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## Note

### 2,4,7-Trinitrofluorenone-modified graphitized carbon black as stationary phase for the gas chromatographic separation of aromatic hydrocarbons

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Many gas chromatographic (GC) methods have been reported for the separation of aromatic compounds. Good results have been obtained by Stuckey<sup>1</sup> who used 1,2,3-tris(2-cyanoethoxy)propane (TCEP) as stationary phase in a single 300-ft. long open-tubular column. With this column he was able to separate 38 aromatic compounds which were eluted as 31 peaks. Ottenstein *et al.*<sup>2</sup> recently developed a suitable method for the separation of a mixture containing benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene, iso- and *n*-propylbenzene and styrene. A near baseline resolution of all of the peaks was achieved within 16 min by use of a column containing 5% SP-1200-1.75% Bentone 34.

Recently, picric acid<sup>3,4</sup> and 1,3,5-trinitrobenzene<sup>5</sup> added in small amounts to graphitized carbon black (GCB) were used as selective modifiers in order to fractionate complex mixtures of aliphatic hydrocarbons. Charge-transfer interactions between the eluate electron donors and electron acceptors in the adsorbed phase were effective in modifying the retention times of unsaturated hydrocarbons. Obviously, the extent of the modification depends on the strength of the electron acceptor used and its concentration on the surface of the GCB. Thus, by careful choice of both the nature and the amount of the electron acceptor, a "tailor-made" column can be obtained for the desired separation. However, for the separation of aromatic hydrocarbons, neither picric acid nor trinitrobenzene can be used as surface modifiers because of their relatively low thermal stability.

2,4,7-Trinitrofluorenone (TNF) is a high-melting good Lewis acid which has already been used as a complexing additive to the stationary phase<sup>5,6</sup>.

The object of this paper is to show that TNF pre-adsorbed on a new type of GCB, Carbo-pack C, can be used for separating aromatic mixtures. In particular, near baseline separation of a mixture of compounds varying from benzene to propylbenzene and including styrene can be achieved with an elution time of *ca.* 15 min by use of 0.33% TNF-modified Carbo-pack C. Graphs of the separation factors for some aromatic pairs and of the thermal stability of the adsorbing system under consideration are reported. Also, the advantage of using hydrogen as carrier gas in order to reduce the analysis time is briefly discussed.

## EXPERIMENTAL

Carbopack C (80–100 mesh) was supplied by Supelco, Bellefonte, Pa., U.S.A. It was ground in order to obtain the 100–120 mesh. Column packings were prepared by dissolving weighed samples of TNF in methylene chloride and adding the solution to a known weight of GCB in a flat dish. The packings were dried slowly at room temperature (20–22°) without stirring, as stirring may cause some crushing of the GCB particles. The dried materials were re-sieved carefully so as to maintain the proper mesh range.

Stainless-steel columns (2 mm I.D.), usually of the coiled type, were packed with this material with the aid of a vibrator. The packing operation is quite critical, and in order to obtain a column of high efficiency it is strongly recommended that the indicated procedure is followed closely. The packing material was added to the column by means of a funnel, and the column was made to vibrate gently and continuously in an uniform way without shock, starting from the bottom of the column and slowly moving to the top. The column must always be rotated in the same direction. Vibration provokes some readjustment of the GCB particles which are more closely packed the more uniform and regular this operation is carried out along the full length of the column. The vibration was repeated several times, and the procedure was concluded when a further slow vibration from the bottom to the top of the column did not affect the height of the carbon level by more than 0.2 mm. When a column is well packed, the amount of Carbopack C should be *ca.* 0.89 g per ml of column volume. The columns were then conditioned overnight at 160°.

A Carlo Erba (Milan, Italy) Model GI gas chromatograph was used. The chromatograph was connected to a Leeds & Northrup Speedomax recorder operating with a 1-mV full-scale response. At the maximum sensitivity of the amplifier system ( $1 \times 1$ ), a current of *ca.* 1.5 pA gives a full-scale response on the recorder. Both extra-pure nitrogen and hydrogen were used as carrier gases. This is important when operating at high temperatures. When less pure gases were used, slight variations in the separation factors of the aromatics were noted.

## RESULTS AND DISCUSSION

Fig. 1 shows a graph of the capacity ratio for *o*-xylene and of the retention times relative to propylbenzene for some aromatic compounds at 180° versus the percentage of TNF added to the carbon surface. Similar plots have been presented and discussed elsewhere<sup>7,8</sup>. It can be seen that the capacity ratio of *o*-xylene decreases continuously as TNF is added to the carbon surface up to a given percentage of TNF. This relative amount should correspond roughly to the amount of TNF needed to form one monolayer.

