DETERMINATION OF SMALL AMOUNTS OF HYDROCARBON IMPURITIES IN C_{10}–C_{18} n-PARAFFINIC FRACTIONS

J. GAWLIK, W. GOLBA AND P. SZYNAGEL

The Institute of Petroleum Processing, Kraków, Łukasiewicza 1 (Poland)

SUMMARY

A method for the quantitative determination of small amounts of hydrocarbons contaminating n-paraffinic fractions of the range C_{10}–C_{18} by using molecular sieve 5A has been developed. The determination is a two-stage analysis. First the sample with an internal reference standard added is analysed in a separating column. The second stage is analogous, with the application of an additional pre-column, packed with molecular sieves which adsorb n-paraffinic hydrocarbons. By comparison of the results of this two-stage analysis, one obtains the contents of impurities in the sample being analysed. For fractions with the wide boiling range of the C_{10}–C_{18} compounds, the impurities at a level of 0.4–10.0% w/w can be determined with satisfactory accuracy. In the case of narrow fractions or when the contamination of individual n-paraffins is to be determined, satisfactory accuracy of analysis was obtained even at low contents of impurities (down to 0.1% w/w).

INTRODUCTION

Normal paraffins of the range C_{10}–C_{18} obtained in the Institute of Petroleum Processing in Kraków, Poland, in the "ITENEX" process, based on the sorptive action of molecular sieve 5A, contain a certain amount of impurities. In general, the contents of the impurities lie between 3 and 6% w/w although in some cases it may be higher or lower. These impurities influence the process of n-paraffin production and the quality and the yield of the final product. Therefore it is important to have a rapid and precise method for the determination of the content of impurities in the C_{10}–C_{18} n-paraffin product.

In the literature, there are many papers concerning the determination of the contents of individual n-paraffins in hydrocarbon mixtures, but there are very few papers dealing with impurities in n-paraffin fractions. Among the latter may be mentioned: LEITHE's method based on formation of tarry substances by *iso*-paraffinic hydrocarbons with antimony pentachloride, but the accuracy of the method lies between 3 and 6% w/w[1]; methods based on the formation of a complex by n-paraffins with urea or thiourea[2–5], but according to STAROBINIEC AND BOLSHOVA[6] these methods are more suitable for higher hydrocarbons; and methods based on the sorptive properties of molecular sieve 5A (refs. 7–11).

Among the methods mentioned above, those based on the application of molecular sieves deserve some attention; their accuracy however, appears to be inadequate for the determination of impurities in n-paraffinic fractions. Other methods, for example those ones based on mass spectroscopy, are not generally available and from the work of CHMIELNICKI et al.[12] on the determination of n-alkanes in the presence of other hydrocarbons, the conclusion must be drawn that the application of this method to the determination of impurities in C_{10}–C_{18} n-paraffinic fractions may involve considerable difficulties.

Even the application of gas chromatography (GC) using capillary columns does not eliminate the errors of determination caused by incomplete separation of all the constituents of the analysed sample, especially—as in the case under consideration— when the constituents have various structures, namely, n-paraffins, iso-paraffins and
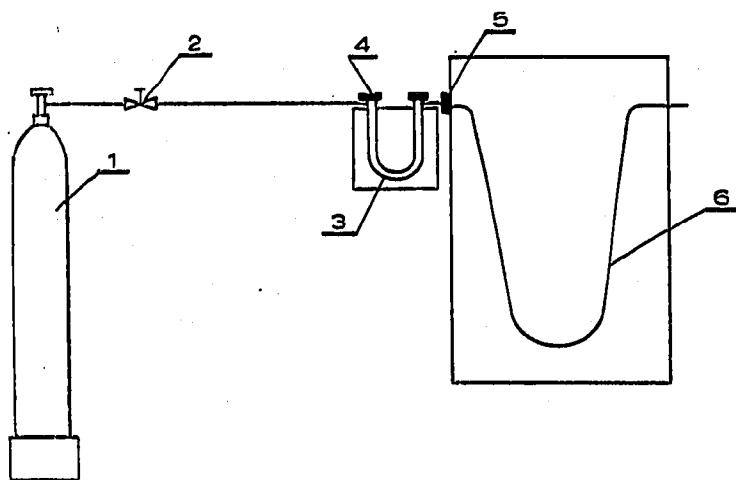
Fig. 1. Diagram showing connection between pre–column packed with molecular sieve 5 A and separating column. 1 = cylinder with carrier gas; 2 = pressure regulator; 3 = pre-column with thermostat; 4 = injection system of pre-column; 5 = injection system of chromatograph; 6 = chromatograph thermostat with separating column.

naphthenic and aromatic hydrocarbons. In such cases, the use of typical capillary columns cannot eliminate overlapping of the peaks of the individual n-paraffins and those of contaminants. As shown below, the amounts of contaminants hidden under the peak areas of n-paraffinic hydrocarbons, when the C_{10}–C_{14} fraction is being analysed on a capillary column, lie between 20 and 30% w/w in relation to the total amount of impurities in the sample.

Therefore, by using the most promising method for the determination of n-paraffins or other hydrocarbons involving the application of molecular sieves, a rapid method for the determination of the total amount of impurities in the C_{10}–C_{18} n-paraffinic fraction was devised. The advantage was taken of the sorptive action of molecular sieve 5A at the very small load on the column, which makes possible the use of GC with flame-ionization detection.

