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Abstract

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Chromatographic Analysis of Mixtures of Hydrocarbons of Composition C_5

In the dehydrogenation of isopentane to isoamylenes and isoprene, multicomponent hydrocarbon mixtures are formed, consisting mainly of hydrocarbons of composition C_5, both saturated and unsaturated. According to the literature and our own data ([1]-[4]), the study of such mixtures is carried out by means of complex and laborious physical and chemical methods of analysis. Therefore, the objective of the present work was to develop a rapid and sufficiently simple method for the quantitative analysis of isopentane-isoprene-isoamylene mixtures.

It is known that chromatographic methods of analysis are the fastest, and many investigators use various chromatographic techniques for the separation of gaseous and liquid hydrocarbons. Among the possible variants of chromatographic analysis, partition chromatography ([5]) and chromatothermography ([6]) have been developed most extensively. In the present investigation, a combination of these chromatographic methods was successfully applied to the analysis of hydrocarbon mixtures of composition C_5. The procedure was developed using pure individual hydrocarbons and their artificial mixtures. For the analysis a universal chromatothermograph ([7]) was used. In this instrument chromatothermography and gas-liquid partition chromatography are carried out. Alumina and diatomite impregnated with dibutyl phthalate (25% of the weight of the sorbent) were used as sorbents. A moving temperature gradient was produced by means of an electric furnace with a temperature drop of 2° per 1 cm of furnace length, with the temperature along the furnace ranging from 20 to 120°. The temperature of the column with diatomite was maintained constant with an accuracy of up to 1°. The carrier gas was air purified from water vapor and acidic and combustible gases. Its linear velocity was measured with a rheometer and was kept constant in individual experiments within the range 120-200 cm/min.

The determination of the concentrations of the mixture components after the sorbent layer was carried out by an instrument based on measurement of the thermal conductivity of gases, while the presence of very small quantities of impurities was established from the thermal effect of combustion of the mixture components. The instrument readings were automatically recorded by an EPP-09 potentiometer with a 10 mV scale. The duration of the analysis was about

2 hours. For analysis, 5 to 15 ml of an air–hydrocarbon mixture, prepared in advance from the samples under study, was taken. The order and time of evolution of the hydrocarbons were established from individual components or from the analysis of artificial mixtures. Since air served as the carrier gas, calibration curves were used in calculating the composition of the mixtures. The content of each component in the mixture was calculated from the fraction represented by the area of its peak on the output curve relative to the total area of the curve.

The experimental material*, obtained in the analysis of artificial mixtures, is presented in Tables 1 and 2, and Fig. 1a shows the separation of a complex ten-component artificial mixture of hydrocarbons of composition C_5 (mixture No. 18). The chromatogram shows a clear separation of all the hydrocarbons of the mixture, with the exception of isopentane and 3-methylbutene-1.

Table 1

Analysis of artificial mixtures

Mixture No.	Composition	Taken, wt. %	Found, wt. %	Error, abs. %	Mixture No.	Composition	Taken, wt. %	Found, wt. %	Error, abs. %
4	Isopentane	54.4	53.7	−0.7	12	Isopentane	83.9	85.8	+1.9
4	2-Methylbutene-2	45.0	46.3	+0.7	12	3-Methylbutene-1	16.1	14.2	−1.9
7	Isopentane	83.7	83.6	−0.1	14	Isopentane	81.2	80.5	−0.7
7	*n*-Pentane	16.3	16.4	+0.1	14	Pentene-2	18.8	19.5	+0.7
8	Isopentane	35.0	36.8	+1.8	16	Isoprene	50.1	48.9	−1.2
8	*n*-Pentane	11.5	11.8	+0.3	16	trans-Piperylene	49.9	51.1	+1.2
8	2-Methylbutene-2	35.0	32.7	−2.3	25	Isopentane	34.7	34.3	−0.4
8	2-Methylbutene-1	18.5	18.7	+0.2	25	3-Methylbutene-1	11.4	11.4	0.0
10	Isopentane	79.1	80.5	+1.4	25	2-Methylbutene-1	13.4	13.5	+0.1
10	2-Methylbutene-1	20.9	19.5	−1.4	25	2-Methylbutene-2	25.5	28.1	+2.6
					25	Isoprene	7.2	5.6	−1.6

25	trans-Piperylene	7.8	7.1	−0.7

Note. Measurement of the areas under the elution curves was carried out with a PP-2K planimeter.

Table 2

Analysis of ten-component artificial mixture No. 18

Composition	Taken, wt. %	Found by planimetry, wt. %	Error, abs. %	Found by equation (1): $\theta = 0.5$, $K\theta = 1.065$, wt. %	Error, abs. %	Found by equation (1): $\theta = 0.75$, $K\theta = 1.66$, wt. %	Error, abs. %	Found by equation (1): $\theta = 0.9$, $K\theta = 2.73$, wt. %	Error, abs. %
Isopentane + 3-Methylbutene-1	30.6	30.3	−0.3	29.1	−1.5	28.4	−2.2	27.7	−2.9
n-Pentane	5.8	5.2	−0.6	5.4	−0.4	5.6	−0.2	5.6	−0.2
Pentene-1	6.2	6.4	+0.2	7.1	+0.9	7.1	+0.9	7.0	+0.8
2-Methylbutene-1	15.4	13.8	−1.6	13.7	−1.7	13.6	−1.8	13.3	−2.1
Pentene-2	6.1	6.1	0.0	6.6	+0.5	6.3	+0.2	6.1	0.0
2-Methylbutene-2	16.3	18.9	+2.6	18.7	+2.4	19.0	+2.7	18.7	+2.4
Isoprene	6.4	6.3	−0.1	6.1	−0.3	6.3	−0.1	6.8	+0.4
trans-Piperylene	6.5	6.5	0.0	6.5	0.0	6.8	+0.3	7.4	+0.9
cis-Piperylene	6.7	6.5	−0.2	6.8	+0.1	6.9	+0.2	7.4	+0.7

