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### Analysis of trimethylnaphthalenes in petroleum by capillary gas chromatography

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Analysis of polymethylnaphthalenes in complex hydrocarbon mixtures is of importance in environmental and geochemical studies. The high toxicity of polymethylnaphthalenes to marine life, caused in part by the relatively high solubility of these petroleum-based hydrocarbons, makes them important targets for environmental monitoring programmes<sup>1-3</sup>. In addition to the toxic effects of alkyl-naphthalenes, several reports indicate that microorganisms preferentially degrade some dimethylnaphthalene isomers, thereby enabling the extent of biodegradation of petroleum to be assessed from the dimethylnaphthalene composition (*e.g.* ref. 4). Changes in the relative abundancies of certain isomers with increasing thermal maturity of sedimentary organic matter have also been reported, and this suggests that alkyl-naphthalenes may have potential for use as petroleum maturation indicators<sup>5,6</sup>.

High-resolution capillary gas chromatography (GC) has been used to separate each of the ten isomeric dimethylnaphthalenes and to examine the composition of isomers in extracts from coals, sediments and petroleum<sup>4,7,8</sup>. Apparently, separation of the more complex mixtures of trimethylnaphthalenes has not been achieved, although the retention behaviour of seven of the fourteen isomers has been described from a study using packed columns<sup>9</sup>.

In this paper we report an analytical procedure suitable for the analysis of trimethylnaphthalene isomers in petroleum using capillary GC. Elution orders are reported for thirteen isomers on capillary columns coated with cross-linked methyl-silicone, 5% phenylmethylsilicone and polar CP Wax 57CB phases.

## EXPERIMENTAL

### *Petroleum fractions*

Alkyl-naphthalene fractions were isolated from Barrow crude (Upper Jurassic, Carnarvon Basin, Australia) and North Apoi crude (Miocene, Nigeria) by preparative thin-layer chromatography (TLC) on alumina<sup>8</sup>.

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*Trimethylnaphthalenes (TMNs)*

2,3,5-TMN ( $\equiv$  1,6,7-) was obtained from Aldrich. The 1,3,7- and 2,3,6-isomers were originally purchased from Aldrich and an unknown commercial supplier and generously donated to us by Prof. L. H. Klemm (University of Oregon, U.S.A.) and Mr. B. Tripp (Woods Hole Oceanographic Institution, U.S.A.) respectively. The 1,4,5- and 1,2,7-isomers were synthesised previously<sup>9</sup> and kindly donated to us. 1,2,5-TMN was obtained by selenium dehydrogenation of a terpenoid acid<sup>10</sup>, followed by recrystallisation of the picrate. Gatterman formylation<sup>11</sup> of 2,3-, 1,4- and 2,6-dimethylnaphthalenes provided samples of 1,2,3-, 1,2,4- and 1,2,6-TMN. 1,4,6-, 1,3,5- and 1,3,8-TMN were obtained by Friedel Crafts syntheses using established procedures<sup>12,13</sup>. A further sample of the 1,3,5-isomer was prepared by isomerisation of 1,4,5-TMN. Intermediates in the syntheses were characterised by IR and mass spectrometry (MS). Spectra compared favourably with literature spectra<sup>11-13</sup>. Confirmation of the structures of the 1,2,4-, 1,2,6-, 1,3,7-, 1,4,5-, 1,4,6-, 1,6,7- and 2,3,6-TMN isomers was obtained by <sup>1</sup>H nuclear magnetic resonance (NMR) (60 MHz). Again, spectra compared favourably with literature data<sup>14</sup>.

*Preparative gas chromatography*

Individual isomers were isolated from mixtures by preparative GC (6-m 15% SE-30 on Chromosorb W, 60-80 mesh) using a Varian Aerograph 700 with helium carrier gas at 200°C oven temperature.

