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SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY LIQUID CHROMATOGRAPHY ON CROSS-LINKED POLYVINYLPYRROLIDONE

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SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) can be separated by liquid chromatography on cross-linked polyvinylpyrrolidone (PVP) stationary phase using a polar solvent as eluent. The order of elution is determined primarily by the number of condensed aromatic rings Efficient separations were obtained with a column packed with 63–90 μm particles of PVP and isopropanol as eluent. Capacity factors (k') ranged from 0.3–10 for PAHs having from one to five aromatic rings, and theoretical plate heights were between 0.3 and 0.5 mm. This technique is being used to assist in the characterization of products from coal liquefaction processes.

INTRODUCTION

There is currently a real need for improved analytical methodology for separating, concentrating, and determining polycyclic aromatic hydrocarbons (PAHs) in a variety of substances. The characterization of materials which are largely a very complex mixture of aromatic hydrocarbons —such as petroleum, petroleum products, coal, and products from coal conversion processes— is an important requirement in the development of energy sources. Determination of trace quantities of PAHs in complex mixtures of other chemical types is also of some significance. Because of their carcinogenic potential and possible environmental damage, there has been considerable concern over the occurrence of trace amounts of PAHs in such diverse materials as air particulates, engine exhausts, tobacco smoke, raw, potable, and waste waters, sea-water, plants, and soils.

In studies of cross-linked polyvinylpyrrolidone (PVP) and other polyamide stationary phases for liquid chromatography (LC) of aromatic acids, aldehydes, and phenols, Olsson and Samuelson[1,2] noted that benzene and naphthalene were also retained and separated on their columns. The applicability of PVP as a stationary phase for chromatography of PAHs has now been investigated in some detail and found to

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provide a simple, inexpensive, and reasonably efficient means of separating many PAHs.

EXPERIMENTAL

Polyclar AT, a commercial cross-linked PVP, was obtained from Serva (Heidelberg, G.F.R.) and 63–90 μm particles isolated by dry sieving. Soluble material was extracted by boiling in 10% HCl for 10 min and residual fines removed by repeated washing and decantation in water.

Equipment for chromatography consisted of a Milton Roy mini pump, Cheminert Model R6031SV sample injection valve, jacketed glass (Cheminert, Type LC-6M) or stainless-steel columns, and an Laboratory Data Control Model 1285 Ultraviolet Monitor operated at 254 nm. Columns were packed by simple sedimentation using a column packing reservoir. Operating pressure depended primarily on the particle size of the PVP packing, and to a lesser extent on the flow-rate and temperature. It rarely exceeded 200 p.s.i. and was usually much lower.

Normally, 5–15 μg of each compound were injected on the column either individually or in mixtures in a volume of 150 μl of isopropanol. Oil samples were diluted as necessary to remain on the scale of the UV monitor. Eluents were filtered and degassed before use.

RESULTS AND DISCUSSION

Elution order of PAHs

Typical chromatograms of mixtures of PAHs are shown in Figs. 1–3. A 360 × 6 mm I.D. column was used, isopropanol as eluent at a flow-rate of 0.3 ml/min,

