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Note

Gas chromatographic separation at 50° of C_4 and C_5 hydrocarbons

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Most column packings for the separation of light hydrocarbons require operation at room temperature or below and even under these conditions the column has a limited life. In a recent paper[1], we showed that C_1–C_4 hydrocarbons, including paraffins, olefins, acetylene and butadiene-1,3, could be readily separated at 50° by using graphitized carbon black (GCB) partially coated with PEG 1500.

More recently, a new GCB, Carbopack C (Supelco, Bellefonte, Pa., U.S.A.), modified with 0.19% of picric acid has been found[2] to give a baseline separation of C_4 hydrocarbons and also propane, propene, *n*-pentane and isopentane at 50° within 15 min. On this column, which was designed especially to separate C_4 hydrocarbons, C_5 hydrocarbons were not completely separated from each other.

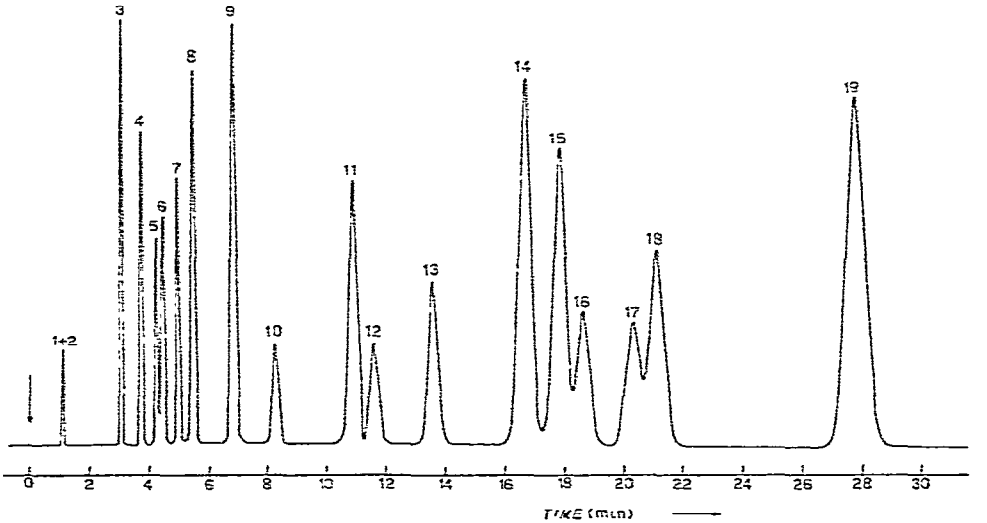

Fig. 1. Chromatogram showing the separation at 50° of a C_4–C_5 hydrocarbon mixture. Column packing, Carbopack C (100–120 mesh) + 0.18% of TNB; 2.5 m × 2 mm I.D. stainless-steel column; pressure drop, 4.6 kg/cm²; carrier gas, hydrogen. 1 = *n*-Propane; 2 = propene; 3 = isobutane; 4 = butene-1; 5 = *n*-butane; 6 = isobutene; 7 = *cis*-butene-2; 8 = *trans*-butene-2; 9 = butadiene-1,3; 10 = cyclopentane; 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.

The C_4 and C_5 hydrocarbons could be separated by decreasing the picric acid content to 0.1%. However, there are difficulties in reproducing this type of column packing, because even very small amounts of a strong π-acid, such as picric acid, when added to the GCB surface modify substantially the retention times of olefins. As a result, small differences in the amount of picric acid present can cause a significant decrease in the resolution of the hydrocarbon mixture.

1,3,5-Trinitrobenzene (TNB) is a considerably weaker π-acid than picric acid, and the amount of TNB deposited on the graphite surface has to be nearly twice that of picric acid in order to induce the same adsorptive effect. When TNB was used as the surface modifier, no difficulties were found in reproducing the column packing with the desired retention characteristics. In addition, we have used TNB-modified GCB at 50° for long periods of time without observing any alteration in its properties.

Fig. 1 shows a chromatogram of the hydrocarbon mixture under consideration eluted at 50° on Carbopack C partially coated with 0.18% TNB. Satisfactory separations of the C_4 and C_5 hydrocarbons were obtained with an analysis time not greater than 29 min. The relatively short analysis time was made possible because hydrogen was chosen as the carrier gas in place of the more commonly used nitrogen. This choice was made on the basis that in gas–solid chromatography, the value of $H_{min.}$ (= minimum plate height at the optimum flow velocity, $\bar{u}_{opt.}$) is scarcely influenced by the nature of the carrier gas, but on the other hand the use of hydrogen has the advantage over nitrogen that the value of $\bar{u}_{opt.}$ is more than double.

In order to obtain a high-efficiency column, the Carbopack C particle size range used was 100–120 mesh. At the optimum carrier gas velocity, the calculated column efficiency was more than 3300 plates per metre.

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