Simple Gas Chromatographic Determination of the Distribution of Normal Alkanes in the Kerosene Fraction of Petroleum

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An internal standard technique has been applied to the determination of the distribution of normal alkanes in the kerosene fraction of petroleum using a capillary column. The applicability of packed columns for such a determination has also been studied and compared with the existing Universal Oil Products (UOP) method.

Keywords: *Normal alkanes determination; subtractive gas chromatography; internal standards technique; molecular sieves*

The determination of the concentration and concentration distribution of normal alkanes in hydrocarbon mixtures is of considerable importance in the petroleum and petrochemicals industries. Normal alkanes from petroleum sources are an important feed stock for the petrochemical industries; the long chain alkanes can be converted to lubricant and fuel additives, plasticisers, industrial surfactants, flotation agents, solvents and raw materials for protein synthesis by means of oxidation, halogenation, esterification, fermentation, etc. Such wide applications have generated a new interest in the refinery processes for recovering long chain alkanes from petroleum. Flow properties, such as viscosity, viscosity index, fluidity, pour point, etc., of heavy petroleum fractions largely depend on the n-alkane content. The distribution of n-C_{11}–n-C_{14} alkanes obtained from the kerosene fraction has immense potential in the manufacture of biodegradable detergents. In view of this importance, various methods and techniques have been proposed to determine the distribution of n-alkanes in the kerosene fraction of petroleum.

The determination of n-alkanes in complex hydrocarbon systems by their selective adsorption on molecular sieve 5A was suggested by Brenner and Coats[1] as early as 1958. Since then the molecular adsorption technique has been invariably used by several workers[2,3] in spite of its limitations. The mechanism of selective adsorption and the structure and properties of molecular sieves have been discussed in detail by many workers. Nelson[4] determined the n-alkane content of petroleum distillates by calculating the difference in mass of the zeolite before and after adsorption. O'Connor and co-workers[5,6] suggested recovering adsorbed n-alkanes from the sieve by a diffusion-controlled process for quantitative determination. Larson and Becker[7] used volumetric techniques for the determination of n-alkanes in olefin-free petroleum distillates.

Whitham[8,9] used a subtractive method using a conventional GLC column with and without a molecular sieve and the n-alkanes were determined by the difference between the two chromatograms. These methods, however, were inadequate for low concentrations of n-alkanes. Eggertsen and Groennings[10] and later Blytas and Peterson[11] modified this method so that n-alkanes were desorbed from the molecular sieve by heating and were then determined on a GLC column. Hydrofluoric acid followed by isooctane extraction[12,13] was used for the recovery of adsorbed n-alkanes by the destruction of the molecular sieve. Petrovic and Vitorovic[14] reported the direct gas chromatographic determination of C_9–C_{14} n-alkanes in the kerosene fraction using an open tubular column of Apiezon L. Hine[15] used an open tubular column for the determination of the total n-alkane content in petroleum fractions. Johanson *et al.*[16] described the possibility of determining hydrocarbons by structural group types in gasoline and distillates.

There is no standard analytical method for the determination of n-alkanes in the kerosene fraction, except for the Universal Oil Products (UOP) method.[17] This method is based on a subtraction technique using two gas chromatographs in series separated by a molecular sieve column, but has certain inherent limitations.

In this paper we propose a simple and straightforward capillary gas chromatographic method for the determination of the n-alkane distribution in straight-run kerosene fractions. The method makes use of the high resolution capability of an open tubular column (WCOT) to separate the n-alkanes from branched components and an internal standard technique[18] for fast, reliable and accurate determinations. A simplified procedure is also discussed utilising the applicability of packed columns for such determinations and is suggested as an alternative to the UOP method.[17]

Experimental

Two gas chromatographs with flame-ionisation detectors were employed, one for the capillary and one for the packed-column studies. The former was a Varian gas chromatograph (Model 3700) with a chromatographic data system (CDS-111) and potentiometric recorder (Model 9176). The provision to install the capillary column was used in order to achieve the separation of individual n-alkanes from branched peaks. A fused-silica open tubular column of 50 m × 0.2 mm with methylsilicone phase of 0.2 μm film thickness was used. The injector and detector blocks were set at 300 and 320 °C, respectively, and the column was programmed from 85 to 250 °C at 4 °C min^{-1} with 4 min of initial hold-up time. Nitrogen was used as a carrier gas at an average linear velocity of 18.5 cm s^{-1}, corresponding to a flow-rate (uncorrected) of 1.5 ml min^{-1}. A 0.1-μl sample was injected with a split ratio of 70 : 1.

