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VOLATILE CONSTITUENTS OF THE PRODUCED WATER EFFLUENT FROM THE BUCCANEER GAS AND OIL FIELD*

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SUMMARY

The volatile constituents of the effluent are concentrated on Tenax-GC using an automated purge-and-trap device and are then examined by combined gas chromatography-mass spectrometry. Some 200 compounds are resolved using a bonded-phase fused-silica column, and they are characterized with the aid of several data manipulation techniques. While the *n*-alkanes are the individual compounds found in highest concentration, the alkylaromatic hydrocarbons comprise a significant proportion of the total hydrocarbons.

INTRODUCTION

Between 1975 and 1980, the Buccaneer Gas and Oil Field, located in the northwestern Gulf of Mexico (50 km south of Galveston, Texas), was studied extensively by 25 research groups working under the aegis of the National Marine Fisheries Service and the Environmental Protection Agency (EPA)¹. Two components of this study focused on the hydrocarbon constituents of the effluents and their distribution in the environment. Brooks *et al.*² examined "gaseous" (C₁-C₅) and "volatile liquid" (C₆-C₁₄) hydrocarbons, while Middleditch and co-workers³⁻¹¹ concentrated on the "high-molecular-weight" (C₁₄+) hydrocarbons. The latter group also performed some analyses of the volatile liquid hydrocarbons¹¹.

Although it had earlier been demonstrated that detailed analyses for volatile liquid hydrocarbons could be performed in the research laboratory by preconcentration on Tenax-GC followed by gas chromatography-mass spectrometry (GC-MS) with glass or metal capillary columns¹², these procedures were time-consuming and impractical for the routine analysis of large numbers of samples. Accordingly, Brooks *et al.* employed the gas chromatographic procedure described by Sauer *et al.*¹³. They reported only eighteen C₆-C₁₄ hydrocarbons in effluents and 30 in seawater². Middleditch and co-workers used the GC-MS procedure mandated by the EPA for organic priority pollutants¹⁴, and characterized 31 volatile constituents of effluents¹¹.

With the expectation that improved analytical techniques might subsequently be developed, representative samples from the Buccaneer field were archived by the various investigators. We have used some of these samples to develop a procedure for the examination of some 200 volatile liquid hydrocarbons in effluents.

* Dedicated to Professor E. C. Horning on the occasion of his 65th birthday.

EXPERIMENTAL

Samples

The effluent discharged from the production platforms in the Buccaneer field consists of small droplets of oil suspended in brine. Thus, the hydrocarbon composition of the effluent is very similar to that of the light oil which floats to the surface in the separator tanks which comprise the final stage of effluent treatment prior to discharge. Samples of separator tank oil were collected from production platform 296-B in the Buccaneer field on January 14, 1979.

Instrument

The gas chromatograph-mass spectrometer employed for these analyses was a modified Finnigan 1020/OWA instrument. Preconcentration of the volatile hydrocarbons was performed using a Hewlett-Packard 7675A automated purge-and-trap device. The effluent tube from this device was connected in place of the carrier gas line to the sample splitter of the gas chromatograph. The gas chromatograph was equipped with a 30 m \times 0.32 mm I.D. DB-5 bonded-phase fused-silica capillary column (J&W Scientific). The outlet of this column was connected directly into the ion source of the mass spectrometer.

Procedure

A 1- μ l volume of the separator tank oil was added to 5 ml of prepurged water in a 15-ml centrifuge tube attached to the purge-and-trap device. The sample was purged with helium for 5 min, and the volatiles collected in the trap containing Tenax-GC. The trap was heated to 200°C for a further 5 min to desorb the volatiles into the gas chromatograph. During the desorption stage, three 5-cm diameter coils of the column (close to the inlet end) were immersed in liquid nitrogen in a polystyrene cup. When the desorption was complete, the liquid nitrogen was removed and the GC-MS analysis was initiated. The column was programmed from 0 to 250°C at 5°C/min. Spectra were scanned from m/z 40 to 500 every 0.5 sec, and were stored on a magnetic disc.

RESULTS AND DISCUSSION

When an automated purge-and-trap device is used with a packed gas chromatographic column, the sample would normally be desorbed onto the column at room temperature. This is impractical with capillary columns, where it is essential that the sample be introduced to the column in a sharp "plug" to preserve the resolution. Since the fused-silica columns are flexible, it was quite convenient to immerse three tight coils of the column in liquid nitrogen during the desorption step. It is possible that the capacity of a small number of coils might be inadequate to contain a large sample, so that break-through and "ghosting" might occur, but we have not encountered this problem. However, this phenomenon was occasionally a problem when, during earlier experiments, we concentrated the sample by freezing a loop of the transfer line between the purge-and-trap device and the gas chromatograph.

Tenax-GC is hydrophobic so that, theoretically, hydrocarbons and related compounds are collected in the trap while water vapor passes through it during the purge cycle. In practice, however, a small amount of water is usually retained in the

trap and is subsequently desorbed into the column along with the volatiles. Repeated use of a purge-and-trap device with columns containing water-sensitive stationary phases (such as silicones) leads to their degradation. This is a particular problem with capillary columns coated with silicone stationary phases. Accordingly, the procedure mandated by the EPA for the analysis of volatile organic priority pollutants employs a packed column containing Carbowax coated with Carbowax.

We have found that a bonded-phase fused-silica column can be used repeatedly with an automated purge-and-trap device without loss of gas chromatographic resolution. Figs. 1-4 show a reconstructed ion chromatogram for an analysis of separator tank oil. The column employed for this analysis had been in almost constant use for 4 months, yet the resolution obtained was still quite adequate.

The high resolution attainable with the bonded-phase fused-silica column dictates that the repetitive mass spectra scans be very fast. With 1-sec scans, it was not possible to reconstruct chromatograms with any degree of fidelity. Even with 0.5-sec scans, we were usually only able to acquire three to four scans per component.

Not all of the components of the sample were fully resolved, but the Finnigan data system provided assistance in the characterization of partially resolved pairs of compounds.

