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ABSTRACT

A survey of analytical methodology was carried out on a pooled sample of oily waste water. This was collected from U.S. Navy vessels. Oily waste water included oily salt water ballast plus bilge waste water. The results are summarized as follows.

I. Microscopy examination showed oil droplets in the 2-25 µm size range. Tiny particles about 1 µm* in size were found adhering to the surface of the oil droplets. After filtration, microscopic examination of filtered particles showed a wide range of particle size to a maximum of about 100 µm*. Scanning electron microscopy was used with x-ray spectroscopy of several individual particles. This indicated evidence for rust where Fe was dominant. Other particles showed Ca dominant, Fe and Si dominant, etc.

II. Thin layer chromatography was carried out using non-polar solvents on silica gel 60 F 254 plates (E. Merck). This showed over 12 distinct fluorescent or UV absorbing spots. This provides a clear indication for the presence of aromatic compounds. A tentative indentification was made of a butylated phenolic anti-oxidant.

III. Gas chromatography of filtered waste water, a CH_2Cl_2 extract and several oil standards showed that the pooled sample was closely matched to marine diesel fuel, although the presence of the fuel could not be ruled out.

IV. High performance liquid chromatography gave several interesting results. The use of GPC with RI and UV detectors showed evidence consistent with C_5-C_{18} alkanes (RI response but non-UV-absorbing) as well as aromatics dominating the C_2-C_5 region (UV absorbing and fluorescent). These results were consistant with the presence of one or more marine diesel fuels, and inconsistent with either jet fuel or lubricating oil. The use of reversed phase HPLC showed that CH_2Cl_2 extraction fails to remove a large cluster of polar and UV absorbing chemicals. The bulk of the volatile compounds were observed in the least polar fraction.

* micrometers

TABLE OF CONTENTS

Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science by John J. Zyren.

FINAL REPORT

This project has involved efforts to classify oily waste water. It has been concluded that the main components of interest are the various possible oils (jet fuel, bunker fuel, and lubricating oil), dissolved salts, particles and, of course, water.

The last phase of the study is reported here in two parts. Both are directed toward the study of the likely oil components in pure form. Part I deals with the development of multiple detector use of high pressure liquid chromatography with a gel permeation separation mode. This shows that the different oil categories exhibit chromatographic patterns that are unique to the category. These patterns are sufficiently distinctive that they may well be unique to different samples within a category, although this would require more testing to be certain. Part II deals with gas chromatographic analysis of the five samples which were examined in Part I. The GC envelopes have sufficient separation that GC may well be a primary method for assessing the volatile oil components in oily waste water.

This leaves the problem of measuring the water soluble non-volatile constituents which may well possess critical properties in terms of potential for environmental damage. Future work, which has been proposed separately, should deal with the non-volatile constituents which are extracted by water from oil, as well as cleansing detergents which are commonly used on naval vessels.

PART I.
MULTI-DETECTOR APPLICATION OF GEL PERMEATION CHROMATOGRAPHY TO NAVAL OILS

(Reference materials for oily waste water study)

Introduction:

Gel permeation chromatography (GPC) is widely used for the separation and analysis of petroleum products.[1-5] Optical detectors are commonly used to monitor sample elution. These include refractive index (RI), ultra-violet absorption (UV) and fluorescence.[6-11] Each detector has its own sensitivity profile and limitation, and each will selectively respond to different chemicals.

The RI detector is often called a universal detector. Its response depends on the difference in refractive index between a sample and reference cell. All chemicals that differ in refractive index from the reference liquid will be detected. Since this difference can be either positive or negative, bi-directional response can be obtained. Done and Reed[11] compiled refractive index measurements for saturated and aromatic hydrocarbons. This data shows for tetrahydrofuram (THF) as the reference, that all peaks except small alkanes will give a positive response. The crossover in response is between C_8 and C_9,[12] although peroxide buildup in the THF can increase this one or two carbon numbers. The sensitivity in the crossover region is therefore small. Also, the overall sensitivity for other compounds is only fair. A more sensitive detector is the ultra-violet (UV) absorbance detector. Its response is based on the relative absorbance of UV light and this usually follows Beer's Law:[13]

$$A = \varepsilon \cdot b \cdot c \qquad (1)$$

where A is the absorbance, ε the molar extinction coefficient, and b is the optical path length. Commercial detectors measure the absorbance from between values of 0.0001 and 2. Molar extinction coefficient values range up to about 10^5. Alkanes and other saturates have quite small extinction coefficients, while unsaturated hydrocarbons, including conjugated unsaturates, have much larger values. A greater level of sensitivity and selectivity is found with the fluorescence detector.[14,15] Fluorescence only occurs with UV absorbing compounds, but not all UV absorbing compounds fluoresce. The fluorescence intensity varies with the wavelength of the exciting UV radiation and the UV spectral absorption pattern varies with different compounds. In addition the emitted fluorescent radiation has a well defined spectral pattern that can be used to aid compound identification. Few chromatographic systems use more than one detector. This study investigates the value of applying a HPLC-GPC system with RI-UV-fluorescence detectors to the characterization and identification of various naval oil samples. This effort is part of the general plan to classify and describe the organic chemical components in oily waste water.

Experimental:

It was necessary to distill the cyclohexane and tetrahydrofuran (THF) solvents prior to their fluorescence use. The THF was distilled in contact with sodium and under nitrogen. This limits peroxide formation.[15]

Gas chromatography of n-alkane calibration standards showed no gross contamination and these were used without further purification.

The five naval samples were stored below 0° in glass containers with aluminum cap liners. Their military specifications are: MDFO (MIL-F-168846), NDFO (MIL-F24397), 2190-TEP (MIL-L17331F), Synthetic lubricant (MIL-L9000G), Jet Propellant, JP-5 (MIL-T56244). In one set of experiments the liquid chromatography was monitored using RI and UV detectors (Waters Associates). Then UV and fluorescence monitoring was carried out in repeated experiments. The later detection was fashioned using a flow-through cell with an Aminco-Bowman Spectrofluorophotometer (Xenon lamp 416-992; photomultiplier tube 1P21; slit arrangement: excitation 1 mm, emission 2 mm, slides 2 mm, meter multiplier 0.3).

Fluorescent spectra were collected using a synthetic quartz (Aminco-Bowman) flow cell. No fluorescent background was observed with the cell although some buildup appeared after three months' use. Connections to the cell were made with 1/16" o.d. teflon tubing.

The gross emission spectrum was taken for each sample in cyclohexane with the excitation wavelength set at 254 nm. The highest intensity emission peak was found and monitored while the excitation wavelengths were then scanned. An excitation wavelength of 265 nm was found to give the greatest emission intensity. All emission spectra were taken using this excitation wavelength.

Calibration of the chromatographic system included measurements of column dimensions, extra-column dead volume, and particle porosity.

The column was 2' x 1/4" glass. The empty column volume (V_C) was measured as the difference between the water-filled and dry weights.

The stationary phase porosity was measured using the recently published[16] method from this laboratory. This was applied as follows. Twenty n-alkane solutes were measured for their GPC retention volume V_R using an RI detector. The particle permeation was set equal to the distribution coefficient, D. This was calculated from the expression

$$D = \frac{V_R - V_O}{V_S} \qquad (1)$$

where V_O is the exclusion volume and V_S is the bulk volume of the stationary phase. The experimentally measured D values were fitted to a least squares line using the equation[17] of Giddings in logarithmic form:

$$- \ln D = g_0 + g_1 L \qquad (2)$$

where L is the solute size. The value of L was taken[18] for the normal alkanes from

$$L = 3.24 + 0.0375 \text{ MW} \qquad (3)$$

where MW is the molecular weight. Since molecular weight and carbon number, n, are related for normal alkanes, C_nH_{2n+2}, we can define a carbon number scale using MW = 12n + (2n + 2) or by substituting,

$$L = 3.32 + 0.525n \tag{4}$$

The g_1 term in Equation 2 is related to the pore diameter by:

$$d_{pore} = \frac{4}{g_1} \tag{5}$$

The g_0 term is the ratio of pore volume to stationary phase volume for zero sized molecules. A possibly more useful measurement is the value for solvent sized molecules. We assigned this value at L = 4.2 Å in the calibration plot shown in Figure 1.

Other system components were the injector (Rheodyne 7105) and the liquid chromatography pump (Waters Associates 6000A). The sample injection volume was 150 μL. The THF solvent flow rate was held at 0.5 mL/minute. The gross sample concentrations were 0.59% in THF. A two pen chart recorder was run at the same speed for all recordings: RI/UV, and UV/fluorescence. Dead volume limitations allowed the UV detector plus only one other detector to be operated in series at the same time. Each chromatographic experiment was repeated three times with alternate detector sequence of RI, fluorescence, and fluorescence spectrum. Emission spectra of separate chromatographic peaks were obtained by stopping the LC solvent flow during the emission scan.

Calibration mixtures were run periodically to test the overall system performance. We found negligible variations in flow rate (<0.2%) or chart speed variations (<0.5%) in any of the calibration tests. (Our data acquisition system was not used for this work because it was restricted to single input channels, a limitation which we only recently removed.)

Results:

The column calibration data are shown in Figure 1. An average pore diameter of 26.3 Å was calculated from the slope (g_1) using Equation 5. The porosity, or pore volume fraction as seen by the solvant, is 0.19; this was read from the abscissa of the least squares line at L = 4.2 Å. The scatter of the points about the line may be real and may be due to imperfections in the pore model, but this does not affect the calibration.

The multi-detector responses are shown in Figures 2, 3 and 4. Table 1 lists the n-values of the major peak-maxima. Thus, this table shows the gross profiles and characteristics of each type of oil.

Each oil sample exhibits a characteristic pattern of multiple detector response. Each sample showed a small number of fluorescent components each with corresponding GPC size characteristic (L- or n-value).

Examination of Table 1 reveals further information. Both fuel oils show a major peak at n = 6.1-6.2 that appears simultaneously on all three detectors. Similarly, the lubricating oils show profiles that differ in only two respects: (1) the synthetic lubricant profile shows a shift to lower carbon numbers and (2) it also shows an additional UV peak not seen on the TEP. The jet propellant had the most greatly retained RI peak at n = 2.6 carbon atoms. Since its RI response was *negative*, it is almost certain to be from small alkanes. Straight chain alkanes of that size could appear only at either n = 2 or n = 3 carbon atoms, so that the peak at n=2.6 is probably from small cyclic or branched alkanes.

The fluorescent peak in the jet fuel at n = 4.5 carbon atoms appears in a location where polynuclear aromatic hydrocarbons (PAH) are known to elute.[15,19-22] Occurrence of a PAH in jet fuel is unlikely, and its fluorescent spectrum was scanned for an identifiable pattern or maxima. This proved fruitless. All of the spectra had very similar shapes. The differences in emission maxima that did appear *could have* been from concentration effects. Hence the identity of the peak cannot be determined using this avenue.

The GPC analysis time was twelve minutes for each sample. With three injections per sample, each complete analysis took less than one hour of run time.

Discussion

Rapid GPC analysis with multiple detectors shows a clear potential for fuel classification. While additional samples are needed to confirm this, the results are quite encouraging. It is not known if the extraction of oil from water, with or without weathering, would show similar patterns. This work needs to be considered.

In our most recent experiments we found that the 12 minute GPC run time can be reduced to two minutes with small gains in peak band width. This is due to the increased linear flow velocity. A shorter, but more efficient column has recently been packed and it shows capability of reducing the 12 minute elution time by a factor of 6 with less effect on band width. In addition, these experiments can now be carried out with minimal operator time since the data acquisition process is now fully automated using our Wang calculator and a home made interface. This results in an additional 3-fold reduction in total analysis time. As a result, we feel that the present system would be a practical approach for routine monitoring of oils as stock materials, or as unknown extracts from oily waste water.

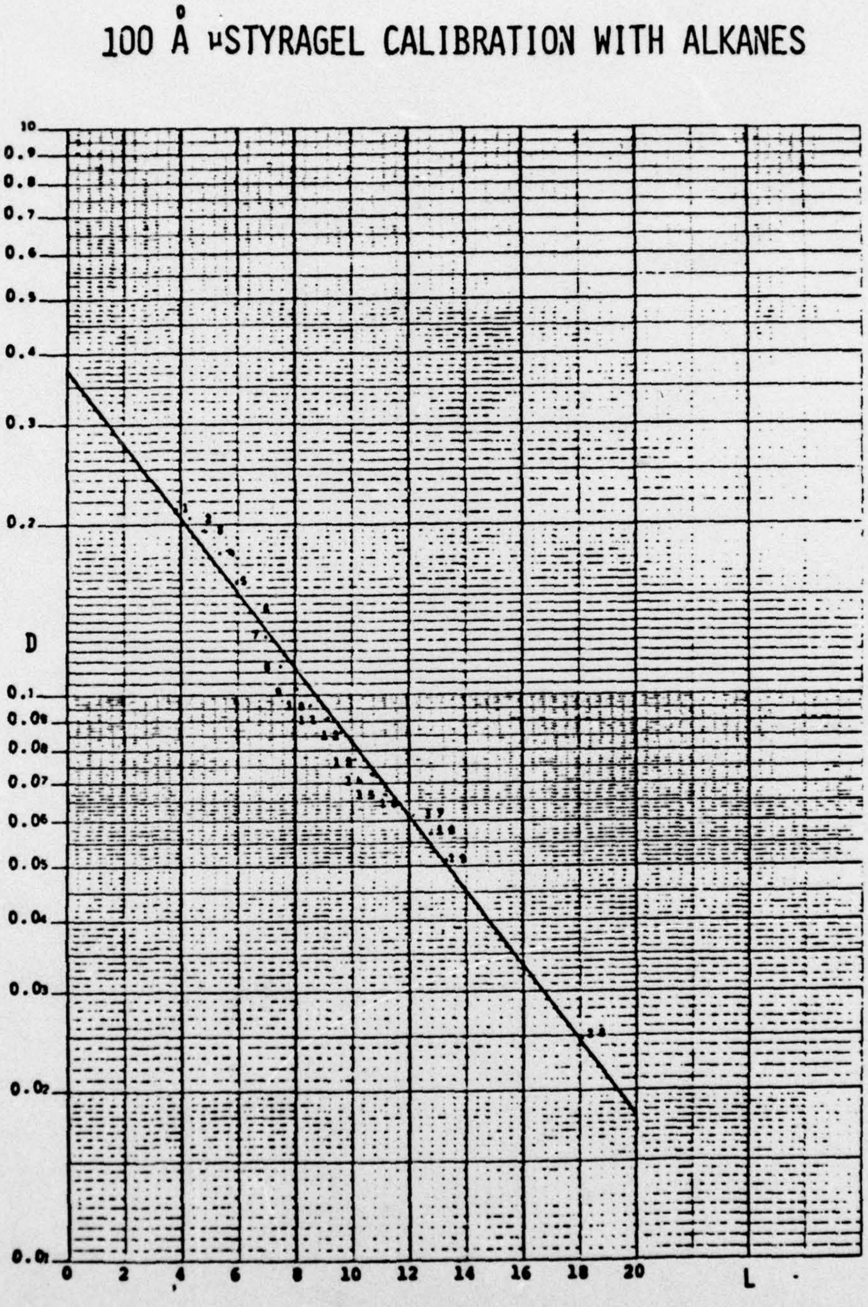
100 Å μSTYRAGEL CALIBRATION WITH ALKANES

Figure 1. The distribution coefficient data for n-alkanes are plotted according to solute size for a PSDVB gel type copolymer (100 Å μStyragel). The solid line through the data is calculated from the parameters (g_1, g_0) of the Giddings' theory. The numbered points correspond to the number or carbon atoms in each alkane. The column parameters are: V_c 18.50mL; V_s 15.75mL; V_o 2.75mL.

