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SINGLE-STEP CAPILLARY COLUMN GAS CHROMATOGRAPHIC METHOD FOR EXTRACTION AND ANALYSIS OF SUB-PARTS PER BILLION (10^9) AMOUNTS OF HYDROCARBONS (C_2 – C_8) FROM ROCK AND CRUDE OIL SAMPLES AND ITS APPLICATION IN PETROLEUM GEOCHEMISTRY

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SUMMARY

A method has been developed for the extraction and analysis of trace amounts of hydrocarbons (C_2 – C_8) in rock samples in a single-step, rapid procedure (complete analysis time *ca.* 40 min). A crushed rock sample (less than 1 g) is placed in the flow system of a capillary column gas chromatograph, the carrier gas serving as the stripping gas. Splitless introduction of the hydrocarbons accumulated in a cold trap ensures a high sensitivity ($10^{-9}\%$, w/w, of rock). Isothermal gas chromatographic analysis allows the application of Kováts retention indices for compound identification. With a slight modification, the hydrocarbon composition of crude oils can be determined by the same procedure. Applications of this type of analysis to petroleum geochemistry are described, involving both hydrocarbon amounts and their molecular composition.

INTRODUCTION

Geochemical studies of light hydrocarbons (molecular range $<C_{10}$) have demonstrated their ubiquitous occurrence in most sedimentary rocks.

For investigations concerning the origin, migration and accumulation of crude oil and natural gas in the subsurface, light hydrocarbons in rock samples have been measured using various extraction techniques combined with gas chromatographic (GC) analysis^{1–8}. Most of these procedures have analytical limitations that reduce their application for routine work in petroleum geochemistry, *e.g.*, large sample requirements, compositional fractionation effects, restricted overall sensitivity with respect to sample size or excessive time requirements.

The method described in this paper combines several advantages, such as small sample size requirements (<1 g of rock), short analysis time (about 40 min), detailed compositional results derived from capillary column GC, high sensitivity (the lowest detectable amount is about $10^{-9}\%$, w/w, of rock), minor fractionation over the complete molecular range and application to crude oil analysis.

The concept of the method is similar to the so-called thermovapourization

technique of Jonathan *et al.*⁹. A detailed description of our method, including the analytical details and limitations, has been published elsewhere¹⁰.

In this work, the method has been applied to some problems encountered in petroleum geochemistry, *e.g.*, detection of light hydrocarbon generation in subsurface sediments, source rock-crude oil correlation based on light hydrocarbon compositional similarities.

EXPERIMENTAL

The analytical apparatus, shown schematically in Fig. 1, consists of a capillary column gas chromatograph that has been substantially modified. For the extraction procedure, a glass tube containing the freshly crushed rock sample and a small portion of granulated dry calcium chloride (No. 9 in Fig. 1) is placed between cold trap (No. 10 in Fig. 1) and carrier gas supply. The sample is stripped by passing a measured volume of hydrogen through the tube at ambient temperature. For this purpose the hydrogen flow-rate is held constant by an all-metal flow controller (Siemens, No. 3 in Fig. 1). As only a fraction of the light hydrocarbons present in the rock is recovered by this method, it is essential that measurements be made under constant conditions with respect to temperature, gas flow-rate and volume.

The back-flush technique employed here is based on Deans' principle of column switching¹¹. The design of the T-union (No. 13 in Fig. 1) is derived from suggestions of Schomburg and co-workers^{12,13}.

