

International Council for
the Exploration of the Sea

C.M. 1974/E : 12
Fisheries Improvement Committee
Ref. Hydrography Committee



On Photochemical Degradation
of Surface Films of Petroleum Hydrocarbons

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SUMMARY

Surface films of a crude oil fraction were exposed to irradiation from different light sources. The physical behaviour is described. Degradation products were isolated and identified. Primarily they are composed of aliphatic and aromatic acids and to a smaller extent of alcohols and phenols. Acids were converted into their methylesters which were identified by combined gas chromatography and mass spectrometry. The amount of oxidation products in the surface film was estimated by measurement of the CO-infrared absorption in the 1700 cm^{-1} region with "Attenuated Total Reflection" (ATR) infrared spectroscopy*. Comparison between the original crude oil fraction and degradation products lead to an estimation of the decomposition rate under natural environmental conditions.

*ATR is also known as "Multiple Internal Reflection" or "Multiple Attenuated Total Reflection" (HARRICK, 1967, BAIER, 1970)

INTRODUCTION

Petroleum hydrocarbon surface films due to oil spills, bilge-pumping etc. are a very common problem in the marine environment. Hence there is an increasing need for research on surface film decomposition. Treatment of floating oil with emulsifiers does not settle the problem but shifts it to the waterbody below. Though some work has been done on the bacterial degradation of surface films, very little information is available on their chemical decomposition. Our research aims at finding out the extent and ways of chemical - especially photochemical - degradation of hydrocarbon surface films.

EXPERIMENTAL

A tank of stainless steel (Fig. 1) was filled with 25 l of sea water. The water had been filtered through Amberlite XAD-2 to remove non-polar organic material. The amount of organic material left was negligible compared with the amount of material extracted from the water samples during the experiments described below.

The water surface was covered with a surface film of 76 g crude oil fraction:

Lybian crude "Es Sider", fraction with boiling range up to 310 °C (oil A).

Oil A covered the total water surface of 50 x 50 cm forming a surface film of 0.036 μ m average film thickness.

The temperature of the water and the air just above the surface was kept at 26 °C by a water cooling system.

Two light sources were used for irradiation. Both were mercury lamps of 400 W. The spectral characteristics of

lamp 2 were very similar to natural sunlight. This is due to some Praseodym iodide in the discharge tube (Osram HQI-TS 400). The other lamp without modifying additions had a high yield of UV emission (lamp 1). The listed values refer to experiments with lamp 1.

Gas chromatographic analysis:

Varian Aerograph Series 1400, FID.

column: 2 m stainless steel 1/8" o.d., packed with 9 % Ucon
50 HP 5100 on Chromosorb W-AW DCMS 80 mesh.

temperature programmed from 40 - 200 °C at 6 °/min.

N₂ : 36 ml/min.

Combined gas chromatography and mass spectrometry:

column: 2 m stainless steel 1/8" o.d., packed with 1 % DEGS
on Chromosorb W-HP, 80 mesh.

temperature programmed from 70 - 210 °C at 10 °/min,

He : 18 ml/min.

Mass spectrometer: Atlas Varian CH-7 with two stage
Biemann-Watson separator and differential pump system.

Total ion current chromatograms permitted the precise
correlation of mass spectra with gas chromatographic peaks.

Mass spectra were obtained under the following conditions:

electron energy: 70 eV, acceleration pot. : 3000 V

beam current: 30 and 100 uA

source temperature: 250 °C

scan: 17 linear

amplifier: 1 - 10 V

filter: 3000 hz

chart speed: 10 cm/sec

Infrared spectroscopy:

Beckmann IR-33 with ATR-attachment (Harrick Sci. Corp.)
using TPMRA-germanium plates (see Fig. 3).

Samples were either taken by penetrating the surface film with the Ge-plates (Baier 1970) or the Ge-plate was covered with an ether solution of the sample. Subsequently the solvent was evaporated in a stream of nitrogen.

At definite times after the beginning of the irradiation samples were taken from the surface film and the water column below.

Surface samples were taken with a screen (5 x 5 cm, mesh size 300/cm²). The adhering oil was washed from the screen with ether. The ether solution was dried over anhydrous sodium sulfate and concentrated for GC analysis. A corresponding sample was taken directly with the Ge-plate and measured by ATR-infrared spectroscopy.

500 ml samples were taken from the water column half way between the surface and the bottom. The samples were extracted with ether, acidified and extracted again. The combined ether extracts were dried, concentrated and also measured by ATR-infrared spectroscopy.

