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ANALYSIS OF THE AROMATIC FRACTION IN GEOTHERMAL FLUIDS

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SUMMARY

Problems connected with analysis of organics in geothermal fluids are discussed. The quantitative analysis of C_6–C_{10} organic components was performed by use of preliminary concentration steps. Particular attention was focused on sampling, transportation, storage and other stages preceding the analysis.

INTRODUCTION

In studies[1,2] of geochemical processes at great depths much attention has been focused on volcanic and/or geothermal gases and vapours. A correlation between the fluid composition and the pressure, P, and temperature, T, is important in establishing the physical and chemical changes taking place in these processes. It is evident that the organic substances play an essential rôle in the fluid composition. However, in theoretical models, only paraffinic hydrocarbons have been taken into consideration[3-6]. This is probably associated with the fact the analysis of organic mixtures are usually involves the C_1–C_4 components[5-7]. The composition of geothermal hydrocarbons is more complex[8,9]. The nature of the hydrocarbon compounds and their origins are problematic[5,6,8,9]. However, volatile compounds with carbon numbers greater than five[8,9] are partially or completely lost during sampling.

In view of the increasing use of geothermal resources and that the power of the generating stations will be 50 000 MW[1,24] (1000 MW is equivalent to 195 000 tons of steam per day), the qualitative measurement of the organic material is essential since the heat-transfer agent can pollute the environment.

The goal of the present study was to determine the content of volatile organics. The samples were taken from different sources of geothermal fluid from South Kamchatka (U.S.S.R.).

EXPERIMENTAL

Fig. 1A shows the procedure for sampling from the natural steam outlet. Steam and vapour–gas mixture enter the condensing coil from the sampler. The sampler (tube-in-tube) consists of two sliding stainless-steel tubes, 60 cm × 7 mm O.D. × 6.5 mm I.D. and 65 cm × 6 mm O.D. × 5.5 mm I.D., joined by a PTFE sleeve. After the sampler is inserted into soil the inner tube is pulled out and the side ports
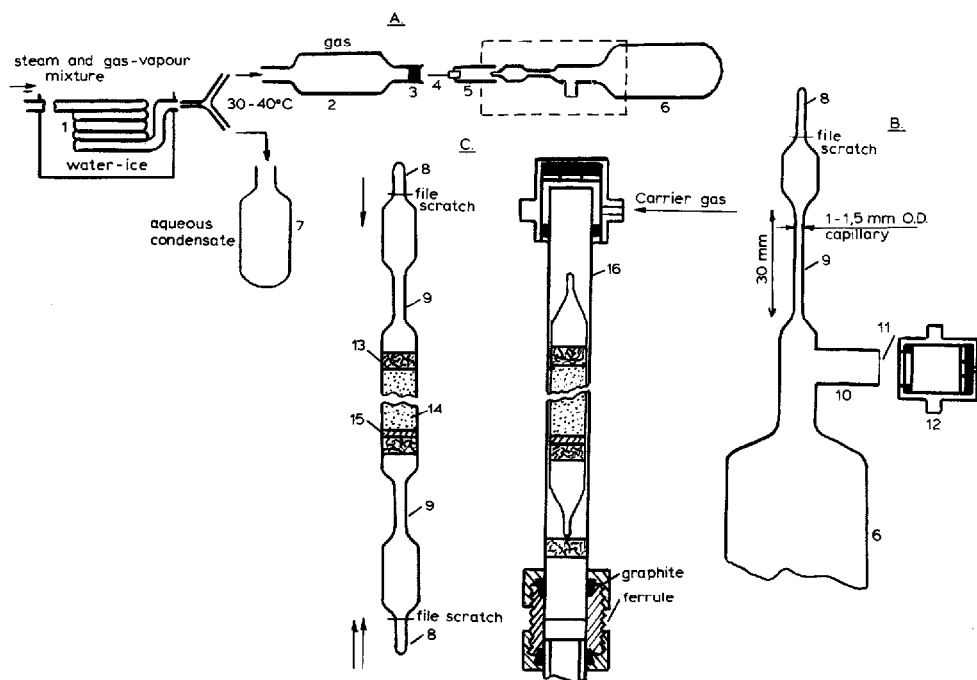
Fig. 1. The sampling system. (A) 1 = Condensing coil 1–4 m × 16 mm; 2 = glass collection vessel; 3 = silicone rubber plug; 4 = syringe needle; 5 = elastic PTFE tube; 6 = evacuated ampoule; 7 = glass bottle for water condensate. (B) Evacuated ampoule for gas sample: 8 = sealed tip; 9 = narrow section; 10 = side tube; 11 = glass partition, wall thickness ≈ 0.1 mm; 12 = self-sealing cap. (C) Trap containing Tenax GC: 13 = glass wool; 14 = Tenax sorbent; 15 = glass-wool filter FSV/A (U.S.S.R.); 16 = stainless-steel tube (220 mm × 6 mm O.D. × 5.5 mm I.D.). Two arrows indicate sampling and gas flow (helium) released from inorganic gases and C_1–C_5 hydrocarbons, one arrow the thermal desorption into the column.