*Capillary gas chromatography*

Capillary GC was performed on Hewlett Packard 5880 chromatographs fitted with 50 m  $\times$  0.2 mm I.D. WCOT columns coated with cross-linked methylsilicone (Hewlett-Packard), 5% phenylmethylsilicone (Hewlett-Packard) or CP Wax 57CB (Chrompack). The oven temperature was held at 40°C for 1 min then programmed at 1°C (silicone phases) or 2°C (Wax) to 230°C. Hydrogen was used as carrier gas at a linear flow velocity of *ca.* 30 cm per sec, and peaks were detected using a flame ionisation detector. Labelled peaks in the figures were identified by co-chromatography, and their purity assessed by GC-MS using an HP 5985B GC-MS system. Chromatography conditions were as outlined above and the ion source temperature was 250°C and the electron ionising voltage was 70 eV.

*NMR*

<sup>1</sup>H NMR spectra were recorded using a Hitachi-Perkin Elmer R-20B at 60 MHz as solutions in tetrachloromethane.

## RESULTS AND DISCUSSION

Fig. 1 shows gas chromatograms of mixtures of the synthetic TMNs using capillary columns coated with the three phases. The use of methylsilicone phase resulted in the coelution of three pairs of isomers (Fig. 1A). Resolution of two of these pairs could be achieved using 5% phenylmethylsilicone phase (Fig. 1B) and the remaining coeluting pair could be separated using a more polar CP Wax phase (Fig. 1C). Although the polar wax phase results in resolution of this (1,4,6- and 1,3,5-) pair, some of the remaining isomers then co-eluted (Fig. 1C). By employing both CP

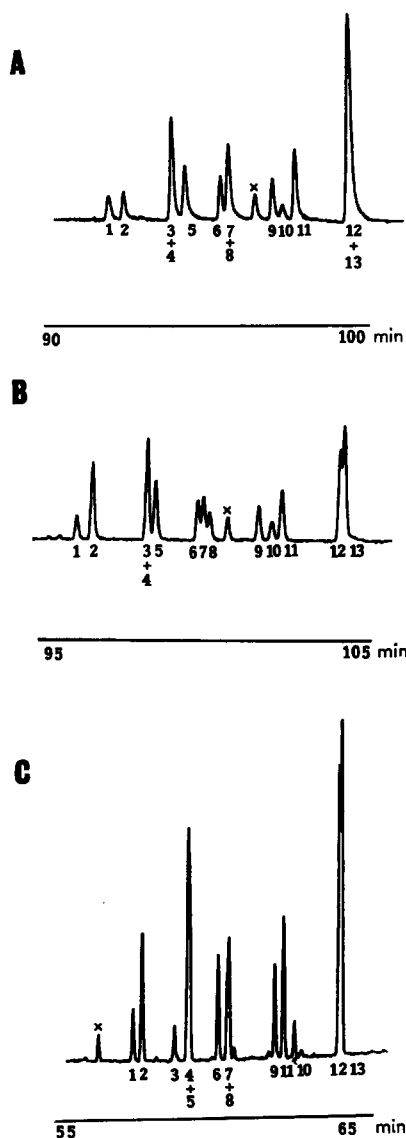


Fig. 1. Capillary gas chromatograms of a mixture of thirteen trimethylnaphthalene isomers using (A) methylsilicone, (B) 5% phenylmethylsilicone and (C) CP Wax 57CB, phases. Peaks: 1 = 1,3,7; 2 = 1,3,6; 3 = 1,4,6; 4 = 1,3,5; 5 = 2,3,6; 6 = 1,2,7; 7 = 1,6,7; 8 = 1,2,6; 9 = 1,2,4; 10 = 1,3,8; 11 = 1,2,5; 12 = 1,2,3; 13 = 1,4,5. X is unknown impurity.

Wax 57CB and 5% phenylmethylsilicone phases, all of the isomers could be separated. The elution order of the thirteen isomers on each column is summarised in Table I.

Fig. 2 shows a gas chromatogram (5% phenylmethylsilicone phase) of an alkylnaphthalene fraction isolated by preparative TLC<sup>8</sup> from a non-biodegraded crude

TABLE I  
ORDER OF ELUTION OF TRIMETHYLNAPHTHALENE ISOMERS

PMS = 5% phenylmethylsilicone; MS = methylsilicone.

