

## Preparation and Characterization of a Water-Soluble Fraction of Crude Oil by a Karr Reciprocating-Plate Countercurrent Extraction Column

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**Abstract.** A 1.8 m × 2.5 cm reciprocating-plate countercurrent extraction column was evaluated for the preparation of WSF (water-soluble fractions) from Flotta North Sea light crude oil. The energy input from the plate reciprocation speeds was found to be the main factor affecting the characteristics of the extracted WSF, and the throughputs of the stock solution or the ratio of seawater to crude oil had little effect on the concentration and composition of the extracted WSF. A combination of a reciprocation speed of 170 strokes/min, a seawater flow rate of 220 ml/min, and a crude oil flow rate of 2.9 ml/min produced a WSF stock solution with a total hydrocarbon concentration of  $13.5 \pm 0.30$  mg/kg ( $n=6$ ) which was more reproducible than that made by a previously used large-scale batch extraction method. A settlement time of 5 h or less for the stock solution allowed a full separation of any dispersed droplets of crude oil from the aqueous phase under the above conditions, but further increases in reciprocation speeds caused difficulties in the final separation of this crude oil. The column extraction method was highly reproducible and gave a more concentrated WSF containing a higher proportion of alkanes than a WSF made by the batch extraction method. Low-boiling aromatics were the main components of the total extracted hydrocarbons of the WSF.

The pollution of the aquatic environment caused by oil spills has led to serious problems for aquatic life. Investigation of the toxicity of crude oil contamination has revealed that the toxicity of oils is apparently due to the water-soluble fraction (WSF) rather than to dispersed droplets (Rice *et al.* 1977). The most immediate effect of oil pollution once a slick is dispersed is the intimate contact of the WSF with fish or other marine organisms.

Many experiments have been conducted on the exposure of different marine and freshwater organisms to various dilutions of the WSF (Davis *et al.* 1992; Heras *et al.* 1992; Lockhart and Danell 1992; Vignier *et al.* 1992); the preparation of the WSF is one of the critical steps necessary to obtain reproducible and precise results. It is difficult to prepare a reproducible WSF stock solution and to continuously supply a fresh stock solution in order to maintain a stable chemical environment in exposure tanks. Different laboratories have used a variety of methods to prepare a WSF, with a wide range of mixing forces, water to oil ratios, and times of settlement (Boylan and Tripp 1971; Katz 1973; Anderson *et al.* 1974; Smith and Cameron 1979; Heras *et al.* 1992). Maher (1982) tended to justify his choice of a mixing method based on gentle oscillation rather than turbulent stirring as this appeared to simulate the most probable environmental situation. However, many different mixing mechanisms occur in the marine environment, and it is impossible to duplicate these natural processes in a laboratory.

Most of the current methods for making a WSF are batch operations, and the stock solution is usually metered into the exposure tanks either continuously (Heras *et al.* 1992) or at certain time intervals (Keck *et al.* 1978). The exposure may also be conducted with no addition of WSF during the entire experimental period (Lee and Nicol 1977). The concentration and composition of the stock solution can change due to any or all of evaporation, biodegradation, photo-oxidation, and adsorption of the WSF on surfaces during the experimental period (Rice *et al.* 1977; Moles *et al.* 1979). This will result in serious variations in the desired WSF concentration during an experiment, especially when a longer-term exposure is required. Continuous-flow test systems have been suggested by Nunes *et al.* (1978) and Johannessen (1983) to solve these problems, but, owing to complications associated with the physical and chemical properties of oils, they have not been widely adopted.

We have, therefore, investigated the continuous production of a WSF. Operation of continuous countercurrent extraction is conducted when one of the phases is dispersed and allowed to pass continuously and countercurrently through the other phase, which is not dispersed. This operational system theoretically gives maximum "efficiency" under equilibrium states (Treybal 1973). Equipment in this category that has been studied and developed includes mechanically assisted gravity de-

