INTER-GOVERNMENTAL MARITIME
CONSULTATIVE ORGANIZATION

MP/CONF/C.2/INF.1
16 October 1973

Original: ENGLISH

IMCO

INTERNATIONAL CONFERENCE ON
MARINE POLLUTION, 1973
Committee II

REPORT ON LOAD-ON-TOP INVESTIGATIONS

Submitted by Norway

Attached hereto for information are the following documents which cover investigations carried out by Norway in assessing the practical implications of load-on-top operations:

1. Load-on-Top Investigations Part I
2. Load-on-Top Investigations Part II
3. Sub-Report on Load-on-Top Investigations Part II
4.* Chemical characterization of crude oil components in ballast and slop water from a very large crude carrier (VLCC) and from model experiments.

* New page 14 to be inserted.

Distribution of the attachment (in English) is limited to this Committee only.

THE SHIP RESEARCH INSTITUTE OF NORWAY

Commission No. 832. 2012

Report No. 1/73

Commission given by: SDS-Project in co-operation with the Norwegian Shipowners Association.

Title of commission: Investigations on the Load-on-Top System.

TITLE OF REPORT: LOAD-ON-TOP INVESTIGATIONS, PART I.

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Oslo, 16th January 1973
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PREFACE

It is recognized that one of the main objectives of the 1973 Conference on Marine Pollution should be to achieve the complete elimination of intentional pollution by oil. That is to eliminate the likely damage to marine resources caused by operational discharge of oily water mixtures. To achieve this goal it is believed that any of the following methods or combination thereof are possible solutions in this respect:

- The use of segregated ballast tanks,
- retention of oil onboard, and
- in-port disposal to shore-reception facilities of the oily mixture.

It is further recognized that the construction of tankers with sufficient segregated ballast capacity will contribute substantially to the reduction of pollution caused by operational discharge. However, one should realize that also this provision has some major shortcomings:

- Unless requiring a segregated ballast tank capacity up to 60 - 70 % of the dw capacity the segregated ballast tanker, on occasion, will have to load ballast in cargo tanks to achieve an acceptable ballast operation condition. As a consequence of this, a segregated ballast tanker must also be equipped with a complete arrangement for application of the Load-on-Top system.

- Even with segregated ballast tanks, it will periodically be necessary to clean the cargo tanks in order to remove sludge build-up and to prepare the ship for dry-docking inspection and repairs. Tankcleaning before drydocking and repairs is found to be one of the major pollution causes.

- The segregated ballast tanker will have an increased freeboard which may effect the ship controllability. This will influence the ship's seaworthiness in an unfavourable way, particularly in wind at low speeds as occurs in harbour and docking situations.

Even if it is realized that the "Load-on-Top" system cannot be operated under all circumstances, it will contribute substantially to a reduced discharge of oil into the sea , and as an overall consideration will give the best result obtainable at the present stage of development.

I INTRODUCTION.

A study of the possible improvements in the operation of crude oil tankers was initiated by Norwegian shipbuilders and owners in 1971. In particular, the processes of tank cleaning and gas freeing attracted attention, and in the course of the study great emphasis was placed on the development of a more efficient and less polluting Load-on-Top-system.

It is felt that the results from the study will be of interest for the recent investigations sponsored by IMCO. This progress report from the Norwegian study is therefore presented, covering tests of different slop tank arrangements both on ships in operation and in model tests.

So far, the study has been carried out according to the following program:

1. To find out what takes place in slop tanks during tank washing 94 water samples were taken onboard 4 crude oil tankers on ballast voyages, and analyzed in laboratories.

2. To investigate the factors that influence the separation of oil in water, a model in scale 1:25 of a three-tank slop tank arrangement was constructed. This arrangement gives possibility for investigation of parameters such as number of tanks, degree of heating, inlet points and inlet nozzles for slop in the tanks. Water samples were taken and analyzed.

3. Piping systems were evaluated in order to be able to unload as much as possible of the cargo oil as well as obtain an effective draining during tank washing.

4. Tank washing equipment and methods for cleaning were discussed.

5. Instrumentation for control of tank atmosphere was investigated.

II CONCLUSIONS.

The result of tests and investigations as listed above, may be summed up as follows:

- Samples of overboard discharge water taken from slop tanks of modern tankers in actual service have proven that the "Load-on-Top"-system as adequately practiced to-day, fulfills the proposed requirements as given in the fourth draft of the 1973-Convention.
- Modern tests of slop tank arrangements have given valuable information with regard to further development of improved slop tanks and settling systems.
- Based on information from model tests and from tankers in service, designers and operators have worked out detailed specifications for an improved "Load-on-Top"-system with the main purpose to reduce pollution of the seas to an absolute minimum and at the same time reducing the risk of maloperation of the "Load-on-Top"-system and reducing the amount of work for the crew.

III SAMPLES FROM SHIPS.

In order to determine the actual oil content in the water which is pumped overboard in connection with cleaning of the cargo tanks, shifting of ballast as well as discharge of water from the slop tank system, a package of sample bottles with instructions for the sampling were sent to four ships to obtain samples at various times during the above mentioned operations.

A total of 94 samples were received from these four ships and quantitatively analyzed for oil content. The methods employed were the infrared spectroscopic method (IR-method) and in a few cases the gravimetric method, both determining the sum (in ppm) of oil components rather than the individual components. While the IR-method is non-destructive and preserves the samples, the gravimetric method involves a step of complete evaporation of the solvent used, and thus leads to loss of lighter components (this weight loss is calculated within the computation of oil content.) A limited number of samples both from the ships and from the model experiments were further analyzed by gas chromatography and combined gas chromatography/mass spectrometry in order to get an impression of the distribution and general nature of the oil components found in washing water. This is further discussed in Appendix A attached to this report.

The result of the analyses of the samples from the ships show that with two slop tanks in series and with a high liquid level in the slop tanks during the washing operation (low ullage) the oil content in the water that is discharged overboard can be kept as low as 25 - 100 ppm. This is when washing with cold water without chemical additives. The analyses of the dirty ballast water from the unwashed cargo tanks show that it is also possible to obtain oil content of this water within the same limits.

During the final decanting of settled water from the primary slop tank to the sea the results show that the oil content of the water is increasing as the oil/water interface is approaching the bottom of the tank. The variation in the results during this operation is assumed to be caused by more or less cautious operation of the discharge pumps.

The four ships that were used in the series were two crude oil tankers of 280.000 tdw, one tanker of 162.000 tdw. and one tanker of 85.000 tdw.

IV MODEL TANK EXPERIMENTS.

a) Description of Experiments.

For the experiments a model tank with linear scale 1:25 was built. The model tank consists of two side tanks of about 400 litres capacity each, and one center tank of about 600 litres. A total of 15 series of experiments were conducted and 200 1 litre water samples were drawn. The oil/water mixtures consisted of fresh water with additions of crude oil. The crude oil had the following specifications:

Type: Arabian Light Crude from Ras Tanura.

Specific gravity: 0,851 g/cm^3

Viscosity: 5,5 CST at 100°F.

Pour point: ÷ 26°C.
Sulphure content: 1,7 weight %.
Reids vapour pressure: 4,6 psi.
Flash point: Less than 0°C.

The oil and water was mixed by the use of an ejector. The water was used as the driving medium and oil was introduced on the suction side of the ejector. Using a driving water pressure of 0,2 kp/cm^2 a total slop quantity of 250 litres per hour was arrived at. In the model experiments this will correspond to the capacit of eight Butterworth Super K washing machines.

During the experiments the following parameters were investigated as to their effect upon the oil/water separation.

The initial oil concentration of the slop.

The method of introducing the slop into the tanks.

The number of slop tanks.
The capacity of the slop tanks.
The temperature in the slop tanks.
The introduction of air in the bottom of the slop tanks.
The addition of chemicals into the slop tank water.

During all experiments the slop water was introduced about halfway up in the primary tank. It was then taken out of this tank near the bottom, and introduced into the secondary tank about halfway up. When three tanks were being used, the water was taken out near the bottom of the secondary tank, and introduced into the tertiary tank about halfway up. To heat the water in the tanks, two heaters each of 1000 w were used. The heating coils were placed about 1/3 of the total tank height from the bottom of the tank.

The primary tank was always filled up completely before the connection to the secondary tank was opened. The primary tank was furthermore constantly being refilled with slop water, so that the level of this tank was kept constant until the secondary tank was filled. When three tanks were being used, the levels in the primary and the secondary tanks were kept constant until the third tank was filled. During all experiments samples were drawn from two levels in the tanks, near the bottom, and in the middle of the tank.

The sampling routine, using two slop tanks in series, was as follows:

Primary tank	Secondary tank	
	2 samples	When the secondary tank is full.
	2 samples	1/2 hour after secondary tank is full.
2 samples	2 samples	1 hour after secondary tank is full.
2 samples	2 samples	The next day.

When experiments using three tanks were conducted, samples were drawn from the secondary and the tertiary tanks only, in accordance with the following routine:

Secondary tank	Tertiary tank	
2 samples		When the secondary tank is full.
2 samples		When the tertiary tank is half full.
2 samples	2 samples	When the tertiary tank is full.
	2 samples	1/2 hour after tertiary tank is full.
	2 samples	1 hour after tertiary tank is full
2 samples	2 samples	The next day.

In some cases samples were also drawn after two or three days. After each experiment the tanks were thoroughly cleaned using water and chemicals of the type Drew ACC-9 and Oil and Grease Remover.

The chemical addition used in experiment No. 12 was:

Ameroid EB-70, Emulsion Breaker, Drew Chemicals.

b) Results and conclusions.

1. The oil content in the water leaving the slop tank system is depending upon two factors:

   a) oil content in the water coming into the system,

   b) time allowed for settling.

   When the settling is over a period of days, the initial oil content does not affect the results.

2. The experiments show that when using a conical expanding outlet on the pipe that introduces the slop into the tank, better results can be obtained than when introducing the slop through a regular cut off pipe.

3. The experiments show that using three slop tanks in series will result in lower oil concentrations in the separated water, as compared with using two slop tanks in series on the condition that the settling period is the same.

4. It was found that a high heating rate in the primary tank improved the oil/water separation considerably. However, the separation can be further improved by using moderate heating in both the primary and the secondary tank.

5. Air was introduced at the bottom of the primary tank and allowed to bubble up through the oil/water mixture. After further settling a minor improvement in the oil/water separation was obtained.

6. The results indicate that by increasing the volume of the primary slop tank better results can be obtained.

V. PROPOSED OUTLINE FOR SPECIFICATIONS FOR AN IMPROVED LOAD-ON-TOP SYSTEM.

A. TANK ARRANGEMENT.

a) Cargo oil tanks.

The basis for this study is a 200. - 350.000 tdw. tanker complying with the 1971 amendments to the Oil Pollution Convention 1954. The tank area is divided by seven bulkheads across and two bulkheads along the ship, giving eight center tanks and eight pairs of wing tanks. Of these tanks all with the exception of wing tanks No. 4 are used for cargo.

b) Ballast tanks.

The wing tanks No. 4 are selected as permanent ballast tanks. This selection is based upon structural considerations as well as considerations of the loading/unloading procedure.

Center tanks No. 1, 3 and 6 are selected for carrying clean ballast.

c) Slop tanks.

The center tank No. 8 is divided using two oil-tight bulkheads across. These three tanks are used as slop tanks and in series to give a stepwise settling. As an alternative the aft wing tanks and the center tank in between may be used as slop tanks.

In the primary slop tank the major part of oil and sediment is felled out and this tank should therefore be easy to clean. This can be accomplished by using flat bottom and sides.

The design of the secondary tank should also be given special consideration to cleaning, and this tank should also have a flat bottom.

The tertiary tank may be of design as a well designed cargo tank.

The capacity of the slop tanks should be based upon the maximum total water flow during tank cleaning, taken as the main parameter, the cargo tank volume being less important. This will result in larger slop tanks than is common to-day. The following criteria seem reasonable for deciding the slop tank capacity:

1. The primary slop tank should have a volume which is at least four times the quantity of water in tons per hour used during normal tank washing procedure at sea.

2. The secondary slop tank should have a volume which is at least twice the volume of the primary slop tank.

3. The tertiary slop tank should have a volume twice the volume of the primary tank. This tank is also used as a reservoir for driving water to the ejectors and for washing water. It is assumed that when the washing is finished, all slop is collected in the primary slop tank.

B. PUMPS.

The ship may have two, three or four cargo oil pumps. A separate ballast pump is installed for the filling and emptying of permanent ballast tanks, as well as for filling of dirty ballast tanks over deck via separate filling lines.

It is desirable to unload as much as possible of the cargo oil and to empty the cargo oil piping system. The stripping pump will be connected to its own line on deck, connected to the manifold midships. This line is to be used for unloading of the oil that remains in the cargo oil piping system after unloading with the sentrifugal pumps and to pump slop ashore. Two ejectors working on the stripping system lines should be installed. The dimensions of the stripping system lines and the ejectors should be based upon the amount of wash water expected.

C. PIPING SYSTEM.

a) Cargo oil piping.

To enable the tanker operator to unload as much as possible of the oil cargo the ship should be listed 2 - 3 degrees to one of the sides during unloading and stripping. It should be one suction in each wing tank and two suctions in each center tank. The suctions are placed in the lowest corner in the tank which will be the aft corner of the tank on the side that the ship is listed to. The second suction in the center tanksis placed near the center beam (on the upper side). The suctions should be placed maximum 40 mm above the bottom and the suction area should be at least 1.5 times the suction pipe area. In connection with the placing of the suctions it is necessary to investigate the ways the oil can flow through the bottom structure to the suctions, and a map of the bottom structure should be drawn showing that all oil on the bottom can flow to the suctions. Extra cut-outs in stiffeners and frames should be made to ensure this.

b) Stripping lines.

As during unloading the ship should be listed 2 - 3 degrees to one side during stripping as well. One stripping suction is placed in each wing tank and one stripping suction in each center tank. The stripping suctions should be placed near the cargo suctions, and shall be placed a maximum of 20 mm above the bottom with a suction area of minimum 1.5 times the pipe area.

The stripping line should be able to strip from two tanks independently. The separate stripping line is connected to the main line using double valves. Further double valves should be fitted in all main suctions and stripping suctions to cargo tanks that are used for dirty and clean ballast. 80 mm quick-connections for hoses with valve are placed on the stripping line, at least one in each tank, and armoured hoses for the removal of sediment are delivered with the ship.

c) Ballast piping.

Separate ballast piping is installed on the deck for filling of dirty ballast.

All permanent ballast tanks shall be filled and emptied with separate ballast lines.

d) Piping system for tank washing.

The piping system for tank washing should be supplied from the cargo oil piping on deck. Either clean sea water (open cycle) or slop water from the tertiary slop tank (closed cycle) can be used. A separate heater with a capacity of at least 350 mm^3 per hour, 90^{0}C, should be installed.

e) Piping system for slop tanks.

The ship should have three slop tanks that can be used in series and the piping system should be arranged to keep the water in the slop tanks at a high level (low ullage).

Al slop should first be pumped into the primary slop tank. To enable washing and inspection of the primary slop tank, the possibility should exist for introduction of slop directly to the secondary slop tank. This connection shall normally be closed an secured.

The slop inlet should be placed at about half the height from the bottom to the surface. The pipe leading the slop into the tank should be fitted with a suitable arrangement to slow down the speed of the water entering to avoid disturbances in the water.

An open pipe that starts about 1 meter above the bottom of the primary slop tank and with an outlet about halfways up the secondary tank should be used for the transfer of the slop from the primary to the secondary tank. A similar arrangement should be used to transfer the slop from the secondary to the tertiary tank. An open overflow pipe that starts about 1 meter above the bottom in each of the secondary and the tertiary tanks may be used to discharge settled slop water overborad. These pipes should be inverted U-shape with their highest point about four meters below deck, thereby ensuring a constant high level in all slop tanks.

f) Monitoring.

The overboard discharge pipes should be fitted with necessary arrangement for installing monitoring equipment.

D. WASHING EQUIPMENT.

Four different alternatives for washing equipment have been considered:

a) Portable equipment in all tanks for washing to hot work standard.

b) Permanent equipment in clean ballast tanks for washing to clean ballast standard and portable equipment in all tanks for washing to hot-work standard.

c) Permanent equipment in all tanks for washing to clean ballast standard and portable equipment in all tanks for washing to hot work standard.

d) Permanent equipment in all tanks for washing to hot work standard.

In order to perform a satisfactory washing to hot work standard, using the poratble washing machines in addition to the permanently installed ones, it might be required to wash wiht warm water.

E. MONITORING OF TANK ATMOSPHERE

The ship should be equipped with portable instruments, approved by the Administration for the measuring of the hydrocarbon gas in air and oxygen in air. The ship should therefore carry at least one instrument that can measure the atmosphere below the Lower Explosion Limit (with scale from 0% to 100% L.E.L.), and at least one instrument that can measure explosive atmospheres and atmospheres above Upper Explosion Limit. In addition, the ship should have at least one approved portable instrument for the measuring of oxygen in air, and in air/inert gas mixture (with measuring area 0 - 21 vol %.)

All measuring instruments that are onboard shall be inspected regularly as prescribed by the Administration. In order to draw samples from the atmosphere at points down in the tanks, the ship should be equipped with a sufficient number of sampling hoses of suitable material.

APPENDIX A

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CHARACTERIZATION OF WATER SOLUBLE COMPONENTS FROM CRUDE OIL AND FROM SLUDGE AND SEDIMENTS FROM CRUDE OIL

STATUS REPORT 2.

1. INTRODUCTION

In an earlier investigation, a total of 94 samples from ships and 200 samples from model tank experiments were quantitatively analyzed for oil content. The methods employed were the infrared spectroscopic method (IR-method) and, in a few cases, the gravimetric method, both determining the sum (expressed as ppm) of oil components rather than the individual components (cfr. our report of June 21, 1972, 72 03 03, JEB/ks).

While the IR-method is non-destructive and preserves the samples, the gravimetric method involves a step of complete evaporation of the solvent used and thus, leads to loss of lighter components (this weight loss is calculated with in the computation of oil content).

In the present investigation, a limited number of samples both from ships and from model experiments have been further characterized by gas chromatography (GC) and by combined gas chromatography - mass spectrometry (GC-MS).

2. GAS CHROMATOGRAPHY (GC)

The samples were either in carbon tetrachloride solution or in carbon disulfide solution and n-dodecan (n-$C_{12}H_{26}$) was used as an external or internal standard for quantitation.

The GC-conditions were as follows:

Instrument: Pye Unicam GC Model 104
Column: 2m 1/8" 3% SE-30 on Chromosorb W 80-100
Carrier gas: 15 ml/min. nitrogen (N_2)
Detector: Flame Ionization (FID)
Detector temperature: 250° C
Column temperature: isothermal 70° C for 5 min., programmed from 70 - 250° C with 5° C/min.

The concentrations (ppb) of the individual oil components were calculated by comparison of peak heights in the chromatograms with the peak height of the standard used.

3. COMBINED GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS)

The GC-MS analysis were performed on a Hitachi-Perkin Elmer RMU-6L MS coupled to a Perkin Elmer Model 801 GC under the GC-conditions described (except carrier gas helium 25 ml/min.), and the mass spectra of separated main components were recorded at 70 eV. The chemical structures of these components were determined when possible.

4. RESULTS AND DISCUSSION

4.1 SAMPLES FROM MODEL TANK

A total of 6 samples have been analyzed by GC and one sample has been analyzed by GC/MS in order to get an impression of the distribution and general nature of the oil components found in washing water. The GC-determinations of this limited number of samples show that the same type of main components are present in the same relative amounts, although the total concentrations vary from sample to sample (determined previously). The GC/MS analysis of sample no. 10 (table 2) shows that both aliphatics and aromatics (benzenes and naphthalenes) are found in the region of fairly volatile components (before C-15), but only paraffinic compounds could be identified above C-15. Approximately 9 percent of a total of 35 ppm (as determined by the IR-method) have been identified by the present method. The total amount of aromatics is approximately 50 percent of identified material.

4.2 SAMPLES FROM SHIPS

A total of 9 samples have been analyzed by GC and one sample (no. 2) has been analyzed by GC/MS from ship no. 4. Since these samples previously were determined by the gravimetric method, the lighter components have disappeared and the first component identified was usually pentadecane (C-15), compound no.70 in table 1. All samples were similar in relative amounts and nature of components identified. Generally, the gravimetric analysis is unsuitable for total determination if further characterization of components present originally is needed.

Two samples from ship no. 3 previously determined by the IR-method have been further characterized by GC and GC/MS (tables 3 and 4). In these samples, the components identified were of the same types as found in the sample from model experiments (table 2).

Between 2 and 3 ppm of a total of approximately 45 ppm could be identified, and the aromatic portions of the identified materials amount to 25 - 30 percent.

4.3 DISCUSSION

In sample no. 10 from model experiments (table 2), 25 percent of total oil components could be identified, where as only 5 - 6 percent could be identified in the samples from ship no. 3 (tables 3 and 4). These components are those most easily volatilized, and thus, the results indicate that the latter samples (from ships) contain less volatile materials. Since, however, a concentration step is involved prior to the determination, these results, although reasonable, have to be interpretated with some caution.

The aromatics identified are substituted benzenes and naphthalenes. Amongst the compounds identified in similar aqueous extracts of crude oil and crude oil fractions, naphthalenes and naphthalene-type compounds are reported to be most toxic to fish, having a general toxicity range of 4 - 5 ppm (see for instance Boylan and Tripp, Nature 230, 44 - 47 (1971)). Such compounds are present in these samples in the sub-ppm range.

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TABLE 1. ANALYSIS OF SAMPLE NO. 2 [illegible] NO. 4

Ref.no[1] for component	Compound	Concentrations Individual components (ppb)	 Total aromatics identified (ppb)	 Total identified (ppm)	 Total in extract[2] (ppm)
70	$n\text{-}C_{15}H_{32}$	95		1.7	90
80	$n\text{-}C_{16}H_{34}$	203			
90	$n\text{-}C_{17}H_{36}$	277			
100	$n\text{-}C_{18}H_{38}$	252			
110	$n\text{-}C_{19}H_{40}$	230			
120	$n\text{-}C_{20}H_{42}$	183			
130	$n\text{-}C_{21}H_{44}$	133			
140	$n\text{-}C_{22}H_{46}$	113			
150	$n\text{-}C_{23}H_{48}$	83			
160	$n\text{-}C_{24}H_{50}$	51			
170	$n\text{-}C_{25}H_{52}$	35			

1) The nos 10, 20, 30,....... refer to the n-alkanes C_9, C_{10}, C_{11},........
Components eluted between n-alkanes are given intermediate nos.

2) Determined by the gravimetric method.

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TABLE 2. ANALYSIS WITH GC/MS OF SAMPLE NO. 10 FROM MODEL EXPERIMENT

Ref.no[1] for component	Compound	Concentrations			
		Individual components (ppb)	Total aromatics identified (ppm)	Total identified (ppm)	Total in extract (ppm)
1	alkyl (C_2) benzene	758	4,4	8.7	35
2		1803			
3		758			
10	n-C_9H_{20}	235			
11	alkyl (C_3) benzene	49			
12		295			
13		374			
14		118			
20	n-$C_{10}H_{22}$	256			
21	alkyl (C_4) benzene	89			
30	n-$C_{11}H_{24}$	305			
31	alkyl (C_5) benzene	39			
32 33	naphthalene + methyl naphthalene or di-methyl indane	39			
40	n-$C_{12}H_{26}$	305			
41	methyl naphthalene	49			
50	n-$C_{13}H_{28}$	355			
60	n-$C_{14}H_{30}$+	364			
61	dimethyl naphthalene				
70	n-$C_{15}H_{32}$	374			
80	n-$C_{16}H_{34}$	364			
90	n-$C_{17}H_{36}$	355			
100	n-$C_{18}H_{38}$	295			
110	n-$C_{19}H_{40}$	276			
120	n-$C_{20}H_{42}$	227			
130	n-$C_{21}H_{44}$	187			
140	n-$C_{22}H_{46}$	148			
150	n-$C_{23}H_{48}$	118			
160	n-$C_{24}H_{50}$	138			
170	n-$C_{25}H_{52}$	59			

1) See note to Table 1.

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TABLE 3. ANALYSIS OF SAMPLE NO. 5 FROM SHIP NO. 3.

Ref.no[1] for component	Compound	Concentrations			
		Individual components (ppb)	Total aromatics identified (ppb)	Total identified (ppm)	Total in extract[2] (ppm)
1	alkyl (C_2) benzene	424	878	2,9	45
10	n-C_9H_{20}	94			
11 12	alkyl (C_3) benzene	27 94			
20	n-$C_{10}H_{22}$	114			
21 22	alkyl (C_4) benzene	37 47			
30	n-$C_{11}H_{24}$	162			
31	alkyl (C_5) benzene	27			
32	naphthalene	27			
40	n-$C_{12}H_{26}$	162			
41	alkyl (C_6) benzene	37			
42	methyl naphthalene	37			
50	n-$C_{13}H_{28}$	175			
51	alkyl (C_7) benzene	27			
52	dimethyl naphthalene	27			
60 61	n-$C_{14}H_{30}$ and dimethylnaphthalene	163			
70	n-$C_{15}H_{32}$	182			
71	alkyl (C_3) naphthalene	67			
80	n-$C_{16}H_{34}$	175			
90	n-$C_{17}H_{36}$	202			
100	n-$C_{18}H_{38}$	168			
110	n-$C_{19}H_{40}$	128			
120	n-$C_{20}H_{42}$	114			
130	n-$C_{21}H_{44}$	87			
140	n-$C_{22}H_{46}$	74			

1) See note in table 1.
2) See note in table 2.

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TABLE 4. ANALYSIS OF SAMPLE NO. 9 [illegible] NO. 3

Ref.no[1] for component	Compound	Concentrations Individual components (ppb)	Total aromatics identified (ppb)	Total identified (ppm)	Total in extract[2] (ppm)
1	alkyl (C_2) benzene	196	554	2,2	44
10	n-C_9H_{20}	101			
11 12	alkyl (C_3) benzene	28 62			
20	n-$C_{10}H_{22}$	112			
21 22	alkyl (C_4) benzene	45 39			
30	n-$C_{11}H_{24}$	129			
31	alkyl (C_5) benzene	28			
32	naphthalene	28			
40	n-$C_{12}H_{26}$	129			
41	alkyl (C_6) benzene	34			
42	methyl naphthalene	34			
50	n-$C_{13}H_{28}$	129			
51	alkyl (C_7) benzene	22			
52	dimethyl naphthalene	22			
60 61	n-$C_{14}H_{30}$ and dimethyl naphthalene	145			
70	n-$C_{15}H_{32}$	145			
71	alkyl (C_3)naphthalene	27			
80	n-$C_{16}H_{34}$	140			
90	n-$C_{17}H_{36}$	145			
100	n-$C_{18}H_{38}$	129			
110	n-$C_{19}H_{40}$	112			
120	n-$C_{20}H_{42}$	89			
130	n-$C_{21}H_{44}$	73			
140	n-$C_{22}H_{46}$	61			

1) See note in table 1.
2) See note in table 2.

THE SHIP RESEARCH INSTITUTE OF NORWAY

Commission No. 832.2012

Report No. 4/73

Commission given by: SDS-Project in cooperation with the Norwegian Shipowners Association

Title of commission: Investigations on the Load-on-Top System

TITLE OF REPORT: LOAD-ON-TOP INVESTIGATIONS, PART II

Prepared by:
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Øystein Hjorteland, Captain

SUMMARY:

The various factors and parameters that influence the use of the LOT system onboard crude oil tankers have been investigated with a view to comply with both the present and proposed new international regulations concerning oil discharged to the sea.

The investigations were carried out during normal operating conditions onboard two Norwegian tankers and, in addition, parallel model experiments were conducted.

This is the summary report. For details, see:

Commission Subreport No 4A/73 for a description of the investigations

and
Commission Subreport No 4B/73 for a description of the methods used for the analyses.

Both subreports contain the results from the samplin

CONTENTS

I CONCLUSIONS.

1. From this investigation, it may be concluded that it is possible to follow the LOT-procedure during normal operating conditions onboard a VLCC and still stay well within the requirements regarding oil content in the effluent according to the 1969-amendments to the 1954 - oil pollution convention and the requirements specified in the proposed 1973 - marine pollution convention.

2. It may further be concluded that the volume of the slop tanks should be increased to improve upon the settling process.

3. On the assumption that ballast water with an oil content below 100 ppm may be discharged outside 50 nautical miles from nearest land, one may expect that the bulk of the ballast water from unwashed tanks may be discharged after a settling period ranging from a few hours up to about 40 hours, depending upon the specific conditions onboard. From the investigation, it may also be concluded that assuming a maximum oil content of 30 ppm, it would have been possible to discharge large quantities of the settled ballast water after 60 hours of settling, and the bulk after settling periods of up to about 100 hours. One center tank could have been pumped almost empty with a discharge oil content of below 20 ppm, but for the other tanks, it took from 80 to 110 hours of settling to come below this oil content in the bulk of their content.

II INTRODUCTION.

A study of the possible improvements in the operation of crude oil tankers was initiated by Norwegian shipowners and shipbuilders in 1971. In Commission Report No. 1/73 detailed specifications for an improved LOT system have been introduced. In order to investigate further the various factors and parameters that influence the use of the LOT system onboard crude oil tankers with a view to comply with both the present and proposed new international regulations concerning oil discharged to sea, the LOT procedure was investigated onboard two Norwegian tankers during normal operating conditions.

The investigation was carried out as follows:

- 318 samples of clean and dirty ballast water and slop were taken onboard a 280.000 tdw. crude oil tanker and analysed.
- 22 samples of dirty ballast water were taken onboard a 240.000 tdw crude oil tanker and analysed.
- 128 samples were taken during model tank experiments in order to establish the relationship between the conditions onboard the 280.000 tdw. tanker under conditions in a tank section model.