in the outer tube are opened. The application of this sampler prevents blocking of the tube channel by clay or rock and permits effective sampling in a short period of time.

It is known that the analysis of hydrocarbons sampled in bottles (containers) yields satisfactory results in the range C_1–C_4[11] or to C_5[12].

The geothermal mixtures were taken from the gas phase (a) into evacuated glass ampoules (Fig. 1B) for a common analysis (inorganic gases and C_1–C_5); (b) into traps for the analysis of volatiles and from the aqueous phase (c) into bottles and traps for analysis of volatiles.

Prior to the sampling the tip (8) of the evacuated ampoule (6) was scratched and elastic PTFE tube connected with the syringe needle (4) was attached. The air from the elastic tube was removed by purging with sampling gas. Then the plug (3) of silicone rubber was pierced by needle (4), the sealed tip (8) was broken and gas from the collection vessel (2) filled the ampoule. After the narrow section (9) of the ampoule was filled, the ampoule was sealed by a microburner. Prior to analysis the self-sealing cap (12) was connected to the side tube (10). Air from the dead volume was removed with helium. The septum and glass partition were pierced by needle

and the ampoule was filled to 1.05 atm with helium. The sample volume taken for the analysis was 0.3–1.0 cm^3.

The volatile organics from the condensing coil were concentrated in the glass traps. The traps were prepared according to the recommendations given in refs. 10, 11, 13, 14. The sample volume was about 10–300 cm^3, with flow-rates 20–40 cm^3/min. The gas was withdrawn with a syringe (50–250 cm^3). The traps (Fig. 1C), 235 mm × 5 mm O.D. × 4 mm I.D. contained Tenax GC (90 mm × 4 mm) and were treated under vacuum before sealing. Prior to the sampling, the tips (8) were filed and broken. After sampling the trap was purged with helium (20 cm^3/min) for 5 min to remove inorganic gases, water and gaseous hydrocarbons. The narrow part of the trap was flame sealed. For sufficient strength and minimum possible sample changes during the process of flame sealing, diameter and length of the narrow section (9) were chosen equal to 1–1.5 mm and 30 mm, respectively (ampoule and trap). Glass traps of the traditional type[15] were also used: 120 mm × 6 mm O.D. × 4 mm I.D., 90 mm × 4 mm Tenax GC.

Fig. 1C shows the method of connection of the trap to the column. The surfaces of the trap were washed with tetrachloromethane and acetone, and the trap was then placed inside a stainless-steel tube (220 mm × 6 mm O.D. × 5.5 mm I.D.). The initial helium flow-rate in the column was reduced, and a blank trace was recorded (Fig. 2.0-0). Then the initial section of the column was cooled with liquid nitrogen. The trap was crushed with tongs and thermal desorption took place.