Figure 2. GPC - RI - UV - Fluorescence Results with Jet Propellant (JP-5)

Raw chromatographic data showing each detector response for each sample. The numbered calibration scale refers to the elution placement of the corresponding n-alkane. The column is 100 Å μstyragel used with a flow rate of 0.5 cc/min.

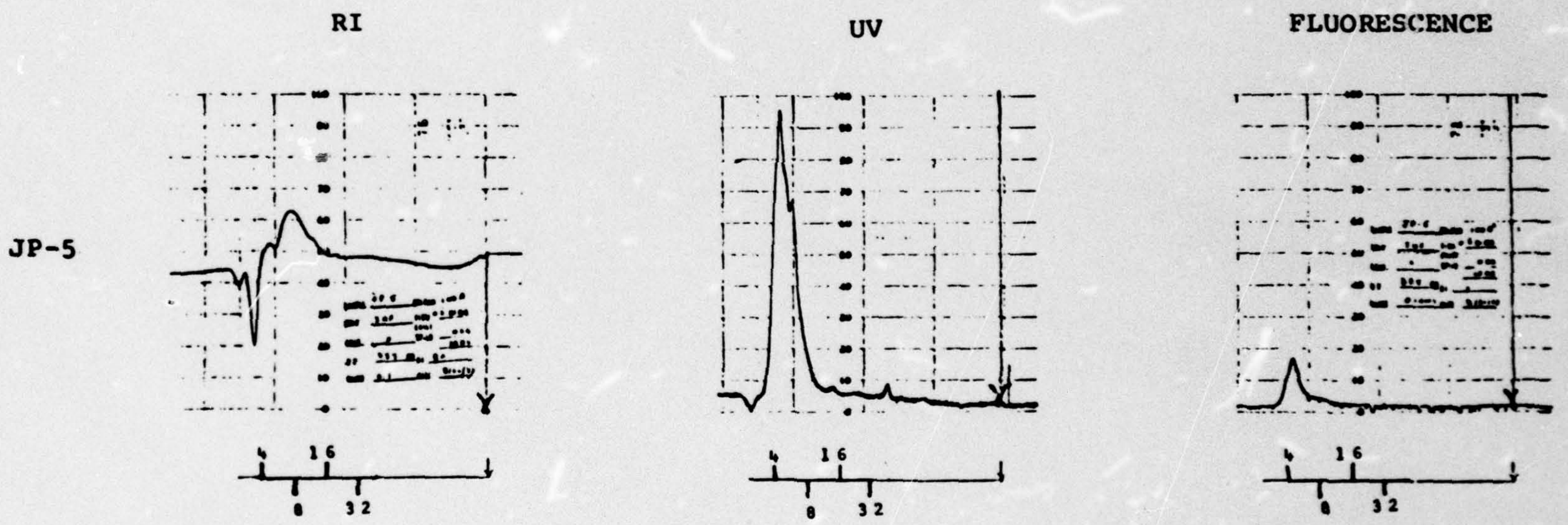

Figure 3. GPC - RI - UV - Fluorescence Results with Two Lubricating Oils

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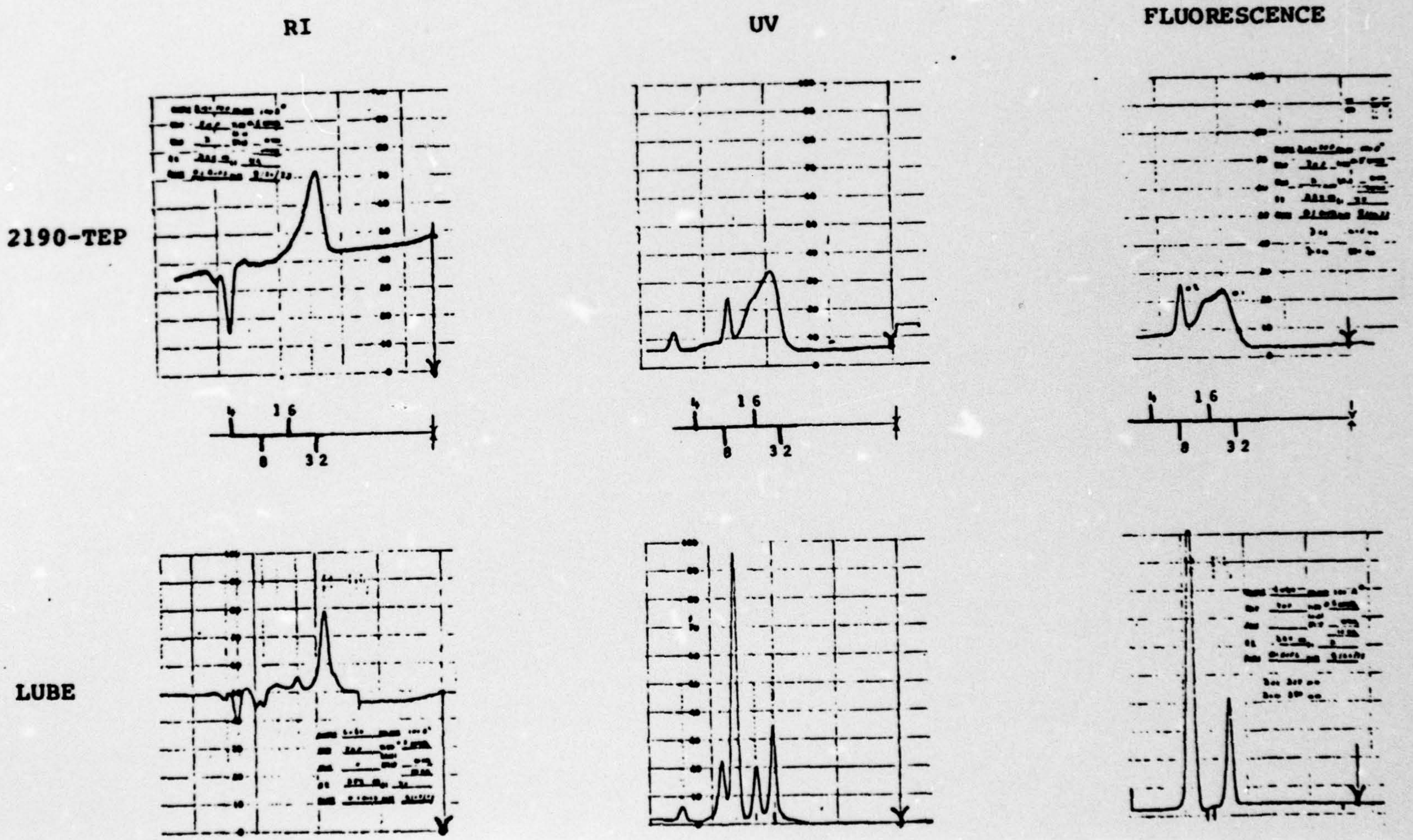
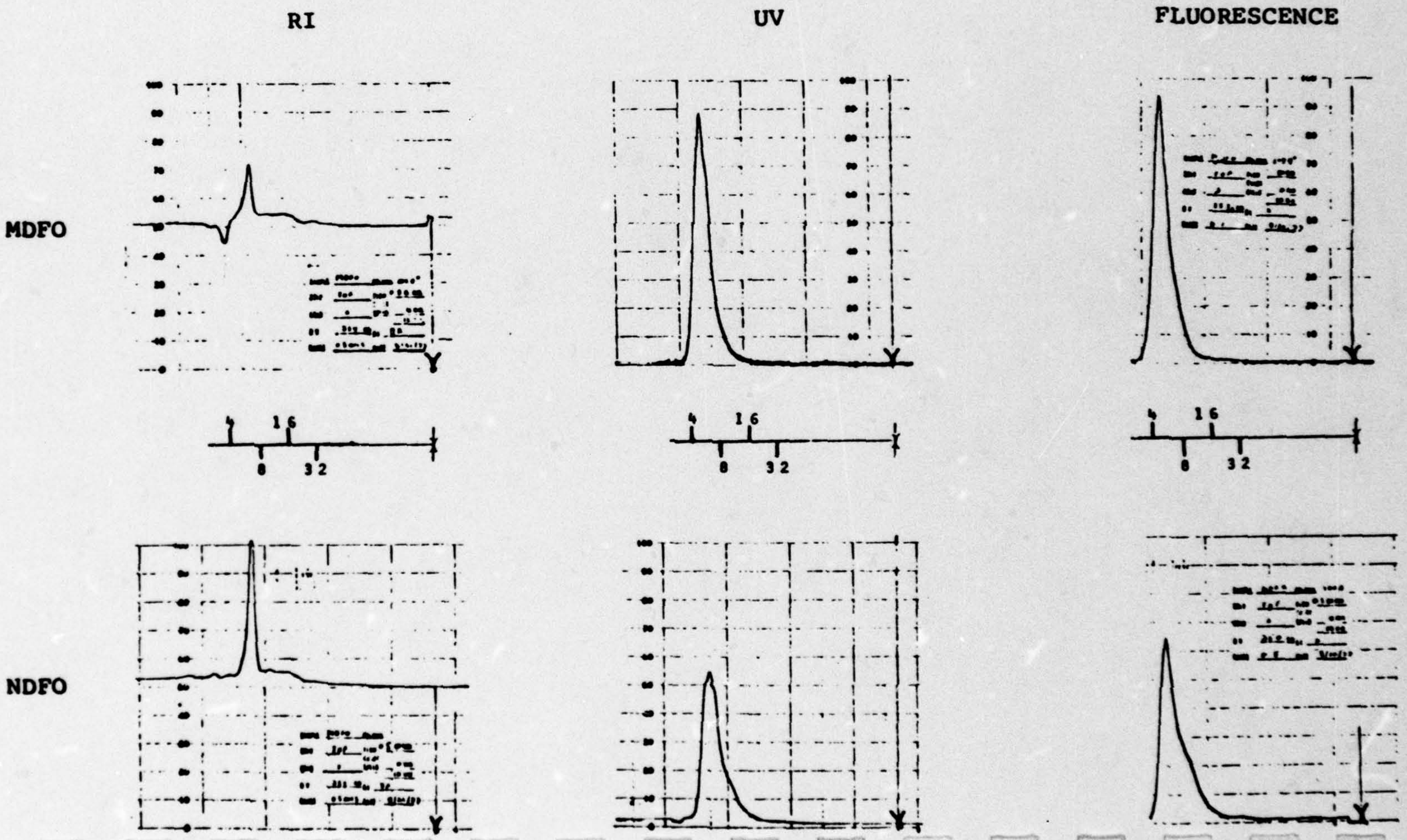


Figure 4. GPC - RI - UV - Fluorescence Results with Two Intermediate Oils

This data is collected under the same conditions as Figure 2.



LOCATION OF MAJOR PEAKS

SAMPLE	DET.	n-VALUES							#
2190-TEP	RI	33.1							1
	UV		23.2	14.8	9.2				3
	FL		23.2		9.2				2
LUBE	RI	28.8							1
	UV		21.2	13.6	9.0	6.5			4
	FL		21.2		9.0				2
MDFO	RI					6.2			1
	UV					6.2	5.1		2
	FL					6.2			1
NDFO	RI					6.1			1
	UV					6.1	5.1		2
	FL					6.1			1
JP-5	RI					7.7		2.6	2
	UV					7.7	4.5		2
	FL						4.5		1

Table 1. The location of major peaks seen by RI, UV and fluorescence detectors is given in terms of where the corresponding n-alkane would elute.

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PART II.

GAS CHROMATOGRAPHIC ANALYSIS OF OIL SAMPLES

Introduction

Gas liquid chromatography was utilized to analyze five oil samples which included MDFO, NDFO, JP5, Synthetic Lube Oil, and 2190 TEP. A mixture of paraffin standards was analyzed under corresponding conditions. Interpretation of chromatograms of the oil samples was facilitated by comparison with the chromatogram of the standard mixture. Efficient chromatograms that clearly distinguished among the oils were obtained within 20 minute analysis times.

Experimental

A 3 ft. by 1/8 in. stainless steel column was packed with 3% Dexsil 300 GC coated on Chromosorb W,AW, of mesh size 80/100. An injection port temperature of 335° C and a detector temperature of 360° C were maintained for all samples. Subsequent to vaporization, samples entered a column held isothermally at 70° C for two minutes and then were temperature programmed at a rate of 16°/min to a final temperature of 350° C. A carrier gas flow rate of 36 ml N_2/min. was employed. Detector gas flow rates were 50 ml H_2/min. and 500 ml. air/min. A sensitivity of 10^{-11} Amp/V and an attenuation of 1024 were used throughout this work.

The above conditions were used in the analysis of NDFO, MDFO, JP5, Synthetic Lube Oil, 2190 TEP, and a standard mixture of alkanes including C-10, C-12, C-14, C-15, C-16, C-17, C-18, C-19, C-28 and C-36. All samples were analyzed using a Varian Aerograph 2800 GC.

Results

The chromatograms of five 0.2 μl oil samples and a 0.2 μl standard mixture appear in Figure 1. A convenient grouping of the chromatograms on the basis of volatility of constituents would be to consider JP5, MDFO, and NDFO to comprise one group and Synthetic Lube Oil and 2190 TEP to constitute a second group. The oil samples of the former group contain relatively volatile components. Those of the latter group possess rather involatile components.

Aside from the presence of relatively volatile components other similarities among JP5, MDFO, and NDFO exist. All three chromatograms possess an unresolved envelope highlighted by hydrocarbon fine structure that is characteristic of fuel oils. The retention distances of a number of paraffins shown in the chromatogram of the standard mixture correspond to retention distances in the chromatograms of JP5, MDFO, and NDFO. At this point, the similarities among the three chromatograms cease.

Although the chromatograms of MDFO and NDFO may appear to be indistinguishable at first glance, different ratios of the constituents of the hydrocarbon fine structure and the absence of very volatile substances in NDFO differentiate them. JP5 lacks a number of hydrocarbons present in the standard mixture and possesses a large amount of very volatile substances. The unresolved envelope in the JP5 chromatogram does not cover a wide boiling range. These factors enable one to distinguish JP5 from MDFO and NDFO. Clearly, the boiling range of JP5 is that of a jet fuel while the boiling ranges of MDFO and NDFO are similar to that of a #2 fuel oil.

The fact that the major constituents of the Synthetic Lube Oil and 2190 TEP are rather involatile suggests that both are lubrication oils. The standard paraffins, C-28 and C-36, are indicative of the boiling points of substances present in the above two oil samples. Both samples display similar high-boiling ranges. However, 2190 TEP affords virtually no fine structure while Synthetic Lube Oil possesses a considerable amount of fine structure. In addition, the peak in the chromatogram of 2190 TEP that corresponds to C-15 of the standard mixture could be used to distinguish 2190 TEP from Synthetic Lube Oil.

In each chromatogram of Figure 1, the first component was identified as acetone which was used for cleaning the syringe. Spurious peaks will be observed which represent septum bleed unless care is taken to properly condition the septa or use commercially available septa which are stable at high temperatures.

Preliminary analyses using temperature programming at rates as slow as 3°/min. and carrier flow rates as low as 25 ml/min. did not provide significantly enhanced resolution of any of the samples. Weighing both time and efficiency considerations, a temperature programming rate of 16°/min. was determined to be optimal.

Conclusion

Three percent Dexsil 300 GC on Chromasorb W, AW, proved to be an excellent packing material. Since it is stable to 450° C, it can safely be employed in high temperature programming. A particular advantage realized was that very involatile components could be removed from the column eliminating memory effects. Silylation of the solid support was not deemed necessary for two reasons. First, no significant tailing was observed and second, silane groups tend to bleed off at 350° C.

Numerous other advantages were realized with the system used. A short column and rapid temperature programming resulted in 20 minutes analysis times. The resultant chromatograms were efficient and did not represent a significant sacrifice in resolution. In addition, only a small quantity of stationary phase was necessary which facilitated reduced cost and rapid preparation of the column.

