DETERMINATION OF HIGH-MOLECULAR-WEIGHT *n*-ALKANES OF PETROLEUM ORIGIN BY HIGH-TEMPERATURE GAS CHROMATOGRAPHY

Pavel ŠIMÁČEK[1,*], Daniel MAXA[2] and Gustav ŠEBOR[3]

Department of Petroleum Technology and Petrochemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail: [1] pavel.simacek@vscht.cz, [2] daniel.maxa@vscht.cz, [3] gustav.sebor@vscht.cz

Received February 23, 2007
Accepted June 3, 2007

This paper deals with the identification and determination of high-molecular-weight *n*-alkanes of petroleum origin using high-temperature gas chromatography (HTGC). Analysed samples, which were the concentrates of saturated hydrocarbons, differed in both the total content of *n*-alkanes and their distribution. They were analysed on various types of HTGC columns differing in length and inner diameter. While the determined total content of *n*-alkanes was comparable for all the chromatographic columns, differences were found in the efficiency of separation of *n*-alkanes over C_{40} as well as in their quantitative elution.

Keywords: High-temperature gas chromatography (HTGC); Petroleum; Saturated hydrocarbons; High-molecular *n*-alkanes.

High-molecular-weight hydrocarbons (HMWHC) present in petroleum, together with asphaltenes, cause serious problems in petroleum transport and storage. HMWHC contain substances commonly referred as petroleum waxes. These compounds typically extend to about C_{70} in most types of petroleum. A few samples of petroleum have been shown to contain these compounds with the carbon number in the range C_{70}–C_{120} (refs[1–4]). Petroleum-derived waxes may be subdivided on the basis of their molecular weight and/or chemical character into two classes – macrocrystalline waxes and microcrystalline waxes. However, the division has not been exactly defined, and several other divisions of waxes can be found in literature. Macrocrystalline waxes are composed mainly of *n*-alkanes with 18 up to ca. 40 carbon atoms in their molecule, while microcrystalline waxes contain mainly branched alkanes and alkyl derivatives of naphthenes with the carbon number typically ranging from 30 to 60 (ref.[5]).

One of the most effective analytical methods for characterization of petroleum waxes is high-temperature gas chromatography (HTGC). In some

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 9, pp. 1295–1305

doi:10.1135/cccc20071295

petroleum samples, waxes are present in a concentrated form. Such samples can be directly analysed by HTGC after dilution with a suitable solvent. Characterization of petroleum tank bottom sludge, pipeline wax deposits or heavy waxy oils was reported[6–8]. On the other hand, in most cases it is necessary to enhance the wax concentration using suitable pre-separation steps. Wax precipitation is a commonly used method for enhancing their concentration[9,10]. This procedure is also used for gravimetric determination of waxes. Clearly, there are other methods enabling to enhance wax concentration, based on the formation of urea adduct[11] or extraction usually followed by preparative liquid adsorption chromatography[12]. An *n*-alkane concentrate can be prepared or first a maltene fraction is separated and subsequently a concentrate of saturated hydrocarbons which can be successively analysed by HTGC.

The first gas chromatographic analysis of waxes on packed columns was reported almost fifty years ago[13]. Peaks of *n*-alkanes C_{20}–C_{70} were resolved in urea-adducible substances, but their separation from other hydrocarbons was poor[13]. The practical temperature limit of most packed columns does not exceed 350 °C; therefore their use for HTGC is limited. The development of capillary columns (WCOT) with a high temperature limit up to 460 °C enabled elution of hydrocarbons with the carbon number higher than 70 and provided much better resolution of *n*-alkanes from other hydrocarbons. Satisfactory resolution of capillary columns caused the adoption of capillary gas chromatography as the ASTM standard test method for the determination of *n*-alkanes in petroleum waxes (C_{16}–C_{44}).

