,9-Dibenzopentacene* | >> 57 |

* Eluted with Aqueous 90% acetonitrile

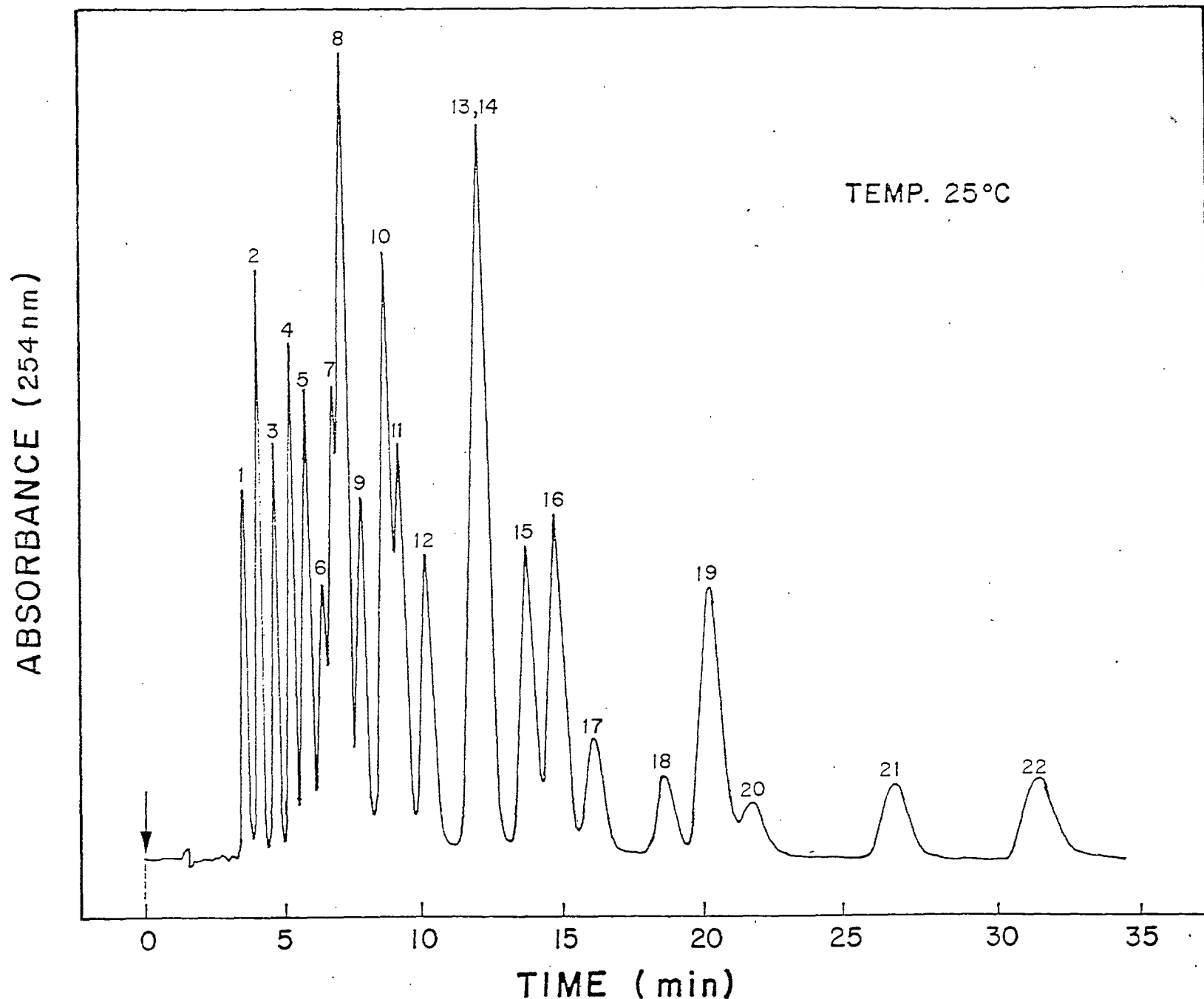


FIGURE 1. Isothermal separation of polynuclear aromatic compounds on silica-C₁₈ column with mobile phase of water-acetonitrile (20:80). 1. Naphthalene, 2. Diphenyl, 3. Fluorene, 4. Phenanthrene, 5. Anthracene, 6. 2-Phenylnaphthalene, 7. Fluoranthene, 8. 9-Methylanthracene, 9. Pyrene, 10. Triphenylene, 11. Difluorenyl, 12. Chrysene, 13. 1,3,5-Triphenylbenzene, 14. 2,2'-Dinaphthyl, 15. 2-Phenylanthracene, 16. 3,4-Benzofluoranthene, 17. 11,12-Benzofluoranthene, 18. 3,4-Benzopyrene, 19. 1,2-5,6-Dibenzanthracene, 20. 1,12-Benzoperylene, 21. 1,2-3,4-Dibenzpyrene

