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GAS CHROMATOGRAPHIC DETERMINATION OF THE COMPOSITION OF UNFRACTIONATED NATURAL HYDROCARBON MIXTURES

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SUMMARY

Procedures developed for determining the fractional composition of crude oils and condensates and for defining the detailed light hydrocarbon content (C_1–C_9) in crude oils, stable condensates and organic matter of rocks and formation waters by multi-dimensional gas chromatography are described. Methods for the determination and prediction of logarithmic retention indices of light hydrocarbons (C_5–C_9) using two stationary phases, squalane and dinonyl phthalate, are proposed. For the first time, the results of the quantitative analysis of complex natural mixtures have been used to identify their components. Possibilities are indicated for improving the detail and reliability of data by means of a combination of quantitative analytical results obtained on capillary columns with the same stationary phase at two temperatures and on the capillary columns with various stationary phases. The rocks in which the organic matter content has been investigated by pyrolysis–gas chromatography were previously powdered only, then they were placed in a reactor and heated stepwise in an inert atmosphere.

INTRODUCTION

Nowadays the application of gas chromatography to the investigation of the composition of complex organic mixtures such as oils, condensates and organic matter in rocks and formation waters involves the use of systems that allow the necessary information to be obtained without any preliminary preparation of the samples[1–4]. The elimination of these labour-consuming and prolonged procedures such as preliminary distillation of complex natural hydrocarbon mixtures, dearomatization of their fractions, preliminary extraction of organic matter from rocks and formation waters and the concentration of extracts by evaporation improves the reliability of the data obtained and allows the necessary detailed information to be obtained using small sample volumes or weights of rock (microlitres, micrograms) with a 10-fold reduction in analysis times.

It is very difficult to employ the existing procedures, based on simulated distillation, for the determination of the fractional composition of crude oils and con-

densates containing components with high boiling points (above 450°C). This is due to the presence of heavy hydrocarbons (C_{37}–C_{40} and higher) and O + S + N compounds (resins, asphaltenes), which can be irreversibly sorbed in the injector of the chromatograph, on its connections and on the sorbent layer of analytical columns, adversely affecting their properties. Heavy components have high retention times, resulting in an increase in analysis times. The application of two-step systems with a pre-column to remove heavy hydrocarbons from the chromatographic system makes it easier to determine the contents of different fractions including the gasoline fractions of oils and condensates.

The second important problem concerns improvements in the methods for handling and interpreting chromatograms, which provide highly detailed and highly reliable information on the composition of complex natural hydrocarbon mixtures using chromatographic columns with relatively low efficiency. In this connection, it is important to be able to combine the quantitative analytical results obtained at various temperatures of capillary columns with the same stationary phase and on columns with different stationary phases in order to identify the components belonging to complex hydrocarbon mixtures and to increase the detail and reliability of the data obtained on their composition. The attraction of quantitative analytical results as an independent method for the identification improves the reliability of the results obtained by using Kováts retention indices.

In this paper a set of gas chromatographic procedures is proposed, including the following:

(1) rapid gas chromatographic determination of the yield of the gasoline and other fractions from oils and condensates;

(2) rapid determination of the detailed composition of wide-boiling gasoline fractions [from temperature of beginning of boiling (t.b.b.) to 152°C] of unfractionated oils and condensates;

(3) handling and interpretation of chromatograms based on using the results of the quantitative analysis of complex hydrocarbon mixtures;

(4) rapid pyrolysis–gas chromatographic technique for the investigation of organic matter;

(5) rapid determination of monoaromatic hydrocarbons in gases, condensates, oils and formation waters on the same equipment;

(6) rapid determination of micro-concentrations of hydrocarbons in organic solvents used as extractants.

DETERMINATION OF FRACTIONAL COMPOSITION OF OILS AND CONDENSATES

The procedure for determining the fractional composition of oils and condensates is based on the application of a two-step gas chromatographic system, the scheme of which is shown in Fig. 1. The use during the analysis of back-flushing of the pre-column 5, installed before the analytical column, allows the determination, under the conditions of simulated distillation, of the fractional composition of crude oils and condensates without the risk of contaminating the analytical column with high-boiling compounds. The system has been designed on the basis of a Chrom-42 chromatograph. The back-flushing device, with pre-column 5 and a six-way switching valve 2 as the main components, can be used with any gas chromatograph in which

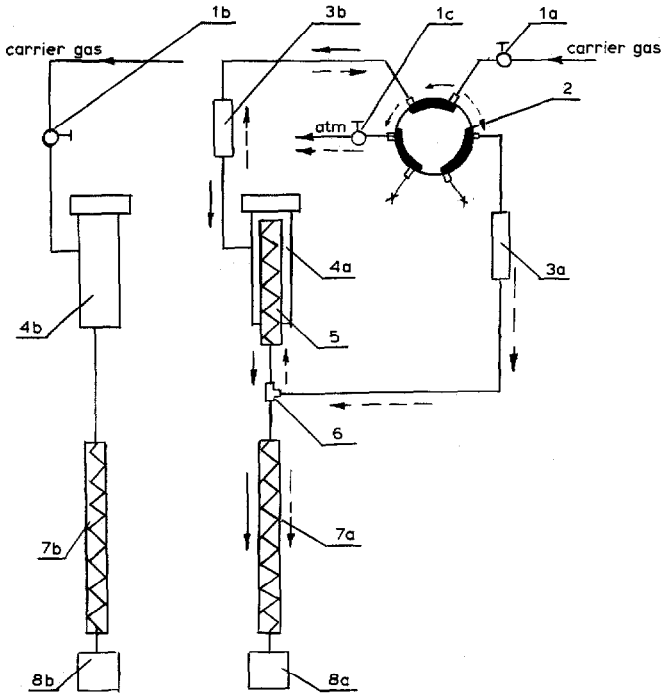


Fig. 1. Schematic diagram of gas chromatograph, 1a,b,c = needle valves; 2 = six-way valve; 3a,b = absorbers; 4a,b = injectors; 5 = pre-column; 6 = effluent splitter; 7a,b = analytical columns; 8a,b = flame ionization detectors.

the device for gas distribution and the oven of the analytical columns 7a and 7b are designed separately. The pre-column 5, packed with Chromaton N AW (grain size 0.20–0.25 mm) containing 18% of SE-30 silicone gum (length of sorbent layer 4.5 cm, diameter 0.3 cm), was installed in the injector 4a of the chromatograph and operated at 250°C. The use of a short pre-column was adopted for the following reasons: (1) small broadening of the chromatographic zones, which leads to an insignificant decrease in the separation efficiency of hydrocarbons and their fractions in the chromatographic system with the pre-column compared with the system without the pre-column; (2) low pre-column resistance to the carrier gas (helium) flow, leading to insignificant changes in its velocity through the column 7a during the revolution of the valve 2 by 60°. The connection of the pre-column with the valve 2, on back-flushing, is fulfilled by means of a chromatograph connection as used for carrier gas splitting when capillary columns are employed. Hence the mounting of the gas chromatographic system does not require any changes to the construction of common chromatographs. To eliminate the baseline drift connected with rapid temperature programming (20°C/min), the analyses of oils and condensates were carried out using a differential procedure on two identical packed columns (247 cm × 3 mm I.D.), work column 7a and reference column 7b, both connected to identical flame ionization detectors. Each column was filled with 5% SE-30 on Chromaton N AW (grain size 0.16–0.20 mm).

To eliminate memory effects, adsorbers 3a (activated carbon CKT, grain size, 0.4–0.6 mm) and 3b (silica gel) were incorporated in the chromatographic system.

The directions of the carrier gas flow are shown by solid arrows (straight-flushing) and by broken arrows (back-flushing).

Choosing the experimental conditions by means of the analysis of a C_6–C_{20} standard mixture, it was established that the following conditions are optimal; supplementary pressure at the inlet of the column in the reference line of the chromatograph, $P_{sup.1}^{str.} = 1.28 \cdot 10^5$ Pa; in the work line of the chromatograph, $P_{sup.2}^{str.} = 1.32 \cdot 10^5$ Pa; $P_{sup.2}^{back} = 1.34 \cdot 10^5$ Pa; volume velocities $V_{\alpha_1}^{str.}$ and $V_{\alpha_2}^{str.}$, measured at ambient temperature at the outlet of the reference and work columns, are equal to 26 ml/min and 28.6 ml/min, respectively; $V_{\alpha_2}^{back} = 25.8$ ml/min; volume velocity at the outlet from the needle valve 1c, $V_{\alpha_2}^{nv} = 3$ ml/min; time interval between sample injection and the revolution of the six-way valve, $\tau^{opt} = 25$ s; $t_{col_1}^{initial} = t_{col_2}^{initial} = 120°C$;

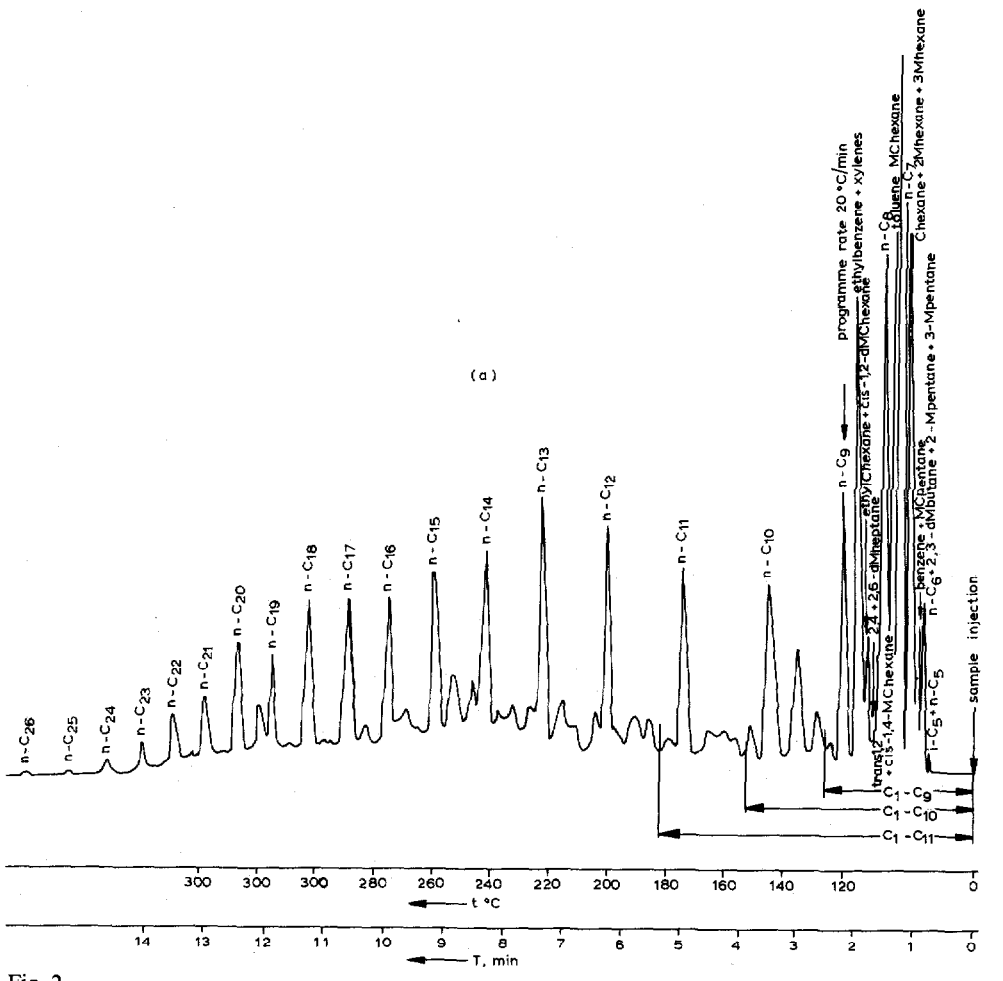


Fig. 2.