One method for detecting partially resolved components relies upon the use of the Biller-Biemann algorithm¹⁵. This procedure indicates scan numbers at which four or more m/z values achieve maximum intensity. This technique is illustrated in Figs. 5-7 for benzene and cyclohexane. The reconstructed ion chromatogram (Fig. 1) contained a peak which maximized at scan 382. The Biller-Biemann algorithm indicated that this peak contained two components, maximizing at scans 381 and 384, respectively. These two spectra are reproduced as Figs. 5 and 6. The spectrum in Fig. 5 is that of cyclohexane, with a molecular ion of m/z 84 and prominent ions of m/z 41, 56, and 69. Fig. 6 gives the spectrum of benzene, with a molecular ion and base peak of m/z 78. Even though these compounds are not resolved, their spectra are remarkably "clean". There is only a small peak of m/z 78 in Fig. 5 and, conversely, only a small peak of m/z 84 in Fig. 6. The Finnigan "spectral enhancement" routine removes these contaminating ions completely. Fig. 7 shows a portion of the reconstructed ion chromatogram along with mass chromatograms for m/z 78 and 84, to illustrate further the degree of resolution between these compounds.

The Biller-Biemann algorithm fails to detect compounds with fewer than four intense ions in their spectra. In such cases reconstructed mass chromatograms can be examined in a search for additional compounds. For example, the algorithm revealed the presence of 2-methylnaphthalene at scan 2810, but gave no indication of the presence of 1-methylnaphthalene. The two most intense ions in the spectra of the methylnaphthalenes are the molecular ion and the $[M-1]^+$ ion, at m/z 142 and 141, respectively. Appropriate mass chromatograms showed that these two ions maximized at scan 2865, and an enhanced spectrum matched with that of 1-methylnaphthalene. This compound coeluted with *n*-tridecane (scan 2869).

Other pairs of unresolved compounds defy deconvolution. *m*-Xylene and *p*-xylene coelute at scan 1195 and have very similar spectra. It is impossible to determine the relative concentrations of these compounds from the data obtained in this analysis. Such analyses will have to await the development of more polar bonded-phase fused-silica columns.

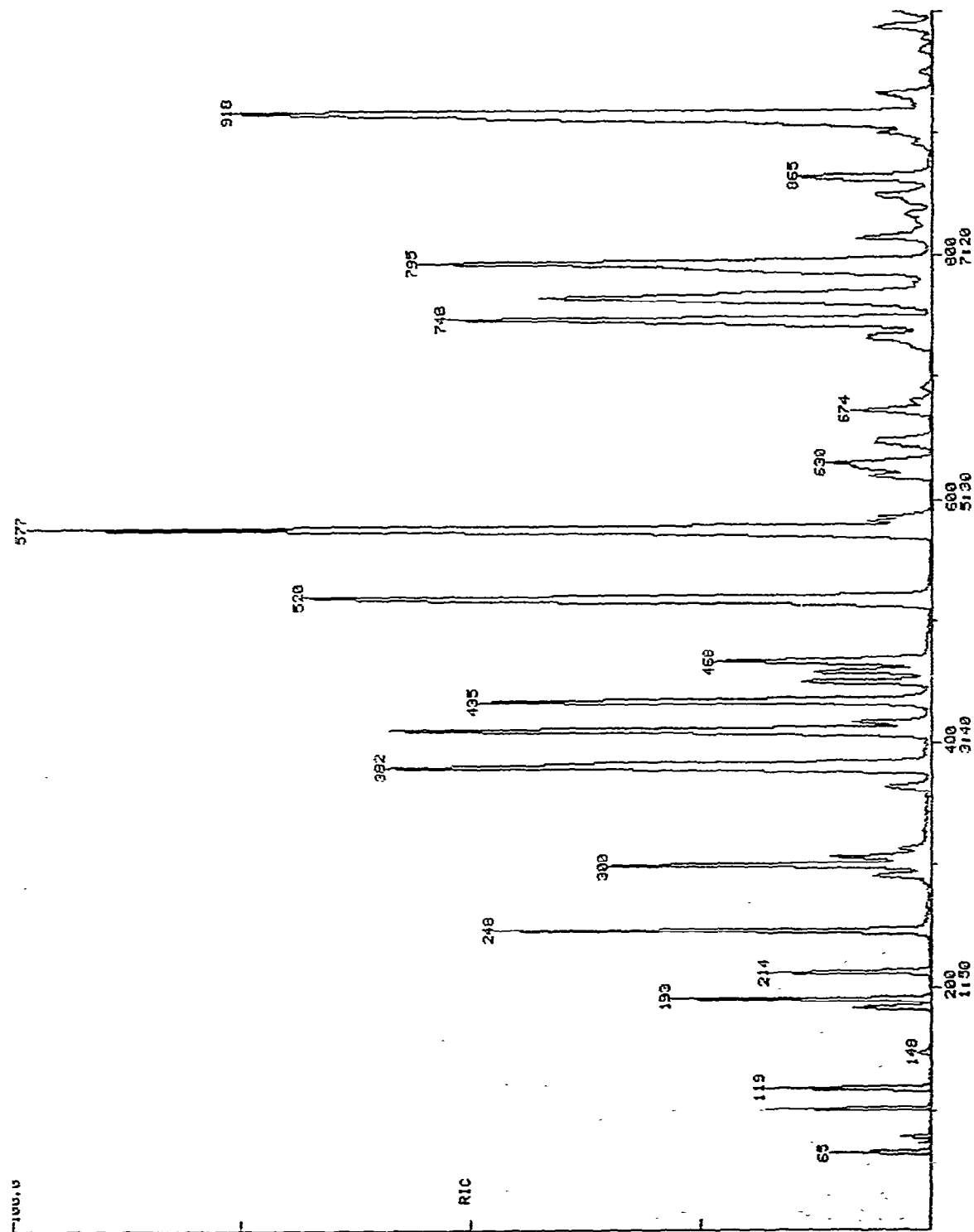


Fig. 1. Reconstructed ion chromatogram of separator tank oil (scans 1-100).