Today, HTGC has a widespread use for simulated distillation (SIMDIST) of various petroleum samples. HTGC also enabled the identification and (semi)quantification of *n*-alkanes in petroleum samples, in which the presence of *n*-alkanes was not assumed. It is possible to use short (3–12 m) wide-bore (0.53 mm ID) capillary columns for characterization of *n*-alkanes in petroleum waxes, but their separation from other hydrocarbons may be insufficient in this case. On the other hand, the use of one column for SIMDIST and simultaneously for wax analysis can be advantageous. Jokuty et al.[12] reported a method for the determination of wax content in petroleum. This procedure consists in isolation of high-boiling saturated hydrocarbons and a subsequent HTGC analysis under standard SIMDIST conditions. Gupta and Severin[14] used a 12 m long, 0.53 mm ID capillary column for the analysis of waxes derived from various Indian petroleum samples. Neto et al.[8] suggested short (3–8 m) and thin (0.32 mm ID or less) columns instead of 20-m or longer columns for high-temperature high-resolution gas chromatography. Del Rio and Philp[15] analysed many samples of microcrystalline waxes and petroleum using a 3-m capillary column.

The purpose of the analysis to be performed is a key factor for the choice of an appropriate chromatographic column. For example Del Neer and Deo[16] used two different columns for the determination of the carbon number distribution of various types of petroleum. A 30-m thin column was used for the characterization of C_5–C_{44} hydrocarbons and a 5-m column with a worse resolution for the characterization of C_{20}–C_{90} hydrocarbons. They found[16] that both columns provided almost the same results in an overlapping region (C_{20}–C_{44}). If the carbon number distribution over C_{20} is the only thing to determine, it is effective to use a short column with a short analysis time. For a better separation of *n*-alkanes, modern longer (15–30 m) narrow-bore (0.32 or 0.25 mm ID) HTGC columns could be more suitable[4,17,18].

In this work, the determination of the total content of high-molecular-weight *n*-alkanes of the petroleum origin and their separation according to the carbon number by HTGC was carried out using capillary columns of different size. Available non-polar or slightly polar metal capillary columns were chosen for the analyses. High-temperature limit was the most important parameter of the columns in order to achieve complete elution of high-molecular-weight hydrocarbons. Polyimide coated fused-silica columns were not tested, because they usually have lower temperature limit (they become fragile at temperatures over ca. 350 °C). Acceptable analysis time (less than one hour) was the second criterion for the choice of analytical column. The results obtained are compared and discussed. So far such a comparison has not been performed.

EXPERIMENTAL

Analysed Samples

For the determination of *n*-alkanes, five samples of petroleum origin differing in the total content of *n*-alkanes and their distribution were chosen. Characteristics of the samples are presented in Table I.

HTGC Analysis

Four HTGC capillary columns were used for analysis. The length of the columns varied from 5 to 30 m and ID from 0.28 to 0.53 mm. All the columns were coated with a non-polar stationary phase. A brief characteristics of the columns used is in Table II.

Although all the analysed samples were “clean”, a guard column was placed before every analytical column using MVSU Mini-Union (SGE) as a connector. Samples were dissolved in carbon disulfide and introduced to the gas chromatograph Trace 2000 (CE Instruments) using an on-column injector. The oven temperature was held at 40 °C for 2 min and then increased at a rate of 15 °C/min to 370 °C for column C and to 410 °C for the others. Then the final temperature was held for 20 to 40 min. A constant flow of helium was set to 1 ml/min for column C and 5 ml/min for the others. The temperature of FID detector was set to 430 °C.

Calculation of the *n*-alkanes content was based on the evaluation of corrected chromatograms obtained by subtraction of a blank run. Integration of *n*-alkane peaks was performed using a valley-to-valley baseline construction. The content of corresponding *n*-alkanes (in wt.%) was calculated using the area of individual *n*-alkane peaks and total area of chromatogram. It was assumed that the FID response is equal for all hydrocarbons. This assumption is acceptable because the analysed samples contained in fact only saturated hydrocarbons.