The organic material extracted from a 3 l water sample after 462 hrs of irradiation (1072 mg) was separated into different compound classes by extracting the ether solution with water at different pH-values.

Extract E1: Extraction with water at pH 1 gave nearly no material.

Extract E2: Extraction with water at pH 8, acidifying the water extract to pH 1 with 2n HCl, extracting with ether, and evaporating the solvent after drying over anhydrous sodium sulfate gave 410 mg of organic material, containing strong acids and more water soluble compounds.

Extract E3: Extraction with water at pH 12 and subsequent treatment like E2 yielded another 113 mg containing weak acids.

E4, the neutral non-polar residue containing hydrocarbons, alcohols, etc., was 558 mg.

The two extracts E2 and E3 were treated with excessive diazomethane in ether at room temperature to convert acids into their methylesters. These were analyzed by combined gas chromatography and mass spectrometry.

RESULTS

Oil A did not form a uniform surface film. This is a common effect observed with mixtures of hydrocarbons containing low boiling and high boiling components as e.g. crude oils or crude oil fractions. This is due to different surface tensions of different hydrocarbons and of water according to the equation

$$F_o = \gamma_o - (\gamma_o + \gamma_{ow}) \quad (\text{Garrett, 1972})$$

F_o = the spreading pressure of the oil

were

γ_w = surface tension of water

γ_o = surface tension of oil

γ_{ow} = interfacial tension between oil and water.

Hydrocarbons on the water surface spread or contract depending upon F_o being positive or negative.

The surface was covered with a thin film of low boiling hydrocarbons containing lenses nearly ten times as thick which contained higher boiling components. During the continuous irradiation the viscosity of the lenses increased until they formed solid film fragments after some three days.

Simultaneously the low boiling parts decreased. After five days - even without agitation of the water and the air above - no hydrocarbons up to seven carbon atoms were found in the surface film. After nineteen days n-octane was reduced to less than 1 % and n-nonane to 39 % of the original amount.

At this time the surface film appeared to be a solid homogenous mass which broke into fragments when moved. The decrease of hydrocarbons is listed in table 1.

As criteria of degradation i.e. photooxidation the intensity of the carbonyl absorption near 1700 cm^{-1} was compared with the intensity of the CH_2 -valence vibration at 2890 cm^{-1} (water samples) and the CH_2 -molecular vibration at 1460 cm^{-1} (surface samples). The ratios are listed below (Table 1).

The different rates of decomposition of straight chain and branched hydrocarbons are calculated from the intensities of gas chromatographic signals of selected hydrocarbons. The intensity ratios of pristane/n-heptadecane, phytane/n-octadecane, and a corresponding isomer/n-tetradecane are listed in table 1.

The two extracts E2 and E3 were analyzed by gas chromatography and mass spectrometry. Identified peaks in the sequence of increasing retention times are listed below (Table 2 and 3). The intensities of gas chromatographic peaks are given in per cent of the maximum signal. These values are followed by mass spectrometric m/e values: molecular peaks and peaks in the order of decreasing intensities which were used for identification.

CONCLUSIONS

A number of experimental results permit the following coarse description of the behaviour and the degradation of hydrocarbon surface films.

The first step after the formation of surface films (oil spill etc.) is a rapid decrease of all low boiling compounds due to air circulation (wind). Even on a calm surface without strong air circulation and at water temperatures of about 25°C all materials with boiling points up to 120°C vanish rapidly, and even materials with higher boiling points show a distinct decrease after a few days.

The oil fraction used in these experiments contains about 20 % of compounds with boiling points below 100°C. No degradation products are to be expected from the lower boiling components of these 20 %, and only little from the less volatile part. The total amount of degradation products isolated after 19 days of irradiation (1072 mg/ 3 l i.e. 8 g total) represents 10 % of the initial 76 g of crude oil fraction. Taking into consideration the lost 20 % this means that approximately 13 % of the remaining crude oil fraction were decomposed. This rate of degradation is about ten times as high as the rate obtained with lamp 2, which nearly represents natural sun light (intense tropical sun). A coarse calculation shows that a 0.04 cm surface film of hydrocarbons is degraded photochemically under natural conditions at a rate of 0.07 %/ day, i.e. more than 3 years for complete decomposition.