This report, Commission Report No. 4/73, contains a summary of the investigations and a discussion of the results. A detailed description of the investigations is contained in Commission Subreport No. 4A/73, "LOT-investigations aboard VLCCs, and on model experiments", while Commission Subreport No. 4B/73 on "Characterization of crude oil components in ballast and slop water from two crude oil tankers and from model experiments" contains a description of the methods used for analyses. These methods include the infrared method for the detection of total oil content in ppm, and the gas chromatography and combined gas chromatography/mass spectrometry methods for detection of the concentration of the individual components of the oil.

III SUMMARY.

1. The data presented in this report are based upon detailed investigations onboard the M/T "Berge Princess" of the shipowners Sig. Bergesen d.y. & Co., on a ballast voyage from Isle of Grain, UK, to Capc Town, and upon a supplementary investigation onboard the T/T "Ferncourt" of the shipowners Fearnley & Eger, on a ballast voyage enroute from Rotterdam to PG. Both ships had carried crude oil from Kuwait with API of about 31.8 on their previous voyages. In addition, data from parallel model experiments are presented.

   M/T "Berge Princess" is equipped with two slop tanks in series, with a combined capacity of about 2.8 % of the cargo carrying capacity.

2. The total amount of oil discharged from the M/T "Berge Princess" on the ballast voyage was 7.53 tons or 1/36.000 of the ship's cargo capacity. This complies with the 1/15.000 cargo limit set by the 1969 amendments to the 1954 oil pollution convention, and the proposed 1/30.000 cargo limit proposed in the draft 1973 convention.

   The ballast was discharged by decanting and by using cargo pumps, and the water from the slop tanks was discharged by decanting and by the use of cargo and stripping pumps.

3. Nine cargo tanks were flushed onboard the M/T "Berge Princess" and the flushing water was pumped into the slop tanks. A small quantity of water was decanted without settling containing 120 ppm of oil, which equals 18 litres per n.mile. After a settling period of 45 hours decanting was continued. The oil content was now 40 ppm or 4.5 litres per n.mile.

4. Dirty ballast was discharged from the M/T "Berge Princess" after a settling period of approximately 130 hours. The most

unfavourable result shows an oil content of 30 ppm or 5.3 litres per n.mile. During the last period of the discharge, the oil content increased to about 200 ppm or 47.5 litres per n.mile.

5. Analyses of the ballast water in an unwashed tank onboard the T/T "Ferncourt" show an oil content well below 20 ppm through the tank even after short settling time.

6. During the washing procedure ejectors were used. The washing water was discharged through the slop tanks. The oil content in the water discharged during tank washing operation started at about 57 ppm and increased to 380 ppm at the end, corresponding to about 5 litres per n.mile and 32 litres per n.mile respectively. The average oil content during the washing was about 145 ppm, which corresponds to about 12 litres per n.mile. The total amount of oil discharged through the full washing procedure was 3.18 tons.

7. After the tank washing procedure and discharge of dirty ballast, discharge of settled water from the slop tanks was continued. The pump speed was reduced as the oil/water interface approached the tank outlet in order to avoid unnecessary discharge of oil. Hence the oil discharge rate only ranged from 6.4 to 15.6 litres per n.mile, while the oil content began at 100 ppm and increased to 900 ppm just before cut-off.

IV DISCUSSION OF THE RESULTS FROM THE SHIPBOARD SAMPLING.

IV A. M/T "BERGE PRINCESS".

The major conclusion to be drawn from the tests is that it was possible for the ship to follow a conventional load on top procedure and still keep the amount of oil discharged to the sea well below the limits given in the 1969 amendments to the 1954 Oil Pollution Convention. This was possible in spite of the fact that this ship had bad weather with heavy seas the first three days of the ballast voyage. This had an unfavourable effect on the settling process of the ballast water. The weather condition on the voyage is listed in Table 17. The tables also include the ship's course, speed and noon position.

Different quantities of oil were left in the tanks selected for the experiments, such that of two identical center tanks one was left with more oil than the other tank, and similarly, for two identical wing tanks. The analysis of the samples drawn from these tanks show that the settled water had lower oil concentration in those tanks that had the larger quantities of oil remaining. Center tank No. 1, for example, had an average oil content of 30 ppm. after 111 hours of settling, while center tank No. 3 had an average oil content of 8 ppm after 112 hours settling. The oil layers measured on the water surface in center tank No. 1 was 15 cm., while the oil layer on the water in center tank No. 3 was 66 cm. This "inversely proportional" tendency could also be noticed in the wing tanks No. 5 Port and Starboard, but not so clearly.

The analysis of the samples that were drawn from the model experiments show small difference between the oil content in the tanks containing much oil and the tanks containing little oil. However, the samples that were drawn from the slop tanks when stripping after simulated flushing of empty cargo tanks was completed, showed higher oil content in the secondary slop tank than in the primary slop tank for all samples after 1 hour, 17 hours, 23 hours, 40 hours and 45 hours settling. The difference in the results from the settling out of the water in the simulated slop tanks show the same tendency as for the slop tanks in M/T "BERGE PRINCESS".

Two slop tanks in series resulted in a fairly good reduction in the oil content of the water that was discharged to the sea from the secondary slop tank (Starboard slop tank) during the washing period. The average oil content of the discharge during the washing of center tanks No. 2 and center tanks No. 5 was about 143 ppm., which equals an oil discharge rate of about 12 l/n.mi. One hour after the washing of center tank No. 2 started, the oil concentration increased to a level of about 280 ppm. which equals 24 l./n.mi., whereafter the concentration decreased. The maximum oil content of the water discharged during washing of center tank No. 5 occurred at the start of washing and the oil content at this point was 250 ppm., which equals 21 l./n.mi.

During the washing period, ejectors were used for stripping, with driving water taken directly from the sea. This gave a large flow through the slop tanks and therefore, a relatively short settling time in the tanks. If a stripping pump had been used for stripping during the tank washing, the flow through the slop tanks would have been reduced to about 1/3, and the settling time would have been increased accordingly. One should expect that under such conditions the oil content of the water discharged would have been further reduced.

If the driving water for the ejectors had been taken from the Starboard slop tank, the total quantity discharged to the sea could have been reduced, but one must assume that the specific oil content of the discharge would have been about the same as measured or possibly higher. This could be caused by the fact that the circulation in the slop tanks would have been the same as when the driving water was taken directly from the sea. Furthermore, with driving water from the Starboard slop tank, the oil content in the slop entering the Port slop tank would have been higher than when clean water is used for driving water. The total slop quantity would have been reduced and possibly the total quantity of oil discharged, as well.

During the experiments, when settled ballast/slop water was discharged overboard, the wake of the ship was kept under constant surveillance to detect possible oil slicks. With the exception of the last minute discharge from the Port slop tank, when the oil content momentarily increased to a value where oil was visible, no oil could be observed behind the ship at any time.

In spite of the fact that in the interest of the experiment a few deviations from normal operating practices were done in order to establish oil content limits, experiments show that the voluntary oil discharge from a 280 000 t.d.w. tanker can, with the execution of reasonable care, be kept well below 10 cu. meters of oil on a ballast voyage, and the maximum oil discharge rate can without difficulty be kept under 30 l./n.mil.

If one assumes that the settled ballast water with oil content below 100 ppm can be discharged to the sea outside the 50 n.mi. limit from nearest land, one could expect to be able to discharge ballast water from unwashed tanks after 12 - 24 hours settling, depending upon the weather conditions. The distance from the oil layer to the suction in the tank when the overboard discharge must be stopped, will depend upon several factors, such as ship movements, pumping capacity and bottom structure of the tanks. When there is no rolling or pitching, and the ballast is discharged with a low pump velocity, one should be able to discharge settled water until oil water interface is about 1.5 m. from the suction. The rest in the tank must then be pumped to the slop tanks for further settling and eventual discharge.

IV B. T/T "FERNCOURT".

A supplementary investigation was conducted onboard the T/T "Ferncourt" Samples were drawn from a center tank containing dirty ballast, and the analysis shows results that are well below 20 ppm. The bulk of the water in the tank could be discharged without coming in conflict with any present and foreseeable near-future regulations.

V DISCUSSION OF THE RESULTS FROM THE TANK SECTION MODEL EXPERIMENTS

The model experiments were conducted in order to establish the relationship between the conditions onboard a tanker and the conditions in a tank section model in a laboratory, and it was attempted to simulate the operations onboard the M/T "Berge Princess" as much as possible. Samples were drawn after the same periods of settling and at depths relative to those onboard. The crude oil used for the experiments was pumped from the ship's cargo in Le Havre and sent to Norway.

It should be kept in mind that the thickness of the oil/water interface will be the same regardless of whether the tank is small or large. The samples from the "center tank" show this clearly since the oil content of the water increases very rapidly as the surface is approached. After 22 hours settling, the increase starts at 48 centimeters below the surface, and increases up to the upper sampling point which is 25 cm below the surface. The increase in oil content diminishes as the settling proceeds, but it is still clearly present in this upper layer after 63 hours of settling. The samples from the "wing tank" does not show the same increase, but an increase can be noticed in the upper layer after 22 hours. After 63 hours settling, the oil content increase in this area is insignificant. This indicates that for the model experiments, one should expect a 25 - 30 cm thick layer below the oil/water interface that will contain a very high oil content.

After 63 hours the water in the "center tank" and the "wing tanks" was discharged, leaving only the oil layer in the tanks. The analysis of the samples drawn during the discharge show an average oil content of 4 ppm.

The sampling series drawn from the "tanks" with much oil remaining show the same tendency as when there were little oil remaining. In this case it also appears to be a 25 - 30 cm thick layer below the oil/water interface that has a relatively high oil content. However, the samples drawn from the water below this layer after 63 hours settling, show the same average oil content (about 4 ppm) as when the tank contains a small quantity of oil remaining.

The third series of samples were drawn from the "tanks" during simulation of a slop tank system. The operation that was simulated was the settling of slop after flushing of empty cargo tanks. It should be noted that the oil content of the settled water in the "tanks" is higher for the secondary "slop tank" which contains fairly little oil, than in the primary "slop tank" that contains considerably more oil. This phenomenon occurs already after 1 hour settling and is clearly evident all the time up to 45 hours settling. This is the same "inversely proportional" tendency that was noted onboard M/T "Berge Princess".

NORGES SKIPSFORSKNINGSINSTITUTT
THE SHIP RESEARCH INSTITUTE OF NORWAY

commission report

Commission No. 832.2012

Report No. 4A/73

Commission given by: SDS-Project in cooperation with the Norwegian Shipowners Association

Title of commission: Investigations on the Load-on-Top System

TITLE OF REPORT: SUBREPORT ON "LOAD-ON-TOP INVESTIGATIONS, PART II"

Prepared by:
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SUMMARY:

This report contains a detailed description of the investigation conducted onboard two Norwegian VLCCs and the parallel model experiments.

For the summary report with the conclusions see:
Commission Report No. 4/73.

For a description of the methods used in the analyses, see:
Commission Subreport No. 4B/73.

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Model experiments:

I INTRODUCTION.

In order to investigate the various factors and parameters that influence the use of the LOT system onboard crude oil tankers with a view to comply with both the present and proposed new international regulations concerning oil discharged to sea, the LOT procedure was investigated onboard two Norwegian tankers during normal operating conditions.

The investigation was carried out as follows:

- 318 samples of clean and dirty ballast water and slop were taken onboard a 280.000 tdw. crude oil tanker and analysed.
- 22 samples of dirty ballast water were taken onboard a 240.000 tdw crude oil tanker and analysed.
- 128 samples were taken during model experiments in order to establish the relationship between the conditions onboard the 280.000 tdw. tanker with the conditions in a tank section model.

The conclusion, a summary and a discussion of the results is contained in Commission Report No. 4/73. This subreport contains a detailed description of the investigations, while Commission Subreport No. 4B/73 on "Characterization of crude oil components in ballast and slop water from two crude oil tankers and from model experiments", contains a description of the methods used for analyses.

II SAMPLING ONBOARD M/T "BERGE PRINCESS"

II A. Description of the ship.

M/T "BERGE PRINCESS" which is owned and operated by Messrs. Sig. Bergesen d.y. & Co., was delivered from Mitsui Chiba Works in 1972. She has an overall length of 329 m., a breadth of about 52 m., and a depth of about 28 m. With a draft of near 22 m., she has a deadweight capacity of about 280 000 tons. The tank section is divided into 6 center tanks and 6 wing tanks on each side. Wing tanks No. 3 Port and Starboard are permanent ballast tanks. On each side aft of wing tanks No. 6 the ship has one slop tank of 3776 cu.meters. The tank arrangement is shown schematically on Figure 1, with the tank volumes in cu.meters.

The ship is equipped with cargo piping system and stripping piping system with connection to all cargo tanks. In addition, the ship has a separate piping system for filling of the permanent ballast tanks. This piping system can also be used to fill clean sea water ballast into wing tanks No. 2 Port and Starboard and wing tanks No. 5 Port and Starboard. These tanks can be shut off by double valves from the cargo piping system, making it possible to fill ballast into these tanks while the unloading is going on from the other tanks.

The inlet to the Port slop tank from the stripping pumps and ejectors enters the tank 5.5 m. above the bottom. In order to let slop water flow from Port slop tank to Starboard slop tank, a 300 mm. diameter pipe is fitted between the tanks. This pipe connects an outlet 1.4 m. above the bottom in the Port slop tank with an inlet 9 m. above the bottom in the Starboard slop tank. A valve which can be operated from deck is fitted in the line. Furthermore, both slop tanks have valves in connection with the stripping lines, and there are valves in the bulkheads between Port and Starboard wing tanks No. 6, respectively. In addition the Starboard slop tank is fitted with a valve on a piping connection to the No. 1 cargo piping line.

The stripping pumps were arranged so that it was very convenient to draw samples of the water on the pressure side of the pumps when they were in use. When the cargo pumps were used, samples were drawn from the suction side of the pumps, both on the top and bottom of the supply piping. When tanks were decanted, however, there were no possibilities of drawing samples in the pump room.

The ship was equipped with inert gas system for all tanks and slop tanks.

II B. Cargo unloading data.

M/S "BERGE PRINCESS" arrived at Lyme Bay on Jan 25, 1973 from Kuwait carrying a full load (272 266 tons) of Kuwait crude oil, with an API of 31.8, and specific gravity of 0.8665 at 60 degrees F. 45960 tons of the cargo was unloaded to another ship in Lyme Bay, after which the ship continued to Le Havre and unloaded another 126 792 tons. One barrel was filled with crude oil from the cargo and sent to Norway for the model experiments. Thereafter the ship continued to Isl. of Grain and unloaded the rest of the cargo. The unloading at Isl. of Grain started on Jan 29. at 1040 and was finished on Jan 30 at 0700. The distribution of the cargo is shown on Figure 2, including the unloading plan for the three ports. The tanks marked with A were unloaded at Lyme Bay, B at Le Havre and C at Isl. of Grain.

Concurrently with the unloading at Isle of Grain, ballast was filled into the permanent ballast tanks wing tanks No. 3 Port and Starboard, cargo tanks wing tanks No. 2 Port and Starboard and wing tanks No. 5 Port and Starboard. Because of the limited draft for departure at Isl. of Grain, wing tanks No. 2 Port and Starboard and No. 5 Port and Starboard were not completely filled before departure. The ballast condition at departure is shown on Figure 3, while Figures 4 and 5 show the ballast condition during the voyage.

Departure Isl. of Grain took place on Jan 30. at 0900, and the ship was abreast of Cape Town on Feb 14. at 1800.

II C. Ballast arrangements, [illegible]hing and sampling.

The outline for the sampling program to be conducted onboard the M/T "BERGE PRINCESS" specifies that samples should be drawn during the settling period of the dirty ballast and during discharge of ballast water. Samples should be drawn from a pair of identical wing tanks, a pair of identical center tanks, as well as from the slop tanks. One of the wing tanks and one of the center tanks should have a relatively large quantity of oil remaining after unloading, comparable to the conditions in tanks that are not properly stripped after unloading, and one wing tank and one center tank should contain as small quantities of oil as possible, comparable to conditions in tanks that are very well stripped after unloading. The tanks selected for monitoring were wing tanks No. 5 Port and Starboard, and center tanks No. 1 and No. 3. Port wing tank No. 5 was stripped extra thoroughly, while Starboard wing tank No. 5 was stripped according to normal good practice. Both center tanks No. 1 and No. 3 were stripped according to good normal practice, and in order to obtain different quantities of oil remaining in these tanks, the piping system was washed into center tank No. 3. Slop tanks were to be filled with slop water from the flushing of the empty cargo tanks, and the stripping pumps should be used for stripping. During the settling of slop water, samples were to be drawn regularly.

Center tanks No. 2 and No. 5 should be washed to clean ballast standard. Samples should be drawn regularly of the water that was discharged overboard from the Starboard slop tank during tank washing, and samples should further be drawn from the settled water in the slop tank during the period after tank washing. The ejector should be used for stripping during tank washing. Samples should also be drawn from the slop water during the last discharge from the slop tanks.

Before departure from Isl. of Grain on Jan 30., wing tanks No. 5 Port and Starboard were filled to an ullage of 13 metres. On Jan [illegible] ballast was discharged from wing tanks No. 2 Port and Starboard, using cargo pump No. 1. Ballast was further pumped out of wing tanks No. 3 Port and Starboard, using clean ballast pump. Center tanks No. 1 and No. 3 were filled to an ullage of 4 m., using cargo pumps No. 2 and 3. The same day, the wing tanks No. 5 Port and Starboard were also filled to an ullage of 4 m., using cargo pump No. 4. Since a valve on the cross-over line on the suction side of the pumps in the pump room was left open, it must be assumed that the ballast that was discharged from wing tanks No. 2 Port and Starboard was drawn into cargo pumps Nos. 2 and 3 and pumped into center tanks Nos. 1 and 3.

II D. Methods for sampling.

Two methods were used for drawing samples of the ballast and slop water from the tanks. The most used method was to lower a hose into the tank and pump the sample out, but samples were also drawn by the use of half liter glass bottles that were lowered into the tank and opened at the desired depth to obtain samples from these specific points. There were two difficulties in connection with the sampling, one of which was the oil layer that was floating on the surface of the ballast water in the tanks, and another one which was the fact that the tanks were under inert gas pressure and it was not desirable to open the tanks too often or longer than necessary.

a) Sampling equipment

The equipment carried along for sampling consisted of:

600 100 ml. dark glass bottles
30 m. 2 in. plastic tube
1 pump
100 m. ½ in. thick walled hose
12 m. 7 in. plastic tube (PVC)
2 units of apparatus to draw samples directly from the [illegible]

level in the tanks, using half litre glass bottles
l measuring tape.

In addition the oil/water interface detector from the ship was used.

b) Hose and pump method, see Figure 6.

In order to avoid contamination of the sampling hose when it was lowered through the oil layer on the top of the water, a 5 meter long 2 in. plastic tube was first lowered into the tank. At the bottom end of the tube a lead plate was fastened to keep the tube in vertical position. To keep the oil from entering the tube when it was lowered through the oil layer, a plastic bag was wrapped over the lower end, and the tube was filled slowly with water as it was lowered down into the tank, keeping the level inside the tube equal to the outside level. When the tube was in desired position, the plastic bag was drawn off by use of a wire and hauled up to deck. In this way a plastic tube was placed in each of the ttanks for sampling To prevent the possibility that some oil might have settled on the surface inside the tube since the sampling pipe was last used, an absorbent material was used before every sampling to clean out any oil inside the tube. To simplify the sampling procedure the half inch sampling hose which was 26 m. long, was marked at 7 m., 16 m., and 25 m. A metal weight was fastened to the end of the hose to make it easier to slide the hose through the plastic tube and to ensure that it would hang as vertical as possible.

The samples were drawn from the tanks using a hand pump. For each level, before samples were drawn, 6 times the total volume of the sampling hose was first pumped through the hose to ensure that there was no contamination in the hose or in the pump. Furthermore, at frequent intervals clean sea water was pumped through the hose an the pump and samples were drawn of the sea water before and after it had passed through the hose pump system. In this way, it could be detected if contamination of the sampling equipment occurred.

c) Sampling glass method, see Figure 7.

In order to make it possible to draw samples from tanks that had a larger ullage than that the pump could draw from, a different sampling method was used. With this method, a half liter sampling bottle was lowered into the tanks with suitable weights, and the sampling cock was opened and closed from the deck when at the desired level. For lowering or pulling up , a measuring tape was first used, but this broke after being used a short time and the wire for closing of the sampling cock was thereafter used for lowering and raising. In this way, this wire was kept in tension, such that the sampling cock was closed at all times during lowering and pulling up.

As shown on Figure 7, the sampling cock is controlled using a thin nylon line which passes through holes in the carrying bracket. It was first intended to use this nylon line all the way up to the deck to control the sampling cock, but the nylon line was too flexible and it was very difficult to have any feeling of the position of the cock. The nylon line was therefore cut about 20 cm. from the carrying bracket and a thin wire was used from there on to the deck. In this way, it was possible to have good control of the cock position. To avoid losing the apparatus into the tank if the nylon line should break, an extra safety loop was attached from the wire to the carrying bracket.

To avoid contaminating the apparatus as it would be if it should pass through the oil layer on the top of the water in the tank, it was here used a 7 in. plastic tube to lower the apparatus through the oil layer down into the water. This plastic tube was lowered in the same way as the 2 in. tube described in the chapter about the sampling hose and pump. When the samples were taken up, part of the content was transferred to the 100 ml. sampling bottles.

This arrangement was in particular intended for use in the slop tanks. Due to the thick oil layer and relatively large variations in ullage in these tanks, however, it became difficult and near impossible to keep the 7 in. plastic tubes clean. Due to the fact that the tanks were under inert gas pressure, the tank hatches could not be kept open at all times to lower or raise the plastic tubes as the ullages varied. As a result, the plastic tubes were contaminated with oil on the inside and could not be used.

For the other tanks the sampling bottle arrangement worked to the satisfaction of the operators.

d) Oil/water interface detection.

In order to measure the oil layer that was floating on the water in the tanks, the ships usual oil/water interface detector was used. When the oil layer was measured it was made several consecutive measurements in each tank. These varied very little which may indicate that this type of oil/water interface detector works very well.

The result of the measurements is shown on Figure 8, and is listed in Table 2 "MEASUREMENT OF OIL LAYER". The figure shows the oil quantity in cu.meters and in per cent of tank volume.

e) Comments concerning ullage.

According to the calibration tables for the ship, the ullage is measured from the ullage hatch on the top of the tank hatch, down to the liquid level. In the report forms for the water samples, the ullage and the depth of the sampling points are measured from the edge of the Butterworth hatch where the samples were drawn.

II E. Description of the sampling.

a) Sea water.

Sampled ahead and behind sampling hose and pump.

Every day one bucket of sea water was drawn from the sea water inlet in the engine room. A sample of the water was first drawn directly from the buckets, thereafter a sample of the water was drawn after it had passed the sampling hose and pump to control the cleanliness of the sampling equipment. On Feb 3. the sea water showed an oil content of 6 ppm after it had passed the sampling hose and the pump. All the other samples showed oil contents of 1 ppm or below this. The result of this sampling is listed in Table 3.

b) Wing tanks No. 2 Port and Starboard.
(16381 m^3. ea., 29.61 m. deep).

Wing tanks No. 2 Port and Starboard were unloaded and stripped on Jan 27. Both tanks were well stripped as usual. The tanks were ballasted with clean sea water, using the clean ballast pump, while the unloading of the other tanks were still going on. The ballasting started on Jan 29. at 2030 hrs and was finished on Jan 30. at 0400 hrs, and the tanks were filled to an ullage of 14 m. The tanks were not filled up because of the limited draft for departure Isle of Grain.

Since it was desired to carry dirty ballast on Center Tanks No. 1 and No. 3, the ballast in wing tanks No. 2 Port and Starboard was discharged on Jan 31. from 1345 until 1800 using cargo pump No. 1. Because of 10 to 15 degrees rolling, the discharge was stopped at an ullage of 27.2 m. on both tanks. This leaves the liquid level 2.41 m. from the bottom. The average oil content of the discharged water was 130 ppm, and the water had been allowed to settle for 35 hours.

At the same time that cargo pump No. 1 was used for discharge from wing tanks No. 2, cargo pumps Nos. 2 and 3 were used to pump ballast water into center tanks No. 1 and 3. In this way the cargo pump No. 1 discharged ballast water to the same cross-over-line through which the other cargo pumps took in sea water, and it must be assumed that the water being discharged from pump No. 1 was drawn into pumps Nos. 2 and 3 and pumped into center tanks Nos. 1 and 3, thus filling these tanks not with clean sea water but with ballast from wing tanks No. 2.

On Feb. 3. the rest of the ballast water in wing tanks No. 2 Port and Starboard was transferred to Port slop tank. The connecting valve between the Port and Starboard slop tanks was open.

The results of the sampling from wing tanks No. 2 Port and Starboard is listed in Table 4.

c) Wing tanks No. 5 Port and Starboard (24585 m^3. ea., 29.6 m. deep).

Wing tanks No. 5 Port and Starboard were unloaded and stripped on Jan 27. While wing tank No. 5 Starboard was well stripped as usual, an effort was made to empty wing tank No. 5 Port thoroughly in order to leave as little oil as possible in this tank. On Jan 29, from 2030 until Jan 30, 0400 both tanks were ballasted with clean sea water, using the clean ballast pump for filling. Both tanks were filled to an ullage of 13 m. The ballasting took place while other tanks were being unloaded. The tanks were not filled completely due to the limited draft for departure Isl. of Grain.

On Jan 31, from 1430 until 1900 more ballast was pumped into the tanks using cargo oil pump No. 4. The tanks were filled to an ullage of 4.0 m. Due to heavy rolling, no samples were drawn of the ballast water until Feb. 1. From then on samples were drawn regularly.

On Feb. 7 0200 until 0445, ballast was pumped out using two cargo pumps until the ullage was 17 m. During the night between Feb 7. and Feb 8. settled ballast water was decanted from the tanks to center tank No. 5. This was continued until the ullage in the wing tanks No. 5 was 22 m. On Feb 7, at 1000 the oil layer on the water in wing tank No. 5 Port was 5 cm. which equals 44 m^3. of oil, and in wing tank No. 5 Starboard, the layer was 13 cm., which equals 113 m^3. of oil.

On Feb 8, from 1807 to 2125, ballast was pumped out from wing tank No. 5, using one cargo pump. The discharge was stopped at an ullage of 28 m., which gave the liquid level of 1.6 m. in the tanks. This leaves 1.55 m. of water below the oil level in wing tank No. 5 Port and 1.47 m. below the oil layer in wing tank No. 5 Starboard.

Discharged overboard from wing tanks No. 5 Port and Starboard:
On Feb 7, 0200 until 0445, 22654 m^3. was discharged with an average oil content of 20 ppm. This equals 0.453 m^3. of oil or 9.6 l./n.mi.
On Feb 8, 1807 to 2125, 10444 m^3. was discharged with an average oil content of 100 ppm. This equals 1,044 m^3. of oil or 19 l/n.mi.
On Feb. 9, wing tanks No. 5 Port and Starboard were stripped into Port slop tank with the valve between the Port and Starbord slop tanks open.

The result of the sampling for wing tanks No. 5 are shown in Tables 5, 6 and 7 and in Table 1 "Summary of settled ballast water and slop water discharged between Feb. 3, and 13, 1973".

d) Center Tank No. 1
(25183 m^3., 31.07 m. deep).

Center Tank No. 1 was unloaded and stripped on Jan. 27. The tank was not washed or flushed before filled with sea water for ballast. The ballasting took place on Jan. 31, from 1320 until 1800. 2324[illegible] of sea water was pumped into the tank, giving an ullage of 4 m.

Due to heavy rolling, samples of the ballast water were not drawn until Feb. 1, at 1400. The ballast water had then settled for 20 hours further samples were drawn at regular intervals from this time on.

On Feb. 6, from 0600 until 0800 ballast water was decanted from the tank until the ullage was 11 meters. This was done to increase the trim by stern for tank washing of Center Tanks Nos. 2 and 5.

On Feb. 7, settled ballast water was decanted from Center Tank No. 1 to Center Tank No. 2 until the ullage in Center Tank No. 1 was 21.5 meters. At 1000, the oil layer on the water in Center Tank No. 1 was 15 cm, which equals 129 m^3 of oil.

On Feb. 8, from 1900 until 2045, the ballast water was discharged from Center Tank No. 1, using one cargo pump. Discharging was stopped at 29.8 meters ullage. The liquid level in the tank at this point was 1.27 meters, which gives 1.12 meters of water below the oil layer.

Quantities discharged from Center Tank No. 1:
On Feb. 6, from 0600 until 0800 - 6013 m^3 was decanted with an average oil content of 30 ppm. This gives 0.110 m^3 of oil, or 5.3 l./n.mile.
On Feb 8, from 1900 until 2045 - 7030 m^3 was pumped out with an average oil content of 200 ppm. This equals 1.426 m^3 of oil, or 47.5 l./n.mile.

On Feb. 9, the remaining 1.27 meters of oil/water in Center Tank No. 1 was stripped into Port sloptank. The valve between Port and Starboard sloptanks was open.

The result of the sampling of Center Tank No. 1 is listed in Table 8 and in Table 1 "Summary of settled ballast water and slop water discharged between 3 Feb and 13 Feb 1973".

e) Center Tank No. 3
(24936 m^3., 30.31 m. deep).

Center Tank No. 3 was unloaded and stripped on Jan. 30, 1973. On Jan. 31, the cargo piping system was flushed and the oil/water mixture was pumped into this tank before it was filled with sea water. Ballasting of the tank took place on Jan. 31, from 1320 until 1800. A total of 22597 m^3. was pumped in, giving an ullage of 4 m.