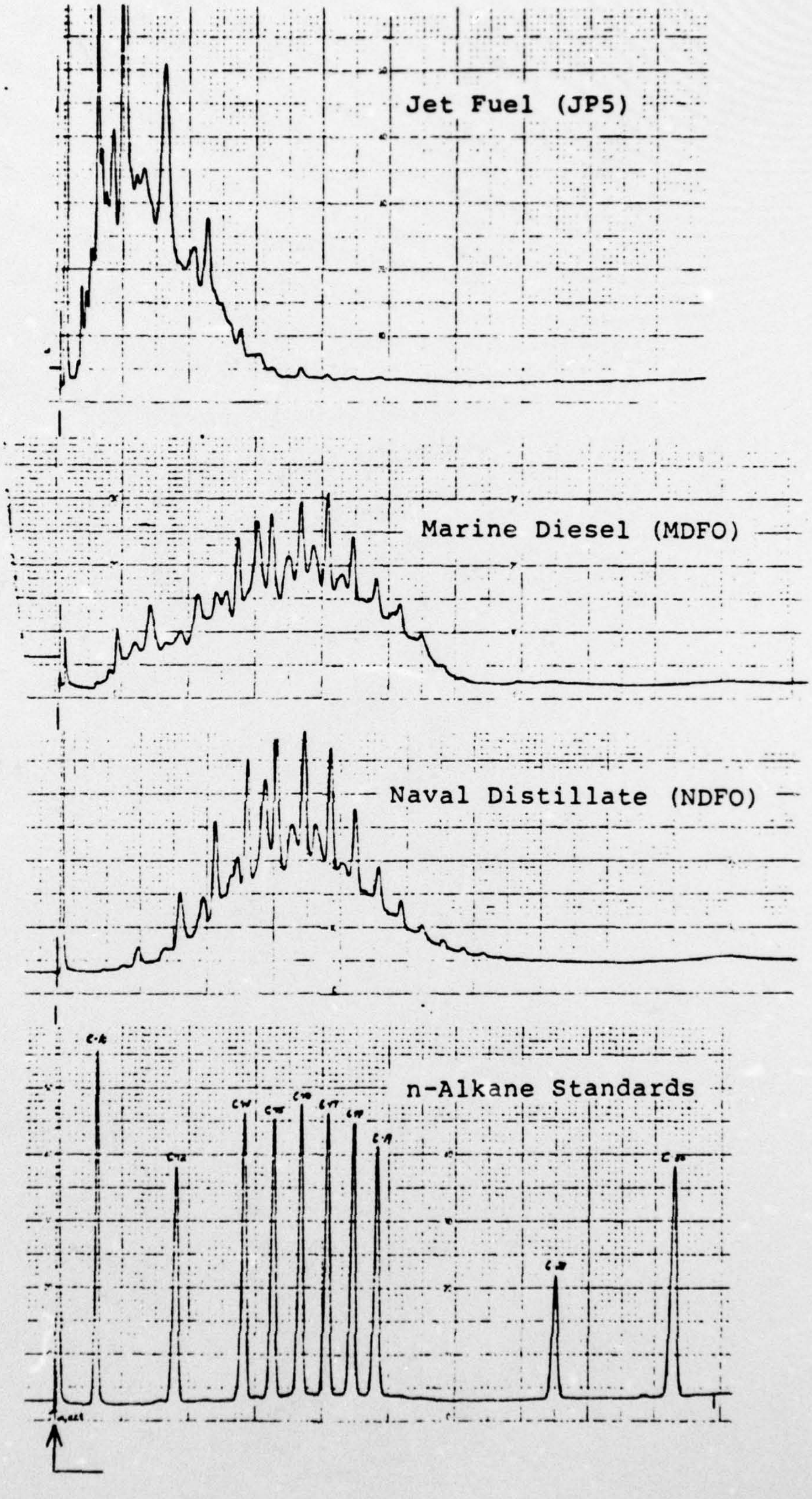
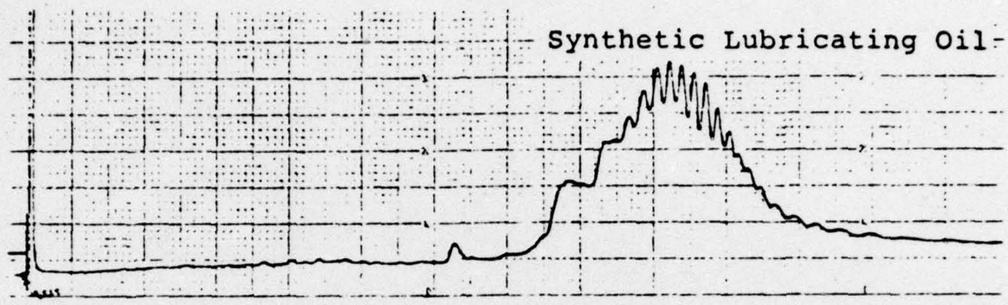
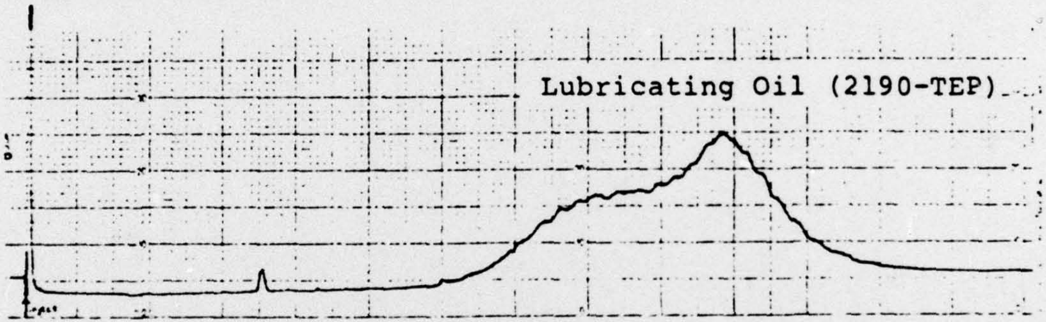
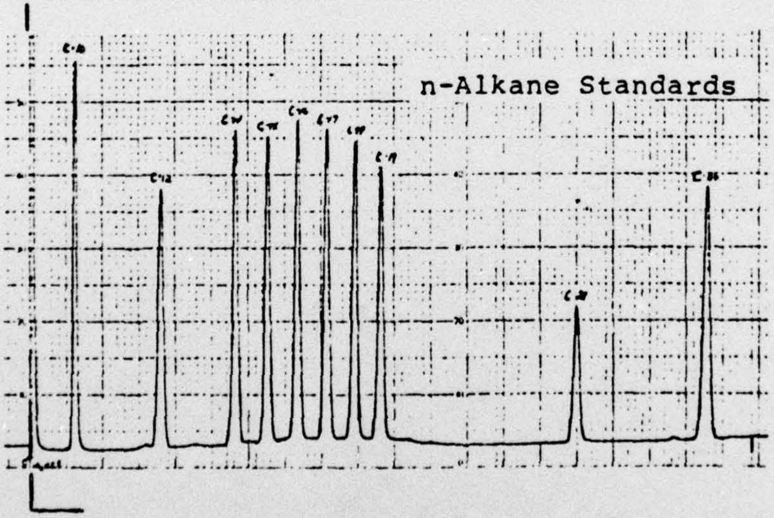


Figure 1. Gas chromatography of oil samples on 3% Dexsil/300GC (Chromosorb W, AW), column: 2mm i.d. x 90 cm., temperature 70°(2 min.) programmed at 16°/min . to 350°.


Synthetic Lubricating Oil


Lubricating Oil (2190-TEP)


n-Alkane Standards

APPENDIX

ANALYSIS OF THE PARTICULATE AND ORGANIC MATERIALS IN OILY WASTE WATER

by

John Joseph Zyren

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Master of Science
1977

APPROVAL SHEET

Title of Thesis: Analysis of the Particulate and Organic Materials in Oily Waste Water

Name of Candidate: John Zyren
Master of Science, 1977

Thesis and Abstract Approved: David H. Freeman
Dr. David H. Freeman
Professor
Department of Chemistry

Date Approved: Aug. 31, 1977

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Degree and date to be conferred: M.S., 1977.

[redacted]

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ABSTRACT

Title of Thesis: Analysis of the Particulate and Organic Materials in Oily Waste Water

John Joseph Zyren, Master of Science, 1977

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The oily waste water was found to contain two different types of contaminants. The major contaminant was an oily residue floating on the surface of the waste water. The second contaminant consisted of particulate materials associated with the oily residue.

The oily residue was found to consist of a very complex mixture of organic contaminants ranging from low molecular weight polymers ($\sim$1 K daltons) to small organic molecules. A sequence of n-alkanes (C_{11} to C_{24}) were identified and found to constitute 70 ppm of the waste water.

The particulate material was found to be present on the surface of the oily droplets, rather than being contained within the droplet. These particulates were found to range in type from protozoan tests to crystalline inorganic materials. The most abundant metallic elements found were iron, calcium, silicon and zinc.

It was concluded that the major source of the organic contamination in the oily waste water was from fuel oil rather than from lubrication oil. The advantages and disadvantages of the analytical techniques used in this study are discussed.

ACKNOWLEDGMENTS

I would like to thank Dr. D. Freeman for suggesting this project and for the unending help and guidance he provided.

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INTRODUCTION

The toxicity of refined oil products has been extensively investigated by various authors. Pulich, et al (1), has found that the water soluble fractions (WSF) of #2 fuel oils display toxic effects on the growth of various microalgae and also inhibit photosynthesis in these organisms. Other writers have found that WSF of fuel oils also have toxic effects on mollusks (2) and sand dollar eggs (3). Anderson, et al (4), have further investigated the organic constituents present in the WSF of fuel oils and have detected both saturated and aromatic hydrocarbons. He concludes that naphthalenes, because of their relatively large concentration, are probably the constituents with the most toxic effects on marine organisms.

More recently, Winters, et al (5) have isolated and identified phenalen-1-one from a #2 fuel oil and found that ppm levels of this compound in water inhibits growth of microalgae. Winters, et al (6) identified 36 different compounds in the WSF of fuel oils by GLC and MS. They found that, in addition to the more commonly described compounds (naphthalenes, benzenes) expected in WSF's, there also occur phenols, anilines and indoles. In a different vein, Larson, et al (7) irradiated a #2 fuel oil with a Hg-vapor lamp to stimulate photo-oxidation of the fuel oil; oxygenated compounds (phenols and peroxides) toxic to baker's yeast were formed. From this brief overview, it is obvious that refined oil products have been found to contain or produce substances toxic to marine organisms.

An oily waste water sample was analyzed in this work. It was obtained from the Naval Research Laboratory. This sample was originally described as water from a ship's bilge and that the principal contaminants were additives extracted from lubrication oil. As our analysis progressed, the sample was later described as a composite sample from the barge onto which Navy ships dump their oily waste water while in harbor (8). We will later show that the latter description is more accurate.

The basic purpose of this study was to investigate the nature and types of contaminants present in the oily waste water and to study and classify their composition. The significance of this study is that ships may accidentally discharge this oily waste waterinto the harbor or sea and it would be beneficial to know how detrimental this substance is to the environment. This work was initially planned to be a general survey of the contaminants present in the waste water. Our approach was to use a variety of different chemical and microscopic techniques to obtain as much general information about the contaminants as possible; this study also evaluated the analytical techniques in terms of their general value for characterization of the organic constituents in oily waste water.

EXTRACTION AND PRECONCENTRATION

Extraction and preconcentration of the oily waste water were necessary because of the difficulty of chromatographic analysis of aqueous solutions and also because the organic constituents were present in too small a quantity to be readily analyzed. The waste water was exhaustively extracted by methylene chloride in a heavier-than-water extraction apparatus (see Fig. 1). The organic extract was concentrated (~20-fold) by vacuum evaporation and was passed through a 0.45 μ Millipore Filter. Some particulate material was found in the filter and was saved for further analysis. The resultant organic extract had a dark greenish-brown color.

Nearly all of the chromatographic and spectroscopic investigations described in this report used this extract rather than the oily waste water itself. The close similarity between the organic extract and the waste water itself will be pointed out in subsequent sections.

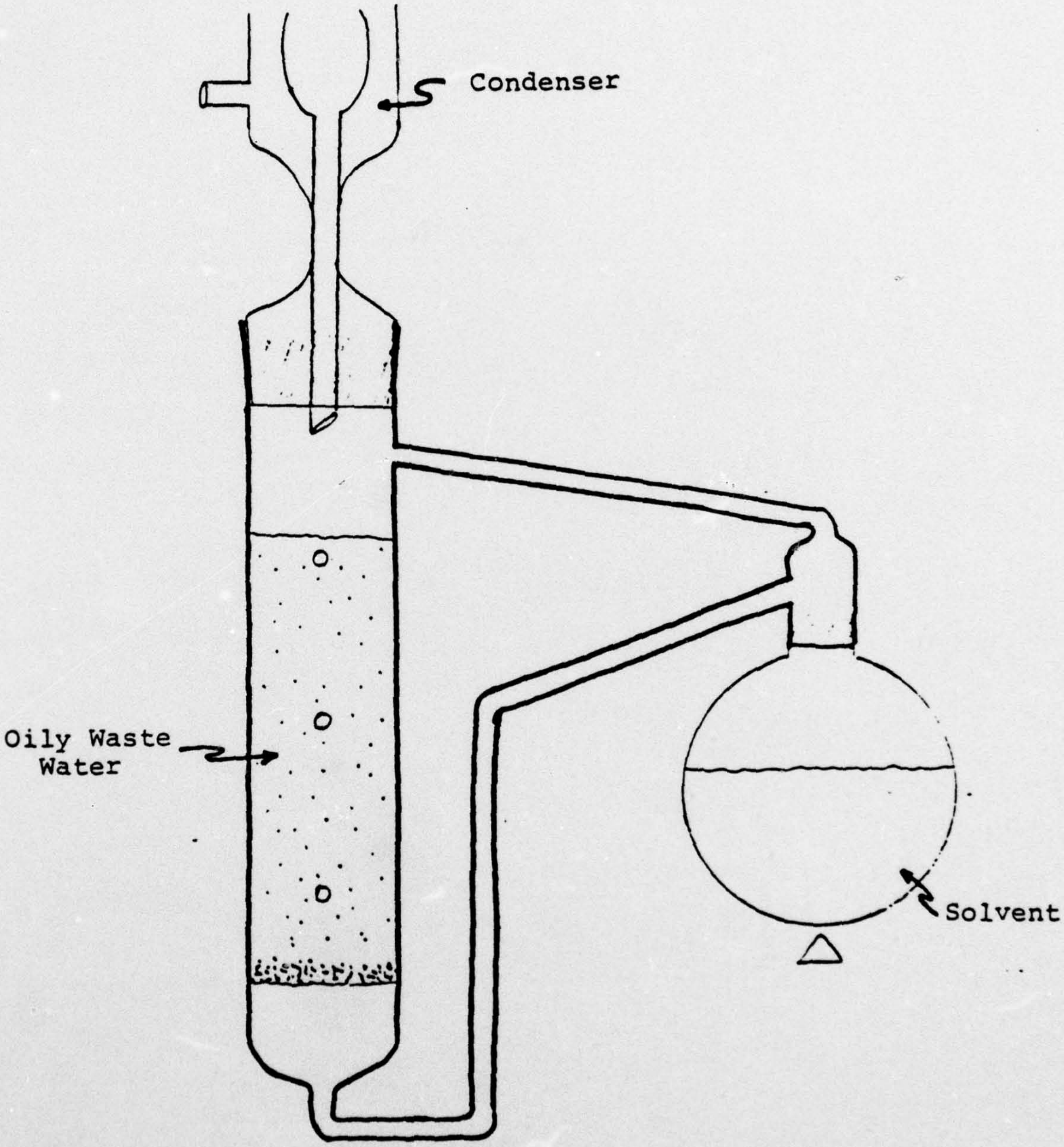


Fig. 1. Solvent Extraction Apparatus

UV-VIS SPECTROPHOTOMETRY

UV-VIS spectrophotometry was performed on the oily waste water extract. The spectrum obtained is shown in Fig. 2; the instrument used was a B&L Spectronic 505 Spectrophotometer. The spectrum shows no distinctive peaks, although two minor slope changes can be seen, one occurring at 415 nm and the other at 590 nm. The gradual increase in absorption with decreasing wavelength seen in the spectrum could be due to non-specific absorption by organic material at the lower wavelengths and/or to light scattered by very small particles which were not removed from the extract by filtration. Due to inhomogeneity of the original sample, in which an oily sludge was immiscibly mixed with water and particulate materials, a reliable spectrum of the oily waste water could not be taken.

