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On the Chromatographic Separation of Aromatic Hydrocarbons from Their Mixture with Organo-Sulfur Compounds

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Numerous attempts to isolate from sulfurous petroleum and from petroleum products obtained from it aromatic hydrocarbons not containing organo-sulfur compounds, with the aid of such adsorbents as silica gel and alumina, have not been successful ([1]-[3]). It therefore seems useful to report some results of the studies we have carried out.

In order to clarify the conditions for the chromatographic separation of aromatic hydrocarbons from their mixture with organo-sulfur compounds that are present in ligroin-kerosene distillates, i.e., in relatively high-boiling petroleum fractions, we tested a number of adsorbents produced by domestic industry—silica gels, aluminum oxide, and activated carbons. The tests were carried out with artificial mixtures. To evaluate the adsorbing capacity of the adsorbents taken by us, the method of frontal chromatography was chosen. Adsorption was carried out from solutions of the substances being tested in technical isooctane in glass columns 50 cm high and 1 cm in diameter, and from the magnitude of the retained volume the value of the specific adsorption was determined (Table 1).

From consideration of Table 1 it follows that typical polar adsorbents (silica gels), nonpolar adsorbents (carbons), and aluminum oxide, which occupies an intermediate position, were subjected to testing. The values given

Table 1

Specific adsorption of certain aromatic hydrocarbons and organo-sulfur compounds from their solutions in technical isooctane (in mM/g)*

Fig. 1. Possible scheme for chromatographic separation of a mixture of aromatic hydrocarbons and organosulfur compounds

Figure 1: Fig. 1. Possible scheme for chromatographic separation of a mixture of aromatic hydrocarbons and organosulfur compounds

Adsorbents	*n*-Butylbenzene (a)**	Naphthalene (b)	α-Methylnaphthalene (c)	Di-*n*-butyl sulfide (A)	Di-*n*-nonyl sulfide (B)	*n*-Propylphenyl sulfide (C)	Di-*n*-butyl disulfide (D)	Benzyl mercaptan (D)
Silica gels:								
	0.21	0.49	0.49	0.35	0.10	0.49	0.29	0.99
	–	0.44	0.64	0.56	–	–	0.50	0.98
	0.66	0.24	0.86	0.90	0.52	1.08	0.63	1.46
Aluminum oxide for chromatography	0.09	0.09	0.18	0.08	0.03	0.05	0.14	0.20
Carbons:								
	0.44	0.46	0.35	0.18	0.06	0.44	0.20	0.88
	–	0.74	1.23	1.67	0.44	1.38	1.02	1.54

* In all cases the initial concentration of the solutions was 300 mM/l.
** a–c and A–D correspond to the letters in Fig. 1.

in the table, the values of specific adsorption vary over wide limits and depend on the nature both of the adsorbents and of the substances adsorbed; moreover, in a number of cases the specific adsorption of aromatic hydrocarbons differs considerably from the specific adsorption of organosulfur compounds.

Fig. 1. Possible scheme for chromatographic separation of a mixture of aromatic hydrocarbons and organosulfur compounds:
a —*n*-butylbenzene, —naphthalene, —methylnaphthalene, **A** —di-*n*-butyl sulfide, —di-*n*-nonyl sulfide, —*n*-propylphenyl sulfide, —di-*n*-butyl disulfide, —benzyl mercaptan, —silica gel of the ShSM grade, —silica gel of the ASM grade, —activated carbon of the AR grade, $\mathbf{Al_2O_3}$ —alumina "for chromatography" ; 1-14 —numbers of the filtrates.

As an example, let us consider the chromatographic separation of a complex mixture consisting of aromatic hydrocarbons and organosulfur compounds for the case in which the adsorption isotherms do not intersect and there is no mutual influence of the components of the mixture. In the case under consideration, the values of specific adsorption given in Table 1 unambiguously characterize the order of emergence of the components of the chromatographed mixture, and also indicate, approximately, the possible completeness of the separation. By using different adsorbents and carrying out repeated chromatography in succession, complete separation of the chromatographed mixture can be achieved. One variant of a possible scheme of such chromatography is shown in Fig. 1.