The second gas chromatograph (Perkin-Elmer Model 3920 B) was installed with a 3 m × 2 mm i.d. packed column of 5% SE-30 (Methyl E-301) on Chromosorb P, 80–100 mesh. The injector and detector temperatures were kept at 300 and 320 °C, respectively. The initial column temperature was 45 °C and it was temperature-programmed at a rate of 4 °C min^{-1}, with an initial hold-up time of 8 min, to a final temperature of 220 °C. Nitrogen was used as the carrier gas with flow-rate of 30 ml min^{-1}, and a 0.2-μl sample was used for the determination. A Spectra-Physics minigrator and recorder were used for computing the data. High purity n-alkanes were used to prepare reference blends and internal standard samples. A de-normalised reference stock was prepared from kerosene samples in two stages for making the calibration blends. The kerosene sample was subjected to urea adduction and the last traces of n-alkanes were removed by molecular sieve adsorp-

tion.[19] The calibration blend was prepared by mixing a known amount of de-normalised reference stock with a pure n-alkane reference blend.

Results and Discussion

The proposed method is based on a wall-coated open tubular column of SE-30 (methylsilicone), which has the best solvent characteristics of a non-polar phase for separating complex hydrocarbon mixtures according to boiling points. Some properties of this capillary column were determined in order to show the efficiency of the stationary phase. The number of theoretical plates of the capillary column used was 254×10^3 with a coating efficiency of 69.8% and a capacity ratio of 5.1 for n-tridecane. The separation number (Trennzahl) for consecutive pairs of n-C_{13} and n-C_{14} was found to be 49.3. This has been used as a measure of column efficiency under temperature-programmed conditions and gives the maximum number of peaks that can be separated between two sequential homologues.

Fig. 1 shows a typical chromatogram of a kerosene sample obtained under the operating conditions outlined above. Each n-alkane has been well separated from the neighbouring branched components by utilising the high resolving power of the capillary column. Two different chromatograms of the sample were recorded; one as above and the other with n-hexadecane added as an internal standard. Area and base-line sensitivity parameters were taken into account for the accurate peak detection using the CDS-111 data system. The values obtained for individual n-alkane concentrations (obtained by area normalisation and internal standard techniques) were found to be in good agreement. The concentration of n-C_{16} in the original kerosene sample was determined by the area normalisation technique for calculating the individual concentration of n-hexadecane. The precision of the above proposed internal standard method was examined by determining five replicate injections of the sample and the standard deviation and coefficient of variation were found to be 0.4726 and 1.5766, respectively, with an average total n-alkane concentration of 29.976%. The reproducibility of individual n-alkane concentrations from run to run is shown in Table 1.

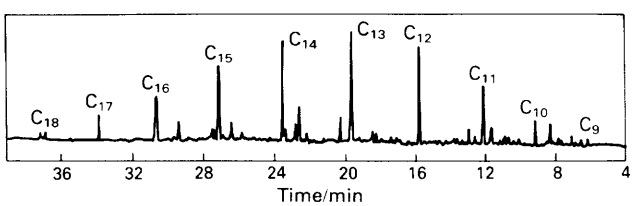

Fig. 1. Kerosene sample on fused-silica capillary column

The peak subtraction technique using a molecular sieve column was applied in order to investigate whether the n-alkanes were masked by branched alkanes. The technique can quantify the extent of contribution of branched to the n-alkanes and the concentration of individual n-alkanes can therefore be determined with high precision. The subtraction was achieved using a Linde molecular sieve 5A packed in the quartz liner of the split injector of the gas chromatograph. The molecular sieve was activated in the injector port itself by heating at 300–350 °C. A section of the subtracted and unsubtracted chromatograms obtained using the capillary column is shown in Fig. 2; it was noticed that the number of branched alkanes obscured by n-alkanes was negligible owing to the high resolution of the capillary column.

Packed-column investigations using a single gas chromatograph with a flame-ionisation detector appear to be promising as an alternative to the UOP method. Data from individual n-alkanes in the same kerosene sample were obtained using a packed column with internal standards. The total concentration of n-alkanes in the sample (Table 2) was 31.372%, which was about 1.396% higher than the value reported when using the fused-silica capillary column. This higher value was expected, owing to the limitations of the packed column in resolving n-alkane peaks from the branched-chain components. The concentration of branched components obscured by n-alkanes was calculated using chromatograms of the sample obtained with and without molecular sieve subtraction (Fig. 3). The deviation in the values obtained for total n-alkane concentration in the kerosene sample using packed and capillary columns does not exceed the error expected in routine GC determinations.

