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ANALYSIS OF AUSTRALIAN CRUDE OILS BY HIGH-RESOLUTION CAPILLARY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

The detailed analysis of Australian crude oils by high-resolution capillary gas chromatography–mass spectrometry is reported. The analyses were conducted by the injection of whole crude oil samples without the use of solvents that preclude a total analysis, or sample fractionation into functional group enriched fractions. Quantitative analysis and the identification of the hydrocarbon constituents of Australian crude oils by gas chromatography–mass spectrometry is demonstrated.

INTRODUCTION

The composition of Australian crude oils has been the subject of a number of studies in recent years. The work has been largely directed by geochemical investigations into crude oil–source rock correlations^{1–11}. Extracts from source rocks and crude oils are extremely complex mixtures of hydrocarbons and other classes of compounds. Petroleum hydrocarbons of geochemical significance (biological markers) such as *n*-alkanes, *iso*- and *anteiso*-alkanes, acyclic isoprenoids, tricyclic diterpenoids, steroids and pentacyclic triterpenoids and aromatic hydrocarbons are identified for correlation purposes. Column chromatography on silica–alumina has frequently been used to separate crude oils into aliphatic, monoaromatic, di- and triaromatic and polar fractions for further gas chromatographic and mass spectrometric study.

A further important area of study is concerned with the identification of the source of oil spills in the marine environment. This is an area of major concern, and much effort has been directed towards the accurate identification of the pollution source. Fingerprinting of crude oils by gas chromatography and mass spectrometry has been widely employed^{12–14}. The characterization of crude oils by gas chromatography on a number of Australian crude oils has been studied by Jackson *et al.*¹⁵. They analysed that fraction of crude boiling between 232 and 316°C (the method of analysis being similar to one recently standardized by the U.K. Institute of Petroleum¹⁶), while other workers have considered the total sample^{17–19}.

Other important areas of application include crude oil and petroleum processing and enhanced oil recovery processes, where detailed information regarding crude oil composition is necessary for rational process design^{20–22}.

The ultimate aim in the evaluation of crude oils is the identification of each compound present and the determination of their relative concentrations. Investigations over several decades have been conducted by the American Petroleum Institute (API) and such work was revolutionized by the advent of capillary chromatography. Early developments in the area have been reviewed by Kurtz²³.

In studies of petroleum processing and enhanced oil recovery processes, hydrocarbon mixtures are characterized in two ways, *viz.*, structural group analyses (where the total alkanes, naphthenes and aromatics are considered; chemical separations in conjunction with chromatography, multiple columns and reaction gas chromatography have all been used, and have been reviewed by Johansen *et al.*²⁴), and boiling range determinations, by either distillation²⁵ or gas chromatographic simulated distillation^{26,27}.

A particular advantage of gas chromatography is that the quantitative response of a flame-ionisation detector is approximately the same for equal weights of any hydrocarbon. Capillary chromatography and the availability of data acquisition systems facilitate the analysis of hydrocarbon mixtures and the substantial success of this approach has been demonstrated by Johansen *et al.*²⁴ and others²⁸⁻³⁰ with gasoline and distillate fractions. The approach is refined by the use of high-resolution capillary gas chromatography-mass spectrometry (GC-MS), and this has been demonstrated for various hydrocarbon mixtures³¹⁻³³.

A detailed analysis of Australian crude oils by high-resolution capillary GC-MS has not been reported previously. This paper presents the results obtained from a detailed analysis of crude oil samples from commercially important Australian hydrocarbon producing basins, which are predominantly light, low-viscosity crudes. Such analyses have been conducted on samples separated into functional-group-enriched fractions, the dilution of whole crude oil samples with frequently used solvents such as *n*-pentane and *n*-hexane, or the analysis of distillate fractions^{32,34-38}.

Australian crude oils, because of their high API gravity, contain a high concentration of low-molecular-weight hydrocarbons and the technique of sample injection without solvent adopted in this investigation allows the identification and quantification of the early eluting components and also a full boiling range determination in one chromatographic analysis. The selection of suitable operating conditions allows a good resolution of most of the crude oil components to be achieved.

GROUP TYPE ANALYSIS

Mass spectrometry has gained wide acceptance in petroleum chemistry as a means of providing structural data on the constituents of petroleum mixtures. The objective of hydrocarbon group analysis is the recognition of compound classes in a sample rather than the determination of individual components. The success of the technique is based on the principle that any given hydrocarbon type can be recognized by a set of specific spectral peaks and that the spectrum of a mixture of hydrocarbons is a composite of the spectra of the individual components making up the mixture. When a set of characteristic peaks are combined arithmetically and treated as a single peak, a distinctive pattern emerges, allowing hydrocarbon type identification.

The determination of hydrocarbon types [*n*-alkanes, *iso*-alkanes, naphthenes (cycloalkanes) and aromatics] is carried out by applying the summation of the mass groups of typical petroleum hydrocarbons as shown in Table I.

TABLE I
CHARACTERISTIC MASS GROUPINGS

Type	<i>m/e</i>
Alkanes	43, 57, 71, 85, 99, 113
Monocycloalkanes	41, 55, 69, 83, 97, 111, 125
Dicycloalkanes	67, 81, 95, 109, ..., 193
Tricycloalkanes	149, 163, 177, ..., 247
Tetracycloalkanes	189, 203, 217, ..., 301
Alkylbenzenes	77, 78, 91, 92, 105, 106, ..., 175, 176
Indanes and/or tetralins	103, 104, 117, 118, ..., 187, 188
Dinaphthenebenzenes	129, 143, 157
Naphthalenes	128, 141, 142, 155, 156, ..., 239, 240
Acenaphthenes	153, 154, 167, 168, ..., 251, 252
Acenaphthylenes	151, 152, 165, 166, ..., 249, 250
Anthracenes	191, 205, 219

In the direct analysis of Australian crude oils by GC-MS, the components of these complex mixtures were separated on a high-resolution capillary column in the gas chromatograph. The components eluted into the ion source of the mass spectrometer, where they were ionized, forming mass fragments with characteristic mass to charge (*m/e*) ratios.

