FOREWORD

Marine contamination by petroleum, whether by natural seepage or by spills from ships at sea, by accidents in harbour or at offshore installations or by atmospheric or terrigenous input is by no means a new or rare phenomenon. In recent years however, the problems have been highlighted not only by the increased utilisation and marine transport of oil but also by a number of spectacular accidents which have raised questions about possible effects on the ecosystem. A number of detailed studies have been carried out in an attempt to answer these questions. The demands for such knowledge have been further increased by the various questions raised as a result of expansion of offshore exploration and exploitation for oil, particularly in environments hostile to these operations, in regions as far apart as the northern North Sea and the coast of Alaska.

Consequently, diverse aspects of the problem are being studied in several parts of the world by chemists and biologists who are often asking the same questions but using different approaches and sometimes producing conflicting views. Against this background, it seemed timely therefore to bring together a group of scientists from university, industry and government, actively engaged in such work, to examine and discuss common problems relevant to petroleum hydrocarbon contamination of the marine ecosystem and so a Workshop was sponsored by the International Council for the Exploration of the Sea, and held in Scotland at Aberdeen in September 1975.

The Workshop considered methodology, occurrence and fate in the environment, and effects on the ecosystem of petroleum hydrocarbons in the sea. Most of the papers presented and updated where necessary, are brought together in the present volume together with an edited version of the recorded discussion that followed each session. Of necessity, the reportage of the discussion is very brief although the proportion of time available for discussion compared favourably with that set aside for formal presentation of the papers. In preparing the discussion reports, the editors were assisted in particular by Dr R. Hardy, Dr R. Johnston, Mr P. R. Mackie and Dr I. C. White, and by comments from several contributors.

No attempt was made to produce specific recommendations but a study of the papers in this volume does give a clear indication of several lines of research which must be followed up before an adequate understanding can be reached of the effects of petroleum in the sea and it is evident that widespread monitoring operations will be fully effective only when the basis of our knowledge has been thus extended.

A list of participants to the workshop may be found in Appendix I.

A. D. McIntyre
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Rapp. P.-v. Réun. Cons. int. Explor. Mer, 171: 101–106. 1977.

PHOTODEGRADATION OF HYDROCARBON SURFACE FILMS

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Photodegradation experiments on crude oil surface films were carried out on natural sea water in an artificial marine system. The compositional changes in the surface film and the organic materials in the water below were investigated. The degradation products were isolated and analyzed. They were found to be primarily aromatic and aliphatic acids, and to a lesser extent alcohols, aldehydes and ketones with the same number of carbon atoms as the original hydrocarbons. A possible reaction scheme was developed based on the amounts and structures of these decomposition products, which were also used together with estimated rates of surface film photochemical decomposition, to suggest possible effects on the marine environment.

INTRODUCTION

The input of large amounts of petroleum hydrocarbons to the marine environment due to oil spills, bilge pumping, atmospheric outfall, waste water input etc., is a very common problem in marine pollution.

A considerable fraction enters the sea by means of floating surface films, where they are subject to physical processes as well as chemical and biological degradation. Some crude oil components have known toxic effects on organisms and there are probably other harmful effects of crude oil such as the blocking of chemical "communication systems" i.e. pheromone systems.

The chemical decomposition might add another group of toxic components, and influence the physical dispersion of oil films. Amounts and types of photochemical degradation products suggest a reaction scheme of photodecomposition and give additional information on the natural fate of crude oil surface films.

The results given should be regarded as preliminary information from continuing work.

METHODS

All experiments were carried out on 25 litres sea water in an artificial marine system (Fig. 69). The sea water had been filtered through Amberlite XAD-2 to reduce non-polar organic material to a negligible amount. Surface films of 0·4 mm thickness were produced on the 50×50 cm water surface by spreading 90 ml of a crude oil fraction, obtained from a Lybian crude "Es Sider", having a boiling range up to 310°C, i.e. the maximum length of straight chain hydrocarbons was 19 carbon atoms. The water was sterilized by 2 g of potassium cyanide and controlled at 26°C by a water cooling system. In a preliminary experiment the mercury lamp of 400 W (over the total spectral range according to the manufacturers specification) was restricted to wavelengths of a minimum of 300 nm, and in later experiments down to 200 nm. Samples taken from the surface and the water below were investigated by gas chromatography and infrared spectrography (ATR-Method, Harrick, 1967).