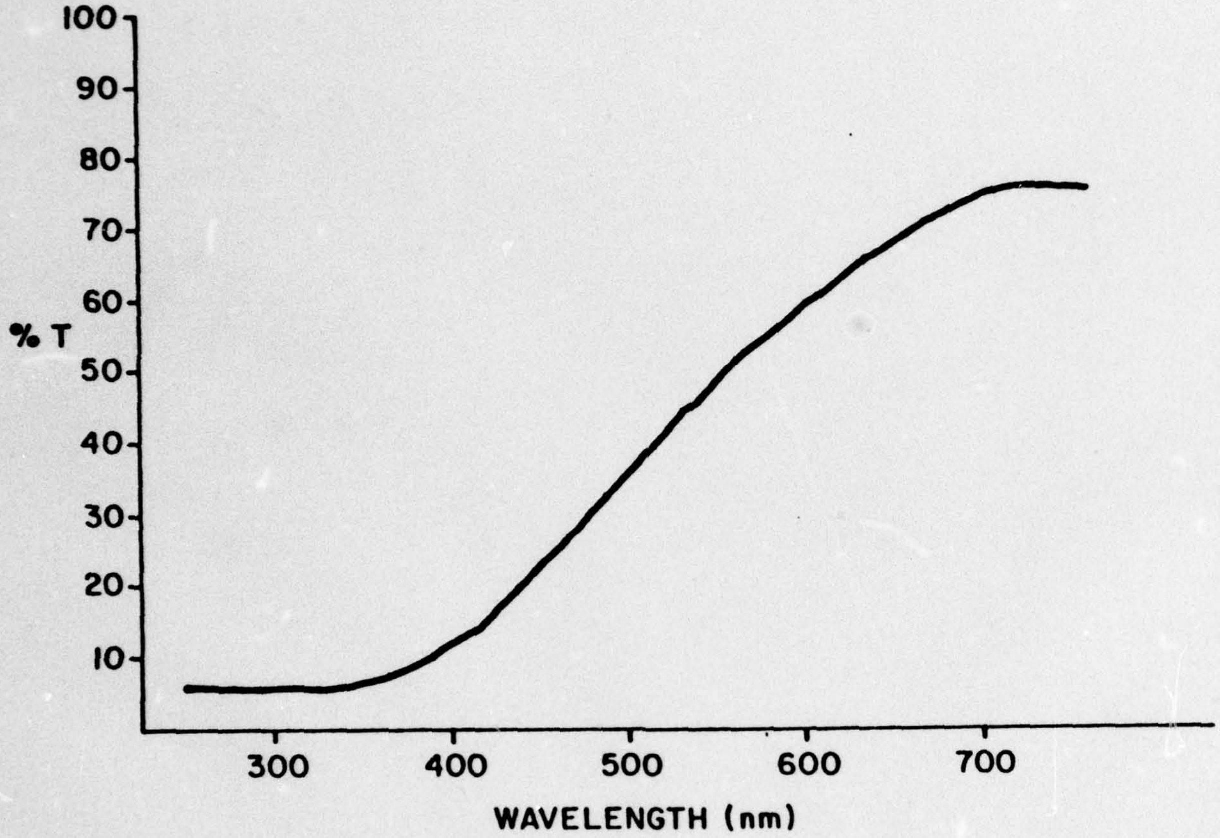


Fig. 2. UV-VIS Spectrum of Waste Water Extract

PARTICULATE MATERIAL

1. Introduction and Light Microscopy

The oily waste water appeared as a greenish mass of water with a greenish-brown oily sludge floating on the surface. Microscopic examination of this organic-rich fraction of the oily waste water revealed that it consisted of tiny droplets of oil suspended in an aqueous medium (plate 1, top left). Closer examination revealed that a reddish-brown particulate material was associated with these droplets of oil (Plate 1, top right). This particulate material averaged about 10μ in size and was intimately associated with the oil droplets. In the photomicrograph, some of the particles can be seen adhering to the surface of the oil droplets.

A sample of the particulate material was prepared for further examination by filtration of the oily waste water with a 0.45μ Millipore filter. The material collected on the filter was extensively washed with methylene chloride to remove any residual organic material. The washed sample was weighed and found to constitute approximately 0.05% by weight of the waste water. The sample was then split into two portions.

The first portion was separated into two density fractions: heavier than 2.5 gm/ml and lighter than 2.5 gm/ml. Each sample was examined microscopically. The heavier fraction (density > 2.5 gm/ml) consisted of reddish-brown

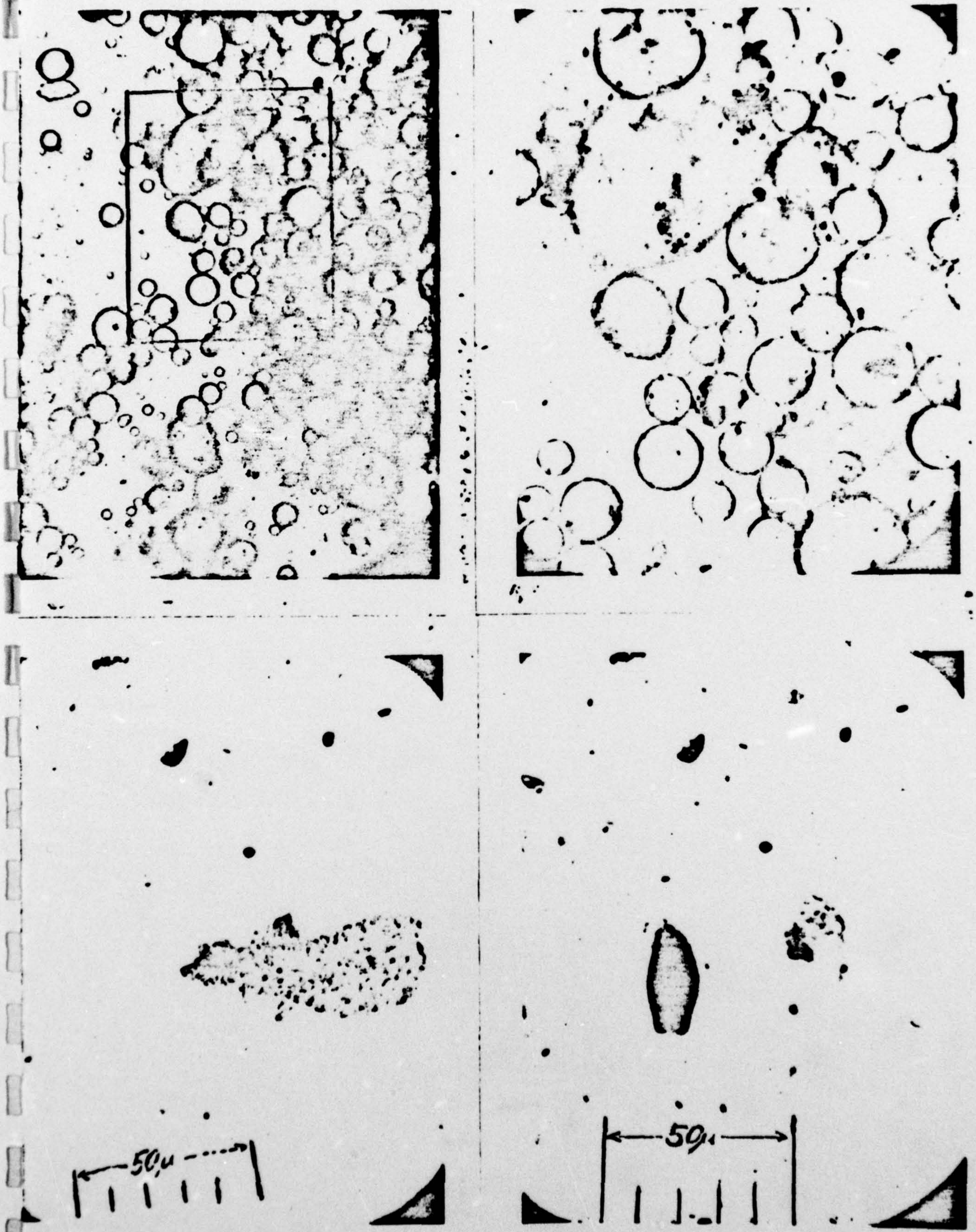
Plate 1. Photomicrographs of oily waste water sample

Top left: Oil fraction of water sample (X300).

Top right: Oil fraction of water sample (enlargement of top left photomicrograph, X625).

Bottom left: Particulate material in water sample heavy fraction (d > 2.5 gm/ml).

Bottom right: Particulate material in water sample light fraction (d < 2.5 gm/ml).


50µ
50µ

glossy shards (Plate 1, bottom left). The lighter particles (density < 2.5 gm/ml) occurred mostly as reddish brown aggregates of material, although more unusual particles, like those shown in Plate 1 (bottom right) did occur. These two photomicrographs show particulate material which is somewhat larger than the bulk of the material in each density fraction.

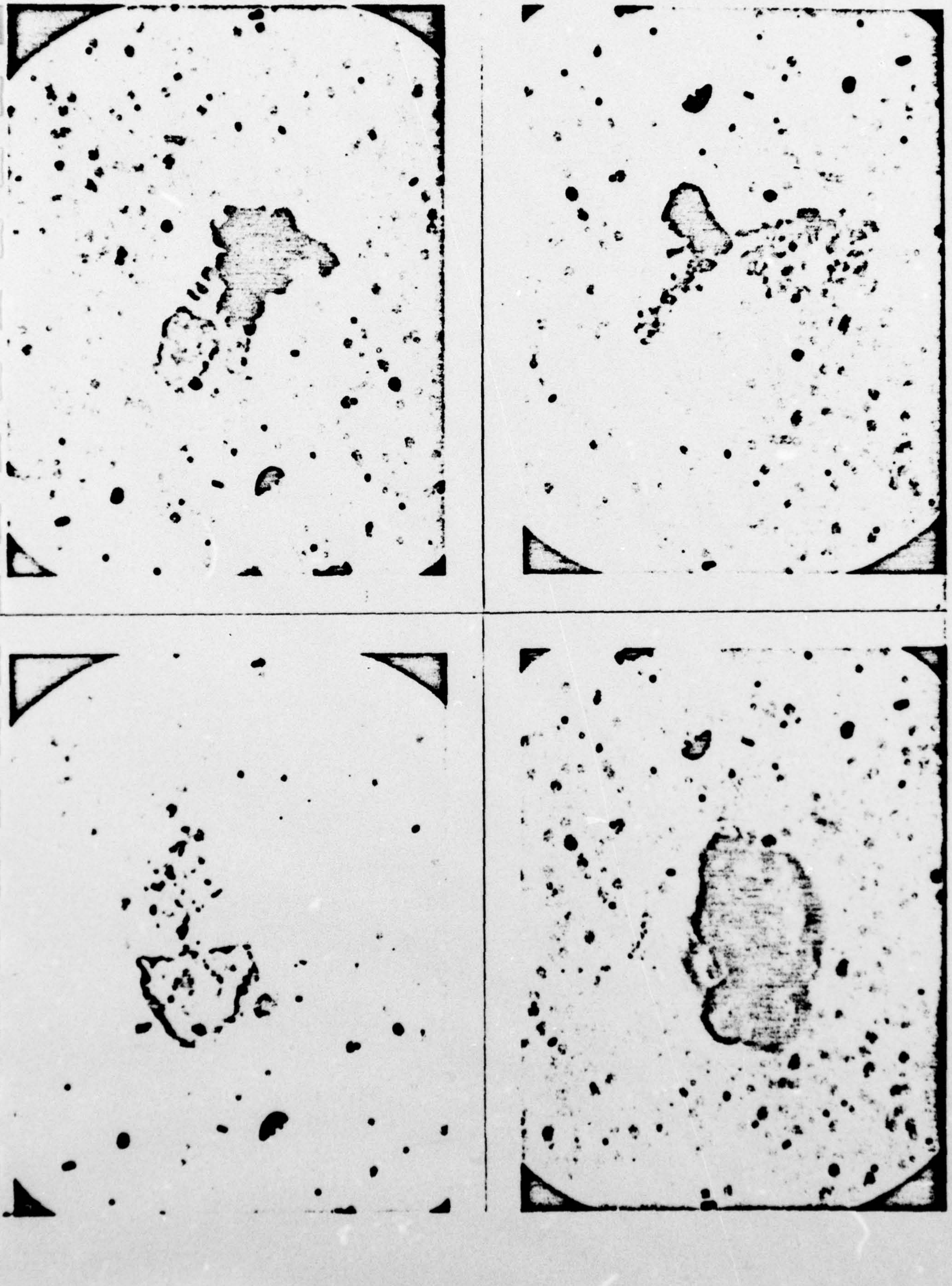
The second portion of the particulate sample was used without any further separation. The sample was disaggregated by sonication and mounted in oil for microscopic examination, but in this sample the major emphasis was on the smaller sizes of particulates. Examples of the particulate materials are shown in Plate 2. This sample was also analyzed by X-ray fluorescence spectrometry and with a scanning electron microscope (SEM).

2. X-Ray Fluorescence Spectrometry

Qualitative X-ray fluorescence studies were attempted on the particulate sample. The analysis was hampered by the small amount of material available. There was insufficient material to give good results on a normal sized X-ray fluorescence specgrometer, so an X-ray milliprobe was used. The milliprobe was set up to determine the first row transition elements, and only these were detected in the sample. The following results were obtained:

Element	Concentration (Estimated)
Fe	2%
Zn	0.1-1%
Cu	0.1-1%
Ni	trace (< 1000 ppm)

Plate 2. Photomicrographs of particulate material oily waste water sample (All photomicrographs are X2500).



3. Scanning Electron Microscopy

Scanning electron microscopy was performed on the particulate sample. Photomicrographs of three different particles are shown in Plates 3, 4 and 5. The particles were selected for their differing chemical compositions, and thus may not be representative of the total sample.

Plate 3 shows what appears to be a crystalline aggregate; some crystal (or cleavage) faces are visible. X-ray analysis by the SEM indicates that the major element present in the aggregate is iron, with many minor elements also being present. The largest peak on the X-ray scan corresponds to chlorine, which is present in the mounting medium.

Plate 4 shows again what appears to be a crystalline aggregate showing a pseudo-hexagonal symmetry. The major element found in the X-ray analysis is calcium, with only traces of other elements. Upon close inspection, the crystals appear orthorhombic. Two sets of interfacial angles were measured: 51.5° and 66.5° (average of two measurements each); these crystals were measured assuming that the crystal face in the plane of the paper is a basal pinacoid, and that the measured faces are prisms or pinacoids. The appropriate angular data for aragonite ($CaCO_3$) is (9)

$$(010) \wedge (110) = 58^\circ 06'$$

$$(110) \wedge (1\bar{1}0) = 61^\circ 54'$$

which does not fit the measured data very well. Identification of these crystals as calcite (trigonal) or CaO

Plate 3. Particulate material isolated by filtration of oily waste water sample.