Some authors have suggested that the behaviour of iso-paraffinic hydrocarbons having a long, straight carbon chain with a methyl group at the end towards molecular sieve 5A is analogous to that of n-paraffins; this suggestion was not confirmed.

EXPERIMENTAL

Determinations were carried out by using a Perkin-Elmer Model F-11 chromatograph, especially adapted for the purpose of this determination, equipped with a flame-ionization detector and with nitrogen as the carrier gas. This apparatus had an additional pre-column, packed with activated molecular sieve 5A, and provided with an independent thermostatic device. The separation was conducted on normal columns and on a capillary column. The scheme of connecting the pre-column with the separating column is shown in Fig. 1.

A sample of C_{10}–C_{18} n-paraffin fraction was prepared for analysis by adding a known amount (5–10% w/w) of internal standard. The sample was analysed twice. First a separation was carried out by using a separating column only and introducing the sample directly into it. A chromatogram of the n-paraffins and impurities with the
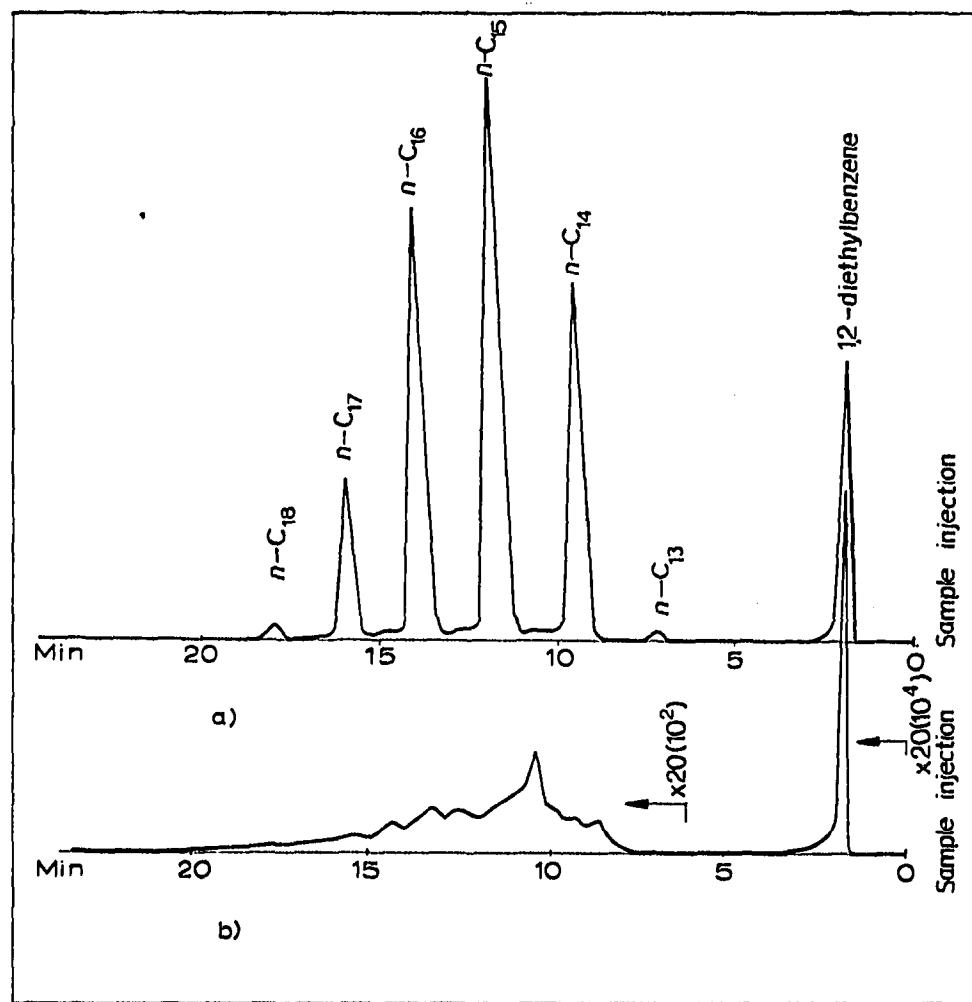
Fig. 2. (a) Chromatogram of C_{14}–C_{18} n-alkane fraction with 1,2-diethylbenzene. Gas chromatograph, Perkin-Elmer Type F 11 with flame-ionization detector. Column length, 1.0 m; I.D., 2.0 mm; packing, Chromosorb W, 60–80 mesh coated with 5.0% of SE-30; temperature, 80–220° programmed at 8°/min. Carrier gas, nitrogen, flow-rate, 50 ml/min. Sample, 0.5 µl. Sensitivity, ×2(10⁴). (b) Chromatogram of impurities of C_{14}–C_{18} n-alkane fraction with 1,2-diethylbenzene. Conditions as in (a) + pre-column, 20 cm × 2 mm, packed with molecular sieve 5 A. Pre-column temperature, 350°.

standard was obtained (Fig. 2a). Secondly, separation was carried out by using the same separating column but having in front of it the pre-column packed with activated molecular sieve 5A. The sample was introduced into the pre-column packed with a molecular sieve. n-Paraffinic hydrocarbons were adsorbed by the molecular sieve in the first column, while internal standards and impurities, after passing intact through the first column, were separated in the separating column.