EXPERIMENTAL

A Hewlett-Packard HP5992B gas chromatograph-quadrupole mass spectrometer and an HP5794A capillary gas chromatograph, with a flame-ionisation detector, were used. The GC-MS system was modified to accept a capillary column and a

TABLE II
GAS CHROMATOGRAPHIC CONDITIONS USED FOR THE ANALYSIS
OF CRUDE OIL SAMPLES

Column:	
Dimensions:	25 m × 0.31 mm I.D.
Material:	Fused-silica
Stationary phase:	OV-101
Film thickness:	0.52 μm
Column temperature:	
Initial isothermal temperature:	-10°C
Initial isothermal period:	2 min
Temperature programme:	3.0°C/min
Final isothermal temperature:	290°C
Final isothermal period:	10 min
Carrier gas:	Helium
Carrier gas flow-rate:	2.0 ml/min
Splitting ratio:	75:1
Injector temperature:	280°C
Sample volume injected:	2.0 μl
Detector for HP5794A system:	Flame ionisation
Detector temperature:	300°C

split-splitless inlet system. The columns used in both chromatographs were fused-silica WCOT capillary columns (25 m × 0.31 mm I.D. with OV-101 bonded polydimethylsiloxane liquid stationary phase. Helium was used as the carrier gas. The instrumental conditions are reported in Table II. Data processing for the HP5794A system was carried out using an HP5880A GC control and data system. The GC-MS was interfaced to an HP9825A data system and an HP9866B printer.

The mass spectrometer was operated in the peakfinder mode, scanning from 20 to 500 a.m.u., and in the selected ion mode (SIM), monitoring up to six ions, each with a dwell time of 100 msec. Typical mass spectrometer conditions used were EM voltage 1800 V and electron energy 70 eV.

Electron-impact mass spectra of the hydrocarbon constituents in a number of crude oils were obtained from a GC-MS analysis. The following crude oils were investigated: (1) Alton A, Bowen-Surat Basin, Queensland; (2) Alton B, Bowen-Surat Basin, Queensland; (3) Tirrawarra, Cooper Basin, South Australia; and (4) Moorari, Cooper Basin, South Australia. The Alton crude oils were supplied by the Bureau of Mineral Resources, Canberra, and the Cooper Basin crude oils by Santos, Adelaide, South Australia.

RESULTS AND DISCUSSION

The crude oils were separated and analysed by capillary GC with flame-ionization detection (FID) and capillary GC-MS. Chromatograms for Tirrawarra crude oil are shown in Figs. 1 and 2.

Fig. 1 shows a portion of the total ion chromatogram of the sample obtained by GC-MS. The single ion trace of m/e 57 was also monitored to indicate the alkane distribution in the crude oil and is shown in the upper trace of Fig. 1.

Fig. 2 shows the full range capillary GC-FID chromatogram for the Tirrawarra crude oil. The hydrocarbon components identified by GC-MS are listed by peak number in Table III, together with the corresponding peak area percentages for the crude oils studied.

In the analysis of multi-component crude oils it is difficult to separate every component, even with high-resolution capillary columns. The separation was optimized by the choice of suitable column (inner diameter, film thickness), carrier gas and GC operating conditions. In this work, OV-101 polydimethylsiloxane was used as the stationary phase in fused-silica capillary columns. Bonded-phase fused-silica columns provide excellent thermal stability (350°C) and a high level of inertness. Fig. 2 shows that most of the peaks are well separated so that it is possible to obtain the mass spectrum of the almost pure components. Partially resolved or peaks of coeluted components were identified from the overall mass spectrum. The hydrocarbon group types were determined from the characteristic fragmentation peaks of the mass spectra, and the molecular weights from the peaks of the molecular ions, the intensity of which, in many instances, is adequate for even coeluted components. The mass spectra of many isomers are virtually identical. In these instances we have reported only the molecular weights and pertaining classes. The technique of selected ion monitoring (SIM) was used for the determination of the molecular weights of compounds that produce only weak parent ions in the total ion mass spectrum. In addition to the interpretation of the mass spectrum for the determination of hydrocarbon group

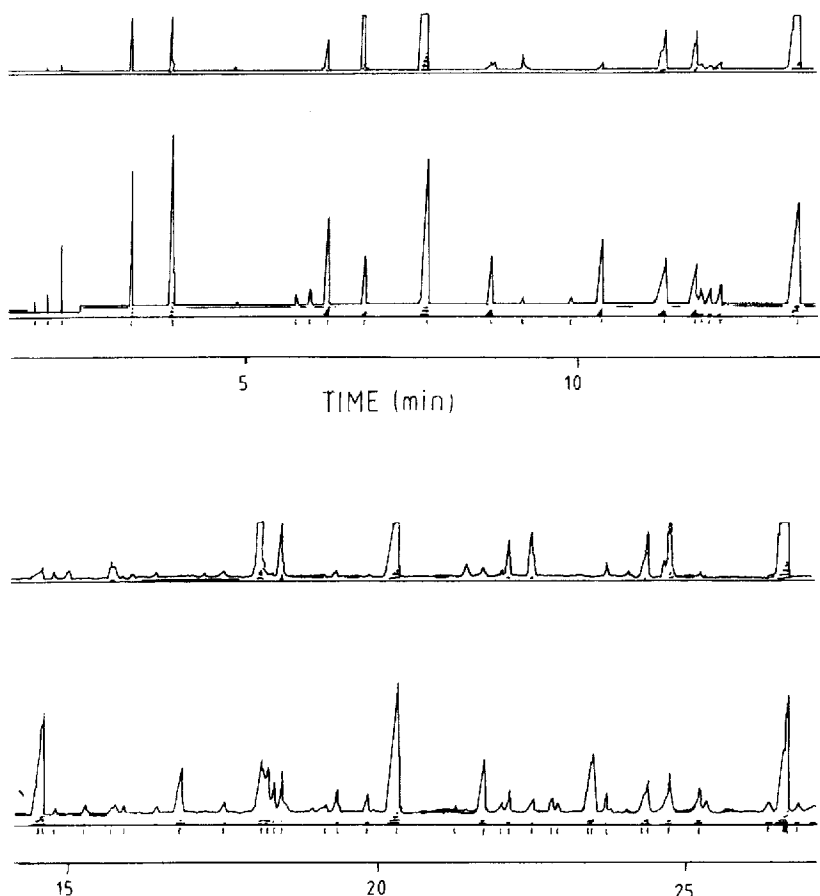


Fig. 1. Portion of the total ion chromatogram of Tirrawarra crude oil. The upper single ion plot of m/e 57 was monitored to profile the crude oils alkane distribution.

types, differences in the mass spectra of isomers are interpreted to provide, in many instances, an independent determination of isomeric hydrocarbons. The Eight Peak Index of Mass Spectra³⁹ and other mass spectrometric references⁴⁰⁻⁴² were used in the identification and compilation of the hydrocarbons listed in Table III.

One shortcoming of GC-MS in the present context is the identification of coeluting components of either long-chain alkyl cycloalkanes or alkylbenzenes with alkanes. The mass spectrum for such hydrocarbons contains peaks characteristic of both cycloalkanes (or benzenes) and alkanes, the molecular ions of these compounds being too weak to be detected in the total ion mass spectrum. In such instances, the identification of only cycloalkanes (or alkylbenzenes) is possible from their characteristic mass fragments, even if they coelute with alkanes. Short-chain alkylcycloalkanes or alkylbenzenes can be differentiated from alkanes, first by the presence of relatively intense molecular ion peaks and second by the presence of alkane mass fragments (Table I) that are too high to be associated with the spectrum of alkylcycloalkanes or alkylbenzenes.

