Journal of Chromatography, 363 (1986) 303–308
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 706

DIRECT GAS CHROMATOGRAPHIC DETERMINATION OF PRISTANE, PHYTANE AND THE CARBON PREFERENCE INDEX IN CRUDE OILS

ADNAN H. H. TAMEESH* and MAZIN H. HANNA
Petroleum Research Centre, Council of Scientific Research, Jadiriyah, Baghdad (Iraq)

(First received January 20th, 1986; revised manuscript received April 7th, 1986)

SUMMARY

The determination of pristane, phytane, the carbon preference index (CPI) and normal hydrocarbons up to C_{36} in crude oils was performed by direct injection of the crude oil into a gas chromatograph. The need to separate the hydrocarbon fraction from crude oil by liquid chromatography, which is commonly used in such work, was eliminated and the results were more reliable. The method employs a small precolumn embodied in the injector, a 25 m × 0.2 mm I.D. wall-coated open tubular SE-30 fused-silica analytical capillary column and a design for a carrier gas switching system. The method proved to be versatile, simple, rapid, efficient and reproducible to ±1.4% relative standard deviation.

INTRODUCTION

Pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) are isoprenoid compounds which play an important role in hypotheses concerning the transformation of natural source materials into petroleum. A knowledge of the concentrations of pristane and phytane together with the ratio of odd/even normal hydrocarbons in sediments and oils provides useful information about the maturation and diagenesis of such sediments or oils. More detailed information can be found elsewhere[1,2]. The procedure usually followed in determining pristane and phytane by gas chromatography was to separate by column liquid or thin-layer chromatography the paraffin fraction of the crude oil or shales[3] or via distillation of the crude oil and then to work with the cut in which these isoprenoids were concentrated[4]. Detailed separations of partial or complete resolution of diastereoisomers of isoprenoids could also be achieved using capillary gas chromatography and columns coated with either polar stationary phases or non-polar Apiezon L and $C_{87}H_{176}$ stationary phases[4–10]. Temperature programming and isothermal regimes have also been employed.

The aim of this work was to develop a rapid, simple, efficient and direct gas chromatographic method for determining pristane, phytane and the carbon preference index (CPI) in samples of crude oils in one straight run without partial preseparations of the samples by other techniques. Previous work on this topic could not be traced in the literature.

0021-9673/86/$03.50

EXPERIMENTAL

A Pye Unicam PU4500 (capillary version) temperature-programmed chromatograph with dual flame ionization detectors (Pye Unicam, Cambridge, U.K.) was used. The chromatograph was connected to a Pye Unicam 4800 Chromatography Video Control Centre via a universal analogue interface and linked to a dual-pen recorder. The column employed was a 25 m × 0.2 mm I.D. WCOT SE-30 fused-silica capillary (SGE, Melbourne, Australia). Helium of 99.996% purity (Air Products, New Malden, U.K.) was used as the carrier gas. The injection port and carrier tubing were modified as follows (see Fig. 1). Initially (mode A), the three-way valve (V_C) connected a–b, closing c, and valve A (V_A) closed, while valve B (V_B) opened. The carrier gas inlet was regulated via a pressure regulator (PR). The needle valves 1 and 4 (NV1 and NV4) were adjusted so that the flow-rate in the capillary column was about 1.2 ml/min with a splitting ratio of 1:20. In mode B, the three-way valve (V_C) connected a–c, keeping b closed. Also, valve A (V_A) was opened, valve B (V_B) was closed and the needle valves 3 and 2 (NV3 and NV2) were adjusted to ensure the same flow-rate in the capillary column. The time between injection of crude oil samples (0.5–1.0 μl) and switching from mode A to B could be adjusted according to the required carbon number range of the crude oil to be analysed.

The pre-column was a 7 cm × 4.0 mm I.D. stainless-steel tube packed with Chromosorb W AW (80–100 mesh) and was placed in the injector. The injector and detector temperature were 350°C and the column temperature was programmed from 100 to 300°C at 2°C/min.

