

Thus, we see that changes in acidity, existent gum content, and mercaptan sulfur content during 5-year storage and in accelerated aging are essentially the same, and are within the limits of error of the method that has been developed. These experimental batches of fuel were also tested by the proposed accelerated aging method after 5 years of storage. In the accelerated test on the samples of fuels I and II from storage, the acidity increased by 0.1 mg KOH/100 ml, i.e., somewhat more than was observed for these batches at the time they were put into storage; in the case of fuel sample III, the acidity number increase was 0.02 mg KOH/100 ml. Despite the slightly greater change in acidity upon accelerated oxidation of fuel samples I and II after 5-year storage, tests in the DTS unit indicated that the thermal stability of these batches remained at a high level (see Table 2).

The results obtained in the accelerated oxidation of jet fuels of different grades under conditions appropriate to the particular grade of fuel (Table 3) demonstrate the feasibility of rating differences in stability of heavy-kerosine type fuels (T-6 and T-8), either without additives or with Ionol or NG-140 antioxidant; the test can also be used to rate DS and DL diesel fuels. In these tests, the quality indices of the diesel fuels changed within the same limits as were observed during 5-year storage in large tanks. These results justify the use of this test method for the heavier distillate fuels.

Fuel samples with lower chemical stability are also lower in thermal stability as determined in the DTS test unit. The accelerated aging method makes it possible, within the course of one week, to obtain data on fuel quality changes that can be obtained in normal storage in large tanks only after a period of 5 years; this means that the time required for the investigation is reduced by approximately 99.5%. This gives a considerable saving in cost of carrying out the studies, and makes it possible to increase the accuracy with which limits of quality change are established, since the analyses before and after aging are performed as parallel determinations.

SEPARATION OF PETROLEUM CUTS AND LUBE OILS WITH DETERGENT ADDITIVES BY MEANS OF TWO-STAGE CONTINUOUS LIQUID CHROMATOGRAPHY

V. A. Zakupra, V. A. Kozak,
N. I. Vykhrestyuk, and D. A. Tkachenko

UDC 543.544:621.892

The application of two-stage continuous liquid chromatography (TCLC) on various adsorbents [1] had made it possible to separate petroleum oils into hydrocarbon groups more sharply than can be done by the use of the GOST 11244-76 method.

Here, we are reporting results from an application of the TCLC technique to the separation of certain relatively low-boiling petroleum cuts and lube oils with detergent additives. The effective separation of petroleum fractions with initial boiling points of 200°C or higher has been achieved principally by the use of an improved eluate vaporizer between the chromatographic stages; in the case of lube oils with detergent additives, this better separation has been achieved by proper selection of the chromatographic conditions. Also, in the example of separation of paraffinic/naphthenic groups of hydrocarbons in a petroleum cut, we have demonstrated the feasibility of using a column with supported urea in the second chromatographic stage.

In separating these petroleum cuts, we have used glass columns in the first and second stages [1]. The eluate between stages is concentrated in two vaporizers (Fig. 1) with a condensation and reflux zone, so that losses of the hydrocarbons being separated through vaporization and carryover by the solvents may be minimized. The operating conditions of the vaporizers are as follows: cooling water temperature in condensation zone 15°C; inert gas (nitrogen) feed rate to vaporizer about 120 ml/min; inert gas temperature at vaporizer inlet 18°C; rate of drop formation on upper dropping tip of vaporizer 3-4 drops/min, and on lower dropping tip about 1 drop/min; other conditions same as described in [1].

All-Union Scientific-Research and Design Institute of the Petroleum Refining and Petrochemical Industry (VNIPKneftekhim). Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 11, pp. 53-56, November, 1979.

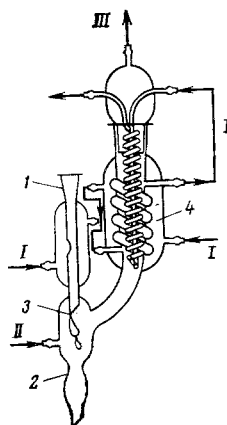


Fig. 1. Diagram of eluate vaporizer: 1, 2) connections to first and second stage columns, respectively; 3) lower dropping tip (for concentrate); 4) condensation and reflux head; I) water; II) inert gas; III) solvent vapor.

