

CHROM. 15,946

## RELATIVE ABUNDANCE OF DIMETHYLNAPHTHALENE ISOMERS IN CRUDE OILS

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(First received November 26th, 1982; revised manuscript received April 20th, 1983)

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### SUMMARY

A procedure has been developed for routine relative quantitative analysis of each of the ten isomeric dimethylnaphthalenes in crude oils. The method requires isolation of an alkylnaphthalene fraction by preparative thin-layer chromatography on activated alumina plates, followed by fused-silica capillary gas chromatography analysis on OV-1 and OV-1701 phases. Because the concentration of 1,8-dimethylnaphthalene in crude oils is so low, it is necessary to carry out a preparative capillary gas chromatography step for analysis of this isomer. In some crude oils, the presence of dimethylbenzothiophenes interferes with the analysis: these components can be removed by treatment of the alkylnaphthalene fraction with *m*-chloroperbenzoic acid prior to analysis.

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### INTRODUCTION

As part of a study into the geochemical significances of changes in the distribution of alkylnaphthalenes, we required to be able to carry out rapid and accurate routine analyses of each of the ten isomeric dimethylnaphthalenes in crude oils. Tesařík *et al.*<sup>1</sup> have summarised attempts to separate dimethylnaphthalenes by both packed column and capillary gas chromatography (GC), and were in fact successful in separating all of the isomers, excepting the 1,6- and 1,7-pair, on a composite column comprised of one column coated with Bentone 34 and dodecyl phthalate (50:50) connected to a column coated with Ucon LB 550 X and tris(cyanoethoxy)propane (TCEP) (85:15). There have also been a number of subsequent reports listing additional retention data on dimethylnaphthalenes and related aromatic compounds which are characteristically found in crude oils<sup>2-4</sup>. In this paper we report a procedure for quantitative analysis of all ten isomeric dimethylnaphthalenes in crude oils. This procedure involved a preliminary isolation of an alkylnaphthalene fraction by thin-layer chromatography (TLC), followed by capillary GC analysis using two columns with different stationary phases.

## EXPERIMENTAL

*Crude oil samples*

The sample described as a Wyoming Pennsylvanian oil was recovered from the Pennsylvanian formation in the Nieber Dome Field in Wyoming, U.S.A. That described as Barrow Upper Jurassic was recovered from the 2040-m level in an Upper Jurassic formation in the Barrow Island oil field, Western Australia.

*Dimethylnaphthalene standards*

The 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 2,3- and 2,6-dimethylnaphthalenes were purchased commercially (Aldrich, Fluka). 1,8-Dimethylnaphthalene was prepared from acenaphthylene according to literature procedures<sup>5</sup>. 1,7-Dimethylnaphthalene was obtained as a mixture by isomerising the 1,8-isomer<sup>6</sup>. The 2,7-isomer was contained in an all-isomer mixture (Aldrich).

*Isolation of alkylnaphthalenes*

Crude oil (80 mg), diluted with dichloromethane if necessary, was applied as a thin band to freshly activated alumina TLC plates (0.75 mm, Merck Alumina G) using a Camag chromatocharger. A reference mixture of dimethylnaphthalenes was spotted at each end of the plate, the plates were developed with pentane and the required band ( $R_f \approx 0.4-0.5$ ) was located using short wavelength UV light. The alkylnaphthalene fraction was extracted from the recovered band of alumina by extraction with dichloromethane (20 ml), and this solution was concentrated to 1–2 ml in a Kuderna–Danish apparatus. In one experiment carried out to assess the extent of fractionation in the procedure, the solution containing the alkylnaphthalene fraction was concentrated to a volume of 250  $\mu$ l. A 50- $\mu$ l sample was set aside for GC analysis and the remaining 200  $\mu$ l were divided into two equal portions. One portion was subjected to TLC under the conditions outlined above, and the second portion was treated similarly, except that the TLC plate was left on the bench for 30 min prior to extraction of the alkylnaphthalene fraction. The two alkylnaphthalene fractions resulting from this procedure were then analysed by GC under standard conditions. Gas chromatograms were recorded using a Hewlett-Packard (HP) 5880 gas chromatograph fitted with a 50-m wall-coated open-tubular (WCOT) column coated with either OV-1 or OV-1701. The oven was held at 30°C for 5 min then temperature programmed at 1° min<sup>-1</sup>, to 270°C. Hydrogen was used as a carrier gas at a flow-rate of 30 cm sec<sup>-1</sup>, and peaks were detected using a flame ionization detector. Mass spectra were recorded using an HP 5985B GC–mass spectrometry (MS) system fitted with a 50-m OV-101 WCOT column operating under the same conditions as the HP 5880. The ion source temperature was 250°C and the electron ionizing voltage was 70 eV.