Moreover, it can be seen that, depending on the surface concentration of the electron acceptor, the selectivity of the adsorbing system under investigation can be considerably modified. In particular, certain modifications in the elution of xylenes are meaningful in illustrating the working mechanism of the TNF–GCB system. On a unmodified GCB surface, *m*-xylene is the first compound to be eluted, whereas *o*- and *p*-xylenes are eluted with almost the same retention time. This effect can be explained by considering that the adsorption of structural isomers on a graphitized

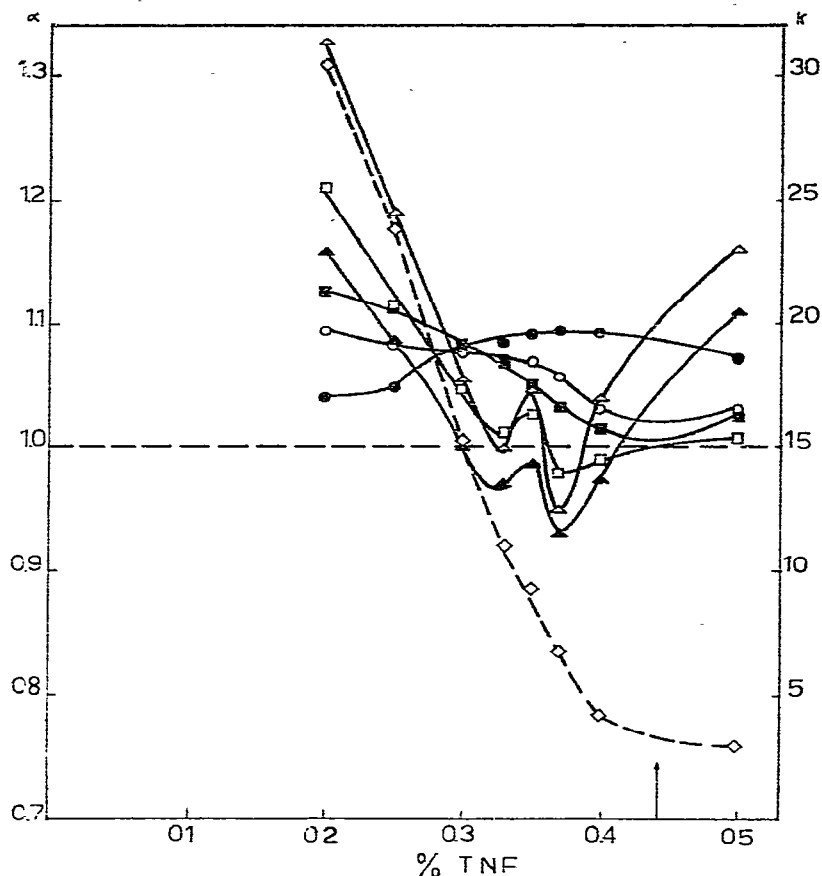


Fig. 1. Graphs of the separation factors ( $\alpha$ ) for some aromatic pairs and of the capacity ratio ( $k$ ) for *o*-xylene (broken line) at 180° versus the amount of TNF added to Carbpacck C. The arrow on the abscissa indicates approximately the completion of one monolayer of the modifying agent.  $\square$  = *m*-Xylene-isopropylbenzene;  $\circ$  = *p*-xylene-*m*-xylene;  $\bullet$  = *o*-xylene-*p*-xylene;  $\blacksquare$  = *sec.*-butylbenzene-*tert.*-butylbenzene;  $\triangle$  = 1,3,5-trimethylbenzene-isobutylbenzene;  $\blacktriangle$  = 1,2,4-trimethylbenzene-butylbenzene.

carbon surface depends strictly on the number of linkages that can come in contact with the adsorbing surface. Therefore, *m*-xylene is more weakly adsorbed than *p*- and *o*-xylenes since in the former case only one CH group of the benzene ring can contact the graphite surface. Also, the adsorption energy for *o*- and *p*-xylene is nearly the same since in each compound two CH groups are in contact with the flat surface of GCB. On the other hand, on adsorption on one layer of TNF, *o*-xylene is more strongly retained than *m*- or *p*-xylene. This behaviour can be explained by the higher electron-donor capacity of *o*-xylene with respect to the other two isomers.

From a practical point of view, it follows that a suitable surface concentration of TNF can be found to achieve the separation of the three isomers of xylene. Fig. 2 shows a chromatogram of the separation of a commonly encountered aromatic mixture on 0.33% TNF-modified Carbpacck C. It can be seen that a near baseline separation of the three xylenes is obtained.