As the result, a chromatogram of impurities and of the internal standard was obtained (Fig. 2b). As the impurities content was very small, it was beneficial to increase the sensitivity of the instrument by about ten times just after registering the peak of the internal standard.

The impurities content in samples of n-paraffin fractions were calculated by comparison of the two chromatograms. Omitting the correction factor for the flame-ionization detector and comparing the areas of peaks obtained in the two chromatograms, the following equation is obtained:

$$z = z_1 \cdot \frac{A}{A_1} \qquad\qquad\qquad (1)$$
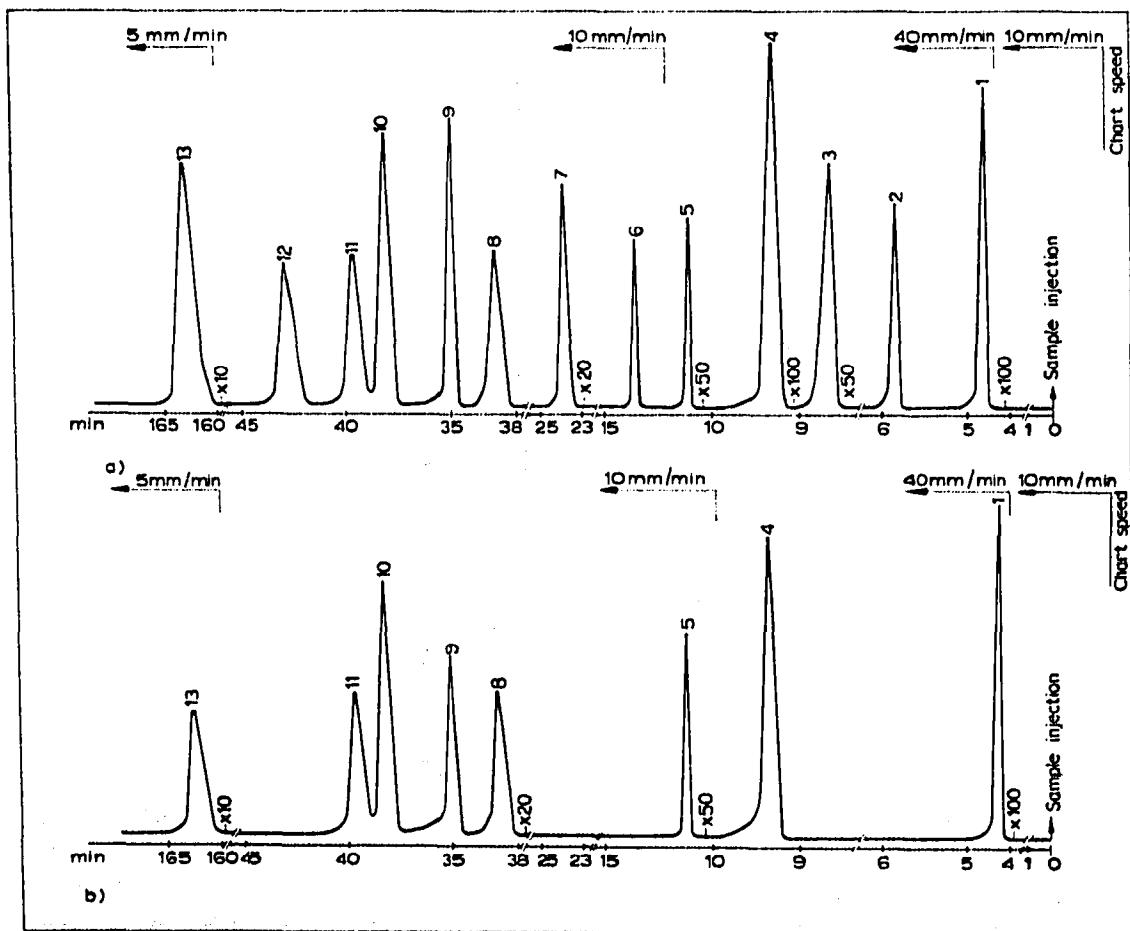
Fig. 3. Chromatogram of standard mixture. (a), Gas chromatograph, Perkin-Elmer Type F 11 with flame-ionization detector. Capillary column, 50 m × 0.25 mm I.D. coated with polyphenyl ether OS 138. Column temperature, 75°. Carrier gas, nitrogen, inlet pressure, 27 p.s.i. Sample, 0.3 μl. (b) Conditions as in (a) with pre-column, 20 cm × 2 mm, filled with molecular sieve 5 A. Pre-column temperature, 320°.

where z = total impurities content in the n-paraffinic fraction (% w/w); z_1 = percentage area of impurities relative to the total area of the peaks in the chromatogram obtained in the analysis using both columns, $i.e.$, column packed with molecular sieve 5A and separating column; A = percentage area of internal standard relative to the total area of the peaks in the chromatogram obtained in the analysis without the molecular-sieve column; and A_1 = percentage area of internal standard relative to the total area of the peaks of the chromatogram obtained in the analysis using both columns. The parameters of analysis are given on the chromatograms.

