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DIRECT GAS CHROMATOGRAPHIC DETERMINATION OF C_9 TO C_{14} *n*-PARAFFINS IN KEROSENE FRACTIONS

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SUMMARY

A new chromatographic method for the direct determination of C_9–C_{14} *n*-paraffins in kerosene fractions of an intermediate base has been developed. The analysis is carried out by using an open tubular column. The contents of *n*-paraffins are calculated by an absolute calibration method, *i.e.*, by comparing the *n*-paraffin peak heights in the sample and reference standard chromatograms. A synthetic mixture of *n*-paraffins dissolved in a molecular-sieve deparaffinized kerosene distillate of a corresponding base was used as reference standard. A coefficient of variation of 1–2 % and a relative error of 2–3% indicate the reliability of the method. The proposed method is advantageous compared with known methods for individual *n*-paraffin determination in kerosene fractions because of the precision and accuracy of the results as well as its relative simplicity and speed. With similar advantages, the new method may replace the usual adsorption methods for the determination of the total content of *n*-paraffins in kerosene fractions.

INTRODUCTION

Some of the important properties of jet and diesel fuels depend on their contents of *n*-paraffins (for example, freezing point, pour point and viscosity). Because of this, a knowledge of the content and the distribution of *n*-paraffins in the gasoline and kerosene range is very helpful in the control of the production of low freezing-point jet fuels and in the evaluation of different processes involving a change of *n*-paraffin content (for instance, isomerization, catalytic reforming, or the manufacture of some detergents). Moreover, there is hope that in the future some analytical methods in the petroleum industry might be based on the content of total or individual *n*-paraffins.

Several methods for the determination of *n*-paraffins by means of molecular sieves are known. Thus, the total content of *n*-paraffins in hydrocarbon mixtures can be determined by adsorption, using an appropriate adsorption apparatus[1–8]. These methods usually take a long time.

The content of individual *n*-paraffins and their total content can be determined in a relatively short time by gas chromatographic (GC) methods[4–10]. These methods when applied for the determination of total content of *n*-paraffins are advantageous compared with adsorption methods, although the accuracy and precision are not as high as with the adsorption methods.

Known GC methods for the determination of individual *n*-paraffins in kerosene fractions are based either on subtractive techniques[4] or on quantitative elution of *n*-paraffins which were selectively adsorbed on a molecular sieve in the first stage[9]. In the subtractive method, the sample has to be analyzed twice: once without and once with a molecular sieve 5A pre-column. This method is not very sensitive. In the desorption method, the sensitivity is higher. A further method has been developed, based on the recovery of adsorbed *n*-paraffins by molecular sieve destruction with hydrofluoric acid, followed by isooctane extraction and by GC analysis[10]. It was shown[10] that the results of this and the previously described method agreed within a range of $\pm 5\%$.

One of the main shortcomings of the above-mentioned GC methods consists in a relatively complex procedure, leading sometimes to unsatisfactory precision. Moreover, special attention has to be paid to the preparation procedure for the molecular sieves[4,5,7], otherwise tailing effects may occur and also some branched paraffins could be adsorbed.

In this paper, a direct GC method for the determination of *n*-paraffins in kerosene-range petroleum fractions has been developed. The results were calculated by comparison of the peak heights of the *n*-paraffins in the samples with those of a reference standard.

The reference standard was prepared by dissolving known amounts of research-grade *n*-paraffins in a corresponding kerosene fraction deparaffinized by molecular sieves 5A. The boiling point range of the samples and the reference standards should be similar. In such a case, a chromatogram of one reference standard may be used for a great number of samples.

The proposed method is simpler than other methods used for the analysis of kerosenes of an intermediate base. The analysis takes only about 30 min and the coefficient of variation and the relative error are about 1–3%, which makes the method advantageous compared with other methods for the determination of *n*-paraffins in kerosene fractions.

EXPERIMENTAL

The instrument used was a Perkin-Elmer gas chromatograph, model 880, equipped with a flame-ionization detector and a Leeds and Northrup 5 mV recorder. A stainless-steel open tubular column (50 m × 0.1 mm) coated with Apiezon L was supplied by Perkin-Elmer. The flow-rates of nitrogen (carrier gas), hydrogen and air were 1–2, 30 and 380 ml/min, respectively, and were measured at the column exit and at the entrance of the detector. The injection port and the detector were kept at temperatures up to 270°C. The column temperature was maintained at 110°C and programmed, after injection, at 2°/min.