Due to heavy rolling of the ship, it was not possible to draw samples of the ballast water before on Feb. 1, at 1435. The dirty ballast water had at this time settled for 20.5 hrs. Following this sampling, further samples were drawn regularly. On Feb. 7, at 1000 hrs., the oil layer on the water in the tank was measured to be 66 cm. which equals 567 m^3. On Feb. 8, settled ballast water was decanted from Center tank No. 3 to Center tank No. 2 until the ullage of Center tank No. 3 was 12.2 m. From 1600 until 1900 the same day, ballast was discharged from center tank No. 3, using two cargo pumps until 1800, and one pump only thereafter. Discharging was stopped at 28.6 m. ullage, which left the liquid level in the tank 1.71 m. above the bottom. This leaves 1.05 m. water below the oil layer.

The quantities discharged overboard from Center tank No. 3 were as follows:
On Feb. 8, 1600 - 1800, 11177 m^3. was discharged, with an average oil content of 15 ppm. This gives 0.168 m^3. of oil or 4.9 l./n.mi.
On Feb. 8. 1800 - 1900, 2920 m^3. was discharged, with an average oil content of 30 ppm. This gives 0.088 m^3. of oil or 5.2 l./n.mi.

On Feb. 8, 1930 to Feb. 9, 0030, the rest (1.71 m.) was stripped from Center tank No. 3 into Port slop tank. The valve between the Port and Starboard slop tanks was open.

The result of the sampling from Center tank No. 3 is listed in Table 9 and in Table 1 "Summary of settled ballast water and slop water discharged between Feb. 3, and Feb. 13, 1973".

f) Center Tank No. 2
(24936 m^3, 30.32 m. deep)

Center Tank No. 2 was unloaded and stripped on Jan. 27. On Jan. 31, at 1100, clean sea water was let into the tank until the water level was 1 meter above the bottom. This water was left in the tank for flushing and was stripped out on Feb. 2, at 200.

On Feb. 6, from 0800 until 1700, Center Tank No. 2 was washed to clean ballast standard. The water from the tank washing was pumped to the slop tanks and samples were drawn as it was discharged from the secondary slop tank. The result of the sampling is listed in Table 14. During the night between 7 and 8 Feb, 15,500 m^3 of settled ballast water from Center Tanks Nos. 1 and 3 was decanted to Cente Tank No. 2.

On Feb. 8, from 1015 until 1530, clean sea water was pumped into Center Tank No. 2 until the ullage was 4 meters. Samples of the ballast water in this tank 15 minutes after the tank was filled showed an oil content of 27 ppm. The result of the sampling is listed in Table 10.

g) Center Tank No. 5
(37404 m^3, 30.31 m. deep)

Center Tank No. 5 was unloaded and stripped on Jan. 30. On Jan 31 at 1100, clean water was drained into the tank until a water level of 1 meter was reached. The water was left in the tank for flushing until it was stripped out on Feb. 3 at 1800. The tank was washed to clean ballast standard from Feb. 6, at 1730, until Feb 7 at 0200. The water from the tank washing was pumped to the slop tanks and samples were drawn as it was discharged from the secondary slop tank. The result of this sampling is listed in Table 15.

During the night between 7 and 8 Feb, 9,500 m^3 settled ballast water from Wing Tanks No. 5, Port and Starboard, was decanted to Center Tank No. 5. On Feb. 8, from 1015 until 1530, clean sea water was pumped into the tank until an ullage of 10 meter was reached. Samples of the ballast water in Center Tank No. 5, 30 minutes after filling was completed, showed oil content of 15 ppm. The result of the sampling is listed in Table 11.

h) Slop Tanks Port and Starboard (3776 m^3. ea., 24.46 m. deep).

According to the calibration table, there remains 217 m^3. in each tank when the ullage is 24.46 m. but the table ends at this point.

On Jan 31, the empty cargo tanks were filled with clean sea water to about 1 m. above the bottom for flushing of the bottom. On Feb. 2 and 3, the tanks were stripped. Stripping pumps were used and the contaminated water was pumped into Port slop tank, with the valve between Port and Starboard slop tanks open. On Feb 3, at 1600, both slop tanks were full and 3 m. was decanted from Starboard slop tank. The decanting stopped at 1615. The total quantity decanted was 602 m^3., with an assumed oil content of 120 ppm, which gives 0.072 m^3. of oil or 18.0 l./n.mi.

At 1800, the stripping after flushing was finished, and at 1900 samples were drawn of the water in the slop tanks. The average oil content in the Port slop tank was 150 ppm, and in the Starboard slop tank 100 ppm. On Feb 5, from 1430 to 1700, settled slop water was decanted from the Starboard slop tank. The valve between Port and Starboard slop tanks was open. The decanting was stopped when the ullage in the Starboard slop tank was 16.5 m. and in the Port slop tank 13.5 m. A total of 4753 m^3. was decanted, with an average oil content of 40 ppm. This equals 0.190 m^3. of oil or 4.5 l./n.mi.

On Feb 5, at 0830, the oil layer on the water in Starboard slop tank was measured to be 18 cm.; this equals 35 m^3. At 1030 the same day. the oil layer on the water in the Port slop tank was measured to be 255 cm., which equals 515 m^3. At 1430 the same day, the average oil content in the water below the oil layer in the Port slop tank was 22 ppm, and in the Starboard slop tank 47 ppm.

On Feb 6, at 0800, washing was started in center tank No. 2, using 11 washing machines with a capacity 35 m^3. for each machine. The tank was stripped, using Port ejector into Port slop tank. The valve between the slop tanks was open. At 0840, cargo pump No. 1 was started to discharge from Starboard slop tank. The quantity discharged was controlled by adjusting the pressure valve for the pump The cargo oil pump was used to discharge the water instead of decanting, in order to be able to draw samples of the water that was discharged. The difference between the liquid levels in the slop tanks was kept to about 7 m. The ullage in the Port slop tank varied between 9 and 5 meters while in the Starboard slop tank, the ullage varied between 16 and 12 meters The flow through the slop tanks was estimated to be 1435 m^3./hour. The average total slop volume in the slop tanks during the washing process was 4300 m^3.

At 1700, the washing of center tank No. 2 was finished. The total volume that was discharged from Starboard slop tank was 11910 m^3 with an average oil content of 125 pp , which equals 1.489 m^3. oil. The discharge took place over a period of 8.3 hours, which resulted in a discharge rate of 10.5 l./n.mi. The maximum oil content of the water that was discharged from the Starboard slop tank during the washing period for center tank No. 2, was 380 ppm, which gives a rate of 32 l./n.mi.

On Feb 6, from 1700 until Feb 7, 0200, center tank No. 5 was washed, using 11 washing machines with a capacity of 35 m^3. each. The same method was used for stripping and discharging from the slop tanks as was used for washing of center tank No. 2. During the 9 hours that the washing went on, 12915 m^3. was discharged from the Starboard slop tank. The discharge had an average oil content of 160 ppm, which equals 2.066 m^3. of oil. This gives a discharge rate of 13.5 l./n.mi. The maximum oil content in the water that was discharged from the Starboard slop tank during this washing period was 248 ppm, which results in a discharge rate of 21 l./n.mi.

On Feb. 7, at 1100, the oil layer in the slop tanks was measured to be 417 cm. thick, which equals 788 m^3. in the Port slop tank and 41 cm. thick, which equals 78 cu.m. in the Starboard slop tank. At this point the ullage in the Port slop tank was 7.3 m., which gives a total slop volume of 2649 cu.m., and the ullage in the Starboard slop tank was 8.4 m., which gives a total slop volume of 2436 cu.m. in this tank. From 1430 until 1700 on the same day, settled slop water was decanted from the Starboard slop tank, with the valve between the Port and Starboard slop tanks open. When the decanting was stopped, the ullage in the Port slop tank was 16 m. and in the Starboard slop tank 20 m. This gives a remaining slop in the tanks of 1107 cu.m. and 561 cu.m., respectively. The total volume discharged was 3417 cu.m. during the 2.5 hrs. Since the settled slop water was decanted rather than being pumped out, there was no possibility of drawing samples of the discharge, and it was therefore estimated that the oil content of the slop water was the same as the last sample drawn during washing, 100 ppm of oil. This would equal 0.342 cu.m. oil or 8.1 l./n.mi.

On Feb 8, 1930, until Feb 9, 0030, center tank No. 3 was stripped into Port slop tank, with the valve between Port and Starboard slop tanks open. On Feb 9, 0830 until 1800, center tank No. 1 and wing tanks No. 5 Port and Starboard were stripped into Port slop tank, with the valve between Port and Starboard slop tanks open. This resulted in ullages of 6.2 m. and 6.8 m. in the Port and Starboard slop tanks, respectively, giving a volume of 2864 cu.m. in the Port slop tank and 2746 cu.m. in the Starboard slop tank. On Feb 9, at 1900, the oil layer on the water in the slop tanks was measured to be 762 cm. thick in the Port slop tank and 48 cm. thick in the Starboard slop tank. This equals 1410 cu.m. and 94 cu.m., respectively.

On Feb 10, at 0850, 15 hours after the last stripping into the slop tanks, discharge of settled slop water from the Starboard slop tank was started. The valve between the Port and Starboard slop tanks open. It was also opened for decanting of Starboard slop tank directly into the sea. At 1135, the valve between the Port and Starboard slop tanks was closed. At this point the ullage in the Port slop tank was 12.8 m. and in the Starboard slop tank 14.4 m. The total discharged volume was 2623 cu.m., with an average oil content of 180 ppm, which equals 0.472 cu.m. of oil. This gives an overboard discharge rate of 10.3 l./n.mi. At 1230, the decanting was stopped but it was continued to discharge from the Starboard slop tank. using a stripping pump. From 1135 until 1230, 712 cu.m. of settled slop was discharged, with an average oil content of 350 ppm. This equals 0.249 cu.m. of oil, which gives a discharge rate of 15.6 l./n.mi.

From 1230 until 1315, the discharge using a stripping pump was continued. In this period, [illegible] slop was discharged, with an average oil content of 400 ppm. This equals 0.077 cu.m. of oil, which results in a discharge rate of [illegible].4 l./n.mi. At 1315, the ullage in the Starboard slop tank was 2[illegible].0 m. The overboard discharge was stopped, and the rest in the Starboard slop tank was stripped over to the Port slop tank. At 1510, the Starboard slop tank was empty and the ullage in the Port slop tank was 10.5 m. The total discharge volume from the slop tanks between 0850 and 1315 was 3506 cu.m., of which 0.7[illegible] cu.m. was oil.

On Feb 13, at 0900, the oil layer on the slop water in the Port slop tank was measured to be 930 cm. thick, which equals 1457 cu.m. of oil. The settling time after last stripping into Port slop tank was at this point, 66 hours. A volume of 1457 cu.m. in the Port slop tank gives an ullage of 13.81 m. At 0935 discharge of settled slop water from the Port slop tank, using one stripping pump, was commenced. At 1130, the ullage was 13.4 m., and oil content of the water after the pump was increasing rapidly. The discharge would therefore normally have been stopped at this point. The total volume discharged between 0935 and 1130 was 528 cu.m. with an average oil content of 640 ppm, which equals 0.338 cu.m. of oil. This gives a discharge rate of 10.5 l. of oil/n.mi.

In the interest of the experiments, it was decided to go beyond normal operating practices and continue the discharge for a few minutes. This was done to obtain samples from the discharge to establish how rapidly the oil content of the discharge increased when the oil/water interface was approached closer than normal practice allows. The discharge was hence continued until 1135, with an additional discharge of 20 cu.m. The ullage in the tank at this time was 13.6 m, and sample 304 drawn at 1135 shows that the oil content at this point was 4%, which results in a discharge rate of [illegible] l/n.mi. With the ullage of 13.6 m, about 1492 cu.m. is left in the tank. Compared with the measurement with the oil layer at 0900, should therefore still be 35 cu.m. of water in the Port slop tank. The result of the sampling from the slop tanks is listed in Tables 12, 13, 14 and 15 and in Table 1 "Summary of Settled Ballast Water and Slop Water discharged between Feb 3 and Feb 13, 1973".

i) Oil Layer Samples.

A total of 13 samples were drawn from the oil layer in the port slop tank, as well as one sample from the oil layer on the ballast water in center tank No. 3. This sample was drawn on Feb 2.

Of the other samples, one was drawn on Feb 3, when the slop tank was filled with slop after the flushing of the empty cargo tanks. The remainder of the samples were drawn from the port slop tank after the last overboard discharge had been stopped. The samples were drawn consecutively at every meter depth in the slop. The result of the analysis show a relatively small variation around 20 - 25 per cent by weight of water in the slop.

The result of the sampling of the oil layers is found in Table 16.

III SAMPLING ONBOARD T/T "FERNCOURT".

An additional shipboard sampling program was conducted onboard the T/T "Ferncourt", belonging to the Fernley & Eger Shipowners of Oslo, Norway. The T/T "Ferncourt" has a deadweight tonnage of 244.000, and the samples were drawn from the center tank No. 3, which has a capacity of 10.000 cu. metres. A total of 21 samples were drawn from the ballast water in this tank, in addition to samples of the cargo oil for analysis reference standard. The T/T "Ferncourt" carried Kuwait crude with API of 31.7 from Mina Al Amadi, and the cargo was unloaded at Rotterdam on Jan 9, 1973. Center tank No. 3 was filled with clean sea water to an ullage of 1.5 m. on Jan 11, 1973, and samples were drawn 3, 8, 14, 32 and 56 hours after the filling was completed. The tank is 28 meters deep, and the samples were drawn from three levels, which were respectively 3.5, 14.0 and 27.0 meters below the deck. The tank was judged to have a relatively large amount of oil remaining. The equipment used for sampling was similar to that described for the shipboard sampling onboard the M/T "Berge Princess". A two-inch tube was placed in position extending below the oil layer on the top of the water, taking care that no oil was allowed inside this tube. A small hose was lowered through the tube down into the tank for sampling. The hose was weighted at the lower end to keep it vertical. On deck, the hose was connected to the suction side of a spray gun, and large quantities of water were allowed to flow through the sampling equipment before the samples were actually taken. The sampling program was conducted by the Shipowner's inspector, who is a chemical engineer, and the samples were stored on glass bottles which were prepared by the Central Institute of Industrial Research, Oslo, as described in the report from this institute in the next section.

The analyses of the samples show that the oil content of the ballast water in the tank is very low. It is, however, interesting to note that the oil content at the upper sampling point is increasing with time. This is probably due to the build-up of the oil layer of the top, causing the oil/water interface to extend further into the tank as the oil layer thickens. The upper sampling point is only two meters below the surface of the ballast in this tank, and it is apparent from the increase in ppm that oil/water interface is approaching this point. It is furthermore clear that it should be possible to discharge the bulk of this ballast directly to the sea without exceeding 30 ppm for instance.

The result of the analysis of the samples is listed in Table 18.

IV TANK SECTION MODEL EXPERIMENTS.

The model experiments were conducted in order to establish the relationship between the conditions onboard a tanker and the conditions in a tank section model in the laboratory. The model experiments herein were meant as reference experiments and it was attempted to simulate the operations onboard the M/T "Berge Princess" as much as possible. Samples were drawn after the same period of settling and at depths relative to those onboard. The crude oil used for the experiments was pumped from the ship's cargo in Le Havre and sent to Norway.

Three series of experiments were conducted, using the tank section model as center tanks and wing tanks with little and much oil remaining, and as slop tanks in series.

IV A. Description of the experiment.

The model experiments were conducted in a tank section model consisting of three different tanks (two wing tanks and one center tank), as shown on Figures 9 and 10. The center tank and the Starboard wing tank were used for dirty ballast tanks. Both wing tanks were used for slop tanks, and the center tank was used to blend oil and water for a simulation of the flushing process. The result of the analysis of the samples is listed in Table 19.

The experiments were conducted as follows:

a) Sample series 1 The center tank and the starboard wing tank were used for "dirty ballast tanks" containing as little oil as possible. The tanks were sprayed with 0.6 % and 0.2 % crude oil, respectively. The tanks were then filled with fresh water until the liquid level was 1 meter above the bottom of the tank. The samples were drawn, following the onboard sampling program as close as possible. Table 19 shows the sampling program and the results of the sampling. After 63 hours, the free water was drained from both tanks.

b) Sample series 2 The center tank and the starboard wing tank were used for "dirty ballast tanks", containing relatively much oil. It was assumed that the oil from the sample series No. 1 remained in the tanks and more oil was added to bring the oil quantity in the tanks to 2.5 % in the center tank and 0.5 % in the wing tank. Sampling was conducted as for sampling series 1.

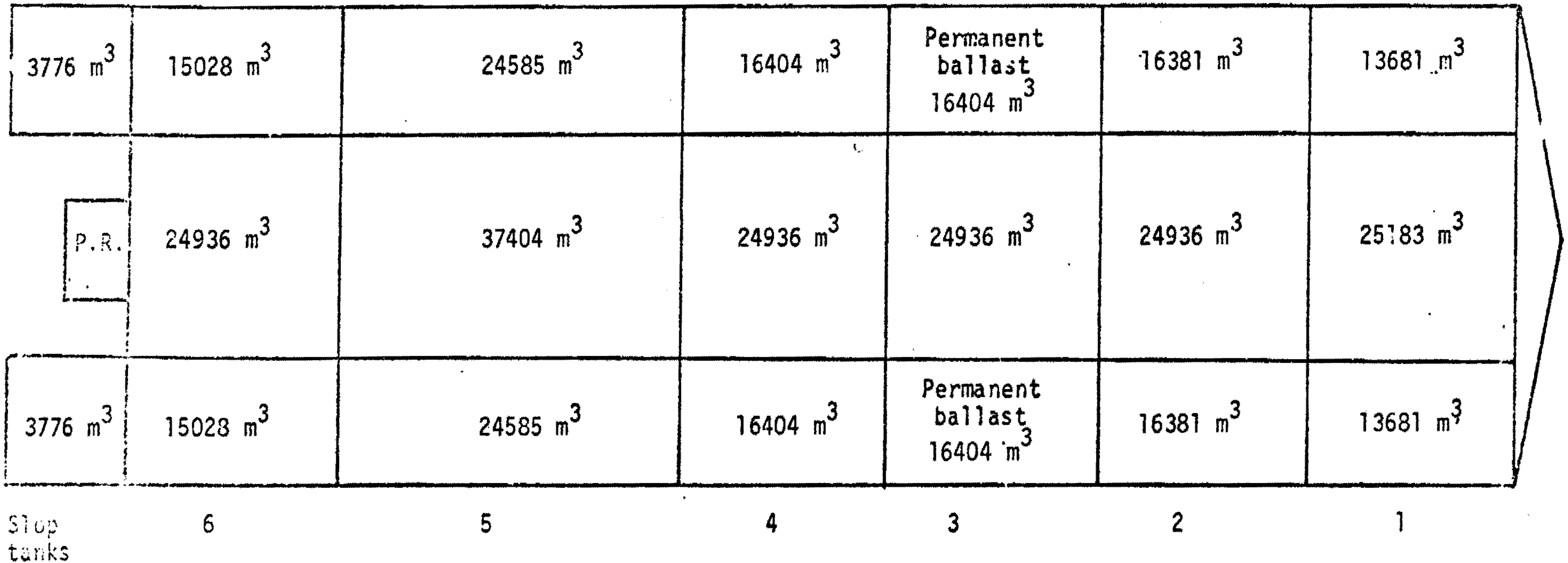
c) Sample series 3 Port and Starboard wing tanks were used for "slop tanks" and it was an open connection between them with an inlet near the bottom of the port wing tank and an outlet around the middle of the starboard wing tank. To simulate the flushing of the cargo tanks, the center tank was used to blend 5.85 litres (7.5%) crude oil and 72 litres (92.5%) of water. This oil/water mixture was pumped from the bottom of the tank and entered the port slop tank about halfway up. A new quantity of the oil/water mixture was then prepared in the center tank and again pumped into the port wing tank. This was repeated another seven times, simulating the pumping of the flushing water from nine cargo tanks, as were done onboard. The sampling program followed the onboard sampling program as closely as possible.

d) Sample series 4 The slop tanks were now full of slop from sample series No. 3. At this point, 38.5 % of the total slop water quantity was drained out, leaving 443 litres of slop. To simulate slop water from the washing process, oil and water was mixed by the use of an ejector, and the mixture was pumped into the primary slop tank (the port tank) about halfway up. The flow corresponded to the flow onboard. Samples were drawn of the oil water mixture in order to control the oil content. Samples were also drawn of the water being discharged. After completion of sample series 4, the slop water was left to settle for 15 hours.

e) Sample series 5 Free water was drained from the secondary slop tank, using the same discharge rate as used during sample series No. 4, until the interface approaced the bottom of the tank. The slop tanks were connected through an open connection. Samples were drawn of the discharge water.

f) Sample series 6 The oil that remained in the secondary slop tank was pumped into the primary slop tank. The content of this tank was allowed to settle for 66 hours. The free water in the tank was thereafter drained with the same discharge rate as used in sample series No. 4, until the interface approached the bottom of the tank. Samples were drawn of the discharge water. In this case samples were also drawn of the oil remaining in the tanks, to find the water content of the oil.

M/T. "BERGE PRINCESS."



	Slop tanks	6	5	4	3	2	1
	3776 m^3	15028 m^3	24585 m^3	16404 m^3	Permanent ballast 16404 m^3	16381 m^3	13681 m^3
	P.R.	24936 m^3	37404 m^3	24936 m^3	24936 m^3	24936 m^3	25183 m^3
	3776 m^3	15028 m^3	24585 m^3	16404 m^3	Permanent ballast 16404 m^3	16381 m^3	13681 m^3

PERMANENT BALLAST TANKS:

Fore peak	:	5953 tons
No. 3 wing tanks	:	33100 tons
Aft peak	:	1355 tons
Total	:	40408 tons

DIMENSIONS

LENGTH	O. A.	1,125′ – 0″	342.900 M
LENGTH	P. P.	1,080′ – 0″	329.184 M
BREADTH	MLD.	170′ – 0″	51.816 M
DEPTH	MLD.	91′ – 0″	27.737 M
DRAFT	SUMMER	71′ – 5 3/16″	21.773 M

TONNAGES

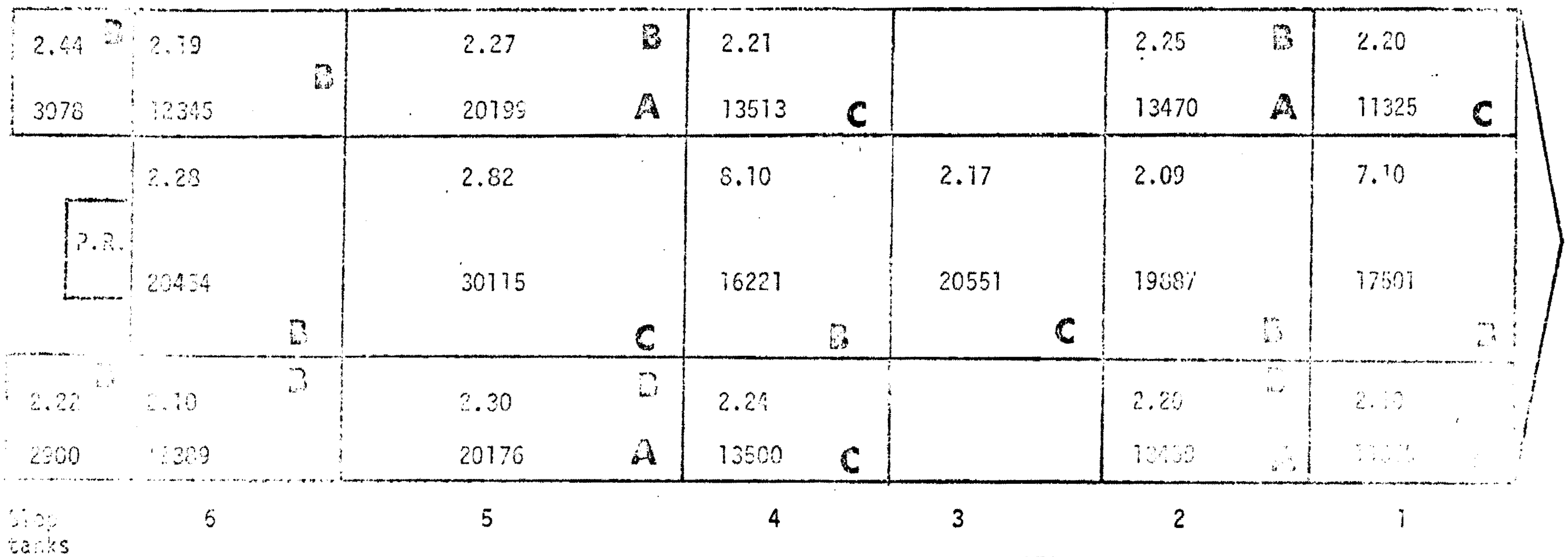
ITEM / TONNAGE	BELOW DECK	GROSS	NET
INTERNATIONAL	138,019.02	139,775.62	104,069.94
SUEZ CANAL	138,051.96	141,916.18	129,637.87

DEADWEIGHT ETC..

ITEM / LOAD LINE	FREE-BOARD	DRAFT	DISPL. LONG TS.	D/W LONG TS.
FRESH TROPICAL	5.000	22.731	327,435	287,050
FRESH	5.515	22.278	320,385	280,010
TROPICAL	5.565	22.226	327,773	287,168
SUMMER	6.018	21.773	320,400	280,015
WINTER	6.471	21.320	313,250	272,834

FIGURE 1

M/T. "BERGE PRINCESS."



On arrival Lyme Bay January 25th, 1973.

272,484 l/tons.

Temp. 62 °F.

Discharged LYME BAY,

A from 2 and 5 P. & S. 45960 l/tons.

Discharged Le Havre 126792 l/tons

from c. 1, 2, 4, 6

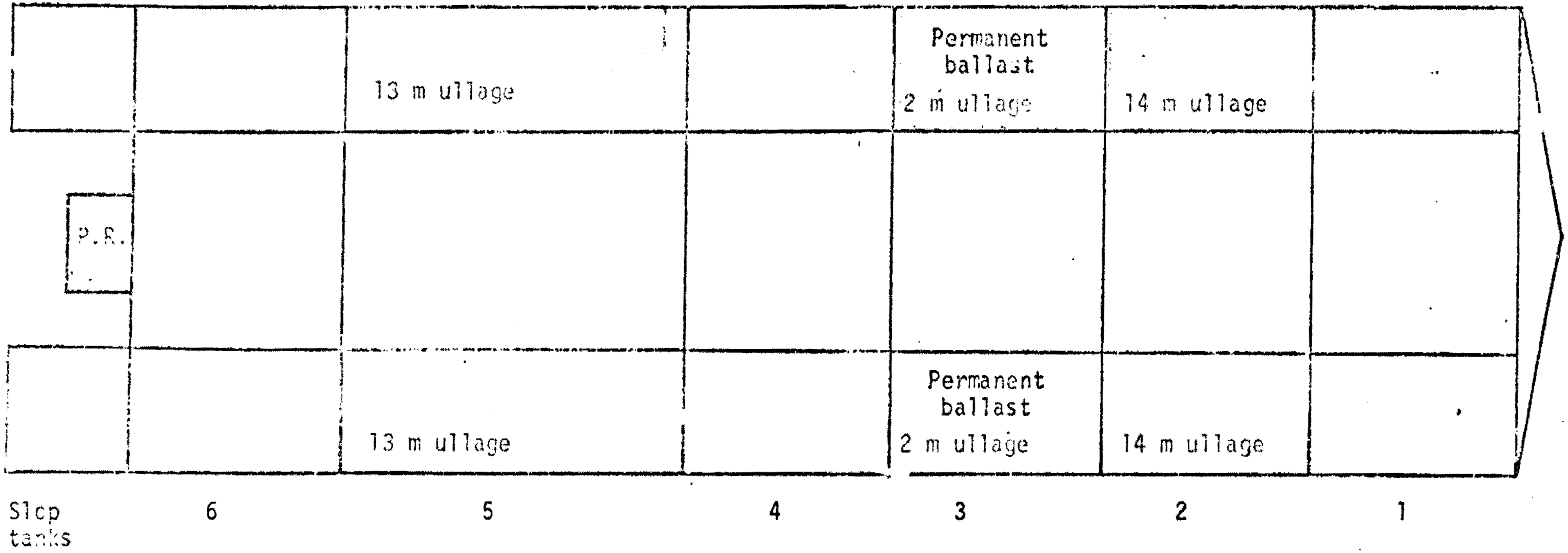
B P. & S. 2, 5, 6 and sloptanks.

C Discharged Isl. of Grain: the rest from C.3, 5.

P. & S. 1, 4.

FIGURE 2

M/T. "BERGE PRINCESS."



