Composition of C_{10} to C_{12} Alkyl-naphthalenes in Various Crude Oils*

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Summary: The analyses of all C_{10} to C_{12} alkyl-naphthalenes in nine crude oils were made by a combined chromatographic and spectrometric method.

The di-aromatic fraction was isolated from the middle distillate (180~300°C) of crude oil by liquid-solid chromatography, and analyzed by gas chromatography using a capillary column. The components inseparable by gas chromatography were determined by infrared spectrometry of the gas chromatographic effluent.

The interference of alkylbenzothiophenes in the infrared spectrometry was avoided by removing them with liquid-liquid chromatography prior to the GC-IR analysis.

The correction for alkylbenzothiophenes in the determination of some alkyl-naphthalenes by capillary gas chromatography was made by using a sulfur selective flame photometric detector.

The precision and accuracy of the method were both 5% relative.

The compositions of C_{10} to C_{12} alkyl-naphthalenes in nine crude oils were determined by this method and compared to each other. As a result, rules were found for the relative distribution of isomers. Furthermore, it was found that there was a marked difference in the relative distribution of isomers in high sulfur crude oils compared to low sulfur ones.

1 Introduction

The analysis of individual alkyl-naphthalenes in petroleum was carried out by Mair, et al. as a part of A.P.I. Research Project 6^{1),2)}. But their works were restricted to one representative crude oil. A similar analysis on a wide variety of crude oils, which would permit us to compare the compositions of alkyl-naphthalenes among various crude oils, has not yet been made. For conducting such an analysis, it was necessary to establish a conventional method of analysis since the procedure used by Mair was so large in scale that it was impractical for analyzing many samples.

This paper reports the results of analyses for all alkyl-naphthalenes up to C_{12} in nine crude oils, and describes the method used for the analyses.

2 Experimental

2.1 Apparatus

The apparatus used in the liquid chromatography (LC) were the same as those described in a previous paper³⁾. The instruments used were as follows:

Gas chromatographs were a Hitachi K-53 gas chromatograph and a Shimadzu GC-5A gas chromatograph. A Hitachi EPI-G3 infrared

spectrophotometer and a Hitachi RMS-4 mass spectrometer equipped with a GC-MS attachment were also used.

2.2 Materials

The materials used in the LC were the same as those described in the previous paper³⁾. The other chemicals used were reagent grade.

2.3 Petroleum Samples Analyzed

The samples analyzed were the straight run distillates from 5 l of crude oils boiling between 180°C to 300°C, and were prepared by a laboratory distillation under reduced pressure with a packed distillation column of 15 theoretical plates. The list of samples is as shown in Table 1.

2.4 Analytical Procedure

2.4.1 Procedure for Low Sulfur Samples

The di-aromatic fraction was isolated from the sample by liquid solid chromatography (LSC) as described in a previous paper³⁾. Accurately

Table 1 List of Sample Analyzed
(180°C to 300°C cut)

Name of Crude Oil	Yield, wt% on Crude Oil	Sulfur, wt% on the Cut
Bunju (South-East Asia)	47.3	0.04
Minas (")	18.3	0.05
Duri (")	15.7	0.07
Arabian L't (Mid-East)	21.8	0.50
Iranian L't (")	19.6	0.62
Iranian H'y (")	21.4	0.45
Khafji (")	19.9	0.82
Kuwait (")	19.3	0.73
Wafra Burgan (")	15.7	0.87

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measured quantities (about 0.5% of the initial sample) of *n*-heptylbenzene were added to the di-aromatic fractions as the internal standards. 10 μ l of the solution was injected into the gas chromatograph operated under the following conditions.

Column: Q-45 Golay column (Apiezon L coated stainless steel capillary of 0.25 mm i.d. and 45 m long). Column temperature: 160°C. Carrier gas: N₂, 1.5 kg/cm². Detector: Flame ionization detector (FID).