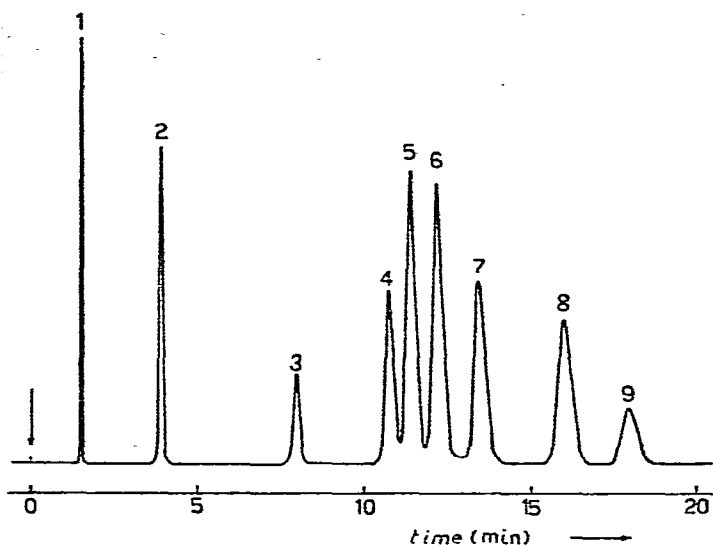


Fig. 2. Chromatogram showing the separation of a characteristic aromatic mixture at  $150^{\circ}$  on a column ( $2.5\text{ m} \times 2\text{ mm I.D.}$ ) containing Carbpacck C (100–120 mesh) modified with 0.33% TNF. Pressure drop,  $5\text{ kg/cm}^2$ ; carrier gas, hydrogen. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = isopropylbenzene; 5 = *m*-xylene; 6 = *p*-xylene; 7 = *o*-xylene; 8 = styrene; 9 = propylbenzene.

Fig. 3 shows a chromatogram of the separation of a more complex aromatic mixture obtained by modifying Carbpacck C with 0.35% TNF. In this case, 1,2,4-trimethylbenzene and *n*-butylbenzene are eluted as one peak. On the other hand, at a higher percentage of TNF the limiting factors become the separation of *tert*-

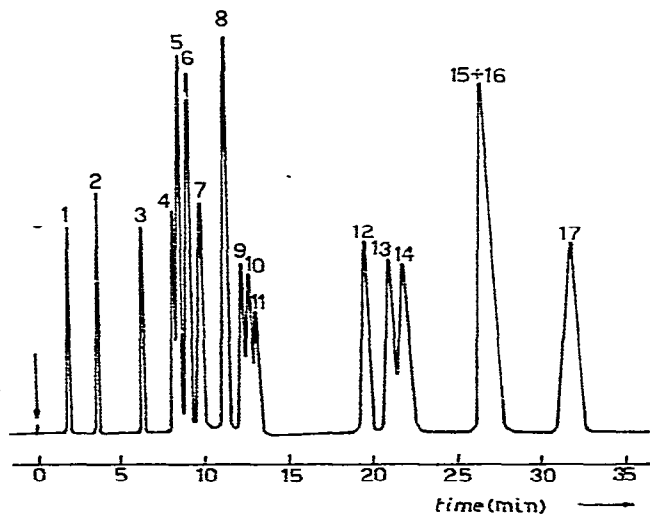


Fig. 3. Chromatogram showing the separation of a complex aromatic mixture at  $168^{\circ}$  on a column ( $3\text{ m} \times 2\text{ mm I.D.}$ ) packed with Carbpacck C (100–120 mesh) modified with 0.35% TNF. Pressure drop,  $5\text{ kg/cm}^2$ ; carrier gas, hydrogen. Peaks 1–8 as in Fig. 2; 9 = *tert*-butylbenzene; 10 = propylbenzene; 11 = *sec*-butylbenzene; 12 = 2-isopropyltoluene; 13 = 1,3,5-trimethylbenzene; 14 = isobutylbenzene; 15 = 1,2,4-trimethylbenzene; 16 = butylbenzene; 17 = 1,2,3-trimethylbenzene.

butylbenzene from propylbenzene and isopropylbenzene from *m*-xylene, while at lower percentages of TNF there is no separation of the *sec.*-butylbenzene-propylbenzene and 1,3,5-trimethylbenzene-isobutylbenzene pairs.

By using both nitrogen and hydrogen as carrier gas, for the TNF-Carbopack packing material, graphs of column efficiency were prepared by varying the linear carrier-gas velocity (Fig. 4). As can be seen, the use of nitrogen allows a slightly lower