TABLE I
Characteristics of the analysed samples of petroleum origin

Sample No.	Characteristics
1	Feedstock for steam cracking (distillation residue of the product of hydrocracking)
2	Concentrate of saturated hydrocarbons separated from petroleum[a])
3	Concentrate of saturated hydrocarbons separated from an urea adduct fraction of petroleum[a])
4	Concentrate of saturated hydrocarbons separated from petroleum storage tank deposits[a])
5	Saturated hydrocarbons separated from toluene-insolubles obtained from petroleum vacuum residue visbreaking[a])

[a] The saturated fractions were obtained using liquid adsorption chromatography on silica gel impregnated with silver nitrate.

TABLE II
Characteristics of the GC columns

Column	Material	*L* m	ID mm	Film µm	Column	Manufacturer	Max. temperature °C
A	Steel	5	0.53	0.17	CP-SimDist	Varian	450
B	Steel	10	0.53	0.17	CP-SimDist	Varian	450
C	Steel	30	0.28	0.10	MXT®-1	Restek	400
D	Al	25	0.53	0.15	HT 5	SGE	460

To quantify and compare the efficiency of the chromatographic columns used, three values of resolution R were calculated for each column using the following formula:

$$R = 2(t_{n+4} - t_n)/1.699(w_n + w_{n+4})$$

where t_n, t_{n+4} is the retention time (in s) of *n*-alkanes with n and $n + 4$ carbon atoms, respectively, w_n, w_{n+4} is the peak width (in s) at its half height for *n*-alkane with n and $n + 4$ carbon atoms, respectively, $n = 20, 30, 40$.

No special mixture was prepared for the calculation of column resolution. The data from chromatograms of sample No. 3 with the highest content of *n*-alkanes were used for this purpose.

RESULTS AND DISCUSSION

As it was mentioned above, the choice of an appropriate chromatographic column is very important in the analysis of petroleum samples by HTGC. The situation is more complicated if characteristics of samples containing compounds higher than C_{70} are required. Although modern long columns have high-temperature limits (mostly over 380 °C), the elution of high-boiling components can be difficult and total time of analysis unacceptably long. This drawback is sometimes compensated by raising final temperature, which often exceeds a maximal temperature limit given by a column manufacturer. This practice can cause a strong bleeding and a decrease in lifetime of the column used. In the case of low concentrations of high boiling *n*-alkanes, good resolution of a long thin column can contrast with its lower capacity and eluting too wide peaks in final isothermal run.

In conditioning of the chromatographic columns used, it was found that after several conditioning steps at temperatures exceeding 400 °C, aluminium chromatographic column (D) was broken. The column was very fragile in comparison with practically unbreakable and flexible metal (probably steel) columns. The risk of column rupture is relatively high, because there is usually some degree of mechanical stress near the injector, detector or in the connection with the pre-column. Therefore, aluminium column was not used for further work. Nevertheless, as it follows from literature, aluminium columns have been frequently used and the described problem has not been reported[14,19–21].

Although column C (T_{max} = 400 °C) was repeatedly carefully conditioned, it showed almost twice higher bleeding in the final isotherm than the other columns used. This column had the bleeding level about 50 mV at 370 °C while the other columns had bleeding less than 30 mV at 410 °C. However, this problem was not too important in the calculations of chromatographic peak areas, because the blank run was always subtracted from a chromatogram to eliminate the baseline drift.

Regarding the oven temperature rate, it was found the rate did not significantly influence the results of analysis. To reach an acceptable time of analysis, a relatively high oven temperature rate was used.

As an example, chromatograms of the analysed samples are presented in Fig. 1 for column C. All the chromatograms obtained using the other columns looked very similar, although the calculated column resolutions differed (Fig. 2). Table III summarizes the total contents of *n*-alkanes and their distribution determined for all the chromatographic columns and the samples used.