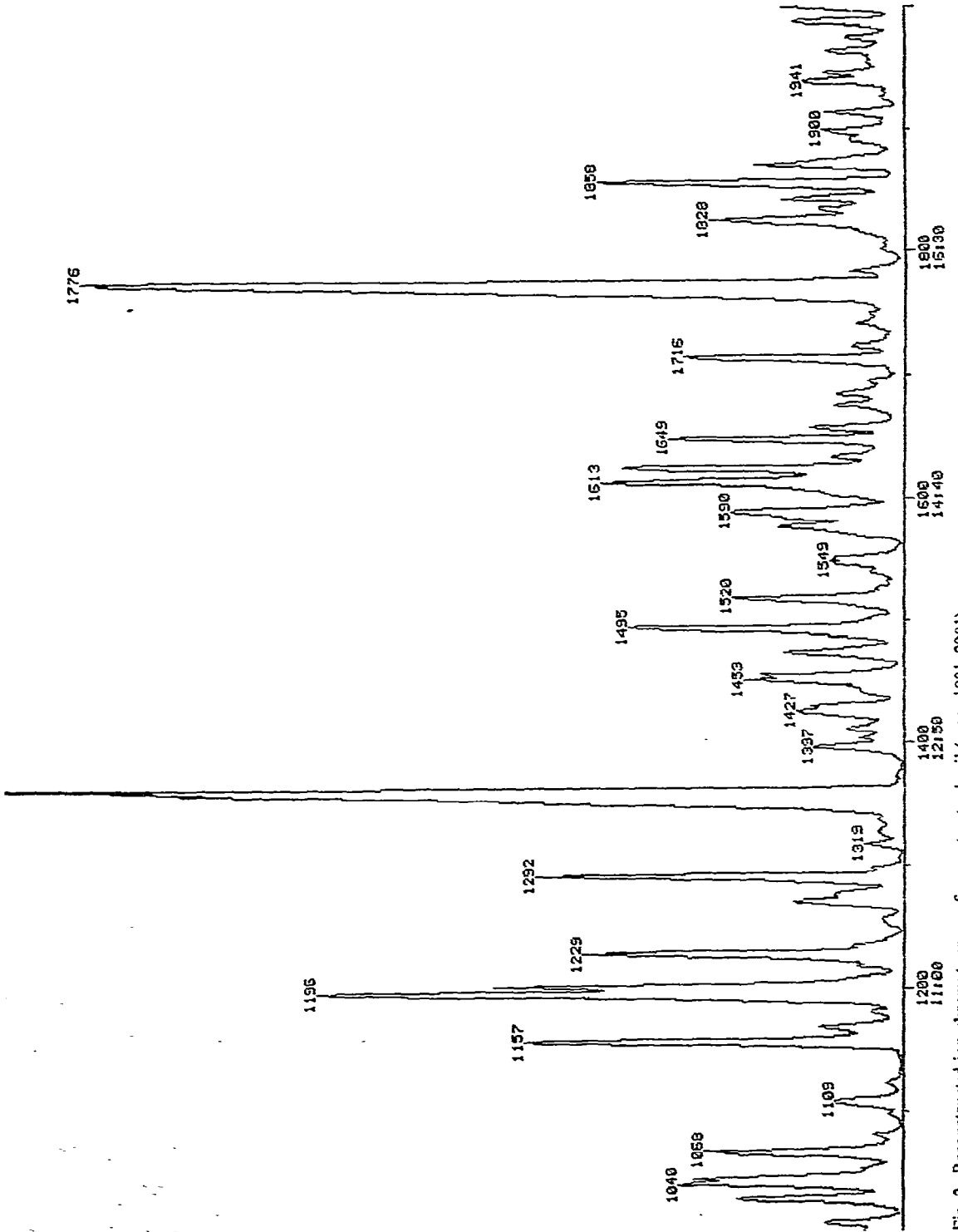


Fig. 2. Reconstructed ion chromatogram of separator tank oil (seams 1001-2001).