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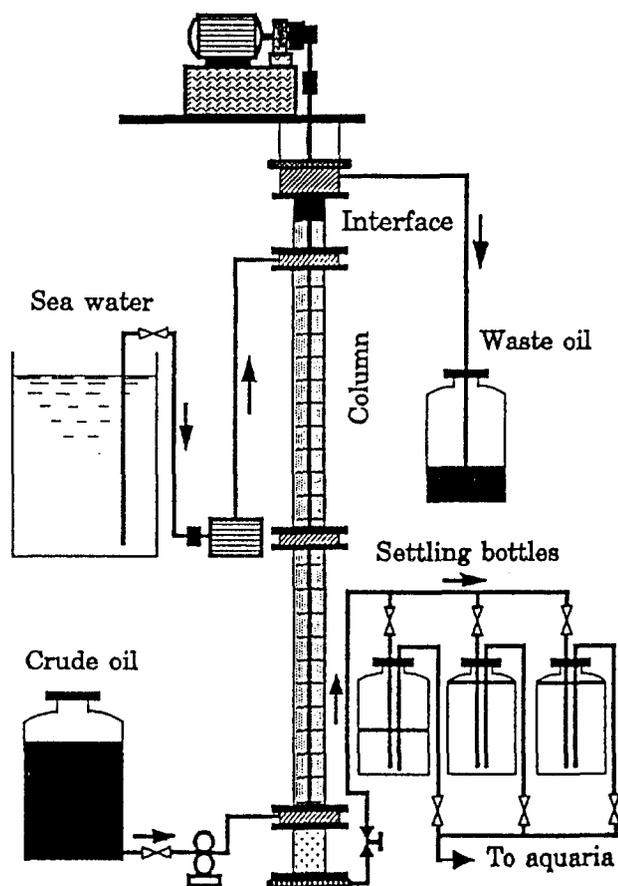


Fig. 1. An outline of equipment used for the preparation of water-soluble fraction of hydrocarbons from crude oil using a Karr reciprocating plate extraction column

vices and centrifugal extractors (Goldberg 1973). Performance data for a 3-in. diameter open type of reciprocating extraction column were first reported by Karr (1959). Since then, various studies on the performance and applications of this type of column have been conducted, including those with a laboratory scale 1-in. diameter column (Lo and Karr 1972). These investigations revealed that the reciprocating extraction column had features of simple construction and easy operation, high versatility and extraction efficiency, and reasonable capacity. The purpose of our work was to investigate the suitability of using a reciprocating plate extraction column for the preparation of WSF. This would provide fresh, reproducible, petroleum water-soluble fractions on a demand basis as stock solutions for long-term exposures of marine organisms to WSF.

## Materials and Methods

### Preparation of Water-Soluble Fraction

Flotta North Sea crude oil, obtained from the Dartmouth, Nova Scotia refinery of Esso Petroleum Canada, was used to prepare the water-soluble fraction. Sand-filtered seawater was supplied by the Aquatron Laboratory of Dalhousie University.

Figure 1 is an outline of the method for the preparation of the WSF of hydrocarbons from crude oil using a Karr reciprocating

plate extraction column. This column was a product of PEGASUS Industrial Specialties Ltd., Agincourt, Ontario (Model KC-1-6, diameter 2.54 cm, plate spacing 5.3 cm, plate stack height 1.83 m). It was fitted with a reciprocating speed adjustment device. The stroke amplitude of the reciprocating plates was set at 2.54 cm. A stainless steel Duplex pump (FR 221-A-117 Frame A, Milton Roy Industries LTD), and a Masterflex pump (Cole-Parmer Instrument Co., Niles, IL) with a standard pump head (Model 6212-14) and Viton tubing, were used to supply seawater and crude oil, respectively. The seawater was metered into the column via the nozzle above the reciprocating plates. Similarly, the crude oil entered the column at a controlled rate via the nozzle below the reciprocating plates. Before admitting crude oil, the entire column was filled with seawater. The interface was established at the midpoint of the upper separation section by adjusting the hand-controlled valve in the bottom discharge line through which the stock WSF solution exited from the column. The reciprocation speeds were varied with the speed adjusting handwheel. Three flow rates of seawater (220, 130, and 66 ml/min), including the maximum and minimum speeds achievable with this pump, were selected and a flow rate of 2.9 ml/min was chosen for crude oil. Reciprocation speeds of 55, 130, 170, 220, and 260 strokes/min corresponding to the scale readings of 2, 4, 5, 6, and 7 were adopted for the experiments. The extractions were conducted at room temperature (25°C). After equilibrium the stock WSF solution was collected into a separatory funnel (8 L) and settled in a cold room (5°C) for 5 h before analyses. A water-soluble fraction was also prepared by a normal batch extraction method (400 L per batch) as reported by Heras *et al.* (1992).