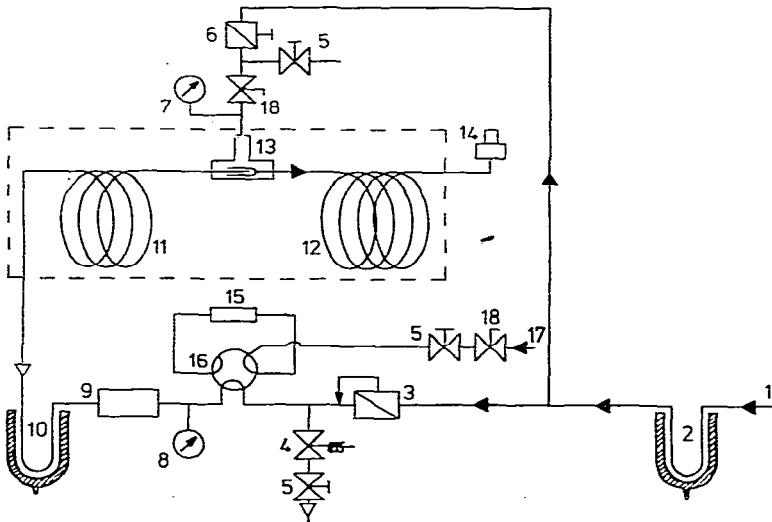


Fig. 1. Schematic representation of capillary column chromatographic system for light hydrocarbon analysis of rock samples using hydrogen stripping. 1 = Hydrogen inlet; 2 = hydrogen purification trap; 3 = flow controller; 4 = solenoid valve; 5 = needle valve; 6 = pressure regulator; 7, 8 = pressure gauges; 9 = sample extraction tube; 10 = cold trap; 11, 12 = capillary column; 13 = T-union; 14 = flame-ionization detector; 15 = gas loop; 16 = six-port valve; 17 = inlet for external standard; 18 = on-off by-pass valve; closed arrows, direction of gas flow; open arrows, reversed flow during back-flush.

Once the sample tube has been replaced with an empty glass tube, GC analysis is started by removing the liquid nitrogen from the cold trap. Subsequent splitless GC analysis is performed isothermally, and hence the components can be identified by their Kováts retention indices. Details of the hydrogen stripping and GC analysis parameters are summarized in Table I.

TABLE I

ANALYTICAL CONDITIONS FOR EXTRACTION AND GAS CHROMATOGRAPHY OF LIGHT HYDROCARBONS (C₂-C₈) FROM ROCK SAMPLES

<i>Operation</i>	<i>Parameter</i>	<i>Condition</i>
Extraction	Stripping gas	Hydrogen
	Flow-rate	10 ml/min
	Stripping time (volume)	10 min (100 ml)
	Temperature	Ambient (22°)
	Sample weight	≤ 1 g
	Sample particle size	0.6-2 mm
GC analysis	Column:	
	Type	SCOT capillary
	Stationary phase	Squalane
	Length	45 m
	Diameter	0.5 mm
	Material	Stainless steel
	Carrier gas	Hydrogen
	Flow-rates:	
	First part (15 m length)	10 ml/min
	Second part (30 m length)	12.5 ml/min
	Reversed flow	10 ml/min
	Temperatures:	
	Oven	60°, isothermal
Flame-ionization detector	100°	

The conditions for light hydrocarbon analysis of crude oils are very similar. However, in order to prevent overloading the capillary, only short stripping times (about 1 min) are applied on a very small amount of crude oil (generally <0.1 mg). The main advantage of this type of crude oil analysis is the absence of any pre-treatment step. Further, the thermal degradation of sensitive compounds that may occur in the heated injection ports of normal gas chromatographs is avoided.

RESULTS AND DISCUSSION

Compound identification

A typical example of a chromatogram, showing the light hydrocarbon distribution of a rock sample from an exploration well, is shown in Fig. 2A. No back-flush was used in this instance. For comparison, Fig. 2B was obtained by utilizing the column back-flush system. Obviously, there is no baseline deviation observed due to flow switching.

Although the initial part of the GC separation is run non-isothermally (warming of sample cold trap), its effect on the precision of retention indices is of minor

