

CHROM. 9129

GAS CHROMATOGRAPHIC ANALYSIS OF ALIPHATIC AND AROMATIC HYDROCARBONS WITH 2,4,5,7-TETRANITROFLUORENONE-MODIFIED GRAPHITIZED CARBON BLACK

ANTONIO DI CORCIA, ARNALDO LIBERTI and ROBERTO SAMPERI

Istituto di Chimica Analitica, Città Universitaria, 00185 Rome (Italy)

SUMMARY

Carbopack C, a graphitized carbon black with a surface area of about 8 m²/g, has been modified with 2,4,5,7-tetranitrofluorenone (TeNF) and used as the packing material for the analysis of aliphatic and aromatic hydrocarbons. By varying the amount of the modifying agent, the packing material was evaluated in terms of selectivity and retention. Carbopack C modified with 0.34% TeNF was found to be capable of separating 25 aromatic hydrocarbons in about 45 min at 183°. By modifying the Carbopack C surface with 0.28% TeNF, rapid separation at 56° of C₄ hydrocarbons could be obtained. By decreasing the amount of TeNF to 0.22%, the separation of alkanes and olefins in the C₄-C₅ range was achieved in 34 min. To reduce the analysis time, hydrogen was used as the carrier gas. The advantage of using hydrogen over nitrogen is discussed in terms of Van Deemter curves.

INTRODUCTION

Many investigators have studied the analysis of hydrocarbons by gas chromatography and many types of liquid phases and adsorbing systems have been suggested. For the separation of light hydrocarbons, say up to C₅, some workers have proposed the use of complicated mixtures of liquid phases, careful treatment of the solid support or multiple columns, thus making the analysis difficult and laborious.

Because of the wide range of volatilities of the hydrocarbons involved, the separations obtained by the use of gas-liquid chromatographic columns are generally unsatisfactory. In addition, in all instances the liquid stationary phases reported in the literature need to be operated at unrealistically low temperatures which cannot be controlled when ordinary gas chromatographic apparatus is used.

Alumina and silica gel, either pure or modified with non-volatile liquids or inorganic salts, have been used successfully by a number of investigators for the analysis of light hydrocarbons¹⁻⁶. A limiting factor in the routine use of these columns, however, is their degradation by trace amounts of moisture in the carrier gas.

n-Octane-Porasil C, which is a stationary phase chemically bonded to a porous silica surface, has been shown to be effective in separating all C₄ isomers with a very short elution time⁷. Even this packing material, however, has the disadvantage that it

must be operated at ambient temperature. In addition, the affinity for water of residual Si-OH groups on the silica surface provokes a gradual change in the chromatographic characteristics of the material.

As far as the analysis of aromatic hydrocarbons is concerned, it has been shown that the use of either very polar liquid phases or an organo-clay, such as Bentone 34, is effective in separating very complex aromatic mixtures. The analysis of 38 aromatic hydrocarbons eluting in 31 peaks has been made possible by the use of 1,2,3-tris-(2-cyanoethoxy)propane (TCEP) as a stationary phase on a 300-ft. long open-tubular column⁸. With an elution time of about 100 min, the separation of 23 isomeric aromatic hydrocarbons in the C₆-C₁₀ range, with *n*-butylbenzene and *m*-diethylbenzene eluting as one peak, has been obtained by Dürbeck⁹ using two columns packed with Bentone 34, one modified with silicone oil and the other with lanolin. Near baseline separation of a mixture containing styrene in the presence of xylenes and propylbenzenes within 15 min has been obtained by Ottenstein *et al.*¹⁰ with the use of 5% SP-1200-1.75% Bentone 34.