Extract E4 - the non-polar neutral compounds, total weight 558 mg - contains about 100 mg of hydrocarbons. That means more than 30 mg hydrocarbons per litre. This is far above the solubility of hydrocarbons in water. We have to conclude the formation of emulsion, particulate hydrocarbons

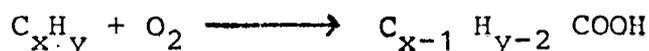
or hydrocarbons adsorbed on other particulate materials even under conditions without mechanical agitation except for thermal convection of the waterbody.

Three main crude oil components show very different decomposition rates in the sequence: aromatics, branched hydrocarbons, straight chain hydrocarbons. The total amount of degradation products contains about 20 % of aromatic material. Initially the crude oil fraction contained less than 5 %. Therefore aromatic compounds seem to be degraded preferably. The comparison of gas chromatographic signals of normal relative to branched hydrocarbons (Table 1) indicates that the latter are decomposed more readily. However, this must be proved by further experiments because the effect could be due to a higher water solubility of branched hydrocarbons.

The principle degradation products are carboxylic acids. Probable intermediate products, alcohols and aldehydes, remain in the surface film and are oxidized rapidly to acids which pass over to the water immediately. The concentration of oxidation products in the surface film does not exceed a certain value (Fig. 2).

Because of the high solubility of carboxylic acids in sea water of pH 8 no further oxidation or decarboxylation is possible. Thus, measurements of formed CO_2 to follow the degradation of emulgated crude oil (Freegarde, 1970) do not seem to be a realistic base for the estimation of natural degradation rates of hydrocarbon surface films. Comparison between the initial crude oil fraction and the identified oxidation products indicates the oxidation of only one methyl- or methylene-group. For example: The maximum chain length of compounds in the oil fraction is 19 carbon atoms. No - or nearly no - n-octadecanoic-acid should be found in case of further oxidation of the initially formed carboxylic acid. However,

n-octadecanoic-acid appears with a GC peak intensity of 25 % of the maximum peak. A very good agreement between the initial oil compounds (Smith, 1968) and oxidation products according to the equation



is found.

The fact that benzoic acid produces the maximum signal in the gas chromatogram of E2 indicates a kind of oxidation which decomposes different alkyl-benzenes to one decomposition product i.e. benzoic acid.

Whether salicylic acids and phthalic acids are formed from oxygen containing components by simple oxidation or from alkyl-benzenes by double oxidation cannot yet be answered.

The formation of salicylic acids seems to be a very interesting effect because of the bacteriostatic activity of salicylic acids, which is expected to influence further biological degradation.

Many of the photo-degradation products are surface active. These compounds may aid in the formation of oil-water emulsions as indicated by the surprisingly high concentration of hydrocarbons in the water below the surface film. Under environmental conditions, this effect may be more important to the disappearance of hydrocarbon surface films than the mere formation of water soluble degradation products.

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Table 1

hrs of irradiation	surface film					water	
	IR ¹⁺) $\frac{\text{CO } 1700}{\text{CH}_2 2890}$	gaschr. ²⁺)			hydrocar. ³⁺) decrease to		IR ¹⁺) $\frac{\text{CO } 1700}{\text{CH}_2 1460}$
		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-C₁₇, phytane/n-C₁₈, and a C₁₄ isomere/n-C₁₄

3+) Decrease of GC signals

Table 2

Extract E2 after esterification: 39 GC peaks >1 % of maximum peak

No	%	m/e	mol.ion 100 %										identified	
													- acid methylester	
1	68	88	74	43	29	57	59						n-butanoic -	
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	27	dimethyl-benzoic -	
		164	133	164	105	77	134						dimethyl-benzoic -	
12	70	164	133	164	105	77	134						methyl-salicylic -	
		166	134	-								-methyl-salicylic-		
13	91	166	134	106	166	39	135							
		164	mixture							47				
		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	27	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 3

Extract E3 after esterification: 42 GC-peaks >1 % of maximum peak

No	%	m/e	ion 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	" "
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

