# Environmental Assessment of the Alaskan Continental Shelf

## Annual Reports of Principal Investigators for the year ending March 1981

## Volume III: Effects of Contaminants

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# Multivariate Analysis of Petroleum Weathering in the Marine Environment - Sub Arctic

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## 1.0 INTRODUCTION

Oil is a complex mixture of hydrocarbons and heterocyclic molecules which, when introduced into the marine environment, undergoes differential dissolution and evaporation, adsorption onto particulate material , photo-oxidation and biological degradation. Additionally, oil as a bulk material is subject to the combined processes of dispersion into the water column and the formation of water-in-oil emulsions (mousse). The magnitude of these processes and their varying rates are dependent upon the specific chemical materials involved and on such "environmental" factors as turbulence, air and water temperature, particulate type and concentration, oil composition, light intensity, and microbial composition and abundance. The purpose of this program has been to investigate the physical and chemical changes which occur to spilled petroleum in the marine environment as a result of the combined actions of these abiotic and biotic factors. Among the processes being examined and quantified are: evaporation, dissolution, microbial oxidation, photo-chemical oxidation, emulsification (mousse formation), adsorption onto particulate material, and the influence of a commercial dispersant on these processes.

Our investigations have been designed to provide qualitative and quantitative information on the fates of specific compounds during oceanic weathering. Ultimately, the goal of this program is to generate a combined component-specific and pseudo-component (boiling point or distillation "cut") model to simulate and predict spilled petroleum behavior as a result of physical/chemical weathering. These models are being developed to encompass specific compound partitioning as well as overall oil mass balance considerations, and they are being tested with observed chemical changes from laboratory and field experiments. The algorithms which make up the computerized model can then be used in a predictive manner to determine the time-dependent chemical compositions and properties of real or simulated oil spills. When coupled to trajectory models, such a physical-chemical weathering model should allow environmental managers to better estimate the impacts from real and

hypothetical oil spill situations. Furthermore, a thorough understanding of the time-dependent compositions and concentrations of spilled petroleum mixtures (including their marine weathering products) will aid in extrapolating the findings from biological effects experiments to real environmental situations.

While this study was initially designed to be an experimental and modeling effort confined to SAI's La Jolla facilities, it was feasible to expand the program to include field studies in the Alaskan subarctic environment of NOAA's Kasitsna Bay laboratory facilities near Homer. At this facility, experiments designed to simulate and quantify open ocean evaporation, dissolution, and microbial and photochemical oxidation processes have been ongoing. Also, in conjunction with other NOAA contractors (Drs. Griffiths and Morita; RU190), experiments designed to evaluate the long-term chemical fate of fresh and weathered oil in sub-tidal sediments have been conducted.* During the most recent field studies at Kasitsna Bay (summer 1981) experiments to examine the long-term chemical fate of fresh oil and mousse in different intertidal regimes were also begun.

As part of our ongoing research into the mechanisms of marine oil weathering, SAI scientists and engineers have continued to participate in several NOAA and BLM-sponsored reviews including: MARINE OIL POLLUTION: FEDERAL PROGRAM REVIEW, conducted for the Inter-agency Committee on Ocean Pollution Research, Development and Monitoring (COPRDM), held in Boulder, Colorado, September 1980; the St. George Basin Synthesis meetings held in Anchorage, Alaska, April 1981; and the National Academy of Sciences Review and Update on the Fate of Petroleum in the Marine Environment, to be held in November, 1981. Background papers were prepared for each of these sessions and are available.

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*Since the information on long-term fate of sedimented oil is pertinent to the overall goals of this program, the results of our efforts with Griffiths and Morita are included as Appendix C of this report.

Many of the results from our multi variant petroleum weathering program have been discussed in detail in interim and progress reports and, therefore, will be repeated herein only as necessary to provide continuity among the key topics being addressed. This report is intended to be an independent document summarizing the program's activities to date, however, it relies in part on the interested expert having access to the preceding progress reports, which have been provided to NOAA's technical monitor. This "annual" report consists of major sections which deal with the modeling and experimental activities as well as updates on our progress in understanding the separate and net effects that the various weathering mechanisms have on spilled oil composition and component distribution.

## 2.0 TOPICAL SUMMARY OF PROGRAM ACTIVITIES

The following outline presents the major program segments and their activities to date in order to provide an overview of the multivariant analysis approach which has been used to generate physical properties data on oil weathering and to formulate an oil weathering simulation model. As mentioned previously, detailed results from many of these activities have been presented in several progress reports; these are contained, along with more recentaccomplishments, in subsequent discussions herein in varying levels of detail as needed to present the program's achievements to date.

### Oil Weathering Model Development

- Mechanisms for handling laboratory and field derived compound specific data have been developed. Time-series reduced gas chromatographic data on specific observed compound concentrations in oil and water have been compared directly to computer-model predictions.

- All reduced gas chromatographic data from oil, water and SPM samples analyzed in La Jolla and/or NOAA's laboratory facility at Kasitsna Bay, Alaska, are now incorporated into SAI's DEC-10 computer which is being used for the oil weathering model. Observed vs predicted component-specific weathering alterations can be evaluated for a wide variety of field and laboratory "environmental" conditions.

- It has become apparent that two submodels - one which is component-specific and one which "weathers" oil in pseudo-components (distillation cuts) - are required to give adequate mass/volume and viscosity/density predictions in addition to providing component concentration information. Algorithms for both approaches have been developed and are presented in this report.

- Pertinent compound-specific and distillation-cut physical property parameter requirements have been defined (Henry's law constants, diffusivities and mass transfer coefficients), and experiments have been conducted to provide needed data.

- Algorithms have been developed to model the following oil weathering processes:

Compound-specific evaporation and dissolution in laboratory stirred tanks.

Pseudo-compound evaporation from ocean surface using various literature sources for mass transfer coefficients.

Compound-specific evaporation from a semi-infinite slick.

Compound-specific evaporation from a finite slick.

Compound-specific dissolution from a semi-infinite slick.

- Computer codes have been written for all the algorithms which are currently in final form. These are being used to compare experimental with theoretical projections, with refinement continuing as necessary.

Oil Characterization

- Liquid-solid column chromatography (L/C) fractionation, capillary gas chromatography (GC), capillary gas chromatography/mass spectrometry (GC/MS), synchronous-scanning UV-fluorescence, distillation cut, viscosity and trace element data were obtained on four selected crude oils (Murban, Cook Inlet, Prudhoe Bay, and Wilmington Crude).
- Prudhoe Bay crude was selected for further analysis and oil weathering studies.

Weathering Processes Investigated Using Prudhoe Bay Crude Oil

- Experiments have been undertaken to obtain laboratory and field rate data on the following oil weathering processes.

  Compound-specific evaporation/dissolution as a function of temperature and the presence or absence of a commercial dispersing agent (Corexit 9527).

  Microbial degradation as a function of nutrient concentrations, the presence or absence of oil, microbial population dynamics, and the source of water (La Jolla vs. Kasitsna Bay) for continuous flow indoor and outdoor aquaria.

  Water-in-oil emulsion (mousse) formation as measured by emulsion stability, kinematic viscosity and density in mousse generated in an ambient-environment outdoor wave tank constructed at Kasitsna Bay.

- Static equilibrium experiments have been undertaken to determine:

  Liquid-liquid partition coefficients of individual components between oil and seawater as a function of temperature (data required for dissolution algorithms of computer model ).

  Partition coefficients of individual oil components between seawater and five representative suspended particulate material types isolated from selected Cook Inlet sediments (required for oil/SPM interaction algorithms).

  Effect of oil on selected SPM sinking rates as a function of particle type and seawater/oil temperature.

  Identification of microbial oxidation products by GC/MS analyses (with and without prior derivatization). Rate data on oxidation product formation are being obtained from flow-through rate experiments referred to above.

- Limited photochemical oxidation experiments have been conducted using simulated irradiation of oil/seawater and oil/seawater/dispersant mixtures in quartz tubes; numerious oxidation products have been tentatively identified by GC/MS analysis.*

Kasitsna Bay Laboratory

- To obtain more valid oil weathering process data representing the subarctic marine environment, a certain amount of field experimentation is necessary to evaluate the effects of specific parameters such as microbial population densities, variable air/water temperature gradients, ambient nutrient and SPM levels, solar radiation input, rainfall, snowfall and other similar factors which cannot be properly simulated in laboratory environments. Recognizing this, after the laboratory and modeling activities had begun in La Jolla, NOAA and SAI investigators designed a major project expansion which would utilize NOAA'S Kasitsna Bay, Alaska, facility. A geochemistry laboratory was established there by SAI chemists and indoor and outdoor aquaria and test tank facilities were constructed.

- All necessary facilities improvements were completed in August 1980 and oil weathering studies in the outdoor and indoor aquaria were initiated in September 1980. Several outdoor tanks were allowed to undergo long-term subarctic ambient weathering

*Due to limitations in resources, further investigation of this area has been postponed to subsequent periods of the program.

from October 1980 through April 1981. Periodic samples from the outdoor flow-through systems were collected; and the analyses of these and the other samples collected during the Spring 1981 (April ) field program are presented. An additional set of outdoor experiments evaluating evaporation/dissolution and microbial processes were initiated to evaluate seasonal (Spring/Summer) perturbations to oil weathering behavior, and results from these studies are also considered.

- The Kasitsna Bay facility was re-occupied in August 1981 and during the Summer/Fall 1981 program, further additions were undertaken and completed, providing a 2,500 liter outdoor wave tank to allow more realistic simulation of subarctic, open ocean oil weathering in the presence of 6- to 10-inch standing- and breaking-wave turbulence. Additional details on the wave tank experiments, extensive summer/fall microbial degradation experiments, oil/suspended particulate material interaction studies and *in situ* chemical weathering studies of stranded oil in selected Intertidal regimes are presented herein.

## 3.0 OIL CHARACTERIZATION

At the onset of the program, four crude oils (representative of a wide variety of oil types) including two crudes produced in Alaska, were selected for detailed chemical analyses. The ultimate purpose of this investigation was to select one of the four crudes for additional detailed weathering characterizations. Crude oils are a naturally occurring complex mixture of organic and inorganic compounds, and the properties of a given crude are dependent upon the original depositional environment, the hydrocarbon sources and the degree of post-depositional maturation and migration. In general, most crudes can be classified into three categories:

- paraffin-based, exemplified by the continental crudes of the mid-United States,
- asphalt-based such as crudes produced in California and the Gulf of Mexico coast of the United States,
- mixed-base crudes such as those from the Middle East and Alaska.

Since the objective of this program is to arrive at a computer model which is applicable to a wide variety of crude petroleums it might be advantageous to select at least one crude from each of the three classes (i.e., paraffin, asphaltic and mixed base). However, the paraffin-based crudes of the first category are not as likely to be involved in contamination of the marine environment, and these crudes have relatively low levels of aromatic compounds, which include the most toxic constituents of crude oil. For these reasons paraffin-based crudes were not included in this study.

Table 3-1 presents gross characterization parameters of the four selected crude oils examined in this study. These include: 1) a relatively high API gravity (lower specific gravity) Murban crude which is designated as an intermediate type or mixed-base crude - this particular crude oil has less sulfur and asphaltic material than most other Middle-East crudes (Evaluation of the World's Important Crudes, 1973); 2) a slightly lower API gravity crude

TABLE 3-1. GROSS CHARACTERIZATIONS OF FOUR SELECTED WHOLE CRUDE OILS.

| Crude Oil | API* Gravity | Specific Gravity g/ml | Viscosity (100°F)* Kinematic c ST | Viscosity (100°F)* Saybolt Sus | Pour Pt** "F | % Asphalt*** | Ni ppm | V ppm | S % | N **** % |
|---|---|---|---|---|---|---|---|---|---|---|
| Murban, Aba Dhabi | 40.5* | ().829 | 2.8 | 35.9 | -20 | 7 | 3.0 | 9.9 | 0.96 | 0.10 |
| Cook Inlet, Alaska | 35.4 | 0.848 | 17 | 85 | -15 | 12 | 1.3 | 0.47 | 0.09 | 0.11 |
| Prudhoe Bay, Alaska | 27.0 | 0.893 | 19 | 84 | -lo | 23 | 13.5 | 28.3 | 0.98 | 0.27 |
| Wilmington, Calif. | 19,4 | 0.938 | 100 | 470 | <5* | 24 | 100 | 80.6 | 1.8 | 9.83 |

Sources:

* Coleman, et al. 1978

** Evaluation of Worlds Important Crudes, 1973

*** Calculated from Conradson carbon value, Coleman et al., 1978

**** Ni, V, S, and N: this study

from Cook Inlet, Alaska, which is representative of oils produced in the sub-arctic environment and which by nature of its production and transport might be expected to be released at sea; 3) a lower API gravity Prudhoe Bay crude oil which would have a high probability of release in arctic regimes during production and in sub-arctic environments during transport and storage; and 4) a low API gravity crude from Wilmington, CA. The data in Table 3-1 illustrate that as the API gravity decreases (density increases) the viscosities of the whole crudes generally increase and the pour points are observed to rise. Percent asphalt content is also observed to increase in going from the higher to lower API gravity crudes selected. Nickel, vanadium, sulfur and nitrogen contents are more variable among the crudes (data generated as part of this study); however, general increases in trace element concentrations are also observed in the trend from higher to lower API gravities. These considerations are important in that asphalts and the presence of trace elements such as nickel, vanadium and sulfur have been implicated in stabilization of water-in-oil emulsions (PAYNE, 1981) and as such, their presence or absence might also be a factor in selecting one representative crude for additional oil weathering studies.

In addition to the whole-crude physical property characterizations and trace element data presented in Table 3-1, each of these four oils was further characterized by separation into aliphatic, aromatic and polar fractions by liquid-solid (silica gel) column chromatography (see Methods, Appendix B), and each fraction was then examined by fused silica capillary column gas chromatography (flame ionization detector) and capillary column gas chromatography/mass spectrometry (GC/MS). Figures 3-1 through 3-4 present the capillary column gas chromatograms obtained on the fractionated Murban, Cook Inlet, Prudhoe Bay and Wilmington Crude Oils, respectively As the figures illustrate, the first three crudes are characterized by a regularly repeating series of n-alkanes and branched and cyclic hydrocarbons in the aliphatic fraction, whereas the Wilmington crude is characterized only by a large Unresolved Complex Mixture (UCM). Likewise, the aromatic fractions from Murban, Cook Inlet, and Prudhoe Bay crudes are very similar (Figures 3-1B

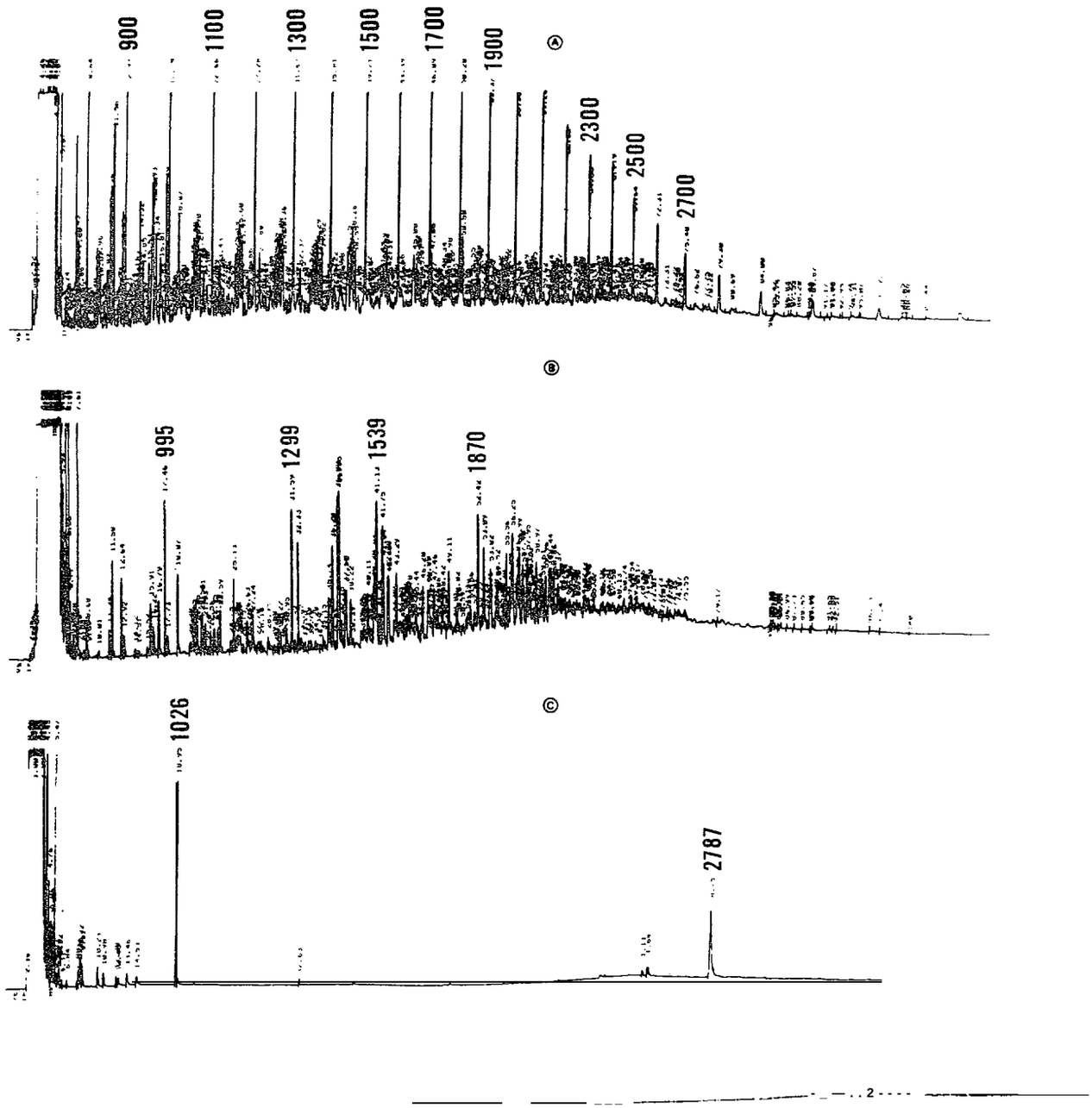



FIGURE 3-1. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON L/C FRACTIONATED MURBAN CRUDE OIL: (A) ALIPHATIC FRACTION (F1); (B) AROMATIC FRACTION (F2); (C) POLAR FRACTION (F3). (KOVAT RETENTION INDICES ARE SHOWN ABOVE SELECTED PEAKS).

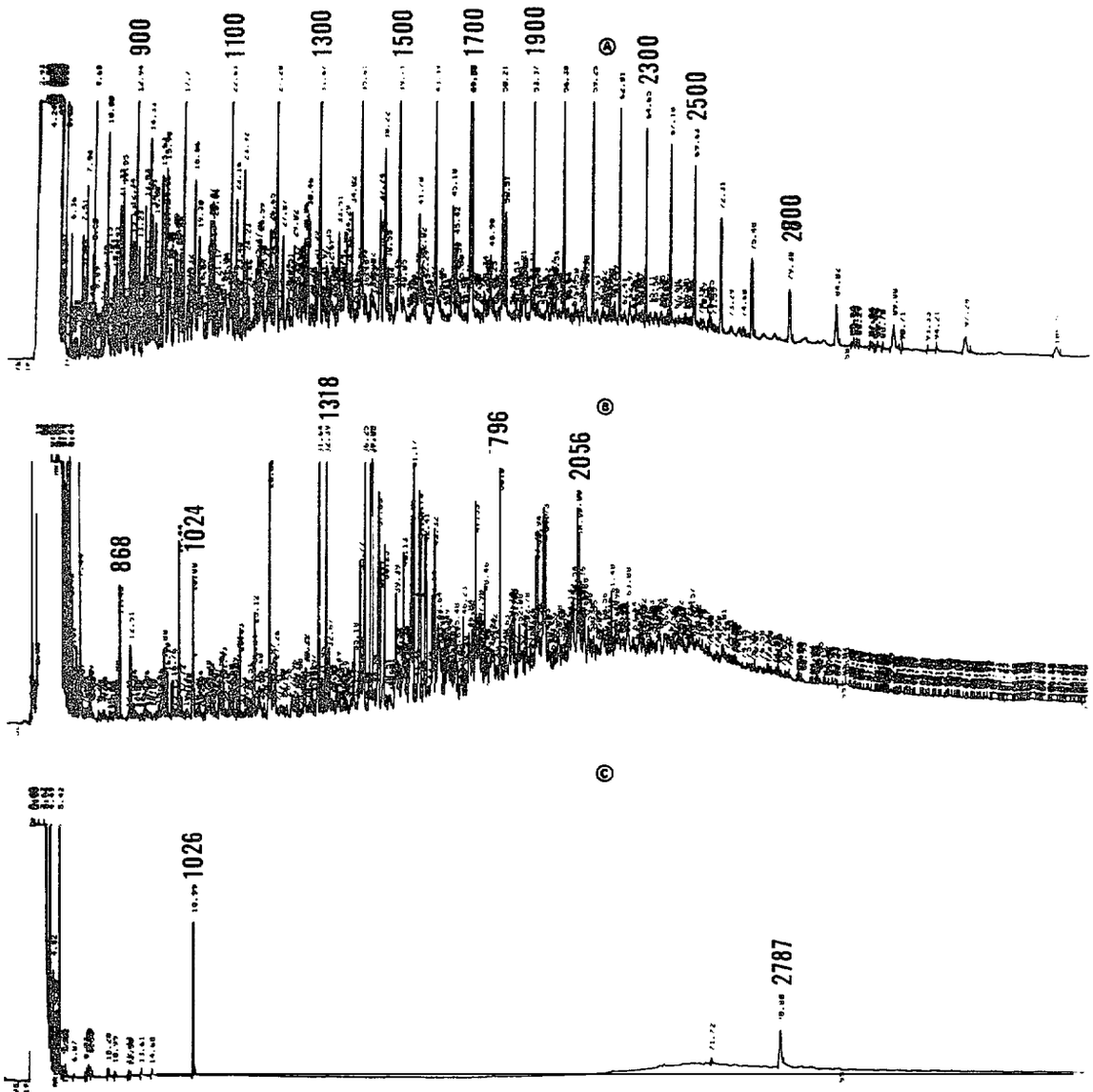



FIGURE 3-2. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON L/C FRACTIONATED COOK INLET CRUDE OIL: (A) ALIPHATIC FRACTION (F1); (B) AROMATIC FRACTION (F2); (C) POLAR FRACTION (F3). (KOVAT RETENTION INDICES ARE SHOWN ABOVE SELECTED PEAKS).

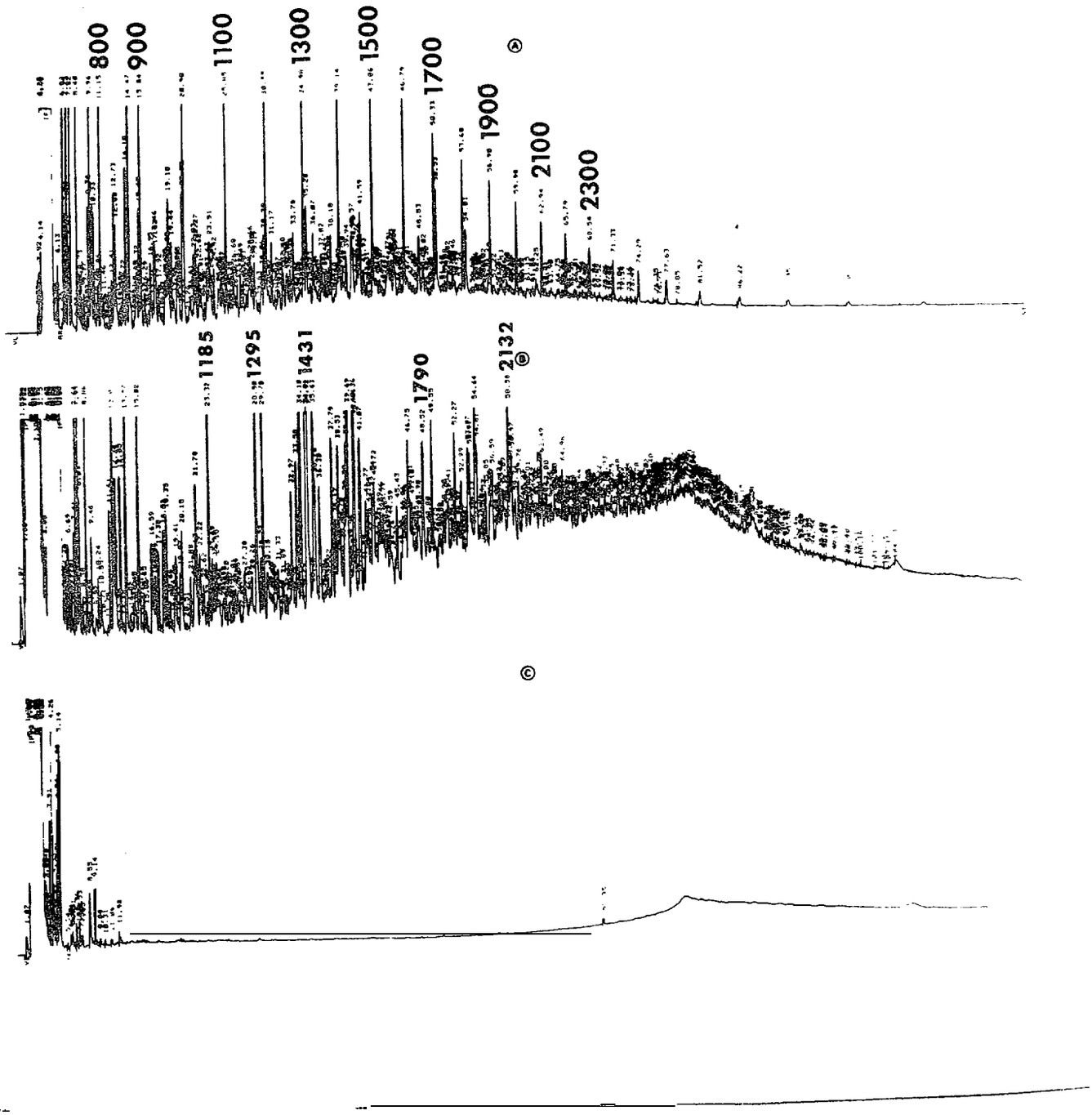



FIGURE 3-3. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON L/C FRACTIONATED PRUDHOE BAY CRUDE OIL: (A) ALIPHATIC FRACTION (F1); (B) AROMATIC FRACTION (F2); (C) POLAR FRACTION (F3). (KOVAT RETENTION INDICES ARE SHOWN ABOVE SELECTED PEAKS).

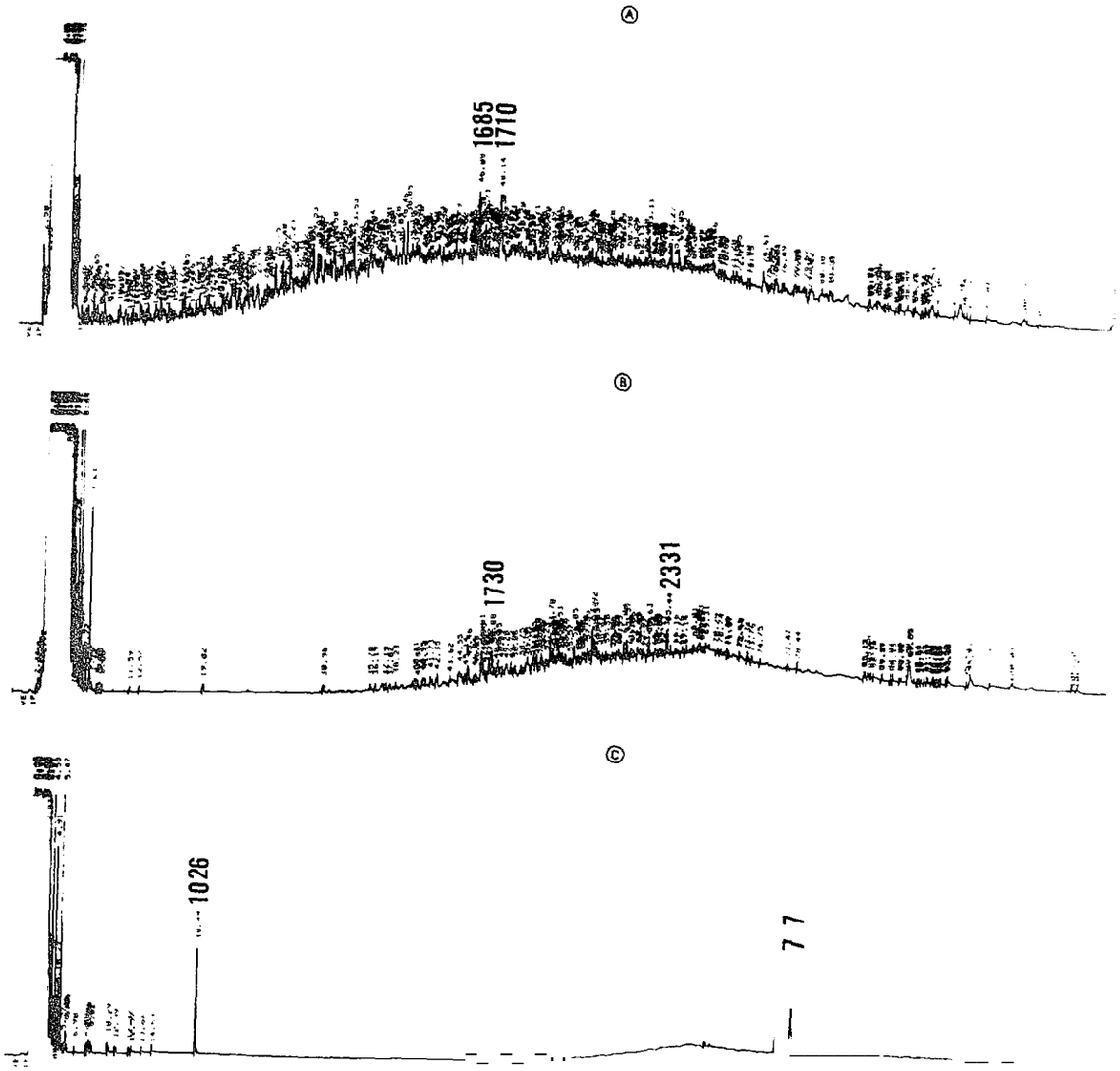



FIGURE 3-4. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON L/C FRACTIONATED WILMINGTON CRUDE OIL: (A} ALIPHATIC FRACTION (F1); (B) AROMATIC FRACTION (F2); (C) POLAR FRACTION (F3). (KOVAT RETENTION INDICES ARE SHOWN ABOVE SELECTED PEAKS).

through 3-3B). The Wilmington crude oil aromatic distribution, however, is skewed to the higher molecular weight compounds. Polar components in the third fraction are observed to be limited in all four of these oils.

Gravimetric data obtained on the aliphatic and aromatic fractions and computer reduced compound-specific concentrations (organized by Kovat retention indices, Kovat 1958) are presented in Tables 3-2 and 3-3 for Murban crude; Tables 3-4 and 3-5 for Cook Inlet crude; Tables 3-6 and 3-7 for Prudhoe Bay crude and Tables 3-8 and 3-9 for Wilmington crude. Compound concentrations for the limited number of components present in the polar (F3) fractions from each oil are shown in Table 3-10. These data were generated on SAI's DEC-10 computer using our compound-specific data reduction program, and such data provide the basis for additional compound-specific weathering phenomena as will be discussed in detail in the next section "Oil Weathering Processes".

Figure 3-5 presents the reconstructed ion GC/MS chromatogram obtained on the aromatic fraction from Prudhoe Bay crude oil, and the individual aromatic components tentatively identified in this fraction are numbered on the chromatogram and listed in Table 3-11. Similar GC/MS data were obtained on the other crudes, however, comparative differences among the crudes can be better illustrated by graphic output such as that shown in Figures 3-6 through 3-8, rather than by tabulated compound identifications and concentrations.

Figure 3-6 presents the individual n-alkane concentrations for Murban crude, Cook Inlet crude and Prudhoe Bay crude, with the inset showing the relative concentrations of isoprenoid compounds in each of these oils. In that the Wilmington crude was not represented by an evenly repeating series of n-alkanes, aliphatic concentrations for that crude are not presented in Figure 3-6. The Cook Inlet crude and Prudhoe Bay crude show very similar trends. whereas the Murban crude is clearly characterized by relatively higher concentrations of the lower molecular weight hydrocarbons.

TABLE 3-2. MURBAN CRUDE OIL CONCENTRATIONS FOR ALIPHATIC FRACTION.

FRACTION 1: HP-RUN-DATE: 10/2 2/1981 HP-RUN-NO: )? HP-BOT-NO: 13

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 3..?100 | 0 | 0 | 0 | 1.440 | 1026.4 |
| 2.00 | 5.3900 | 0 | 0 | 0 | 1.440 | 195.91 |
| 3.00 | 7.4300 | 0 | 0 | 0 | 1.440 | 1079.7 |
| 4.00 | 7.6600 | 0 | 0 | 0 | 1.440 | 482.57 |
| 5.00 | 7.8600 | 0 | 0 | 0 | 1.440 | 279.37 |
| 6.00 | 8.6400 | 603 | 0 | 0 | 1.440 | 4477.0 |
| 7.00 | 9.7400 | 826 | 0 | 0 | 1.440 | 499.65 |
| .4.00 | 9.9600 | 831 | 0 | 0 | 1.440 | 504.46 |
| 9.00 | 10.920 | 9s3 | 0 | 0 | 1.440 | 488.62 |
| 10.0 | 11.560 | 868 | 0 | 0 | 1.440 | 3614.0 |
| 11.0 | 12.620 | 893 | 0 | 0 | 1.440 | 1145.9 |
| 1.2.0 | 12.930 | 900 | 0 | 0 | 1.440 | 6541.1 |
| 13.0 | 13.700 | 917 | 0 | 0 | 1.440 | 195.56 |
| 14.0 | 14.110 | 924 | 0 | 0 | 1.440 | 552.50 |
| 15.0 | 14.330 | 929 | 0 | 0 | 1.440 | 587.88 |
| 16.0 | 14.520 | 933 | 0 | 0 | 1.440 | 1266.2 |
| 17.0 | 14.850 | 940 | 0 | 0 | 1.440 | 898.38 |
| 18.0 | 15.530 | 953 | 0 | 0 | 1.440 | 971.73 |
| 19.0 | 16.340 | 970 | 0 | 0 | 1.440 | 1566.b |
| 20.0 | 16.810 | 980 | 0 | 0 | 1.440 | 717.41 |
| 21.0 | 17.030 | 984 | 0 | 0 | 1.440 | .25s.17 |
| 22.0 | 17.490 | 994 | 0 | 0 | 1.440 | 1678.0 |
| 23.0 | 17.790 | 1000 | 0 | 0 | 1.440 | 6646.0 |
| 24.0 | 18.870 | 1022 | 0 | 0 | 1.440 | 884.00 |
| 25.0 | 20.340 | 1052 | 0 | 0 | 1.440 | 780.98 |
| 26.0 | 20.580 | 10s7 | 0 | 0 | 1.440 | 744.32 |
| 27.0 | 20.720 | 1060 | 0 | 0 | 1.040 | 353.39 |
| 28.0 | 20.900 | 1064 | 0 | 0 | 1.440 | 8.30.30 |
| 29.0 | 22.000 | 1086 | 0 | 0 | 1.440 | 760.69 |
| 30.0 | 22.660 | 1100 | 0 | 0 | 1.440 | 7770. b |
| 31.0 | 23.430 | 1117 | 0 | 0 | 1.440 | 618.52 |
| 3.2.0 | 23.650 | 11.21 | 0 | 0 | 1.440 | 314.78 |
| 33.0 | 23.870 | 1126 | 0 | 0 | 1.440 | 436.31 |
| 34.0 | 24.250 | 1134 | 0 | 0 | 1.440 | 296.63 |
| 35.0 | 24.440 | 1139 | 0 | 0 | 1.440 | 316.'27 |
| 36.0 | 24.620 | 1147 | 0 | 0 | 1.440 | 483.82 |
| 37,0 | 25.190 | 1155 | 0 | 0 | 1.440 | 1258.0 |
| 3.9.0 | 25.400 | 1159 | 0 | 0 | 1.440 | .4.?3.50 |
| 39.0 | 2s.600 | 1164 | 0 | 0 | 1.440 | 1013.7 |
| 40.0 | 25.910 | 1170 | 0 | 0 | 1.440 | 719.59 |
| 41.0 | 26.200 | 1177 | 0 | 0 | 1.440 | 20.?. s0 |
| 42.0 | 26.660 | 1107 | 0 | 0 | 1.440 | 530.62 |
| 43.0 | 26.870 | 1191 | 0 | 0 | 1.440 | 198.05 |
| 44.0 | 27.280 | .200 | 0 | 0 | 1.430 | 7788.1 |
| 49.0 | 27.680 | 1213 | 0 | 0 | 1.440 | 5.39.99 |
| 46.0 | 26. 510 | 1228 | 0 | 0 | 1.440 | 208.44 |
| 47.0 | 28.040 | 1240 | 0 | 0 | 1.440 | 222.20 |
| 48.0 | 29.670 | 1258 | 0 | 0 | 1.440 | 449.88 |
| 49.0 | 30.080 | 1263 | 0 | 0 | 1.440 | 877.04 |
| 50.0. | 30..360 | 1270 | .0. | 0 | 1.440 | 450.92 |
| 51.0 | 30.790 | 1279 | 0 | 0 | 1.450 | 286.46 |
| 52.0 | 31.230 | 1289 | 0 | 0 | 1.450 | 233.33 |
| 53.0 | 31.670 | 1300 | 0 | 0. | 1.450 | 8169.3 |
| 54.0 | 32.370 | 1316 | 0 | 0 | 1.440 | 539.79 |
| 55.0 | 32.650 | 1323 | 0 | 0 | 1.430 | 52.7.82 |
| 56.0 | 33.040 | 1333 | 0 | 0 | 1.420 | 276.92 |
| 57.0 | 33.520 | 1344 | 0 | 0 | 1.420 | 490.39 |
| 58.0 | 33.760 | 1350 | 0 | 0 | 1.410 | .?32.95 |
| 59.0 | 34.080 | 1358 | 0 | 0 | 1.410 | 460.04 |
| 60.0 | 34.290 | 1363 | 0 | 0 | 1:400 | 125.66 |
| 61.0 | 34.580 | 1370 | 0 | 0 | 1.400 | 734.22 |
| 62.0 | 34.820 | 1376 | 0 | 0 | 1.s90 | 695.01 |
| 63.0 | 35.810 | 1400 | 0 | 0 | 1.380 | 6548.0 |
| 64.0 | 36.220 | 1410 | 0 | 0 | 1.390 | 451.27 |
| 65.0 | 37.750 | 1449 | 0 | 0 | 1.440 | 665.58 |
| 66.0 | 38.0.30 | 1458 | 0 | 0 | 1.450 | 310.20 |
| 67.0 | 38.260 | 1462 | 0 | 0 | 1.460 | 807.97 |
| 68.0 | 38.550 | 1470 | 0 | 0 | 1.470 | 747.11 |
| 69.0 | 39.710 | 1500 | 0 | 0 | 1.510 | 6913.3 |
| 70.0 | 41.490 | 1548 | 0 | 0 | 1.500 | 637.40 |
| 71.0 | 41.690 | 1553 | 0 | 0 | 1.500 | ●:a.z9 |
| 72.0 | 42.040 | 1563 | 0 | 0 | 1.500 | 707..26 |
| 73.0 | Q.?.310 | 1570 | 0 | 0 | 1 .500 | 361.98 |
| 74.0 | 4s.080 | 1591 | 0 | 0 | 1.s00 | 194.35 |
| 75.0 | 43.390 | 1600 | 0 | 0 | 1.500 | 5925.5 |
| 76.0 | 45.080 | 1648 | 0 | 0 | 1.550 | 1821.5 |
| 77. k | 45.420 | 1658 | 0 | 0 | 1.560 | 489.0a |
| 78.0 | 45.600 | 1663 | 0 | 0 | 1 .s60 | 291.18 |
| 79.0 | 45.870 | 1670 | 0 | 0 | 1.570 | 376.65 |
| .90.0 | 46.690 | 1700 | 0 | 0 | 1.600 | 5527.8 |
| al. o | 47.060 | 1710 | 0 | 0 | 1.500 | 497.15 |
| 82.0 | 48.340 | 1743 | 0 | 0 | 1.9*0 | 757.28 |
| 83.0 | 48.980 | 1763 | b | 0 | 1.540 | 315.89 |
| 84.0 | 49.250 | 1771 | 0 | 0 | 1.s30 | 204.46 |
| 85.0 | 50.200 | 1800 | 0 | 0 | 1.510 | 4193.8 |
| 86.0 | 50.500 | 1815 | 0 | 0 | 1.440 | 632.91 |
| 87.0 | 51.590 | 1842 | 0 | 0 | 1.7.30 | 651.36 |
| 88.0 | 52.020 | 1897 | 0 | 0 | 1.880 | .294.55 |
| woo | 52.200 | 1863 | 0 | 0 | '1.920 | 296.29 |
| 90.0 | 52.460 | 1871 | 0 | 0 | 1.970 | 416.88 |
| 91.0 | 53.370 | 1900 | 0 | 0 | 2.160 | 5078.5 |
| 92.0 | 56.3s0 | 2000 | 0 | 0 | 1.560 | 3791.2 |
| 93.0 | 57.490 | 2036 | 0 | 0 | f.580 | 310.88 |
| 94.0 | 9a..450 | 2071 | 0 | 0 | 1.590 | .219.71 |
| 95.0 | 59..?60 | 2100 | 0 | 0 | 1.610 | 3161.,? |
| 96.0 | 60.340 | 2139 | 0 | 0 | 1.620 | 210.90 |
| 97.0 | 61.270 | 2172 | 0 | 0 | 1.640 | 3.?1.96 |
| 98.0 | 62.020 | 2200 | 0 | 0 | 1.650 | 2950.3 |
| 99.0 | 63.000 | 2237 | 0 | 0 | 1.660 | 623.33 |
| 100. | 64.650 | 2300 | 0 | 0 | 1.740 | 2698.1 |
| 101. | 65.590 | 2337 | 0 | 0 | 1.700 | 211.89 |

FRACTION 1: HP-RUN-DATE: 10/22/1981 HP-RUN-NO: 37 HP-BOT-NO: 13

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 10.2. | 67,190 | 2400 | 0 | 0 | 1.630 | 2226.7 |
| 103. | 68.040 | 2434 | 0 | 0 | 1.650 | 216.63 |
| 104. | 69.640 | 2500 | 0 | 0 | 1.670 | 1925.0 |
| 105. | 70.500 | 2532 | 0 | 0 | 1.680 | 213.54 |
| 106. | 72.310 | 2600 | 0 | 0 | 1.720 | 1895.1 |
| 107. | 75..200. | 2700 | 0 | 0 | 2.56 0 | 2205.8 |
| 108. | 76.6,50 | 2729 | 0 | 0 | 2.320 | 296.82 |
| 109. | 79.300 | 2800 | 0 | 0 | 1.770 | 1302.8 |
| 110. | 84.000 | 2900 | 0 | 0 | 1.850 | 1066.3 |
| 111. | 85.740 | 2940 | 0 | 0 | 1.870 | 258.29 |
| 112. | 89.870 | 3000 | 0 | 0 | 1.920 | 866.60 |
| 113. | ● 7.avg. | 3100 | 0 | 0 | 2.630 | 1028.1 |
| 114. | 106.51 | 3200 | 0 | 0 | .2.320 | 662.13 |
| 115. | 106.51 | 3200 | 13 | 0 | 2.s,?0 | .00000 |

TOTAL RESOLVED HYDROCARBON = 154001.4
TOTAL UNRESOLVED HYDROCARBON = 1S5S08.5
RESPONSE FACTOR AV. FOR C - 1000 TO 3000 FOR UCM = 1.714239
RAT IO: RESOLVED/UNRESOLVED = 0.988402

SUM OF THE N-ALKANES = 75961.44
SUM OF THE EVEN N-ALKANES = 38150.2
SUM OF THE ODD N-ALKANES = 37811.24

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 1.437679E-2
RATIO: ODD/EVEN N-ALKANES = 0.991115
RATIO: PRISTANE/C-17 = 8.993653E-2
RATIO: PHYTANE/C-18 = 0.150916
RATIO: PRISTANE/PHYTANE = 0.785492
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = 0.973365

Weight Distribution of Murban Crude by Fraction

| Fraction | Weight (mg/g) |
|---|---|
| 1 | 369 |
| 2 | 123 |
| 3 | 53.3 |

TABLE 3-3. MURBAN CRUDE OIL CONCENTRATIONS FOR AROMATIC FRACTION.

FRACTION:2 HP-RUN-DATE:10/22/1981 HP-RUN-NO: 38 HP-BOT-NO: 15

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 5.0700 | 0 | 0 | 0 | 1.440 | 22366. |
| 2.00 | 5.1900 | 0 | 0 | 0 | 1.440 | 7530. |
| 3.00 | 5.2900 | 0 | 0 | 0 | 1.440 | 21833. |
| 4.00 | 5.3400 | 0 | 0 | 0 | 1.440 | 11195. |
| 5.00 | 5.4600 | 0 | 0 | 0 | 1.440 | 15563 |
| 6.00 | 5.5500 | 0 | 0 | 0 | 1.440 | 18429. |
| 6.50 | 5.6200 | 700 | 0 | 0 | .0000 | .00000 |
| 7.00 | 5.8[illegible]00 | 700 | 0 | 0 | 1.440 | 1816. |
| 8.00 | 5.9300 | 721 | 0 | 0 | 1.440 | 106.15 |
| 9.00 | 6.3600 | 726 | 0 | 0 | 1.440 | 870.19 |
| 10.0 | 6.5600 | 735 | 0 | 0 | 1.440 | 61.969 |
| 11.0 | 6.6200 | 735 | 0 | 0 | 1.440 | 332.76 |
| 12.0 | 6.7700 | 7a0 | 0 | 0 | 1.440 | 43.073 |
| 12.5 | 8.4900 | 800 | 0 | 0 | .0000 | .00000 |
| 13.0 | 7.6100 | t e e | 0 | 0 | 1.440 | 282.57 |
| 14.0 | 11.240 | 863 | 0 | 0 | 1.440 | 59.143 |
| 15.0 | 13.300 | 871 | 0 | 0 | 1.440 | 199.92 |
| 14.0 | 12.640 | 895 | 0 | 0 | 1.440 | 163.78 |
| 16.5 | 12.840 | 900 | 0 | 0 | .0000 | .00000 |
| 17.0 | 12.920 | 902 | 0 | 0 | 1.440 | 43.927 |
| 18.0 | 15.910 | 963 | 0 | 0 | 1.440 | 158.62 |
| 19.0 | 16.220 | 969 | 0 | 0 | 1.440 | 64.858 |
| 20.0 | 16.740 | 981 | 0 | 0 | 1.440 | 126.05 |
| 21.0 | 17.460 | 995 | 0 | 0 | 1.440 | 352.77 |
| 21.5 | 17.710 | 1000 | 0 | 0 | .0000 | .00000 |
| 22.0 | 17.730 | 1000 | 0 | 0 | 1.440 | 44.710 |
| 23.0 | 18.870 | 1026 | 0 | 0 | 1.460 | 221.95 |
| 24.0 | 20.290 | 1053 | 0 | 0 | 1.440 | 41.222 |
| 25.0 | 23.050 | 1068 | 0 | 0 | 1.440 | 57.632 |
| 26.0 | 21.930 | 1086 | 0 | 0 | 1.440 | 94.191 |
| 27.0 | 22.560 | 1099 | 0 | 0 | 1.440 | 65.244 |
| 27.5 | 22.600 | 1100 | 0 | 0 | .0000 | .00000 |
| 28.0 | 22.950 | 1108 | 0 | 0 | 1.440 | 76.890 |
| 29.0 | 23.390 | 1117 | 0 | 0 | 1.440 | 67.528 |
| 30.0 | 23.590 | 1121 | 0 | 0 | 1.440 | 103.48 |
| 31.0 | 26.750 | 1146 | 0 | 0 | 1.440 | 55.852 |
| 32.0 | 3s.1s0 | 1155 | 0 | 0 | 1.440 | 234.02 |
| 33.0 | 26.630 | 1187 | 0 | 0 | 1.440 | 67.137 |
| 34.0 | 27.240 | 1200 | 0 | 0 | 1.430 | 122.79 |
| 35.0 | 28.950 | 1239 | 0 | 0 | 1.440 | 87.257 |
| 36.0 | 30.0s0 | 1280 | 0 | 0 | 1.450 | 77.553 |
| 37.0 | 31.590 | 1249 | 0 | 0 | 1.450 | 830.37 |
| 38.0 | 31.620 | 1300 | 0 | 0 | 1.450 | .00000 |
| 39.0 | 32.330 | 1317 | 0 | 0 | 1.440 | 290.31 |
| 40.0 | 32.670 | 1325 | 0 | 0 | 1.430 | 37.539 |
| 41.0 | 35.760 | 1399 | 0 | 0 | 1.380 | 198.27 |
| 42.0 | 35.760 | 1400 | 0 | 0 | 1.380 | .00000 |
| 43.0 | 36.200 | 1411 | 0 | 0 | 1.390 | 338.86 |
| 44.0 | 36.820 | 1427 | 0 | 0 | 1.410 | 282.00 |
| 45.0 | 36.950 | 1430 | 0 | 0 | 1.420 | 206.19 |
| 46.0 | 37.150 | 1435 | 0 | 0 | 1.420 | 46.474 |
| 47.0 | 37.600 | 1447 | 0 | 0 | 1.440 | 120.51 |
| 48.0 | 37.350 | 1451 | 0 | 0 | 1.440 | 85.203 |
| 49.0 | 38.220 | 1463 | 0 | 0 | 1.460 | 117.97 |
| 50.0 | 39.660 | 1500 | 0 | 0 | 1.510 | .00000 |
| 51.0 | 40.110 | 1512 | 0 | 0 | 1.510 | 143.78 |
| 52.0 | 40.790 | 1530 | 0 | 0 | 1.510 | 119.26 |
| 53.0 | 40.940 | 1534 | 0 | 0 | 1.510 | 126.10 |
| 54.0 | 41.130 | 1539 | 0 | 0 | 1.510 | 320.19 |
| 55.0 | 41.440 | 1548 | 0 | 0 | 1.500 | 83.108 |
| 56.0 | 41.750 | 1556 | 0 | 0 | 1.500 | 136.32 |
| 57.0 | 42.380 | 1573 | 0 | 0 | 1.500 | 60.466 |
| 58.0 | 43.020 | 1590 | 0 | 0 | 1.500 | 68.804 |
| 59.0 | 43.290 | 1598 | 0 | 0 | 1.500 | 161.38 |
| 60.0 | 43.360 | 1600 | 0 | 0 | 1.500 | .00000 |
| 61.0 | 43.650 | 1608 | 0 | 0 | 1.510 | 71.931 |
| 62.0 | 44.270 | 1626 | 0 | 0 | 1.530 | 69.228 |
| 63.0 | 44.450 | 1631 | 0 | 0 | 1.530 | 41.585 |
| 64.0 | 45.440 | 1659 | 0 | 0 | 1.560 | 84.789 |
| 65.0 | 46.200 | 1681 | 0 | 0 | 1.580 | 132.30 |
| 66.0 | 46.800 | 1698 | 0 | 0 | 1.600 | 105.74 |
| 67.0 | 46.860 | 1700 | 0 | 0 | 1.600 | .00000 |
| 68.0 | 47.080 | 1710 | 0 | 0 | 1.500 | .00000 |
| 69.0 | 47.460 | 1718 | 0 | 0 | 1.580 | 196.08 |
| 70.0 | 04.420 | 1746 | 0 | 0 | 1.560 | 97.316 |
| 71.0 | 49.110 | 1767 | 0 | 0 | 1.540 | 186.79 |
| 72.0 | 50.020 | 1795 | 0 | 0 | 1.510 | 55.686 |
| 73.0 | 50.180 | 1800 | 0 | 0 | 1.510 | .00000 |
| 74.0 | 50.510 | 1815 | 0 | 0 | 1.440 | .00000 |
| 75.0 | 51.110 | 1829 | 0 | 0 | 1.700 | 45.577 |
| 76.0 | 51.290 | 1835 | 0 | 0 | 1.730 | 74.174 |
| 77.0 | 51.560 | 1843 | 0 | 0 | 1.790 | 52.425 |
| 78.0 | 52.010 | 1857 | 0 | 0 | 1.680 | 101.06 |
| 79.0 | 52.420 | 1870 | 0 | 0 | 1.970 | 470.68 |
| 80.0 | 53.090 | 1892 | 0 | 0 | 2.100 | 402.54 |
| 81.0 | 53.340 | 1900 | 0 | 0 | 2.160 | .00000 |
| 82.0 | 53.820 | 1915 | 0 | 0 | 2.060 | 215.10 |
| 83.0 | 54.520 | 1939 | 0 | 0 | 1.920 | 106.13 |
| 84.0 | 54.670 | 1944 | 0 | 0 | 1.890 | 66.789 |
| 85.0 | 55.300 | 1964 | 0 | 0 | 1.770 | 73.466 |
| 86.0 | 55.560 | 1973 | 0 | 0 | 1.720 | 275.57 |
| 87.0 | 96.000 | 1984 | 0 | 0 | 1.630 | 73.068 |
| 88.0 | 56.250 | 1996 | 0 | 0 | 1.580 | 367.74 |
| 89.0 | 56.560 | 2000 | 0 | 0 | 1.560 | .00000 |
| 90.0 | 56.810 | 2015 | 0 | 0 | 1.570 | 92.288 |
| 91.0 | 56.990 | 2021 | 0 | 0 | 1.570 | 231.47 |
| 92.0 | 57.400 | 2036 | 0 | 0 | 1.580 | 107.13 |
| 93.0 | 57.950 | 2055 | 0 | 0 | 1.590 | 237.79 |
| 94.0 | 58.970 | 2090 | 0 | 0 | 1.600 | 275.58 |
| 95.0 | 59.240 | 2100 | 0 | 0 | 1.610 | .00000 |
| 96.0 | 59.610 | 2113 | 0 | 0 | 1.610 | 184.98 |

FRACTION:2 HP-RUN-DATE:10/22/1981 HP-RUN-NO: 38 HP-BOT-NO: 15

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 97.0 | 59.960 | 2126 | 0 | 0 | 1.620 | 239.34 |
| 98.0 | 60.440 | 2143 | 0 | | | 133.64 |
| 99.0 | 60 | 2158 | 0 | | | 137.60 |
| 100. | 61.370 | 2177 | 0 | 0 | | 140.03 |
| 101. | 61.660 | 2195 | 0 | 0 | 1.640 | 58.671 |
| 102. | 61.990 | 2200 | 0 | 0 | 1.650 | .00000 |
| 103. | 62.140 | 2205 | 0 | 0 | 1.650 | 63.213 |
| 104. | 62.440 | 2217 | 0 | 0 | 1.660 | 56.003 |
| 105. | 64.320 | 2288 | 0 | 0 | 1.730 | 59.906 |
| 106. | 64.630 | 2300 | 0 | 0 | 1.740 | .70060 |
| 107. | 66.910 | 2389 | 0 | 0 | 1.640 | 52.644 |
| 108. | 67.170 | 2400 | 0 | 0 | 1.630 | .00000 |
| 109. | 68.740 | 2464 | 0 | 0 | 1.660 | 48.519 |
| 110. | 69.540 | 2497 | 0 | 0 | 1.670 | 62.150 |
| 111. | 69.610 | 2500 | 0 | 0 | 1.670 | .00000 |
| 112. | 71.580 | 2573 | 0 | 0 | 1.700 | 46.185 |
| 113. | 72.300 | 2600 | 0 | 0 | 1.720 | .00000 |
| 114. | 75.440 | 2700 | 0 | 0 | 2.560 | .00000 |
| 115. | 79.280 | 2800 | 0 | 0 | 1.770 | .00000 |
| 116. | 84.000 | 3900 | 0 | 0 | 1.850 | .00000 |
| 117. | 89.860 | 3000 | 0 | 0 | 1.920 | .00000 |
| 118. | 97.230 | 3100 | 0 | 0 | 2.630 | .00000 |
| 119. | 106.49 | 3200 | 0 | 0 | 3.320 | .00000 |

TOTAL RESOLVED HYDROCARBON = 11[illegible].1
TOTAL UNRESOLVED HYDROCARBON = 31[illegible].1
RESPONSE FACTOR AV. FOR C - 1500 TO 3100 FOR UCM = 1.[illegible]
RATIO: RESOLVED/UNRESOLVED = 3.590606

SUM OF THE N-ALKANES = 122.7935
SUM OF THE EVEN N-ALKANES = 122.7935
SUM OF THE ODD N-ALKANES = 0

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 0
RATIO: ODD/EVEN N-ALKANES = 0
RATIO: PRISTANE/C-17 = 0
RATIO: PHYTANE/C-18 = 0
RATIO: PRISTANE/PHYTANE = 0
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = 1.098496E-3

TABLE 3-4. COOK INLET CRUDE OIL CONCENTRATIONS FOR ALIPHATIC FRACTION.

