

QUANTITATIVE DETERMINATION OF THE NORMAL PARAFFIN HYDROCARBONS  
IN KEROSENE-GASOIL FRACTIONS

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In recent years the processes for isolating normal paraffin hydrocarbons from petroleum fractions by means of synthetic zeolites and crystalline urea have been developed intensively.

In connection with this it is of interest to find a suitable and accurate method for the quantitative determination of the concentration of normal paraffin hydrocarbons in petroleum fractions and also in the normal paraffin concentrates and denormalizates, which are the products of the indicated processes.

Methods are described in the literature for the determination of the total concentration of normal paraffins in petroleum products by vapor-phase adsorption on CaA type zeolite for the gasoline fractions [1, 2] and by using crystalline urea for the fractions which contain C<sub>15</sub> and higher normal paraffins [3]. The method of liquid-phase adsorption on CaA zeolite has gained widespread use for determining the concentration of the normal paraffins in kerosene-gasoil fractions [4-6].

This work is devoted to the selection of the conditions for the quantitative determination of the normal paraffin hydrocarbon concentration in kerosene-gasoil fractions by direct distillation and in the products from the separation of these fractions in the denormalization process on CaA type zeolite. It is not always possible to use the urea method [3] for determining the normal paraffin hydrocarbons under the conditions which have been developed for the analysis of low-melting paraffins and diesel fuel because of the instability of the complex of urea with the normal C<sub>8</sub>-C<sub>15</sub> paraffins, which are present in the kerosene fractions, at room temperature. In carrying out this study, the method of determining the normal paraffins by liquid-phase adsorption on CaA zeolite, which was suggested by Larcon and Becker [4], based on the change (decrease) in the liquid volume because of the adsorption of the normal paraffins from the hydrocarbon mixture by the coarse CaA zeolite at room temperature, was used as the base. As we know, CaA zeolite is a highly selective adsorbent for extracting normal paraffins from hydrocarbon mixtures of petroleum fractions. The high absorption capacity of the CaA zeolite to normal paraffins makes it possible to use this zeolite for the almost complete extraction of them from hydrocarbon mixtures.

Some changes were introduced into the Larcon and Becker method with the aim of simplifying and accelerating the determination and to make it suitable to carry out a large number of analyses, which is necessary for controlling the operation of units for the isolation of the normal paraffin hydrocarbons from petroleum fractions. These changes consisted in making use of standard 25 ml picnometers rather than special vessels, using grains of the 0.4 to 0.8 mm fraction composition instead of 1.5, and the use of isooctane instead of cyclohexane as the solvent.

Other authors [5, 6] have suggested carrying out the adsorption of the normal paraffins at elevated temperature to accelerate the analysis by making use of special vessels with reflux condensers.

The method which we used is as follows. Twelve gram samples of CaA type zeolite grains are placed in beakers of heat-resistant glass with ground glass stoppers on analytical balances and they are dehydrated at 400 to 500°C in a muffle furnace for 2-3 h. Then the beakers with the zeolite are cooled to room temperature in a desiccator and the zeolite is rapidly transferred into calibrated 25 ml picnometers (AUSS 7465-55) after which 10 ml of a mixture, made by diluting the sample product with isooctane so that the concentration of the normal paraffins in this mixture does not exceed 5-6% of the zeolite weight, is poured into the picnometers. Preliminary experiments showed that for a low concentration of the normal paraffins in the mixture the accuracy of the determination decreases and for a high concentration, the time required for the quantitative adsorption of the normal paraffins from the solution increases. The picnometers are kept at room temperature for one day; after this time the adsorption of all of the normal paraffins from the mixture is completed.

TABLE 1. Accuracy of Determining the Concentration of Normal Paraffin Hydrocarbons in Artificial Mixtures and in Petroleum Products on Zeolites

Product	Concentration of normal paraffins in the sample, % by wt.		Error, relative, %
	True	Found	
n-C <sub>11</sub>	100	98	2.0
n-C <sub>12</sub>	100	99	1.0
n-C <sub>13</sub>	100	101	1.0
n-C <sub>16</sub>	100	98	2.0
n-C <sub>12</sub> + n-C <sub>16</sub>	100	96	4.0
Low melting paraffins from the Grozny paraffin based petroleum	90*	89	1.1
Diesel fuel from Grozny paraffin based petroleum	20*	20.2	1.0
Normal paraffins, isolated on zeolites from the 280-300°C fraction of Stavropol'skii petroleum	96*	96.0	0.0

\* Determined by the method of isolating the normal paraffin hydrocarbons with crystalline urea at room temperature.