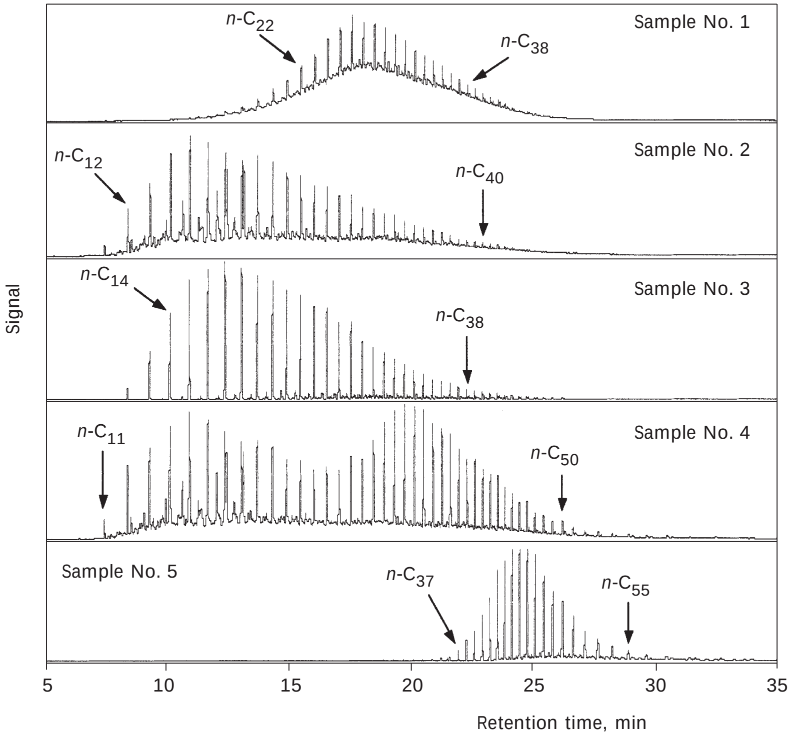

FIG. 1
Chromatograms of the analysed samples obtained using column C

TABLE III
Total content of *n*-alkanes and their distribution determined in the analysed samples

Sample No.	Column	First *n*-alkane	Last *n*-alkane	Total *n*-alkane wt.%
1	A	C_{12}	C_{47}	7.1
	B	C_{12}	C_{47}	7.6
	C	C_{12}	C_{48}	6.7
2	A	C_{11}	C_{47}	15.9
	B	C_{11}	C_{47}	16.2
	C	C_{11}	C_{50}	15.3
3	A	C_{12}	C_{62}	73.1
	B	C_{12}	C_{60}	73.6
	C	C_{12}	C_{61}	74.2
4	A	C_{10}	C_{70}	24.8
	B	C_{10}	C_{71}	26.3
	C	C_{10}	C_{69}	25.5
5	A	C_{19}	C_{80}[a]	49.3
	B	C_{19}	C_{80}[a]	52.4
	C	C_{19}	C_{70}	55.7

[a] Originally identified *n*-alkanes (see the text).

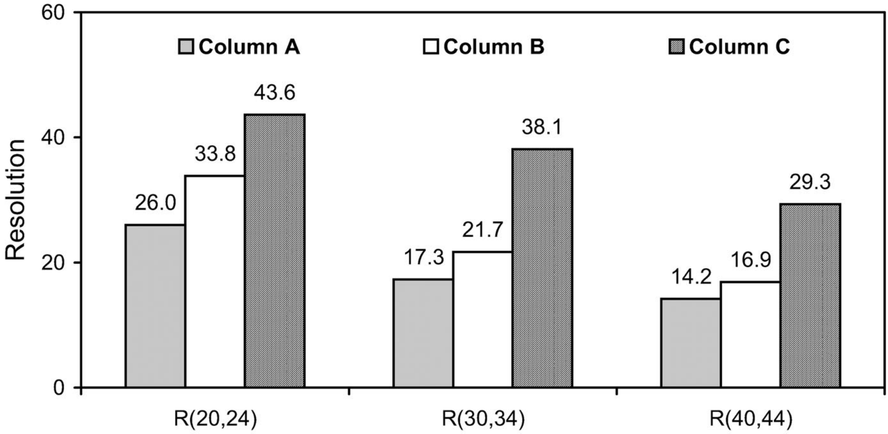

FIG. 2
Calculated resolutions (*R*) of the columns used

Differences among the total contents of *n*-alkanes determined on the individual chromatographic columns are not too significant. No systematic deviation depending on the number of carbon atoms of *n*-alkanes was found. The efficiency of the used columns influenced the shape of chromatographic curve and hence the area of the peaks integrated. Therefore some differences were found in the determined contents of individual *n*-alkanes. The worst accordance was observed for sample No. 1 in the range of C_{21}–C_{27} and for sample No. 5 containing the highest amount of high-molecular-weight hydrocarbons.