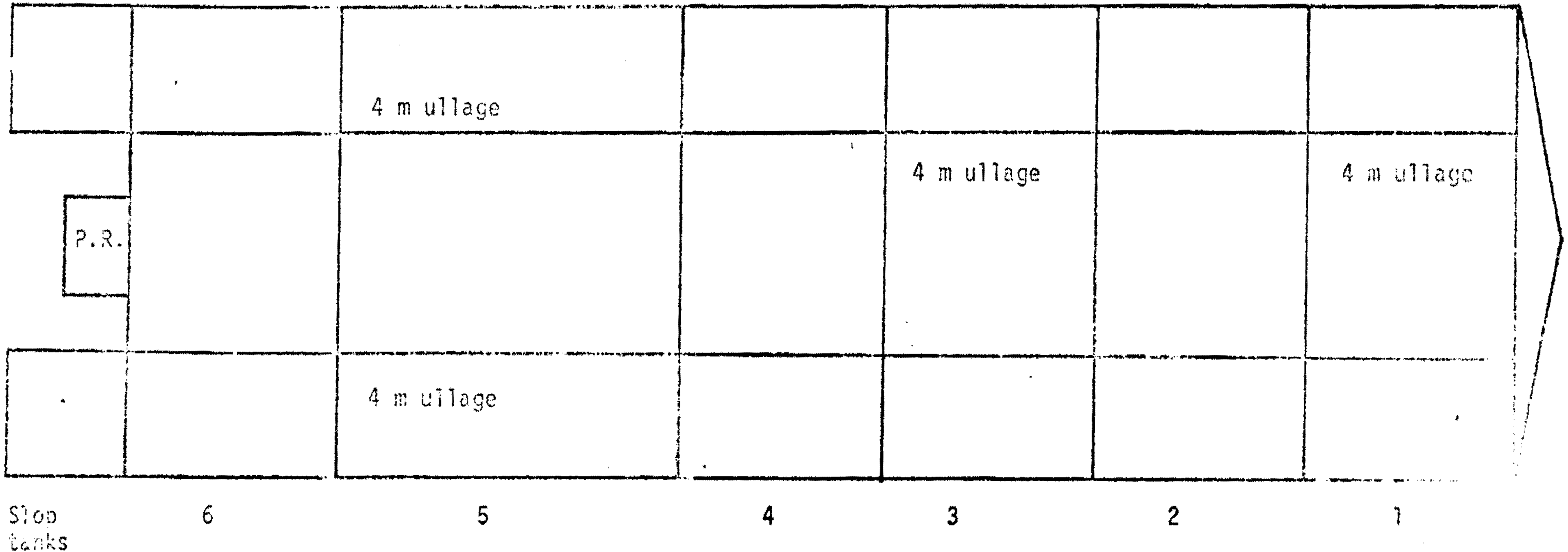
BALLAST AT DEPARTURE ISL. OF GRAIN ON JANUARY 30th, 1973.

Dirty ballast W.2	P.& S. :	18034 m^3
Dirty ballast W.5	P.& S. :	28812 m^3
Clean ballast W.3	P.& S. :	31114 m^3
Total ballast:		77960 m^3

Draft F. 8,0 m A 10,0 m M. 9,0 m.

FIGURE 3

M/T. "BERGE PRINCESS."



BALLAST ON JANUARY 31st, 1973, AT 1900 HOURS.

Dirty ballast C.1 : 23245 m^3
Dirty ballast C.3 : 22597 m^3
Dirty ballast W.5 P.& S.: 44500 m^3

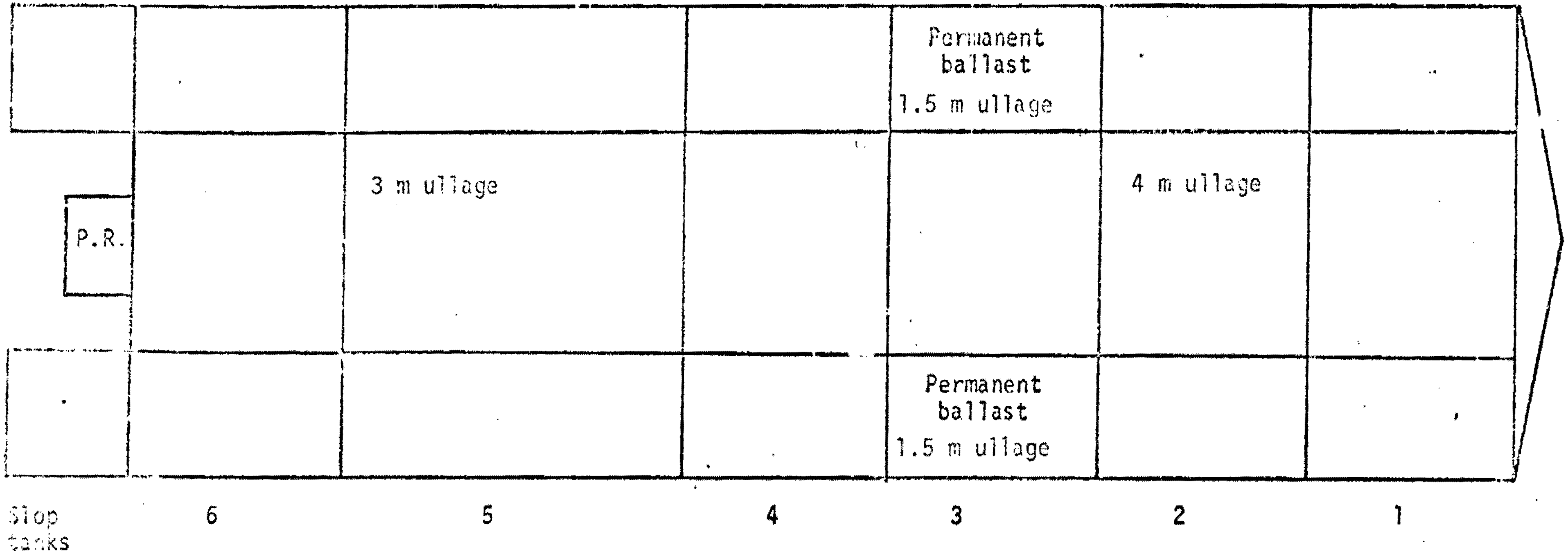
Ballast : 90342 m^3
Dirty water for flushing: 7000 m^3

Total Ballast : 97342 m^3

Draft: F. 9,2 m A. 11,2 m M. 10,2 m.

FIGURE 4

M/T. "BERGE PRINCESS."



BALLAST DISTRIBUTION AFTER TRANSFER ON FEBRUARY 8th, 1973.

Clean ballast C.2 : 22607 m^3
Clean ballast C.5 : 35186 m^3
Clean ballast W.3 P.& S.: 31732 m^3

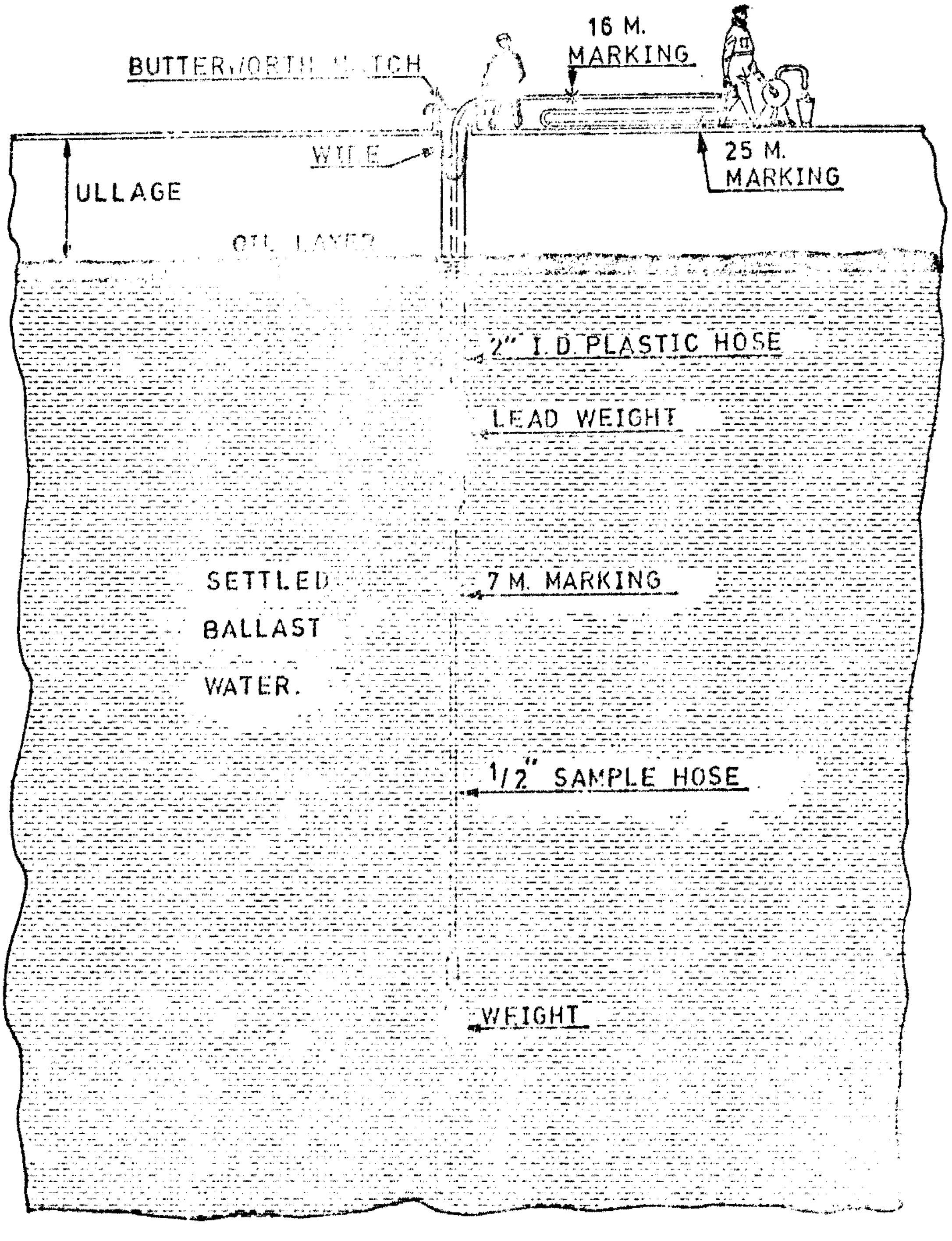
Ballast : 89525 m^3
Slop : 7000 m^3

Total : 96525 m^3

Draft: F.8,5 m A. 11,5 m M. 10,0 m.
Draft: F.8,7 m A. 10,7 m M. 9,7 m

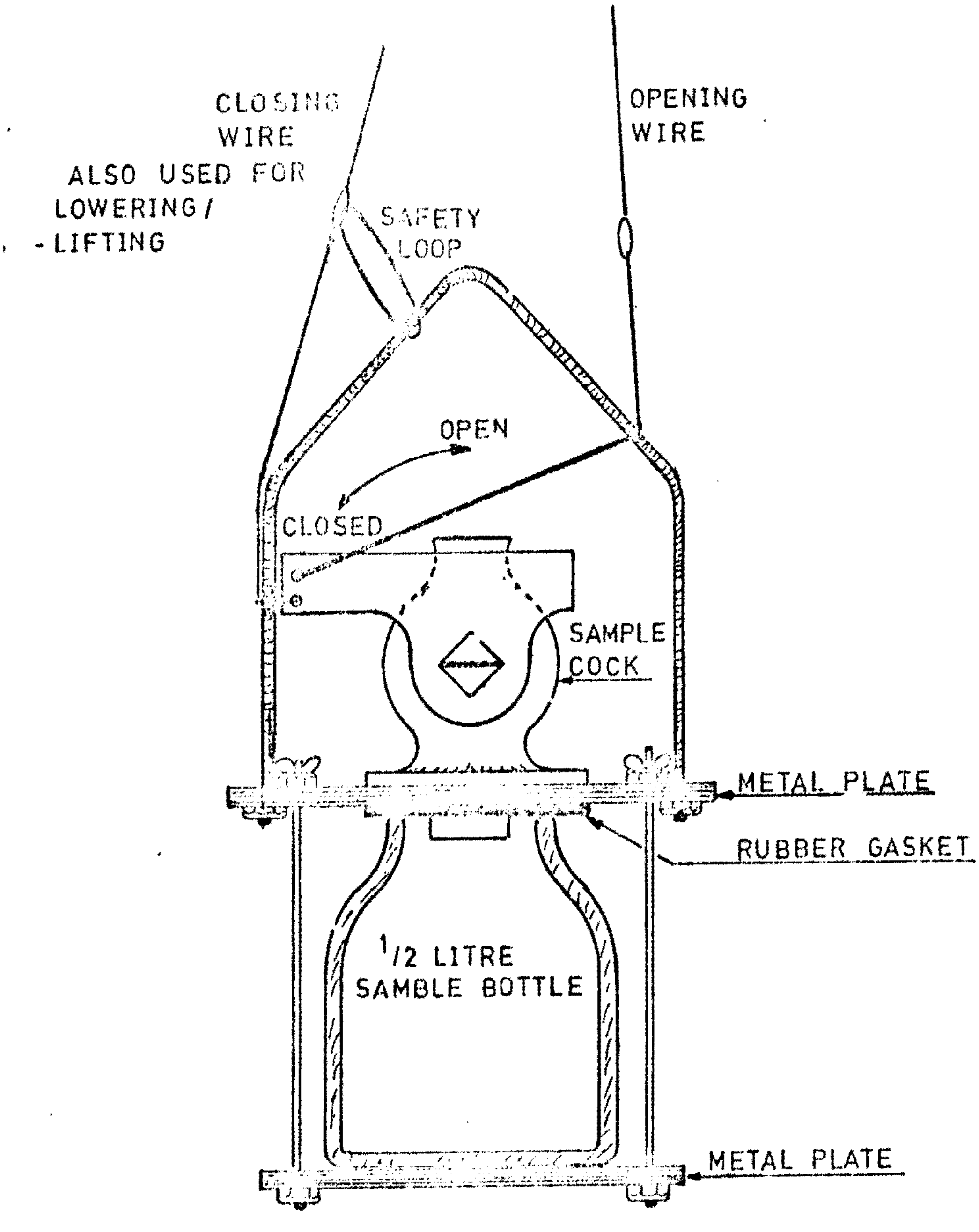
10/2 Slop: 2000 m^3

FIGURE 5



Hose sampling method.

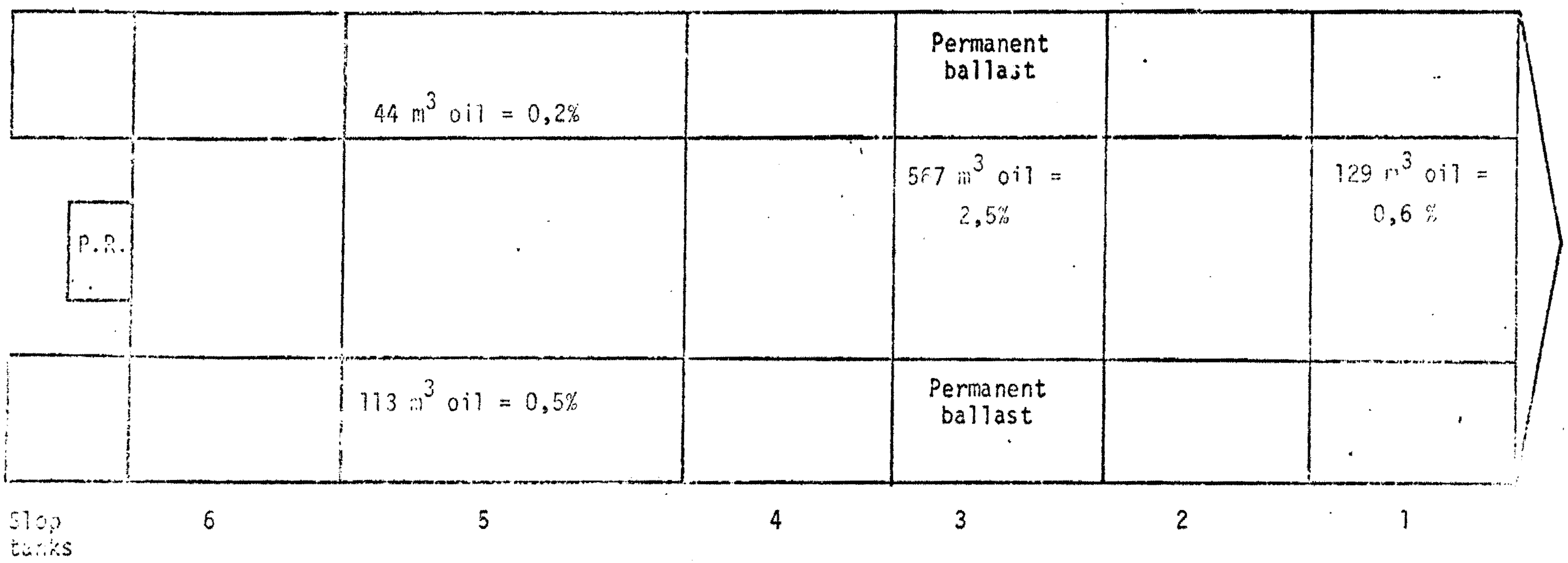
FIGURE 6



Sampling glass method.

FIGURE 7

M/T. "BERGE PRINCESS."



FEBRUARY 4th, 1973.

MEASURED OIL LAYER ON TOP OF BALLAST WATER IN UNWASHED CARGO TANKS, SHOWN IN CU.METRES AND PERCENT OF TANK VOLUME.

FIGURE 8

TANK SECTION MODEL USED AS "DIRTY BALLAST TANKS"

——— " ——— " ——— SLOPTANKS AFTER FLUSHING OF CARGO TANKS.

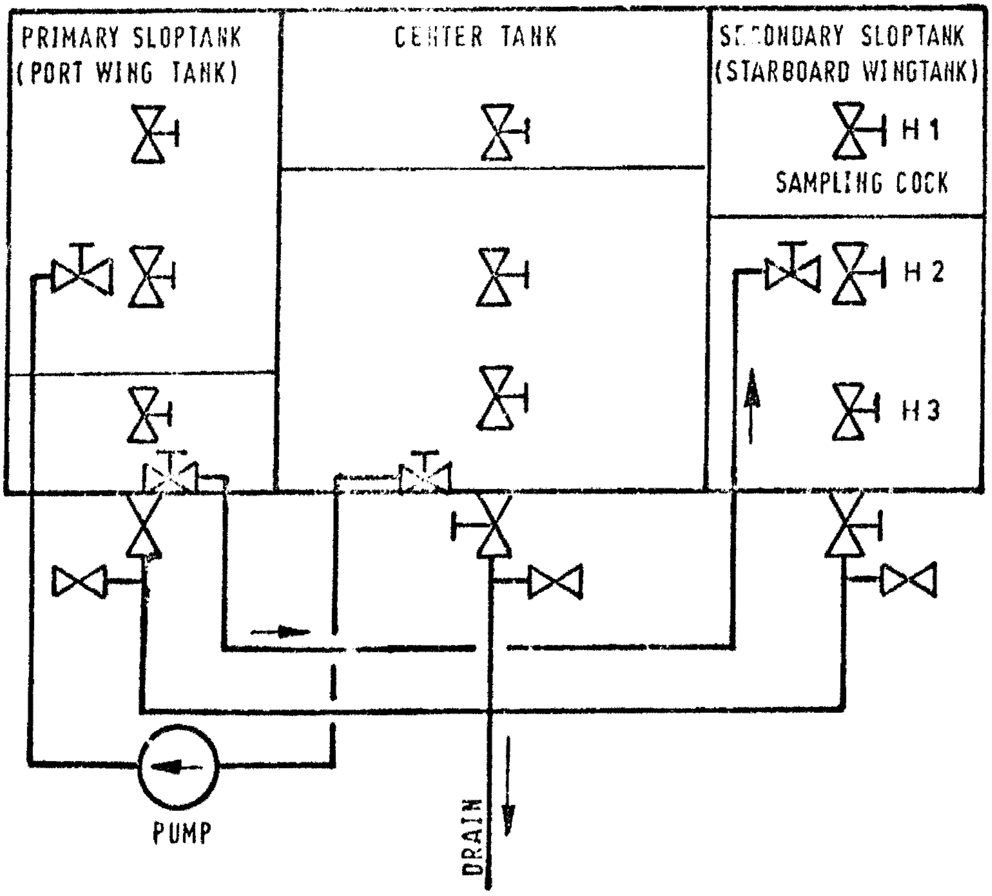


FIGURE 9

TANK SECTION MODEL SKETCH NO. 1	
MARITIME PROTECTION A/S.	D 73 - 1

TANK SECTION MODEL USED AS SLOP TANK DURING TANKWASHING.

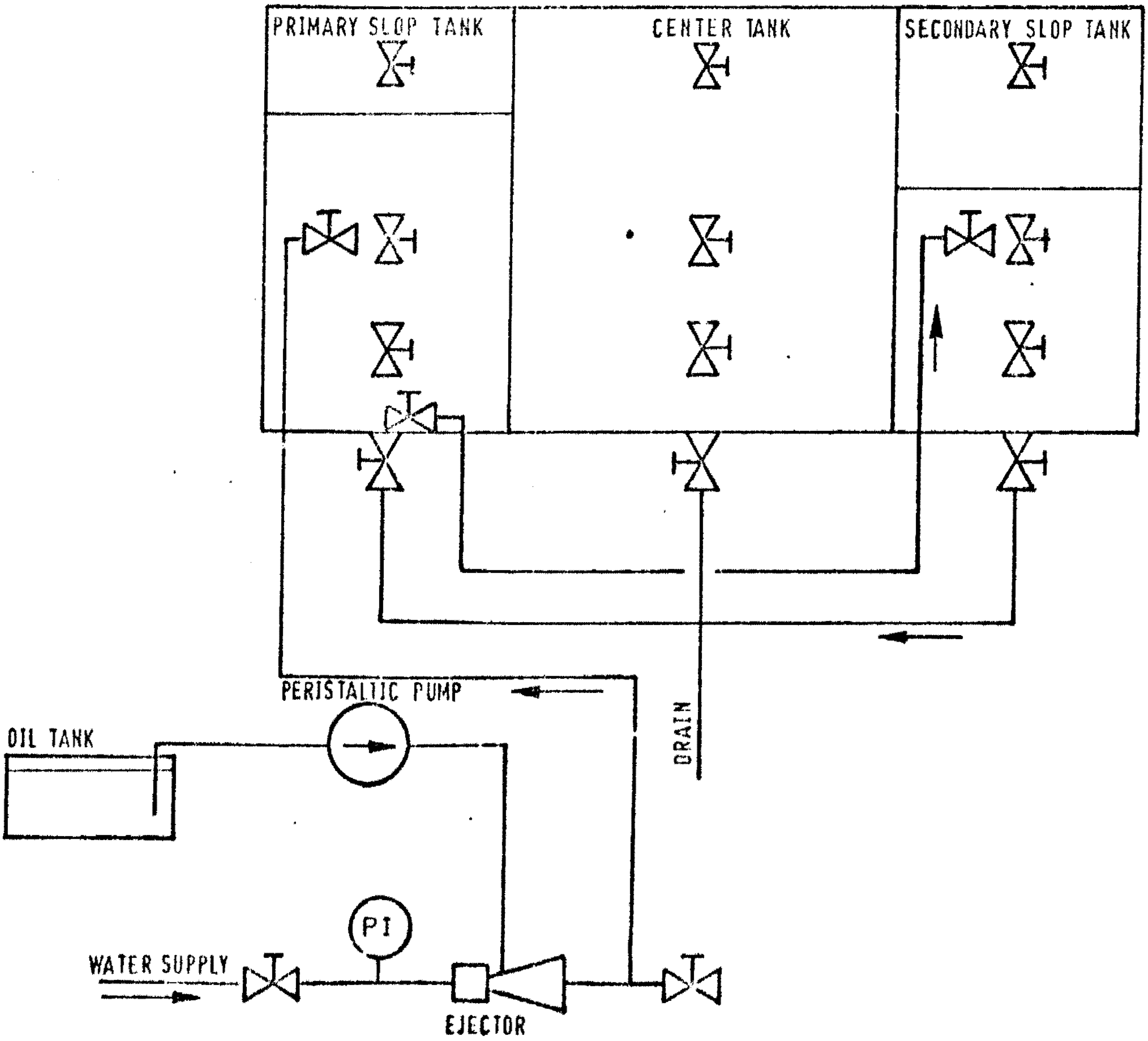


FIGURE 10

TANK SECTION MODEL SKETCH NO. 2		
MARITIME PROTECTION A/S.	D 73 - 2	

TABLE I

NSFI

SUMMARY OF SETTLED BALLAST WATER AND SLOP WATER DISCHARGED BETWEEN FEBRUARY 3 D AND 13TH, 1973.

Date	Time	Tank	m^3/h.	Total m^3.	ppm.	Oil m^3.	Oil l/n. mi.	Remarks
3/2	1600-1615	Slop S	2408	602	120	0,072	18.0	Decanted
5/2	1430-1700	Slop S	1743	2615	40	0.105	4.5	Decanted
"	"	Slop P	1425	2138	40	0.086	4.5	Decanted via slop S.
6/2	0600-0800	C1	3007	6013	30	0.180	5.3	Decanted
"	0840-1700	Slop S	1435	11910	125	1.489	10.5	Washing C2,stripped with ejector to slop P. Decanted from slop P. to S. and further into the sea by cargo pump. Max.380 ppm 32 l/n.mi.
"	1700-	Slop S	1435	12915	160	2.066	13.5	Washing C5, same method
7/2	0200							as for C2.
"	0200-0415	W5 P.S.	8350	22654	20	0.453	9.6	Discharged to 17 m.ull.
"	1430-1700	Slop P.S.	2278	3417	100	0.342	8.1	Decanted via slop S.
8/2	1600-1800	C3	5588	11177	15	0.168	4.9	Pumped out, 2 pumps.
"	1800-1900	C3	2920	2920	30	0.088	5.2	Pumped out, 1 pump.
"	1807-2125	W5 P.S.	5805	10444	100	1.044	19.3	Pumped out.
"	1900-2045	C1	4073	7130	200	1.426	47.5	Pumped out.
10/2	0850-1135	Slop P.S.	954	2623	180	0.472	10.3	Pumped out, using one stripping pump and decanted.
"	1135-1230	Slop S	800	712	350	0.249	15.6	Pumped out, using one stripping pump and decanted.
"	1230-1315	Slop S	228	171	450	0.077	6.4	Pumped using one stripping pump.
13/2	0935-1130	Slop P	275	528	640	0.338	10.5	Pumped using one stripping pump.

Sum discharged overboard: 97960 8.655

In addition , as an experiment to establish the rise of the oil content as the interface is approached:

1130-1135 Slop P 250 20 4% 0.800 533

TABLE 2.

MEASUREMENT OF OIL LAYER, USING "OIL/WATER INTERFACE DETECTOR".

DATE	TIME	TANK	OIL LAYER CM	OIL VOLUME CU.M	REMARKS
5/2	1000	C 3	66	567	112 hours settling. Relatively large quantity of oil, because the piping system was washed into this tank.
7/2	1000	C 3	66	567	160 hours settling.
8/2	1900	C 3			Rest in the tank when overboard discharge was stopped = 1467 m^3.
	Ullage 28,60 m = 1,70 m liquid depth				
5/2	0930	C 1	10	86	111,5 hours settling.
7/2	1000	C 1	15	129	160 hours settling.
8/2	2045	C 1			Rest in the tank when overboard discharge was stopped = 1083 m^3.
	Ullage 29,80 = 1,27 m liquid depth.				
5/2	0900	W 5 S	13	113	101 hours settling.
7/2	1000	W 5 S	13	113	159 hours settling.
8/2	2125	W 5 S			Rest in the tank when overboard discharge was stopped = 1343 m^3.
	Ullage 28,00 m = 1,60 m liquid depth.				
5/2	0830	W 5 P	3	26	109, 5 hours settling.
7/2	1000	W 5 P	5	44	159 hours settling.
8/2	2125	W 5 P			Rest in the tank when overboard discharge was stopped = 1343 m^3.
	Ullage 28,00 m = 1,6 m liquid depth.				

TABLE 2, CONTINUED.

DATE	TIME	TANK	OIL LAYER CM	OIL VOLUME CU.M.	REMARKS.
5/2	1030	Slopt. P	255 cm	511	41 hours settling after draining after flushing.
7/2	1100	Slopt. P	417 cm	788	9 hours settling after washing of C 2 and C 5.
9/2	1900	Slopt. P	762 cm	1410	1 hour after stripping of C 1, C 3 and W 5 P & S finished.
13/2	0900	Slopt. P	930 cm	1457	66 hours settling after slop from slop tank S was stripped over to this tank (P
13/2	1135	Slopt. P			Rest in the tank when the overboard discharge was stopped = 1492 m^3.
	Ullage 13,60 m.				
5/2	0830	Slopt. S	18 cm	37	37 hours settling after draining after flushing.
7/2	1100	Slopt. S	41 cm	77	9 hours settling after washing.
9/2	1900	Slopt. S	48 cm	94	1 hour after stripping.
10/2	1315	Slopt. S			Rest in the tank when the overboard discharge was stopped = 476 m^3 This quantity was pumped to sloptank P.
	Ullage 21,00 m.				

TABLE 3.

TYPE OF SAMPLES:

SEA WATER

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
29/1	1700	1	sea			IR	1 ppm	13 m. below sea level. Isl. of Grain.
30/1	0800	2	"			IR	1 "	13 m. " " " " "
1/2	0830	30	"			IR	1 "	Eng. room cooling water intake.
2/2	0830	55	"				1 "	" " " " "
"	"	56	"			IR	1 "	After passing sampling hose and pump.
"	1530	69	"			IR	1 "	" " " "
3/2	0815	83	"			IR	1 "	Before passing hose and pump.
		84	"				1 "	After " " "
"	1500	97	"			IR	1 "	Before passing hose and pump.
		98	"				6 "	After " " "
4/2	0900	121	"			IR	1 "	Before passing hose and pump
		122	"				1 "	After " " "
"	1530	141	"			IR	1 "	Before passing hose and pump
		142	"				1 "	After " " "
5/2	0830	153	"			IR	2 "	Before passing hose and pump
"	"	154	"				1 "	After " " "
6/2	0830	175	"			IR	1 "	Before passing hose and pump
		176	"				1 "	After " " "
8/2	1000	227	"			IR	1 "	Eng. room cooling water intake.

TABLE 3, CONTINUED.