### Extraction of Hydrocarbons for Gas-Liquid Chromatography

The hydrocarbons in the stock solution were recovered according to the Murray microextraction procedure (Murray 1979; Murray *et al.* 1984); an extraction flask of 1 L capacity was constructed with a side arm and a capillary tube at the top-center of the flask as described by Murray (1979). The WSF (980 ml) was placed in the flask. The flask was stoppered, and the mixture was shaken with hexane (1 ml, BDH, Omnisolv grade) for 1 min. The layers were allowed to settle for a minimum of 15 min in a domestic refrigerator (5°C) to permit the hexane droplets dispersed throughout the aqueous phase to collect on the upper surface. The hexane layer was directed to the centre capillary tube by adding chilled distilled water through the side arm, while tilting the flask at an angle of 45°. Two  $\mu\text{l}$  of the hexane layer from the capillary tube were taken into a 10  $\mu\text{l}$  Hamilton GC syringe containing 0.2  $\mu\text{l}$  of clean hexane, followed by 1  $\mu\text{l}$  of a hexane solution of *n*-heneicosane. Both were injected simultaneously into the GLC (gas-liquid chromatograph). Quantitative analyses were based on the use of *n*-C<sub>21</sub> as the internal standard, and the concentrations of hydrocarbons in the samples were calculated according to correction factors from a published report (Ernst *et al.* 1989).

### Gas-Liquid Chromatography

The hydrocarbon analyses were conducted with a Perkin Elmer (Norwalk CT) 8420 capillary gas chromatograph equipped with a flame ionization detector (FID) and a split injection system (split ratio 1:55). The analysis was conducted on a DB-1 (methyl silicone) fused silica capillary column (60 m, 0.25 mm ID, 0.25  $\mu\text{m}$  film thickness). Conditions and temperature were: FID, 280°C; injector, 280°C. The column temperature was programmed as follows: initial temperature, 45°C held for 15 min; increased at a rate of 13°C min<sup>-1</sup>; final temperature 280°C, held for 25 min. The carrier gas was helium at a pressure of 138 kPa and hydrogen and air pressures were 90 and 159 kPa, respectively.

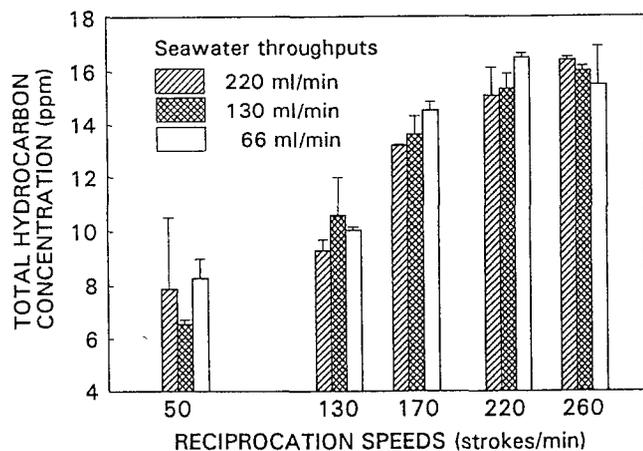


Fig. 2. Effect of reciprocation speeds and seawater throughputs on the extraction of WSF from crude oil

## Results and Discussion

### Extraction of the Water-Soluble Fraction

Many experimental parameters affect the extraction of WSF from crude oil, *i.e.*, type of oil, degree and duration of agitation, ratio of crude oil to seawater, and settling time required to achieve a stable distribution of hydrocarbons between the aqueous and oil phases. The results showed that the concentrations of continuously extracted WSF were principally related to the reciprocation speeds of the column agitator, whereas the throughputs of the stock solution had little effect under the experimental conditions (Figure 2). Two critical reciprocation speeds were observed. Below 130 strokes/min, the crude oil droplets were not well dispersed, and much less WSF was extracted compared to higher speeds. At or above 170 strokes/min dispersion of the crude oil was excellent and the concentration of the lower molecular weight hydrocarbons increased sharply (Figure 3). At the reciprocation speed of 170 strokes/min, the effect of seawater flow rate on the extraction of hydrocarbons into WSF was very low, with coefficients of variation of only 4% (flow rate was varied from 66 to 220 ml/min).