Fig. 1: artificial marine system

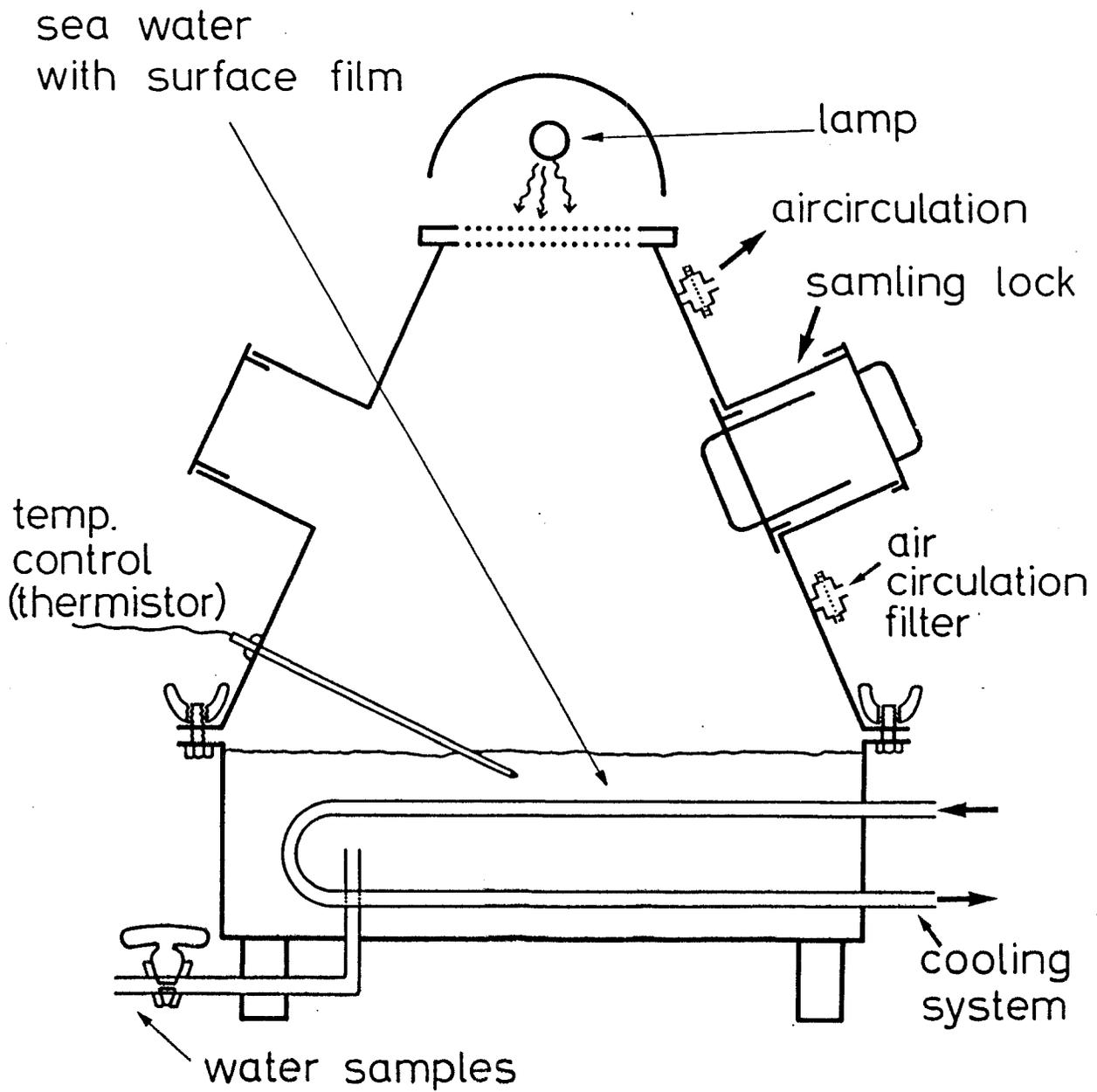
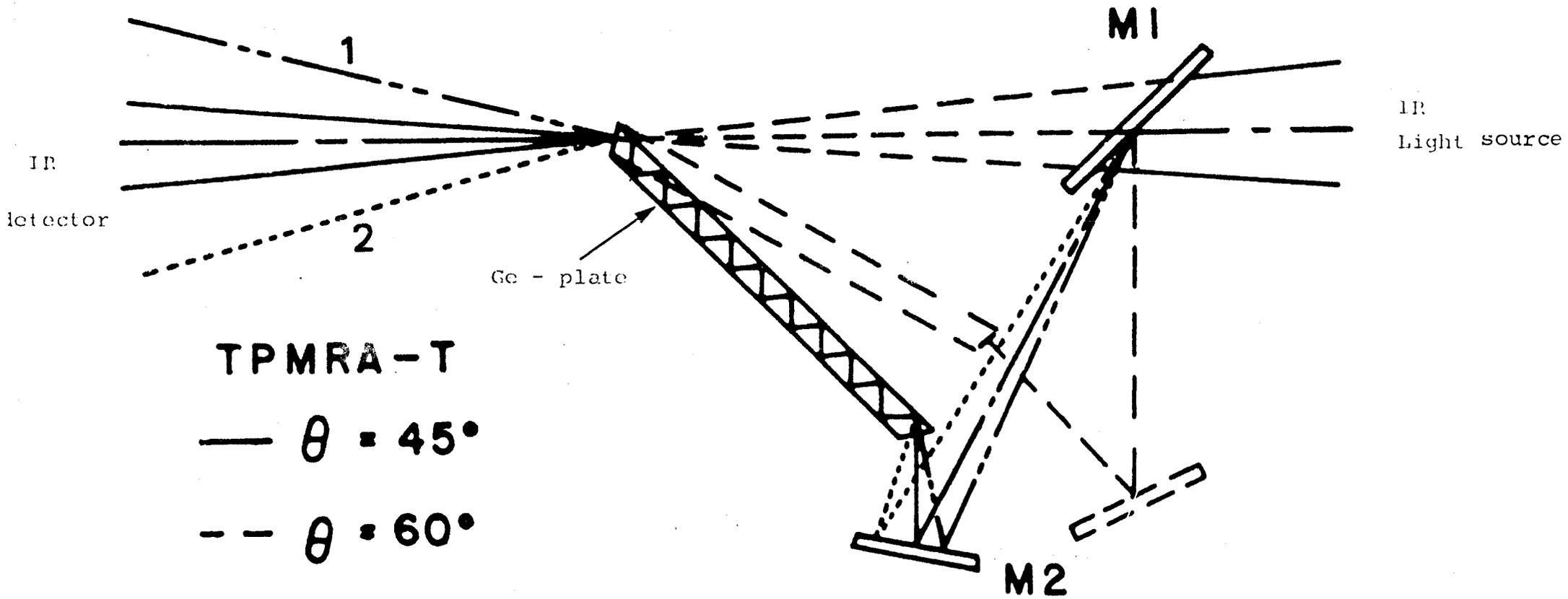


