Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Gas-Solid Chromatography with an Organic Phase: A Study of the Properties of Thermal Graphitized Carbon Black Modified with Anthraquinone

Claire Vidal-madjar[a]; Georges Guiochon[a]
[a] LABORATOIRE DU PROFESSEUR L. JACQUÉ, ECOLE POLYTECHNIQUE, PARIS, FRANCE

To cite this Article Vidal-madjar, Claire and Guiochon, Georges(1967) 'Gas-Solid Chromatography with an Organic Phase: A Study of the Properties of Thermal Graphitized Carbon Black Modified with Anthraquinone', Separation Science and Technology, 2: 2, 155 — 167
To link to this Article: DOI: 10.1080/01496396708049923
URL: http://dx.doi.org/10.1080/01496396708049923

SEPARATION SCIENCE, 2(2), 155–167 (1967)

Gas–Solid Chromatography with an Organic Phase: A Study of the Properties of Thermal Graphitized Carbon Black Modified with Anthraquinone

CLAIRE VIDAL-MADJAR and GEORGES GUIOCHON
LABORATOIRE DU PROFESSEUR L. JACQUÉ,
ECOLE POLYTECHNIQUE,
PARIS, FRANCE

Summary

When an organic solid substance such as anthraquinone is deposited on an homogeneous graphitized carbon black such as Sterling M. T., a new solid support is obtained. This adsorbent is of type III of Kiselev's classification; it adsorbs, nonspecifically, hydrocarbons and molecules with π electrons or unshared electron pairs, such as ketones, esters, ethers, alkyl chlorides, and aromatic hydrocarbons. The kinetic-mass-transfer term is very small for these compounds, less than 10^{-4} sec.

The adsorption enthalpy of these compounds is lower than on pure graphitized carbon black; this permits them to be eluted at much lower temperatures.

The adsorbent keeps some properties of the carbon black which are different from those of anthraquinone alone, i.e., meta and para xylenes are well resolved, whereas ortho and para xylene are not.

Graphitized carbon blacks with great homogeneous surfaces are very suitable adsorbents for gas-solid chromatography. They have been used with the same ease and often in much the same way as liquid stationary phases: they have been deposited on the walls of capillary columns (*1*), on glass beads (*2*), and on polyethylene powder (*3*); they have been put in the large pores of modified silica gels (*4*), and they have been used as the packing material in conventional packed columns (*5–8*) and in packed capillary columns (*9*).

Kiselev (7) has shown that this support, which has a chemically saturated surface, behaves as a nonspecific adsorbent (class I). The retention time of aromatic and unsaturated hydrocarbons, of ethers, ketones, nitriles, and amines, is of the same order as that of the saturated hydrocarbons of the same molecular weight. With flame-ionization detectors it is easy to work in the linear range of the adsorption isotherms, and for nearly all solutes the elution peak is symmetrical.

The general disadvantages of graphitized carbon blacks are its poor mechanical stability and the high adsorption energy caused by the large concentration of carbon atoms on the adsorbent surface. Moreover, these blacks have a large surface area (about 10 m^2/g). Therefore the column temperature needs to be higher than with usual packings in gas-liquid chromatography. The benefit of having a stationary phase which is stable enough to be used at high temperatures is nullified by the fact that high-molecular-weight organic molecules to be analyzed are decomposed at the temperatures which would be needed for their elution.

To allow working at lower temperature it would be necessary to decrease the adsorption energy of the solutes on the surface of graphitized carbon black. This may be achieved by depositing on this surface a layer of an organic solid.

The use of an organic solid phase as an adsorbent in gas-solid chromatography was first reported by Scott, who impregnated Celite with benzophenone and obtained good efficiencies for alkanes at temperatures well under the melting point (*10*). Recently we reported on the properties of benzophenone deposited on graphitized carbon black Sterling F. T. and on Chromosorb W (*11*). The best results were obtained with the first packing. The surface of this adsorbent has a high density of π electrons, so it belongs to type III of Kiselev's classification (*4*). We observed that this adsorbent has a nonspecific retention and a good efficiency for molecules with π bonds or unshared electron pairs (benzene, ether, acetone); the adsorption energy is decreased. This phase gives a specific adsorption of molecules with some electron affinity. The lack of homogeneity of this surface results in peak tailing and change of retention time with the amount of sample injected for phenols, alcohols, and amines.