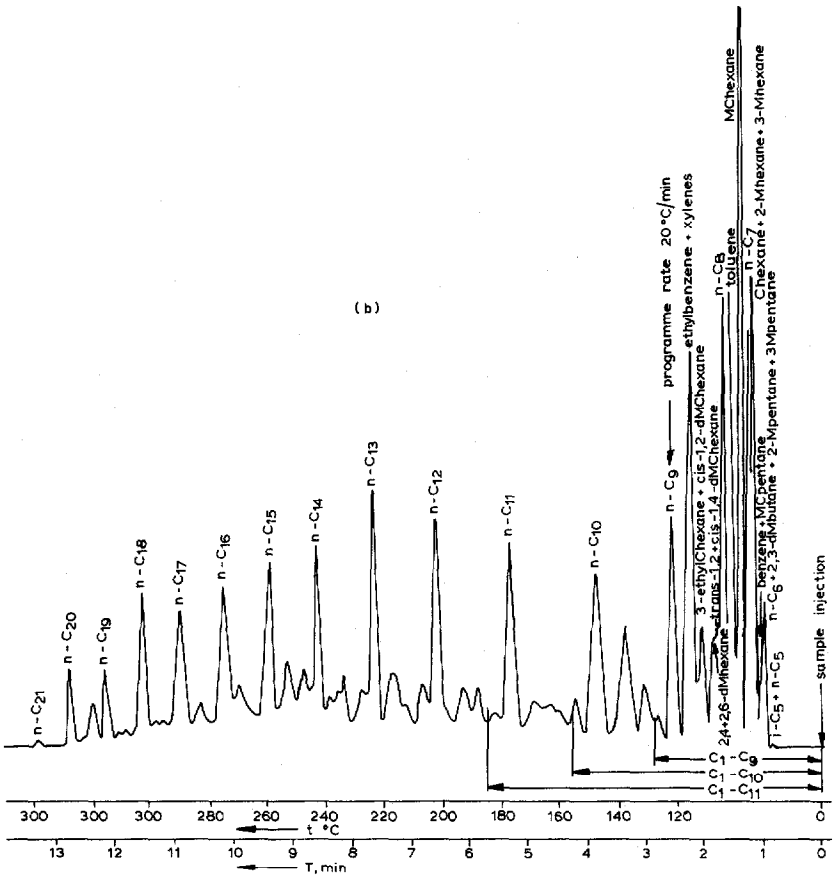


Fig. 2. Chromatogram of the condensate obtained under (a) straight-flushing conditions and (b) back-flushing conditions on a 247 cm × 3 mm I.D. packed column. (a) $t_{col.}^{initial} = 120°C$; $P_{sup.1}^{str.} = 1.27 \cdot 10^5$ Pa; $P_{sup.2}^{str.} = 1.32 \cdot 10^5$ Pa; $t_{inj.} = 250°C$; $t_{det.} = 240°C$. (b) $t_{col.}^{initial} = 120°C$; $P_{sup.1}^{str.} = 1.27 \cdot 10^5$ Pa; $P_{sup.2}^{str.} = 1.32 \cdot 10^5$ Pa; $P_{sup.2}^{back\text{-}flush} = 1.34 \cdot 10^5$ Pa; $V_{\alpha 1}^{str.} = 26.0$ ml/min; $V_{\alpha 2}^{str.} = 28.4$ ml/min; $V_{\alpha 2}^{back\text{-}flush} = 26.0$ ml/min; $V_{nv}^{back\text{-}flush} = 3$ ml/min; $t_{pre\text{-}col.} = 250°C$.

$t_{pre\text{-}col} = 250°C$; $t_{det} = 240°C$; $V_{H_2} = 30$ ml/min; $V_{air} = 400$ ml/min. Chromatography of the oils and condensates began under isothermal conditions, then at the moment of eluting the maximum of the n-C_9 peak linear temperature programming was begun at a rate of 20°C/min and continued to 300°C, after which isothermal conditions were maintained. The proximity of $V_{\alpha_1}^{str.}$ and $V_{\alpha_2}^{back}$ ensures baseline stability under the conditions of temperature programming. To speed up regeneration of the pre-column after the analysis was completed, the septum of injector was pricked with the needle of a medical syringe. It was established that analysis under the above conditions, when $\tau^{opt} = 25$ s, leads to distortion of the results for hydrocarbon content beginning only from n-C_{17} (n-heptadecane). This allows the determination of the yield of any fractions boiling up to the boiling-point of n-C_{17}.

Typical chromatograms of a condensate obtained under (a) straight-flushing conditions and (b) back-flushing conditions are shown in Fig. 2. The intervals of

recording the fractions C_1–C_9 (t.b.b.–152°C), C_1–C_{10} (t.b.b.–177°C) and C_1–C_{11} (t.b.b.–199°C) are illustrated. The yield of these fractions can be easily calculated by the internal standard method, taking into account the area measured by the integrator under the outlet curve corresponding to a particular fraction. It is advisable to use as an internal standard a mixture of C_{13}–C_{15} *n*-alkanes. The application of back-flushing results in compounds having the boiling points above 358°C (boiling point of *n*-C_{21}) not entering the analytical column, which allows heavy oils to be analysed. As can be seen from the chromatograms, using sample volumes of $q \leq 1$ μl for 13–16 min one can obtain not only quantitative data on the fractional composition of the samples, but also qualitative information on their groups and individual compositions, which is of importance for the choice of the optimal conditions for the further detailed analysis of oils and condensates by means of capillary gas chromatography and for their preliminary geological–geochemical comparison. In particular, the data on the fractional composition are used for the determination of the

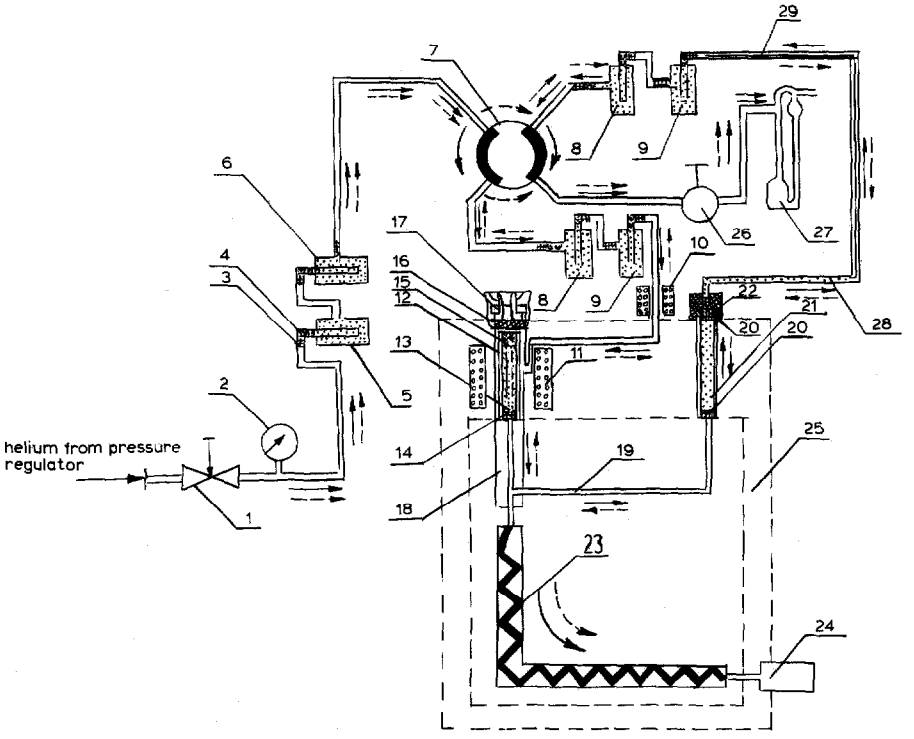


Fig. 3. Scheme of using the back-flushing system for the analysis of stable condensates and crude oils. 1 = Needle valve; 2 = manometer; 3, 14, 20 = copper nets; 4, 15 = glass wool; 5 = adsorber with $Mg(ClO_4)_2$ as a drier; 6 = adsorber with a drier (molecular sieve 5 Å of grain size 0.5–1.0 mm); 7 = four-way tap; 8 = adsorber with adsorbent (CKT activated carbon of grain size 0.4–0.6 mm); 9 = adsorber with adsorbent (molecular sieve 5 Å of grain size 0.5–1 mm); 10 = moving oven for heating communication tube; 11 = oven for injector heating; 12 = injector; 13 = inlet piece with sorbent (18% SE-30 on Chromaton N AW of grain size 0.20–0.25 mm); 16 = silicone-rubber septum; 17 = union nut; 18 = tube connecting the injector with capillary column; 19 = capillary for controlling the carrier gas stream to be released; 21 = 80 mm × 2 mm I.D. stainless-steel tube with solid support; 22 = vacuum rubber tube; 23 = capillary column; 24 = flame ionization detector; 25 = oven; 26 = needle valve; 27 = rheometer; 28 = CKT activated carbon layer of grain size 0.4–0.6 mm; 29 = copper wire.

contents of different components in the whole sample (condensate or oil) by means of capillary gas chromatography. The determination of the fractional composition of condensates and light oils can be carried out according to the technique described previously[5], *i.e.*, without using a pre-column and back-flushing of carrier gas. In this instance, the possibility exists of determining also the temperature of the end of boiling of the samples.

RAPID DETERMINATION OF DETAILED COMPOSITION OF WIDE-BOILING GASOLINE FRACTIONS (t.b.b.–152°C) OF UNFRACTIONATED OILS AND CONDENSATES

The procedure for the detailed determination of the composition of unfractionated oils and condensates, taking into account the peculiarities of their composition, is based on the use of a two-step gas chromatographic system (Fig. 3) with back-flushing of pre-column 13 installed before the 50 m × 0.22 mm I.D. open-tubular stainless-steel capillary column 23. The capillary column was dynamically coated using the well known procedure with 10% solutions of the stationary phase (squalane) in *n*-hexane. The system installed on the basis of the Chrom-41 chromatograph allows the fractionation of crude oils and stable condensates and does not require any changes to the construction of the gas chromatograph. The back-flushing device can be used with any gas chromatograph in which the system for gas distribution and the column oven are in different devices. The important feature of the back-flushing system is remote control of the carrier gas (helium) flows, achieved through the effluent splitter 19 by means of the four-way valve 7 installed together with the back-flushing device beyond the chromatograph. Design features of the injector 12 of the Chrom-4 and Chrom-5 series of chromatographs make it possible to employ the inlet piece 13, in this injector being a pre-column packed with Chromaton N AW (grain size 0.20–0.25 mm) containing 18% of SE-30. Using the short pre-column (3.7 cm × 3 mm I.D.) with a non-polar stationary phase allows, with a high splitting ratio (125:1–160:1), the efficiency of separation (80 000 theoretical plates) observed in experiments without back-flushing to be maintained and also the stability of the Kováts retention indices used for identification to be retained.

Under the conditions of straight-flushing (the direction of helium flow is shown by solid arrows) the carrier gas enters the pre-column 13 (t_{inj} = 190°C). On passing through the sorbent layer, helium enters tube 18, at the outlet of which its flow is branched. The lesser flow is directed to the capillary column 23 and the greater (97–99%) flow, which passes through the capillary (flow splitter) 19, the tube 21 packed with solid support [dried Celite 545 (60–80 mesh)], the tube (36 cm × 2 mm I.D.) the front portion (23.5 cm length) of which is packed with activated carbon CKT (grain size 0.4–0.6 mm) layer 28, adsorbers 8 and 9, used for elimination of the memory effect and packed with molecular sieve 5 Å (grain size 0.5–1.0 mm) and with activated carbon CKT (grain size 0.4–0.6 mm), the switching four-position valve (four-way stopcock) 7 and the needle valve 26, is released. The splitting ratio was regulated by the needle valve 26 and the flow velocity at its outlet was measured by the rheometer 27. After injection of the sample of crude oil or stable condensate (sample volume q = 0.2–0.5 μl), stopcock 7 is turned by 90° in 18–19 s and the system begins to operate under conditions of pre-column back-flushing (the direction of the flow of helium, used as a carrier gas, is shown by broken arrows). Under these

conditions, during the elution of hydrocarbons from the capillary column simultaneous regeneration of the pre-column sorbent occurs. Heavy hydrocarbons and other high-boiling compounds are back-flushed from the pre-column and enter the communication tube heated at 200°C by the moving oven 10, and then these compounds are irreversibly sorbed in adsorbers 8 and 9.

The experiments with standard mixtures allowed the selection of the optimal conditions for carrying out analysis, which were as follows: $t_{cap.col.}$ = 50 and 70°C; $t_{pre\text{-}col.}$ = 185–190°C, t_{det} = 55 and 75°C (flame ionization detector), P_{sup} = (2.48–2.55) · 10^5 Pa, linear velocity α = 26–29 cm/s, velocity (V_α^{nv}) of the carrier gas flow, released into the atmosphere and regulated with the needle valve 26 and measured at room temperature, is 60–160 ml/min, the optimum time interval, τ^{opt}, between sample injection and revolution of stopcock 7 is 18–20 s, V_{H_2} = 30 ml/min and V_{air} = 400 ml/min.