The last binary mixture of hydrocarbons was separated separately on aluminum oxide with the use of chromatothermography (Fig. 2). From the analysis of

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

mixture No. 25 (Table 1) it is also evident that isopentane and 3-methylbutene-1 can be determined with sufficient accuracy in a complex mixture when they are present together. The tabulated data on the analysis of artificial mixtures indicate a satisfactory accuracy of the results.

* A. I. Karymova and P. S. Pavlova took part in the work.

An important element of the chromatographic analysis of hydrocarbon mixtures is the interpretation of the effluent curve. Since the content of components in a mixture is determined from measurements of the areas of the effluent curve, various methods are used in calculating the areas. For example, the determination of the area is replaced by measurement of the concentration at the maximum of the effluent curve ($C_{\max}$), assuming that $C_{\max}$ is a quantity proportional to the measured area (^{8}). In this case, however, it is necessary to observe the experimental conditions strictly and to calibrate the apparatus for all the individual components of the mixture. To measure the area rapidly, the area is sometimes (^{9}) calculated as the product of the peak height by the band width at the point where the concentration of the component $C = 0.5C_{\max}$. Such an approximation is sufficient when the components of the mixture are completely separated. However, it is practically inapplicable when the separation criterion $K < 1/2$ (^{10}).

Fig. 1. Chromatograms of the mixtures studied. **a:** left—artificial mixture No. 18, right—pentane-amylene fraction of catalytic cracking gasoline (b.p. 26-39°); **b:** left—product of isopentane dehydrogenation (alumina-chromia-potassium catalyst, 550°, space velocity 1 hour^{-1}), right—gasoline gas fraction (b.p. 20-39°).

Fig. 2. Chromatogram of a binary mixture of isopentane and 3-methylbutene-1 (mixture No. 12).

In chromatographic analysis of hydrocarbon mixtures one has to deal with insufficiently complete separation of the mixture components. In view of this, a method is proposed here for calculating the composition of the mixture, based on the assumption that a Gaussian distribution is applicable for a linear adsorption isotherm (^{11}). Then, in general form, the area q, corresponding to a given amount of component in the mixture, will be determined by the equation:

$$q = K_\theta C_{\max} \mu_\theta, \tag{1}$$

where K_θ is the proportionality coefficient, and μ_θ is the band width corresponding at this point of the curve to a definite value of the ratio $\theta = C/C_{\max}$. For values of θ equal to 0.5, 0.75, and 0.9, the coefficient K_θ, as calculations show, is equal to 1.065, 1.66, and 2.73, respectively. Depending on the degree of separation of the components of the mixture, in calculating the area of the elution curve one must choose one or another of the three values of K_θ and the corresponding μ_θ.

To check the proposed method for calculating the composition of a mixture, the areas were calculated by different methods. Such calculations were carried out for an artificial ten-component mixture No. 18 (Table 2). From the calculations presented it is clear that calculations according to equation (1) with different values of K_θ give satisfactory agreement both with one another and with the data obtained by planimetry, as well as with the results of preparing the mixture. The same conclusion was obtained in processing about 30 elution curves of catalysts from the dehydrogenation of isopentane and of light gasoline fractions.

Figs. 1a and b illustrate the application of the chromatographic method to the study of the products of the catalytic conversion of hydrocarbons (dehydrogenation of isopentane) and to the study of the composition of light gasoline fractions. These data show the relationship between the principal components of the mixture and the impurities, which is of great importance for investigating catalytic processes and for deciding the question of the direction in which petroleum fractions should be used.

Using as an example the analysis of a fraction (b.p. 20–39°) of catalytic-cracking gas gasoline (Fig. 1b), a detailed decoding of its composition is given, with determination of the impurities to the main product of the fraction—isopentane. In addition to isopentane (88.6 wt. %), impurities were found in the fraction in amounts up to 1 wt. % of three hydrocarbons (isobutane, 3-methylbutene-1, and pentene-1) and from 1 to 2 wt. % of seven hydrocarbons (*n*-butane, cis- and trans-butenes-2, *n*-pentane, 2-methylbutene-1, pentene-2, and 2-methylbutene-2).

The universal apparatus can also be used to determine the purity of hydrocarbons. Thus, isopentane isolated from natural-gas condensate contained, as impurities, 1 wt. % *n*-butane and 0.4 wt. % *n*-pentane. Thus, in the present investigation, on the basis of chromatographic methods, a method was developed for the quantitative analysis of complex mixtures of hydrocarbons of composition C_5 of various structures with admixture of lighter hydrocarbons.

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