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V. G. Berezkin and L. S. Polyak

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Abstract

Full Text

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Some Features of Gas-Liquid Chromatography of Paraffins and Aromatic Hydrocarbons C_7-C_{12}

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At the present time gas chromatography is becoming the principal method for the analysis of volatile substances, and for the analysis of complex hydrocarbon mixtures the methods of gas-liquid chromatography are used predominantly. Gas-liquid chromatography satisfies the basic requirements of an analytical method: good reproducibility of the qualitative characteristic of the compound being analyzed (retention time), high resolving power, high sensitivity (especially when ionization detectors are used), and great flexibility of the method, which, by proper selection of the selective stationary liquid phase, makes it possible to alter the resolving power of the column in the desired direction.

A promising direction in gas chromatography is the development of modification methods in order to obtain solid sorbents with a reproducible and homogeneous surface ([1,2]). To solve this problem, in our opinion, it is not advisable to carry out surface treatment aimed at converting individual active surface groups into predetermined ones. It is more promising to produce a continuous coating of the surface with a thin layer of a solid polymer (for example, by radiation polymerization), or to create special polymer sorbents. By changing the type of polymer, it will apparently be possible to vary over wide limits the chemical nature of the surface and, consequently, the resolving power of the sorbent.

Fig. 1. Diagram of the chromatographic setup: **1** —katharometer, **2** —sample-introduction device, **3** —chromatographic column, **4** —converter, **5** —recording device, **6, 7** —thermostats.

In gas-liquid chromatography the correct choice of the stationary liquid phase is of decisive importance. The literature ([3]) describes the use of various highmolecular-weight silicone oils for the analysis of high-boiling organic compounds of various classes. However, as a rule, chromatographic studies indicate only the grade of the oil, without specifying its structure and composition. The present work describes a procedure for analyzing hydrocarbons of composition C_7–C_{12} on the domestic methylphenylpolysiloxane oil PFMS-4 (4).

The schematic diagram of the chromatographic apparatus used in the work is shown in Fig. 1. The column and the katharometer are thermostated at different temperatures: the column at an elevated temperature, the katharometer at 30°. To increase the sensitivity of the instrument, the hydrocarbon being analyzed was subjected to conversion before reaching the katharometer, and the direct measurement of the compounds being analyzed was carried out with respect to hydrogen (5). The use of a chromatograph with conversion of the compounds being analyzed simplifies the design of the instrument and the processing of the results, and increases the sensitivity of the apparatus. The sensitivity of the apparatus was about 6000 mV · ml/mg according to Porter. The accuracy of determination was ±5 rel. %.

The composition of the mixture being analyzed was calculated by the formula

$$i = \frac{S_i/n_i}{\sum_{z=1}^{q} S_z/n_z} \cdot 100 \text{ (mol. \%)},$$

where S_z is the area of the chromatographic peak, and n_z is the correction coefficient, equal to the number of hydrogen atoms in the molecule.

Table 1

Relative retention times of hydrocarbons of composition C_7—C_{12} on PFMS-4 at 140°

Compound	Relative retention time	Compound	Relative retention time
Dodecane	1.00	2,2,4-Trimethylheptane	0.980
3-Methylundecane	0.850	3-Ethylheptane	0.880
4-Methylundecane	0.795	2,4,6-Trimethylheptane	0.830
6-Methylundecane	0.795	3-Methyloctane	0.830
2,3-Dimethyldecane	0.770	4-Methyloctane	0.825
5-Propylnonane	0.670	2-Methyloctane	0.810

Compound	Relative retention time	Compound	Relative retention time
2,4,4-Trimethyl-5-ethylheptane	0.600	Octane	0.595
Undecane	0.585	2,2,4,4-Tetramethylpentane	0.550
Decane	0.345	3-Methylheptane	0.510
Nonane	0.200	2-Methylheptane	0.480
Nonane	1.00	Benzene	0.470
Mesitylene	2.40	2,2,4-Trimethylpentane	0.370
Propylbenzene	2.20	Cyclohexane	0.370
Cumene	1.85	Heptane	0.365
2,2,4,4,5-Pentamethylhexane	1.80	3-Ethylpentane	0.360
Decane	1.80	3-Methylhexane	0.305
o-Xylene	1.70	2-Methylhexane	0.285
m-Xylene	1.40	Hexane	0.200
p-Xylene	1.40		

The column length was 5 m, the internal diameter 6 mm. Diatomaceous brick of the 0.2–0.3 mm fraction was impregnated with PFMS-4 silicone oil in a weight ratio of 100 : 15. The efficiency of the chromatographic column was about 3000 theoretical plates (for undecane at 140°).