The concentration of each compound was calculated by assuming that the relative peak area values can be taken as relative concentrations by weight. 2,6- and 2,7-dimethylnaphthalenes gave one peak and were calculated together as a sum. 1,6- and 1,3-dimethylnaphthalenes were treated similarly.

In order to determine the relative distribution of these four compounds, GC-IR analysis was carried out as follows. The di-aromatic fraction was evaporated on a water bath to remove the LSC eluent (*n*-pentane and ethylether), and 10 μ l of the resulting residue was injected into the gas chromatograph operated under the following conditions.

Column: 3 mm i.d. and 5 m long stainless steel tube. Liquid phase: Propane deasphalted asphalt of a middle East crude, 10 wt% on solid support. Solid support: Diasolid M, 40 to 50 mesh. Column temperature: 200°C. Carrier gas: He, 50 ml/min. Collecting trap: 1 mm i.d. and 50 cm long stainless steel tube dipped in an ice bath.

2,6- plus 2,7-dimethylnaphthalenes and 1,6- plus 1,3-dimethylnaphthalenes were collected in respective traps, and washed out with 1 to 2 ml of carbon disulfide. Each washing was concentrated to about 20 μ l on a water bath and transferred into 0.1 mm thick microvolume cells. Infrared absorption spectra from 900 cm⁻¹ to 700 cm⁻¹ were recorded and absorbances of following bands were read.

2,6-dimethylnaphthalene: 810 cm⁻¹

2,7-dimethylnaphthalene: 830 cm⁻¹

1,6-dimethylnaphthalene: 780 cm⁻¹

1,3-dimethylnaphthalene: 765 cm⁻¹

The concentrations of each compound other than 2,7-dimethylnaphthalene were calculated by using the predetermined their absorptivities of the pure compounds.

For 2,7-dimethylnaphthalene, the "average

absorptivity of dimethylnaphthalene" was used (Refer to 3.2).

2.4.2 Procedure for High Sulfur Samples

The isolation of the di-aromatic fraction and gas chromatographic analysis of it with a Q-45 Golay column were similar to those for the low sulfur sample. But, in the case of the high sulfur samples, C₁₀ alkylbenzothiophenes merged with the peaks of 1-ethylnaphthalene and 2,6- plus 2,7-dimethylnaphthalenes. Correction for the sulfur compounds on these peaks was made by using a sulfur selective flame photometric detector (FPD) (Refer to 3.3).

The separation of dimethylnaphthalenes and C₁₀ alkylbenzothiophenes was carried out prior to GC-IR analysis of 2,6-, 2,7-, 1,6-, and 1,3-dimethylnaphthalenes, by means of liquid liquid chromatography (LLC) described in a previous paper³⁾.

The GC-IR procedure for the LLC fraction was similar to that described in 2.4.1.

3 Discussion of Analytical Procedure

3.1 Analytical Gas Chromatography

The gas chromatographic separation of an alkyl-naphthalene mixture was reported by numerous investigators, and it seemed to be difficult to separate all compounds up to C₁₂. The column used gave the chromatogram, shown in Fig. 1, which was basically similar to, but superior in plate number to, that reported by Walker et al.⁴⁾. 2,6- and 2,7-Dimethylnaphthalenes were not separated as reported Walker et al., Mostecký et al.,⁵⁾ and 1,6- and 1,3-dimethylnaphthalenes also gave only one peak, though Mostecký reported their partial separation⁵⁾. Methylbiphenyls did not merge with any alkyl-naphthalene peak, differing from Mostecký's observation. But the marketed Q-45 columns differed from one another in separation ability and separation characteristics, and with some columns, operations at two different column temperatures between 140°C to 180°C were necessary to separate all peaks in Fig. 1.