The melting point of benzophenone (49°C) prevents the use of this new stationary phase at high temperatures. So, to diminish

the adsorption energy of the solutes on carbon blacks we have studied the properties of anthraquinone deposited on the graphitized carbon black, Sterling M. T. The chemical structure of this compound has the same features which make benzophenone attractive, but it can withstand much higher temperatures.

EXPERIMENTAL

The apparatus was made in our laboratory using a flame-ionization detector (*12*) and a splitting system which allows the injection of samples smaller than 10^{-6} g. The inlet pressure is controlled with

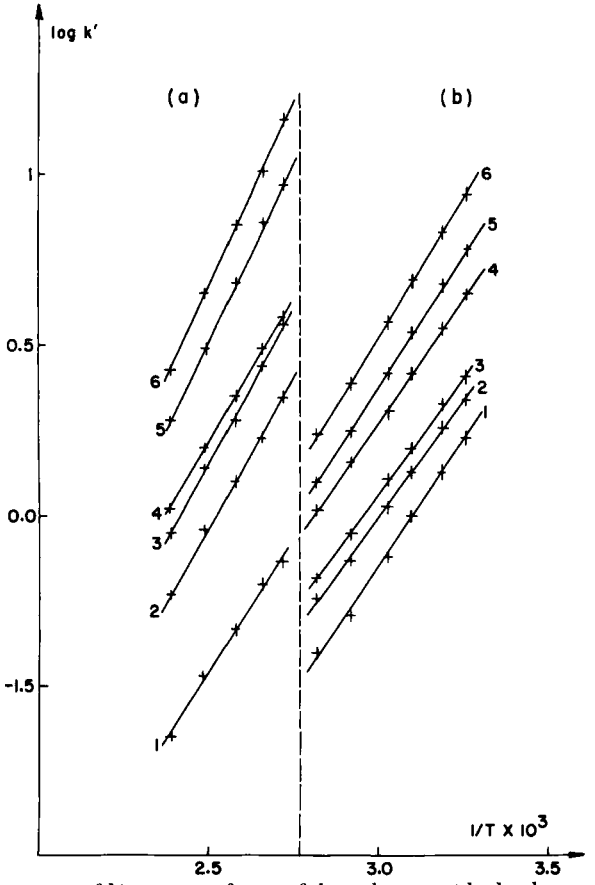

FIG. 1. Variation of k', capacity factor of the column, with absolute temperature. Column packing: (a) Sterling M. T., (b) 5% anthraquinone on Sterling M. T. See compound name, Table 1.

a Negretti and Zambra valve. Columns are made with stainless-steel tubing 2 mm I.D. and are 1 or 2 m long.

To deposit anthraquinone on graphitized carbon black Sterling M. T. (Cabot Co., Cambridge, Mass.) we have proceeded as indicated by Brodasky (*8*)—anthraquinone was dissolved in toluene. The liquid is mixed up with the support (5% anthraquinone on Sterling M. T.) at 110°C, until the complete evaporation of toluene. The solid is then sieved and the fraction 100–160 μ is retained. The mass of packing is 2.0 g per meter of column.

The isosteric adsorption enthalpy ΔH is calculated from the slope of the straight line obtained by plotting the logarithm of the column capacity factor $k' = (t_R - t_0)/t_0$, where t_R and t_0 are retention times of the compound and of air, respectively, versus the reciprocal of the absolute temperature T (cf. Fig. 1).

The latent heat of vaporization ΔH_v is determined from the variation of the vapor pressure with absolute temperature (*13*).

The diffusion coefficient of the solute in the gas phase, D_g, has been calculated according to the Chapman-Enskog equation (*14*).

RESULTS

Enthalpy of Adsorption

The adsorption enthalpy has been measured for various compounds on Sterling M. T. with 5% anthraquinone and on pure Sterling M. T. The values are given in Table 1 together with the latent heat of vaporization of these compounds, ΔH_v.