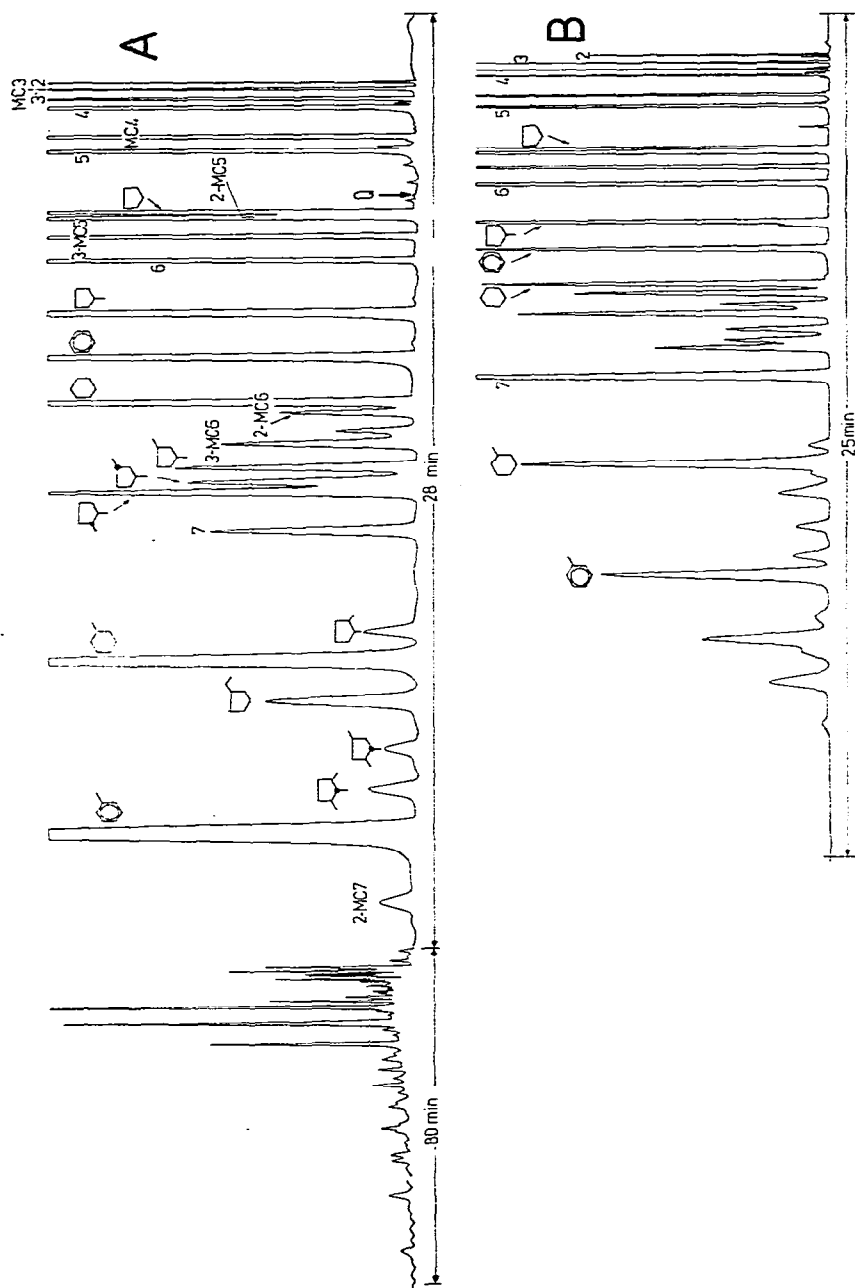


Fig. 2. Gas chromatograms of light hydrocarbons (molecular range C_2-C_7) obtained by hydrogen stripping of a typical rock sample. A, Without back-flush; B, with back-flush. Small peak between pentane and cyclopentane, marked Q in chromatogram A, represents the lowest detectable amount of $1.2 \cdot 10^{-11}$ g in this molecular range. Abbreviations used for peak identification (unless chemical structures are given): 2 = ethane; 3 = propane; 4 = butane; 5 = pentane; 6 = pentane; 7 = heptane; MC3 = isobutane; MC4 = isopentane; 2-MC5 = 2-methylpentane; 3-MC5 = 3-methylpentane; 2-MC6 = 2-methylhexane; 3-MC6 = 3-methylhexane; 2-MC7 = 2-methylheptane.

importance. The compounds are identified by comparison with literature data for both Kováts indices and their corresponding temperature coefficients¹⁴.

A small peak between pentane and cyclopentane in Fig. 2A, marked Q, represents the lowest detectable amount of about $1.2 \cdot 10^{-11}$ g in this molecular range.