After 19 days of irradiation a 3 litre water sample was taken and extracted with ether, acidified, and

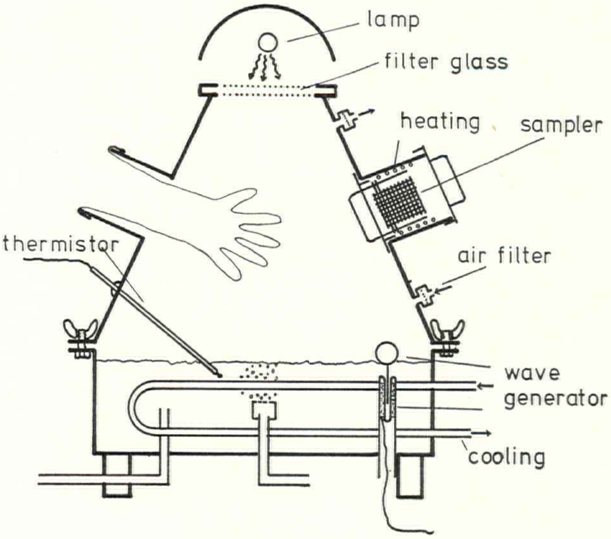


Figure 69. Artified marine system.

Table 28. Ratios of carbonyl IR-absorption. GC-ratios. Hydrocarbon decrease

Hrs of irradiation	Surface film IR[1] CO 1700 / $CH_2$2890	Surface film Gaschr.[2]			Surface film Hydrocar.[3] decrease to		Water IR[1] CO 1700 / $CH_2$1460
		% pr/C_{17}	% ph/C_{18}	% iso/C_{14}	%n-C_9	n-C_8	
0 (oil fr.)	0	50·5	36·2	43·0	100	100	0
4	< 1	50·5	34·5	43·5	97	95	< 1
53	5	50·0	33·0	41·5	66	39	51
126	20	49·4	32·7	39·5	62	32	59
170	25	47·9	31·8	37·5	56	22	82
295	28	46·8	30·9	36·0	43	8	136
462	31	45·4	26·7	30·3	39	< 1	178

[1] Ratio of IR-absorption (cm^{-1})

[2] Ratio of GC-signal: pristane/n-C_{17}, phytane/n-C_{18}, and a ^{14}C isomer/n-C_{14}.

[3] Decrease of GC-signals.

further extracted. The organics in the combined ether extracts were separated into different compound classes, by extracting with water at different pH values.

Amounts and characterisation of the extracts:

E 1: extracted with water at pH 1
less than 10 mg.

E 2: extracted with water at pH 8
410 mg, "strong" acids.

E 3: extracted with water at pH 12
110 mg, "weak" acids.

E 4: 460 mg, hydrocarbons (110 mg), alcohols (250 mg), ketones (200 mg).

The IR-spectra of E 4 showed a strong —OH signal and strong —CO signal. Tests with Fehlings-reagent showed the absence of aldehydes.

The acids, in E 2 and E 3, were converted into their

Table 29. Mass spectrometric data

No.	%	m/e mol. ion	Extract E2 after esterification: 39 GC-peaks > 1% of maximum peak 100 %											Identified – acid methylester
1	68	88	74	43	29	57	59							n-propanoic-
2	31	130	74	43	27	29	41	87	59	88	99	101	115	methyl-pentanoic-
3	72	130	74	43	29	87	59	99	71					n-hexanoic-
4	18	144	74	29	41	43	87	55	59	88	113	101	129	2-methyl-hexanoic-
5	82	144	74	41	43	87	29	55	59	101	113			n-heptanoic-
6	50	158	74	29	87	41	43	55	57	127	101			n-octanoic-
7	11	172	74	43	41	87	55	57	29	69	141			n-nonanoic-
8	100	136	105	77	51	136	50	106						benzoic-
9	16	150	43	119	91	44	150							2-phenyl-acetic-
10	78	150	119	91	150	65	120							m-methyl-benzoic-
11	64	152	120	92	152	39	121	65	63	64	93			salicylic dimethyl-benzoic-
		164	133	164	105	77	134							salicylic dimethyl-benzoic-
12	70	164	133	164	105	77	134							salicylic methyl-salicylic-
		166	134	–										salicylic-methyl-salicylic-
13	91	166	134	106	166	39	135							
		164	mixture											
		178												
		192												
14	17	178	147	146	178	91	119	118	39	77	51	163		trimethyl-benzoic-
15	22	178	147	146	178	119	91	118	39	77				trimethyl-benzoic- (?)
		180												
16	16	194	163	135	194	76	50	75	164					dimethyl-isophthalate
17	12	192	177	43	45	145	161	56	91	59	99	27	29	*tert.* butyl-benzoic-
18	46	194	163	194	77	164	135							dimethyl-terephthalate