A detailed description of the arrangement and function of the different components, the choice of the experimental conditions and the analytical procedure are given elsewhere[1]. It should be noted that the analysis performed under the conditions when τ^{opt} = 18–20 s ensures entry of all hydrocarbons up to C_{11} into the capillary column, ensuring that their contents correspond to the initial composition of the samples. When analysing gasoline fractions (t.b.b.–152°C), the capillary column was regenerated ($t_{cap.col.}$ = 125°C, α = 45 cm/s) after *n*-C_9, being eluted for 35 min when the needle valve 26 is closed. Regeneration of the capillary column is necessary because some of the heavier hydrocarbons (sometimes up to C_{13}–C_{14}) together with C_1–C_9 hydrocarbons penetrate into the capillary column. The front portions of the chromatograms were obtained at $t_{cap.col.}$ = 30°C and τ^{opt} = 17 s to determine separately hydrocarbons 11, 12 and 13 (Figs. 4 and 5 and Table I).

Chromatograms of the gasoline fraction (C_1–C_9) of the unfractionated condensate No. 1 and oil, obtained under back-flushing conditions at 50 and 70°C, respectively, are illustrated in Figs. 4 and 5. As many as 196–198 saturated and aromatic hydrocarbons, the full list of which is given in ref. 6, were identified in the gasoline fractions (t.b.b.–152°C). Some of these compounds are also indicated in Table I and in ref. 1.

The light condensate No. 2, the gasoline fraction yield of which is 79.6 wt%, was chosen for the comparison of the analytical results obtained during back-flushing of the pre-column and according to the ordinary procedure. It allowed without any difficulty the chromatogram of the gasoline fraction to be obtained without recourse to back-flushing.

Good agreement between the quantitative results of the analysis of condensate No. 2 (Table I) and the identity of the chromatograms obtained as a result of using the various analytical procedures confirm the reliability of the proposed technique. The data on the content of some hydrocarbons chosen at random are compared in Table I. These data were obtained by means of a combination of the quantitative analytical results measured at two operating temperatures (50 and 70°C) using an IT-1 digital integrator in two series of experiments, *i.e.*, without back-flushing[6] and with back-flushing.

The procedure developed offers new possibilities for increasing the overall speed of analysis up to 10-fold in comparison with earlier procedures, as a result of eliminating the stage involving the preliminary fractionation of oils and condensates,

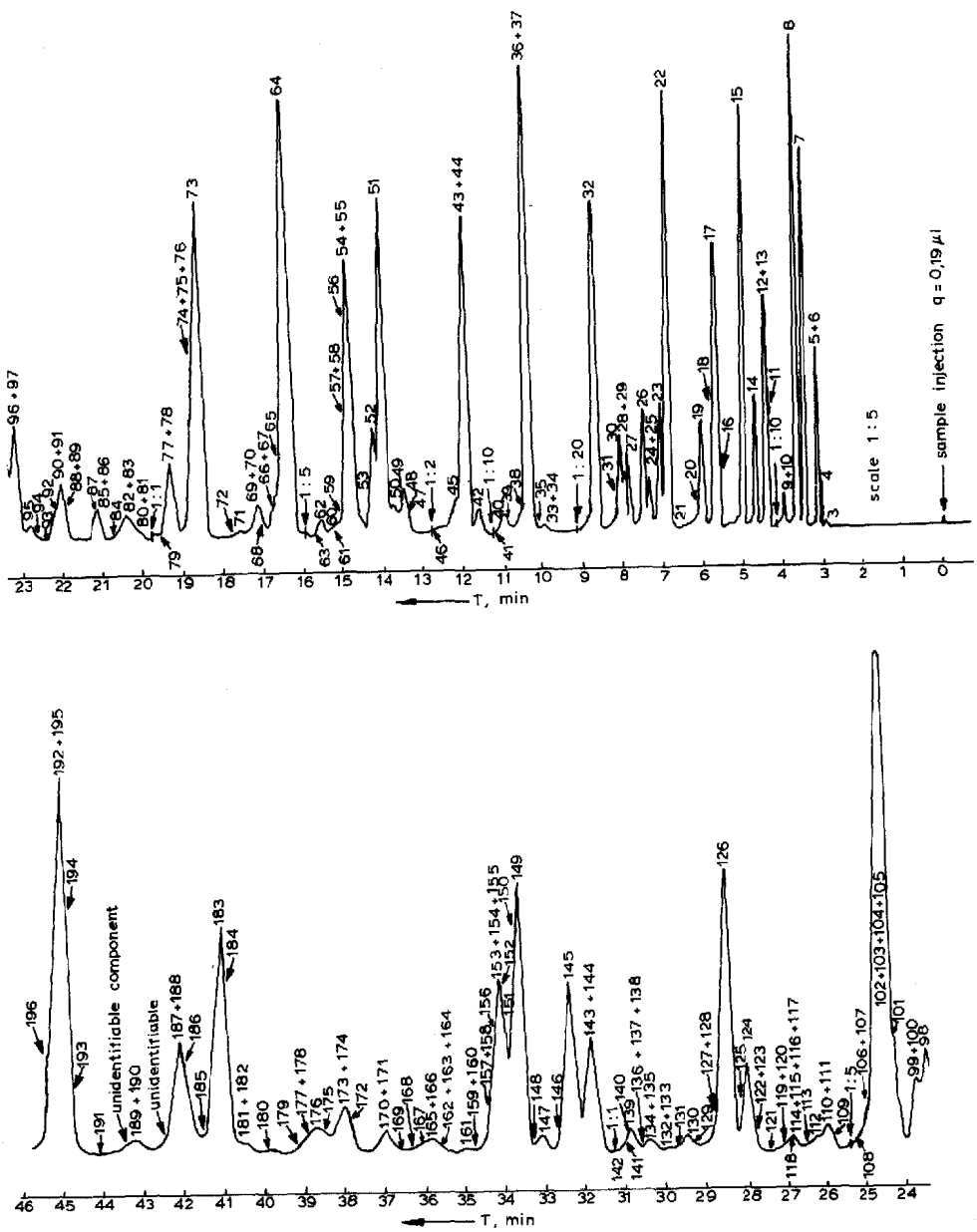


Fig. 4. Chromatogram of gasoline fraction of unfractionated condensate No. 1 obtained under back-flushing conditions at $t_{cap.col.}$ = 50°C (squalane stationary phase), $P_{sup.}$ = 2.53 · 10^5 Pa, α = 28.3 cm/s, V_a^{av} = 120 ml/min, t_{inj} = 190°C, $\tau^{opt.}$ = 19 s.

of applying relatively short capillary columns and of reducing the duration of their regeneration. In turn, the elimination of the entry of high-boiling hydrocarbons into the capillary column and of contaminating it with non-volatile materials and, as a consequence, the reduction of the duration of capillary column regeneration at ele-

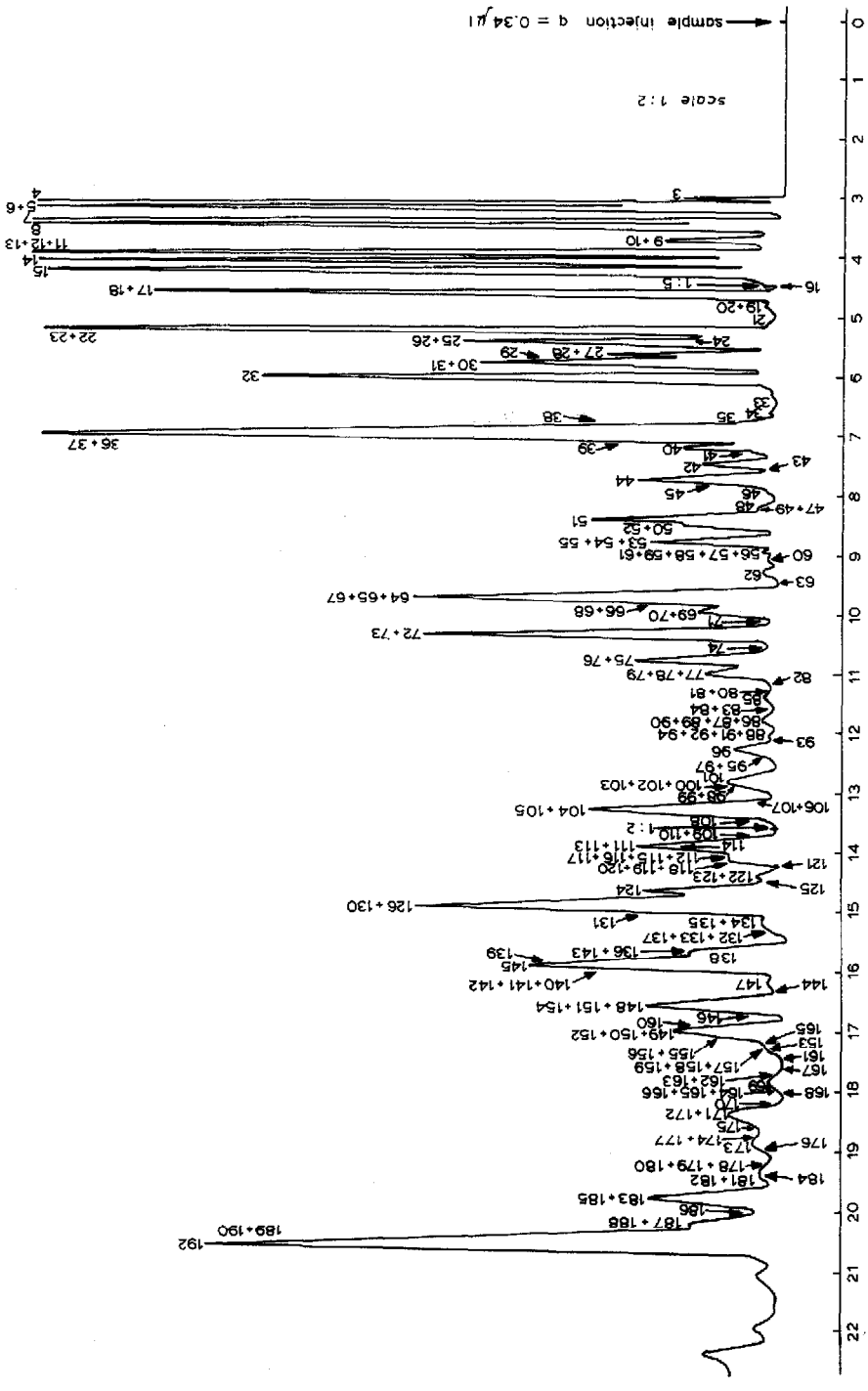


Fig. 5. Chromatogram of gasoline fraction of unfractionated crude oil obtained under back-flushing conditions at $t_{cap.col.}$ = 70°C, (squalane stationary phase), $P_{sup.}$ = 2.53 · 10^5 Pa, α = 26.8 cm/s, V_{α}^{inj} = 60 ml/min, t_{inj} = 185°C, τ^{opt} = 20 s.