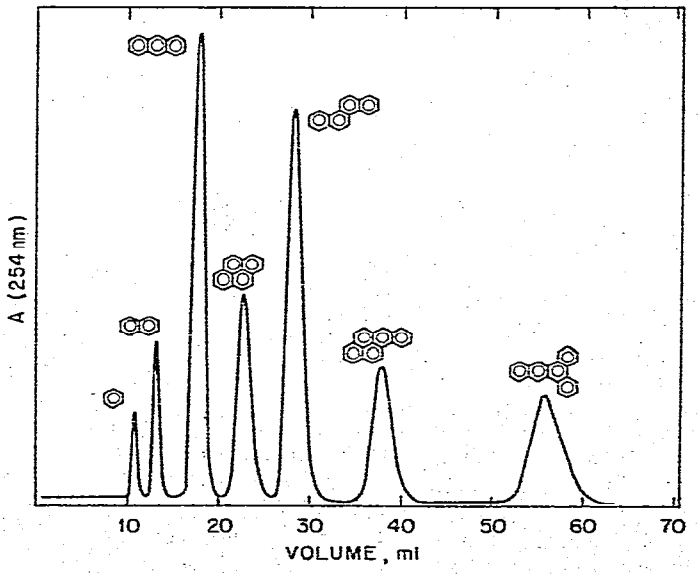

Fig. 1. Separation of benzene, naphthalene, anthracene, pyrene, chrysene, benzo[*a*]pyrene, and dibenz[*a*,*c*]anthracene on PVP. Column, 360 × 6 mm I.D.; packing, 63–90 μm PVP; eluent, isopropanol; flow-rate, 0.3 ml/min; column temperature, 62°.

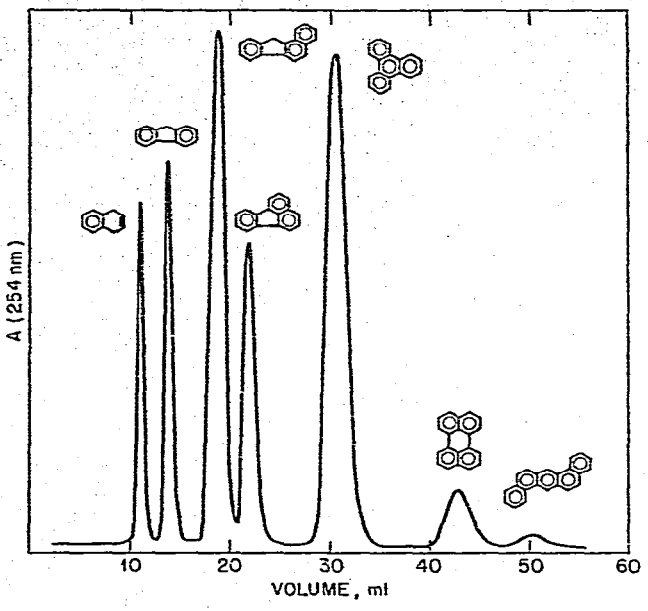

Fig. 2. Separation of 1,4-dihydronaphthalene, fluorene, benzo[*a*]fluorene, fluoranthene, triphenylene perylene and dibenz[*a*,*h*]anthracene on PVP. Conditions, as in Fig. 1.

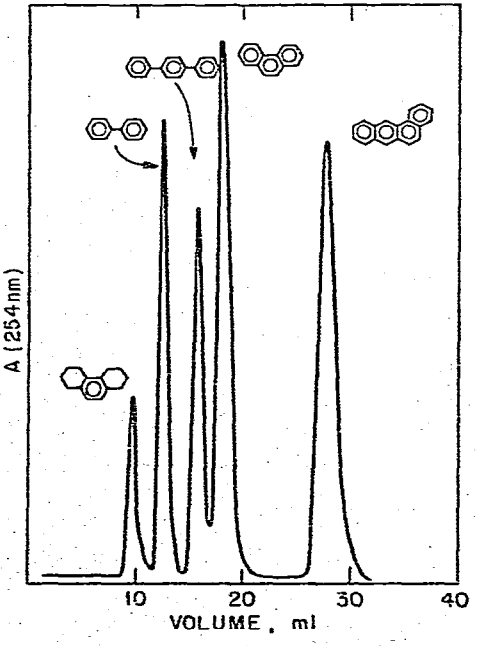

Fig. 3. Separation of octahydrophenanthrene, biphenyl, *p*-terphenyl, phenanthrene, and benz[*a*]-anthracene on PVP. Conditions, as in Fig. 1.