The adsorbing surface of graphitized carbon black (GCB) partially modified with various electron-acceptor compounds has been shown to be very effective in separating both aliphatic and aromatic complex mixtures. Interactions between electron-donor adsorbates and electron-acceptor pre-adsorbed compounds modify the selectivity characteristics of the GCB surface. The extent of this modification is dependent strictly upon the surface concentration of the modifier as well as its complexing ability. Carbopack B, which is a GCB with a surface area of about 100 m²/g, has been modified with a very strong Lewis acid-type compound, picric acid¹¹. By the use of this packing material, the analysis at 46° of 20 light impurities contained in a pure-grade 1,3-butadiene has been made possible. Using picric acid as a selectivity modifier, Carbopack C (surface area about 8 m²/g) is able to give baseline separation at 50° of C₄ hydrocarbons plus isopentane and *n*-pentane within about 15 min¹². Carbopack C modified with 1,3,5-trinitrobenzene (TNB) has proved to be useful for the analysis of a C₄-C₅ hydrocarbon mixture containing both olefins and alkanes in 30 min at 50°¹³. In the analysis of aromatic hydrocarbons, a suitable surface modifier was found to be 2,4,7-trinitrofluorenone (TNF). Baseline separation of styrene in the presence of xylenes and propylbenzenes has been achieved in approximately 15 min by using 0.33% TNF-modified Carbopack C¹⁴.

For general purposes, the above-mentioned electron acceptors have some limitations. Thus, for the analysis of aromatic hydrocarbons, neither picric acid nor TNB can be used as a surface modifier because of their relatively low thermal stability. Conversely, TNF-modified Carbopack C columns did not have the necessary capability, as shown by picric acid and TNB, of separating complex light hydrocarbon mixtures.

The object of this paper is to show that by using 2,4,5,7-tetranitrofluorenone (TeNF) as the modifying agent of the Carbopack C surface, tailor-made columns can be made for the analysis of complex mixtures of both aliphatic and aromatic hydrocarbons. Thus, by using a 0.28% TeNF-modified Carbopack C column at 56°, the complete separation of C₄ hydrocarbons plus isopentane and *n*-pentane can be achieved in 17 min. By slightly decreasing the percentage of TeNF, to 0.22%, hydrocarbons in the C₄-C₅ range can be separated at 50° in about 35 min. On a 3-m long column packed with 0.34% TeNF-modified Carbopack C at 183°, the separation of

25 aromatics in the C_6 - C_{10} range has been obtained within 45 min. The advantage of using hydrogen as carrier gas to reduce the analysis time is also briefly discussed.

EXPERIMENTAL

Carbopack C was supplied by Supelco (Bellefonte, Pa., U.S.A.) as 80-100 mesh and was ground further to 100-120 mesh.

Column packings were prepared by dissolving weighed amounts of TeNF 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 this operation would crush the GCB particles. The dried materials were re-sieved accurately so as to maintain the proper mesh range.

Glass columns of I.D. 1.8 mm, usually of the coiled type, were packed with this material with the aid of a vibrator. The packing operation is critical and, in order to obtain high-efficiency columns, it is strongly recommended that the following procedure should be followed closely. Packing material is added to the column by means of a funnel and the column is vibrated gently and continuously in a uniform manner without shocks, starting from the bottom of the column and slowly moving up to the top. The column must always be rotated in the same direction. Vibration causes some re-adjustment 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. Vibration is repeated several times and the packing can be terminated when a further vibration set from the bottom to the top affects the level of the carbon inside the column by less than 0.2 mm. When a column is correctly packed, the amount of Carbopack C should be about 0.89 g per millilitre of the column volume.

After packing the columns were conditioned overnight at 180°. A Carlo Erba Model GI gas chromatograph was used connected to a Leed and Northrup Speedomax recorder operating with a 1-mV full-scale response. At the maximum sensitivity of the amplifier system (1×1), about 1.5 pA gave full-scale response on the recorder. Both extra-pure nitrogen and hydrogen were used as carrier gases. This precaution is important when operating at high temperatures; when gases of ordinary purity were used, slight variations in the separation factors of aromatic hydrocarbons were noted. Chemicals were obtained from commercial sources. Ethyltoluenes, isopropyltoluenes and *n*-propyltoluenes were prepared by the Friedel-Crafts reaction.

RESULTS AND DISCUSSION

In Table I are reported retention indices at 180° of benzene, toluene and ethylbenzene calculated for adsorption on a bare carbon surface and for Carbopack C modified with increasing amounts of TeNF. These values can be useful in evaluating the extent of modifications in the adsorption process caused by pre-adsorption of electron-acceptor molecules on the carbon surface. Firstly, it appears that retention indices increase linearly as the surface concentration of TeNF is increased. This result seems to indicate that 1:1 partial charge-transfer complexes are formed on the carbon surface between aromatic hydrocarbons and TeNF.