Geochemical applications

Hydrocarbon generation in the subsurface. In order to show the increasing generation of hydrocarbons from the high-molecular sedimentary organic matter (kerogen) with increasing depth (and hence temperature), two rock samples (depth 1380 and 2050 m) from an exploration well were selected for comparison and the results are shown in Fig. 3. Both rock samples have almost identical organic carbon contents and belong to the same stratigraphic unit. Hence, the amounts of hydrocarbons generated (see Table II) differ, primarily owing to an increase in reaction rate with increasing temperature ($\Delta T \approx 30^\circ$). The ratios of certain hydrocarbon concentrations measured in both samples are listed in Table II and interpreted as generation indices in this particular geological situation. Generally, the lighter molecules

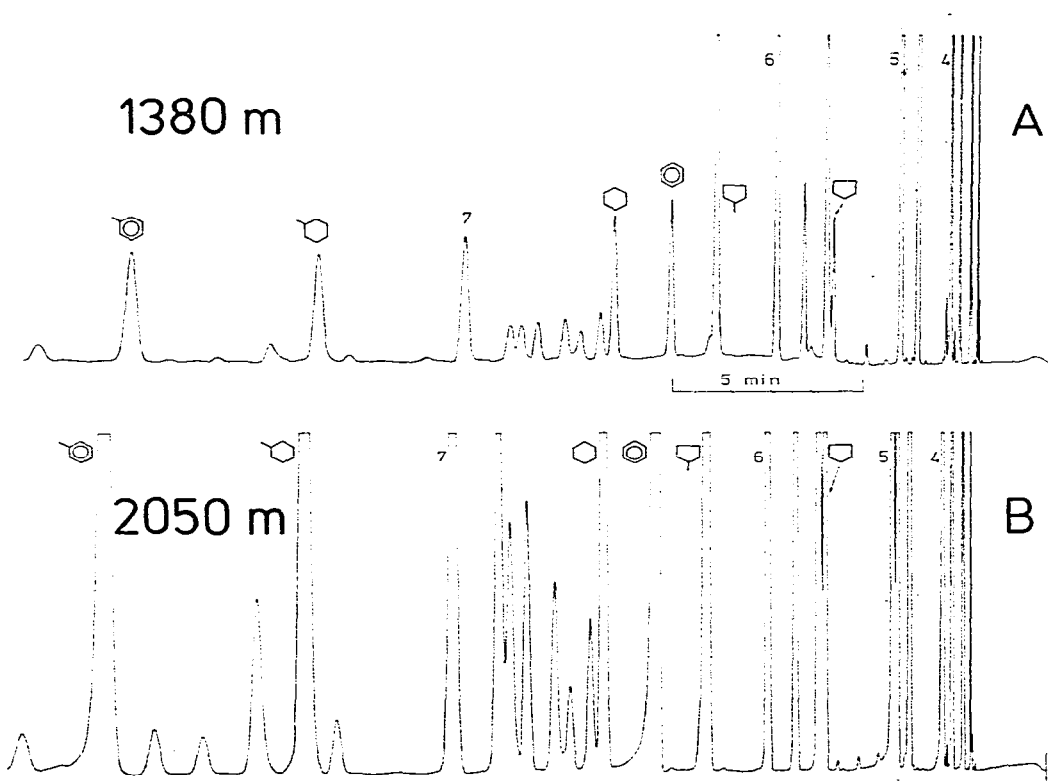


Fig. 3. Light hydrocarbons in two rock samples recovered from different depths (1380 and 2050 m) of an exploration well showing effect of subsurface temperature increase on generation of hydrocarbons. For peak identification see Fig. 2. Quantitative results for some selected compounds are summarized in Table II.

TABLE II

EFFECT OF BURIAL DEPTH (AND HENCE TEMPERATURE) ON GENERATION OF LIGHT HYDROCARBONS IN A SOURCE ROCK-TYPE SHALE

Both rock samples were from the same well and stratigraphic unit. For chromatograms see Fig. 3.