An experimental check of one variant of the chromatographic separation scheme shown in Fig. 1 was carried out by us using an artificial mixture consisting of *n*-butylbenzene, naphthalene, α-methylnaphthalene, di-*n*-butyl sulfide, di-*n*-nonyl sulfide, isohexylphenyl sulfide*, di*-n-*butyl disulfide, and benzyl mercaptan, dissolved in technical isooctane. The concentration of each component of the mixture was 300 mM/l. This mixture, in an amount of 20 ml, was applied to silica gel of the ShSM grade, with which a glass column 1 m high and 10 mm in diameter had been filled. After washing the adsorbed substances with a mixture of isooctane and acetone taken in a volume ratio of 15 : 1, three chromatographic filtrates—Nos. 1, 2, and 3—were obtained. Filtrate No. 4, containing benzyl mercaptan, was obtained as a result of washing it with pure acetone. Filtrate No. 1 was applied to activated carbon of the AR grade, with which a glass column analogous to that indicated above had been filled. After washing with isooctane, two filtrates were obtained: No. 5, containing* n-*butylbenzene, and No. 6, containing di*-n*-nonyl sulfide. Filtrates Nos. 2 and 3 were chromatographed on silica gel of the ASM grade, as a result of which filtrates Nos. 7, 8, 9, and 10 were obtained. Filtrates Nos. 7 and 10 were chromatographed, respectively, on AR carbon and alumina of the grade "for chromatography." In this process filtrates Nos. 5, 11, 12, and 13 were obtained. The latter was then chromatographed on AR carbon, as a result of which filtrate No. 14 was obtained, containing isohexylphenyl sulfide in admixture with α-methylnaphthalene. The results of the chromatography are summarized in Table 2, consideration of which indi— testifies to insufficiently complete chromatographic separation of the mixture we took. The comparatively small yields of the isolated components of the mixture are explained by the consumption of substance for analysis in the course of monitoring the chromatographic filtrates. Only *n*-butyl-

Table 2

Results of chromatography of an artificial eight-component mixture of aromatic hydrocarbons and organosulfur compounds

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* It was established by special experiments that the values of specific adsorption of isohexylphenyl sulfide and *n*-propylphenyl sulfide on the adsorbents tested were practically identical.

Chromatographed mixtures	Adsorbent grades	No.	Composition	Yield as % of content in the initial mixture
Initial mixture	ShSM	1	–	–
Initial mixture	ShSM	2	–	–
Initial mixture	ShSM	3	–	–
Filtrate No. 1	AR	4	benzyl mercaptan	72
Filtrate No. 1	AR	5	*n*-butylbenzene	35
Filtrate No. 1	AR	6	di-*n*-nonyl sulfide	48
Filtrate No. 2	ASM	7	–	–
Filtrate No. 2	ASM	8	di-*n*-butyl sulfide	21
Filtrate No. 3	ASM	9	mixture of naphthalene with di-*n*-butyl sulfide	81 (disulfide)
Filtrate No. 3	ASM	10	–	–
Filtrate No. 7	AR	5	*n*-butylbenzene	60
Filtrate No. 7	AR	11	di-*n*-butyl disulfide	traces
Filtrate No. 10	Al_2O_3	12	mixture of α-methylnaphthalene with di-*n*-butyl disulfide	–
Filtrate No. 10	Al_2O_3	13	–	–
Filtrate No. 13	AR	8	di-*n*-butyl sulfide	24

Filtrate No. 13	AR	14	mixture of α-methylnaphthalene with isohexylphenyl sulfide	—

benzene, benzyl mercaptan, di-*n*-butyl sulfide, and di-*n*-nonyl sulfide were isolated in pure form; α-methylnaphthalene, naphthalene, isohexylphenyl sulfide, and also di-*n*-butyl disulfide were not isolated in pure form, as had been assumed according to the scheme shown in Fig. 1. The discrepancy between the scheme and the final experimental results can be explained by intersecting adsorption isotherms and, possibly, by the mutual influence of the components being separated. It must be assumed that, in order to solve the problem of separating a mixture of aromatic hydrocarbons and organosulfur compounds, it is necessary to carry out studies on the adsorption isotherms of as large a number as possible of the compounds mentioned.