Fig. 3: ATR - attachment



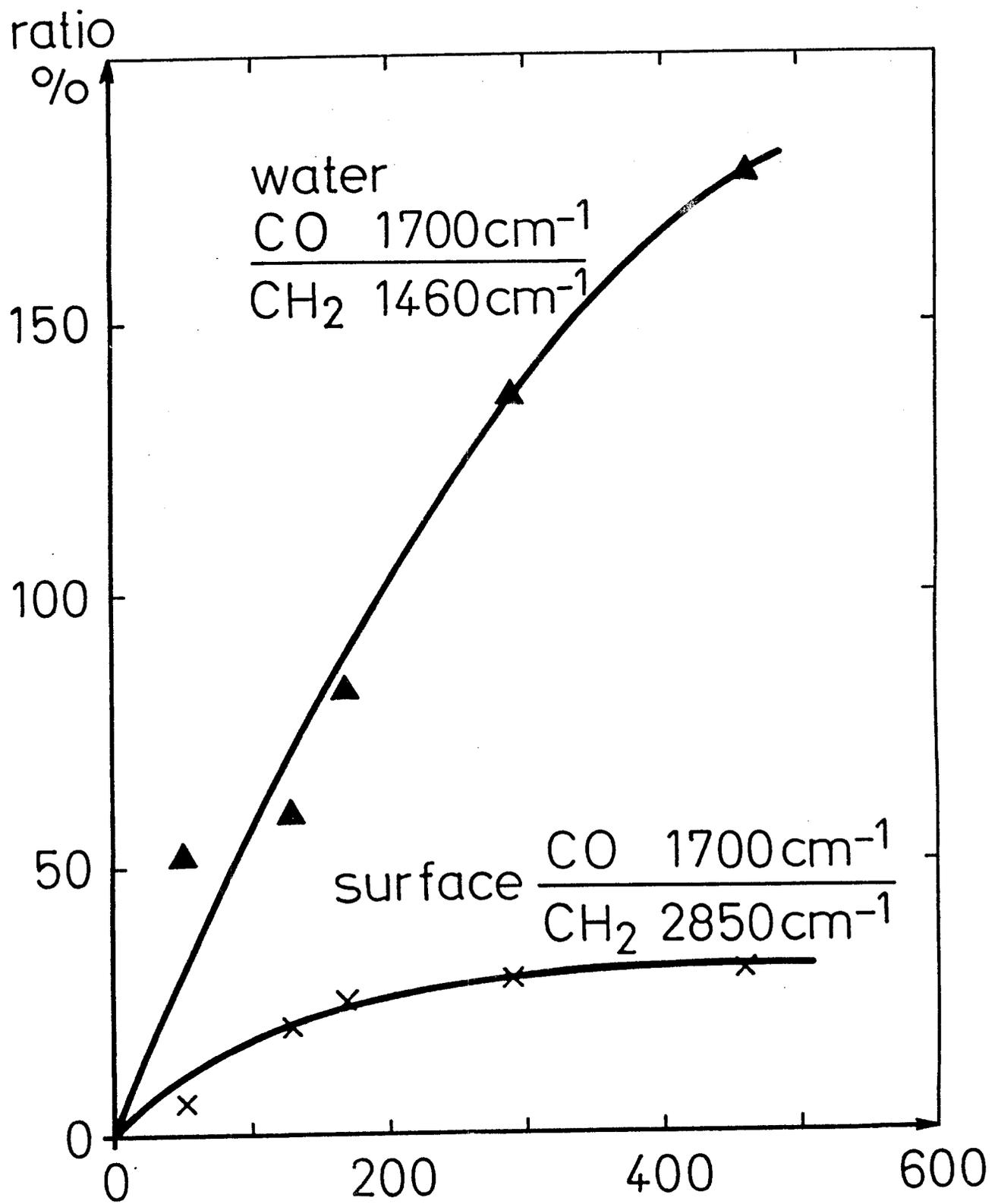


Fig.2 Increase of oxidation products given by the ratios of IR absorption of CO/CH₂