TABLE I

ELUTION PARAMETERS FOR POLYCYCLIC AROMATIC HYDROCARBONS ON PVP

Compound	V_R			k'		
	22°	*42°*	*62°*	*22°*	*42°*	*62°*
1,2,3,4,5,6,7,8-Octahydrophenanthrene	11.1	9.9	9.0	0.58	0.42	0.29
Benzene	12.0	11.1	10.1	0.72	0.59	0.45
1,4-Dihydronaphthalene	12.9	11.5	10.5	0.85	0.64	0.50
Acenaphthene	15.7	13.7	11.8	1.24	0.96	0.69
9,10-Dihydroanthracene	15.9	13.4	11.7	1.27	0.92	0.67
Biphenyl	16.2	13.6	11.8	1.31	0.94	0.69
Naphthalene	16.8	14.3	12.4	1.40	1.04	0.77
9,10-Dihydrophenanthrene	17.4	14.4	12.3	1.48	1.06	0.75
Fluorene	19.3	15.6	13.2	1.76	1.22	0.88
Acenaphthylene	22.1	17.8	14.5	2.16	1.54	1.07
1,2-Dihydropyrene	25.3	19.3	15.3	2.62	1.76	1.18
p-Terphenyl	25.9	19.1	15.0	2.70	1.73	1.14
5,12-Dihydrotetracene	26.8	19.7	15.5	2.83	1.81	1.21
Anthracene	28.7	21.4	16.8	3.10	2.06	1.40
Phenanthrene	30.5	22.1	17.2	3.35	2.15	1.46
Benzo[*b*]fluorene	33.9	24.0	18.0	3.85	2.42	1.57
Benzo[*a*]fluorene	34.3	24.0	18.0	3.90	2.42	1.57
Pyrene	43.4	29.7	21.4	5.20	3.24	2.06
Fluoranthene	43.6	28.7	20.8	5.23	3.10	1.97
1,3,5-Triphenylbenzene	44.0	27.2	18.3	5.29	2.88	1.62
Benz[*a*]anthracene	65.8	40.3	26.4	8.40	4.75	2.78
Chrysene	68.4	40.7	26.8	8.78	4.82	2.83
Triphenylene	77.2	45.4	29.2	10.0	5.49	3.17
Benzo[*a*]pyrene	—	—	36.1	—	—	4.16
Perylene	—	—	41.0	—	—	4.86
Dibenz[*a*,*h*]anthracene	—	—	48.1	—	—	5.87
Dibenz[*a*,*c*]anthracene	—	—	53.2	—	—	6.60

and a column temperature of 62°. Numerical data for the elution volume (V_R) and capacity factor (k') of all compounds tested are given in Table I. Retention on PVP evidently depends primarily on the total number of condensed aromatic rings; the greater the number of rings the greater the retention. Members of the same class of compounds (non-condensed, pericondensed, catacondensed, fluorene derivatives) having different numbers of aromatic rings are well separated from one another. In general, it appears that for compounds having the same number of aromatic rings, non-condensed systems and pericondensed systems elute earlier than catacondensed. Partially reduced compounds elute earlier than their completely unsaturated counterparts —octahydrophenanthrene, dihydrophenanthrene, and phenanthrene elute in that order— usually appearing close to other compounds with the same number of unsaturated rings. Similarly, because of their partially saturated cyclopentadiene ring, fluorene derivatives also elute before condensed hydrocarbons with the same ring number; fluorene elutes before *p*-terphenyl and anthracene, benzofluorene and fluoranthene elute before chrysene.

The mechanism for the interaction of PAHs with PVP has not been elucidated yet. It does seem likely, however, that with isopropanol or other unmixed solvents, separations are effected via adsorption rather than partition. Hydrogen bonding

obviously plays no part. Compared with octadecyl reversed-phase packings[3,4] there are several differences in the elution order, the position of the non-condensed PAHs in particular, which suggest significant differences in bonding mechanisms.

Effect of eluent composition

PVP swells slightly in polar solvents (water, alcohols) and contracts in non-polar (cyclohexane, benzene). Thus far, in all chromatographic applications polar solvents have been employed. Isopropanol was selected rather than the lower alcohols because it is a much better solvent for complex mixtures of relatively non-polar organic compounds, and also causes fewer practical problems in chromatography such as degassing in the pump or detector. Mixtures of water and isopropanol were tested as eluents for PAHs with the results shown in Fig. 4. Using eluents containing a high volume percentage of water, elution times for PAHs were very long and such eluents are impractical for separation of compounds with four or more aromatic rings. As the water content of the eluent is decreased elution volumes also decrease, reaching a minimum with about 3:1 isopropanol–water. With 100% isopropanol, however, elution volumes are again larger. Similar effects have previously been observed with silica packings[5,6] and attributed to selective adsorption of water from mixed eluents