The dominant compound classes corresponding to these esters are:
aliphatic carboxylic acids C-numbers < 10; benzoic acids; salicylic acids; phthalic acids.

Table 30. Mass spectrometric data

No.	%	m/e mol. ion	Extract E3 after esterification: 42 GC-peaks > 1% of maximum peak 100%											Identified – acid-methylester
1	13	144	74	43	87	41	88	55	29	57	59	101		2-methyl-hexanoic-
2	27	172	88	41	43	55	29	57	101	74	87	59	69	2.4-dimethyl-heptanoic-
3	77	158	74	87	43	41	29	27	55	57	59			*n*-octanoic-
4	45	186	74	88	41	87	55	43	29	57	69	101	27	2.4-dimethyl-octanoic-
5	100	172	74	87	41	43	55	29	57	59	88	69		*n*-nonanoic-
6	43	186	88	74	41	55	43	29	57	69	87	101	27	2-methyl-nonanoic-
7	54	186	74	87	41	43	55	29	57	69	59	88	75	*n*-decanoic-
8	27	200	88	41	74	43	29	69	55	87	57	101		2-methyl-decanoic-
9	72	198	44	75	31	45	46	27	43	41	74	87	88	not ident.
10	10	152	43	41	99	55	73	29	69	45	27	102	152	not ident.
11	18	242	85	41	43	74	87	55	29	56	57	69	27	7-methyl-tridecanoic-
12	61	270	74	87	43	41	55	57	69	59	143			*n*-hexadecanoic-
13	34	284	41	43	88	55	29	74	69	57	101	87		2-methyl-heptadecanoic-
14	25	298	74	87	43	41	55	29	57	69	147	83		*n*-octadecanoic-

15 to 22 are mixed mass spectra of aliphatic and probably unsaturated and alicyclic carboxylic acids which cannot be identified because of overlapping aromatic signals.

The dominant compound classes:
aliphatic esters; some unsaturated and alicyclic acids; in higher molecular regions aromatic acids similar to Extract 2.

methylesters by treatment of the ether solution with excess diazomethane at room temperature. These were analyzed by combined gas chromatography and mass spectrometry.

The peak intensities for each total ion current recording (per cent of the maximum peak), and mass spectrometric identifications are given in Table 29 and Table 30.

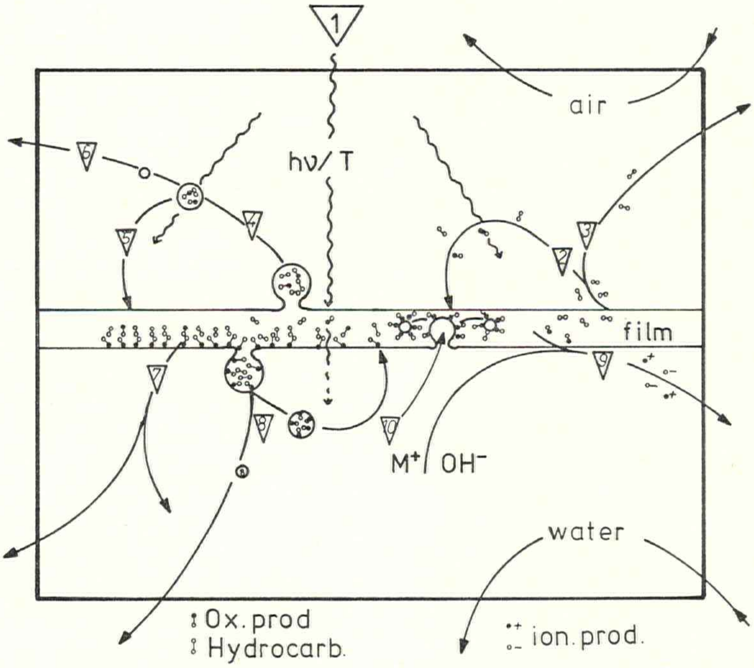


Figure 70. Schematic diagram of physical and chemical processes within the system. 1, Incident light energy and associated temperature increase; 2, Recycled evaporated material; 3, Lost evaporated material; 4, Aerosol formation; 5, Recycled aerosol; 6, Lost aerosol material; 7, Dissolution of soluble film material (+ losses); 8, Formation of oil-water emulsions (partly recycled); 9, Transfer of film material into soluble charged products; 10, Formation of water-in-oil emulsions.