When there are aromatic hydrocarbons present in the impurities of the n-paraffin fraction, and also when an aromatic hydrocarbon is used as the internal standard, the column packed with the molecular sieve is heated to a temperature at least 50° higher than the boiling temperature of the highest-boiling aromatic hydrocarbon contained in the sample. This procedure lowers the sorptive action of the molecular sieve towards the aromatic hydrocarbons.

TABLE I

HYDROCARBONS IN REFERENCE MIXTURE

No.	Component	Producer	Purity (% w/w)	Contents of the component in reference mixture	
				Calculated from weight added	Calculated from 6 successive chromatographic determinations as the arithmetic mean
1	Cyclooctane	Schuchardt, G.F.R.	>99	7.3	7.0
2	n-C_{11}	Fluka AG, Switzerland	99.48	6.0	5.9
3	n-C_{12}	L. Light, Great Britain	>99	5.7	5.5
4	n-Butylbenzene	Fluka AG	99.72	14.8	14.7
5	2-Methyl-dodecane	Inst. of Petr. Chem. Synthesis. Academy of Sciences, Moscow, U.S.S.R.	>99[a]	6.1	6.1
6	n-C_{13}	Fluka AG	99.82	6.0	6.2
7	n-C_{14}	Fluka AG	>99	5.7	5.9
8	2-Methyl-tetradecane	Inst. of Petr. Chem. Synthesis. Academy of Sciences, Moscow, U.S.S.R.	>99[a]	6.0	6.0
9	Naphthalene	Schuchardt	>99[a]	7.8	8.0
10	Pentamethyl-benzene	Schuchardt	>99[a]	9.6	9.6
11	5-Butyl-dodecane	Inst. of Petr. Chem. Synthesis. Academy of Sciences, Moscow, U.S.S.R.	>99[a]	6.1	6.1
12	n-C_{15}	Fluka AG	>99	6.2	6.1
13	Hexamethyl-benzene	Eastman Organic, Rochester, U.S.A.	>99[a]	12.7	12.9

[a] The purity was determined in two analyses carried out each time on two different columns, one coated with polyphenyl ether, the other with Apiezon L. The purity of the other components is given by the producer's guarantees.

TABLE II

SORPTIVE ACTION OF MOLECULAR SIEVE 5 A ON *iso*-PARAFFINIC HYDROCARBONS

a = the values of the ratio of peak area of the reference hydrocarbon to that of the *iso*-paraffinic hydrocarbon obtained by analysis on separating columns only. b = the values as above, obtained by analysis on separating columns connected with a pre-column packed with molecular sieve 5 A.

Reference hydrocarbon/ iso-paraffinic hydrocarbon	*Ratio of peak area of reference hydrocarbon to that of the iso-paraffinic hydrocarbon*									
	Mixture 1		*Mixture 2*		*Mixture 3*		*Mixture 4*		*Mixture 5*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Cyclooctane/ 2-methyldodecane	1.28	1.33	0.36	0.34	0.56	0.54	0.53	0.56	0.61	0.62
Cyclooctane/ 2-methyltetradecane	1.11	1.14	0.32	0.33	0.43	0.50	0.52	0.51	0.66	0.68
Cyclooctane/ 5-butyldodecane	1.10	1.16	0.33	0.31	0.43	0.45	0.48	0.49	0.52	0.49
5-Butyldodecane/ 2-methyldodecane	1.16	1.12	1.11	1.13	1.18	1.21	1.10	1.15	1.17	1.23
5-Butyldodecane/ 2-methyltetradecane	1.24	1.27	1.20	1.26	1.30	1.29	1.20	1.23	1.28	1.33

In order to define the accuracy of the method and to investigate the sorption activity of molecular sieves towards *iso*-paraffins having a long straight carbon chain with a methyl group at the end of it and towards aromatic hydrocarbons under the conditions of analysis, a series of determinations were made with specially prepared reference mixtures. They were made of high-purity *n*-paraffins, *iso*-paraffins, cyclo-paraffins and aromatic hydrocarbons (guaranteed by the producers). All the components were of the boiling range of C_{10}–C_{18} *n*-paraffins. Detailed data for the reference hydrocarbons used are presented in Table I. A series of determinations were carried out with the prepared mixtures using as the separating column a capillary tube, 50 m × 0.25 mm, coated with polyphenyl ether OS-138 (Perkin-Elmer). The conditions used in the determinations performed are given in Fig. 3. The chromatogram in Fig. 3a was obtained by analysis of the mixture of reference hydrocarbons on a capillary column. Fig. 3b is a chromatogram obtained for a sample of reference hydrocarbons using the same capillary column connected with a pre-column packed with molecular sieve 5A. The results for the determinations of the contents of the individual components of the reference mixture, which are the arithmetic mean values of six successive analyses of the mixture, are given in Table I. On the basis of the prepared mixtures of reference hydrocarbons, the observations show the behaviour of *iso*-paraffinic and aromatic hydrocarbons towards molecular sieve 5A. The results are given in Tables II and III. Table II illustrates the results of the sorptive action of molecular sieve 5A on *iso*-paraffins having a long straight carbon chain with a methyl group on the 2-C atom. Determinations were carried out with a seven-component mixture of reference hydrocarbons, consisting of three *n*-paraffins (C_{12}, C_{13}, C_{14}), three *iso*-paraffins (2-methyldodecane, 2-methyltetradecane, 5-butyldodecane) and a cyclic hydrocarbon (cyclooctane) as the internal standard.