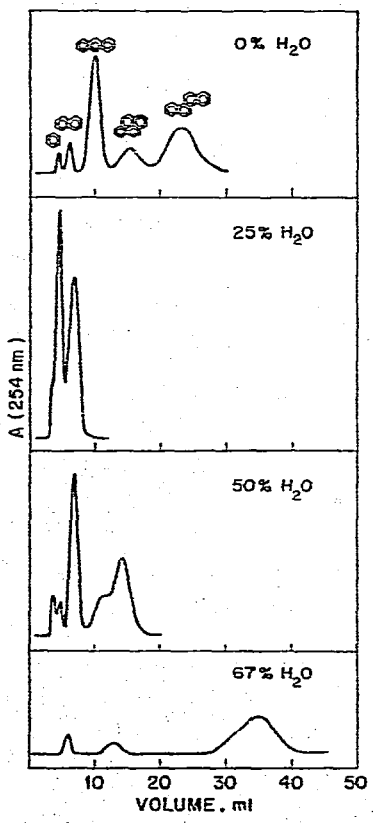

Fig. 4. Effect of eluent composition (water–isopropanol mixtures) on the separation of PAHs. Column, 250 × 4.5 mm I D ; packing, 63–90 μm PVP; flow-rate, 0.3 ml/min; temperature, 22°.

on the packing. As the composition of eluent changes from isopropanol to isopropanol–water the surface of the packing becomes coated with a water-rich phase and adsorption of PAHs is consequently weaker. With increasing water in the eluent the surface of the PVP gradually becomes loaded with an adsorbed liquid phase and there is a continuous transition from liquid–solid adsorption of PAHs to a liquid–liquid partition system. As the water content of the mobile phase further increases, one would then expect the PAHs to preferentially partition into the immobilized phase. As a result, there are two possibilities for gradient elution. One might add small amounts of water to isopropanol to decrease the k' values of late eluting components or, if the solubility of the sample permits, add isopropanol to a water-rich starting mixture.

Effect of flow-rate

Plate heights, and hence column resolution, depend on the velocity of the mobile phase. Although the precise theoretical background relating to this effect is at present the subject of some discussion[7] this dependence can usually be described by the expression[8] $H = Du^n$, with n having a value of approximately 0.4. The effect of flow-rate was tested, with the results shown in Fig. 5. For most compounds n was between 0.35 and 0.45 at low flow-rates; phenanthrene and fluorene were exceptions, having n values of 0.1–0.2.

For the larger 6 mm I.D. columns a flow-rate of 0.3 ml/min (0.25 mm/sec) was selected as a reasonable compromise between best resolution and speed of separation.

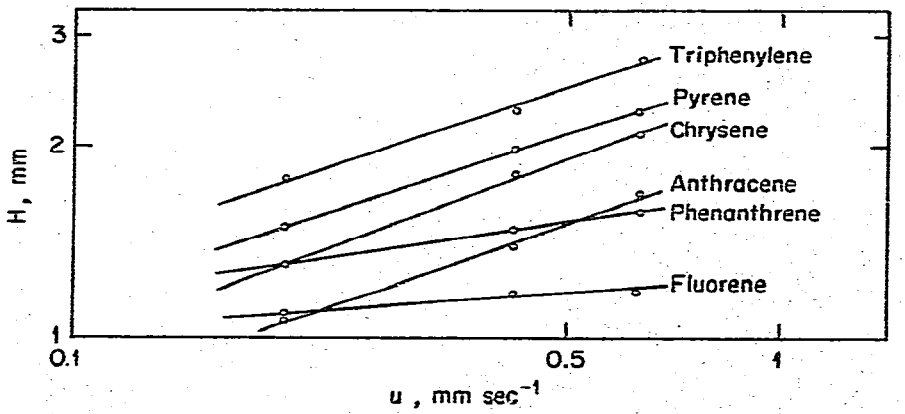

Fig. 5. Effect of flow-rate on plate height. Column, 250 × 4.5 mm I.D.; packing, 63–90 μm PVP; eluent, isopropanol; temperature, 22°.