TABLE 2. Reproducibility of the Results of Determining the Normal Paraffin Hydrocarbons on Zeolites

Samples of products	Concentration of normal paraffins, % by wt.					Average value	Error, relative, %
	1	2	3	4	5		
Kerosene from Stavropol'skii petroleum	20	20.5	19.8	—	—	20.0	1.2
Products from the process of isolating normal paraffins from kerosene 220-280°C fractions of Stavropol'skii petroleum							
raw material	22	21.5	21.5	21.5	23	22.0	2.3
isoparaffins 1	6.2	6.0	5.8	—	—	6.0	1.3
isoparaffins 2	2.25	2.2	2.45	—	—	2.3	4.35
The 270-300°C fraction of the kerosene from Stavropol'skii petroleum	39	40	40.5	—	—	40	1.2
Paraffins from the 270-300°C fraction of Stavropol'skii petroleum	93	97	98	96	—	96	1.6
Low melting paraffins from the Grozny paraffin-based petroleum	86	85	85	86	—	85.5	0.58
Diesel fuel from the Grozny paraffin based petroleum	20.5	21	28	20	—	20.3	2.1

The adsorption of the normal paraffins by the zeolite is accompanied by the displacement of the air present in the pores of the zeolite, which has no effect on the absorption capacity of the zeolite but which may decrease the rate of adsorption somewhat.

The air bubbles, displaced from the zeolite pores by the normal paraffins, are partially held between its grains. In order to be freed of the air bubbles, the picnometers are rapped lightly for several minutes and then the picnometers are filled to the mark with isooctane from a 10 ml burette.

A blank experiment is carried out in the same way, differing only in that 10 ml of pure isooctane is poured into the picnometer with the zeolite rather than the mixture.

The difference in the volumes of isooctane needed to fill the picnometers to the mark in the working and blank experiments corresponds to the volume of normal paraffins absorbed by the zeolite. This difference must be corrected by a value which takes into account the difference in the volumes of the picnometers in the working and blank experiments.

The volume concentration of the normal paraffins in the starting sample is calculated by the formula:

$$c = \frac{\Delta v_c \cdot a \cdot 100}{v_s} \% \text{ vol.},$$

where  $\Delta v_c$  is the corrected difference in the volumes of isooctane added to the picnometers in the working and blank experiments, ml;  $v_s$  is the volume of the mixture being analyzed which is poured into the picnometer in the working experiment, equal to 10 ml;  $a$  is the multiple for the dilution of the sample with isooctane.

The method was checked on a number of artificial mixtures prepared by mixing the individual normal  $C_{11}$ – $C_{16}$  paraffin hydrocarbons (purity 99% and over) with isooctane and on samples of diesel fuel and low-melting paraffin which contains the  $C_{16}$  and higher normal paraffins and which have been analyzed by the urea method at room temperature.

Table 1 shows that the error in determining the normal paraffins by the described method is, as a rule, 1-2 relative % and the results of the determination are in good agreement with the data of determination by the urea method.

The results of the analysis of kerosene-gasoil fraction samples and of the products of their denormalization on zeolite are shown in Table 2. The deviation between parallel determinations is 1-2% and, in the case of low concentrations of the normal paraffins, they reach 4 relative %.

The experiment carried out using the described method shows its simplicity and that it is possible to analyze small samples of the product and simultaneously analyze a large number of samples.

As has already been pointed out, the time necessary for the adsorption of the normal paraffin hydrocarbons at room temperature is equal to 24 h.

The duration of the analysis can be decreased markedly if the picnometers with the zeolite and with the sample being analyzed are set in an ultrasonic field; in this case the adsorption time for the normal paraffins on the zeolite is decreased to 15-20 min.

#### LITERATURE CITED

1. E. S. Levchenko, *Novosti Neftyanoi i Gazovoi Tekhniki*, Ser.: Neftepererabotka i Neftekhimiya, No. 9 (1962).
2. L. N. Kvitkovskii and E. V. Grushetskaya, *Khimiya i Tekhnol. Topliv i Masel*, No. 3 (1962).
3. V. V. Veselov, *Khimiya i Tekhnol. Topliv i Masel*, No. 1 (1960).
4. L. P. Larcon and H. C. Becker, *Anal. Chemistry*, 32, No. 9 (1960), p. 1215.
5. Rennak et al., *J. Pract. Chem.*, 29, No. 3-6 (1965), p. 271.
6. Bacurova Emilia, *Ropa Uhlie*, No. 7 (6) (1965), p. 171-173.