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THE USE OF HIGH EFFICIENCY PACKED COLUMNS FOR GAS-SOLID CHROMATOGRAPHY

III. SEPARATION OF DEUTERIUM SUBSTITUTED COMPOUNDS

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SUMMARY

Gas–solid chromatography with packed columns is used for the separation of some polar and nonpolar isotopic pairs.

The technique involves the use of graphitized carbon black modified with proper amounts of suitable liquid phases. A comparison with capillary columns shows that in many cases these can be conveniently substituted by packed columns. The technique is useful either for the study of isotope effects or for analytical uses.

The gas chromatography of isotopically substituted molecules is of interest both as an analytical tool and as a method for investigating isotope effects.

There are several reports in the literature concerning the separation of various isotopic mixtures by exploiting isotope effects either in gas–liquid (GLC) or in gas–solid (GSC) systems using capillary or packed columns[1–4].

The use of capillary columns involves a rather sophisticated technique and the chemist is often discouraged by the operative difficulties encountered in preparing high resolution capillary columns with particular liquid phases.

Our efforts have recently been directed to the exploitation of high resolution packed columns, so that gas chromatography can be used as a routine method of analysis of isotopic mixtures as well as a simple technique for the study of isotope effects.

The exploitation of the gas chromatographic properties of Graphon[5], which is a graphitized carbon black with a surface area of about 100 m^2/g, has made it possible to extend the use of gas–liquid–solid chromatography (GLSC) to the elution of polar and H-bonding compounds. This macroporous adsorbent, whose surface properties are the same[6] as those of the other graphitized carbon blacks with lower surface areas, like FT or MT, exhibits a higher mechanical resistance, so that packing of long columns with relatively high permeability is possible.

This paper reports the separation of some polar isotopic pairs (CH_3OH–CD_3OH; C_2H_5OH–C_2D_5OH; CH_3CN–CD_3CN) obtained by GLSC employing Graphon partially coated with 1.5% w/w of TEPA.

The separation of C_2H_6–$C_2H_3D_3$–C_2D_6 and C_2H_4–C_2D_4 isotopic molecules has also been achieved with a 15-m column packed with Graphon deactivated with only 0.1% w/w of glycerol.

Furthermore, the analysis of all deuterated isotopic methanes is reported; they are eluted at −78° by means of a 120-m column packed with Graphon deactivated by 0.1% of squalane.

EXPERIMENTAL

Experiments, as far as polar isotopic pairs are concerned, have been carried out using a commercial gas chromatograph (Carlo Erba ATC/f, model C) equipped with a thermal conductivity detector. The separations were performed in a temperature range between +50° and +90°, with an accuracy of ±0.3°.

After some preliminary experiments to eliminate severe tailing of the peaks of the compounds considered, due to some hydrophilic sites on the Graphon, the adsorbent was partially coated with 1.5% w/w of TEPA (tetraethylenepentamine), which provided a surface coverage of about 5%. This addition of liquid phase, due to specific lateral interactions between the functional groups of the liquid phase and the eluate, increased the retention times and separation factors, so that elution of the isotopic mixtures at temperatures above room temperature was possible.

A 15 m × 4 mm I.D. stainless steel tube packed with Graphon (40–60 mesh) was chosen. The column had a theoretical plate value of 16,000 referred to CH_3CN and 13,000 referred to CH_3OH. Hydrogen was used as carrier gas. The pressure drop did not exceed 3 kg/cm^2.

Separations of C_2H_6–$C_2H_3D_3$–C_2D_6 and C_2H_4–C_2D_4 were performed in the temperature range between +37.5° and −41.5°, with an accuracy of ±0.2°. Low-temperature measurements were carried out using a methanol–dry ice cryostat (Lauda, G.F.R.) which refrigerated the thermostatic bath, in which the column was immersed. The gas chromatograph was slightly modified so that it would bear inlet pressures of 10–12 atm and operate at a low temperature, as previously described[4].

The 15 m long, 2 mm I.D. column was packed with Graphon 60–80 mesh coated with glycerol 0.1% w/w, which provided a surface coverage of about 3%. In this way, tailing of the ethylene peak, still present when squalane is used as deactivant, is fully eliminated. The column had a theoretical plate value of 26,000 referred to C_2H_6 and 21,000 referred to C_2H_4. In this case the pressure drop was 8–12 kg/cm^2.