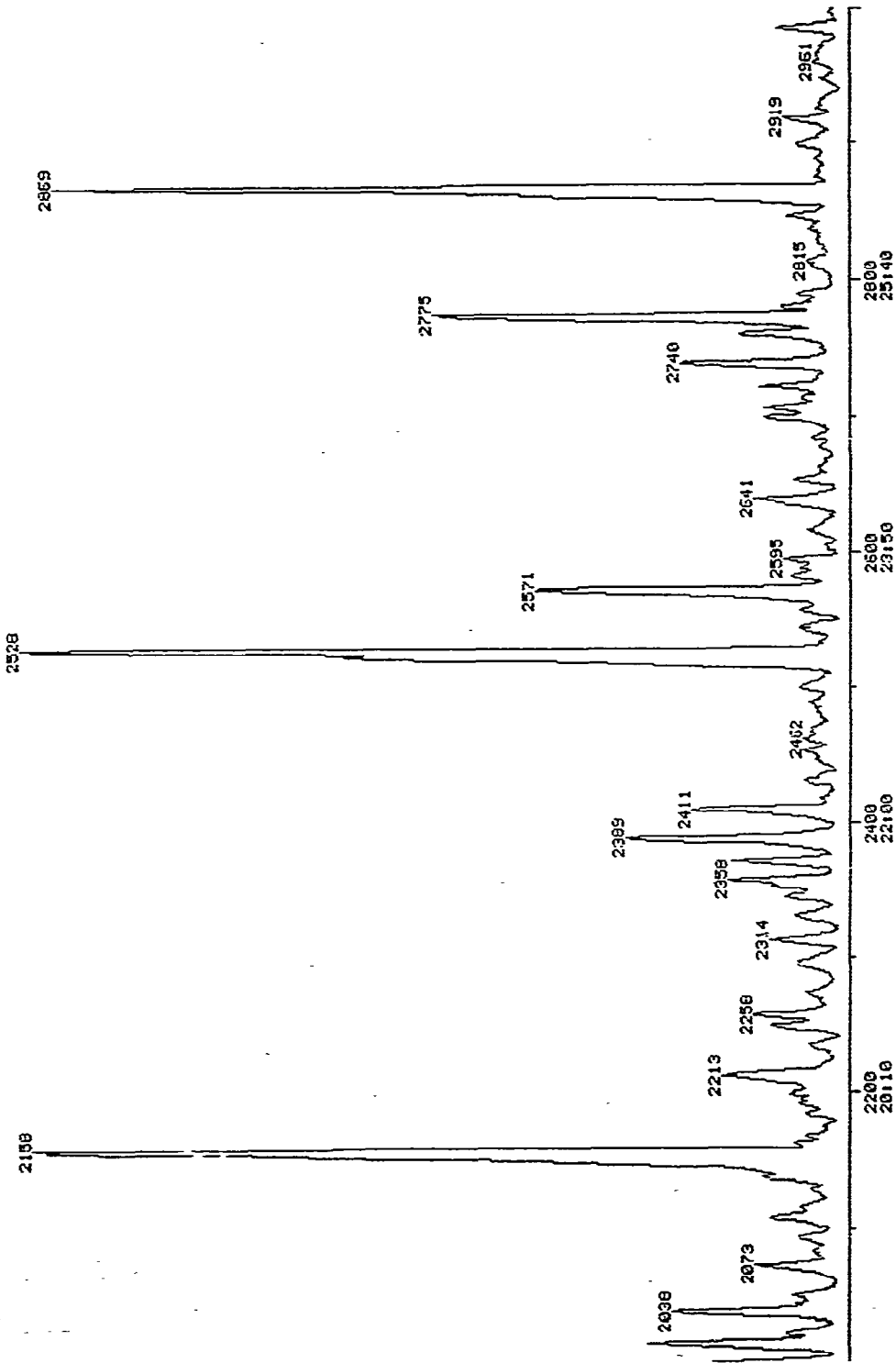


Fig. 3. Reconstructed ion chromatogram of separator tank oil (scans 2001-3001).

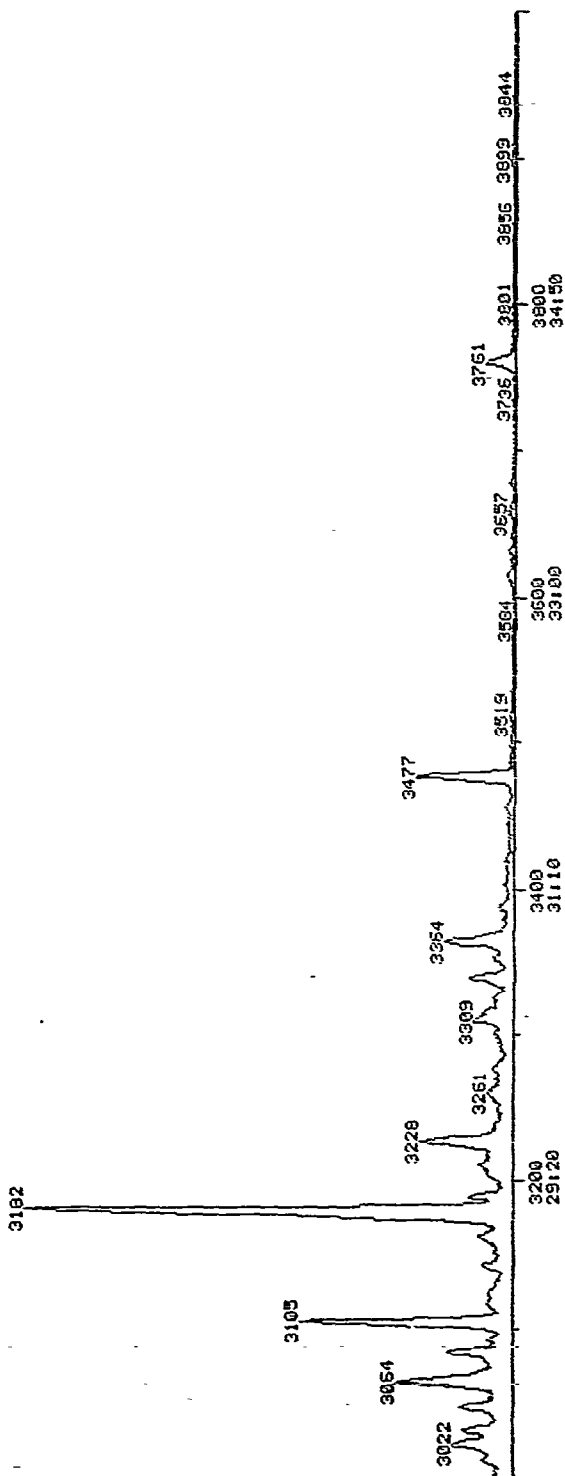


Fig. 4. Reconstructed ion chromatogram of separator tank oil (scans 3001-4001).

47532.
10.