FRACTION:1 HP-RUN-DATE:10/21/1981 HP-RUN-NO: 31 HP-BOT-NO: 1

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 2.00 | 5.0500 | 0 | 0 | 0 | 1.440 | 1256.4 |
| 3.00 | 5.1000 | a | 0 | 0 | 1.440 | 3006.5 |
| 4.00 | 5.2000 | 0 | 0 | 0 | 1.440 | 7834.6 |
| 5.00 | 5.3900 | 0 | 0 | 0 | 1.440 | 1968.5 |
| 6.00 | 5.5100 | 0 | 0 | 0 | 1.440 | 249.29 |
| 7.00 | 5.8000 | 700 | a | 0 | 1.440 | 2S3S.0 |
| 8.00 | 6.3600 | 719 | 0 | 0 | 1.440 | 509.92 |
| 9.00 | 7.5100 | 759 | 0 | 0 | 1.440 | 617.92 |
| 10.0 | 7.6300 | 764 | 0 | 0 | 1.4.30 | 147.39 |
| 11.0 | 7.7600 | 766 | 0 | 0 | 1.440 | 409.47 |
| 1.5.0 | 7.9400 | 77a | 0 | 0 | 1.●40 | 1028.8 |
| 1s.0 | 8.6000 | 790 | a | 0 | 1.440 | 186.35 |
| la. 0 | 8.6000 | 797 | 0 | 0 | 1.440 | 239.S5 |
| 15.0 | 8.6800 | 800 | a | 0 | 1.440 | 1712.3 |
| 16.0 | 8.8900 | 805 | 0 | 0 | 1.440 | 306.56 |
| 17.0 | 9.5300 | 820 | 0 | 0 | 1.440 | 203.21 |
| 131.0 | 9.7900 | 826 | 0 | 0 | 1.440 | 457.30 |
| 19.0 | 18.000 | 831 | 0 | 0 | 1.440 | 1909.9 |
| 20.0 | 10.730 | 848 | 0 | 0 | 1.440 | 897.27 |
| 21.0 | 10.930 | 853 | 0 | 0 | 1.440 | 806.74 |
| 22.0 | 11.530 | 862 | 0 | 0 | 1.440 | 1751.6 |
| 29.0 | 11.590 | 867 | 0 | 0 | 1.440 | 2241.6 |
| 24.0 | 12.340 | 886 | 0 | 0 | 1.440 | 570.09 |
| 25.0 | 12.630 | 893 | 0 | 0 | 1.440 | 836.68 |
| 26.0 | 12.940 | 900 | 0 | 0 | 1.440 | 5395.7 |
| 27.0 | 13.230 | 906 | 0 | 0 | 1.440 | 611.81 |
| 2s.0 | 13.360 | 909 | 0 | 0 | 1.440 | 242.75 |
| 2*. O | 13. 830 | 916 | 0 | 0 | 1.440 | 790.75 |
| 30.0 | 14.110 | 924 | 0 | 0 | 1.440 | 607.18 |
| 31.0 | 14.330 | 929 | 0 | 0 | 1.440 | 1863.5 |
| 32.0 | 14.510 | 933 | a | 0 | 1.440 | 1241.1 |
| 33.0 | 14.860 | 940 | a | 0 | 1.080 | 1377.1 |
| 3a. o | 15.090 | 945 | 0 | 0 | 1.440 | 286.06 |
| 39.0 | 15.530 | 958 | 0 | 0 | 1.440 | 1712.3 |
| 36.O | 15.860 | '460 | 0 | 0 | 1.440 | 188.36 |
| 37.0 | 15.9 10 | 963 | 0 | 0 | 1.440 | 369.79 |
| 38.0 | 16.2 10 | 982 | 0 | 0 | 1.440 | 273.82 |
| 39.0 | 17.0 10 | 4704 | 0 | 0 | 1.440 | 356.65 |
| 40.0 | 17.1 10 | 987 | 0 | 0 | 1.860 | 335.92 |
| 41.0 | 17.4 10 | 993 | 0 | 0 | 1.440 | 1313.7 |
| 42.0 | 17.7 0 | 1000 | 0 | 0 | 1.440 | 6695.2 |
| 43.0 | 18.1 10 | 1008 | 0 | 0 | 1.440 | 588.12 |
| 44.0 | 18.1 10 | toll | 0 | 0 | 1.440 | 279.23 |
| 45.0 | in.8*13 | 1022 | 0 | 0 | 1.440 | 2296.7 |
| 46.0 | 19.300 | 103! | 0 | 0 | 1.440 | 1008.s |
| 47.0 | 19.670 | 1039 | 0 | 0 | 1.440 | 162.95 |
| 48.0 | 19.5 10 | 1046 | 0 | 0 | 1.440 | 169.25 |
| 49.0 | 20.1 10 | 10%? | 0 | 0 | 1. | 254.38 |
| 50.0 | 20.4 10 | 1056 | 0 | 0 | 1. | 336.91 |
| S3 .0 | 20.5 10. | 1057 | 0 | 0 | 1. | 162.66 |
| 52.0 | 20.4 10 | 1060 | 0 | 0 | 1. | 440.21 |
| 53.0 | 20.860 | 1064 | 0 | 0 | 1.440 | 1056..2 |
| 54.0 | 21.170 | ..107o | 0 | 0 | 1.440 | 360.05 |
| 55.0 | 21.620 | 1079 | a | 0 | 1.440 | 189.26 |
| 56.0 | 21.870 | 1084 | 0 | a | 1.440 | .2s7.08 |
| 57.0 | 22.060 | 1088 | 0 | 0 | 1.440 | 329.09 |
| 58.0 | 22.630 | 1100 | 0 | 0 | 1.440 | 7113.a |
| 59.0 | 23. 160 | 1111 | 0 | 0 | 1.440 | 1252.1 |
| 60.0 | 23.400 | 1117 | 0 | 0 | 1.440 | 587.10 |
| 61.0 | 23.600 | 1121 | 0 | 0 | 1.440 | 213.39 |
| 62.0 | 23.920 | 1128 | 0 | 0 | 1.440 | 1655.6 |
| 63.0 | 24.230 | 1134 | 0 | 0 | 1.460 | 840.32 |
| 64.0 | 2a. 460 | 1139 | 0 | 0 | 1.440 | 4331.s7 |
| 65.0 | 25.170 | 11s5 | 0 | 0 | 1.440 | 911..?s |
| 66.0 | .35.390 | 1159 | 0 | a | 1.440 | 621.41 |
| 67.0 | 25.590 | 1164 | 0 | a | 1 .600 | 704.67 |
| 68.0 | 25.900 | 1670 | 0 | 0 | 1.440 | S.S6..32 |
| 69.0 | 26.250 | 7 | 0 | 0 | 1.440 | 146.67 |
| 70.0 | .26.6S0 | 1186 | 0 | 0 | 1 .440 | 1012.6 |
| 71.0 | 26.860 | 1191 | 0 | 0 | 1.440 | 674.61 |
| 72.0 | 27.200 | 1200 | 0 | 0 | 1.430 | 7804.0 |
| 73.0 | 27.630 | 1207 | 0 | 0 | 1.440 | 205.19 |
| 74.0 | 27.870 | 1213 | 0 | 0 | 1.440 | 925.99 |
| 75.0 | 28.300 | ..1224 | a | 0 | 1.440 | 279.52 |
| 76.0 | 28.510 | 1228 | 0 | 0 | 1.440 | 309.80 |
| 77.0 | 29.020 | 1239 | 0 | a | 1.440 | 659.24 |
| 7s.0 | 29.870 | 1258 | a | 0 | 1.440 | 274.39 |
| 79.0 | 30.060 | 1263 | 0 | 0 | 1 .440 | 882.64 |
| 80.0 | 30.460 | 1272 | 0 | 0 | 1.450 | 467.51 |
| 81.0 | 30.780 | 1279 | 0 | 0 | 1.4s0 | 316.81 |
| 82.0 | 30.970 | 1284 | 0 | 0 | 1.450 | 158.26 |
| 83.0 | 31.220 | 1289 | 0 | 0 | 1.450 | 565.67 |
| 84.0 | 31. 670 | 1300 | 0 | 0 | 1.490 | 7596.8 |
| 85.0 | 31.970 | 1307 | 0 | 0 | 1.440 | 381.35 |
| 86.0 | 32.390 | 1316 | 0 | 0 | 1.440 | 670.89 |
| 87.0 | 32.670 | 1324 | 0 | 0 | 1.430 | 451.64 |
| 88.0 | 33.300 | 1339 | 0 | 0 | 1.420 | 185.11 |
| 89.0 | 33. s10 | 1344 | 0 | 0 | 1.420 | 1142.6 |
| 90.0 | 34.080 | 1350 | 0 | 0 | 1.410 | 356.38 |
| 91.0 | 34.290 | 1365 | 0 | 0 | 1.400 | 521..54 |
| 92.0 | 34.580 | 1370 | 0 | 0 | 1.400 | 361.59 |
| 93.0 | 36.820 | 1376 | 0 | 0 | 1.390 | 1148.1 |
| 94.0 | 33S.920 | 1 39.? | 0 | 0 | 1.380 | 157. s3 |
| 95.0 | 35.810 | 1.s00 | 0 | 0 | 1.380 | 6143.5 |
| 96.0 | 36.820 | 1425 | 0 | 0 | 1.410 | 215.04 |
| 99.0 | 37.780 | 1449 | 0 | a | 1.440 | 1846.8 |
| 98.0 | 3a. 060 | 1458 | 0 | 0 | 1.450 | 276. 84 |
| 99.0 | 38.220 | 1461 | 0 | 0 | 1.460 | 1647.8 |
| 100. | 38. s50 | 1070 | 0 | 0 | 1.470 | 619.79 |
| lot. | 38.840 | 1477 | 0 | 0 | 1.460 | 252.12 |
| 102. | 39.3s0 | 1490 | 0 | 0 | 1 .s00 | 224.17 |

FRACTION:1 HP-RUN-DATE:10/21/1981 HP-RUN-NO : 31 HP-BOT-NO: 1

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 103. | 39.710 | 1500 | 0 | 0 | 1.510 | 6885.5 |
| 104. | 40.050 | 1509 | 0 | 0 | 1.510 | 447.67 |
| 105. | 41.400 | 1588 | 0 | 0 | 1 .s00 | 391.46 |
| 106. | 41.700 | 15%X | 0 | 0 | 1.500 | 932.17 |
| 107. | 42.020 | 1562 | 0 | 0 | 1.900 | 562.93 |
| 108. | 42.290 | 1570 | 0 | 0 | 1.500 | |
| 109. | 43.390 | 1600 | 0 | 0 | 1.900 | 9339.2 |
| tie. | 45.100 | 1648 | 0 | 0 | 1.550 | 1865.6 |
| 111. | 45.420 | 1657 | 0 | 0 | 1.560 | 756.45 |
| 112. | 45.590 | 1662 | 0 | 0 | 1.560 | 271.47 |
| 113. | 45.860 | 1670 | 0 | 0 | 1 .s70 | 225.35 |
| 114. | 46.900 | 1700 | | | 1.600 | 6452.8 |
| 119. | 47.080 | 1710 | | | 1.500 | 3129.7 |
| 116. | 48.340 | 1743 | 0 | 0 | 1.560 | 539.57 |
| 117. | 48.980 | 1762 | 0 | 0 | 1.560 | 641.51 |
| 118. | 49.250 | 1770 | 0 | 0 | 1.9s0 | 160.10 |
| 119. | 50.230 | 1800 | 0 | 0 | 1.510 | 3485.1 |
| .1.20. | 50.510 | 1015 | 0 | 0 | 1.440 | 1065.1 |
| 121. | 51.530 | 1441 | 0 | 0 | 1.780 | 389.20 |
| 122. | 52.010 | 1856 | 0 | 0 | 1.880 | 223.88 |
| 123. | 52.210 | 1863 | 0 | 0 | 1..920 | 272.53 |
| 124. | S3.11O | 1.391 | 0 | 0 | 2.100 | 587.96 |
| 125. | 53.370 | 1900 | 0 | 0 | 2.160 | 4628.1 |
| 126. | 55.270 | 1963 | 0 | 0 | 1.760 | 183.31 |
| 123. | 56.380 | 2000 | 0 | 0 | 1.560 | 3046.8 |
| 128. | 57.500 | 2039 | 0 | 0 | 1.560 | 176.43 |
| 129. | 59.250 | .2100 | 0 | 0 | 1.61o | 2912.6 |
| 130. | 61.280 | 2173 | 0 | 0 | 1.680 | 198.28 |
| 131. | 61.090 | 2181 | 0 | 0 | 1.640 | 210.20 |
| 132. | 62.010 | 2200 | 0 | 0 | 1.650 | 26.3.9..3 |
| 133. | 64.650 | 2300 | 0 | 0 | 1.760 | 2613.3 |
| 13.4. | 65.110 | 231a | 0 | 0 | 1.720 | 240.29 |
| 135. | 67.160 | 2400 | 0 | 0 | 1.630 | 2171.3 |
| 136. | 69.630 | 2500 | 0 | 0 | 1.670 | 1794..3 |
| 137. | 72.310 | 2600 | 0 | 0 | 1.720 | 1916.9 |
| 138. | 75.480 | 2700 | 0 | 0 | 2.560 | 2245.0 |
| 139. | 79.300 | 2800 | 0 | 0 | 1.770 | 1238.9 |
| 140. | 84.020 | 2900 | 0 | 0 | 1.850 | 1136.3 |
| 141. | 89.800 | 3000 | 0 | 0 | 1.920 | 98.9.7s |
| 142. | 97.280 | 3100 | 0 | 0 | 2.630 | 989.35 |
| 143. | 106. 52 | 3200 | 0 | 0 | 2.320 | 530.60 |
| 144. | 10*. S? | 3200 | 0 | 0 | 2.520 | .00000 |

TOTAL RESOLVED HYDROCARBON = 17915s. s
TOTAL UNRESOLVED HYDROCARBON . 211498.7
RESPONSE FACTOR AV. FOR C - 700 TO 2900 FOR UCM = 1.701876
RATIO: RESOLVED/UNRESOLVED = 0.847076

SUM OF THE N-ALKANES = 70600.0'3
SUM OF THE EVEN N-ALKANES = 35349. 81
SUM OF THE ODD N-ALKANES = 35250.23

RATIO: (PRISTANE+PHYTANE) /(N-ALKANES) = 0.0596988
RATIO: ODD/EVEN N-ALKANES - 0.9971S3
RATIO: PRISTANE/C-17 = 0.702859
RATIO: PHYTANE/C-18 = 0.311339
RATIO: PRISTANE/PHYTANE = 2.884348
RATIO: (N-ALKANES) / (BRANCHED HYDROCARBONS) = 0.650359

Weight Distribution of Cook inlet Crude by Fraction

| Fraction | Weight (mg/g) |
|---|---|
| 1 | 803 |
| 2 | 64.6 |
| 3 | 127 |

TABLE 3-5. COOK INLET CRUDE OIL CONCENTRATIONS FOR AROMATIC FRACTION.

FRACTION:2 HP-RUN-DATE:10/21/1981 HP-RUN-NO: 32 HP-BOT-NO: 3

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 5.1s00 | 0 | 0 | 0 | 1.440 | 2491.7 |
| 2.00 | 5.2100 | 0 | 0 | 0 | 1.440 | 792.16 |
| 2.50 | 5.6200 | 700 | 0 | 0 | .0000 | .00000 |
| 3.00 | 5.7900 | 705 | 0 | 0 | 1.440 | 2473.2 |
| 4.00 | 6.2300 | 721 | 0 | 0 | 1.440 | 1439.9 |
| 5.00 | 6.4200 | 728 | 0 | 0 | 1.440 | 150.45 |
| 6.00 | ?.0300 | 749 | 0 | 0 | 1.440 | 45.534 |
| 7.00 | 7.4400 | 763 | 0 | 0 | 1.440 | 422.83 |
| 7.90 | 8.4900 | 800 | 0 | 0 | .0000 | .00000 |
| 8.00 | 11.080 | 860 | 0 | 0 | 1.440 | 24.547 |
| 9.00 | 11.430 | 868 | 0 | 0 | 1.440 | 158.93 |
| 9.50 | 12.040 | 900 | 0 | 0 | .0000 | .00000 |
| 10.0 | 12.510 | 893 | 0 | 0 | 1.440 | 133.41 |
| 11.0 | 15.880 | 962 | 0 | 0 | 1.440 | 93.352 |
| 12.0 | 16.190 | 969 | 0 | 0 | 1.440 | 51.234 |
| 13.0 | 16.760 | 980 | 0 | 0 | 1.440 | 54.587 |
| 1[illegible]-c | 17.440 | 994 | 0 | 0 | 1.440 | 286.82 |
| 14.5 | 17.710 | 1000 | 0 | 0 | .0000 | .00000 |
| 15.0 | 18.880 | 1024 | 0 | 0 | 1.440 | 262.96 |
| 16.0 | 20.280 | 1053 | 0 | 0 | 1.440 | 33.044 |
| 17.0 | 21.930 | 1086 | 0 | 0 | 1.440 | 69.648 |
| 18.0 | 22.640 | 1100 | 0 | 0 | 1.440 | 27.983 |
| 18.8 | 22.600 | 1100 | 0 | 0 | .0000 | .00000 |
| 19.0 | 23.420 | 111'9 | 0 | 0 | 1.440 | 65.698 |
| .20.0 | 23.630 | 1122 | 0 | 0 | 1.440 | 81.521 |
| 21.0 | 24.510 | 1141 | 0 | 0 | 1.440 | 33.662 |
| 22.0 | 24.790 | 1146 | 0 | 0 | 1.440 | 40.122 |
| 23.0 | 25.600 | 1165 | 0 | 0 | 1.440 | 40.225 |
| 24.0 | 26.180 | 117? | 0 | 0 | 1.440 | 23.415 |
| 25.0 | 26.660 | 1188 | 0 | 0 | 1.440 | 410.90 |
| 26.0 | 26.820 | 1192 | 0 | 0 | 1.440 | 39.85s |
| 27.0 | 27.200 | 1200 | 0 | 0 | 1.430 | .00000 |
| 2s.0 | 27.260 | 1200 | 0 | 0 | 1.430 | 75.094 |
| 29.0 | 28.[illegible]00 | 1228 | 0 | 0 | 1.440 | 28.949 |
| 30.0 | 28.960 | 1239 | 0 | 0 | 1.440 | 40.922 |
| 31.0 | 29.360 | 1248 | 0 | 0 | 1.440 | 28.678 |
| 32.0 | 29.600 | 1253 | 0 | 0 | 1.440 | 36.598 |
| 33.0 | 30.970 | 1285 | 0 | 0 | 1.450 | 49.908 |
| 38.0 | 31.620 | 1300 | 0 | 0 | 1.450 | .00000 |
| 39.0 | 31. 640 | 1300 | 0 | 0 | 1.450 | 1203.7 |
| 36.0 | 31.950 | 1307 | 0 | 0 | 1.440 | 54.434 |
| 37.0 | 32.390 | 1318 | 0 | 0 | 1.440 | 732.28 |
| 3a.0 | 32.670 | 1325 | 0 | 0 | 1.430 | 87.609 |
| 39.0 | 33.490 | 1395 | 0 | 0 | 1.620 | 38.629 |
| 40.0 | 34.290 | 1364 | 0 | 0 | 1.400 | 20.120 |
| 41.0 | 34.990 | 1381 | 0 | 0 | 1.390 | 26.759 |
| 42.0 | 35.180 | 1385 | a | 0 | 1.390 | 85.650 |
| 43.0 | 35.760 | 1400 | 0 | 0 | 1.380 | .00000 |
| 44.0 | 35.770 | 1400 | 0 | 0 | 1.380 | 241.65 |
| 45.0 | 36.250 | 1412 | 0 | 0 | 1.390 | 627.73 |
| 46.0 | 36.880 | 182.s | 0 | 0 | 1.410 | 571.49 |
| 47.0 | 37.020 | 1432 | 0 | 0 | 1.420 | 229.48 |
| 48.0 | 37.630 | 1447 | 0 | a | 1.440 | 257.16 |
| 49.0 | 37.770 | 1451 | 0 | 0 | 1.440 | 38.288 |
| 50.0 | 36.,?50 | 1463 | 0 | 0 | 1.460 | 261.57 |
| 51.0 | 38.810 | 1478 | 0 | 0 | 1.440 | 22.044 |
| 52.0 | 39.390 | 1493 | 0 | 0 | 1.s00 | 142.38 |
| 53.0 | 39.660 | 1500 | 0 | 0 | 1.510 | .00000 |
| 54.0 | 39.740 | 1502 | 0 | 0 | 1.510 | 12.082 |
| 59.0 | 40.130 | 1512 | 0 | 0 | 1.510 | 173.73 |
| 56.0 | 40.590 | 1525 | 0 | 0 | 1.510 | 62.959 |
| 57.0 | 40.820 | 1531 | 0 | 0 | 1.510 | 55.243 |
| 58.0 | 00.969 | 1535 | 0 | 0 | 1.510 | 144.61 |
| 59.0 | 41.170 | 1s00 | 0 | 0 | 1.510 | 229.77 |
| 60.0 | 41 .660 | 338 | 0 | 0 | 1.500 | 26.979 |
| 61.0 | 41.780 | 15s7 | 0 | 0 | 1.500 | 91.616 |
| 62.0 | 42.410 | 1574 | 0 | 0 | 1.500 | 498.40 |
| 63.0 | 43.140 | 1594 | 0 | 0 | 1.500 | 164.99 |
| 64.0 | 43.320 | 1598 | 0 | 0 | 1.5ee | 169.26 |
| 65.0 | 43.360 | 1600 | 0 | 0 | 1.5{10 | .00000 |
| 66.0 | 43.640 | 1608 | 0 | 0 | 1.510 | 70.557 |
| 67.0 | 44.310 | 1627 | 0 | 0 | 1.s?10 | 74.776 |
| 68.0 | 44.490 | 1632 | 0 | 0 | 1.5?10 | 47.388 |
| *V. O | 45.000 | 1646 | 0 | 0 | 1.550 | 39.506 |
| 70.0 | 45.170 | 1651 | 0 | 0 | 1.390 | 38.891 |
| 71.0 | 45.480 | 1660 | 0 | 0 | 1.S60 | 69.522 |
| 72.0 | 46.230 | 1682 | 0 | a | L.580 | 97.665 |
| 73.0 | 46.490 | 1689 | 0 | 0 | 1.s90 | 45.581 |
| 74.0 | 46.840 | 1699 | 0 | 0 | 1 boo | 180.56 |
| 75.0 | 46.860 | 1700 | 0 | 0 | 1.600 | .00000 |
| 7*. O | 47.080 | 1718 | 0 | 0 | 1.500 | .00000 |
| ??.0 | 47.160 | 1709 | 0 | 0 | 1.590 | 35. 004 |
| 78.0 | 47.530 | 1720 | 0 | 0 | 1.580 | 293.69 |
| 79.0 | 47.900 | 1731 | 0 | 0 | 1.s70 | 52.290 |
| 80.0 | 48.460 | 1748 | 0 | 0 | 1.590 | 154.86 |
| 31.0 | 89.030 | 1765 | 0 | 0 | 1.540 | 29.367 |
| 82.0 | 49.240 | 1771 | 0 | 0 | 1 .s30 | 21.953 |
| 83.0 | 49.740 | 1786 | 0 | 0 | 1.520 | 40.629 |
| 84.0 | 50.070 | 1796 | 0 | 0 | 1.91$ | 323.08 |
| 85.0 | 50.180 | 1800 | 0 | 0 | 1.510 | .00000 |
| 86.0 | 50.510 | 1815 | 0 | 0 | 1.440 | .00000 |
| $7.0 | 50. 630 | 1814 | 0 | 0 | 1.600 | 29.517 |
| 0.3.0 | 51.140 | 1830 | 0 | 0 | 1.700 | 93.9.23 |
| 89.0 | 51.320 | 1836 | 0 | 0 | 1.740 | 26.118 |
| 9*. O | 51.600 | 1844 | 0 | 0 | 1.000 | 62.087 |
| 91.0 | 52.080 | 1860 | 0 | 0 | 1.900 | 136.38 |
| 9.3.0 | 52.3.20 | 1S67 | 0 | 0 | 1.950 | 64.794 |
| 93.0 | 52.590 | 1876 | 0 | 0 | 2.000 | 38.983 |
| 94.0 | 52.780 | 1882 | 0 | 0 | 2.040 | 93.215 |
| 95.0 | 53.260 | 1897 | 0 | 0 | 2.140 | 99.833 |
| 96.0 | 53.340 | 1900 | 0 | 0 | 2.160 | .00000 |

FRACTION:2 HP-RUN-DATE:10/21/1981 HP-RUN-NO: 32 HP-BOT-NO: 3

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 97.0 | 53.750 | 1913 | 0 | 0 | 2.070 | .209.93 |
| 98.0 | 53. *MO | 1919 | 0 | 0 | 2.080 | 221 .00 |
| 99.0 | 54.200 | 1'92A | 0 | 0 | 1.990 | |
| 100. | 54.570 | 1940 | a | 0 | 1.910 | |
| 101. | 54.730 | 1946 | 0 | 0 | 1.800 | 129.83 |
| 102. | 55.850 | 1983 | 0 | 0 | 1.660 | 25.299 |
| 103. | 56.080 | 1990 | 0 | 0 | 1.610 | 88.162 |
| 104. | 56.360 | 2000 | 0 | 0 | 1.560 | .00000 |
| 109 | 37.1s0 | 2026 | 0 | 0 | 1.570 | 38.463 |
| 106. | 58.000 | 2056 | 0 | 0 | 1.590 | 259.17 |
| 107. | 58.170 | 2062 | 0 | 0 | 1.590 | 120.36 |
| 108. | 58.360 | 2069 | 0 | 0 | 1.590 | 69.395 |
| 109. | 58. 680 | .3080 | 0 | 0 | 1.600 | 23.171 |
| 110. | 59.080 | 2098 | 0 | 0 | 1.600 | 68.066 |
| 111. | 59.240 | 2100 | 0 | 0 | 1.610 | .0(3000 |
| 112. | 59.300 | 2102 | 0 | 0 | 1.610 | 31 es? |
| 113. | 99.550 | 2111 | 0 | 0 | 1.610 | 53.660 |
| 150. | 60.560 | 2168 | 0 | 0 | 1.630 | 89.195 |
| 115. | 61.150 | 2169 | 0 | 0 | 1.630 | 5A.396 |
| 116. | 61.400 | 2178 | 0 | 0 | 1.640 | 125.11 |
| 117. | 61.900 | 2196 | 0 | 0 | 1.640 | 51.897 |
| 118. | 61.990 | ?.s00 | 0 | 0 | 1.650 | .00000 |
| 119. | 63.080 | 2241 | 0 | 0 | 1.690 | 93.961 |
| 120. | 64.620 | 2299 | 0 | 0 | 1.740 | 25.774 |
| 121. | 64.630 | 2300 | 0 | 0 | 1.740 | .00000 |
| 122. | 66.640 | 2367 | 0 | 0 | 1.650 | 73.826 |
| 1 2 3 . | 67.170 | 2400 | 0 | 0 | 1.630 | .00006 |
| 124. | 67.270 | 2408 | 0 | 0 | 1.640 | 58.015 |
| 1.3s. | 69.570 | 2498 | 0 | 0 | 1.670 | 61.089 |
| 126. | 69.610 | 2500 | 0 | 0 | 1.670 | .00000 |
| 127. | 72.3oo | 2600 | 0 | 0 | 1.720 | .00000 |
| 128. | 7.?.810 | 2616 | 0 | 0 | 1.890 | 61 .907 |
| 129. | ?5.370 | 2697 | 0 | 0 | 2.540 | 37.175 |
| 130. | 75.440 | 2700 | 0 | 0 | 2.560 | .00000 |
| 1s1. | 76.580 | 2729 | 0 | 0 | 2.330 | 42.131 |
| 132. | 79.280 | 2800 | 0 | 0 | 1.770 | .00000 |
| 1 33. | 84.000 | ,2900 | 0 | 0 | 1.850 | ,00000 |
| 134. | 89.860 | 3000 | 0 | 0 | 1.920 | ,00000 |
| 135. | 97.230 | 3100 | 0 | 0 | 2.630 | .00000 |
| 136. | 100.49 | 3200 | 0 | 0 | 2.320 | .00000 |

TOTAL RESOLVED HYDROCARBON = 20856.13
TOTAL UNRESOLVED HYDROCARBON = 32399.1
RESPONSE FACTOR AV. FOR C - 1500 TO 3100 FOR UCM = 1.803576
RATIO: RESOLVED/UNRESOLVED = 0.643726

SUM OF THE N-ALKANES = 0
SUM OF THE EVEN N-ALKANES = 0
SUM OF THE ODD N-ALKANES = 0

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 0
RATIO: ODD/EVEN N-ALKANES = 0
RATIO: PRISTANE/C-17 = 0
RATIO: PHYTANE/C-18 = 0
RATIO: PRISTANE/PHYTANE = 0
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = 0

TABLE 3-6. PRUDHOE BAY CRUDE OIL CONCENTRATIONS FOR ALIPHATIC FRACTION.

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATIO TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 6.87700 | 0 | 0 | 0 | 1.900 | 222.26 |
| 2.00 | 6.6600 | 0 | 0 | 0 | 1.400 | 503.98 |
| 3.00 | 7.4000 | 700 | 0 | 0 | 1.900 | 772.90 |
| 4.00 | 8.7600 | 730 | 0 | 0 | 1.900 | 220.44 |
| 9.00 | 8.9900 | 759 | 0 | 0 | 1.900 | 1211.2 |
| 6.00 | 9.3900 | 770 | 9 | 0 | 1.900 | 151.87 |
| 7.00 | 9.8300 | 790 | 0 | 0 | 1.900 | 68.620 |
| 8.00 | 10.110 | 800 | 0 | 0 | 1.900 | 1672.0 |
| 9.00 | 11. 080 | 821 | 0 | 0 | 1.900 | 30.366 |
| 10.0 | 11 .350 | 827 | 0 | 0 | 1.900 | 9 5.709 |
| 11.0 | 11.650 | 833 | 0 | 0 | 1.900 | 194.90 |
| 12.0 | 11.790 | 836 | 0 | 0 | 1.900 | 107.53 |
| 13.0 | 12.470 | 851 | 0 | 0 | 1.900 | 31.594 |
| 14.0 | 12.640 | 855 | 0 | 0 | 1.400 | 48.322 |
| 15.0 | 13. o% | 863 | 0 | 0 | 1.900 | 593. 76 |
| 16.0 | 13.610 | 871 | 0 | 0 | 1.900 | 1629.6 |
| 17.0 | 14.200 | 888 | 0 | 0 | 1.900 | 32.560 |
| 18.0 | 14.500 | 896 | 0 | 0 | 1.900 | 2215.27 |
| 19.0 | 14.750 | 900 | 0 | 0 | 1.900 | 1000.3 |
| 20.0 | 15.150 | 908 | 0 | 0 | 1.900 | 41.800 |
| 21.0 | 15.610 | 917 | 0 | 0 | 1.900 | 29.476 |
| 22.0 | 15.800 | 921 | 0 | 0 | 1.900 | 253.09 |
| 23.0 | 16.130 | 927 | 0 | 0 | 1.900 | 26.606 |
| 24.0 | 16.310 | 931 | 0 | 0 | 1.900 | 19.959 |
| 25.0 | 16.630 | 933 | 0 | 0 | 1.900 | 147.04 |
| 26.0 | 16.820 | 941 | 0 | 0 | 1.900 | 173.7.? |
| 27.0 | 17.620 | 957 | 0 | 0 | 1.900 | 193.63 |
| 28.0 | 17.840 | 941 | 0 | 0 | 1.900 | 50.313 |
| 29.0 | 17.990 | 960 | 0 | 0 | 1.900 | 3.39.79 |
| 30.0 | 18.320 | 971 | 0 | 0 | 1.900 | 460.17 |
| 31.0 | 18.980 | 984 | 0 | 0 | 1.900 | 525.15 |
| 32. o | 19.620 | 997 | 0 | 0 | 1.900 | 233.69 |
| 33.0 | 19.760 | 1000 | 0 | 0 | 1.900 | 806.36 |
| 34.0 | 20.320 | 1011 | 0 | 0 | 1.900 | 32.461 |
| 35.0 | 20.470 | 1014 | 0 | 0 | 1.900 | 57. 809 |
| 36.0 | 20.800 | 1023 | 0 | 0 | 1 *900 | 183.15 |
| 37.0 | 21.110 | 1027 | 0 | 0 | 1.400 | 245.25 |
| 38.0 | 21.470 | 1034 | 0 | 0 | 1.900 | 176. 60 |
| 39.0 | 21.690 | 1039 | 0 | 0 | 1.900 | 110.11 |
| 40.0 | 22.130 | 1048 | 0 | 0 | 1.900 | 99.164 |
| 41.0 | 22.400 | 1055 | 0 | 0 | 1.900 | 160.00 |
| 42.0 | 22.740 | 1060 | 0 | 0 | K 9 @ | 325.59 |
| 43.0 | 23.270 | 1071 | 0 | 0 | 1.900 | 181.56 |
| 44.0 | 23.7'30 | 1081 | 0 | 0 | 1.900 | 32.780 |
| 45.0 | 23.870 | 1083 | 0 | 0 | 1.900 | 27.952 |
| 46.0 | 24.030 | 1086 | 0 | 0 | 1.900 | 44.553 |
| 47.0 | 24. 190 | 1089 | 0 | 0 | 1 .900 | 149.12 |
| 48.0 | 28.710 | 1100 | 0 | 0 | 1.900 | 1540.3 |
| 49.0 | 25.070 | 1106 | 0 | 0 | 1.900 | 31.424 |
| 50. o | 25.240 | 1111 | 0 | 0 | 1.900 | 35.194 |
| 51.0 | 25. 480 | 1117 | 0 | 0 | 1.900 | 169.07 |
| 52.0 | 25.680 | 11.31 | 0 | 0 | 1.900 | 22.700 |
| 53.0 | 25.900 | 1127 | 0 | 0 | 1-900 | 140.61 |
| 54.0 | 26.270 | 1133 | 0 | 0 | 1.900 | 205.11 |
| 55.0 | 26.470 | 1136 | 0 | 0 | 1.900 | 82.415 |
| 56.0 | 26.630 | 1141 | 0 | 0 | 1.900 | 84.914 |
| 57.0 | 27.040 | 1150 | 0 | 0 | 1.900 | 101. 47 |
| 58.0 | 27.360 | 1157 | 0 | 0 | 1.900 | 55.861 |
| 59.0 | 27.470 | 1159 | 0 | 0 | 1.900 | 57.13[ |
| 60.0 | 27.699 | 1164 | 0 | Q | 1.900 | 146.53 |
| 61.0 | 28.000 | 1171 | 0 | 0 | 1.900 | S06.20 |
| 62.0 | 2a.430 | 11.s0 | 0 | 0 | 1.900 | 41.080 |
| 63.0 | 28.650 | 1169 | 0 | 0 | 1.900 | 288. 49 |
| 64.0 | 29.060 | 1193 | 0 | 0 | 1.908 | 190.33 |
| 65.0 | 29.370 | 1200 | 0 | 0 | 1.860 | 1241.8 |
| 66.0 | 29.980 | 1213 | 0 | 0 | 1.890 | 272.23 |
| 67. o | 30.630 | 1228 | 0 | 0 | 1.890 | 90.111 |
| 68.0 | 30.840 | 1233 | 0 | 0 | 1.890 | 96.531 |
| 69.0 | 31.240 | 1242 | 0 | 0 | 1.900 | 72.615 |
| 70.0 | 31.680 | 1252 | 0 | 0 | 1.900 | 244.49 |
| 71.0 | 31.960 | 1258 | 0 | 0 | 1.900 | 96.603 |
| 72.0 | 32.170 | 1263 | 0 | 0 | 1.900 | 165.73 |
| 73.0 | 32.570 | 1272 | 0 | 0 | 1.910 | 495.52 |
| 74.0 | 33.410 | 1292 | 0 | 0 | 1.910 | 25.825 |
| 75.0 | 33.760 | 1300 | 0 | 0 | 1.920 | 1247. ! |
| 76.0 | 34.010 | 1306 | 0 | 0 | 1.920 | 3?I.&Q |
| 79.0 | 34.280 | 1311 | 0 | 0 | 1.920 | .36.S36 |
| 78.0 | 34.500 | 1317 | 0 | 0 | 1.930 | 75.993 |
| 79.0 | 34.760 | 1324 | 0 | 0 | 1.950 | 270.40 |
| 80.0 | 39.730 | 1347 | 0 | 0 | 1.940 | 264.84 |
| 81.0 | 36.170 | 139a | 0 | 0 | 1.960 | 109.64 |
| 82.0 | 36.380 | 1363 | 0 | 0 | 1.950 | 101.73 |
| 83.0 | 36.660 | 1370 | 0 | 0 | 1.950 | 98.982 |
| 84.0 | 36.928 | 1376 | 0 | 0 | 1.950 | 290.29 |
| 85.0 | 37.290 | 13a5 | 0 | 0 | 1.960 | 24.823 |
| 86.0 | 37.630 | 1393 | 0 | 0 | 1.960 | 98.636 |
| 87.0 | 37.890 | 1400 | 0 | 0 | 1.960 | 12S0.7 |
| 88.0 | 38.200 | 1407 | 0 | 0 | 1.970 | 51.772 |
| 89.0 | 30.2.30 | 1419 | 0 | 0 | 1.990 | 158.12 |
| 90.0 | 39.200 | 1434 | 0 | 0 | 2.010 | 1249.79 |
| 91.0 | 39.790 | 1448 | 0 | 0 | 2.020 | 35.%30 |
| 92.0 | 39.930 | 1452 | 0 | 0 | 2.030 | 102.34 |
| 93.0 | 40.160 | 1458 | 0 | 0 | 2.030 | 32.13'2 |
| 94.0 | 40.310 | 1462 | 0 | 0 | 2.040 | 210.76 |
| 95.0 | 40.630 | 1470 | 0 | 0 | 2.050 | 147.10 |
| 96.0 | 41.040 | 1480 | 0 | 0 | 2.060 | 31.088 |
| 97.0 | 01.700 | 1500 | 0 | 0 | 2.080 | 1485.5 |
| 98.0 | 42.060 | 1508 | 0 | 0 | 2.080 | 57.090 |
| 99.0 | 42.520 | 1520 | 0 | 0 | 2.090 | 47.564 |
| 100. | 42.740 | 1526 | 0 | 0 | 2.090 | 25.770 |
| 101. | 43.380 | 1542 | 0 | 0 | a.090 | 34.977 |
| 102. | 43.540 | 1548 | 0 | 0 | 2.090 | 115.13 |
| 103. | 43.870 | 1557 | 0 | 0 | 2.090 | 166.07 |
| 100. | 44.110 | 1563 | 0 | 0 | 2.090 | 50.379 |
| | 44.56 | 1575 | 0 | 0 | 2.090 | 288 |
| | 44.820 | 1583 | 0 | 0 | 2.100 | 99.971 |
| 107. | 45.440 | 1600 | 0 | 0 | [illegible] | [illegible] |
| 108. | 45.640 | 1605 | 0 | 0 | 2.110 | 59.216 |
| 109. | 46.030 | 1617 | 0 | [illegible] | [illegible] | [illegible] |
| 110. | 46.350 | 1626 | 0 | 0 | .3.170 | 77.078 |
| 111. | 46.660 | 1635 | 0 | 0 | 2.190 | 36.170 |
| 112. | w.19* | 1649 | 0 | 0 | 2.230 | 248.75 |
| 1 W. | 47.618 | 1662 | 0 | 0 | 2.260 | 109.18 |
| 114. | 48.900 | 1670 | 0 | 0 | 2.10 | 120.60 |
| 11s. | 48.910 | 1700 | 0 | 0 | 2.360 | 995.06 |
| 116. | 49.110 | 1710 | 0 | 0 | 3:290 | 638.20 |
| 117. | 49.980 | 1732 | 0 | 0 | 2.290 | 96.746 |
| 118. | 50.340 | 1745 | 0 | 0 | 2.240 | 48.5 |
| 119. | S0.040 | 1752 | 0 | 0 | 2.250 | 45.636 |
| 120. | 50.830 | 1756 | 0 | 0 | 2.230 | 28.929 |
| 121. | 51.000 | 1763 | 0 | 0 | 2.220 | 61.780 |
| 122. | 51.690 | 1784 | 0 | 0 | 2.180 | 51.411 |
| 123. | 52.210 | 1800 | 0 | 0 | 2.140 | .223,03 |
| 124. | 52.530 | 1815 | 0 | 0 | 2.270 | 532.36 |
| 125. | 53.340 | 1835 | 0 | 0 | 2.280 | 32.253 |
| 126. | 53.550 | 1842 | 0 | 0 | 2.310 | 91.029 |
| 127. | 54.470 | 1871 | 0 | 0 | 2.420 | 49.609 |
| 128. | 55.140 | 1892 | 0 | 0 | .2.900 | 65.152 |
| 129. | 51.370 | 1900 | 0 | 0 | 2.530 | 753.89 |
| 130. | 55.640 | 1909 | 0 | 0 | 2.550 | 30.201 |
| 131. | 57.100 | 1957 | 0 | 0 | 2.690 | 46.663 |
| 132. | 58.310 | 2000 | 0 | 12 | 2.810 | 842.36 |
| 133. | 59.520 | 2039 | 0 | 0 | 2.990 | 154.89 |
| 134. | 60.530 | .3074 | 0 | 0 | 3.150 | 145.79 |
| 135. | 61.260 | 2100 | 0 | 0 | 3.270 | 610.26 |
| 136. | 63.020 | 2163 | 0 | 0 | 3.S70 | 76.649 |
| 137. | 63.690 | 2187 | 0 | 0 | 3.690 | 55.736 |
| 138. | 64.840 | 2200 | 0 | 0 | 3.750 | 832.65 |
| 139. | 65.030 | 2236 | 0 | 0 | 3.860 | 98.829 |
| 140. | 65.730 | 2263 | 0 | 0 | 3.930 | 99.231 |
| 141. | 66.720. | 2300 | 0 | 0 | 4.040 | 714..71 |
| 142. | 69.310 | 2400 | 0 | 0 | 4.660 | 726.08 |
| 143. | 70.990 | 2461 | 0 | 0 | 4.610 | 52.954 |
| 144. | 72.030 | 2500 | 0 | 0 | 4.580 | 643.89 |
| 14s. | 73.410 | 2532 | 0 | 0 | 4.730 | .51.040 |
| 146. | 73.860 | 2561 | 0 | 0 | 4.860 | 118.35 |
| 147. | 75.010 | 2600 | 0 | 0 | 5.030 | 596.84 |
| 148. | 76.100 | 2631 | 0 | 0 | 5.900 | 103.93 |
| 149. | 77.040 | 2659 | 0 | 0 | 6.640 | 102.77 |
| 150. | 78.460 | 2700 | 0 | 0 | 7.160 | 323.16 |
| 151. | 82.520 | 2800 | 0 | 0 | 5.960 | 361.19 |
| 152. | 87.480 | 2900 | 0 | 0 | 6.440 | 195.04 |
| 153. | 89.230 | 2928 | 0 | 0 | 6.640 | 147.81 |
| 154. | 93.580 | 3000 | 0 | 0 | 7.120 | 272.89 |
| 155. | 102.11 | 3100 | 0 | 0 | 9.630 | 300.68 |
| 156. | 108.59 | 3200 | 0 | 0 | 8.830 | 287 .53- |
| 157. | 110.59 | 3200 | 0 | 0 | 9.650 | .00000 |

TOTAL RESOLVED HYDROCARBON = 42256.59
TOTAL UNRESOLVED HYDROCARBON = 152822.6
RESPONSE FACTOR AV. FOR C - 1200 TO 3100 FOR UCM = 4.222611
RATIO: RESOLVED/UNRESOLVED = 0.276507

SUM OF THE N-ALKANES = 15937 .11
SUM OF THE EVEN N-ALKANES ..,$.371
SUM OF THE ODD N-ALKANES "78?0,736

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 7.351602E-2
RATIO: ODD/EVEN N-ALKANES = 0.927945
RATIO: PRISTANE/C-17 = 0.648072
RATIO: PHYTANE/C-18 = 0.648625
RATIO: PRISTANE/PHYTANE = 1.200857
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = [illegible]