Molecular sieves 5A, 60–80 mesh, were supplied by Linde Co. The sieves were activated by heating in a vacuum for 2 h at 250–300°C. The deparaffinization of kero-

sene fractions to obtain solvents for reference standard preparation was carried out according to method B of CHEN AND LUCKI[3], modified for kerosene-range products. Partial evaporation of light components did not cause a substantial change of the solvent composition and hence did not affect the reliability of the method. The C_9–C_{14} research-grade *n*-paraffins were supplied by Phillips Petroleum Company. Samples of 3–4 μl were injected by using a Hamilton syringe. Before entering the open tubular column, the samples were split from 700:1 up to 900:1.

RESULTS AND DISCUSSION

Samples

Kerosene fractions of an intermediate base boiling up to about 250°C were investigated because they are very important in the production of low freezing-point jet fuels. Samples with different characterization factors* were chosen so as to check the dependence of the method on the general composition of the samples.

Synthetic samples were also made by dissolving known amounts of *n*-paraffins in the deparaffinized kerosene.

Reference standards

By using reference standards prepared on the basis of deparaffinized kerosene fractions as solvents, it was possible to eliminate the effect of a background, resulting from overlapping peaks, on the accuracy of *n*-paraffin determinations. If a reference standard consisting of a mixture of pure *n*-paraffins were to be used, it would be impossible to avoid this effect.

To illustrate the dependence of the results on the type of solvent used for the preparation of the reference standard, analyses of five naphtha jet fuels were carried out by using two different reference standards (Table I). Columns A and B in Table I contain results obtained by using reference standards consisting of synthetic mixtures of pure *n*-paraffins dissolved in isooctane (A) and in deparaffinized samples (B) as solvents. Approximately the same absolute deviation was observed with all five samples. With more efficient columns absolute deviations would be lower, but certain overlapping of peaks would still occur. This means that the chemical nature of the solvents used for the preparation of reference standards is important.

Analysis of unknown samples

As an illustration, chromatograms of a sample and a reference standard are shown in Fig. 1. The sample (A) consisted of a kerosene-range fuel. The chromatogram B belongs to the reference standard consisting of a synthetic mixture of the same *n*-paraffins dissolved in the same kerosene but which had been previously deparaffinized. In other words, the reference standard B represents a good reference standard for the sample A.

* The characterization factor is an index of the chemical character of pure hydrocarbons and petroleum fractions. It was originally defined as the cube root of the average molal boiling point divided by the specific gravity at 60°F. It has since been related to viscosity, aniline point, molecular weight, critical temperature, percentage of hydrocarbon, etc., so that almost any laboratory data can be used to estimate the factor. It may be considered as an approximate index of paraffinicity, with high values corresponding to high degrees of saturation.

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TABLE I

DETERMINATION OF C_{10}–C_{12} *n*-PARAFFINS IN FIVE NAPHTHA JET FUELS BY USING TWO DIFFERENT REFERENCE STANDARDS (A AND B)

Component	*Sample*														
	1			*2*			*3*			*4*			*5*		
	A	*B*	*Abs. dev.*	*A*	*B*	*Abs. dev.*	*A*	*B*	*Abs. dev.*	*A*	*B*	*Abs. dev.*	*A*	*B*	*Abs. dev.*
n-C_{10}	9.8	9.0	0.8	9.0	8.3	0.7	8.8	8.0	0.8	11.0	10.1	0.9	10.8	10.0	0.8
n-C_{11}	9.7	8.3	1.4	9.4	8.2	1.2	8.7	7.4	1.3	9.8	8.4	1.4	7.3	6.2	1.1
n-C_{12}	2.5	2.0	0.5	2.3	2.1	0.2	3.2	2.6	0.6	0.5	0.4	0.1	0.6	0.5	0.1
Total	22.0	19.3	2.7	20.7	18.6	2.1	20.7	18.0	2.7	21.3	18.9	2.4	18.7	16.7	2.0