For *n*-pentane, *n*-hexane, and benzene the adsorption enthalpy is about 2 kcal/mole less when anthraquinone is deposited on the

TABLE 1

Isosteric Enthalpy of Adsorption on the Two Different Solid Surfaces

No.	Compound	ΔH_v, kcal/mole	ΔH, kcal/mole	
			Sterling M. T.	5% anthraquinone on Sterling M. T.
1	Diethyl ether	7.5	7.1	6.0
2	Acetone	7.8	8.1	6.4
3	*n*-Pentane	6.9	8.5	6.4
4	Cyclohexane	7.9	7.8	6.7
5	Benzene	8.1	9.6	7.1
6	*n*-Hexane	7.8	9.9	7.5

graphitized carbon black. For cyclohexane the difference is only 1 kcal/mole. The adsorption enthalpy on anthraquinone is generally lower than the enthalpy of vaporization. This phenomenon has also been observed by Kiselev (*4*) for benzene and *n*-hexane on silica-gel surfaces modified by grafting trimethyl silyl groups.

For the same packing density, a given value of k' is obtained for a compound at 130°C on pure Sterling M. T. and at about 60°C on Sterling M. T. coated with anthraquinone. This phenomenon results from the decrease of the adsorption enthalpy; the specific surface areas of both adsorbents are roughly the same. Measurements carried out by the BET method give a surface of 10 m^2/g for Sterling M. T. and of 9.2 m^2/g for 5% anthraquinone on Sterling M. T.

Column Efficiency and Permeability

Symmetrical peaks are eluted from the column packed with 5% anthraquinone on Sterling M. T. for saturated, unsaturated, and aromatic hydrocarbons, for alkyl chlorides, ketones, and ethers. The minimum value of the plate height is about 0.8 mm with both stationary phases. This value is higher than the one usually obtained with conventional adsorbents used in gas-solid chromatography. Columns are very difficult to pack with pure or coated blacks, and the packing is not as homogeneous as with conventional solids. The carbon black particles are very brittle and break during column filling. That explains also why the permeability of these columns is very low, about 0.3×10^{-7} cm^2, whereas with glass beads of the same average diameter a permeability of 1.5 to 1.8×10^{-7} cm^2 is usually obtained.

Kinetic-Mass-Transfer Term

The kinetic-mass-transfer term C_k is related to the average plate height H according to the equation (*15*)

$$H = H_g f + C_l u_0 j$$

where H_g is the gas-phase contribution and u_0 the outlet linear velocity; f and j are pressure correction factors given by