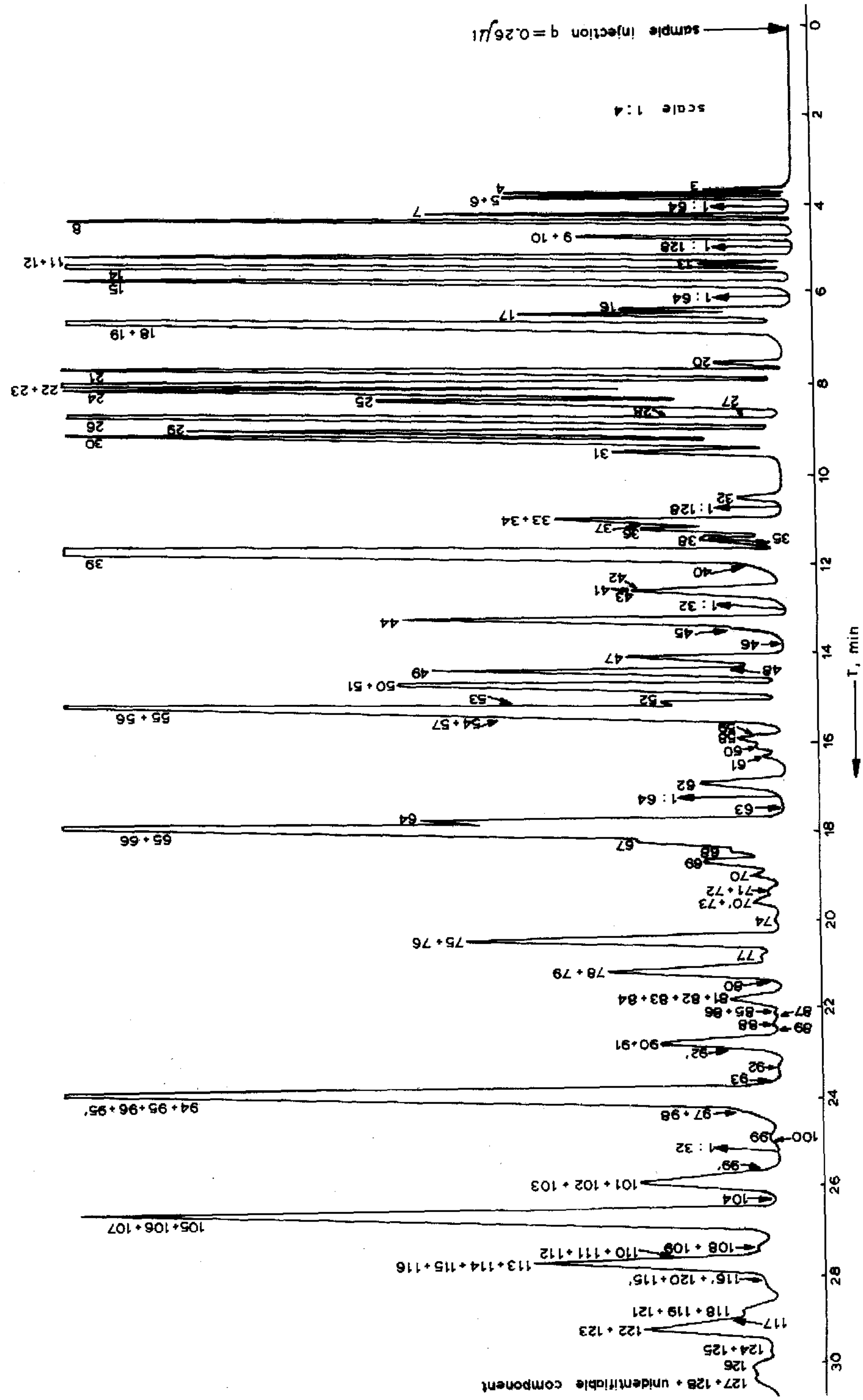
vated temperature increase its operating stability and lifetime. Several microlitres of sample are required in order to obtain detailed information on the composition of oils and condensates. The scheme proposed for using the back-flush pre-column system in combination with the capillary column can be applied to determinations other than those of low-boiling hydrocarbons in oils and condensates. It is necessary to carry out correctly the selection of the optimal chromatographic parameters (column length $L_{cap.col.}$, $t_{cap.col.}$, flow-rate, splitting ratio, stationary phase, t_{inj}, τ^{opt}, etc.) for the analysis of a particular fraction. Characteristics such as the analysis time, the reliability of the results and the degree of detail of the information obtained on the composition of a sample depend on the above parameters.

CHROMATOGRAM HANDLING AND INTERPRETATION BASED ON QUANTITATIVE ANALYSIS OF COMPLEX HYDROCARBON MIXTURES

The use of 50-m capillary columns characterized by a relatively low separation efficiency (80 000–110 000 theoretical plates) may be beneficial in terms of reducing the total analysis times and the possibility of analysing complex hydrocarbon mixtures by ordinary procedures that do not employ preliminary sample distillation into narrow fractions[6]. However, analyses on such columns can involve difficulties in connection with the necessity to obtain detailed information on the composition of the samples. Methods of obtaining great detail on composition, based on a combination of quantitative analytical results obtained at two column temperatures with the same stationary phases [squalane and dinonyl phthalate (DNP)], are considered here. The results of the quantitative analysis were also used for the varification of the validity of preliminary identification made on the basis of logarithmic Kováts retention indices, for the prediction of unidentifiable components eluted together with identified hydrocarbons, and for solving other problems of identification. In particular, the Kováts retention indices of about 175 hydrocarbons on DNP have been defined on the basis of a comparison of the quantitative analytical results obtained on capillary columns with different stationary phases for natural samples having the same qualitative, but considerably variable quantitative, composition. Thus, the total identification of C_1–C_9 hydrocarbons contained in the gasoline fractions (t.b.b.–152°C) has been achieved.

The use of the results of quantitative analysis for the identification of components of complex organic mixtures such as wide-boiling gasoline fractions of oils and condensates seemed to be possible for the following reasons: (1) a variable temperature dependence of the retention indices of components belonging to different groups of hydrocarbons (*n*-alkanes, mono-, di-, tri-, and tetraalkyl-substituted isoalkanes, cyclopentane and cyclohexane naphthenes with various configurations and various number of alkyl radicals, arenes), which leads to changes in the order of elution of components as a result of variations in the column temperature with the same stationary phase; (2) various orders of elution of components from columns with different stationary phases; (3) better precision of peak-area measurements owing to the use of digital or electronic integrators; (4) large differences in the composition of natural samples used.

At each temperature the quantitative analysis was carried out using peak areas by means of simple normalization on the basis of averaging the results of three mea-


sample injection q = 0.26 μl
scale 1 : 4
127 + 128 + unidentifiable component
T, min

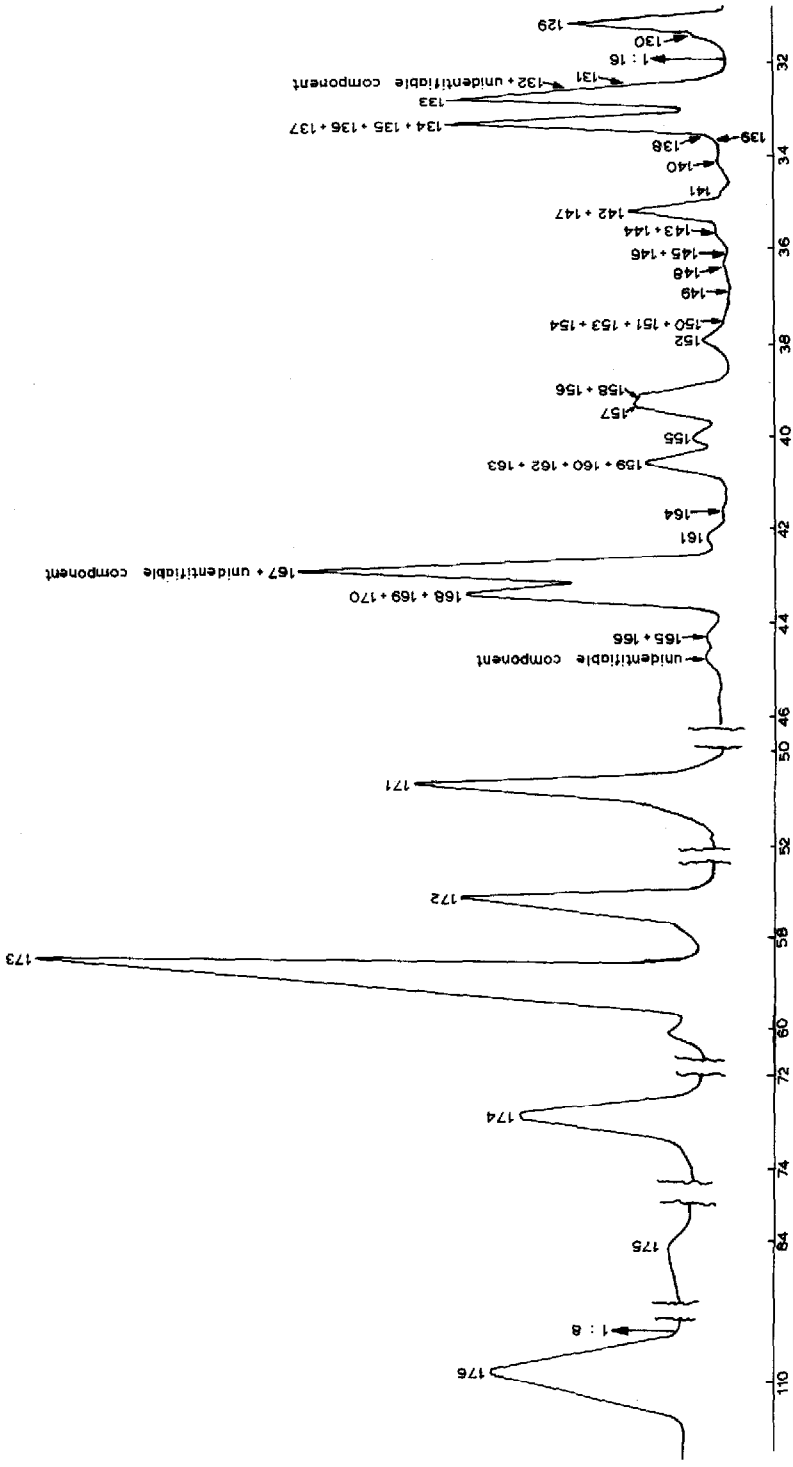


Fig. 6. Chromatogram of gasoline fraction of unfractionated condensate No. 2 obtained at $t_{cap.col.}$ = 50°C (DNP stationary phase), $P_{sup.}$ = 1.42 · 10^5 Pa, α = 23.3 cm/s, V_{α}^{av} = 42.3 ml/min, $t_{inj.}$ = 190°C.

TABLE I

HYDROCARBON CONTENT OF THE GASOLINE FRACTION OF CONDENSATE NO.2

Not less than two analyses were carried out at each temperature (50 and 70°C) and the results were averaged.

No. of hydrocarbon on chromatogram (squalane stationary phase)	*Hydrocarbon**	*Concentration (wt.-%) obtained (calculated in gasoline fraction)*	
		With back-flushing of pre-column (α = 26.4–28.4 cm/s, V_α^{nv} = 160 ml/min)	*By ordinary method (α = 27.9–28.4 cm/s, V_α^{nv} = 64.5–72 ml/min)*
3	Propane	0.0024	0.0025
7	Isopentane	0.41	0.49
8	*n*-Pentane	0.86	0.91
11	Cpentane	0.27	0.28
12	2,3-dMbutane	0.71	0.72
13	2-Mpentane	3.99	4.07
14	3-Mpentane	2.72	2.68
17	MCpentane	2.73	2.95
19	Benzene	1.39	1.62
22	Chexane	7.08	7.37
25	1,1-dMCpentane	0.99	0.96
26	3-Mhexane	3.11	3.02
27	*cis*-1,3-dMpentane	1.70	1.76
28	3-Ethylpentane	0.17	0.15
35	1,1,3-TriMCpentane	0.67	0.62
37	MChexane	18.1	17.3
44	Toluene	4.82	4.84
46	2,3,4-TriMpentane	0.35	0.31
50	1,1,2-TriMCpentane	0.27	0.30

54 + 55	3-Mheptane + 3-ethylhexane	1.72	1.76
66	1,1-dMChexane	0.43	0.49
69 + 70	*trans*-1,3-EthylMCpentane + *trans*-1,2-EthylMCpentane	0.56	0.58
73	*n*-Octane	0.10	0.052
77 + 78	*cis*-1,4-dMChexane + *trans*-1,3-dMChexane	0.94	0.91
85	2,2-dMheptane	0.060	0.070
95	1,1-dM-3-EthylCpentane	0.056	0.061
96	2,6-dMheptane	0.62	0.57
118	1,*cis*-3,*cis*-5-TriMChexane	0.16	0.22
124	*p*-Xylene	1.24	1.17
126	*m*-Xylene	3.54	3.53
129 + 130 + 131	3,4-MEthylhexane + 2,3-dMheptane + 3,3-Methylhexane	0.56	0.50
154	3-Moctane	0.46	0.44
139 + 140	1,*cis*-3,*trans*-5-TriMChexane + bicyclo[3.3.0]octane	0.52	0.53
172	*trans*-1,2-MpropylCpentane	0.15	0.13
173	1,1,2-TriMChexane	0.074	0.084
183	*cis*-1,3-MEthylChexane	0.82	0.74
186	IsobutylCpentane	0.046	0.042
192	*n*-Nonane	0.049	trace

* Abbreviations: M = methyl, d = di, C = cyclo.

surements assuming the correction factors to be unity. The error of determination for concentrations of about 5 wt.-% did not exceed 5% relative, increasing to 10% for concentrations of the order of 1%. Under these conditions, the relative standard deviation varied from 3 to 5%.