RESULTS

The processes involved are summarised in Figure 70.

a) Physical

The oil fraction did not form a uniform surface film, which is a common effect observed with mixtures of hydrocarbons containing both low and high boiling components, e.g. crude oil fractions (Garrett, 1972).

The surface was covered with a film of low boiling hydrocarbons, containing lenses of the higher boiling compounds, nearly ten times as thick. The viscosity of the film increased with the irradiation, until after three days solid fragments were visible, the low boiling fraction simultaneously decreasing.

After nineteen days *n*-octane was reduced to less than 1 % of the original amount. Examples of the decrease in hydrocarbons are listed in Table 28.

Within nineteen days of irradiation, the initial, light yellow transparent film gradually changed to an opaque red-brown and then grey-brown layer, some fragments of which clung to the tank wall at the water-air interface, having the appearance of tar-balls.

The underlying sea water changed from a clear to colloidal solution showing a Tyndall-effect.

b) Chemical

The reaction products extracted from the sea water were found to be carboxylic acids (20 % aromatic, 28 % aliphatic), alcohols (23 %) and ketones (18 % aliphatic only).

To enable the effect of photo-oxidation to be estimated, the intensities of the IR-spectroscopic carbonyl absorption near 1700 cm^{-1} were compared with that of the CH_2-bond vibration 2890 cm^{-1} (water samples) and the CH_2-molecular vibration at 1460 cm^{-1} (surface samples) (Figs. 71, 72 and 73, Table 28). Gas chromatograms of surface samples (Fig. 74) show a change of intensity ratios for selected branched/normal alkanes, which are quoted for pristane/*n*-heptadecane, phytane/*n*-octadecane and a corresponding isomer/*n*-tetradecane (Table 28).

From the preliminary experiment, photo-oxidation of hydrocarbon (crude oil) surface films is very low with radiation greater than 300 nm, but increases by at least two orders of magnitude if the spectral range is widened to 200 nm.

The UV-spectrum of the crude oil fraction shows an increasing absorption starting at 260 nm due to the presence of aromatics and sulphur compounds.

CONCLUSIONS

At temperatures below 30°C no chemical reaction involving oxygen and hydrocarbons is possible in the dark. The initiating radiation which could start photoreaction i.e. radical oxidation, must be in a range where absorbance by the molecules occurs. As the absorbance of the crude oil fraction starts at 260 nm (increasing to lower wavelengths) it seems reasonable that nearly no oxidation products are to be found when irradiated with light limited to 300 nm.

