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EVALUATION OF MODIFIED GRAPHITIZED CARBON BLACK FOR THE ANALYSIS OF LIGHT HYDROCARBONS

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SUMMARY

Vulcan-G, a graphitized carbon black, has been modified with polyethylene glycol 1500 and picric acid for use in analysis of C_1 – C_4 hydrocarbons. By varying the amounts of the modifying agents, the packing material was evaluated in terms of selectivity and retention. Vulcan-G modified with 2.8% PEG 1500 was found to be capable of separating a C_1 – C_4 hydrocarbon mixture in 19 min at 48°. The analysis of 20 light impurities contained in purum-grade 1,3-butadiene was performed at 46° in about 30 min by using Vulcan-G modified with 4.8% picric acid.

INTRODUCTION

Many investigators have studied the analysis of C_1 – C_4 hydrocarbons by gas chromatography and many types of liquid phases and adsorbing media have been used. However, very few of the systems reported in the literature are completely satisfactory. Some workers have suggested 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. Also, in all instances the liquid stationary phases reported in the literature have the disadvantage that they must be operated at unrealistically low temperatures that cannot be controlled when working with commercial gas chromatographic apparatus.

Olefins form molecular complexes with π -acceptors, which has been taken advantage of in mixing various π -acceptors^{1–3} with liquid phases in order to increase the selectivity of gas chromatographic columns. However, this method is suitable only for research purposes and cannot be used in practical analytical applications owing to the chemical and thermal instability of the complexing agents.

Alumina and silica gel, both pure and modified with several non-volatile liquids and inorganic salts, have been used successfully by a number of investigators^{4–9}. The main problem encountered in the routine use of these columns is the af-

finitly of the uncovered solid fraction for water, which causes the retention times of hydrocarbons to change considerably.

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 in a very short elution time¹⁰. However, even this packing material has the disadvantage that it must be operated at temperatures that cannot be controlled with commercial gas chromatographic apparatus. 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.

Porapaks Q (ref. 11) and N (ref. 12) have been used in the analysis of C₁-C₄ hydrocarbons. Their main advantage is that they can be used at temperatures above 50°. On the other hand, they are not particularly efficient in fractionating all C₄ isomers.

Graphitized carbon black (GCB) provides good separations of hydrocarbon gases. Schneider *et al.*¹³ used a 10 m × 0.25 mm I.D. capillary column filled with squalane-modified GCB in order to separate a C₁-C₄ hydrocarbon mixture containing 20 components with an analysis time not greater than 24 min.

In this paper is reported an evaluation of the chromatographic behaviour of GCB modified with various amounts of either polyethylene glycol (PEG) 1500 and picric acid for the fractionation of light hydrocarbons. In order to improve the repeatability of our results in routine analysis, we tried to avoid the use of difficult operating conditions and complicated gas chromatographic devices. In particular, we chromatographed C₁-C₄ hydrocarbon mixtures at temperatures that could easily be controlled with commercial chromatographic apparatus. By using GCB modified with 2.8% PEG 1500, the separation of C₁-C₄ hydrocarbons was achieved at 48° with an analysis time of 19 min. Also, for the analysis of light hydrocarbon impurities contained in purum-grade 1,3-butadiene, we found the use of GCB modified with 4.8% picric acid to be suitable.

EXPERIMENTAL

The graphitized carbon black (GCB) used, Vulcan-G (specific surface area, *ca.* 110 m²/g), was supplied by Supelco, Bellefonte, Pa., U.S.A., as Carbopack B. The GCB had a particle-size range of the 60-80 mesh, and was ground in order to obtain smaller particlesize ranges (80-100 and 100-120 mesh).

Column packings were prepared by dissolving weighed samples of PEG 1500 in methylene chloride and adding the solution to a known weight of GCB in a flat dish. Methanol was used as the solvent for picric acid. The packings were dried slowly at room temperature without stirring, which would have caused some crushing of the GCB particles. The dried materials were re-sieved so as to maintain the proper mesh range.

With the materials prepared in this fashion, columns made from stainless-steel tubing (2 mm I.D.) were packed with the aid of a vibrator. In order to maintain uniformity of the packed material, it was necessary that the void tubing should be previously coiled and ready for connection to the gas chromatograph. The columns were then conditioned for 12 h at 140° when using PEG 1500 and at 100° when using picric acid for modifying the GCB.