The calculation of gasoline fraction composition was carried out by the tabular method as described previously[6]. In this method, hydrocarbons were distributed into groups for each of which a combination of the quantitative analytical results was effected. With the 50-m squalane capillary column, the number of such groups was 46 and with the 50-m DNP capillary column it was 58. Examples of the combination of the quantitative analytical results obtained at 50 and 70°C for condensates Nos. 3 and 4 for the two groups of components are given in Table II (squalane stationary phase). The total calculation of the gasoline fraction composition (squalane) was described earlier[6]. With the DNP capillary column the combination of the quantitative analytical results was carried out on the basis of data obtained at 50 and 60°C.

Let us consider the examples in Table II in detail. In compliance with the results of preliminary identification (squalane), 2,3-dMpentane (group 15) is eluted together with 1,1-dMCpentane, but at 70°C 2,3-dMpentane gives an independent peak before 1,1-dMCpentane, which at 70°C is eluted together with 3-Mhexane (Figs. 4 and 5). The results of the quantitative analysis for condensate No. 3 are as follows: 2,3-dMpentane + 1,1-dMCpentane, 1.68% (50°C); 3-Mhexane, 3.12% (50°C); 2,3-dMpentane, 0.92% (70°C); 1,1-dMCpentane + 3-Mhexane, 3.96% (70°C). Based on the data obtained at a single temperature, it is impossible to confirm that 1,1-dMCpentane is present in the condensate or to determine its content. The combi-

TABLE II

EXAMPLES OF CALCULATION OF CONTENTS OF SEVERAL COMPONENTS OF GASOLINE FRACTIONS

Component	*No. of component on chromatogram*	*Component content (wt.-%)*					
		Condensate No. 3			*Condensate No. 4*		
		50°C	*70°C*	*Combination of results*	*50°C*	*70°C*	*Combination of results*
2,3-dMpentane	24	1.68	0.92	0.92	1.05	0.70	0.70
1,1-dMCpentane	25			0.80			0.42
3-Mhexane	26	3.12	3.96	3.12	1.96	2.44	1.96
Σ_{15}		4.80	4.88	4.84	3.01	3.14	3.08
cis-1,3-dMChexane	64	10.80	11.71	11.04	4.64	4.28	4.33
trans-1,4-dMChexane	65						
cis-1,3-EthylMCpentane	67	1.48		0.42	0.62		0.28
1,1-dMChexane	66		1.12	1.08		0.34	0.33
2,2,4-TriMChexane	68			0.05			0.02
trans-1,3-EthylMCpentane	69	1.14	1.09	0.09	0.56	0.54	0.54
trans-1,2-EthylMCpentane	70						
Σ_{29}		13.42	13.92	13.67	5.82	5.16	5.50

nation of the data may permit these two questions to be answered unambiguously. We determined 1,1-dMCpentane in two ways: (1) 3.96 − 3.12 = 0.84 wt.-%; (2) 1.68 − 0.92 = 0.76 wt.-%. The similarity of these results confirms the validity of the identification of 1,1-dMCpentane. Its actual concentration is taken to be 0.5 · (0.84 + 0.76) = 0.80 wt.-%. It should be noted that in the above instance the method of additions cannot give an unambiguous answer about the presence of the 1,1-dMCpentane in the sample.

To determine separately *cis*-1,3-dMChexane and *trans*-1,4-dMChexane + *cis*-1-ethyl-3-MCpentane, related to the 29th group, we find previously the 1,1-dMChexane content and the total content of hydrocarbons Nos. 65 and 67. Illustrated by the example of condensate No. 3, [66] = 1.12 − 0.05 = 1.07 wt.-% and [65 + 67] = 1.48 − 1.07 = 0.41 wt.-%. Further, the value 11.71 wt.-%, representing [64 + 65 + 67] found at 70°C, is divided in the ratio of 10.80:0.41 and the values obtained are averaged with the values 10.80 wt.-% and 0.41 wt.-%, respectively. We then have [64] = 0.5(11.28 + 10.80) = 11.04 wt.-% and [65 + 67] = 0.5(0.43 + 0.41) = 0.42 wt.-%. Similar calculations have also been made for condensate No. 4.

Using the approach developed, it is possible to determine separately arenes in non-dearomatized fractions[6].

DNP was chosen as a second stationary phase not only because of its higher selectivity (in comparison with squalane) with respect to a number of hydrocarbons, particularly naphthenes, but also the selective retention of arenes, ensuring rapid analyses (from 40 to 60 min at 60 and 50°C) of gasoline fractions because of its relatively low polarity. The use of the DNP capillary column enabled both the detail of information on the composition of wide-boiling gasoline fractions to be increased and the correctness of identifications made with the squalane capillary column to be confirmed.

Kováts retention indices on hydrocarbons on DNP are very limited in the literature, are often contradictory[7,8] and refer to the temperature range 70–110°C[8], which is not always advisable for the analysis of gasoline fractions. Relatively exact data on a very limited number of isoalkanes (15 compounds) measured at 60°C have been reported[7]. In this connection, the problem of the determination and prediction of the retention indices for the majority of the C_5–C_9 hydrocarbons is of great interest.

Separation of the gasoline fractions on the DNP capillary columns* was carried out on a Chrom-5 chromatograph equipped with a flame ionization detector at carrier gas linear velocities corresponding to the Van Deemter curve minimum: at $t_{cap.col.}$ = 50°C, α = 23.4–23.8 cm/s (P_{sup} = 1.45 · 10^5 Pa); at $t_{cap.col.}$ = 60°C, α = 23.7–24.5 cm/s (P_{sup} = 1.5 · 10^5 Pa). The part of the carrier gas stream that was released into the atmosphere was equal to 40–45 ml/min, corresponding to a splitting ratio of 43:1–50:1. Sample injection (q = 0.06–0.3 μl) was carried out at t_{inj} = 185–190°C. The separation efficiency of the capillary column, measured using C_8–C_9 arenes and

* The 50 m × 0.25 mm I.D. column was dynamically coated twice with a 10% solution of DNP in acetone. After evaporating the solvent in a flow of helium, the column was installed in the oven of the Chrom-5 chromatograph without connecting it to the detector and heated stepwise in small steps in a flow of carrier gas at temperatures ranging from ambient to 120°C, and then the column was subjected to conditioning at 120°C (isothermal) for 3 h.

C_8–C_9 *n*-alkanes under the above conditions, was 114 000–119 000 theoretical plates. For the purpose of measuring hydrocarbon retention indices, *I*, chromatograms of five unfractionated condensates, having the same qualitative but considerably different quantitative compositions, were obtained on capillary columns impregnated with squalane (50 and 70°C) and DNP (50 and 60°C). The essence of the method for determining *I* values on the DNP column consists in a comparison of peak areas measured in units of concentration from the chromatograms obtained on the squalane and DNP columns for natural samples having the same qualitative but substantially different quantitative compositions. The method is suitable for any stationary phase and for any classes of compounds in instances when the identification of all compounds for one of the stationary phases (squalane in the case under consideration) is known.

The determination of the retention indices on DNP is based on four principles: (1) if two (or more) hydrocarbons A and B correspond to the same chromatographic zone, the retention index of component A is determined by the chromatogram of the condensate in the gasoline fraction of which the content of component A predominates over that of the other components and, hence, in this instance component A determines the location of the peak maximum; (2) as the quality of resolution of neighbouring components depends on their content in the sample, if there is partial overlap of the chromatographic zones of components A and B, the retention values are determined by the chromatogram in which the best quality of resolution can be observed; (3) symmetrical peaks corresponding to the concentrations belonging to the linear portion of the solubility isotherm are used for retention index measurements; (4) the retention indices of components whose concentrations are small (0.01–0.001%) are determined by the chromatogram where these components provide independent individual peaks.

The example of using the quantitative analytical results for defining the retention values is illustrated by Table III, in which the concentrations of six hydrocarbons (Nos. 33–38) measured on a capillary column for the above-mentioned five condensates are given.

The *I* value of benzene (No. 34) eluted together with 2,2,3,3-tetraMbutane (No. 33) and 2,5-dMhexane (No. 37) should be determined by the chromatograms of condensates Nos. 1 and 2, while the *I* value of 2,5-dMhexane (No. 37) must be

TABLE III

CONTENT (WT.-%) OF HYDROCARBONS NOS. 33–38 IN DIFFERENT CONDENSATES [CALCULATED IN GASOLINE FRACTION (t.b.b. –152°C)]

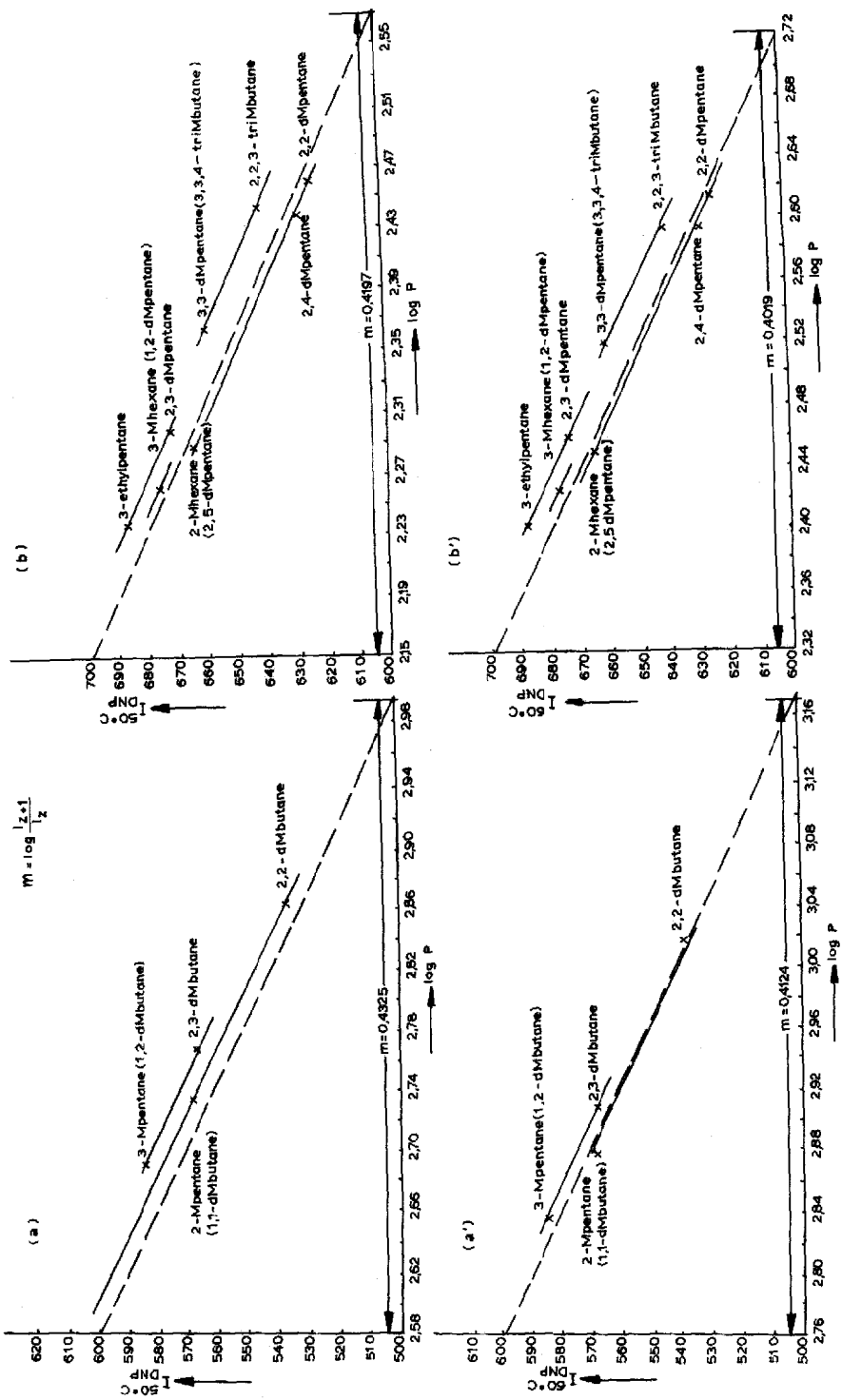
Condensate	*Hydrocarbon*					
	No. 33	*No. 34*	*No. 35*	*No. 36*	*No. 37*	*No. 38*
No. 1	0.10	1.51	0.32	0.65	0.84	0.62
No. 2	Trace	1.06	0.29	0.37	0.38	0.21
No. 3	0.04	0.17	0.082	0.072	0.94	1.24
No. 4	0.10	0.26	0.27	0.52	0.36	0.31
No. 5	0.15	0.23	0.23	1.59	0.70	0.75

defined by the chromatogram of condensate No. 3. The *I* value of 1,1,3-triMCpentane (No. 36) is determined by the chromatograms of all the condensates, except for condensate No. 3, on the chromatogram of which this component does not give a distinct maximum at 50°C. The *I* value of 2,4-dMhexane (No. 38), being separated poorly with *cis*-1,2-dMCpentane (No. 35) at 50°C, was determined by the chromatogram of condensate No. 3 in which the concentration of hydrocarbon No. 38 exceeds that No. 35 approximately 15-fold. In addition, we took into account the *I* values of the maximum of the peak of 2,4-dMhexane measured by the chromatograms of other condensates (Nos. 1, 2 and 5) regarding the availability of the turning point on the plot of the outlet curve corresponding to hydrocarbons Nos. 35 and 38. The *I* value of *cis*-1,2-dMCpentane (No. 35) determined by the chromatograms of the condensates Nos. 1, 2 and 4 for which typical is the best "seemed separation" of hydrocarbons Nos. 35 and 38 associated with commensurability of their concentrations in these condensates. The validity of the identification (DNP stationary phase) is confirmed by the coincidence of the quantitative analytical results obtained on columns with different stationary phases. Thus, the bulk concentrations of hydrocarbons Nos. 35 and 38 measured by the use of the DNP column for condensates Nos. 1, 3, 4 and 5 are 0.83%, 1.26%, 0.47% and 1.18%, respectively. These values are adequately consistent with the data in Table III. The second convincing evidence of the validity of the approach proposed for the identification of the components of complex mixtures and based on using the results of quantitative analysis, is the coincidence of the