Weight Distribution of Prudhoe Bay Crude by Fraction

| Fraction | Weight (mg/g) |
|---|---|
| 1 | 879 |
| 2 | 75 |
| 3 | 613 |

TABLE 3-7. PRUDHOE BAY CRUDE OIL CONCENTRATIONS FOR AROMATIC FRACTION,

FRACTION:2 HP-RUN-DATE: 9/22/1981 mua-7i0i 72 HP-SOT-NO: 9

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SU BGROUP | GO VAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 5.0700 | 0 | 0 | | | 198.85 |
| 1.S0 | 5.1400 | 700 | 0 | 0 | | .00000 |
| 2.00 | 5.2000 | 700 | 0 | 0 | 1.720 | 30. s.23 |
| 3.00 | 5.3200 | 708 | 0 | 0 | 1.720 | 10S0.7 |
| *.00 | 5.5900 | 719 | 0 | 0 | 1.720 | 259.28 |
| See | 5.7200 | 725 | 0 | 0 | 1.720 | 40.506 |
| 6.00 | 6.5500 | 761 | 0 | 0 | 1.720 | 1362.0 |
| 7.00 | 6.6500 | 765 | o | 0 | 1.720 | 31.096 |
| 8.00 | 7.1300 | 786 | 0 | 0 | 1.720 | 29.295 |
| 9.00 | 7.2600 | 792 | 0 | 0 | 1.720 | 89.482 |
| 9.50 | 7.4s00 | 800 | 0 | 0 | .0000 | .00000 |
| 10.0 | 7.4500 | 800 | o | 0 | 1.720 | 93.026 |
| 11.0 | 7.6600 | 805 | 0 | 0 | 1.720 | 28.500 |
| 12.0 | 10.040 | 841 | 0 | 0 | 1.720 | 474.62 |
| 13.0 | 10.390 | 870 | 0 | 0 | 1.720 | 1794.1 |
| 13.5 | 11.470 | 9 o o | 0 | 0 | .0000 | .00000 |
| 14.0 | 11.910 | 905 | 0 | 0 | 1.720 | 88.766 |
| 15.0 | 12.870 | 925 | o | 0 | 1.720 | 118.70 |
| 16.0 | 14.830 | 949 | 0 | 0 | 1.720 | 90. 858 |
| 17.0 | 14.270 | 954 | 0 | 0 | 1.720 | 220.08 |
| 18. O | 14.680 | 963 | 0 | 0 | 1.720 | 736.48 |
| 19.0 | 18.970 | 969 | 0 | 0 | 1.720 | 309.65 |
| 20.0 | 15. 530 | 980 | 0 | 0 | 1.720 | 299.91 |
| 21.0 | 16.160 | 993 | 0 | 0 | 1.720 | 926.70 |
| 21.5 | 16.488 | 1000 | a. | 0 | .0000 | .00000 |
| 22.0 | 17.040 | 1012 | 0 | 0 | 1.720 | 60.596 |
| 23.0 | 17. boo | 1023 | 0 | 0 | 1.720 | 452.93 |
| 24.0 | 18.240 | 1036 | 0 | 0 | 1.720 | 55.931 |
| 25.0 | 19.030 | 1053 | o | 0 | 1.720 | 304.00 |
| 2*. O | 19.250 | 1057 | o | 0 | 1.720 | 94.556 |
| 27.0 | 19.380 | 1060 | 0 | 0 | 1.720 | 75.039 |
| 28.0 | 19.770 | 1062. | 0 | 0 | 1.720 | 168.90 |
| 29.0 | 20.340 | 1080 | 0 | 0 | 1.720 | 326.51 |
| 30.0 | 20.680 | 1 087 | 0 | 0 | 1.720 | 261.53 |
| 3s.0 | 20.970 | 1095 | o | 0 | 1.720 | 31.137 |
| 31.5 | 21.320 | 1100 | 0 | 0 | .0000 | .00000 |
| 32.0 | 21.410 | 1102 | 0 | 0. | 1.720. | 25.659 |
| 3s.0 | 21.630 | 1107 | 0 | 0 | 1.720 | 23.976 |
| 34.0 | 23.190 | 1140 | o | 0 | 1.720 | 164.11 |
| 35.0 | 23.480 | 1147 | 0 | 0 | 1.720 | 210.96 |
| 36.0 | 23.820 | 1154 | o | 0 | 1.720 | 152.70 |
| 37.0 | 24.090 | 1159 | o | 0 | 1.720 | 58.627 |
| 38.0 | 24.360 | 1164 | 0 | 0 | 1.720 | 126.06 |
| 39.0 | 24.500 | 1169 | o | 0 | 1.720 | 127.45 |
| 80.0 | 24.870 | 1177 | o | 0 | 1.720 | 85.472 |
| 41.0 | 25.290 | 1186 | 0 | 0 | 1.720 | 20.66 |
| 42.0 | 25.540 | 1191 | o | 0 | 1.720 | 27.456 |
| 43.0 | 25.710 | 1195 | o | 0 | 1.720 | 92.759 |
| 44.0 | 25.830 | 1200 | 0 | 0 | 1.720 | 135.14 |
| 45.0 | 25.940 | 1200 | 0 | 0 | 1.720 | .00000 |
| 46.0 | 26.160 | 120s | 0 | 0 | 1.720 | 27.690 |
| 47.0 | 26.450 | 1211 | 0 | 0 | 1.720 | 21.965 |
| 48.0 | 27.130 | 1227 | 0 | 0 | 1.720 | 17x. 69 |
| 49.0 | 27.670 | 1239 | 0 | 0 | 1.720 | 106.25 |
| 50.0 | 28.010 | 1247 | a. | 0 | 1.720 | --laq.a$- |
| 91.0 | 28.240 | 1252 | 0 | 0 | 1.720 | 91.939 |
| 52.0 | 28.650 | 1262 | 0 | 0 | 1.720 | 76.356 |
| 53.0 | 28.950 | 1269 | 0 | 0 | 1.720 | 184.60 |
| 54.0 | 29.410 | 1279 | o | 0 | 1.720 | 57.255 |
| 55.0 | 29.600 | 1283 | 0 | 0 | 1.720 | 60.080 |
| 56. 0 | 30.200 | 1297 | 0 | 0 | 1.720 | 1250.5 |
| 57.0 | 30.300 | 1300 | 0 | 0 | 1.720 | .00000 |
| 58.0 | 30.560 | 1306 | 0 | 0 | 1.710 | 77.748 |
| 59.0 | 30.940 | 1315 | 0 | 0 | 1.700 | 737.95 |
| 60.0 | 31.270 | 1323 | 0 | 0 | 1.690 | 149.40 |
| 61.0 | 31.880 | 1330 | 0 | 0 | 1.670 | 46.904 |
| b a a | 32.160 | 1348 | 0 | 0 | 1.660 | 46.013 |
| 63.0 | 32.620 | 1356 | 0 | 0 | 1.650 | 25.069 |
| 64.0 | 3a. 870 | 1362 | 0 | 0 | 1.640 | 47.801 |
| 65.0 | 33.260 | 1372 | 0. | 0 | 1.630 | 30.491 |
| 66.U | 3s.760 | 1384 | 0 | 0 | 1.610 | 125.32 |
| 67.0 | 34.330 | 15*FJ | 0 | 0 | 1.600 | 176.99 |
| 68.0 | 34.610 | 1400 | 0 | 0 | 1.590 | .00000 |
| b?. O | 38. 500 | 1402 | 0 | 0 | 1.600 | 33.488 |
| 70.0 | 34.780 | 1409 | 0 | 0 | 1.610 | 530.99 |
| 11.0 | 39.390 | 1425 | 0 | 0 | 1.630 | 359.91 |
| 7a. o | 35.s10 | 1428 | 0 | 0 | 1.630 | 171.79 |
| ?3.0 | 35.920 | 1438 | 0 | 0 | 1.640 | 25.701 |
| 74.0 | 36.160 | 1445 | 0 | 0 | 1 .A% | 1●3.qo |
| 75.0 | 36.290 | 1448 | 0 | 0 | 1.650 | 40.603 |
| 7*. O | 36.770 | 1460 | 0 | 0 | 1.670 | 277.89 |
| 77.0 | 37.350 | 1475 | o | 0 | 1.690 | 84.677 |
| 78.0 | 37.940 | 1490 | 0 | 0 | 1.710 | 155.97 |
| 79.0 | 38.290 | 1900 | 0 | 0 | 1 .720 | .00000 |
| 80.0 | 38.320 | 1s00 | 0 | 0 | 1.720 | 138.36 |
| 81.0 | 38.670 | 1s10 | 0 | 0 | 1.71O | 209.85 |
| 82.0 | 3*4.110 | 1522 | 0 | 0 | 1.71O | 61.565 |
| 83.0 | 39.350 | 1528 | 0 | 0 | 1.710 | 76.088 |
| 84.0 | 39.4*O | 1532 | 0 | 0 | 1.710 | 67.565 |
| 09.0 | 39.660 | 1537 | 0 | 0 | 1.700 | 163.18 |
| 86. 0 | 39.980 | 1546 | 0 | 0 | 1.700 | 50.688 |
| 87.0 | 40.270 | 1554 | 0 | 0 | 1.700 | 360.57 |
| 80.0 | 40.910 | 1571 | 0 | 0 | 1.690 | 382.99 |
| 89.0 | 41.580 | 1509 | 0 | 0 | 1.680 | 83.018 |
| 90.0 | a/.790 | 1595 | 0 | 0 | 1.680 | 105.44 |
| 91.0 | 41.990 | 1600 | 0 | 0 | 1.660 | .00000 |
| 92.0 | 42.140 | 160s | 0 | 0 | 1.700 | 23.659 |
| 93.0 | 42.800 | 1624 | 0 | 0 | 1.770 | 65.828 |
| 94.0 | ●2.990 | 1629 | 0 | 0 | 1.790 | 56.629 |
| 95.0 | 43.430 | 1642 | 0 | 0 | 1.530 | 51.286 |
| 96.0 | 43.970 | 1656 | 0 | 0 | 1.890 | 30.'977 |

FRACTION:2 HP-RUN-DATE: 9/22/1981 HP-RUN-NO: 72 HP-SOT-NO: 9

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 97.0 | 44.550 | 1674 | o | 0 | 1.950 | 23.556 |
| 98.0 | .720 | | | | | 23.060 |
| 9*. O | 84.870 | 1683 | o | 0 | 1.980 | 28.234 |
| 100. | 45.300 | 1696 | 0 | 0 | 2.020 | 26.795 |
| 101. | .430 | 700 | | | | .00000 |
| 102. | 45.630 | 1V1O | 0 | 0 | 2.200 | 106.89 |
| 103. | 45.940 | 1715 | 0 | 0 | 1.980 | 179.71 |
| 104. | 46.320 | 1727 | 0 | 0 | 1.960 | 80.193 |
| 109. | 46.590 | 1735 | o | 0 | 1.930 | 24.762 |
| 106. | 46.890 | 1744 | 0 | o | 1.900 | 102.68 |
| 107. | 47.540 | 1764 | 0 | o. | 1.850 | .202.57 |
| 108. | 48.450 | 1791 | 0 | 0 | 1.760 | 198.98 |
| 109. | 48.720 | 1800 | 0 | 0 | 1.740 | .00000 |
| 110. | 49.060 | 1815 | 4 | 0 | 1.700 | .00000 |
| 111. | 49.560 | 1826 | 0 | 0 | 1.960 | 46.389 |
| 1ts. | 49.800 | 1834 | 0 | 0 | 2.070 | 83.000 |
| 113. | 50.010 | 1841 | 0 | 0 | 2.130 | 43.110 |
| 114. | So. 820 | 1866 | 0 | 0 | 2.380 | 227.38 |
| 115. | 50.980 | 1871 | 0 | 0 | 2.430 | 36.169 |
| 116. | 51.170 | 1878 | 0 | 0 | 2.480 | 93.966 |
| 117. | 91. 470 | 16s7 | 0 | 0 | 2.570 | 131.40 |
| 118. | 51.670 | 1893 | 0 | 0 | 2.630 | 61.880 |
| 119. | 51.860 | 1900 | 0 | 0 | 2.690 | .00000 |
| 120. | 52.110 | 190e | 0 | 0 | 2.630 | 96.167 |
| 121. | 52.290 | 1910 | 0 | 0 | 2.500 | 102.86 |
| 122. | 52.910 | 1935 | 0 | 0 | 2.410 | 180.62 |
| 123. | 53.060 | 1940 | 0 | 0 | 2.370 | 75.793 |
| 124. | 53.940 | 1949 | 0 | 0 | 2.130 | 72.737 |
| 125. | 54.790 | 1997 | 0 | 0 | 1.900 | 25.529 |
| 126. | 54.850 | 2000 | 0 | 0 | 1.890 | .00000 |
| 127. | 55.140 | 2010 | 0 | 0 | 1.890 | 22.603 |
| 128. | 55.860 | 2035 | 0 | 0 | 1.890 | 28.007 |
| 129. | 56.290 | 2050 | 0 | 0 | 1.900 | 218.64 |
| 130. | 56.500 | ao57 | 0 | 0 | 1.900 | 67.069 |
| 131. | 56.670 | 2063 | 0 | 0 | 1.900 | 28.102 |
| 132. | 57.010 | 2075 | 0 | 0 | 1.900 | 52.911 |
| 133. | 57.340 | 2087 | 0 | 0 | 1.900 | 115.85 |
| 134. | 57.660 | 2098 | 0 | 0 | 1.910 | 85.896 |
| 135. | 57.710 | 2100 | 0 | 0 | 1.910 | .00000 |
| 136. | 58.280 | 2120 | 0 | 0 | 1.900 | 63.968 |
| 137. | 59.440 | 2163 | 0 | 0 | 1.880 | 67.191 |
| 138. | 59.700 | 2172 | 0 | 0 | 1.880 | 112.33 |
| 139. | 60.160 | 2189 | 0 | 0 | 1.870 | 28.102 |
| 140. | 60.440 | 2208 | 0 | 0 | 1.870 | .00000 |
| 141. | 60.500 | 2202 | 0 | 0 | 1 .S20 | 45.016 |
| 142. | 61.930 | 2256 | 0 | 0 | 1.870 | 67.085 |
| 143. | 63.040 | 2298 | 0 | 0 | 1.870 | 23.278 |
| 1ea. | 63.070 | 2300 | 0 | 0 | 1.870 | .00000 |
| 145. | 63.680 | 2328 | 0 | 0 | 1.830 | 23.304 |
| 146. | 65.530 | 2808 | 0 | 0 | 1.700 | .00000 |
| 147. | 67.740 | 2469 | 0 | 0 | 1.660 | 29.996 |
| 148. | 67.990 | 2900 | 0 | 0 | 1.650 | .00000 |
| 149. | 69.240 | 2552 | 0 | 0 | 1.650 | 41.619 |
| 150. | 70.370 | 2600 | 0 | 0 | 1.650 | .00000 |
| 151. | 70.590 | 2607 | 0 | 0 | 1.700 | 25.283 |
| 152. | 7s.1s0. | 2700 | 0 | 0. | 2.300 | .00000 |
| 193. | 76.440 | 2800 | 0 | 0 | 1.640 | .00000 |
| 154. | 80.500 | 2900 | 0 | 0 | 1.680 | .00000 |
| 155. | 85.500 | 3000 | 0 | 0 | 1.8s0 | .00000 |
| 156. | 91.750 | 3s 00 | 0 | 0 | 3.840 | .00000 |

TOTAL RESOLVED HYDROCARBON = 22520.58
TOTAL UNRESOLVED HYDROCARBON = 36669.98
RESPONSE FACTOR AV. FOR C - 1400 TO 3200 FOR UCM = 1.965737
RATIO: RESOLVED/UNRESOLVED = 0.614142

SUM OF THE N-ALKANES = 0
SUM OF THE EVEN N-ALKANES = 0
SUM OF THE ODD N-ALKANES = 0

TABLE 3-8. WILMINGTON CRUDE OIL CONCENTRATIONS FOR ALIPHATIC FRACTION.

FRACTION:1 HP-RUN-DATE:10/21/1981 HP-RUN-NO: 34 HP-BOT-NO: 1

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 9.0100 | 0 | 0 | 0 | 1.440 | 540.74 |
| 2.00 | 5.1600 | 0 | 0 | 0 | 1.440 | 17970. |
| 3.00 | 5.3200 | 0 | 0 | 0 | 1.440 | 1414.6 |
| 4.00 | 5.7900 | 0 | 0 | 0 | 1.440 | 1043.3 |
| 5.00 | 15.120 | 0 | 0 | 0 | 1.440 | 82.352 |
| 6.00 | 16.460 | 0 | 0 | 0 | 1.440 | 76.485 |
| 7.00 | 16.650 | 0 | 0 | 0 | 1.440 | 91.486 |
| 8.00 | 17.790 | 1000 | 0 | 0 | 1.440 | 77.525 |
| 9.00 | 18.210 | 1009 | 0 | 0 | 1.440 | 78.936 |
| 10.0 | 19.060 | 1027 | 0 | 0 | 1.440 | 92.822 |
| 11.0 | 19.670 | 1040 | 0 | 0 | 1.440 | 82.797 |
| 12.0 | 20.900 | 1066 | 0 | 0 | 1.440 | 145.77 |
| 13.0 | 21.400 | 1076 | 0 | 0 | 1.440 | 111.46 |
| 10.0 | 21.710 | 1083 | 0 | 0 | 1.440 | 80.644 |
| 15.0 | 23.200 | 1115 | 0 | 0 | 1.440 | 77.228 |
| 16.0 | 23.460 | 1120 | 0 | 0 | 1.440 | 80.198 |
| 17.9 | 23.900 | 1131 | 0 | 0 | 1.S340 | 317.65 |
| 1.3.0 | 24.640 | 1105 | 0 | 0 | 1.440 | 109.53 |
| 19.0 | 24.900 | 11S1 | 0 | 0 | 1.440 | 10.2.62 |
| 20.0 | 25.750 | 1169 | 0 | 0 | 1.440 | 225.82 |
| 21.0 | 26.400 | 11S2 | 0 | 0 | 1.440 | 172.95 |
| 22.0 | 26.720 | 1189 | 0 | 0 | 1.440 | 167.45 |
| 23.0 | 27.230 | 1200 | 0 | 0 | 1.430 | 236.43 |
| 24.0 | 26.520 | 1229 | 0 | 0 | 1.440 | 106.79 |
| 25.0 | 29.S30 | 1252 | 0 | 0 | 1.440 | 139.65 |
| 26.0 | 30.010 | 1263 | 0 | 0 | 1.440 | 143..S2 |
| 27.0 | 31.580 | 1300 | 0 | 0 | 1.450 | 139.56 |
| 28.0 | 33.270 | 1340 | 0 | 0 | 1.420 | 75.580 |
| 29.0 | 33.530 | 1340 | 0 | 0 | 1.410 | .705.90 |
| 30.0 | 34.210 | 1362 | 0 | 0 | 1.400 | 83.654 |
| 31.0 | 35.760 | 1400 | 0 | 0 | 1.3.S0 | .00000 |
| 32.0 | 36.910 | 1426 | 0 | 0 | 1.410 | 128.37 |
| 33.0 | 37.280 | 14ab | 0 | 0 | 1.440 | 117.04 |
| 38.0 | 37.0?0 | 1453 | 0 | 0 | 1.450 | 122.81 |
| 3s.0 | 38.460 | 1462 | 0 | 0 | 1.460 | 295..?4 |
| 36.0 | 38.850 | 1471 | 0 | 0 | 1.470 | 249.05 |
| 37.0 | 40.100 | 1S00 | 0 | 0 | 1.s10 | 85.398 |
| 38.0 | 4.?.500 | 1600 | 0 | 0 | .1.500 | 93.802 |
| 39.0 | ● a.5ao | 1647 | 0 | 0 | 1.s50 | 140.10 |
| 40.0 | 46.080 | 1685 | 0 | 0 | 1.580 | 287.25 |
| 41.0 | 46.300 | 1690 | 0 | | 590 | 113.58 |
| 42.0 | 46.710 | 1700 | 0 | 0 | 1.600 | 153.16 |
| 43.0 | 48.140 | 1710 | 0 | 0 | 1.500 | 350.08 |
| 44.0 | | 1800 | 0 | 0 | 1.510 | 102.09 |
| 45.0 | | 1815 | 0 | 0 | 1.440 | 127.47 |
| 4?.O | 53.340 | 1900 | 0 | 0 | 2.160 | .00000 |
| 47.0 | 56.030 | 2000 | 0 | 0 | 1.560 | 101.89 |
| 48.0 | 57.160 | 2035 | 0 | 0 | 1.580 | 82.645 |
| 49.0 | 59..?40 | 2100 | 0 | 0 | 1.610 | .00000 |
| 50.0 | -63.110 | 2200 | 0 | 0 | 1.650 | 279.55 |
| 51.0 | 65.270 | .3300 | 0 | 0 | 1.740 | 117.53 |
| 52.0 | 66.0s0 | 2400 | 0 | 0 | 1.630 | 160.37 |
| 53.0 | 69.610 | 2500 | 0. | 0. | 1.670.. | .00000 |
| 50.0 | 7,3.300 | 2600 | 0 | 0 | 1.7.?0 | .00000 |
| 55.0 | 74.610 | 2700 | 0 | 0 | 2.s60 | 342.38 |
| 56.0 | 79.280 | 2800 | .0 | 0 | 1.770 | .00000 |
| 57.0 | 84.000 | 2900 | 0 | 0 | .850 | .00000 |
| 59.0 | 91 .s30 | 3000 | 0 | 0 | 1.920 | 213.71 |
| 59.0 | 94.360 | 3049 | 0 | 0 | 2.270 | 325.16 |
| 60.0 | 97.230 | 3100 | 0 | 0 | 2.630 | .00000 |
| 61.0 | 100.76 | 3138 | 0 | 0 | 2.520 | 138.29 |
| 62.0 | 106.49 | 3.?00 | 0 | 0 | 2.320 | .00000 |

TOTAL RESOLVED HYDROCARBON = 28358.51
TOTAL UNRESOLVED HYDROCARBON = 179975
RESPONSE FACTOR AV. FOR C - 1000 TO 3100 FOR UCM = 1.762911
RATIO: RESOLVED/UNRESOLVED = 0.157569

SUM OF THE N-ALKANES . 2023.472
SUM OF THE EVEN N-ALKANES = 1185.446
SUM OF THE ODD N-ALKANES . 838.0258

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 0.236006
RATIO: ODD/EVEN N-ALKANES = 0.706929
RATIO: PRISTANE/C-17 = 2.285708
RATIO: PHYTANE/C-18 = 1.248612
RATIO: PRISTANE/PHYTANE = 2.746258
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = 7.683572E-2

Weight Distribution of Wilmington Crude by Fraction

| Fraction | Weight (mg/g) |
|---|---|
| 1 | 205 |
| 2 | 335 |
| 3 | 204 |

TABLE 3-9. WILMINGTON CRUDE OIL CONCENTRATIONS FOR AROMATIC FRACTION.

FRACTION: HP-RUN-DATE: 10/21/1981 HP-RUN-NO: 55 HP-BUT-NO: 9

| PEAK NUMBER | RETENTION TIME | KOVAT INDEX | KOVAT SUBGROUP | KOVAT GROUP | RESPONSE FACTOR | CONCENTRATION TOTAL |
|---|---|---|---|---|---|---|
| 1.00 | 5.3500 | 0 | 0 | 0 | 1.440 | 273.42 |
| 2.00 | 5.6000 | 0 | 0 | 0 | 1.440 | 507.48 |
| 2.50 | 5.6200 | 700 | 0 | 0 | .0000 | .00000 |
| 3.00 | 5.8200 | 705 | 0 | 0 | 1.440 | 2570.7 |
| 4.00 | 5.9000 | 706 | 0 | 0 | 1.440 | 170.29 |
| 5.00 | 6.3600 | 717 | 0 | 0 | 1.440 | 1402.1 |
| 6.00 | 6.6400 | 724 | 0 | 0 | 1.440 | 584.55 |
| 7.00 | 7.6300 | 746 | 0 | 0 | 1.440 | 442.19 |
| 8.00 | 27.240 | 1200 | 0 | 0 | 1.430 | .00000 |
| 9.00 | 31.620 | 1300 | 0 | 0 | 1.450 | .00000 |
| 10.0 | 35.760 | 1400 | 0 | 0 | 1.380 | .00000 |
| 11.0 | 39.660 | 1500 | 0 | 0 | 1.510 | .00000 |
| 12.0 | 43.360 | 1600 | 0 | 0 | 1.500 | .00000 |
| 13.0 | 44.550 | 1634 | 0 | 0 | 1.530 | 232.30 |
| 14.0 | 46.810 | 1698 | 0 | 0 | 1.600 | 103.07 |
| 15.0 | 46.860 | 1700 | 0 | 0 | 1.600 | .00000 |
| 16.0 | 47.080 | 1710 | 0 | 0 | 1.500 | .00000 |
| 17.0 | 47.880 | 1730 | 0 | 0 | 1.570 | 100.29 |
| 18.0 | 50.180 | 1800 | 0 | 0 | 1.510 | .00000 |
| 19.0 | 50.510 | 1815 | 0 | 0 | 1.440 | .00000 |
| 20.0 | 53.340 | 1900 | 0 | 0 | 2.160 | .00000 |
| 21.0 | 53.700 | 1911 | 0 | 0 | 2.080 | 200.20 |
| 22.0 | 56.050 | 1989 | 0 | 0 | 1.620 | 189.65 |
| 23.0 | 56.360 | 2000 | 0 | 0 | 1.560 | .00000 |
| 24.0 | 57.390 | 2035 | 0 | 0 | 1.580 | 113.34 |
| 25.0 | 57.920 | 2054 | 0 | 0 | 1.580 | 184.18 |
| 26.0 | 59.240 | 2100 | 0 | 0 | 1.610 | .00000 |
| 27.0 | 61.090 | 2167 | 0 | 0 | 1.630 | 156.63 |
| 28.0 | 61.370 | 2177 | 0 | 0 | 1.640 | 113.98 |
| 29.0 | 61.990 | 2200 | 0 | 0 | 1.650 | .00000 |
| 31.0 | 64.630 | 2300 | 0 | 0 | 1.740 | .00000 |
| 31.0 | 65.440 | 2331 | 0 | 0 | 1.710 | 101.68 |
| 32.0 | 67.170 | 2400 | 0 | 0 | 1.630 | .00000 |
| 33.0 | 69.610 | 2500 | 0 | 0 | 1.670 | .00000 |
| 34.0 | 72.300 | 2600 | 0 | 0 | 1.720 | .00000 |
| 35.0 | 75.440 | 2700 | 0 | 0 | 2.560 | .00000 |
| 36.0 | 79.280 | 2800 | 0 | 0 | 1.770 | .00000 |
| 37.0 | 84.000 | 2900 | 0 | 0 | 1.850 | .00000 |
| 38.0 | 89.860 | 3000 | 0 | 0 | 1.920 | .00000 |
| 39.0 | 97.230 | 3100 | 0 | 0 | 2.630 | .00000 |
| 40.0 | 106.49 | 3200 | 9.. | 0 | 2.320 | .00000 |

TOTAL RESOLVED HYDROCARBON = 7446.003
TOTAL UNRESOLVED HYDROCARBON = 67236.01
RESPONSE FACTOR AV. FOR C - 1600 TO 3100 FOR UCM = 1.821669
RATIO: RESOLVED/UNRESOLVED = 0.1107443

SUM OF THE N-ALKANES = 0
SUM OF THE EVEN N-ALKANES = 0
SUM OF THE ODD N-ALKANES = 0

RATIO: (PRISTANE+PHYTANE)/(N-ALKANES) = 0
RATIO: ODD/EVEN N-ALKANES = 0
RATIO: PRISTANE/C-17 = 0
RATIO: PHYTANE/C-18 = 0
RATIO: PRISTANE/PHYTANE = 0
RATIO: (N-ALKANES)/(BRANCHED HYDROCARBONS) = 0

TABLE 3-10. POLAR (F3) FRACTION COMPONENTS FOR THE FOUR SELECTED CRUDES.

Murban Crude Oil Concentrations for Polar Fraction

| Retention Time (rein) | Ko va t | Concentration (μg/g) |
|---|---|---|
| 18.95 | 1026 | 121. |
| 78.75 | 2787 | 116. |

Cook Inlet Crude Oil Concentrations for Polar Fraction

| Retention Time (rein) | Ko va t | Concentration (μg/g) |
|---|---|---|
| 18.99 | 1026 | 151. |
| 78.80 | 2787 | 111. |

Prudhoe Bay Crude Oil Concentrations for Polar Fraction

| Retention Time (rein) | Kovat | Concentration (μg/g) |
|---|---|---|
| 5.14 | 640 | 6 4 . 4 |
| 8.55 | 806 | 49.6 |
| 9.14 | 861 | 28.4 |

Wilmington Crude Oil Concentrations for Polar Fraction

| Retention Time (rein) | Kovat | Concentration (μg/g) |
|---|---|---|
| 18.99 | 1026 | 211. |
| 78.76 | 2787 | 224. |

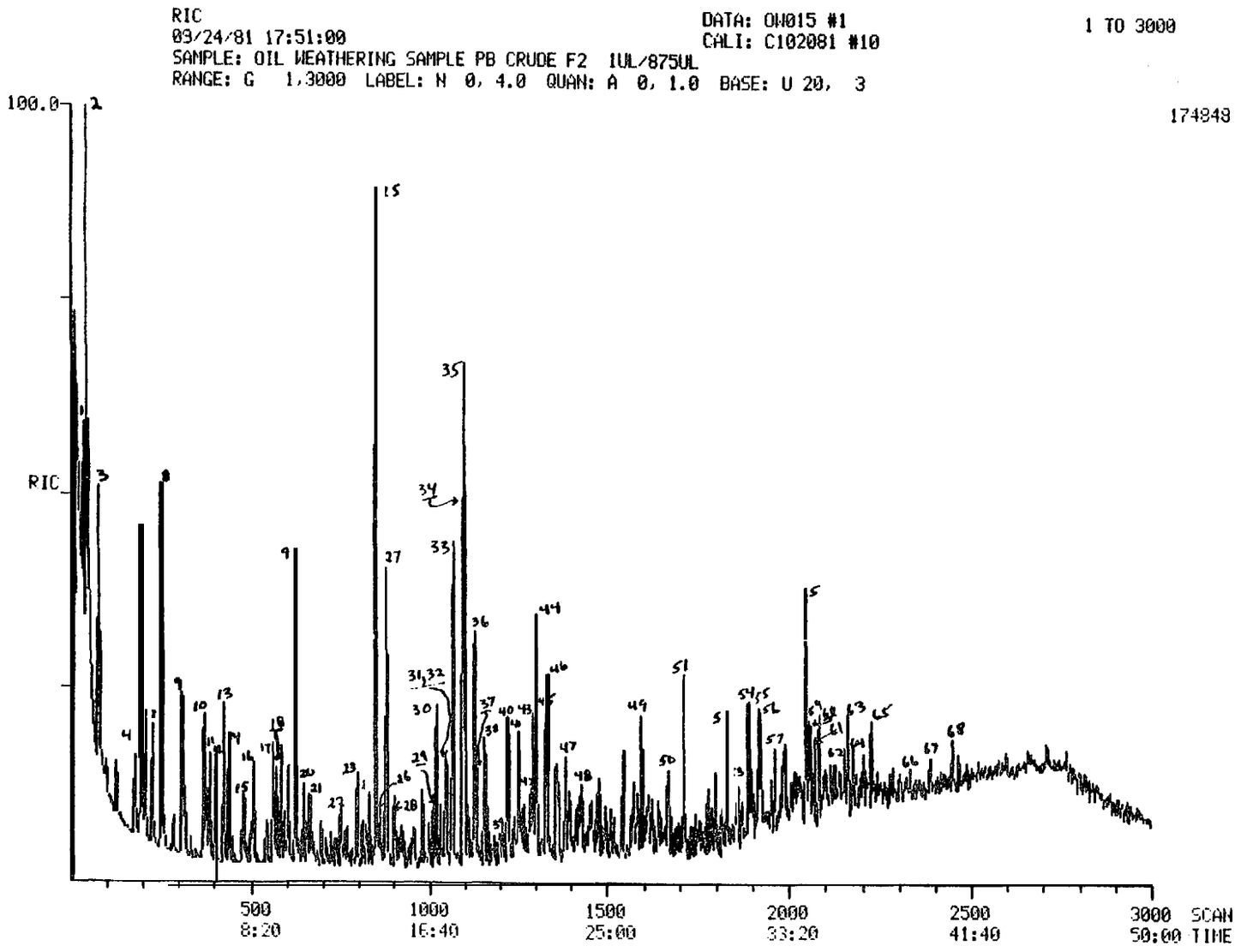



FIGURE 3-5. RECONSTRUCTED ION CHROMATOGRAM RIC) GENERATED FROM GC/MS ANALYSES OF THE AROMATIC FRACTION (F2) OF PRUDHOE BAY CRUDE OIL. IDENTIFICATIONS OF THE NUMBERED PEAKS ARE PRESENTED IN TABLE 3-11.

TABLE 3-11. GC/MS IDENTIFICATIONS OF SELECTED COMPONENTS IN THE AROMATIC FRACTION OF PRUDHOE BAY CRUDE OIL (SEE FIGURE 3-5).

| | |
|---|---|
| 1 | ethyl benzene |
| 2 | p-xylene |
| 3 | o-xylene |
| 4 | n-propylbenzene |
| 5 | ethylmethyl benzene |
| 6 | trimethy?benzene |
| 7-9 | $C_3$ benzenes |
| 10 | methylpropyl benzene |
| 11-13 | $C_4$ benzenes |
| 14 | ethyldimethyl benzene |
| 15 | $C_4$ benzene |
| 16 | tetramethyl benzene |
| 17 | unsaturated C4 benzene (possibly a methyl indane) |
| 18 | $C_4$ benzene |
| 19 | naphthalene |
| 20,21 | unsaturated $C_5$ benzenes (possibly $C_2$ indanes) |
| 22 | unsaturated $C_6$ benzene (possibly a $C_2$ tetral in) |
| 23,24 | $C_6$ benzenes |
| 25 | 2-methyl naphthalene |
| 26 | unsaturated $C_6$ benzene (possibly a $C_2$ tetral in) |
| 27 | l-methyl naphthalene |
| 28 | unsaturated $C_6$ benzene (possibly a $C_2$ tetral in) |
| 29 | $C_7$ benzene |
| 30 | biphenyl |
| 31 | 2-ethylnaphthal ene |
| 32 | l-ethyl naphthalene |
| 33-38 | dimethylnaphthal enes |
| 39 | $C_3$ naphthalene |
| 40 | methylbiphenyl |
| 41 | 2-isopropylnaphthal ene |
| 42 | l-isopropylnaphthalene |
| 43-46 | trimethylnaphthal enes |
| 47 | fluorene |
| 48 | dimethylbiphenyl |
| 49 | methylfluorene |
| 50 | dibenzothiophene |
| 51 | phenanthrene |
| 52,53 | methyl dibenzothiophenes |
| 54-56 | methyl phenanthrenes |
| 57 | $C_2$ napthothiophenes |
| 58-61 | dimethyl phenanthrenes |
| 62-65 | $C_3$ phenanthrenes |
| 66 | benzonaphthothiophene |
| 67 | chrysene or benz (a)anthracene |
| 68 | phthalate ester |

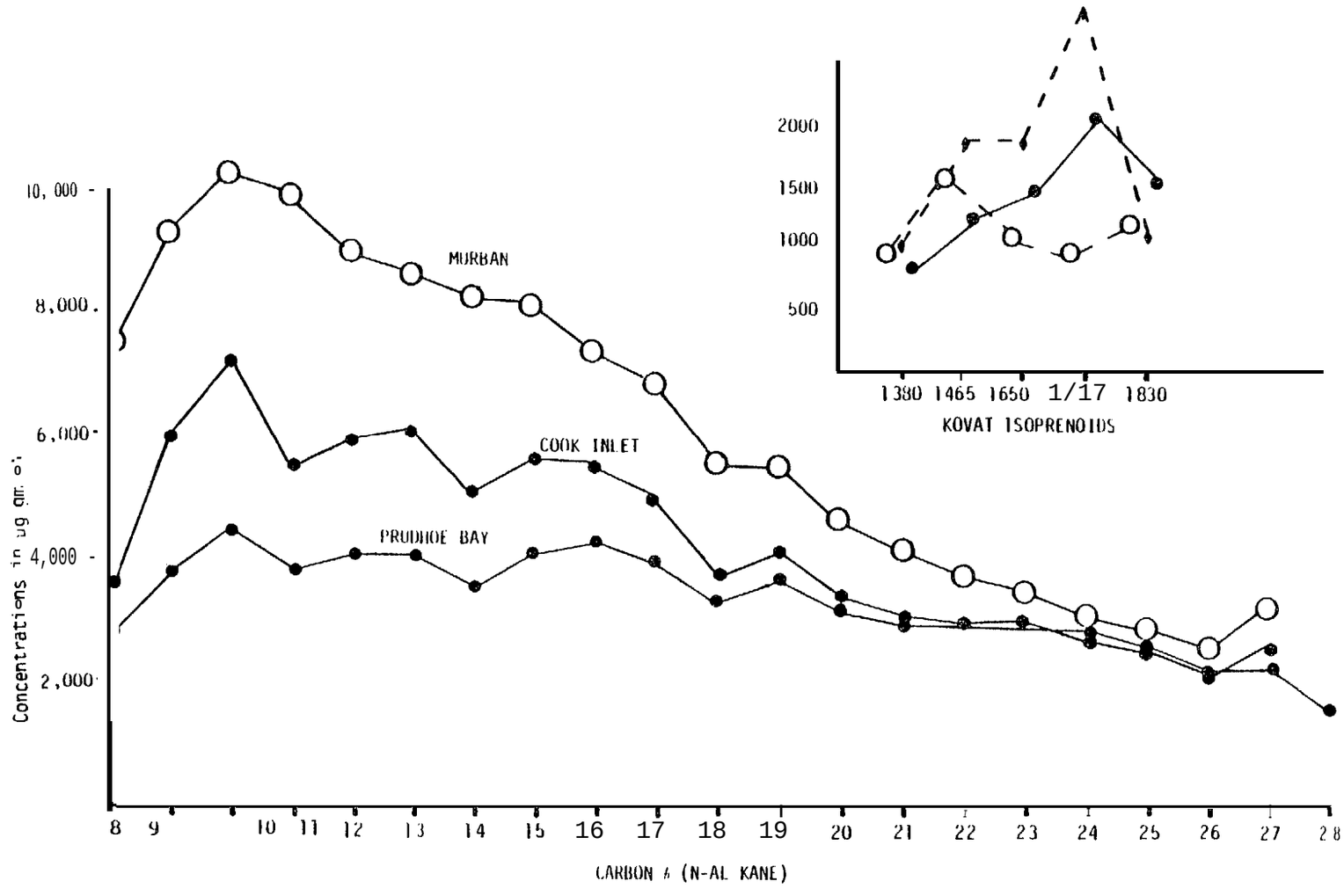
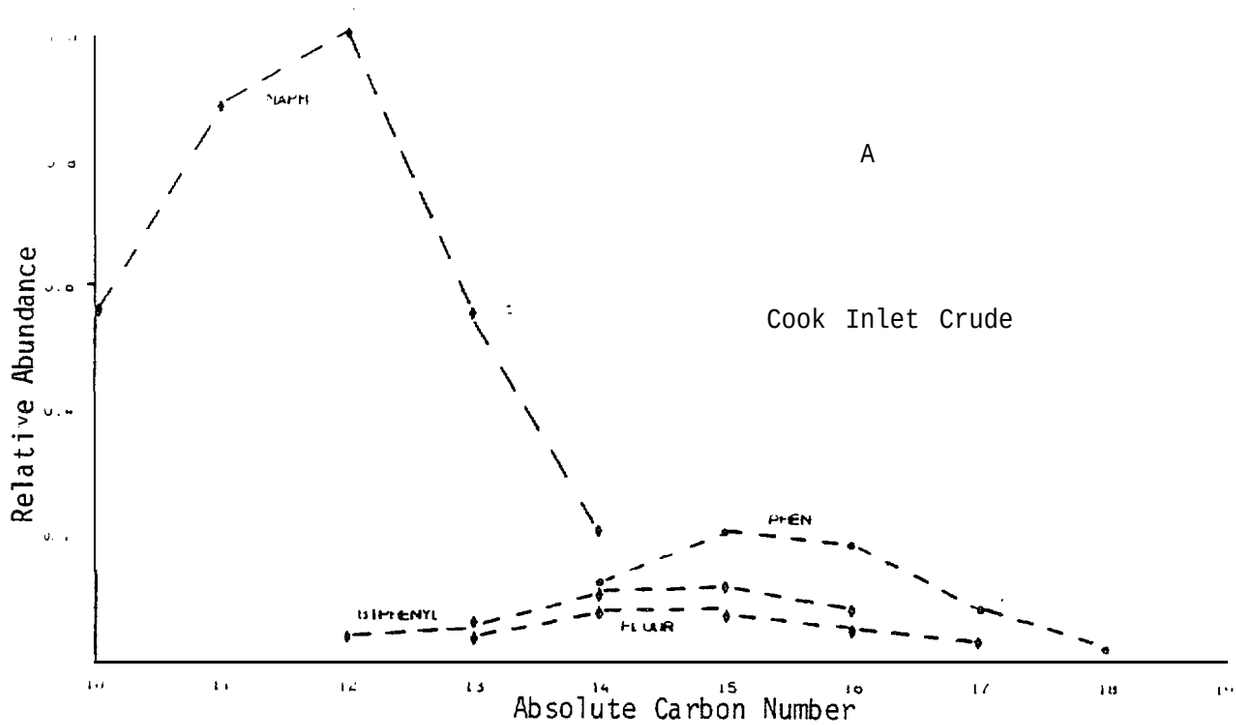



FIGURE 3-6. ALIPHATIC (n-alkane and isoprenoid) CARBON DISTRIBUTIONS FOR PRUDHOE BAY, COOK INLET AND MURBAN (middle east) CRUDE OILS.



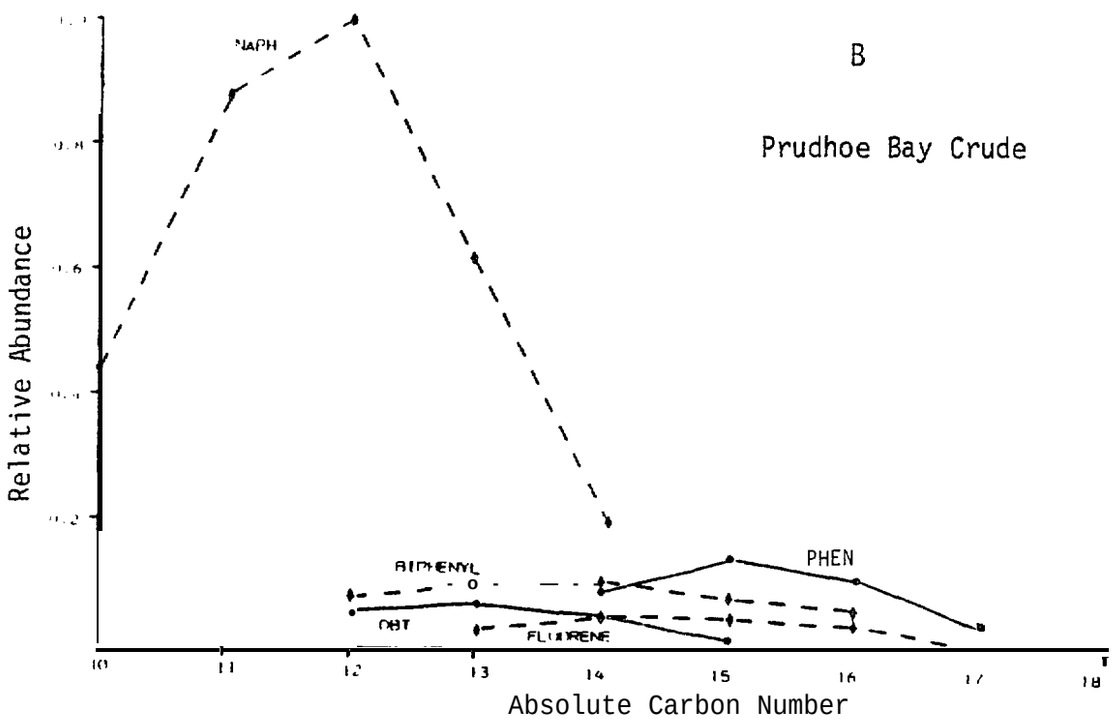




FIGURE 3-7. RELATIVE ABUNDANCE PLOTS FROM SELECTIVE ION MONITORING (GCMS) OF THE MAJOR ALKYL SUBSTITUTED AROMATIC SERIES DETECTED IN COOK INLET (TOP) AND PRUDHOE BAY (BOTTOM) OILS. (NAPH - naphthalene; PHEN- phenanthrenes; DBT - dibenzothiophenes; FLUOR - fluorenes)

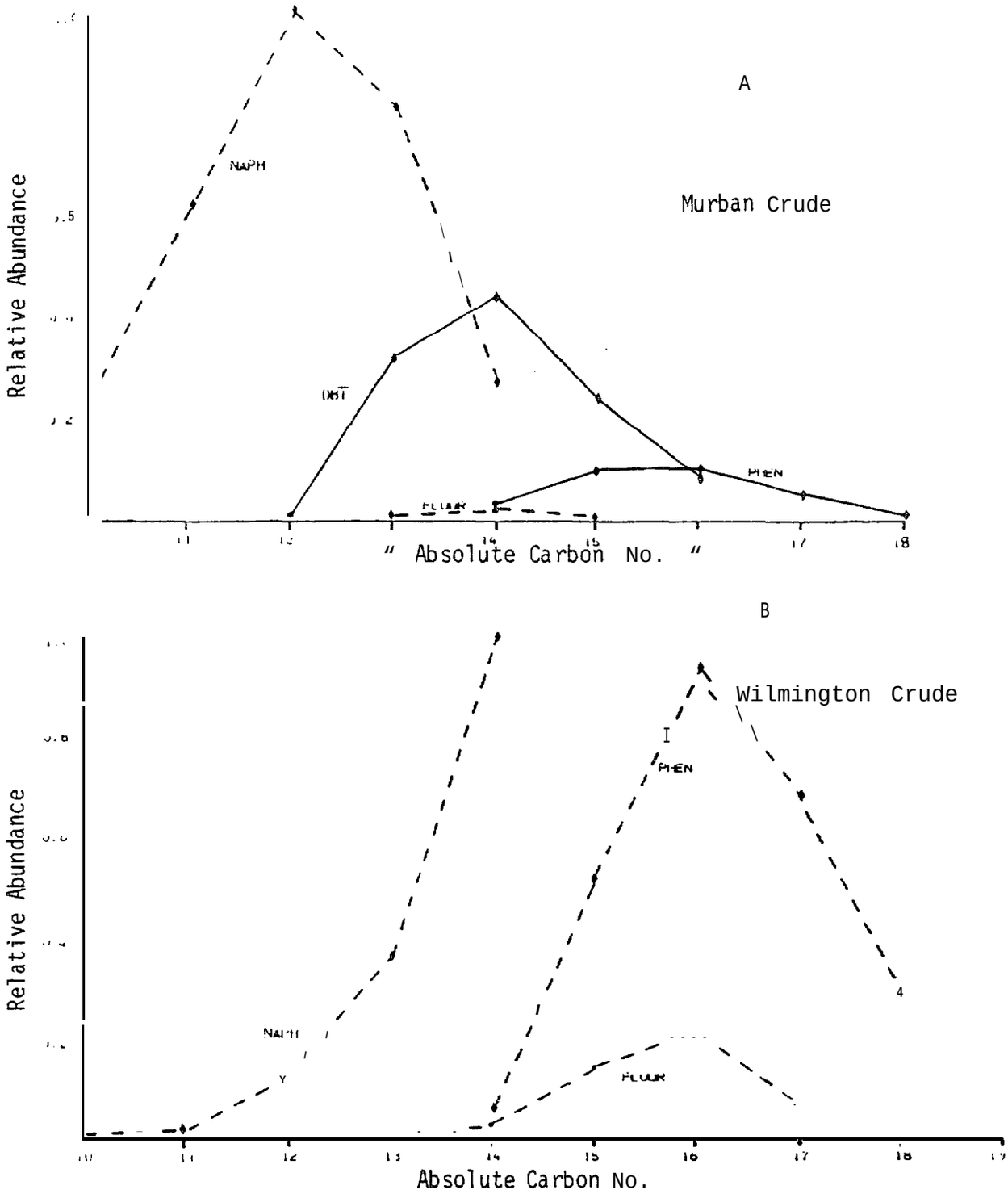



FIGURE 3-8. RELATIVE ABUNDANCE PLOTS FROM SELECTIVE ION MONITORING (GCMS) OF THE MOLECULAR ION FOR THE MAJOR ALKYL SUBSTITUTED AROMATIC SERIES DETECTED IN THE MURBAN (TOP) AND LONG BEACH (BOTTOM) CRUDE OILS. (Abbreviations as in Figure 3-7)

Even more striking similarities of the two Alaskan crude oils are depicted in Figure 3-7, which shows the relative abundance of alkyl-substituted polynuclear aromatic (PNA) hydrocarbons as derived from selected ion monitoring GC/MS analyses. Figure 3-7A presents the relative abundance of the PNAs for Cook Inlet crude and Figure 3-7B presents the same data for Prudhoe Bay crude oil. It should be noted that in these oils, as in many other crudes, the alkyl-substituted polynuclear aromatic compounds are Predominant over the non-substituted parent compounds. In Figure 3-7 the parent hydrocarbon is denoted by the first data point nearest the origin of the Absolute Carbon Number coordinate, and the degree of alkyl-substitution is then shown to increase with, for example, 11 representing methyl naphthalene, 12 representing dimethyl naphthalene, etc. In comparing Prudhoe Bay and Cook Inlet crudes it can be seen that the relative "abundance of alkyl-substituted naphthalenes are nearly identical, and similar trends are observed for biphenyl, fluorene and phenanthrene. In this instance, Cook Inlet crude shows some evidence of slightly higher relative levels of alkyl-substituted phenanthrene. Of these two oils, only Prudhoe Bay crude oil contained significant concentrations of the alkyl-substituted sulfur-heteroaromatic dibenzothiophenes. This is also reflected in the difference in weight percent sulfur of the two crudes as shown by the data in Table 3-1. Figure 3-8 presents the relative abundance plots for the alkyl-substituted polynuclear aromatic hydrocarbons in Murban Crude and Wilmington crude. The alkyl-substituted naphthalene composition of Murban crude is similar to that observed for the two Alaskan crudes; however, this oil contains significantly higher levels of alkyl-substituted dibenzothiophenes, and again the weight percent sulfur in the crude is somewhat higher. The alkyl-substituted naphthalene distribution for Wilmington crude is significantly different from the other three oils considered, and of the four crudes it has the highest relative abundance of phenanthrene and fluorene.

Interestingly, there were no significant levels of dibenzothiophene detected. BALL and RALL (1962) have shown that the sulfur content of the low-boiling (up to 250°C) fractions of Wilmington crude is predominantly in

the form of alkyl thiophenes and saturated cyclic sulfides. The bulk of the sulfur-containing components, however, were in the residue and were not characterized in that study. It should be noted from the data in Table 3-1 that the Wilmington crude also had the highest levels of the trace elements nickel and vanadium.

Another significant feature of the relative abundance plots for aliphatic and aromatic hydrocarbons is that the crudes with higher API gravities (lower specific gravities) also tend to have higher relative concentrations of the lower molecular weight, and less dense, aliphatic and aromatic hydrocarbons. That is, the Wilmington crude with the lowest API gravity is not represented by lower molecular weight aliphatic materials and the aromatic fractions are skewed towards the more highly alkyl -substituted phenanthrenes and fluorenes. As the data in Table 3-1 illustrate, the lower API gravity crudes also tend to have higher weight percent asphalts.

Synchronous scanning spectrofluorometry has also been used to characterize the polynuclear aromatic hydrocarbons content of crude oil and sediments and waters exposed to crude oils (WAKEHAM, 1977; GORDON et al., 1976; VO-DINH et al., 1978; BOEHM and FIEST, 1980) and this technique was also used in our studies to characterize the four selected crude oils examined. Families of aromatic hydrocarbons can be revealed by this method (LLOYD, 1971) and synchronous scan UV fluorescence spectra of the four crudes are shown in Figures 3-9, 3-10 and 3-11. These spectra were obtained on a Perkin-Elmer model MPF-44A high performance fluorescence spectrofluorometer with the exitation and emission monochromoters offset by 30 nm. The combined excitation emission spectra were obtained over the range of 230 to 600 nm. In general, monocyclic aromatic hydrocarbons emit most strongly in the 28(I to 290 nm region, dicyclic aromatics such as alkyl-substituted naphthalenes emit at about 310 to 320 nm; 3 and 4 ring aromatics emit in the range of 340 to 380 nm and compounds with greater than 5 rings emit in the range of 400 to 470 nm.

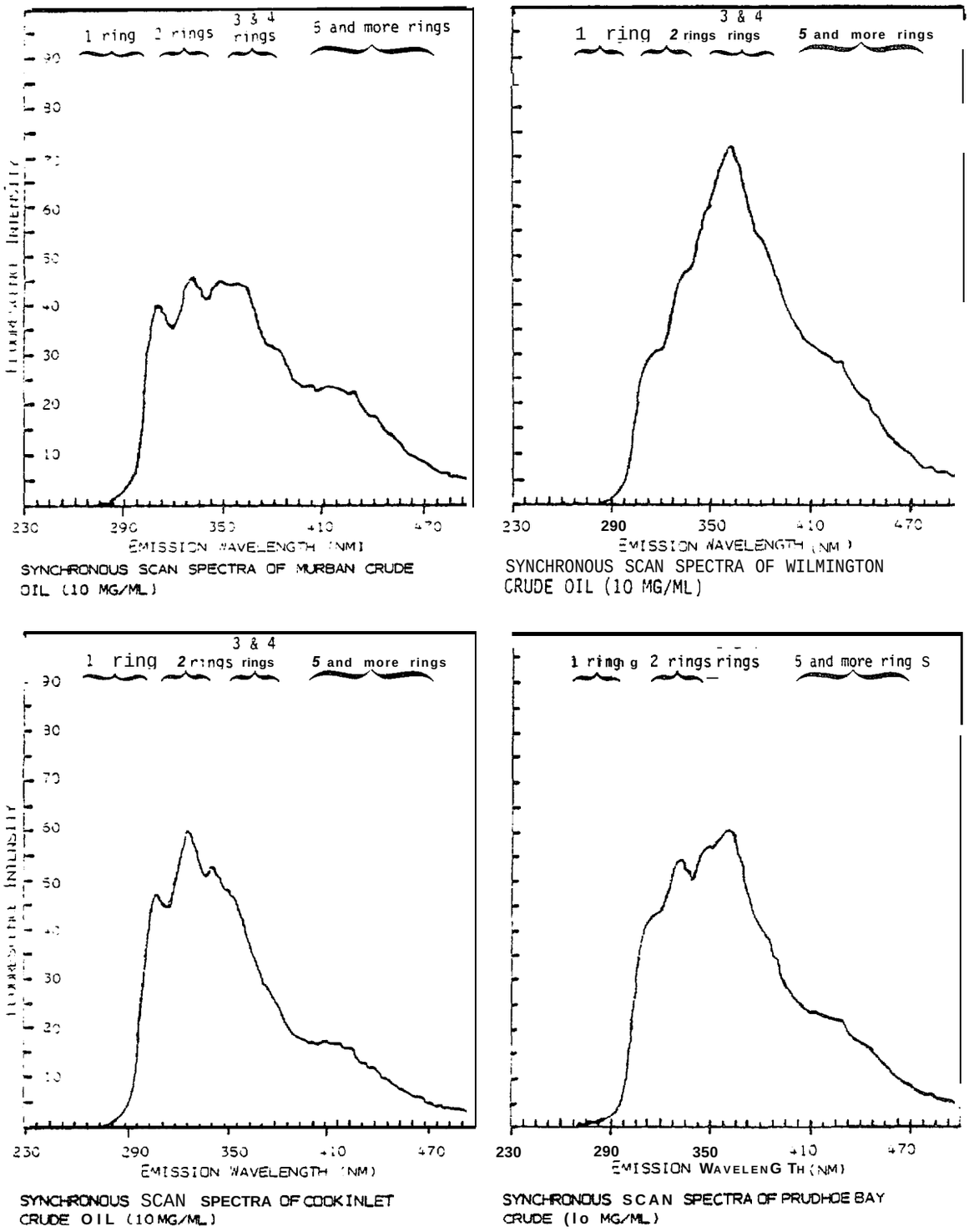



FIGURE 3-9. SYNCHRONOUS SCAN UV FLUORESCENCE SPECTRUM OF 10 mg/ml CONCENTRATION OF THE FOUR SELECTED CRUDE OILS.