Mair et al. reported that 1,8-dimethylnaphthalene was not detected¹⁾. Even if the compound were present, it may be difficult to determine by gas chromatography using this procedure, because its retention volume was considerably larger than other isomers^{4),5)} and it may be merged in any C₁₃ alkyl-naphthalene peak. The existence of the compound was searched by means of

N: Naphthalene MN: Methyl-naphthalene BP: Biphenyl
 2,6-, 2,7-,....., : Dimethyl-naphthalene
 Sample: Bunju 180~300°C cut, di-aromatic fraction

Fig. 1 Gas Chromatogram of Di-aromatic Fraction

Fig. 2 GC-MS Chromatograms of Di-aromatic Fraction

GC-MS. The scanning magnetic field of the mass spectrometer was fixed at $m/e=156$ (parent mass of dimethylnaphthalene), and the chromatogram of $m/e=156$ and total ions were recorded at the same time.

The chromatograms were as shown in **Fig. 2**. The peaks in the chromatogram of total ions were identified by taking their mass spectra. The parent masses determined in this manner were also shown in the **Fig. 2**. From those spectra it was proved that the peaks in the chromatogram of $m/e=156$ were all due to isotope ions of 155 masses which were the main fragment ions of C_{13} alkylnaphthalenes ($m/e=170$). No peak remained after subtracting the isotope contributions.

The possible maximum quantities of 1,8-dimethylnaphthalene estimated from the S/N ratio of the method used were below 1% of total dimethylnaphthalenes present.

As the relative response of the FID used lay in

the range of 0.95 to 1.05 for all available pure alkylnaphthalene compounds on comparison to 1-methylnaphthalene, the calculation was made without using response factors.

3.2 GC-IR Analysis

In order to search for a suitable liquid phase for the preparative GC of alkylnaphthalenes, a comparative study was made among Apiezon L, Silicone SE-30, Silicone-KF 96 and petroleum asphalts. As the result of the study, propane deasphalted asphalt of a Middle East crude proved to be the best for the purpose, because the decrease of plate number with increase of sample size was the least and loss of the liquid phase from the column could be minimized with it. This liquid phase has been proved in the author's laboratory to be excellent also for general use at column temperature up to 300°C⁽⁶⁾.

Prior to the infrared analysis of 2,6-, 2,7-, 1,6-, and 1,3-dimethylnaphthalenes, the absorptivities of each compound must be determined. Since

Table 2 Summed Intensity of Absorption Bands of Dimethylnaphthalenes in the Range of 700~900 cm^{-1}

Compound	Intensity*	Band Position (cm^{-1})
1,2-DMN	44	737, 770, 804
1,3-DMN	46	743, 770, 841, 857
1,4-DMN	44	752, 821
2,3-DMN	43	743, 870
1,5-DMN	48	784
1,6-DMN	42	747, 783, 812, 869
2,6-DMN	35	810, 872
Average	43.4	

* Absorptivity (cm , W/V % in CS_2)

pure 2,7-dimethylnaphthalene was not available, its absorptivity was assumed on the following basis: The sum of the intensity values of the absorption bands corresponding to CH out-of-plane bending vibrations of a naphthalene ring was approximately constant among the isomers of dimethylnaphthalene. The data are as shown in **Table 2**. The average value in **Table 2** was taken as the absorptivity of 2,7-dimethylnaphthalene. A searching of the absorption bands assigned to 2,7-dimethylnaphthalene in the spectra of actual samples was made by comparison with the published spectrum,⁷⁾ and the band occurring at 830 cm^{-1} was the only one observed. The spectra of an actual sample was as shown in **Fig. 3**.

The di-aromatic fraction of the high sulfur sample contained alkylbenzothiophenes. The major components of the C_{10} alkylbenzothiophenes could not be separated from the 2,6-, 2,7-, 1,6-, and 1,3-dimethylnaphthalenes by preparative GC using any liquid phase available. Since alkylbenzothiophenes also have intense bands in the same wave number region as alkyl-naphthalenes, interference of C_{10} alkylbenzothiophenes in the IR analysis of the GC fractions was unavoidable.