The analysis of isotopic methanes was carried out on a special gas chromatograph equipped with a thermostatic bath at −78° (acetone–dry ice). Particular attention has been devoted to the detector. The effluent from the column, about 250 ml/min, was split and about 5% of it was sent to a flame ionization detector. An additional flow of hydrogen was used at the splitting point as scavenging gas so that dead volumes were avoided. In this way, a double advantage is obtained. Firstly, most of the sample remains intact, which is useful if preparative chromatography is being considered; secondly, the sensitivity of the thermal conductivity detector is much lower than that of the flame ionization detector, and furthermore, the sensitivity of the former would be lowered by using such high flow rates. A detection limit about 1000 times lower is attained, even though 95% of the sample injected is not passing through the detector.

All the compounds were from commercial sources, but the mixture of deuterated methanes was prepared according to a procedure previously described[2].

RESULTS AND DISCUSSION

Fig. 1 shows the plot of the logarithm of the ratio of the retention volumes of hydrogen and the deuterated species *vs.* $1/T$. As can be seen, all the isotopic mixtures eluted show an abnormal isotope effect (*i.e.* the heavier species is eluted first) and a relationship of the type $\ln(V_R)_H/(V_R)_D = B/T + C$ describes the variation of the separation factor with the temperature.

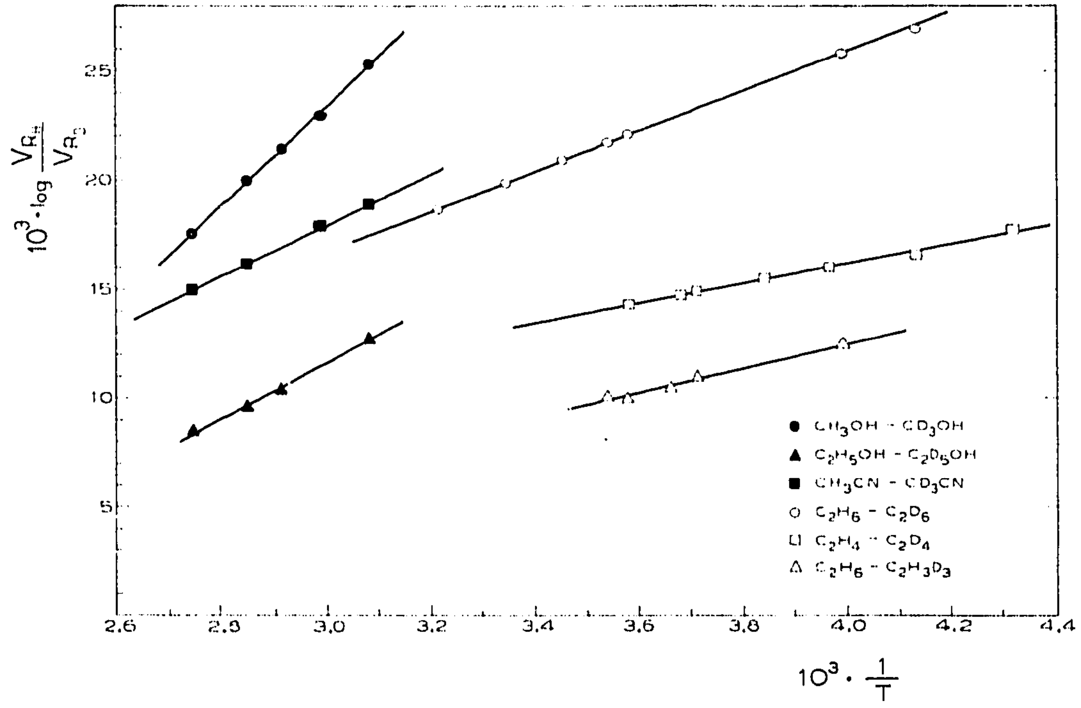

Fig. 1. Plot of the logarithms of ratios of the retention volumes *vs.* $1/T$.

