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High-Pressure Gas Chromatography and Chromatography with Supercritical Fluids. IV. Fluid-Solid Chromatography

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Summary

A chromatographic separation process is described which uses a supercritical fluid as mobile phase in combination with a solid adsorbent. Experiments have been conducted at temperatures of 200–250°C in the pressure range of 30–50 kg/cm² with *n*-pentane and isopropanol as examples of mobile fluids and alumina as the adsorbent.

The new technique, which may be called "fluid-solid chromatography" (FSC), is applicable to heavy substances which are difficult or even impossible to handle by normal gas-chromatographic methods. With FSC, such substances can be eluted in a short time and yield symmetrical peaks. Other attractive features include a high degree of flexibility and rapidity. It owes its versatility to the ease with which the separation pattern can be changed by variations of phase system, pressure, and temperature.

The most important features of FSC are illustrated with several examples, including the analysis of tars.

In an earlier article we described the use of supercritical fluids as mobile carriers in conjunction with liquid stationary phases for the chromatographic separation of heavy substances (*1*). This so-called fluid-liquid chromatography (FLC), was shown to be a very versatile and rapid separation method, as we had predicted before on the basis of the effect of pressure in gas-liquid chromatography (*2,3*).

In the present study we have investigated the replacement of the stationary liquid by solid adsorbents. This form of chromatography may be called fluid-solid chromatography (FSC).

SOLID ADSORBENTS IN GAS CHROMATOGRAPHY

The spectacular development of gas-liquid chromatography (GLC) and its widespread use are in remarkable contrast with the limited application of gas-solid chromatography (GSC), which is, in fact, the older of the two techniques. This lack of acceptance of GSC can be attributed to two factors:

1. The adsorption affinity of most adsorbents is too high, which results in excessively long elution times except for adsorbates of very low boiling points.

2. The adsorption isotherm is usually nonlinear in the concentration range of interest, which results in an asymmetry of peaks vitiating the separation. The situation is more favorable as the operating temperature is higher relative to the boiling point of the adsorbate.

With the commonly used adsorbents the operating temperature should, as a rule, be some 100–300°C above the boiling points of the substances to be analyzed to satisfy the requirements of reasonable elution times and peak symmetry. In consequence, GSC requires considerably higher temperatures than GLC. This explains why the latter technique is usually preferred, except for the separation of permanent gases, where the operating temperature for GSC is quite convenient.

The possibilities of GSC may be enlarged by modifying the usual adsorbents so as to obtain a more homogeneous surface of lower adsorption affinity. For instance, in the classical example of Eggertsen et al. (*4*) the performance of a furnace carbon black was improved by coating with 1.5 wt. % of squalane. Scott (*5,6*) similarly modified a low-surface alumina adsorbent by heating, followed by treatment with sodium hydroxide. With adsorbents thus deactivated, Scott (*5*) and Huyten and Van Beersum (*7*) were able to analyze hydrocarbons boiling up to about 500°C at temperatures of about 400°C.

Although the above-mentioned authors have shown that GSC can be applied to heavy substances (provided they are sufficiently stable), they did not succeed in getting further than is possible with GLC. From the work of Huyten and Van Beersum (*7*) it follows that even with the optimally modified adsorbents a GSC separation comparable to one in GLC still calls for a higher operating temperature, nullifying the advantage of the higher thermal stability of the

stationary phase in GSC. Scott and Phillips (*8*) compared GSC with GLC and also found that GSC requires a higher temperature for the same speed of analysis, notwithstanding the fact that the alumina adsorbent they used was quite effectively modified with sodium iodide.

SOLID ADSORBENTS IN FLUID CHROMATOGRAPHY

If the low-pressure carrier gas in GSC is replaced by a supercritical fluid, the distribution equilibria will probably be shifted for two reasons. First, there will be an increased tendency of adsorbate molecules to move into the fluid phase owing to molecular interactions in the latter. Our work on FLC (*1*) has shown that this effect alone can be very appreciable, corresponding to a "volatility enhancement" by anything up to a factor of 10^4. Second, with a carrier fluid which is to some extent adsorbed too, the adsorption of sample molecules will be reduced as a result of competition. The role which adsorbed carrier fluid molecules play is analogous to that of the "modifiers" in the preceding section. Thus, in FSC the adsorbent is "modified" in situ to an extent which may be varied by changing the temperature and pressure.*

The above considerations render it likely that the use of supercritical fluids as mobile phases and adsorbents as stationary ones will open up far better possibilities of separating heavy substances than does GSC.

EXPERIMENTAL

Apparatus

Liquid mobile carrier, contained in a high-pressure cylinder under nitrogen pressure, is fed to the column via an electrically heated tube and a temperature-conditioning tube. The latter is kept in the same air thermostat as the column.

* Such a "modification" can have far-reaching consequences. With strongly adsorbed carrier fluids the distinction between FSC and FLC may even vanish. For instance, we may have a high-pressure carrier fluid under such conditions that capillary condensation takes place, in which case it is perhaps more appropriate to regard the technique as FLC, with the mobile phase and the stationary liquid phase composed of essentially the same kind of molecules.

Small samples (about 15 μl of a dilute solution*) are introduced into the column by means of a pneumatically operated high-pressure injector. The column effluent is cooled to obtain a liquid before the pressure is released. The eluted components are detected in the liquid stream by means of an ultraviolet-absorption monitor.

A more detailed description of the apparatus has been given in a previous paper (*1*).

Columns

The columns were constructed from 6 mm i.d. stainless-steel tubing. Four straight sections of 25 cm were interconnected by capillaries to give a total column length of 1 m.

The column filling consisted of 120–140 mesh alumina, which was obtained by sieving a commercial product. This product,† a basic alumina of activity grade I (Brockmann scale), was not treated any further for the FSC experiments.

Mobile Phases

The products used as representatives of nonpolar and polar carrier fluids were the same as in our FLC study:

n-Pentane: $T_{crit} = 196.62°C$; $P_{crit} = 33.31$ atm; $d_{crit} = 0.238$ g/ml (*9*)

Isopropanol: $T_{crit} = 235.25°C$; $P_{crit} = 47.02$ atm; $d_{crit} = 0.2727$ g/ml (*10*)

The purity of both products is about 99%.