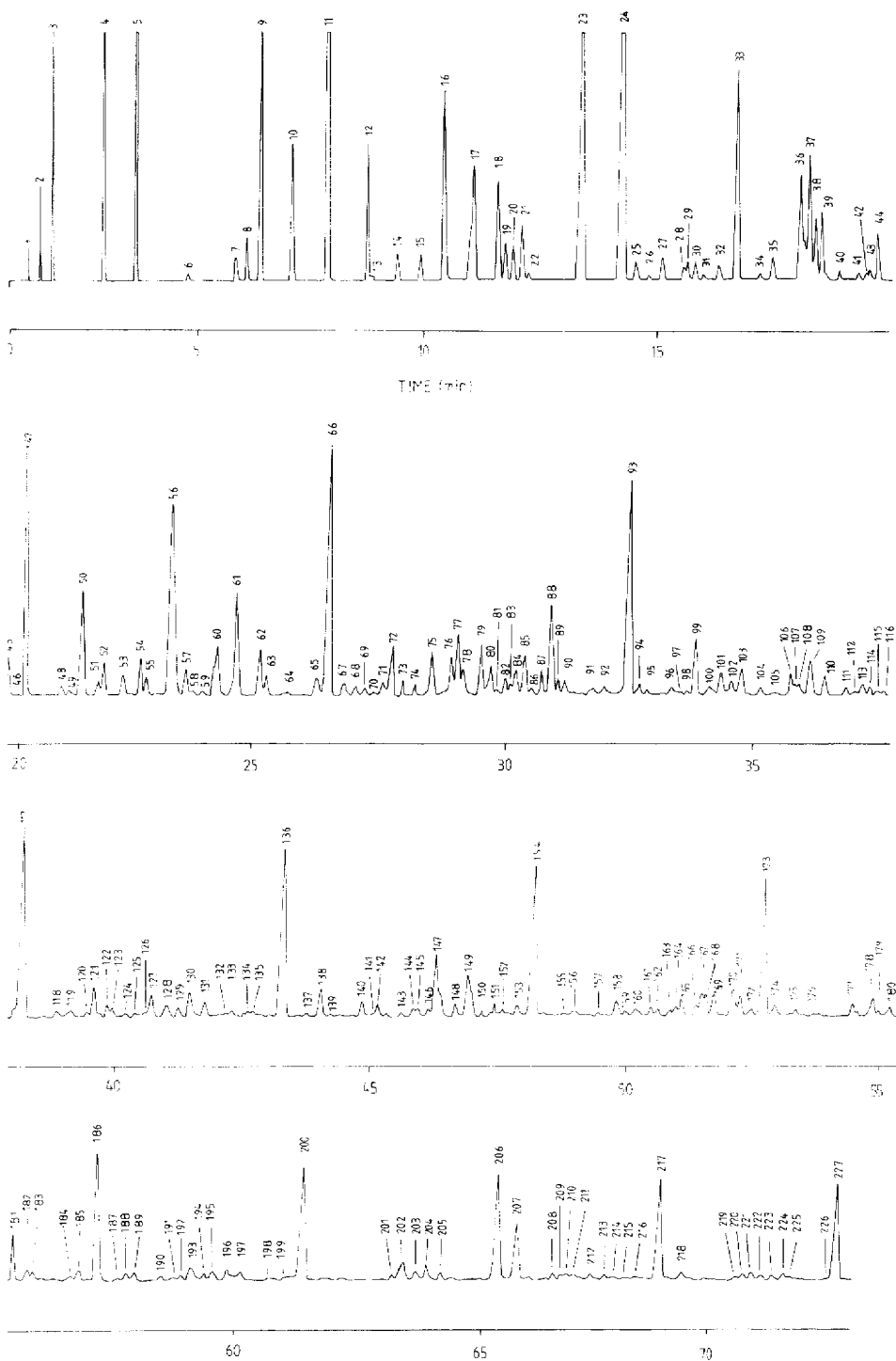


Fig. 2.

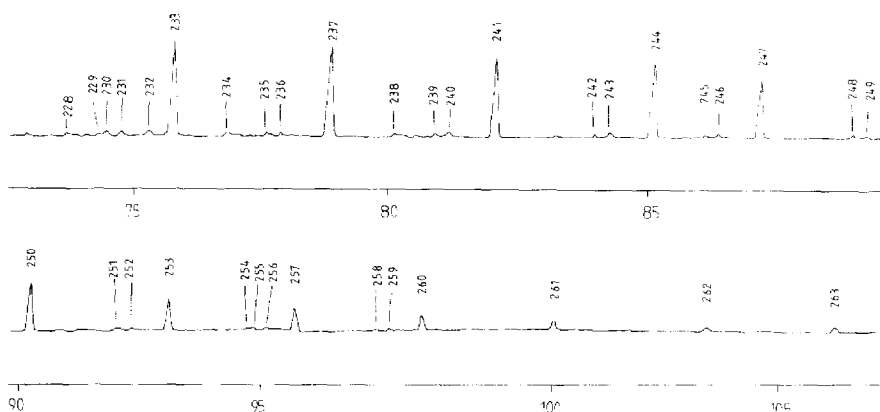


Fig. 2. Chromatogram of Tirrawarra crude oil. Column and conditions as in Table II. The components, identified by peak number, are listed in Table III.

Under the experimental conditions used, GC-MS failed to detect a number of components present in very low concentrations and those components which were close to other components present in much higher concentrations. It was possible to identify a number of these components owing to their presence in higher concentrations in different crude oils. By the direct injection of a crude oil sample on to a capillary column without the use of commonly used solvents such as *n*-pentane or *n*-hexane (thus eliminating the problems associated with solvent effects^{4,3}), it was possible to separate, identify and quantify the light-end components and also to achieve a full boiling range analysis of the crude oils studied.