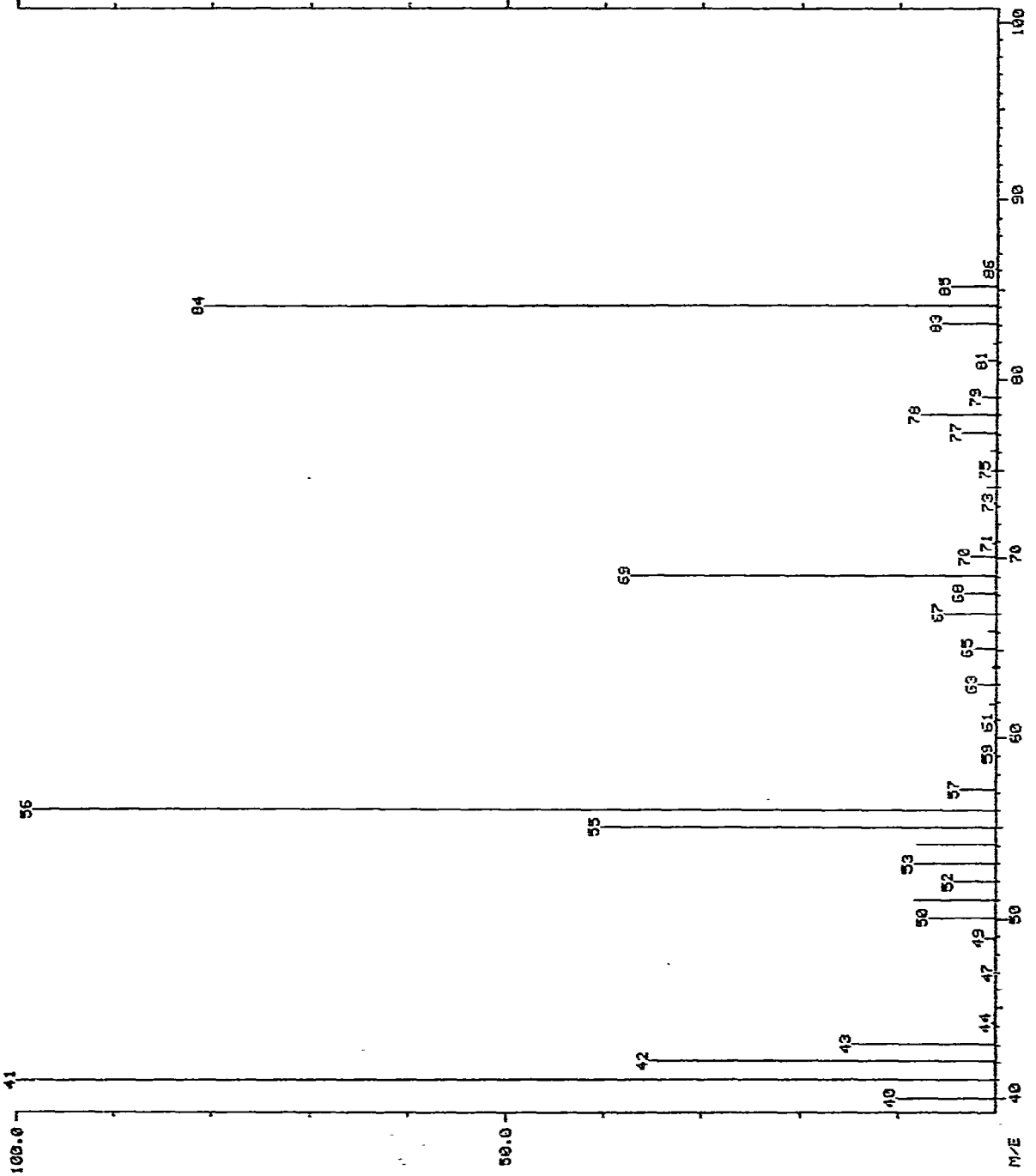


Fig. 5. Mass spectrum of scan 381 from the chromatogram shown in Fig. 1.

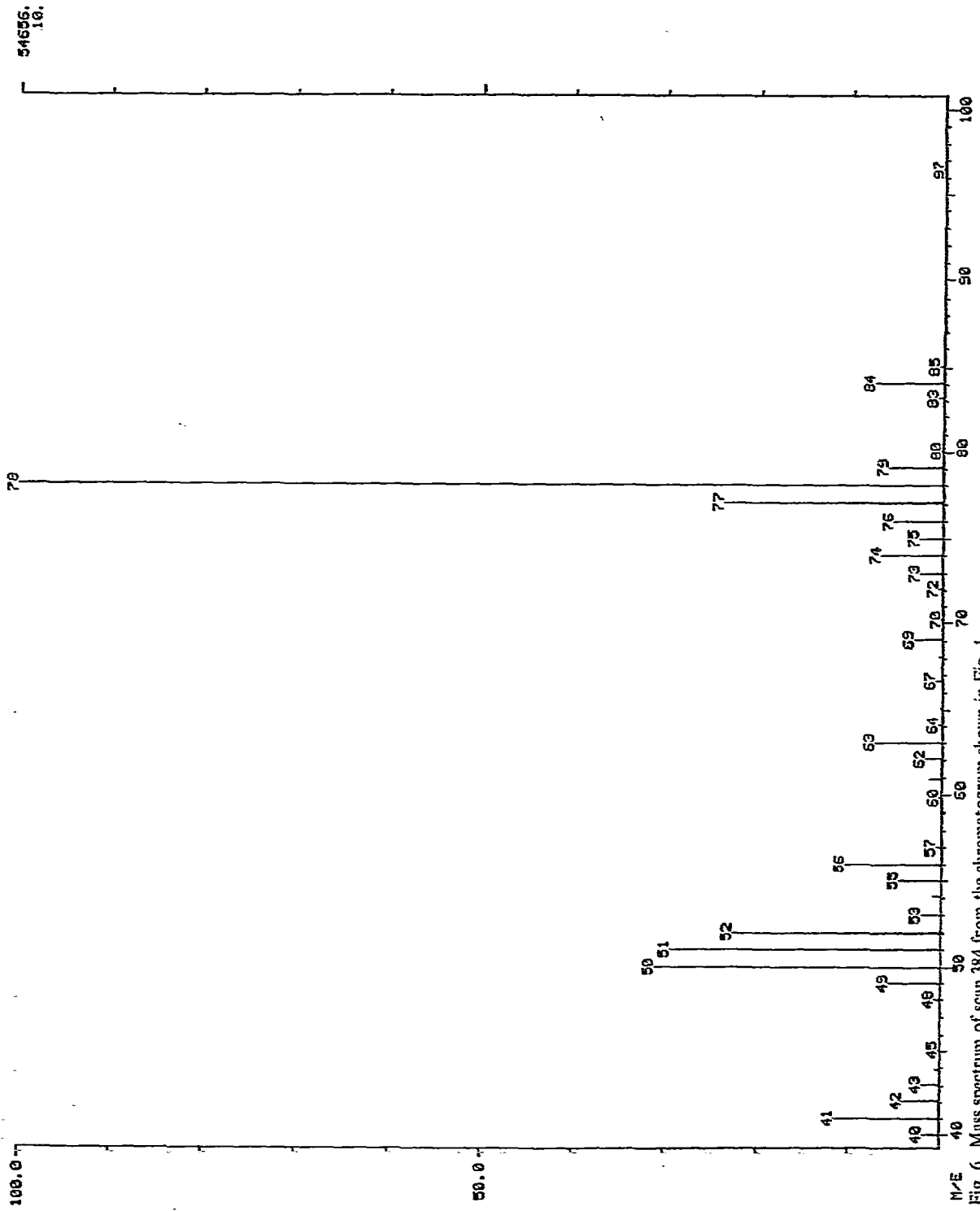


Fig. 6. Mass spectrum of scan 384 from the chromatogram shown in Fig. 1.