RESULTS AND DISCUSSION

Different time lap adjustments between mode A and B switching system (Fig. 1) gave good flexibility for the selection of a particular cut in crude oil hydrocarbon

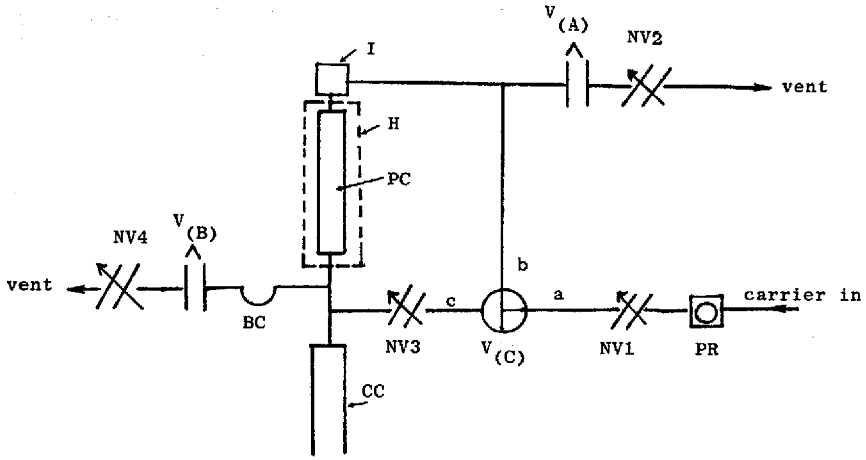

Fig. 1. Schematic diagram showing injector, pre-column and valve system used. NV = needle valve; $V_{(A)}$ and $V_{(B)}$ = on/off valves; $V_{(C)}$ = three-way valve; PR = pressure regulator; I = injector; H = injector heater; CC = capillary column; BC = buffer column; PC = pre-column.

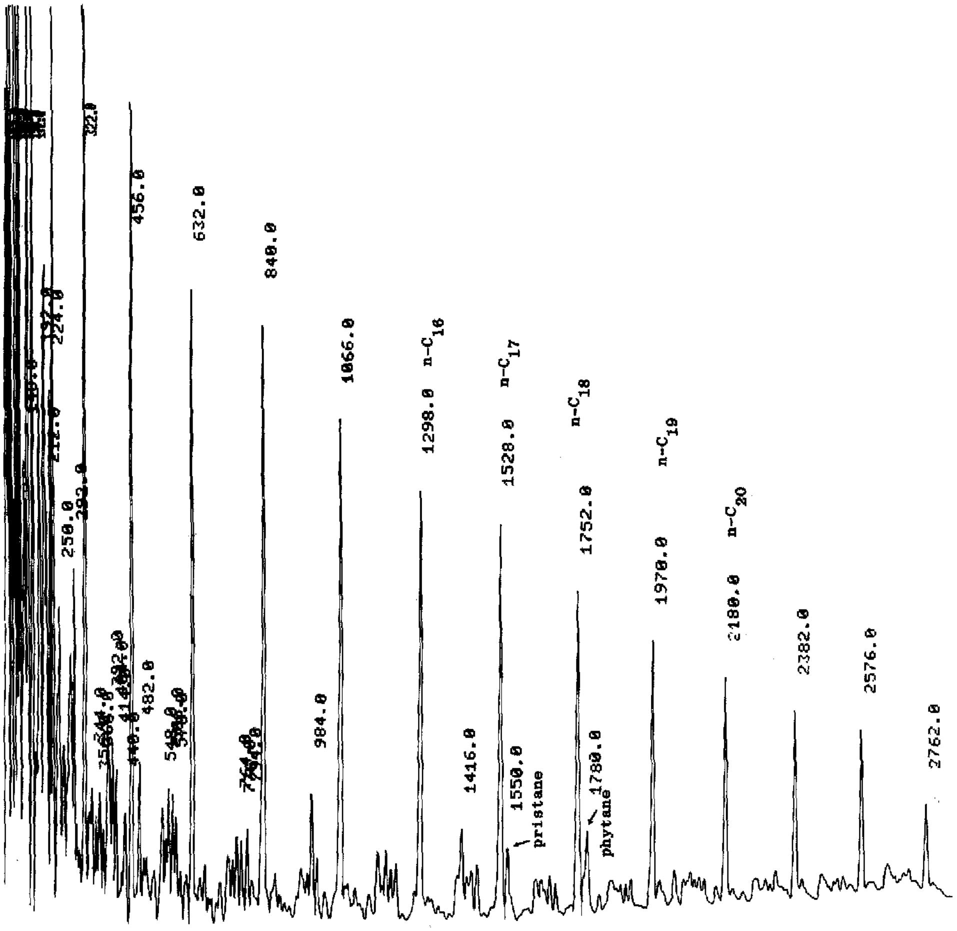

Fig. 2. Chromatogram showing direct analysis of crude oil with a 3-min time lap between switching from mode A to mode B.