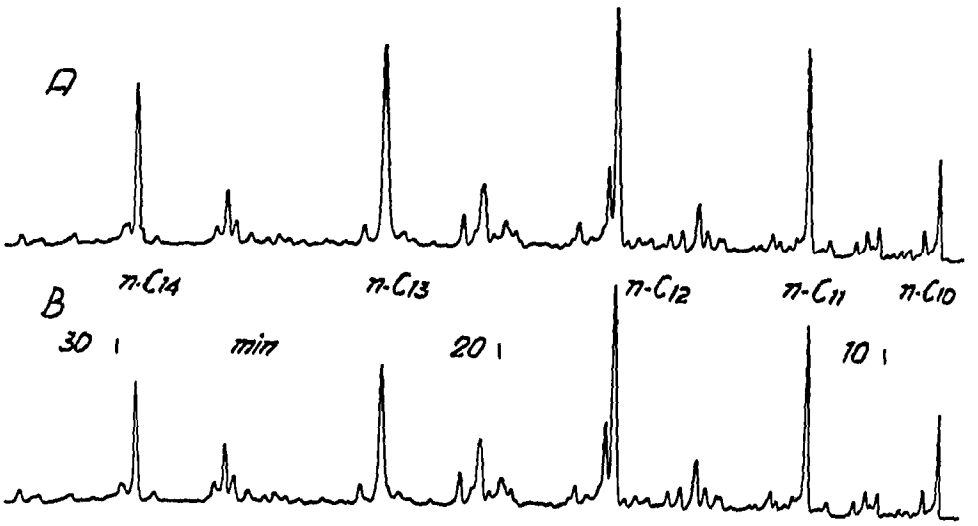

Fig. 1. Chromatograms of a kerosene sample (A) and a reference standard (B).

TABLE II

DETERMINATION OF THE CONTENT OF C_9–C_{14} *n*-PARAFFINS IN A SAMPLE WITH A CHARACTERIZATION FACTOR OF 11.9

Component	*Content (wt.-%)*						*Average*	*Standard deviation*	*Coefficient of variation*
	1	*2*	*3*	*4*	*5*	*6*			
n-C_9	0.54	0.51	0.54	0.53	0.53	0.53	0.53	0.0119	2.3
n-C_{10}	1.31	1.27	1.30	1.30	1.31	1.30	1.30	0.0158	1.2
n-C_{11}	4.62	4.43	4.58	4.54	4.55	4.53	4.54	0.0751	1.7
n-C_{12}	5.13	5.03	5.16	5.13	5.13	5.09	5.12	0.0514	1.0
n-C_{13}	4.48	4.31	4.40	4.40	4.43	4.38	4.40	0.0672	1.5
n-C_{14}	3.96	3.79	3.84	3.86	3.94	3.86	3.88	0.0672	1.7
Total	20.04	19.34	19.82	19.76	19.89	19.69	19.77	0.2765	1.4

The repeatability of the method was examined by analyzing a number of samples having a characterization factor in the range 11.5–12.0. The coefficient of variation was found to be 1–2%. As an example, results obtained by analysis of a kerosene fraction of a characterization factor 11.9 are given in Table II.

Analysis of synthetic mixtures

Since the kerosene fractions to be examined might be of various origins, particular attention was paid to the checking of the accuracy of the results depending on the composition of the sample. Special emphasis in these studies was given to the evaluation of the effect caused by a difference in the chemical nature of the samples and reference standards. In this sense, the possibility of using one reference standard for analyzing many different synthetic samples similar to kerosenes of an intermediate base was examined. For this purpose a number of synthetic mixtures of different characterization factors were made. Concentrations of *n*-paraffins in the samples and the reference standards in most cases differed by up to about 60%.

The dependence of the accuracy of the method on the reference standard used was investigated by analyzing ten synthetic samples. Results, each representing an

TABLE III

ANALYSIS OF VARIOUS SYNTHETIC MIXTURES OF C_9–C_{14} *n*-PARAFFINS

Sample	*Component (wt.-%)*								
	n-C_9			*n*-C_{10}			*n*-C_{11}		
	Added	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*
1	0.71	0.65	8.5	1.40	1.45	3.6	3.90	3.75	3.8
2	–	–	–	1.86	1.84	1.1	2.00	1.97	1.5
3	–	–	–	1.78	1.76	1.1	3.00	2.94	2.0
4	–	–	–	–	–	–	3.40	3.30	0.6
5	0.83	0.78	6.0	1.50	1.54	2.7	2.94	3.10	2.9
6	0.70	0.68	2.8	1.38	1.40	1.5	3.37	3.42	1.5
7	2.00	1.98	1.0	2.93	2.98	1.7	4.00	3.90	2.5
8	–	–	–	0.94	1.00	6.4	1.52	1.55	2.0
9	–	–	–	1.43	1.47	2.1	3.74	3.90	4.1
10	0.40	0.35	12.5	0.87	0.90	3.4	1.62	1.77	9.2

average of two determinations, are given in Table III. The same reference standards were used for the following groups of samples: 1, 8 and 10; 2, 3 and 4; and 5, 6 and 7. For sample 9 an extra reference standard was used. The greatest difference between the characterization factors of the samples and the standards was 0.3 unit, except for sample 9 where it was 0.4 unit. Sample 10 should be treated as a special example as far as its composition is concerned, and this sample will be discussed later.