*Isolation of 1,8-dimethylnaphthalene by preparative capillary GC*

An alkylnaphthalene fraction was chromatographed on the HP 5880 system fitted with a 50-m OV-101 capillary column. When the 1,2-dimethylnaphthalene peak had just eluted, the detector end of the column was quickly removed from the FID, withdrawn through the oven door and the oven door was closed immediately to allow the temperature program to continue. The effluent from the column was bubbled

through dichloromethane (10 ml) for 3 min, then the section of the column protruding from the oven was broken off and any material condensed on its surface was collected by forcing dichloromethane (200  $\mu$ l) through the tubing with a syringe. The combined dichloromethane solutions were concentrated to 10  $\mu$ l using a Kuderna-Danish apparatus prior to analysis by GC-MS.

#### *Oxidation of sulphides to sulphones*

*m*-Chloroperbenzoic acid (2 mg) was added to the alkylnaphthalene fraction extracted from the alumina of the TLC plate with dichloromethane (20 ml) and the mixture was allowed to stand at ambient temperature for 10 min. The solution was then passed through a column of basic alumina (5 g, Woelm W200 Basic) to remove sulphones and acidic material.

## RESULTS AND DISCUSSION

The complex composition of crude oils is evident from the partial GC trace of the Barrow Upper Jurassic oil which is shown in Fig. 1. Preparative TLC of this oil on a freshly activated alumina plate under carefully controlled and standardised conditions provided an alkylnaphthalene fraction. The capillary GC traces of this alkylnaphthalene fraction on a OV-1 column is shown in Fig. 1b. That carried out using an OV-1701 column is shown in Fig. 1c. Except for 2,7-dimethylnaphthalene, where published retention index data<sup>2,4</sup> were used, assignment of peaks was made by coinjection of authentic standards. The possibility of coelution of other compounds with the dimethylnaphthalenes was eliminated by GC-MS analysis. Examination by GC-MS of extracts of the regions of the plate immediately above and below the region isolated confirmed that this fraction contains all of the naphthalenes, methylnaphthalenes and dimethylnaphthalenes in the oil sample.

Excepting for 1,5- and 2,3-isomers, which coeluted, all of the dimethylnaphthalenes were resolved on the OV-1 column under the conditions employed. On the OV-1701 column, these isomers were resolved, but in this case, the 2,6- and 2,7-isomers coeluted, and the 1,3- and 1,7-isomers were poorly resolved. The distribution of dimethylnaphthalenes in the Barrow Upper Jurassic oil can therefore be obtained from these two chromatograms. The mean values obtained from five replicate analyses are shown in Table I, column 1. The reproducibility of the analysis is  $\pm 3\%$ .

As might have been expected on the basis of thermodynamic data<sup>7</sup>, 1,8-dimethylnaphthalene is usually not detected in crude oils<sup>8</sup> or coal tars<sup>1</sup>. A tiny peak at a retention time very similar to that of 1,8-dimethylnaphthalene is indicated in Fig. 1b. Coinjection with authentic material showed that it was not the 1,8-isomer, and GC-MS analysis confirmed that this isomer was not present in sufficient quantity for direct analysis to be possible. A fraction containing 1,8-dimethylnaphthalene and acenaphthylene was therefore obtained by preparative capillary gas chromatography. This was analysed by GC-MS: the areas of the peaks due to 1,8-dimethylnaphthalene in the *m/z* 141 and 156 mass fragmentograms were compared with the areas of the peaks due to acenaphthylene in the *m/z* 153 and 154 mass fragmentograms; finally, after correction had been made for detector response, the level of 1,8-dimethylnaphthalene could be related to those of the other isomers via their ratios to the level