Effect of temperature

To study the effect of column temperature on retention, chromatograms were run at 22°, 42°, and 62°. These data are included in Table I and typical chromatograms shown in Fig. 6. Two separate effects were evident, a decrease in elution volumes and a reduction in peak widths with increasing tempe ature. The former can be attributed to a negative enthalpy of adsorption on PVP. A few compounds with approximately the same elution volumes at room temperature have significantly dif-

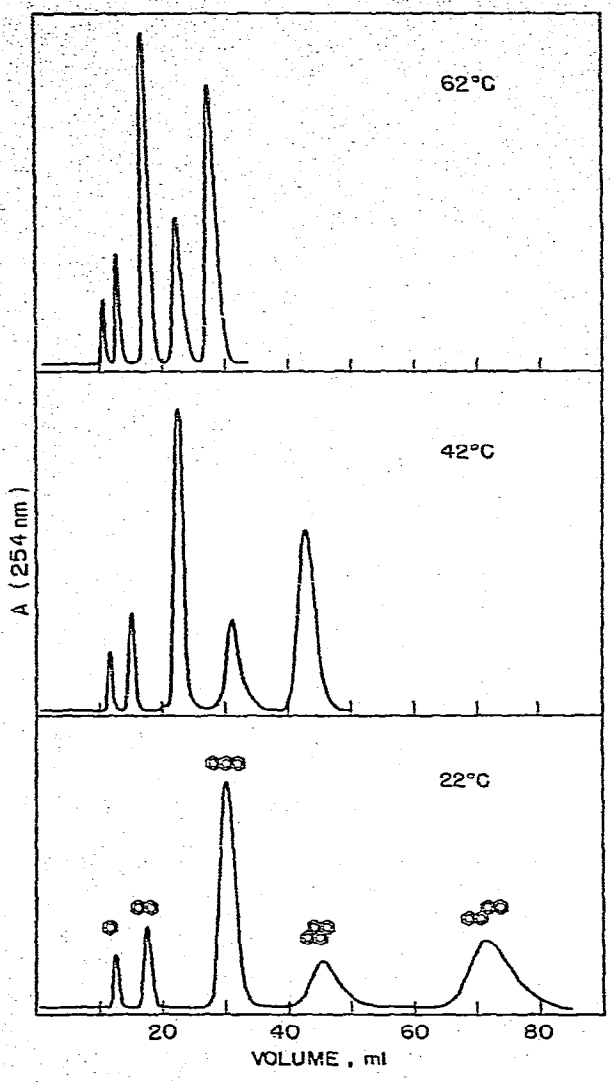

Fig. 6. Effect of column temperature on the separation of PAHs. Conditions, as in Fig. 1.

ferent heats of adsorption and temperature control or programming may be helpful in effecting separations. In Fig. 7, the log of k' is plotted *vs.* reciprocal temperature so that the slopes of the straight lines are proportional to the heat of adsorption. The most striking case is that of 1,3,5-triphenylbenzene, which elutes close to pyrene at 22° but much earlier and well separated from pyrene at 62°. Other instances of changes in elution order with temperature can be found in the data in Table I.

Peak narrowing, and a reduction in plate height, is probably largely due to a substantial decrease in the viscosity of isopropanol at elevated temperatures, and consequently faster kinetics in the mass transfer processes on the column. The change in plate heights as a function of temperature, shown in Fig. 8, roughly parallels the