The reproducibility for the extraction of WSF using this column was tested. The results of Table 1 revealed that the reproducibility of this column method was much better than that produced by normal batch extraction method (400 L each time). The total hydrocarbon concentration was  $13.5 \pm 0.3$  mg/kg ( $n=6$ ) extracted at reciprocation speeds of 170 strokes/min and a seawater flow rate of 220 ml/min; with the normal batch extraction it was only  $11.03 \pm 2.33$  ( $n=12$ ).

### Separation of Dispersed Crude Oil from the Aqueous Phase

A period of time is needed for the subsequent separation of dispersed oil droplets from the water phase. Two well-resolved GC peaks are convenient for this assessment. The ratio of  $C_{13}$  *n*-alkane + 2-methylnaphthalene to 1-methylnaphthalene was used as an indicator for the involvement of undissolved oil droplets in seawater as it is well recognized that the *n*-alkanes

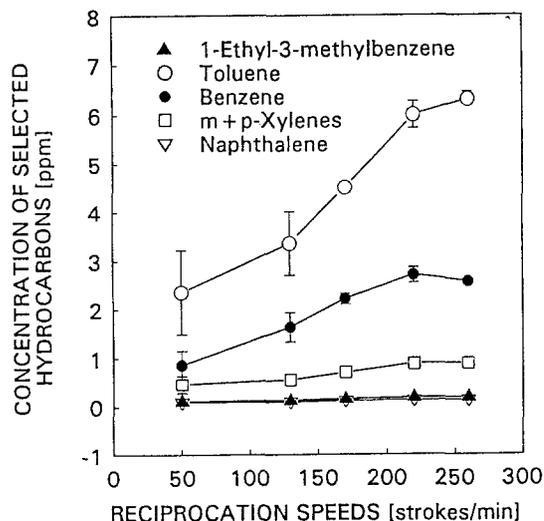


Fig. 3. Effect of reciprocation speeds on the extraction of individual hydrocarbons of water-soluble fraction

from  $C_{11}$  upward generally have a very low solubility in water compared with aromatic hydrocarbons (McAuliffe 1966; Sutton and Calder 1974; Clark 1977; Burris and MacIntyre 1984). After 1 h of settlement, many oil droplets were still present, as indicated by the high ratio of alkanes to aromatic hydrocarbons, but the stock solution was almost free of oil droplets after 2 h of settlement. Further settlement continuously decreased crude oil inclusion but at a very slow rate. The stock solution was considered to be essentially free of crude oil droplets after 5 h of settlement.

### Characteristics of the Water-Soluble Fraction

The two methods presented the same profile of water-soluble hydrocarbons dissolved in water (Table 1), but the column method had slightly lower aromatic hydrocarbon percentages and higher alkane percentages (71.92% and 21.73%) compared with those from the normal batch extraction method (85.42% and 11.1%). The slight differences of WSF composition were probably caused by the evaporation of low boiling alkane components during the long term mixing (24 h) and settling periods (48 h) of the normal batch extraction method. In both methods, the aromatic hydrocarbons were highly enriched (see column WSF, Figure 4b) compared with the crude oil hydrocarbon profile (Figure 4a). The alkanes from  $C_{11}$  upward were negligible in the WSF solution, which means that it was essentially free of crude oil suspension. The monoaromatic hydrocarbons, such as benzene, toluene, xylene, and ethylbenzene, were the main components among the aromatic hydrocarbons. These are the major sources of the toxicity of crude oil and were largely responsible for the fluctuations of WSF concentration in different batch extractions. Our experimental results on composition of the WSF extracted from Flotta North Sea crude oil were quite similar to those previously reported by Heras *et al.* (1992) and by Widdows *et al.* (1982), who worked with the same oil. Figure 5 is a typical GLC chromatogram of the water-soluble hydrocarbons extracted by the reciprocating extraction column.