Top: Scanning electron micrograph of particle (X5600).

Bottom: X-ray spectrum (0.000 to 10.230 keV) of same particle. Qualitative analysis: Fe $\gg$ Zn, Ca, S, P, Si $>$ Mg, Al, K.

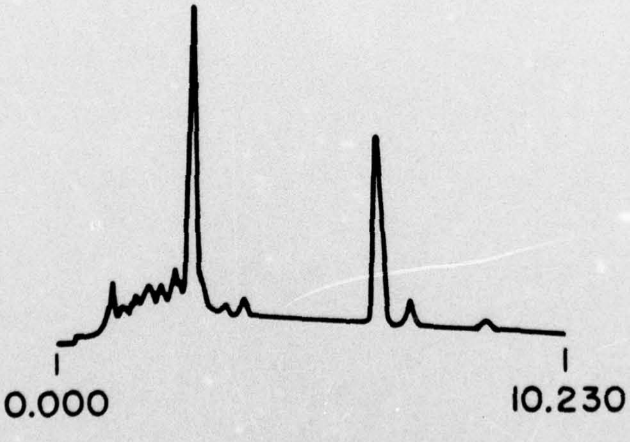

0.000
10.230

Plate 4. Particulate material isolated by filtration of oily waste water sample.

Top: Scanning electron micrograph of particle (X11,000).

Bottom: X-ray spectrum (0.000 to 10.230 keV) of same particle. Qualitative analysis: Ca $\gg$ Fe, Si, S.

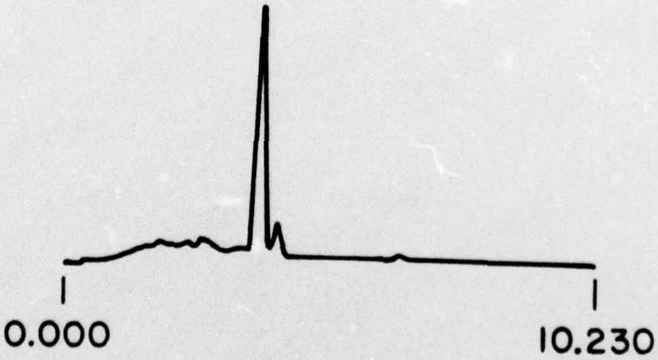
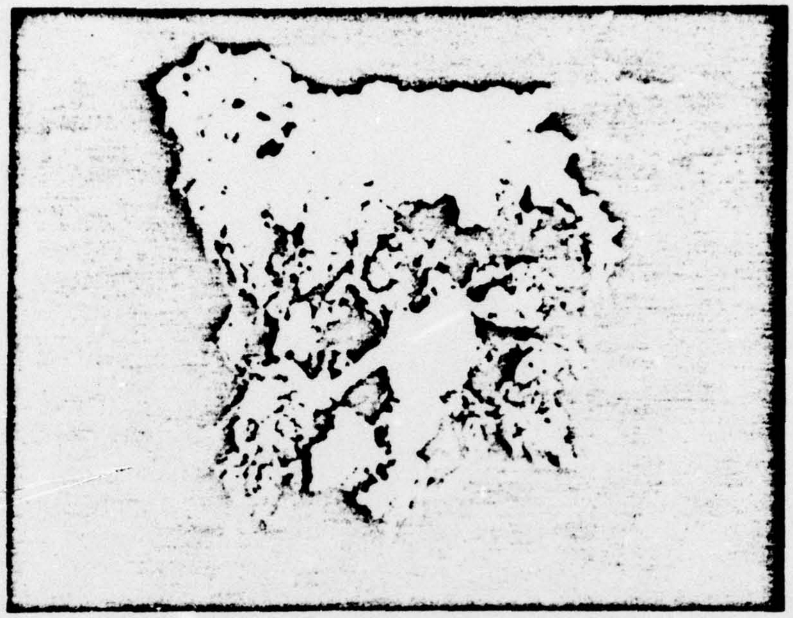
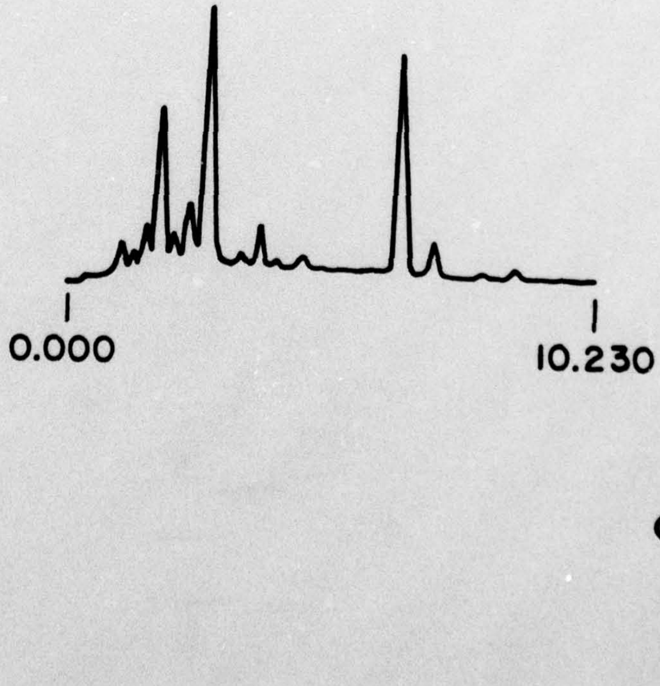

0.000
10.230

Plate 5. Particulate material isolated by filtration of oily waste water sample.

Top: Scanning electron micrograph of particle (X1150).

Bottom: X-ray spectrum (0.000 to 10.230 keV) of same particle. Qualitative analysis: Fe > Si >> Cu, S > Al, Zn, Mg, P, K, Ti Cr, Mn (?).





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(isometric periclase structure) is also ruled out.

Plate 5 shows what appears to be a large particle coated with a heterogeneous mix of smaller particles. The chemical composition of the aggregate is quite varied with iron and silicon being the most abundant elements (the largest peak in the X-ray scan is chlorine, again due to the mounting medium). The iron X-ray and silicon X-ray maps of this particle are shown in Plate 6. The iron X-ray map indicates that the particle has iron uniformly distributed throughout; the particle may in fact be an iron or steel fragment. A silicon X-ray map indicates that some of the surface particles contain large quantities of silicon; it should also be noted tnat not all of the surface particles contain large amounts of silicon.

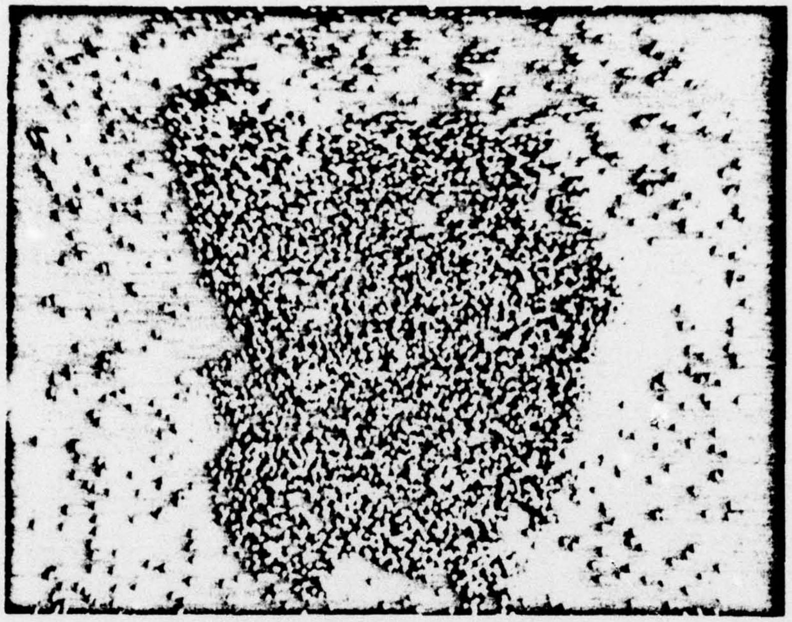
4. Conclusion

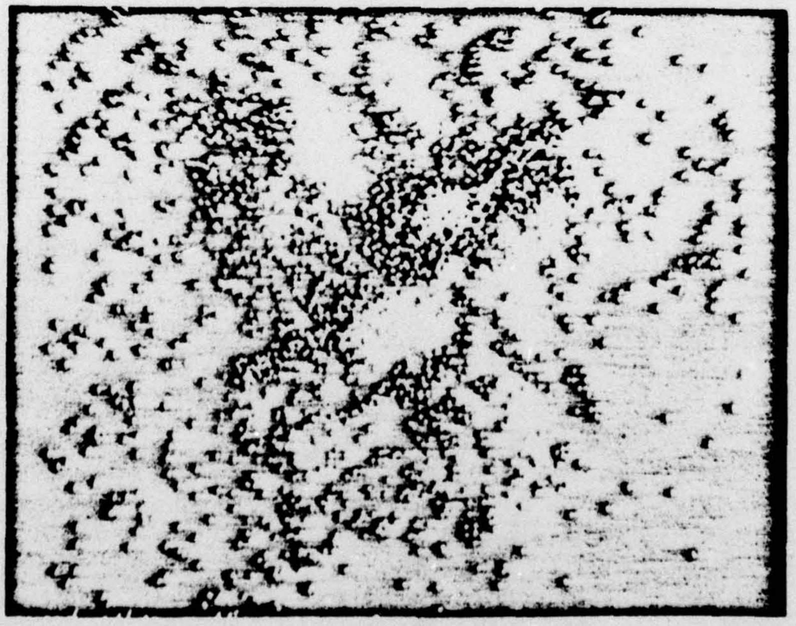
The particulate material found in the oily waste water was a very heterogeneous mixture of constituents with a very large size range. These particulates constitute approximately 0.05% by weight of the oily waste water. The majority of the particulates visible with a light microscope at moderate magnification were transparent to translucent reddish-brown grains, approximately 10 nm in size, and were mainly found associated with (in many cases <u>on</u> the surface of) oil droplets in the waste water. Scanning electron microscopy revealed that many of the smaller grains were crystalline aggregates with a varied composition, with iron appearing to be the most prevalent element.

Plate 6. X-ray photo maps of particle in Plate 5.

Top: Fe.

Bottom: Si.





THIN-LAYER CHROMATOGRAPHY

A preliminary attempt at the separation of the organic constituents in the oily waste water was performed with thin-layer chromatography. This technique has been much used as a rapid method for the determination of the type of petroleum product present in an unknown sample (10, 11) and also has been used more specifically to identify constituents and additives in lubrication oils (12). Thin-layer chromatography has an advantage over gas-liquid chromatography because specific functional group reactions are much more easily performed on the separated products, but a price is paid for this convenience in the lower separation ability of the thin-layer plates.

The work described below was performed on pre-coated Silica Gel 60 F 254 aluminum-backed plates having a layer thickness of 0.25 mm (available from E. Merk). The solvents used were of reagent or spectro grade quality, with no prior purification. The samples were filtered chloroform extracts of the waste water and the oily waste water itself.

The thin-layer chromatography of the waste water extracts yielded about a dozen distinct spots on the thin-layer plate when a non-polar developing solvent was used. Very polar solvents (e.g. water or methanol did not appear to produce any migration of the constituents from the origin; this behavior is taken to mean that the individual constituents are not soluble in such solvents. Development of the plate with non-polar solvents (e.g. carbon tetrachloride or benzene) gave rise to many different spots with R_f varying from 0.0 to 0.90. The spots were visualized using the inherent UV-absorbing and/or fluorescing capabilities of the constituents or by charring the plate with dichromate-sulfuric acid (13).

There has been no positive identification of the constituents of the various spots on the developed thin-layer plates, but suggestions can be made for certain groups of spots. It is suspected that some of the spots may be due to aromatic hydrocarbons because of the UV-absorbence (and/or fluorescence) displayed by some spots and also because of the relatively non-polar nature of the constituents in the spots as evidenced by their migratory behavior in various solvents. There is an indication that one of the spots with a large R_f (R_f = 0.80) may be a phenolic antioxidant. This particular spot shows the proper chromatographic behavior (large R_f) in various solvents (12), UV light absorption, and the reddish-brown diazonium coupling product (of tetra-azotized-o-dianisidine - T.O.D.) typical of a butylated phenol (12). Less specifically, this spot also is readily oxidized by the dichromate-sulfuric acid charring reagent; this fact also gives credence to the possible presence of an anti-oxidant.

The thin-layer chromatography of the oily waste water was attempted using non-polar developing solvents, but reproducible results could not be obtained. Spotting of the crude oily waste water on a thin-layer plate resulted in a greenish-brown spot at the origin which may be due to insoluble (particulate ?) constituents. A somewhat similar spot also occurred with the waste water extract, although the spot in this case is due to soluble materials. Irrespective of the solvent used to develop the plate, the greenish-brown at the origin was seen to undergo little or no migration.

In summary, thin-layer chromatographic analysis of the waste water extract was successful because reproducible separations of the constituents were obtained. The information derived from the various separations using different solvents indicated that the oily waste water is a very complex system of organic contaminants.

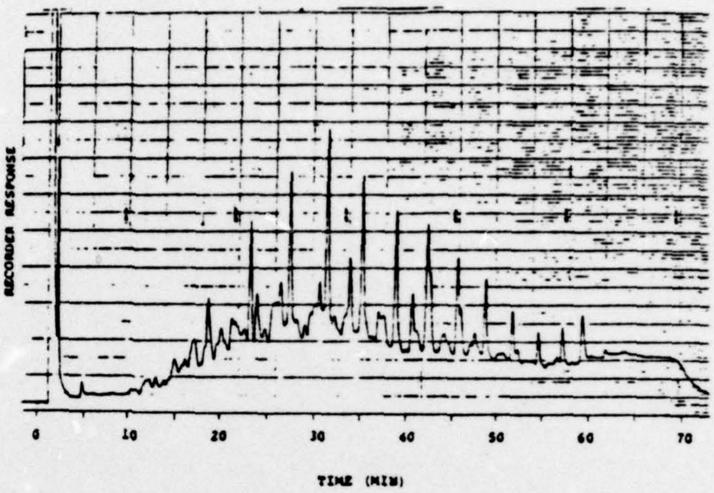
GAS-LIQUID CHROMATOGRAPHY

The gas-liquid chromatographic analyses were performed with two major objectives in mind: (1) a comparison of the oily waste water with a typical fuel oil and lubrication oil to determine if there are any similarities between the organic materials in the waste water and the two oil products, and (2) the identification of classes and/or individual compounds in the oily waste water. The work was performed with a Tracer Model MT-220 gas chromatograph equipped with a Flame Ionization Detector; columns packed with OV-1 (methyl silicone), a non-polar stationary phase, were used exclusively.