In order to avoid the interference, separation of dimethylnaphthalenes and C_{10} alkylbenzothiophenes had to be made prior to GC-IR analysis. The separation could be made satisfactorily with liquid-liquid chromatography using a mixture of dimethylsulfoxide and dimethylformamide as the liquid phase and calcined alumina as a solid support³⁾.

3.3 Correction of Sulfur Compounds by FPD

Figure 4 illustrates the gas chromatograms of a high sulfur di-aromatic fraction using FID and FPD as the respective detector. The peaks in the chromatogram using FPD were proved to be C_{10} alkylbenzothiophenes by GC-MS. It is

(I) 2,6-plus 2,7-Dimethylnaphthalene fraction
(II) 1,6-plus 1,3-Dimethylnaphthalene fraction
① 2,6-Dimethylnaphthalene, ② 2,7-Dimethylnaphthalene, ③ 1,7-Dimethylnaphthalene, ④ Unknown, ⑤ 1,3-Dimethylnaphthalene, ⑥ 1,6-Dimethylnaphthalene

Fig. 3 Infrared Spectra of GC Fractions

—: Chromatogram by FID
----: Chromatogram by FPD
Sample: Wafra Burgan 180~300°C cut, di-aromatic fraction

EN: Ethylnaphthalene

DMN: Dimethylnaphthalene

①, ②, ..., ⑤: C_{10} Alkylbenzothiophene

Fig. 4 Chromatogram of High Sulfur Di-aromatic Fraction

obvious that 2,6-plus 2,7-dimethylnaphthalenes and 1-ethylnaphthalene can not be determined by only GC using FID. Separation by LLC, though possible, is inconvenient in determining

the overall composition. So a study was made on the use of FPD to determine the alkylbenzothiophenes to be subtracted from the peaks in question.

Quenching, though significant in general use of FPD⁸⁾, was considered to be minor, because the quantities of hydrocarbon introduced into the detector together with sulfur were very small (10^{-7} – 10^{-8} g in the case of 2,6- plus 2,7-dimethylnaphthalenes) and the ratio of hydrocarbon to sulfur was also small (less than 10/1). Simple confirmation on the problem was made with mixtures of naphthalene and benzothiophene, and it was proved that the response of the FPD for 5×10^{-9} g of benzothiophene was not affected by less than 5×10^{-7} g of naphthalene.

Since each peak of C₁₀ alkylbenzothiophenes was not identified as an individual compound, plotting the calibration curve of concentration vs. detector response for each peak was impossible. So relative amounts were at first calculated using the calibration curve of benzothiophene under the following assumptions. (1) The slopes of the log-log calibration curves of C₁₀ alkylbenzothiophenes were all equal to that of benzothiophene.

Table 3 Relative Amounts of Alkylbenzothiophenes Determined by FID and FPD (Alkylbenzothiophene 5/Alkylbenzothiophene 4)

Sample Name	Detector		Difference (% of FID Value)
	FID	FPD	
Arabian L't	2.28	2.06	-10
Iranian L't	2.20	2.41	+10
Iranian H'y	2.42	2.69	+11
Khafji	1.50	1.48	-1
Kuwait	1.44	1.32	-8
Wafra Burgan	1.27	1.20	-6

phene. (2) The log-log calibration curves of C₁₀ alkylbenzothiophenes were all the same. Next, the values of relative amounts were converted to absolute ones by the relationship between the values of FID and FPD response on peaks 4 and 5 in Fig. 4.

The ratio of peak 4 to peak 5 can be obtained by either FID or FPD. So comparison between these two values reveals the reliability of the estimation described here. The data are as shown in Table 3.

The error was about 10% relative.

3.4 Precision and Accuracy

The results of an examination for the precision and accuracy of the method are as shown in Table 4. The accuracy was estimated by an addition of pure compounds to a sample.

The repeatability (deviation) was about 5% relative, and the difference between the observed and true values was estimated to be in the range of repeatability.