SEA WATER

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
9/2	0900	252				IR	1 ppm	Eng. room cooling water intake
10/2	0830	253				IR	1 "	" " " " "
11/2	0930	286				IR	1 "	" " " " "
13/2	0900	293				IR	1 "	Before passing hose and pump
		294				IR	2 "	After " " "

TABLE 4.

WING TANKS NO. 2 PORT AND STARBOARD

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
31/1	1400	5	2 PS	Pumproom	T 16.00		120 ppm	T: Top of suction line.
"	"	6	"	"	B "		114 "	B: Bottom of suction line.
"	1415	7	"	"	T 17.05		106 "	
"	"	8	"	"	B "		94 "	Settling time: 30/1.0400 - 31/1.1345 =
"	1430	9	"	"	T 18.10		112 "	33 hrs. 45 min.
"	"	10	"	"	B "		91 "	Cargo pump no. 1 used. Started 1345.
"	1500	11	"	"	T 20.10		132 "	Discharge rate: 4350 tons/hour
"	"	12	"	"	B "		120 "	At 1600 reduced to 2200 tons/hour
"	1530	13	"	"	T 22.00		150 "	
"	"	14	"	"	B "		93 "	Pump stopped at 1800. Ullage 27,30 m.
"	1600	15	"	"	T 23.50		137 "	Tank depth 29,61 m.
"	"	16	"	"	B "		123 "	Because of an open line on the cross-
"	1615	17	"	"	T 23.90		143 "	over-line in the pump room it must be
"	"	18	"	"	B "		88 "	assumed that what was discharged from
"	1630	19	"	"	T 24.30		126 "	cargo pump No. 1 was drawn into
"	"	20	"	"	B "		93 "	cargo pumps Nos. 2 and 3 and trans-
"	1645	21	"	"	T 24.70		158 "	ferred to center tanks Nos. 1 and 3
"	"	22	"	"	B "		136 "	which were ballasted at this time.
"	1700	23	"	"	T 25.10		143 "	
"	"	24	"	"	B "		143 "	
"	1715	25	"	"	T 25.60		160 "	
"	"	26	"	"	B "		146 "	
"	1730	27	"	"	T 26.20		148 "	
"	"	28	"	"	B "		142 "	
"	[illegible]	29	"	"	B 27.20		199 "	

TABLE 5.

WINGTANK NO. 5 P.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
30/1	1630	4	5 P	21 m	12.80 m		6 ppm	12.5 hrs. settling. Sample bottle used.
1/2	1100	31	"	7 m	2.8 m	IR	77 "	16.0 hrs. settling. Pumpe and hose used for sampling.
"	1115	32	"	16 m	"	IR	75 "	16.0 hrs. settling.
"	1130	33	"	25 m	"	IR	75 "	16.5 " "
"	1600	43	"	7 m	"	IR	63 "	21.0 " "
"	1605	44	"	16 m	"	GC	68 "	2100 " "
"	1615	45	"	25 m	"	IR	67 "	21.25 " "
2/2	0900	57	"	7 m	2.8 m	IR	40 "	38.0 hrs. settling.
"	"	58	"	16 m	"	IR	42 "	" " "
"	"	59	"	25 m	"	IR	40 "	" "
"	1530	70	"	7 m	2.8 m	IR	39 "	44.5 hrs. settling.
"	"	71	"	16 m	"	IR	41 "	
"	"	72	"	25 m	"	IR	42 "	
3/2	0830	85	"	7 m	2.8 m	IR	27 "	61.5 hrs. settling.
		86		16	2.8 m	IR	28 "	
		87		25			28 "	
	1500	99	"	7 m	"		25 ppm	68 hrs. settling.
		[illegible]		16		IR	27	
				25			28	

TABLE 5, CONTINUED.

WINGTANK NR. 5 P.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
4/2	0830	135	5 P	7 m	2.8 m	IR	21 ppm	85.5 hrs. settling.
		136	"	16 m	"	GC	20 "	
		137	"	25 m	"	IR	22 "	
5/2	0830	164	"	7 m	2.8 m	IR	18 "	109.5 hrs. settling. 3 cm. oil.
		165		16 m			16 "	
		166		25 m			17 "	
6/2	0830	177	"	7 m	2.8 m	IR	17 "	133.5 hrs. settling.
		178	"	16 m			18 "	
		179	"	25 m			18 "	
7/2	1000		"		15.8 m			5 cm. oil. (by oil/water interface detector) 44 m^3

TABLE 6.

WINGTANK NO. 5 S.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
30/1	1600	3	5 S	21 m	12.00		6 ppm	12 hrs. settling. Sampling bottle used.
1/2	1300	34	"	7	2.6 m	IR	78 "	18 hrs. settling. Pump and hose used for sampling.
	1315	35	"	16	"	IR	62 "	
"	1330	36	"	25	"	IR	82 "	
"	1620	46	"	7	"	GC		21.5 hrs. settling.
"	1625	47	"	16	"	or		
"	1630	48	"	25	"	GC/MS		
2/2	0915	60	"	7 m	"	IR	45 "	38 hrs. settling.
"	"	61	"	16 m	"	IR	46 "	
"	"	62	"	25 m	"	IR	38 "	
"	1545	73	"	7 m	"	IR	37 "	44.5 hrs. settling.
"	"	74	"	16 m	"	IR	35 "	
"	"	75	"	25 m			40 "	
3/2	0900	88	"	7 m	"	IR	25 "	62 hrs. settling.
		89		16 m	"	IR	25 "	
		90		25 m		IR	27 "	
"	1515	102	"	7 m	"		27 "	68 hrs. settling.
		103		16 m			24 "	
		104		25 m		IR	25 "	

TABLE 6, CONTINUED.

WINGTANK NR. 5 S.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
4/2	0900	126	5 S	7 m	2.6 m	IR		86 hrs. Settling.
		127	"	16 m	"	GC		
		128	"	25 m	"	IR		
5/2	0900	155	"	7 m	2.6 m	IR	17 ppm	110 hrs. settling.
		156	"	16 m		"	17 "	13 cm. oil.
		157		25 m		"	16 "	
6/2	0900	180	"	7 m	2.6 m	IR	17 "	134 hrs. settling.
		181		16 m		"	15 "	
		182		25 m		"	15 "	
7/2	1000		"		15.8 m			13 cm. oil (by oil/water interface detector) 113 m^3

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
				BELOW DECK		METHOD	CONC.	
7/2	0230	223 B	P.room		5 P&S: 6m.		20 ppm	At 0210 commenced pumping out ballast
		224 T					20 "	from wingtanks 5 P. & S.
	0300	225 B				IR	17 "	2 cargo pumps used. 8350 T/H.
		226 T					18 "	Total Disch. 22654 m^3
								B = bottom of suction line.
								T = Top " " "
								151 hrs. settling (Wingtanks 5 P & S)
								At 0445 7/2, deballasting stopped.
8/2	1820	235 T	P.room		22.9 m		63 ppm	1805 commenced deballasting 5 P&S.
	1845	237 T	"		23.5 m		60 "	Ullage P&S = 22 m.
	1900	239 T	"		23.8 m		60 "	2125 deballasting completed.
	1930	240 T	"		25.5		94 "	Ullage P. 28.0 m, S. 28.0 m.
	2000	242 T	"		26.5	IR	86 "	1.60 m over bottom. 1.47 m. on 5 and
	2050	246 T	"		27.4 m		111 "	1.55 m på P. under oil layer.
	2055	247 T	"				97 "	Samples taken in the pump room, suction
	2100	248 T	"				105 "	side of pump no. 2.
	2105	249 T	"		27.7 m		115 "	T = top of suction line.
	2115	250 T	"		27.9 m		116 "	Settling time : 183 hrs.
								Depth of WT 5 = 29.60 m.

SETTLED DIRTY BALLAST WATER.

WINGTANKS NO. 5 P&S.

TABLE 8. CENTER TANK NO. 1

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
1/2	1400	37	C 1	7 m	1.94 m	IR	123 ppm	20.0 hrs. settling. Pump and hose used for sampling.
"	1410	38	"	16 m	"	"	73 ppm	
"	1420	39	"	25 m	"	"	117 ppm	
"	1640	49	"	7 m	"	"	108 ppm	22.7 hrs. settling.
"	1655	50	"	16 m	"	GC		
"	1710	51	"	25 m	"	IR	113 ppm	
2/2	0930	63	"	7 m	"	IR	46 ppm	39.5 hrs. settling.
		64		16 m	"	"	109 ppm	
		65		25 m		"	105 ppm	
"	1600	76	"	7 m	"	"	109 ppm	46 hrs. settling.
		77		16 m	"	"	93 ppm	
		78		25 m		"	98 ppm	
3/2	0930	91	"	7 m	"	"	83 ppm	63.5 hrs. settling.
"		92		16 m	"	"	73 ppm	
		93		25 m	"	"	75 ppm	
"	1600	105	"	7 m	"	"	85 ppm	70.5 hrs. settling.
		106	"	16 m	"	"	83 ppm	
		107	"	25 m		"	64 ppm	
3/2	1600	108	C 1	7 m	1.94 m	IR	73 ppm	Sampling point 5 m from bulkheads.
		109	"	16 m		"	65 ppm	
		110		25 m		"	66 ppm	

TABLE 8, CONTINUED. CENTER TANK NO. 1

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
4/2	0930	129	C 1	7 m	1.94 m	IR	57	87.5 hrs. settling. Sampling point 5 m from bulkheads.
		130	"	16 m	"	GC		
		131	"	25 m	"	IR	54 ppm	
5/2	0930	158	"	7 m	"	"	30 ppm	111.5 hrs. settling. " " " 10.0 cm. oil.
		159		16 m		"	28	
		160		25 m		"	29 ppm	
7/2	1000		"		11 m			15 cm. oil (by oil/water interface detector). 129 m^3.
8/2	1930	241 T		P.room	24.5 m		116 ppm	1900 commence pumping out ballast from C 1. Ullage 21.5 m. 2045 deballasting stopped. Ullage 29.8 m. = 1.27 m from bottom. 1.12 m under the oil layer. Samples taken in the pumproom, suction side of pump no. 4. T = top of suction line. Settling time: 193.5 hrs. Depth of C 1 = 31.07 m.
	2000	243 T		"	26.7 m	IR	193	
	2020	244 T		"	28.1 m		280 ppm	
	2035	245 T			29.0 m		282 ppm	

TABLE 9.

CENTER TANK NO. 3.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
1/2.	1435	40	C. 3	7 m	2.9 m	IR	17 ppm	20.5 hrs. settling. Pump and hose sampling.
"	1450	41	"	16 m	"		18 "	
"	1505	42	"	25 m	"		16 "	
"	1715	52	"	7 m	"	GC or GC/MS		23.5 hrs. settling .
"	1725	53	"	16 m	"			
"	1735	54	"	25 m	"			
2/2.	1000	66	"	7 m	"	IR	11 "	40 hrs. settling
"		67	"	16 m	"		11 "	
"		68	"	25 m	"		12 "	
"	1630	79	"	7 m	"	IR	6 "	46,5 hrs. settling
"		80	"	16 m	"		10 "	
"		81	"	25 m	"		11 "	
3/2.	1000	94	"	7 m	"	IR	9 "	64 hrs. settling
"		95	"	16 m	"		9 "	
"		96	"	25 m	"		11 "	
"	1630	111	"	7 m	"	IR	11 "	70.5 hrs. settling
"		112	"	16 m	"		10 "	
"		113	"	25 m	"		9 "	

TABLE 9, CONTINUED. CENTER TANK NO. 3.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
4/2.	1000	132	C. 3	7 m	2.9 m	GC or GC/MS		88 hrs. settling. Pump and hose used for sampling
		133	"	16 m	"			
		134	"	25 m	"			
5/2.	1000	161	"	7 m	"	IR	7 ppm	112 hrs. settling. 66 cm oil.
		162	"	16 m	"		7 "	
		163	"	25 m	"		8 "	
6/2.	1000	183	"	7 m	"	IR	8 "	136 hrs. settling.
		184	"	16 m	"		8 "	
		185	"	25 m	"		7 "	
7/2.	1000		"		"			66 cm. oil (by oil/water interface detector). 6567 m^3.
8/2.	1730	234		P. room	21 m	IR	12 "	1600 commenced pumping out ballast from C 3. Ullage 12.2 m. 1900 deballasting stopped. Ullage 28.6 m. 1.70 m. above the bottom. 1.04 m. under the oil layer. Samples taken in the pumproom, suction side of pump no. 4. T = top of suction line.. Settling time: 190 hrs. Depth of C 3 = 30,30 m.
	1820	236		"	26.4 m		26 "	
	1845	238		"	27.7 m		33 "	

TABLE 10.

CLEAN BALLAST C 2

TYPE OF SAMPLES:

ATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
8/2	1545	228	C 2	7 m	4 m		36	C 2 completed ballasted 1530 8/2.
		229		16 m			21	Sample bottle used.
		230		25 m			25	Settling time = 15 min.
11/2	0930	282	"	7 m	4 m		26	Sample bottle used.
		283	"	16			25	Settling time 66 hrs.
		284		25			23	
13/2	0900	287	"	7 m	4 m		24	Hose and pump used.
		288	"	16 m			24	Settling time 112.5 hours.
		289	"	25 m	"		23	

TABLE 11.

CLEAN BALLAST C 5.

TYPE OF SAMPLES:

ATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
8/2	1600	231	C 5	7 m	3 m		23	C 5 completed ballasted 1530 8/2.
		232		16 m			16	Sample bottle used.
		233		25 m			5	Settling time : 30 min.
11/2	0930	285	"	12 m	3 m		15	Sample bottle used. Settling time : 66 hrs.
13/2	0930	290	"	7 m	3 m		9	Hose and pump used.
		291	"	16 m			9	Settling time : 114 hrs.
		292	"	25 m			13	

TABLE 12.

PORT SLOP TANK

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
3/2.	1830	114	Slop P.	7 m			192 ppm	1 hr. settling
"		115		16 m	2.3 m.	IR	123 "	
		116		25 m			154	
4/2.	1030	138	"	7 m	"	IR	82 "	17 hrs settling
		139	"	16 m	"	GC		
		140	"	25 m		IR	99 "	
"	1600	146	"	7 m	"		32 "	22.5 hrs. settling.
		147	"	16 m	"	IR	35 "	
		148	"	25 m	"		32 "	
"	1700	151	"	7 m	"	IR	69 "	23.5 hrs. settling. Sample bottle used.
		152	"	14 m	"		86 "	
5/2.	1030	167	"	7 m	"	IR	55 "	41 hrs. settling. " " "
		168		14 m				255 cm. oil = 515 m^3 " " "
"	1430	171	"	7 m	"	IR	22 "	45 hrs. settling. " " "
		172		14 m	"		21 "	
7/2.	1100		"		7.3 m			417 cm. oil (by oil/water interface detector) 788 m^3. 9 hours settling after end of washing.

TABLE 12, CONTINUED.

PORT SLOP TANK

TYPE OF SAMPLES:

ATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
9/2.	1900		Slop P.		6.2 m.			762 cm. oil = 1410 m^3 (using oil/water interface detector) 1 hr. after stripping completed from C1 and C3 plus W5 P & S.
13/2.	0940	295	Slop P.	P. room	10.6 m.	IR	575 ppm	66.5 hrs. settling time after the last stripping of slop from slop tank S was completed. According to "oil/water interface detector" before commencing stripping from slop tank P today: 1457 m^3 oil (930 cm). Commenced stripping 0935 Ull. 10.5 Completed stripping according to normal operation at 1130 Quantity discharged 528 m^3. Samples taken from the pressure side of the port stripping pump.
	0950	296			11.0 m		368 "	
	1000	297			11.3 m		312 "	
	1015	298			11.8		388 "	
	1030	299			12.4		620 "	
	1045	300			12.7		655 "	
	1100	301			12.9		1290 "	
	1115	302			13.2		830 "	
	1130	303			13.4		975 "	
	1135	304			13,6		4.8%	For the purpose of the experimennt stripping continued beyond normal practice until 1135, Ullage = 13.6 m. Additional quantity discharged = 20 m^3.

TABLE 13. STARBOARD SLOPTANK

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
3/2	1900	117	Slop S	7 m	2.3 m	IR	74	1 hr. settling.
		118		16 m	"	"	98	
		119		25 m	"	"	108	
4/2	0830	123	"	7 m	"	"	34	15.5 hrs. settling.
		124	"	16 m	"	GC		
		125	"	25 m	"	IR	43	
"	1600	143	"	7 m	"	"	65	23 hrs. settling.
		144	"	16 m	"	"	74	
		145	"	25 m	"	"	79	
"	1630	149	"	7 m	"	"	40	23.5 hrs. settling. Sample bottle used.
		150	"	14 m	"	"	44	
5/2	0830	169	"	7 m	"	"	23	39.5 hrs. settling. 18 cm. oil = 35 m^3
		170	"	14 m	"	GC		
"	1430	173	"	7 m	"	IR	42	45.5 hrs. settling.
		174		14 m	"	"	52	
7/2	1100		"		8.4 m			41 cm oil (using oil/water interface detector) 78 m^3. 9 hrs. settling after end of washing.

TABLE 13, CONTINUED.

TYPE OF SAMPLES:

STARBOARD SLOPTANK:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
9/2	1900		Slop S		6.8 m			48 cm oil = 94 m^3 (using oil/water interface detector) One hr. after stripping completed C 1, C 3 and W 5 P&S.
10/2	0855	254	Slop S	P. room	6.9 m S	IR	200 ppm	0850 commenced pumping from slop tank S. to sea. Valve between slop tank P and S open. P. 6.2 m, S 6.8 m. 1135 valve between slop tanks closed. P 12.8 m, S 14.4 m. 1315 Ullage S. 21.0 m. Remaining quantity in slop tank S pumped over to slop tank P. Total quantity pumped to sea 3506 m^3. Samples taken from the pressure side of the pump. (stripping pump). Settling time after last stripping 15 hrs.
	0900	255			7.0 m	"	181 "	
	0905	256			7.5 m	GC	174 "	
	0930	257			9.3 m	IR	128 "	
	0945	258			10.1 m	"	134 "	
	1000	259			10.8 m	"	141 "	
	1015	260			11.5 m	"	164 "	
	1030	261			12.2 m	"	171 "	
	1045	262			12.7 m	"	181 "	
	1100	263			13.5 m	GC		
	1115	264			13.9 m	IR	210 "	
	1130	265			14.4 m	"	173 "	
	1145	266			14.7 m	"	226 "	
	1200	267			15.5 m	"	284 "	
	1220	268			18.3 m	"	366 "	
	1230	269			19.2 m	"	405 "	
	1245	270			19.6 m	"	388 "	
	1300	271			20.4 m	GC		
	1315	272			21.0 m	IR	493 "	
	1330	273			21.7 m	"	615 "	

TABLE 13, CONTINUED. STARBOARD SLOPTANK.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
10/2	1345	274	Slop S	P.room	22.3 m	IR	795 ppm	
	1400	275			23.0 m	"	745 "	
	1415	276			23.6 m	"	845 "	
	1430	277			24.2 m	"	2355 "	
	1445	278					2600 "	
	1500	279					2.8 %	1510 Starboard slop tank empty. Ullage Port slop tank 10.5 m. When ullage in slop tanks is 24.45 m, the remaining quantity is 217 m^3 in each tank.
	1505	280					Sludge, Sediments	
	1510	281						

TABLE 14.

SETTLED SLOP WATER DURING CLEANING OF CENTER TANK NO. 2.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
6/2	0845	186 B	Slop S.	-	P 9m S 13m	IR	99 ppm	Sample taken in pump room, suction
		187 T				"	94 "	side of pump No. 1.
	0900	188 B			9 16	"	234 "	B = bottom of suction line
		189 T				GC		T = Top " " "
	0915	190 B			" "	IR	246 "	
		191 T				"	288 "	
	0930	192 B			" "	"	260 "	At 0800 tank cleaning commenced C2.
		193 T				"	380 "	" 1700 tank cleaning completed "
	0945	194 B			" "	"	282 "	At 0840 discharge cargo pump No. 1
		195 T				"	285 "	started from slop tank S [illegible] via
	1000	196 B			" "	"	213 "	S. sea valve.
		197 T				"	228 "	
	1000	198 T			8 15	"	198 "	
	1100	199 B			" "	"	155 "	
		200 T				"	158 "	
	1130	201 T			7 14	"	112 W	
	1200	202 B			" "	"	127 "	
		203 T			" "	GC		
	1230	204 T			" "	IR	110 "	
	1300	205 T			" "	"	104 "	
	1400	20[illegible] T			6 13	"	94 "	
	1[illegible]	207 T			" "	GC	95 "	
	1[illegible]				" "	IR		
					" "	"	72 "	
					" "	"	57 "	

TABLE 15.

SETTLED SLOP WATER DURING CLEANI
OF CENTRE TANK NO. 5.

TYPE OF SAMPLES:

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
6/2	1800	211 B	Slop S		P.5m S.13m	IR	248 ppm	Samples taken in the pump room,
		212 T			" "	"	156 "	suction side of pump No. 1.
	1900	213 T			5 16	"	151	
	2000	214 T			6 16	"	141 "	B.= Bottom of suction line.
	2100	215 T			" "	"	148 "	T.= Top " " . "
	2200	216 B			" "	"	133 "	
		217 T			" "	"	143 "	At 1730 cleaning centre tank No.5 com-
	2300	218 T			" 15	"	196 "	mence. At 0200 7/2. cleaning completed.
	2400	219 T			" 14	"	228 "	
7/2	0100	220 T			" 15	"	186	From slop tank S to sea via sea
	0200	221 B			" "	"	92 "	valve S, using Cargo pump No. 1.
		222 T			" "	"	101 "	

TABLE 16. OIL LAYER SAMPLES.

TYPE OF SAMPLES: OIL LAYER SAMPLES

DATE	TIME	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
							The figures below show weight per cent of water in slop.	
2.2.	1630	82	C.3		2,9 m		16 %	On top of dirty ballast water.
3.2	1700	120	Slop P.		2.0 m		38 %	On top of slop water, after flushing.
		318					18 %	Top of slop.
13.2.	1300	305	Slop P.	15,0 m	13,6 m		25 %	Sample bottle used.
		306		16,0 m	13,6 m		20 %	1,5 hrs. after stripping of free water completed.
		307		17,0 m	13,6 m		19 %	
		308		18,0 m	13,6 m		20 %	
		310		20,0 m	13,6 m		21 %	
		311		21,0 m	13,6 m		23 %	
		313		23,0 m	13,6 m		23 %	
		314		24,0 m	13,6 m		24 %	
		315		25,0 m	13,6 m		27 %	
		316		26,0 m	13,6 m		26 %	
		317		28,0 m	13,6 m		27 %	

TABLE 17.

WEATHER DATA INCLUDING SHIP'S POSITION, COURSE AND SPEED.

							TEMPERATURE C.					
DATE	TIME	POSITION	COURSE	SPEED	WIND	SEA	AIR	SEA	BALLAST	ULLAGE	SHIP'S ROLLING TO EACH SIDE(°)	REMARKS
30/1	1200	Dower Strait	-	15	S.V.3	2	12	8	-	-	-	
31/1	1200	N.48 26 W5 34	209	16	N.V.6	5	8	10			15	
1/2	1200	N.42 44W 9 51	200	16,3	N.V.6	6	11	13	10	11	15 - 18	
2/2	0900		"	16,5	N.NE.4	4	12	15	9	10		
	12CON	N36 30 W12 47	"	"	"	"	14	"			5	
	1600		198	17,0	"	"	15	16	10	16	2 - 3	
3/2	0800		"	17,2	NE.5	4	15	17	12	12	2 - 3	
	1200	N29 59 W15 21	196	"	"	"	17	18			2 - 3	
	1600		"	"	"	"	18	"	16	23	2 - 3	
4/2	0800		192	"	"	"	17	17	13	19	2 - 3	
	1200	N.23 20 W17 15	"	"	N.4	"	20	18			2 - 3	
	1600		"	"	"	"	"	"	16	25	2 - 3	
5/2	0800		179	"	"	3-4	"	"	13	15	2 - 3	
	1200	N.16 38 W17 45	"	"	"	"	22	19			2 - 3	
	1600		"	"	"	"	24	"	19	29	2 - 3	
6/2	0800		153	"	N.W.5	"	20	24	16	17	2	
	1200	N.0950 W16 51	"	"	N.W.4	"	26	25			2	
	1600		143	"	"		27	26			2	

TABLE 17, CONTINUED.

WEATHER DATA INCLUDING SHIP'S POSITION, COURSE AND SPEED.

							TEMPERATURE C.					
DATE	TIME	POSITION	COURSE	SPEED	WIND	SEA	AIR	SEA	BAL-LAST	ULL-AGE	SHIP'S ROLLING TO EACH SIDE (°)	REMARKS
7/2	0800		143	17,5	N.V.2	2	28	30			2	
	1200	N04 12 V 12 36	"	"	"	"	30	"			2	
	1600		"	"	S.S.E.3	3	31	29			2	
8/2	0800		"	17,2	S.S.E.4	"	27	27			2	
	1200	S01 18 V 8 27	"	"	"	"	31	28			2	
	1600		"	"	S.S.E.5	4	30	"			2	
9/2	0800		"	17,0	S.E.5	"	27	"			2	
	1200	S 06 27 V 04 26	"	16,8	"	"	30	"			2	
	1600		"	16,8	S.E.6	5	28	27			3 - 4	
10/2	0800		"	"	S.E.4	"	25	26			5 - 6	
	1200	S 11 54 V 00 27	"	16,7	"	4	28	"			5 - 6	
	1600		"	"	"	"	27	25			3 - 4	
11/2	0800		"	"	"	"	24	24			5 - 6	
	1200	S17 17 E 03 42	"	"	"	"	26	"			5 - 6	
	1600		"	"	"	"	25	23			5 - 6	
12/2	0800		142	16,5	S.E.6	5	23	22			5 - 6	
	1200	S 22 29 E 97 59	"	"	"	"	26	"			5 - 6	
	1600		"	"	"	"	23	"			5 - 6	

TABLE 17, CONTINUED.

WEATHER DATA INCLUDING SHIP'S POSITION, COURSE AND SPEED.

							TEMPERATURE C.					
DATE	TIME	POSITION	COURSE	SPEED	WIND	SEA	AIR	SEA	BALLAST	ULLAGE	SHIP'S ROLLING TO EACH SIDE (°)	REMARKS
13/2	0800		142	16,5	S.S.E.5	4 - 5	22	20			5 - 6	
	1200	S 27 26 E 12 05	"	"	"	"	26	22			5 - 6	
	1600		"	"	"	"	23	"			5 - 6	
14/2	0800		"	17,0	S.S.E.2	3	21	19			2	
	1200	S 32 44 E 17 02	"	"	Var. 2	"	25	"			2	

TYPE OF SAMPLES: SAMPLES FROM T/T "FERNCOURT".

DATE	HOURS AFTER BALL. COMPL.	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
an.11, 73	0		C 3		1,5 m			The letters A, B and C are used to identify the individual samples when more than one sample is drawn from one sampling point.
	3	H3A	C 3	3,5 m	1,5 m	IR	3 ppm	
	3	H3B	C 3	3,5 m	1,5 m	IR	3 ppm	
	3	M3	C 3	14,0 m	1,5 m	IR	3 ppm	
	3	D3A	C 3	27.0 m	1,5 m	IR	3 ppm	
	3	D3B	C 3	27,0 m	1,5 m	IR	4 ppm	
	3	D3C	C 3	27,0 m	1,5 m	IR	4 ppm	
	8	H8A	C 3	3,5 m	1,5 m	IR	5 ppm	
	8	h8B	C 3	3,5 m	1,5 m	IR	5 ppm	
	8	M8A	C 3	14,0 m	1,5 m	IR	4 ppm	
	8	M8B	C 3	14,0 m	1,5 m	IR	4 ppm	
	8	D8A	C 3	27,0 m	1,5 m	IR	4 ppm	
	8	D8B	C 3	27,0 m	1,5 m	IR	4 ppm	
	14	H14	C 3	3,5 m	1,5 m	IR	13 ppm	
	14	m14	C 3	1,4 m	1,5 m	IR	5 ppm	
	14	D14	C 3	27,0 m	1,5 m	IR	4 ppm	

TABLE 18.

SAMPLES FROM T/T "FERNCOURT".

TABLE 18. CONTINUED.

SAMPLES FROM T/T "FERNCOURT".

TYPE OF SAMPLES: SAMPLES FROM T/T "FERNCOURT", continued.

DATE	HOURS AFTER BALL. COMPL.	SAMPLE NO.	SAMPLING POINT		ULLAGE	DETERMINATION		REMARKS
			TANK	BELOW DECK		METHOD	CONC.	
	32	H32A	C 3	3,5 m	1,5 m	IR	50 ppm	
	32	H32B	C 3	3,5 m	1,5 m	IR	31 ppm	
	32	M32A	C 3	14,0 m	1,5 m	IR	8 ppm	
	32	M32B	C 3	14,0 m	1,5 m	IR	9 ppm	
	32	D32	C 3	27,0 m	1,5 m	IR	7 ppm	
	56	M56	C 3	14,0 m	1,5 m	IR	6 ppm	
		D56	C 3	27,0 m	1,5 m	IR	5 ppm	

SAMPLE SERIES NO. 1 A, "DIRTY BALLAST TANKS".

Center tank contains 0.6% crude oil of tank volume.

0 hours	18 h		22 h		40 h		46 h		63 h	
Room temp.: 12°C Water temp.: 4°C	10°C 7.5°C		10°C 8°C		10°C 8°C		11°C 3°C		8.5°C 8.5°C	
Distance above tank bottom	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm
H_1 74 cm	$c_{1,1}$	10	$c_{1,3}$	650	$c_{1,9}$	2	$c_{1,11}$	2	$c_{1,13}$	135
H_2 51.5 cm			$c_{1,4}$	18					$c_{1,14}$	4
H_3 6.5 cm			$c_{1,5}$	16					$c_{1,15}$	12

Wing tank contains 0.2% crude oil of tank volume.