TABLE III

ANALYTICAL DATA FROM THE ANALYSIS OF AUSTRALIAN CRUDE OILS BY GC-FID AND GC-MS

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
1	1.21	0.053	0	0	0.064	Propane
2	1.45	0.189	0	0.172	0.213	Isobutane
3	1.68	0.804	0	0.145	0.180	<i>n</i> -Butane
3a	1.81	0	0	0.015	0.014	2,2-Dimethylpropane
4	2.71	1.484	0	0.842	0.898	Isopentane
5	3.34	2.366	0	0.520	0.697	<i>n</i> -Pentane
6	4.38	0.042	0	0.095	0.061	2,2-Dimethylbutane
7	5.35	0.141	0	0.052	0.046	Cyclopentane
8	5.56	0.276	0	0.260	0.235	2,3-Dimethylbutane
9	5.85	1.633	0	0.914	0.974	2-Methylpentane
10	6.46	0.872	0	0.531	0.525	3-Methylpentane
11	7.45	3.398	0.016	1.064	1.478	<i>n</i> -Hexane
12	8.56	1.014	0	0.434	0.447	Methylcyclopentane
13	8.63	0.042	0	0.062	0.065	Unknown
14	9.05	0.171	0	0.159	0.162	Dimethylpentane
15	9.86	0.201	0	0	0	Benzene

(Continued on p. 312)

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
16	10.34	1.555	0.063	1.450	1.265	Cyclohexane
17	11.37	1.358	0.181	1.120	1.169	2-Methylhexane
18	11.87	0.846	0.147	0.600	0.647	3-Methylhexane
19	12.01	0.305	0.040	0.163	0.178	Dimethylcyclopentane
20	12.16	0.289	0.042	0.151	0.164	Dimethylcyclopentane
21	12.34	0.456	0.069	0.301	0.308	Dimethylcyclopentane
22	12.47	0.054	0	0.061	0.061	Unknown
23	13.56	3.762	0.942	1.964	2.479	<i>n</i> -Heptane
24	14.36	4.952	1.474	4.865	5.036	Methylcyclohexane
25	14.61	0.135	0.047	0.120	0.127	Trimethylcyclopentane
26	14.86	0.033	0	0.035	0.038	Unknown
27	15.14	0.196	0.064	0.138	0.166	Ethylcyclopentane
28	15.57	0.104	0.067	0.131	0.144	Dimethylhexane
29	15.64	0.160	0.096	0.121	0.133	Dimethylhexane
30	15.79	0.160	0.070	0.142	0.157	Trimethylcyclopentane
31	15.95	0.046	0.260	0.066	0.067	Dimethylhexane
32	16.26	0.122	0.056	0.126	0.137	Trimethylcyclopentane
33	16.64	1.987	0.753	0.253	0.242	Toluene
34	17.07	0.048	0.026	0.061	0.062	Trimethylcyclopentane
35	17.34	0.219	0.125	0.285	0.299	C ₈ Isoalkane
36	17.89	1.277	0.796	1.130	1.280	C ₈ Isoalkane
36a	17.96	0	0.172	0	0	Unknown
37	18.06	1.286	0.939	1.543	1.634	Dimethylcyclohexane
38	18.18	0.570	0.430	0.433	0.474	Dimethylcyclohexane
39	18.32	0.662	0.596	0.533	0.595	C ₈ Isoalkane
40	18.44	0.101	0.078	0.162	0.158	Unknown
41	18.54	0.068	0.042	0.079	0.093	Methylethylcyclopentane
42	18.98	0.061	0.045	0.062	0.071	C ₈ Isoalkane
43	19.05	0.107	0.070	0.143	0.155	Methylethylcyclopentane
44	19.23	0.443	0.355	0.524	0.539	Dimethylcyclohexane
45	19.74	0.358	0.296	0.398	0.424	Dimethylcyclohexane
46	19.85	0.025	0	0.035	0.068	Unknown
47	20.17	3.391	2.933	2.384	3.655	<i>n</i> -Octane
47a	20.21	0	0	0	0.572	Isoalkane
47b	20.84	0	0	0	0.019	Unknown
48	21.17	0.079	0.079	0.120	0.121	Dimethylcyclohexane
49	21.31	0.037	0.057	0.040	0.039	C ₉ Isoalkane
50	21.58	1.089	1.045	1.035	1.101	Ethylcyclohexane + C ₉ isoalkane
51	21.90	0.153	0.155	0.329	0.339	Tetramethylcyclopentane
52	22.02	0.325	0.337	0.525	0.542	C ₉ Isoalkane
53	22.41	0.239	0.324	0.287	0.297	C ₉ Isoalkane
53a	22.53	0	0	0.030	0.032	Unknown
54	22.76	0.348	0.306	0.130	0.109	Ethylbenzene
55	22.88	0.165	0.213	0.189	0.201	Trimethylcyclohexane
55a	23.00	0	0	0.051	0.051	Unknown
56	23.39	2.969	2.917	0.941	0.708	<i>p</i> - + <i>m</i> -Xylene
57	23.67	0.227	0.232	0.425	0.437	C ₉ Isoalkane
58	23.80	0.007	0.053	0	0.036	C ₉ Isoalkane
59	24.00	0.048	0.008	0.048	0.049	C ₉ Isoalkane
59a	24.18	0	0.390	0	0	C ₉ Isoalkane

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
60	24.32	0.737	0.637	0.784	0.839	C ₉ Isoalkane
60a	24.59	0	0	0.172	0.184	Unknown
61	24.69	1.142	1.305	0.710	0.651	<i>o</i> -Xylene
62	25.17	0.503	0.638	0.560	0.574	Methylethylcyclohexane
63	25.30	0.195	0.257	0.157	0.162	Methylethylcyclohexane
63a	25.58	0	0.017	0	0.033	Unknown
64	25.71	0.032	0.037	0.041	0.038	Unknown
65	26.28	0.246	0.326	0.328	0.331	Methylethylcyclohexane
66	26.54	2.984	3.728	2.953	3.208	<i>n</i> -Nonane
67	26.82	0.162	0.186	0.183	0.178	Isopropylbenzene
68	27.05	0.096	0.050	0.157	0.161	C ₃ Cyclohexane
69	27.24	0.087	0.109	0.096	0.093	Methylethylcyclohexane + isoalkane
70	27.43	0.039	0.057	0.083	0.078	C ₁₀ Isoalkane
71	27.61	0.182	0.242	0.140	0.141	C ₁₀ Isoalkane
72	27.76	0.446	0.570	0.416	0.425	C ₃ Cyclohexane
72a	27.96	0	0.036	0	0	Unknown
73	28.05	0.180	0.254	0.193	0.195	C ₄ Cyclopentane + isoalkane
74	28.32	0.125	0.174	0.168	0.162	C ₁₀ Isoalkane
75	28.57	0.469	0.648	0.543	0.523	<i>n</i> -Propylbenzene + isoalkane
76	28.96	0.469	0.455	0.883	0.851	Isoalkane + methylethylbenzene
77	29.08	0.625	0.806	0.339	0.283	Methylethylbenzene
78	29.18	0.279	0.338	0.248	0.224	Methylethylbenzene
79	29.54	0.521	0.735	0.389	0.316	Trimethylbenzene
80	29.74	0.370	0.443	0.288	0.285	C ₁₀ Isoalkane
81	29.86	0.059	0.100	0.078	0.085	C ₁₀ Isoalkane
82	30.02	0.163	0.196	0.131	0.106	Methylethylbenzene
83	30.14	0.099	0.168	0.132	0.130	C ₁₀ Isoalkane
84	30.24	0.268	0.423	0.335	0.338	C ₁₀ Isoalkane
85	30.41	0.399	0.605	0.572	0.570	C ₁₀ Isoalkane
86	30.55	0.067	0.103	0.081	0.084	C ₁₀ Isoalkane
87	30.76	0.251	0.418	0.305	0.307	C ₁₀ Isoalkane
88	30.95	0.930	1.248	0.503	0.403	Trimethylbenzene
89	31.07	0.161	0.253	0.163	0.163	C ₄ Cyclohexane
90	31.21	0.168	0.254	0.187	0.186	C ₄ Cyclohexane
91	31.79	0.136	0.211	0.167	0.158	C ₄ Cyclohexane
92	32.00	0.119	0.177	0.122	0.151	C ₄ Benzene + C ₄ cyclohexane
93	32.52	2.785	3.799	3.460	3.459	<i>n</i> -Decane
94	32.69	0.129	0.175	0.128	0.115	C ₄ Benzene + isoalkane + C ₅ cyclopentane
95	32.84	0.055	0.077	0.046	0.160	C ₄ Cyclohexane + C ₁₁ isoalkane
95a	33.14	0	0	0.054	0.054	Unknown
96	33.34	0.130	0.213	0.260	0.265	C ₁₁ Isoalkane + C ₄ cyclohexane