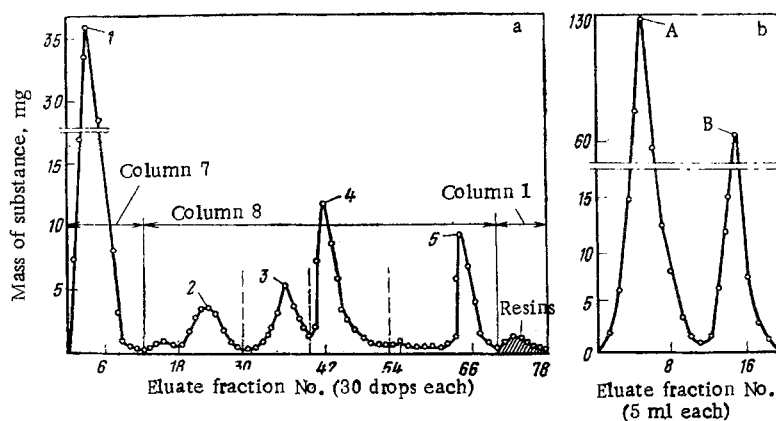


Fig. 2. Liquid chromatograms: a) TLC separation of 230-340°C cut from Stavropol' crude; b) urea-column separation of the group (peaks 1 and 2) of recovered paraffinic/naphthenic hydrocarbons. Vertical dashed lines indicate the regions for collection of hydrocarbons (peaks); peak A represents isoparaffins and naphthenes, peak B n-paraffins.

A typical liquid chromatogram for the separation of a 230-240°C cut from Stavropol' crude is shown in Fig. 2a. Results from a calculation of the yields of hydrocarbon groups recovered, based on this chromatogram and on a chromatogram for the separation of a 200-280°C cut from crudes produced in the Dnepr-Donetsk Basin, are summarized in Table 1. As can be seen from the chromatogram, the material is separated cleanly into five hydrocarbon fractions and a resinous part; also, the repeatability of results in parallel experiments is good, and the chromatographic losses are relatively low (see Table 1).

TABLE 1. Results from TLC Separation of Various Petroleum Products (all results referred to initial sample)

Sample	Mass of original sample, g	Yield of hydrocarbon fractions recovered, * mass %						Chromatographic losses, mass %
		paraffinic/naphthenic		aromatic			resinous part	
		fraction 1	fraction 2	fraction 3	fraction 4	fraction 5		
200-280°C from Dnepr-Donetsk Basic crude	0,5484	73,0	1,5	8,2	10,6	5,2	0,3	1,2
	0,5477	68,7	2,5	6,5	10,9	3,3	0,4	7,7
	0,5621	73,5	0,9	6,6	9,6	4,7	0,2	4,5
Average	—	71,8 (75,1)	1,6 (1,7)	7,1 (7,4)	10,4 (10,9)	4,4 (4,6)	0,3 (0,3)	4,4 (0,0)
230-340°C from Stavropol' crude	0,5987	71,6	4,7	3,6	8,7	3,8	2,0	5,6
	0,5532	77,0	4,7	4,0	8,5	3,9	1,4	0,5
	0,5465	73,0	4,5	4,3	9,4	3,8	2,1	2,9
Average	—	74,0 (76,3)	4,6 (4,8)	3,9 (4,0)	8,9 (9,2)	3,8 (3,9)	1,8 (1,8)	3,0 (0,0)
Blend of AVS-5 oil and MASK additive concentrate (11%)†	0,2432	48,1	1,6	22,8	9,8	5,7	5,9	6,1
	0,2427	53,1	1,7	23,1	9,8	3,5	4,5	4,3
	0,2482	53,9	0,8	23,7	9,7	4,3	4,7	2,9
Average	—	53,7 (54,0)	1,4 (1,4)	23,2 (24,4)	9,8 (10,3)	4,5 (4,7)	5,0 (5,2)	4,4 (0,0)

* Values in parentheses include chromatographic losses, distributed in proportion to the yields of the hydrocarbon fractions and resinous part.

† Composition of MASK additive concentrate, determined in accordance with procedure given in [5], is as follows (in mass %): calcium alkylsalicylate 22.4 and 21.4; alkylphenols and alkylphenol ethers 27.3 and 27.9; mineral oil 39.2 and 38.4; loss in separation (including calcium carbonate, calcium hydroxide, and solid contaminants) 11.3 and 12.3.

TABLE 2. Results from Mass Spectrometric Determination* of Structural-Group Composition of Hydrocarbon Fractions Recovered in TLC Separation of Petroleum Cuts