It may be concluded that one reference standard can be used for the analysis of a number of samples of different compositions. Such a conclusion is certainly valid if the difference between the characterization factor of the sample and the reference standard is reasonable. This conclusion may be supported by the chromatograms

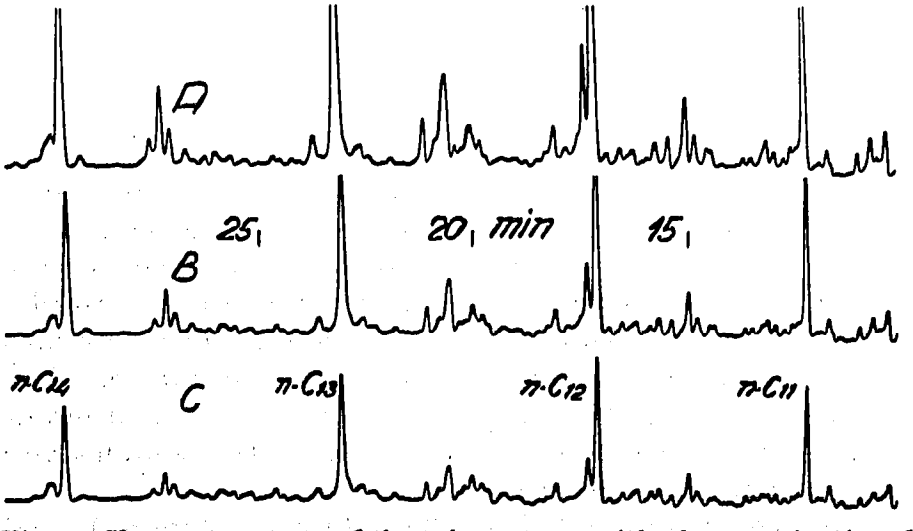

Fig. 2. Chromatograms of three kerosenes with characterization factors of 11.9 (A), 11.7 (B) and 11.5 (C).

i-C_{12}			*n*-C_{13}			*n*-C_{14}			*Total*		
Added	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*	*Added*	*Found*	*Rel. error (%)*
4.71	4.78	1.5	3.46	3.47	0.3	3.06	3.04	0.7	17.24	17.15	0.5
2.69	2.74	1.9	2.86	2.91	1.8	2.70	2.74	1.5	12.11	12.20	0.7
3.75	3.63	3.2	3.05	2.94	3.6	2.78	2.70	2.9	14.36	14.02	2.4
4.57	4.47	2.2	3.46	3.57	3.2	2.45	2.52	2.9	13.88	13.86	0.1
3.69	3.74	2.2	2.93	2.82	3.1	2.12	2.20	2.8	14.01	14.18	1.2
5.28	5.35	1.3	3.45	3.35	2.9	3.10	3.12	0.6	17.28	17.32	0.2
6.07	5.95	2.0	4.58	4.52	1.3	2.86	2.97	3.8	22.44	22.30	0.3
–	–	–	2.09	2.02	3.2	1.69	1.63	3.5	6.24	6.20	0.6
5.05	5.28	4.3	4.20	4.13	1.6	3.27	3.35	2.4	17.70	18.30	3.4
2.37	2.48	4.6	2.16	2.28	5.5	1.55	1.79	9.6	8.97	9.47	5.3

shown in Fig. 2 for three samples of different characterization factors: 11.9 (A), 11.7 (B) and 11.5 (C). The background at the points of elution of *n*-paraffins is similar. This means that one can expect that, if the difference in the chemical nature of the reference standards and the samples under examination is kept within reasonable limits, the accuracy of the method should not be affected substantially.

A more obvious illustration of the effect of the nature of the solvent used for reference standard preparation on the accuracy of the results is shown in Table IV. A synthetic mixture of *n*-paraffins in a *n*-paraffin-free solvent of a characterization factor 11.9 was analyzed, and the results were calculated by using three different reference standards with characterization factors of 11.9, 11.7 and 11.5; the results are given in columns 1, 2 and 3, respectively. As shown, the accuracy decreased slightly with the increase of the difference between the characterization factors of the sample and the reference standard.