(Continued on p. 314)

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
97	33.53	0.042	0.058	0.079	0.072	Unknown
98	33.65	0.050	0.096	0.082	0.080	C ₁₁ Isoalkane
99	33.82	0.576	0.828	0.734	0.716	Methyl (C ₃ cyclohexane) + isoalkane
100	34.11	0.173	0.274	0.200	0.198	Isoalkane + C ₅ cyclopentane
101	34.34	0.259	0.388	0.275	0.255	C ₄ Benzene + isoalkane
102	34.54	0.221	0.332	0.141	0.133	C ₄ Benzene
103	34.74	0.366	0.586	0.339	0.319	C ₄ Benzene + C ₅ cyclohexane + decahydronaphthalene
104	35.12	0.093	0.133	0.109	0.103	C ₄ Benzene
105	35.40	0.067	0.087	0.062	0.072	C ₁₁ Isoalkane
106	35.72	0.240	0	0	0	Unknown
107	35.80	0.091	0.052	0.324	0.332	C ₄ Benzene + isoalkane
108	35.88	0.141	0.250	0.172	0.178	Isoalkane + methylindane
109	36.10	0.438	0.671	0.571	0.569	C ₄ Benzene + isoalkane
110	36.42	0.230	0.368	0.327	0.334	C ₁₁ Isoalkane
111	36.83	0.090	0.147	0.059	0.079	C ₄ (Methylcyclohexane)
112	37.02	0.067	0.103	0.046	0.069	C ₄ (Methylcyclohexane) + isoalkane
113	37.16	0.154	0.238	0.143	0.164	C ₄ Benzene + C ₅ cyclohexane
114	37.30	0.094	0.147	0.070	0.095	C ₅ Benzene + isoalkane + C ₅ cyclohexane
115	37.49	0.081	0.153	0.043	0.085	C ₅ Cyclohexane + C ₅ benzene
116	37.60	0.063	0.093	0.019	0.078	C ₃ (Ethylcyclohexane) + C ₅ benzene + isoalkane
117	38.09	2.577	3.706	3.628	3.530	<i>n</i> -Undecane
117a	38.35	0	0	0.030	0	Unknown
117b	38.44	0	0	0	0.046	Unknown
118	38.75	0.106	0.167	0.092	0.132	C ₄ (Methylcyclohexane) + methyldecahydronaphthalene
119	39.03	0.144	0.222	0.193	0.247	C ₅ Benzene + isoalkane
120	39.36	0.098	0.156	0.067	0.093	Methyl (C ₃ benzene) + isoalkane + cycloalkane (154)
121	39.50	0.323	0.551	0.348	0.349	Isoalkane + C ₅ benzene + cycloalkane (154)
122	39.77	0.136	0.113	0.082	0.077	Isoalkane + tetrahydronaphthalene + methyldecahydronaphthalene
123	39.87	0.106	0.171	0.113	0.109	C ₅ Benzene + isoalkane
124	40.13	0.074	0.110	0	0	Unknown
125	40.31	0.041	0.100	0.042	0.038	C ₅ Benzene + C ₅ cyclohexane
125a	40.35	0	0.038	0.040	0.044	Unknown
126	40.51	0.025	0.083	0	0.077	C ₁₂ Isoalkane
127	40.66	0.257	0.376	0.229	0.115	Naphthalene
128	40.97	0.204	0.380	0.287	0.277	C ₅ Benzene

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
129	41.19	0.115	0.217	0.167	0.158	C ₁₂ Isoalkane
130	41.42	0.319	0.500	0.464	0.441	C ₁₂ Isoalkane
131	41.73	0.177	0.281	0.273	0.270	C ₁₂ Isoalkane
131a	41.85	0	0.036	0	0	Unknown
131b	42.00	0	0.040	0	0	Unknown
132	42.14	0.094	0.096	0.163	0.153	C ₆ Benzene + C ₆ cyclohexane
133	42.25	0.074	0.125	0.056	0.055	C ₆ Cyclohexane
133a	42.44	0	0.074	0	0	Cycloalkane (168)
134	42.58	0.114	0.080	0.206	0.198	C ₁₂ Isoalkane
135	42.68	0.067	0.066	0.079	0.074	Unknown
135a	42.93	0	0.044	0	0	Unknown
136	43.30	2.022	2.853	3.300	3.211	<i>n</i> -Dodecane
136a	43.51	0	0.047	0	0	Unknown
137	43.72	0.050	0.055	0.062	0.059	Cycloalkane (168) + isoalkane
137a	43.80	0	0	0.044	0.041	Isoalkane
138	44.02	0.319	0.452	0.546	0.514	Isoalkane + C ₆ benzene + cycloalkane (168)
139	44.20	0.036	0.033	0.048	0.045	Unknown
139a	44.34	0	0.027	0	0	C ₆ Benzene + isoalkane + cycloalkane (168)
139b	44.66	0	0.027	0.074	0.071	C ₆ Cyclohexane
140	44.84	0.183	0.239	0.163	0.159	C ₁₃ Isoalkane
141	45.06	0.030	0	0	0	Unknown
142	45.17	0.151	0.127	0.080	0.083	Isoalkane + C ₇ cyclopentane
142a	45.29	0	0.056	0	0.050	C ₆ Benzene + C ₇ cyclohexane
143	45.64	0.045	0.066	0.065	0.063	C ₆ Benzene + isoalkane + cycloalkane (182)
144	45.87	0.094	0.166	0.144	0.142	C ₁₃ Isoalkane
145	45.96	0.097	0.158	0.143	0.133	C ₁₃ Isoalkane
146	46.18	0.095	0.178	0.129	0.127	Methylnaphthalene + C ₁₃ isoalkane
146a	46.30	0	0	0.170	0.124	Unknown
147	46.34	0.969	1.283	0.428	0.404	Methylnaphthalene + C ₁₃ isoalkane ●
148	46.72	0.129	0.214	0.215	0.203	C ₁₃ Isoalkane
149	46.96	0.661	1.021	0.804	0.719	Methylnaphthalene + C ₁₃ isoalkane
150	47.18	0.051	0.098	0.070	0.065	Unknown
151	47.41	0.050	0.103	0.055	0.051	C ₇ Cyclohexane
152	47.67	0.031	0.067	0.050	0.049	C ₇ Cyclohexane
153	47.85	0.110	0.166	0.069	0.069	C ₇ Cyclohexane + dimethyltetrahydro-naphthalene
154	48.19	1.845	2.649	3.315	3.121	<i>n</i> -Tridecane
154a	48.36	0	0.084	0.052	0.055	Unknown
154b	48.74	0	0.083	0.082	0.093	Isoalkane
155	48.95	0.050	0.067	0	0	Unknown
156	49.02	0.049	0.076	0.132	0.159	C ₁₄ Isoalkane + cycloalkane (182)