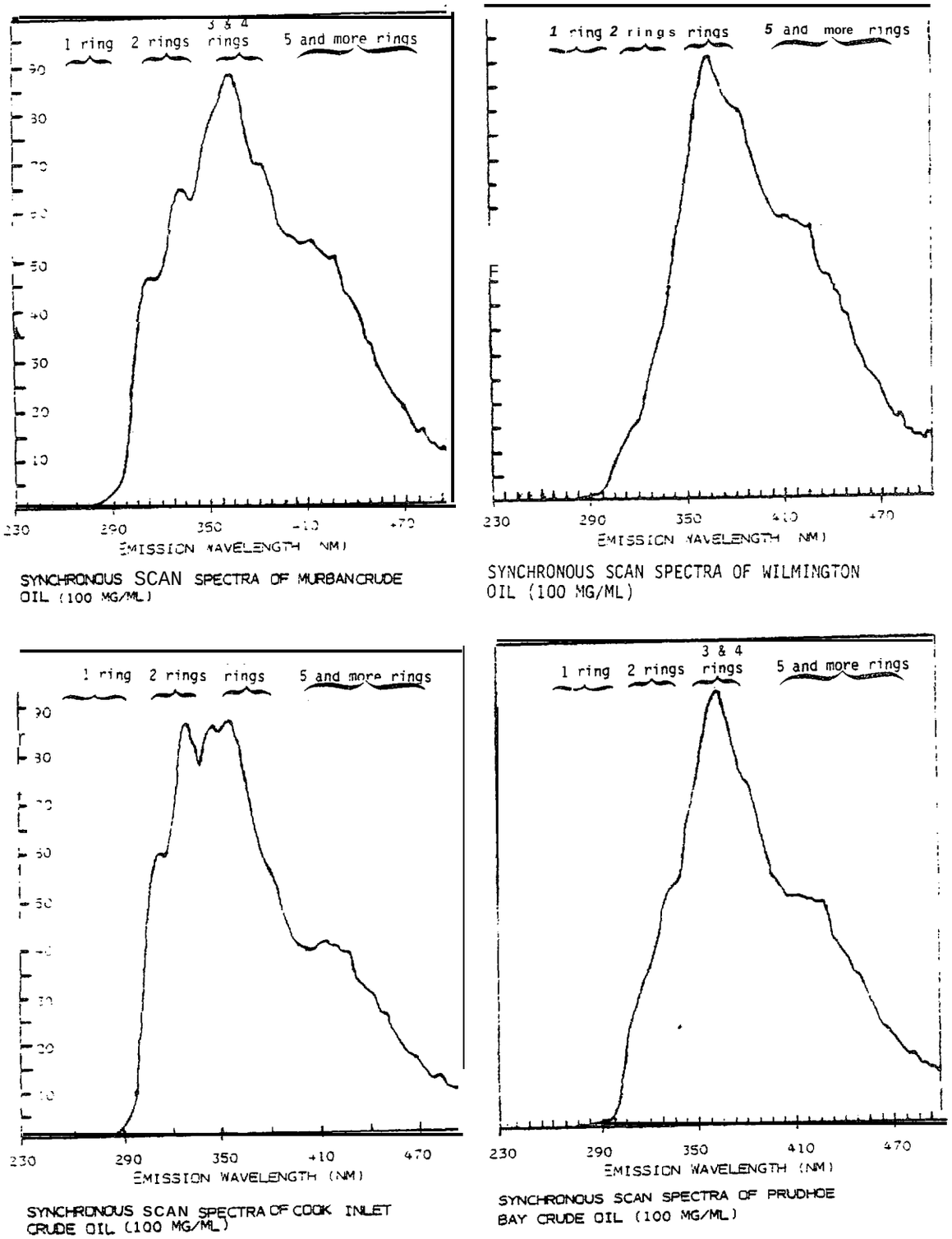



FIGURE 3-10. SYNCHRONOUS SCAN UV FLUORESCENCE SPECTRUM OF 100 mg/ml CONCENTRATIONS OF THE FOUR SELECTED CRUDE OILS.

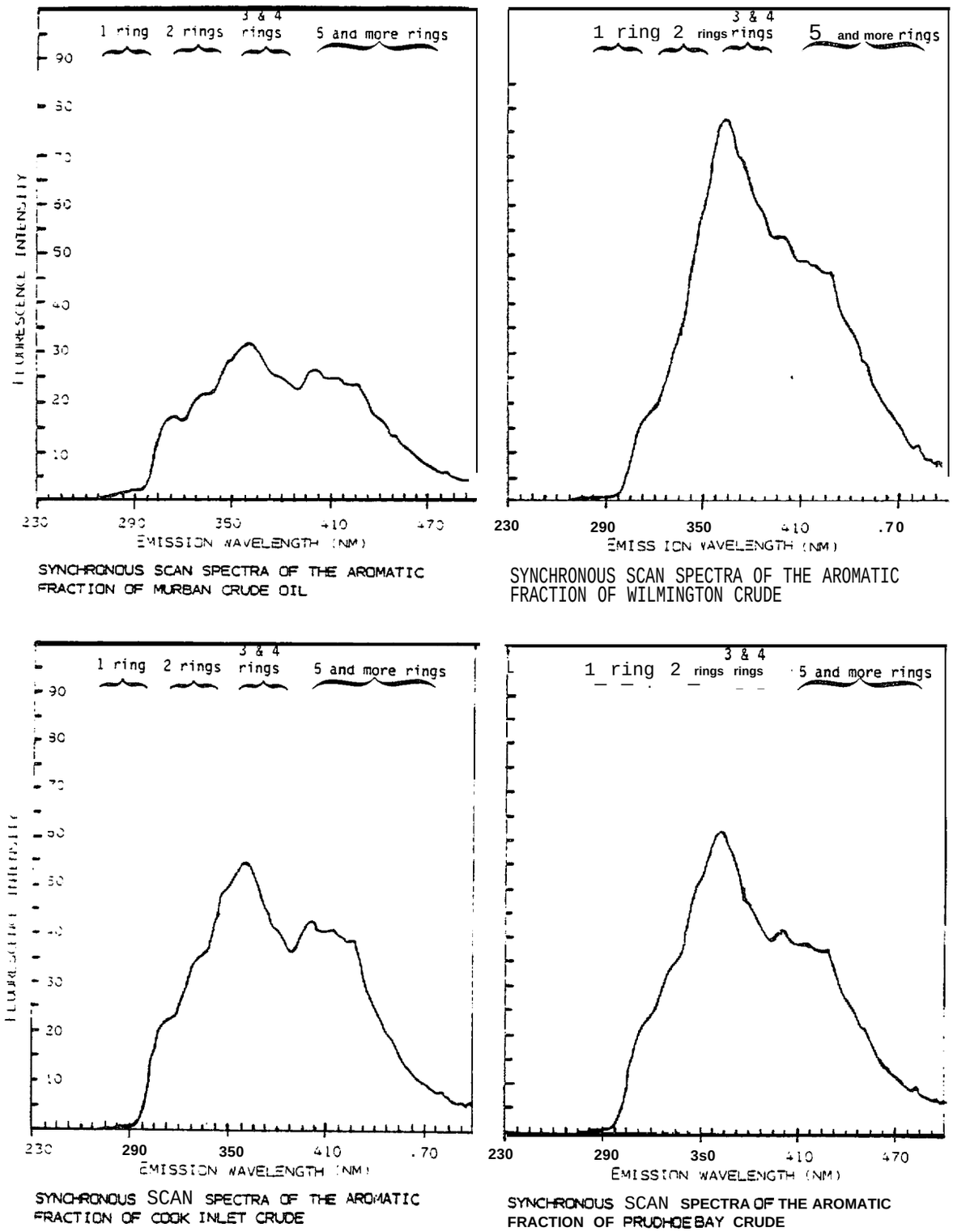



FIGURE 3-11. SYNCHRONOUS SCAN UV FLUORESCENCE SPECTRUM OF THE AROMATIC FRACTIONS OF THE FOUR SELECTED CRUDE OILS.

The four crudes shown in, Figure 3-9 were scanned at concentrations of 10 mg/ml in spectral grade cyclohexane and the spectra shown in Figure 3-10 were obtained at concentrations of 100 mg/ml. It can be seen from the spectra presented in Figures 3-9 and 3-10 that at lower concentrations better fluorescence resolution for the small ringed compounds is obtained at the lower wavelengths. At higher concentrations, greater fluorescence and resolution is observed for the 4 and 5 ring compounds, reflecting the effective energy transfer processes which occur at higher concentrations (JOHN and SOUTAR, 1976; VO-DIDH et al.)

From the spectra of the whole crude oil samples it appears that Cook Inlet and Murban crude oils contain a higher abundance of 2 and 3 ring aromatic compounds with Prudhoe Bay crude being intermediate and Wilmington having the lowest relative abundance of these compounds. As noted above, these compositional differences are also illustrated by the relative abundance PNA plots presented in Figures 3-7 and 3-8. The 4 and 5 ring aromatics appears to be more concentrated in the Wilmington and Murban crude oils. Figure 3-11 presents the synchronous scan UV-fluorescence spectra obtained on the aromatic fractions of each of the selected oils, and while the results are similar to those obtained for the unfractionated oils, a slight relative increase in fluorescence from the 3, 4, and 5 ring compounds can be observed.

While component-specific data are necessary for developing an oil weathering model , additional data are also required to enable a mass balance approach describing the state of an actively weathering oil slick. As was discussed in the previous sections on modeling, it is not possible to develop a mass balance model of oil weathering if only specific organic compounds, or even confined groups of compounds, are considered. Thus, to obtain information on the overall mass balance for various spilled crude oils, fractional distillation data are required of the type routinely used in the petroleum industry for overall oil characterizations. With such an approach, compounds can be grouped into pseudo-component classes based on their boiling points,

and cumulative percent compositional data can be obtained on crudes as a function of the true boiling point distillation curve. Tables 3-12 through 3-15 present the fractional-distillation cut data (COLEMAN et al, 1978) for Murban, Cook Inlet, Prudhoe Bay and Wilmington crudes, respectively. The percent composition of each fractional cut is presented by boiling point, and the cumulative volume percent and API gravity of each distillation cut are also given. From this data, it can be seen that cumulative percent distilled can vary significantly from oil to oil , and it is also possible to see how different oil compositions are skewed to higher or lower molecular weight components. Note that the relative percent of nondistillable residue increases from Murban crude (19. 1%) to Cook Inlet (25.6%) to Prudhoe Bay crude (36.3%) to Wilmington crude (53.3%) in line with the relative compositions of higher molecular weight materials, percent asphalt and (to a general extent) Kinematic and Saybolt viscosities. Not surprisingly, a relatively smooth decreasing trend in API gravity is also observed with each distillate cut. Figure 3-12 presents the true boiling point distillation curves showing the cumulative volume percent of each crude distilled vs. true boiling point in "F UP to the limit of the nondistillable stillpot residual. Similar plots will be utilized extensively with the development of the pseudo component oil weathering model, and predicted vs. observed (as derived from capillary GC data) distillation curves will be used to compare oil weathering model output and observed field data.

In examining the detail from Tables 3-12 through 3-15, and the curves presented in Figure 3-12, it can be seen that significant portions of each of the crudes occur in the non-distillable residuum with boiling points above 790°F. Thus, while Murban and Cook Inlet crudes have 80% and 71% distillable components, Prudhoe Bay crude oil and Wilmington crude oil have distillable fractions consisting of only 62.6% and 46.3% of the starting oil, respectively. The steepness of the boiling point distillation temperature vs. percent distilled curves in Figure 3-12 also shows the relative differences in percent higher molecular weight non-boiling components. That is, the steeper the

TABLE 3-12. FRACTIONAL 9ISTILLATION DATA ON MURBAN BAB-BU HASA ABU DHABI CRUDE OIL.

| Fraction No. | Cut Temp °F | Volume Percent | Cumulative Percent | "API 60°F | Cumulative % Based on Total Distillable Only |
|---|---|---|---|---|---|
| 1 | 122 | 1.7 | 1.7 | 96.7 | 2.1 |
| 2 | 167 | 2.9 | 4.6 | 86.2 | 5.7 |
| 3 | 212 | 4.9 | 9.5 | 70.6 | 11.8 |
| 4 | 257 | 6.0 | 15.5 | 62.3 | 19.4 |
| 5 | 302 | 6.7 | 22.2 | 55.7 | 27.7 |
| 6 | 347 | 6.4 | 28.6 | 51.6 | 35.7 |
| 7 | 392 | 5.7 | 34.3 | 48.5 | 42.8 |
| 8 | 437 | 5.6 | 39.9 | 45.6 | 49.8 |
| 9 | 482 | 5.9 | 45.8 | 43.0 | 57.2 |
| 10 | 527 | 4.9 | 50.7 | 40.0 | 63.3 |
| 11 | 580 | 5.7 | 56.4 | 35.8 | 70.4 |
| 12 | 638 | 5.6 | 62.0 | 34.0 | 77.4 |
| 13 | 685 | 6.5 | 68.5 | 30.0 | 85.5 |
| 14 | 738 | 6.0 | 74.5 | 28.4 | 93.0 |
| 15 | 790 | 5.6 | 80.1 | 26.6 | 100 |

% Non-distillable residuum: 19.1; cumulative % 99.2; 'API 16.7

% Asphalt in residuum: 30

TABLE 3-13. FRACTIONAL DISTILLATION DATA ON COOK INLET, ALASKA CRUDE OIL (McArthur River Field).

| Fraction No. | Cut Temp °F | Volume Percent | Cumulative Percent | 'API 60°F | Cumulative % Based on Total Distillable Only |
|---|---|---|---|---|---|
| 1 | 122 | 2.4 | 2.4 | 89.2 | 3.4 |
| 2 | 167 | 2.5 | 4.9 | 77.2 | 6.9 |
| 3 | 212 | 5.9 | 10.8 | 65.0 | 15.1 |
| 4 | 257 | 6.1 | 16.9 | 59.5 | 23.7 |
| 5 | 302 | 5.1 | 22.0 | 55.4 | 30.8 |
| 6 | 347 | 5.2 | 27.2 | 50.8 | 38.1 |
| 7 | 392 | 4.9 | 32.1 | 46.5 | 45.0 |
| 8 | 437 | 5.1 | 37.2 | 43.0 | 52.2 |
| 9 | 482 | 5.2 | 42.4 | 39.6 | 59.5 |
| 10 | 527 | 5.0 | 47.4 | 37.0 | 66.5 |
| 11 | 580 | 3.3 | 50.7 | 32.8 | 71.1 |
| 12 | 638 | 5.2 | 55.9 | 31.3 | 78.4 |
| 13 | 685 | 7.0 | 62.9 | 28.7 | 88.2 |
| 14 | 738 | 4.2 | 67.1 | 26.6 | 94.1 |
| 15 | 790 | 4.2 | 71.3 | 25.0 | 100 |

% Non-distillable residuum: 25.6; cumulative % 96.9: °API 11.6

% Asphalt in residuum: 35

TABLE 3-14. FRACTIONAL DISTILLATION DATA ON PRUDHOE BAY, ALASKA CRUDE OIL.

| Fraction No. | Cut Temp °F | Volume Percent | Cumulative Percent | °API 60°F | Cumulative % Based on Total Distillable Only |
|---|---|---|---|---|---|
| 1 | 122 | | | | |
| 2 | 167 | 2.1 | 2.1 | 72,7 | 3.4 |
| 3 | 212 | 2.6 | 4.7 | 64.2 | 7.5 |
| 4 | 257 | 3.5 | 8.2 | 56.7 | 13.1 |
| 5 | 302 | 3.6 | 11.8 | 51.6 | 18.8 |
| 6 | 347 | 3.7 | 15.5 | 47.6 | 24.8 |
| 7 | 392 | 3.5 | 19.0 | 45.2 | 30.4 |
| 8 | 437 | 4.3 | 23.3 | 41.5 | 37.2 |
| 9 | 482 | 4.8 | 28.1 | 37,8 | 44.9 |
| 10 | 527 | 5.0 | 33.1 | 34.8 | 52.9 |
| 11 | 580 | 2.8 | 35.9 | 30.6 | 57.3 |
| 12 | 638 | 6.5 | 42.4 | 29.1 | 67.7 |
| 13 | 685 | 6.8 | 49.2 | 26.2 | 78.6 |
| 14 | 738 | 6.0 | 55.2 | 24.0 | 88.2 |
| 15 | 790 | 7.4 | 62.6 | 22.5 | 100 |

% Non-distillable residuum: 36.3; cumulative % 98.9; °API 11.4

% Asphalt in residuum: 57

TABLE 3-15. FRACTIONAL DISTILLATION DATA ON WILMINGTON, CALIFORNIA CRUDE OIL.

| Fraction No. | Cut Temp °F | Volume Percent | Cumulative Percent | 'API 60°F | Cumulative % Based on Total Distillable Only |
|---|---|---|---|---|---|
| 1 | 122 | | | | |
| 2 | 167 | | | | |
| 3 | 212 | 2.3 | 2.3 | 68.6 | 5.0 |
| 4 | 257 | 2.4 | 4.7 | 58.7 | 10.2 |
| 5 | 302 | 2.4 | 7.1 | 53.0 | 15.3 |
| 6 | 347 | 2.5 | 9.6 | 48.1 | 20.7 |
| 7 | 392 | 2.8 | 12.4 | 43.2 | 26.8 |
| 8 | 437 | 3.6 | 16.0 | 38.8 | 34.6 |
| 9 | 482 | 4.4 | 20.4 | 35.4 | 44.1 |
| 10 | 527 | 5.3 | 25.7 | 32.3 | 55.5 |
| 11 | 580 | 4.7 | 30.4 | 26.8 | 65.7 |
| 12 | 638 | 6.3 | 36.7 | 24.5 | 79.3 |
| 13 | 685 | 4.1 | 40.8 | 22.3 | 88.1 |
| 14 | 738 | 5.5 | 46.3 | 20.3 | 100 |
| 15 | 790 | * | | | |

% Non-distillable residuum: 53.5; cumulative % 99.6; 'API 8.9

% Asphalt in residuum: 42

* Distillation discontinued at 740°F

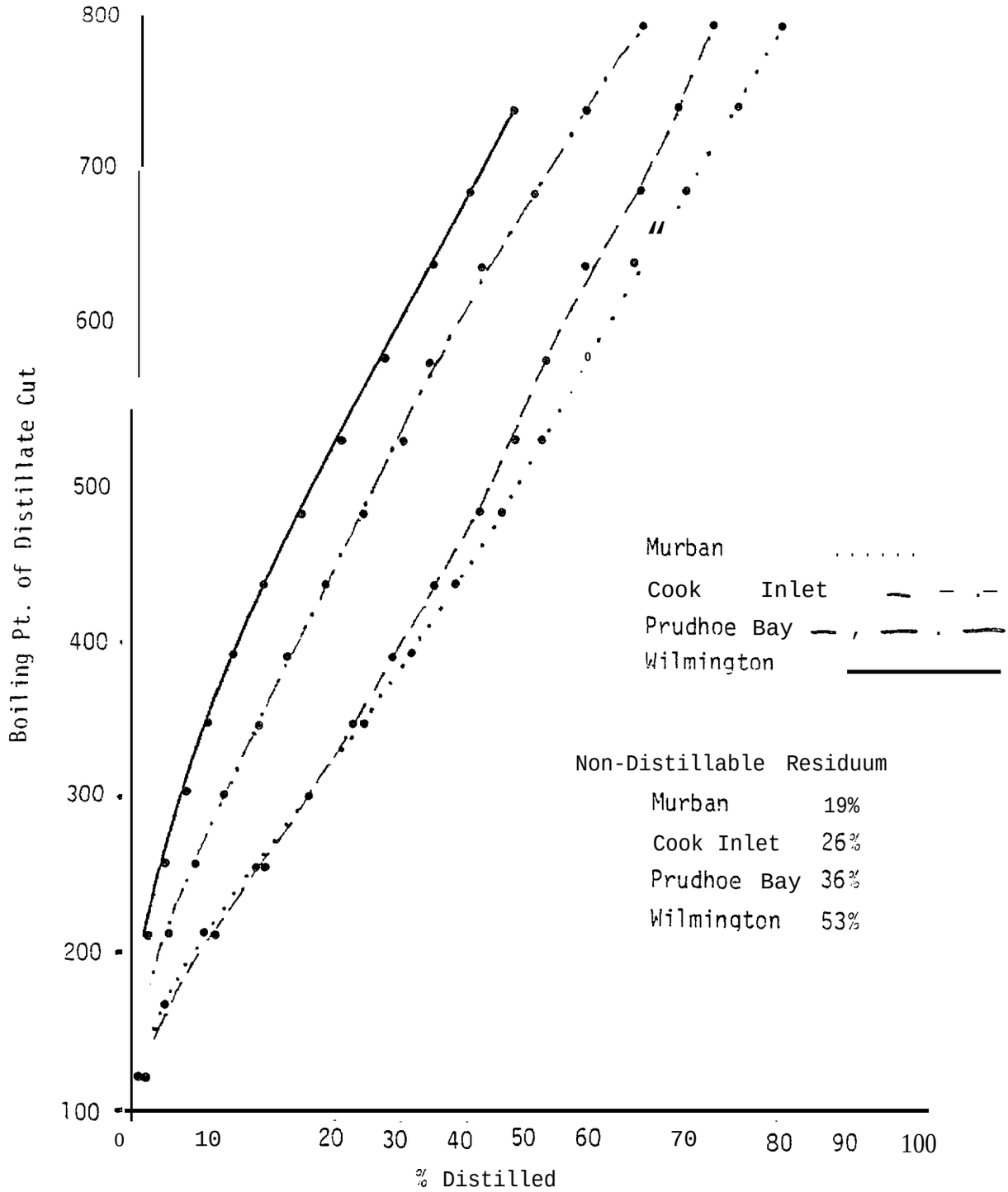



FIGURE 3-12. BOILING POINT DISTILLATION CURVES FOR THE FOUR SELECTED CRUDE OILS STUDIED.

curve in Figure 3-12 the more components present boiling above 790°F. Figure 3-13 shows the cumulative boiling point distributions for the four crudes based on the total distillable fractions only. That is, it is a temperature vs. percent distilled curve for the fraction of the oil which can be distilled below 790°F, and thus, the weight of each distillate cut has been normalized to the overall weight of the total distillate obtained. What this data shows is that at a given temperature less total material of the distillable fraction has been distilled for Prudhoe Bay and Wilmington crude vs Murban and Cook Inlet crude, and this again reflects the somewhat higher molecular weight component concentrations of the Prudhoe Bay and Wilmington crude oils.

Selection of Prudhoe Bay Crude Oil for Further Oil Weathering Studies

Based on the results just presented, Prudhoe Bay crude oil was selected as being the best candidate for extensive sub-arctic weathering studies. Prudhoe Bay crude oil has an API gravity somewhat lower than the Murban or Cook Inlet crudes, yet its aliphatic fraction is represented by an evenly repeating series of alkanes (unlike the Wilmington crude) which facilitates examination of microbial degradation processes. Also, Prudhoe Bay crude oil has a relatively high percent asphaltic fraction and intermediate levels of nickel, vanadium, sulfur and nitrogen, making it an ideal oil for extended studies investigating the formation of water-in-oil emulsions or mousse (PAYPIE, 1981). As demonstrated by the synchronous scan UV fluorescence data and the selected ion monitoring relative abundance plots for the polynuclear aromatic hydrocarbons, Prudhoe Bay crude oil is intermediate in overall aromatic hydrocarbon composition. On this basis, the Prudhoe Bay crude is a good representative selection for toxicity determinations on weathered crude oil. Finally, while both Cook Inlet crude oil and Prudhoe Bay crude oil have a higher potential of being released in sub-arctic environments, the selection of Prudhoe Bay crude over Cook Inlet crude was supported by the fact that it contains relatively higher levels of the alkyl-substituted dibenzothiophenes.

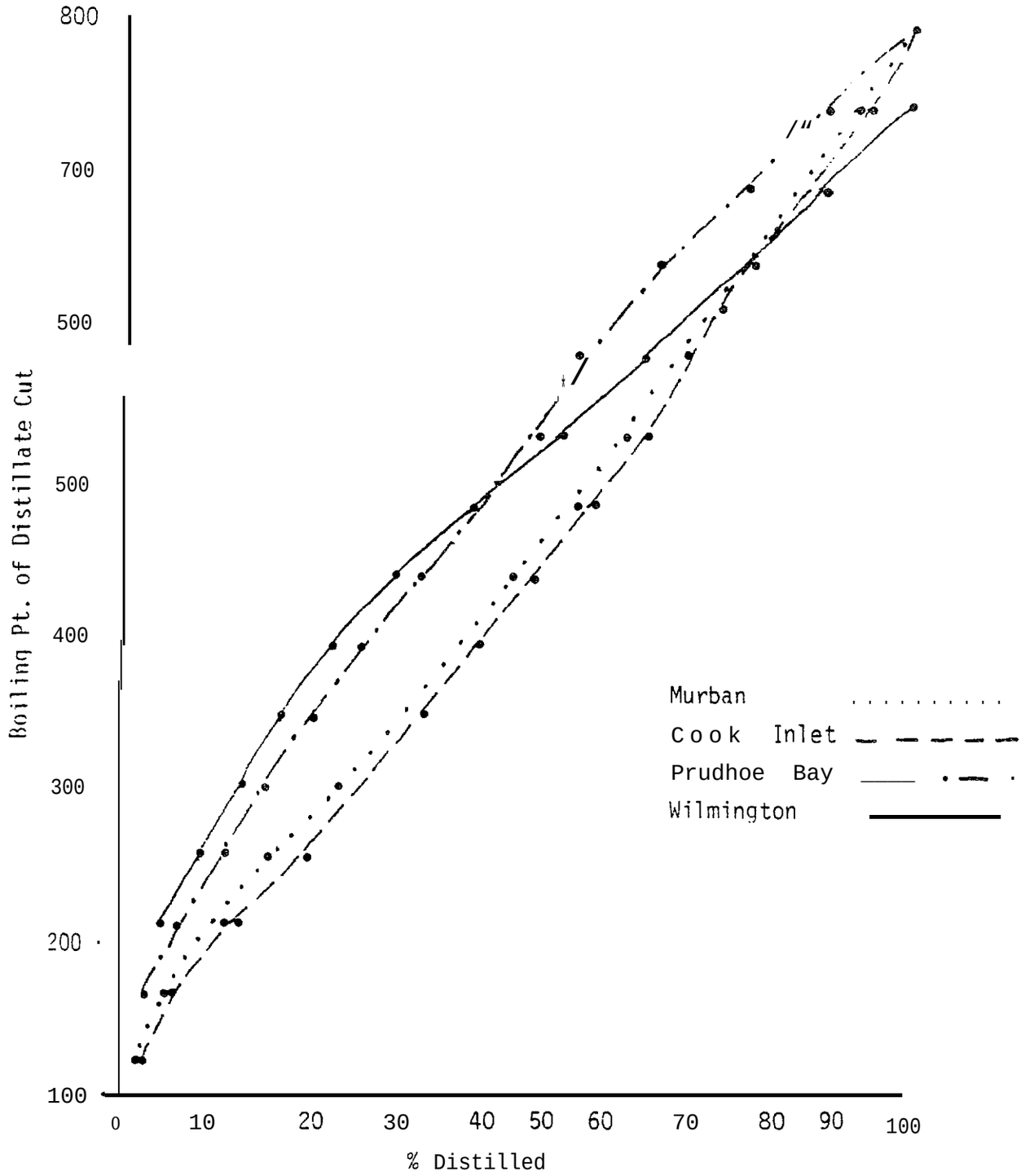



FIGURE 3-13. CUMULATIVE BOILING POINT DISTILLATION CURVES FOR THE TOTAL DISTILLABLE FRACTIONS OF THE FOUR CRUDE OILS STUDIED.

## 4.0 OIL WEATHERING MODEL DEVELOPMENT

The objectives for a mathematical model of oil weathering on the ocean surface are to temporally predict both the mass of oil remaining in the slick and the chemical composition and physical properties of the oil slick. These two objectives require that oil composition be described in terms of both specific components and component categories, or "pseudocompounds." Pseudocomponent classification has been widely used in the petroleum industry to describe crude oil because of the inherent interest in bulk oil characteristics and accounting for total mass. A specific-component description is of more interest to describing spilled oil as a changing source of foreign chemicals to an aquatic ecosystem, but the complexity of oil composition makes it impractical to keep track of bulk oil mass in terms of individual components.

The mathematical models presented in this report are in various stages of development and computerization. The most developed to date are those describing the evaporation and dissolution processes, and present for the first time a coupling of the two types of material balance models (specific- and pseudo-component) in a form that will provide environmental predictions. These models incorporate the concepts of interracial mass transfer, the considerations of both mechanically well-stirred and stagnant oil phases, the effects of slick spreading, and the boundary conditions imposed on the oil by the environment. In addition, these models include descriptive predictions of specific compound concentrations in the air and water columns in contact with a slick or other spilled oil phase.

Both portions of the model require distinct and independent mathematical formulations. In order to predict the mass of oil remaining in a slick as a function of time, a method of characterizing the bulk oil with respect to the various transport processes that alter and dissipate oil must be utilized. The total oil mass cannot be characterized by its individual components because of their number and complexity, and the limitations of analysis. To compensate for these limitations, the pseudo-component approach "cuts" oil into a number of fractions, assigning appropriate physical properties to each.

In attempting to predict the mass of oil remaining in a slick, the two most important mass transport processes to consider are evaporation and dissolution. Of these two, evaporation appears to have the greater influence, certainly over short time scales, making vapor pressure an especially important oil characteristic. Adequate description of the dissolution process, on the other hand, requires water volubility information. The pseudo-component approach to describe these processes is to cut the oil into a number of fractions based on properties of distillation fractions.

The pseudo-component approach, which is that taken in virtually all previous efforts to model oil weathering, is singularly useful for providing total material balances with time for spilled oil (especially for slicks). However, this approach does not predict the time-dependent material balance for specific chemical components. In order to obtain component-specific information, component specific physical properties (e.g., solubilities, vapor pressures and other phase partitioning parameters) must be used. There have been no other functional component specific models developed previously. Ironically, most of the data generated when an actual oil spill has occurred have been component-specific concentrations across phase boundaries.

Although evaporation and dissolution are the oil-weathering processes of most importance during the initial stages of a spill, other longer-term weathering processes destroy and produce compounds to a degree that is important to any component-specific model. In the case of autoxidation, a compound may chemically react to become an aldehyde, ketone, alcohol or carboxylic acid, all of which are more soluble in the water column than are the precursor hydrocarbon compounds. Similarly, metabolizes of microbial degradation have physical properties markedly different from their corresponding parent compounds. Such "fringe" processes, which are not unimportant, are typically more complex than are the evaporation and dissolution processes, increasing the complexity of their mathematical descriptions.

In discussing the segments of the model which follow, three basic aspects have been considered for each oil weathering process:

(1) physical properties (of bulk oil and specific components)

(z) mass balance equations (for specific components and pseudo-components)

(3) environmental parameters (which the oil encounters upon being spilled)

Physical properties include the thermodynamic and transport characteristics required to describe a particular process. In the cases of evaporation and dissolution, thermodynamic properties are the vapor pressures, Henry's law coefficients, solubilities, and mixing rules, while the transport properties include diffusivities, viscosities and, again, mixing rules.

## 4.1 Pseudo-Component Marine Evaporation of Oil

Predicting the quantity of oil in the slick as a function of time requires that a total mass balance approach be used. It is not possible to write a total material balance for crude oil by using component specific information. If one tries to use component specific information, it soon becomes apparent that all the components in crude oil will never be identified, thus precluding an accounting of the total mass of the oil. No predictive equations have ever been successfully developed based on specific components where the purpose of prediction was a total mass balance for oil.

The question then is raised as to how one uses bulk properties of the oil to make specific predictions? The petroleum industry refers to these bulk properties of oil as "characterization parameters". The characterization of an oil must be done with respect to a specific prediction as the objective. For example, when the prediction (process design or mathematical model) is a process that involves vapor-liquid transport, the characteristic parameters are then vapor pressures or partial pressures. When the prediction is the Performance of a catalytic reformer where naphthas are converted to aromatics,

the characteristics required on the catalytic reformer feedstock are combined contents of paraffins-olefins-naphthas-aromatics, referred to as PONA. Kinetic equations use PONA values as starting concentrations along with kinetic constants to predict the product from the catalytic reforming process. Both these examples illustrate a pseudo-component model, sometimes referred to as a "lumped" model.

In predicting the mass of oil remaining in an oil slick as a function of time as evaporation proceeds, characterization of the oil must be with respect to vapor pressure. An overall mass balance utilizes the vapor pressure and environmental parameters to predict loss of oil and, therefore, mass of oil remaining in the slick. The following discussion considers: 1) tile procedure for characterizing crude oils with respect to pseudo-component vapor pressures and 2) the pertinent equations for the overall mass balance as they apply to the use of the overall oil weathering model.

### 4.1.1 Pseudo-Component Characterization of Crude Oil

The standard inspections on a crude oil include distillation, density of the distillate cuts, and viscosity of the distillate cuts. There are virtually no component-specific data that can be obtained which will allow adequate prediction of the bulk properties of the oil. The standard distillation data come from either a true boiling point distillation or an ASTM (American Society for Test and Materials) D-86 distillation; both are carried out at one atmosphere total pressure. Each of these distillations can be carried out at 10 mm Hg total pressure to obtain information on the less volatile fractions of the oil.

Either distillation is conducted in a manner such that the distillate fractions are collected separately (i.e., the fraction distilling at 50 to 75°C is physically separated from the fraction distilling at 75 to 100"C). The total number of fractions collected is usually five to seven, but can be as many as 20. Characteristic data for the distillate fractions include the

temperatures at the beginning and end of each fraction (or "cut"), sometimes in the form of a continuous curve of temperature vs percent distillate. The API (American Petroleum Institute) gravity for each cut is then measured, as is occasionally the viscosity of each cut.

Given the boiling point (1 atm) and API gravity of each cut (or pseudo-component), the vapor pressure of the cut as a function of temperature can be calculated. First, the molecular weight and critical temperature of the cut are calculated according to the following correlation (FALLON and WATSON, 1944):

$$Y = C_1 + C_2X_1 + C_3X_2 + C_4X_1X_2 + C_5X_1^2 + C_6X_2^2 \tag{4.1}$$

where $X_1$ is the boiling point ("F) at one atmosphere, $X_2$ is the API gravity, and the constants $C_1$ to $C_5$ have the values indicated in Table 4-1. Similarly, the critical temperature can be calculated from the same equation form using the indicated constant values in Table 4-1.

Next the equivalent paraffin carbon number is calculated according to (GAMSON and WATSON, 1944):

$$N_c = (MW - 2)/14 \tag{4.2}$$

The critical volume is then calculated according to:

$$V_c = (1.88 + 2.44\ Nc)/0.044 \tag{4*3}$$

TABLE 4-1. CORRELATION EQUATION CONSTANTS FOR THE CHARACTERIZATION OF NARROW BOILING PETROLEUM FRACTIONS (see text for equation form).

| PROPERTY | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|---|---|---|---|---|---|---|
| Molecular weight $t_b \leq 500°F$ | 6.241 E+01 | -4.595E-02 | -2.836E-01 | 3.256E-03 | 4.578E-04 | 5.279E-04 |
| Molecular weight $t_b > 500$ | 4.268E+02 | -1.007 | -7.491 | 1.380E-02 | 1.047E-03 | 2.621E-02 |
| Critical temperature to $\leq 500$ | 4.055E+02 | 1.337 | -2.662 | -2.169E-03 | -4.943E-04 | 1.454E-02 |
| Critical temperature $t_b > 500$ | 4.122E+02 | 1.276 | -2.865 | -2.888E-03 | -3.707E-04 | 2.288E-02 |
| b′ | 1.237E-02 | 2.516E-01 | 4.039E-02 | -4.024E-02 | ----- | ----- |
| Kinematic vis, CS @ 122°F API $\leq 35$ | -4.488E-01 | -9.344E-04 | 1.583E-02 | -5.219E-05 | 5.2688-06 | 1.536E-04 |
| Kinematic vis, CS @ 122°F API > 35 | -6.019E-01 | 1.793E-03 | -3.159E-03 | -5.1E-06 | 9.067E-07 | 3.522E-05 |

and the critical pressure is calculated from:

$$P_c = \frac{20.8T_c}{(v_c - 8)} + P_c' \tag{4.4}$$

where $P_c'$ = 10 to (correct the critical pressure correlation from a strictly paraffinic mixture to a naphtha-aromatic-paraffin mixture). Next a parameter (b) is calculated according to

$$b = b' - 0.02 \tag{4.5}$$

where

$$b' = C_1 + C_2 N_c + C_3 N_c^2 + C_4 N_c^3 \tag{4.6}$$

and the values of the constants $C_1$ to $C_4$ are indicated in Table 4-1.

A final parameter designated as A is then calculated according to:

$$A = \frac{T_{r_b}}{T_{r_b} - 1} \left\{ \log_{10} (P_{r_b}) \exp \left[ -20(T_{r_b} - b)^2 \right] \right\} \tag{4.7}$$

where $T_{r_b}$ and $P_{r_b}$ are the reduced temperature and pressure at the normal boiling point. The vapor pressure equation which can be used down to 10 mm Hg is:

$$\log_{10} p_r = \frac{-A(1 - T_r)}{T_r} - \exp \left[ -20(T_r - b)^2 \right] \tag{4.8}$$

where A, h, $T_c$ and $P_c$ were determined from the normal boiling point and API gravity of the cut. The temperature at which the vapor pressure is 10 mm Hg can be obtained by the root-finding algorithm of Newton-Raphson.

Below 10 mm Hg, the vapor pressure is calculated according to the Clausius-Clapeyron equation as follows (GAMSON and WATSON, 1944):

$$\ln \frac{P_2}{P_1} = \frac{\lambda_0}{RT_c} \int_{T_{r_1}}^{T_{r_2}} \frac{(1 - T_r)^{0.38}}{T_r^2} dT_r \tag{4.9}$$

and is based on the law which states the ratio of the heat of vaporization, $\lambda$, to $(1 - T_r)^{0.38}$ is a constant at any temperature. The latent heat of vaporization is calculated from the slope of the natural log of the vapor pressure equation with respect to the temperature at the temperature where the vapor pressure is 10 mm Hg. Thus, in the above equation, $P_2$ is the 10 mm Hg vapor pressure at the temperature, $T_r$, previously determined.

A sample calculation for the characterization of Prudhoe Bay crude oil is presented in Tables 4-2 and 4-3A. Table 4-2 presents the standard inspections (COLEMAN, 1978; PPC, 1973) for the crude and is the starting point for the characterization calculations. Note that the distillation in Table 4-2 was conducted at 40 mm Hg for cuts 11 to 15. Thus, these cut temperatures must be corrected to one atmosphere (API, 1976). Table 4-3A presents the computer generated output along with the corrected cut temperatures, and a calculation of the vapor pressures at an environmental temperature of 55°F. The characterizations of Cook Inlet, Murban, and Wilmington crudes are presented in Tables 4-35 to 4-3D, and the vapor pressures calculated from these characterizations are presented in Table 4-3E for all four crudes.

TABLE 4-2. STANDARD INSPECTIONS FOR PRUDHOE BAY CRUDE OIL (COLEMAN, 1978).

Item 9

Sample 71011

IDENTIFICATION

Prudhoe Bayfield
Sadlerochit, Triassic
8,890 - 9,008 feet

Alaska
North Slope

GENERAL CHARACTERISTICS

Gravity, specific 0.893 Gravity, ° API 27.0 Pour point, ° F. 15
Sulfur, percent, 0.82 Color, brownish black
Viscosity, Saybolt Universal at 77° F, 111 sec; 100° F, 84 sec Nitrogen, percent, 0.230

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 741 mm. Hg
First drop, 81 ° F.

| Fraction No. | Cut temp. ° F. | Percent | Sum percent | Sp. gr. 60/60° F. | ° API at 60° F. | C. | Refractive index, $n_D$ at 20° C | Specific dispersion | S. U. vis. 100° F. | Cloud pnt. ° F. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 122 | | | | | | | | | |
| 2 | 157 | 2.1 | 2.1 | 0.693 | 72.7 | - | 1.38591 | 127.9 | | |
| 3 | 212 | 2.6 | 4.7 | .723 | 64.2 | 23 | 1.40312 | 139.0 | | |
| 4 | 257 | 3.5 | 8.2 | .752 | 56.7 | 27 | 1.22 | 141.9 | | |
| 5 | 303 | 3.6 | 11.8 | .773 | 51.6 | 30 | 1.43082 | 147.0 | | |
| 6 | 347 | 3.7 | 15.5 | .790 | 47.6 | [illegible] | 1.43222 | 149.6 | | |
| 7 | 393 | 3.5 | 19.0 | .811 | 45.2 | 30 | 1.44626 | 152.1 | | |
| 8 | 437 | 4.3 | 23.3 | .818 | 41.5 | 33 | 1.45528 | 154.7 | | |
| 9 | 482 | 4.8 | 20.1 | .836 | 37.8 | 36 | 1.46565 | 157.0 | | |
| 10 | 527 | 5.0 | 33.1 | .851 | 34.8 | 38 | 1.47467 | 160.5 | | |
| STAGE 2—Distillation restricted at 40 Hg | | | | | | | | | | |
| 11 | 392 | 2.8 | 35.9 | 0.879 | 30.6 | | 1.48218 | 161.5 | 40 | 10 |
| 12 | 437 | 6.5 | 42.4 | .881 | 29.1 | | 1.48650 | 168.6 | 45 | 30 |
| 13 | 482 | 6.8 | 49.2 | .897 | 26.2 | 49 | 1.49477 | 169.4 | [illegible] | 50 |
| 14 | 527 | 6.0 | 55.2 | .910 | 24.0 | 52 | | | 93 | 70 |
| 15 | 572 | 7.4 | 62.6 | .919 | 22.5 | 53 | | | 176 | 90 |
| Residuum | | 36.3 | 98.9 | .990 | 11.4 | | | | | |

Carbon residue, Conradson: Residuum 11.6 percent; crude 4.7 percent.

Residuum:
Sulfur, percent, -
Nitrogen, percent, -

APPROXIMATE SUMMARY

| | Percent | Sp. gr. | ° API | Viscosity |
|---|---|---|---|---|
| Light gasoline | 4.7 | 0.710 | 67.9 | |
| Total gasoline and naphtha | 19.0 | 0.762 | 54.2 | |
| Kerosene distillate | 4.3 | .818 | 41.5 | |
| Gas oil | 18.4 | .860 | 33.1 | |
| Nonviscous lubricating distillate | 11.0 | .887-.911 | 28.0-23.9 | 50-100 |
| Medium lubricating distillate | 8.1 | .911-.922 | 23.9-22.0 | 100-200 |
| Viscous lubricating distillate | 1.8 | .922-.924 | 22.0-21.6 | Above 200 |
| Residuum | 36.3 | .990 | 11.4 | |
| Distillation loss | 1.1 | | | |

TABLE 4-3A. SUMMARY OF THE TBP CUTS CHARACTERIZATION FOR PRUDHOE BAY, ITEM 9, SAMPLE 71011.

SUMMARY OF TBP CUTS CHARACTERIZATION FOR: PRUDHOE BAY, ITEM9, SAMPLE 71011

| | TN | A P | VOL | MW | TC | PC | VC | A | B | T10 | VIS | NC | NS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.670E+02 | 7.270E+01 | 2.123E+00 | 8.921E +01 | 9.310E+02 | 3.030E+01 | 3.802E+02 | 3.227E+00 | 1.976E-01 | 4.604E+02 | 4.144E-01 | 3 | 1 |
| 2 | 2.120E+02 | 6.420E+01 | 2.629E+00 | 1.015E+02 | 9.802E+02 | 3.654E+01 | 4.370E+02 | 3.311E+00 | 2. 111E-01 | 4.959E+02 | 4.919E-01 | 3 | 1 |
| 3 | 2.570E+02 | 5.670E+01 | 3.539E+00 | 1 . 139E+02 | 1 .040E+03 | 3.514E+01 | 4.860E+02 | 3.391E+00 | 2.220E-01 | 5.315E+02 | 6.006E-01 | 3 | 1 |
| 4 | 3.020E+02 | 5.160E+01 | 3 .640E+00 | 1 .270E+02 | 1 .091 E+03 | 3.365E+01 | 5.410E+02 | 3.493E+00 | 2.341E-01 | 5.677E+02 | 7.474E-01 | 3 | 1 |
| 5 | 3.470E+02 | 4.760E+01 | 3.741E+00 | 1 .481 E+02 | 1.139E+03 | 3.210E+01 | 6.015E+02 | 3.612E+00 | 2.440E-01 | 6.044E+02 | 9.433E-01 | 3 | 1 |
| 6 | 3.920E+02 | 4. 520E+01 | 3.539E+00 | 1.607E+02 | 1.184E+03 | 3.062E+01 | 6.713E+02 | 3.767 E+00 | 2.554E-01 | 6.420E+02 | 1 .20011100 | 3 | 1 |
| 7 | 4.370E+02 | 4. 150E+01 | 4 .340E+00 | 1.779E+02 | 1.230E+03 | 2.942E+01 | 7.396E+02 | 3.909E+00 | 2.643E-01 | 6.796E+02 | 1.555E+00 | 3 | 1 |
| 11 | 4.820E+02 | 3.780E+01 | 4. 853E+00 | 1.960E+02 | 1.275E+03 | 2.834E+01 | 8. 111E+02 | 4.059E+00 | 2.724E-01 | 7.176E+02 | 2.046E+00 | 3 | 1 |
| 9 | 5.270E+02 | 3.480E+01 | 5.056E+00 | 2.125E+02 | 1.323E+03 | 2.760E+01 | 0.76 5E+02 | 4. 178E+00 | 2 .789E-01 | 7.551E+02 | 2.000E100 | 3 | 1 |
| 10 | 5.900E+02 | 3.060E+01 | 2.831E+00 | 2.429E+02 | 1 .302E+03 | 2.615E+01 | 9.969E+02 | 4.424E+00 | 2.890E-01 | 8.097E+02 | 3.309E+00 | 3 | 1 |
| 11 | 6.400E+02 | 2.910E+01 | 6 . 572E+00 | 2.736E+02 | 1.423E+03 | 2.481E+01 | 1.119E+03 | 4.689E+00 | 2.974E-01 | 8.540E+02 | 5.367E+00 | 3 | 1 |
| 12 | 6.850E+02 | 2.620E+01 | 6.876E+00 | 2.980E+02 | 1.464E+03 | 2.398E+01 | 1.218E+03 | 4.892E+00 | 3.032E-01 | 8.949E+02 | 9.259E+00 | 3 | 1 |
| 13 | 7.350E+02 | 2.400E+01 | 6.067E+00 | 3.320E+02 | 1.506E+03 | 2.297E+01 | 1.350E+03 | 5.177E+00 | 3.097E-01 | 9.411E+02 | 1.812E+01 | 3 | 1 |
| 14 | 7.900E+02 | 2.250E+01 | 7.482E+00 | 3.757E+02 | 1.547E+03 | 2.180E+01 | 1.523E+03 | 5.581E+00 | 3.166E-01 | 9.943E+02 | 4.046E+01 | 3 | 1 |
| 15 | 8.500E+02 | 1.140E+01 | 3.670E+01 | 6.000E+02 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 1.810E+02 | 0 | 0 |

TB . NORMAL BOI LI NG TEMPERATURE, DEG F
AI>I = API GRAVITY
VOL = VOLUME PER CENT OF TOTAL CRUDE
MW = MOLECULAR WEIGHT
TC = CRITICAL TEMPERATURE, DEG HANK I NE
PC = CRITICAL PRESSURE . ATMOSPHERES
VC CRITICAL VOLUME, CC/MOLE
A AND B ARE PARAMETERS IN THE VAPOR PRESSURE EQUATION
T10 IS THE TEMPERATURE IN DEG n WHERE THE VAPOR PRESSURE IS 10 MM HG
VIS IS THE KINEMATIC VISCOSITY IN CENTI STOKES AT 122 DEG F
NC = ERROR CODE, SHOULD JE LESS THAN 20
NS = ERROR CODE, SHOULD BE EQUAL TO 1
IGNORE THE ERROR CODES FOR COMPONENT NUMBER 1 5
CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: PRUDHOE DAY, ITEM 9, SAMPLE 71011

VAPOR PRESSURE IN ATMOSPHERES AT 3. 200E+0 1 DEG t

| | VP |
|---|---|
| 1 | 3.704E-02 |
| 2 | 1.086E-02 |
| 3 | 2. 504E-03 |
| 4 | 5.643E-04 |
| 5 | 1.123E-04 |
| 6 | 1.955E-05 |
| 7 | 3.176E-06 |
| n | 4.635E-07 |
| 9 | 6.603E-08 |
| 10 | 3.052E-09 |
| 11 | 1.049E-10 |
| 12 | 1.422E-11 |
| 13 | 5.662E-13 |
| 14 | 8.024E-15 |

TABLE 4-3B.

SUMMARY OF TBP CUTS CHARACTERIZATION FOR: COOK INLET, ALASKA
ITEM 7, SAMPLE 72025

| | TB | API | SPG | VOL | MW | TC | PC | VC | A | B | T10 | VIS | NC | NS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.22E+02 | 8.92E+01 | 6.30E-01 | 2.48E+00 | 7.80E+01 | 8.75E+02 | 4.01E+01 | 3.44E+02 | 3.15E+00 | 1.83E-01 | 4.25E+02 | 3.74E-01 | 3 | 1 |
| 2 | 1.67E+02 | 7.72E+01 | 6.96E-01 | 2.58E+00 | 9.07E+01 | 9.27E+02 | 3.77E+01 | 3.94E+02 | 3.25E+00 | 1.99E-01 | 4.61E+02 | 4.20E-01 | 3 | 1 |
| 3 | 2.12E+02 | 6.50E+01 | 7.08E-01 | 6.09E+00 | 1.02E+02 | 9.84E+02 | 3.64E+01 | 4.38E+02 | 3.32E+00 | 2.12E-01 | 4.96E+02 | 4.92E-01 | 3 | 1 |
| 4 | 2.57E+02 | 5.95E+01 | 7.28E-01 | 6.30E+00 | 1.16E+02 | 1.04E+03 | 3.47E+01 | 4.93E+02 | 3.42E+00 | 2.24E-01 | 5.32E+02 | 5.99E-01 | 3 | 1 |
| 5 | 3.02E+02 | 5.54E+01 | 7.44E-01 | 5.26E+00 | 1.31E+02 | 1.08E+03 | 3.30E+01 | 5.52E+02 | 3.55E+00 | 2.36E-01 | 5.69E+02 | 7.41E-01 | 3 | 1 |
| 6 | 3.47E+02 | 5.08E+01 | 7.63E-01 | 5.37E+00 | 1.46E+02 | 1.13E+03 | 3.16E+01 | 6.13E+02 | 3.67E+00 | 2.47E-01 | 6.05E+02 | 9.33E-01 | 3 | 1 |
| 7 | 3.92E+02 | 4.65E+01 | 7.81E-01 | 5.06E+00 | 1.62E+02 | 1.18E+03 | 3.04E+01 | 6.77E+02 | 3.79E+00 | 2.56E-01 | 6.43E+02 | 1.19E+00 | 3 | 1 |
| 8 | 4.37E+02 | 4.30E+01 | 7.97E-01 | 5.26E+00 | 1.80E+02 | 1.23E+03 | 2.92E+01 | 7.47E+02 | 3.94E+00 | 2.65E-01 | 6.80E+02 | 1.54E+00 | 3 | 1 |
| 9 | 4.82E+02 | 3.96E+01 | 8.13E-01 | 5.37E+00 | 1.98E+02 | 1.27E+03 | 2.81E+01 | 8.21E+02 | 4.10E+00 | 2.73E-01 | 7.19E+02 | 2.02E+00 | 3 | 1 |
| 10 | 5.27E+02 | 3.70E+01 | 8.25E-01 | 5.16E+00 | 2.16E+02 | 1.32E+03 | 2.72E+01 | 8.91E+02 | 4.23E+00 | 2.80E-01 | 7.56E+02 | 2.67E+00 | 3 | 1 |
| 11 | 5.80E+02 | 3.48E+01 | 8.47E-01 | 3.41E+00 | 2.41E+02 | 1.37E+03 | 2.61E+01 | 9.91E+02 | 4.43E+00 | 2.89E-01 | 8.02E+02 | 2.97E+00 | 3 | 1 |
| 12 | 6.38E+02 | 3.23E+01 | 8.54E-01 | 5.37E+00 | 2.79E+02 | 1.42E+03 | 2.45E+01 | 1.14E+03 | 4.75E+00 | 2.99E-01 | 8.55E+02 | 5.05E+00 | 3 | 1 |
| 13 | 6.85E+02 | 2.37E+01 | 8.60E-01 | 7.25E+00 | 3.07E+02 | 1.46E+03 | 2.35E+01 | 1.25E+03 | 4.99E+00 | 3.05E-01 | 8.97E+02 | 8.67E+00 | 3 | 1 |
| 13 | 7.35E+02 | 2.96E+01 | 8.80E-01 | 4.33E+00 | 3.45E+02 | 1.50E+03 | 2.24E+01 | 1.40E+03 | 5.33E+00 | 3.12E-01 | 9.47E+02 | 1.72E+01 | 3 | 1 |
| 15 | 7.90E+02 | 2.30E+01 | 8.89E-01 | 4.33E+00 | 3.87E+02 | 1.54E+03 | 2.14E+01 | 1.57E+03 | 5.73E+00 | 3.18E-01 | 9.98E+02 | 3.65E+01 | 3 | 1 |
| 16 | 8.50E+02 | 1.76E+01 | 9.72E-01 | 2.69E+01 | 6.00E+02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.79E+02 | 0 | 0 |

TB = NORMAL BOILING TEMPERATURE, DEG F
API = API GRAVITY
VOL = VOLUME PER CENT OF TOTAL CRUDE
MW = MOLECULAR WEIGHT
TC = CRITICAL TEMPERATURE, DEG RANKINE
PC = CRITICAL PRESSURE, ATMOSPHERES
VC = CRITICAL VOLUME, CC/MOLE
A AND B ARE PARAMETERS IN THE VAPOR PRESSURE EQUATION
T10 IS THE TEMPERATURE IN DEG R WHERE THE VAPOR PRESSURE IS 10 MM HG
VIS IS THE KINEMATIC VISCOSITY IN CENTISTOKES AT 122 DEG F
NC = ERROR CODE, SHOULD BE LESS THAN 20
NS = ERROR CODE, SHOULD BE EQUAL TO 1
IGNORE THE ERROR CODES FOR COMPONENT NUMBER 16

TABLE 4.3-C.