<i>Stationary phases</i>		
<i>PMS</i>	<i>MS</i>	<i>CP Wax 57CB</i>
1,3,7	1,3,7	1,3,7
1,3,6	1,3,6	1,3,6
1,4,6 + 1,3,5	1,4,6 + 1,3,5	1,4,6
2,3,6	2,3,6	1,3,5 + 2,3,6
1,2,7	1,2,7	1,2,7
1,6,7	1,6,7 + 1,2,6	1,2,6 + 1,6,7
1,2,6	1,2,4	1,2,4
1,2,4	1,3,8	1,2,5
1,3,8	1,2,5	1,3,8
1,2,5	1,4,5 + 1,2,3	1,2,3
1,2,3		1,4,5
1,4,5		

oil sample. The relative abundances of the trimethylnaphthalene isomers in this oil and in a second non-biograded crude oil were determined by automatic peak area integration of gas chromatograms obtained on the 5% phenylmethylsilicone phase. The values obtained are shown in Table II. It is interesting to note the restricted isomeric compositions of these oils. Isomers with *peri*-disubstituted methyl groups

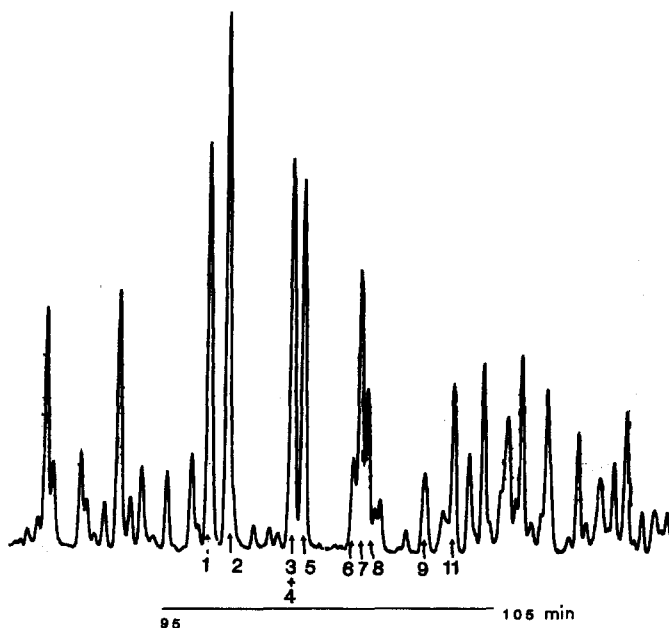


Fig. 2. A capillary gas chromatogram of the alkylnaphthalene fraction of a crude oil (Barrow Upper Jurassic, Australia) using 5% phenylmethylsilicone. Peak identifications as in Fig. 1.

TABLE II

## DISTRIBUTIONS OF TRIMETHYLNAPHTHALENE ISOMERS IN TWO CRUDE OIL SAMPLES

Values are expressed as a percentage of the total trimethylnaphthalenes.

Trimethylnaphthalene isomer	Peak number in Fig. 2	Crude oil	
		Barrow (%)	N. Apo (%)
1,3,7	1	16.7	17.3
1,3,6	2	22.8	27.1
1,4,6 and 1,3,5	3, 4	17.5	17.0
2,3,6	5	14.6	10.1
1,2,7	6	.0	4.4
1,6,7	7	10.8	7.1
1,2,6	8	5.0	8.2
1,2,4	9	4.0	1.1
1,2,5	11	5.6	7.7

such as 1,3,8-TMN are not present in concentrations which are readily measured, while those isomers with two  $\alpha$ -substituents are present in lower amounts than those with two and three  $\beta$ -substituents. These observations are consistent with those made for the dimethylnaphthalenes in non-biodegraded petroleum<sup>5,8,14</sup> and in coal tar<sup>15</sup> where a very low relative abundance of  $\alpha\alpha$ -isomers and a predominance of  $\beta\beta$ -isomers has been noted, with intermediate values for most  $\alpha\beta$ -isomers. This had led to the suggestion that the isomeric distribution of dimethylnaphthalenes varies with thermal maturity in coals and crude oils and can be used as a measure of rank or maturity<sup>5,6</sup>. Detailed accounts of the effects of thermal maturation on the composition of trimethylnaphthalenes in petroleum and sediments will be presented elsewhere.

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