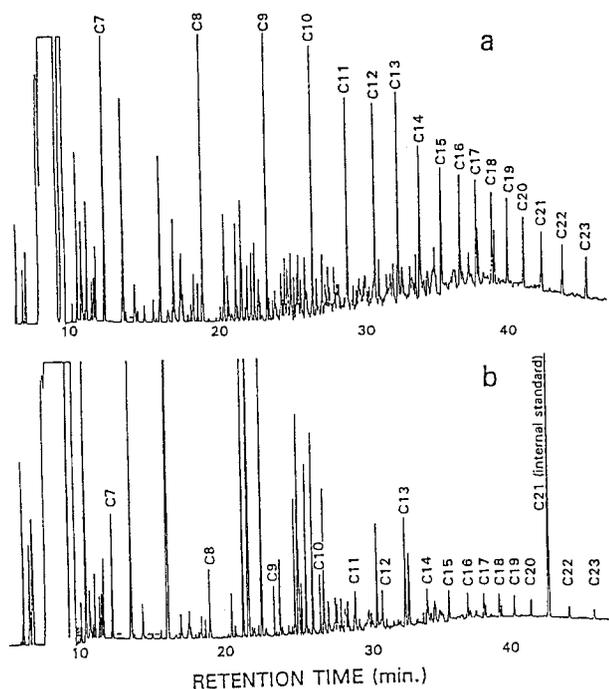
**Table 1.** Relative concentration of hydrocarbon components in stock water-soluble fraction extracted from Flotta North Sea crude oil by a Karr reciprocating plate countercurrent extraction column and by a usual batch extraction method. Reciprocation speed, 170 strokes/min; throughput, 220 ml/min. Values are means  $\pm$  SD of results from three separate extractions

Component	Concentration	
	Column method	Batch method
Total hydrocarbons (mg/kg)	13.51 $\pm$ 0.30 (n = 6)	11.03 $\pm$ 2.33 (n = 12)
<b>Aromatics (wt%)</b>		
Benzene	15.82 $\pm$ 0.67	22.24 $\pm$ 5.14
Toluene	36.21 $\pm$ 1.64	31.94 $\pm$ 2.55
Ethylbenzene	3.64 $\pm$ 0.16	4.99 $\pm$ 0.53
<i>m</i> + <i>p</i> Xylene	5.38 $\pm$ 0.24	7.69 $\pm$ 0.92
<i>o</i> -Xylene	3.31 $\pm$ 0.16	4.80 $\pm$ 0.61
Isopropylbenzene	0.37 $\pm$ 0.01	0.65 $\pm$ 0.18
Propylbenzene	0.73 $\pm$ 0.03	1.16 $\pm$ 0.25
1-Ethyl-3-methylbenzene	1.18 $\pm$ 0.06	2.22 $\pm$ 0.70
1-Ethyl-4-methylbenzene	0.44 $\pm$ 0.03	0.40 $\pm$ 0.29
1,3,5-Trimethylbenzene	0.17 $\pm$ 0.01	0.27 $\pm$ 0.05
1-Ethyl-2-methylbenzene	0.60 $\pm$ 0.03	0.94 $\pm$ 0.15
1,2,4-Trimethylbenzene	0.72 $\pm$ 0.04	1.13 $\pm$ 0.18
1,2,3-Trimethylbenzene	0.60 $\pm$ 0.04	1.00 $\pm$ 0.21
Tetramethylbenzenes	0.09 $\pm$ 0.00	0.15 $\pm$ 0.02
C <sub>4</sub> -benzenes	0.07 $\pm$ 0.03	2.80 $\pm$ 1.41
Naphthalene	0.88 $\pm$ 0.07	0.94 $\pm$ 0.67
C <sub>13</sub> Alkane + 2-Methylnaphthalene	0.55 $\pm$ 0.03	0.64 $\pm$ 0.22
1-Methylnaphthalene	0.45 $\pm$ 0.01	0.56 $\pm$ 0.29
1,1'-Biphenyl	0.02 $\pm$ 0.00	0.03 $\pm$ 0.02
C <sub>14</sub> Alkane + Ethylnaphthalene	0.12 $\pm$ 0.01	0.05 $\pm$ 0.04
Dimethylnaphthalenes	0.32 $\pm$ 0.05	0.54 $\pm$ 0.26
C <sub>15</sub> Alkane + Propylnaphthalene	0.13 $\pm$ 0.07	0.00 $\pm$ 0.00
C <sub>3</sub> -Naphthalenes	0.12 $\pm$ 0.07	0.28 $\pm$ 0.07
Total aromatics	71.92 $\pm$ 3.46	85.42 $\pm$ 14.76
<b>Alkanes (wt%)</b>		
Cyclohexane	11.05 $\pm$ 0.65	4.88 $\pm$ 3.71
2-Methylhexane	0.63 $\pm$ 0.04	0.48 $\pm$ 0.47
Isooctane	1.35 $\pm$ 0.13	1.25 $\pm$ 0.50
<i>n</i> -Heptane	2.01 $\pm$ 0.08	0.38 $\pm$ 0.05
Methylcyclohexane	4.41 $\pm$ 0.09	2.33 $\pm$ 0.34
Dimethylcyclohexanes	1.00 $\pm$ 0.07	0.91 $\pm$ 0.19
<i>n</i> -Octane	0.62 $\pm$ 0.10	0.27 $\pm$ 0.07
Ethylcyclohexane	0.27 $\pm$ 0.02	0.23 $\pm$ 0.06
<i>n</i> -Nonane	0.06 $\pm$ 0.01	0.02 $\pm$ 0.01
<i>n</i> -Decane	0.20 $\pm$ 0.02	0.17 $\pm$ 0.05
<i>n</i> -Hendecane	0.11 $\pm$ 0.03	0.14 $\pm$ 0.03
<i>n</i> -Dodecane	0.02 $\pm$ 0.00	0.04 $\pm$ 0.03
Total Alkanes <sup>a</sup>	21.73 $\pm$ 1.24	11.10 $\pm$ 5.51
<b>Unknown (wt%)</b>	5.12	3.48