(Continued on p. 316)

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
157	49.47	0.038	0.053	0.083	0.078	C ₁₄ Isoalkane + C ₇ cyclohexane
158	49.84	0.195	0.296	0.166	0.160	<i>n</i> -C ₇ Cyclohexane
159	50.01	0.059	0.077	0.047	0.047	C ₈ Cyclopentane + C ₇ benzene
160	50.19	0.140	0.165	0.140	0.112	Diphenyl + C ₇ benzene + dihydroanthracene
161	50.52	0.115	0.182	0.154	0.148	C ₁₄ Isoalkane
162	50.66	0.077	0.125	0.112	0.106	C ₁₄ Isoalkane
163	50.88	0.070	0.125	0.104	0.100	C ₁₄ Isoalkane + ethylnaphthalene
164	51.00	0.119	0.168	0	0	C ₁₄ Isoalkane
165	51.12	0.214	0.310	0.437	0.401	C ₁₄ Isoalkane
165a	51.23	0	0	0.048	0.043	Unknown
166	51.42	0.114	0.185	0.248	0.226	Dimethylnaphthalene
167	51.52	0.267	0.339	0	0	C ₁₄ Isoalkane
168	51.60	0.220	0.320	0	0	Dimethylnaphthalene
169	51.78	0.262	0.410	0.388	0.360	C ₁₄ Isoalkane
170	52.17	0.369	0.564	0.159	0.136	Dimethylnaphthalene
171	52.30	0.246	0.352	0.095	0.080	Dimethylnaphthalene
172	52.51	0.109	0.163	0.089	0.081	Cycloalkane + alkylbenzene + trimethyltetrahydronaphthalene
173	52.80	1.724	2.443	3.237	2.973	<i>n</i> -Tetradecane + dimethylnaphthalene
174	53.00	0.193	0.306	0.160	0.143	Cycloalkane + alkylbenzene
174a	53.32	0	0	0.072	0	Unknown
175	53.41	0.114	0.161	0.228	0.278	Dimethylnaphthalene + cycloalkane
176	53.76	0.036	0.064	0.052	0.054	C ₃ Naphthalene + cycloalkane + alkylbenzene
177	54.56	0.187	0.282	0.116	0.109	<i>n</i> -C ₈ Cyclohexane
178	54.96	0.289	0.443	0.327	0.298	C ₁₅ Isoalkane + C ₈ cyclohexane + diphenylmethane
179	55.09	0.079	0.127	0.115	0.111	C ₁₅ Isoalkane + C ₈ benzene
180	55.31	0.151	0.244	0.205	0.188	C ₁₅ Isoalkane + diphenylmethane
181	55.58	0.515	0.833	0.748	0.697	Acyclic isoprenoid
182	55.84	0.131	0.221	0.264	0.247	C ₁₅ Isoalkane + C ₃ naphthalene
183	55.96	0.116	0.177	0	0	C ₈ Benzene + C ₃ naphthalene
183a	56.29	0	0.062	0	0	Unknown
184	56.69	0.084	0.154	0	0	Cycloalkane (210) + diphenylethane
185	56.88	0.137	0.236	0.030	0.026	C ₃ Naphthalene + cycloalkane (210) + C ₉ benzene

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
186	57.15	1.681	2.405	3.017	2.756	<i>n</i> -Pentadecane
187	57.52	0.057	0.093	0.103	0.104	Cycloalkane
188	57.70	0.098	0.171	0.157	0.145	C ₃ Naphthalene + cycloalkane
189	57.86	0.114	0.177	0	0	C ₃ Naphthalene + cycloalkane + C ₉ benzene
189a	58.05	0	0	0	0.057	C ₁₆ Isoalkane
190	58.41	0.083	0.164	0.021	0.104	C ₃ Naphthalene + C ₉ benzene
191	58.62	0.058	0.077	0.050	0.074	Unknown
192	58.81	0.073	0.114	0	0	C ₉ Benzene + diphenylethane + methylacenaphthylene
193	59.00	0.225	0.368	0.266	0.466	<i>n</i> -C ₉ Cyclohexane
194	59.28	0.089	0.143	0.182	0.206	Diphenylethane + C ₁₆ isoalkane
195	59.44	0.134	0.237	0.187	0.190	C ₉ Benzene + cycloalkane + diphenylethane
196	59.74	0.087	0.252	0.218	0.212	Acyclic isoprenoid
196a	59.90	0	0	0.052	0.051	C ₁₆ Isoalkane
197	60.01	0.078	0.188	0.179	0.174	C ₁₆ Isoalkane
198	60.55	0.052	0.036	0	0	Cycloalkane + ditolylmethane
199	60.87	0.024	0.064	0.060	0.057	C ₄ Naphthalene + diphenylethane
199a	60.96	0	0.086	0	0	Unknown
200	61.26	1.334	1.953	2.752	2.484	<i>n</i> -Hexadecane
200a	61.60	0	0.065	0.073	0.065	Unknown
200b	61.75	0	0	0.061	0.053	Isoalkane
200c	61.92	0	0.052	0	0	Unknown
200d	62.75	0	0.063	0	0	Alkylbenzene + cycloalkane
201	63.01	0.050	0.096	0.090	0.080	Cycloalkane + C ₄ naphthalene
202	63.25	0.344	0.571	0.420	0.381	<i>n</i> -C ₁₀ Cyclohexane
203	63.49	0.119	0.212	0.113	0.112	C ₁₇ Isoalkane + ditolylmethane
204	63.71	0.183	0.285	0.199	0.174	C ₁₇ Isoalkane
205	63.99	0.068	0.122	0.161	0.144	C ₁₇ Isoalkane
205a	64.12	0	0.078	0	0	Unknown
206	65.16	1.365	1.939	2.611	2.315	<i>n</i> -Heptadecane
207	65.52	0.765	1.255	0.819	0.736	Pristane (2,6,10,14-tetramethylpentadecane)
207a	65.67	0	0.079	0	0	Unknown
207b	66.03	0	0.052	0	0	Unknown
208	66.24	0.083	0.101	0	0	Phenanthrene + C ₁₀ cyclopentane
209	66.79	0.077	0.121	0.110	0.099	Alkylbenzene
210	66.90	0.030	0.054	0.038	0.035	Unknown
210a	67.09	0	0.168	0.044	0.120	<i>n</i> -C ₁₁ Cyclohexane
211	67.13	0.113	0	0.082	0	Unknown