A Carlo Erba (Milan, Italy) Model GI gas chromatograph was used. The

chromatograph was connected to a Leeds and Northrup Speedomax Model G recorder operating with a 1-mV full-scale response. At the maximum sensitivity of the amplifier system (1×1), about 1.5 pA gives full-scale response on the recorder. Nitrogen was used as the carrier gas.

RESULTS AND DISCUSSION

In chromatography, the smaller the particle size the faster is the rate of mass transfer and hence the greater is the efficiency. In Fig. 1 are shown Van Deemter curves for three particle size ranges of Vulcan-G modified with 1.5% PEG 1500 packed in a 2.2-m stainless-steel column. The abscissa also shows the pressure drop needed in order to obtain a given linear carrier gas velocity for each particle size range. This was included with a view to obtaining high-efficiency packed columns consistently with the pressure capability of commercial gas chromatographs, which is generally 5 kg/cm². From Fig. 1 it can be seen that by using the 100–120 mesh range the column efficiency is about 3300 plates per metre of column length. Similar results were obtained by using Vulcan-G modified with picric acid.

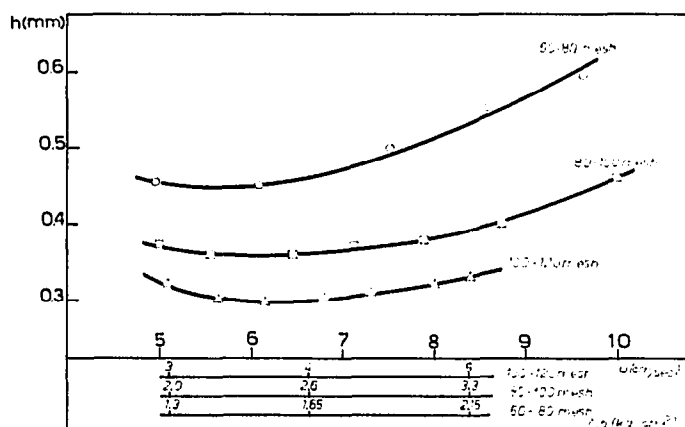


Fig. 1. Van Deemter curves for three particle size ranges. The abscissa also gives the different pressure drops relative to a given linear gas velocity for each particle size range. Column, 2.2 m \times 2 mm I.D.; packing material, Vulcan-G modified with 1.5% PEG 1500; temperature, 50°; eluted compound, *trans*-2-butene.

Fig. 2 shows a graph of separation factors for some hydrocarbon pairs of interest and the capacity ratio for *trans*-2-butene (broken line) at 50° versus the percentage of PEG 1500 added to the carbon surface. Similar plots have been presented and discussed elsewhere¹⁴⁻¹⁶.

The graphitized carbon surface retains molecules on the basis of their geometrical structures and polarizabilities. Conversely, unsaturated hydrocarbons can be polarized by the functional groups of PEG 1500. It seems likely, however, that these dipole-induced dipole type lateral interactions that occur on the carbon surface are rather weak. This accounts for the fact that in the sub-monolayer region, additions of PEG 1500 to the carbon do not cause large changes in the separation factors.