In gas-liquid chromatography, by making use of a suitable stationary phase, such as TCEP, benzene can be eluted even after dodecane⁸. On the other hand,

TABLE I
RETENTION INDICES AT 180° AS A FUNCTION OF PERCENTAGE OF TeNF

Hydrocarbon	TeNF (%)						
	0	1	2	3	4	5	6
Benzene	555	577	600	620	642	666	686
Toluene	685	706	727	745	768	788	808
Ethylbenzene	742	767	793	817	843	867	892

even when adsorption occurs on a monolayer of TeNF, benzene is eluted before heptane. It can be deduced, therefore, that also on a substantially modified GCB surface conventional adsorption forces are still important in the elution process.

By varying the surface concentration of the modifying agent, column selectivity can be changed continuously. This effect is well illustrated in Fig. 1, where retention times relative to propylbenzene for a number of aromatic hydrocarbons are plotted

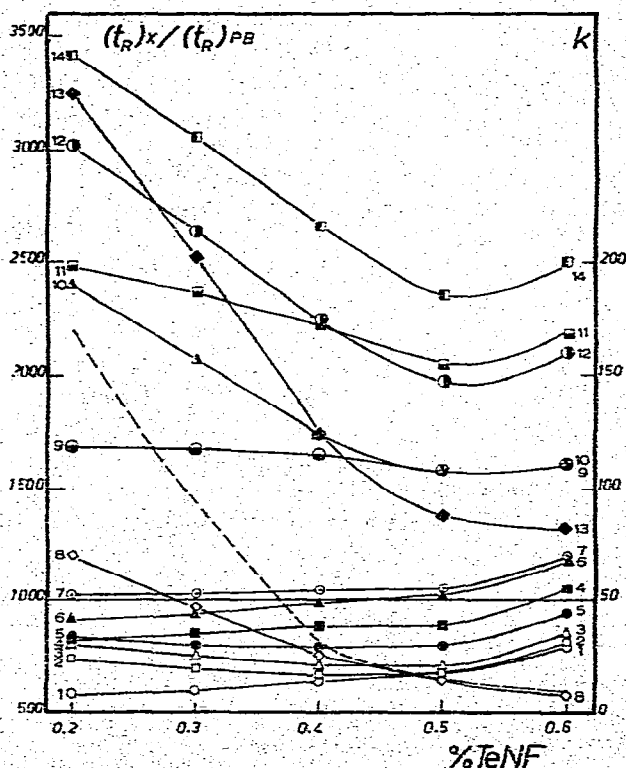


Fig. 1. Plots of corrected retention times relative to *n*-propylbenzene (PB) for aromatic hydrocarbons plus *n*-nonane and *n*-decane, and capacity ratio (*k*) for decane (broken line) at 180° versus the amount of TeNF added to Carboxpack C. 1 = Isopropylbenzene; 2 = *m*-xylene; 3 = *p*-xylene; 4 = *o*-xylene; 5 = styrene; 6 = *tert*-butylbenzene; 7 = *sec*-butylbenzene; 8 = *n*-nonane; 9 = isobutylbenzene; 10 = 1,3,5-trimethylbenzene; 11 = *n*-butylbenzene; 12 = 1,2,4-trimethylbenzene; 13 = *n*-decane; 14 = 1,2,3-trimethylbenzene.

as a function of the percentage of TeNF added to GCB. The variation of the capacity ratio of decane is also reported. Analogous plots have been presented and discussed elsewhere¹⁵⁻¹⁷. It can be seen that the capacity ratio of decane decreases rapidly as the amount of TeNF added to the carbon surface increases, up to a given TeNF percentage. As demonstrated elsewhere¹⁶, this amount should correspond roughly to the amount of TeNF needed to form a more or less closely packed monolayer.

Certain modifications induced in the elution of xylenes as the amount of the modifying agent is varied are meaningful in illustrating the working mechanism of the TeNF + GCB system.