As far as polar isotopic mixtures are concerned, it is interesting to note that the highest isotope effect is shown by the isotopic pair CH_3OH-CD_3OH.

The relative differences in polarizability ($\Delta\alpha/\alpha$), shown in Table I, can partially account for the higher isotope effect shown by the CH_3OH-CD_3OH isotopic system with respect to the isotopic pair CH_3CN-CD_3CN, but this difference does not justify the lower isotope effect for the isotopic pair, C_2H_5OH-C_2D_5OH. Tentatively, the above disagreement can be explained if it is assumed that the substitution of protium for deuterium atoms in the methyl group slightly decreases the strength of the hydrogen bond between the alcoholic and the amino group of TEPA, introducing an isotope effect of the second order. In this hypothesis, the isotope effect on the OH group works in the same direction as the differences in polarizability and the two effects cannot be easily divorced.

As would be expected from the differences in polarizability, the separation of

TABLE I

NUMERICAL VALUES FOR THE ISOTOPE EFFECT FOR THE PAIRS INVESTIGATED

Isotopic pair	$Q_H - Q_D$ *(cal/mole)*[a]	$B \cdot 10^3$ *(K)*	$C \cdot 10^3$	$\Delta a/a \cdot 10^2$
CH_3OH–CD_3OH	105	52.5	−105	0.85
C_2H_5OH–C_2D_5OH	58	29.0	− 61	0.92
CH_3CN–CD_3CN	51	25.5	− 35.5	0.55
C_2H_6–C_2D_6	43	21.5	− 25.0	1.2
C_2H_6–$C_2H_3D_3$	~23	11.5	− 18.0	0.60
C_2H_4–C_2D_4	21	10.5	− 5.0	0.85

[a] Differences of chromatographic molar heats.

C_2H_6 and C_2D_6 is better than that between C_2H_4 and C_2D_4. It is noteworthy that the values of the B and C terms on Graphon, shown in Table I, are approximately equal to those obtained on FT (ref. 7), a graphitized carbon black with a surface area of about 15 m^2/g. This confirms the experimental results obtained by KISELEV[6], that the surface properties of these carbon blacks are the same in spite of the differences in the surface

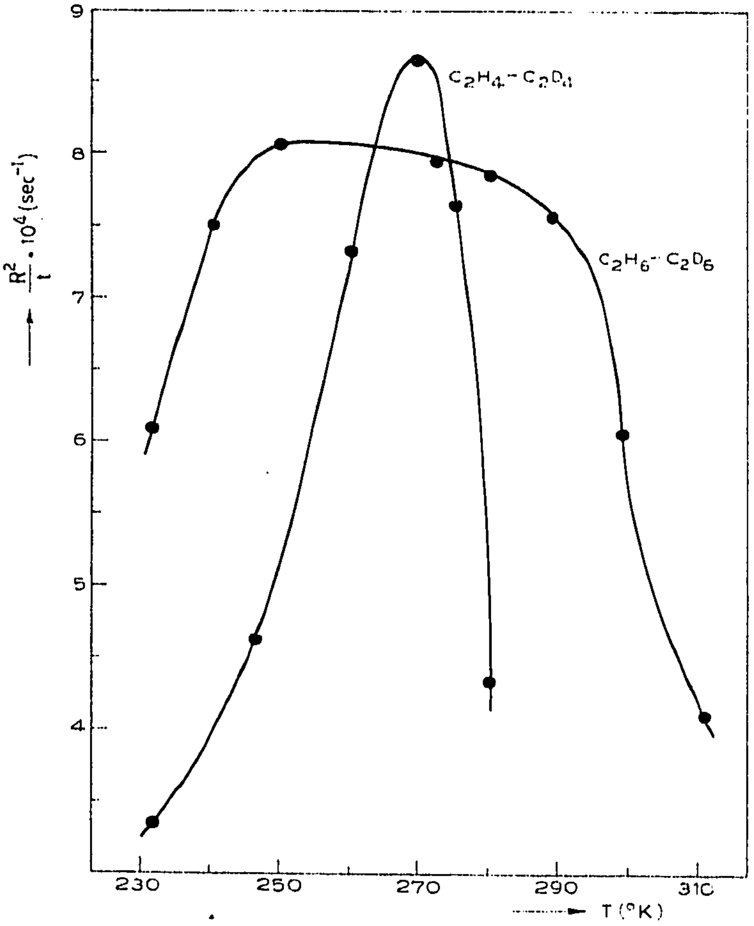

Fig. 2. Graph showing the ratio R^2/t *vs.* temperature for the pairs ethane–ethane-D_6, ethylene–ethylene-D_4.

area. Furthermore, the above results show that glycerol at such low coverages ($\theta = 3 \cdot 10^{-2}$) acts as a deactivant only, and it does not modify the surface properties of Graphon substantially.