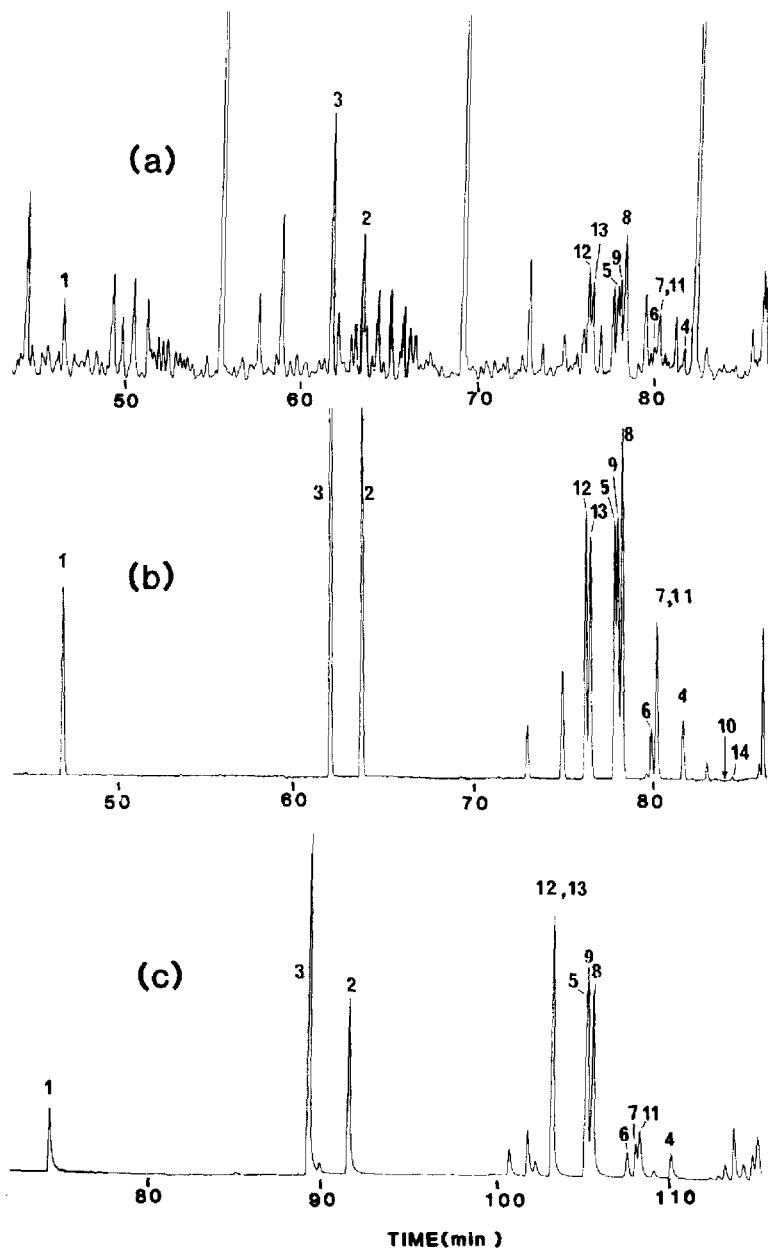


Fig. 1. Capillary GC traces of the Barrow Upper Jurassic crude oil (a) and its alkylnaphthalene fraction using OV-1 (b) and OV-1701 (c) columns. Peaks were assigned as: 1 = naphthalene; 2 = 1-methylnaphthalene; 3 = 2-methylnaphthalene; 14 = acenaphthylene; dimethylnaphthalenes (see Table I).

of acenaphthylene. In the case of the Barrow Upper Jurassic oil, the 1,8-isomer was found to account for approximately 0.003% of the dimethylnaphthalenes.

The boiling points of dimethylnaphthalenes range from 262°C for the 2,6- and 2,7-isomers to 277°C for the 1,8-isomer. We were therefore concerned that fraction-

TABLE I

RESULTS FROM ANALYSES OF ALKYLNAPHTHALENES IN BARROW UPPER JURASSIC CRUDE OIL

Values are percentages of the sum of the areas of the peaks due to the dimethylnaphthalene isomers. Values for sample 1 are the means of five replicate analyses. Values for sample 2 were obtained after reduction of sample solution volume to 250  $\mu$ l. Values for sample 3 were obtained by repeating the TLC procedure on sample 2. Sample 4 was obtained from sample 2 by repeating the TLC procedure and allowing the plate to stand at ambient temperature for 30 min before isolation of the alkyl-naphthalene fraction and GC. n.d. = Not determined.