SUMMARY OF TBP CUTS CHARACTERIZATION FOR: MURBAN, ABU DHABI
ITEM 99999 SAMPLE 9999C

| | TB | API | SPGC | VOL | MW | TC | PC | VC | A | B | T10 | VIS | NC | NS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.22E+02 | 9.67E+01 | 6.10E-01 | 1.71E+00 | 7.95E+01 | 8.73E+02 | 3.95E+01 | 3.50E+02 | 3.16E+00 | 1.85E-01 | 4.25E+02 | 3.93E-01 | 3 | 1 |
| 2 | 1.67E+02 | 8.62E+01 | 6.39E-01 | 2.92E+00 | 9.39E+01 | 9.21E+02 | 3.67E+01 | 4.07E+02 | 3.29E+00 | 2.03E-01 | 4.62E+02 | 4.35E-01 | 3 | 1 |
| 3 | 2.12E+02 | 7.06E+01 | 6.88E-01 | 4.94E+00 | 1.05E+02 | 9.78E+02 | 3.56E+01 | 4.49E+02 | 3.37E+00 | 2.14E-01 | 4.97E+02 | 4.96E-01 | 3 | 1 |
| 4 | 2.57E+02 | 6.23E+01 | 7.18E-01 | 6.05E+00 | 1.17E+02 | 1.03E+03 | 3.42E+01 | 5.00E+02 | 3.46E+00 | 2.26E-01 | 5.33E+02 | 5.98E-01 | 3 | 1 |
| 5 | 3.02E+02 | 5.57E+01 | 7.43E-01 | 6.75E+00 | 1.31E+02 | 1.08E+03 | 3.30E+01 | 5.43E+02 | 3.55E+00 | 2.36E-01 | 5.69E+02 | 7.41E-01 | 3 | 1 |
| 6 | 3.47E+02 | 5.16E+01 | 7.60E-01 | 6.45E+00 | 1.47E+02 | 1.13E+03 | 3.15E+01 | 5.76E+02 | 3.68E+00 | 2.47E-01 | 6.06E+02 | 9.31E-01 | 3 | 1 |
| 7 | 3.92E+02 | 4.85E+01 | 7.73E-01 | 5.75E+00 | 1.64E+02 | 1.18E+03 | 3.01E+01 | 6.05E+02 | 3.83E+00 | 2.57E-01 | 6.43E+02 | 1.18E+00 | 3 | 1 |
| 8 | 4.37E+02 | 4.56E+01 | 7.87E-01 | 5.65E+00 | 1.83E+02 | 1.22E+03 | 2.88E+01 | 7.09E+02 | 4.00E+00 | 2.67E-01 | 6.81E+02 | 1.52E+00 | 3 | 1 |
| 9 | 4.82E+02 | 4.30E+01 | 7.97E-01 | 5.95E+00 | 2.03E+02 | 1.26E+03 | 2.76E+01 | 8.38E+02 | 4.19E+00 | 2.75E-01 | 7.20E+02 | 1.98E+00 | 3 | 1 |
| 10 | 5.27E+02 | 4.00E+01 | 8.11E-01 | 4.94E+00 | 2.22E+02 | 1.31E+03 | 2.67E+01 | 9.13E+02 | 4.29E+00 | 2.82E-01 | 7.57E+02 | 2.61E+00 | 3 | 1 |
| 11 | 5.80E+02 | 3.58E+01 | 8.31E-01 | 5.75E+00 | 2.40E+02 | 1.36E+03 | 2.56E+01 | 1.02E+03 | 4.50E+00 | 2.91E-01 | 8.04E+02 | 3.71E+00 | 3 | 1 |
| 12 | 6.36E+02 | 3.40E+01 | 8.40E-01 | 5.65E+00 | 2.87E+02 | 1.41E+03 | 2.40E+01 | 1.17E+03 | 4.84E+00 | 3.01E-01 | 8.57E+02 | 4.82E+00 | 3 | 1 |
| 13 | 6.85E+02 | 3.00E+01 | 8.61E-01 | 6.55E+00 | 3.12E+02 | 1.45E+03 | 2.33E+01 | 1.27E+03 | 5.04E+00 | 3.06E-01 | 8.98E+02 | 6.39E+00 | 3 | 1 |
| 14 | 7.36E+02 | 2.84E+01 | 8.70E-01 | 6.05E+00 | 3.53E+02 | 1.49E+03 | 2.21E+01 | 1.43E+03 | 5.41E+00 | 3.13E-01 | 9.49E+02 | 1.62E+01 | 3 | 1 |
| 15 | 7.96E+02 | 2.66E+01 | 8.86E-01 | 5.65E+00 | 3.95E+02 | 1.53E+03 | 2.11E+01 | 1.60E+03 | 5.83E+00 | 3.19E-01 | 1.00E+03 | 3.42E+01 | 3 | 1 |
| 16 | 8.50E+02 | 1.67E+01 | 9.39E-01 | 1.93E+01 | 6.00E+02 | 0.00E+00 | 0.00E+00 | 0.90E+03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.35E+02 | 0 | 0 |

TB = NORMAL BOILING TEMPERATURE, DEG F
API = API GRAVITY
VOL = VOLUME PER CENT OF TOTAL CRUDE
MW = MOLECULAR WEIGHT
TC = CRITICAL TEMPERATURE, DEG RANKINE
PC = CRITICAL PRESSURE, ATMOSPHERES
VC = CRITICAL VOLUME, CC/MOLE
A AND B ARE PARAMETERS IN THE VAPOR PRESSURE EQUATION
T10 IS THE TEMPERATURE IN DEG R WHERE THE VAPOR PRESSURE IS 10 MM HG
VIS IS THE KINEMATIC VISCOSITY IN CENTISTOKES AT 122 DEG F
NC = ERROR CODE, SHOULD BE LESS THAN 20
NS = ERROR CODE, SHOULD BE EQUAL TO 1
IGNORE THE ERROR CODES FOR COMPONENT NUMBER 16

TABLE -3D.

SUMMARY OF TBP CUTS CHARACTERIZATION FOR WILMINGTON, CALIFORNIA
ITEM 94, SAMPLE 71052

| | TB | API | SPG R | VOL | MW | TC | PC | VC | A | B | T10 | VIS | NC | NS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.12E+02 | 6.86E+01 | 6.95E-01 | 2.30E+00 | 1.04E+02 | 6.80E+02 | 3.59E+01 | 4.45E+02 | 3.35E+00 | 2.13E-01 | 4.97E+02 | 4.94E-01 | 3 | 1 |
| 2 | 2.57E+02 | 5.87E+01 | 7.31E-01 | 2.40E+00 | 1.15E+02 | 7.04E+03 | 3.48E+01 | 4.91E+02 | 3.4[illegible]E+00 | 2.24E-01 | 5.32E+02 | 5.99E-01 | 3 | 1 |
| 3 | 3.02E+02 | 5.30E+01 | 7.54E-01 | 2.40E+00 | 1.29E+02 | 7.09E+03 | 3.34E+01 | 5.45E+02 | 3.5[illegible]E+00 | 2.35E-01 | 5.68E+02 | 7.45E-01 | 3 | 1 |
| 4 | 3.47E+02 | 4.81E+01 | 7.74E-01 | 2.51E+00 | 1.44E+02 | 7.14E+03 | 3.21E+01 | 6.03E+02 | 3.62E+00 | 2.45E-01 | 6.05E+02 | 9.42E-01 | 3 | 1 |
| 5 | 3.92E+02 | 4.32E+01 | 7.96E-01 | 2.81E+00 | 1.59E+02 | 7.19E+03 | 3.10E+01 | 6.63E+02 | 3.73E+00 | 2.54E-01 | 6.41E+02 | 1.21E+00 | 3 | 1 |
| 6 | 4.37E+02 | 3.88E+01 | 8.17E-01 | 3.6[illegible]E+00 | 1.75E+02 | 7.24E+03 | 3.09E+01 | 7.27E+02 | 3.85E+00 | 2.63E-01 | 6.78E+02 | 1.58E+00 | 3 | 1 |
| 7 | 4.82E+02 | 3.54E+01 | 8.33E-01 | 4.4[illegible]E+00 | 1.93E+02 | 7.28E+03 | 3.07E+01 | 7.98E+02 | 4.00E+00 | 2.71E-01 | 7.16E+02 | 2.08E+00 | 3 | 1 |
| 8 | 5.27E+02 | 3.23E+01 | 8.49E-01 | 5.3[illegible]E+00 | 2.09E+02 | 7.33E+03 | 3.05E+01 | 8.61E+02 | 4.12E+00 | 2.77E-01 | 7.54E+02 | 2.02E+00 | 3 | 1 |
| 9 | 5.80E+02 | 2.68E+01 | 8.79E-01 | 4.7[illegible]E+00 | 2.29E+02 | 7.39E+03 | 3.02E+01 | 9.40E+02 | 4.24E+00 | 2.85E-01 | 7.98E+02 | 3.20E+00 | 3 | 1 |
| 10 | 6.38E+02 | 2.45E+01 | 8.92E-01 | 6.3[illegible]E+00 | 2.59E+02 | 7.44E+03 | 3.00E+01 | 1.06E+03 | 4.52E+00 | 2.94E-01 | 8.49E+02 | 5.80E+00 | 3 | 1 |
| 11 | 6.85E+02 | 2.23E+01 | 9.04E-01 | 4.1[illegible]E+00 | 2.86E+02 | 7.48E+03 | 2.97E+01 | 1.17E+03 | 4.74E.00 | 3.00E-01 | 8.91E+02 | 1.04E+01 | 3 | 1 |
| 12 | 7.38E+02 | 2.03E+01 | 9.16E-01 | 5.5[illegible]E+00 | 3.26E+02 | 7.52E+03 | 2.96E+01 | 1.30E+03 | 5.03E.00 | 3.08E-01 | 9.40E+02 | 2.16E+01 | 3 | 1 |
| 13 | 8.50E+02 | 8.90E+00 | 9.91E-01 | 5.36E+01 | 6.00E+02 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E.00 | 0.00E+00 | 0.00E+00 | 2.10E+02 | 0 | 0 |

TB = NORMAL BOILING TEMPERATURE, DEG F
API = API GRAVITY
VOL = VOLUME PER CENT OF TOTAL CRUDE
MW = MOLECULAR WEIGHT
TC = CRITICAL TEMPERATURE, DEG RANKINE
PC = CRITICAL PRESSURE, ATMOSPHERES
VC = CRITICAL VOLUME, CC/MOLE
A AND B ARE PARAMETERS IN THE VAPOR PRESSURE EQUATION
T10 IS THE TEMPERATURE IN DEG R WHERE THE VAPOR PRESSURE IS 10 MM HG
VIS IS THE KINEMATIC VISCOSITY IN CENTISTOKES AT 122 DEG F
NC = ERROR CODE, SHOULD BE LESS THAN 20
NS = ERROR CODE, SHOULD BE EQUAL TO 1
IGNORE THE ERROR CODES FOR COMPONENT NUMBER 13

TABLE 4-3E.

CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION : PRUDHOE BAY , ALASKA

VAPOR PRESSURE IN ATMOSPHERES AT 5.540E+01 DEG F

| | VP |
|---|---|
| 1 | 7.751E-02 |
| 2 | 2.440E-02 |
| 3 | 6.852E-03 |
| 4 | 1.644E-03 |
| 5 | 3.617E-04 |
| 6 | 7.046E-05 |
| 7 | 1.283E-05 |
| 8 | 2.115E-06 |
| 9 | 3.394E-07 |
| 10 | 3.193E-08 |
| 11 | 1.556E-09 |
| 12 | 1.255E-10 |
| 13 | 4.983E-12 |
| 14 | 1.264E-13 |

CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: COOK INLET, ALASKA

VAPOR PRESSURE IN ATMOSPHERES AT 5.540E+01 DEG F

| | VP |
|---|---|
| 1 | 2.280E-01 |
| 2 | 7.673E-02 |
| 3 | 2.430E-02 |
| 4 | 6.680E-03 |
| 5 | 1.561E-03 |
| 6 | 3.402E-04 |
| 7 | 6.809E-05 |
| 8 | 1.247E-05 |
| 9 | 1.945E-06 |
| 10 | 3.071E-07 |
| 11 | 2.770E-08 |
| 12 | 1.275E-09 |
| 13 | 9.292E-11 |
| 14 | 3.248E-12 |
| 15 | 7.181E-14 |

CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION : MUBDAN, ABU DHABI

VAPOR PRESSURE IN ATMOSPHERES AT 5.540 E+01 DEG F

| | VP |
|---|---|
| 1 | 2.279E-01 |
| 2 | 7.565E-02 |
| 3 | 2.368E-02 |
| 4 | 6.517E-03 |
| 5 | 1.555E-03 |
| 6 | 3.350E-04 |
| 7 | 6.459E-05 |
| 8 | 1.110E-05 |
| 9 | 1.657E-06 |
| 10 | 2.699E-07 |
| 11 | 2.295E-08 |
| 12 | 1.051E-09 |
| 13 | 7.944E-11 |
| 14 | 2.40:11:- 12 |
| 15 | 4.950E-14 |

CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: WILMINGTON, CALIFORNIA

VAPOR PRESSURE IN ATMOSPHERES AT 5.540E+01 DEG F

| | VP |
|---|---|
| 1 | 2.389E-02 |
| 2 | 6.728E-03 |
| 3 | 1.613E-03 |
| 4 | 3.583E-04 |
| 5 | 7.427E-05 |
| 6 | 1.411E-05 |
| 7 | 2.361E-06 |
| 8 | 3.822E-07 |
| 9 | 4.110E-08 |
| 10 | 2.372E-09 |
| 11 | 1.997E-10 |
| 12 | 9.010E-12 |

### 4.1.2 Pseudo-Component Evaporation Model on the Ocean Surface

The evaporation model which predicts the oil remaining in a slick is derived from the physical properties of the oil cuts and a total material balance. From the previous discussion a number of pseudo-components are defined. For each pseudo-component the vapor pressure, molecular weight and initial quantity are known, and a material balance can be written to include each:

$$\frac{dM_i}{dt} = -K_p A X_i P_i^* \quad \text{for } i = 1, 2, \ldots\ldots\ldots \text{total number of components} \tag{4.10}$$

where it is assumed that the oil slick is well stirred and a pseudo-Raoult's law applies as the mixing rule. In this rate equation, $M_i$ is the number of moles of component i in the oil slick, $P_i^*$ is the vapor pressure at the prevailing environmental temperature, A is the area of the slick, $K_p$ is an overall mass-transfer coefficient based on partial pressure driving forces, and xi is the mole fraction of component i in the slick. The differential equations are all coupled through the mole fraction term where the total number of moles appears in the denominator.

The over-all mass-transfer coefficient can be calculated two different ways. One way is the approach of MACKAY and MATSUGU, 1976:

$$K = 0.0292\, U^{0.78}\, X^{-0.11}\, S.^{-0.67} \tag{4.11}$$

where U is the wind velocity in m/hr, X is the slick diameter (assumes circular slick), and Sc is the Schmidt number (2.7). This expression is a correlation and is the proper mass transfer coefficient to multiply by the partial pressure to obtain the rate.

Implicit in the rate equation for the i-th component is the assumption that the partial pressure in the bulk atmosphere is zero. It can then be seen that the mass transfer coefficient above takes into account an averaging effect whereby the evaporation rate on the downwind portion of the slick is lower than the upwind portion due to the fact that $P_i$ becomes finite in the air immediately over the oil slick in the direction of the wind.

Another approach to calculating overall mass transfer coefficients is that of TREYBAL, 1955, and LISS, 1974:

$$\frac{1}{K} = \frac{1}{k_g} + \frac{H^*}{k_\ell} \tag{4.12}$$

where $k_g$ is the individual gas-phase mass-transfer coefficient, $k_\ell$ is the individual liquid-phase mass-transfer coefficient and H* is the Henry's law coefficient which is defined by:

$$Pi \equiv H^* x_i \tag{4.13}$$

The units on $k_g$ for a partial pressure driving force are typically moles/($m^2$ hr atm), the units on k for a mole fraction driving force is moles/($m^2$ hr), and the units on H* are atm. The individual mass transfer coefficients, $k_\ell$ and $k_g$, must then be obtained from actual data in a manner similar to that used to deduce K in equation (4.11).

The other bulk property of interest for the oil slick is its viscosity. When oil is spilled on the ocean surface, the viscosity is low enough so that mixing occurs and the well-mixed oil-phase assumption is valid. However, as evaporation occurs the viscosity increases because the low-viscosity fractions are removed. The viscosity "blending" relationship used to predict the bulk viscosity as a function of composition is:

$$\ln\mu_{mix} = \sum_{i=1} x_i \ln\mu_i \quad \text{for } i = 1, 2, \ldots \tag{4.14}$$

Therefore, in order to predict viscosity as a function of time the viscosity of the individual fraction from the distillation characterization must be known. If these data are not available then the viscosity of the cut can be estimated from the correlation form indicated in equation (4.1) where the predicted quantity is $\log_{10}$ of the kinematic viscosity at 122°F in centistokes and the constants $C_1$ to $C_5$ are presented in Table 4-1 (HOUGEN, 1965). The viscosity for each cut can then be scaled with respect to temperature according to (GOLD, 1969):

$$\ln \frac{\mu}{\mu_o} = 5.2 \times 10^{-4}\left(\frac{1}{T} - 0.00172\right) \tag{4.15}$$

where T is in degrees R (Rankine scale). This viscosity equation does not take into account water-in-oil emulsion (mousse) formation (MACKAY, 1980).

The area for mass transfer in equation (4.10) is calculated from the rate at which the oil spreads on the water surface. Considerable research has been devoted to the spreading of oil on the water surface, however, many of the resulting models are still relatively elementary. We have relied on the MACKAY, 1980 version.

Oil is assumed to spread in thick and thin slicks, with the thick slick feeding the thin slick. Using arguments based on observation, the area of the thin slick is given by:

$$\frac{dA_1}{dt} = k_1 A_1^{1/3} \exp\left[-k_2/Z\right] \tag{4.16}$$

where $A_1$, is the area, $k_1$ and $k_2$ are constants and Z is the thickness of the thick slick. The thick slick area is given by:

$$\frac{dA_2}{dt} = k_3 Z^{1.33} A_2 - k_4 A_1 / Z \tag{4.17}$$

where $A_2$ is the area of the thick slick and $k_3$ and $k_4$ are constants. The area and thickness are related by the mass (moles) of oil in the slick and the bulk density, and the oil remaining in the slick is obtained from the previous differential equations describing the pseudo-component material balances.

Constants for the above equations are $k_1 = 1$, $k_2 = 0.0015$, $k_3 = 150$ and $k_4 = 1 \times 10^{-6}$. The units on the variables are meters and seconds. The thick oil slick is assumed to have an initial thickness of 2 cm and the thin slick area is assumed to be 8 times the thick area. The thin oil slick thickness is set at 1 micrometer.

The evaporation model just described could be used to predict mass transfer from a spilled oil mass over any time period. However, it is known through observation that an oil slick eventually becomes rigid and is not well-stirred at longer (greater than a few days) time intervals. Therefore, we have established a criterion to guage when a slick becomes rigid based on bulk viscosity (presently a value of 1000 centipoises is being used). A more sophisticated approach would be to include information on the sea state and the Reynold's stress at the air-sea interface; however, such data are difficult to come by in quantitative form.

Equations (4.1) through (4.17) represent the pseudo-component mathematical model describing the weathering of an oil slick due to evaporation. The material balance approach incorporates physical properties, mass balance, and the effect of environmental conditions. Figure 4-1 summarizes the flow of information that occurs in this model.

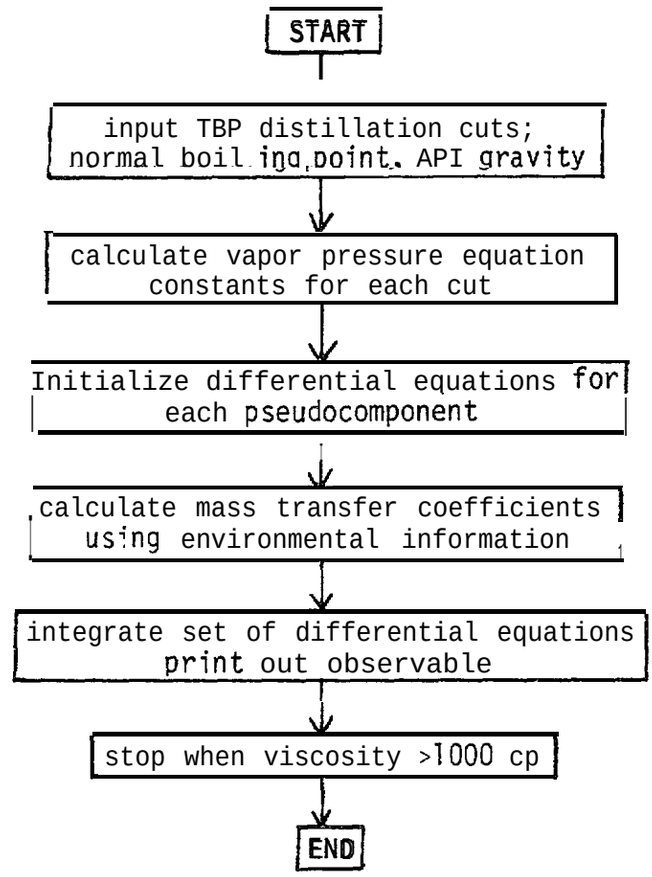



FIGURE 4-1. CALCULATION STEPS FOR PREDICTING SLICK MASS DUE TO EVAPORATION USING PSEUDOCOMPONENTS.

The results of an evaporation calculation for Prudhoe Bay crude oil are presented in Figures 4-2 and 4-3, and in Appendix A. Figure 4-2 presents the starting distillation curve (at time zero) and curves at other times up to 500 hours. Figure 4-3 presents the predicted gas-chromatograph curve where the residuum has been deleted and the curves renormalized. These. results were obtained for a mass-transfer coefficient calculated from the MACKAY and MATSUGU (1976) correlation for a 10 knot wind.

When an oil slick becomes "rigid" due to increasing viscosity, the components leave the slick by diffusion, but mathematically the slick can still appear to be well-stirred. Section 4.6.3 presents a discussion for a criterion to determine when internal circulation in an oil slick ceases. In order for an oil slick to appear well-stirred when in fact it is a slab, the diffusivity, the convective mass transfer coefficient, the Henry's law coefficient and the slick thickness must satisfy a certain relation. The following section presents a discussion of this relation, which is called the mass-transfer "Biot" number, and how the modeling mathematics can be simplified by evaluating this relationship.

## 4.2 The Influence of Mechanical State on an Oil Slick

In essentially all of the previously published modeling work on oil weathering by the processes of evaporation and dissolution, the oil phase has been modeled as a well-stirred phase, resulting in a decaying exponential expression. Another modeling assumption which might be applied to an oil phase is that diffusion controls the mass transfer of components, at least under certain conditions. The well-stirred oil assumption is not universally appropriate since there can be conditions under which an oil phase is stagnant and not mechanically stirred. However, if the rate of evaporation (or dissolution) is the rate limiting step, then the concentration gradients in the oil phase can "keep up" with the evaporation rate at the surface and the "oil phase appears well-stirred (i.e., no concentration gradients exist). The rate of evaporation or dissolution can be expected to be rate limiting when the

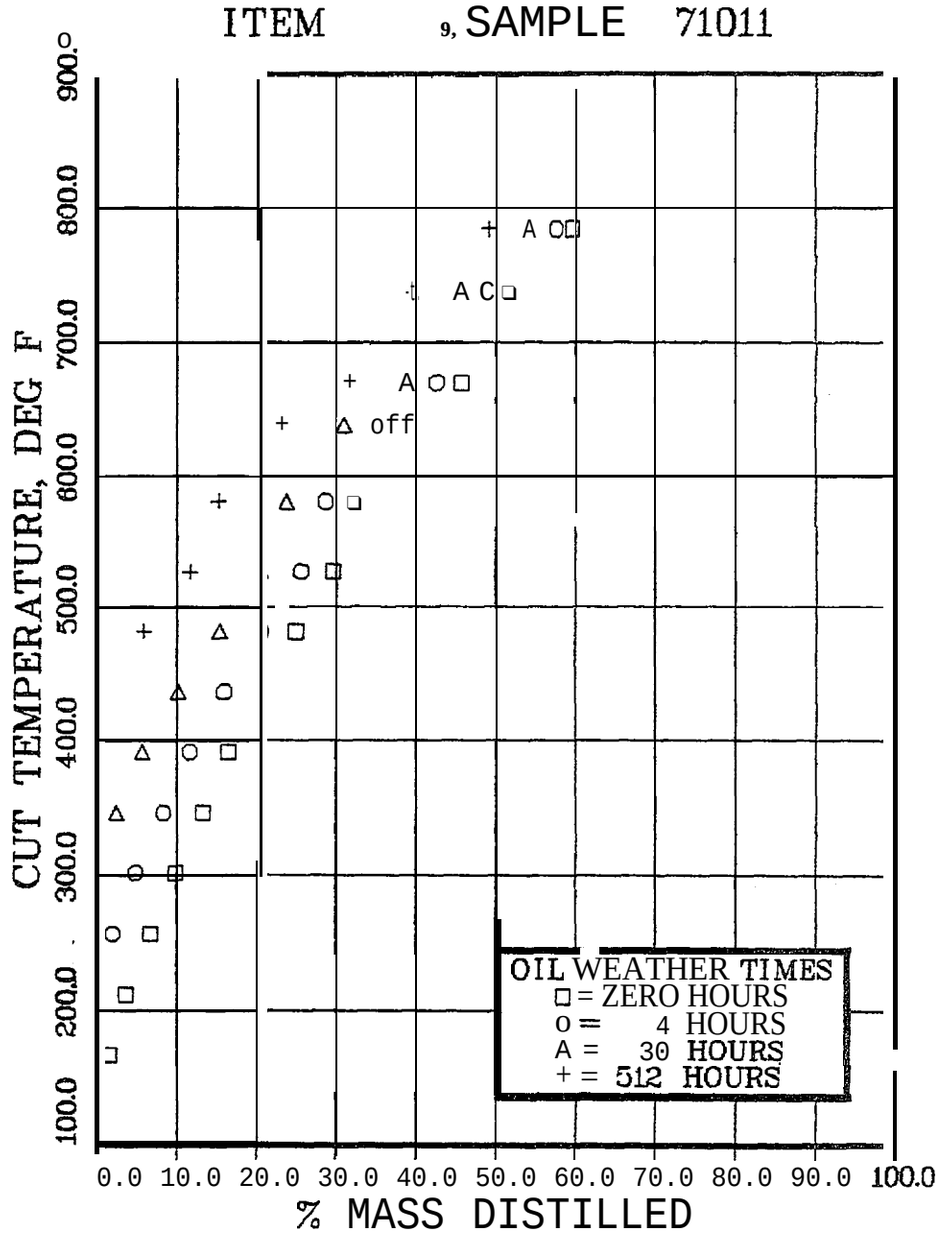



FIGURE 4-2. PREDICTED TOTAL DISTILLATION CURVES FOR WEATHERED OIL AT 55° F.

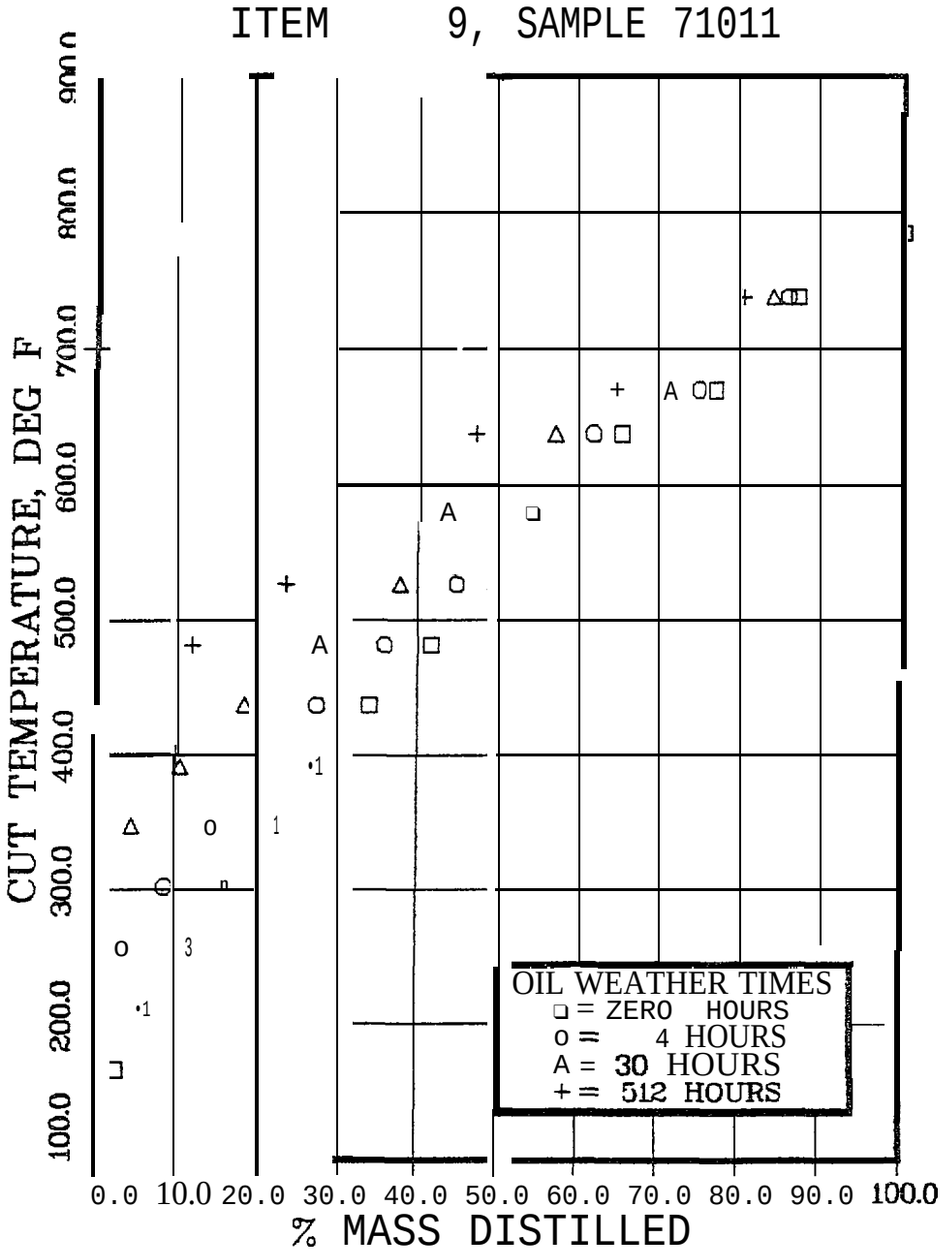



FIGURE 4-3. PREDICTED GC DISTILLATION CURVES FOR WEATHERED OIL AT 55° F.

partial pressure or volubility of the component of interest is quite small, or when a crust or skin has formed on the oil surface.

The following discussion examines a criterion for invoking the well-stirred oil phase assumption by invoking results from corresponding heat transfer problems. This criterion is then examined for the physical properties of the components of interest for evaporation from an oil slick. Finally, the results of a numerical experiment are presented which demonstrate that a decaying exponential model can fit the data from an evaporation experiment where the evaporation is diffusion controlled within the bulk oil phase.

### 4.2.1 Modeling Assumptions

In heat transfer problems involving flat plates and a surface heat transfer coefficient, there are two problem solutions termed the "thin" and "thick" plate solutions. A thin plate does not have sufficient internal thermal resistance relative to the surface resistance to support temperature gradients. In other words, the surface resistance to heat transfer is much greater than the internal resistance. As a result the temperature of a thin plate is essentially uniform and the thin plate problem solution is the same as that obtained for a well-stirred phase comprising the plate. A particular plate can be classified as thermally thick or thin according to the Biot number (ROHSENOW and HARTNETT, 1973) which is:

$$Bi \equiv \frac{h\delta}{K} \quad \text{(dimensionless)} \tag{4.18}$$

where h is the surface conductance, $\delta$ is the plate thickness and K is the thermal conductivity. Roughly, for a flat plate with the convective boundary condition:

$$\text{thin, } Bi < 0.1 \text{ ; thick, } Bi > 0.1 \tag{4.19}$$

The Biot number as defined above is the same as H in the solutions for the temperatures of a well-stirred fluid in contact with a slab with "radiation" boundary conditions (JAEGER, 1945).

The corresponding Biot number for mass transfer problems involving flat plates is obtained by examining the following equations for heat and mass transfer:

$$-K \left.\frac{dT}{dx}\right|_{x=0} = h(T_m - T) \tag{4.20}$$

where T is the temperature of the solid at the interface and $T_m$ is the temperature of the convective medium. The corresponding equation for mass transfer is:

$$-\mathscr{D} \left.\frac{dc}{dx}\right|_{x=0} = h(C_m - CM^*) \tag{4.21}$$

where $\mathscr{D}$ is the diffusion coefficient in the slab, C is the concentration in the slab at the interface, Cm is the concentration of the convective medium, $C_m^*$ is the hypothetical concentration of the convective medium in equilibrium with C, and h is now the convective mass-transfer coefficient. The equilibrium relationship required is assumed to be a Henry's law type expressed as:

$$CM^* = \xi C \tag{4.22}$$

Equations (4.21) and (4.22) are not in the same form because of the equilibrium relationship that exists in the mass transfer case. However, making the change of variable $C_m^* = \xi C$ in the later equation yields:

$$-\mathscr{D}\frac{dc}{dx}\bigg|_{x=0} = \xi h(\overline{C}_m - C) \tag{4.23}$$

Now, compared to the heat transfer Biot number, the Biot mass-transfer number becomes:

$$Bi(mass) = \frac{h\xi\delta}{\mathscr{D}} \tag{4.24}$$

In order to use the Biot number criterion to determine if an oil slick is diffusion-controlled, the quantity $\xi$ in the Henry's law expression is required. The following calculation illustrates the assumptions and data required to calculate $\xi$. The starting point for the calculation is:

$$C_a = \xi C_\ell \tag{4.25}$$

where $C_a$ is the concentration in the air, gin/cc; $C_\ell$ is the concentration in the liquid, gm/cc; and" $\xi$ is dimensionless.

In the absence of experimental measurements of $\xi$, a conventional Raoult's law is assumed:

$$Pi = x_i P_{vp} \tag{4.26}$$

where Pi is the partial pressure of component i, xi is the mole fraction, and $P_{Vp}$ is the pure component vapor pressure. In order to use this expression, it must be assumed that:

$$C_a = \left[\frac{M_i}{RT}\right] P_{vp} \left[\frac{M_o}{\rho_o} \frac{1}{M_i}\right] C_\ell \tag{4.27}$$

where $M_i$ is the molecular weight of the component of interest, $M_o$ is the mean molecular weight of the oil , and $P_{Vp}$ is the bulk oil density. The quantity $RT/M_i$ converts $C_a$ to partial pressure and the quantity $M_o/(P_{vp}M_i)$ converts $C_\ell$ to mole fraction; thus recovering Raoult's law as used here. The dimensionless Henry's law constant sought becomes:

$$\xi \equiv \frac{P_{vp}M_o}{\rho_o RT} \tag{4.28}$$

which has units of (gm-mole i)/(gm-mole oil) and is unitless according to the use of mo"le fraction in Raoult's law.

In order to illustrate the calculation of the Biot mass-transfer number, the vapor pressures for hydrocarbons containing 6 to 18 carbon atoms can be predicted from (BUTLER, 1975):

$$Pi = \exp\ [10.94 - 1.06N_i] \tag{4.29}$$

where Pi is the vapor pressure in mm Hg at 20°C and $N_i$ is the number of carbon atoms. The quantity $\xi$ becomes:

$$\xi = \frac{\exp\ [10.94 - 1.06N_i]\ M.}{760\rho_o RT} \tag{4.30}$$

Assuming a mean molecular weight for the oil of 300 gms/gm-mole and a bulk oil density of 0.8 $gm/cm^3$, Equation (4.30) becomes:

$$\xi = 2 \times 10^{-5} \exp [10.94 - 1.06N_i] \tag{4.31}$$

at 20″ C, and the above can be used to calculate the Biot mass-transfer number.

In order to calculate the Biot mass-transfer number, the diffusivity of the component of interest, the convective mass-transfer coefficient and oil thickness must be estimated. For the diffusivity a value of $10^{-6}$ $cm^2/sec$ is used (REID, 1977); a slick thickness of 0.5 cm, and for the convective mass-transfer coefficient a value of 1000 cm/hr (0.28 cm/see; LISS, 1974). The Biot mass-transfer number becomes:

$$Bi \equiv 1.4 \times 10^{-5} \xi \tag{4.32}$$

or, using the expression for :

$$Bi = 2.8 \exp [10.94 - 1.06N_i] \tag{4.33}$$

Table 4-4 presents the Biot mass transfer number for hydrocarbons containing 6 to 20 carbon atoms. This table indicates that the "thin" plate solution (i.e., the well-stirred phase assumption) is satisfactory, and that it canbe used for hydrocarbons $n\text{-}C_{14}$ and higher in carbon number. Thus, for these compounds the evaporation rate is so small that the diffusion transport rate can "keep up," and the concentration profiles within the oil are "flat." However, for hydrocarbons containing 13 carbon atoms or less, the evaporation rate is much greater than the diffusion rate. As a result concentration profiles can be present in the oil phase and the well-stirred oil-phase assumption should not be used.

It is important to recognize the assumptions used to calculate the Biot mass-transfer number. The diffusivity assumed is $10^{-6}$ $cm^2/see$, and it is

TABLE 4-4. BIOT MASS TRANSFER NUMBER ($\mathscr{D}=10^{-6}$ cm²/see, $\delta$=0.5 cm, h=1000 cm/hr, T=20°C).

| $N_i$ (carbon atoms) | Bi (dimensionless) | |
|---|---|---|
| 6 | 273 | |
| 7 | 94 | |
| 8 | 33 | |
| 9 | 11 | |
| 10 | 4 | |
| 11 | 1.4 | |
| 12 | 0.5 | |
| 13 | 0.16 | diffusion controlled (convection> diffusive rate) |
| 14 | 0.05 | (diffusive rate>convective) |
| 15 | 0.02 | well-stirred |
| 16 | 0.006 | |
| 17 | 0.002 | |
| 18 | 0.0008 | |
| 19 | 0.0003 | |
| 20 | 0.0001 | |

conceivable that a value of $10^{-7}$ to $10^{-9}$ $cm^2/sec$ is real . Since the diffusivity appears in the denominator of the Biot mass transfer number, all the values presented in Table 4-4 could increase accordingly. Also there are no data available to determine the real value of the equilibrium constant, $\xi$, and it is not readily known how close to reality the calculated values are.

### 4.2.2 Material Transport Under Diffusion-Controlled Evaporation

The previous discussion presents information on the criterion for the assumption of a well-stirred oil phase for modeling the evaporation oil-weathering process. It was pointed out that many assumptions were required to perform the calculation of the Biot mass transfer number and these assumptions definitely require refinement. However, whether or not the evaporation process is diffusion-controlled it must be recognized that experimentally the well-stirred oil phase model, which is a decaying exponential, appears to fit the observed data quite well. Therefore, it is worthwhile to examine the mathematics of a diffusion controlled slab from which components are evaporating and compare the observable variable with a first order decay law. The observable variable is the concentration of the component of interest in the air stream, or the bulk average concentration in the fluid, as a function of time.

The numerical experiment performed here was that of calculating the theoretical air phase concentration of a component evaporating from a diffusion-controlled slab, and then fitting by least squares a decaying exponential to the "data".

The concentration profiles in a diffusion controlled slab from which a component of interest is evaporating are (CARSLAW and JAEGER, 1959):

$$\frac{C}{C_o} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(2n-1)} \cos\left\{\frac{(2n-1)\pi x}{2\ell}\right\} \exp\left[-\frac{(2n-1)^2\pi^2\theta}{4}\right] \qquad (4.34)$$

where $C_o$ is the initial concentration throughout and $\theta$ is the dimensionless time: $\mathcal{D}t/\ell^2$. The evaporation rate, and hence the concentration of the component of interest in an air stream above the surface, is the derivative of the above expression evaluated at the evaporating surface. The derivative need not be multiplied by the area and diffusivity since these quantities only "scale" the calculated concentration, and thus the calculated concentration in the air stream is in arbitrary units.

The results of this numerical experiment are presented in Figures 4-4 through 4-6. In each of the figures the fitting curve, which is $A*\exp[-k\theta]$, has four symbols marking it, and the theoretical curve is the one with no symbols running from a dimensionless time of 0.1 to 1.5. In Figure 4-4 the fitted curve covers one e-folding time; i.e., the time required for the theoretical curve to decrease by l/e = 0.367, beginning at $\theta = 0.1$. In Figures 4-5 and 4-6 the fitted curves cover two and three e-folding times, respectively.

The result of this numerical experiment is that the fitted $A*\exp[-k\theta]$ curves cannot be distinguished in a laboratory experiment from the theoretical curve. In other words, performing a laboratory experiment on evaporation, fitting the data to $A*\exp[-k\theta]$, and obtaining an apparently good fit of the data is not sufficient to draw a conclusion about which mechanism is controlling.

The results of this numerical experiment can be used to obtain a single exponential expression to predict the decay of the air-phase concentration above a diffusion-controlled slab in the following way. Note that over the range of dimensionless time from 0.1 to 1.5 the "k" in the exponential fit is about -2.5. Thus, $\exp[-kt]$ where $k = 2.5\mathcal{D}t/\ell^2$, and t is time in seconds, provides a good fit to the data over the range of the independent variable examined.

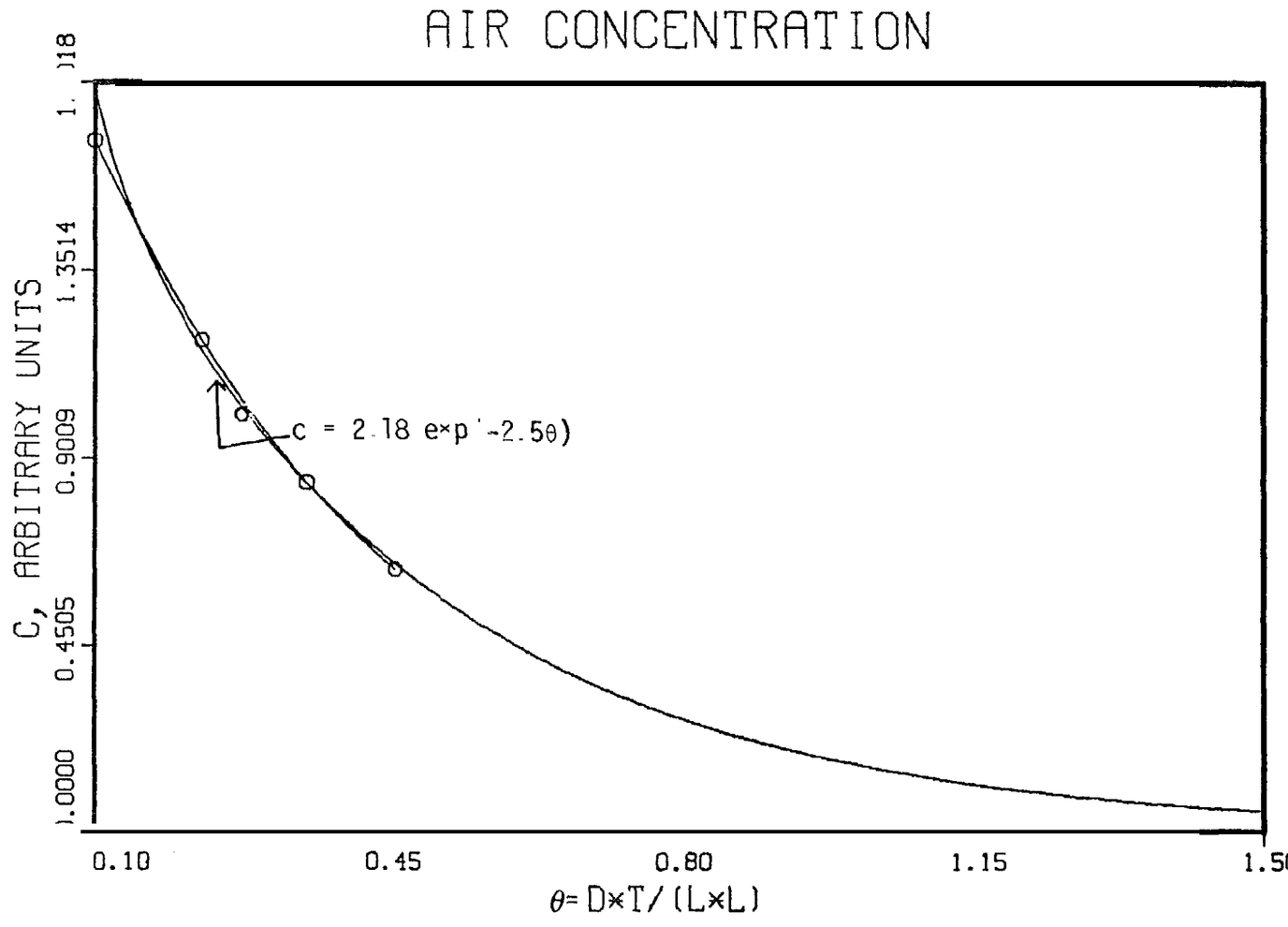



FIGURE 7-4. THEORETICAL AIR CONCENTRATION OF AN EVAPORATING COMPONENT ABOVE A DIFFUSION CONTROLLED SLAB AND A LEAST SQUARES EXP(-kθ).

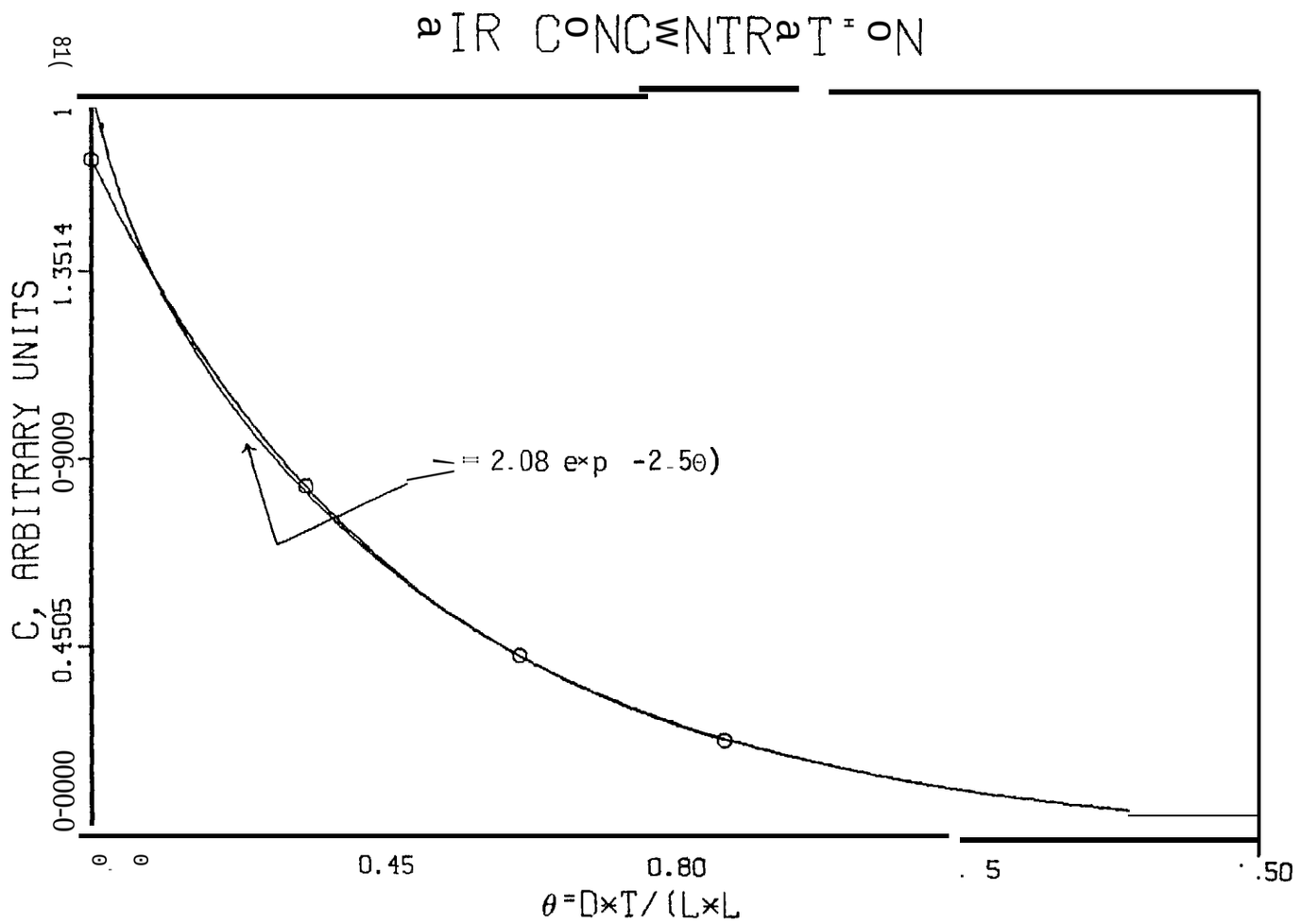



FIGURE 4-5. THEORETICAL AIR CONCENTRATION OF AN EVAPORATING COMPONENTS ABOVE A DIFFUSION CONTROLLED SLAB AND A LEAST SQUARES EXP(-kθ)

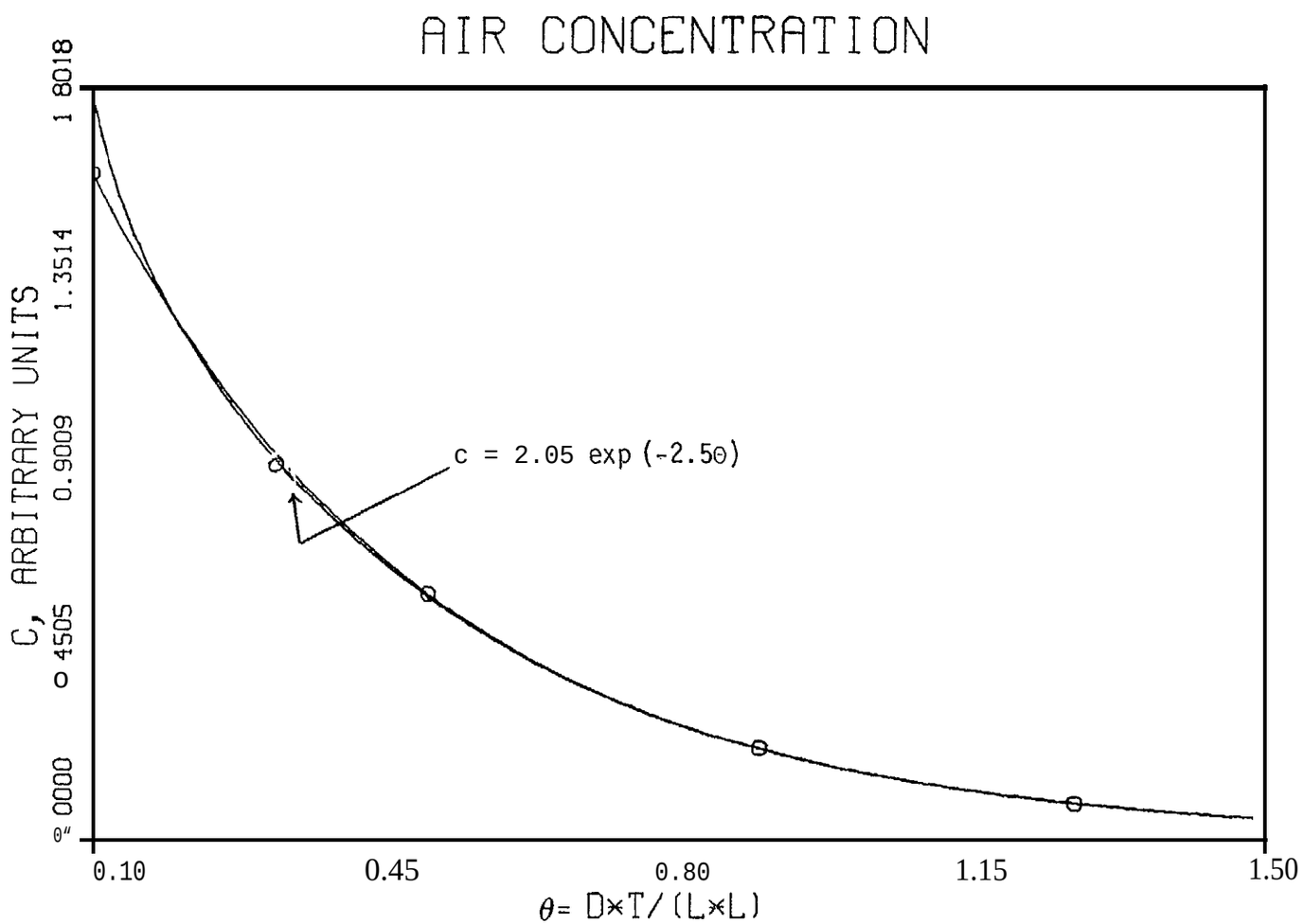



FIGURE 4-6. THEORETICAL AIR CONCENTRATION OF AN EVAPORATING COMPONENT ABOVE A DIFFUSION CONTROLLED SLAB AND A LEAST SQUARE EXP(-kθ).