<sup>a</sup>Except alkanes of C<sub>13</sub> upward

Figure 3 shows the partitioning equilibrium between oil and water attained at different reciprocation rates for individual hydrocarbons. Benzene is the most soluble component and the solubility of the five compounds shown in Figure 3 decreases in the following order: benzene, toluene, *m*+*p*-xylene, 1-ethyl-3-methylbenzene, and naphthalene (Clark 1977). Due to the low solubility of naphthalene and 1-ethyl-3-methylbenzene in seawater, partitioning equilibrium is rapidly attained even at low reciprocation speeds (Figure 3). Toluene showed the largest change in concentration in seawater with increases in reciprocation speeds, although its solubility was three times less than that of benzene. There is much more toluene than benzene present in crude oil, and the combination of solubility in water and amount in crude oil results in a higher concentration of toluene

present in the WSF. The increase in reciprocation speeds has a direct effect on the contacting area between the two phases. The higher the contacting area, the faster the mass transfer. Figure 3 also shows that reciprocation speeds between 130 and 220 strokes/min were more effective for the extraction of low boiling aromatics than other hydrocarbons. At reciprocation speeds above 220 strokes/min, this benefit diminished. The fine oil droplets produced under higher reciprocation speeds caused serious problems in the separation of these droplets from seawater and larger amounts of crude oil were still present in the water phase even after five h of settlement. Figure 4b is a GLC chromatogram of the water soluble fraction prepared at a reciprocation speed of 260 strokes/min analyzed after 5 h of settlement at 5°C. It still somewhat resembles the parent crude oil



**Fig. 4.** (a) GLC chromatogram of Flotta North Sea crude oil; (b) GLC chromatogram of water-soluble fraction extracted from the same crude oil by reciprocating plate extraction column under conditions of an excessive reciprocation speed (260 strokes/min) at a flow rate of seawater of 220 ml/min and a flow rate of crude oil of 2.9 ml/min; settling time, 5 h at 5°C

(Figure 4a) in respect to *n*-alkanes (compare Figure 5 of a superior WSF also prepared with Karr column).

### Practical Applications

It is difficult to compare the experimental results reported for bioassay or exposure studies because of different oils and methods used in the preparation of a WSF, and consequent variations in the concentration and composition of a WSF from batch to batch. It was clear that the major variation is related to the more volatile components, *i.e.*, benzene and toluene. There are two types of biological effects of the WSF on marine organisms, namely acute and chronic; the former is caused primarily by the low boiling aromatics, whereas the latter might be caused by all fractions, but the most important substances are probably still those with relatively low volatility. It is quite obvious that a preparation of a WSF with a reproducible high amount of lower boiling aromatics is very important for the exposure or bioassay experiments.