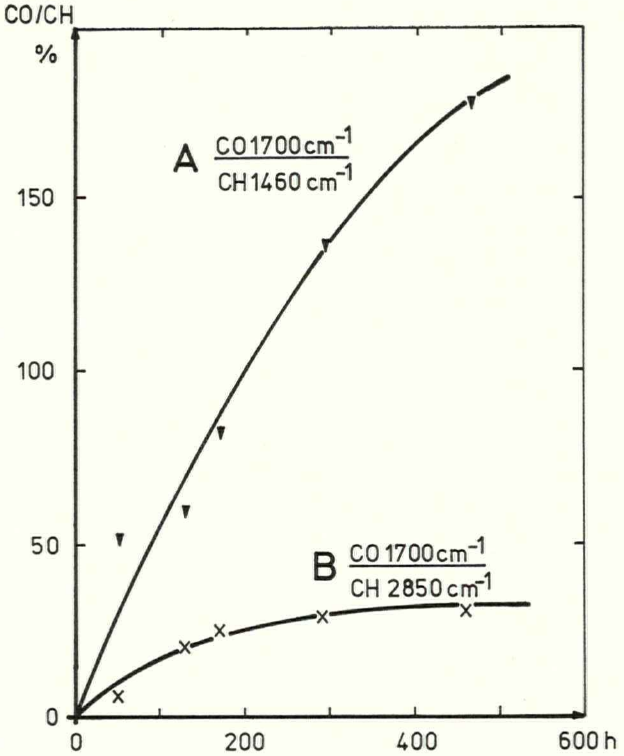


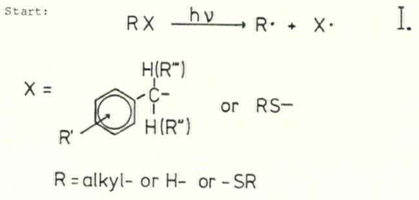
Figure 71. Ratios of CO/CH from IR-spectra.

From the amount of aromatics in the original hydrocarbon film and their amount in the degradation products (3 % and 20 %, respectively) the preferential decomposition of the aromatics is obvious. This indicates the importance of aromatics as initiators of photo-oxidation.

Thus, compound classes are present which could very likely start the photoreaction by absorbing light of about 250 nm and forming reactive radicals:

a) alkyl-aromatic compounds,

b) sulphur containing compounds of the type R-S-R or R-S-H and R-S-S-R.



The radicals R· and X· are able to abstract a hydrogen atom from a tertiary carbon atom. The change in intensity ratios of branched/*n*-hydrocarbons (Fig. 74, Table 28) suggests a higher decomposition rate of the branched hydrocarbons. It is interesting to note that the relative proportion of *n*-alkanes does not increase in a significant manner, which implies their degradation (Fig. 74, Table 28).

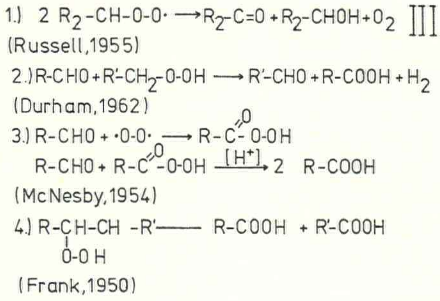
To initiate the photo-oxidation of *n*-alkanes i.e. formation of a secondary C-radical, a more reactive radical is required. This can be obtained by reaction of the initially formed radical R· or X· and the oxygen molecule which is a di-radical, yielding peroxi-radicals.

Further reaction with a radical of type R· or X· leads to peroxides. Light of the 250 nm region is able to fragment peroxides into two oxy-radicals. The abstraction of a hydrogen atom from an alkane changes the oxy-radical to an alcohol, this reaction is exothermic because of the high bonding energy of the —O—H bonding.

$$\begin{aligned}
&R\cdot + HR' \longrightarrow RH + R'\cdot \quad , R' = t\text{-alkyl-}\\
&R'\cdot + \cdot O\text{-}O\cdot \longrightarrow R'\text{-}O\text{-}O\cdot\\
&R'\text{-}O\text{-}O\cdot + HR' \longrightarrow R'\text{-}O\text{-}OH + R'\cdot \qquad\qquad \text{II.}\\
&\qquad\qquad + R\cdot \longrightarrow R'\text{-}O\text{-}O\text{-}R\\
&\left.\begin{aligned}&R'\text{-}O\text{-}O\text{-}R \xrightarrow{h\nu} R'\text{-}O\cdot + R\text{-}O\cdot\\ &2\ R'\text{-}O\text{-}O\cdot \rightarrow [\quad] \longrightarrow 2R'\text{-}O\cdot + O_2\end{aligned}\right\}\text{(Pryor,1974)}\\
&R'\text{-}O\cdot + RH \longrightarrow R'\text{-}OH + R\cdot
\end{aligned}$$

The formation of *t*-butanol from a *t*-butoxy-radical yields 110 kcal/mole, the reaction still being exothermic even if the hydrogen is extracted from a primary C-atom (98—102 kcal/mole).

A number of well known reaction mechanisms convert or fragment the intermediate peroxides or hydroperoxides to carboxylic acids, aldehydes, ketones and alcohols. Aldehydes and alcohols can easily be oxidized to carboxylic acids by reaction with peroxides (except *t*-alcohols which are inert). The absence of aldehydes in the oxidation products indicates the occurrence of these reactions.