These discussions have presented criteria to determine if an evaporating oil slick should be modeled as a well-stirred or stagnant phase. The method for that determination has been based on the Biot mass-transfer number in much the same way the presence of laminar flow is based on the Reynolds number. However, the data required to calculate the Biot mass-transfer number are not readily available, and estimates of these data must be made.

The primary reason for wanting to know if the oil phase is well-stirred or stagnant is that each of these states require different data and equations for model development. If an oil slick is diffusion-controlled, wind speed will not affect the average, time-dependent composition of the diffusing component in the oil mass. On the other hand, if the oil phase is well-stirred the wind speed will have an affect on the average composition of the oil.

Even though an oil phase can be diffusion controlled, it has been demonstrated that a decaying exponential will fit the air phase concentration data quite well. Thus, if an experiment is conducted to determine if evaporation from an oil slick is occurring from a well-stirred phase, it is necessary to obtain a good fit to the data but not sufficient to distinguish a well-stirred from a diffusion-controlled phase.

## 4.3 Component-Specific Evaporation from a Finite Oil Slick

The component-specific approach to model the evaporation process cannot predict the total mass of oil remaining in a slick. This approach can yield component-specific concentrations in the oil as a function of time when coupled to a pseudo-component overall material balance. For each specific component the rate of loss of component i from the slick takes the same form as a pre-defined pseudo-component:

$$\frac{dC_i}{dt} = -KAHiCi \quad \text{for } i = 1, 2, \ldots\ldots\ldots \tag{4.35}$$

where $C_i$ is the concentration of component i in the oil, Hi is the Henry's law coefficient for the i-th component, and K and A are the same as those used in the pseudo-component equations. There is no "closure" on the total mass of oil remaining in the slick when the above equation is used because the index i does not include all species. Therefore, the closure of the material balance can be handled in any of three ways:

1) ignore the decreasing slick mass and integrate equation (4.35) directly;

2) decrease the slick mass for those compounds for which a differential equation is written;

3) use the pseudo-component material balance to calculate a total slick mass and use this information in the differential equation.

Using the last approach, the rate of loss of component i from the slick is written the same as before but now with the concentration $C_i$ as:

$$C_i = g_i/M_T \tag{4.36}$$

where $g_i$ is the mass of i and MT is the total mass of oil. $M_T$ is calculated from the pseudo-component differential equations.

This approach to component-specific evaporation modeling will predict an increase in concentration with respect to time for those compounds with very low or essentially zero vapor pressures. While approach 2) above would also do the same, the error in predicting the total mass of oil remaining in the slick is not known, and it is believed the pseudo-component prediction will yield the best results when coupled to the component-specific model.

## 4.4 Component-Specific Evaporation from a Semi-Infinite Oil Slick

The foregoing discussion on evaporation of components, from an oil slick does not take into account the fact that the partial pressure in the air of all the components being transported from the oil through evaporation will not necessarily be zero. For example, when the Henry's law coefficient of a compound is very low, it takes only a very small amount of it to saturate the air, which is the case with a very volatile compound such as naphthalene. Also, since the air above an oil slick is not of infinite "volume" due to finite turbulent diffusivities which form transport boundaries, it is necessary to consider the effects of these conditions on component-specific transport.

Consider an oil slick beinq continuously emitted from a point source onto the ocean surface as shown in Figure 4-7. This slick is referred to as the semi-infinite slick. By writing differential material balances for both the oil and air phases the following set of equations describes the evaporation of component i:

$$U_a \frac{\partial C_a}{\partial x} = \bar{\mathscr{D}}_z \frac{\partial^2 C_a}{\partial z^2} \tag{4.37}$$

$$C_a(x) = 0 \quad \text{at} \quad Z = \infty \tag{4.38}$$

$$C_a(Z) = 0 \quad \text{at} \quad x = O \tag{4.39}$$

$$\frac{dC_H}{dx} = \frac{H\bar{\mathscr{D}}_z}{\bar{U}_o \delta} \left. \frac{dC_a}{dz} \right|_{z=0} \tag{4.40}$$

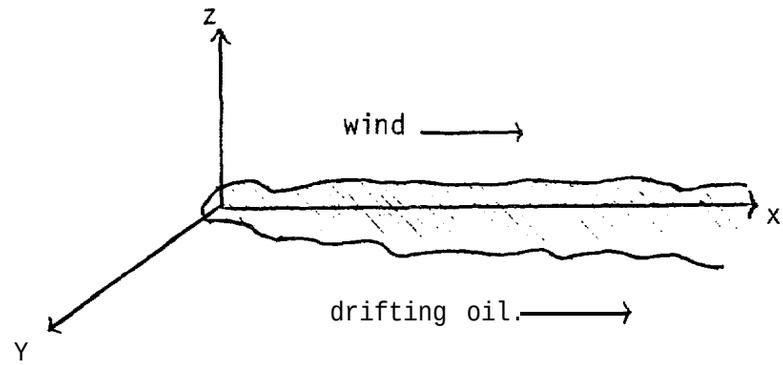



FIGURE 4-7. CONTINUOUS OIL SLICK WITH ORIGIN AT x = 0; SURFACE IS IN y-x PLANE

$$\frac{dC_H}{dx} = -\frac{K_o}{\bar{U}_o \delta}\left[C_H - C_a\Big|_{z=0}\right] \tag{4.41}$$

$$C_H = HC_i \quad \text{at} \quad x = 0 \tag{4.42}$$

where C is the concentration of the species of interest with the subscipt "a" denoting the air, H denoting the oil, i denotes the X = 0 concentration, $U_a$ is the mean wind speed, $\bar{\mathscr{D}}_z$ is the turbulent diffusivity in the air, H is the Henry's law coefficient, U. is the oil velocity, $\delta$ is the slick thickness, and K. is the over-all mass-transfer coefficient. This derivation essentially follows that of SUTTON (1943) in which the evaporation of water from lakes was studied. A modification of Sutton's derivation was made here where the over-all mass-transfer coefficient was-introduced so that the results of other researchers can be utilized. The width of the slick does not appear in the above equations as a result of the assumption that the slick width is constant. This assumption will generally be valid only in the case where the oil is emitted to the surface slowly.

Equations (4.37) through (4.42) can be solved by Laplace transforms. The quantity of interest is the concentration of a specific component in the oil, and the solution is:

$$\frac{C}{C_o} = \frac{1}{\alpha}\exp\left[kx\alpha^2\right]\operatorname{erfc}\left[\alpha\sqrt{kx}\right] + \frac{1}{\beta}\exp\left[kx\beta^2\right]\operatorname{erfc}\left[\beta\sqrt{kx}\right] \tag{4.43}$$

where $\alpha$ and $\beta$ are the roots of:

$$q^2 + \frac{\tilde{H}}{K}q + \frac{\tilde{H}}{k} = 0 \tag{4.44}$$

which may be complex. The other terms are defined as:

$$\tilde{H} = \frac{K_o}{\bar{U}_o \delta} \tag{4.45}$$

and

$$K \equiv \frac{H\bar{\mathcal{D}}_z}{\bar{U}_o \delta} \tag{4.46}$$

and

$$k \equiv \frac{\bar{U}_a}{\bar{\mathcal{D}}_z} \tag{4.47}$$

This model for a semi-infinite oil slick will not predict an increase in concentration with respect to time for the less volatile compounds in the oil phase due to the fact that an over-all material balance is not considered here as it is in the pseudo-component model. However, the above model will predict what combinations of parameters are important in invoking the zero air phase concentration assumption. Equations 4.43 through 4.47 show that the oil-phase concentration can be adequately predicted by assuming a zero air-phase partial pressure for small distances from the oil release point. However, for large distances from the oil release point, the zero air-phase partial-pressure assumption is not always adequate to predict the oil-phase concentrations and the above equations must be used.

Figures 4-8 and 4-9 present the calculations of the relative concentration of a specific compound in a semi-infinite oil slick for the parameters indicated in the figure legends. Also presented in these figures is the oil concentration when a zero partial pressure for this species is assumed to exist in the air phase. For the case of a 10 knot wind, the error introduced in assuming a zero partial pressure is approximately a factor of 10 at a downwind distance of one kilometer. This error rapidly increases with distance and thus shows that the zero-partial-pressure assumption should not be used, but. that equations 4.43 through 4.47 must be used to predict the oil-phase concentration as a function of downwind distance for the parameters specified. The case of a 40 knot wind is presented in Figure 4-8 and shows that the error at one kilometer is essentially zero and does not become significant until 5 kilometers. This result is expected because a strong wind lowers the partial pressure above the slick. For less than a 10 knot wind the error in assuming a zero partial pressure will be quite large. These results are being used to determine when the zero partial-pressure assumption can (or can not) be involved.

## 4.5 Component-Specific Dissolution from a Semi-Infinite Oil Slick

The dissolution of specific components from an oil slick into the water column is described mathematically in much the same way as evaporation. However, dissolution accounts for only a small reduction of the slick mass compared to evaporation. The pertinent physical property required to describe dissolution is the liquid-liquid partition coefficient which is the analogy of Henry's law for evaporation.

Unfortunately there is no characterization process for dissolution that can he applied to the bulk oil in the same manner that distillation is used to characterize the oil with respect to evaporation. There have been two attempts to classify the oil into pseudo-components with respect to solubility, one by YANG and WANG (1977), but was not carried through to the quantitative stage, and another due to MACKAY (1980) where only two major "cuts" were

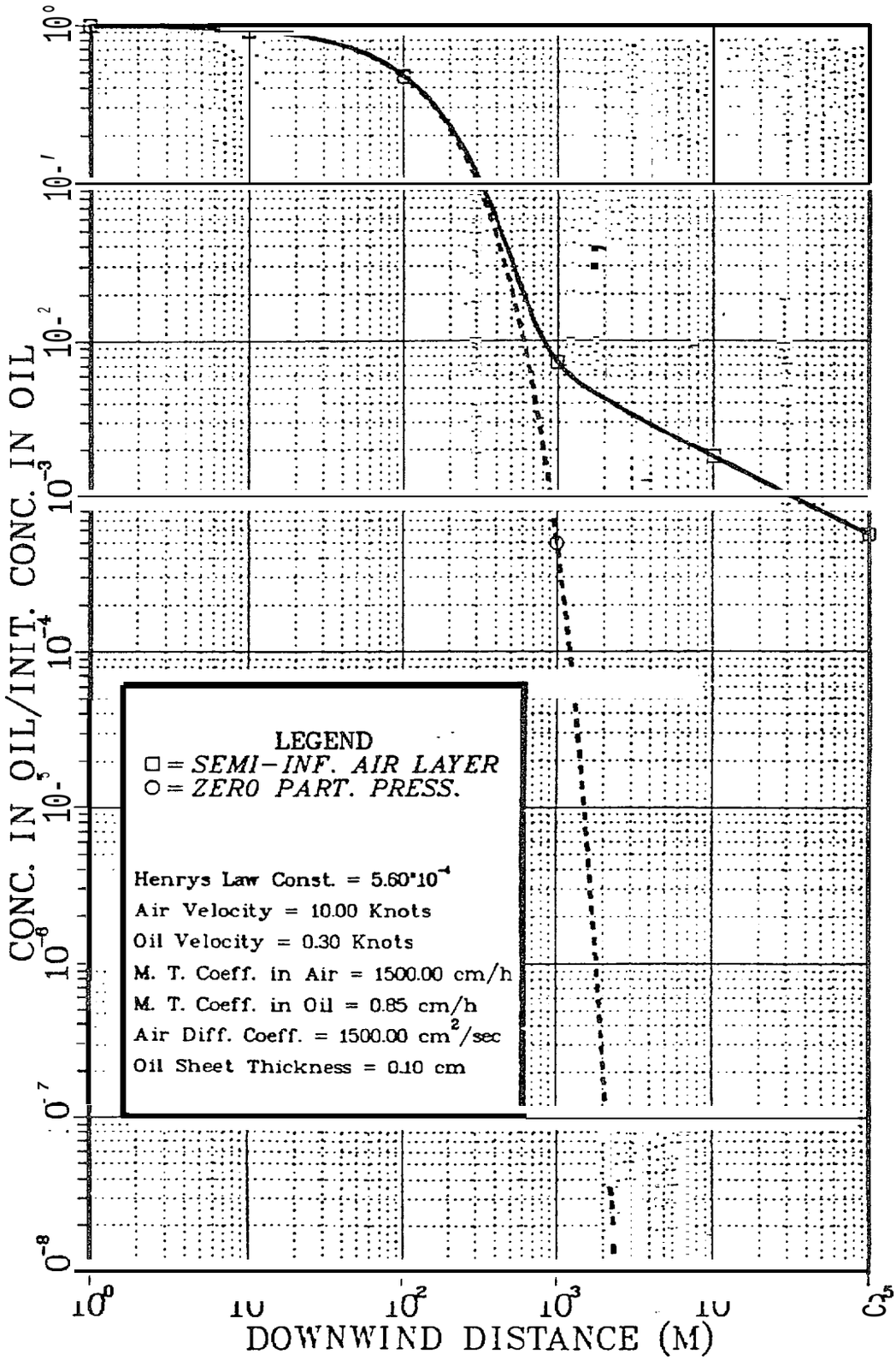



FIGURE 4-8. PREDICTED OIL-PHASE CONCENTRATION IN A SEMI-INFINITE OIL SLICK FOR A 10 KNOT WIND.

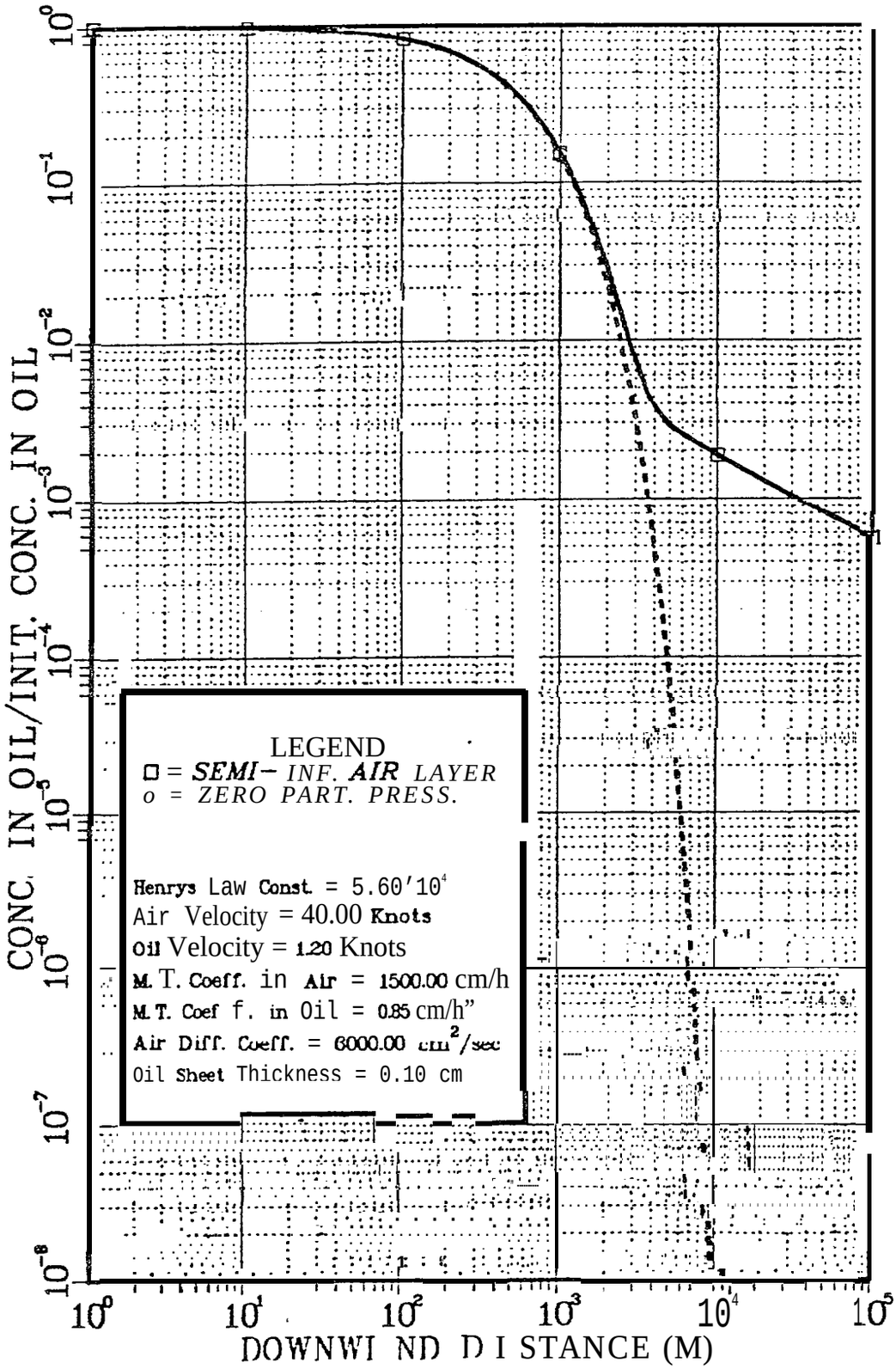



FIGURE 4-9. PREDICTED OIL-PHASE CONCENTRATION IN A SEMI-INFINITE OIL SLICK FOR A 40 KNOT WIND.

recognized. Since dissolution apparently accounts for a relatively small mass loss from the slick, an independent component-specific approach to dissolution is being utilized in our model.

Required physical property data required are liquid-liquid partition coefficients, referred to in the content of our work as m-values. It must be emphasized that pure component volubility data alone are not useful in obtaining m-values, because these types of data only yield information about the chemical potential of the species in the aqueous phase. What is needed along with pure component volubility data is the chemical potential of the species in the oil phase. Henry's law data coupled with volubility and vapor pressure data will provide a computed m-value through calculation, while liquid-liquid equilibrium experiments measure the m-value directly.

The dissolution oil weathering process is used to calculate species concentrations in the water column, not to account for the mass balance of the oil slick itself. The appropriate equations for a well-stirred slick with the coordinate reference shown in Figure 4-10 are:

$$\frac{\partial C_w}{\partial t} = \bar{\mathscr{D}}_w \frac{\partial^2 C_w}{\partial x^2} \tag{4.48}$$

$$C_w(x) = 0 \quad \text{at} \quad t = 0 \tag{4.49}$$

$$\frac{dC_w}{dx} = 0 \quad \text{at} \quad x = \ell, \; t > 0 \tag{4.50}$$

$$\frac{dC_m}{dt} = \frac{\bar{\mathscr{D}}_w}{m\delta} \frac{dC_w}{dx} \quad \text{at} \quad x = 0, \; t > 0 \tag{4.51}$$

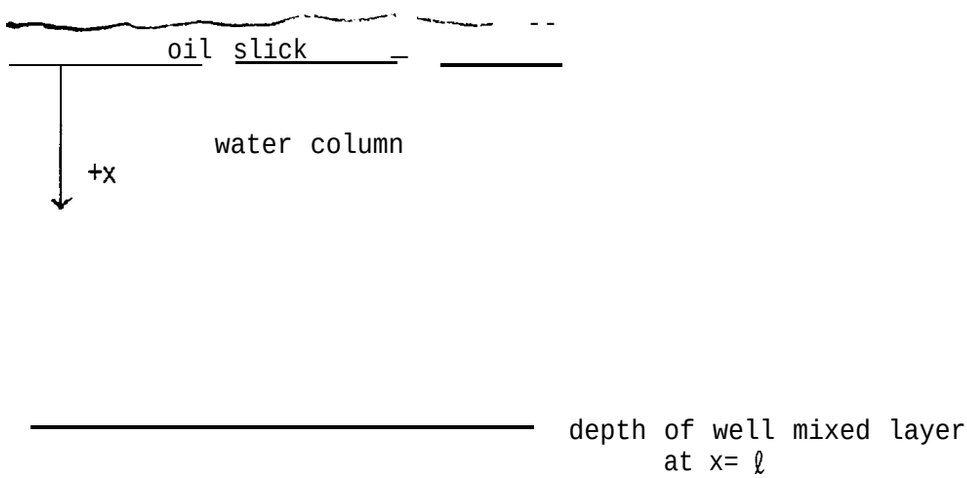



FIGURE 4-10. ILLUSTRATION OF COORDINATE FRAME FOR DISSOLUTION OF HYDROCARBONS INTO WATER COLUMN.

$$\frac{dC_m}{dt} = -\frac{K.}{\delta}[C_m - C_w] \text{ at } \quad x = 0 \tag{4.52}$$

$$C_m = C_m^{\circ} \quad \text{at } t = 0$$

where $C_w$ is the concentration of the species of interest in the water column, Cm is the concentration of the species of interest in the oil divided by the partition coefficient m, m is defined as the concentration in the oil divided by the concentration in the water at equilibrium, $\bar{\mathscr{D}}_w$ is the turbulent diffusivity in the water column, $\delta$ is the slick thickness, K. is the over-all mass-transfer coefficient, and $C_m^o$ is the initial Cm concentration in the oil.

The types of compounds to which the above problem solution will be applied are presented in Table 4-5 (MACKAY and SHIU, 1977). These compounds represent the polynuclear aromatic. -hydrocarbons which are likely to have the significant environmental toxic effects. The solutions represented by the above equations apply only strictly for the case where there is no evaporation. This condition is approximated when there is a crust on the oil or the dissolution rate is much greater than the evaporation rate. Likewise, the solution to the corresponding evaporation problem applies only strictly for the case where there is no dissolution, which is approximated when the evaporation rate is much greater than the dissolution rate. When evaporation and dissolution are both important, a "three-slab" problem results; however, this Particular condition would be unlikely in a mathematical sense.

## 4.6 Comprehensive Aspects of Model Development

The previous discussions on model development did not include water-in-oil dispersions or microbial processes. The current plan for bringing these oil-weathering processes into the model is to incorporate the direction provided by MACKAY (1980) for the dispersion and mousse formation processes and the findings of the current microbial work as it becomes available.

TABLE 4-5. COMPOUNDS OF IMPORTANCE IN AQUATIC ENVIRONMENT (MACKEY & SHIU, 1977).

| pd | Solubilities Exptl mg/L | Solubilities Exptl $x_w$, mole fraction $\times 10^9$ |
|---|---|---|
| Indan, $C_9H_{10}$ | 109.1 * 1.02 | 16650 |
| Naphthalene, $C_{10}H_8$ | 31.7 ± 0.26 | 4460 |
| 1-Methylnaphthalene, $C_{11}H_{10}$ | 28.5 * 0.3 | 3550 |
| 2-Methylnaphthalene, $C_{11}H_{10}$ | 25.4 ± 0.2 | 3220 |
| 1,3-Dimethylnaphtha lene, $C_{12}H_{12}$ | 8.0 ± 0.5 | 920 |
| 1,4-Dimethylnaphthalene, $C_{12}H_{12}$ | 11.4 ± 0.1 | 1310 |
| 1,5-Dimethylnaphthalene, $C_{12}H_{12}$ | 3.36 * 0.04 | 377 |
| 2,3-Dimethylnaphthalene, $C_{12}H_{12}$ | 3.0 * 0.01 | 347 |
| 2,6-Dimethylnaphthalene, $C_{12}H_{12}$ | 2.0 * 0.02 | 233 |
| 1-Ethylnaphthalene, $C_{12}H_{12}$ | 10.7 ± 0.3 | 1240 |
| 1,4,5-Trimethylnaphthalene, $C_{13}H_{14}$ | 2.1 ± 0.1 | 215 |
| Biphenyl, $C_{12}H_{10}$ | 7.0 ± 0.06 | 815 |
| Acenaphthlene, $C_{12}H_{10}$ | 3.93 ± 0.014 | 459 |
| Fluorene, $C_{13}H_{10}$ | 1.98 ± 0.04 | 214 |
| Phenanthrene, $C_{14}H_{10}$ | 1.29 ± 0.07 | 130 |
| Anthracene, $C_{14}H_{10}$ | 0.073 ± 0.005 | 7.57 |
| 2-Methylanthracene, $C_{15}H_{12}$ | 0.039 * 0.004 | 3.67 |
| 9-Methylanthracene, $C_{15}H_{12}$ | 0.261 ± 0.002 | 24.4 |
| 9, 10-Dimethylanthracene, $C_{16}H_{14}$ | 0.056 ± 0.0005 | 4.80 |
| Pyrene, $C_{16}H_{14}$ | 0.135 ± 0.005 | 12.0 |
| Fluoranthene, $C_{16}H_{10}$ | 0.26 ● 0.002 | 22.8 |
| 1,2-Benzofluorene, $C_{17}H_{10}$ | 0.045 ± 0.0012 | 3.75 |
| 2,3-Benzofluorene, $C_{17}H_{10}$ | 0.0020 ± 0.00003 | 0.956 |
| Chrysene, $C_{18}H_{12}$ | 0.0020 ● 0.00017 | 0.158 |
| Triphenylene, $C_{18}H_{12}$ | 0.043 ● 0.00013 | 3.39 |
| Naphthacene, $C_{18}H_{12}$ | 0.00057 * 0.00003 | 0.037 |
| 1,2-Benzanthracene, $C_{18}H_{12}$ | 0.014 ± 0.0002 | 1.10 |
| 7,12-Dimethyl-1,2-benzanthracene, $C_{20}H_{16}$ | 0.061 ± 0.0006 | 4.26 |
| Perylene, $C_{20}H_{12}$ | 0.0004 ± 000002 | 0.0283 |
| 3,4-Benzopyrene, $C_{20}H_{12}$ | 0.0038 ± 0.00031 | 0.273 |
| 3-Methylcholanthrene, $C_{21}H_{16}$ | 0.0028 ± 0.000021 | 0.192 |
| Benzo[g,h,i]perylene, $C_{22}H_{12}$ | 0.000264 0.00001 | 0.0173. |
| Coronene, $C_{24}H_{12}$ | 0.00014 ● 0.00002 | 0.00856 |

The logic involved in performing a calculation utilizing both pseudo-component and specific-component models is shown in Figure 4-11. The most important mass balance calculation is the pseudo-component evaporation process from which the slick mass and viscosity are obtained. Dissolution is not assumed to significantly affect. slick mass. In parallel to the pseudo-component evaporation process, the component-specific evaporation and dissolution processes are calculated. These calculations proceed initially assuming a well-stirred slick state and continue until the viscosity reaches some pre-specified value at which the slick becomes rigid. At this point the diffusion equation is used to calculate component specific concentrations according to the previous discussion of the Biot mass-transfer number.

### 4.6.1 Measurement of Henry's Law Coefficient

The need for specific thermodynamic information to describe interphase mass transport was presented in the discussions of component-specific evaporation and dissolution. The vapor-liquid equilibrium data required are called Henry's law coefficients (H). The Henry's law coefficient pertains to that portion of the phase equilibrium diagram where the ratio of phase concentrations is constant, which is the case when the concentration of the species of interest in one phase is small (e.g., oxygen in water).

Henry's law coefficients appear in the flux expressions and the overall mass-transfer coefficients which describe interphase mass transfer. The reason for the appearance of H in the flux expression is that a concentration difference between two phases is not sufficient information to identify in which direction mass will transfer. If the system is not at equilibrium, mass will transfer in the direction toward equilibrium. The information required to determine which way mass will transfer is the chemical Potential of the species in each phase because the chemical potential is the potential for mass transfer. The Henry's law coefficient provides the method to map the concentration in one phase to the same chemical potential basis as the other phase. By using H, the correct driving force can be written for mass transfer.

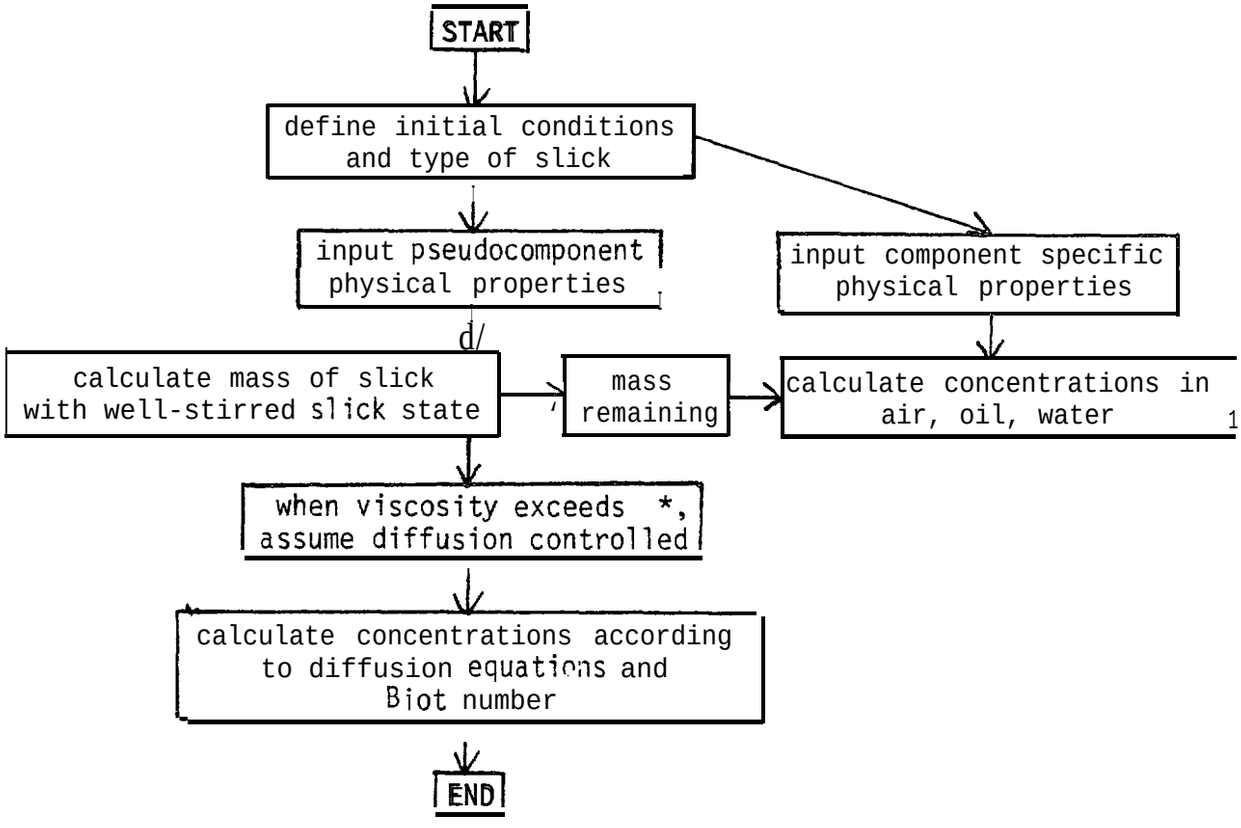



FIGURE 4-11. LOGIC FOR USING PSEUDOCOMOPNENT AND SPECIFIC COMPONENT MODELS IN OIL WEATHERING.

The over-all mass-transfer coefficient also utilizes H in a manner that takes into account the relative volubility of the species of interest in each phase. There is virtually no way to determine the relative mass transfer resistances without H (TREYBAL, 1955; LISS, 1974).

The technique originally described by MCAULIFFE (1966) to measure Henry's law coefficients using gas chromatography involves multiple equilibrations of equal volumes of aqueous and gaseous phases. A large glass syringe with a Luer-Lok fitting is filled 1:1 with liquid and clean nitrogen or air. The syringe is then capped off and agitated vigorously to create an equilibrium between phases. Most of the gas is then flowed through a gas sample loop which is an integral part of the analytical system (a gas chromatograph). At some point in this flow, a valve is turned and the gas in the loop (typically 0.1 to 10 ml) is introduced into the gas chromatography. The rest of the gas is discharged from the syringe and fresh gas in introduced. The process is repeated a number of times.

The mathematical description of this procedure using equal volumes was given by McAullife and yields:

$$\log G_n = an + b \tag{4.54}$$

$$a = -\log (t\text{-}l + 1) \tag{4.55}$$

$$b = \log HX_o \tag{4.56}$$

where $G_n$ is the amount of the compound of interest in the gas during the n-th equilibration, H is Henry's law coefficient, and X. is the original amount of the compound in the system. Equation (4.54) shows that a plot of the log of compound concentration (or GC peak height) vs equibration number n gives a straight line. The negative slope of this line gives the log of (H + 1).

In measurements of Henry's law coefficients for petroleum components, it is not necessarily convenient to use equal volumes of liquid and gaseous phases. Some compounds have large distribution coefficients and some have relatively small values. Also, when the fresh oil/air system is measured, it has been found to not be desirable to deal with 25 ml of oil in the partitioning syringe. Therefore, a re-derivation of equations (4.54) through (4.56) for unequal volumes of gas/liquid has been done. Considering a measurement system with unequal liquid and gas volumes, VI and $V_g$, respectively, $G_i$ can be defined as the amount of a distributing component in the gas phase during the i-th equilibration. Similarly, $L_i$ is the amount in the liquid phase during the i-th equilibration. The total amount of the substance is:

$$x_i = G_i + L_i \tag{4.57}$$

and the Henry's law coefficient becomes:

$$H = \frac{\text{concentration in gas}}{\text{concentration in liquid}} = \frac{G_i V_L}{V_g L_i} \tag{4.58}$$

r can be defined as:

$$r = \frac{V_L}{V_g} \tag{4.59}$$

and as a result the gas phase amount, $G_i$, can be re-expressed:

$$G_i = X_i - L_i = X_i - \frac{rG_i}{H} = \frac{Hx_i - rG_i}{H} \tag{4.60}$$

$$HG_i = Hx_i - rG_i \tag{4.61}$$

$$G_i = \frac{HX_i}{r + H} \tag{4.62}$$

$$G_i = \frac{(H/r)x_i}{1 + H/r} \tag{4.63}$$

Similarly, the liquid phase amount, $L_i$, can be written:

$$L_i = \frac{x_i}{1 + H/r} \tag{4.64}$$

The fractional amounts the component in the gas and liquid phases, $f_g$ and $f_L$, respectively, can be expressed as:

$$f_g = \frac{G_i}{x_i} = \frac{(H/r)x_i}{x_i(1 + H/r)} = \frac{Ii/r}{(1 + H/r)} \tag{4.65}$$

$$f_L = \frac{L_i}{Xi} = \frac{x_i}{x_i(1 + H/r)} = \frac{1}{(1 + H/r)} \tag{4.66}$$

For subsequent equilibrations (i.e., i+1, i+2 . . . . i+n), equation (4.63) can be generalized to:

$$G_{i+1} = \frac{(H/r)}{1 + H/r}\left[x_i - \frac{Ii/r}{1 + H/r}\, x_i\right] \tag{4.67}$$

or redefining the subscripts finally yields:

$$G_m = \frac{(H/r)x_o}{(H/r + I)^m} \tag{4.68}$$

$G_m$ can be experimentallyobtainedas component-specific gas chromatographic data, and if equation (4.68) is rearranged to logarithmic form it takes on a linear form ($y = mx + b$) - a plot of log $G_m$ vs ($m$) has a slope equal to $-\log(H/r + 1)$. Only one phase of the system needs to be sampled, any ratio of volumes can be used, many compounds can be measured at one time, and standards do not have to be run since only relative amounts are used in the calculations.

Henry's law coefficients have been measured in this study using equation (4.6?3). A 50 ml glass Hamilton gas-tight syringe with a Luer fitting is used along with a sample loop (of. varying sizes) installed into a six-port Valco valve which allows the 100p gas to be initially purged to the atmosphere prior to introduction into the carrier gas of the gas chromatography. The valve is enclosed in an insulated enclosure, heated, and temperature controlled. The gas is delivered to the valve by l/16-inch tubing. In order to avoid inconsistencies and pressure differences which could effect equilibrium, the syringe is discharged with a Sage Instruments Syringe infusion pump set at a very slow rate. A Hewlett-Packard 5731A gas chromatography with a flame ionization detector and 3385A Automatic Integration System has been employed. A 6-ft glass column packed with 1% SP-1OOO on Carbopak B 60/80 is currently beinq used, and plans for future studies incorporate the use of a 30-m glass capillary column using SE-54 or SE-30 as the liquid phase.

In order to verify the ability of this experimental technique, a number of measurements have been made on hydrocarbons dissolved in distilled water. The extent of "known" Henry's law data is very limited, however a few literature values (MACKAY, 1975) have been found for comparison. Typically, the compound of interest is equilibrated with distilled water in a separator

funnel for a number of hours. Then the water can be taken from the funnel stopcock directly into the syringe. Figure 4-12 presents a plot of resultant data for benzene and Table 4-6 presents some of the data obtained so far in this program which can be compared to previously measured values.

The technique is reproducible, with a scatter in the data of about 10 to 20 percent. All of the Henry's law values are in approximate agreement with the literature values except for iso-octane. This has not been explained, but it is suspected that the previously cited value is incorrect.

Currently, Henry's law measurements on the oil-air system are being completed. This is requiring the use of a capillary column for enhanced analytical resolution. The combination of the two columns will enable us to obtain Henry's law coefficients for all of the compounds that partition to a reasonable extent to the gaseous phase.

In order to get H values for compounds that have very low partial pressures in oil, a slightly different approach is being taken. Instead of sampling the gas, the liquid (oil) is sampled after every 5 or 10 equilibrations. The partitioning theory presented for water is applicable, however the measurement technique is the same except that the liquid sample involves the oil being dissolved in an appropriate amount of solvent ($CS_2$) and analyzed directly.

### 4.5.2 Diffusion Coefficients for Volatile Components Through Oil

To fully develop a model for oil weathering it is necessary to have diffusion coefficients for a variety of components in oil. Two problems pose obstacles to straight-forward application of the diffusion equations to describe the migration of components within an oil mass. First, the oil is usually in the form of a continually spreading slick and the continually altering thickness of the slick is a complicating factor. In addition, as lighter components are lost from the surface of the slick and skins begin to

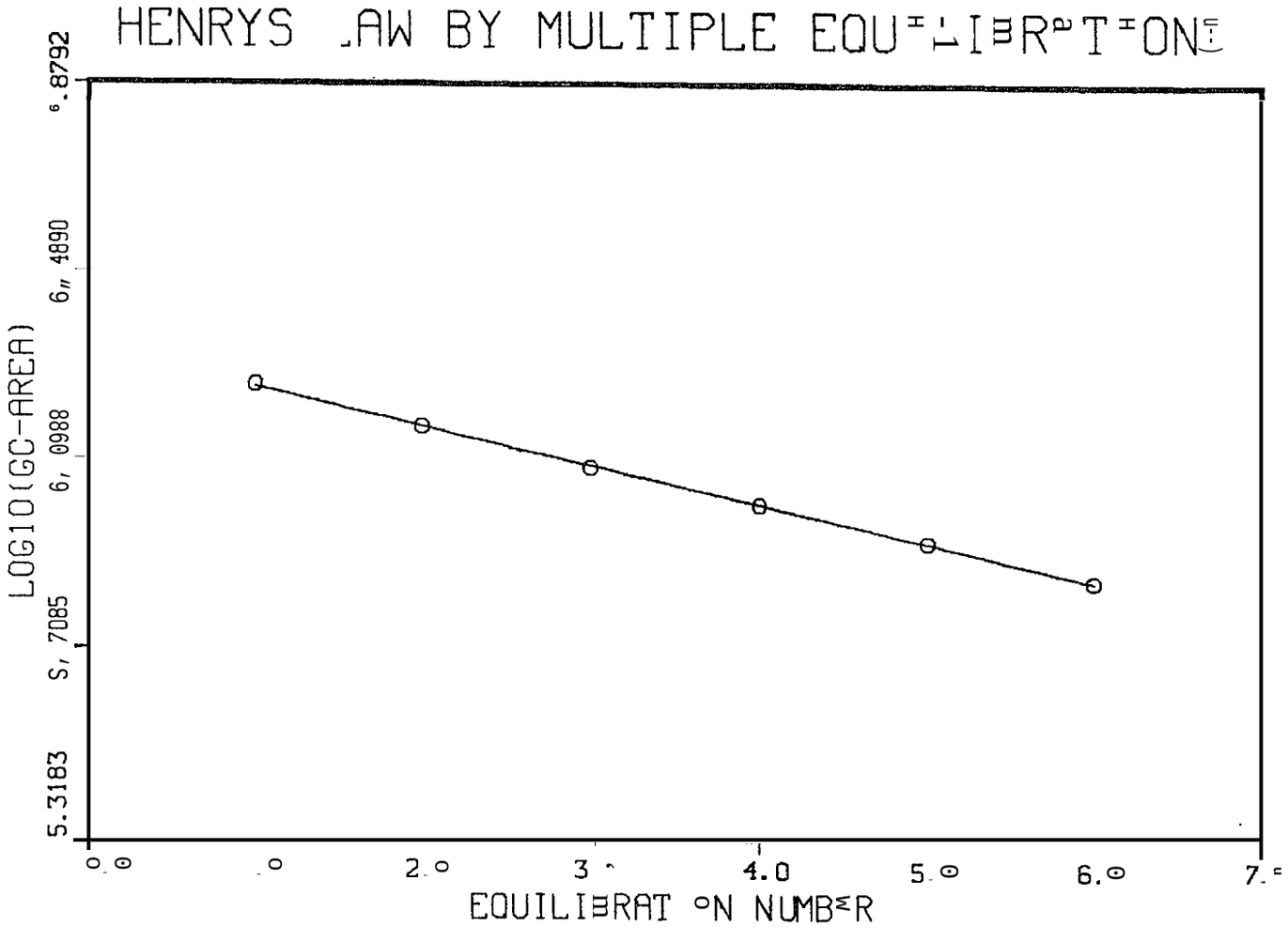



FIGURE 4-2. EXPERIMENTAL DATA FOR BENZENE.

TABLE 4-5. HENRY'S LAW RESULTS.

| Compound | Ratio $\frac{V_\ell}{V_s}$ ** | r * | H(atm $m^3$/mole) | H(literature) | $\frac{H}{H(lit.)} \times 100$ |
|---|---|---|---|---|---|
| Benzene | 25/25 | -.9980 | $5.5 \times 10^{-3}$ | $5.5 \times 10^{-3}$ | 100 |
| Benzene | 14/36 | -.9997 | $4.3 \times 10^{-3}$ | | 78 |
| Benzene | 25/25 | -.9998 | $5.0 \times 10^{-3}$ | | 98 |
| Benzene | 25/25 | -. 999B | $5.0 \times 10^{-3}$ | | 91 |
| Benzene | 14/36 | -. 9998 | $4.9 \times 10^{-3}$ | | 90 |
| Benzene | 14/36 | -.9999 | $4.8 \times 10^{-3}$ | | 87 |
| Toluene | 25/25 | -.9999 | $5.3 \times 10^{-3}$ | $6.68 \times 10^{-3}$ | 79 |
| Toluene | 21/19 | -. 9B90 | $5.6 \times 10^{-3}$ | | 84 |
| Iso-octane | 31/19 | -.990 | ~0. 18 | 3.04 | 5.9 |
| Iso-octane | 31/19 | -.997 | 0.098 | | 3.2 |
| n- Hexane | 31/19 | --- | 0.87 | 1.20 | 72.5 |
| n- Hexane | 36/14 | --- | 1.04 | 1.20 | 87.1 |
| Benzene/ Toluene*** | 26/24 | -. 9985/-. 9948 | $5.04 \times 10^{-3}/5.07 \times 10^{-3}$ | $5.5 \times 10^{-3}/6.68 \times 10^{-3}$ | 91/76 |

* correlation coefficient

** $V_\ell$ = volume of liquid, $V_g$ = volume of gas

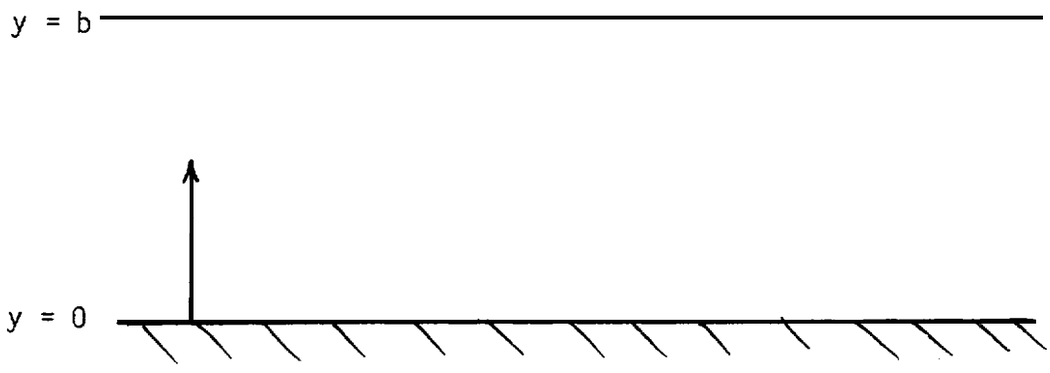
*** combined Benzene/Tel uene

form, the impact on transfer of components across that interface is major. It is important, therefore, to be able to account for changing slick thickness and for slick skin permeability.

This section treats these points, beginning with multicomponent diffusion and commenting on the problems of developing a model that accounts for slick thinning. As an outgrowth of this, an approach is explained for treating laboratory experimental data in a way that will yield diffusion coefficients free from the effect of thinning. Problems associated with modeling skin formation are discussed, and an approach is presented.

4.6.2.1 Diffusion Through a Thinning Slick

This case can be thought of in terms of one-dimensional diffusion through a plane slab of thickness b. Assuming an impenetrable barrier at the plane boundary (.Y = 0). Also, at y = b, it is assumed that the ambient medium is sufficiently stirred. that all volatiles are at zero concentration in that plane.



If $b = b_o$ = constant, and if diffusivity $\mathscr{D}$ is also constant, the (molar) concentration of any species is given by:

$$\frac{C}{C_o} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[\frac{-(2n+1)^2 \pi^2 \mathscr{D} t}{4b_o^2}\right] \cos\left[\frac{(2n+1)\pi y}{2b_o}\right] \tag{4.69}$$

where Co is the (assumed uni form) concentration at $t = o$. After some interval of time, t, the amount of the volatile species remaining in the slab is:

$$\int_0^b c\,dy = \frac{8\,C_o b}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 \mathscr{D} t}{4b^2}\right] \tag{4.70}$$

and the mass loss up to time t is:

$$MC_o b_o \left[1 - \int_0^{\phi} (C/C_o)\, dy/b_o\right] \tag{4.71}$$

where M = molecular weight and $\phi \equiv b/be$.

If an assumption is made that the volumes of all components are addictive, then the mass loss may be related to slab thickness as follows:

$$\rho_L (b_o - b) = \sum_i M_i C_{o_i} b_o \left[1 - \int_0^{\phi} (C/C_o)_i\, dy/b_o\right] \tag{4.72}$$

where $\rho_L$ is the mass density of the slab, and the summation is over all volatile speci es,.

If one makes a "quasi-steady state" assumption, stipulating that equation *(4.70)* is valid even for b varying with time, then an algebraic equation for b(t) is obtained:

$$1 - \phi = \sum_i m_i \left[ 1 - \frac{8\phi}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[ \frac{-(2n+1)^2 \pi^2 \mathscr{D}_i t}{4b^2} \right] \right] \qquad (4.73)$$

or

$$1 - \phi = \sum_i m_i \left[ 1 - \frac{8\phi}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[ \frac{-(2n+1)^2 \pi^2 \tau_i}{4\phi^2} \right] \right] \qquad (4.74)$$

where

$$\phi = b/be, \quad \tau_i = \mathscr{D}_i t/b_o^2, \quad m_i = \frac{M_i C_{o_i}}{\rho_L} \qquad (4.75)$$

One would expect this quasi-steady state assumption to be reasonably accurate for short time ($\phi \approx 1$).

In principle one could use equation (4.74) to calculate diffusion coefficients $\mathscr{D}_i$ from observations of $\phi(\tau)$. For a multicomponent system this would be impractical, since a multivariable fit of data on $\phi(\tau)$ would be required. Since the accuracy of equation (4.74) for large time periods is questionable, and since one would have to go to large time in order to have reasonable precision in data for $\phi(\tau)$, the use of equation (4.74) for determination of $\mathscr{D}_i$ is not suggested for multicomponent systems.

Having completed this analysis, it was concluded that the proper alternative approach should be to determine diffusion coefficients by monitoring the role of release of each species from the slab, at short time intervals

($\phi = 1$). This is done by measuring the appearance of each species in an inert stream that sweeps across the slab. If a sweep stream, initially free of every diffusing species, is provided at a flowrate $q_0$ (volume/time), then the concentration of each species in that stream may be found, assuming constant pressure isothermal conditions in the sweep stream. If $\rho_G$ is the density of the sweep gas, then the rate of flow of gas into the system is $\rho_G q_0$.

The mass rate of flow of diffusants into the system is $\sum AM_i N_i$, where A is the exposed area of the slab and $N_i$ is the molar flux of species i from the slab. The mass fraction of species i in the exit stream is:

$$x_i = \frac{AM_i N_i}{\rho_G q_0 + \sum AM_i N_i} \tag{4.76}$$

It is anticipated that $\sum AM_i N_i \ll \rho_G q_0$, therefore:

$$x_i = \frac{AM_i N_i}{\rho_G q_0} \tag{4.77}$$

Hence, from a measurement of each $X_i$, each $N_i$ is found, to then be correlated to individual component diffusivities $\mathscr{D}$.

To avoid problems with the reduction in slab thickness, an expression for $N_i$ that is accurate over small time interval is derived from the Leveque solution:

$$N_i = C_{oi}\sqrt{\mathscr{D}_i/\pi t} \tag{4.78}$$

Thus, xi(t) should be measured to determine $N_i(t)$, and from the slope of a plot Of $N_i$ VS $t^{-1/2}$, $\mathscr{D}$ can be found.