541556.

78.023
± 0.500

38454.

84.025
± 0.500

249500.

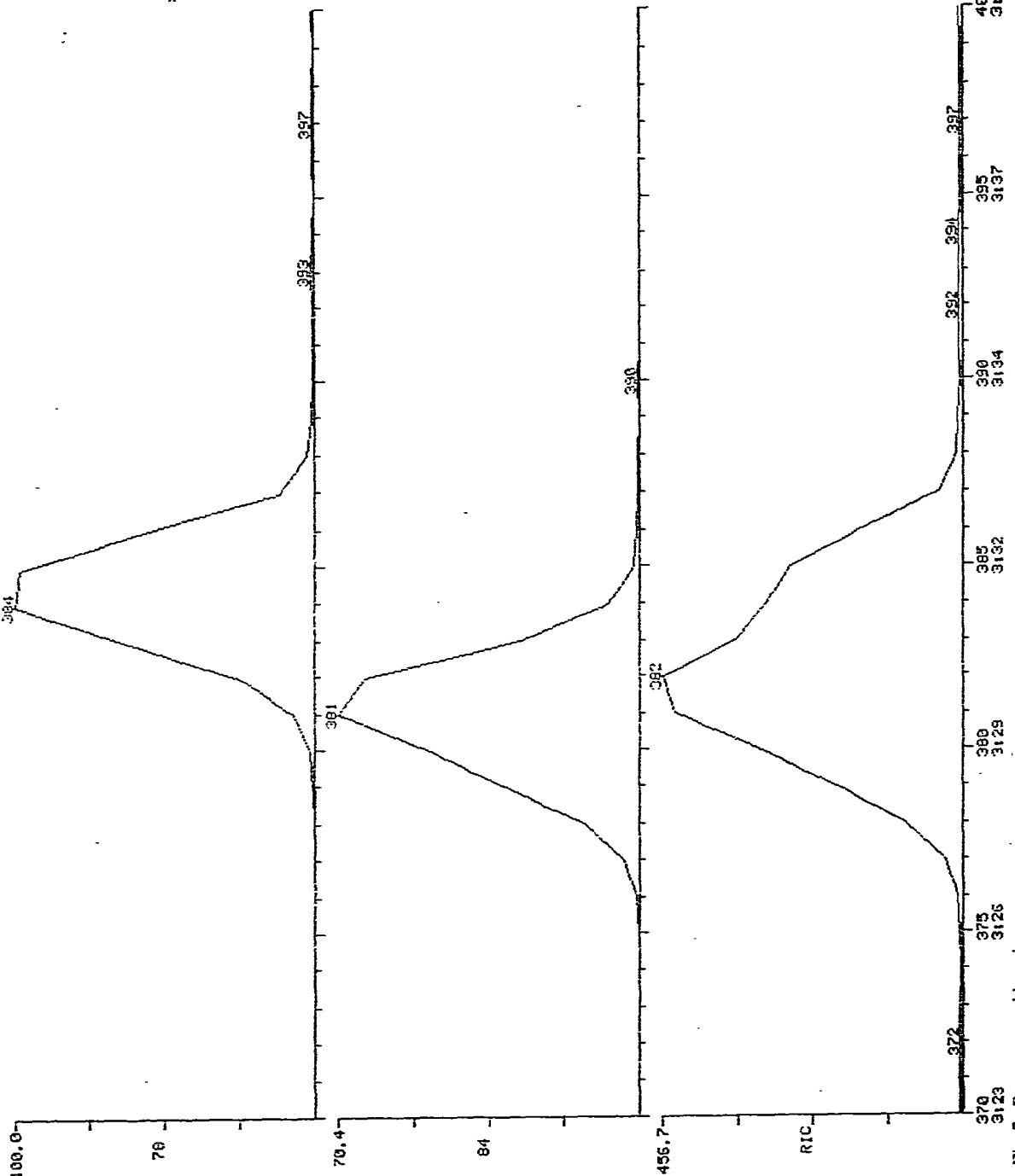


TABLE I
VOLATILE CONSTITUENTS OF OIL FROM SEPARATOR TANK

Scan	Formula	Identity	Scan	Formula	Identity
65	CO ₂	Carbon dioxide	978	C ₈ H ₁₆	?
74	C ₄ H ₁₀	2-Methylpropane	988	C ₉ H ₂₀	Alkane
79	C ₄ H ₁₀	<i>n</i> -Butane	1002	C ₈ H ₁₆	<i>cis</i> -1,2-Dimethylcyclohexane
103	C ₅ H ₁₂	2-Methylbutane	1008	C ₉ H ₂₀	2,4-Dimethylheptane
119	C ₅ H ₁₂	<i>n</i> -Pentane	1028	C ₈ H ₁₆	Ethylcyclohexane
148	C ₆ H ₁₄	2,2-Dimethylbutane	1039	C ₉ H ₂₀	2,6-Dimethylheptane
185	C ₆ H ₁₄	2,3-Dimethylbutane	1045	C ₉ H ₁₈	1,1,3-Trimethylcyclohexane
193	C ₆ H ₁₄	2-Methylpentane	1068	C ₉ H ₂₀	3,5-Dimethylheptane
214	C ₆ H ₁₄	3-Methylpentane	1081	C ₉ H ₂₀	Alkane
248	C ₆ H ₁₄	<i>n</i> -Hexane	1109	C ₉ H ₁₈	Trimethylcyclohexane
292	C ₇ H ₁₆	2,2-Dimethylpentane	1123	C ₉ H ₁₈	Trimethylcyclohexane
300	C ₆ H ₁₂	Methylcyclopentane	1157	C ₈ H ₁₀	Ethylbenzene
308	C ₇ H ₁₆	2,4-Dimethylpentane	1170	C ₈ H ₁₄	?
315	C ₇ H ₁₆	Alkane	1181	C ₉ H ₂₀	Alkane
365	C ₇ H ₁₆	3,3-Dimethylpentane	1196	C ₈ H ₁₀	<i>m</i> - + <i>p</i> -Xylene
381	C ₆ H ₁₂	Cyclohexane	1203	C ₉ H ₂₀	2-Methyloctane
384	C ₆ H ₆	Benzene	1229	C ₉ H ₂₀	3-Methyloctane
411	C ₇ H ₁₆	2-Methylhexane	1258	C ₁₀ H ₂₀	?
418	C ₇ H ₁₄	1,1-Dimethylcyclopentane	1271	C ₉ H ₂₀	1-Ethyl-4-methylcyclohexane
435	C ₇ H ₁₆	3-Methylhexane	1277	C ₉ H ₂₀	Ethylmethylcyclohexane
451	C ₇ H ₁₄	?	1292	C ₈ H ₁₀	<i>o</i> -Xylene
459	C ₇ H ₁₄	?	1319	C ₉ H ₁₆	?
468	C ₇ H ₁₄	<i>cis</i> -1,2-Dimethylcyclopentane	1339	C ₁₁ H ₂₂	Diethylmethylcyclohexane