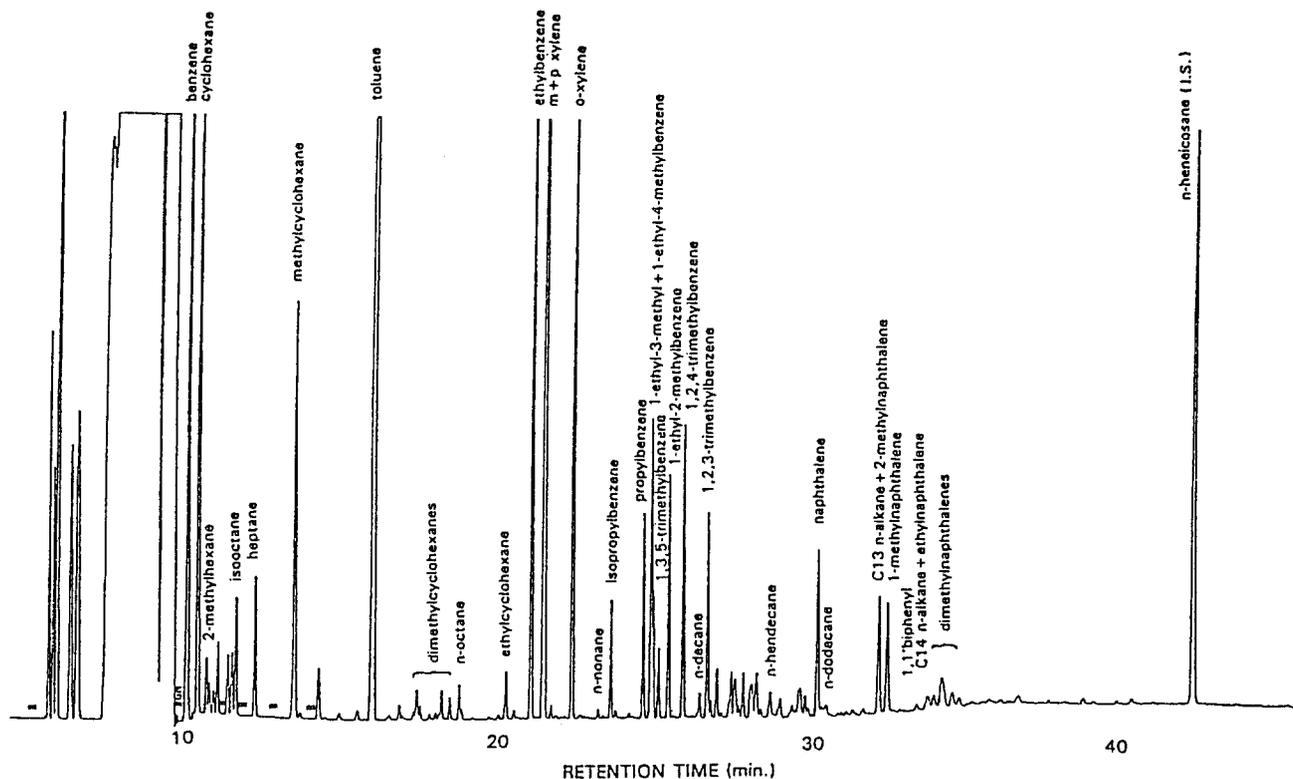
Another recurring difficulty has been the effect of vapor losses from the WSF solution during exposure or bioassay experiments, resulting in exposure to decreasing concentrations of toxicants. Anderson *et al.* (1974) found that gentle aeration of the oil-in-water dispersions resulted in a loss of 80–90% of the aqueous hydrocarbons in 24 h. Craddock (1977) recommended that additional aeration should not be used with volatile toxicants, but suggested that if the dissolved oxygen levels are below saturation, aeration may be used. To solve these problems, a fresh, reproducible stock WSF solution should be con-

tinuously added to the exposure tanks. When diluted with fresh seawater, it can bring enough oxygen to support the experimental organisms and avoid stress. In contrast to the large (70 L) WSF storage reservoirs from our batch operations (Heras *et al.* 1992), a number of 4-L settling bottles were used for the collection from the column, settling (2 h), and continuous supplying of WSF to our fish exposure tanks. Only 30 min to 2 h were needed to empty one bottle of stock WSF solution. During this short time, the composition was stable. Extraction of crude oil using a reciprocating countercurrent column could provide an ideal way to meet all requirements of continuous preparation of WSF if a continuous centrifuge step was also provided for fast removal of the fine droplets from the WSF.