Material	Sequence No. of fract. recovered (peak on liquid chromatogram)	Content of hydrocarbon structures, mass % relative to original sample												total
		paraffinic	naphthenic				alkylbenzenes	indans (or tetralins)	dinaphtheno-benzenes	naphthalenes	acenaphthenes	fluorenes	phenanthrenes	
			monocyclic	bicyclic	tricyclic	tetracyclic								
200-280°C cut from Dnepr-Donetsk Basin crude	1	40,4	15,6	12,1	5,3	1,7	0,0	—	—	—	—	—	—	75,1
	2†	—	—	—	—	—	—	—	—	—	—	—	—	1,7
	3	—	—	—	—	—	4,8	1,8	0,5	0,1	0,0	0,0	0,2	7,4
	4	—	—	—	—	—	2,8	1,2	0,8	4,8	1,2	0,0	0,1	10,9
	5‡	—	—	—	—	—	—	—	—	—	—	—	—	4,6
230-240°C cut from Stavropol' crude	1	40,3	19,6	9,1	4,2	3,1	0,0	—	—	—	—	—	—	76,3
	2	2,2	1,1	0,5	0,4	0,4	0,2	—	—	—	—	—	—	4,8
	3	—	—	—	—	—	2,0	1,1	0,7	0,2	0,0	0,0	<0,1	4,0
	4	—	—	—	—	—	0,7	0,6	1,2	3,5	1,4	0,8	1,0	9,2
	5‡	—	—	—	—	—	—	—	—	—	—	—	—	3,9

* Conditions for taking mass spectra in MX-1303 instrument and procedures used in calculating mass spectra have been described in [1].

† Fractions contain mainly isoparaffinic and naphthenic hydrocarbons and a very small amount of aromatic hydrocarbons; the latter were not investigated in detail because of the low content.

‡ Fraction did not vaporize completely in the ion source of the mass spectrometer; material consists mainly of heterocyclic polycyclic aromatic compounds.

On the basis of the data of Table 2 and the curves for molecular mass distribution of the alkylbenzene and naphthalene structures (these curves are not given here), we may conclude that the TLC technique will give a rather clean separation of aromatic hydrocarbons according to the indicated structural types, and also a better differentiation according to molecular mass. In the groups of paraffinic/naphthenic hydrocarbons that were recovered (see Table 2, fraction 2), the content of aromatic (alkylbenzene) structures is very small, and hence the mass spectrometric determinations of paraffinic, isoparaffinic, and naphthenic structures in these groups are fully reliable.

TABLE 3. Results from Liquid Chromatographic Separation, in Column with Urea, of 230–340°C Cut from Stavropol' Crude and Paraffinic/Naphthenic Hydrocarbons Recovered from This Cut by Means of TLC

Sample	Mass of original sample, g	Yield of hydrocarbon groups recovered, mass % relative to 230–340°C cut*		Chromatographic loss, mass % relative to amount of sample fed to urea column
		n-paraffins	isoparaffins and naphthenes†	
Group of paraffinic/naphthenic hydrocarbons (peaks 1 and 2 in Fig. 2)	0,4288	(17,5) ‡	(63,1)	0,2
	0,4261	(18,9)	(63,3)	0,0
	0,3992	(16,7)	(63,0)	0,1
	Average	(27,7)	(63,1)	0,1
230–340°C cut	1,0011	17,0	82,5	0,5
	1,0128	19,0	80,9	0,1
	0,9985	16,5	82,8	0,7
	Average	17,5(17,6)	82,1(82,4)	0,4(0,0)

* I.e., on original samples weighing 0.5987, 0.5532, and 0.5465 g, respectively (see Table 1).

† The value shown for the 230–340°C in this cut includes the aromatic hydrocarbons and resinous part in addition to the isoparaffinic and naphthenes.

‡ The values in parentheses include the chromatographic loss, distributed in proportion to the yields of the hydrocarbon groups.

For a more detailed analysis of the paraffinic/naphthenic hydrocarbons, we carried out a liquid chromatographic separation of these materials in a column with urea, on a scale of separation corresponding to the mass of these materials recovered as a result of a single TLC separation. We introduced certain modifications into the procedure described in [3, 4], as required by the present purposes. The chromatography was carried out in a vertical glass column, 400 × 7 mm, with a thermostated jacket, pressure feed bottle, and a drawn-out lower end plugged with glass wool. The column was filled with a mixture (2 : 1 by mass) of finely pulverized dry urea and porcelain chips (0.2–0.3 mm) that had been pretreated with HCl, washed, and dried; the water temperature in the jacket was held at 25°C. The bed of adsorbent in the column was wetted with 20 ml of a mixture of anhydrous benzene with 5% anhydrous methanol; then a weighed sample of the hydrocarbons (dissolved in 15 ml of the indicated solvent mixture) was introduced, and was eluted with 60 ml of benzene, holding the temperature at 25°C during these operations (eluate collected in flask I). In order to decompose the adduct formed by the urea with the n-paraffins, the column bed was washed with 40 ml of benzene at a temperature of 80.1°C (this eluate was collected in flask II). After drying off the solvents, the material remaining in flask I consisted of isoparaffins and naphthenes, and the material remaining in flask II consisted of n-paraffins.