### 4.6.2.2 Rate of Slick Thinning

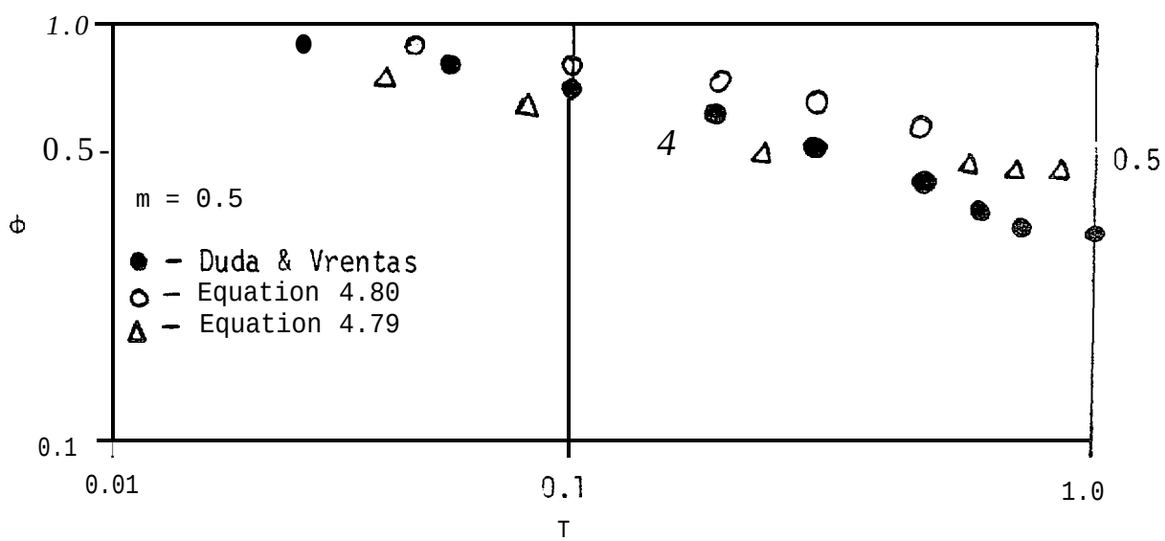
Although we have avoided treating the reduction in slab thickness as a variable in measuring diffusion coefficients, it is important to get some idea of the rate of thinning. From equation (4.74) for a single diffusing species, we must solve for $\phi$:

$$\phi = \frac{1 - m}{1 - \frac{8m}{\pi^2} \sum_{n=0} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 \tau}{4\phi^2}\right]} \tag{4.79}$$

Again for short time intervals, it is convenient to use the Leveque solution for N, and find $\phi$ from:

$$\phi = 1 - \frac{2m}{\sqrt{\pi}} \tau^{1/2} \tag{4.80}$$

Another approach to this problem is to apply the perturbation solution as described by DUDA and VRENTAS (1969). Since only the first few terms are used, the available solution is restricted to small values of M. A comparison of solutions is:



Equation (4.80) is expected to be valid only for small $\tau$. Equation (4.79) shows (correctly) that $\phi$ approaches a value of l-m at long $\tau$. Also, the Duda and Vrentas solution is inaccurate over its mid-range, where it predicts that $\phi$ falls below $\phi = 0.5$. It does correctly give $\phi = 0.5$ as $\tau$ exceeds 3. The Duda and Vrentas solution is probably accurate at small $\tau$. The value of $m = 0.5$ examined here ($m = -N_b$ in their notation) is a little large for their perturbation solution.

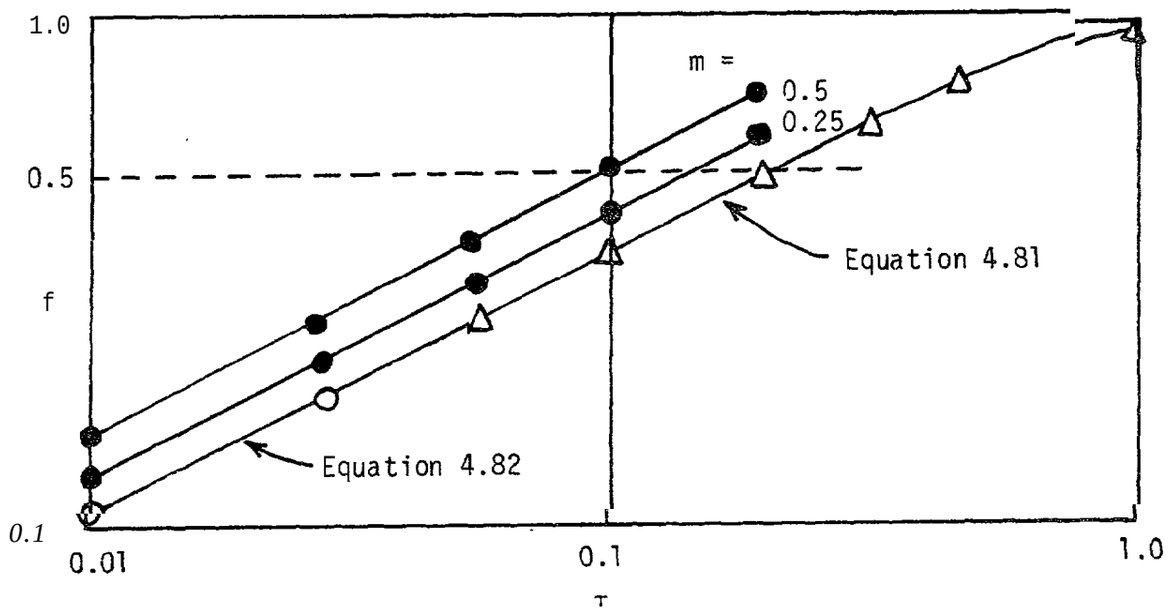
It is interesting to examine the fractional loss of a species from the slab, as a function of time. We expect that slab thinning will increase the rate of loss, but we do not know the degree of this increase. If the thickness remained uniform, the fraction of each species remaining would be found from:

$$f = 1 - \frac{8}{\pi^2} \sum_{n=0} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2\pi^2\tau}{4}\right] \tag{4.81}$$

or, for short times:

$$f \approx \frac{2}{\sqrt{\pi}} \tau^{1/2} \tag{4.82}$$

The figure following shows f calculated using the above equations as well as f using the Duda and Vrentas solution. As expected, taking account of slab thinning leads to more rapid loss of diffusible species.




Even though the Duda and Vrentas solution is suspect in its mid-range for such large values of m, it is still useful to observe the effect of slab thinning on the half-time for release of a volatile component. For a slab of uniform thickness, the half-time is found to be $\tau_{1/2} = 0.2$. For m = 0.25 we find $\tau_{1/2} = 0.15$, and for m = 0.5, the value is reduced to $\tau_{1/2} = 0.1$.

### 4.6.3 The Role of Internal Circulation in the Weathering of a Thin Oil Slick

When a slick of oil floats upon a rough sea, its motion is determined by the local wind and wave action. These external forces could be strong enough to produce motion within the slick. Previous analyses of weathering have focussed on mass transfer by diffusion within the slick, and on convection across the slick/water and slick/air interfaces. Our efforts have attempted to produce a model that allows an estimate of the extent of internal motion, and the degree to which that motion enhances mass transfer of components to the environment.

The simplest model is derived from Figure 4-13 which shows an idealized oil slick. The slick is taken to be a slab of uniform thickness, H, and length, L, in the wind direction and we assume $L \gg H$. Further, the width normal to the wind direction, W, also is assumed to satisfy $W \gg H$. The wind generates a shear stress $\tau$ on the upper surface, which produces a velocity, V, in the wind direction, along the plane of the slick/air interface. We assume that the slick is stationary with respect to the water, or equivalently that V is measured relative to the mean velocity of the slick with respect to the water. Thus the physical model is as shown in Figure 4-14.

We are interested in the velocity profile v(y), and in then examining the effect of velocity on mass transfer at the slick/air interface. The velocity profile, under the approximations, satisfies:

$$0 = -\frac{\partial p}{\partial x} + \mu \frac{\partial^2 v}{\partial y^2}$$

$$v = V \quad \text{at} \quad y = H \qquad (4.83)$$

$$v = 0 \quad \text{at} \quad y = 0$$

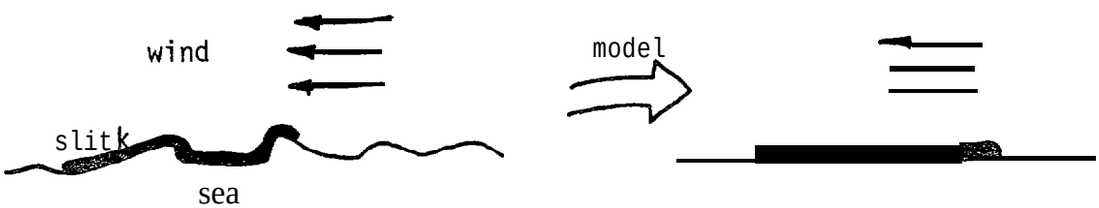



FIGURE 4-13. OIL SLICK ON THE SEA.

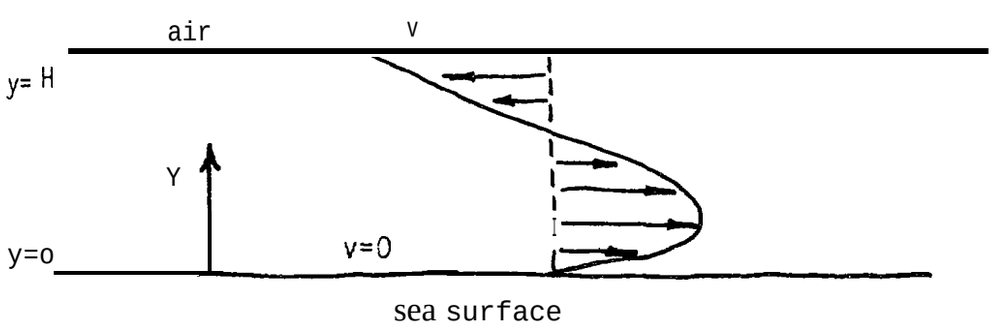



FIGURE 4-14. CIRCULATION WITHIN THE SLICK

and is found to be:

$$v = V\frac{y}{H} - \frac{1}{2\mu}\, y(H - y)\frac{\partial p}{\partial x} \tag{4.84}$$

We have assumed that $\partial p/\partial x$ is independent of y, equivalent to the assumption that the velocity is everywhere parallel to the planes (i.e., at both y = 0 and y = H). Of course this would not be true near the edges of the slick, where the flow reverses and returns across the lower region of the slick. We envision the flow induced in the slick by the wind to be like the motion of a tractor tread. The gradient $\partial p/\partial x$ is not known, but may be found by invoking the assumption that there is no net flow of oil in the x-direction:

$$\int_0^H v\, dy = 0 \tag{4.85}$$

Upon imposing this constraint we find:

$$\frac{\partial p}{\partial x} = \frac{6\mu V}{H^2} \tag{4.86}$$

and the velocity field is given as:

$$v = V\frac{y}{H}\left(2 - \frac{3y}{H}\right) \tag{4.87}$$

Next we examine the effect of this velocity field on mass transfer across the plane y = H. The basic case for comparison is the pure diffusion control situation, where there is no motion within the slab. From the classical solution to the pure diffusion problem we find:

$$\frac{C}{C_o} \approx \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4}\frac{\mathscr{D}}{H^2}t\right) \quad \text{for} \quad \frac{\mathscr{D}t}{H^2} > 0.2 \tag{4.88}$$

where $\mathscr{D}$ is the diffusion coefficient of some species through the oil, and C/C. is the fraction of the diffusible species remaining after time t. We may regard the term:

$$t_D \equiv \frac{4H^2}{\pi^2 \mathscr{D}} \tag{4.89}$$

to be a diffusion "time scale".

We can now impose a shear stress exerted by the wind which can set the slick liquid into circulation.. Circulation aids diffusion by bringing regions of high concentration in the diffusible species into closer contact with the interface. In a sense this reduces the diffusion distance and should speed up the rate of removal by diffusion. We have investigated the magnitude of this enhanced removal, and how it might be correlated with slick and wind Parameters.

A model can be formed alongthephysicalbounds shown in Figure 4-15. Near the region y = H, we assume a classic Leveque-type diffusion problem. The circulating flow is mixed in the lower part of the slick and becomes the feed for the Leveque flow. Schematically, we separate the upper and lower regions into a diffusion region and a mixing region, connected by the circulating flow q. The magnitude of the circulating flow can be gotten from:

$$q/w = \int_{\frac{2}{3}H}^{H} v\,dy = \frac{4HV}{27} \cdot \frac{H^2\tau}{27\mu} \tag{4.90}$$

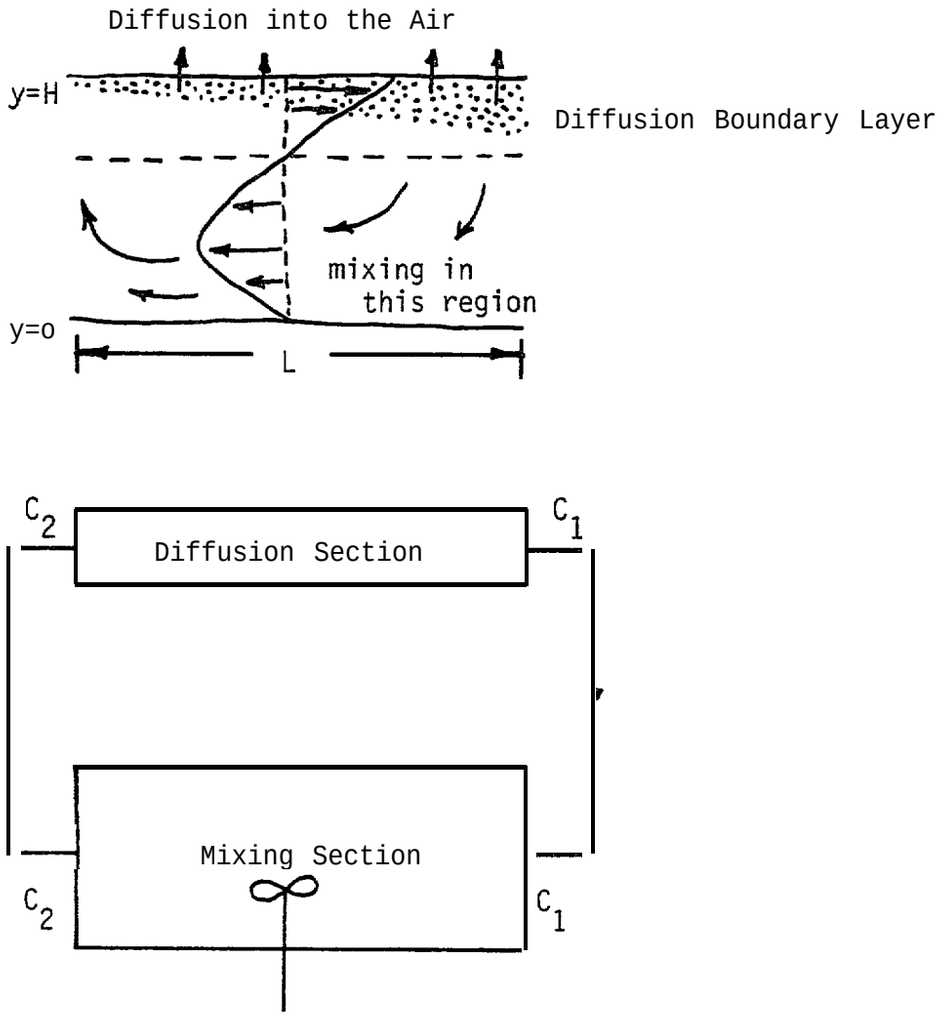



FIGURE 4-15. A MODEL FOR DIFFUSION WITH CIRCULATION

where W is the unit width in the z-direction. Along the slick/air interface the velocity is related to the shear stress $\tau$ by:

$$\tau = \mu \left.\frac{\partial v}{\partial y}\right|_{H} = 4\mu \frac{V}{H} \tag{4.91}$$

An average velocity of circulation as may be defined as:

$$\bar{V} = \frac{q/W}{H/3} = \frac{H\tau}{9\mu} \tag{4.92}$$

The Leveque solution gives:

$$\frac{C_2}{C_1} = 1 - 0.186(3)^{1/3} \left(\frac{9\Delta L}{\bar{V}B^2}\right)^{2/3} \tag{4.93}$$

where $C_1$ and $C_2$ are defined as in Figure 4-15, $B = \frac{1}{3}H$ and $V = H^2/9\mu$; more simply:

$$\frac{C_2}{C_1} = 1 - 21.7\left(\frac{\Delta L \mu}{\tau H^3}\right)^{2/3} \tag{4.94}$$

For a simple stirred tank of volume v, a material balance can be stated as:

$$v\frac{dC_2}{dt} = q\left(C_2 - C_1\right) = -21.7\left(\frac{\Delta L \mu}{\tau H^3}\right)^{2/3} q\, C_2 \tag{4.95}$$

and the solution for $C_2$ is expressed:

$$\frac{C_2}{C_{2_0}} = \exp\left(-t/t_c\right) \tag{4.96}$$

Thus we find, using Equations (4.90) and (4.95), that an appropriate time scale for circulation-enhanced loss is:

$$t_c = 0.8\left(\frac{L\mu H^3}{\mathcal{D}^2\tau}\right)^{1/3} \tag{4.97}$$

Of particular interest is the ratio $t_D/t_c$, which provides a measure of enhanced removal associated with circulation. We find:

$$E \equiv \frac{t_D}{t_c} = \frac{1}{2}\left(\frac{\tau H^3}{L\mu\mathcal{D}}\right)^{1/3} \tag{4.98}$$

If we go back to Equation (4.91), we may write E as:

$$E = \frac{1}{2}\left(\frac{4\,VH^2}{L\mathcal{D}}\right)^{1/3} = 0.79\left(\frac{VH}{\mathcal{D}}\;\frac{H}{L}\right)^{1/3} \tag{4.99}$$

Even though we do not know V (it is related to the unknown $\tau$) equation (4.99) is a useful form because it has the appearance of a Peclet number:

$$Pe = VH/\mathcal{D} = \frac{\tau H^2}{4\mu\mathcal{D}} \tag{4.100}$$

and:

$$E = 0.79(Pe/A)^{1/3} \tag{4.101}$$

where the aspect ratio A = L/H appears.

While this model has several assumptions and uncertainties, it provides the opportunity to assess the role of certain physical events that occur during the weathering process:

Slick Spreading

As H decreases and L increases, we see that E decreases. Thus, as spreading occurs, diffusion control dominates any effects of internal circulation.

Viscosity increase through loss of volatiles

Since a rough approximation for diffusion coefficients of volatiles in a viscous liquid suggests that $\mathscr{D} \approx 1/\mu$ , we expect that the Peclet number will remain constant at fixed H. Thus the aging of the slick per se does not change the balance between diffusion and convection as the dominant mode of volatiles loss.

In order to assess the importance of interns? circulation, in the context of this model, we must estimate the magnitude of E. This requires data from which the shear stress at the sea surface may be estimated. However, typical values of V, H, and $\mathscr{D}$ (e.g., V = 10 cm/s, H = 2 cm, $\mathscr{D} = 10^{-7}$ $cm^2/s$) and aspect ratio (L/H = 200) give an estimate for E of about $10^2$, representing a significant enhancement in the rate of loss of volatiles. This circulation model assumes that the slick may spread across the sea surface, but that its motion is laminar. Another type of internal circulation is possible, driven by wave action which is shown in Figure 4-16.

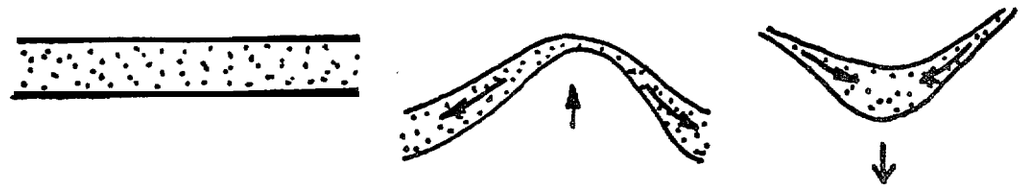


FIGURE 4-16. WAVE ACTION AS A MEANS OF PERIODIC MIXING ON A LOCAL SCALE.

A localized area within a large slick may alternately be thinned and thickened as the surface of the sea undergoes wave motion. We might regard this as a complete mixing process at that local level, and a model which accounts for this phenomenon might be taken along the following lines:

- diffusion occurs from a uniform slab;
- the slab is instantaneously mixed periodically;
- diffusion occurs during intervals between mixing.

This is a relatively simple model to assess. Define $t_M$ as the time interval between mixes (We expect that $t_M$ is related to the temporal periodicity of the waves). If the slick has a mean concentration, Co, of some species at time $t = 0$, then after an interval, $t_M$, the slick will be mixed and its mean concentration will be:

$$C_1 = C_o \left[1 - \left(4 \mathcal{D} t_M / \pi H^2\right)^{1/2}\right] = C_o(1 - F) \tag{4.102}$$

The slick will then continue to lose volatiles by diffusion, as before, except that the initial mean concentration is now $C_1$. In general, we would find, after n "mixes":

$$C_n = C_{n-1}(1 - F) \tag{4.103}$$

arid the solution of this difference equation, assuming F is constant, is:

$$C_n = C_o(1 - F)^n \tag{4.104}$$

We may compare this solution to that for quiescent diffusion in the absence of mixing:

$$C/C_o = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4}\frac{\mathcal{D}}{H^2}t\right) + \frac{8}{9\pi^2}\exp\left(-\frac{9\pi^2}{4}\frac{\mathcal{D}t}{H^2}\right) + \cdots \quad (4.105)$$

and is we plot $C/C_o$ vs $\mathcal{D}t/H^2$ (Figure 4-17) we see that:

$$t = n\,t_M \quad (4.106)$$

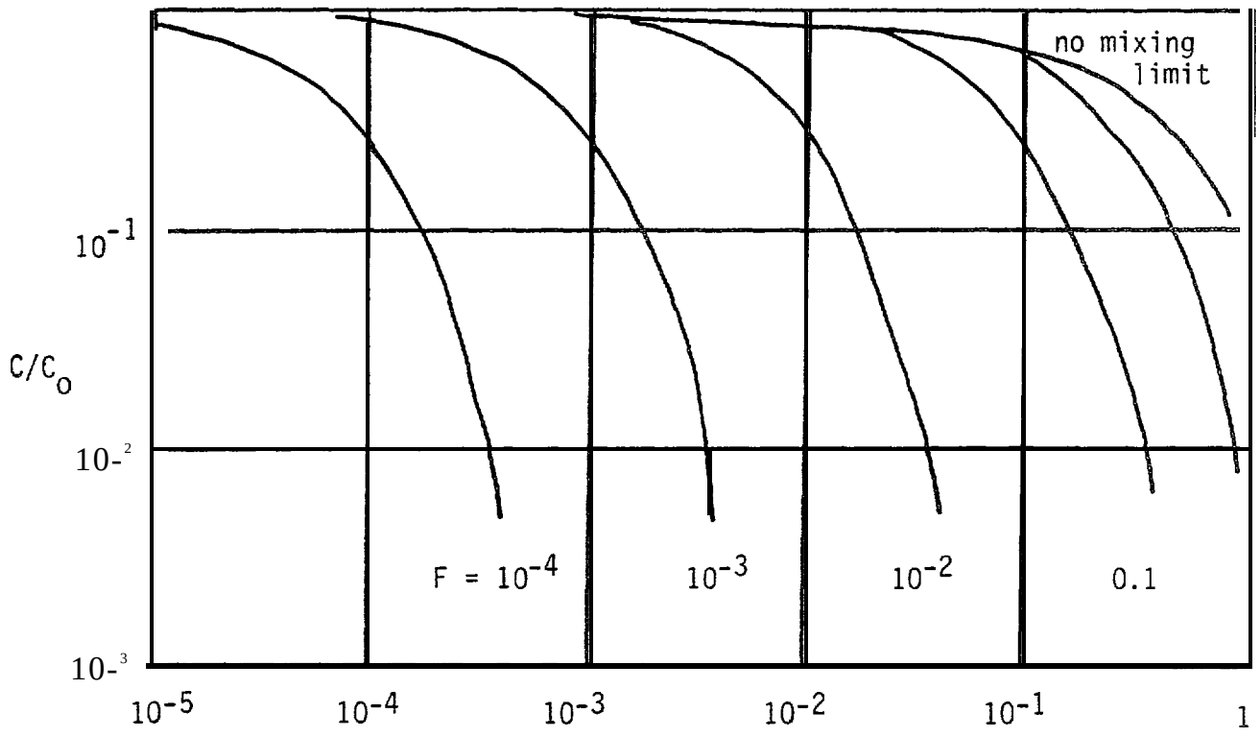
As expected, periodic mixing enhances the rate of loss of volatiles, the extent of enhancement depending upon the parameter F. From the half-times of these curves we may define a measure of the extent of enhancement by mixing, $E_M$, as:

$$E_M = \frac{\tau_{1/2}(\text{pure diffusion})}{\tau_{1/2}(\text{periodic mixing})} \quad (4.107)$$

Figure 4-18 shows Em plotted as a function of F. Reasonable values of F can be estimated from:

$$F = \left(4\mathcal{D}t_M/\pi H^2\right)^{1/2} \quad (4.108)$$

We expect that H is of order 1 cm, with a range of perhaps 0.5 to 2 cm. The magnitude of $\mathcal{D}$ will depend strongly upon which volatile species is considered and might range from $10^{-8}$ to $10^{-6}$ $cm^2/s$. The wave interval, $t_M$, might take on values in the range 1 to 10 sec. F, then, would be in the range $10^{-4} \leq F \leq 10^{-2}$. If these estimates are reasonable, then it appears that this periodic mixing mechanism exerts a tremendous degree of enhancement of loss of volatiles on the slick in comparison to the pure, static diffusion model.




$$\mathscr{D}t/H^2 = \frac{\pi n}{4}F^2$$

FIGURE 4-17. EFFECT OF MIXING ON CONCENTRATION

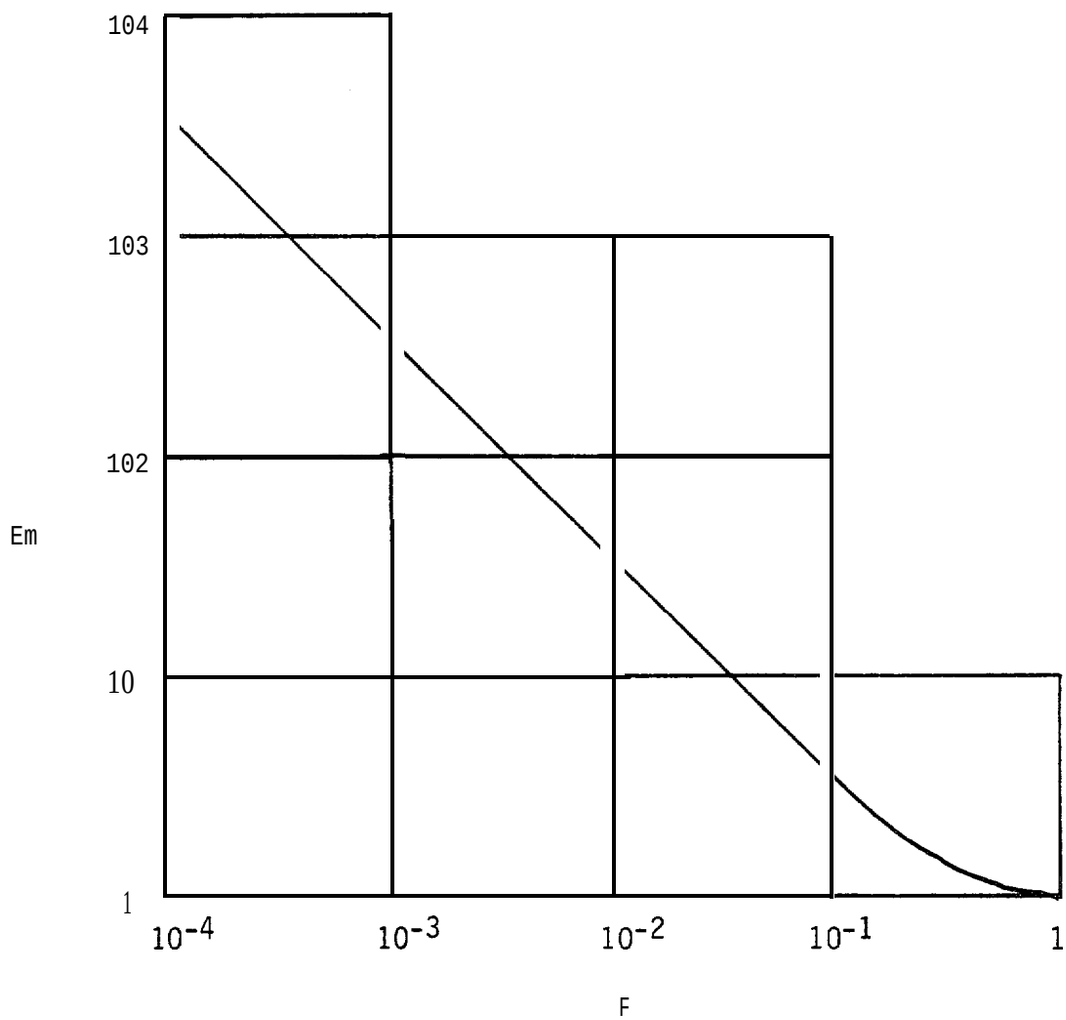



FIGURE 4-18. DEPENDENCE OF ENHANCEMENT FACTOR ON F

One difficulty with this approach is that it provides no connection between wave dynamics and the periodic mixing action, except through the time scale $t_M$. Nor does it address the question of whether the degree of mixing depends upon the viscosity of the oil. An "aged" slick will potentially be too viscous to be mixed by a wave. An expression to account for the ability of a wave to distort a slick, introducing slick viscosity and wave energy terms, is currently being contemplated.

## 5.0 EXPERIMENTAL PROGRAM RESULTS -- LA JOLLA, CALIFORNIA AND KASITSNA BAY, ALASKA

### 5.1 Evaporation/Dissolution Rate Determinations

Evaporation and dissolution are the two major weathering processes affecting oil after it is released into seawater; in some instances most of the volatile compounds may be lost by evaporative processes within 24 to 48 hours (JORDAN and PAYNE, 1980). The composition of an oil slick, its surface area and physical Properties, the wind velocity, air and sea temperatures, sea state, and the intensity of solar radiation can all affect hydrocarbon evaporation rates (WHEELER, 1978).

Given sufficient time, evaporative processes can remove most of the volatile hydrocarbons with molecular weights less than nC-15, and in general pentadecane is the lightest normal alkane commonly found in weathered oils and tar balls (PAYNE, 1981). Further, it is rare to find hydrocarbons lighter than nC-12 in seawater extracts not associated with oil spill events. The volatile compounds encompassed below nC-15 make up anywhere from 20-50% of most crude oils, and the distillation curve data shown in Figure 3-12 illustrate that these components make up 50% of the overall mass of Murban crude, 46% of Cook Inlet crude, 31% of Prudhoe Bay crude and 25% of Wilmington crude oils. Hydrocarbon components with molecular weights less than nC-15 can make up as much as 75% or more in refined petroleum products and they constitute 10% or less of residual fuel oils such as Bunker C (CLARK and BROWN, 1977).

While other studies have been completed to determine the relative importance of evaporation vs dissolution for such compounds as benzene and cyclohexane (HARRISON et al., 1975; MCAULIFFE, 1977; SMITH and MCINTYRE, 1971), carefully controlled experiments were clearly required to examine the simultaneous affects of evaporation and dissolution on oil weathering. Acquisition of such data is critical for modification of algorithms and input components for the oil-weathering computer model and verification of predicted output where environmental parameters such as wind speed and air and water temperature could be controlled. To support this requirement, an evaporation/

dissolution chamber was constructed to allow simultaneous, compound-specific concentration determinations in air, oil and water phases such that evaporative and dissolution process rates could be determined as a function of time. Figure 5-1 presents three schematic diagrams of the evaporation/dissolution chamber showing its component parts and functional design, and Figure 5-2 shows the assembled evaporation/dissolution chamber. The circular design of the tank allows air to pass over the slick on a one time basis where an estimated 90% of the air flow is diverted up the exhaust vent showed in Figure 5-1A and out of the exhaust port into a vented duct. The velocity of the air stream is controlled by baffled systems on the blower shown in the foreground of Figure 5-2, and air velocities over the slick are measured using a Kurz air velocity meter installed 5 cm above the oil/seawater interface. To minimize sample contamination during experimental studies, the tank has been fabricated entirely of glass, stainless steel , anodized aluminum and teflon. The circular design was chosen over other shapes (e.g., rectangular) such that wind driven oil would not accumulate or pile up at one end of the chamber. In this manner a continuous oil slick can be maintained to simulate the conditions of airflow over a large surface oil slick.

For ambient temperature (19 to 23°C) studies, the chamber is assembled in a dedicated laboratory facility controlled by standard air conditioning. Lower temperature studies at 13 and 3°C have been conducted within a specially designed cold room where air and water temperatures can be carefully controlled and maintained. (In this enclosed chamber, lower molecular weight hydrocarbons lost due to evaporation processes are vented outside the laboratory. ) Seawater for the system is obtained from the flow-through seawater aquarium supply source at Scripps Institution of Oceanography and filtered (0.45 m glass fiber filters) before use. During an experimental run, time series air samples are obtained by adsorbing volatile components onto Tenax® columns using a technique described in greater detail later (and in Appendix B), water column samples are obtained through the stopcocks in the sides of the chamber and "grab" oil samples are obtained through a specially designed sampling port in the top of the air-flow manifold. To ensure homogeneity in

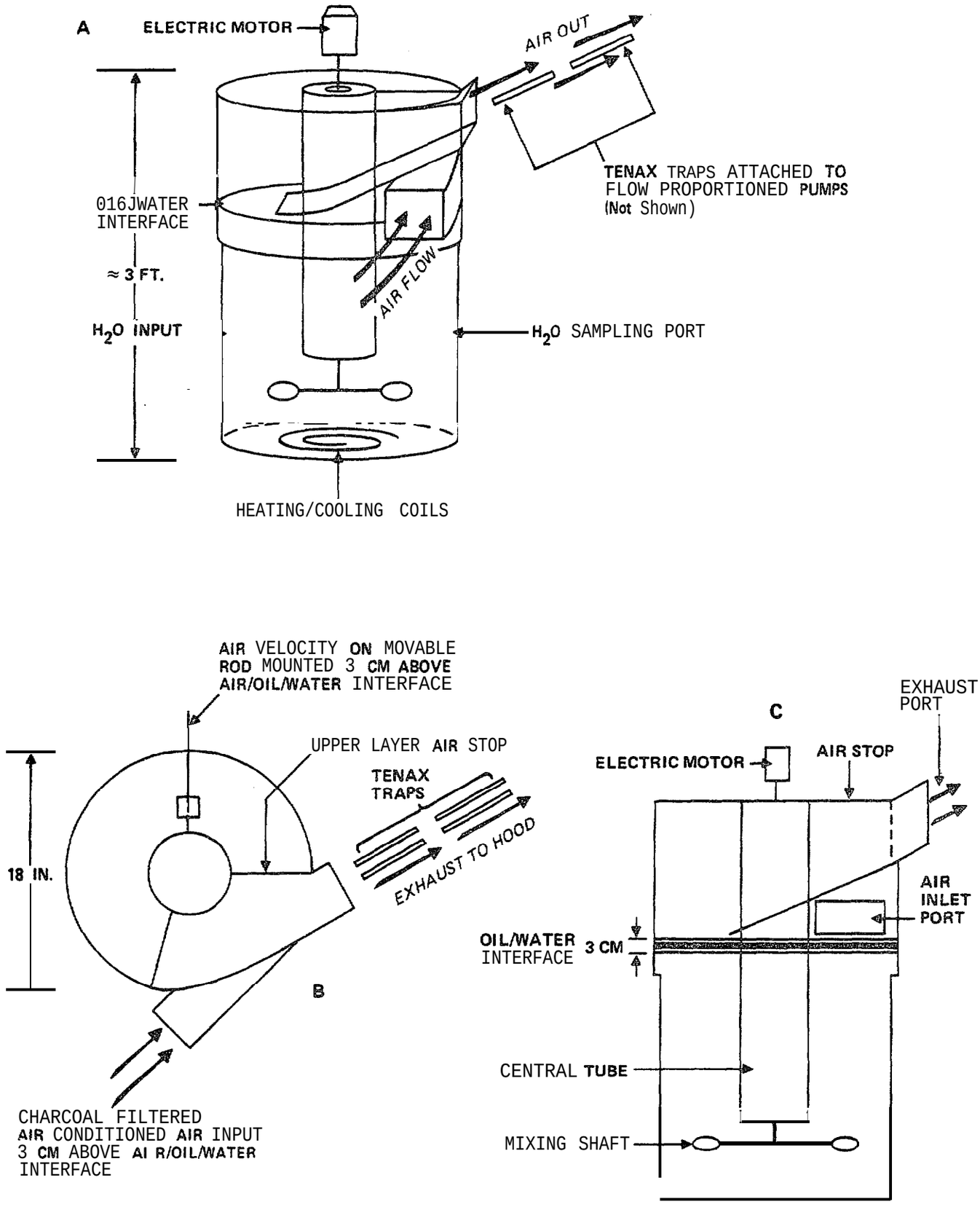



FIGURE 5-1. PROTOTYPE TANK DESIGN FOR EVAPORATION/DISSOLUTION EXPERIMENTS.

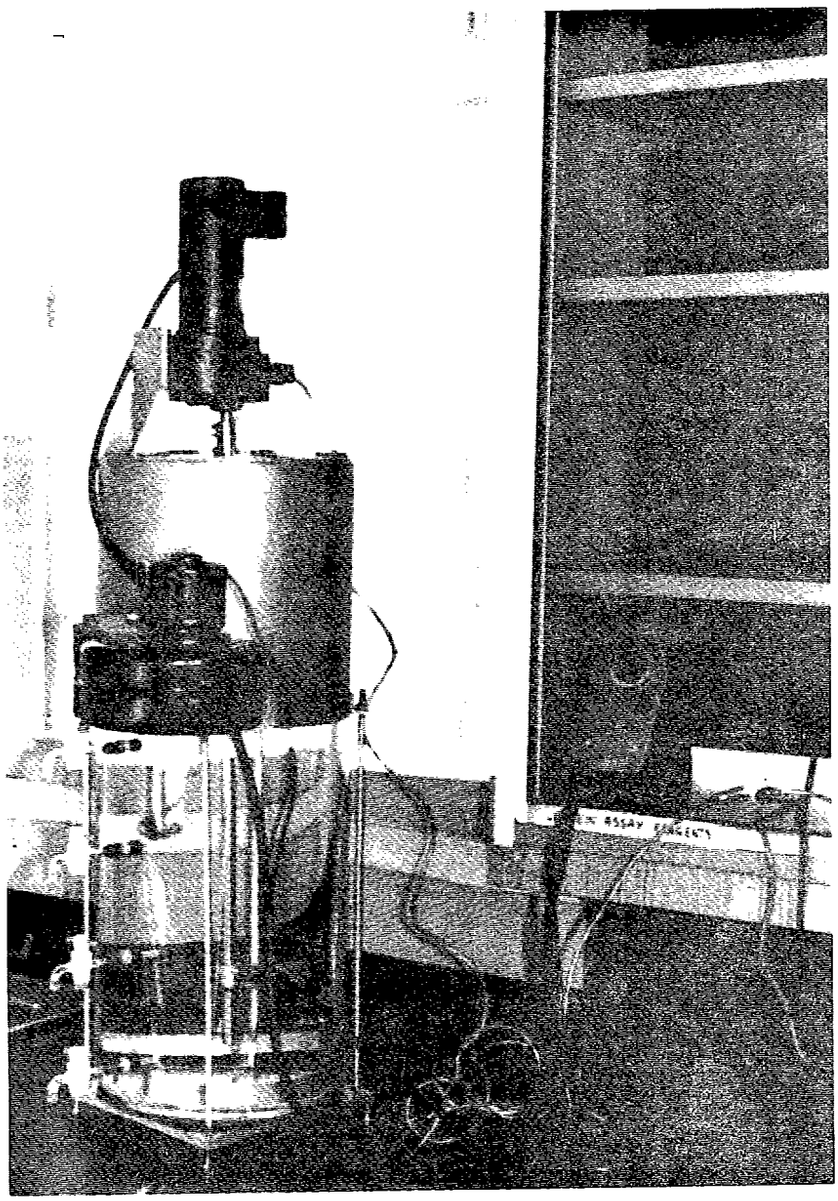


FIGURE 5-2. ASSEMBLED EVAPORATION/DISSOLUTION CHAMBER UTILIZED FOR COMPONENT SPECIFIC EVAPORATION/DISSOLUTION RATE DETERMINATIONS AS A FUNCTION OF TEMPERATURE AND WIND SPEED -- LA JOLLA, CALIFORNIA.

the water column, the water is agitated from below by means of a rotating paddle capable of generating eddy diffusion coefficients ranging from 10 to 100 $cm^2/sec$ (September 1980 Quarterly Report).

### 5.1.1 Results of Evaporation/Dissolution Chamber Experiments - La Jolla

Before experimental studies on such a complex mixture as Prudhoe Bay crude oil were initiated, evaporation/dissoluti on experiments were completed using a simple, component mixture consisting of benzene, toluene, and cyclohexane at less than full saturation concentrations. The application of the results from these experiments toward the oil weathering model development was presented in detail in Sections 2.4.4 and 2.4.6, respectively, of our November 1980 Interim Quarterly Report.

After completing preliminary evaluation of the evaporation/dissolution chamber with the three component m'ixture mentioned above, a series of oil weathering experiments were undertaken with Prudhoe Bay crude oil at ambient (19 to 23°C) temperatures and at 3°C in the presence and absence of Corexit 9527. Table 5-1 presents computer listings of the time series oil and water samples collected in conjunction with these experiments. Each data entry in the table includes the chromatographic identifiers for the whole oil or aliphatic, aromatic and polar fractions of the representative samples as stored in the experiment (EXP) data base of the oil weathering model. From these sample-specific identifiers, individual compound concentrations can be retrieved from the computer data base for any desired fraction as a function of time and environmental conditions. At this time data for atmospheric volatile compound concentrations are still being obtained and reduced manually (Tenax® trap experiments) ; however, the reduced data output are then being entered into the computer for generation of time series decay curves for volatile compound losses.

Figure 5-3 presents time series packed column FID gas chromatograms obtained on the volatile components in the air above the spilled oil slick at

TABLE 5-1. COMPUTER LISTING OF SAMPLES FROM EVAPORATION/DISSOLUTION RUN #4 (19°C WITHOUT COREXIT).

LISTING OF HISTORY DATASET PAGE 1 OCT-28-1981

EXPERIMENT: EVAP 4 PRINCIPAL INVESTIGATOR: JRP
LOG PAGE: 0
STATUS: FIN
START DATE: FEB-11-1981
END DATE: FEB-11-1981

THIS WAS THE FOURTH RUN OF THE EVAPORATION/DISSOLUTION TANK USING PRUDHOE BAY CRUDE AND SEAWATER AS THE TWO PHASES. MOD-RATE MIXING AND WIND CONDITIONS WERE EMPLOYED.

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-28-1981

EXPERIMENT: EVAP 4
MEDIUM: OIL FRACTION TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 58 | 1 FEB-26-1981 | 3 | 0 | .00 | 17.30 | 17.30 | NO | 3.70 | 80.00 | |
| 53 | 3 FEB-26-1981 | 6 | 0 | .00 | 18.10 | 18.10 | NO | 3.70 | 80.00 | |
| 78 | 5 FEB-26-1981 | 9 | 0 | .00 | 18.40 | 18.40 | NO | 3.70 | 80.00 | |
| 67 | 13 FEB-25-1981 | 12 | 0 | .00 | 18.30 | 18.30 | NO | 3.70 | 80.00 | |
| 68 | 15 FEB-26-1981 | 24 | 0 | .00 | 17.10 | 17.10 | NO | 3.70 | 80.00 | |
| 5 | 7 MAR-06-1981 | 36 | 0 | .00 | 17.73 | 17.70 | NO | 3.70 | 80.00 | |
| 82 | 11 FEB-27-1981 | 48 | 0 | .00 | 17.70 | 17.70 | NO | 3.70 | 80.00 | |
| 83 | 13 FEB-27-1981 | 72 | 0 | .00 | 17.90 | 17.90 | NO | 3.70 | 80.00 | |
| 84 | 15 FEB-27-1981 | 120 | 0 | .00 | .00 | .00 | NO | 3.70 | 80.00 | |
| 87 | 17 FEB-27-1981 | 168 | 0 | .00 | .00 | .00 | NO | 3.70 | 80.00 | |
| 88 | 88 FEB-27-1981 | 194 | 0 | .00 | .00 | .00 | NO | 3.70 | 80.00 | |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-28-1981

EXPERIMENT: EVAP 4
MEDIUM: OIL FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 26 | / FEB-16-1981 | 0 | [illegible] | .00 | .00 | 15.50 | NO | 3.70 | 80.00 | |
| 27 | FEB-16-1981 | [illegible] | 30 | .00 | .00 | 16.30 | NO | 3.70 | 80.00 | |
| 28 | 5 *CO-,*-IS*! | 3 | 0 | .00 | .00 | 7. 30 | NO | 3.70 | 80.00 | |
| 29 | 7 FEB-16-1981 | [illegible] | [illegible] | .00 | 16.10 | 16.10 | NO | 3.70 | 80.00 | |
| 31 | FEB-16-1981 | [illegible] | 0 | .00 | 16.40 | .00 | N | 3.70 | 80.00 | |
| 32 | 32 FEB-17-1981 | 12 | 0 | .00 | 16.30 | 16.30 | NO. | 3.70 | 80.00 | |
| 33 | 13 FEB-17-1981 | 24 | 0 | .00 | 17.10 | 17.10 | NO | 3.70 | 80.00 | |
| 34 | 15 FEB-17-1981 | 35 | 45 | .00 | .00 | .00 | NO | 3.70 | 80.00 | |
| 35 | 17 FEB-17-1981 | 48 | 0 | .00 | 17.70 | 17.70 | NO | 3.70 | 80.00 | |
| 46 | 11 FEB-18-1981 | 72 | 30 | .00 | 17.90 | 17.90 | NO | 3.70 | 80.00 | |
| 47 | 13 FEB-18-1981 | 144 | 45 | .00 | .00 | .00 | NO | 3.70 | 80.00 | |
| 48 | 15 FEB-18-1981 | 168 | 15 | .00 | 18.60 | 18.60 | NO | 3.70 | 80.00 | |
| 49 | 17 FEB-18-1981 | 194 | 15 | .00 | 18.00 | 18.00 | NO | 3.70 | 80.00 | |
| 52 | 1 FEB-19-1981 | 220 | 0 | .00 | 17.90 | 17.90 | NO | 3.70 | 80.00 | |
| 53 | 3 FEB-19-1981 | 288 | 0 | .00 | 18.00 | 18.00 | NO | 3.70 | 80.00 | |
| 15 | 5 FEB-20-1981 | 337 | 0 | .00 | 18.60 | 18.60 | NO | 3.70 | 80.00 | |
| 16 | 7 FEB-20-1981 | 384 | 0 | .00 | 15.90 | 15.90 | NO | 3.70 | 80.00 | |
| 17 | 9 FEB-20-1981 | 460 | 15 | .00 | 18.30 | 18.30 | NO | 3.70 | 80.00 | |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-28-1981

EXPERIMENT: EVAP 4
MEDIUM: WATER FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 218 | 7 FEB-13-1981 | 1 | 30 | .00 | 18.30 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 219 | 9 FEB-13-1981 | 3 | 0 | .00 | 17.30 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 220 | 11 FEB-13-1981 | 6 | 0 | .00 | 18.10 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 221 | 13 FEB-13-1981 | 9 | 0 | .00 | 18.40 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 222 | 15 FEB-13-1981 | 12 | 0 | .00 | 18.30 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 1 | 25 FEB-14-1981 | 24 | 0 | .00 | 17.10 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| 2 | 27 FEB-14-1981 | 36 | 0 | .00 | .00 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| , | 29 FEB-14-1981 | 48 | 0 | .0. | 17.70 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| • | 5 FEB-15-1981 | 72 | 0 | .00 | 17.90 | .00 | NO. | 3.70 | 80.00 | VOL WATER: 1 L. |
| 635 | FEB-14-1981 | 144 | 0 | .00 | .00 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| / | / FEB-14-1981 | 168 | 0 | .00 | 18.60 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |
| / | 3 FEB-14-1981 | 194 | 0 | .00 | 18.00 | .00 | NO | 3.70 | 80.00 | VOL WATER: 1 L. |

TABLE 5-1. COMPUTER LISTING OF SAMPLES FROM EVAPORATION/DISSOLUTION RUN #5 (19°C WITHOUT COREXIT). (Continued).

LISTING OF HISTORY DATASET PAGE 1 OCT-28-1981

PRINCIPAL 1NVE911G11OU1 JLL

EXPERIMENT: EVAP 5
LOG PAGE: 01
STATUS: FIN
START DATE: APR-24-1981
END DATE: JUN-04-1981

THIS WAS THE FIFTH RUN OF THE EVAPORATION DISSOLUTION TANK. PRUDHOE BAY CRUDE AND SEAWATER WERE THE TWO PHASES. TURBULENCE SETTING WAS 44 IN REVERSE, AND THE AIR FLOW GAUGE READS .99

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: EVAP 5
MEDIUM: OIL FRICTION TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING % |
|---|---|---|---|---|---|---|---|---|---|
| 49 | 3 JUN-26-1981 | 0 | 30 | .00 | 21.20 | 21.20 | No | .99 | 44.00 |
| 43 | 5 JUN-17-1981 | 2 | 0 | .00 | 21.40 | 21.40 | NO | .99 | 44.00 |
| 64 | 7 JUN-18-1981 | 24 | 15 | .00 | 21.00 | 21.00 | NO | .99 | 44.00 |
| 65 | 9 JUN-18-1981 | 96 | 30 | .00 | 21.00 | 21.00 | NO | .99 | 44.00 |
| 51 | 7 JUN-27-1981 | 71 | 0 | .00 | 20.90 | 20.90 | NO | .99 | 44.00 |
| 54 | 1 JUN-27-1981 | 171 | 0 | .00 | 22.50 | 22.50 | NO | .99 | 44. |
| 56 | 5 JUN-27-1981 | 288 | 0 | .00 | 20.30 | 20.30 | NO | .99 | 44.00 |
| 58 | 9 JUN-27-1981 | 454 | 0 | .00 | 21.50 | 21.50 | No | .99 | 44.00 |
| 70 | 13 JUN-28-1981 | 576 | 0 | .00 | 22.20 | 22.20 | NO | .99 | 48.00 |
| 64 | 19 JUN-28-1981 | 982 | 0 | .00 | .00 | [illegible] | NO | .99 | 44.00 |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: EVAP 5
MEDIUM: OIL FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING |
|---|---|---|---|---|---|---|---|---|---|
| 50 | 5 JUN-26-1981 | 0 | 30 | .00 | 21.20 | 21.20 | No | | .44.00 |
| 66 | 11 J,SN-in-Iq*I | 2 | 0 | .00 | 21.40 | 21.40 | NO | | 44.00 |
| 72 | 13 JUN-18-1981 | 24 | 15 | .00 | 21.00 | 21.00 | No | .99 | 44.00 |
| 52 | 9 JUN-27-1981 | 71 | 0 | .00 | 20.90 | 20.90 | No | .99 | 44.00 |
| 55 | 3 JUN-27-1981 | 171 | 0 | .00 | 22.50 | 22.50 | NO | .99 | 4a.00 |
| 57 | 7 JUN-27-1981 | 288 | 0 | .00 | 20.30 | 20.30 | NO | .99 | 44.00 |
| 59 | 11 JUN-27-1981 | 454 | 0 | .00 | 21.50 | 21.50 | NO | .99 | 44.00 |
| 61 | 15 JUN-28-1981 | 576 | 0 | .00 | 22.20 | 22.20 | NO | .99 | 44.00 |
| 65 | 21 JUN-28-1981 | 982 | 0 | .00 | .00 | .00 | No | .99 | 44.00 |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: EVAP 5
MEDIUM: WATER FRACTION TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING |
|---|---|---|---|---|---|---|---|---|---|
| 18 | 23 JUN-30-1981 | 0 | 0 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 19 | 25 JUN-30-1981 | 0 | 15 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 20 | 27 JUN-30-1981 | 0 | 30 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 21 | 29 JUN-30-1981 | 2 | 0 | .00 | 21.40 | 21.40 | NO | .99 | 44.00 |
| 67 | 3 JUL-07-1981 | 12 | 0 | .00 | 21.00 | 21.00 | No | .99 | 44.00 |
| 68 | 5 JUL-07-1981 | 24 | 15 | .00 | 21.00 | 21.00 | [illegible] | .99 | 44.00 |
| 69 | 7 JUL-07-1981 | 46 | 30 | .00 | 21.00 | 21.00 | No | .99 | 44.00 |
| 71 | 11 JUL-07-1981 | 71 | 0 | .00 | 20.90 | 20.90 | NO | .99 | 44.00 |
| 5.9 | 19 JUL-15-1981 | 96 | a. | .00 | 20.40 | 20.40 | NO | .99 | 44.00 |
| 78 | 3 JUL-08-1981 | 120 | 0 | .00 | 21.00 | 21.00 | NO | .99 | 44.00 |
| 80 | 5 JUL-08-1981 | 147 | 0 | .00 | 22.30 | 22.30 | NO | .99 | 44.00 |
| 82 | 7 JUL-08-1981 | 171 | .0.. | .00 | 22.50 | 22.50 | NO | .99 | 44.00 |
| 83 | 9 JUL-08-1981 | 196 | 0 | .00 | 21.40 | 21.40 | NO | .4* | 44.00 |
| 84 | 11 JUL-08-1981 | 238 | 0 | .00 | 21.60 | 21.60 | NO | .99 | 44.00 |
| 92 | 5 JUL-09-1981 | 288 | .0 | .00 | 20.30 | 20.30 | NO | .99 | 44.00 |
| 93 | 7 JUL-09-1981 | 336 | 0 | .00 | .00 | 400 | NO | .99 | 44.00 |
| 59 | 21 JUL-15-1981 | 416 | 0 | .00 | 23.40 | 23.00 | NO | .99 | 44.00 |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: EVAP 5
MEDIUM: WATER FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 5 JUN-29-1981 | 1 | 0 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 9 | 7 JUN-29-1981 | | 15 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 10 | 9 JUN-30-1981 | 1 | 30 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 11 | 11 JUN-30-1981 | 1 | 0 | .00 | 21.20 | 21.20 | NO | .99 | 44.00 |
| 12 | 13 JUN-30-1981 | 2 | 0 | .00 | 21.40 | 21.40 | No | .99 | 44.00 |
| 13 | 15 JUN-30-1981 | 3 | 0 | .00 | 21.50 | 21.50 | NO | .99 | 44.00 |
| 7 | 3 JUN-29-1981 | 5 | 30 | .00 | 22.10 | 22.10 | NO | .99 | 44.00 |
| 24 | 5 JUL-01-1981 | 12 | 0 | .00 | 21.00 | 21.00 | NO | .99 | 44.00 |
| 25 | 7 JUL-01-1981 | 24 | 15 | .00 | 21.00 | 21.00 | NO | .99 | 44.00 |
| 27 | 11 JUL-01-1981 | 46 | 30 | .00 | 21.00 | 21.00 | No | .99 | 44.00 |
| 39 | 3 JUL-02-1981 | 71 | 0 | .00 | 20.90 | 20.90 | NO | .99 | 44.00 |
| 40 | 5 JUL-02-1981 | 96 | 0 | .00 | 22.50 | 22.50 | NO | .99 | 44.00 |
| 41 | 7 JUL-02-1981 | 120 | 0 | .00 | 21.60 | 21.60 | NO | .9S | 44.00 |
| 42 | 9 JUL-03-1981 | 147 | 0 | .00 | 22.30 | 22.30 | NO | .99 | 44.00 |
| 113 | 11 JUL-03-1981 | 171 | 0 | .00 | 22.50 | 22.50 | NO | .99 | 44.00 |
| 44 | 13 JUL-03-1981 | 196 | 0 | .00 | 21.90 | 21.90 | NO | .99 | 44.00 |
| 45 | 15 JUL-03-1981 | 239 | 0 | .00 | 21.60 | 21.60 | NO | .99 | 44.00 |
| 47 | 19 JUL-03-1981 | 339 | 0 | .00 | [illegible] | [illegible] | NO | .99 | 44.; |

TABLE 5-1. COMPUTER LISTING OF SAMPLES FROM EVAPORATION/DISSOLUTION RUN #6 (3°C WITHOUT COREXIT). (Continued).