analyses. This is demonstrated in Figs. 2, 3 and 4, which represent time laps of 3, 10 and 30 min, respectively. The hydrocarbons allowed to enter the analytical column were up to C_{23}, C_{25} and C_{36} for the corresponding times above. Thus, in an analysis requiring, for example, calculations of pristane, phytane, C_{17} and C_{18} ratios only, the present technique allows a much faster analysis, hence permitting a larger number of samples to be run per working day. Moreover, the time needed for sample preparation was reduced to the minimum as there was no need for column or TLC pre-separations or evaporation of solvents. This would also imply more accurate results because such pre-separations could result in erroneous measurements of pristane and phytane concentrations, as was demonstrated by Semkin *et al.*[11] when they passed *n*-hexane containing equal weights of pristane and phytane through a silica gel column and found that out of twenty eluted fractions, there were seven fractions containing more (up to 2 times) pristane than phytane.

Fig. 4 shows a representative detailed chromatogram of a crude oil run using the present method for the calculations of pristane, phytane, C_{17} and C_{18} concen-

Fig. 3. Chromatogram showing direct analysis of crude oil with a 10-min time lap between switching from mode A to mode B.

trations and CPI, *i.e.*, the ratio, by weight, of odd/even molecules. The CPI is calculated using the following equation[12]:

$$\mathrm{CPI} = \frac{1}{2}\left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}}\right)$$

Table I shows the results for CPI and pristane/phytane, pristane/C_{17} and phytane/C_{18} ratios for five different samples of crude oils. Table II shows a comparison of the above data when obtained by the present method and that commonly used

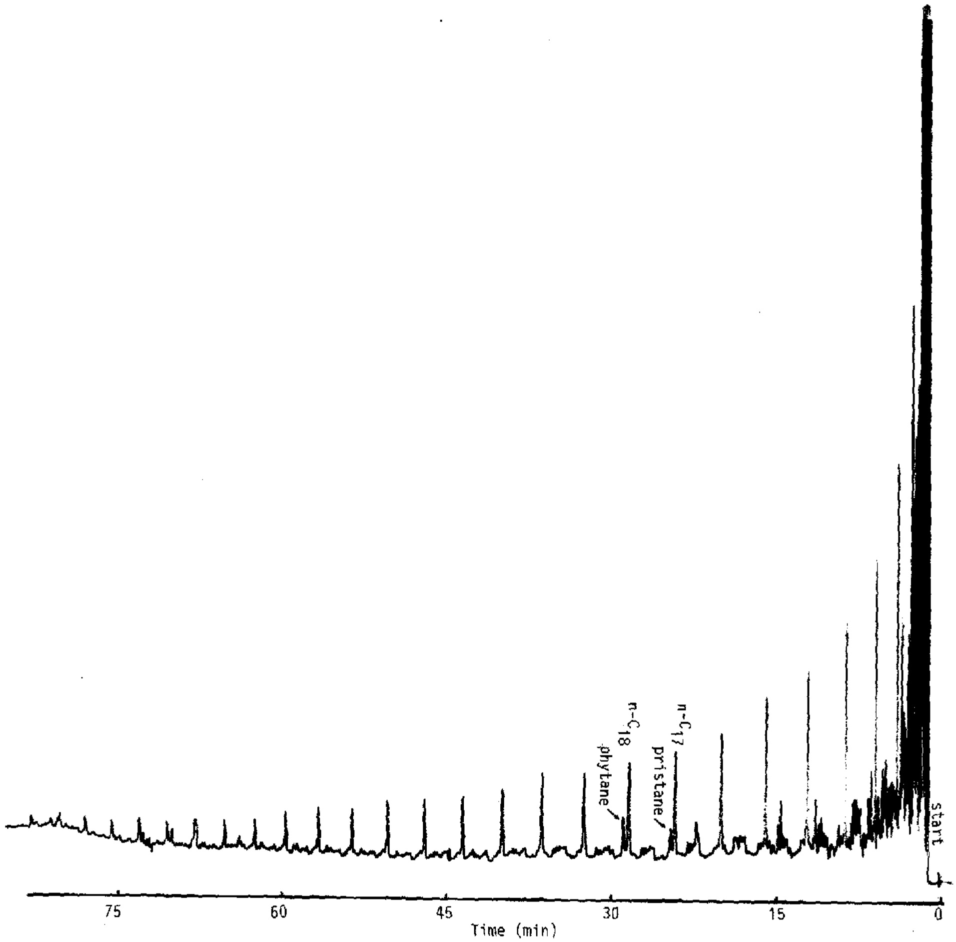

Fig. 4. Representative chromatogram for a crude oil analysis up to C_{36} by direct injection of sample and a 30-min time lap between switching from mode A to mode B.