Parameter	Chromatogram (Fig. 3)		Generation index
	A	B	
Depth (m)	1380	2050	—
Sample weight (g)	0.82	0.89	—
Organic carbon content (wt.-%)	1.6	1.7	—
Concentration (ppb*)			
Butane	19.4	275	14
Pentane	18.4	129	7.0
3-Methylpentane	3.3	19.7	6.0
Hexane	8.5	27.4	3.2
Heptane	6.0	26.4	4.4
Benzene	4.5	101	22
Toluene	8.0	46.9	5.9
Cyclopentane	2.2	25.0	11
Methylcyclopentane	10.0	102	10
Cyclohexane	4.8	30.9	6.4
Methylcyclohexane	6.3	43.9	7.0

* ppb here means 10^{-9} g of hydrocarbon per gram of rock normalized to a 100-ml stripping gas volume.

are generated from the kerogen at higher rates than the heavier molecules during a temperature increase².

Oil-source rock correlation. Correlating crude oil and natural gas accumulations with the residual hydrocarbons in source rocks provides important information to the exploration geologist. Correlation based on hydrocarbons (molecular range $<C_{10}$), which represent main constituents of most crude oils, appears to be possible¹⁵. In the particular example described below, the possible genetic relationship between one oil sample and a series of rock samples collected between depths of 2250 and 3890 m in an exploration well was investigated. Fig. 4 shows the chromatograms of the crude oil (A) and four selected rock samples from different depths [2390 m (B), 2570 m (C), 3090 m (D) and 3750 m (E)] that are representative of certain intervals. The crude oil is characterized by relatively high cyclohexane-benzene and methylcyclohexane-toluene ratios (see Table III). Among the rock samples from this well only those from 2570 and 3750 m show a similar cycloalkane-aromatic hydrocarbon ratio. In particular, the match of the oil with the sample from 2570 m is almost perfect.

The results of a statistical evaluation¹⁶ of the same situation are shown in Fig. 5. Eight concentration ratios (methylbutane-butane, methylbutane-pentane, 2-methylpentane-3-methylpentane, cyclohexane-methylcyclopentane) were calculated from each chromatogram and subjected to cluster analysis¹⁷. The relationship between the oil and the hydrocarbons in the rock samples is demonstrated here by a diagram that shows the correlation coefficients between the measurements of the rocks and the oil as a function of depth. On the basis of a similarity limit of 0.80 for the correlation coefficient, two intervals show significant similarities with the oil, the shallow-