TABLE IV

KOVÁTS RETENTION INDICES OF SOME HYDROCARBONS (DNP STATIONARY PHASE)

No. of component on chromatogram	*Component*	*Measured by chromatograms of condensates*		*Measured by chromatograms of reference mixtures*	
		50°C	*60°C*	*50°C*	*60°C*
7	Isopentane	473.2	473.6	474.4	–
13	Cyclopentane	578.05	581.3	577.3	579.3
17	2,4-dMpentane	628.0	629.3	627.6	628.5
21	2-Mhexane	665.4	665.6	665.7	666.0
22	2,3-dMpentane	673.4	674.7	672.7	673.5
23	Cyclohexane	671.5	674.7	671.6	674.6
24	3-Mhexane	676.2	677.25	676.1	677.25
28	2,2,4-TriMpentane	687.4	688.35	687.0	688.2
34	Benzene	723.7	726.1	723.4	725.9
81	2,4-dMheptane	818.1	818.2	818.5	818.6
96	Toluene	830.1	833.0	829.9	833.0
105	EthylChexane	843.2	846.4	843.3	846.45
122	1,*cis*-3,*cis*-5-TriMChexane	853.7	855.9	853.5	855.6
133	1,*cis*-3,*trans*-5-TriMChexane	867.6	870.9	868.1	871.9
171	Ethylbenzene	918.1	921.9	918.2	921.5
172	*p*-Xylene	931.6	935.6	931.6	934.6
173	*m*-Xylene	934.5	938.7	934.5	937.8
174	*o*-Xylene	959.4	963.4	959.3	962.6
175	Cumene	975.25	977.5	974.9	977.4


(a)
(a')
(b)
(b')
$I_{DNP}^{50°C}$
log P
$m = \log \frac{I_{z+1}}{I_z}$
3-Mpentane (1,2-dMbutane)
2-Mpentane (1,1-dMbutane)
2,3-dMbutane
2,2-dMbutane
m=0,4325
m=0,4124
3-ethylpentane
3-Mhexane (1,2-dMpentane)
2,3-dMpentane
2-Mhexane (2,5-dMpentane)
3,3-dMpentane(3,3,4-triMbutane)
2,2,3-triMbutane
2,4-dMpentane
2,2-dMpentane
m=0,4197
m=0,4019

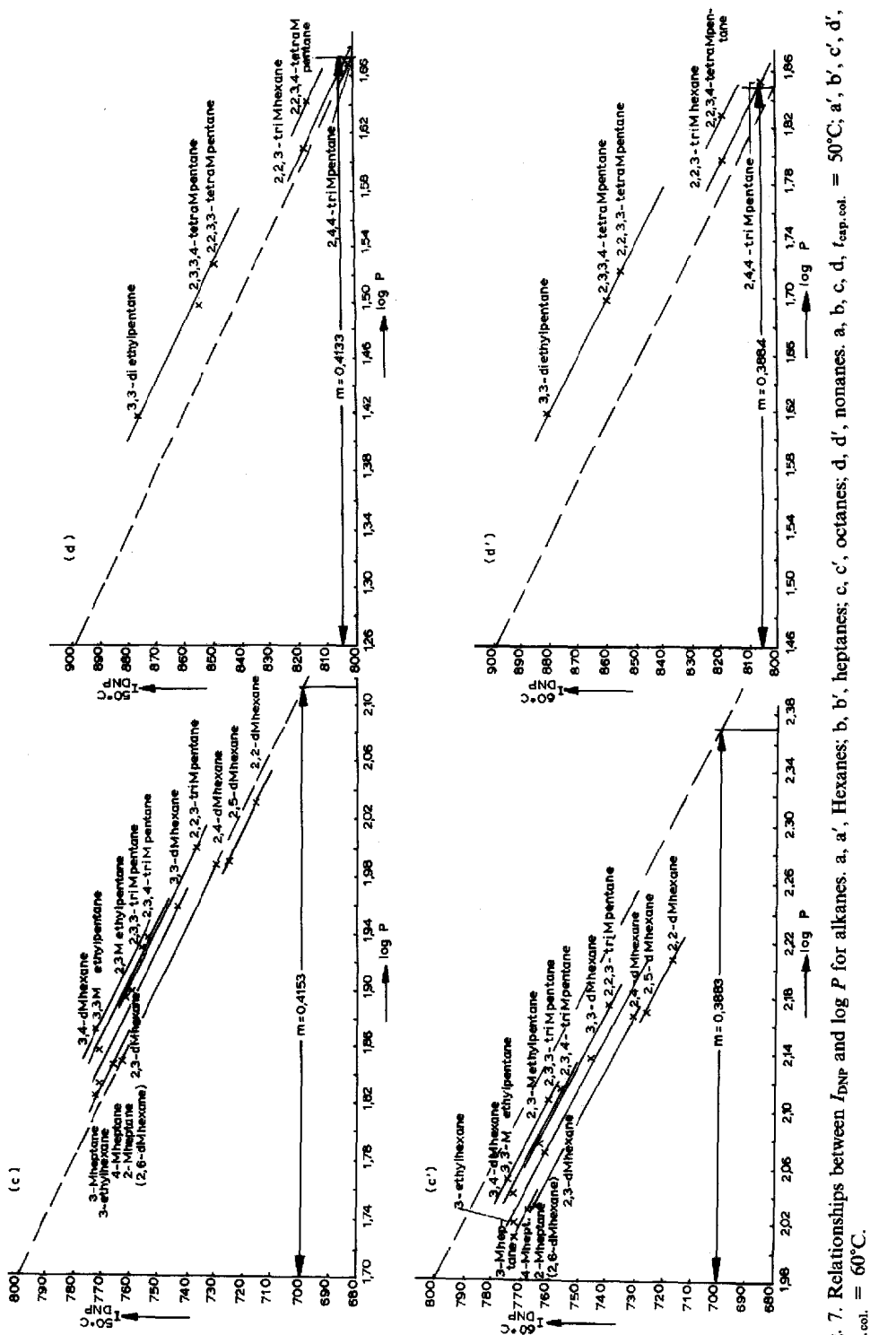


Fig. 7. Relationships between I_{DNP} and log P for alkanes. a, a', Hexanes; b, b', heptanes; c, c', octanes; d, d', nonanes. a, b, c, d, $t_{cap.col.} = 50°C$; a', b', c', d', $t_{cap.col.} = 60°C$.

I values (50 and 60°C) measured by the chromatograms of natural and standard mixtures for a number of compounds (Table IV). The I values of 175 low-boiling hydrocarbons were measured by the chromatograms of five condensates. This permitted us to complete, using DNP stationary phase, the total identification of the hydrocarbons present in wide-boiling gasoline fractions of oils and condensates. The chromatogram of the gasoline fraction of one of the unfractionated condensates (No. 2) obtained on the DNP capillary column is shown in Fig. 6 ($t_{cap.col.} = 50°C$). It should be noted that the hydrocarbon numbers in the chromatograms obtained on the squalane (Figs. 4 and 5) and DNP (Fig. 6) columns do not coincide.

The I values of hydrocarbons obtained at 50 and 60°C on the DNP columns were plotted against log P (where P is the vapour pressure of the sorbate at the column temperature). It was found that the relationships $I = f(\log P)$ are a family of parallels with the same angle coefficient $K = -100/\log(l_{z+1}/l_z)$ (where l_z *and* l_{z+1} are the adjusted retention distances of n-alkanes with z and $z + 1$ carbon atoms, respectively). It is important to note that the points which correspond to the components with similar structures of molecules having close values of activity coefficients in the stationary phase lie on the same line of the family.

Fig. 7, in which the dependences for C_6–C_9 isoalkanes are shown, confirms the above. The results are completely consistent with theoretical concepts following from the combined examination of the expressions for the Kováts retention index and the Herington equation and, therefore, proves the validity of the identification of low-boiling C_5–C_9 hydrocarbons made for DNP stationary phase.

It should be noted that the above method of information handling, based on the combination of quantitative analytical results obtained at different temperatures and on the columns with various stationary phases, can be used not only for capillary columns of any length, but also for packed columns.

This method is also applicable to hydrocarbon mixtures and to complex mixtures of any organic compounds that are characterized by different temperature dependences of their retention parameters and different orders of elution of components from columns with various stationary phases.

RAPID PYROLYSIS–GAS CHROMATOGRAPHIC TECHNIQUE FOR THE INVESTIGATION OF ORGANIC MATTER

Pyrolysis–gas chromatography (PGC) is widely applied in geochemical research because of its advantages such as rapidity, high sensitivity, very small samples, simplicity of equipment and the possibility of working with standard devices.

On the one hand, PGC enables hydrocarbon (HC) compositions to be examined, which is essential for characterizing the origin and type of organic matter[9–11] and, on the other, it can be used for determining the hydrocarbon potential of source rocks and the migration of hydrocarbons out of the rocks[12–14].

In this section, a variation of the PGC technique is described for the purpose of characterizing (1) the total HC content, (2) the total HC content in the range C_{8+} and (3) some individual HC contents up to C_8.

The PGC system (Fig. 8) consists of a reactor (9) inserted into a furnace (10) and a gas chromatograph (LChM-8MD) having two flame ionization detectors. One of them (6b) determines the total hydrocarbon content and the other one (6a) the

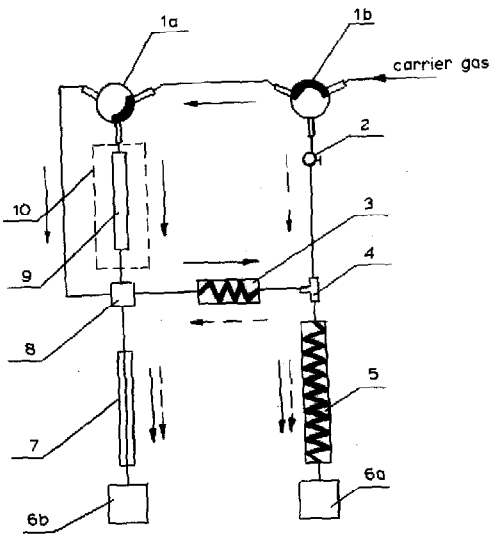


Fig. 8. Schematic diagram of pyrolysis arrangement. 1a,b = three-way taps; 2 = needle valve; 3 = pre-column; 4 = effluent splitter; 5 = analytical column; 6a,b = flame ionization detectors; 8 = four-way effluent splitter; 9 = reactor; 10 = furnace.

individual composition of some hydrocarbons up to C_8. The PGC system also includes a chromatographic column (5) and a pre-column (3) interfaced with an effluent splitter (4) and also a capillary resistor (7) connected with detector 6b and a four-way valve (8). Two three-way taps have been added: tap 1a is for the inlet of the carrier gas flow and the tap 1b for changing the direction of the carrier gas flow in the pre-column after the necessary hydrocarbons have been eluted.