Determination of Distribution Coefficients

In conformity with out study of FLC, k' values are defined by

$$t_R = (1 + k')t_G$$

where t_R is the emergence time of the substance under consideration and t_G the holdup time of a nonadsorbed compound in an experiment at constant flow rate.

Since the UV-absorption monitor allowed only the detection of

* 0.1–1 wt. % in *n*-heptane or 1,2-dichloroethane. In the case of very sparingly soluble substances a saturated solution was employed.

† Obtained from M. Woelm, Eschwege, Germany.

aromatic compounds, we used benzene for determining t_G. Although benzene is not completely inert, the retention of this substance under the conditions adopted is probably quite small.

In most of the experiments the velocity of the carrier fluid amounted to a few centimeters per second. The pressure drop across the column was mostly less than 1 kg/cm²; the reported pressures are those at the column inlet.

RESULTS AND DISCUSSION

Applicability of FSC to Substances of Low Volatility

A comparison of the potentialities of FSC and high-temperature GSC for heavy substances can be made on the basis of polynuclear aromatic hydrocarbons. These compounds are particularly well suited to the latter technique because of their exceptionally high thermal stability. Two limiting factors will be considered, viz., elution time and peak asymmetry.

Limitation by Elution Time. Figure 1 shows k' values of condensed polyaromatic hydrocarbons as a function of boiling point for FSC

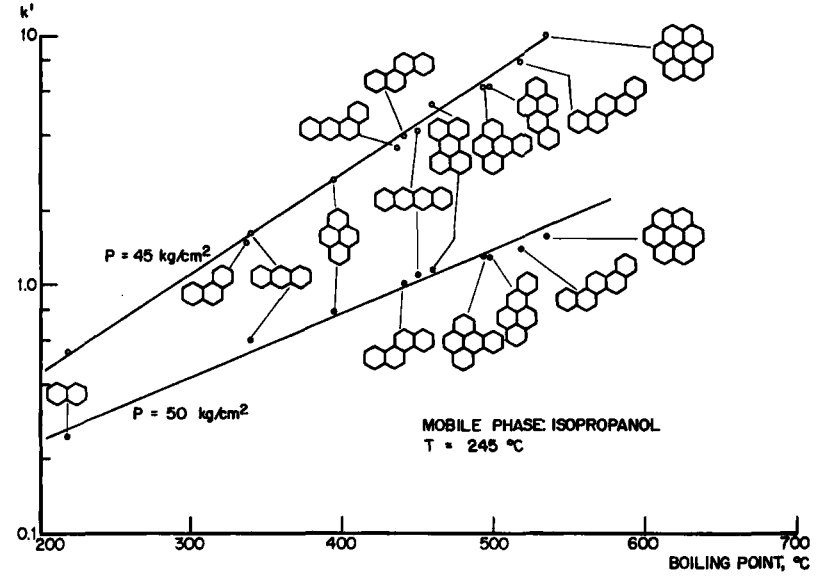

FIG. 1. Distribution coefficients of condensed polynuclear aromatic hydrocarbons.

with isopropanol as mobile phase. As found earlier in FLC (*1*), the relation between log k' and boiling point is approximately linear.

For the column of 1 m length operated at a carrier velocity of 1.7 cm/sec, the elution time in minutes is numerically the same as $1 + k'$. From Fig. 1 it can be inferred that at 245°C and 50 kg/cm² the analysis of substances boiling around 500°C takes only a few minutes.

These results may be compared with data obtained by high-temperature GSC (*7*). With the latter technique, the alumina adsorbent as such could not be used at all for substances in the boiling range of interest. The alumina was therefore modified by first heating at 980°C for about 5 hr and then adding so much of an aqueous sodium

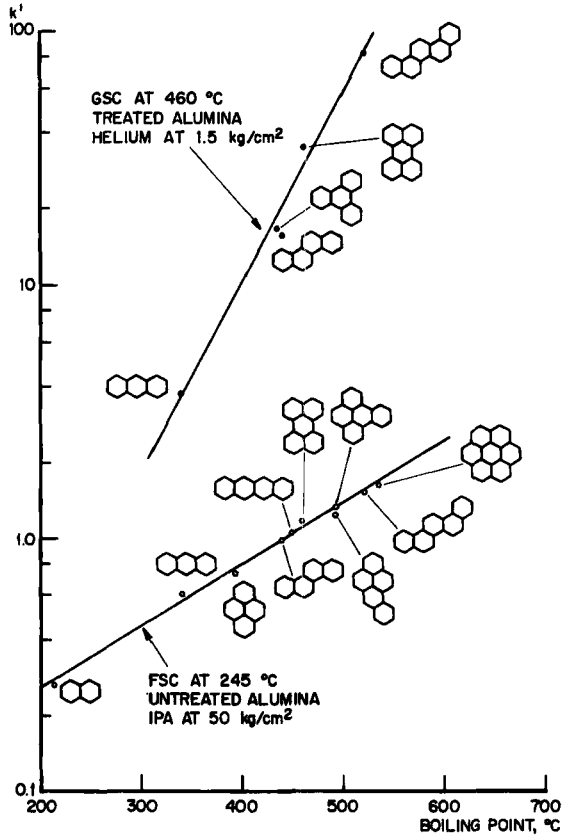

FIG. 2. Comparison of retention in high-temperature GSC and FSC.

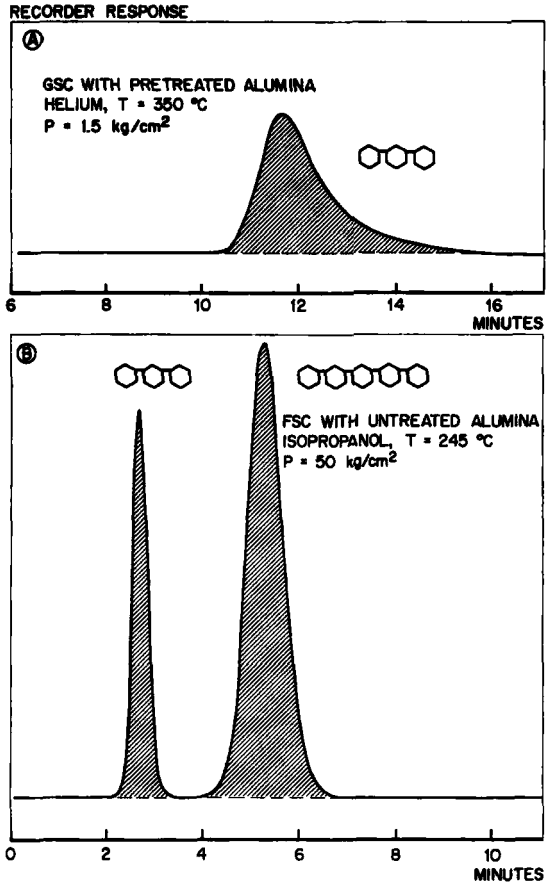

FIG. 3. Comparison of peak symmetry in high-temperature GSC and FSC.

hydroxide solution as to leave 1 wt. % of NaOH after evaporation of water.