Fig. 2 shows the behavior of the factor R^2/t *vs.* temperature, t being the elution time and R the resolution of the isotopic pair according to the definition $R = \Delta t/w$, where Δt is the difference in retention time of the two species and w the width of the peak at the base expressed in the same units as t. As already reported[2], the factor R^2/t is important for determining the experimental conditions required to get the best separation for a given pair in the minimum time. As can be seen, this factor shows a sharp maximum in the case of C_2H_4–C_2D_4, while the range of temperature for which optimum conditions for the separation are obtained in the case of the isotopic pair, C_2H_6–C_2D_6, is rather extended. This is due to the fact that the separation factor of the latter increases steeply inversely with temperature, so that the two counteracting terms balance each other over a wide range. In the case of ethylene, the separation factor increases to a smaller extent, so that an "optimum" of temperature exists for the best separation. The same figures are not reported for the other isotopic pairs examined, since the temperature is much less critical for their R^2/t factor.

Fig. 3 illustrates the best separations obtained for the pairs investigated. A better separation is obtained for methanol, with respect to methanol-D_3, than that obtained on capillary columns and reported previously[8]. The same can be said for the separation C_2H_6–$C_2H_3D_3$–C_2D_6. Separations of this kind by packed columns have already been reported in the literature[3], but our results represent a large improvement in analysis time, temperature and resolution. Moreover, a comparison of analysis time and resolution of the isotopic pair C_2H_6–C_2D_6 shows that Graphon is a better