On the unmodified GCB surface, *m*-xylene is the first to be eluted, whereas *o*- and *p*-xylenes have nearly the same retention times. This effect can be explained by considering that the adsorption of structural isomers on the flat carbon surface depends strictly upon the number of linkages that can come into contact with the adsorbing surface. Therefore, *m*-xylene is more weakly adsorbed than either *o*- or *p*-xylene, as for the former only one CH group of the benzene ring can contact the graphite surface whereas for the latter two isomers the adsorption energies are nearly identical as in both instances two CH groups are in contact with the adsorbing surface.

On the other hand, from the plot reported above it can be seen that on a monolayer of TeNF molecules deposited on GCB, *o*-xylene is more strongly retained than

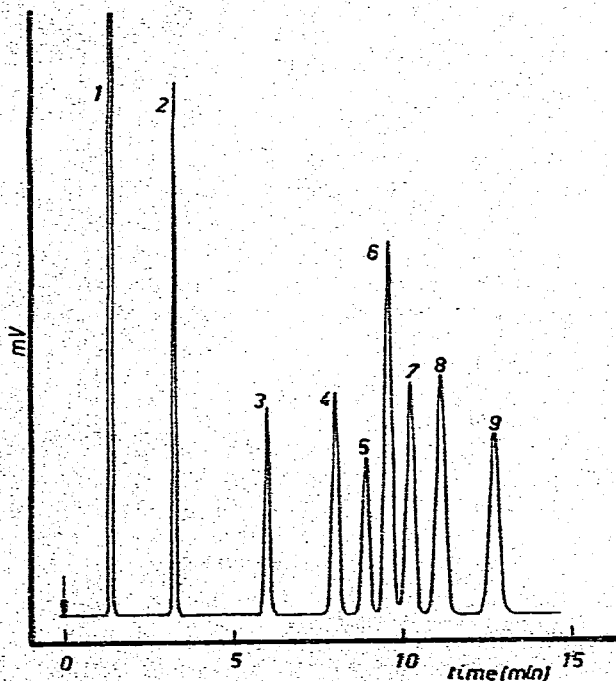


Fig. 2. Gas chromatogram of aromatic hydrocarbons at 187° on a 3 m × 1.8 mm I.D. column containing Carbowack C (100-120 mesh) modified with 0.34% TeNF. Pressure drop, 5.0 kg/cm²; linear carrier gas velocity, 11.7 cm/sec; carrier gas, hydrogen. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = isopropylbenzene; 5 = *m*-xylene; 6 = *p*-xylene; 7 = *o*-xylene; 8 = styrene; 9 = *n*-propylbenzene.