$$f = \frac{9}{8} \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2}$$

$$j = \frac{3}{2} \frac{P^2 - 1}{P^3 - 1}$$

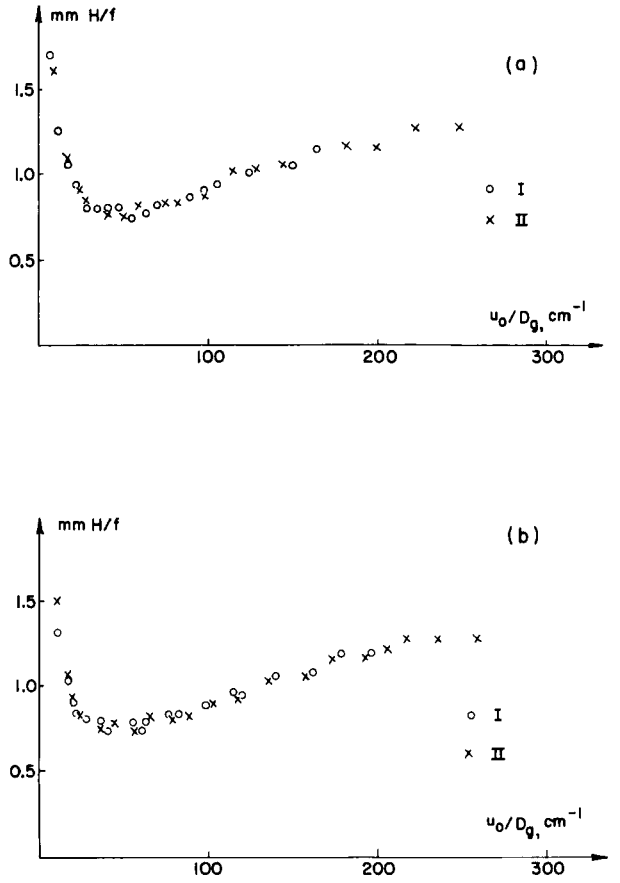

FIG. 2. Plot of H/f against u_0/D_g. Column packed with 5% anthraquinone on Sterling M. T., 100–160 μ. Length, 1 m; temperature, 58°C; carrier gas: I, hydrogen, II, argon. (a) Cyclohexane: $D_g(H_2) = 0.41$ cm²/sec, $D_g(Ar) = 0.09$ cm²/sec. (b) Benzene: $D_g(H_2) = 0.48$ cm²/sec, $D_g(Ar) = 0.09$ cm²/sec.

where P is the ratio of inlet to outlet pressure. The kinetic-mass-transfer term C_k can be calculated (*15*) from the difference between the plots of H/f versus u_0/D_g for two different carrier gases such as argon and hydrogen (Fig. 2).

The kinetic-mass-transfer term C_k for cyclohexane and benzene on Sterling M. T. coated with anthraquinone is too small to be measured owing to the dispersion of the experimental points (cf. Fig. 2a and 2b) no difference can be seen between the curves ob-

tained with argon and hydrogen. This means that C_k is less than 10^{-4} sec for cyclohexane or benzene on this support.

This low value shows that the modified carbon black actually behaves like a solid support with an average desorption time of less than 10^{-4} sec when it gives nonspecific adsorption (*16*). In gas-liquid chromatography the term of resistance to mass transfer in the liquid phase C_l, which is related to the rate of diffusion of the solute in the liquid phase, is usually a few milliseconds. This result underlines the advantage of gas-solid chromatography over gas-liquid chromatography. But to have the full benefit of small C_k values, it is necessary to lower the H_g term by using a support which should be more mechanically stable than graphitized carbon black.

Thermal Stability

It is possible to use the modified adsorbent at temperatures up to about 160°C. At this temperature the vapor pressure of anthraquinone is 0.1 mm Hg. Should this be the equilibrium pressure in column and the carrier gas be saturated, it would be possible to work for 200 hours with a flow rate of 10 cm^3/min, after which time all the anthraquinone would be flushed out of the column. The experiment is in fair agreement with this result; after a few days at 160°C the column performances decrease. Because of this temperature limitation, anthraquinone is not more useful than many conventional liquid stationary phases for the analysis of high-boiling compounds.

The modified adsorbent would have been thermally more stable if a monolayer had been deposited on the surface of the graphitized carbon black. It is difficult to produce such a monolayer of a solid substance which cannot be spread as uniformly as a liquid on the carbon surface and accumulates in some parts of the support during its crystallization.

The fact that the performances of the columns decrease progressively during their thermal degradation shows that either there is not a stable monolayer of anthraquinone adsorbed on the carbon black surface or that such a monolayer does not play an important role in the properties of the modified solid.

Gas-Chromatographic Properties

Owing to the low adsorption energy, the elution times are shorter on the modified adsorbent than on the pure graphitized carbon