In the chromatographic separation in the urea column, whether operating on the paraffins and naphthenes recovered by the TLC method or on the original 230–340°C petroleum cut from Stavropol' crude, highly reproducible results and good agreement of results were obtained, and the chromatographic losses were small (Table 3). An analysis of the groups of n-paraffins (see Fig. 2b) by means of gas-liquid chromatography (Fig. 3) confirms the sharpness of separation of n-paraffins from branched-chain and naphthenic hydrocarbons in the urea column. These results show that, in order to improve the separation of paraffinic/naphthenic hydrocarbons from petroleum cuts with initial boiling points of 200°C or higher, a column with urea should be installed in the TLC system of columns in place of the usual second-stage column with ASM silica gel; the indicated hydrocarbons (total of fractions 1 and 2, see Table 1) pass into the urea column after complete removal of solvents.

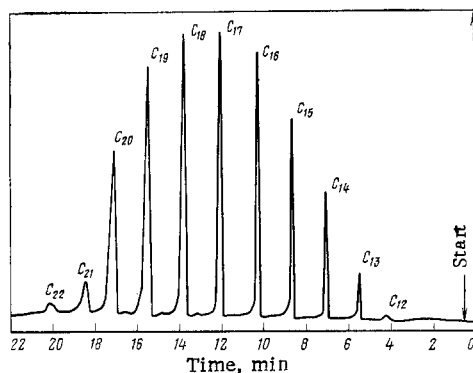


Fig. 3. Gas-liquid chromatogram for separation of n-paraffin group (peak B in Fig. 2) recovered by liquid chromatography (urea column) of paraffinic/naphthenic hydrocarbons from 230-340°C cut of Stavropol' crude. Conditions of chromatography: capillary column 5000 × 0.25 mm with Apiezon L; flame ionization detector; carrier gas hydrogen; column temperature programmed from 150 to 350°C at a heating rate of 6°C/min; sample volume 1 μ liter.

For the separation of the ASV-5 oil with the sulfonate additive S-150, as reported in [6], the first-stage column in the TLC (column 1) was packed with Grade ASK silica gel containing 30-40% water; this packing was chosen so as to give breakdown of the colloidal system and separation of the hydrocarbon (oil) part from the sulfonate. For separation of this same oil with the alkylsalicylate additive MASK, column 1 was packed with ASK silica gel in a two-section bed (one section of activated gel and another of gel containing 30% water), giving the same effect with this additive, i.e., separation of the oil part from the alkylsalicylate [5].

The results obtained in the TLC separation of the ASV-5 oil with the MASK additive are listed in Table 1. The conditions of separation were the same as in [1], with the following exception: Column 1 was packed with activated ASK silica gel to a height of 380 mm, and then with an additional 120 mm of the same fraction of ASK silica gel containing 30% water; the combined (total) bed of silica gel in column 1 was wetted with 6 ml of n-hexane, after which the sample of oil (containing MASK additive), diluted with 0.5 ml of n-hexane, was fed to the column.

By a comparison of the results from separation of the ASV-5 oil (see Table 1 in [1]) and the blend of this oil with 11% of the MASK additive concentrate (see Table 1 in the present article), along with IR spectroscopic data, we can conclude that the calcium alkylsalicylate additive is concentrated almost entirely in the resinous compound fraction, and the alkylphenols and alkylphenol ethers are concentrated in fraction 5. The sulfonate part of the additive S-150 is concentrated in these same fractions.

From the results obtained in these studies, we find that it is possible to separate blends of detergent additives in oils, so as to obtain a concentrate of the "active" ingredient, and simultaneously to determine the contents of the principal groups of hydrocarbons in the oil; by means of this approach, comparative analyses can be made of monotypical additive oil formulations, or changes in their chemical composition during service may be determined.

LITERATURE CITED

1. V. A. Zakupra, V. A. Kozak, É. V. Kolosova, et al., *Khim. Tekhnol. Topl. Masel*, No. 3, 58-63 (1978).
2. GOST [All-Union State Standard] 11244-76; Petroleum; Method of Determination of Potential Contents of Distillate and Residual Lubricating Oils.
3. D. Stejaru and Popescu, *Rev. Chem. (Romania)*, 20, No. 10, 629-632 (1969).
4. S. R. Sergienko, E. I. Talalaev, V. A. Zakupra, et al., *Izv. Akad. Nauk Turkm. SSR Ser. Fiz.-Tekh. Khim. Biol. Nauk*, No. 1, 46-50 (1973).
5. V. A. Zakupra, S. V. Timoshenko, Yu. T. Gordash, et al., *Khim. Tekhnol. Topl. Masel*, No. 5, 57-60 (1976).
6. V. A. Zakupra, S. V. Timoshenko, O. L. Glavati, et al., *Neftepererab. Neftekhim.*, No. 6, 34-36 (1975).