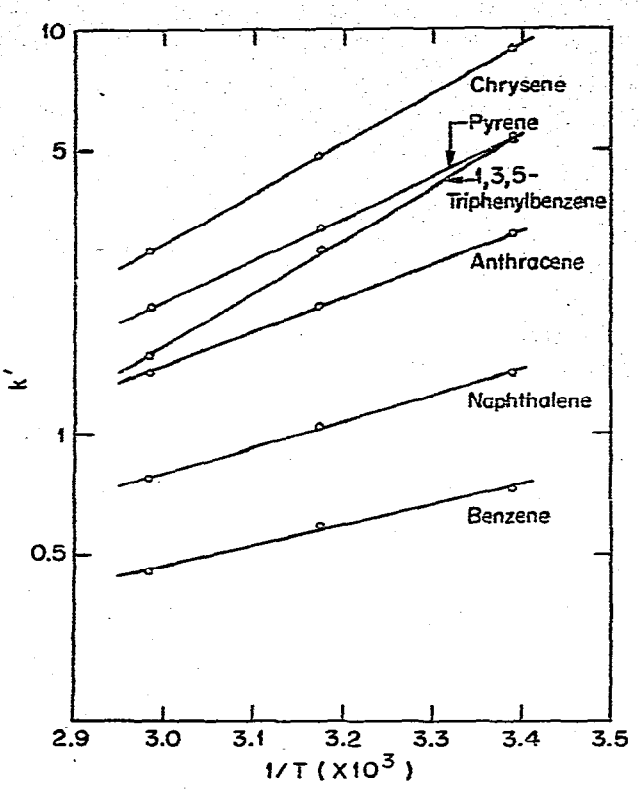

Fig. 7. Capacity factors as a function of temperature.

decrease in viscosity of isopropanol, although there are undoubtedly other factors involved. The average plate height for 27 compounds was 0.3 mm at 62° compared to 0.5 mm at 22°.

Applications

At present the primary application has been to assist in the characterization of synthetic oils derived from coal liquefaction processes[9] and other complex mixtures. A slightly longer column (500 × 6 mm I.D.) was used, an eluent flow-rate of about 0.3 ml/min, and a temperature of 62°.

Fig. 9 shows a chromatogram of Synthoil, a heavy oil product from a catalytic coal hydrogenation process. The oil was pretreated by first removing the benzene insolubles and the hexane insolubles (asphaltenes). The hexane was evaporated and the residue taken up in isopropanol in which it was entirely soluble. Two dilutions were run, one at ten times the concentration of the other and monitored on a non-linear scale. Although this material is far too complex to resolve individual components, the chromatogram shows that it contains primarily mono-, di-, and tri-aromatics, all of which elute within less than 90 min, and that compounds with four or more aromatic rings also constitute a considerable fraction. The structure in the chromatogram at just over 1 h is in the acenaphthylene/*p*-terphenyl area, and that at about 1.5 h in the fluoranthene/pyrene area, but these should not be considered definite iden-

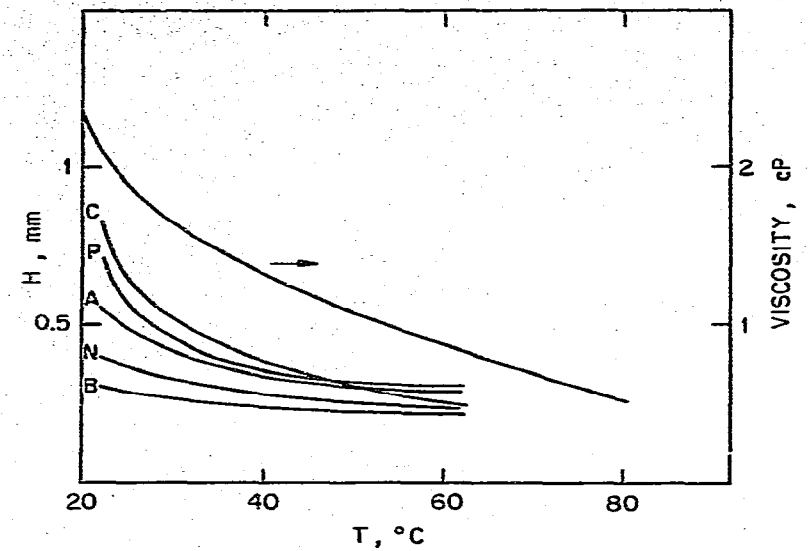

Fig. 8. Effect of temperature on plate heights. B, N, A, P, C refer to benzene, naphthalene, anthracene, pyrene, and chrysene, respectively. The top line is the viscosity of isopropanol (right-hand scale).