In Fig. 2, k' values in GSC at 460°C (with modified alumina) are compared with FSC data (at 245°C, with untreated alumina). If we take a k' value of 100 as representing a practical limit,* we find that even at 460°C GSC is limited to substances boiling below 550°C. The limit for FSC, however, seems to be much farther away. Extrapolating the straight line in Fig. 2, we may speculatively locate

* This corresponds to an analysis time of the order of 1 hr for a column of a few meters length at a carrier fluid velocity of a few centimeters per second.

it at a boiling point of about 1000°C for the present conditions, which are not necessarily the most severe ones.

Limitation by Peak Symmetry. Figure 3(A) shows the *m*-terphenyl peak obtained by GSC at 350°C. It is seen that the pretreatment of the adsorbent, while improving peak shape, still fails to give a completely symmetrical peak for this substance at a temperature near its boiling point (364°C).

By contrast, the *m*-terphenyl peak obtained in FSC [Fig. 3(B)] is sharp and almost perfectly symmetrical. This result is noteworthy, considering that the working temperature is lower and the adsorbent has not been pretreated. Figure 3(B) shows that *m*-quinquephenyl gives a practically symmetrical peak, too, although its boiling point (576°C) is more than 300°C above the working temperature.

Effect of Operating Parameters on Speed of Elution and Separation Pattern

Effect of Pressure. Comparing the lines for $P = 45$ kg/cm² and $P = 50$ kg/cm² in Fig. 1, we see that at higher pressures k' values are lower. In other words, at higher pressures a substance is less

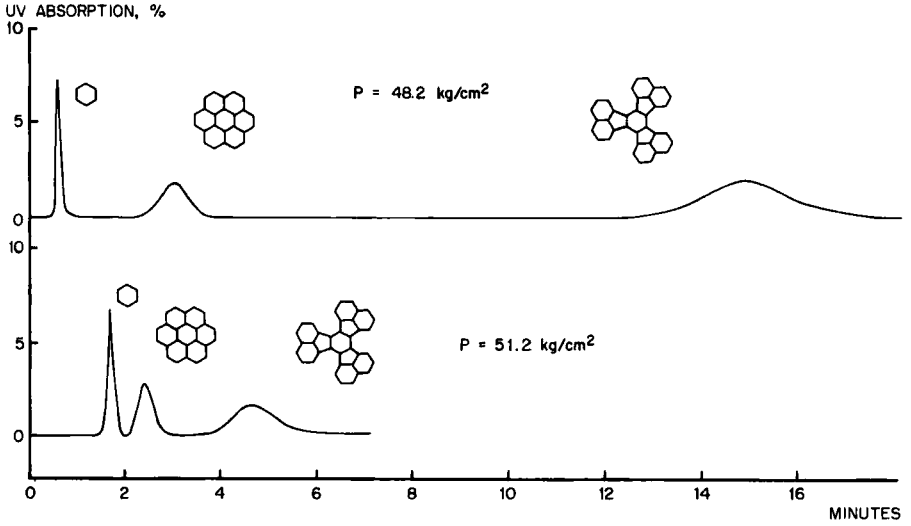

FIG. 4. Effect of pressure on the elution of coronene and decacyclene. Alumina column with isopropanol as a mobile fluid; $T = 245$°C.

readily adsorbed and consequently its elution proceeds faster. We also see that at the higher pressure the slope of the line is lower, or, putting it differently, light/heavy selectivity diminishes at higher pressures. This is completely in line with our earlier findings in high-pressure GLC and FLC (*1,2*).

As an example of the pronounced effect of pressure on elution time, Fig. 4 shows the separation of coronene from decacyclene at pressures only 3 kg/cm² apart. This small difference suffices to speed up the elution of the latter substance (which is expected to boil around 800°C) by a factor of about 3, even though the linear velocity at the higher pressure is appreciably smaller.

In our work on FLC we showed that pressure not only influences the speed of elution, but it may also change the separation pattern. The latter effect is also observed in FSC. From Table 1 it can be inferred that, with isopropanol as the mobile fluid, the elution order of 9,10-diphenylanthracene and picene is reversed when the pressure is changed from 45 to 50 kg/cm². With *n*-pentane as the mobile fluid, the same occurs for the pair 1,1′-binaphthyl/phenanthrene when the pressure is increased from 41 to 50 kg/cm².

Effect of Temperature. In FLC temperature has a large effect on partition coefficients, especially in the neighborhood of the critical points. Both the speed of elution and the separation pattern are influenced. That analogous effects occur in FSC appears from Fig. 5, where k' values of a number of aromatic hydrocarbons boiling between 337 and 450°C have been plotted against operating temperature. All curves show a maximum, below which k' drops steeply with decreasing temperature. In the temperature range below this

TABLE 1

Distribution Coefficients of Some Hydrocarbons in FSC as a Function of Pressure (alumina column)

Solute	Mobile fluid	Temperature, °C	k' at a pressure of		
			41 kg/cm²	45 kg/cm²	50 kg/cm²
9,10-Diphenylanthracene	Isopropanol	245	—	6.9	1.57
Picene	Isopropanol	245	—	7.9	1.39
1,1′-Binaphthyl	*n*-Pentane	213	4.38	—	1.89
Phenanthrene	*n*-Pentane	213	3.61	—	2.19