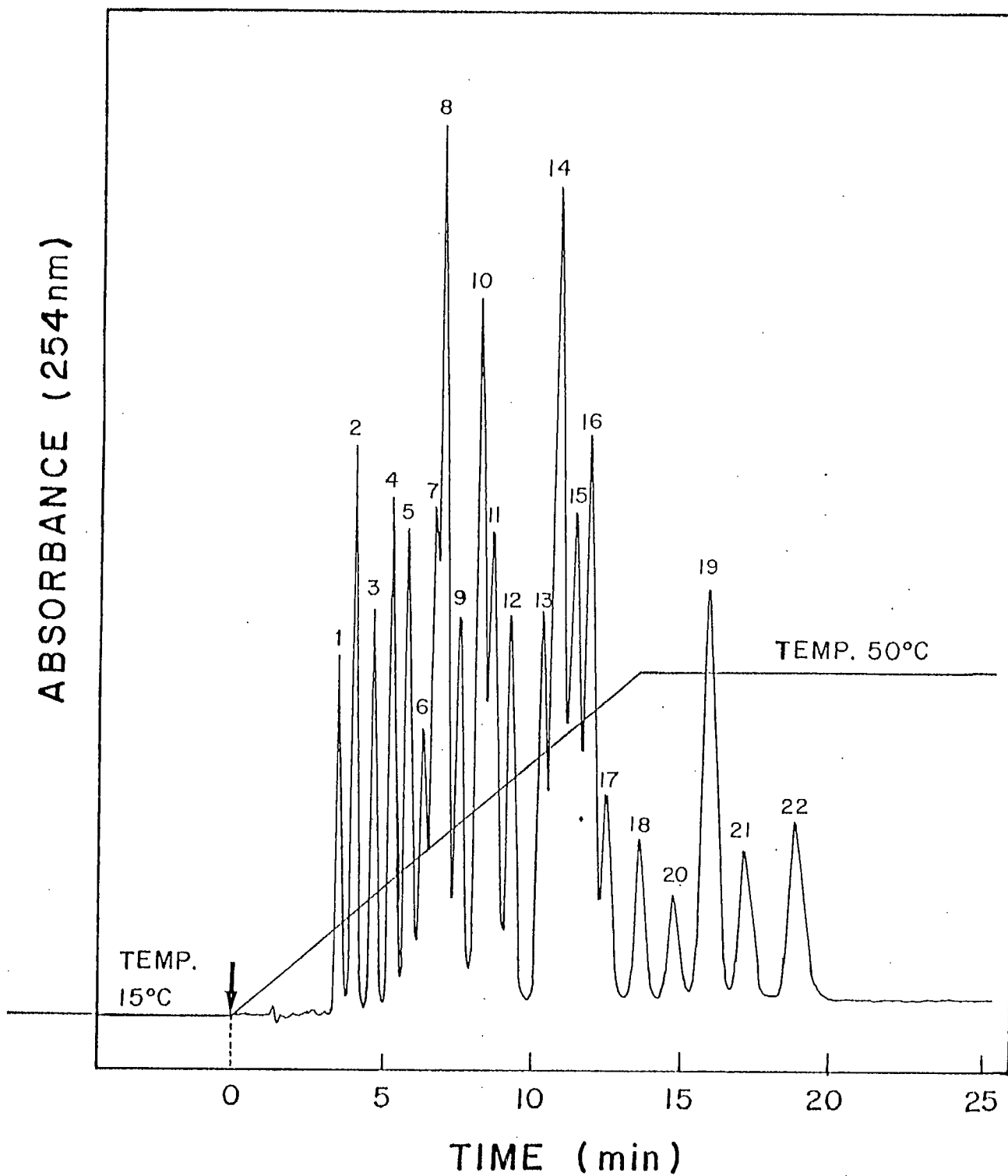


FIGURE 2. Gradient temperature separation of compounds shown in Figure 1.

| COMPOUNDS | DETECTION | CHROMATOGRAMS |
|--|--|--------------------|
| A. o-TERPHENYL B. ANTHRACENE | λ_{EX} 238nm λ_{EM} 370nm UV 254nm | 11°C 25°C 45°C |
| A. m-TERPHENYL B. FLUORANTHENE | λ_{EX} 265nm λ_{EM} 352nm UV 254nm | 11°C 25°C 45°C |
| A. 1,1'-DINAPHTHYL B. TRIPHENYLENE | λ_{EX} 265nm λ_{EM} 352nm UV 275nm | 10°C 35°C 65°C |
| A. 1,3,5-TRIPHENYL-BENZENE B. CHRYSENE | λ_{EX} 265nm λ_{EM} 352nm UV 254nm | 10°C 15°C 20°C |
| A. 1,3,5-TRIPHENYL-BENZENE B. 4-METHYLPYRENE | λ_{EX} 265nm λ_{EM} 352nm UV 254nm | 12°C 20°C 30°C |
| A. 9,10-DIMETHYL-1,2-BENZOANTHRACENE B. 3,4-BENZOFLUORANTHENE | λ_{EX} 265nm λ_{EM} 420nm UV 254nm | 15°C 25°C 45°C |
| A. 9,10-DIPHENYL-ANTHRACENE B. 1,2,5,6-DIBENZO-ANTHRACENE | λ_{EX} 265nm λ_{EM} 425nm UV 254nm | 25°C 30°C 35°C |

FIGURE 3. Changes in elution sequence with temperature changes.