Fig. 4: ATR-spectra surface

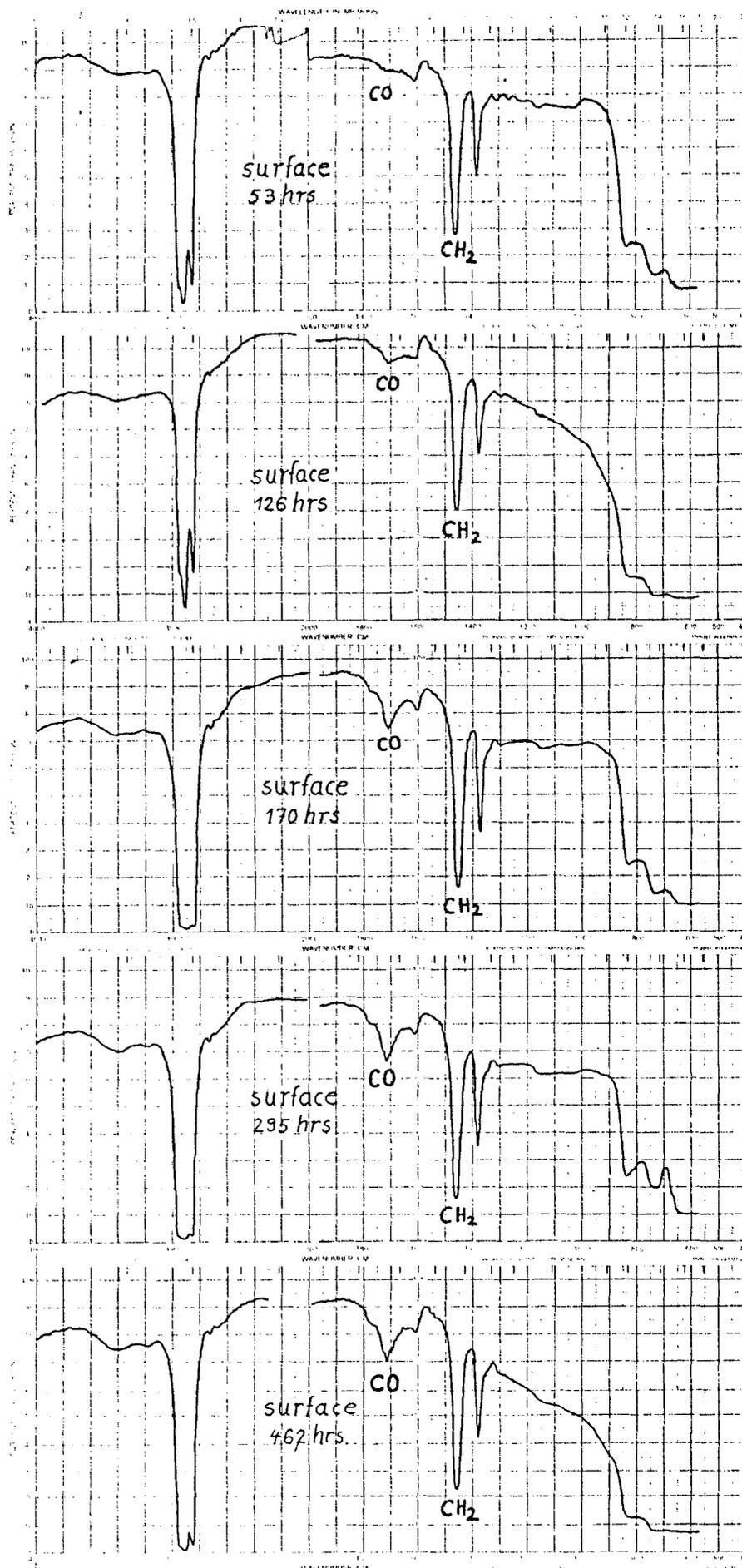


Fig. 5: ATR-spectra