As expected, the best separation of peaks, nearly to baseline, was observed in the case of very high *n*-alkane content (sample No. 3). In chromatograms of other samples, typical shoulders could be observed regardless of which column was used. This is also the case of sample of petroleum deposits (Fig. 1, sample No. 4) containing relatively great amount of *n*-alkanes.

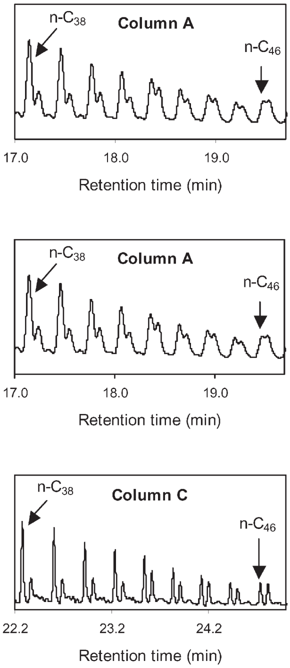

FIG. 3
Chromatograms of sample No. 3 in the range of C_{38}–C_{46}

The best resolution on column C influenced separation of *n*-alkanes in the sample of fraction giving urea adduct (sample No. 3). This effect is the most significant in the range over C_{40}, where peaks co-eluting on columns A and B were completely separated on column C (Fig. 3). This influenced the determined content of individual *n*-alkanes, which was in sample No. 3 very low (each <0.2 wt.%). Column C provided better separation of hydrocarbons over C_{40} also in other cases, as it is shown for sample No. 5 in Fig. 4.

The presence of *n*-alkanes over C_{70} in sample No. 5 is very probable, but it could not be confirmed on column C, because only hydrocarbons up to C_{70} were completely eluted from this column in a preset time (Fig. 5). This explains great differences in the carbon numbers of the last identified *n*-alkanes in this sample (Table III). Correct quantification of *n*-alkanes over C_{70} on columns A and B is not possible, but the total content of assumed *n*-alkanes C_{70}–C_{80} determined originally did not exceed 0.5 wt.%.

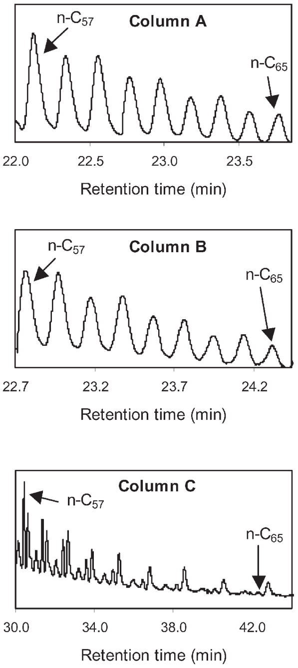

FIG. 4

Chromatograms of sample No. 5 in the range C_{57}–C_{65} (worse efficiency of columns A and B caused erroneous determination and identification of high-molecular-weight *n*-alkanes)

Regarding all the above-mentioned facts, it can be stated that the determined *n*-alkanes content need not always correspond to the real content in the analysed sample. In spite of this fact, HTGC makes possible to obtain valuable information about the total content and distribution of *n*-alkanes in various samples of petroleum origin.