1. Oily Waste Water

The non-polar organic material in the oily waste water is quite distinctive; a typical gas-liquid chromatogram of the methylene chloride extract is shown in Fig. 3. The direct gas-liquid chromatographic analysis of the oily waste water itself was attempted, but with limited success. The organic-rich surface layer of the waste water, which consists of minute oil droplets floating in the aqueous medium, was mechanically separated from the bulk of the aqueous phase and injected directly into the gas-liquid chromatograph. The chromatogram of this oil phase, see Fig. 3 (bottom), is nearly identical to that of the organic (methylene chloride) extract. This great similarity between the organic-rich layer of the water and the methylene chloride extract indicated that most, if not all, of the non-polar constituents in the organic extract of the waste

Waste Water Extract



Oily Waste Water
(Organic Layer)

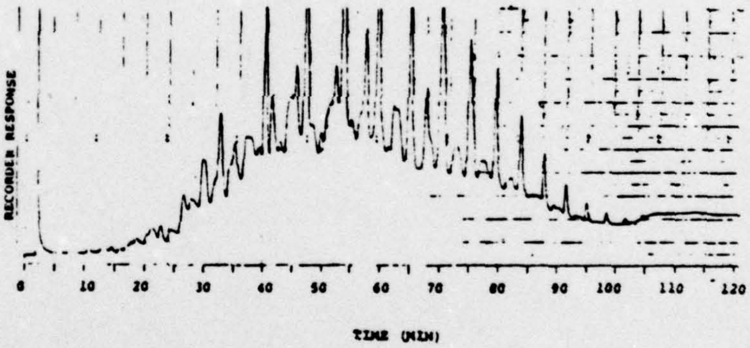


Fig. 3. Gas-Liquid Chromatogram of Oily Waste Water and Extract.

Carrier Gas: Nitrogen (27 ml/min)
Temperature: init.: 70° (4 min) (top fig.)
60° (6 min) (bottom)
prog.: 3°/min (top)
2°/min (bottom)
final: 250° (10 min) (top)
270° (20 min) (bottom)
Column: ¼in X 6ft, 5% OV-1 on 80/100 mesh GasChrom S

water were the same as those in the organic-rich layer of the oily waste water itself. An analysis of the bulk aqueous portion of the oily waste water by GLC was attempted, but without success. This was due to the effect that the water in the column had on the separation -- i.e. steam distillation of the organic constituents and column stationary phase, and/or the small quantities of non-polar organic material dissolved in the aqueous phase.

Several things can be said concerning the nature of the non-polar organic constituents in the oily waste water from the evidence in the chromatographic data. First of all, the large singular equidistant peaks superimposed upon unresolved background gives the chromatogram a distinctive character which should allow it to be distinguished from the other oil products analyzed in this series of experiments. These large peaks probably indicate the presence of members of a homologous series of compounds -- e.g. n-alkane hydrocarbons (14). The detection and quantitation of n-alkanes are discussed in a later section. Another important feature is the large number of compounds in the sample; at least 100 peaks or shoulders can be seen in chromatograms of the oily waste extract. In addition to the peaks and shoulders, there also occurs in the low to moderate boiling range, a broad featureless "humpane" structure on which the other peaks are superimposed. This humpane feature, a common occurrence in the chromatographic work which accompanies primitive atmosphere random synthesis simulation experiments in studies of chemical evaluation, is due to the near simultaneous elution of many similar compounds (15).

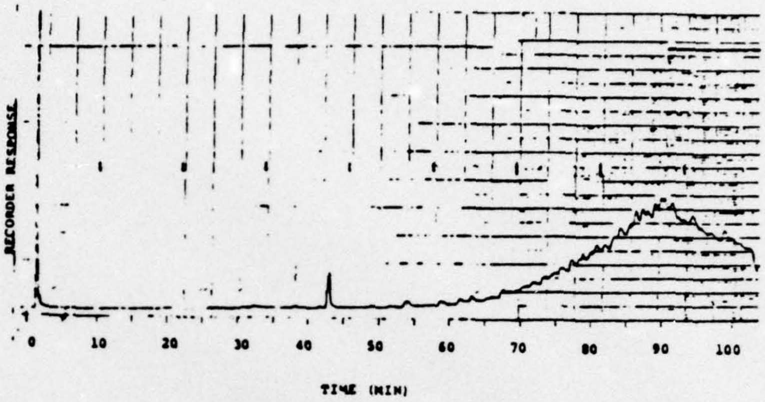
2. Lubrication Oil

In order to be able to compare the oily waste water analysis with some "standard" substances, a typical Navy lubrication oil (2190 TEP, MIL-1733F AM2, Steam Turbine) and Navy fuel oil (MIL-F-24397, ND, California #2) were analyzed under chromatographic conditions similar to those for the waste water. The chromatographic analyses of these substances were much easier to perform because of the absence of an interfering aqueous phase. In most cases, the anlyses were performed by directly injecting the filtered oil product into the gas chromatograph. In this section the chromatographic results for the lubrication oil are discussed; the next section will discuss the results for fuel oil.

The lubrication oil is a multicomponent mixture consisting mostly of high boiling constituents(see Fig. 4). The major portion of this oil elutes from the chromatograph at high column temperatures; this portion has at least 50 components which were not completely resolved. The oil also has one major constituent which elutes much earlier than the majority of the constituents.

A methanol extraction of the lubrication oil was performed by shaking the methanol and oil together and then removing the methanol phase; this solution was then analyzed bt gas-liquid chromatography (see Fig. 4). It was found that the methanol extract of the oil contained only a single major component which eluted much earlier than the major portion of the constituents in the oil.

Lubrication Oil



Lubrication Oil
(MeOH Extract)

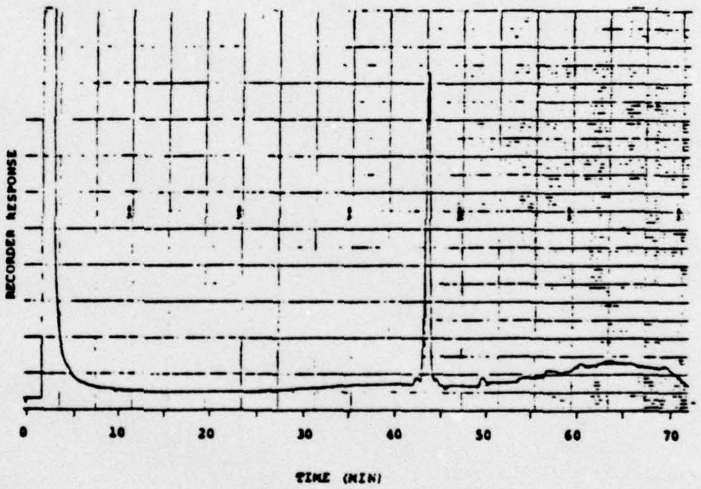


Fig. 4. Gas-Liquid Chromatogram of Lubrication Oil and Methanol Extract

Carrier Gas: Nitrogen (27ml/min)
Temperature: init.: 75° (5 min) (top Fig.)
70° (4 min) (bottom)
prog.: 2°/min (top)
3°/min (bottom)
final: 250° (20 min) (top)
250° (10 min) (bottom)
Column: ¼in X 6ft, 5% OV-1 on 80/100 mesh GasChrom S

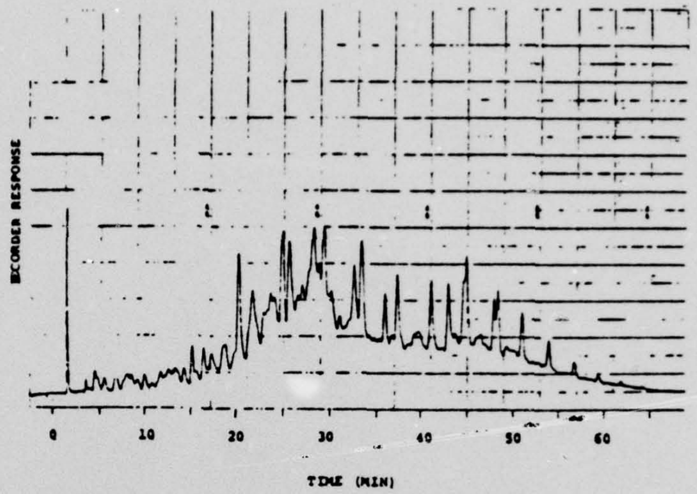
The higher boiling constituents appear not to have been extracted by the polar solvent.

From the above information, we can say that most of the constituents in the lubrication oil are non-polar and are of relatively large molecular weight ($MW > 300$). The oil also contains a polar constituent, perhaps of lower molecular weight. Since a normal mineral oil contains only non-polar compounds (viz straight-and branched-chain paraffins, alkylated naphthenes, alkylated aromatic hydrocarbons, and some asphaltenes (16), this polar constituent might be an oil additive.

3. Fuel Oil

The fuel oil is also a multicomponent complex system. A typical gas-liquid chromatogram shows a number of large peaks, and some smaller ones, superimposed on an unresolved baseline (see Fig. 5). The large number of peaks in the chromatogram indicates that the fuel oil contains many constituents; over 100 peaks and shoulders can be found. Another interesting characteristic of the fuel oil is that it contains constituents which elute over a very wide range of temperatures, from volatile substances (eluting immediately after the solvent peak) to substances with low volatility (late eluting). The volatile components constitue a minor but significant fraction in the fuel oil. Another prominent feature in the chromatogram is the occurrence of a humpane feature in the moderate boiling range.

Fuel Oil



Fuel Oil
(MeOH Extract)

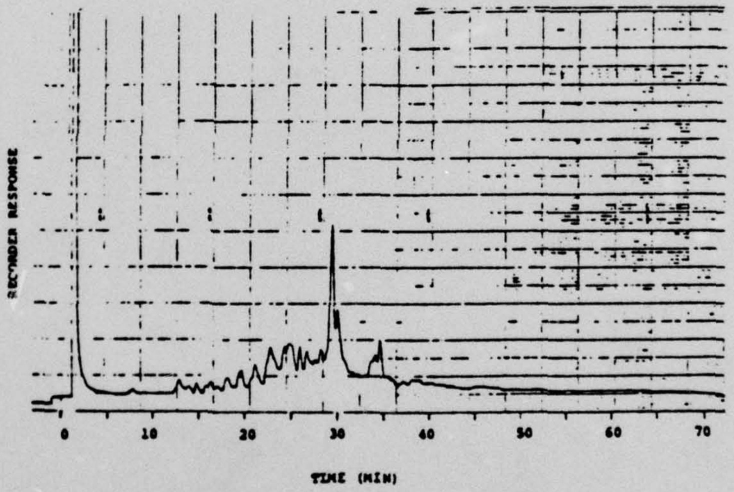


Fig. 5. Gas-Liquid Chromatogram of Fuel Oil and Methanol Extract

Carrier Gas: Nitrogen (27 ml/min)
Temperature: init.: 70° (4 min)
prog.: 3°/min
final: 250° (10 min)
Column: ¼in X 6ft, 5% OV-1 on 80/100 mesh GasChrom S

A methanol extraction was performed on the fuel oil in a manner similar to that described for the lubrication oil. Gas-liquid chromatographic analysis of this extract showed that this extract contained a large number of constituents; more than 80 peaks or shoulders were found (see Fig. 5). These constituents were generally low to moderate boiling components of the fuel oil. Very few of the higher boiling components appeared to be extractable into a polar solvent.

4. Discussion

In the previous three sections, the results of the gas-liquid chromatographic analyses for the oily waste water, lubrication oil and fuel oil were discussed individually. Therein it was noted that the chromatograms of each of these substances were different and some inferences were made about the constituents. In this section, the similarities and differences of the oil products will be discussed, with emphasis on their comparison with the oily waste water.

The lubrication oil is quite distinctive when compared to either the fuel oil or the waste water extract because of the absence of significant numbers of constituents in the low to moderate boiling range and because of the predominance of high boiling compounds in the sample; this elution profile is just the opposite of that which occurs in the other two samples. From this evidence we can draw the conclusion that lubrication oil does not appear to be the dominant type of contamination in the oily waste water. As a further check, some of the lubrication oil was dissolved in the solvent (methylene chloride) used to extract the oily waste water. It was found that the lubrication oil dissolves completely in the solvent, and the gas-liquid chromatography results were very similar to those for the neat oil. This tends to confirm the above conclusion that the lubrication oil, if present in the oily waste water, should have been extracted by the solvent, and thus detected in the chromatographic analysis of the oily waste water.

The fuel oil is much more similar to the organic contaminants in the oily waste water than is the lubrication oil. Generally speaking, the gas-liquid chromatograms of the two substances appear similar. Both the fuel oil and waste water extract have the major quantity of constituents eluting in the moderate boiling range, with lesser amounts in the low to high boiling ranges. One major difference between the two substances is that the fuel oil contains small but significant amounts of very volatile constituents, whereas the waste water does not; however, this may be due in part to the method of collection of the waste water and also to its exposed nature, where the more volatile components could have evaporated away. Another difference is that the mass of the major components (largest peaks) in the fuel oil appear to be present in more uniform quantities than are the major constituents in the oily waste water.

A good test of how closely the constituents in the fuel oil resemble the individual constituents in the oily waste water is to coinject the fuel oil and waste water extract into the chromatograph and observe the chromatogram. If the two materials are similar and/or identical, then the resulting chromatogram will have many of the peaks of one substance superimposed on peaks of the other, these superimposed peaks will be enhanced in size, and the resulting chromatogram will look similar to one or both of the substances (17); just the opposite would be true if the substances have dissimilar constituents. This experiment was performed by mixing the waste water extract and fuel oil together, and injecting the solution; the resulting chromatogram is shown in Fig. 6. The coinjection chromatogram is found to be nearly identical to that of the oily waste water (extract). From this evidence, it appears that many of the constituents which comprise the fuel oil are also present as contaminants in the oily waste water. It can further be said that probably the major source of contamination in the oily waste water is by a fuel oil.

The methanol extractions of the fuel oil and lubrication oil were performed in order to demonstrate that certain constituents in these oils are sufficiently polar so as to be extractable by methanol and perhaps even by an aqueous solvent. As such, they may be more of an environmental hazard than the non-polar constituents because they would be dissolved in the water and could be more widely distributed.