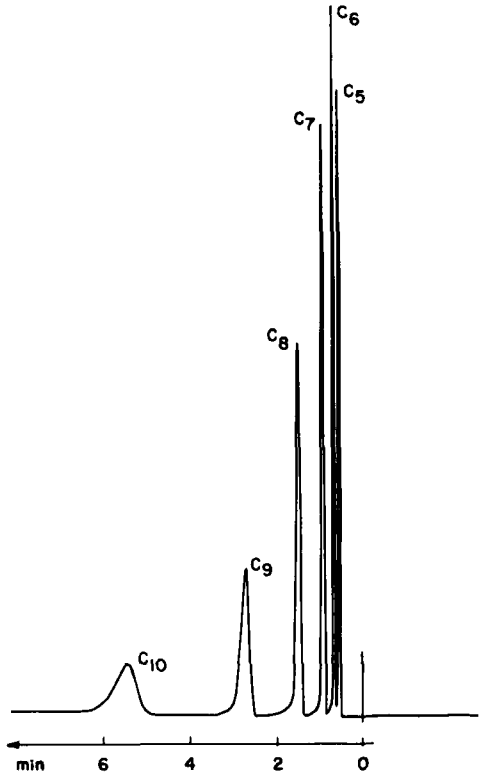

FIG. 3. Analysis of *n*-alkanes (*n*-pentane to *n*-decane). Column packed with 5% anthraquinone on Sterling M. T. 100–160 μ. Length, 2 m; carrier gas, hydrogen; $u_0 = 34$ cm/sec; inlet pressure, 5 kg/cm^2; temperature, 160°C.

black. At 160°C, *n*-decane is eluted in 6 min from a 2-m column and an outlet velocity of 34 cm/sec with hydrogen as carrier gas, whereas *n*-pentane and *n*-hexane are still well resolved (Fig. 3).

Symmetrical peaks are obtained with ethers, ketones, and esters (Fig. 4), with alkyl chlorides (Fig. 5), and with aromatic hydrocarbons (Fig. 6). The same separation of aromatic hydrocarbons can be obtained with graphitized carbon black, but it needs a temperature of 150°C instead of 65°C.

On the anthraquinone-coated carbon black, as well as on the pure carbon, meta and para xylenes are partly resolved, whereas para and ortho xylenes are not. This shows that there is an important contribution of adsorption on the carbon black surface to the net retention on the anthraquinone-coated carbon black. When benzophenone, the adsorption properties of which are very near those of

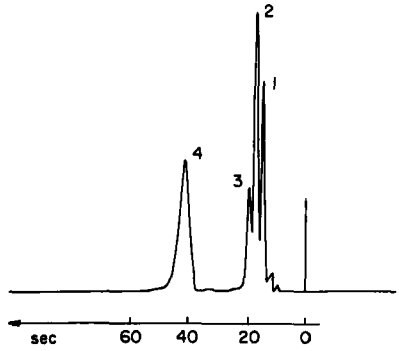

FIG. 4. Analysis of (1) diethyl ether, (2) ethyl formiate, (3) acetone, (4) ethyl acetate. Column packed with 5% anthraquinone on Sterling M. T. 100–160 μ. Length, 1 m; carrier gas, hydrogen; $u_0 = 60$ cm/sec; inlet pressure, 4 kg/cm^2; temperature, 65°C.

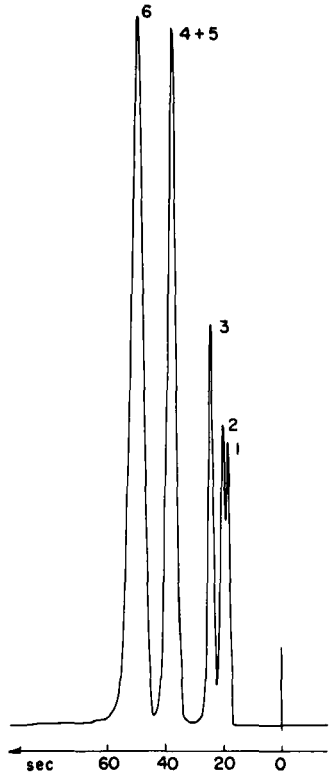

FIG. 5. Analysis of alkyl chlorides; same conditions as for Fig. 4. (1) *trans*-1,2 dichloroethylene, (2) *cis*-1,2 dichloroethylene, (3) *t*-butyl chloride, (4) *s*-butyl chloride, (5) *i*-butyl chloride, (6) *n*-butyl chloride.