The results of the study of hydrocarbon separation at 140° on PFMS-4 are presented in Table 1. The reproducibility is $\alpha \pm 3\%$. Relative retention times were determined for 35 hydrocarbons, mainly for alkanes. Figure 2 shows the dependence of the logarithm of the retained volume (α) on the boiling temperature of the corresponding compounds. At the same boiling temperature, aromatic compounds (curve 2) are characterized by substantially longer retention times than alkanes (curve 1). Thus, for example, the retention time of cumene is 1.86 times greater than the retention time of nonane, although the boiling temperatures of these compounds are very close (b.p. of nonane 150.8°, b.p. of cumene 152.4°). This result is quite natural, since one should expect a specific interaction of the chromatographed aromatic compounds with the phenyl groups of the silicone oil.

Fig. 2. Dependence of the logarithm of the retained volume on boiling temperature. 1 —alkanes, 2 —aromatic compounds.

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In this connection it is expedient to use methylphenylpolysiloxane oil for separating alkanes and aromatics in fractions preliminarily obtained on a column with a nonpolar stationary liquid phase. It should be noted that the separation of aromatic compounds proceeds considerably better on PFMS-4 silicone than on silicone oil of grade

DC[6], and the separation of alkanes and aromatic hydrocarbons is better than on E-301 silicone[7].

To study the temperature dependence, the relative retention times of several alkanes were measured at a column temperature of 90°.

In Fig. 3 the relative retention times (with respect to *n*-nonane) of hydrocarbons, measured at temperature $t_1 = 140°$, are presented as a function of the relative retention times of these compounds at $t_2 = 90°$. As follows from Fig. 3, the relative retention times obtained on the same column at two temperatures are connected by a linear relationship:

$$\alpha(t_1) = K\alpha(t_2) + \beta,$$

where K, β are certain constants.

Fig. 3. Dependence of the relative retention times of alkanes for two temperatures on PMS-4 silicone oil. Alkanes (in order of increasing α): 2-methylhexane, 3-methylhexane, heptane, 2-methylheptane, 3-methylheptane, octane, 2-methyloctane, 3-methyloctane, nonane

The proper choice of experimental temperature is of primary importance for separating a definite group of hydrocarbons, and also for determining the optimum duration of analysis. However, obtaining the retention times of the compounds being analyzed at several temperatures requires carrying out a large number of experiments and is not always possible because of the absence of the necessary compounds. Use of the dependence indicated above makes it possible, from known relative retention times for one temperature, to calculate the relative retention times for any other temperature, provided that a limited number of experiments are carried out to determine the constant coefficients of the equation K and β. A linear dependence for relative retention times is also found for other stationary liquid phases and other classes of compounds. For example, in Fig. 4, in coordinates $(\alpha - 1)$, the dependence of the relative retention times of aromatic compounds is presented when *n*-decyl phthalate[6] is used as the stationary liquid phase.

Fig. 4. Dependence of the relative retention times of aromatic hydrocarbons on *n*-decyl phthalate[6] in coordinates $(\alpha - 1)$. Hydrocarbons (in order of increasing α): toluene, ethylbenzene, *m*-xylene, *o*-xylene; cumene, *m*-ethyltoluene, mesitylene, *o*-ethyltoluene

Let us note that from the basic equation

$$\lg \alpha_i = \lg \frac{P_{st}}{P_i} + \lg \gamma_i$$

(P_{st} and P_i are the saturated vapor pressures of the standard and of the given compound at the experimental temperature, γ_i is the relative activity coefficient) and Trouton' s rule $\Delta H = KT_{\text{boil}}$, by simple transformations a dependence of the form

$$\lg \alpha = K \Delta T_{\text{boil}} / T + g$$

or

$$\lg \alpha_i = A \cdot T_{\text{boil}} + B$$

can be derived.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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REFERENCES

1. V. S. Vasil' eva, I. V. Drogaleva, A. V. Kiselev, A. Ya. Korolev, K. D. Shcherbakova, DAN, 136, 852 (1961).
2. D. Whate, Nature, 179, 1075 (1957).
3. C. J. Hardy, F. H. Pollard, J. Chromatogr., 2, 1 (1959).
4. V. G. Berezkin, I. M. Kustanovich, L. S. Polak, N. Ya. Chernyak, DAN, 131, 593 (1960).
5. E. E. Green, Nature, 180, 295 (1957).
6. D. Jentzsch, G. Bergmann, Zs. analyt. Chem., 170, 239 (1959).

7. A. A. Zhukhovitskii, M. S. Semikina, N. M. Turkel' taub, Chemistry and Technology of Fuels and Oils, No. 11, 57 (1960).

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