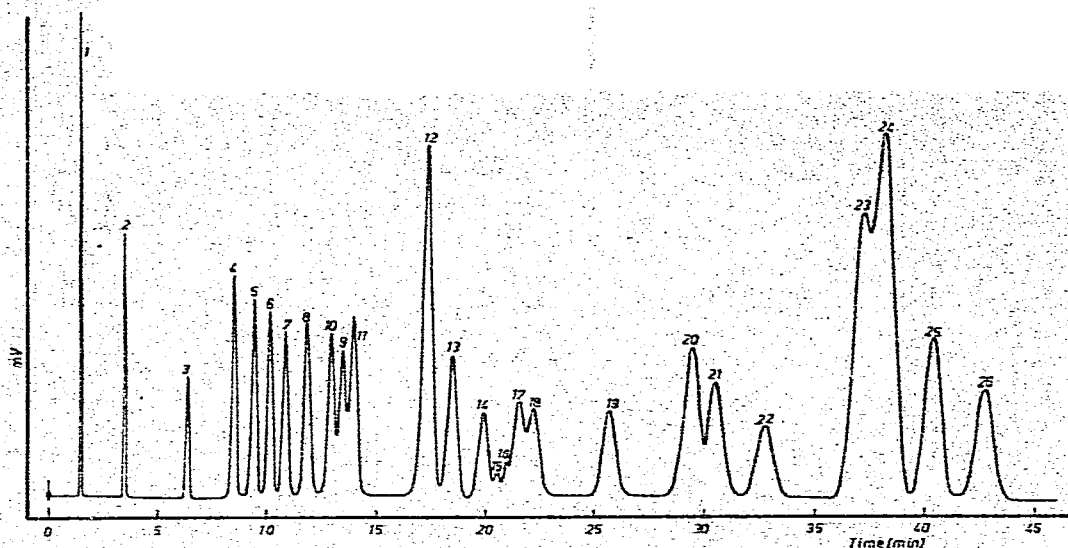


Fig. 3. Gas chromatogram of a complex aromatic mixture in the C_6 - C_{10} range at 183° . Column characteristics, operating conditions and peaks 1-9 as in Fig. 2; 10 = *tert.*-butylbenzene; 11 = *sec.*-butylbenzene; 12 = *m*-ethyltoluene; 13 = *p*-ethyltoluene; 14 = *o*-ethyltoluene; 15 = *m*-isopropyltoluene; 16 = *o*-isopropyltoluene; 17 = *p*-isopropyltoluene; 18 = isobutylbenzene; 19 = 1,3,5-trimethylbenzene; 20 = *n*-butylbenzene; 21 = 1,2,4-trimethylbenzene; 22 = *m*-propyltoluene; 23 = 1,2,3-trimethylbenzene; 24 = *p*-propyltoluene; 25 = *o*-propyltoluene.

the *m*- + *p*-xylene pair. This behaviour is accounted for by considering that *o*-xylene has a higher capability than the other isomers of establishing charge-transfer interactions with TeNF. For the purpose of separation, this favourable situation can be exploited by choosing a suitable amount of TeNF to be added to Carbpac C.

Fig. 2 is a chromatogram showing the rapid separation, obtained by using 0.34% TeNF-modified Carbpac C, of an aromatic mixture that can be encountered in certain industrial streams. It can be seen that a base-line separation of the three xylene isomers has been achieved. Interestingly, ethylbenzene is much less retained than the xylenes, which renders possible an accurate determination of xylenes contained as impurities in pure-grade ethylbenzene.

By slightly decreasing the column temperature, the same column packing can be used to analyze a more complex aromatic mixture, as shown in Fig. 3. It can be seen that good separations of many aromatic hydrocarbons in the C_6 - C_{10} range have been obtained, except for isopropyltoluenes. In addition, a critical factor is the separation of *tert.*-butylbenzene, *sec.*-butylbenzene and *n*-propylbenzene. In fact, by slightly decreasing the percentage of TeNF, *n*-propylbenzene tends to be eluted with *sec.*-butylbenzene, whereas at higher percentages of TeNF *tert.*-butylbenzene and *n*-propylbenzene are eluted as one peak. Tetramethylbenzenes are the last to be eluted on this column packing. However, under the operating conditions used, these compounds are too strongly retained and 1,2,4,5- and 1,2,3,5-tetramethylbenzenes are eluted as one peak.

The TeNF + Carbpac C adsorbing system can also be used effectively to analyze light hydrocarbon mixtures. In Table II are reported changes in retention times,

TABLE II

RETENTION TIMES RELATIVE TO *n*-BUTANE AT 50° AS A FUNCTION OF PERCENTAGE OF TeNF

Hydrocarbon	TeNF (%)			
	5	4	3	2
Isobutane	776	741	697	672
<i>n</i> -Butane	1000	1000	1000	1000
Butene-1	1060	993	910	840
Isobutene	1224	1170	1109	1040
<i>cis</i> -Butene-2	1395	1337	1260	1169
<i>trans</i> -Butene-2	1355	1337	1341	1319
Butadiene-1,3	2048	1990	1785	1551
Cyclopentane	2758	2602	2279	2006
Isopentane	3130	3447	3503	3396
<i>n</i> -Pentane	4188	4973	5384	5425
3-Methylbutene-1	2950	3011	2885	2671
Cyclopentene	3477	3447	3170	2843
Pentene-1	4116	4428	4417	4166
2-Methylbutene-1	4595	4918	4842	4469
<i>cis</i> -Pentene-2	4806	5142	5110	4682
<i>trans</i> -Pentene-2	4695	5142	5335	5149
2-Methylbutene-2	5992	6886	7295	7120