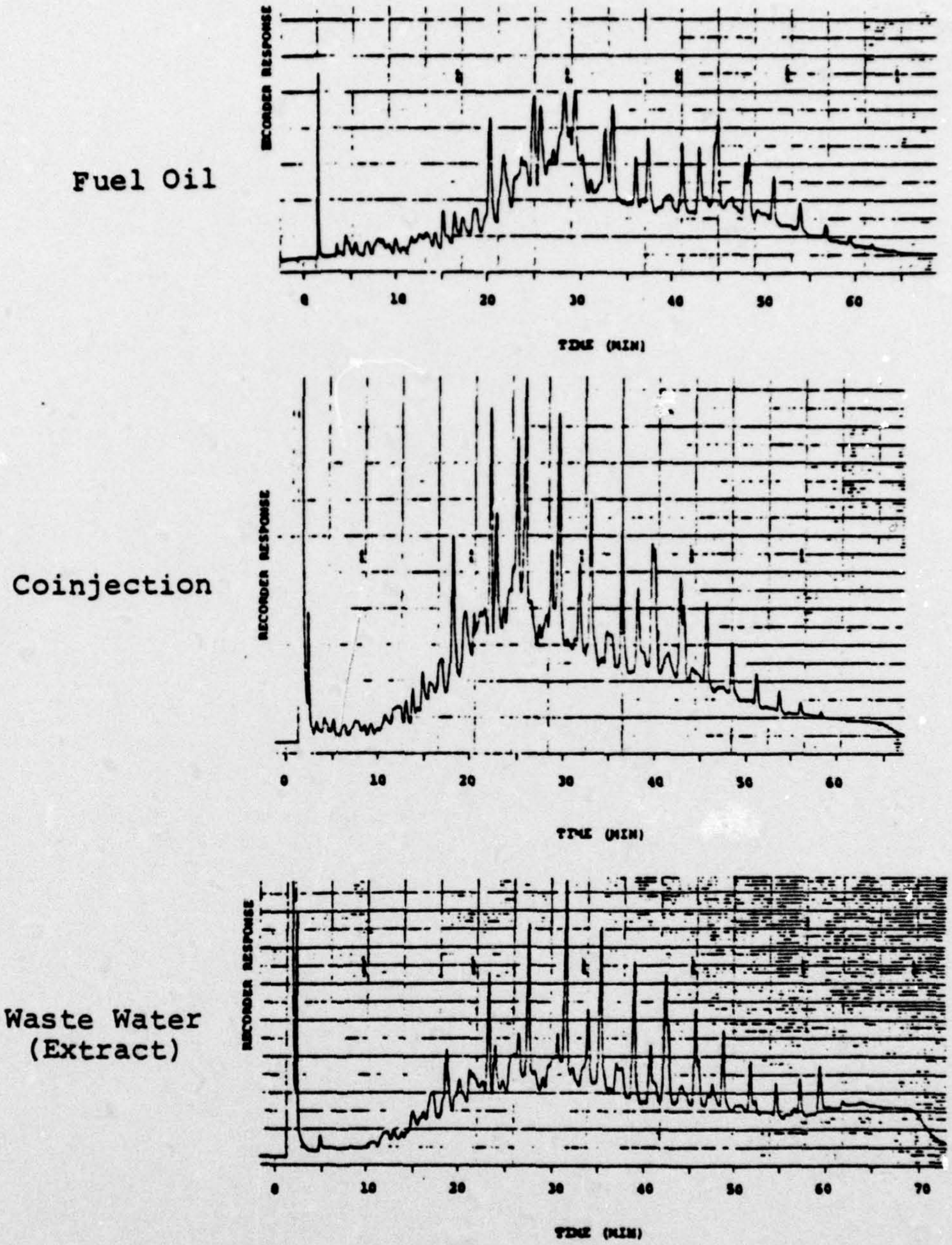


Fig. 6. Gas-Liquid Chromatogram of the Coinjection of Fuel Oil and Waste Water Extract

Carrier Gas: Nitrogen (27 ml/min)
Temperature: init.: 70° (4 min)
prog.: 3°/min
final: 250° (10 min)
Column: ¼in X 6ft, 5% OV-1 on 80/100 mesh GasChrom S

LIQUID CHROMATOGRAPHY

Analysis of the oil samples was also performed by liquid chromatography to complement the information obtained by gas chromatography. Two different liquid chromatographic techniques were utilized to analyze the individual oils and also to compare the organic contaminants in the oily waste water with the fuel oil and lubrication oil. Gel permeation chromatography, a separation technique based principally on the size of individual molecules in solution, was used in an attempt to determine the range of molecular weights occurring in each of the oil samples. Reversed-phase liquid chromatography, a separation technique based on molecular polarities, was used to obtain information on the molecular polarities of the UV-absorbing constituents in each of the oils. The results of the analyses using each of these techniques will be discussed separately as they have quite different interpretations.

1. Gel Permeation Chromatography

The gel permeation chromatography experiments were performed to obtain information on the molecular weight ranges of the organic constituents in the oily waste water extract, the fuel oil and the lubrication oil. In these experiments, a microporous PSDVB (8% cross-linked) gel was used as the stationary phase and tetrahydrofuran as the mobile phase. The column had previously been calibrated for molecular size (molecular weight) using n-alkanes as standards (18). Two detectors (RI and UV were used in order to be able to determine which molecular size fractions contain UV-absorbing materials. The results for each of the oil products are reported below.

a) Oily Waste Water

The oily waste water mainly contains materials of relatively low molecular size, some constituents of which do not have significant UV-absorption (see Fig 7). Some material also occurs in a larger molecular size fraction ($MW > 1000$), and is UV-absorbing, but this fraction constitutes only a minor portion of the total amount of organic material. The major portion of the organic constituents occur in a fraction with a very broad molecular size range, varying from C_{18} to C_7 (if expressed as n-alkanes) and showing variations in UV-absorbing character over this range. The UV-absorbing material appears to be concentrated in the lower size range of the main fraction, viz the C_{12} to C_7 n-alkanes portion, whereas the higher molecular size portion, that ranging from C_{18} to C_{12} n-alkanes, does not appear to have significant UV-absorption properties. It is probable that the high molecular size portion (C_{18} to C_{12}, non UV-absorbing) may consist of aliphatic hydrocarbons and the lower molecular size portion (C_{12} to C_7, UV-absorbing) consists of aromatic compounds.

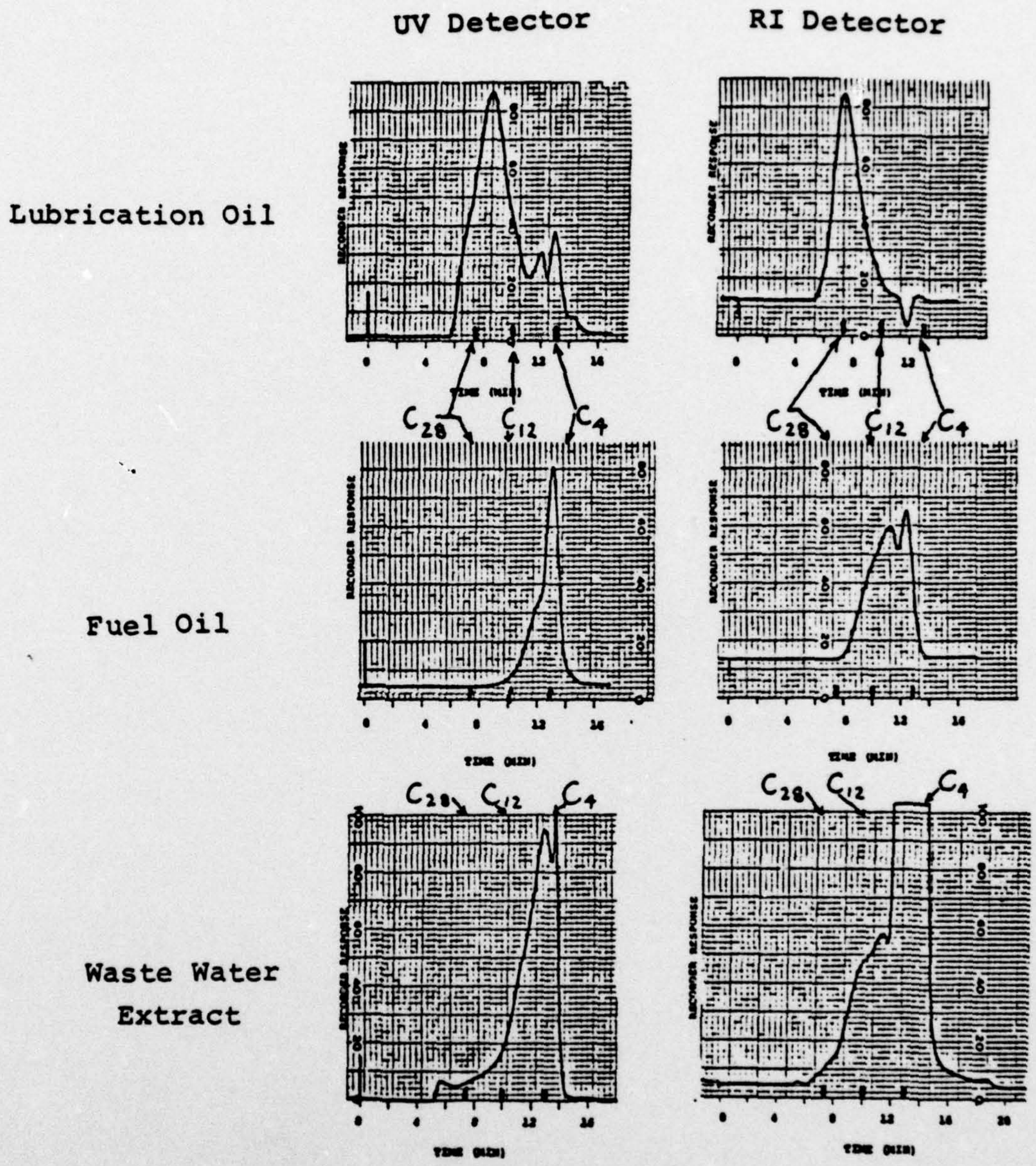


Fig. 7. Liquid Chromatogram (GPC) of Oil Products (C_6 is n-hexane, etc.)

Flow Rate: 0.5 ml/min
Solvent: tetrahydrofuran
Column: GKL-11(PSDVB); (6.1mm X 30cm)
Detector: RI; UV(254)

b) Lubrication Oil

The lubrication oil contains materials with a wide range of molecular sizes, most of which appear to have significant UV absorption properties. There are four distinct molecular size fractions. The first and largest has a molecular size range from C_{40} to C_{10} (n-alkanes) and has significant UV absorption. This fraction contains the major mass ($>90\%$) of the lubrication oil, as determined by the relative sizes of the RI detector peaks. The second fraction has a calibrated molecular range from C_{10} to C_5 (n-alkanes). The material in this fraction is again UV-absorbing, but is distinctive in that these constituents have a lower refractive index than does the solvent, tetrahydrofuran. The next two fractions, consisting of sizes C_5 to C_2 and less than C_2 (n-alkanes) are present in lesser quantities than the first two fractions, but both contain material which is UV absorbing. Since few compounds smaller than butane have large UV absorptivities (at $\lambda = 254$ nm), the constituents eluting in the two small molecular size fractions appear to be somewhat odd. But Popl, et. a., have found that polynuclear aromatic hydrocarbons seem to have an affinity for a polystyrene stationary phase (18) and thus will elute from the column later than would normally be expected if no interaction occurs between the solute and stationary phase (19).

The constituents in the lubrication oil are, on the average, of much higher molecular weight than the oily waste waterorganic constituents, and exhibit greater degrees of UV absorption. The UV-absorbing constituents in the lubrication oil occur in the entire range of molecular sizes, whereas in the oily waste water extract, only some fractions are UV absorbing.

c) Fuel Oil

The fuel oil is found to contain materials in two different molecular size fractions. The first fraction elutes in the calibrated size range of the C_{18} to C_5 n-alkanes and does not absorb in the UV. The second size fraction elutes in the range of C_5 to C_2 (n-alkanes) and absorbs in the UV region. The larger size fraction may contain aliphatic hydrocarbons because of the RI response, their known presence in the sample, and the negligible amount of UV absorption. The possibility that the second fraction (C_5 to C_2) may have aromatic hydrocarbon constituents has been discussed in a previous section. The presence of a size fraction which is not UV absorbing serves to distinguish the fuel oil from the lubrication oil. This fraction elutes in the same general size range as the non-UV absorbing fraction in the oily waste water extract and demonstrates the similarity of the fuel oil to the organic contaminants in the waste water.

2. Reversed-phase Liquid Chromatography

Liquid-solid partition chromatography is a separation technique based on the partitioning of the solute molecules between the mobile phase and the stationary phase. Our use of reversed-phase liquid chromatography involves the use of a polar mobile phase and a non-polar bonded stationary phase (ODS). Reversed-phase liquid chromatography separates molecules on the basis of the their polarities, the more polar molecules being eluted before the less polar ones.

Reversed-phase liquid chromatography was used in this investigation in two different capacities. The first was to compare the oily waste water with the methylene chloride extract of the same, in order to determine how complete the extraction was. The second purpose of the chromatography was to compare how closely the UV absorbing constituents in the fuel oil, lubrication oil and waste water extract compare with each other in regard to the molecular polarities of the various constituents.

a) Oily Waste Water

An experiment was performed using reversed-phase liquid chromatography in a solvent program mode to determine how effectively the methylene chloride extraction proved in removing the organic constituents from the oily waste water. The liquid chromatographic apparatus used is shown in Fig. 8. The gradient program enhanced the separation, as compared to an isocratic mode, of the early eluting compounds while decreasing the separation of the more retained substances. This program mode was quite useful because gas-liquid chromatography had been used to investigate extensively the less polar (late eluting) fraction.

The results of the chromatography (see Fig. 9) shows that the methylene chloride extraction procedure does not extract the polar UV absorbing constituents that were present in the oily waste water. These hydrophyllic constituents

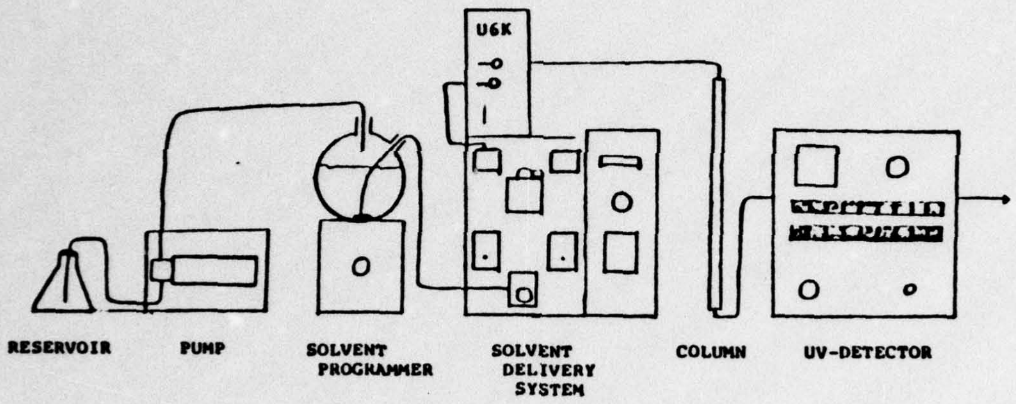
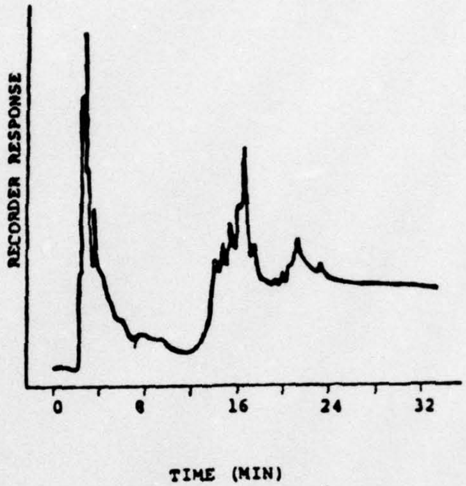


Fig. 8. Liquid Chromatography System (inc. Solvent Programmer)

Oily Waste Water



Waste Water Extract

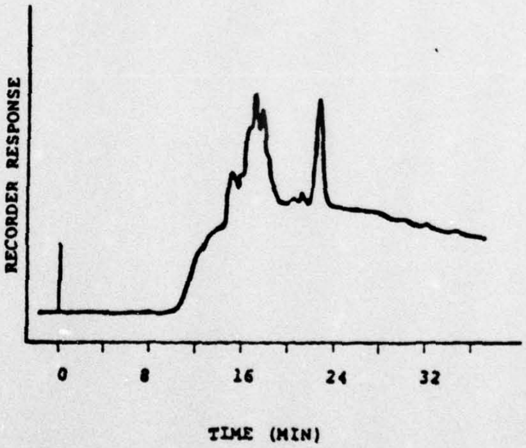


Fig. 9. Liquid Chromatogram (Reversed-phase) of Oily Waste Water

Flow Rate: 1.0 ml/min
Solvent: acetonitrile/water (1:4) + 1.0 ml/min acetonitrile
Column: µ-Bondapak C18 (4mm X 30cm)
Detector: UV (254nm)

are probably dissolved in the aqueous phase rather than being contained in the film of organic material at the waste water surface. It was also found that the non-polar constituents are adequately removed by the extraction procedure.

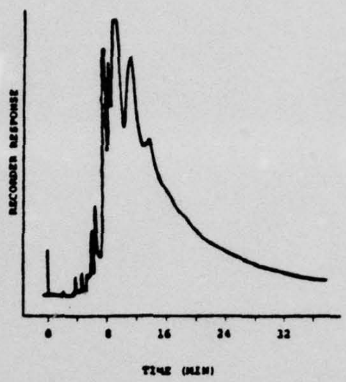
b) Comparison of the Lubrication Oil, Fuel Oil and Waste Water Extract

High pressure liquid chromatographic separations were performed to determine how closely the UV absorbing constituents in the three oil samples compare with respect to their polarities. The analyses were performed in an isocratic elution mode because the elution behavior of the UV absorbing constituents indicated no need for use of a solvent program. The solvent used for elution, acetonitrite/water (1:1), gave incomplete separation of the individual peaks, but 15 + peaks or shoulders could still be distinguished in the individual chromatograms (see Fig. 10). The chromatographic results for each sample will be discussed in separate comparisons of the oil samples with the waste water extract.