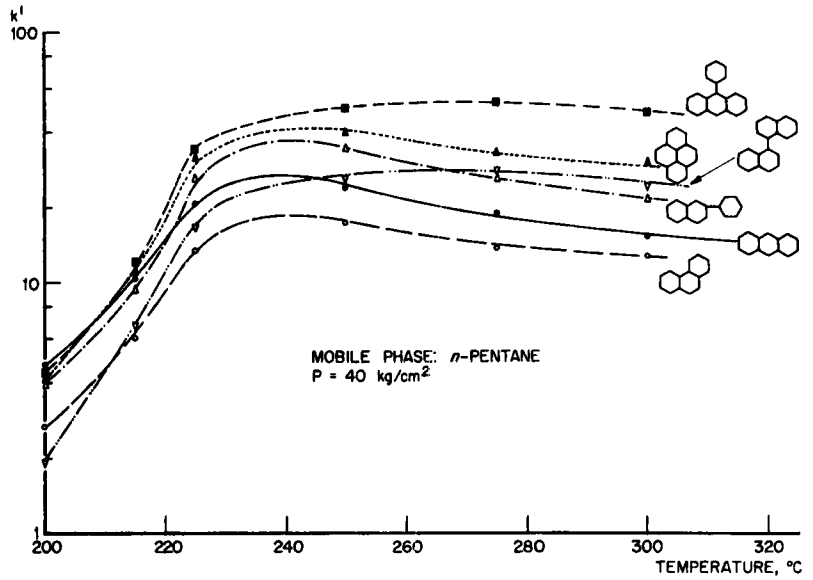

FIG. 5. Effect of temperature on distribution coefficients.

maximum, the tendency of an adsorbate to move into the fluid phase increases accordingly as the temperature is lower. Evidently, the increasing molecular interactions in the fluid phase (resulting from a higher fluid density at lower temperature) play a dominating role here.

This does not hold for temperatures higher than those corresponding with the above-mentioned maximum. Here the situation is the same as in normal GSC: at higher temperatures elution is accelerated.

Although the curves for different solutes are qualitatively the same, they have their maxima at different locations. The slopes on either side of the maxima may also be different. This may result in crossing of the curves, implying that at different operating temperatures the order of elution may differ. The change in elution order by variation of temperature is clearly demonstrated in Fig. 6 with the adsorbate pair anthracene/1,1-binaphthyl as an example.

Effect of the Nature of the Mobile Phase. In Fig. 7, k' values of β-substituted naphthalenes have been plotted against the number of carbon atoms for FSC with *n*-pentane and isopropanol as mobile fluids. The points for naphthalene and its 2-*n*-hexyl and

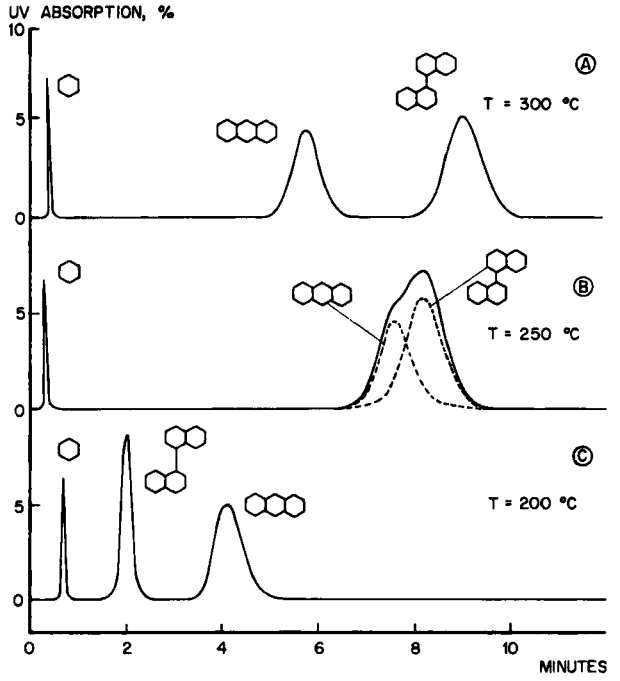

FIG. 6. Effect of temperature on the separation of anthracene from 1,1′-binaphthyl. Alumina column with *n*-pentane as a mobile fluid; $P = 40$ kg/cm².

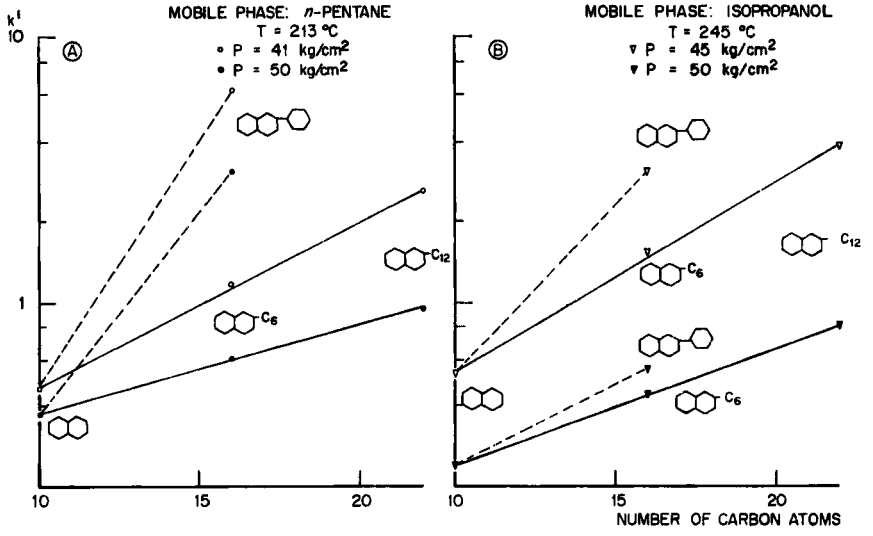

FIG. 7. Distribution coefficients of 2-substituted naphthalenes.

2-*n*-dodecyl derivatives can be connected by a straight line, as is to be expected for members of a homologous series. We shall, therefore, consider these lines to represent the homologous series of 2-*n*-alkylnaphthalenes.

The points for 2-phenylnaphthalene in Fig. 7 lie above the respective lines for the alkylnaphthalenes. The retardation of 2-phenylnaphthalene vis-à-vis 2-*n*-hexylnaphthalene may be expressed as a carbon atom increment ΔC, which is the difference in carbon atom number between 2-phenylnaphthalene and a 2-*n*-alkylnaphthalene having the same k' value.