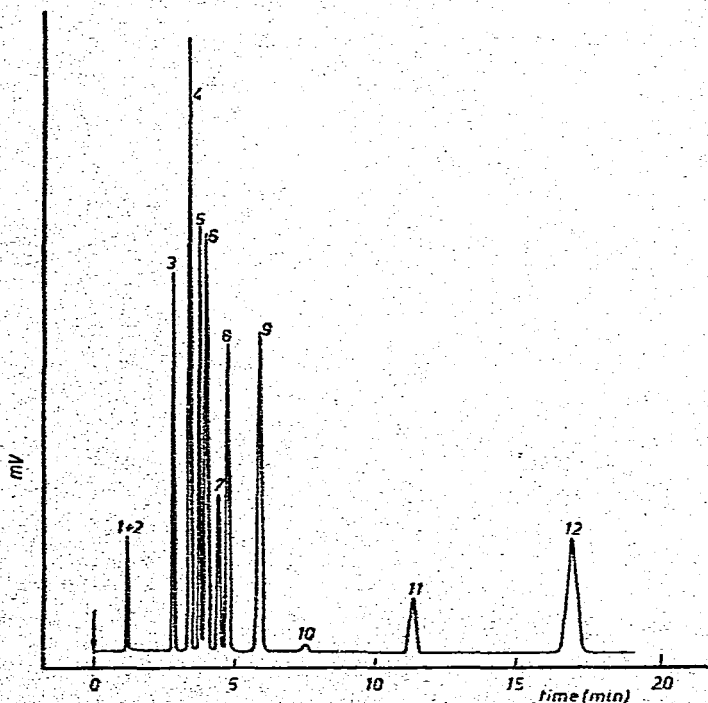


Fig. 4. Chromatogram of C_4 hydrocarbons at 56° on a 3 m \times 1.8 mm I.D. column containing Carbo-pack C (100–120 mesh) modified with 0.28% TeNF. Pressure drop, 5.0 kg/cm²; linear carrier gas velocity, 11.8 cm/sec; carrier gas, hydrogen. 1 = *n*-Propane; 2 = propene; 3 = isobutane; 4 = butene-1; 5 = *n*-butane; 6 = isobutene; 7 = *cis*-butene-2; 8 = *trans*-butene-2; 9 = 1,3-butadiene; 10 = cyclopentane; 11 = isopentane; 12 = *n*-pentane.

relative to that of *n*-butane, of alkanes and olefins in the C_4 - C_5 range at 50° as the percentage of TeNF is varied. Even in this instance, modifications in the selectivity characteristics of the carbon surface are induced via charge-transfer interactions that take place between unsaturated hydrocarbons and TeNF molecules.

Rapid base-line separation of the C_4 hydrocarbons and isopentane and *n*-pentane at 56° could be obtained by using 0.28% TeNF-modified Carboxpack C, as shown in Fig. 4. From a practical point of view, it is noteworthy that this column packing can be operated at 56° . This is a realistic column temperature that can be easily controlled in most gas chromatographs.

The column packing mentioned above has the same capability as a 0.18% picric acid-modified Carboxpack C column for separating C_4 hydrocarbons¹². With the former, however, propane and propene, which may be present in a typical C_4 hydrocarbon mixture of interest in the petroleum industry, cannot be separated.

By using the same column packing mentioned above for the analysis of a C_4 - C_5 hydrocarbon mixture, *trans*-pentene-2 and *n*-pentane are eluted with nearly the same retention times. This limitation can be eliminated by simply decreasing the amount of complexing agent deposited on the GCB surface. In this way, *n*-pentane, which is more strongly adsorbed on the bare surface of GCB than the branched olefin, will be retarded with respect to *trans*-pentene-2. Fig. 5 shows a chromatogram of the hydrocarbon mixture under consideration eluted at 50° on Carboxpack C partially coated