water samples

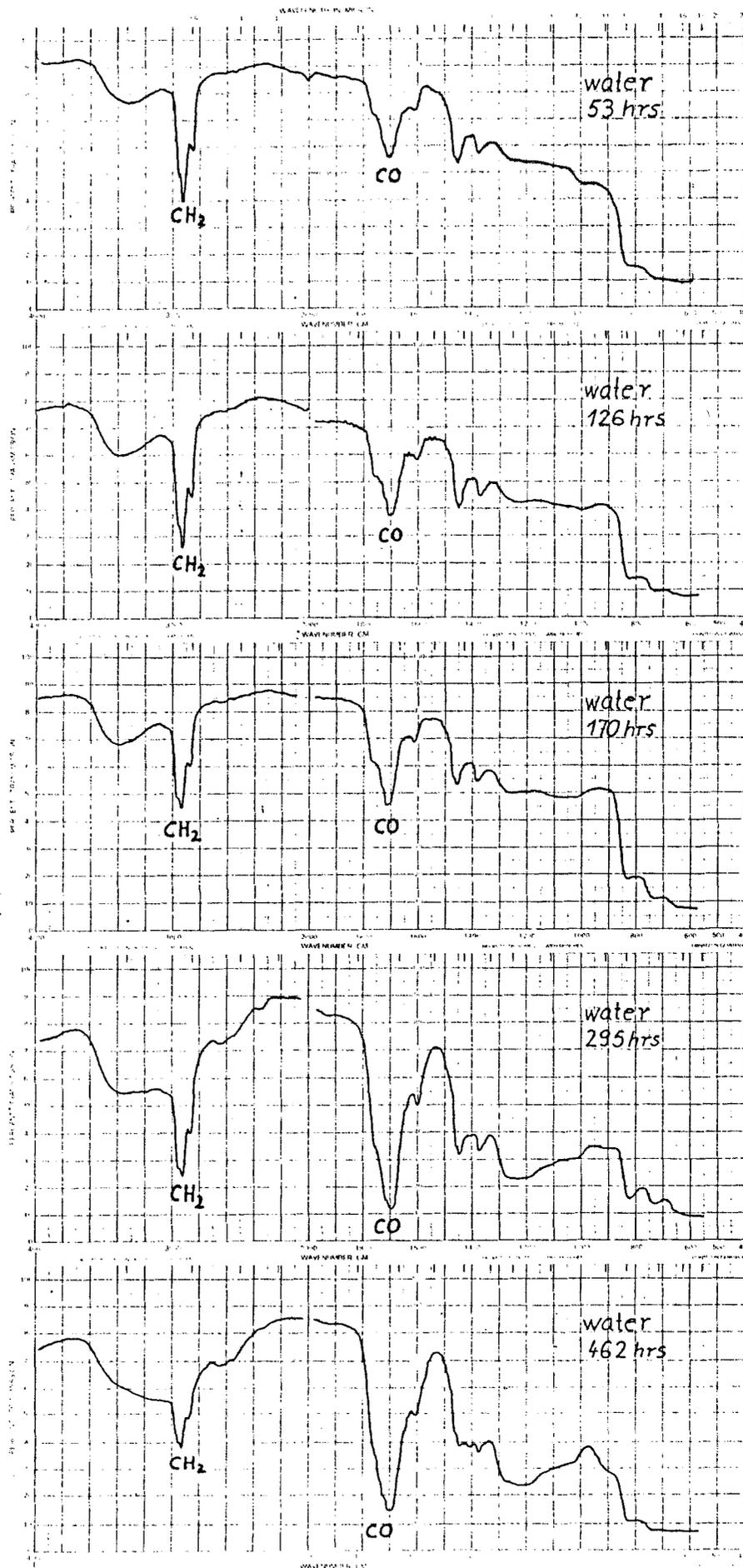


Fig. 6 Gaschromatograms of surface film