Compound	Peak No.	Alkyl-naphthalene fractions			
		1	2	3	4
1,2-Dimethylnaphthalene	4	3.7	3.7	3.8	3.7
1,3-Dimethylnaphthalene	5	15.4	15.6	15.5	16.0
1,4-Dimethylnaphthalene	6	3.0	2.9	2.9	3.0
1,5-Dimethylnaphthalene	7	4.0	4.0	4.0	4.0
1,6-Dimethylnaphthalene	8	21.2	21.2	21.1	21.1
1,7-Dimethylnaphthalene	9	15.6	15.3	15.4	15.0
1,8-Dimethylnaphthalene	10	0.003	n.d.	n.d.	n.d.
2,3-Dimethylnaphthalene	11	6.6	6.7	6.8	6.7
2,6-Dimethylnaphthalene	12	16.0	15.9	15.9	15.9
2,7-Dimethylnaphthalene	13	14.5	14.6	14.5	14.5

ation might occur during our analytical procedure, particularly in the TLC step. In order to eliminate the possibility that losses occur during evaporation of the dichloromethane solvent an alkyl-naphthalene fraction was evaporated to 250  $\mu$ l, and the residue was analysed by GC; Table I, sample 2. The TLC procedure was repeated on two 100- $\mu$ l portions of this residue: in one case, however, the TLC plate was allowed to stand on the bench for 30 min before the alkyl-naphthalene band was removed. Analysis of these two fractions was carried out and the results are presented in Table I: samples 4 and 3 respectively. The values in this table show that there is no relative enrichment or depletion of any of the dimethylnaphthalene isomers.

Attempted quantitative analysis of the dimethylnaphthalene isomers in the alkyl-naphthalene fraction of some oils is frustrated by the co-elution of dimethylbenzothiophenes with the dimethylnaphthalenes. This problem can be overcome by oxidising the interfering benzothiophenes to the corresponding sulphones using the method of Hunt and Shabanowitz<sup>9</sup>. The dichloromethane solution of the alkyl-naphthalene fractions was simply treated with excess of *m*-chloroperbenzoic acid at room temperature for 10 min, then the reaction products and excess reagent were removed by passing the solution through a short column of basic alumina. The eluate was analysed by GC without further purification. Fig. 2a shows the GC profile of the alkyl-naphthalene fraction of the Wyoming, Pennsylvanian oil; Fig. 2b shows the same region of the GC trace of the same fraction after treatment to remove the dimethylbenzothiophenes.

## ACKNOWLEDGEMENTS

This work was undertaken as part of a National Energy Research, Development and Demonstration Programme administered by the Department of National

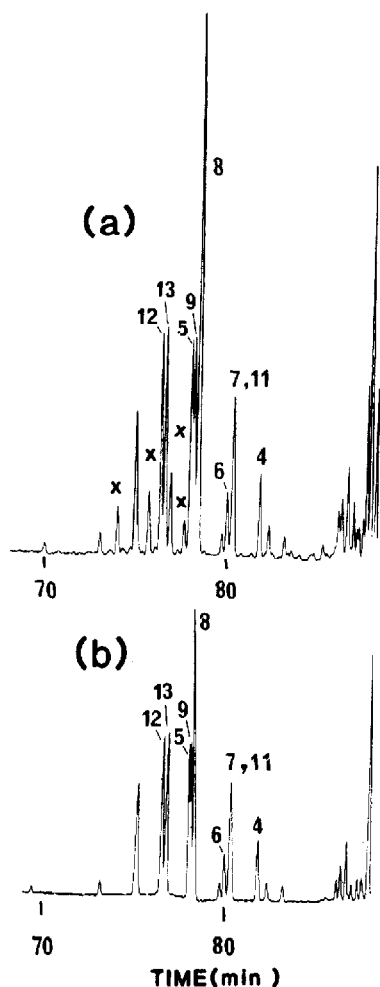


Fig. 2. Capillary GC traces of the alkylnaphthalene fraction of Wyoming Pennsylvania crude oil before (a) and after (b) peracid treatment. Peaks labelled X represent isomeric dimethylbenzothiophenes; for other peak assignments refer to Table I and Fig. 1.

Development (Australia). We also thank Dr. J. K. Volkman for helpful discussions and suggestions.

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