Similarly, Table III shows the results of investigations of the sorptive action of molecular sieve 5A on *iso*-paraffins in the presence of aromatic hydrocarbons. Deter-

minations were carried out on a thirteen-component reference mixture, containing the same components as the previous mixture and also n-butylbenzene, naphthalene, pentamethylbenzene, hexamethylbenzene, n-pentadecane and n-undecane. In both cases, cyclooctane and 5-butyldodecane were used as the internal reference hydrocarbons. 5-Butyldodecane, in comparison with the other iso-paraffins, should have the weakest sorptive affinity towards molecular sieve 5A, because iso-paraffins with a methyl radical at the 2-C atom undergo partial sorption by molecular sieve 5A (ref. 13).

The repeatability of the method was also verified by the analysis of n-paraffin fractions obtained in the "ITENEX" process, consisting of C_{10}–C_{18} hydrocarbons. The contents of aromatic hydrocarbons in the samples of n-paraffins analysed constituted about 20% of the total amount of impurities. Aromatic hydrocarbons were determined by UV spectrophotometry[14].

TABLE III

SORPTIVE ACTION OF MOLECULAR SIEVE 5A ON iso-PARAFFINIC AND AROMATIC HYDROCARBONS
a and b as in Table II.

Reference hydrocarbon/ aromatic or iso-paraffinic hydrocarbon	Ratio of peak area of reference hydrocarbon to that of the iso-paraffinic or aromatic hydrocarbon									
	Mixture 1		Mixture 2		Mixture 3		Mixture 4		Mixture 5	
	a	b	a	b	a	b	a	b	a	b
Cyclooctane/ n-butylbenzene	0.51	0.52	0.44	0.46	0.51	0.55	0.52	0.54	0.62	0.65
Cyclooctane/ 2-methyldodecane	1.18	1.16	1.10	1.10	1.18	1.23	1.15	1.13	1.20	1.19
Cyclooctane/ 2-methyltetradecane	1.23	1.19	1.09	1.13	1.26	1.30	1.29	1.33	1.28	1.29
Cyclooctane/ naphthalene	0.94	1.18	0.81	1.17	0.94	1.23	0.95	1.23	0.75	1.04
Cyclooctane/ pentamethylbenzene	0.73	0.70	0.71	0.69	0.84	0.81	0.85	0.86	0.65	0.66
Cyclooctane/ 5-butyldodecane	1.21	1.19	1.07	1.05	1.16	1.18	1.21	1.18	1.25	1.23
Cyclooctane/ hexamethylbenzene	0.59	0.90	0.49	0.95	0.59	1.11	0.59	1.15	0.52	1.10
5-Butyldodecane/ n-butylbenzene	0.42	0.46	0.41	0.48	0.44	0.49	0.43	0.48	0.49	0.54
5-Butyldodecane/ 2-methyldodecane	0.97	0.95	1.03	1.05	0.96	1.00	0.98	1.02	1.12	1.11
5-Butyldodecane/ 2-methyltetradecane	1.02	1.03	1.02	1.03	1.09	1.13	1.07	1.11	0.98	1.00
5-Butyldodecane/ naphthalene	0.77	1.02	0.76	1.10	0.81	1.07	0.79	1.04	0.77	1.05
5-Butyldodecane/ pentamethylbenzene	0.60	0.60	0.66	0.63	0.73	0.71	0.71	0.72	0.80	0.79
5-Butyldodecane/ hexamethylbenzene	0.49	0.88	0.46	0.94	0.51	0.94	0.49	1.08	0.55	0.99

In order to increase the statistical data needed for the evaluation of the repeatability of the method and for the determination of the mean error of analysis, the determinations were carried out in columns with different packings and for each analysis an optimal set of conditions was selected.

TABLE IV

THE RESULTS OF DETERMINATIONS OF CONTENTS OF HYDROCARBON IMPURITIES IN C_{10}–C_{14} AND C_{14}–C_{18} n-PARAFFIN FRACTIONS

Fraction	Series	No. of determination	Contents of impurities (% w/w)		Deviation from the arithmetic mean value, d	Relative error of determination expressed as percentage of arithmetic mean value	Mean square deviation	Conditions of determination[a]		
			Found	Arithmetic mean value				Column	Temp.	Standard
C_{10}–C_{14}	I	1	5.6	5.7	−0.1	1.8	0.120	A	PR	ECH
		2	5.9		+0.2	3.5		A	IT	ECH
		3	5.7		0.0	0.0		A	IT	3MH
		4	5.7		0.0	0.0		B	PR	3MH
		5	5.8		+0.1	1.8		C	PR	1,2DEB
		6	5.6		−0.1	1.8		D	IT	ECH
	II	1	5.8	5.7	+0.1	1.8	0.127	B	IT	ECH
		2	5.5		−0.2	3.5		B	PR	ECH
		3	5.6		−0.1	1.8		D	IT	CO
		4	5.7		0.0	0.0		D	IT	ECH
		5	5.6		−0.1	1.8		A	PR	ECH
		6	5.8		+0.1	1.8		D	IT	ECH
	III	1	5.9	5.8	+0.1	1.8	0.120	C	PR	1,2DEB
		2	5.8		0.0	0.0		C	PR	1,2DEB
		3	5.6		−0.2	3.5		D	IT	ECH
		4	5.8		0.0	0.0		A	IT	3MH
		5	5.7		−0.1	1.8		A	PR	3MH
		6	5.9		+0.1	1.8		D	IT	CO
C_{14}–C_{18}	I	1	3.3	3.2	+0.1	3.1	0.156	A	PR	3MH
		2	3.1		−0.1	3.1		A	PR	3MH
		3	3.2		0.0	0.0		A	IT	ECH