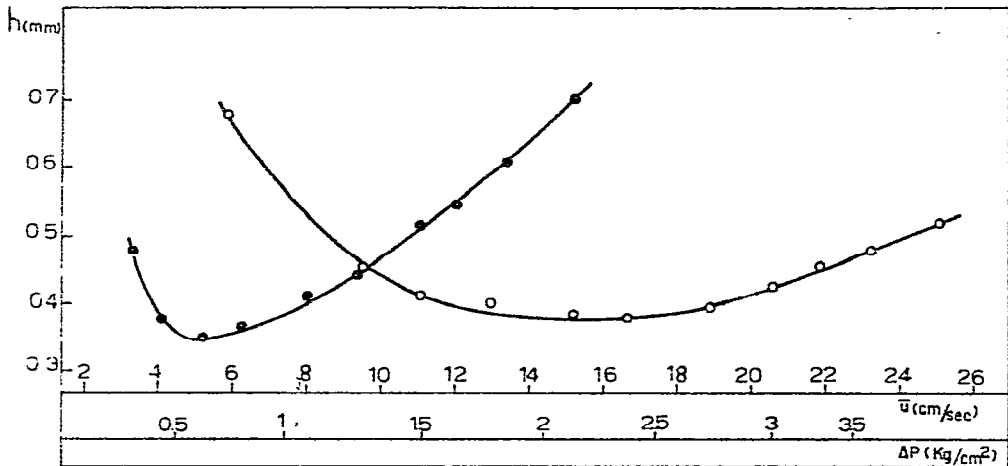


Fig. 4. Van Deemter curves obtained by using two carrier gases. Column (1.4 mm × 2 mm I.D.) packing material, Carbopack C (100-200 mesh) modified with 0.33% TNF; temperature, 150°; eluted compound, ethylbenzene. The different pressure relative to a given linear carrier-gas velocity, is given on the abscissa. ○ = Hydrogen; ● = nitrogen.

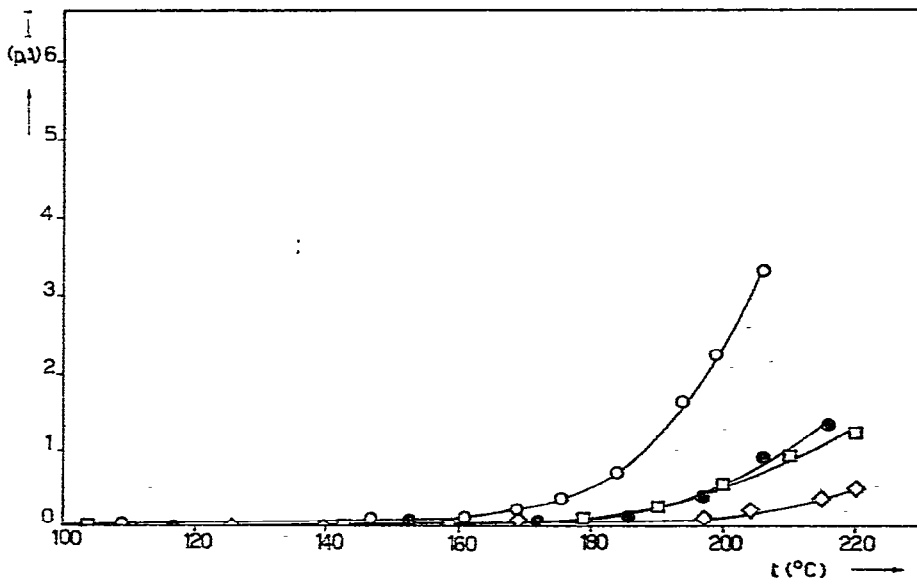


Fig. 5. Graphs of ion background current of a flame ionization detector versus the column temperature for Carbopack C + 0.25% TNF (○), Carbopack C + 0.4% TNF (□), Carbopack C + 0.5% TNF (◇), and Carbopack C + 0.7% TNF (●).

$H_{\min}$  to be attained. However, it appears that, with the use of hydrogen, this type of column packing can be operated at very high linear carrier-gas velocities without significant loss of efficiency.

As reported earlier<sup>8</sup>, the thermal stability of modified GCB is dependent on the surface concentration of the selectivity modifier as well as on its chemical nature. Fig. 5 shows a graph of the thermal stabilities of some columns packed with TNF-modified Carbopack C obtained by measuring the background ion currents with a flame ionization detector. As can be seen, these column packings have good thermal stability up to 180°, except for 0.25% TNF-modified Carbopack C.

#### REFERENCES

- 1 C. L. Stuckey, *J. Chromatogr. Sci.*, 7 (1969) 177.
- 2 D. M. Ottenstein, D. A. Bartley and W. R. Supina, *Anal. Chem.*, 46 (1974) 2225.
- 3 A. Di Corcia and R. Samperi, *J. Chromatogr.*, 107 (1975) 99.
- 4 A. Di Corcia and R. Samperi, *Anal. Chem.*, 47 (1975) 1853.
- 5 A. Di Corcia and R. Samperi, *J. Chromatogr.*, 117 (1976) 199.
- 6 R. O. C. Norman, *Proc. Chem. Soc., London*, (1958) 151.
- 7 A. Di Corcia, *Anal. Chem.*, 45 (1973) 493.
- 8 A. Di Corcia, A. Liberti and R. Samperi, *Anal. Chem.*, 45 (1973) 1228.