tifications. In contrast, the chromatogram of a synthetic oil from the COED (char oil energy development) process (Fig. 10) shows a much smaller fraction eluting after more than 90 min. COED oil is produced by high-temperature pyrolysis of coal and is a lighter oil containing no significant quantities of benzene insolubles or asphaltenes, and is readily miscible with isopropanol. Hydrogenation of COED oil yields as one

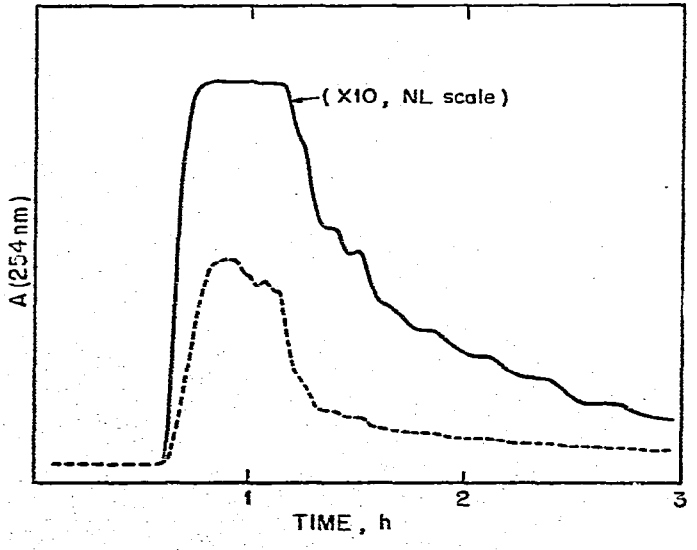

Fig. 9. Chromatogram of Synthoil. Column, 500 × 6 mm I.D.; packing, 63–100 μm PVP; eluent, isopropanol; flow-rate, 0.3 ml/min; temperature, 62°.

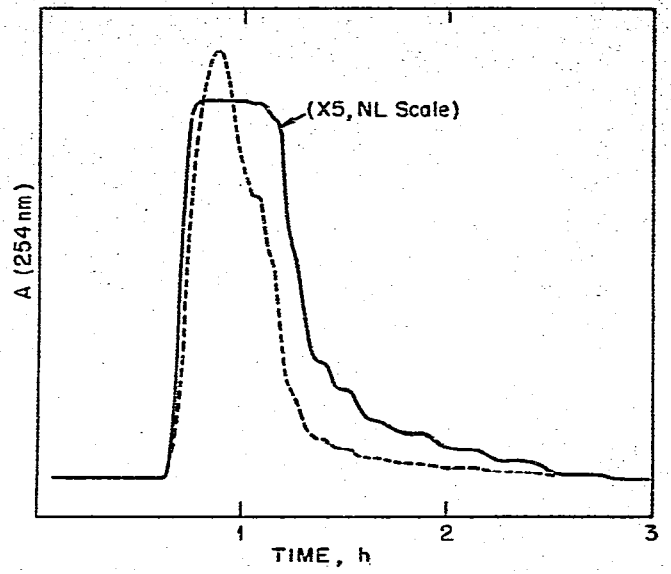

Fig. 10. Chromatogram of COED Syncrude. Conditions, as in Fig. 9.

product a light hydrotreated oil, a light colored, non-viscous, largely aliphatic oil. Its chromatogram in Fig. 11 indicates a much less complex mixture of aromatic substances. The four prominent peaks in the chromatogram correspond roughly to unresolved mixtures of mono-, di-, tri-, and tetra-aromatics in that order. There is very little material heavier than pyrene/fluoranthene.