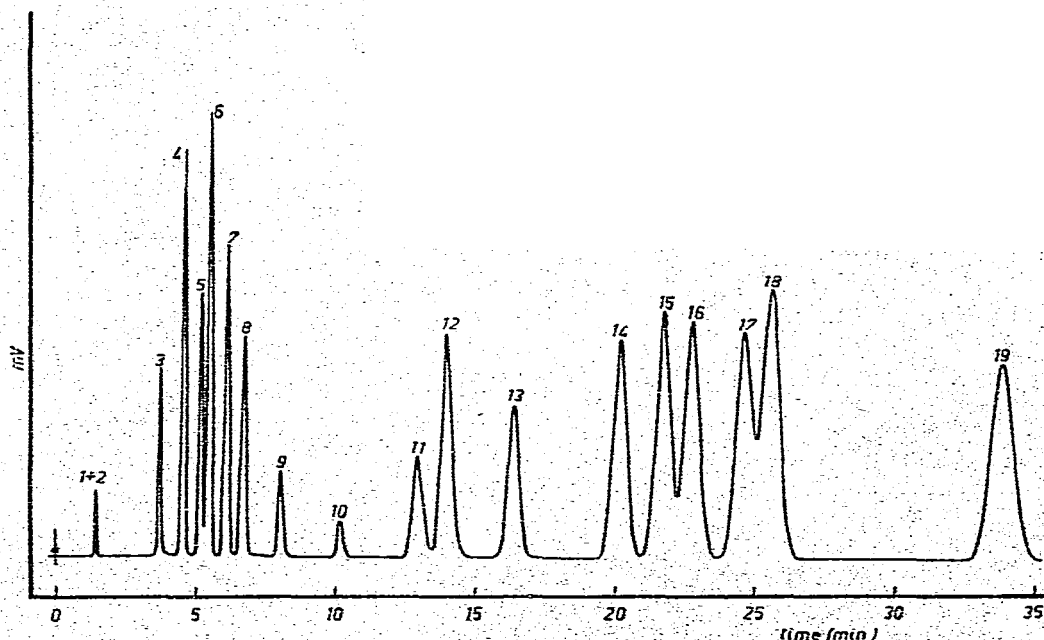


Fig. 5. Chromatogram showing the separation at 50° of a C_4 - C_5 hydrocarbon mixture on a 3 m \times 1.8 mm I.D. column containing Carboxpack C (100-120 mesh) modified with 0.22% TeNF. Pressure drop, 3.0 kg/cm²; linear carrier gas velocity, 9.1 cm/sec; carrier gas, hydrogen; peaks 1-10 as in Fig. 4; 11 = 3-methylbutene-1; 12 = cyclopentene; 13 = isopentane; 14 = pentene-1; 15 = 2-methylbutene-1; 16 = *cis*-pentene-2; 17 = *trans*-pentene-2; 18 = *n*-pentane; 19 = 2-methylbutene-2.

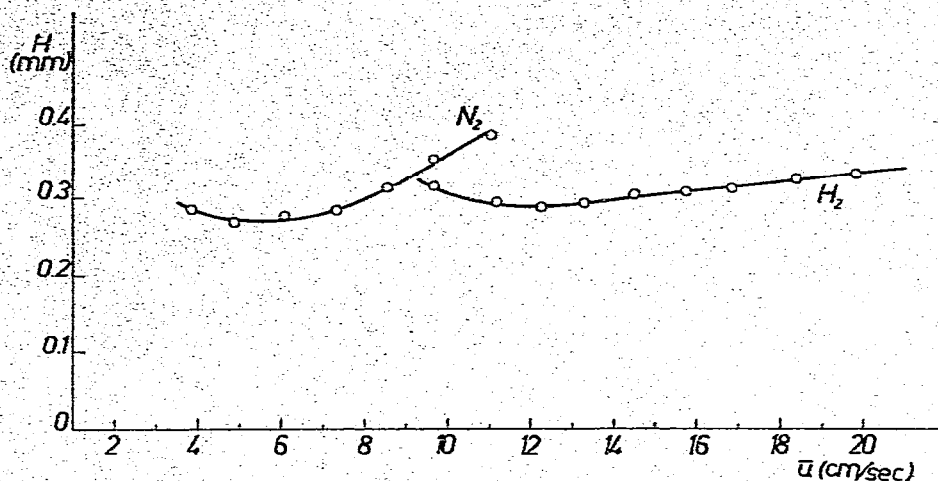


Fig. 6. Van Deemter curves for two different carrier gases (hydrogen and nitrogen). Column, 1.20 m \times 2 mm I.D.; packing material, Carbowack C modified with 0.4% TeNF; temperature, 50°; eluted compound, *n*-pentane.

with 0.22% TeNF. Satisfactory separations of the C₄ and C₅ hydrocarbons were obtained with an analysis time not greater than 35 min.