TABLE I

CPI AND PRISTANE/PHYTANE, PRISTANE/n-C_{17} AND PHYTANE/n-C_{18} RATIOS FOR SOME CRUDE OILS

Crude oil sample No.	*CPI*	*Pristane/ phytane*	*Pristane/ n-C_{17}*	*Phytane/ n-C_{18}*
1	0.98	0.801	0.216	0.320
2	1.01	0.987	0.357	0.417
3	0.95	0.869	0.357	0.469
4	0.96	0.850	0.377	0.510
5	1.05	0.992	0.296	0.351

TABLE II

COMPARISON BETWEEN RESULTS OBTAINED BY PRESENT METHOD AND THE COMMONLY USED METHOD[3] FOR CRUDE OIL SAMPLE 1*

Method	*CPI*	*Pristane/ phytane*	*Pristane/ n-C_{17}*	*Phytane/ n-C_{18}*
This work	0.98	0.801	0.216	0.320
Ref. 3	0.98	0.846	0.225	0.310

* See Table I.

for using pre-separations of hydrocarbons by column chromatography and evaporation of the solvent[3]. The results found by the latter method indicated that there was a slight increase in pristane relative to phytane and their ratios to C_{17} and C_{18} normal hydrocarbons in comparison with the direct method used in this work. This observation is in accord with that of Semkin *et al.*[11]. It can be suggested that the adsorptivity of phytane is slightly higher than that of pristane on silica gel in a liquid chromatographic column when using a non-polar solvent such as *n*-hexane. This would result in uneven desorption rates of both isoprenoids in such a separation process.

The reproducibility of the method was investigated and the results showed that when the same sample was run four times, the results were reproducible to ±1.4% relative standard deviation.

The pre-column used can be applied in up to five runs, after which a fresh column is desirable.

ACKNOWLEDGEMENTS

The authors thank Dr. Yehya Kassim Al-Habah, Director of Geological Laboratories, Iraqi National Oil Co., Baghdad, for his interest, useful discussions and supply of some samples of crude oils. Thanks are also due to Mr. A. K. Abdul-Sada for his help with some of the experimental work.

REFERENCES

1 B. P. Tissot and D. H. Welte (Editors), *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, Springer, New York, 1978.

2 W. G. Meinschein, in G. Eglinton and M. T. J. Murphy (Editors), *Organic Geochemistry, Methods and Results*, Springer, New York, 1969, Ch. 13.

3 A. Y. Huc and J. G. Roucaché, *Anal. Chem.*, 53 (1981) 914.

4 H. Borwitzky and G. Schomburg, *J. Chromatogr.*, 240 (1982) 307.

5 R. L. Patience, D. A. Yon, G. Ryback and J. R. Maxwell, in A. G. Douglas and J. R. Maxwell (Editors), *Advances in Organic Geochemistry 1979*, Pergamon, Oxford, 1980, p. 287.

6 A. S. Mackenzie, R. L. Patience and J. R. Maxwell, *Geochim. Cosmochim. Acta*, 44 (1980) 1709.

7 R. L. Patience, S. J. Rowland and J. R. Maxwell, *Geochim. Cosmochim. Acta*, 42 (1978) 1871.

8 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.

9 R. E. Cox, J. R. Maxwell, R. G. Ackman and S. N. Hooper, *Can. J. Biochem.*, 50 (1972) 1238.

10 J. R. Maxwell, R. E. Cox, R. G. Ackman and S. N. Hooper, in H. R. von Gaertner and H. Wehner (Editors), *Advances in Organic Geochemistry 1971*, Pergamon, Oxford, 1972, p. 277.

11 V. I. Semkin, S. K. Lezina and M. S. Vigdergauz, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 27 (1984) 215; *C.A.*, 100 (1984) 159142c.

12 E. E. Bray and E. D. Evans, *Geochim. Cosmochim. Acta*, 22 (1961) 2.