TABLE IV

DETERMINATION OF *n*-PARAFFINS IN A SYNTHETIC KEROSENE BY USING THREE DIFFERENT REFERENCE STANDARDS

Compound	*Amount added (%)*	*Reference standard*								
		1			*2*			*3*		
		Found (%)	*Abs. dev.*	*Rel. error (%)*	*Found (%)*	*Abs. dev.*	*Rel. error (%)*	*Found (%)*	*Abs. dev.*	*Rel. error (%)*
n-C_{10}	1.38	1.40	0.02	1.5	1.36	0.02	1.5	1.33	0.05	3.7
n-C_{11}	3.37	3.42	0.05	1.5	3.34	0.03	0.9	3.24	0.13	3.9
n-C_{12}	5.28	5.35	0.07	1.3	5.30	0.02	0.4	5.08	0.20	3.8
n-C_{13}	3.45	3.35	0.10	2.9	3.56	0.11	3.2	3.48	0.03	0.8
n-C_{14}	3.10	3.12	0.02	0.6	3.18	0.08	2.6	3.03	0.07	2.2
Total	16.58	16.64	0.06	0.4	16.74	0.16	1.0	16.16	0.42	2.5

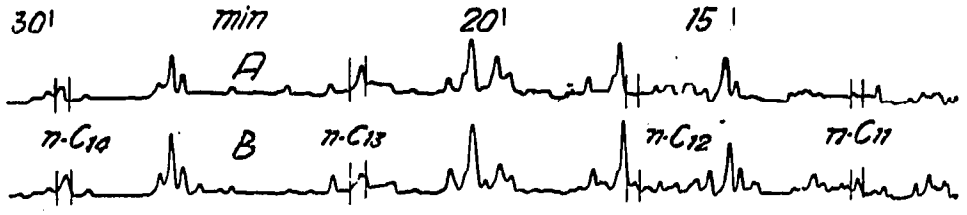

Fig. 3. Chromatograms of deparaffinized kerosene fractions of characterization factors 11.5 (A) and 11.9 (B).

On the basis of results obtained, it can be concluded that for kerosene fractions of an intermediate base, the maximum difference between the characterization factors of the sample and the reference standard should not be more than a few tenths of a unit.

However, the necessity for using a proper deparaffinized solvent for the preparation of the corresponding reference standard should be pointed out. In the chromatograms of kerosene-range samples, overlapping of the peaks of *n*-paraffins and of other hydrocarbons is inevitable; in the samples of higher characterization factors, the overlapping compounds are primarily branched paraffins. The potential effect of the accompanying hydrocarbons may be estimated from Fig. 3. Chromatograms A and B correspond to *n*-paraffin-free kerosene fractions whose characterization factors prior to deparaffinization were 11.5 and 11.9, respectively. It is obvious that a fraction with a higher characterization factor contains more branched paraffins at the points of elution of *n*-paraffins. According to this observation, it can be concluded that for the preparation of reference standards containing relatively low concentrations of *n*-paraffins, deparaffinized kerosene fractions of similar chemical nature should be used as solvents. Only in that case would the effect of overlapping branched hydrocarbons not be considerable. Otherwise, the accuracy of the results would be affected much more.

This effect has been demonstrated in the case of sample 10, Table III, which was prepared by using a solvent consisting of a deparaffinized kerosene of an inappropriate characterization factor. Because of this, the results for sample 10 were considerably higher than expected.

Since quantitative ratios of different hydrocarbon types in the fuels are nearly constant regardless of the origin of the crude oil[11], elution of greater amounts of some other hydrocarbons at the points of elution of *n*-paraffins should not be expected.

In general, the smaller the difference between chemical nature and composition of the samples and those of the reference standards, the higher the accuracy of the method will be.

The method described can also be applied to the determination of *n*-paraffins in kerosenes of a paraffinic base, but a proper reference standard should be used. The applicability of the method for the determination of *n*-paraffins in samples of a naphthenic base is questionable, because of the relatively low concentration of *n*-paraffins in these kerosene fractions. Mixing of kerosenes of a naphthenic base with reference standards of an intermediate or paraffinic base, in appropriate proportions, prior to analysis, would be one possible approach which might lead to the successful application of the proposed method to the analysis of such samples. However, this will be the subject of further investigations on the applicability of the method.

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