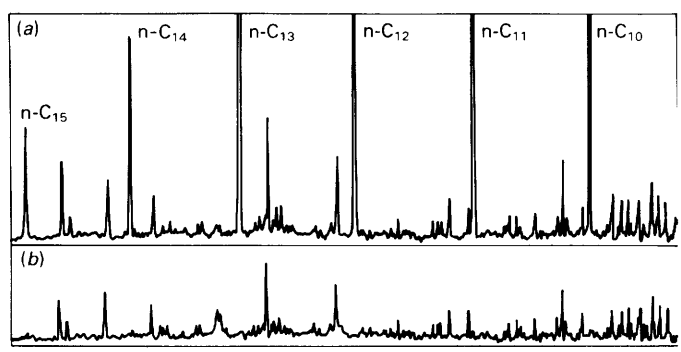

Fig. 2. Section of chromatogram of kerosene sample on capillary column (*a*) without molecular sieve and (*b*) with molecular sieve

Table 1. Repeatability and precision in capillary-column method

n-Alkane components	Concentration, % *m/m*					Average, % *m/m*	Standard deviation, % *m/m*	Coefficient of variation, %
	1	2	3	4	5			
C-8	0.28	0.26	0.29	0.29	0.30	0.2840	0.0152	5.3401
C-9	0.84	0.85	0.88	0.88	0.91	0.8720	0.0277	3.1822
C-10	2.42	2.45	2.52	2.52	2.57	2.4960	0.0602	2.4138
C-11	5.09	5.25	5.14	5.15	5.00	5.1260	0.0913	1.7805
C-12	6.31	6.20	6.37	6.39	6.51	6.3560	0.1135	1.7856
C-13	6.00	5.89	6.06	6.10	6.21	6.0520	0.1186	1.9600
C-14	4.53	4.45	4.58	4.66	4.68	4.5800	0.0946	2.0655
C-15	2.28	2.31	2.37	2.40	2.44	2.3600	0.0652	2.7624
C-16	0.78	0.79	0.81	0.82	0.84	0.8080	0.0239	2.9548
C-17	0.36	0.35	0.37	0.37	0.38	0.3660	0.0114	3.1152
C-18	0.32	0.31	0.33	0.33	0.34	0.3260	0.0114	3.4975
C-19	0.19	0.19	0.20	0.20	0.21	0.1980	0.0084	4.2256
C-20	0.15	0.14	0.15	0.16	0.16	0.1520	0.0084	5.5043
Total	29.55	29.44	30.07	30.27	30.55	29.976	0.4726	1.5766

Table 2. Repeatability and precision in packed-column method

n-Alkane components	Concentration, % *m/m*					Average, % *m/m*	Standard deviation, % *m/m*	Coefficient of variation, %
	1	2	3	4	5			
C-8	0.27	0.29	0.31	0.30	0.33	0.3000	0.0224	7.4536
C-9	0.89	0.93	0.98	1.01	1.05	0.9720	0.0634	6.5230
C-10	2.49	2.56	2.63	2.67	2.70	2.6100	0.0851	3.2623
C-11	5.13	5.22	5.24	5.32	5.40	5.2620	0.1026	1.9492
C-12	6.38	6.31	6.53	6.44	6.60	6.4520	0.1157	1.7917
C-13	6.08	6.2	6.19	6.38	6.38	6.246	0.1310	2.098
C-14	4.68	4.75	4.84	4.89	4.93	4.818	0.1022	2.1217
C-15	2.59	2.61	2.60	2.72	2.75	2.654	0.0750	2.8272
C-16	0.87	0.89	0.90	0.83	0.86	0.87	0.0274	3.1478
C-17	0.54	0.51	0.52	0.49	0.51	0.514	0.0181	3.5300
C-18	0.29	0.28	0.31	0.30	0.31	0.2980	0.0130	4.3753
C-19	0.24	0.21	0.23	0.23	0.25	0.2320	0.0148	6.3933
C-20	0.13	0.14	0.16	0.14	0.15	0.1440	0.0114	7.9179
Total	30.58	30.90	31.44	31.72	32.22	31.372	0.65093	2.075

Table 3. Accuracy and coefficient of variation in packed-column method

n-Alkane components	Actual concentration, % *m/m*	Observed concentration, % *m/m*					Coefficient of variation, %	Accuracy, %
		1	2	3	4	5		
C-11	4.18	4.25	4.35	4.4	4.1	4.3	2.69	2.39
C-12	4.80	4.90	4.94	5.0	4.75	4.88	1.89	1.87
C-13	3.87	4.0	3.95	3.85	4.15	4.10	2.98	3.61
C-14	2.08	2.10	2.15	2.2	2.3	2.22	3.44	5.48
C-15	0.75	0.72	0.77	0.70	0.67	0.75	5.40	4.50
Total	15.68	15.97	16.16	16.15	15.97	16.25	0.78	2.64