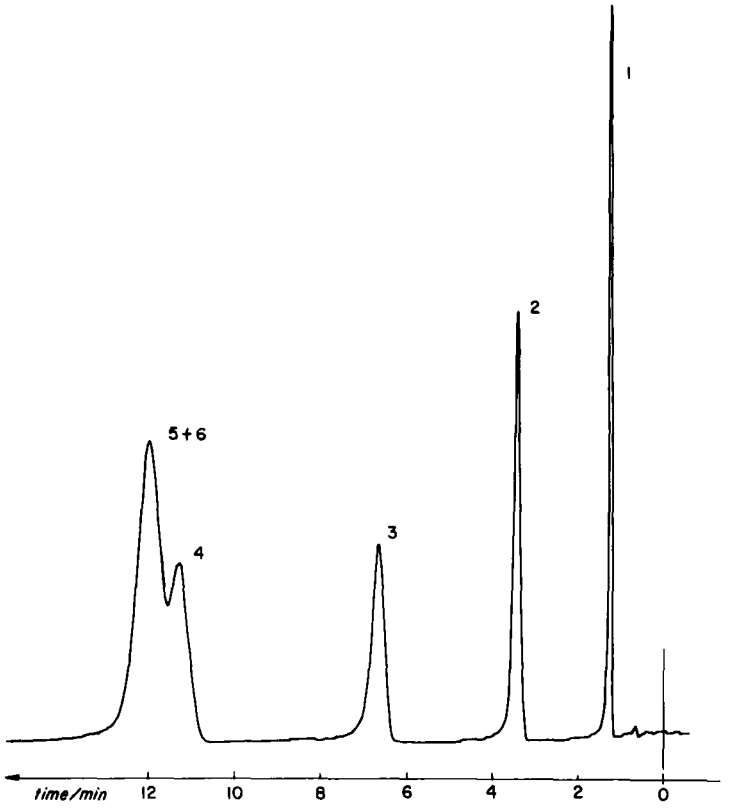

FIG. 6. Analysis of aromatic hydrocarbons. Same conditions as for Fig. 3 except temperature 65°C. (1) benzene, (2) toluene, (3) ethylbenzene, (4) *m*-xylene, (5) *p*-xylene, (6) *o*-xylene.

anthraquinone, is deposited on Chromosorb, meta and para xylenes are eluted in the same time and are resolved from ortho xylene; moreover, ethyl benzene is eluted just before meta and para xylenes (*11*). Thus the comparison of the elution pattern of the C_8 aromatic hydrocarbons on these two adsorbents shows that anthraquinone is not uniformly coated on the carbon surface, so that the adsorbent keeps some properties of the graphitized carbon black.

The anthraquinone surface presents a specific adsorption toward molecules with mobile hydrogen which can give specific interactions with the π electrons of anthraquinone, such as alcohols which are more retained on this surface than on graphitized carbon black alone and are eluted with a slight tailing (Fig. 7).

The last chromatogram (Fig. 8) shows the elution of aniline,

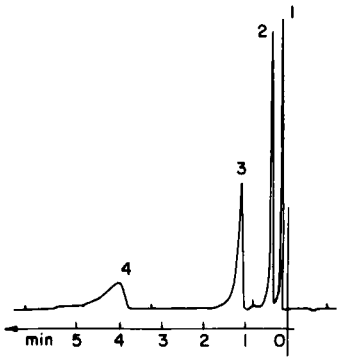

FIG. 7. Analysis of alcohols, same conditions as for Fig. 4. (1) methanol, (2) propanol-1, (3) butanol-1, (4) pentanol-1.

nitrobenzene, and dimethylaniline at 165°C. The peaks are tailing only slightly. It must be considered, however, that such an analysis is still uncommon by gas-solid chromatography and would be impossible on most usual adsorbents.

Kiselev (*17*) has resolved aniline, N-methyl aniline, N-dimethylaniline, and nitrobenzene on pure graphitized carbon black. The peaks were more symmetrical, but roughly the same capacity factor as those shown in Fig. 8 is observed at a higher temperature.

The aliphatic amines and phenols are greatly retained and tail badly, so that this new adsorbent cannot be used for their analysis.

CONCLUSION

This work shows that it is possible to modify some of the adsorption properties of graphitized carbon blacks by depositing a layer of an organic solid substance on its surface.