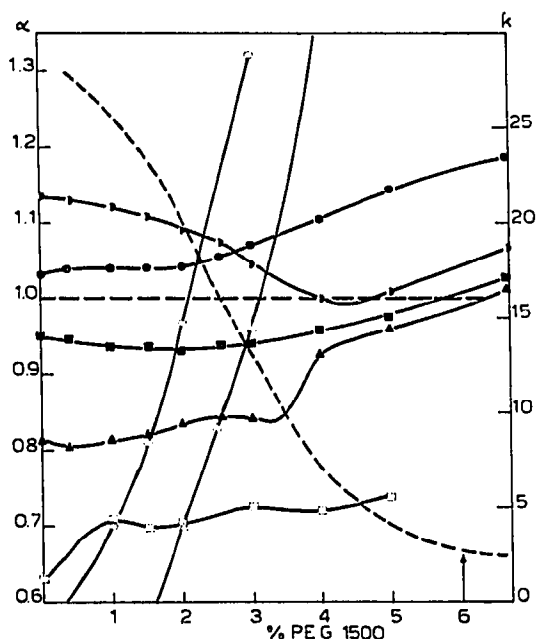


Fig. 2. Plots of the separation factors (α) for some hydrocarbon pairs (full line) and capacity ratio (k) for *trans*-2-butene (broken line) at 50° versus the amount of PEG 1500 added to Vulcan-G. The arrow on the abscissa indicates roughly the completion of one monolayer of the modifying agent. ○, Acetylene-ethylene; △, acetylene-ethane; □, ethylene-ethane; ■, propene-propane; ●, *cis*-2-butene-butane; ▲, *cis*-2-butene-*trans*-2-butene; ●, 1,3-butadiene-*cis*-2-butene.

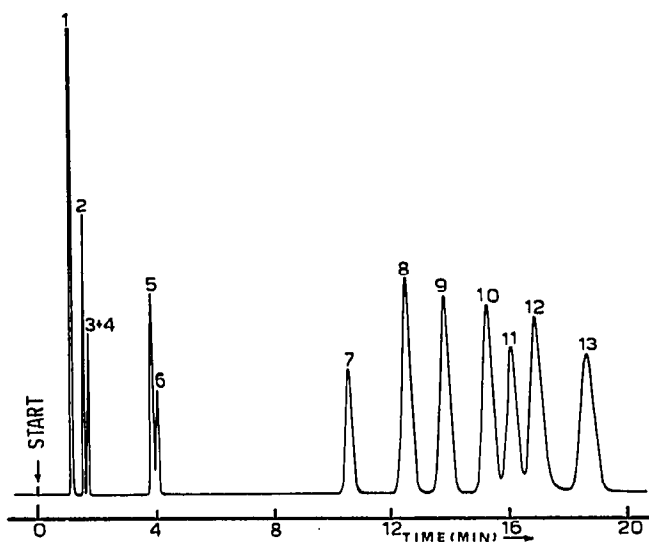


Fig. 3. Gas chromatogram of C_1 - C_4 hydrocarbons at 48° on a 3 m \times 2 mm I.D. column containing Vulcan-G (100-120 mesh) modified with 2.8% PEG 1500. Pressure drop, 4.9 kg/cm². 1, Methane; 2, ethylene; 3, acetylene; 4, ethane; 5, propene; 6, propane; 7, isobutane; 8, 1-butene; 9, isobutene; 10, butane; 11, *cis*-2-butene; 12, 1,3-butadiene; 13, *trans*-2-butene.

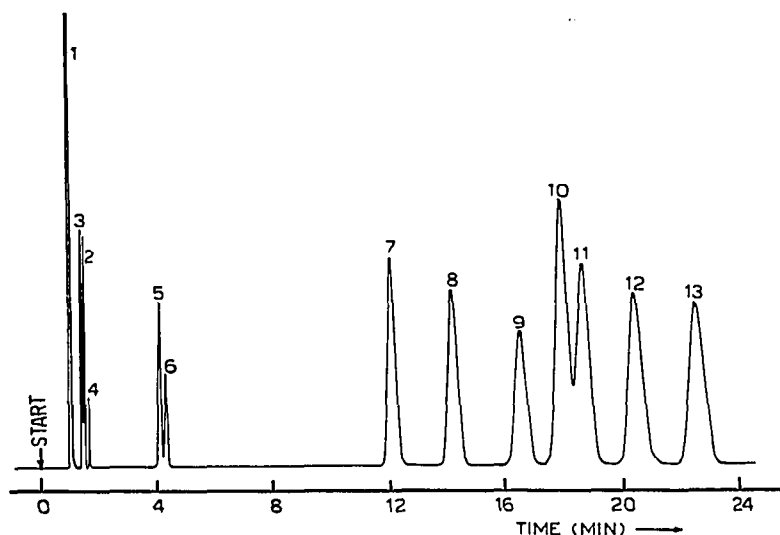


Fig. 4. Gas chromatogram of C₁-C₄ hydrocarbons at 50° on a 3 m × 2 mm I.D. column containing Vulcan-G (100-120 mesh) modified with 1.5% PEG 1500. Pressure drop, 4.9 kg/cm². Peaks as in Fig. 3.