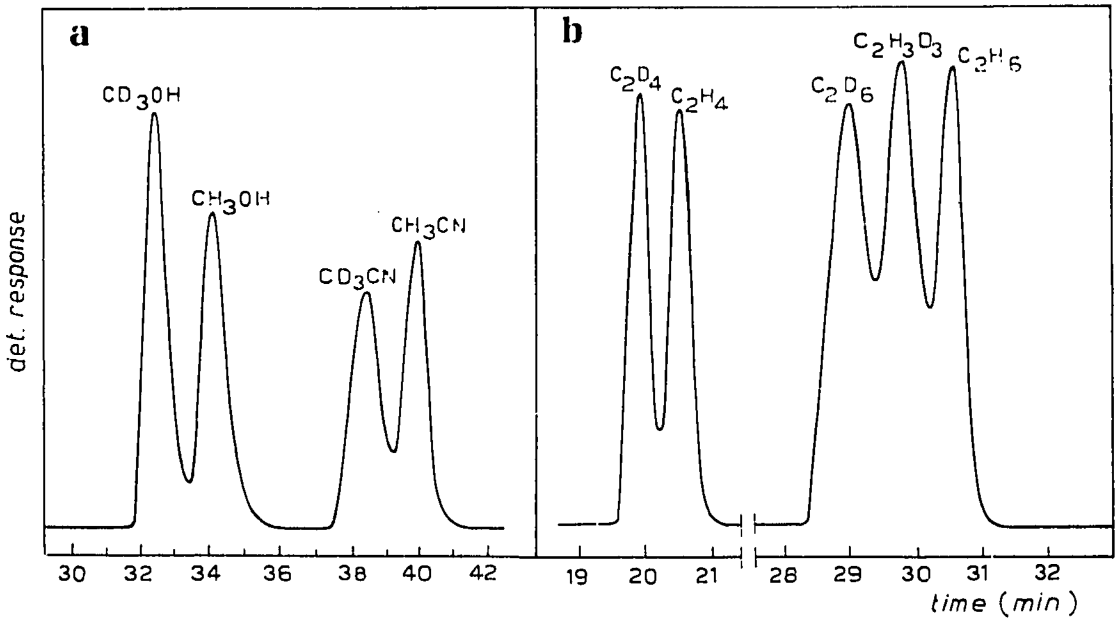

Fig. 3. Separations of methanol–methanol-D_3, methylcyanide–methylcyanide-D_3, ethylene–ethylene-D_4, ethane–ethane-D_3–ethane-D_6. Columns: (a) 15 m × 4 mm I.D. stainless steel column packed with Graphon 40–60 mesh, coated with TEPA 1.5% w/w; temperature, 63°; flow rate, 120 ml/min; inlet pressure, 3 kg/cm^2. (b) 15 m × 2 mm I.D. column packed with Graphon 60–80 mesh coated with 0.1% glycerol w/w; temperature, −22.5°; flow rate, 72 ml/min; inlet pressure, 11 kg/cm^2.

medium than Porapak[9] since in our case the R^2/t ratio is more than doubled at the same temperature.

The separation of ethylene–ethylene-D_4 is not as good as that reported in literature[10]. However, we wish to point out that this separation was carried out in order to get further information about the isotope effect on physical adsorption, and not for analytical use.

Lastly, the separation of all deuterated methanes is shown in Fig. 4. This separation has often been reported in the literature[11]. However, it was obtained by means of capillary columns at liquid nitrogen temperature and using a mixture of nitrogen and helium as carrier gas. The technique used in this work is much simpler and does not require any special equipment. Furthermore, the detection limit for trace components is about ten times lower with the present technique.

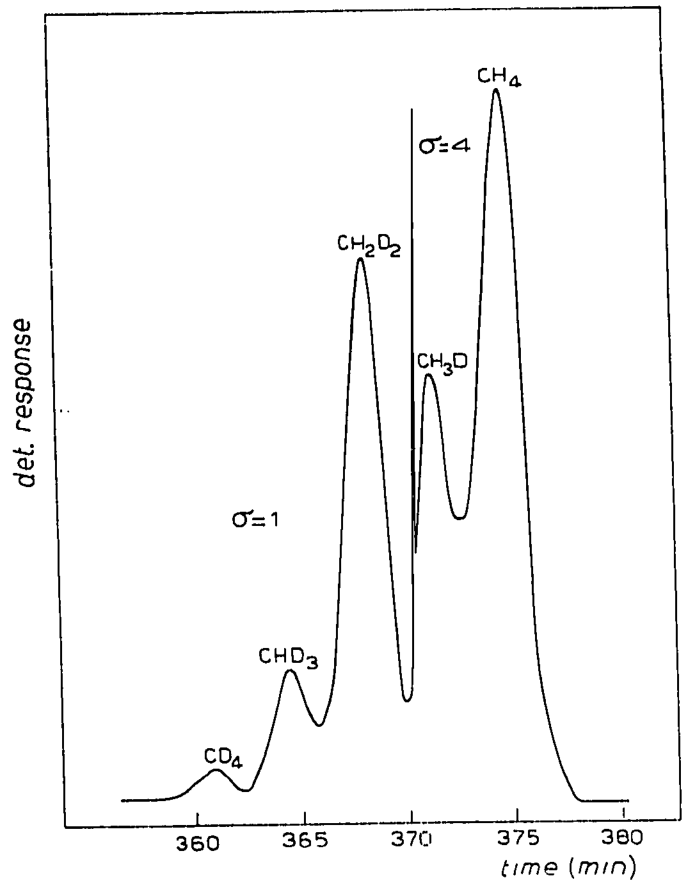

Fig. 4. Chromatogram showing the separation of deuterated methanes. Column: 120 m × 4 mm I.D. copper column packed with Graphon 40–60 mesh coated with 0.1% squalane w/w; temperature, $-78°$; flow rate, 250 ml/min; inlet pressure, 13.5 kg/cm^2.

The results of this investigation show that high efficiency packed columns can be competitive and, in some cases, better than capillary columns as regards resolution and analysis time.

The technique of gas–liquid–solid chromatography with packed columns is useful for the investigation of the isotope effect, and offers a very simple method of analysis for isotopic mixtures, at the same time allowing isotopic separations at more convenient temperatures.

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