Aqueous condensate was collected in 200-cm^3 glass bottles (Fig. 1A) which were then closed with PTFE caps. The volatile organics were trapped as described by O'Brien and McTaggert[16]. The 10 ml of condensate were pipetted onto a small pore glass disk. The dissolved hydrocarbons were purged with helium at room temperature during 20 min, at a flow-rate of 30 cm^3/min. The condensate *in situ* was also passed through the trap with Tenax GC as described by Mieure and Dietrich[17].

The samples were collected from the following sources. (1) Lower Koshelevskii thermal field, height 750 m above sea-level. Well 9 was drilled to a depth of about 600 m, the effluent gas from the well orifice had a pressure of about 1 atm and ambient temperature; flow-rate about 10 l/min. Well 10a was drilled to a depth of 1000 m, the temperature being ⩾300°C. The samples were taken from the side pipe-outlet, the well orifice being closed. After condensation geothermal steam from well 10a consists of 2 l of gas and 1 kg of water. (2) East Pauzhetskii thermal field, height 300 m above sea-level, a 98°C fumarole. The samples were collected from a depth of 0.25 m. After condensatuion geothermal steam from fumarole consists of 1 l of gas and 1 kg of water.

The analyses were made 10–14 days after sampling. Varian Aerograph 1800 and Pye 104 gas chromatographs equipped with an integral device Kent Chromalog 2 were used. Detection of the column effluent was by means of a flame ionization detector and a thermal conductivity cell. Gas chromatographic–mass spectrometric (GC–MS) analysis were performed on an LKB-9000 mass spectrometer. The trapping procedures and chromatographic conditions were the same as for GC. The separations were carried out with 2 m × 2 mm I.D. glass columns packed with Porapak Q (60–80 mesh) (Waters Assoc., Milford, MA, U.S.A.), Tenax GC (60–80 mesh) (Chrompack, Middelburg, The Netherlands), molecular sieves 5A (50–80 mesh) (Alltech, Arlington Heights, IL, U.S.A.), Chromosorb W AW (80–100 mesh) coated
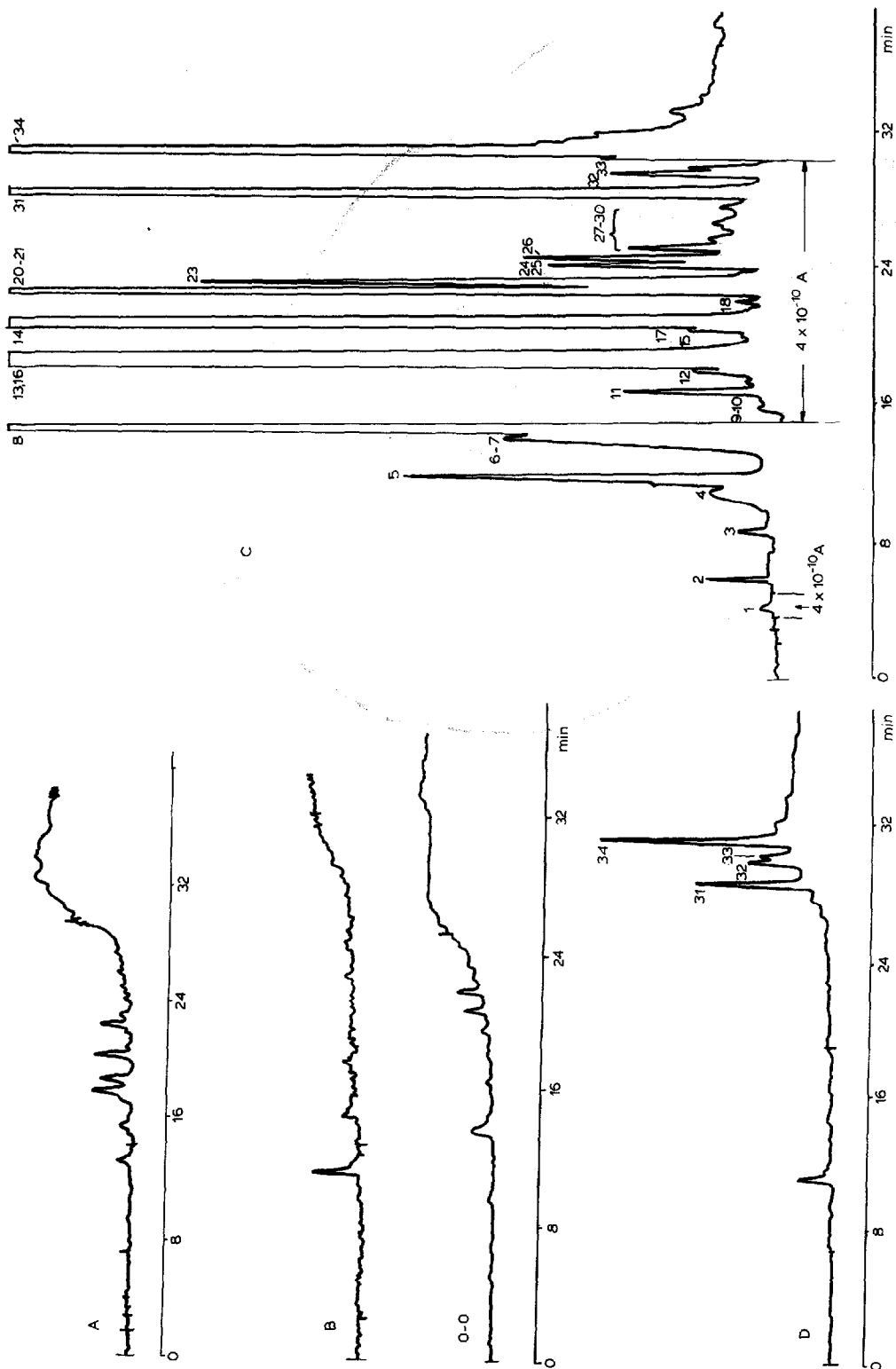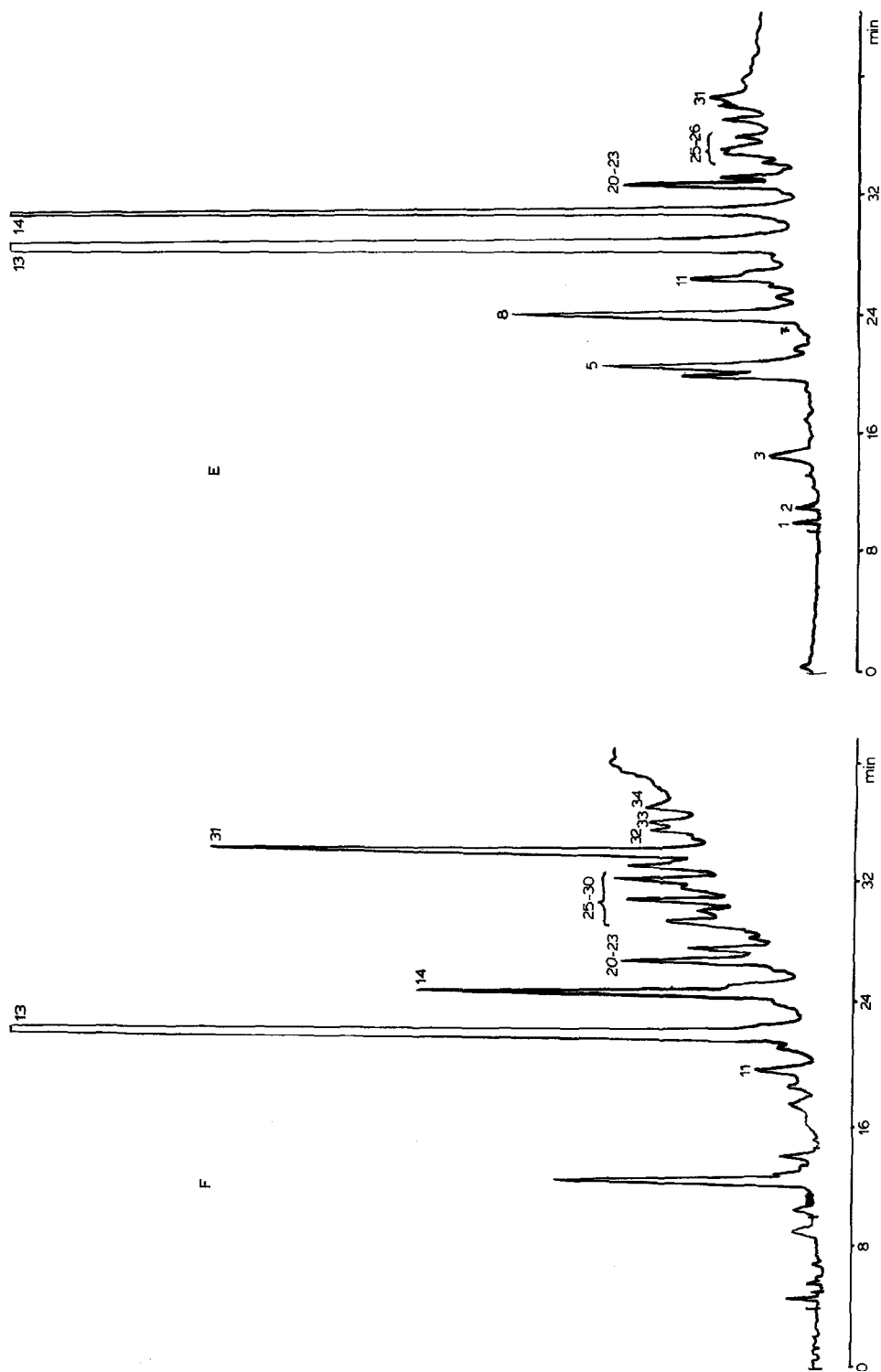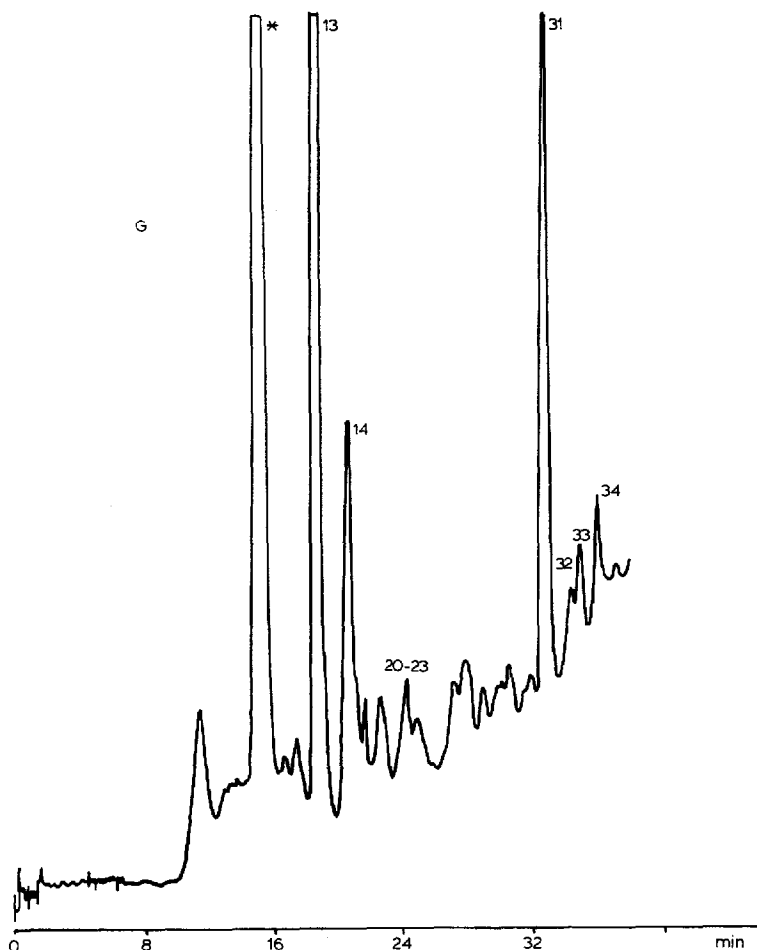
Fig. 2.