The isolation of *n*-butylbenzene from its mixture with di-*n*-butyl sulfide, di-*n*-butyl disulfide, and benzyl mercaptan was achieved by us by chromatography under analogous conditions on silica gel of the ASM grade. Displacement was carried out with a solution of acetone in technical isooctane (1 : 15 by volume).

The chromatogram shown in Fig. 2 convincingly demonstrates that *n*-butylbenzene can be well isolated chromatographically from its mixture with di-*n*-butyl sulfide, di-*n*-butyl disulfide, and benzyl mercaptan, and also, it must be assumed, from analogous mixtures of organosulfur compounds. In those filtrates that contained *n*-butylbenzene, no organosulfur compounds were detected; and, conversely, in filtrates containing total sulfur, *n*-butylbenzene was absent.

As in the preceding experiment, we see that the magnitude of the specific adsorption obtained under definite conditions does not always unambiguously characterize the degree of separability of the substances chromatographed, nor the order of their elution, and that a mutual influence of the adsorbed substances takes place. Thus, for example, on the basis of the magnitude of the specific adsorption on ASM silica gel, it could have been expected that *n*-butylbenzene would be difficult to separate from di-*n*-butyl disulfide. However, experiment shows that *n*-butylbenzene is eluted in pure form and that di-*n*-butyl disulfide is eluted after the emergence of *n*-butylbenzene.

Under conditions analogous to those in which the experiments with artificial mixtures were carried out, chromatography was performed on a mixture of aromatic hydrocarbons and organosulfur compounds isolated from the 194–214° fraction of Tuymazy crude oil by chromatographic means (Fig. 3). From consideration of the curves it follows that a considerable part of the aromatic hydrocarbons is separated without admixture of organosulfur

Fig. 2. Chromatogram of an artificial mixture of *n*-butylbenzene and organosulfur compounds on silica gel ASM: 1 —*n*-butylbenzene, 2 —*n*-dibutyl disulfide, 3 —*n*-butyl sulfide, 4 —mixture of sulfide with mercaptan, 5 —benzyl mercaptan

Figure 2: Fig. 2. Chromatogram of an artificial mixture of *n*-butylbenzene and organosulfur compounds on silica gel ASM: 1 —*n*-butylbenzene, 2 —*n*-dibutyl disulfide, 3 —*n*-butyl sulfide, 4 —mixture of sulfide with mercaptan, 5 —benzyl mercaptan

Fig. 3. Chromatogram of a mixture of aromatic hydrocarbons and organosulfur compounds isolated from the 194–214° fraction of Tuymazy crude oil. Adsorbent —silica gel ASM. 1 —n_D^{20}, 2 —total sulfur

Figure 3: Fig. 3. Chromatogram of a mixture of aromatic hydrocarbons and organosulfur compounds isolated from the 194–214° fraction of Tuymazy crude oil. Adsorbent —silica gel ASM. 1 —n_D^{20}, 2 —total sulfur

compounds. It should be noted that in those filtrates for which the refractive index was equal to 1.4048, organosulfur compounds were absent, and the formalite reaction was positive, which indicated the separation of aromatic hydrocarbons without admixture of organosulfur compounds.

Fig. 2. Chromatogram of an artificial mixture of *n*-butylbenzene and organosulfur compounds on silica gel ASM: 1 —*n*-butylbenzene, 2 —*n*-dibutyl disulfide, 3 —*n*-butyl sulfide, 4 —mixture of sulfide with mercaptan, 5 —benzyl mercaptan

Fig. 3. Chromatogram of a mixture of aromatic hydrocarbons and organosulfur compounds isolated from the 194–214° fraction of Tuymazy crude oil. Adsorbent —silica gel ASM.
1 —n_D^{20}, 2 —total sulfur

The results of chromatographing both artificial mixtures and the narrow fraction isolated from sulfurous crude oil indicate the fundamental possibility of chromatographic separation of mixtures of aromatic hydrocarbons and organosulfur compounds, as well as the need for further systematic study of this question.

Laboratory assistant G. P. Gribkova took part in the experimental part of the work.

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Note: Figure translations are in progress. See original paper for figures.