Water-Soluble Hydrocarbons From Crude Oil

by C. C. LEE, W. K. CRAIG,
and P. J. SMITH
Department of Chemistry and Chemical Engineering
University of Saskatchewan
Saskatoon, Saskatchewan, Canada S7N OWO

When spills of crude oil occur on bodies of water, even after the clean-up, water-soluble components from the oil may remain and continue to exert their effects on the environment. We have, therefore, undertaken a study on the nature and amounts of water-soluble materials that can be derived from crude petroleum oils. After the present work has started, BOYLAN and TRIPP (1971) reported the identification of a large number of aromatic hydrocarbons (chiefly alkylated benzenes and naphthalenes) in the sea-water extracts of several crude oils and a kerosene. In the present communication, we report the results from studies on the water-soluble components from 10 oil samples and discuss the differences between these findings and those of BOYLAN and TRIPP (1971).

Seven of the crude oil samples were supplied by the Research Council of Alberta. These were obtained directly from the well-head in different fields in the Province of Alberta and represent oils of different geological ages (Table I). The remaining three samples were imported crude oils supplied by Gulf Oil Canada Ltd. (Table II). The Alberta oils were extracted with distilled water while the imported oils were extracted with distilled water and with a 3.5% NaCl solution to simulate sea-water. The extraction was effected by the "slow stirring" procedure of BOYLAN and TRIPP (1971) (25 ml. oil in 1.5 l H_2O gently stirred with a magnetic stirrer for 12 hr. at room temperature). BOYLAN and TRIPP (1971) have pointed out that with turbulent mixing, the results were complicated by the presence of fine droplets of oil suspended in the aqueous extract. In the present work, it was found that even with "slow stirring", emulsified oil droplets were likely present in the aqueous phase. When the aqueous phase was separated from the oil and then extracted with pentane and concentrated as described by BOYLAN and TRIPP (1971), a typical gas chromatogram of the resulting residue is given in Fig. 1, which showed a fair extent of similarity to the chromatograms reported by BOYLAN and TRIPP (1971). On the other hand, if the aqueous extract was filtered through a layer of $CaCO_3$ on a Buchner funnel to break up and remove any oil emulsion (BECHER, 1965) and then further clarified by filtration through a layer of celite before being extracted with pentane and concentrated, the resulting residue from such a filtered aqueous extract gave a much simpler gas chromatogram as typified by Fig. 2. It is reasonable to assume that Fig. 2 represents the chromatogram of the more truly water-

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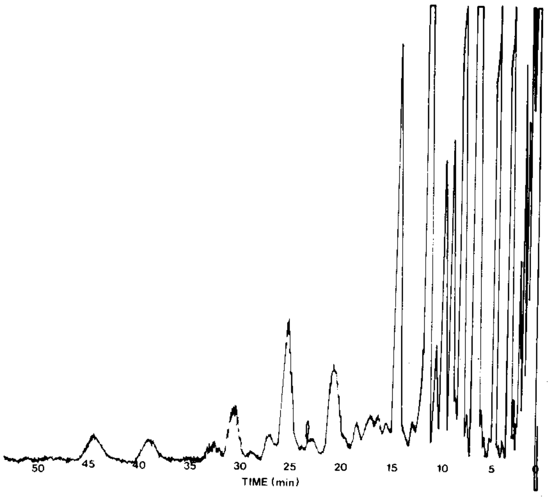

Fig. 1. Gas chromatogram of materials derived from unfiltered aqueous extract of oil sample No. 10 (Carbowax column at 180°C)

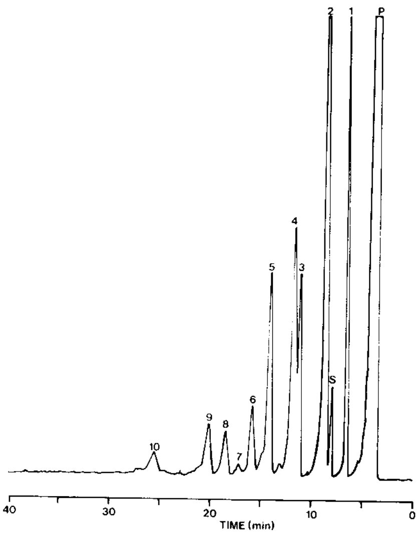

Fig. 2. Gas chromatogram of materials derived from filtered aqueous extract of oil sample No. 10 (Carbowax column at 135°C)

soluble components in the aqueous extract of crude petroleum oil.

Identifications of the different peaks in the gas chromatogram were based on retention times (25 ft. x 1/8 in. column packed with 25% Carbowax 20M on Chromosorb P or with 5% SE-30 on Chromosorb W using an Aerograph 200 gas chromatograph with flame ionization detector), mass spectrometry (Perkin-Elmer model 990 gas chromatograph interfaced to an AEI MS12 mass spectrometer), and comparisons of the gas chromatograms and mass spectra with those of authentic compounds. With reference to Fig. 2, besides the solvent peak P (pentane) and the internal standard S (isobutyl acetate), peaks 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, respectively, were identified as benzene, toluene, ethylbenzene, m- and p-xylenes, o-xylene, m- and p-ethyltoluenes, mesitylene, o-ethyltoluene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene.