(Continued on p. 318)

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
211a	67.21	0	0.049	0	0	Unknown
212	67.48	0.085	0.123	0.156	0.137	C ₁₈ Isoalkane + alkylbenzene
213	67.76	0.060	0.088	0.114	0.103	C ₁₇ Isoalkane + cycloalkane
214	67.92	0.049	0.070	0	0	Unknown
215	68.20	0.051	0.080	0	0	Unknown
216	68.36	0.046	0.079	0	0	Unknown
217	68.82	1.266	1.743	2.371	2.052	<i>n</i> -Octadecane
218	69.28	0.083	0.236	0.184	0.159	Phytane (2,6,10,14-tetramethylhexadecane)
219	69.65	0	0.043	0	0	Alkylbenzene
220	70.35	0.044	0.074	0.080	0.072	Unknown
221	70.52	0.078	0.111	0	0	Cycloalkane (238) + methylphenanthrene
222	70.67	0.091	0.121	0.041	0.034	Cycloalkane + methylphenanthrene
223	70.88	0.069	0.105	0.078	0.068	<i>n</i> -C ₁₂ Cyclohexane + alkylbenzene
224	71.08	0.073	0.100	0.118	0.107	C ₁₉ Isoalkane
225	71.33	0.109	0.160	0.129	0.107	Methylphenanthrene + C ₁₉ isoalkane
226	71.46	0.061	0.085	0	0	Cycloalkane
227	72.41	1.250	1.694	2.129	1.807	<i>n</i> -Nonadecane
228	73.77	0.071	0.116	0.093	0.083	Cycloalkane + dimethylphenanthrene
228a	74.06	0	0.036	0	0	C ₂₀ Isoalkane + alkylbenzene
229	74.34	0.032	0.056	0.046	0	Cycloalkane
230	74.50	0.076	0.113	0.119	0.100	<i>n</i> -C ₁₃ Cyclohexane
231	74.78	0.091	0.104	0.079	0.079	C ₂₀ Isoalkane + dimethylphenanthrene
231a	75.07	0	0	0.025	0	Unknown
232	75.30	0.121	0.126	0.063	0.071	Dimethylphenanthrene + cycloalkane
232a	75.43	0	0.030	0	0	Unknown
233	75.78	1.154	1.511	1.774	1.474	<i>n</i> -Eicosane
234	77.05	0.090	0.111	0	0.063	Unknown
234a	77.57	0	0.026	0	0	Unknown
235	77.78	0.058	0.073	0.108	0.093	Cycloalkane
235a	77.83	0	0.031	0.021	0	C ₂₁ Isoalkane
236	78.06	0.052	0.061	0.079	0.067	Cycloalkane + alkylbenzene
237	79.00	1.094	1.451	1.463	1.206	<i>n</i> -Heneicosane
237a	79.23	0	0.063	0	0	Unknown
238	80.17	0.028	0.053	0.079	0.066	Alkylbenzene + cycloalkane
238a	80.55	0	0.040	0	0	Alkylbenzene + cycloalkane
239	80.93	0.046	0.073	0.078	0.052	Acyclic isoprenoid
240	81.18	0.102	0.140	0.161	0.108	Cycloalkane

TABLE III (continued)

Peak No.	Retention time (min)	Peak area (%)				Compound (mol.wt.)
		Tirrawarra	Moorari	Alton A	Alton B	
241	82.09	0.977	1.310	1.161	0.965	<i>n</i> -Docosane
241a	83.16	0	0.084	0	0	Alkylbenzene + cycloalkane
242	83.89	0.031	0.064	0.045	0.043	Cycloalkane
242a	84.06	0	0.024	0	0	Alkylcyclopentane
243	84.20	0.085	0.163	0.083	0.086	Alkylcyclohexane
244	85.05	0.891	1.235	0.971	0.829	<i>n</i> -Tricosane
244a	86.05	0	0.072	0	0	Cycloalkane
245	86.83	0.040	0.057	0.059	0.050	Isoalkane
246	87.07	0.071	0.096	0.077	0.060	Cycloalkane
247	87.88	0.682	0.991	0.606	0.531	<i>n</i> -Tetracosane
247a	88.84	0	0.060	0	0	Cycloalkane
248	89.62	0.053	0.069	0.088	0.045	Cycloalkane
249	89.86	0.050	0.074	0	0	Cycloalkane
250	90.61	0.554	0.862	0.425	0.392	<i>n</i> -Pentacosane
250a	91.03	0	0.040	0	0	Unknown
250b	91.51	0	0.051	0	0	Cycloalkane + alkylbenzene
251	92.27	0.054	0.095	0.093	0.071	Cycloalkane + alkylbenzene
252	92.52	0.033	0.066	0	0	Cycloalkane
252a	92.84	0	0.025	0	0	Alkylcyclohexane + alkylbenzene
253	93.23	0.363	0.601	0.219	0.211	<i>n</i> -Hexacosane
253a	94.11	0	0.053	0	0	Unknown
253b	94.41	0	0.028	0	0	Cycloalkane + alkylbenzene
254	94.73	0.017	0.027	0	0	Cycloalkane
255	94.85	0.031	0.045	0	0	Cycloalkane + alkylbenzene
256	95.09	0.030	0.049	0	0	Alkylcyclohexane Alkylbenzene
256a	95.49	0	0.017	0	0	Unknown
257	95.77	0.301	0.534	0.156	0.163	<i>n</i> -Heptacosane
258	97.32	0.029	0.042	0	0	Cycloalkane
259	97.58	0.023	0.042	0	0	Unknown
259a	98.04	0	0.018	0	0	Alkylcyclohexane
260	98.21	0.172	0.324	0.090	0.083	<i>n</i> -Octacosane
261	100.73	0.138	0.258	0.056	0.068	<i>n</i> -Nonacosane
262	103.67	0.072	0.149	0	0	<i>n</i> -Triacontane
263	107.17	0.053	0.104	0	0	<i>n</i> -Henetriacontane

Table III shows the components present in the four crude oil samples analysed. In the chromatogram shown in Fig. 2, 263 peaks were detected by GC-FID, and of these 206 were positively identified by GC-MS, the unidentified components representing a maximum of only 2.40% for the Moorari crude and approximately 1.5% for the other crudes. None of the unidentified components is present in concentrations greater than 0.18%.