The efficiency of the extraction of WSF by the reciprocating plate column depends on the flow rate of seawater, ratio of seawater to crude oil, and stroke amplitude, but particularly on the reciprocation speed as also reported by Lo and Karr (1972). Both high and low reciprocation speeds are not suitable due to the incomplete extraction of crude oil, high variations in the WSF concentration, and the formation of emulsions. Irrespective of different column models, the most suitable speed would be the point at which the crude oil is just completely dispersed into droplets, and no ascent of the crude oil along the column wall or reciprocating rod is observed. If the ratio of water to crude oil is to be further increased, *i.e.*, by decreasing the flow rate of crude oil or by increasing the flow rate of seawater, it would also be expected that the WSF solution would present the same composition and no large difference in the concentration would be observed. However, an increase in flow rate of seawater increased the linear speed of water inside of the column which resulted in more fine droplets of crude oil leaving the column with the seawater. Physical inclusion of crude oil in water could also be observed at high reciprocation speeds.

Oil can become associated with an aqueous phase in a variety of different ways, such as an emulsion, a dispersion (Peake and Hodgson 1966), or dissolved in water. Since some of the hydrocarbons in the water phase were not present in a truly dissolved form, the hydrocarbon composition in these stock solutions closely resembled that of the parent oil. This phenomenon was also observed in the WSF solution prepared by batch extraction methods with violent mixing instead of gentle stirring (Boylan *et al.* 1971; Gordon *et al.* 1973; Anderson *et al.* 1974). Shaw (1977) pointed out that unless the settling time was quite long (on the order of weeks or months), the stirring of crude oil and seawater would result in a non-equilibrium, non-steady system containing hydrocarbons associated with water in various ways. However, under the optimized countercurrent extraction conditions (170 strokes/min), most of the crude oil was disengaged from the water phase after only 2 h of settlement.

Siron *et al.* (1987) analyzed both total hydrocarbons and non-hydrocarbon components dissolved in seawater, and found that very polar oil compounds were present in the resulting WSF of crude oil. They observed that the solubles included a strong unresolved envelope of a complex mixture of less-volatile hydrocarbons that appeared in the GLC chromatogram after the more-volatile hydrocarbons. In the WSF prepared by the column extraction method only a very small envelope of late-eluting materials was found on the GLC chromatograms of the extracts from the cleared stock solution; it became larger as more crude oil remained in the water phase. The envelope of such materials could be removed through treatment of the aqueous extract on active silica gel (Boylan and Tripp 1971) and was



**Fig. 5.** GLC chromatogram of water-soluble fraction extracted by reciprocating plate countercurrent column under ideal conditions of reciprocation speed (170 strokes/min) at a flow rate of seawater of 220 ml/min and a flow rate of crude oil of 2.9 ml/min; settling time, 5 h at 5°C

due mostly to polar aromatic materials. These materials are presumably a function of the hydrocarbon mixture used and are not associated with the particular method of preparation of the WSF.

## Conclusions

The reciprocating plate extraction column for the production of stock WSF solutions provided very stable and reproducible hydrocarbon characteristics. The equilibrium rates of extraction of different hydrocarbons were inversely related to their solubilities in the seawater. Higher proportions of low-boiling aromatics were transferred to the water-soluble fraction, an important consideration for tainting or toxicity tests of the WSF of crude petroleum or petroleum products. Compared to batch extraction methods more *n*-alkanes were found in the WSF from the column.

The reciprocating plate countercurrent column is in one sense a duplication of surface mixing in oil spill situations. It is capable of semicontinuously supplying fresh WSF stock solutions which are especially suitable for flow-through experiments of long term exposure or bioassay where the requirement is to continuously provide a metered input of WSF with low fluctuations in composition and concentration during the experiments.

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