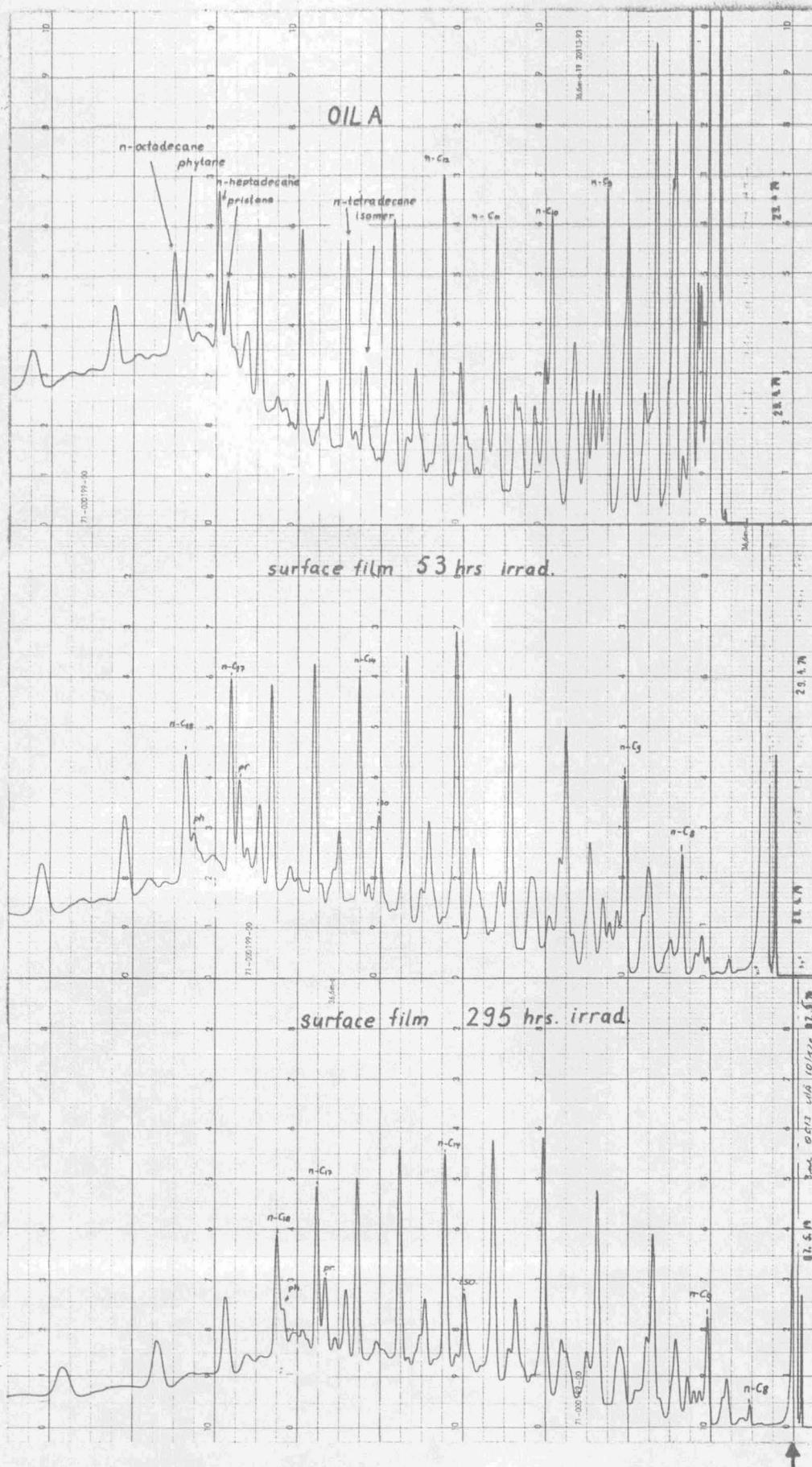


Fig. 6 Gaschromatograms of surface film