Hydrogen was used as the carrier gas in place of the more commonly used nitrogen. The reason for this choice is made clear from two Van Deemter curves obtained by using both hydrogen and nitrogen on TeNF-modified Carbowack C (Fig. 6). As can be seen, the value of H_{\min} is scarcely affected by the nature of the carrier gas. On the other hand, by using hydrogen, the maximum column efficiency is obtained at far higher linear carrier gas velocities than with nitrogen. In addition, the right-hand branch of the Van Deemter curve is smoothed when hydrogen is used. From a theoretical point of view, this effect can be accounted for qualitatively by considering that at high linear carrier gas velocities H depends mainly upon two terms, that is C_g and C_k . The first term represents diffusion in the gas phase and is proportional to the ratio d_p^2/D_g , where d_p is the mean particle diameter of the packing material and D_g is the molecular diffusion coefficient for the gas phase. The second term is related to the time necessary to establish equilibrium between the gas and adsorbed phases. On an homogeneous adsorbing surface, which is the case for Carbowack C, the time to reach equilibrium is very low, so C_k is negligible compared with C_g . It follows, therefore, that at high linear carrier gas velocities the plate height can be minimized by using a small particle diameter and a low-viscosity gas, such as hydrogen. From a practical point of view, when the analysis time is a critical factor, the use of hydrogen has the advantage over nitrogen that an equal peak resolution can be attained by reducing the elution time.

As far as the thermal stability of the column material under investigation is concerned, it has been found that columns can be operated up to about 210°. Such a packing material has been used at 200° for several weeks without observing any alteration. However, when working at high temperatures, columns must be operated by

using extra-pure gases in order to prevent slow chemical decomposition of the modifying agent by trace impurities contained in ordinary-grade gases. This decomposition results in a slow, continuous variation of the retention times of the eluates.

REFERENCES

- 1 T. Bellar, J. E. Sigsby, C. A. Clemons and A. P. Altshuller, *Anal. Chem.*, 34 (1962) 763.
- 2 F. H. Huyten, G. W. A. Rijnders and W. V. Beersun, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1963, p. 335.
- 3 C. G. Scott, *J. Inst. Petrol.*, 45 (1959) 115.
- 4 T. A. Bellar and J. E. Sigsby, *Environ. Sci. Technol.*, 1 (1967) 309.
- 5 E. Jeung and H. L. Helwig, *Symposium on Air Pollution, 144th National Meeting, American Chemical Society, Los Angeles, Calif., April 1963*.
- 6 C. J. Kuley, *Anal. Chem.*, 35 (1963) 1472.
- 7 J. N. Little, W. A. Dark, P. W. Farlinger and K. J. Bombaugh, *J. Chromatogr. Sci.*, 8 (1970) 647.
- 8 C. L. Stuckey, *J. Chromatogr. Sci.*, 7 (1969) 177.
- 9 H. W. Dürbeck, *Z. Anal. Chem.*, 251 (1970) 108.
- 10 D. M. Ottenstein, D. A. Bartley and W. R. Supina, *Anal. Chem.*, 46 (1974) 2225.
- 11 A. Di Corcia and R. Samperi, *J. Chromatogr.*, 107 (1975) 99.
- 12 A. Di Corcia and R. Samperi, *Anal. Chem.*, 47 (1975) 1853.
- 13 A. Di Corcia and R. Samperi, *J. Chromatogr.*, 117 (1976) 199.
- 14 A. Di Corcia, R. Samperi and G. Capponi, *J. Chromatogr.*, in press.
- 15 A. Di Corcia, *Anal. Chem.*, 45 (1973) 492.
- 16 A. Di Corcia, A. Liberti and R. Samperi, *Anal. Chem.*, 45 (1973) 1228.
- 17 A. Di Corcia and A. Liberti, *Advan. Chromatogr.*, in press.