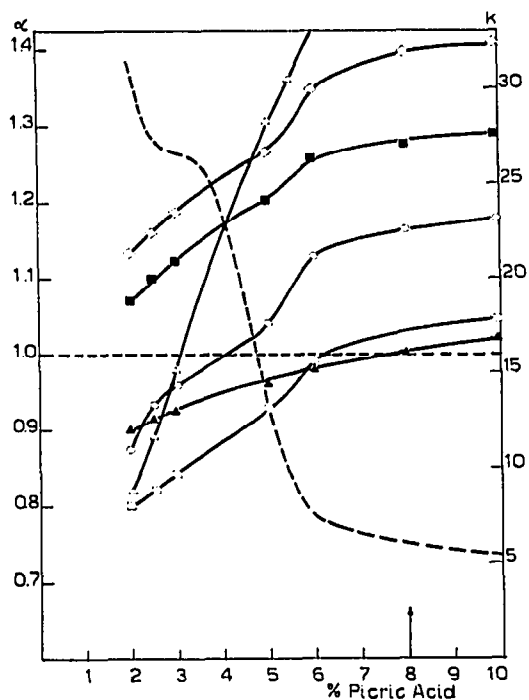


Fig. 5. Plots of the separation factors for some hydrocarbon pairs (full line) and capacity ratio for *trans*-2-butene (broken line) at 50° versus the amount of picric acid added to Vulcan-G. The arrow on the abscissa indicates roughly the completion of one monolayer of the modifying agent. Δ , Acetylene-ethane; \square , ethylene-ethane; \blacksquare , propene-propane; \circ , 1-butene-butane; \diamond , isobutene-butane; \blacktriangle , *cis*-2-butene-*trans*-2-butene.

The monitoring of light hydrocarbons in the atmosphere is of importance as some hydrocarbons can participate in photochemical reactions. Olefins and 1,3-butadiene generally react rapidly in such reactions, while paraffins and acetylene react slowly or not at all. Hence, there is the need to separate the former compounds from the latter in a reasonable elution time by making use of a simplified chromatographic system. The use of packing materials whose operating temperatures are less than 46–47° should be avoided, as this is the minimum temperature that can be controlled with a commercial gas chromatographic apparatus.

In this connection and taking into account the graph discussed above, we found it suitable to use a 3-m column packed with Vulcan coated with 2.8% PEG 1500 for the analysis of a C₁–C₄ hydrocarbon mixture. The chromatogram is shown in Fig. 3.

It should be pointed out that for several months a chromatographic material similar to that discussed here has been used successfully in the analysis of light hydrocarbons in the urban atmosphere¹⁷. Also, the relatively high thermal stability of such packing material¹⁵ permits the determination of hydrocarbons higher than C₄.

The separation of acetylene from ethane could be accomplished by decreasing the PEG 1500 coating to 1.5%. It can be seen from the chromatogram in Fig. 4 that this column packing is able to separate the C₂ hydrocarbons and also to enhance the separation of propene–propane. However, this is possible only at the expense of the separation of the butane-*cis*-2-butene pair and an increase in the analysis time.

Fig. 5 shows a graph similar to that reported above obtained by modifying Vulcan-G with increasing amounts of picric acid, which is a strong π -acid: It can be seen that pre-adsorbed Lewis-acid type molecules on the graphitized carbon surface