H_1 74 cm	$w_{1,2}$	9	$w_{1,6}$	14	$w_{1,10}$	9	$w_{1,12}$	4	$w_{1,16}$	4
H_2 51.5 cm			$w_{1,7}$	3					$w_{1,17}$	2
H_3 6.5 cm			$w_{1,8}$	2					$w_{1,18}$	3

The following quantities of crude olje are sprayed on the bulkhead and the bottom in the center tanks and starboard wing tanks:

C.T. 3.25 litres crude oil
W.T. 0.72 litres crude oil.

The tanks are then filled with fresh water until the surface is 1 meter above the bottom. The total liquid quantity is at this point: C.T. 540 litres, W.T. 360 litres.

Samples are drawn according to the above table.

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TABLE 19.

TABLE 19, CONTINUED.

NSFI

After 63 hours, the free water in the lower section of the tanks is drained out, leaving only the oil layer on the top.

The samples are drawn according to the following table.

	CENTER TANK		WING TANK	
Drained slop in % of tank volume	Sample No.	Concentration ppm	Sample No.	Concentration ppm
10%	$c_{1,19}$	3	$w_{1,28}$	2
20%	$c_{1,20}$	3	$w_{1,29}$	3
30%	$c_{1,21}$	3	$w_{1,30}$	3
40%	$c_{1,22}$	3	$w_{1,31}$	3
50%	$c_{1,23}$	3	$w_{1,32}$	4
60%	$c_{1,24}$	3	$w_{1,33}$	3
70%	$c_{1,25}$	4	$w_{1,34}$	4
80%	$c_{1,26}$	4	$w_{1,35}$	4
90%	$c_{1,27}$	5	$w_{1,36}$	4

The discharge rate is reduced towards the end of the draining to avoid turbulence at the outlet.

Disregarding the relatively small quantities of oil contained in the water that is discharged, it is assumed that the tanks contain the same quantities of oil after completion of the sampling series as they contained at the beginning.

SAMPLING SERIES NO: 2, "DIRTY BALLAST TANKS".

Center tank contains 2.5% crude oil of tank volume.

0 hours	18 h		24 h		40 h		46 h		63 h	
Room temp.: 9°C Water temp.: 4°C	10°C 6.5°C		10°C 7°C		8.5°C 8.0°C		10°C 8°C		9°C 8°C	
Distance above tank bottom	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm
H_1 74 cm	$c_{2,1}$	6	$c_{2,3}$	338	$c_{2,9}$	4	$c_{2,11}$	3	$c_{2,13}$	18
H_2 51.5 cm			$c_{2,4}$	5					$c_{2,14}$	3
H_3 6.5 cm			$c_{2,5}$	12					$c_{2,15}$	6

Wing tank contains 0.5% crude oil of tank volume

H_1 74 cm	$w_{2,2}$	2	$w_{2,6}$	11	$w_{2,10}$	2	$w_{2,12}$	2	$w_{2,16}$	5
H_2 51.5 cm			$w_{2,7}$	2					$w_{2,17}$	2
H_3 6.5 cm			$w_{2,8}$	4					$w_{2,18}$	2

The following quantities of oil remain from sample series No. 1: In the center tank, 3.25 litres, in the wing tank, 0.72 litres.
To increase the oil content to the desired level for this series, the following oil quantities are sprayed into the tanks:
In the center tank, 10.25 litres,
In the wing tank, 1.08 litres.
The tanks are then filled with fresh water until the surface is 1 meter above the bottom. The total liquid level is then,
in the center tank, 540 litres,
in the wing tank, 360 litres.

The samples are drawn according to the above table.

TABLE 19, CONTINUED.

NSFI

After 63 hours, the free water in the lower section of the tanks are drained, leaving only the oil layer in the tanks.

The samples are drawn according to the table below.

After the free water is drained out, it remains the following quantities of oil: In the center tank, 13.5 litres,
In the wing tank, 1.8 litres.

Drained slop in percent of tank volume	CENTER TANK		WING TANK	
	Sample No.	Concentration ppm	Sample No.	Concentration ppm
10%	$c_{2,19}$	14	$w_{2,28}$	2
20%	$c_{2,20}$	5	$w_{2,29}$	2
30%	$c_{2,21}$	5	$w_{2,30}$	2
40%	$c_{2,22}$	4	$w_{2,31}$	2
50%	$c_{2,23}$	4	$w_{2,32}$	3
60%	$c_{2,24}$	4	$w_{2,33}$	2
70%	$c_{2,25}$	5	$w_{2,34}$	3
80%	$c_{2,26}$	5	$w_{2,35}$	5
90%	$c_{2,27}$	5	$w_{2,36}$	4

The discharge rate is reduced towards the end of the draining to avoid turbulence near the outlet.

TABLE 19. CONTINUED.

NSFI

SAMPLING PROGRAM NO. 3, "FLUSHING OF TANKS".

The center tank shall be filled with 5.85 litres of oil. The oil is sprayed on the lower part of the tank bulkheads. The tank is then filled with 78 litres of fresh water. This gives an oil content of 7.5%. This mixture is pumped from the bottom of the tank and into the port slop tank, about halfway up. There shall be an open connection between the bottom of the port slop tank and the middle of the starboard slop tank. This mixing/pumping is done 9 times, simulating the flushing of nine cargo tanks. The total quantity of liquid in the slop tank should then be 720 litres. The center tank and the starboard wing tanks should be full at this point.

PRIMARY SLOP TANK.

0 hours	1 h		17 h		23 h		40 h		45 h	
Room temp.: 9°C	9°C		8°C		7.5°C		6.5°C		6.5°C	
Water temp.: 4°C	5°C		6.5°C		6.5°C		5.5°C		5.5°C	
Distance from interface	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm
H1 15 cm	$s_{3,1}$	323	$s_{3,3}$	95	$s_{3,7}$ A og B	A-96 B-54	$s_{3,9}$	51	$s_{3,11}$	50
H2 41 cm			$s_{3,4}$	64					$s_{3,12}$	45

SECONDARY SLOP TANK

Distance from interface	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm	Sample No.	Concentration ppm
H_1 25 cm	$s_{3,2}$	405	$s_{3,5}$	108	$S_{3,8}$ A og B	A-78 B-78	$s_{3,10}$	59	$s_{3,13}$	80
H_2 48 cm			$s_{3,6}$	89					$s_{3,14}$	56

Samples drawn according to the table.

The capital letters A and B are used to identify the samples when more than one sample is drawn from one point at the time.

TABLE 19, CONTINUED

NSFI

SAMPLING PROGRAM NO. 4, "TANK WASHING".

The slop tanks are now full of slop from the flushing. There shall be an open connection between the bottom of the primary slop tank and the middle of the secondary slop tank.
38,5% of the total slop quantity (equalling 272 litres) shall be drained out. This leaves 443 litres of slop in the tanks.
Washing water mixed with oil shall be pumped into the first slop tank about halfway up, at the same time that the secondary slop tank is opened for decanting to keep the slop level in the primary tank constant.

The discharge rate shall be adjusted so that the slop will take about 3 hours through both the tanks.

I	Required oil quantity in the	1st hour,	5%	crude oil, i.e.	141 litres water,	7.4 litres crude oil,
	" " " " "	2nd " ,	2%	" " "	146 " " ,	3.0 " " "
	" " " " "	3rd " ,	0.2%	" " "	147 " " ,	0.3 " " "
II	" " " " "	4th " ,	5 %	" " "	141 " " ,	7.4 " " "
	" " " " "	5th " ,	2%	" " "	146 " " ,	3.0 " " "
	" " " " "	6th " ,	0.2%	" " "	147 " " ,	0.3 " " "

To obtain a constant oil rate, a peristaltic pump was used.

Room temp.: water temp.:	6.5^{o}C 5.0^{o}C			
TIME	Inlet		Outlet	
	Sample No.	Concentration ppm	Sample No.	Concentration ppm
15 min.	I 4,1A	48000	A.4,2	313
30 "	B	61563	A.4,3	330
45 "	C	50313	A.4,4	199
60 "			A.4,5	230
15 min.	I 4,6	16188	A.4,7	200
30 "			A.4,8	191
45 "			A.4,9	155
60 "			A.4,10	139
15 min	I 4,11	2267	A.4,12	114
30 "			A.4,13	103
45 "			A.4,14	92
60 "			A.4,15	73

6.5^{o}C 6.5^{o}C			
Inlet		Outlet	
Sample No.	Concentration ppm	Sample No.	Concentration ppm
I 4,16A	71250	A.4,17	322
B		A.4,18	257
		A.4,19	257
		A.4,20	43
I 4,21	15729	A.4,22	39
		A.4,23	49
		A.4,24	42
		A.4,25	51
I 4,26	10208	A.4,27	45
		A.4,28	39
		A.4,29	46
		A.4,30	45

The pumped oil quantity deviates a little from the required quantities. This is because the peristaltic pump was not quite adjustable for the required values. However, samples of the slop pumped into the tanks will give the actual oil content.
The slop is to be left for 15 hours for settling.

SAMPLING PROGRAM NO. 5, "DRAINING".

Free water is drained from the secondary slop tank until all the water has been discharged. The slop tanks shall have an open connection between them as previously.

The discharge rate is about 147 litres/hour.

TIME	SAMPLE NO.	CONCENTRATION PPM.
0	A 5,1	8
1/2 h	A 5,2	15
1 h	A 5,3	13
2 h	A 5,5	8
Room temp. Water temp.	6,5^{0}C 6,0^{0}C	

The tank shall be drained until the interface approaches the outlet.

The discharge rate shall be reduced towards the end of the draining to avoid turbulence near the outlet.

TABLE 19, CONTINUED.

NSFI

SAMPLING PROGRAM NO. 6, "DRAINING".

The/water remaining in the secondary slop tank after sample series No. 4, is pumped into the primary slop tank.
The primary slop tank is then left to settle for 66 hours.
All the water is thereafter drained from the bottom of the primary slop tank, using a discharge rate of about 147 litres per hour.

TIME	SAMPLE NO.	CONCENTRATION PPM.
0	$A_{6,1}$	25
1/2 h	$A_{6,2}$	4604
(1 h	$A_{6,3}$)	
Room temp. Water temp.	8°C 8°C	

Samples of the discharge water is drawn every half hour. The discharge is continued until the interface approaches the outlet. Thereafter , samples are drawn from different levels in the remaining slop. The discharge rate is reduced towards the end of the draining, to avoid turbulence near the outlet. Two samples were drawn from the remaining slop in the primary slop tank.

DISTANCE FROM THE TANK BOTTOM	SAMPLE No.	CONCENTRATION
6.5 cm	slop 7,1	1.5%
38 cm	slop 7,2	97 %

TABLE 19, CONTINUED.

Commission No. 832.2012 for
The Ship Research Institute of Norway

Subreport No. 4 B/73

Chemical characterization of crude oil components in ballast and slop water from a very large crude carrier (VLCC) and from model experiments

CIIR Report No. 452-721109 - June 1973

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CHEMICAL CHARACTERIZATION OF CRUDE OIL COMPONENTS IN BALLAST AND SLOP WATER FROM A VERY LARGE CRUDE CARRIER (VLCC) AND FROM MODEL EXPERIMENTS

SUMMARY

As part of the studies proposed in Commission No. 832.2012, Report No. 2/73 "Outline of experiments, load-on-top system", this report presents results from the chemical characterization of crude oil components found in ballast and slop water from a very large crude carrier (VLCC) and from model experiments. The oil content has been determined in 276 samples from a VLCC and in 126 samples from model experiments, using a method based on extraction into an organic solvent followed by quantification by infrared (IR) spectroscopy. In water samples that were particularily rich in oil (slop), the content of water has been determined by azeotropic distillation. A number of aliphatic and aromatic components both in the original crude oil and in water samples have been identified by combined gas chromatography/mass spectrometry (GC-MS). Low and high temperature gas chromatographic (GC) analyses have been carried out on a total of 23 samples in order to estimate relative concentrations of individual components as well as variations in total contents of aliphatics and aromatics, respectively.

The water samples have been received without any further knowledge of the basis for their selection. In this report, the analytical results are presented in tabulated forms, and only a general discussion of the analytical methods employed together with a broad classification of the GC-samples as being very rich, rich, intermediate or low in aromatics has been included.

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1. INTRODUCTION

As part of the studies proposed in Commission No. 832.2012, Report No. 2/73 "Outline of experiments, load-on-top system" (ref. 1), a total of 315 samples from a very large crude carrier (VLCC) and 128 samples from model experiments have been analyzed and characterized by chemical methods. In this report, the methods employed as well as all analytical data obtained will be presented and discussed in some detail.

2. ANALYTICAL METHODS

The water samples collected from the VLCC were to be analyzed for total content of crude oil (ppm) and individual components identified and quantified, whereas the samples from model experiments were to be analyzed only quantitatively. For the latter type of analysis, the infrared spectroscopic (IR) method was chosen, and for the further characterization and identification, suitable methods included gas liquid chromatography (GC) and combined gas liquid chromatography/mass spectrometry (GC/MS). In some of the samples of slop, the water content was determined by azeotropic distillation with toluene. These methods, with experimental details as well as the techniques employed for the storage of samples and for the extraction of crude oil components from samples, are described in the following.

2.1 SAMPLE STORAGE

For preservation of the water from the time of sampling until the analyses, aqueous sulphuric acid (1 ml, 3 N) was added to the empty sampling bottles (100 ml dark brown glass bottles with screw cap, see fig. 2). Thus, the resulting mixtures obtained a pH of approximately 1.5 - 2.0, and algal or bacterial growth in the samples was avoided during transport and storage.

2.2 IR-METHOD

General

The IR-method is used for quantitative estimation of the total content of oil in water. It is fairly rapid and well suited for routine analyses of a large number of samples. Furthermore, the method is non-destructive, and thus, the samples can be preserved for further investigations. The main limitations are a) lack of specificity, i.e. total extractable organics (also other than oil components) containing aliphatic carbon-hydrogen bonds will be determined; b) since aromatic carbon-hydrogen bonds have absorption bands outside the spectral region employed, values for samples that are rich in aromatics might be too low when compared with commonly employed standards; and c) although sufficient for the present purpose, the sensitivity is somewhat limited and often inadequate when sample volumes are small and concentrations of oil are low.

Experimental details

The procedure employed in the present investigation is based on a common and widely accepted method (ref. 2 and 3). Experimental details were as follows:

The water sample was transferred to a separatory funnel (250 ml glass funnel with a Teflon stop cock, see fig. 2). The sample flask was rinsed with carbon tetrachloride (10 ml, Merck, Uvasol grade), which was then added to the funnel and used for quantitative extraction of oil components by shaking (15 min) in a shaking machine (horizontal stroke ca. 6 cm, speed approximately 170 strokes per min, see fig. 1). When the samples were rich in oil, additional carbon tetrachloride was added in portions of 10 ml to the funnel before shaking until a suitable dilution was obtained. After settling (10 min), the organic layer (10 ml) was transferred to a regular glass tube (15 ml, see fig. 3), the volume marked and the sample kept in a refrigerator before analysis. For quantification, an aliquot (ca. 4 ml) was transferred to a quartz cell (1 cm), and the spectral region from about 2.9 to 4.2 μm (3400 to 2400 cm^{-1}) was recorded against a compensating carbon tetrachloride blank (see fig. 8) in a Perkin Elmer Model 457 Double Beam Grating Infrared Spectrophotometer (see fig. 5) operating at slow mode (100 cm^{-1} per min). The absorbances at 3.42 µm (2920 cm^{-1}) and 3.50 µm (2860 cm^{-1}) were added, and the concentration of extractable oil components in the sample was determined directly from a standard curve based on the actual oil that had been transported.

Samples with absorbances larger than approximately 0.9 had to be diluted before final quantification.

Discussion

Due to impurities, the carbon tetrachloride blank showed small background absorptions at 3.42 and 3.50 µm. Varying somewhat from bottle to bottle, this absorption could be significantly reduced, but not completely removed by treatment with Molecular Sieve 5A. Therefore, the solvent was used without pretreatment and care was taken to use solvent from the same bottle for extraction and dilution as well as in the IR reference cell.

The "Florisil" treatment for "removal of non-hydrocarbons" (ref. 2) was not used in the present procedure. Preliminary experiments had shown rather small effects on the absorbances at 3.42 and 3.50 µm, and omittance of this step made the procedure simpler and more rapid. Since this step was also omitted during the preparation of the calibration curve, the error was thereby further reduced and was considered negligible.

The yield of extraction was tested in several experiments prior to the work-up of the actual samples. In the procedure described above, an almost quantitative recovery of oil components was obtained from the water phase, and the single extraction step was as effective as two or three extractions with smaller amounts of solvent (the amount of solvent employed was substantially larger than recommended in ref. 2; i.e. 50 ml of carbon tetrachloride per 3 litres of water).

The calibration curve was based on the actual oil that had been transported (Mena Crude (Kuwait), API 31.8, sp.g. 0.8665, T=82°F).

Being a little higher, these values differed somewhat from those obtained from a recommended (ref. 3) synthetic standard blend routinely used in our laboratories for quantification of unknown samples.

2.3 GC-METHOD

General

The gas liquid chromatographic (GLC or GC) analytical method is widely employed for the characterization and qualitative and quantitative analyses of organic components (also recommended in ref. 2). In principle, a given component (or a mixture of components) is injected as a liquid (or in solution) into the GC where it is vaporized and carried through a separation column in a stream of carrier gas (usually nitrogen, N_2, or helium, He). Ideally, components will be completely separated and registered individually in a suitable detector (the general response flame ionization detector (FID) is commonly used for hydrocarbon analyses). The detector signals are amplified and visualized on a strip chart recorder. The peaks in the resulting gas chromatogram can be quantified either by manual methods (measurements of peak heights etc.), or an electronic integrator can be employed in the calculations. The use of an internal or an external standard is recommended for precise determinations.

The general requirements are

a) all components in a given mixture have to be vaporized at the given injector temperature (up to approximately 300°C) for complete analysis;

b) all components should be thermally stable during the whole chromatographic sequence;

c) individual components should be present in concentrations of at least a few nanograms (ng) per ml (ppb); and

d) for exact quantification, all components in a given mixture have to be completely separated and linear reponse curves should be recorded for each component by the use of pure standards.

With rather complex mixtures (such as crude oil), several compromises have to be reached. For complete characterization of the low boiling components in a given crude oil, a high resolution capillary column must be employed. Higher boiling components can be further characterized with a high capacity packed column operating at higher temperatures. Still, components boiling above approximately 350-400°C will not be vaporized and analyzed under ordinary GC conditions.

Experimental details

Sample volumes of 100 ml with expected low oil contents of a few ppm, seriously restricted the maximum amount of organic solvent that could be employed. Furthermore, since preconcentration of an extract by evaporation causes heavy loss of volatile components, the following experimental procedure was used for extraction of oil components prior to GC (and GC/MS) analysis:
To the sample bottle was added carbon disulfide (0.3 ml, Merck pro analysi), the screw cap was fitted with aluminium foil prerinsed with the same solvent and the mixture was shaken in a shaking machine (15 min) and immediately transferred to a separatory funnel (250 ml). After settling (10-15 min), approximately 10 ml of the content was transferred to a centrifuge tube (10 ml). After centrifugation (5 min, 1500 rpm, see fig. 4), the organic layer containing the oil components was found as a small droplet in the bottom of the tube (see fig. 3). From this droplet, aliquots (1 µl) were removed for GC (or GC/MS) analyses by the use of a hypodermic syringe (10 µl) pushed through the water layer.

The instruments used in the GC analyses were the following (see fig. 6):
Gas chromatograph: Perkin Elmer Model 900.
Recorder: Hitachi Perkin Elmer Model 159 (1 mV).
Integrator: Varian Aerograph Model 480 Electronic Integrator.

The experimental conditions for the low temperature GC were as follows:

Column: "SCOT" 50 feet x 0.02 inches ID
Polyphenylether OS-138 (theoretical plates (n) = 32.000 or 2.100 per metre).
Carrier gas: 4 ml per min nitrogen (N_2) through the column (split 1:3)
Detector: Flame ionization FID (single)
Detector temperature: 200 °C
Injector temperature: 150 °C
Column temperatures: Isothermal 10 °C for 3 min; programmed run 10-190 °C with 6 °C per min; isothermal 190 °C for approximately 10 min
Injected volumes: 1 µl of the carbon disulfide solutions;
0.2 µl of the pure oil sample.

The experimental conditions for the high temperature GC were as follows:

Column: 2 M 3.6 % SE 30 on Chromosorb W 80-100 mesh (theoretical plates (n)=3000 or 1500 per metre)
Carrier gas: 30 ml per min nitrogen (N_2) through the column
Detector: Flame ionization FID (double)
Detector temperature: 300 °C
Injector temperature: 300 °C
Column temperatures: Isothermal 150 °C for 1 min, programmed run 150-290 °C with 6 °C per min; isothermal 290 °C for approximately 10 min
Injected volumes: 1 µl of the carbon disulfide solutions;
0.4 µl of the pure oil sample

In the low temperature GC, the resolution of components were high and the integrator could be used for all peak area measurements. Furthermore, a number of components could be identified prior to the GC/MS analysis by comparison with chromatograms of mixtures of pure standards. These standards were also used for the determination of individual response curves. In the high temperature GC, the integrator was not capable of adjusting itself to the elevated base line, and peak areas in these chromatograms were computed by multiplying the values of the peak height by the width at one-half height.

Discussion

The main objectives behind the GC determinations were:

a) obtaining optimum separation of individual components,

b) determining relative concentrations of individual components,

c) determining variations in total contents of aliphatics and aromatics respectively,

d) determination of absolute concentrations was concidered being less important and could only be roughly estimated by the selected method.

The extraction step was critical and had to be performed in such a way that a) the largest number of components would be present in sufficient concentration for detection and identification, and that b) if possible, it should be quantitative for all components present and no preferential extraction of any component should take place.

These requirements restricted the total amount of organic solvent that could be employed and excluded the use of a preconcentration step by evaporation. In order to test the described GC extraction procedure, sea water (100 ml) was mixed with weighed amounts of crude oil in glass bottles and placed in the shaking machine. The resulting samples were low in overall concentrations of crude oil, varying between 150 and 500 ppm and thus, were of the same order of magnitude as a number of the actual samples. Extraction with 0,3, 0,5 or 0,7 ml of carbon disulfide (which has a very low response in FID) followed by centrifugation and analyses by low temperature GC showed the following:

a) all components in the original oil (including the volatiles) were present in the extract,

b) no preferential extraction of any component seemed to have taken place, and

c) the resulting volume of carbon disulfide after centrifugation varied from sample to sample, and, thus, it is more precise determining relative concentrations of individual components rather than absolute values.

Furthermore, when centrifuged samples were kept at 4 °C for some time (for example 15 days), repeated analysis showed larger concentrations of all components, probably caused by dissolution of solvent into the water phase.

2.4 GC/MS-METHOD

General

Mass spectrometry combined with gas chromatography (GC/MS) is considered one of the most versatile methods in modern organic analytical chemistry. It combines the advantages of GC with absolute structure identification of the individual components. In particular, the combination with high resolution GC offers the possibilities for rapid identification of a large number of components in rather complex mixtures. In principle, individual components that are eluted from the GC pass through a capillary tube into the ion source in the MS. Here, the molecules are split into positively charged fragments which are then removed by a strong negative electric field followed by deflections in a magnetic field. Thereby, these charged species are selected and determined according to their mass to charge ratio, and the molecular weight and structure of the original molecule can be interpreted from the recorded line spectrum.

Detection limits are of the order of a few ppb, and for complete identification, components should be sufficiently pure or well separated from other components and be thermally stable in the vapor phase.

Experimental details

The extraction procedure was the same as used for the GC-determinations and is already described in detail (page 7). The following instruments and conditions were used in the GC/MS analyses (see fig. 7):

Mass spectrometer: Hitachi-Perkin Elmer RMU 6L

Gas chromatograph: Perkin Elmer Model 801

Column: As for the low temperature GC

Carrier gas: 4 ml per min helium (He) through the column

Make up gas for the mass spectrometer: 11 ml per min He
Detector: Total ion current (TIC)
Column temperatures: Isothermal 15 °C for 5 min; programmed run 15-190 °C with 5 °C per min; isothermal at 190 °C
Ionization chamber temperature: 240 °C
Electron energy: 70 eV
Injected volumes: 0.3 µl of the carbon disulfide solutions;
0.1 µl of the pure oil sample (used without a split).

Discussion

The main objective behind the GC/MS determinations was identification of as many components as possible both in water samples as well as in the original oil. Selection of samples for this analysis was based on the results obtained by GC in order to get complete identification of all components present throughout the samples. In addition to pure standards and the actual oil, samples being rich in aromatics as well as samples containing all types of hydrocarbons were analyzed by this method.

2.5 Determination of water content

In some of the samples that were very rich in oil (collected from the top of the slop tanks), the content of water was determined by azeotropic distillation with toluene. In the procedure employed, the sample was distilled with toluene (100 ml, Merck pro analysi) in a round bottomed glass flask (500 ml). The water phase was collected by condensation and the volume was measured in a graduated cylinder when no more water could be removed from the mixture.

3. RESULTS AND DISCUSSION

Details regarding the selection of water samples have not been available during the present study. Consequently, only results from the chemical analyses of the samples will be presented and discussed in the following.

3.1 Determination of total oil contents

A total of 276 samples from a VLCC and 126 samples from model tank experiments have been analyzed by the IR-method (page 3) and the results are summarized in table 1 and 2, respectively. Most of the values are expressed as mg per litre of sample, which are almost the same as ppm (sp.g. of sea water is approximately 1.025). Some of the recorded spectra of extracted water samples differ from that of the standard crude oil. In some cases, new bands occur in the region of aromatic carbon-hydrogen absorption (denoted "a" in the tables), whereas in other spectra, variations in relative intensities between the aliphatic absorption bands are observed (denoted "b" in the tables).

Samples that are rich in aromatics would give absorptions of the former type, whereas a difference in the distribution between branched and straight chain hydrocarbons could alter the pattern of absorption bands as observed in the latter cases.

3.2 Determination of water content

The content of water has been determined (page 11) in 16 samples from a VLCC and in 2 samples from model experiments, and the results in table 1 and 2 are expressed as percent by weight.

3.3 GC/MS - determinations

In order to identify the largest number of components encountered in this investigation, samples were selected for determination by GC/MS on basis of their gas chromatograms. For establishment of suitable analytical conditions as well as some useful reference data, a syntetic standard mixture consisting of n-alkanes (C_5 - C_{16}) and aromatics (benzene, toluene, ethylbenzene, m-xylene and naphthalene) were analyzed by the described method (page 10). Typical examples of mass spectra of alkanes and of aromatic compounds are shown in fig. 9 and 10, respectively.

The analysis of the original crude oil resulted in the recording of 100 mass spectra. Most of the compounds seen in the chromatogram (fig. 11) have been fully identified, either by comparison with available reference data or by the aid of molecular weights and given fragment patterns. In some cases, compounds have been characterized by their general molecular formula and by further structural information obtained from their mass spectra. Thus, an unknown aliphatic compound might be listed as C_8H_{18} (an octane isomer) and an aromatic compound as an alkyl (C_4) benzene isomer (a benzene ring substituted either by a butyl, propyl and methyl, two ethyls, one ethyl and two methyls, or four methyl groups).

Furthermore, one sample rich in both aliphatics and aromatics (sample No. 271) as well as two samples very rich in aromatics (sample No. 54 and No 132) have been characterized by this method. From sample No. 271, a total of 70 mass spectra were recorded, whereas 23 compounds could be identified in sample No. 132 (No. 54 was lower in concentration of oil and little structural information could be obtained from this sample). The structural information obtained may be seen from tables 3, 6 and 8.

3.4 GC-determinations

In addition to the actual crude oil and several synthetic standards, a total of 23 samples from a VLCC have been analyzed by the GC-methods previously described (page 6). One sample (No. 189) was lost before the final analysis. The actual samples were selected in such a way as to "a" fulfil the main objectives (see page 9) and "b" obtain information about possible correlations between different ship operative procedures and variations in the observed relative amounts and general nature of individual oil components found in the water phase (detailed descriptions of the samples are not available here). The analyses have resulted in a rather large amount of experimental data, and in the following, some of the more important conclusions will be presented and discussed.

Crude oil

The crude oil was chromatographed both by low (see fig. 11) and high temperature GC-techniques, and table 3 and 4 summarize the nature of individual components identified together with elution temperatures, absolute values and values relative to n-heptane for peak areas, and, for a few components only, a rough estimate of absolute concentrations in the injected extract. Where two (or more) components are not resolved, peak areas are displaced to the right in the table column. In this original material, aliphatic components dominate, and, based on values obtained from the low temperature GC, constitute more than 80 % of total material encountered (see fig. 14).

Oil in slop tank

The GC-determinations show that the sample analyzed (No. 312) is very similar to the original oil, except that in the high temperature chromatogram (see fig. 13 and table 5), higher boiling aliphatic constituents (C_{29} and above) are present in somewhat larger concentrations. Since the solubilities of higher boiling fractions of crude oil are reported to be extremely low (see e.g. ref. 4), this is to be expected.