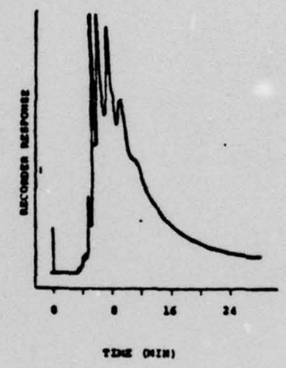
i) Waste Water Extract -- Lubrication Oil Comparison

The UV absorbing substances in the lubrication oil are quite different than those found in the oily waste water extract. As a whole, the substances in the lubrication oil are less polar than those in the waste water extract. Although some constituents in the lubrication oil have polarities similar to those in the extract (i.e. some elution time), these substances constitute only a minor portion of the lubrication oil (see Fig. 10).

Lubrication Oil



Fuel Oil



Waste Water Extract

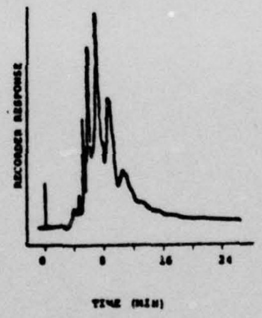


Fig. 10. Liquid Chromatogram (Reversed-phase) of Oil Products

Flow Rate: 1.0 ml/min
Solvent: acetonitrile/water (1:1)
Column: Partisil-ODS (4.6mm X 25cm)
Detector: UV(254nm)

ii) Waste Water Extract -- Fuel Oil Comparison

The polarity of the UV absorbing constituents of the fuel oil is very similar to those in the oily waste water extract; this is in contrast to the lubrication oil constituents as discussed above. A further indication of this similarity is the appearance of the two chromatograms (see Fig. 10) showing that each contain the same set of at least 4 major constituents with numerous other smaller components.

3. Conclusion

It has been found by gel permeation chromatography that the fuel oil and lubrication oil are easily distinguishable from each other by the presence or absence of material with UV chromophores in the respective size fractions and that the waste water also has a non-UV absorbing fraction. This evidence for the difference between the lubrication and fuel oils confirms that the major source of the organic contamination of the oily waste water is from a fuel oil, and that the lubrication oil contamination appears to be of only minor importance.

The results of the reversed-phase chromatography show that the UV-absorbing organic contaminants in the oily waste water are closely similar to components found in fuel oil than to those found in lubrication oil. This is based on the analysis of a class of compounds (probably aromatic hydrocarbons) and is the same as the conclusion reached in previous sections (viz. GLC and GPC) where the entire sample was characterized.

LIQUID CHROMATOGRAPHY - PAH's

A preliminary investigation was performed to determine the possible presence of polynuclear aromatic hydrocarbons (PAH's) in the oily waste water. Published work by Boden (20) indicates that PAH's can be separated on a μ-Bondapak C_{18} column using acetonitrite/water (60:40) as the isocratic elument. Experiments were performed to attempt the separation of phenanthrene and chrysene under the conditions suggested by Boden (20); the only experimental difference was that the detector used in this study monitored the column effluent at 254 nm. For some unknown reason, the separation factor value found (α=1.9) for the standard compounds was significantly poorer than that reported (α=20) in Boden's work (20). Because of this, it was found necessary to decrease the amount of acetonitrile in the solvent; a solvent with composition acetonitrile/water (42:58) was found to separate phenanthrene and chrysene adequately (α=6.9). This is the solvent used in the work subsequently described.

The experiment included the chromatography of the oily waste water and the two standards using the conditions mentioned above. The resulting chromatogram for the waste water extract is shown in Fig. 11 along with the elution time of the two standards. From these results it appears that some of the substances contained in the oily waste water

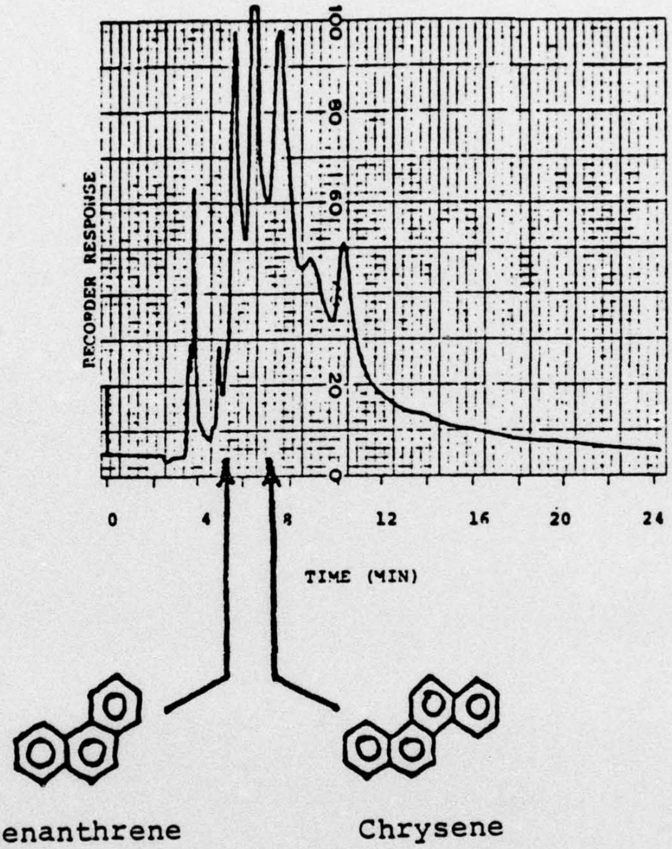


Fig. 11. Liquid Chromatogram(Reversed-phase) of Waste Water Extract Showing Elution Times of Phenanthrene and Chrysene

Flow Rate: 1.0 ml/min
Solvent: acetonitrile/water (42:58)
Column: Partisil-ODS (4.6mm X 25 cm)
Detector: UV(254nm)

elute at the same general time as do typical PAH's, so that serious consideration should be given to the possibility that the oily waste water may contain such compounds. It is a well established fact that some 4 to 6 ring polynuclear aromatic hydrocarbons are chemical carcinogens (21) and if present they could have deleterious effects on the quality of the environment.

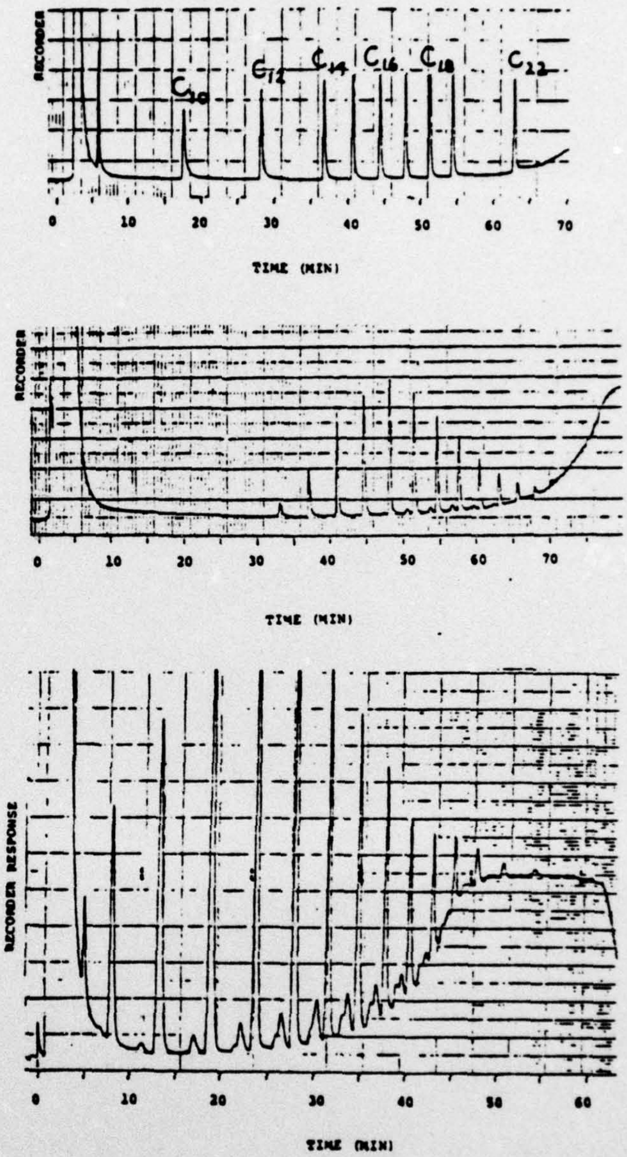
ALKANES

n-Alkanes were qualitatively and semi-quantitatively determined by the use of a technique called urea adduction (22). The theory behind this technique was investigated by Schiessler and Flitter two decades ago (23). They found that urea will crystallize in the presence of a suitable guest molecule into an elongated hexagonal prism with a longitudinal cavity of 5.0Å diameter; suitable guests were found to be linear molecules having a diameter less than 5Å. n-Alkanes, because they are linear molecules with a diameter of approximately 4.5Å, make excellent guest molecules. The urea adduction technique is commonly used to detect the presence of and to quantitate n-alkanes in geochemical analyses (24).

For this work, the urea adduction was used in conjunction with gas-liquid chromatography to identify n-alkane hydrocarbons in the oily waste water and to derive a semi-quantitative estimate of their concentration. The procedure was very similar to that used by Meinschein and Kenny (25). A large excess of a saturated urea in methanol solution was added to the waste water extract; crystallization of the urea adduct was immediate, but the mixture was allowed to stand for two days to ensure that the crystallization went to completion. The adduct crystals were then collected by filtration on a Millipore Filter and washed with small amounts of benzene. The crystals were transferred to a beaker, were decomposed by heating with a small amount of water and the hydrocarbons isolated by extracting the aqueous solution four times with 0.2 ml of hexane. The extract was then diluted to 1.0 ml volume with additional hexane.

n-Alkane standards show the gas chromatogram typical of members of homologous series (see Fig 12 top). Equal amounts of each n-alkane standard were injected, and the measure of quantitation used (area of peak) indicated that the actual response of the Flame Ionization Detector gave values which varied less than 10% of absolute magnitude. The quantitation of the urea adduct was based on the average detector response in terms of amount of the standard injected (in area units per microgram of standard). This was used to calculate the amount of alkane from the peak area on the chromatogram of the urea adduct. Comparison of the chromatogram of the standard n-alkanes with the oily waste water extract chromatograms shows that the large singularpeaks appearing in the chromatogram correspond to the n-alkanes.

The gas-liquid chromatogram of the hexane extract of the decomposed adduct is shown in Fig 12 (middle). The individual alkanes produce distinct and well separated peaks, thus making quantitation possible. A smooth distribution of n-alkanes is found, with no odd-even predominance, peaking at C_{17} and decreasing in amount with higher and lower carbon numbers. Small amounts of other compounds occur, eluting between the major n-alkane peaks. These peaks are shown in greater detail in Fig 12 (bottom). From their similar appearance and relative position between the n-alkane peaks, these



n-Alkane Standard

Urea Adduct

Urea Adduct

Fig. 12. Gas-Liquid Chromatogram of Urea Adduct of Oily Waste Water and n-Alkane Standards

Carrier Gas: Nitrogen (32 ml/min)
Temperature: init.: 60°(7 min) (top & middle)
140°(10 min) (bottom)
prog.: 3°/min
final: 260°(20 min) (bottom)
Column: ¼in X 6ft, 5% OV-1 on 80/100 mesh
Gas Chrom S

peaks may be due to another homologous series of compounds (alkanes ?) present in the oily waste water. Oro, et al (26) have found that iso- and anteiso-alkanes containing a certain number of carbon atoms will elute immediately preceding the elution of the n-alkane with the same number of carbon atoms. Perhaps these smaller peaks are iso-alkanes, but further work (e.g. GC-MS) would be required to identify them.

Quantitation of the results reveals that the oily waste water contains approximately 70 ppm n-alkanes; Table 1 shows the breakdown into the individual alkanes and the quantities of each. Because of the experimental procedure used, viz. multiple extractions, solvent evaporation, etc., the data are reliable only to the most significant digit.

Table 1

Quantities of n-Alkanes in Oily Waste Water

n-Alkane	Concentration (ppm)
C_{12}	3.6
C_{14}	10.7
C_{15}	12.1
C_{16}	10.3
C_{17}	9.1
C_{18}	7.2
C_{19}	5.6
C_{22}	1.5
C_{11}, C_{13}, C_{20}, C_{21}, C_{23}, C_{24} (standards unavailable)	14.0

CONCLUSION

The oily waste water was found to contain at least two different types of contaminants. The major contaminant was an oily residue which was found floating on the surface of the waste water. The second contaminant consisted of particulate materials which were found associated with the oily residue. There is the possibility of a third type of contaminant -- those organic materials dissolved in the aqueous phase of the waste water, but these were not analyzed as a part of this study.

The particulate material was found to be present mainly on the surface of the oil droplets, rather than being contained within the body of the droplet. This material consisted of a wide variety of constituents ranging from what appeared to be protozoan tests, too wholly inorganic materials. The inorganic materials were found to contain iron, calcium, silicon and zinc as the most abundant metallic elements present; in addition, some of the particles were found to have crystal-like faces.

The oily residue was the principal contaminant present in the oily waste water. This oily residue was found to contain a very complex mixture of organic compounds ranging in molecular size from low molecular weight ($\sim$ 1000 daltons) polymeric materials to small organic molecules. The major source of these contaminants was found to be fuel oils rather than the lubrication oils and other sources, also some contribution from these sources seems likely.

The techniques used for the analysis of the oily residue of the waste water produced information that varied widely in quality and quantity. The analytical methods used were:

1. UV-VIS Spectrophotometry - yielded the least information about the oily residue. The spectrum obtained showed a monotonically increasing absorption by the sample with decreasing wavelength of light; no distinct peaks were evident. As a diagnostic tool, UV-VIS spectrophotometry was not useful for the complex sample used in this study.

2. Thin-Layer Chromatography - was found to be an easily used rapid technique with low resolving power for complex mixtures. TLC was found useful because it indicated that the oily residue was a complex mixture of constituents, allowed tentative identification of an antioxidant by specific chemical tests and also indicated that absorption HPLC would not be useful on the crude residue. TLC was found to have limited use for resolving individual constituents in a complex mixture.

3. Gel Permeation Chromatography - was used for the determination of the molecular size range of the oily residue. It was used both for an absolute size calibration of n-alkanes in the oily residue and for a relative size calibration of the oily residue and for a relative size calibration of the oily residue with respect to fuel oil and lubrication oil. The major disadvantage of GPC was its low resolving power for individual constituents in a complex mixture.

4. Gas-Liquid Chromatography - was used for the separation and analysis of the non-polar constituents in the oily residue. GLC was used to demonstrate the presence of over 100 constituents in the oily residue, to show the similarity of the oily residue to a fuel oil and to identify and quantitate a homologous series of alkanes present in the oily residue. GLC was the most useful analytical tool used in this study and further work, especially with a capillary system, should prove very useful for the determination of individual compounds in the oily residue.

5. Reversed-Phase Liquid Chromatography - was used for the analysis of the crude oily waste water and also the extract of the waste water. HPLC was used to show that the exhaustive extraction of the oily waste water was not complete and also to show the possible presence of PAH's in the oily residue. The major disadvantage of HPLC analysis was found to be the lack of sensitive universal detector.

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