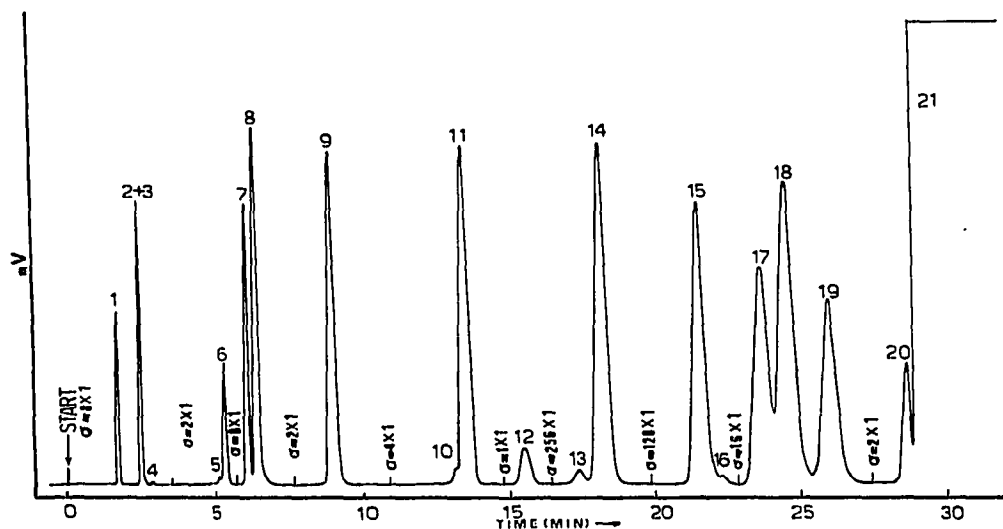


Fig. 6. Light impurities in purum-grade 1,3-butadiene at 46° on a 4 m × 2 mm I.D. column containing Vulcan-G (100–120 mesh) modified with 4.8% picric acid. Pressure drop, 4.9 kg/cm². 1, Methane (10 ppm); 2, ethylene (12 ppm); 3, ethane (7 ppm); 4, acetylene (0.3 ppm); 5, cyclopropane (0.4 ppm); 6, propane (5 ppm); 7, propene (46 ppm); 8, propadiene (70 ppm); 9, propyne (13 ppm); 11, isobutene (61 ppm); 13, butane (210 ppm); 14, 1-butene (5500 ppm); 15, isobutene (2500 ppm); 17, *cis*-2-butene (270 ppm); 18, *trans*-2-butene (390 ppm); 21, 1,3-butadiene; 10, 12, 16, 19 and 20, unidentified peaks.

can modify considerably the elution order for a mixture containing both unsaturated and saturated hydrocarbons. In such a situation, the adsorption characteristics of the carbon surface are largely modified by strong lateral interactions through partial charge transfer between the π -acceptor and unsaturated hydrocarbons.

When picric acid is added to Vulcan-G, 1,3-butadiene is the last of the C₄ hydrocarbons to be eluted, which has practical utility in the determination of light impurities in butadiene. Fig. 6 shows a chromatogram of light impurities contained in purum-grade 1,3-butadiene (Fluka, Buchs, Switzerland). The optimum coating of picric acid for the maximum number of peaks to be obtained appeared to be 4.8%. Methanol, which is present in butadiene, was eluted well after butadiene.

REFERENCES

- 1 B. W. Bradford, D. Harvey and D. E. Chalkey, *J. Inst. Petrol., London*, 41 (1955) 80.
- 2 G. P. Cartoni, R. S. Lowrie, C. S. G. Phillips and L. M. Venanzi, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 273.
- 3 E. Gil-Av and V. Schurig, *Anal. Chem.*, 43 (1971) 2030.
- 4 T. Bellar, J. E. Sigsby, C. A. Clemons and A. P. Altshuller, *Anal. Chem.*, 34 (1962) 763.
- 5 F. H. Huyten, G. W. A. Rijnders and W. V. Beersum, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1963, p.335.
- 6 C. G. S. Scott, *J. Inst. Petrol., London*, 45 (1959) 115.
- 7 T. A. Bellar and J. E. Sigsby, *Environ. Sci. Technol.*, 1 (1967) 309.
- 8 E. Jeung and H. L. Helwig, *Symposium on Air Pollution, 144th National Meeting, American Chemical Society, Los Angeles, Calif., April 1963*.
- 9 C. J. Kuley, *Anal. Chem.*, 35 (1963) 1472.
- 10 J. N. Little, W. A. Dark, P. W. Farlinger and K. J. Bombaugh, *J. Chromatogr. Sci.*, 8 (1970) 647.
- 11 M. Papic, *J. Gas Chromatogr.*, 6 (1968) 493.
- 12 C. A. Cramers and J. Rijks, *J. Chromatogr.*, 65 (1972) 29.
- 13 W. Schneider, H. Bruderreck and I. Halász, *Anal. Chem.*, 36 (1964) 1533.
- 14 A. di Corcia, *Anal. Chem.*, 45 (1973) 492.
- 15 A. di Corcia, A. Liberti and R. Samperi, *Anal. Chem.*, 45 (1973) 1228.
- 16 A. di Corcia and R. Samperi, *Anal. Chem.*, 46 (1974) 977.
- 17 F. Bruner, P. Cicciooli and F. di Nardo, *J. Chromatogr.*, 99 (1974) 661.