520	C ₇ H ₁₆	<i>n</i> -Heptane	1363	C ₉ H ₂₀	<i>n</i> -Nonane
577	C ₇ H ₁₄	Methylcyclohexane	1397	C ₉ H ₁₆	?
587	C ₈ H ₁₈	Alkane	1405	C ₉ H ₁₈	Isopropylcyclohexane
619	C ₇ H ₁₄	Ethylcyclopentane	1427	C ₁₀ H ₂₂	Alkane
626	C ₈ H ₁₈	Alkane	1431	C ₉ H ₁₂	Ethylmethylbenzene
631	C ₈ H ₁₈	2,4-Dimethylhexane	1452	C ₉ H ₁₈	<i>n</i> -Propylcyclohexane
646	C ₈ H ₁₆	1,2,4-Trimethylcyclopentane	1457	C ₁₀ H ₂₂	Alkane
649	C ₈ H ₁₈	Alkane	1476	C ₁₀ H ₂₂	Alkane
674	C ₈ H ₁₆	?	1495	C ₁₀ H ₂₂	Alkane
682	C ₈ H ₁₈	Alkane	1520	C ₁₀ H ₂₂	Alkane
692	C ₈ H ₁₈	Alkane	1549	C ₁₀ H ₂₂	Alkane
725	C ₈ H ₁₄	?	1553	C ₉ H ₁₂	<i>n</i> -Propylbenzene
733	C ₈ H ₁₈	2,3-Dimethylhexane	1578	C ₁₀ H ₂₂	Alkane
748	C ₇ H ₈	Toluene	1590	C ₉ H ₁₂	Ethylmethylbenzene
765	C ₈ H ₁₈	2-Methylheptane	1613	C ₁₀ H ₂₂	Alkane
789	C ₈ H ₁₆	Dimethylcyclohexane	1616	C ₉ H ₁₂	1,2,4-Trimethylbenzene
795	C ₈ H ₁₈	Alkane	1624	C ₁₀ H ₂₂	2-Methylnonane
815	C ₈ H ₁₆	<i>cis</i> -1,3-Dimethylcyclohexane	1633	C ₁₀ H ₂₂	Alkane
835	C ₈ H ₁₆	Ethylmethylcyclopentane	1649	C ₁₀ H ₂₂	3-Methylnonane
850	C ₈ H ₁₆	4-Octene	1658	C ₉ H ₁₂	Ethylmethylbenzene
865	C ₈ H ₁₆	<i>trans</i> -1,2-Dimethylcyclohexane	1676	C ₁₀ H ₂₀	Methylpropylcyclohexane
892	C ₉ H ₁₈	?	1686	C ₁₀ H ₂₀	?
901	C ₈ H ₁₆	Dimethylcyclohexane	1716	C ₉ H ₁₂	Trimethylbenzene
918	C ₈ H ₁₈	<i>n</i> -Octane	1724	C ₁₀ H ₂₀	Methylpropylcyclohexane
950	C ₈ H ₁₆	?	1771	C ₁₀ H ₁₄	Butylbenzene
968	C ₉ H ₂₀	Alkane	1776	C ₁₀ H ₂₂	<i>n</i> -Decane

(Continued on p. 170)

TABLE I (continued)