The standard operating conditions for GC analysis are as follows: analytical column, 300 cm × 4 cm I.D., stainless steel, packed with 15% 1,2,3-tris(β-cyanethoxypropane) on Chezasorb AW; pre-column, 50 cm × 4 cm I.D., stainless steel, packed with 5% SE-30 on Chromaton N AW; oven temperature, 80°C; operating range of the reactor furnace, 125, 250 and 350°C; gas carrier, helium; flow-rate of helium to the detector, with straight-flushing (solid arrow in Fig. 8) 12.3 cm^3/min from the capillary resistor and 40.0 cm^3/min from the analytical column, and with back-flushing (dashed arrow) 9.0 cm^3/min and 42.2 cm^3/min, respectively.

The PGC procedure is as follows. A whole rock sample ground to 0.25–0.5 mm particle size is placed (20–40 mg) in a reactor, which is inserted in a furnace and, heated to 120°C. The sample is heated at 120°C in a helium atmosphere for 10 min (the positions of taps 1a and 1b is shown in Fig. 8), then tap 1a is turned and a portion of helium is sent to the reactor, which carries out the hydrocarbons evolved from the rock matrix. One part of the evolved hydrocarbons is directed to a capillary resistor and then to detector 6a for measuring the total yield of volatile HC. The other portion of the gas flow is directed to the pre-column which serves two functions: on the one hand it passes hydrocarbons lighter than C_8 (octane) and, on the other, it retains hydrocarbons heavier than C_8 (nonane). The retained HC are removed from the pre-column by means of the inverse carrier gas flow (tap 1b) and are measured as a total peak on detector 6b. The pyrolysis experiments at 250 and 350°C are

carried out in the same manner as at 125°C. Chromatograms are recorded simultaneously by two potentiometers. Areas of peaks are measured by means of a U-02 integrator.

Whole-rock samples containing various sedimentary organic matter have been investigated by this technique.

Table V shows that the different types of original organic matter (humic or sapropelic) generate hydrocarbons that differ in both amount and composition. For example, predominantly humic organic matter (derived largely from higher plant materials) in sample No. 1116-V4 generates up to 95% of aromatic hydrocarbons (mainly benzene) in the first heating step, whereas sapropelic organic matter (derived largely from algae) in sample No. 42-BP does not contain such hydrocarbons.

It is interesting that humic organic matter can generate more light hydrocarbons than sapropelic organic matter. For example, sample No. 6-U215 generates 74–99% of heavy oil-like hydrocarbons in all three steps of pyrolysis, whereas sample No. 158-4C generates only 17.8%.

The minimum amount of aromatic hydrocarbons contained in light fractions is found in the samples having sapropelic organic matter.

TABLE V

PYROLYSIS–GAS CHROMATOGRAPHIC RESULTS FOR ORGANIC MATTER

Sample	*Rock type*	*Organic matter type**	*Temperature (°C)*	*Total yield of HC (wt.-%)*	*Hydrocarbon content (%)*		
					C_{8+}	C_1–C_8	
						*Me–Na***	*Ar***
6-U215	Shale	S:	125	0.032	74.0	98.7	1.3
			250	0.120	99.0	97.9	2.1
			350	0.160	78.0	96.2	3.8
42-BP	Siltstone	S	125	0.001	66.5	100.0	0
			250	0.005	69.5	100.0	0
			350	0.012	32.0	100.0	0
647-DV	Sludge	H-S	125	0.007	55.0	76.9	23.1
			250	0.140	40.0	98.6	1.4
			350	0.220	38.0	97.4	2.6
1066-UT	Aleurite	S-H	125	0.005	19.0	94.0	6.0
			250	0.030	49.0	91.2	8.8
			350	0.023	43.0	89.6	10.4
1116-V4	Siltstone	S-H	125	0.102	11.5	3.4	94.6
			250	0.120	50.5	43.9	56.1
			350	0.082	52.0	33.3	66.7
141-CM	Sandstone	H	125	0.002	75.5	33.3	66.7
			250	0.004	17.0	78.8	21.2
			350	0.016	15.5	90.1	9.9
158-4C	Clay	H	125	0.002	0	0	0
			250	0.007	17.8	76.1	23.9
			350	0.014	17.3	92.1	7.9

* S = Sapropelic organic matter; H = humic organic matter; H-S = predominantly sapropelic organic matter; S-H = predominantly humic organic matter.

** Me–Na = methane–naphthene HC; Ar = aromatic HC.

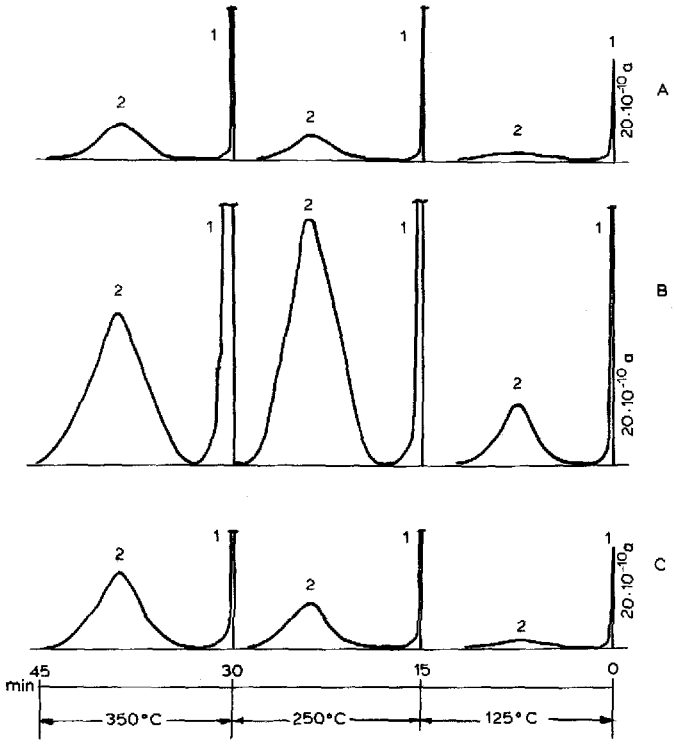


Fig. 9. Variation in hydrocarbon yields from argillites of different ages by the vertical well section. 1, Total hydrocarbon yield; 2, total hydrocarbon yield of C_{8+}. (A) Lower Cretaceous; (B) Upper Jurassic; (C) Middle–Lower Jurassic.

Table V gives an idea of the dynamics of the hydrocarbons yield depending on variations in temperature. It shows that an increase in the experiment temperature generally results in an increase in the bulk of hydrocarbons in which light hydrocarbons are predominant.

Figs. 9 and 10 reveal the pattern of changes in the yield of total and individual HC up to C_8 in argillites from the vertical well section which have different compositions of organic matter.

Fig. 9 shows the total yield of hydrocarbons with a direct flow of carrier gas in the pre-column and the yield of hydrocarbons heavier than C_8 with a back-flow in the pre-column. According to Fig. 9, sample B, having mainly sapropelic organic matter, generates the bulk of the heavy HC (up to 99%); sample C generates slightly less HC (60–40%) and sample A about 20–40%.

Fig. 10 illustrates the yield of methane–naphthene hydrocarbons, benzene and toluene contained in the light pyrolytic fraction in the same samples. Increasing humic materials in rocks (samples A and C) cause a substantial generation of aromatic hydrocarbons. Sample B, having predominantly sapropelic organic matter, generates substantially less aromatic hydrocarbons.

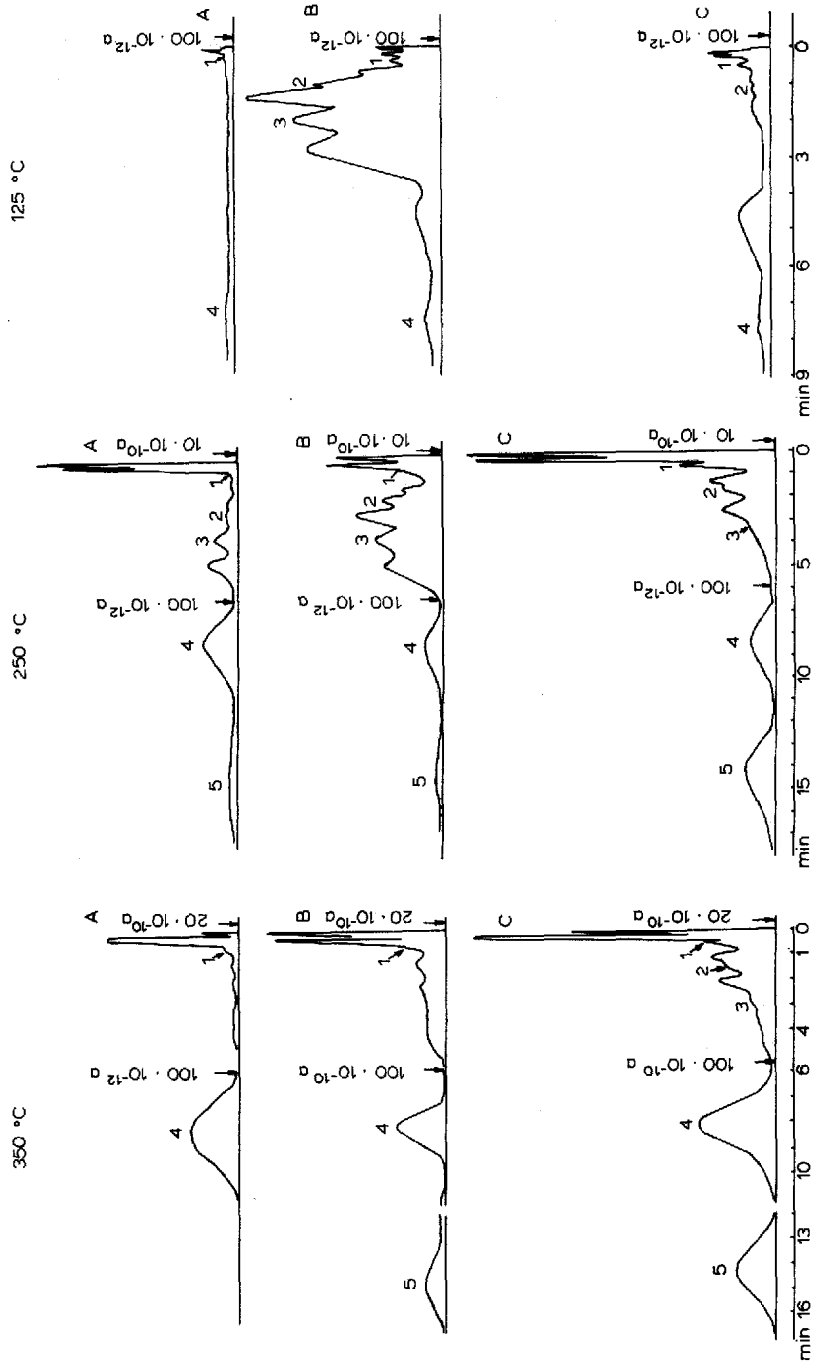


Fig. 10. Variation in C_1–C_8 hydrocarbon yield from argillites of different ages by the vertical well section. 1 = *n*-Hexane; 2 = *n*-heptane; 3 = *n*-octane; 4 = benzene; 5 = toluene. (A) Lower Cretaceous; (B) Upper Jurassic; (C) Middle–Lower Jurassic.

RAPID DETERMINATION OF MONOAROMATIC HYDROCARBONS IN GASES, CONDENSATES, CRUDE OILS AND SUBSURFACE WATERS WITH THE SAME DEVICE

The investigastion of crude oils and condensates in the Urengoi multi-bedded field by GC has shown[15] that the information obtained on the monoaromatic hydrocarbon content can be used for the study of forming hydrocarbon accumulation. In particular, it has been ascertained that the ratio of total *m*- and *p*-xylenes to ethylbenzene concentration is not changed on phase crossing in the system gas–crude oil–water and also during migration of gaseous and liquid hydrocarbons.

Chromatographic methods are highly sensitive and rapid, but when they are applied to the analysis of crude oils to determine benzene and its homologues, they lose their rapidity because the gasoline fractions are subjected to the analysis. Separation into fractions is time consuming.