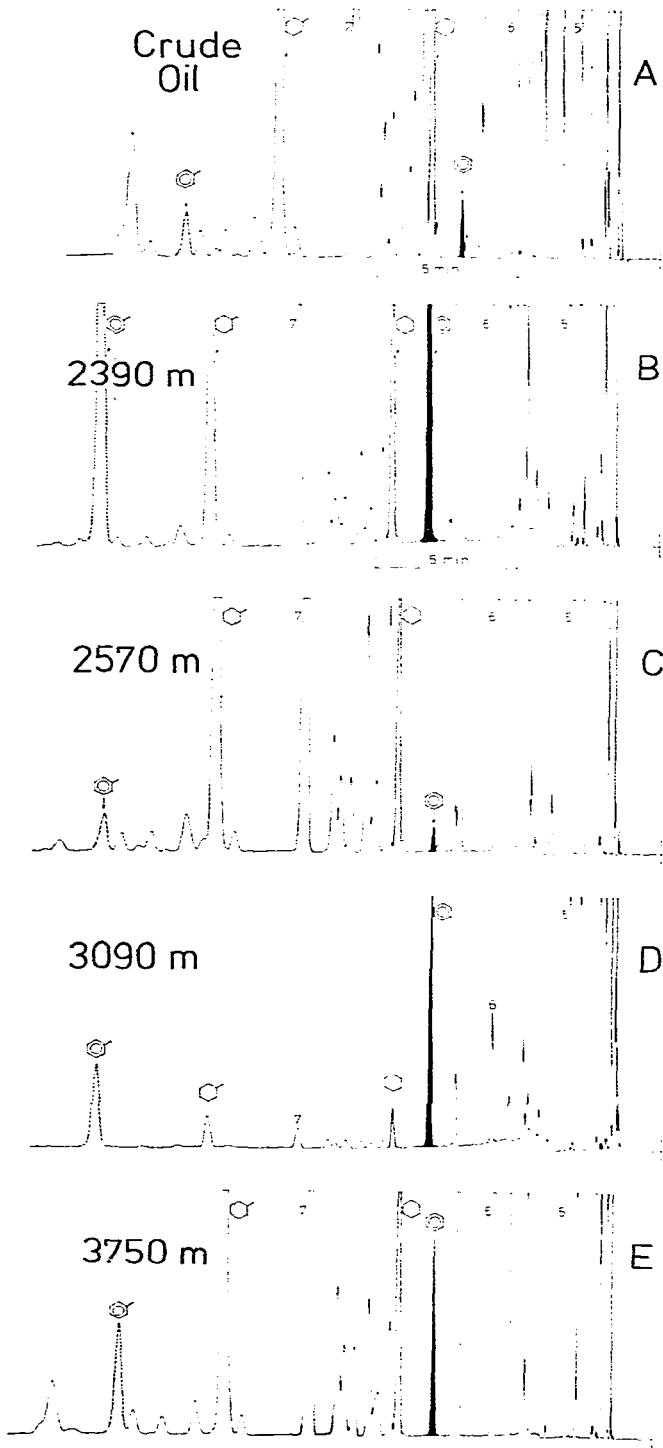


Fig. 4. Light hydrocarbon chromatograms of a crude oil (A) and four rock samples (B-E) whose hydrocarbon composition is representative for adjacent depth intervals in an exploration well. For peak identification see Fig. 2. Quantitative results of selected compounds (shaded peaks) are summarized in Table III.

TABLE III

COMPARISON OF LIGHT HYDROCARBON CONCENTRATION RATIOS IN A CRUDE OIL (A) AND FOUR SELECTED ROCK SAMPLES (B-E) FROM DIFFERENT DEPTHS OF AN EXPLORATION WELL

For chromatograms see Fig. 4.

Chromatogram (Fig. 4)	Depth (m)	Concentration ratio	
		Cyclohexane-benzene	Methylcyclohexane-toluene
A	Crude oil	20	13
B	2390	0.55	0.60
C	2570	21	16
D	3090	0.16	0.28
E	3750	4.1	4.0

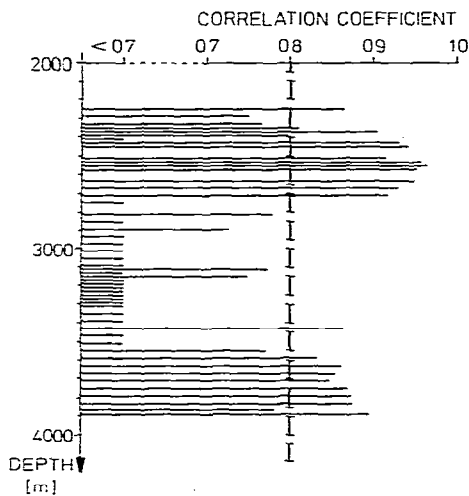


Fig. 5. Compositional similarities between oil and rock samples. Cluster analysis of one crude oil and 51 rock samples from an exploration well (see Fig. 4) based on eight different parameters (concentration ratios) calculated from light hydrocarbon data. The similarity values (correlation coefficients) between the rock sample and the oil sample are plotted against depth. A similarity limit of 0.80 is represented by a broken line.

er interval showing the greater similarity. This is in good agreement with the visual interpretation of the chromatograms shown in Fig. 4. From other geological informations it can be deduced that the interval represented by sample C is not a source rock, but a zone which is impregnated by migrated petroleum. The interval represented by sample E or the appropriate lateral equivalents can be considered as a likely source rock for the oil.

CONCLUSION

The method for combined extraction and GC analysis of light hydrocarbons in rock and crude oil samples might be extended in several ways. According to Fig.

2A the complete analysis in the molecular range $\geq C_8$ seems to be a promising development for producing additional chemical information. For this purpose it may be necessary to replace the steel capillary with a high-resolution glass capillary column and to incorporate a flow-switch system that ensures a higher precision of retention index measurements¹⁸. As a result of an increased separation efficiency, even in the molecular range discussed in this paper, new aspects might be encountered which could form the basis of further geochemical interpretation.

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