4 Results and Discussion

The results of the analyses are given in Table 5. The relative abundances of dimethylnaphthalene isomers calculated from Table 5 are as shown in Table 6. From these results the following rules were found to hold on the relative distribution of alkylnaphthalene isomers in petroleum.

(1) Low sulfur crude oils

a. Within the subsets of methylnaphthalenes, ethylnaphthalenes, and dimethylnaphthalenes, the relative abundances of isomers are approximately invariant among the different crude oils.

b. In mono-alkylnaphthalenes substitution in position 2 is predominant. The ratio of 2-alkyl

Table 4 Precision and Accuracy (Bunju 180~300°C cut, wt%)

Compound	Precision				Accuracy		
	I	II	III	Deviation %	Added	Found	Difference %
Naphthalene	1.54	1.55	1.64	2.9			
1-MN	1.59	1.61	1.69	3.3	1.04	1.09	4.8
2-MN	2.75	3.00	2.99	4.9			
1-EN	0.13	0.13	0.13	0.0			
2-EN	0.38	0.34	0.35	5.9			
1,2-DMN	0.19	0.17	0.17	6.8	1.03	1.01	1.9
1,3-DMN	0.42	0.50	0.45	8.8	0.82	0.92	12.2
1,4-DMN	0.17	0.17	0.18	3.5			
2,3-DMN	0.31	0.32	0.35	6.4			
1,5-DMN	0.13	0.13	0.14	4.5			
1,6-DMN	2.06	1.78	1.94	7.3	1.19	1.15	3.4
1,7-DMN	0.70	0.65	0.69	3.8			
2,6-DMN	0.76	0.76	0.84	5.8	0.45	0.44	2.2
2,7-DMN	0.63	0.60	0.60	2.8			
Average				4.8			4.9

MN: Methylnaphthalene, EN: Ethylnaphthalene, DMN: Dimethylnaphthalene

Table 5 C₁₀ to C₁₂ Alkyl-naphthalenes in Various Crude Oils (wt% in 180~300°C cut)

	Low Sulfur Crude Oil			High Sulfur Crude Oil					
	Bunju	Minas	Duri	Arabian Light	Iranian Heavy	Iranian Light	Khafji	Kuwait	Wafra Burgan
Naphthalene	1.54	0.20	0.07	0.06	0.13	0.13	0.07	0.11	0.13
1-MN	1.59	0.28	0.14	0.22	0.30	0.30	0.14	0.22	0.26
2-MN	2.75	0.50	0.26	0.19	0.37	0.39	0.14	0.22	0.27
1-EN	0.13	0.02	0.03	0.04	0.04	0.04	0.03	0.03	0.04
2-EN	0.38	0.08	0.09	0.07	0.09	0.08	0.05	0.06	0.08
1,2-DMN	0.19	0.05	0.07	0.08	0.08	0.07	0.05	0.06	0.09
1,3-DMN	0.42	0.13	0.15	0.13	0.13	0.17	0.08	0.09	0.13
1,4-DMN	0.17	0.04	0.05	0.07	0.06	0.06	0.04	0.05	0.06
2,3-DMN	0.31	0.08	0.11	0.04	0.06	0.06	0.03	0.03	0.04
1,5-DMN	0.13	0.04	0.06	0.11	0.07	0.08	0.06	0.08	0.09
1,6-DMN	2.06	0.62	0.71	0.28	0.35	0.35	0.19	0.24	0.30
1,7-DMN	0.70	0.16	0.17	0.13	0.17	0.18	0.09	0.11	0.14
2,6-DMN	0.76	0.23	0.23	0.11	0.16	0.18	0.07	0.10	0.12
2,7-DMN	0.63	0.16	0.13	0.08	0.11	0.13	0.05	0.07	0.09
BT-1	—	—	—	0.01	0.02	0.02	0.02	0.02	0.03
BT-2	—	—	—	0.01	0.01	0.01	0.01	0.01	0.02
BT-3	—	—	—	0.01	0.01	0.02	0.01	0.02	0.03
BT-4	—	—	—	0.04	0.04	0.04	0.04	0.05	0.07
BT-5	—	—	—	0.09	0.09	0.09	0.06	0.07	0.08

MN: Methyl-naphthalene, EN: Ethyl-naphthalene, DMN: Dimethyl-naphthalene
 BT: Alkylbenzothiophene, 1,2,, correspond to those in Fig. 4.

