

Retention data of C₃ and C₄ hydrocarbons at low temperatures

Near room temperature, gas chromatographic separation of C₄ hydrocarbons is unsatisfactory since their boiling points are too close to each other and solubilities in polar solvents are so poor that good resolution is not obtained by non-polar and polar liquid phases. Adequate separation can be obtained only by complicated column combinations¹ or by gas-solid chromatography using special adsorbents². The most difficult problem of the analysis is the separation of isobutene and butene-1. PORTER AND JOHNSON³ used *n*-heptane and *n*-octane as liquid phases for analysis of low hydrocarbons at -78°C . The retention times of the C₄ hydrocarbons, however, were very long.

In the present experiments, 15.25 wt.% β,β' -oxydipropionitrile on firebrick support was used at 0, -32 , -40 , -45 , -50 , and -57°C . Stainless steel columns (2 m in length and 6 mm I.D.) were surrounded by a glass jacket cooled with a thermostat. Ethanol was used as cooling medium. The thermal conductivity detector and the sample injector of the Willi Giede GCHF 18 gas chromatograph were at room temperature.

TABLE I
RETENTION VOLUMES OF SOME C₃ TO C₄ HYDROCARBONS AT DIFFERENT TEMPERATURES

Hydrocarbon	0°C	-32°C	-40°C	-45°C	-50°C	-57°C
Propane	9.6	22.9	28.7	37.1	44.5	56.3
Propylene	18.3	49.0	62.3	77	92	120
Isobutane	20.8	65.4	89.5	114	149	216
<i>n</i> -Butane	29.8	92.7	133	172	227	337
<i>n</i> -Butene-1	46.1	169	240	305	406	609
Isobutene	47.5	191	262	328	432	622
<i>trans</i> -Butene-2	—	228	329	413	550	825
<i>cis</i> -Butene-2	85.5	280	404	516	681	1015
Butadiene-1,3	137.4	463	669	851	1133	1703

TABLE II
CONSTANTS FOR EQUATION (1)

Hydrocarbon	A	B
Propane	802	1.96
Propylene	848	1.84
Isobutane	1028	2.45
<i>n</i> -Butane	1110	2.63
<i>n</i> -Butene-1	1156	2.57
Isobutene	1154	2.54
<i>trans</i> -Butene-2	1169	2.50
<i>cis</i> -Butene-2	1105	2.12
Butadiene-1,3	1127	1.99

Retention volumes measured from the air peak are listed in Table I. The relationship between retention volumes (V_R) and temperature was found to follow the equation:

$$\log V_R = A/T - B \quad (1)$$

where T is the absolute temperature of the column. Values for constants A and B are shown in Table II.

A mixture of these hydrocarbons (a C_4 cut of pyrolysis product of a Romashkino naphtha) was analysed, and -40°C appeared to be the optimum temperature

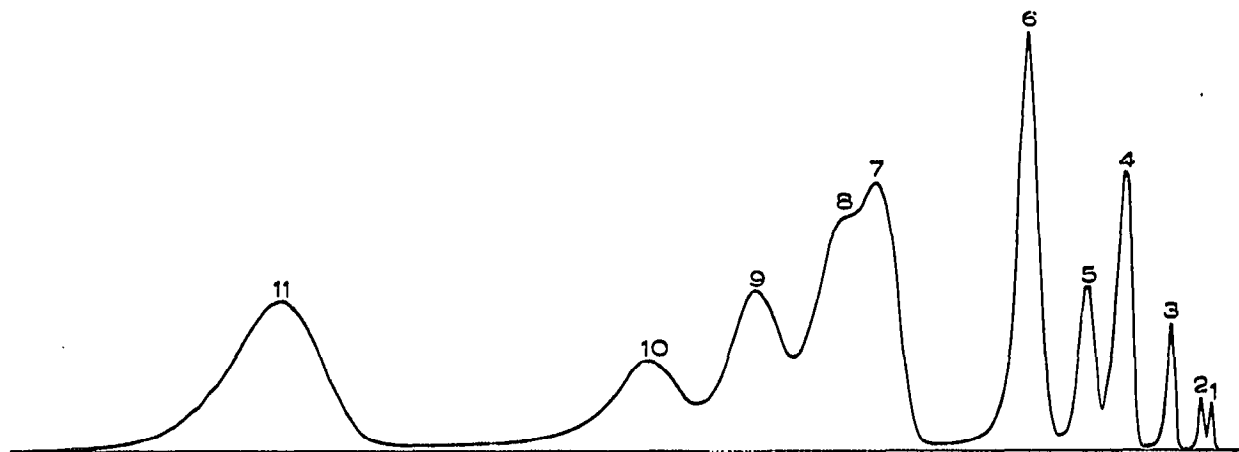


Fig. 1. Chromatogram of a mixture of hydrocarbons at -40°C . 1 = Air; 2 = ethane; 3 = propane; 4 = propylene; 5 = isobutane; 6 = *n*-butane; 7 = *n*-butene-1; 8 = isobutene; 9 = *trans*-butene-2; 10 = *cis*-butene-2; 11 = butadiene-1,3.

for gas chromatographic separation. Below this temperature further improvement in the resolution was hindered by broadening of the peaks. A typical chromatogram at -40°C is shown in Fig. 1. Even butene-1 and isobutene could be detected separately.

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Gas chromatography of isomeric butyl halides

Studies of alkyl rearrangements occurring during the preparation of alkyl halides have necessitated the development of methods for the analysis of mixtures of isomers¹. Alkyl halides are important starting materials in many organic syntheses, *e.g.* in the Wurtz and Grignard reactions, and methods for assessing their isomeric purity are therefore important. Whilst the *n*- and *tert.*-butyl halides were readily separated on a number of stationary phases, including squalane, dinonyl phthalate, and bis (2-cyanoethyl) ether, the *sec.*- and isobutyl halides had identical retention

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