Fig. 2. Separations obtained with a Pye 104 gas chromatograph and a glass column of Tenax GC (2 m × 2 mm I.D.). Carrier gas (helium) flow-rate: 21 cm³/min. Temperatures of injector and flame ionization detector: 250°C. Electrometer sensitivity: 10^{-11} A (attenuator × 4). Temperature programme: initial, room temperature for 4 min, then raised at 8.5°C/min to 300°C, isothermal for 8 min. Thermal desorber programmed at 100°C/min to 300(350)°C, then isothermal for 8 min. Column inlet frozen at liquid nitrogen temperature during injection from the sampling trap. (A) Blank chromatogram for a standard trap containing Tenax GC; no sampling. (0-0) Blank chromatogram of the column. (B) Blank chromatogram of a control trap containing Tenax GC; no sampling. (C) Chromatogram of volatile components from a gas sample. Collection site: Lower Koshelevskii thermal field, well 10a. (D) Repeated chromatogram of the same sample, desorption temperature 350°C. (E) Chromatogram of volatile components from a gas sample. Collection site: East Pauzhetskii thermal field, fumarole. The column inlet was cooled to −196°C for 8 min, then a linear temperature porogramme from 20 to 300°C at 10°C/min was applied. (F) Chromatogram of an effluent water sample, from a fumarole, using the purge and trap technique. (G) Chromatogram of organic compounds recovered from an aqueous sample by direct collection in the trap. The asterisk indicates an artifact peak.