Table 6 Relative Abundances of Dimethyl-naphthalene Isomers
(Total of dimethyl-naphthalene=100)

	Low Sulfur Crude Oils	High Sulfur Crude Oils
1,2-DMN	3~4	6~9
1,3-DMN	8~9	11~13
1,4-DMN	3	5~6
2,3-DMN	5~6	4~5
1,5-DMN	2~4	6~11
1,6-DMN	38~42	27~29
1,7-DMN	10~13	13~14
2,6-DMN	14~15	11~14
2,7-DMN	8~12	8~10
Total	100	100
1,6+1,7	51~52	40~42
2,6+2,7	21~26	18~24
1,5	2~4	6~11
Total	77~80	69~72
Total	20~23	28~31

to 1-alkyl is 1.8 for methyl-naphthalenes and 3.3 for ethyl-naphthalenes.

c. In dimethyl-naphthalenes, the isomers having one methyl group on each ring (1,6-, 1,7-, 2,6-, 2,7-, and 1,5- isomers) amount, in total, to 80% of the dimethyl-naphthalenes.

d. In the dimethyl-naphthalenes having one methyl group on each ring, the isomers with one methyl group in position 1 and the other in position 2 (1,6- and 1,7 isomers) are the most predominant in total, and those with both methyl groups in position 2 (2,6- and 2,7 isomers) are

Table 7 Comparison of Relative Isomer Abundances between Low Sulfur Crude and High Sulfur Crude

	Low Sulfur Crude Oils	High Sulfur Crude Oils
2-MN/1-MN	1.8	1.1
2-EN/1-EN	3.3	2.0
(1,6+1,7) DMN/(2,6+2,7) DMN	2.1	2.0
1,6-DMN/1,5-DMN	14.0	3.4
3.8	2.4

MN: Methyl-naphthalene, EN: Ethyl-naphthalene
 DMN: Dimethyl-naphthalene

second. Those with both methyl groups in position 1 (1,5- and 1,8- isomers) are far smaller than others. Above all, 1,8-dimethyl-naphthalene was not detected in any crude oil.

(2) High sulfur crude oils.

The rules found in low sulfur crude oils hold also for high sulfur crude oils qualitatively. In addition, there is a marked difference in the values of relative abundances of isomers in high sulfur crude oils compared to those of low sulfur crude oils. That is to say, in low sulfur crude oils, the predominant isomers are more predominant as compared with high sulfur crude oils.

The comparison of the relative abundances between low sulfur crude oils and high sulfur crude oils is as shown in **Table 7**. The above mentioned tendency can be seen from the Table.

If it is assumed that the predominant isomers are the more stable ones, the composition of the low sulfur crude oil can be considered to be more stabilized compared with the high sulfur crude oil.

5 Conclusion

The analyses of all C_{10} to C_{12} alkyl-naphthalenes in nine crude oils were made by a combined method of chromatography and spectrometry. Several difficulties encountered in the intended analysis were all satisfactorily solved. The isolation method for alkyl-naphthalenes was established previously³⁾. The components inseparable in gas chromatography were determined by a simple GC-IR technique. Lack of pure compounds for calibration work in the IR and FPD analyses was solved by introducing reasonable assumptions.

Thus a convenient and reliable analytical procedure was established. The compositions of C_{10} to C_{12} alkyl-naphthalenes in nine crude oils were determined by this method and compared to each other. As the result, rules on the relative

distribution of isomers were found. Furthermore, a marked difference was found between the relative distributions of isomers in high and low sulfur crude oils.

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