When anthraquinone is used as the organic substance, an adsorb-

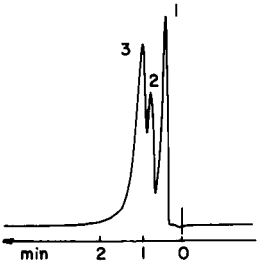

FIG. 8. Analysis of (1) aniline, (2) nitrobenzene, (3) dimethylaniline. Same conditions as for Fig. 4, except temperature 165°C. Inlet pressure 5 kg/cm², $u_0 = 96$ cm/sec.

ent of type III of Kiselev's classification is obtained. This adsorbent has some very useful chromatographic properties: Its surface is fairly homogeneous, the kinetic-mass-transfer term is less than 10^{-4} sec for nonspecifically adsorbed compounds, and the adsorption enthalpy is lower than on pure carbon black. This decrease in the adsorption enthalpy is very large, especially for long-chain alkanes and for aromatic hydrocarbons. It allows us to make useful separations at temperature much lower than with the pure graphitized carbon black.

Some specific properties of the pure graphitized carbon black can be observed with the modified adsorbent; the relative retention depends on the geometric structure of the isomer in much the same way as with pure carbon black. Ortho xylene is more retained than meta xylene; *n*-alkanes are much more retained than branched and cyclic hydrocarbons with the same carbon number.

Molecules with mobile hydrogen, such as alcohols, which can give specific interaction with the π electrons of anthraquinone, are more retained and give slightly tailing peaks. To resolve highly polar compounds such as phenols and alkyl amines, the use of anthraquinone is not convenient, because its surface is not as homogeneous and nonselective as the surface of pure carbon black.

If an organic solid substance with a different electronic structure is used, other specific separations could be achieved, as examplified by those obtained by Scott and Phillips (*18*).

However, the search for new organic adsorbents must be directed mainly toward compounds which are thermally more stable than anthraquinone and can be used at high temperature (i.e., up to 300°C at least) or eventually in temperature programming without producing baseline drift or noise, and with no column degradation after extensive use. Such an adsorbent would be very useful in the analysis of low-vapor-pressure compounds.

REFERENCES

1. I. Halasz and C. Horvath, *Nature*, **197**, 71 (1963).
2. I. Halasz and C. Horvath, *Anal. Chem.*, **36**, 1178 (1964).
3. C. G. Pope, *Anal. Chem.*, **35**, 654 (1963).
4. A. V. Kiselev, in *Gas Chromatography 1962* (M. van Swaay, ed.), Butterworth, London, 1963, p. XXXIV.
5. R. L. Gale and R. A. Beebe, *J. Phys. Chem.*, **68**, 555 (1964).
6. S. Ross, J. K. Saelens, and J. P. Olivier, *J. Phys. Chem.*, **66**, 696 (1962).

7. A. V. Kiselev, in *Gas Chromatography 1964* (A. Goldup, ed.), Butterworth, London, 1965, p. 238.
8. T. F. Brodasky, *Anal. Chem.*, **36,** 1604 (1964).
9. W. Schneider, H. Bruderreck, and I. Halasz, *Anal. Chem.*, **36,** 1533 (1964).
10. C. G. Scott, in *Gas Chromatography 1962* (M. van Swaay, ed.), Butterworth, London, 1963, p. 36.
11. C. Vidal-Madjar and G. Guiochon, *Bull. Soc. Chim. France*, **1966,** 1096.
12. I. Halasz and G. Schreyer, *Chem. Ing. Tech.*, **32,** 675 (1960).
13. Handbook of Chemistry and Physics, 42nd ed. (C. D. Hodgman, ed.), Chemical Rubber Co., Cleveland, Ohio, 1961.
14. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York 1954, p. 539.
15. J. C. Giddings and P. D. Schettler, *Anal. Chem.*, **36,** 1483 (1964).
16. J. C. Giddings, *Anal. Chem.*, **36,** 1170 (1964).
17. A. V. Kiselev, in *Gas Chromatographie 1965*, Vorträge des V-Symposiums über Gas-Chromatographie in Berlin, Mai 1965 Nachtrag, p. 59.
18. C. G. Scott and C. S. G. Phillips, in *Gas Chromatography 1964* (A. Goldup, ed.), Butterworth, London, 1965, p. 266.

Received by editor December 2, 1966
Submitted for publication December 27, 1966