	4	3.4		+0.2	6.2		A	IT	ECH
	5	3.5		+0.3	9.4		B	PR	3MH
	6	3.1		−0.1	3.1		B	PR	ECH
	7	3.2		0.0	0.0		B	IT	ECH
	8	3.1		−0.1	3.1		B	IT	3MH
	9	3.1		−0.1	3.1		C	PR	1,2DEB
	10	3.0		−0.2	6.2		C	IT	1,2DEB
II	1	3.3	3.5	−0.2	5.7	0.120	B	PR	3MH
	2	3.3		−0.2	5.7		B	PR	3MH
	3	3.4		−0.1	2.8		B	IT	ECH
	4	3.4		−0.1	2.8		B	IT	ECH
	5	3.5		0.0	0.0		B	PR	ECH
	6	3.5		0.0	0.0		C	PR	1,2DEB
	7	3.5		0.0	0.0		C	PR	1,2DEB
	8	3.6		+0.1	2.8		C	PR	1,2DEB
	9	3.6		+0.1	2.8		A	IT	ECH
	10	3.6		+0.1	2.8		A	IT	CO
III	1	3.2	3.2	0.0	0.0	0.130	C	PR	1,2DEB
	2	3.3		+0.1	3.1		C	PR	1,2DEB
	3	3.0		−0.2	6.2		C	PR	1,2DEB
	4	3.3		+0.1	3.1		C	PR	1,2DEB
	5	3.1		−0.1	3.1		C	PR	1,2DEB
	6	3.2		0.0	0.0		A	IT	ECH
	7	3.4		+0.2	6.2		A	IT	3MH
	8	3.2		0.0	0.0		A	IT	ECH
	9	3.0		−0.2	6.2		A	IT	3MH
	10	3.2		0.0	0.0		B	PR	ECH

[a] The characteristics of the columns used in the analysis (A, B, C, D) are given in the text. Temperature conditions: IT = isothermal, PR = temperature-programmed. Reference standards used: 3MH = 3 methylheptane, ECH = ethylcyclohexane, CO = cyclooctane, 1,2DEB = 1,2-diethylbenzene.

The following separating columns were employed:

A: Steel column, 2.5 m long, 5.0 mm I.D., packed with Chromosorb P, 60–80 mesh, containing 10% of Apiezon L.

B: Steel column, 2.0 m long, 2.0 mm I.D., packed with Chromosorb W, 60–80 mesh, containing 3% of SE-30.

C: Steel column, 1.0 m long, 2.0 mm I.D., packed with Chromosorb W, 60–80 mesh, containing 5% of SE-30.

D: Capillary steel column, 50.0 m long, 0.25 mm I.D., coated with polyphenyl ether OS-138.

The analyses were carried out under isothermal conditions and also with temperature-programming.

TABLE V

RESULTS OF THE DETERMINATION OF CONTENTS OF IMPURITIES IN REFERENCE MIXTURE

No. of mixture	No. of determinations	Contents of impurities (% w/w)			Deviation from actual value, d	Relative error of determination expressed as percentage of actual value
		Calculated	Found	Arithmetic mean value		
I	1	8.2	8.4	8.2	+0.2	2.4
	2		8.3		+0.1	1.2
	3		8.1		−0.1	1.2
	4		8.3		+0.1	1.2
	5		8.2		0.0	0.0
	6		8.4		+0.2	2.4
	7		8.0		−0.2	2.4
	8		8.4		+0.2	2.4
	9		8.2		0.0	0.0
	10		8.0		−0.2	2.4
II	1	3.5	3.7	3.6	+0.2	5.7
	2		3.6		+0.1	2.9
	3		3.4		−0.1	2.9
	4		3.8		+0.3	8.6
	5		3.7		+0.2	5.7
	6		3.7		+0.2	5.7
	7		3.6		+0.1	2.9
	8		3.4		−0.1	2.9
	9		3.5		0.0	0.0
	10		3.7		+0.2	5.7
III	1	1.4	1.3	1.3	−0.1	7.1
	2		1.4		0.0	0.0
	3		1.2		−0.2	14.3
	4		1.2		−0.2	14.3
	5		1.3		−0.1	7.1
	6		1.2		−0.2	14.3
	7		1.3		−0.1	7.1
	8		1.4		0.0	0.0
	9		1.2		−0.2	14.3
	10		1.3		−0.1	7.1

Additional analyses were carried out using various internal standards representing all the structural groups of hydrocarbons occurring in the impurities. The following internal standards were used: 3-methylheptane, 1,2-diethylbenzene and