with 3% OV-225, both from Varian Aerograph. A capillary column (100 m × 0.3 mm I.D.) containing UCON 50HB-2000 was used (Perkin-Elmer).

Quantitative measurements of the compounds were made by comparing the peak areas of the sample with those of calibration mixtures. Calibration solutions

TABLE I

POSSIBLE QUANTITATIVE CHANGES IN THE CONCENTRATION (ARBITRARY UNITS) OF THE SAMPLE IN GLASS BOTTLES WITH INJECTOR OR CAP HAVING A SILICONE RUBBER SEPTUM*

Component	Time (days)		
	0	5	30
Propane	800	800	780
2-Methylpropane	99	96	86
n-Butane	173	132	100
2-Methylbutane	38	31	13
n-Pentane	44	24	7

* For example, Microsep F-174.

with concentrations of 10 000, 1000, 100 and 10 ppm (w/w) were prepared in tetrachloromethane and o-xylene for benzene, toluene, o-xylene, naphthalene and n-hexane on the same day as the analysis.

RESULTS AND DISCUSSION

Some difficulties were encountered in the quantitation of organic compounds in the geothermal sample. The sampling techniques used previously[18] could not provide accurate quantitation of the (hydrocarbon) abundance for carbon numbers above five. Control measurements using bottles with different types of silicone rubber (including PTFE coating) seals showed significant losses of hydrocarbons during the first days of storage (Table I).

Attention was given previously[19,20] to the accidental formation of compounds as a result of flame sealing. Glass with a low melting point (Type S 52-1) (U.S.S.R.) was used. Insignificant amounts of olefins (<0.005%, w/w) can be formed due to flame sealing of 200-cm³ ampoules (Fig. 1B), filled with a propane–butane mixture.

Field and laboratory analyses of gas samples have been reported[7,21].

Fig. 2B shows a blank chromatogram of a control trap which underwent all methodological and analytical operations. Fig. 2A presents a blank chromatogram of a control trap of the traditional type. The comparison of the chromatographic profiles indicates that during storage and transportation of a polymer in the trap (Fig. 1C) there is no contamination by impurities from the atmosphere.

The series connection of traps used for sampling of the geothermal gases showed that n-hexane may break through a sorbent layer if the sample volume is 400–450 cm³.

It is evident from the chromatogram (Fig. 2G) of the sample taken from the aqueous condensate that aromatic hydrocarbons represent the main constituents. However the separation using direct injection into a column was not satisfactory due to the large amount of water.