From the values of ΔC given in Table 2, it is seen that the system *n*-pentane/alumina shows considerably more type selectivity than isopropanol/alumina. This does not seem illogical, since in the latter case the "polar" character of the adsorbent is counteracted by the polar character of the mobile fluid. Also, the effect of pressure is different with the two mobile fluids studied. Whereas with *n*-pentane ΔC increases at higher pressures (owing to diminished light/heavy selectivity), it decreases with isopropanol at higher pressures.

The above results illustrate that it is possible to vary type selectivity within wide limits even though only one adsorbent is used. The type selectivity obtainable is considerably higher than in normal gas chromatography, as evidenced by the fact that the replacement of a hexyl group by a phenyl group may correspond to nearly 20 additional methylene units.

Figure 8 provides another example of the effect of the mobile phase on the separation pattern. The elution order of the two aromatic hydrocarbons 2-phenylnaphthalene (bp 359.8°C) and 1,1′-bi-

TABLE 2

Effect of Mobile Phase on Type Selectivity in FSC with Alumina (adsorbates: β-substituted naphthalenes)

Mobile fluid	Temperature, °C	Pressure, kg/cm²	ΔC^a
n-Pentane	213	41	12
n-Pentane	213	50	19
Isopropanol	245	45	4
Isopropanol	245	50	2

[a] Number of additional methylene groups equivalent to one aromatic ring.

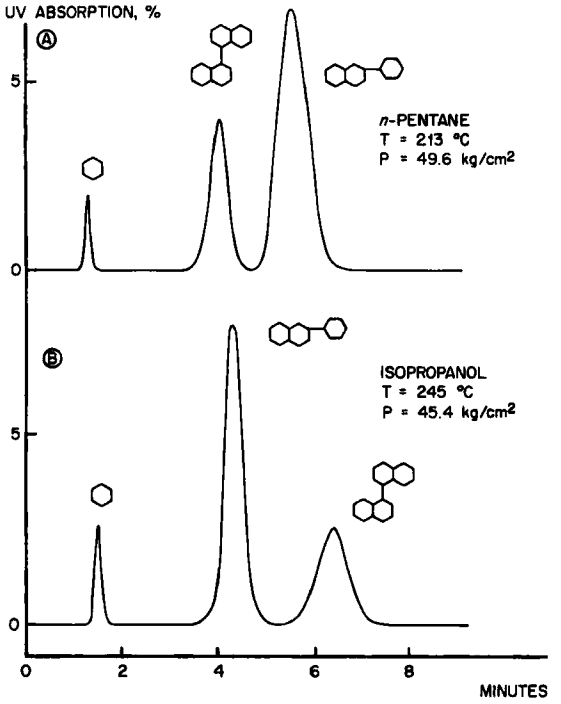

FIG. 8. Effect of mobile phase on the elution order of 1,1'-binaphthyl and 2-phenylnaphthalene.

naphthyl (bp > 360°C) is reversed if we change from *n*-pentane to isopropanol as the mobile fluid.

Speed and Efficiency of Separation

Our previous work concerning the effect of pressure on plate heights of packed GLC columns (*3*) has led to the conclusion that the use of supercritical mobile fluids should be very attractive with an eye to speed and efficiency of separation. It has been anticipated that fluid chromatography will be a faster technique than liquid chromatography. Our work on FLC has substantiated this conclusion (*1*).

The arguments which we put forward to explain why FLC can be a fast and efficient separation technique also apply to FSC. These arguments need not, therefore, be mentioned anew.

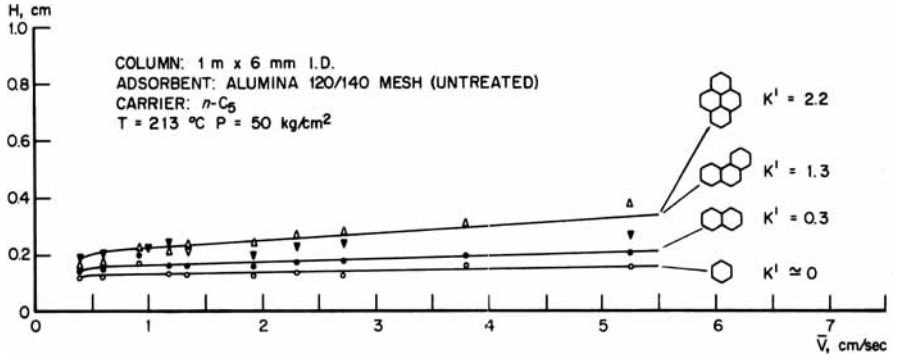

FIG. 9. Plate-height curves in FSC.

Figure 9 shows some plate-height data collected for an alumina column with supercritical *n*-pentane as the mobile fluid. Plate heights of the order of a few millimeters can be obtained at velocities of a few centimeters per second. These velocities are comparable to those normally used in gas chromatography and are two or three orders of magnitude higher than the ones commonly employed in liquid chromatography.

The possibility of carrying out fast analyses by FSC is demon-

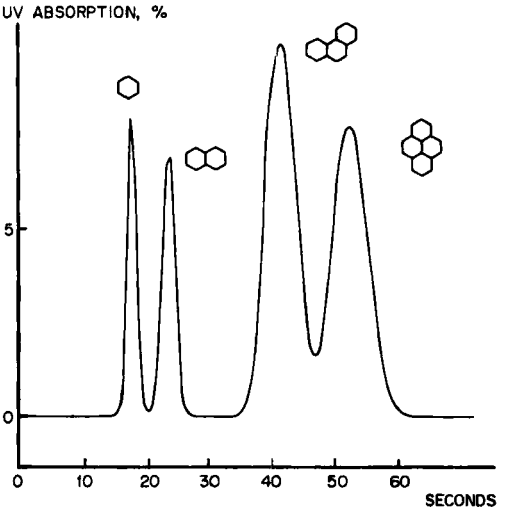

FIG. 10. Example of a fast separation with FSC. Alumina column with *n*-pentane as a mobile fluid; $T = 213°C$; $P = 50$ kg/cm².

strated in Fig. 10, which is a chromatogram of a four-component mixture. The nearly complete separation is accomplished within 60 sec.

Miscellaneous Examples of FSC Separations

Separation of Kata-Condensed Aromatics According to Ring Number. Figure 11 shows the separation of benzene, naphthalene, phenanthrene, 1,2-benzanthracene, and picene with isopropanol as a mobile fluid. The chromatogram covers a boiling range between 80 and 518°C.