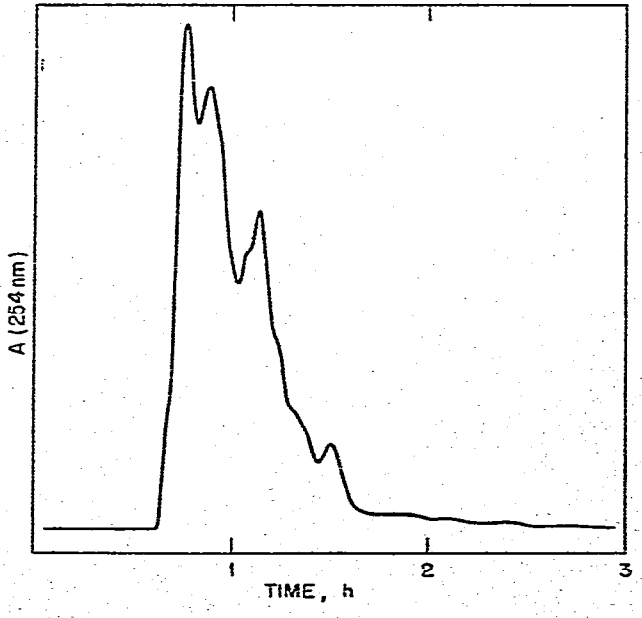

Fig. 11. Chromatogram of COED light hydrotreated oil. Conditions, as in Fig. 9.

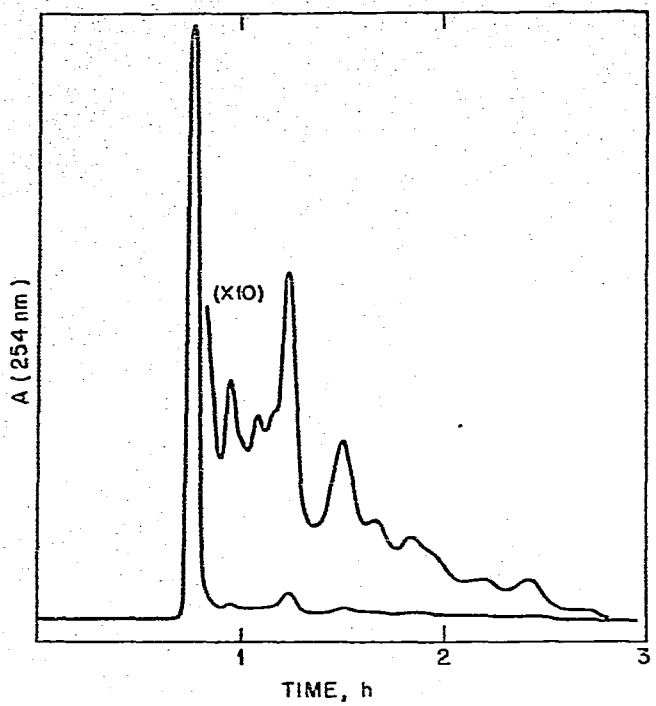

Fig. 12. Chromatogram of perchloroethylene scrubber solution. Conditions, as in Fig. 9.

The chromatogram shown in Fig. 12 is of a different kind of material, a perchloroethylene scrubber solution used to trap off-gases from a vapor phase carbon deposition process. After filtering out elemental carbon and other insoluble material, the filtrate was diluted with isopropanol. The chromatogram shows that the solution contains primarily perchloroethylene and simple aromatic compounds eluting in under 1 h. There are also peaks corresponding in elution volume to anthracene/phenanthrene at 1.2 h, pyrene/fluoranthene at 1.5 h, chrysene at 1.8 h, and benzo[*a*]pyrene at 2.4 h, plus other peaks. No definite identifications have been made yet.

In the course of work with oil samples, we observed that the capacity of PVP columns was quite high. There was no degradation of resolution on analytical columns even with samples representing as much as 5 mg of original oil, although the UV detector was frequently overloaded.

The PVP columns used in this work are far from optimum in many respects and substantial improvements are possible. Selection of smaller, more uniform particle size PVP, and longer columns, ought to result in improved resolution. Furthermore, it seems feasible to prepare a chemically bonded PVP phase on microparticulate silica, perhaps by the vinyl polymerization technique suggested by Wheals[10], to provide a modern, well engineered LC packing. At present we intend to take advantage of the simplicity, low cost, and high capacity of PVP columns to scale up to the preparative range. Collected fractions will then be further analyzed by high-performance LC or other high-resolution methods.

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