Water samples

Judged by their low temperature gas chromatograms some of the samples show distinct differences in the distribution between aliphatic and aromatic constituents. In sample No. 271 (table 6), which is fairly rich in total oil, aromatics are present in a total concentration not very different from that in the crude oil (see also fig. 14), but in several other samples (examplified by No. 132, fig. 12 and 14), aromatic compounds have been enriched to a very large degree. As can be seen from table 8, the compounds that have been most enriched are aromatics like benzene, toluene, xylene and various other alkylbenzenes together with some of the lower aliphatics (boiling up to n-heptane). Some naphtalenes are also preent in this sample. It has been found unnecessary to tabulate values for all the other samples that have been analyzed by GC. However, some conclusions can be drawn when the distribution between aliphatic and aromatic constituents are being compared. In table 9, the samples (denoted by their numbers) have been arranged according to the degree of enrichment.

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TABLE 1

DETERMINATION OF OIL (IR-METHOD) AND OF WATER (AZEOTROPIC DISTILLATION) IN SAMPLES FROM A VLCC

Sample no.	Concentration of oil (mg per litre)	Sample no.	Concentration of oil (mg per litre)
1	1[a]	31	77
2	< 1	32	75
3	6	33	75
4	6[b]	34	78
5	120	35	62
6	114	36	82
7	106	37	123
8	94	38	73
9	112	39	117
10	91	40	17[a]
11	132	41	18[a]
12	120	42	16[a]
13	150	43	63
14	93	44	68
15	137	45	67
16	123	46	
17	143	47	
18	88	48	
19	126	49	108
20	93	50	
21	158	51	113
22	136	52	
23	148	53	
24	143	54	
25	160	55	1
26	146	56	1
27	148	57	40
28	142	58	42
29	199	59	40
30	< 1	60	45

TABLE 1 (p. 2)

Sample no.	Concentration of oil (mg per litre)	Sample no.	Concentration of oil (mg per litre)
61	46	91	83
62	38	92	73
63	46	93	75
64	109	94	9[a]
65	105	95	9[a]
66	11[a]	96	11[a,b]
67	11[a]	97	<1
68	12[a]	98	6
69	<1	99	25
70	39	100	27
71	41	101	28
72	42	102	27
73	37	103	24
74	35	104	25
75	40	105	85
76	109	106	83
77	93	107	64
78	98	108	78
79	6	109	65
80[a,b]	10[a,b]	110	66
81[a,b]	11[a,b]	111	11[a]
82		112	10
83	< 1	113	9[b]
84	< 1	114	192
85	27	115	123
86	28[a]	116	154
87	28	117	74
88	25	118	98
89	25	119	108
90	27	120	

TABLE 1 (p. 3)

Sample no.	Concentration of oil (mg per litre)	Sample no.	Concentration of oil (mg per litre)
121	<1	151	69
122	<1	152	86[a]
123	34[a]	153	2
124		154	1
125	43[a]	155	17[a]
126		156	17
127		157	16[a]
128		158	30[a]
129	57	159	28[a]
130		160	29[a]
131	54	161	7[a,b]
132		162	7[a,b]
133		163	8[a,b]
134		164	18[a]
135	21[a]	165	16
136	20[a]	166	17[a]
137	22[a]	167	55
138	82	168	
139		169	23[a]
140	99	170	
141	<1	171	22[a]
142	<1	172	21[a]
143	65	173	42[a]
144	74	174	52[a]
145	79	175	<1
146	32	176	<1
147	35[a]	177	17[a]
148	32	178	18[a]
149	40	179	18
150	44[a]	180	17[a]

TABLE 1 (p. 4)

Sample no.	Concentration of oil (mg per litre)	Sample no.	Concentration of oil (mg per litre)
181	17	211	248
182	15[a]	212	156
183	8[a,b]	213	151
184	8[a,b]	214	141
185	7[a,b]	215	148
186	99	216	133
187	94	217	143
188	234	218	196
189		219	228
190	246	220	186
191	288	221	92
192	260	222	101
193	380	223	20
194	282	224	20
195	285	225	17
196	213	226	18
197	228	227	<1
198	198	228	36
199	155	229	21
200	158	230	25
201	112	231	23
202	127	232	16
203		233	5
204	110	234	12
205	104	235	63
206	94	236	26
207		237	60
208	95	238	33
209	72	239	60
210	57	240	94

TABLE 1 (p. 5)

Sample no.	Concentration of oil (mg per litre)	Sample no.	Concentration of oil	
			(mg/l)	(g/l)
241	116	271		
242	86	272	493	
243	193	273	615	
244	280	274	795	
245	282	275	745	
246	111	276	845	
247	97	277		2,4
248	105	278		2,6
249	115	279		28,1
250	116	280		
251		281		
252	< 1	282	26	
253	< 1	283	25	
254	200	284	23	
255	181	285	15	
256	174	286	< 1	
257	128	287	24	
258	134	288	24	
259	141	289	23	
260	164	290	9	
261	171	291	9	
262	181	292	13	
263		293	< 1	
264	210	294	2	
265	173	295	575	
266	226	296	368	
267	284	297	312	
268	366	298	388	
269	405	299	620	
270	388	300	655	

TABLE 1 (p. 6)

Sample no.	Concentration of oil (mg/l)	Concentration of oil (g/l)
301		1,3
302	830	
303	975	
304		47,5
305		

Sample no.	Content of water (per cent by weight)
82	16
120	38
251	9
305	25
306	20
307	19
308	20
309	11
310	21
311	23
313	23
314	24
315	27
316	26
317	27
318	18

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a = addition IR-absorption bands, probably due to aromatics

b = relative intensities of hydrocarbon absorption bands varying from the standard

TABLE 2

DETERMINATION OF OIL (IR-METHOD) AND OF WATER (AZEOTROPIC DISTILLATION) IN SAMPLES FROM MODEL TANK EXPERIMENTS.

Sample no.	Concentration of oil (mg/l)	Concentration of oil (g/l)
A 4,29	46	
A 4,30	45	
A 5,1	8	
A 5,2	15	
A 5,3	13	
A 5,4	sample lost	
A 5,5	8	
S 3,1	323	
VA 6,1	25	
VA 6,2		4,6
A 4,20	43	
I 4,21		15,7
A 4,22	39	
A 4,23	49	
A 4,24	42	
A 4,25	51	
A 4,26		1,2
A 4,27	45	
A 4,28	39	
I 4,11		2,3
A 4,12	114	
A 4,13	103	
A 4,14	92	
A 4,15	73	
A 4,16		71,1
A 4,17	322	
A 4,18	257	
A 4,19	257	
I 4,2	313	
I 4,3	330	
I 4,4	199	
I 4,5	230	
I 4,6		16,2
I 4,7	200	
A 4,8	171	
A 4,9	155	
A 4,10	139	
S 3,9	51	
S 3,10	59	
S 3,11	50	
S 3,12	45	
S 3,13	80	
S 3,14	56	
I 4,1 A		48,0
I 4,1 B		61,6
I 4,1 C		50,3
S 3,2	405	
S 3,3	95	
S 3,4	64	
S 3,5	108	
S 3,6	89	
S 3,7 A	46	
S 3,7 B	54	
S 3,8 A	78	
S 3,8 B	78	
W 2,28	2	
W 2,29	2	
W 2,30	2	
W 3,31	2	
W 3,32	3	
W 3,33	2	
W 3,34	3	

TABLE 2 (p. 2)

Sample no.	Concentration of oil (mg per litre)
W 3,35	5
W 3,36	4
C 2,19	14
C 2,20	5
C 2,21	5
C 2,22	4
C 2,23	4
C 2,24	4
C 2,25	5
C 2,26	5
C 2,27	5
W 2,10	2
C 2,11	3
W 2,12	2
C 2,13	18
C 2,14	3
C 2,15	6
W 2,16	5
W 2,17	2
W 2,18	2
C 2,1	6
C 2,2	2
C 2,3	338
C 2,4	5
C 2,5	12
W 2,6	11
W 2,7	2
W 2,8	4
C 2,9	4
W 1,28	2
W 1,29	3
W 1,30	3
W 1,31	3
W 1,32	4
W 1,33	3
W 1,34	4
W 1,35	4
W 1,36	4
C 1,19	3
C 1,20	3
C 1,21	3
C 1,22	3
C 1,23	3
C 1,24	3
C 1,25	4
C 1,26	4
C 1,27	5
W 1,10	9
W 1,12	4
C 1,11	2
C 1,13	135
C 1,14	4
C 1,15	12
W 1,16	4
W 1,17	2
W 1,18	3
C 1,1	10
W 1,2	9
C 1,3	650
C 1,4	18
C 1,5	16
W 1,6	14

TABLE 2 (p. 3)

Sample no.	Concentration of oil (mg per litre)
W 1,7	3
W 1,8	2
C 1,9	2

Sample no.	Content of water (per cent by weight)
7,1	1,5
7,2	97

A rather large number of these samples showed variations in the relative intensities of hydrocarbon absorption bands when compared with the standard.

TABLE 3

LOW TEMPERATURE GC-DATA FOR CRUDE OIL

Component	Formula	Elution temperature (°C)	Peak area x)	Peak area x) relative to n-heptane	Estimated concentration mg/ml of oil
methane	CH_4	10			
ethane	C_2H_6	10	557	2	
propane	C_3H_8	10	974	4	
butane	C_4H_{10}	10	5212	19	
i-pentane	C_5H_{12}	10	8742	33	
n-pentane	C_5H_{12} (n)	11	16551	62	3,5
2-methylpentane	C_6H_{14}	25	10716	40	
3-methylpentane	C_6H_{14}	29	9379	35	
n-hexane	C_6H_{14} (n)	34	22585	84	7,5
2,2-dimethylpentane	C_7H_{16}	40			
methylcyclopentane	C_6H_{12}	44	4359	16	
2-methylhexane	C_7H_{16}	51	7614	28	
3-methylhexane	C_7H_{16}	54	12583	47	
alkane (C_7)	C_7H_{14}	57			
n-heptane	C_7H_{16} (n)	60	26762	100	
n.i.	-	67	2931	11	
methylcyclohexane	C_7H_{14}	69	7685	29	
alkene (C_7)	C_7H_{14}	72	2144	8	

TABLE 3 (p. 2)

Component	Formula	Elution temperature (°C)	Peak x) area	Peak area x) relative to n-heptane	Estimated concentration mg/ml of oil
alkene (C_8)	C_8H_{16}	73	2309	9	
benzene	C_6H_6	73			
2-methylheptane	C_8H_{18}	76,5	13216	49	
3-methylheptane	C_8H_{18}	78	7833	29	
alkene (C_8)	C_8H_{16}	84	3185	12	
n-octane	C_8H_{18} (n)	86	24218	90	
alkane (C_9)	C_9H_{20}	91	3107	12	
alkane (C_9)	C_9H_{20}	93	2585	10	
alkene (C_9)	C_9H_{18}	98			
toluene	C_7H_8	99	10042	38	2,0
2-methyloctane	C_9H_{20}	100,5	7072	26	
3-methyloctane	C_9H_{20}	102	6886	26	
n-nonane	C_9H_{20} (n)	109	22778	85	7,0
alkene (C_9)	C_9H_{18}	113	2029	8	
alkane (C_{10})	$C_{10}H_{22}$	115,5	5422	20	
n.i.	-	117	4325	16	
alkene (C_9)	C_9H_{18}	120	8098	30	
ethylbenzene	C_8H_{10}	120			
p-xylene	C_8H_{10}	122	7874	29	3,0
m-xylene	C_8H_{10}	122			

TABLE 3 (p. 3)

Component	Formula	Elution temperature (°C)	Peak[x)] area	Peak area[x)] relative to n-heptane	Estimated concentration mg/ml of oil
alkane (C_{10})	$C_{10}H_{22}$	123	9031	3	
alkene (C_{10})	$C_{10}H_{20}$	124,5	2662	10	
o-xylene	C_8H_{10}	129	5249	20	2,5
n-decane	$C_{10}H_{22}$ (n)	130,5	23170	87	
i-propylbenzene	C_9H_{12}	130,5			
alkane (C_{11})	$C_{11}H_{24}$	134	5485	20	
n-propylbenzene	$C_{11}H_{24}$	139	1932	7	
n.i.	-	139			
alkene (C_{11})	$C_{11}H_{22}$	141	13503	50	
ethylmethylbenzene	C_9H_{12}	141			
ethylmethylbenzene	C_9H_{12}	144,5	4840	18	
n.i.	-	144,5			
alkane (C_{11})	$C_{11}H_{24}$	146	3387	13	
ethylmethylbenzene	C_9H_{12}	146			
trimethylbenzene	C_9H_{12}	148,5	-		
n-undecane	$C_{11}H_{24}$ (n)	150	27988	105	
alkyl (C_4) benzene	$C_{10}H_{14}$	150			
n.i.	-	153	4867	18	

TABLE 3 (p. 4)

Component	Formula	Elution temperature (°C)	Peak area x)	Peak area x) relative to n-heptane	Estimated concentration mg/ml of oil
n.i.	-	155	3007	11	
(1,2-diethylbenzene)	$C_{10}H_{14}$	157	5167	19	
alkyl (C_4) benzene	$C_{10}H_{14}$	159	2013	8	
(methylpropylbenzene)	$C_{10}H_{14}$	160,5	6485	24	
alkane (C_{12})	$C_{12}H_{26}$	162	6833	26	
alkyl (C_4) benzene	$C_{10}H_{14}$	164	4909	18	
n.i.	-	164			
alkyl (C_4) benzene	$C_{10}H_{14}$	165	3690	14	
n.i.	-	167	2738	10	
n-dodecane	$C_{12}H_{26}$ (n)	169	23327	87	
n.i.	-	172	3253	12	
alkyl (C_5) benzene	$C_{11}H_{16}$	174	3648	14	
alkyl (C_5) benzene	$C_{11}H_{16}$	178	8488	32	
alkane (C_{14})	$C_{14}H_{30}$	180	8065	30	
n.i.	-	181	3996	15	
n.i.	-	183	4765	18	
n-tridecane	$C_{13}H_{28}$ (n)	186	22543	84	
alkyl (C_5) benzene	$C_{11}H_{16}$	186			
alkane (C_{14})	$C_{14}H_{30}$	190	7996	30	
alkyl (C_6) benzene	$C_{12}H_{18}$	190			

TABLE 3 (p. 5)

Component	Formula	Elution temperature (°C)	Peak area x)	Peak area x) relative to n-heptane	Estimated concentration mg/ml of oil
alkane (C_{14})	$C_{14}H_{30}$	190	9595	36	
n-tetradecane	$C_{14}H_{30}$ (n)	190	23374	87	
n.i.	-	190	10732	40	
methylnaphthalene	$C_{11}H_{10}$	190	2790	10	
n-pentadecane	$C_{15}H_{32}$ (n)	190	21043	79	
n-hexadecane	$C_{16}H_{34}$ (n)	190	13357	50	
n-heptadecane	$C_{17}H_{36}$ (n)	190	-	-	

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n.i. = not identified

x) values for nonresolved components are displaced to the right

TABLE 4

HIGH TEMPERATURE GC-DATA FOR CRUDE OIL

Component	Formula	Elution temperature (°C)	Peak area	Estimated concentration mg/ml in oil
n-hexadecane	$C_{16}H_{34}$ (n)	171	2128	6,7
	$C_{17}H_{36}$ (n)	179	1952	6,1
	$C_{18}H_{38}$ (n)	189	2112	6,6
	$C_{19}H_{40}$ (n)	199	1280	4,0
n-eicosane	$C_{20}H_{42}$ (n)	209	1056	3,3
	$C_{21}H_{44}$ (n)	219	816	2,6
	$C_{22}H_{46}$ (n)	228	688	2,2
	$C_{23}H_{48}$ (n)	237	576	1,8
	$C_{24}H_{50}$ (n)	246	480	1,5
n-pentacosane	$C_{25}H_{52}$ (n)	255	384	1,2
	$C_{26}H_{54}$ (n)	263	368	1,2
	$C_{27}H_{56}$ (n)	271	288	0,9
	$C_{28}H_{58}$ (n)	278	256	0,8
	$C_{29}H_{60}$ (n)	286	144	0,5
n-triacontane	$C_{30}H_{62}$ (n)	290	224	0,7
	$C_{31}H_{64}$ (n)	290	160	0,5
	$C_{32}H_{66}$ (n)	290	192	0,6
	$C_{33}H_{68}$ (n)	290	96	0,3
	$C_{34}H_{70}$ (n)	290	96	0,3

TABLE 5

HIGH TEMPERATURE GC-DATA FOR SAMPLE NO. 312(SLOP)

Component	Formula	Elution temperature (°C)	Peak area	Estimated concentration mg/ml in oil
n-hexadecane	$C_{16}H_{34}$ (n)	171	2336	7,3
	$C_{17}H_{36}$ (n)	179	2144	6,7
	$C_{18}H_{38}$ (n)	189	2000	6,3
	$C_{19}H_{40}$ (n)	199	1360	4,3
n-eicosane	$C_{20}H_{42}$ (n)	209	1152	3,6
	$C_{21}H_{44}$ (n)	219	880	2,8
	$C_{22}H_{46}$ (n)	228	768	2,4
	$C_{23}H_{48}$ (n)	237	624	2,0
	$C_{24}H_{50}$ (n)	246	512	1,6
n-pentacosane	$C_{25}H_{52}$ (n)	255	472	1,5
	$C_{26}H_{54}$ (n)	263	432	1,4
	$C_{27}H_{56}$ (n)	271	336	1,1
	$C_{28}H_{58}$ (n)	278	352	1,1
	$C_{29}H_{60}$ (n)	286	336	1,1
n-triacontane	$C_{30}H_{62}$ (n)	290	624	2,0
	$C_{31}H_{64}$ (n)	290	736	2,3
	$C_{32}H_{66}$ (n)	290	784	2,5
	$C_{33}H_{68}$ (n)	290	696	2,2
	$C_{34}H_{70}$ (n)	290	696	2,2

TABLE 5 (p. 2)

Component	Formula	Elution temperature (°C)	Peak area	Estimated concentration mg/ml in oil
n-pentatriacontane	$C_{35}H_{72}$ (n)	290	512	1,6
	$C_{36}H_{74}$ (n)	290	520	1,6
	$C_{37}H_{76}$ (n)	290	432	1,4
	$C_{38}H_{78}$ (n)	290	448	1,4
	$C_{39}H_{80}$ (n)	290	400	1,3
n-tetracontane	$C_{40}H_{82}$ (n)	290	240	0,8
	$C_{41}H_{84}$ (n)	290	160	0,5

TABLE 6

LOW TEMPERATURE GC-DATA FOR SAMPLE NO. 271

Component	Formula	Elution temperature (°C)	Peak area x)	Peak area x) relative to n-heptane	Estimated concentration mg/ml in CS_2 extract
methane	CH_4	10	136	1	
ethane	C_2H_6	10	1340	9	
propane	C_3H_8	10	739	5	
butane	C_4H_{10}	10	4324	30	
i-pentane	C_5H_{12}	10	3782	26	
n-pentane	C_5H_{12} (n)	11	7087	49	0,3
solvent	CS_2				
n-hexane	C_6H_{14} (n)	34	9638	67	0,4
methylcyclopentane	C_6H_{12}	44	2534	18	
2-methylhexane	C_7H_{16}	51	3896	27	
3-methylhexane	C_7H_{16}	54	7024	49	
n-heptane	C_7H_{16} (n)	60	14426	100	0,5
n.i.	-	67	790	5	
methylcyclohexane	C_7H_{14}	69	4437	31	
benzene	C_6H_6	73	7467	52	0,3
2-methylheptane	C_8H_{18}	76,5	7438	52	
3-methylheptane	C_8H_{18}	78	4319	30	
alkene (C_8)	C_8H_{16}	84	1770	12	
n-octane	C_8H_{18} (n)	86	13365	92	0,5

TABLE 6 (p. 2)

Component	Formula	Elution temperature (°C)	Peak area[x)]	Peak area[x)] relative to n-heptane	Estimated concentration mg/ml in CS_2 extract
alkane (C_9)	C_9H_{20}	91	1623	11	
alkane (C_9)	C_9H_{20}	93	1329	9	
alkene (C_9)	C_9H_{18}	98	-	-	
toluene	C_7H_8	99	18870	131	0,6
2-methyloctane	C_9H_{20}	100,5	3631	25	
3-methyloctane	C_9H_{20}	102	3486	24	
n-nonane	C_9H_{20} (n)	109	11264	78	0,4
alkene (C_9)	C_9H_{18}	113	928	6	
alkane (C_{10})	$C_{10}H_{22}$	115,5	2539	18	
n.i.	-	117	1891	13	
alkene (C_9)	C_9H_{18}	120	5026	35	
ethylbenzene	C_8H_{10}	120			
p-xylene	C_8H_{10}	122	5358	37	0,2
m-xylene	C_8H_{10}	122			
alkane (C_{10})	$C_{10}H_{22}$	123	5357	37	
alkene (C_{10})	$C_{10}H_{20}$	124,5	1049	7	
o-xylene	C_8H_{10}	129	4161	29	0,1
n-decane	$C_{10}H_{22}$ (n)	130,5	9126	63	
i-propylbenzene	C_9H_{12}	130,5			

TABLE 6 (p. 3)

Component	Formula	Elution temperature (°C)	Peak[x)] area	Peak area[x)] relative to n-heptane	Estimated concentration mg/ml in CS_2 extract
alkane (C_{11})	$C_{11}H_{24}$	134	2087	14	
n-propylbenzene	C_9H_{12}	139	798	6	
ethylmethylbenzene	C_9H_{12}	141	6213	43	
ethylmethylbenzene	C_9H_{12}	144,5	1846	13	
ethylmethylbenzene	C_9H_{12}	146	1462	10	
n-undecane	$C_{11}H_{24}$ (n)	150	9653	67	
alkyl (C_4) benzene	$C_{10}H_{14}$	150			
n.i.	-	153	1443	10	
n.i.	-	155	803	6	
(1,2-diethylbenzene)	$C_{10}H_{14}$	157	1975	14	
alkyl (C_4) benzene	$C_{10}H_{14}$	159	610	4	
alkyl (C_4) benzene	$C_{10}H_{14}$	160,5	1774	13	
alkyl (C_4) benzene	$C_{10}H_{14}$	162	2059	14	
n.i.	-	162			
alkyl (C_4) benzene	$C_{10}H_{14}$	164	1352	9	
alkyl (C_4) benzene	$C_{10}H_{14}$	165	1148	8	
n.i.	-	167	820	6	
n-dodecane	$C_{12}H_{24}$ (n)	169	5943	41	
n.i.	-	172	943	7	

TABLE 6 (p. 4)

Component	Formula	Elution temperature (°C)	Peak[x)] area	Peak area[x)] relative to n-heptane	Estimated concentration mg/ml in CS_2 extract
alkyl (C_5) benzene	$C_{11}H_{16}$	174	923	6	
alkyl (C_5) benzene	$C_{11}H_{16}$	178	2078	14	
alkane (C_{14})	$C_{14}H_{30}$	180	2111	15	
n.i.	-	183	969	7	
n-tridecane	$C_{13}H_{28}$ (n)	186	5841	40	
alkyl (C_6) benzene	$C_{12}H_{18}$	190	1991	14	
naphthalene	$C_{10}H_8$	190	791	5	
alkane (C_{14})	$C_{14}H_{30}$	190	2267	16	
n-tetradecane	$C_{14}H_{30}$ (n)	190	4408	31	
methylnaphthalene	$C_{11}H_{10}$	190	109	0,7	
n-pentadecane	$C_{15}H_{32}$ (n)	190	2300	16	
n-hexadecane	$C_{16}H_{34}$ (n)	190	1388	10	
dimethylnaphthalene	$C_{12}H_{12}$	190			
trimethylnaphthalene	$C_{13}H_{14}$	190	100	0,7	

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n.i. = not identified

x) see footnote in table 3

TABLE 7

HIGH TEMPERATURE GC-DATA FOR SAMPLE NO. 271

Component	Formula	Elution temperature (°C)	Peak area	Estimated concentration (mg/ml) in CS_2 - extract
n-hexadecane	$C_{16}H_{34}$ (n)	171	243	0,29
	$C_{17}H_{36}$ (n)	179	216	0,26
	$C_{18}H_{38}$ (n)	189	186	0,22
	$C_{19}H_{40}$ (n)	199	138	0,17
n-eicosane	$C_{20}H_{42}$ (n)	209	118	0,14
	$C_{21}H_{44}$ (n)	219	90	0,11
	$C_{22}H_{46}$ (n)	228	80	0,10
	$C_{23}H_{48}$ (n)	237	64	0,08
	$C_{24}H_{50}$ (n)	246	56	0,07
n-pentacosane	$C_{25}H_{52}$ (n)	255	46	0,06
	$C_{26}H_{54}$ (n)	263	42	0,05
	$C_{27}H_{56}$ (n)	271	34	0,04
	$C_{28}H_{58}$ (n)	278	32	0,04
	$C_{29}H_{60}$ (n)	286	28	0,03
n-triacontane	$C_{30}H_{62}$ (n)	290	40	0,05
	$C_{31}H_{64}$ (n)	290	50	0,06
	$C_{32}H_{66}$ (n)	290	53	0,06
	$C_{33}H_{68}$ (n)	290	39	0,05
	$C_{34}H_{70}$ (n)	290	64	0,08
n-pentatriacontane	$C_{35}H_{72}$ (n)	290	36	0,04
	$C_{36}H_{74}$ (n)	290	40	0,05
	$C_{37}H_{76}$ (n)	290	49	0,06
	$C_{38}H_{78}$ (n)	290	40	0,05

TABLE 8

LOW TEMPERATURE GC-DATA FOR SAMPLE NO. 132

Component	Formula	Elution temperature (°C)	Peak area[x)]	Peak area relative to n-heptane[x)]	Estimated concentration mg/ml in CS_2 extract
methane	CH_4	10	139	24	
ethane	C_2H_6	10	1857	321	
propane	C_3H_8	10	682	118	
butane	C_4H_{10}	10	4033	698	
i-pentane	C_5H_{12}	10	1517	262	
n-pentane	C_5H_{12} (n)	11	2299	398	0,1
solvent	CS_2				
n-hexane	C_6H_{14} (n)	34	2021	350	0,1
methylcyclopentane	C_6H_{12}	44	1132	196	
2-methylhexane	C_7H_{16}	51	272	47	
cyclohexane	C_6H_{12}	54	3803	658	
n-heptane	C_7H_{16} (n)	60	578	100	< 0,1
methylcyclohexane	C_7H_{14}	69	532	92	
benzene	C_6H_6	73	15182	2627	0,5
2-methylheptane	C_8H_{18}	76,5	330	57	
3-methylheptane	C_8H_{18}	78	197	34	
alkene (C_8)	C_8H_{16}	84	62	11	
n-octane	C_8H_{18} (n)	86	369	64	
toluene	C_7H_8	99	31758	5494	> 1,0

TABLE 8 (p. 2)

Component	Formula	Elution temperature (°C)	Peak area x)	Peak area x) relative to h-heptane	Estimated concentration mg/ml in CS_2 extract
n-nonane	C_9H_{20} (n)	109	333	58	
ethylbenzene	C_8H_{10}	120	4045	700	0,15
p-xylene	C_8H_{10}	122	9791	1694	0,4
m-xylene	C_8H_{10}	122			
o-xylene	C_8H_{10}	129	6231	1078	0,2
i-propylbenzene	C_9H_{12}	130,5	279	48	
alkane (C_{11})	$C_{11}H_{24}$	134	133	23	
n-propylbenzene	C_9H_{12}	139	307	53	
ethylmethylbenzene	C_9H_{12}	141	1545	267	
ethylmethylbenzene	C_9H_{12}	144,5	1566	271	
trimethylbenzene	C_9H_{12}	150	2075	359	
trimethylbenzene	C_9H_{12}	156	1042	180	
alkyl (C_4) benzene	$C_{10}H_{14}$	182	290	50	
naphthalene	$C_{10}H_8$	190			
methylnaphthalene	$C_{11}H_{10}$	190			
dimethylnaphthalene	$C_{12}H_{12}$	190			

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x) See footnote in table 3.

TABLE 9

GC-SAMPLES CHARACTERIZED BY THE DISTRIBUTION BETWEEN ALIPHATIC AND AROMATIC CONSTITUENTS (SAMPLE NUMBERS ARE GIVEN IN THE TABLE)

Content of aromatics relative to aliphatics			
Very high	High	Intermediate	Low
	46		
	47		
	48		
		50	Crude oil
52			
53			
54			
	124		
126			
127			
128			
		130	
132			
133			
134			
	139		
	168		
170			
		203	
		207	
		263	
		271	
			312 (slop)

Figure 1.

Shaking machine with separatory funnels mounted.

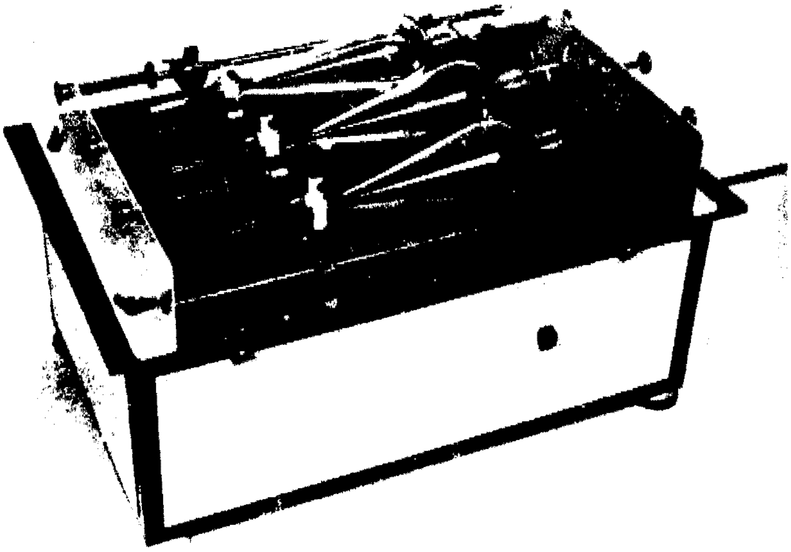

Figure 2.