TABLE VI

RESULTS OF DETERMINATION OF THE CONTENTS OF IMPURITIES ($<1\%$ w/w) IN THE MIXTURE OF n-PARAFFIN REFERENCE HYDROCARBONS

No.	Impurities content in n-C_{11-13} mixture (% w/w)			Deviation from actual value	Relative error expressed as percentage of actual value	Impurities content in n-C_{12} paraffin determined chromatographically		Deviation from arithmetic mean	Percentage of arithmetic mean	Mean square deviation
	Calculated	Determined	Arithmetic mean			Found	Arithmetic mean			
1	0.35	0.37	0.36	+ 0.02	5.7	0.41	0.41	0.00	0.00	0.0088
2		0.36		+ 0.01	2.9	0.41		0.00	0.00	
3		0.37		+ 0.02	5.7	0.41		0.00	0.00	
4		0.35		0.00	0.0	0.39		− 0.02	4.88	
5		0.36		+ 0.01	2.9	0.42		+ 0.01	2.44	
6		0.36		+ 0.01	2.9	0.41		0.00	0.00	
7		0.35		0.00	0.0	0.41		0.00	0.00	
8		0.36		+ 0.01	2.9	0.40		− 0.01	2.44	
9		0.38		+ 0.03	8.6	0.41		0.00	0.00	
10		0.35		0.00	0.0	0.40		− 0.01	2.44	
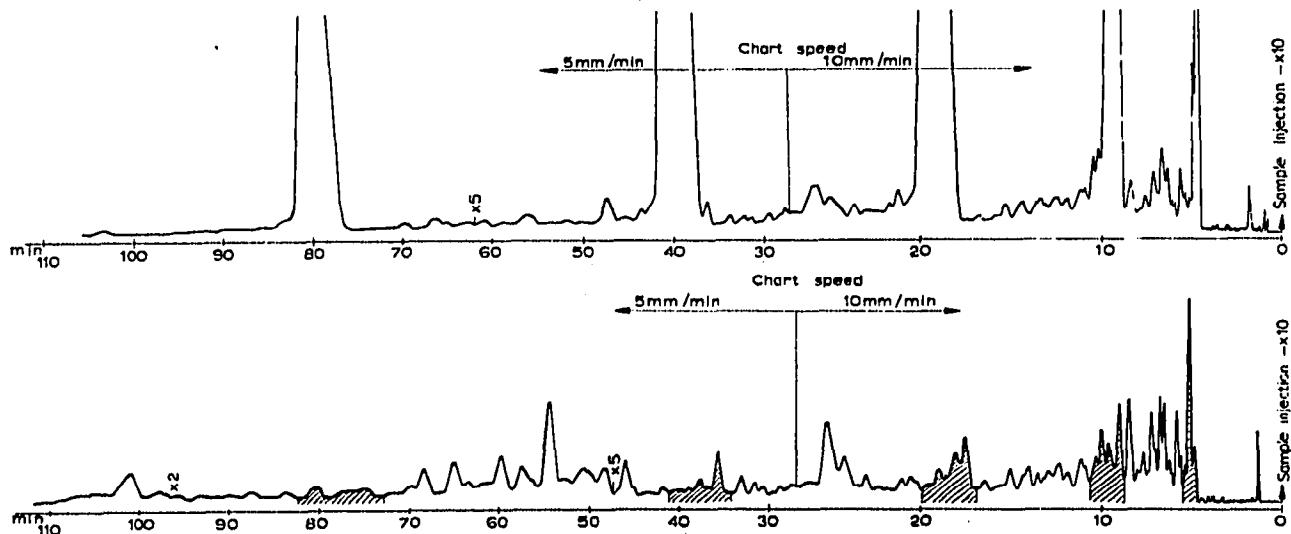
Fig. 4. (a) Chromatogram of $C_{10}-C_{14}$ n-alkane fraction. Gas chromatograph, Perkin-Elmer Type F 11 with flame-ionization detector. Capillary column, 50 × 0.25 mm I.D. coated with polyphenyl ether OS 138. Column temperature, 75°. Carrier gas, nitrogen; inlet pressure, 27 p.s.i. Sample, 0.4 µl. (b) Chromatogram of impurities of $C_{10}-C_{14}$ n-alkane fractions. Conditions as in (a).

ethylcyclohexane, all of which had > 99.9% purity, ascertained on various capillary columns, coated with polar and non-polar phases (polyphenyl ether and Apiezon L). The results of the analyses are given in Table IV.

For a fuller illustration of the accuracy of our method, the impurities contents in model mixtures, made up from reference n-paraffins $(C_{11}-C_{14})$, and in denormalisate obtained from the "ITENEX" unit were determined; the denormalisate was completely free of n-paraffins. The results are shown in Table V.

Additional investigations were carried out with a mixture containing a small quantity of impurities (<1%). A reference mixture of n-paraffins $(C_{11}-C_{13})$ was prepared especially for this purpose. According to the producer's guarantee, the purity of the individual hydrocarbons were n-C_{11}, 99.48%; n-C_{13}, 99.82%; and n-C_{12}, >99%. Before preparing the mixture, the purity of the n-C_{12} hydrocarbon was determined by using the method described here. The results of the analysis are given in Table VI, which also contains the results of the determination of impurities in the mixture of these three hydrocarbons, in the ratio 3:3:4.