The GC technique that we developed previously enables condensates and crude oils to be analysed without any preliminary treatment[16]. When the crude oil is very viscous it is necessary to dissolve it in tetradecane to decrease the viscosity. The GC system (Fig. 11) is mounted in the oven of a Tsvet-101 gas chromatograph. There are two packed columns, one of which can operate under back-flushing conditions. The direction of carrier gas flow in this column is changed by a two-position, six-

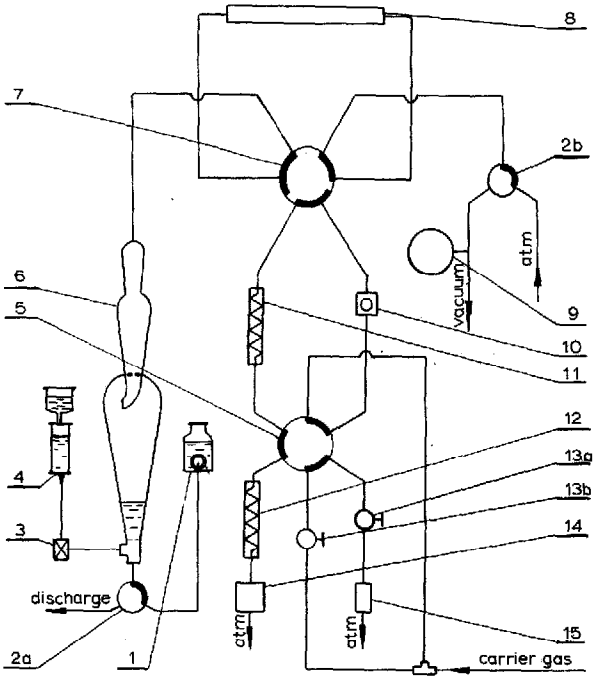


Fig. 11. Schematic diagram of GC arrangement used for the determination of aromatic hydrocarbons in gases, condensates, crude oils and formation waters. 1 = Balancing bottle; 2a,b = three-way taps; 3 = test-tube clamp; 4 = glass cylinder; 5 = six-way tap; 6 = degasser; 7 = three-position sampling valve; 8 = trap; 9 = vacuum gauge; 10 = injector; 11, 12 = chromatographic columns; 13a,b = needle valves; 14 = flame ionization detector; 15 = adsorber.

way tap (5). Thereby, the flow of carrier gas in column 12 is maintained constant due to valve 13b, whose resistor is the same as that of a column 11.

A flame ionization detector (14) is installed downstream of the output of column 12. An adsorber of hydrocarbons (15) packed with activated carbon in installed after valve 13a.

Column 11 (0.3 m × 3 mm I.D.) is packed with 5% SE-30 on Chromaton N AW and column 12 (3.0 m × 3 mm I.D.) is packed with 15% β,β'-oxydipropionitrile on Chromasorb. The sample (0.5–5.0 μl) is injected into the evaporator (10) by a microsyringe with the position of tap 5 as shown in Fig. 11. The vapour phase is entrained by the carrier gas into column 11, from which a partially separated phase passes through one of the holes of tap 5 to column 12. The components are eluted in succession from column 11 according to their boiling points, the high-boiling hydrocarbons remaining in column 11 being taken by the carrier gas through valve 13a into the absorber. The renegeration of the sorbent in this column is carried out isothermally and continues up to the beginning of the next experiment.

The duration of the black-flushing is determined from the analytical results for arene mixtures obtained under the standard conditions of the chromatographic experiment.

Fig. 12 shows the gas chromatogram of a condensate obtained with back-flushing 4 min after the beginning of the experiment. The components of interest (ethylbenzene and xylenes) can be reliably determined. In the gas analysis, the sample volumes taken are 0.5–5.0 cm^3. Sample weighing is carried out with a syringe or a sample-tap 7.

In the analysis of water samples by GC[17], the sample (5–10 ml) is first placed in a preparatory device. The sample is filled into the lower part of vessel 4, and the upper part of the vessel is filled with distillate, heated to boiling. The test-tube clamp 3 is open and liquid and then free air pass into a preliminarily evacuated degasser

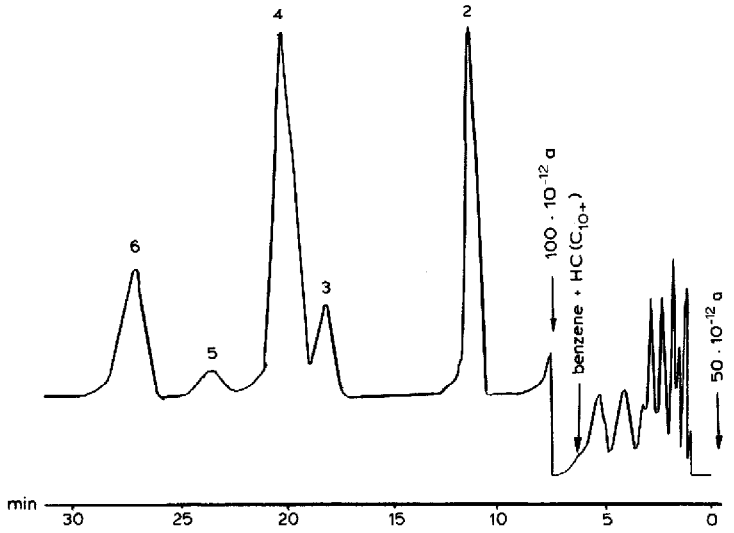


Fig. 12. Chromatogram of condensate. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*- and *p*-xylene; 5 = cumene; 6 = *o*-xylene.

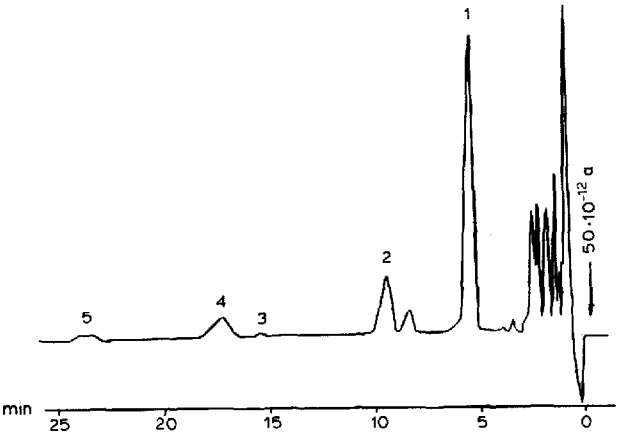


Fig. 13. Chromatogram of a subsurface water. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*- and *p*-xylene; 5 = *o*-xylene.

(6). Constant gases and hydrocarbons extracted from the sample solution in the gas phase are displaced by air into trap 8 of the six-way, three-position tap 7, from which the carrier gas removes them to the pre-column 11, and analysis begins. A gas chromatogram of subsurface water analysis is shown in Fig. 13.

This device provides for the almost complete extraction of any HC, including monoaromatic HC, from aqueous solution with any mineralization. The sensitivity of the determination of aromatic hydrocarbons is 0.01–0.001 mg/l.

RAPID DETERMINATION OF HYDROCARBON MICRO-CONCENTRATIONS IN ORGANIC SOLVENTS USED AS EXTRACTANTS

Rocks and formation waters contain small amounts of organic compounds (less than 10^{-4} wt.-%). To improve the sensitivity of the determination of these compounds, extracts are evaporated with the result that the information on the content of low hydrocarbons up C_9 is completely lost.

The GC device developed by us previously enables the sensitivity of hydrocarbon determination to be increased by a factor of 10^2 and, as a consequence, the low hydrocarbons can be reliably determined in liquid extracts without their evaporation. The increase in the sensitivity of hydrocarbon determination is achieved by increasing the organic solvent sample size, extracting the low HC from the organic solvent and by concentrating the latter at a thermal adsorption accumulator. A schematic diagram of the device is shown in Fig. 14.

Th experiment is carried out in the following manner. Liquid extract is injected by means of a syringe into an evaporater heated to 250°C. The carrier gas passing through the needle valve lc removes the vapour phase from the evaporater 3a into the column 4. The components eluted from the pre-column 4 pass through the capillary valve 8 to the flame ionization detector 7b and to a thermal adsorption accumulator 5, which is situated at the inlet of the capillary column 6. The direction of the carrier gas flow in this case is shown by solid arrows.

At the moment when the nonane peak is recorded by detector 7b the system

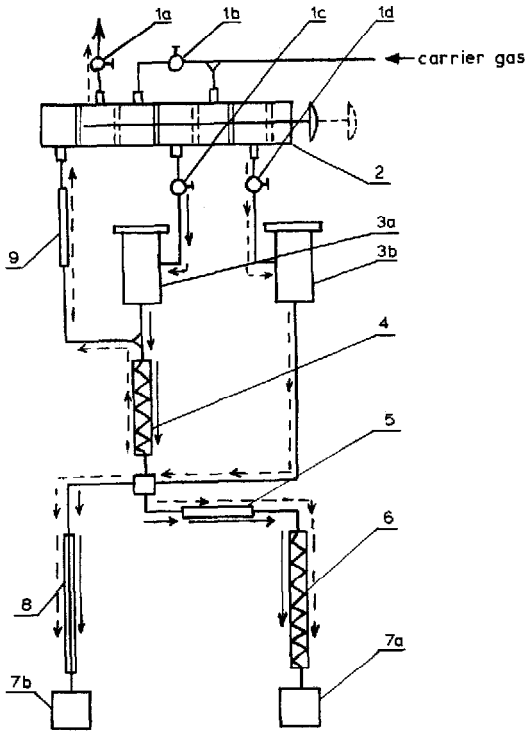


Fig. 14. Schematic diagram of arrangement for determination of low hydrocarbons in organic solvents. 1a,b,c,d = Needle valves; 2 = six-way tap; 3a,b = evaporators; 4 = pre-column; 5 = thermal adsorption accumulator; 6 = capillary column; 7a,b = flame ionization detectors; 8 = capillary valve; 9 = absorber for hydrocarbons.

is transferred to back-flushing conditions by means of the tap 2. In Fig. 14 the gaskets are shown by dashed lines, and the direction of the carrier gas flow is marked by dashed arrows. In this case the direction of the carrier gas flow in the pre-column 4 is reversed. The extract is eluted from the pre-column 4 to the absorber 9. Hence regeneration of the pre-column sorbent is performed under isothermal conditions and completed during the chromatographic analysis of the low hydrocarbon concentrate contained in the cold trap of the thermal absorption accumulator 5. The analysis begins from the moment of removing cold trap and its heating.

As shown by the analysis of the toluene and octane, the sensitivity of the determination of these hydrocarbons can be increased more than 800-fold. An initial solution containing both toluene and octane in equal concentrations (2 wt.-%) in decane was prepared for carrying out these experiments. In addition, five solutions were prepared by diluting the initial solution with decane 5-, 10-, 50-, 100- and 800-fold. The volume of sample was 0.1 μl for the initial solution and 0.5, 1.0, 5, 10 and 80 μl, respectively, for the others. As would be expected, the same amounts of toluene and octane are placed in the trap as correspond to the areas of the toluene and octane peaks after separating them on the capillary column. The differences between the areas of peaks of these components in all experiments are less than 15%.

Using the suggested gas circuit allows one to eliminate completely the memory

effect that may remain from the previous experiment, because the direction of the pure carrier gas flow through the tap 2 and evaporators 3a and 3b do not change. This device can be applied for the rapid analysis of condensates and crude oils without any preliminary preparation for determining the low hydrocarbons up to C_9.

CONCLUSIONS

The application of the described two-step GC systems, including an analytical packed or capillary column and a short packed pre-column functioning under straight- and back-flushing conditions, allows a 10-fold reduction in the total duration of determinations when analysing crude oils and stable condensates, an improvement in the reliability of the GC analytical results and necessary information to be obtained on the fractional composition of samples with injection of not more than 1 μl of sample. This is due to the elimination of time-consuming operations of preliminary sample preparation prior to the GC analysis. The rapidity of obtaining detailed information on the individual compositions of oils and condensates is also due to the use of relatively short capillary columns (shorter than 50 m).

The important distinguishing feature of the method of handling the experimental data is the combination of quantitative analytical results obtained at different temperatures on the same capillary column and on columns coated with different stationary phases. As a consequence, it is possible to increase the detail of information obtained on composition and to use, for the first time, the results of the quantitative analysis of complex mixtures for identification purposes.

PGC enables one to investigate the organic matter composition of rocks. Also, it permits information to be obtained on the total hydrocarbon yield, C_{8+} hydrocarbon yield and some individual hydrocarbons up to C_8. Rapidity is achieved by analysing the whole rock sample without preliminary treatment. About 40–100 mg of whole rock are necessary for one experiment.

Rapidity of the GC determination of monoaromatic hydrocarbons in crude oils, condensates, gases and water samples is achieved by using two columns, one operating under back-flushing conditions, and also by employing a device for the preparation of the liquid sample to be analysed on the chromatograph.

Rapidity and high sensitivity of the determination of low-boiling hydrocarbon micro-concentrations in rocks and extracts are achieved by using a large sample volume (up to 80 μl) of organic solvent, isolating the fraction of low-boiling hydrocarbons and concentrating the fraction in a thermal adsorption accumulator.

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