Quantitative estimations of the various components for each gas chromatogram were made by using a known weight of isobutyl acetate as an internal standard and correcting each peak area, including that of the internal standard, with an appropriate relative sensitivity factor (DIETZ, 1967) determined by calibrations using known weights of authentic compounds. The results are summarized in Tables I and II. It can be seen from these Tables that the same aromatic hydrocarbons were found in the filtered aqueous extract of each of the 10 oil samples studied. The relative distributions of these compounds, however, do vary for the different oil samples. It is also seen that salt water extracted from the oil lesser amounts of these aromatic hydrocarbons than distilled water (Table II).

It is of interest to note that the first four chromatographic peaks identified by BOYLAN and TRIPP (1971) were m- and p-ethyltoluenes, mesitylene and o-ethylbenzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene. These compounds correspond to the last five peaks obtained in the present study. Thus, the present experiments gave the qualitative and quantitative estimates of the lower boiling aromatic hydrocarbons in the aqueous extracts of crude oil while the work of BOYLAN and TRIPP (1971) showed many other higher boiling materials.

BOYLAN and TRIPP (1971) have suggested the possibility of using differences in the relative amounts of naphthalenes in the aqueous extract as a means of rapid identification of the oil. In the present study, the naphthalenes were not detected. The relative composition of the hydrocarbons that were detected did differ for the different oils and in principle these differences could serve as an aid in the identification of the original oil. However, the data in Table II indicate only fair reproducibility in the relative composition for duplicate runs. The gas chromatogram of the soluble components from an oil, therefore, should not be regarded as an absolute "finger-print" of that oil.

TABLE I

Relative Composition of Water-Soluble Components in Aqueous Extracts of Alberta Oils

Sample No.	Field (pool)	Relative Composition[a], %									
		1	2	3	4	5	6	7	8	9	10
Upper Cretaceous											
1	Pembina (Cardium)	5.9	44.7	8.1	11.7	12.5	3.0	1.5	2.0	4.9	5.8
2	Joarcan (Viking)	2.6	20.0	10.1	23.6	13.0	6.4	3.7	3.2	11.0	6.3
Lower Cretaceous											
3	Leduc-Woodbend (Blairmore)	24.8	30.8	4.5	16.2	9.4	2.1	1.5	1.0	6.9	3.0
4	Gilby (Basal Mannville B)	10.4	44.7	8.2	17.2	9.1	2.0	1.0	0.9	4.0	2.5
Carboniferous											
5	Turner Valley (Rundle)	8.2	36.7	9.6	21.0	11.0	2.6	1.5	1.3	5.2	2.9
Upper Devonian											
6	Redwater (D-3)	7.6	28.2	13.4	14.4	10.4	2.8	3.3	2.6	10.9	6.6
7	Swan Hills (Beaverhill Lake A)	5.7	19.5	9.9	22.9	13.3	2.7	2.2	1.3	14.8	7.6

[a] Components 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 are, respectively, benzene, toluene, ethylbenzene, *m*- and *p*-xylenes, *o*-xylene, *m*- and *p*-ethyltoluenes,mesitylene, *o*-ethyltoluene, 1,2,4-trimethylbenzene and 1, 2, 3-trimethylbenzene.

TABLE II

Relative Composition of Water-Soluble Components in Aqueous Extracts of Imported Oils

Sample No.	Expt.[b]	Relative Composition[a], % 1	2	3	4	5	6	7	8	9	10	Total Solubles, ppm.
African												
8	A	16.2	36.7	5.2	18.5	8.1	2.0	1.4	1.2	6.0	4.6	0.35
	B	14.8	34.4	3.6	19.3	9.0	1.9	2.4	1.9	6.6	6.5	0.50
	C	8.8	39.7	4.2	17.5	8.8	1.7	3.2	1.9	7.5	6.8	0.23
Arabian												
9	A	15.3	28.5	12.9	16.7	11.6	4.5	0.6	3.7	4.1	1.7	1.15
	B	15.4	30.8	12.0	15.9	11.4	4.5	1.1	3.1	3.7	2.0	1.42
	C	10.4	46.3	9.9	12.4	10.2	3.2	0.6	2.4	3.2	1.5	0.70
Venezuelan												
10	A	14.0	28.7	14.0	18.2	11.0	3.6	0.7	3.8	4.4	1.7	1.55
	B	14.9	28.2	14.0	16.8	11.3	4.0	1.0	3.4	4.3	2.3	1.17
	C	13.2	45.1	8.9	14.7	8.9	2.9	0.8	2.3	2.6	1.0	0.44

[a] Components 1 to 10 as in Table I. [b] Expt. A and B from duplicate extractions with distilled water; Expt. C from extraction with 3.5% NaCl solution.

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