Separation of Isomeric Bi- and Triaryls. Figure 12(A) is a chromatogram of a synthetic mixture of benzene, biphenyl, *o*-terphenyl and *p*-terphenyl. The last two isomeric hydrocarbons are well separated in the order of their boiling points (332 and 364°C, respectively).

As is clear from Fig. 12(B), the two isomeric binaphthyls 1,1'-binaphthyl (bp > 360°C) and 2,2'-binaphthyl (bp 452°C) are also easily separated by FSC.

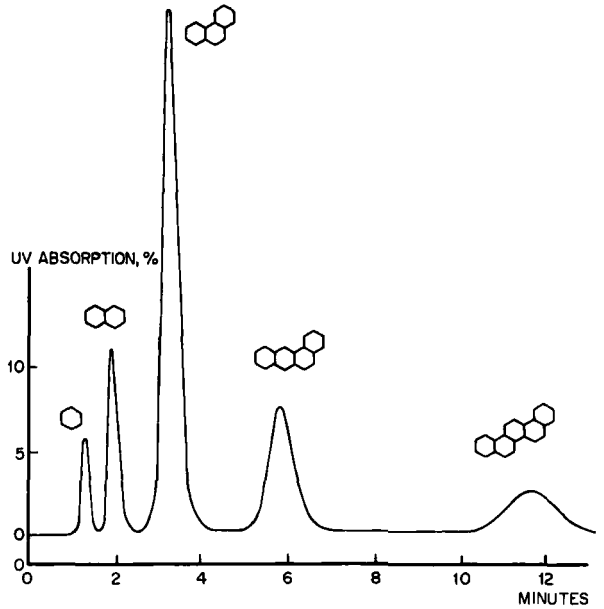

FIG. 11. Separation of some condensed aromatic hydrocarbons. Alumina column with isopropanol as a mobile fluid; $T = 245°C$; $P = 45.2$ kg/cm^2.

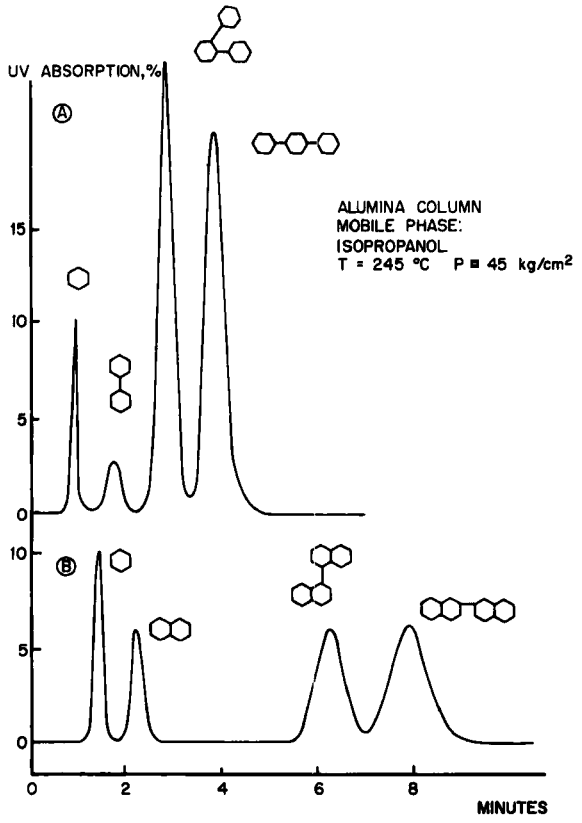

FIG. 12. Separation of isomeric bi- and triaryls.

Separation of Close-Boiling Polynuclear Aromatics. Figure 13(A) illustrates the ready separation of phenanthrene (bp 336.8°C) from anthracene (bp 339.9°C) by FSC with *n*-pentane as a mobile fluid under near critical conditions. Figure 13(B) is a chromatogram obtained under similar conditions with a mixture containing 1,2-benzpyrene (bp 493°C) and 3,4-benzpyrene (bp 495°C). These isomers are also separated completely.

The ease with which these separations are achieved by FSC justifies some further discussion. As regards anthracene/phenanthrene, the relative retention of this pair of substances on common isotropic liquid stationary phases suitable for high-temperature

GLC is very close to unity.* In consequence, no separation is obtained in packed GLC columns.† Nor are they separated by high-temperature GSC with NaOH-modified alumina (*7*).

For the separation of these substances by FSC, the adsorbent plays a leading role. This conclusion can be drawn from the fact that they are not separated by FLC under otherwise comparable conditions. The conditions of the fluid phase are also of interest,

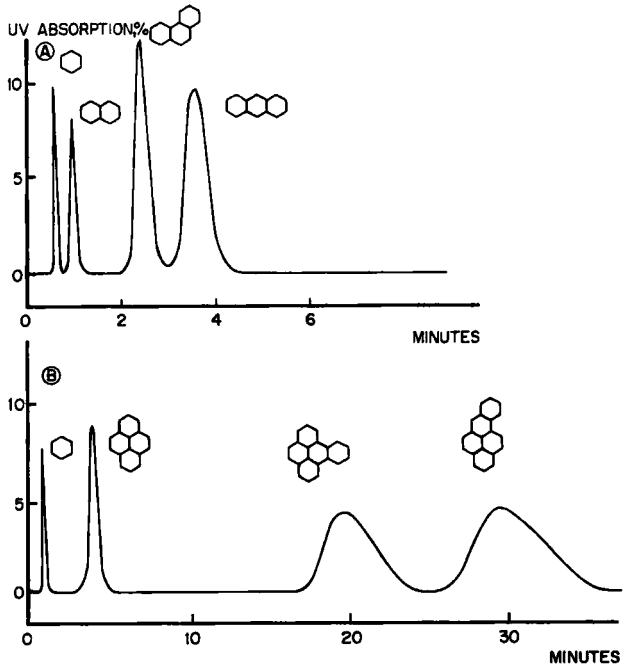

FIG. 13. Separation of isomeric condensed polynuclear aromatic hydrocarbons. Alumina column with *n*-pentane as a mobile fluid; $T = 200°C$; $P = 39.8$ kg/cm^2.

