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## Note

### Surface-layer sorbents for group analysis of aromatic hydrocarbons in petroleum distillates

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For the determination of aromatic content of petroleum distillates, having boiling points up to 220°, various schemes of analysis of gasoline group composition were used.

The separation of aromatic hydrocarbons is usually effected on columns with cyanoethylated stationary liquids<sup>1,2</sup> followed by chromatographic analysis of the individual separated aromatics<sup>3,4</sup>. The following methods have also been used to determine the total amount of aromatic hydrocarbons: liquid adsorption chromatography on silica gel, a variant of fluorescence indicator analysis<sup>5</sup>; adsorption on calcium zeolite 10X at 300–350° followed by removal of the aromatic hydrocarbons by programming the temperature to 400° (ref. 6–8) or by using different chemical methods<sup>9,10</sup>.

In the works cited<sup>1–8</sup> the research workers were faced with complicated chromatographic analyses of the group compositions of petroleum distillates containing aromatics, and in many cases only their total content is determined.

The present paper describes a method of gas adsorption analysis of aromatics based on their preliminary isolation by adsorption on silica gel and subsequent analysis on a surface-layer sorbent<sup>11,12</sup>. This method has been applied to the analysis of aromatic hydrocarbons having boiling points within the range 80–235°, and a separation of the aromatics into groups is made according to the number of carbon atoms in molecules.

Silica gel dust was used as a fine-grained adsorbent. It was impregnated with a 0.25% solution of sodium hydroxide in order to shorten the analysis time, decrease the analysis temperature and to make possible the group analysis of the aromatics.

## EXPERIMENTAL AND RESULTS

In a surface-layer sorbent the active agent (sorbent) is uniformly distributed over the exterior surface of a grain, and the sorptive processes do not take place throughout the grain but only in a shallow surface layer equal to the depth of the layer of the active adsorbent. This explains the high efficiency of surface-layer sorbents which is attained by decreasing the resistance to mass transfer and shortening the diffusion paths of compounds to be chromatographed (see, for instance, ref. 13).

In the present work, the adsorbent was prepared by coating Celite-545 (80–100 mesh) with silica gel dust by mechanical shaking for 10 h and subsequent removal of the excess of dust. The fine-grained particles of silica gel powder enter the macropores of the large porous carrier with a small specific surface area and are held in it by adhesive forces. As an active adsorbent we used silica gel developed by the All-Union research institute of petroleum refining especially for fluorescence indicator analysis. Characteristics of the silica gel used were as follows:

Bulk density, 0.64 g/ml.

Geometric structure: surface, 550–650 g/ml; pore volume, 0.5–0.7 ml/g; medium radius of pores, 14–23 Å.

In order to avoid the possible overlapping of paraffinic and naphthenic hydrocarbons, the straight gasoline cut (b.p. 45–220°) under investigation was subjected to separation on a liquid column with a fluorescent indicator to isolate the aromatics. The indicator used in this analysis permits a clear determination of the zones of not only the paraffinic naphthenic aromatics, but also of the olefinic hydrocarbons in the case of catalytic gasoline analysis in daylight (without a UV light source).

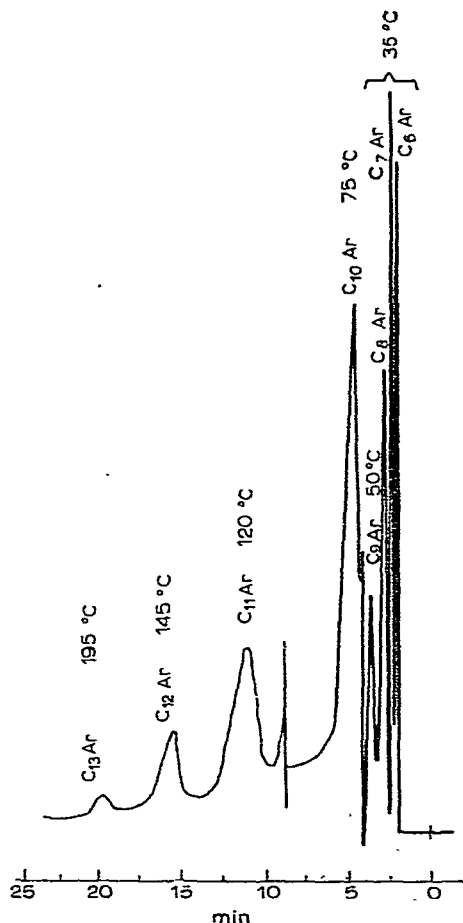


Fig. 1. Chromatogram of a concentrate of  $C_6$ – $C_{13}$  aromatic hydrocarbons.

The analysis of the C<sub>6</sub>-C<sub>13</sub> aromatic hydrocarbon concentrate showed that, owing to a substantial decrease in the catalytic activity of the silica gel as a result of alkaline treatment the temperature of separation of the aromatics of a given mass decreased below their boiling points by an average of 50°. Thus benzene, toluene and C<sub>8</sub> aromatics were eluted at 35°; increasing the separation temperature to 50° led to the separation of C<sub>9</sub> hydrocarbons, and C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub> and C<sub>13</sub> aromatics were separated when the temperature was increased further to 195° at the rate of 8°/min. The separation temperature of C<sub>13</sub> aromatics having boiling points of ca. 235° was 195° (Fig. 1).

The analysis was carried out on a serial TSVET-100 chromatograph equipped with a flame ionization detector. The column was a stainless steel tube (1.00 m × 3 mm) filled with silica gel dust impregnated with a 0.25% solution of NaOH on Celite-545 (80-100 mesh) (20% of carrier weight). The carrier gas (nitrogen) flow-rate was 25 ml/min, and the total elution time was 20-25 min. Quantitation of a chromatogram as shown in Fig. 1 was carried out by using the coefficients obtained in the analysis of artificial mixtures of aromatics under similar conditions.

The method described has permitted the determination of the group distribution of aromatics in a straight run petroleum distillate boiling within the range 45-220°.

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