An analysis of the composition of the crude oils studied in terms of functional groups is presented in Table IV. The total alkane contents of the Tirrawarra, Moor-

ari, Alton A and B crudes are 61.90, 61.35, 67.40 and 67.75%, respectively. Significant differences exist between the light-end (up to *n*-heptane) compositions of the four crudes. The Alton crudes are identical, but the Tirrawarra and Moorari crudes are distinctively different, having compositions of 21.30 and 1.50%, respectively. The alkane compositions heavier than *n*-heptane are essentially identical, with the alkane content of the Tirrawarra crude being approximately 15% less than that of the other three crudes. The naphthene contents of the alkane fraction above *n*-heptane are very similar for all four crudes. One of the most significant differences between the crudes is the aromatic contents. The Alton crudes contain significantly less (approximately 40%) aromatics than the Tirrawarra and Moorari crudes. The Tirrawarra and Moorari aromatic contents differ by only 3%.

A qualitative appraisal of the Australian crude oils studied was conducted by determining the hydrocarbon distribution by carbon number (Table V). The Tirrawarra crude has the highest individual concentration of species up to *n*-octane (*n*-C₈), and the lowest individual concentration of species from *n*-C₈ up to *n*-hentricontane (*n*-C₃₁). Concentrations of components from *n*-nonane (*n*-C₉) up to *n*-tridecane (*n*-C₁₃) are highest for the Moorari crude, and then essentially identical for Moorari and the Alton crudes up to *n*-docosane (*n*-C₂₂), Moorari has the highest concentration of species from *n*-C₂₃ up to *n*-C₃₁.

TABLE IV

ALKANE, NAPHTHENE AND AROMATIC (PNA) CONTENT OF AUSTRALIAN CRUDE OILS

Group	Crude oil			
	Tirrawarra	Moorari	Alton A	Alton B
<i>C</i> ₁ - <i>C</i> ₇ content:				
Alkanes	18.81	1.29	8.80	9.80
Naphthenes	2.21	0.21	2.55	2.41
Aromatics	0.20	0.0	0.0	0.0
Unknowns	0.10	0.0	0.12	0.13
Total <i>C</i> ₁ - <i>C</i> ₇	21.32	1.50	11.47	12.34
<i>C</i> ₇ - <i>C</i> ₃₁ content:				
Alkanes	43.09	60.06	58.60	57.95
Naphthenes	17.28	15.48	17.23	17.60
Aromatics	17.11	20.56	11.35	10.95
Unknowns	1.20	2.40	1.35	1.16
Total <i>C</i> ₇ - <i>C</i> ₃₁	78.68	98.50	88.53	87.66
Total hydrocarbons:				
<i>n</i> -Alkanes	41.05	42.13	45.87	45.39
Isoalkanes	20.85	19.22	21.53	22.36
Total alkanes	61.90	61.35	67.40	67.75
Naphthenes	19.49	15.69	19.78	20.01
Aromatics	17.31	20.56	11.35	10.95
Unknowns	1.30	2.40	1.47	1.29
Total	100.00	100.00	100.00	100.00

TABLE V
DISTRIBUTION OF CRUDE OIL COMPONENTS BY CARBON NUMBER

Carbon number	Crude oil			
	Tirrawarra	Moorari	Alton A	Alton B
<i>n</i> -C ₁	0.0	0.0	0.0	0.0
<i>n</i> -C ₂	0.0	0.0	0.0	0.0
<i>n</i> -C ₃	0.053	0.0	0.0	0.064
<i>n</i> -C ₄	0.993	0.0	0.317	0.393
<i>n</i> -C ₅	3.961	0.0	1.429	1.655
<i>n</i> -C ₆	9.132	0.079	4.748	4.985
<i>n</i> -C ₇	14.418	3.712	9.837	11.277
<i>n</i> -C ₈	14.219	12.267	10.753	12.283
<i>n</i> -C ₉	10.301	13.712	10.858	10.421
<i>n</i> -C ₁₀	7.814	11.309	9.465	9.050
<i>n</i> -C ₁₁	6.465	9.487	7.798	7.639
<i>n</i> -C ₁₂	4.774	7.058	6.403	6.152
<i>n</i> -C ₁₃	4.399	6.538	6.108	5.881
<i>n</i> -C ₁₄	4.370	6.640	6.566	6.147
<i>n</i> -C ₁₅	3.243	4.986	4.940	4.712
<i>n</i> -C ₁₆	2.129	3.391	3.725	3.511
<i>n</i> -C ₁₇	1.984	3.355	2.815	3.502
<i>n</i> -C ₁₈	1.869	2.628	2.860	2.415
<i>n</i> -C ₁₉	2.313	3.417	3.397	2.893
<i>n</i> -C ₂₀	1.343	1.880	2.054	1.708
<i>n</i> -C ₂₁	1.294	1.713	1.650	1.429
<i>n</i> -C ₂₂	1.153	1.639	1.479	1.191
<i>n</i> -C ₂₃	1.007	1.570	1.104	0.958
<i>n</i> -C ₂₄	0.793	1.136	0.742	0.701
<i>n</i> -C ₂₅	0.657	1.025	0.518	0.437
<i>n</i> -C ₂₆	0.450	0.848	0.312	0.282
<i>n</i> -C ₂₇	0.379	0.713	0.156	0.163
<i>n</i> -C ₂₈	0.224	0.386	0.090	0.083
<i>n</i> -C ₂₉	0.138	0.258	0.056	0.068
<i>n</i> -C ₃₀	0.072	0.149	0.0	0.0
<i>n</i> -C ₃₁	0.053	0.104	0.0	0.0
Total	100.00	100.00	100.00	100.00

CONCLUSIONS

The combination of high-resolution capillary column gas chromatography and mass spectrometry has made it possible to identify most of the hydrocarbon constituents of Australian crude oils, separated in the gas chromatograph, by means of their mass spectra. Using this approach for the analysis of whole crude oil samples, it is possible to obtain a full boiling range analysis of crude oils. For the crude oils studied, a minimum of 263 peaks were separated and more than 370 of the major alkane, naphthene and aromatic hydrocarbon compounds present in the crude oils were positively identified.

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