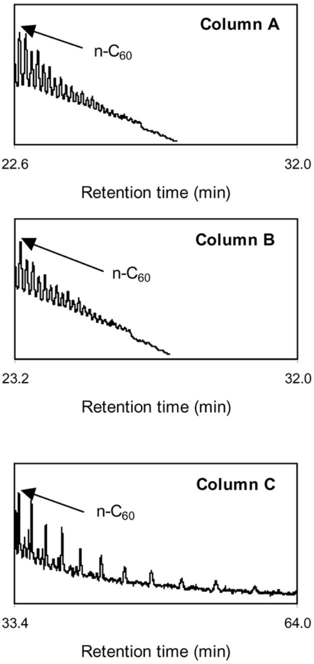

FIG. 5
Elution of hydrocarbons over C_{60} present in sample No. 5 (incomplete elution on column C due to low maximum allowable column temperature)

CONCLUSIONS

Although the efficiency of the chromatographic columns used in HTGC analysis differed, the differences in the total content of high-molecular-weight *n*-alkanes determined in samples of petroleum origin were not too significant. Regarding the determined contents of individual *n*-alkanes, no systematic deviation depending on their carbon number was found.

On the other hand, the efficiency of a chromatographic column influenced the determination of individual high-molecular-weight *n*-alkanes.

Relatively low resolution of the used chromatographic columns (A and B) and wrong integration of peaks corresponding to individual *n*-alkanes led to inaccurate results due to peaks overlapping in the region of C_{50}^{+} hydrocarbons. Although recommended for high-temperature applications, aluminium column showed poor mechanical strength and vulnerability to breakage after exposing to temperature above 400 °C.

The authors gratefully acknowledge the Ministry of Education, Youth and Sports of the Czech Republic (project No. MSM 6046137304).

REFERENCES

1. Lipsky S. R., Duffy M. L.: *J. High Resolut. Chromatogr.* **1986**, *9*, 376.
2. Lipsky S. R., Duffy M. L.: *J. High Resolut. Chromatogr.* **1986**, *9*, 725.
3. Philp R. P.: *J. High Resolut. Chromatogr.* **1994**, *17*, 398.
4. Thanh N. X., Hsieh M., Philp R. P.: *Org. Geochem.* **1999**, *30*, 119.
5. Mansori G. A.: http://www.uic.edu/~mansoori/Wax.and.Waxy.Crude_html.
6. Fazal S. A., Zarapkar S. S., Joshi G. C.: *Fuel Sci. Technol. Int.* **1995**, *13*, 881.
7. Roehner R. M., Fletcher J. V., Hanson F. V.: *Energy Fuels* **2002**, *16*, 211.
8. Aquino Neto F. R., Cardoso J. N., Santos Pereira A., Zupo Fernandes M. C., Caetano C. A., Castro Machado A. L.: *J. High Resolut. Chromatogr.* **1994**, *17*, 259.
9. Burger E. D., Perkins T. K., Striegler J. H.: *J. Petrol. Technol.* **1981**, *33*, 1076.
10. Philp R. P., Bishop A. N., Del Rio J. C., Allen J.: *Geological Society Special Publication* **1995**, *86*, 71.
11. Purhoit R. C., Agrawal K. M., Joshi G. C.: *Fuel Sci. Technol. Int.* **1993**, *11*, 665.
12. Jokuty P., Whiticar S., Wang Z., Landriault M., Sigouin N., Mullin J.: *Spill Sci. Technol. Bull.* **1996**, *3*, 195.
13. Ludwig F. J.: *Anal. Chem.* **1965**, *37*, 1732.
14. Gupta A. K., Severin D.: *Petrol. Sci. Technol.* **1997**, *15*, 943.
15. Del Rio J. C., Philp R. P., Allen J.: *Org. Geochem.* **1992**, *18*, 541.
16. Neer L. A., Deo M. D.: *J. Chromatogr. Sci.* **1995**, *33*, 133.
17. Killops S. D., Carlson R. M. K., Peters K. E.: *Org. Geochem.* **2000**, *31*, 589.
18. Hsieh M., Philp R. P.: *Org. Geochem.* **2001**, *32*, 955.
19. Durand J. P., Bré A., Bébouléne J. J., Ducrozet A., Carbonneaux S.: *J. Chromatogr. Sci.* **1998**, *36*, 431.
20. Hong Z., Guanghui H., Cuishan Z., Peirong W., Yongxin Y.: *Org. Geochem.* **2003**, *34*, 1037.
21. Kumar S., Gupta A. K., Agrawal K. M.: *Petrol. Sci. Technol.* **2003**, *21*, 1253.