* Stationary phases examined include various silicone oils (*11,12*), silicone gum rubbers (*13,17*), silicone greases (*7,14,15*), Apiezon L (*11,12,16,18*), polystyrene (*12*), and neopentyl glycol succinate (*11*) in the temperature range between 175 and 300°C.

† The separation of anthracene from phenanthrene has been reported by Grant (*19*), using a capillary column of 500,000 theoretical plates, and by Cantuti et al. (*20*), using a capillary column of 40,000 theoretical plates with silicone gum rubber SE-52 as the stationary phase.

TABLE 3

Distribution Coefficients of Anthracene and Phenanthrene in FSC as a Function of Temperature (alumina column)[a]

Temperature, °C	k'		$\frac{k'_{anthracene}}{k'_{phenanthrene}}$
	Phenanthrene	Anthracene	
200	2.68	4.74	1.77
215	6.28	10.3	1.64
225	13.8	21.0	1.52
250	17.2	24.9	1.45
275	13.9	19.2	1.38
300	12.8	15.2	1.19

[a] With *n*-pentane as mobile phase; $P = 40$ kg/cm².

however, as can be seen from the data presented in Table 3. These may also serve to reconcile the separation obtainable by FSC with the coincidence of peaks in high-temperature GSC. In FSC the ratio of the k' values of anthracene and phenanthrene tends to unity with higher temperature and less dense mobile phase. Thus, as the operating conditions move in the direction of high-temperature GSC, the separation of anthracene from phenanthrene deteriorates.

The separation of 1,2-benzpyrene from 3,4-benzpyrene (which is of practical interest since they have widely different carcinogenic properties) is also difficult to effect by GLC. For example, with sili-

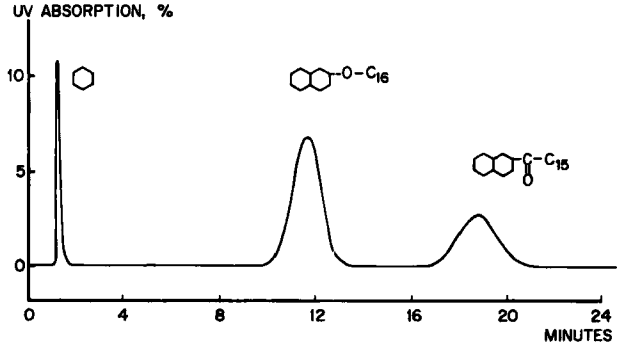

FIG. 14. Separation of 2-naphthyl hexadecyl ether from 2-naphthyl pentadecyl ketone. Alumina column with isopropanol as a mobile fluid; $T = 245$°C; $P = 45.4$ kg/cm².

cone gum rubber SE-52 as the stationary phase in a capillary column of 40,000 theoretical plates, only a partial separation was obtained by Cantuti et al. (*20*).

Separation of Heavy Oxygenated Compounds. No examples are known of the applicability of high-temperature GSC to heavy substances outside the hydrocarbon field. That FSC can cope effectively with nonhydrocarbons is illustrated in Fig. 14, showing the separation of 2-naphthyl hexadecyl ether from 2-naphthyl pentadecyl ketone. Apart from the different functional groups these two substances have nearly the same molecular weight and structure.

Analysis of a Coal Tar. Figure 15 is a chromatogram of a coal tar, as used in bitumen blending. The separation was carried out with isopropanol as the mobile fluid.

Since coal tar pitch consists predominantly of unsubstituted polynuclear aromatic hydrocarbons and heterocyclic analogues,* the chromatogram bears some relation to Fig. 1 and the record shown in Fig. 11. The location of the peaks of several substances known to be present in coal tar pitch has been indicated in Fig. 15. After the pronounced composite peak attributable to phenanthrene, anthracene, fluoranthene, and pyrene, the chromatogram exhibits a series of peaks descending in height. These roughly correspond to polynuclear hydrocarbons of increasing molecular weight and ring number, the last peaks probably representing seven- and eight-ring aromatics. This result is compatible with earlier studies of the composition of coal tar, which had led Franck (*21*) to deduce that about 90% of a typical coal tar pitch may consist of three- to seven-ring aromatics.

Analysis of a Polyphenyl Tar. Figure 16 shows the analysis of a polyphenyl tar, a brittle black resin obtained as a residue from the flash distillation of a neutron-irradiated terphenyl mixture. In this analysis we applied a pressure-programming technique to accelerate the elution of the heavier part while retaining the separation in the lighter range.

Peak A in Fig. 16 corresponds to *o*-terphenyl, while peak B can be attributed to *m*- and *p*-terphenyl. The pronounced peak C has its location in the region where condensed four-ring aromatics are to be found. Such an aromatic, viz., triphenylene, may be formed

* Methyl substituents and phenolic hydroxyl groups occur only in the lower-boiling tar fractions. In the fractions boiling above 400°C no compounds with side groups have yet been found, except for some nitriles. See, e.g., (*21*).