The repeated gas extraction of the aqueous samples showed that naphthalene is not completely extracted from the condensate, 5–15% being left behind.

Check, control and analysis procedures allow an estimation of the sample contamination level, the recovery, qualitative and quantitative composition (Fig. 2A–G). Except for the volatile compounds, the composition was refined by use of a capillary column (Fig. 3).

Table II presents the results of the analyses of organic compounds with concentrations $\geqslant 1$ ppm (w/w). This limit is due to contamination during storage and procedures preceding the analysis. It does not complicate estimation of the relationships between the main classes of organic compounds. The GC analysis showed that the net concentration of aromatic hydrocarbons with $T_{boiling} = 80–220°C$ is comparable with that of $C_2–C_{11}$ alkanes, and that cycloparaffins are present in relatively small amounts. The sample volume was *ca.* 10–300 cm^3, with flow-rates of 20-40 cm^3/min. The systematic error in the measurement of sample volume (STP) was not higher than 8% and consists of errors due to changes in atmospheric P, T conditions (2%), of the volume determination during the sampling by syringe (5%) and probably a correction factor of gas humidity of 5%.

Comparison of the results for the Lower Koschelevskii and East Pauzhetskii thermal fields revealed the similarity in the distribution of $C_1–C_5$ alkanes, benzene–alkylbenzenes and naphthalene–alkylnaphthalenes. Similar results have been reported by Nehring and Valette-Silver[22]. Apparently, the observed hydrocarbon composition and their relationships are associated with the deep geothermal origin. It is important to note that aromatic hydrocarbons are predominant in the $C_6–C_{10}$ range.

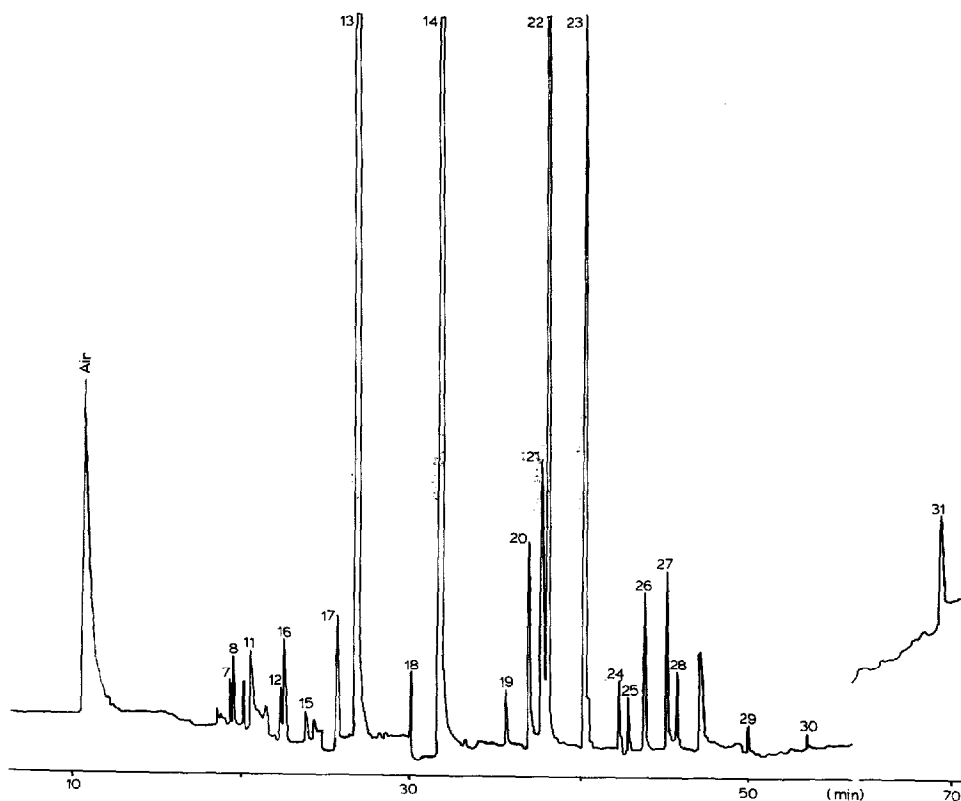Fig. 3. Separation of volatile organic components obtained with an LKB-9000 chromatograph and a nickel column (100 m × 0.3 mm). Carrier gass (helium) flow-rate: 2 cm^3/min. Injector and separator temperatures: 130°C. Desorption temperature: 300°C. The sample effluent was split in the ratio 1:25. Column inlet frozen with liquid nitrogen for 6 min. Column temperature programme: initial, room temperature, then raised at 2°C/min to 150°C.