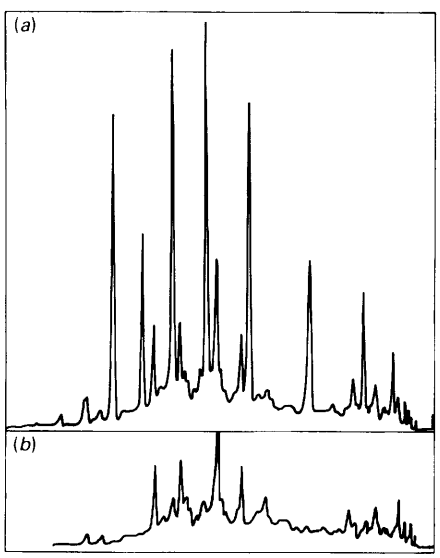

Fig. 3. Kerosene sample on packed column (*a*) without molecular sieve and (*b*) with molecular sieve

In order to check the precision and accuracy of the packed-column method, a high purity calibration blend was prepared by weighing portions of a de-normalised kerosene reference stock and a blend of pure n-alkanes from n-undecane to n-pentadecane. The calibration blend was determined on the packed column and the concentration of each n-alkane was calculated and compared with the actual values. The agreement between the actual and observed concentrations was found to be between 1.875 and 5.48%, as shown in Table 3, and the coefficient of variation was 0.78%.

The proposed packed-column method has many advantages over the UOP method.[17] The flame-ionisation detector that was used in place of the thermal-conductivity detector, apart from being more sensitive, has the distinct advantage of having the same quantitative response to equal masses of any hydrocarbon, thus avoiding having to account for the response factors of individual components. Peak broadening, which may be caused by the use of a transfer line in the UOP method,[17] is eliminated by using a single gas chromatograph. Also, the optimisation of the detector current in both gas chromatographs in order to match the detector signals for the relative distribution of an isoalkane blend is not required in the proposed method. The total n-alkane concentration depends on the factor used for the conversion of area percent. to mass percent. in the non-distributive mode. Any error in preparing the calibration blend will affect the total concentration of n-alkanes obtained for the sample. As the sample is injected twice in the proposed method (with and without the molecular sieve) the accuracy in a sample injection of 0.2 μl is well within acceptable limits.

Conclusion

The proposed internal standard method for the determination of normal alkanes using a fused-silica capillary column is both fast and reliable. The proposed method using a packed column is simpler and more sensitive than the existing UOP method[17] for the determination of normal alkanes and gives reasonable accuracy compared with an open tubular column.

References

1. Brenner, N., and Coates, V. J., *Nature, (London)*, 1958, **181**, 1401.
2. Barall, E. M., and Bauman, F. J., *J. Gas Chromatogr.*, 1964, **2**, 256.
3. Beroza, M., and Insco, M. N., *in* Ettre, L. S., and McFadden, W. H., *Editors,* "Ancillary Technique of Gas Chromatography," Wiley-Interscience, New York, 1969, pp. 89–114 and 127–130.
4. Nelson, K. H., *Anal. Chem.*, 1957, **29**, 1026.
5. O'Connor, J. G., and Norris, M. S., *Anal. Chem.*, 1960, **30**, 701.
6. O'Connor, J. G., Burrow, F. H., and Norris, M. S., *Anal. Chem.*, 1962, **34**, 83.

7. Larson, L. P., and Becker, H. C., *Anal. Chem.*, 1960, **32**, 1215.
8. Whitham, B. T., *Nature (London)*, 1958, **182**, 392.
9. Whitham, B. T., *Nature (London)*, 1961, **192**, 966.
10. Eggertsen, F. T., and Groennings, S., *Anal. Chem.*, 1961, **33**, 1147.
11. Blytas, G. C., and Peterson, D. L., *Anal. Chem.*, 1967, **39**, 1434.
12. Knight, H. S., *Anal. Chem.*, 1967, **39**, 1452.
13. Brunnock, J. V., *Anal. Chem.*, 1966, **8**, 1648.
14. Petrovic, K., and Vitorovic, D., *J. Chromatogr.*, 1972, **65**, 155.
15. Hine, B. T., *Chromatographia*, 1984, **18**, 679.
16. Johanson, N. G., Ettre, L. S., and Miller, R. L., *J. Chromatogr.*, 1983, **256**, 393.
17. "Normal Paraffins by Subtractive Gas Chromatography," UOP VO8-411-75, Universal Oil Products Inc., Des Plaines, IL, 1975.
18. "Application Laboratory Report," No. 1005, Hewlett Packard, Avondale, PA, 1966.
19. Chen, N. Y., and Lucki, S. J., *Anal. Chem.*, 1970, **42**, 508.

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