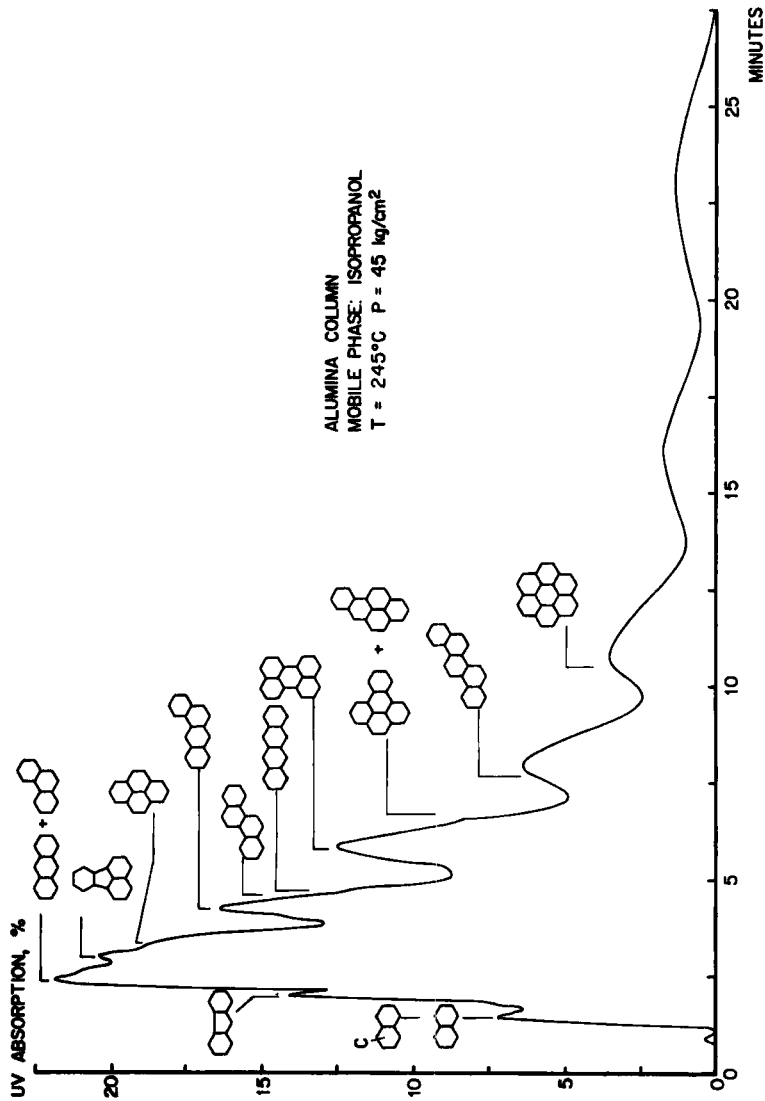

FIG. 15. Chromatogram of coal tar.

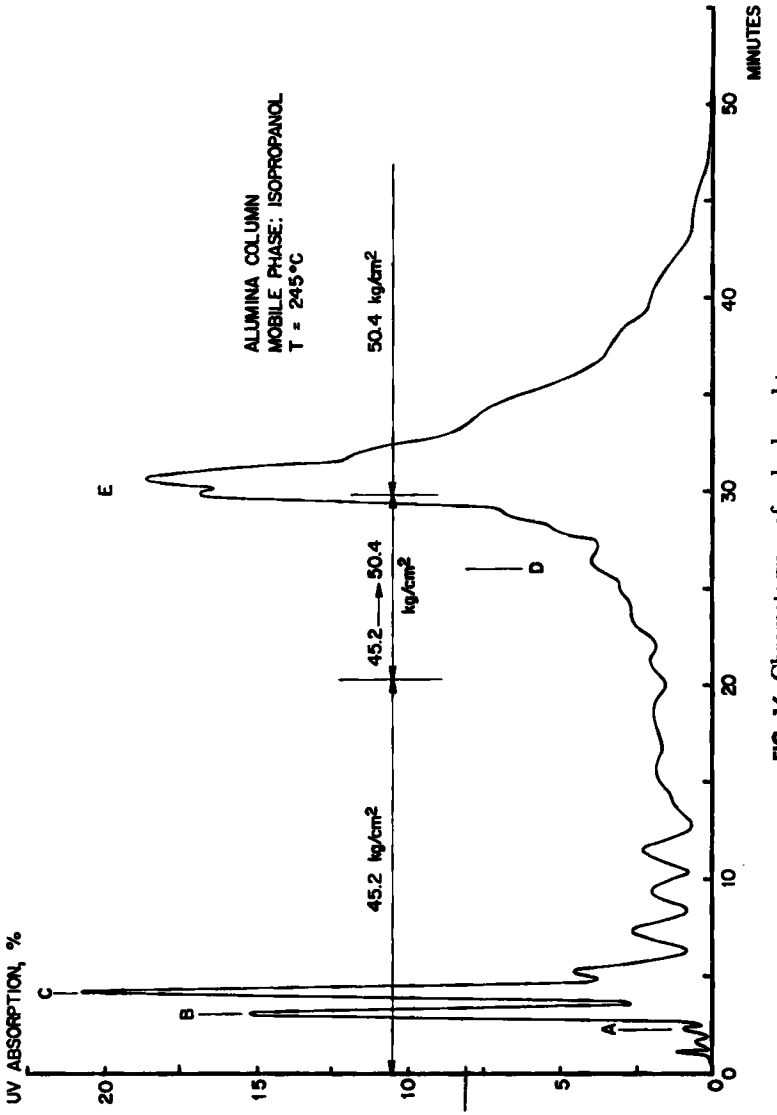

FIG. 16. Chromatogram of polyphenyl tar.

from *o*-terphenyl by hydrogen abstraction and formation of an intramolecular bond.*

In view of the complexity of the product (as evidenced by the chromatogram) and the lack of suitable model substances, no further attempts were made to identify peaks. We can, however, form some idea of the molecular weight of the heavier part. The approximate location of the *m*-quinquephenyl peak, when chromatographed under similar conditions, is indicated by D in Fig. 16. It seems probable, therefore, that the pronounced peaks at E represent six-ring aromatics, while the trailing end of the chromatogram should contain products of still higher molecular weight.

CONCLUSIONS

With untreated alumina as an adsorbent it is possible to analyze heavy products by fluid-solid chromatography. High-boiling substances may be eluted rapidly and give rise to symmetrical peaks. Hence, FSC appears to have considerably greater potentialities than high-temperature GSC.

As regards applicability to heavy substances, flexibility, speed, and ease of manipulation, FSC and FLC have much in common. While the latter technique per se offers many possibilities, as demonstrated earlier (*1*), the use of solid adsorbents enlarges the scope of fluid chromatography. For instance, close-boiling isomeric hydrocarbons are more easily separated by FSC.

In comparison with liquid-solid chromatography (LSC), FSC offers distinct advantages by its greater speed and the larger freedom in varying the operating conditions to suit a particular separation. Whereas in liquid chromatography a change in operating conditions is usually brought about by substituting another solvent, the characteristics of the chromatographic system in FSC can be varied in a more convenient way, viz., by utilizing the pronounced effects of temperature and pressure.

The latter operating parameters can easily be changed even during a chromatographic run. A technique of pressure-programmed FSC seems to be quite feasible and will be somewhat analogous to temperature-programmed GLC or LSC with gradient elution. Compared with the latter technique, pressure-programmed FSC

* Gudzinowicz and Smith (22) indeed found triphenylene in a similar product which they analyzed by high-temperature GLC (silicone grease column at 303°C).

has the great advantage that the system can be easily restored to initial conditions after completion of a chromatographic run.

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