At right:	Sampling bottles (100 ml dark brown glass bottles with screw cap).
At left:	Separatory funnels (250 ml glass funnels with Teflon stop cock); samples extracted into carbon tetrachloride after settling.

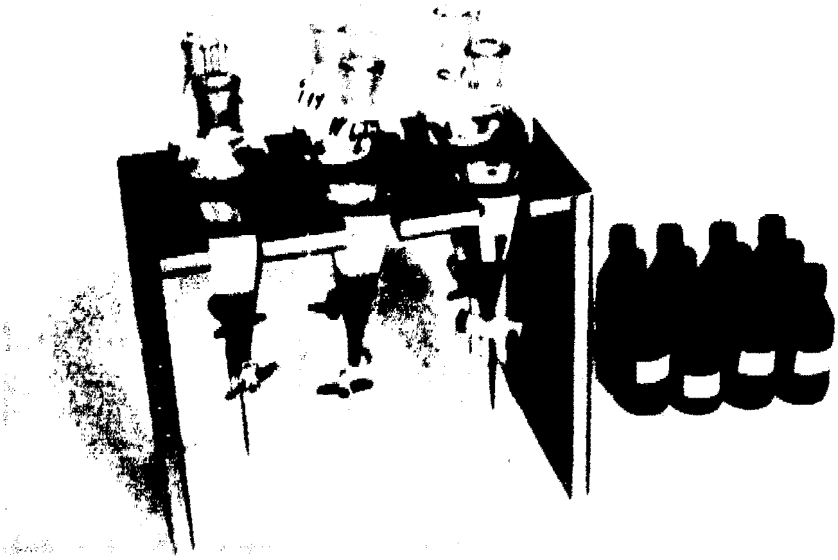

Figure 3.

At right: Samples extracted into carbon tetrachloride and kept in glass tubes.

At left: Samples extracted into carbon disulfide after sentrifugation.

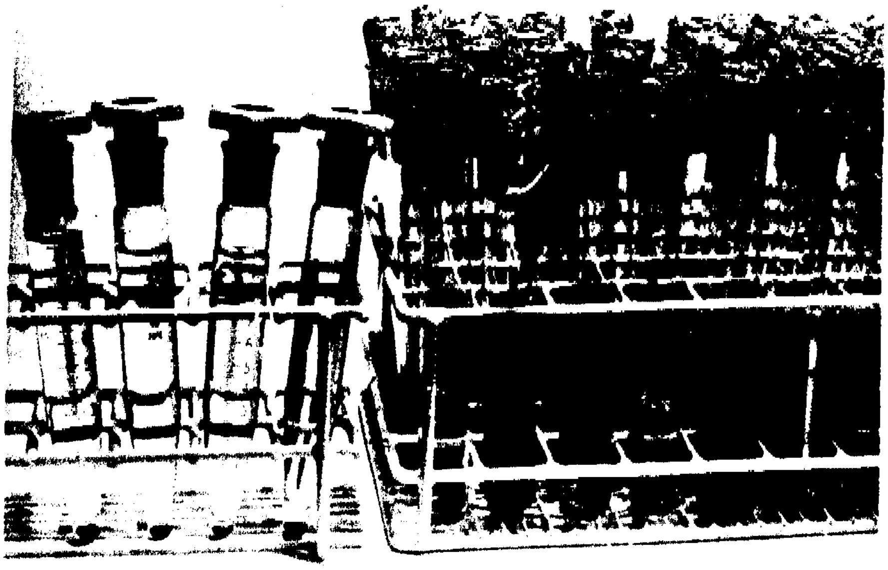

Figure 4.

Sentrifugation of samples extracted with carbon disulfide.

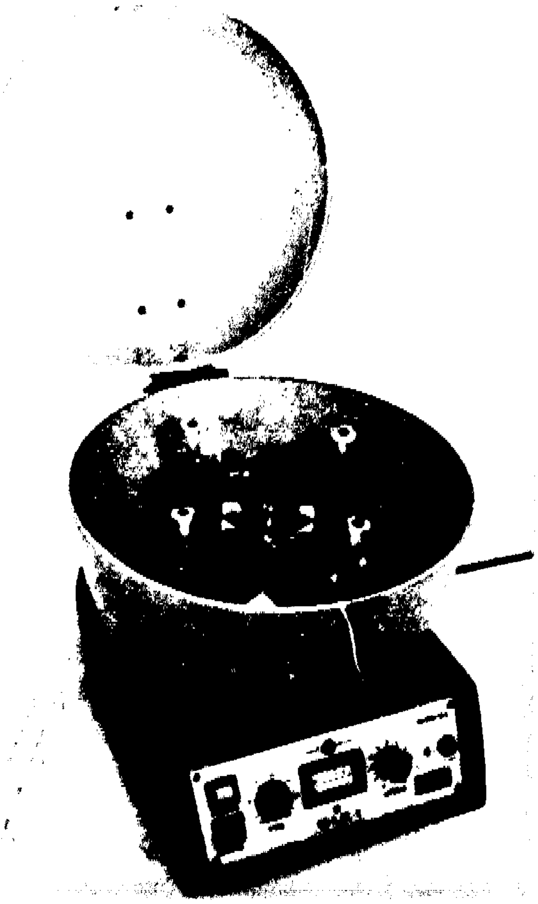

Figure 5.

Infrared spectrophotometric determination of samples extracted with carbon tetrachloride.

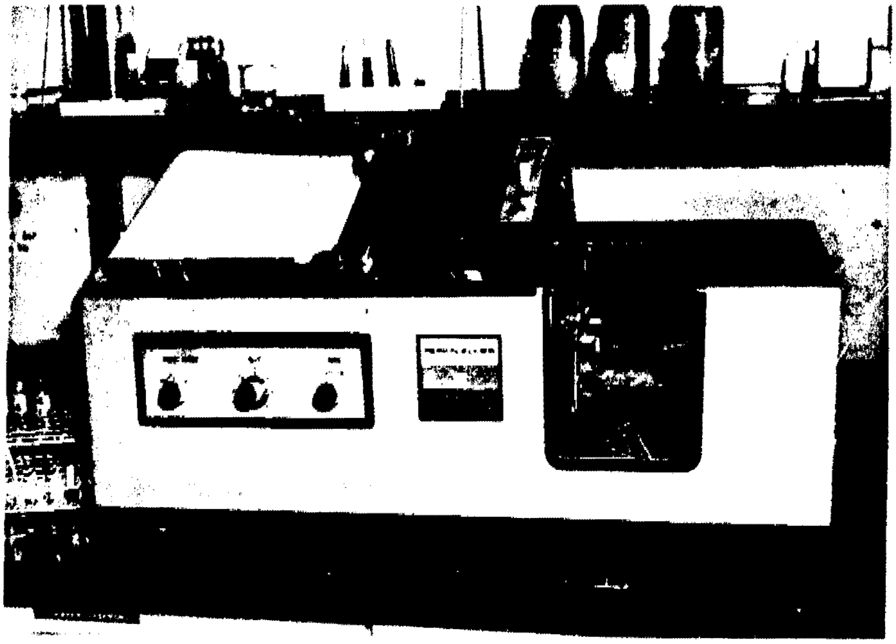

Figure 6.

Gas chromatographic determination of samples extracted with carbon disulfide.

Figure 7.

Combined gas chromatographic-mass spectrometric determination of samples extracted with carbon disulfide.

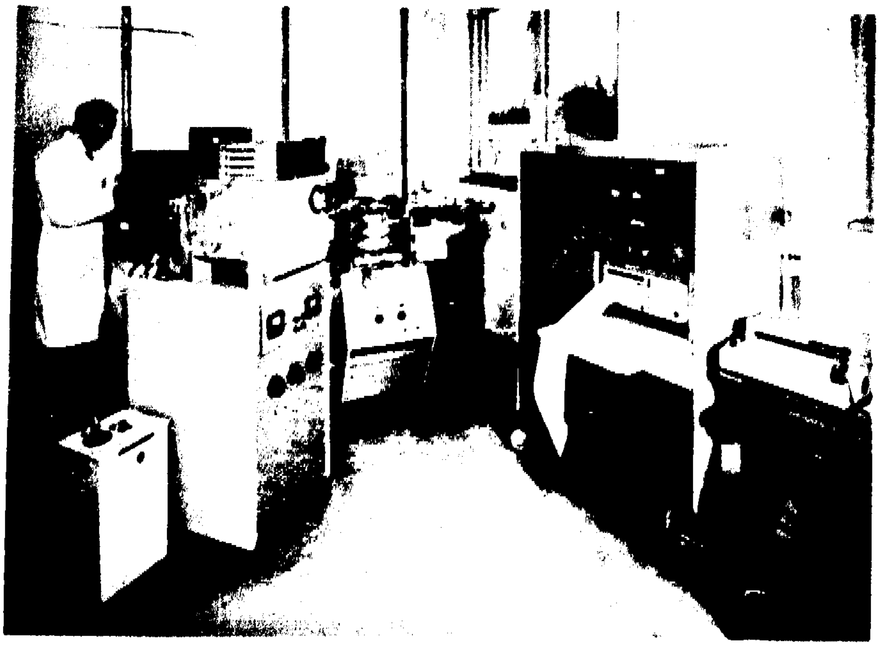

Figure 8.

IR-spectrum of actual crude oil in carbon tetrachloride solution (200 mg per litre) recorded from 3400 to 2400 cm^{-1}.

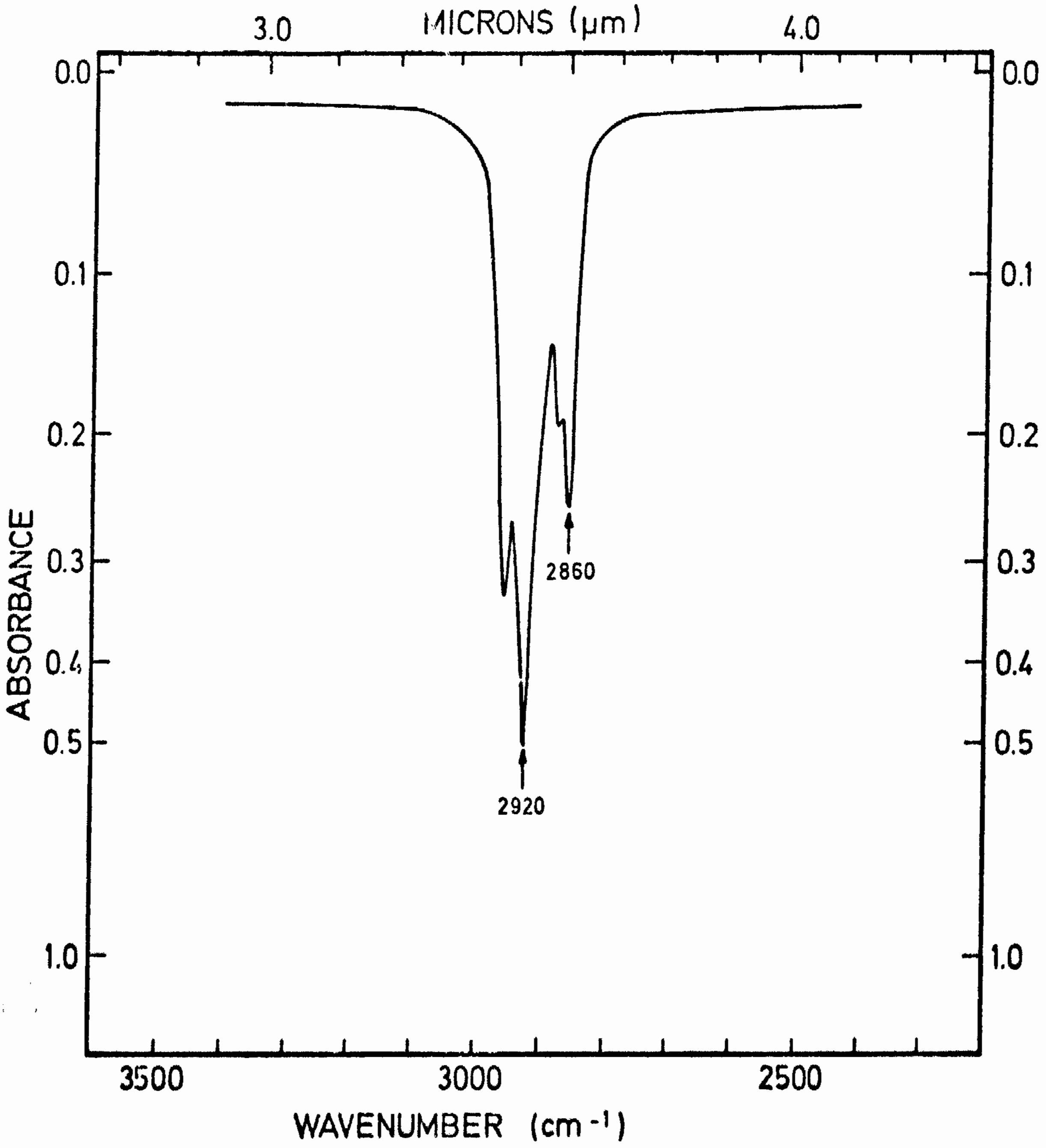

Figure 9

Mass spectrum of n-decane

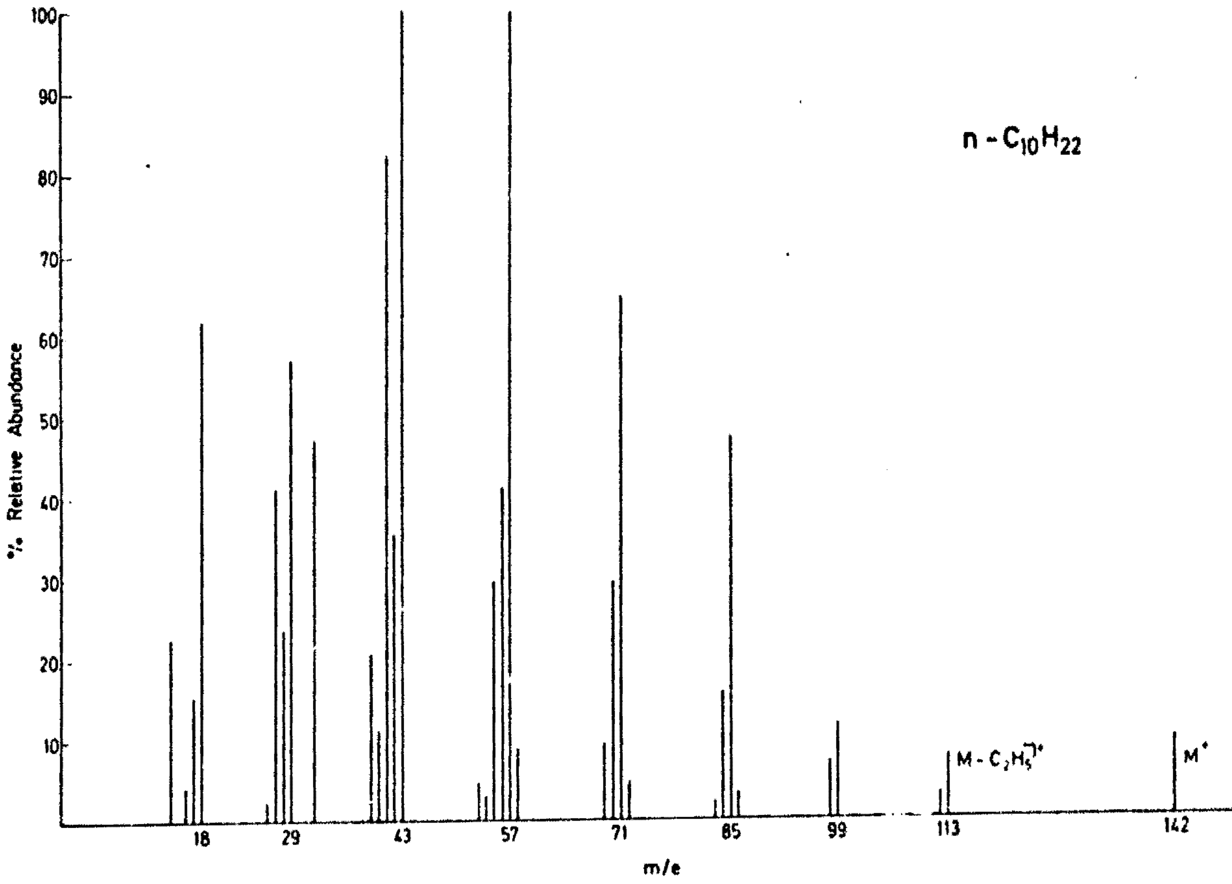

Figure 10

Mass spectrum of ethylbenzene

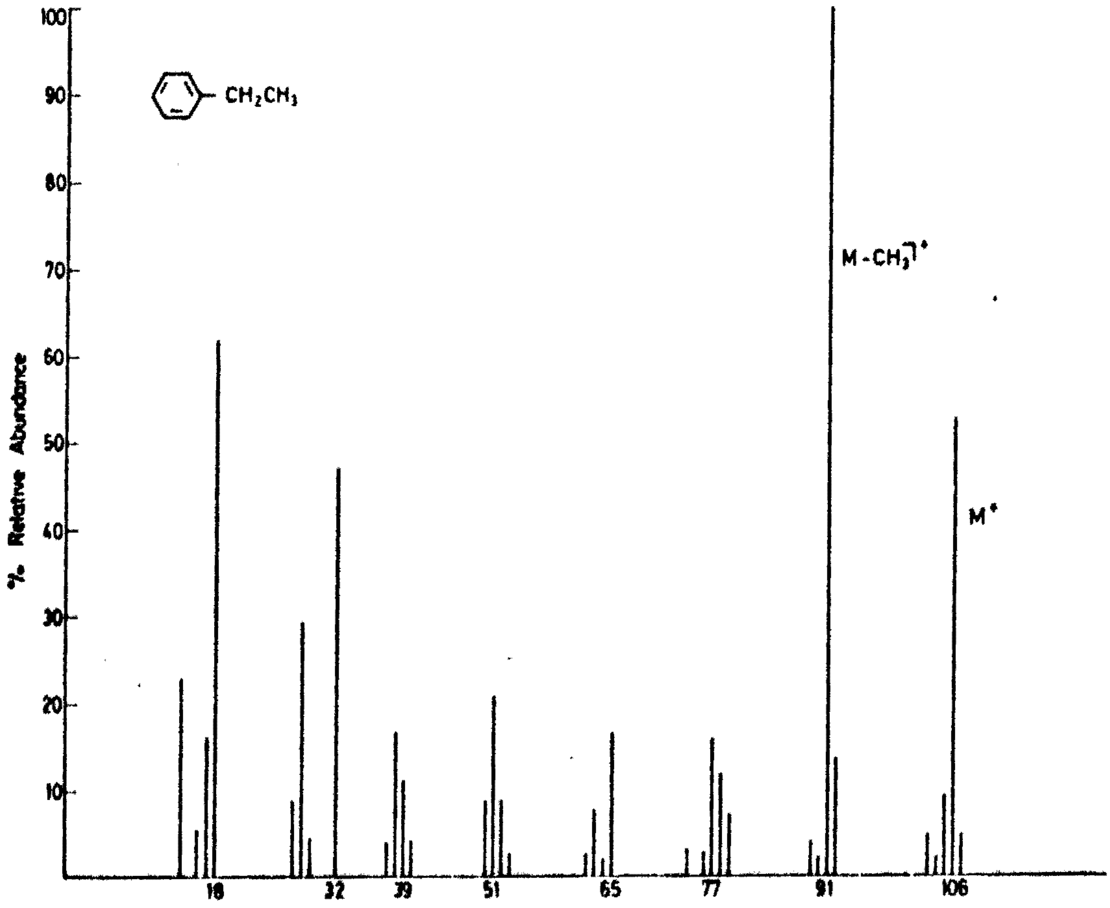

Figure 11

Low temperature gas chromatogram of crude oil.

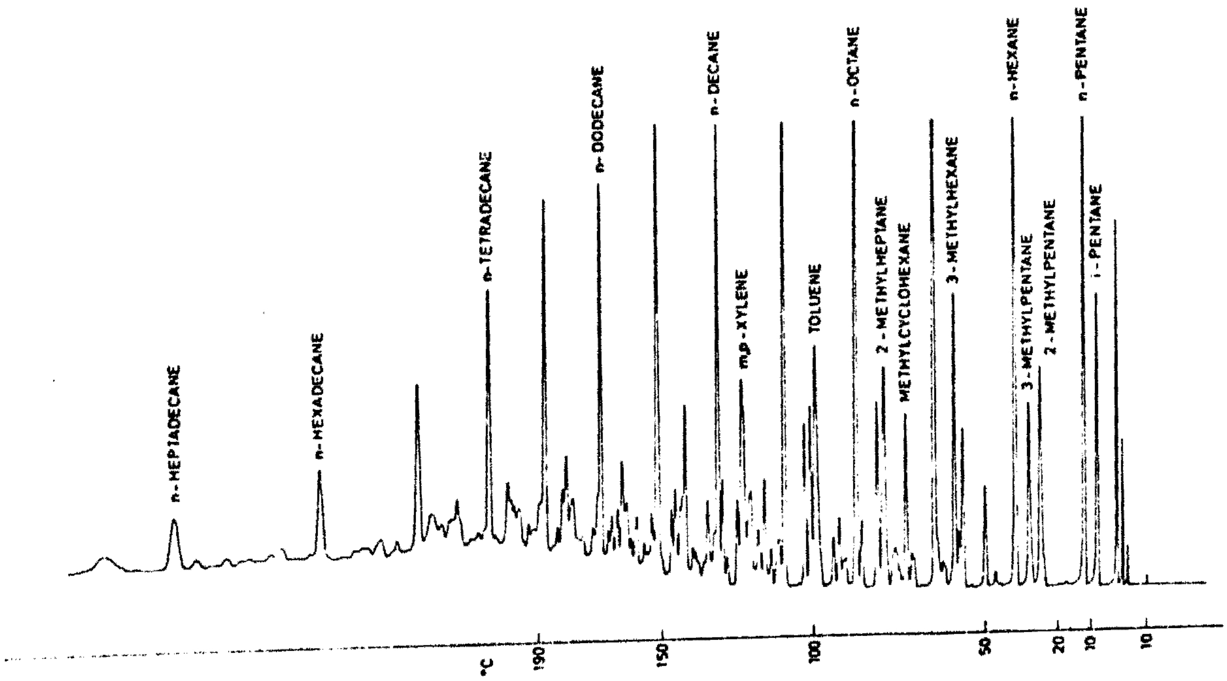

Figure 12

Low temperature gas chromatogram of sample no. 132.

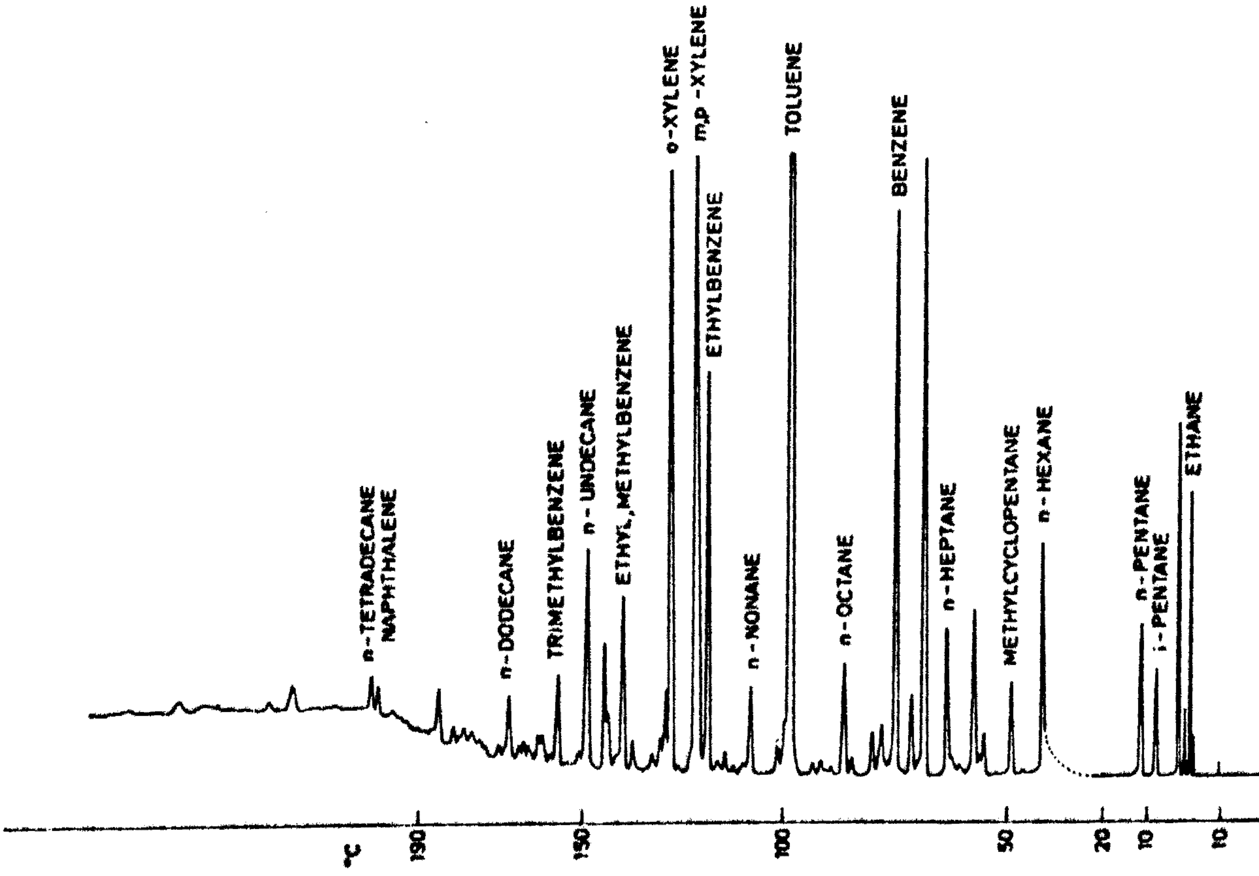

Figure 13

High temperature gas chromatogram of sample no. 312.

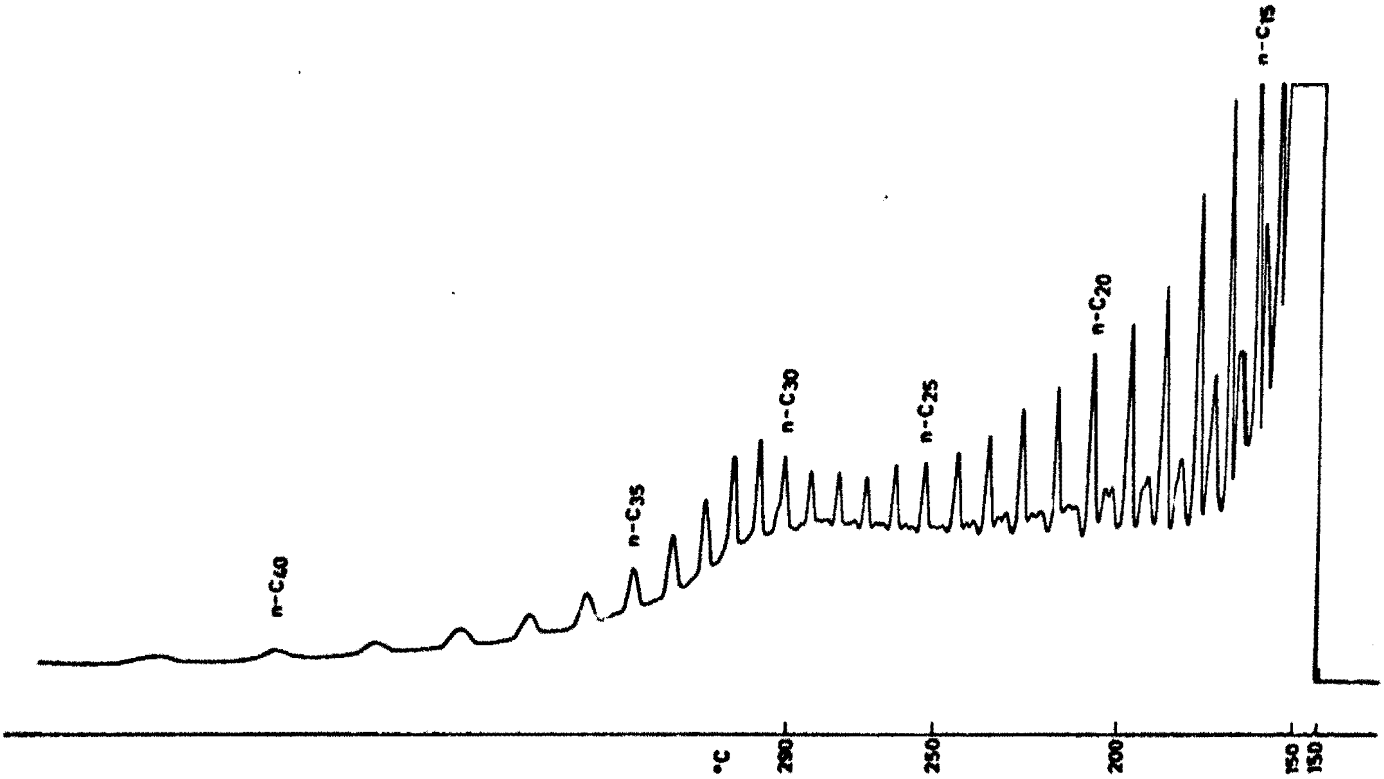

Figure 14

Distribution between aliphatic and aromatic compounds in crude oil and in samples no. 271 and 132 (calculations are based on low temperature GC-data in tables 3, 6 and 8).