Scan	Formula	Identity	Scan	Formula	Identity
1786	C ₁₀ H ₁₄	Methylpropylbenzene	2462	C ₁₃ H ₂₈	Alkane
1828	C ₉ H ₁₂	Ethylmethylbenzene	2472	C ₁₂ H ₁₈	Trimethylpropylbenzene
1836	C ₁₀ H ₁₄	Methylisopropylbenzene	2490	C ₁₂ H ₂₄	Methylpentylcyclohexane
1844	C ₁₀ H ₁₄	Methylisopropylbenzene	2500	C ₁₂ H ₂₀	?
1858	C ₁₁ H ₂₄	Alkane	2528	C ₁₂ H ₂₆	<i>n</i> -Dodecane
1871	C ₁₀ H ₂₀	Butylcyclohexane	2542	C ₁₂ H ₁₆	?
1897	C ₁₀ H ₁₄	Butylbenzene	2557	C ₁₃ H ₂₈	Alkane
1900	C ₁₁ H ₂₄	Alkane	2571	C ₁₃ H ₂₈	Alkane
1915	C ₁₁ H ₂₄	Alkane	2582	C ₁₃ H ₂₈	Alkane
1940	C ₁₀ H ₁₈	Decalin?	2588	C ₁₂ H ₁₈	Dimethylbutylbenzene
1947	C ₁₀ H ₁₄	Methylpropylbenzene	2595	C ₁₂ H ₂₈	Alkane
1964	C ₁₀ H ₁₄	Butylbenzene	2605	C ₁₂ H ₁₈	Dipropylbenzene
1975	C ₁₀ H ₁₄	Ethylidimethylbenzene	2616	C ₁₃ H ₂₈	Alkane
1983	C ₁₁ H ₂₄	Alkane	2641	C ₁₂ H ₂₄	Hexylcyclohexane
2000	C ₁₁ H ₂₄	Alkane	2655	C ₁₃ H ₂₈	Alkane
2002	C ₁₀ H ₁₄	Methylpropylbenzene	2663	C ₁₃ H ₂₈	Alkane
2015	C ₁₁ H ₂₄	2-Methyldecane	2678	C ₁₂ H ₁₈	Butylethylbenzene
2022	C ₁₁ H ₂₄	Alkane	2685	C ₁₃ H ₂₈	Alkane
2033	C ₁₁ H ₂₄	3-Methyldecane	2701	C ₁₃ H ₂₈	Alkane
2044	C ₁₀ H ₁₄	Methylpropylbenzene	2708	C ₁₃ H ₂₈	Alkane
2050	C ₁₀ H ₁₄	Methylpropylbenzene	2710	C ₁₂ H ₁₈	Dimethylbutylbenzene
2073	C ₁₀ H ₁₄	Methylpropylbenzene	2715	C ₁₃ H ₂₈	Alkane
2084	C ₁₀ H ₁₄	Methylpropylbenzene	2723	C ₁₃ H ₂₈	Alkane
2094	C ₁₀ H ₁₄	Methylpropylbenzene	2740	C ₁₃ H ₂₈	2-Methyltridecane
2103	C ₁₁ H ₁₈	?	2762	C ₁₃ H ₂₈	Alkane
2115	C ₁₁ H ₂₂	Pentylcyclohexane	2775	C ₁₃ H ₂₈	3-Methyltridecane
2136	C ₁₁ H ₁₆	Isobutyltoluene	2781	C ₁₄ H ₃₀	Alkane
2148	C ₁₀ H ₁₄	Ethylidimethylbenzene	2791	C ₁₄ H ₃₀	Alkane
2158	C ₁₁ H ₂₄	<i>n</i> -Undecane	2810	C ₁₁ H ₁₀	2-Methylnaphthalene
2163	C ₁₂ H ₂₀	?	2815	C ₁₃ H ₂₆	?
2168	C ₁₂ H ₂₆	Alkane	2848	C ₁₃ H ₂₆	?
2186	C ₁₀ H ₁₄	Diethylbenzene	2865	C ₁₁ H ₁₀	1-Methylnaphthalene
2194	C ₁₁ H ₁₆	Dimethylpropylbenzene	2869	C ₁₃ H ₂₈	<i>n</i> -Tridecane
2200	C ₁₀ H ₁₄	Methylpropylbenzene	2899	C ₁₄ H ₃₀	Alkane
2213	C ₁₁ H ₂₀	Methyldecalin	2919	C ₁₄ H ₃₀	Alkane
2236	C ₁₂ H ₂₆	Alkane	2961	C ₁₄ H ₂₆	?
2250	C ₁₂ H ₂₆	Alkane	2987	C ₁₃ H ₂₆	Heptylcyclohexane
2258	C ₁₁ H ₂₂	Pentylcyclohexane	3022	C ₁₄ H ₃₀	Alkane
2262	C ₁₁ H ₁₆	Ethylpropylbenzene	3032	C ₁₄ H ₃₀	Alkane
2268	C ₁₁ H ₁₆	Dimethylpropylbenzene	3047	C ₁₄ H ₃₀	Alkane
2275	C ₁₂ H ₂₆	Alkane	3064	C ₁₄ H ₃₀	2-Methyltetradecane
2295	C ₁₁ H ₁₆	Ethylpropylbenzene	3084	C ₁₄ H ₃₀	Alkane
2298	C ₁₂ H ₂₆	Alkane	3105	C ₁₄ H ₃₀	1-Methyltetradecane
2314	C ₁₀ H ₁₄	Tetramethylbenzene	3163	C ₁₂ H ₁₂	Dimethylnaphthalene
2330	C ₁₁ H ₁₆	Isobutyltoluene	3182	C ₁₄ H ₃₀	<i>n</i> -Tetradecane
2345	C ₁₁ H ₁₈	?	3210	C ₁₂ H ₁₂	Dimethylnaphthalene
2358	C ₁₂ H ₂₆	Alkane	3221	C ₁₂ H ₁₂	Dimethylnaphthalene
2372	C ₁₂ H ₂₆	Alkane	3228	C ₁₅ H ₂₈	?
2389	C ₁₂ H ₂₆	2-Methylundecane	3309	C ₁₄ H ₂₈	Octylcyclohexane
2407	C ₁₂ H ₁₈	Dimethylbutylbenzene	3340	C ₁₅ H ₂₈	?
2411	C ₁₂ H ₂₆	3-Methylundecane	3364	C ₁₅ H ₃₂	2-Methylpentadecane
2420	C ₁₀ H ₈	Naphthalene	3477	C ₁₅ H ₃₂	<i>n</i> -Pentadecane
2448	C ₁₂ H ₁₈	Dimethylbutylbenzene	3761	C ₁₆ H ₃₄	<i>n</i> -Hexadecane

CONCLUSIONS

Some 200 components of produced water effluent from the Buccaneer field have now been characterized, considerably more than were previously identified. The most abundant single compounds are the *n*-alkanes, while alkylaromatic hydrocarbons are also present in a relatively high aggregate concentration.

The use of bonded-phase fused-silica columns allows one to examine effluent samples by combining an automated purge-and-trap device with a gas chromatograph-mass spectrometer. The sample is loaded into the purge tube and the operation of the device is initiated. Further operator intervention is only required when the desorption is complete: the cooled portion of the column is removed from the liquid nitrogen and data acquisition is initiated. Thus, the procedure is amenable to repetitive analyses.

While it has been demonstrated that some 200 components of an effluent can be resolved and characterized, it is unlikely that such detailed analyses would be needed repetitively. Manipulation of the data to provide target compound analyses for selected compounds could be performed simultaneously with data acquisition for subsequent samples if, as in the Finnigan instrument, the data system can be used in the foreground/background mode with priority interrupt.

ACKNOWLEDGEMENTS

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