III.

$$\begin{aligned}
&1.)\ 2\ R_2\text{-CH-O-O}\cdot \longrightarrow R_2\text{-C=O} + R_2\text{-CHOH} + O_2\\
&\text{(Russell,1955)}\\
&2.)\ R\text{-CHO} + R'\text{-}CH_2\text{-O-OH} \longrightarrow R'\text{-CHO} + R\text{-COOH} + H_2\\
&\text{(Durham,1962)}\\
&3.)\ R\text{-CHO} + \cdot O\text{-}O\cdot \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-O-OH}\\
&\quad R\text{-CHO} + R\text{-}\overset{O}{\overset{\|}{C}}\text{-O-OH} \xrightarrow{[H^+]} 2\ \ R\text{-COOH}\\
&\text{(McNesby,1954)}\\
&4.)\ R\text{-}\underset{\text{O-OH}}{\underset{|}{C}}\text{H-CH-R'} \longrightarrow R\text{-COOH} + R'\text{-COOH}\\
&\text{(Frank,1950)}
\end{aligned}$$

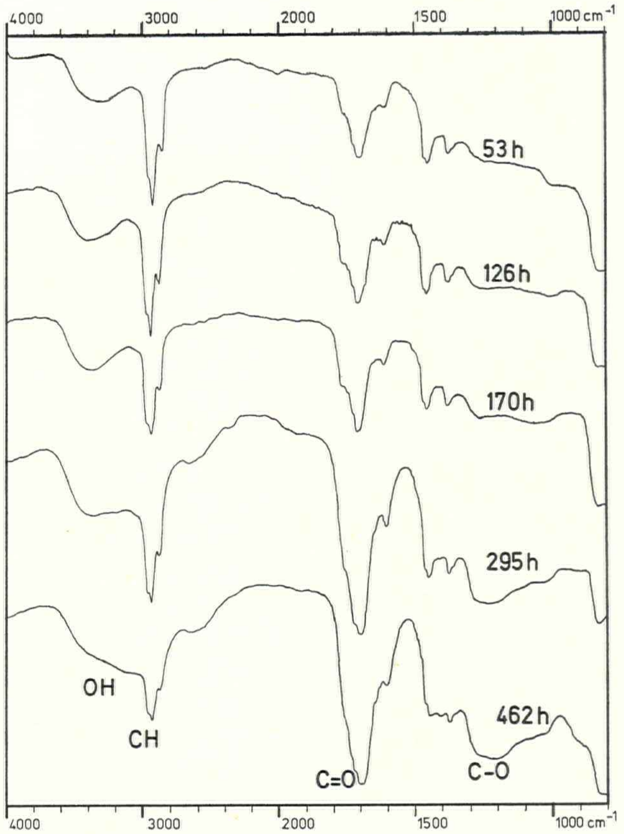


Figure 72. Time interval IR-spectra (water samples).

Carboxylic acids are surface active materials because of their hydrophilic and hydrophobic nature. As indicated by the increase of carbonyl components in the surface film, which approaches a constant value, they pass to the water phase immediately, where they are no longer subject to photo-oxidation. Additionally, a second or third oxidation of a hydrocarbon should cause a significant loss of long chain carboxylic acids in the oxidation products. However, even *n*-octadecanoic acid is present with a GC-peak intensity of 25 % of the maximum peak.

The formation of surfactants obviously affects the physical dispersion of the crude oil surface film. The hydrocarbon concentration below the surface film is some 300 µg/ml which is far above the water solubility of hydrocarbons. Additionally, the amount of water in the surface film increased to several times the weight of hydrocarbons, both effects being due to the formation of oil/water and water/oil emulsions respectively, enhanced by the formation of surfactants.

In calculating the effects of the photo-oxidation of hydrocarbon surface films in the natural environment, with respect to the experimental results, the following suggestions could be made:

The amount of decomposed materials i.e. decompo-

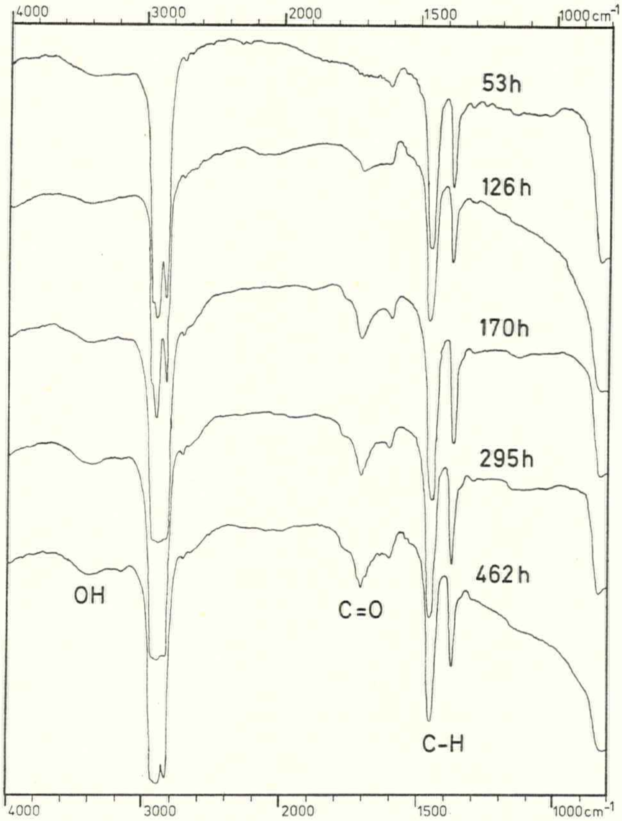


Figure 73. Time interval IR-spectra (surface samples).

sition rate (some 0·7 %/day) seems to be of less importance. The decomposition rate will depend very much on the type and composition of the crude oil film (amounts of aromatics, sulphur components etc.).

The time required for physical dispersion of a surface film will be considerably shorter in areas with high sun input i.e. more photo-oxidation compared to low sun input areas. Because of the surfactants formed, the concentration of hydrocarbons in the water below the surface film will be relatively high in "photo-active" areas, and thus the surface film dispersed within a shorter time but into a smaller water mass than in low sun input areas.

Photo-oxidation, in causing a higher aqueous hydrocarbon concentration and an additional class of possibly toxic compounds, does not seem to settle the problem of floating oil films but only introduces new problems.

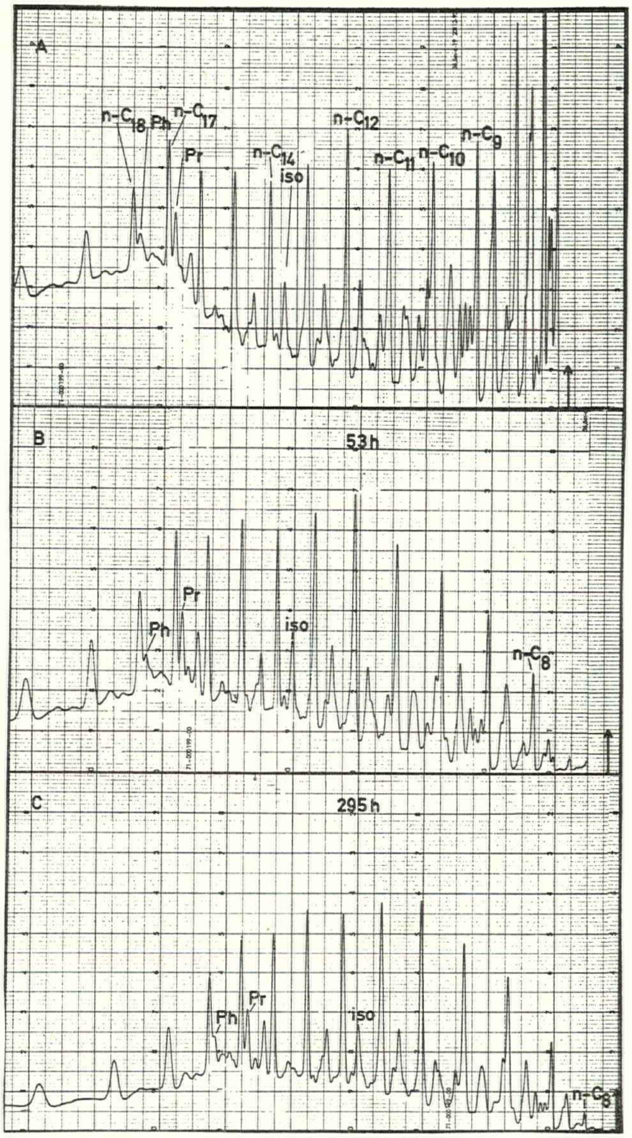


Figure 74. Gas chromatograms of surface film.

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