TABLE II

CONCENTRATIONS OF ORGANIC COMPONENTS (ppm, w/w) IN THE GAS PHASE FROM WELLS AND A FUMAROLE

A + sign indicates that the compound was identified.

Compound		Wells			Fumarole gas vapour (water phase) September 1983
		No. 9 August 1981	No. 9 August 1982	No. 10a August 1982	
1	Methane	122 100	121 860	46 800	10 000
2	Ethane	6000	6426	2600	38
3	Propane	2100	2458	778	13
4	2-Methylpropane	282	341	92	2.5
5	n-Butane	420	552	161	3.5
6	2,2-Dimethylpropane	9	6	3.5	
7	2-Methylbutane	113	100	31	1
8	n-pentane	126	130	42	1
9	Cyclopentane	+	+	+	
10	Hexane isomers	+	+	+	
11	n-Hexane	+	25	15	< 1
12	Cyclohexane	+	+	+	
13	Benzene	1930	1560	2028	54 (15)*
14	Toluene	750	629	650	6 (2.5)
15	Methylcyclohexane		+	+	
16	n-Heptane	+	20	13	
17	n-Octane	+	16	9	
18	n-Nonane	+	9	6	
19	n-Decane	+	7	2	
20	Ethylbenzene	33	26	39	
21	p-Xylene	43	30	47	1.5 (1)**
22	m-Xylene	196	144	191	
23	o-Xylene	145	90	154	
24	n-Undecane		8	1	
25	Propylbenzene	+	6	3	
26	Methylethylbenzene	+	13	6	+ (1)**
27–30	ΣC3-benzenes, possible C4-benzene	+	65	36	
31	Naphthalene	+	201	61	1 (4)
32	1-Methylnaphthalene	+	+	+	(+)
33	2-Methylnaphthalene	+	+	+	(+)
34	Biphenyl	+	+	+	(+)

* Values in parentheses were obtained for the gas phase.
** The total content of C_2-benzenes and C_3-benzenes was determined.

It was suggested previously[23] that geothermal hydrocarbons can be redistributed fractionally. The fluid mixture artificially separated *in situ* into a gas and a condensate at 30–40°C and $P = 1$ atm confirms this. The abundance of benzene, toluene, xylenes and ethylbenzene, naphthalene in an aqueous condensate is 30, 40, 60, 380% respectively of their abundance in the gas phase (Table II, last column). In real cases and under different conditions the fractionation could be more complicated but, obviously, with enrichment of an aqueous condensate by high-molecular-weight compounds.

The use of the preliminary concentration on polymer sorbents together with the method of gas sampling allows an improvement in geochemical analysis. Un-

doubtedly, the data presented in Table II about volatile organic compounds should be taken into account when considering the origin of geothermal hydrocarbons and the rôle of organic substances in this natural phenomenon.

CONCLUSIONS

The investigations made it possible:

(1) To estimate the quantitative and qualitative features of the C_1–C_{12} organic compositions in high-temperature geothermal fluids.

(2) To show that under hydrothermal conditions, hydrocarbon fractionation may occur, resulting in enrichment of condensation waters with high-molecular-weight compounds.

(3) To show that the aromatic hydrocarbons are predominant in the range C_6–C_{10}, *i.e.*, aromatic hydrocarbons: (n-alkanes + cycloalkanes) $\gg$ 10.

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