Two other analyses were carried out to investigate the possibilities of applying chromatographic analysis, using capillary columns of high separating ability, for the determination of impurity contents in a $C_{10}-C_{14}$ n-paraffin fraction. The first one was carried out on the $C_{10}-C_{14}$ n-paraffin fraction from the "ITENEX" process, and the other was conducted with denormalisate of the first fraction. On comparison of the two chromatograms obtained, we found the areas of impurity constituents which in the first analysis were hidden under the peak areas of n-paraffins. Chromatograms of these two analyses are shown in Figs. 4a and 4b.

DISCUSSION

On the basis of the results obtained and presented in Table IV, a high repeat-

ability of the determinations is confirmed. The deviation from the arithmetic mean expressed as the relative error of determination, does not exceed the error occurring in routine determinations by using GC. The relatively large amount of statistical data based on the analyses on different separating columns and under different conditions support the high repeatability of this method. The data contained in Table V, representing the results of determinations of known amounts of impurities in the form of denormalisate in the mixtures of reference *n*-paraffins, allow for the assumption that the accuracy of the determination lies within the limits of the error of routine analysis when the impurities content is in the range 1–10%. When the amount of impurities is relatively small (*ca.* 1%) in an analysed sample, the value of the error is quite large, but it is still admissible. *Iso*-paraffinic, naphthenic and aromatic hydrocarbons contained in denormalisate do not greatly affect the accuracy of the analysis carried out under normal conditions. Data reported by WIEL[13] for the sorptive action of molecular sieves towards *iso*-paraffins having a long straight carbon chain with a methyl group at the end or towards naphthenic hydrocarbons with a long straight carbon chain attached, have not been confirmed under the conditions of analysis used by us. This is understandable as in the present method the contact time of the sample and molecular sieves is much shorter than the one employed by WIEL. Also, he proved the existence of the relation between the quantity of the above-mentioned constituents adsorbed and their contact time with molecular sieves.

The results in Table II support the neglect of the sorptive action of molecular sieve 5A towards *iso*-paraffins. The ratios of the areas of individual *iso*-paraffins to the area of reference hydrocarbons are equal within the limits of determination error, whether molecular sieve 5A was used in the analysis or not. The results of O'CONNOR AND NORRIS[15] give additional confirmation of the occurrence of negligible adsorption of *iso*-paraffins with a long, straight carbon chain on molecular sieves. However, they are desorbed by almost 100% under the conditions in which *n*-paraffins are hardly desorbed. On the basis of the results in Table III for the adsorption of *iso*-paraffins by molecular sieves, it can be stated that the majority of reference aromatic hydrocarbons used did not undergo sorption by molecular sieves under the analysis conditions used. The present authors have observed in their previous work[16], that, when the temperature of pre-column is lower than, equal to or only slightly higher than the boiling range of the aromatic hydrocarbons being analysed, these hydrocarbons are partially adsorbed by molecular sieves. However, if the temperature of the pre-column is higher by 50° than the boiling temperature of the hydrocarbons, adsorptivity becomes unnoticeable. In spite of keeping the temperature of the pre-column according to the requirements given in Table III, the results point distinctly to the partial sorption of naphthalene and hexamethylbenzene by molecular sieve 5A. The authors are unable to explain this phenomenon, particularly that pentamethylbenzene which is structurally very similar to hexamethylbenzene, was not adsorbed in the course of the same analysis.

On the basis of the results presented in Tables II–V, it may be assumed that in spite of the possibility of slight adsorption of some hydrocarbons such as naphthalene, hexamethylbenzene and possibly others by molecular sieves, the determination of the total contents of hydrocarbon impurities in C_{10}–C_{18} *n*-paraffin fractions with this method is characterized by high precision within the defined limits of their contents. The feasibility of the determination of total contents of impurities by using GC

even with application of capillary columns with very high solvency but without a pre-column packed with molecular sieves, is not acceptable. As is evident from the chromatograms in Figs. 4a and 4b, the amount of impurities whose peaks are covered by the peaks of n-paraffins constitutes about 30% of the total quantity of impurities contained in the sample being analysed. Such an error of determination is too great to be permissible.

From the data in Table VI, based on the analysis of the mixture of reference n-paraffins with impurity contents <1% w/w, it can be inferred that the contents of impurities, for fractions of narrow boiling range, can be determined with satisfactory accuracy down to 0.1% w/w. The results for impurity contents obtained for the mixture analysed indicate the high accuracy of the applied method (also in the range 0.1–1.0%), which can be seen by comparing the experimental data with the data calculated on the basis of producer's guarantees for the reference hydrocarbons.

The lower accuracy of the method when analysing the reference mixture with a 1.4% impurities content (Table V) is explained either by the possible effect of the boiling range of the impurities introduced (C_{10}–C_{18}) or by the number and variety of individual components of normalisate used for contamination. Also, some of the hydrocarbons present in denormalisate may be partially adsorbed by molecular sieves.

The results in Table VI suggest that the method described may also be applied to the determination of the purity of n-paraffin reference hydrocarbons.

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