LISTING OF HISTORY DATASET PAGE 1 OCT-20-1981

EXPERIMENT: EVAP 6 PRINCIPAL INVESTIGATOR: JLL

STATUS: FIN
START: FRI JUL 03- 1981
ENDATE: 08.. .70L. 51

THE SYSTEM ... OF THE EVOTANK ... ENTRATHERMAL, DEGREE CELCIUS ... WIND SPEED .99 AND TURBULENCE ... 286 MLS. OPUIL WAS ADDED TO APPROX. 25 LIT ERS OF SEAWATER

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-20-1981

EXPERIMENT: EVAP 6
MEDIUM: OIL FRAC TEOM TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | PRESE | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 15 AUG-14-1981 | 0 | 30 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 28% THRU LC |
| 40 | 15 AUG-14-1981 | 7 | 0 | 3.00 | 3.00 | .00 | | NO | .99 | 44.00 | 6.25 THRU LC |
| 41 | 17 AUG-14-1981 | 4 | 0 | 3.00 | 3.00 | 1.41 | | NO | .99 | 44.00 | 16% THRU LC |
| 42 | 19 AUG-15-1981 | 6 | 0 | 3.00 | 1 a * | 3.00 | | NO | .99 | 44.00 | 2.86 THRU LC |
| 21 | AUG-15- 1981 | 9 | 0 | 1.09 | | 3.00 | 3.00 | NO | .99 | 44.00 | THRU LC |
| | 2 AUG-1 5-1981 | | | | | | | | | | |
| 7 | 17 AUG-1-1 981 | 19 | * | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 1 0.25% THRU LC |
| 17 | 19 AUG-18-1981 | 24 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 5% THRU LC |
| 18 | AUG-1 -,$*1 | 35 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 5% THRU LC |
| 19 | 19 AUG-19-1981 | 46 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 5% THRU LC |
| 20 | 21 AUG-19-1 981 | Γ. | 30 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 4% THRU LC |
| 6 | 3 AUG-28-1981 | 146 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 6.25% THRU LC |
| 42 | 11 SEP-21-1981 | 222 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 8.64% THRU LC |
| 43 | 15 SEP-22-1981 | 284 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 4% THRU LC |
| 44 | 15 SEP-22-1981 | 305 | 0 | 3.00 | 3.00 | 3.00 | | NO | .99 | 44.00 | 4% THRU LC |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-20-1981

EXPERIMENT: EVAP 6
MEDIUM: OIL FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 49 | AUG-15-1981 | 0 | 30 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 50 | 9 AUG-15-1981 | 2 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 47 | 3 AUG-15-1981 | 0 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 51 | 13 AUG-15-1981 | 4 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 52 | 15 AUG-16-1981 | 9 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 53 | 15 AUG-18-1981 | 11 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 6.61% ON LC |
| 36 | 29 AUG-21-1981 | 26 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 5% ON LC |
| 39 | 31 AUG-21-1981 | 35 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 5% ON LC |
| 40 | 33 AUG-21-1981 | 46 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 5% ON LC |
| 41 | 35 AUG-22-1981 | 74 | 30 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 4% ON LC |
| 4 | 14 AUG-28-1981 | 95 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 5.90% ON LC |
| 5 | 1 AUG-28-1981 | 146 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 6.25% ON LC |
| 60 | 1 SEP-23-1981 | 222 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 8.64% ON LC |
| 69 | 3 SEP-22-1981 | 286 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | 4% ON LC |
| 66 | 1 SEP-22-1981 | 305 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |

EXPERIMENT: EVAP 6
MEDIUM: WATER FRACTION TYPE: 3

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 5 AUG-17-1981 | 0 | 10 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 7 | 13 AUG-17-1981 | 0 | 30 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 5 | 9 AUG-17-1981 | -1 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 12 | 5 AUG-18-1981 | 2 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 14 | 7 AUG-18-1981 | 4 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 16 | 13 AUG-18-1981 | 6 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 26 | 9 AUG-19-1981 | 11 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 30 | 17 AUG-20-1981 | 19 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 31 | 19 WC-81 | 24 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 33 | 21 AUG-21-1981 | 48 | 0 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 35 | 23 AUG-21-1981 | 74 | 30 | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 37 | 27 AUG-21-1981 | 146 | 0 | 3.00 | 3.00 | 3.00 | | .99 | 44.00 | |
| 19 | 21 SEP-21-1981 | 284 | | 3.00 | 3.00 | 3.00 | NO | .99 | 44.00 | |
| 34 | 7 SEP-23- 1981 | 305 | 0 | 1.90 | 3.00 | 3.00 | NO | .99 | 44.00 | |

TABLE 5-1. COMPUTER LISTING OF SAMPLES FROM EVAPORATION/DISSOLUTION RUN #7 (3°C WITH COREXIT). (Continued).

LISTING OF HISTORY DATASET PAGE 1 OCT-28-1981

EXPERIMENT: EVAP 7 PRINCIPAL INVESTIGATOR: TLL
LOG PAGE: 46
STATUS: FI'
START DATE: AUG-27-1981
END DATE: SEP-21-1981

THE CONDITIONS IN THIS E/D RUN WERE IDENTECAL TO THOSE OF E/D 6 (3 DEGREE ISO.) EXCEPT THAT 10 MLS. OF COREXIT WAS WELL MIXED IN THE OIL BEFORE IS WAS SPILLED.

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: EVAP 7
MEDIUM: WATER FRACTION TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 93 | 0 SEP-09-1981 | 0 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 91 | 0 SEP-08-1981 | 0 | 15 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 90 | 0 SEP-08-1981 | 0 | 30 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 89 | 0 SEP-08-1981 | 1 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 88 | 0 SEP-08-1981 | 2 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 87 | 0 SEP-08-1981 | 4 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 86 | 0 SEP-08-1981 | 8 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | OIL/COR=20 |
| 85 | 0 SEP-08-1981 | 12 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | OIL/COR=20 |
| 80 | 0 SEP-04-1981 | 30 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 79 | 0 SEP-04-1981 | 48 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 78 | 0 SEP-04-1981 | 96 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 96 | 0 SEP-09-1981 | 192 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |
| 95 | 0 SEP-09-1981 | 299 | 0 | 3.00 | 3.00 | 3.00 | YES | .99 | 44.00 | VOA ON 5 MLS. | VOL OIL/COR=20 |

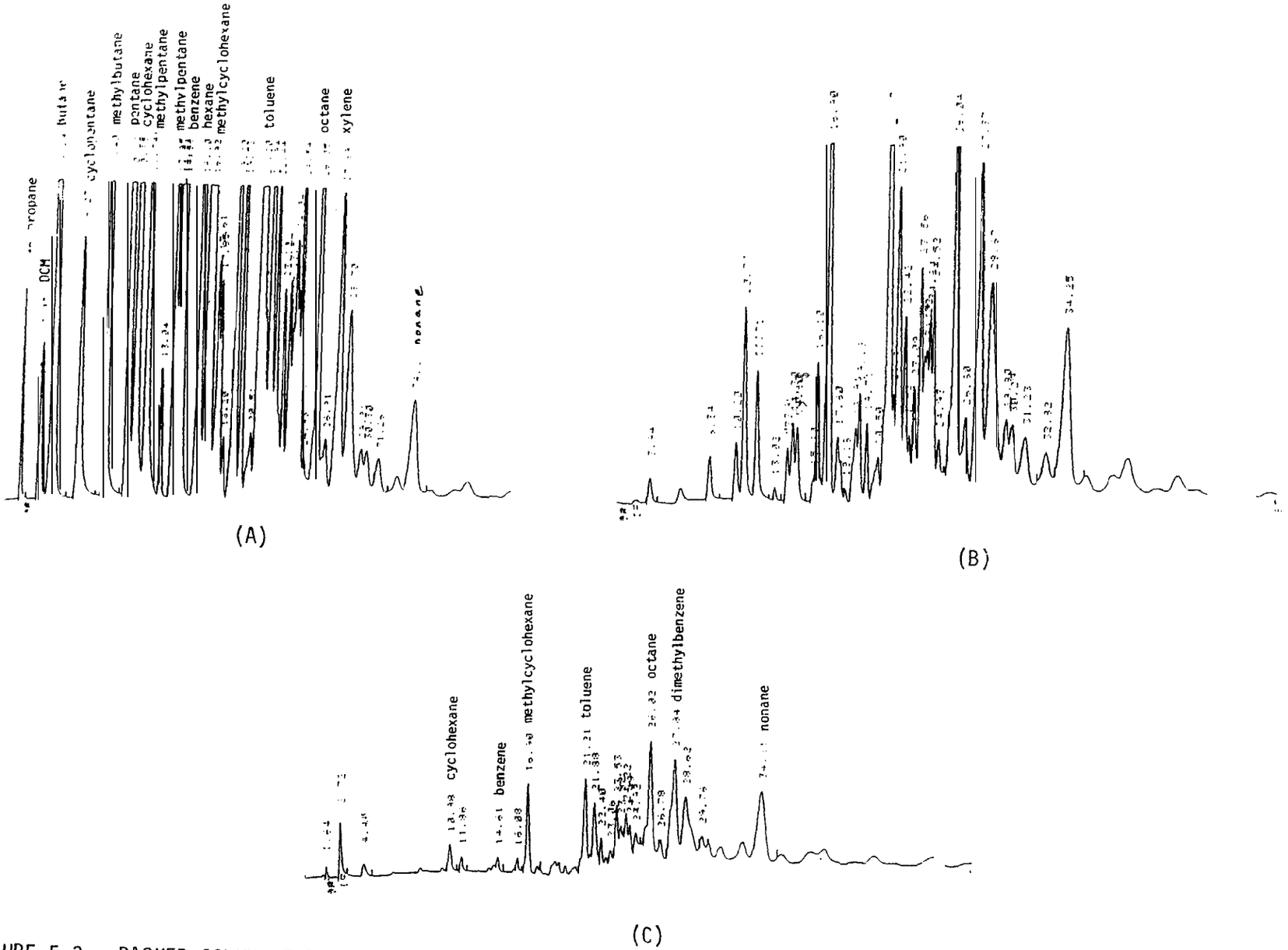



FIGURE 5-3. PACKED COLUMN FLAME IONIZATION DETECTOR GAS CHROMATOGRAMS OBTAINED ON HEAT-DESORBED VOLATILE COMPONENTS TRAPPED ON TENAX® FROM EVAPORATION/DISSOLUTION EXPERIMENT COMPLETED AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND (E/D-4). (A) AIR SAMPLE 15 MINUTES AFTER THE SPILL (FRONT TRAP); (B) AIR SAMPLE 6 HOURS AFTER THE SPILL (FRONT TRAP); (C) AIR SAMPLE 12 HOURS AFTER THE SPILL (FRONT TRAP); (D) BACKUP IN-SERIES TRAP 15 MINUTES AFTER THE SPILL SHOWING LIMITED BREAKTHROUGH OF ONLY 4 INDIVIDUAL ALIPHATIC COMPONENTS; (E) BACKGROUND AIR SAMPLE (CONTROL) COLLECTED BEFORE SPILL INITIATED. ALL SAMPLES OBTAINED BY VACUUM TRAPPING EXHAUST AIR STREAM FROM EVAPORATION/DISSOLUTION CHAMBER AT A FLOW RATE OF 25 ML/MIN FOR 60 SECONDS.

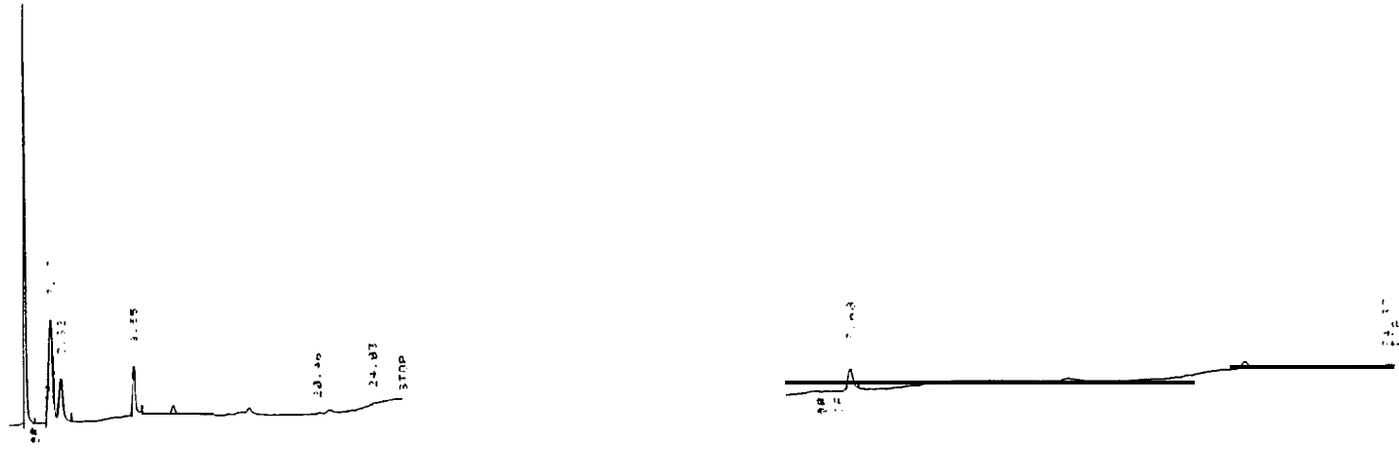



FIGURE 5-3. PACKED COLUMN FLAME IONIZATION DETECTOR GAS CHROMATOGRAMS OBTAINED ON HEAT-DESORBED VOLATILE COMPONENTS TRAPPED ON TENAX® FROM EVAPORATION/DISSOLUTION EXPERIMENT COMPLETED AT 9°C UNDER INFLUENCE OF A 7 KNOT WIND (E/D-4). (A) AIR SAMPLE 15 MINUTES AFTER THE SPILL (FRONT TRAP); (B) AIR SAMPLE 6 HOURS AFTER THE SPILL (FRONT TRAP); (C) AIR SAMPLE 12 HOURS AFTER THE SPILL (FRONT TRAP); (D) BACKUP IN-SERIES TRAP 15 MINUTES AFTER THE SPILL SHOWING LIMITED BREAKTHROUGH OF ONLY 4 INDIVIDUAL ALIPHATIC COMPONENTS; (E) BACKGROUND AIR SAMPLE (CONTROL COLLECTED BEFORE SPILL INITIATED. ALL SAMPLES OBTAINED BY VACUUM TRAPPING EXHAUST AIR STREAM FROM EVAPORATION/DISSOLUTION CHAMBER AT A FLOW RATE OF 25 ML/MIN FOR 60 SECONDS (Continued)

19°C (Evaporation/Dissolution Run 4 ; denoted E/D-4). This technique allows quantitation of lower molecular weight compounds ranging from propane through nonane as a function of time. As the chromatograms in Figure 5-3, B and C illustrate very rapid losses of lower molecular weight components below octane are observed. The chromatogram in Figure 5-3D shows the in-series backup Tenax trap from the 15 minute sample, and only limited breakthrough of lower molecular weight compounds such as butane and methylbutane are noted. Figure 5-3E presents a time zero Tenax background air control sample showing no component contamination before the spill occurred. Additional details on the sampling procedure and methodology for analyses of volatiles using this Tenax trap procedure are presented in Appendix B - Methods.

From the type of data obtained and shown in Figure 5-3 it is possible to generate time series airborne concentrations of these volatile compounds as shown by the data in Table 5-2 and the graphs in Figure 5-4. Clearly, airborne concentrations of monocyclic aromatics such as benzene and toluene are observed to fall off rapidly to non-detectable levels within 7 to 8 hours under these conditions. Similar exponential decay curves are observed for volatile aliphatic compounds such as pentane, methylpentane and octane (Figure 5-5).

Simultaneously collected water samples analyzed by a purge and trap technique similar to that developed by BELLAR and LICHTENBERG, (1974) allows determination of water column concentrations of these same volatilecomponents as a function of time, Table 5-3 and Figure 5-6 present such time series data (from FID-4) for benzene, toluene, cyclohexane and xylene. In the water column data, an initial increase in aromatic hydrocarbon concentrations is noted with the concentration maximum occurring after 4-5 hours. Under these conditions, the absolute maximum of individual compounds are determined by the seawater volubility of the compound of interest and its mole fraction in the parent oil. After the maximum concentration buildup at 4-5 hours (controlled by compound specific mass transfer coefficients) exponential decreases in the water-borne concentrations are then noted due to the gradual seawater/air Partitioning and evaporative loss of these compounds.

TABLE 5-2. TIME-SERIES AIR-BORN CONCENTRATIONS OF VOLATILE COMPONENTS ABOVE PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER A 7 KNOT WIND. (Tenax samples from E/D-4).

| Compound | time 0 | 30 min | 45 min | 1 hour | 1 hour 15 min | 1 hour 30 min | 1 hour 45 min | 2 hrs | 7.5 hrs | 3 hrs | 4 hrs | 5 hrs | 6 hrs | 8 hrs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.0226 L | .0255 | .0286 | .0273 L | 028 | .0245 | .0176 | .028 | .077 | .031 | . 025 | .0316 | .070 | .024 |
| Butane | 11.9 | 3.54 | 3.05 | 2.65 | 1.17 | ND | ND | ND | ND | ND | NO | NO | NO | NO |
| Cyclopentane | 2.46 | 0.761 | 0.689 | 0.382 | ND | NO | NO | NO | ND | ND | ND | ND | ND | ND |
| Methylbutane | 7.30 | 2.22 | 2.59 | 1.08 | 1.19 | 0.675 | 1727 | 0.439 | 0.592 | ().241 | ND | NO | ND | ND |
| Pentane | 16. I | 3.88 | 3.50 | 1.79 | 1.64 | 0.816 | 0.682 | 0.496 | 0.426 | 0.222 | NO | ND | NO | ND |
| Cyclohexane | 7.52 | 2.70 | 2.80 | 1.39 | 1.36 | 0.816 | 0.682 | 0.488 | 0.454 | 0.323 | 0.320 | 0.?53 | 0.85 | NO |
| Methylpentane | 7.32 | 2.34 | 2.21 | 1.14 | 1.19 | 0.537 | 0.565 | 0.400 | 0.557 | 0.180 | ND | NO | NO | No |
| Benzene | 3.8 | 1.17 | 1.18 | 0.670 | 0.670 | 0.653 | 1.08 | 0.748 | 0.636 | 0.355 | 0.160 | 0.443 | 0.003 | NO |
| Hexane | 12.0 µg/l | 4.78 | 6.29 | 3.30 | 3.89 | 2.12 | 2.39 | 2.62 | 4.95 | 0.806 | 1.68 | 1.77 | 0.550 | ND |
| Methylcyclohexane | 15.6 | 5.64 | 5.63 | 3.11 | 3.14 | 1.48 | 1.47 | 1.25 | 1.23 | 0.717 | 0.247 | 0.222 | ND | ND |
| 101 uene | 14.3 µg/l | 4.98 | 5.17 | 2.97 | 2.79 | 1.55 | 1.42 | 0.975 | 0.864 | 0.484 | 0.20 | 0.253 | ND | NO |
| Ethyl Benzene | 1.47 | 0.576 | 0.555 | 0.318 | 0.306 | ND | ND | NO | NO | NO | ND | ND | NO | NO |
| Cumene & n-octane | 6.08µg/l | 2.63 | 2.60 | 1.75 | 1.63 | 1.35 | 1.27 | 1.20 | 1.09 | 0. 806 | 0.520 | 0.348 | ND | ND |

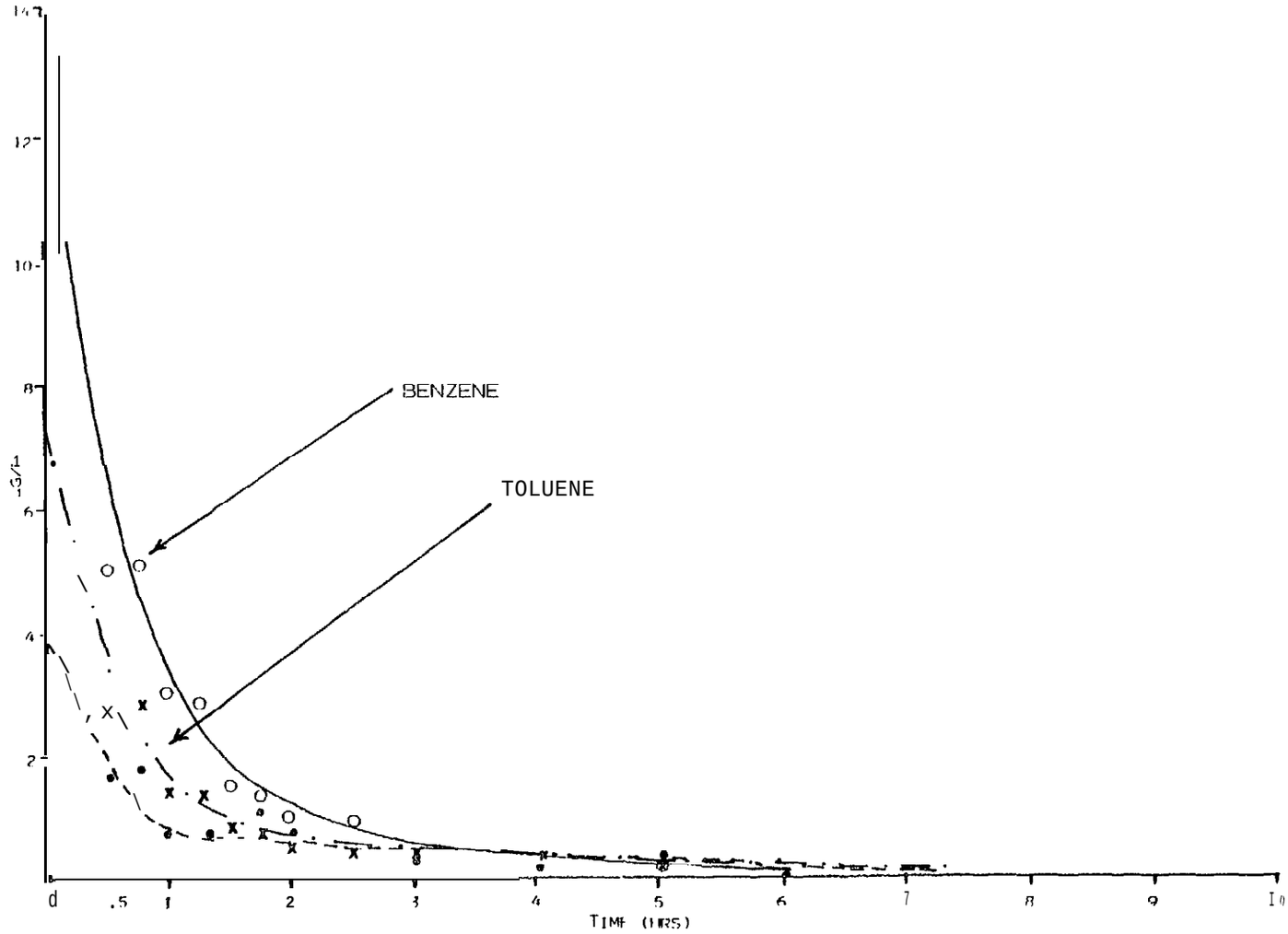



FIGURE 5-4, VOLATILE AROMATIC COMPONENT CONCENTRATIONS IN THE AIR STREAM ABOVE A 200 ml "SLICK" OF PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND. (Evaporation/dissolution chamber run 4).

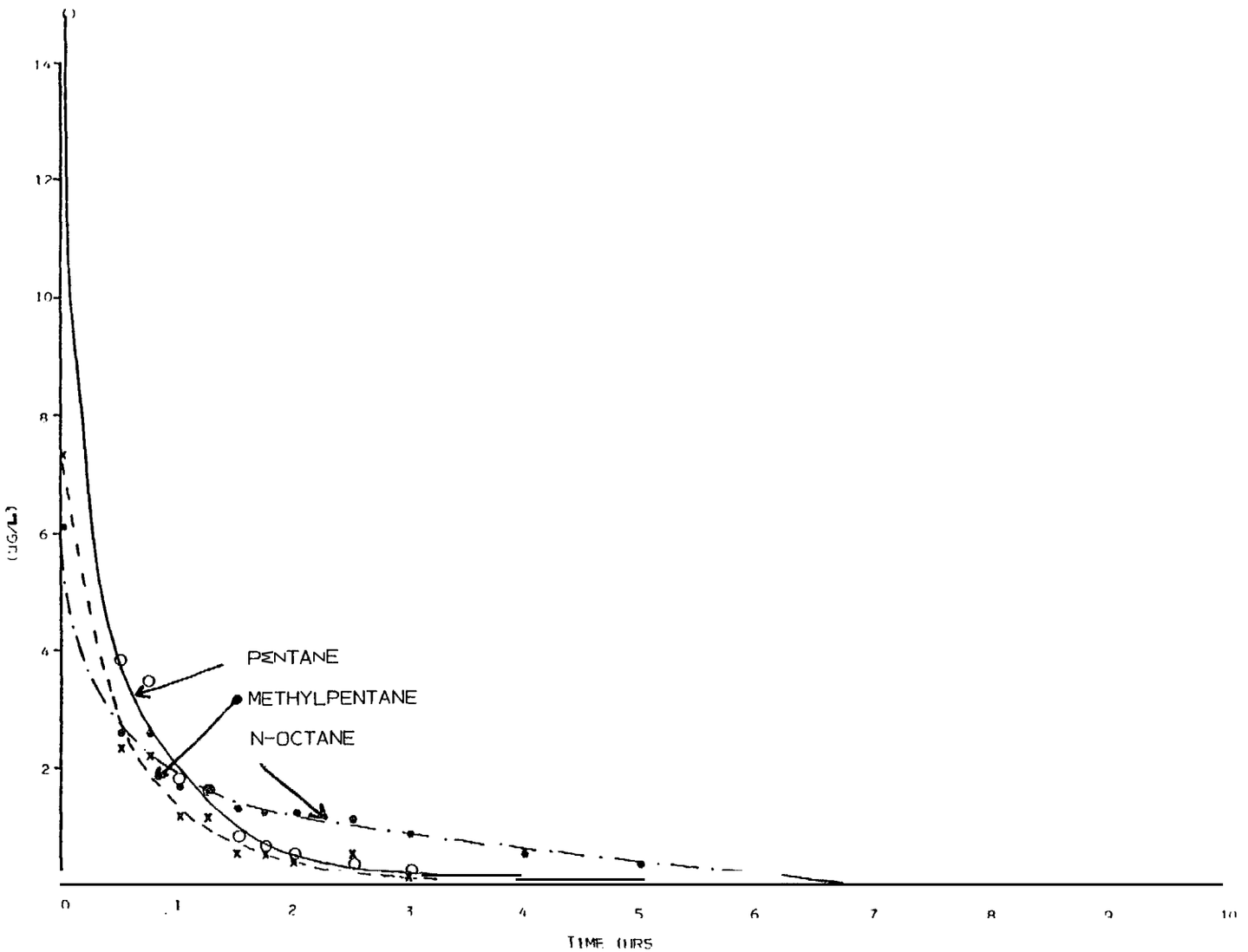



FIGURE 5-5. VOLATILE ALIPHATIC COMPONENT CONCENTRATIONS IN THE AIR STREAM ABOVE A 200 $m^2$ "SLICK" OF PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT W $N_2$ (Evaporation/dissolution chamber run 4).

TABLE 5-3. TIME-SERIES WATER COLUMN CONCENTRATIONS OF LOWER MOLECULAR WEIGHT ALIPHATIC AND AROMATIC COMPONENTS FROM PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND. (Evaporation/dissolution Exp-4; purge and trap analyses after Bellar & Lichtenberg, 1974).

| Compound | 15 min | 30 min | 45 min | 1 hour | 1.5 hours | 7 hours | 2.5 hours | 6 hours | 11 hours | 20 hours | 26 hours | 32 hours | 38 hours | 44 hours | 50 hours | 56 hours | 62 hours |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cyclopentane | 43.7 | 48.7 | 54.6 | 54.6 | 48.7 | 63.9 | 61,7 | 64.0 | 48 0 | 31.0 | 25 2 | 1 9 4 | 13.0 | 8.21 | 3.59 | No | NO |
| Methylbutane | 21.4 | 23.? | 24.2 | 24.2 | ,74.4 | 27.0 | 76.0 | 27.1 | 21.1 | 15.1 | 13.3 | 10.8 | 7 51 | 5 01 | 2.75 | ND | ND |
| Pentane | 96.? | 90.1 | 98.4 | 98.0 | 58.6 | 108.0 | 105.0 | 67.4 | 58.6 | 42.0 | 30.4 | 40.6 | 25 6 | 17.8 | 6 7 | 7.6 | NI) |
| Cyclohexane | 50.7 | 50.0 | 52.4 | 53.0 | 61.4 | 62.4 | 67.6 | 59 8 | 44.0 | 30.4 | 26 8 | 21.2 | 15. 0 | 10.7 | 6.2 | 1.8 | ND |
| Methylpentane | 57.6 | 54.7 | 57.2 | 57.4 | 59.8 | 64.6 | 66.3 | 57.6 | 42.8 | 79.7 | 25 1 | 21.9 | 15.1 | 10.7 | 4.60 | ND | ND |
| Benzene | 424.0 | 494. 0 | 588. 0 | 647.0 | 661.0 | 669.0 | 688.0 | 482.0 | 309.0 | 136.0 | 1.21 | 69.0 | 71 6 | 0800 | ND | ND | ND |
| Methylcyclohexane | 36.6 | 28.0 | 28.1 | 27.0 | 27.7 | 30.1 | 31.5 | 26.4 | 18.7 | 13,9 | 12.7 | 11.0 | 8.01 | 5.61 | 3.32 | No | ND |
| Toluene | 377.0 | 354.0 | 492.0 | 650.0 | 604.0 | 608. 0 | 680.0 | 406.0 | 7 3 1 . ( 1 | 77.0 | ND | 49.6 | 3. 80 | ND | ND | NO | ND |
| Ethyl Benzene | 19.5 | 11.4 | 19.3 | 375.0 | 26.8 | 25.8 | 34.3 | | | | | | | | | | |
| nOctane | 6.40 | 4.20 | 4.6 | 6.6 | 5.7 | 4.2 | 5.41 | 3.40 | 3.20 | 2.80 | 1 60 | 1.80 | 1 60 | 1 20 | 1 20 | 1 20 | ND |

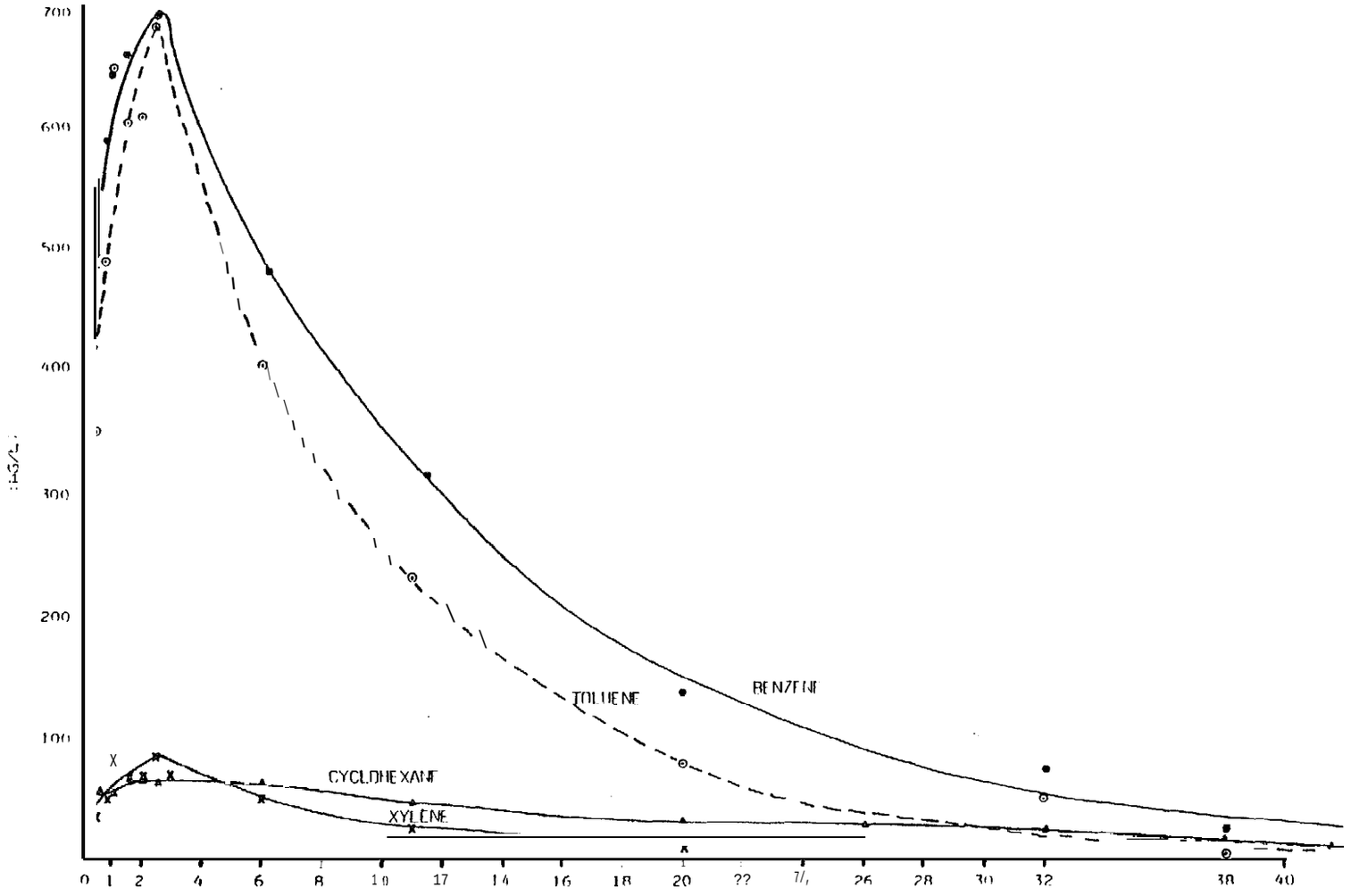



FIGURE 5-6. WATER COLUMN CONCENTRATIONS OF LOWER MOLECULAR WEIGHT AROMATIC COMPONENTS FROM PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND. (Evaporation/dissolution Exp-4; purge and trap analyses after Bellar & Lichtenberg, 1974).

Intermediate and higher molecular weight component-specific data can only be generated by more detailed time-series sampling, methylene chloride extraction and fractionation of oil and water phases followed by capillary gas chromatographic analyses. Figure 5-7 presents the time-series FID capillary column gas chromatograms obtained on the aliphatic fractions of the oil samples from one such evaporation run (E/D-4) undertaken at 19°C under the influence of 7 knotwinds. Sampling times for the chromatograms shown in Figure 5-7 are as follows: A, 0 hours; B, 2 hours; C, 1 day; D, 3 days; E, 7 days; F, 12 days; G, 24 days; and H, 41 days. Quite clearly, general evaporative trends can be observed from the chromatograms, Figure 5-7, and rapid loss of compounds below Kovat index 1000 are observed after as little as 2 hours. The time series concentration profiles for the intermediate and higher molecular weight compounds are somewhat more subtle with only limited additional losses occurring and Tables 5-4 and 5-5 present time series concentrations of selected aromatic hydrocarbons in the oil and sub-surface water column, respectively.

Examination of the myriad of peaks in the time series chromatograms and the data in Tables 5-4 and 5-5 clearly shows the efficacy of developing a sound data management system for handling the extensive array of compound-specific data in the oil and water phases during the weathering process. Specifically, for each sample phase (oil, water and air) at each sampling time, literally hundreds of component-specific concentrations are generated. While such data can be worked up manually and plotted as shown in Figures 5-8 through 5-13, comparisons of oil weathering behavior as a function of temperature (or the presence or absence of dispersants, etc.) can best be accomplished through computer manipulation of data. Further, comparison of predicted vs. observed compound-specific (or even pseudo-component or distillation unit) data for oil weathering behavior can only be handled with an advanced data system such as the one being utilized in this program. During development of this GC data base system, however, it was necessary to manually reduce and plot some of the initial individual compound time dependent concentrations as shown in Figures 5-8 through 5-13. Figures 5-14 and 5-15 present

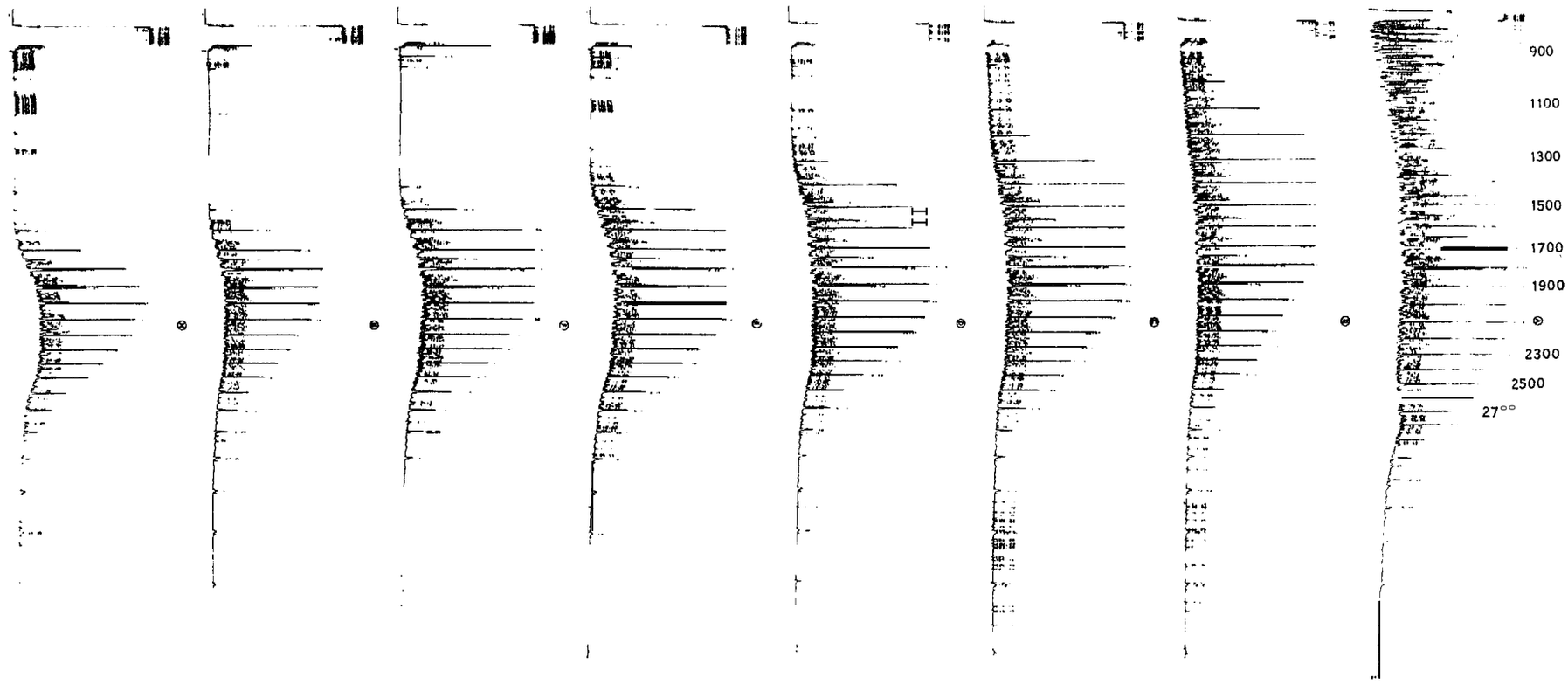



FIGURE 5-7. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND (E/D-4). SAMPLING TIMES: (A) ZERO HOURS; (B) 2 HOURS; (C) 1 DAY; (D) 3 DAYS; (E) 7 DAYS; F) 12 DAYS; (G) 24 DAYS; AND (H) 41 DAYS.

TABLE 5-4. TIME DEPENDENT AROMATIC COMPOUND CONCENTRATIONS IN OIL EXTRACTS FROM EVAPORATION/ DISSOLUTION WEATHERING AT 19°C UNDER A 7 KNOW WIND (Concentrations in μg/g).

| COMPOUND | RT (min) | Kovat | 0 hrs. | 1.5 hr | 3.0 | 6.0 | 8.75 | 12.0 | 24.0 | 35.75 | 48.0 | 72.5 | 140.75 | 168.25 | 192.25 | 270. | 288. | 337. | 384. | 460.25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethylbenzene | 7.77 | 857 | 26.9 | | 16.3 | 18.7 | | | | | | | | | | | | | | |
| 1,4 & 1,3 dimethylbenzene | 7.69 | 867 | 118. | 124. | 131. | 119.1 | 78.5 | 26.6 | 26.1 | | | | | | | | | | | |
| 1,2 dimethylbenzene | 8.59 | 899 | 114. | 94.1 | 102. | 69.6 | 63.3 | 21.4 | 12.2 | | | | | | | | | | | |
| Propylbenzene | 11.18 | 958 | 12.6 | 15.9 | 14.8 | 15.9 | | | | | | | | | | | | | | |
| 1 ethyl-2 methylbenzene | 11.81 | 959 | 138. | 105. | 103. | 71.6 | 50.8 | 13.8 | | | | | | | | | | | | |
| 1 methyl-ethylbenzene | 12.68 | 977 | 74.7 | 78.3 | 77.1 | 49.9 | 31.7 | | | | | | | | | | | | | |
| 1,2,4 trimethylbenzene | 13.40 | 998 | 263. | 370. | 303. | 200. | 176. | 60.3 | 18.1 | | | | | | | | | | | |
| 1,2,3 trimethylbenzene | 14.86 | 1049 | 230 | 288 | 274. | 186. | 120. | 56.5 | | | | | | | | | | | | |
| 2,3 dihydro-1H indene | 15.49 | 1011 | | 21.6 | 19.7 | 12.7 | | | | | | | | | | | | | | |
| 2,3-dihydro-1-methyl-1H-indene | 18.21 | 1002 | 820 | 122. | 114. | 95.3 | 66.7 | 29.2 | | | | | | | | | | | | |
| 1,2,3,5 tetramethylbenzene | 21.65 | 1140 | 83.8 | 127. | 126. | 97.8 | 69.3 | 56.6 | 23.7 | | | | | | | | | | | |
| 1,2,3,4 tetrahydronapthalene | 22.09 | 1156 | 83.2 | 148. | 139. | 128. | 102. | 55.0 | | | | | | | | | | | | |
| Napthalene | 23.26 | 1179 | 299. | 523. | 513. | 424. | 304. | 227. | 79.3 | | 18.3 | 18.1 | | | | | | | | |
| 1 methylnapthalene | 29.57 | 1300 | 560. | 948. | 990. | 905. | 738. | 697. | 441. | 120 | 166 | 310. | 84.1 | 45.1 | 33.3 | 21.1 | | | | |
| 2 methylnapthalene | 28.77 | 1288 | 890. | 1500. | 1530. | 1430. | 1150. | 1050. | 661. | 161. | 513 | 419. | 88.8 | 35.4 | 29.4 | 16.8 | | | | |
| 1,1 biphenyl | 32.85 | 1375 | 182. | 248. | 260. | 244. | 122. | 125. | 163. | 131. | 80.9 | 25.8 | 12.0 | 22.1 | 15.8 | 16.6 | 8.82 | | | |
| 2 ethylnapthalene | 33.45 | 1387 | 124. | 223. | 234. | 220. | 196. | 182. | 130. | 24.0 | 148. | 144 | 80.1 | 52.9 | 50.7 | 38.1 | 25.1 | 22.8 | | |
| 1,5 dimethylnapthalene | 33.94 | 1398 | 510. | 828. | 859. | 812. | 736. | 708. | 613. | 248. | 557 | 576. | 384. | 284. | 287. | 185. | 124 | 124. | 79.7 | 59.4 |
| 2,3, dimethylnapthalene | 34.62 | 1413 | 208. | 221. | 227. | 205. | 167. | 195. | 160. | 140. | 147 | 127. | 77.1 | | 127 | 33.3 | 65.5 | 77.7 | 56.7 | 45.9 |
| 1,1 methylene bis-benzene | 37.64 | 1481 | 281. | 459. | 469. | 475. | 394. | 391. | 339. | 208. | 300 | 411. | 328. | 222 | 253 | 227. | 193 | 194. | 156 | 137. |
| Dibenzothiophene | 40.32 | 1544 | 246. | 316. | 334. | 310. | 276. | 285. | 318. | 267. | 239. | 156 | 123 | 297 | 112 | 314 | 157 | 127. | 356 | 449. |
| Phenanthrene | 49.38 | 1770 | 207. | 257. | 270. | 264. | 230. | 238. | 260. | 246 | 244 | 200 | 274. | 248 | 271. | 259 | 175 | 111 | 281. | 151. |
| 4 methyldibenzothiophene | 52.05 | 1845 | 176. | 248. | 249. | 250. | 223. | 221. | 253. | 222 | 244 | 223. | 264 | 233 | 252. | 241. | 114 | 136 | 259. | 160 |
| 2 methylphenanthrene | 53.58 | 1883 | 120. | 161. | 158. | 149. | 151. | 150. | 160. | 147. | 147 | 162 | 150. | 159. | 158 | 148. | 163. | 139 | 179. | 198 |
| 9 methlphenanthrene | 54.42 | 1918 | 188. | 212. | 215. | 213. | 178. | 197. | 216. | 195. | 200 | 207 | 199 | 201. | 172. | 18. | 141 | 253. | 224 | 222. |
| 2,3 dimethylphenanthrene | 58.16 | 2027 | 242. | 260. | 275. | 264. | 225. | 243. | 275. | 250. | 249. | 271. | 255. | 241. | 252. | 193. | 114. | 187 | 302. | 182. |

TABLE 5-5. TIME DEPENDENT AROMATIC COMPOUND CONCENTRATIONS IN WATER EXTRACTS BENEATH A SLICK UNDERGOING EVAPORATION/DISSOLUTION WEATHERING AT 19°C UNDER A 7 KNOT WIND. (Concentration in µg/l ).

| Compound | RT (fain) | Kovat | 0 hr | 1.5 | 3.0 | 6.0 | 9.75 | 12.0 | 24.0 | 35.75 | 48.0 | 72.5 | 148.75 | 16:1.75 | 194.25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethylbenzene | 3.?? | 857 | | 10.6 | ?1.0 | 22.7 | 17.6 | 17.5 | 3.54 | 5.32 | 4.51 | | 1.23 | | 2.80 |
| 1,4 1 1, 1-dimethylbenzene | 7.64 | 867 | | 55.2 | 73.7 | 98.7 | 44.5 | 64.4 | 18.6 | 29.? | 16.1 | | 9.15 | | 6.70 |
| I .7 dimethylbenzene | 8.59 | 893 | | 30.2 | 41.5 | 55.9 | 4?.3 | 40.1 | 120. | 17.4 | 8.42 | | 2.61 | | 1.87 |
| Propylbenzene | 11.38 | 951 | | 3.19 | 1247 | on. 6 | 170 | 61.0 | | 59.4 | 2.92 | | | | |
| 1-ethyl-2-methylbenzene | 11.81 | 959 | | 6.97 | 13.2 | 18.2 | 14.64 | 13.R | | 4.92 | 1.92 | | | | |
| 1-methylethylbenzene | 12.68 | 977 | | 3.89 | 1. 111 | 11. ? | 8.85 | 9.0! | ?.17 | 4.09 | 1.08 | | | | |
| 1,2,4 -trimethylbenzene | 13.40 | 991 | | 12.6 | 10.9 | 21.9 | 3.01 | 14 1 | 6.26 | 3.75 | 3.11 | | | | |
| 1,2, x- trimethylbenzene | 14.86 | 1019 | | 8.16 | 10.6 | 18.6 | 7.40 | 11.9 | 8.30 | 9.48 | | | | | |
| 7, 1-dihydro 1n. indane | 15.49 | 1011 | | | 1.51 | 2.17 | 2.01 | 1.18 | | 1.14 | 4.25 | | | | |
| 7,1-dihydro- 1-methyl-1H-indan | 18.21 | 1082 | | | 1.61 | 2.97 | 3.81 | 7.05 | 1 17 | ?.17 | | | | | |
| 1,2, 1,5 tetramethylbenzene | 21.65 | 1148 | | | | | | | | 1.1? | | | | | |
| 1 ,2, 1,4-tetrahydronapthalem | 22.09 | 1156 | | | | 2.51 | 1.87 | 7.00 | 1.80 | 2,95 | 1.47 | | | | |
| Napthalene | 23.26 | 1179 | | 14.4 | 11.2 | 35.5 | 6.77 | .17. n | 32.4 | 18.3 | 21.6 | | | | |
| 1-Methylnapthalene | 29.57 | 1304 | | 4.43 | 1.48 | 7.52 | | 7.12 | ?4.6 | 24.4 | 22.4 | 9.32 | 4 09 | 1.67 | |
| 2-Methylnapthalene | 28.77 | 1288 | | 5.98 | 1.81 | 9.36 | | 1.76 | 10.6 | 3?. ? | ?6.6 | 8.27 | 4.09 | 2.17 | 1.46 |
| 1,1-bi-phenyl | 32.85 | 1375 | | | | | | 1.98 | 4.06 | 5.59 | 3.90 | 2.05 | 1.31 | | |
| 2-ethylnapthalene | 33.45 | 1387 | | | | | | | | ?.17 | | | | | |
| 1,5-dimethylnapthalene | 33.94 | 1398 | | | | | | | 3.86 | 1.67 | | 7.34 | 2.76 | 1.51 | |
| 2 3-dimethylnapthalene | 34.62 | 1413 | | | | | | | 1.40 | | 1.19 | | 1.49 | | 1.47 |
| 1,1-methylene-bisbenzene | 37.64 | 1481 | | | | | | | | | 1.50 | | | | |
| 1,6,7-trimethylnapthalene | 39.52 | 1525 | | | | | | | | | | | | | |
| Dibenzothiophene | 48.32 | 1744 | | | | | | | | | | | | | |
| Phenanthrene | 49.34 | 1771 | | | | | | | | | | | | | |
| 4-methyldibenzothiophene | 52.05 | 1845 | | | | | | | | | | | | | |
| 2-methylphenanthrene | 53.50 | 1887 | | | | | | | | | | | | | |
| x-methylphenanthrene | 54.42 | 1911 | | | | | | | | | | | | | |
| 2,3-dimethylphenanthrene | 58.36 | 2027 | | | | | | | | | | | | | |

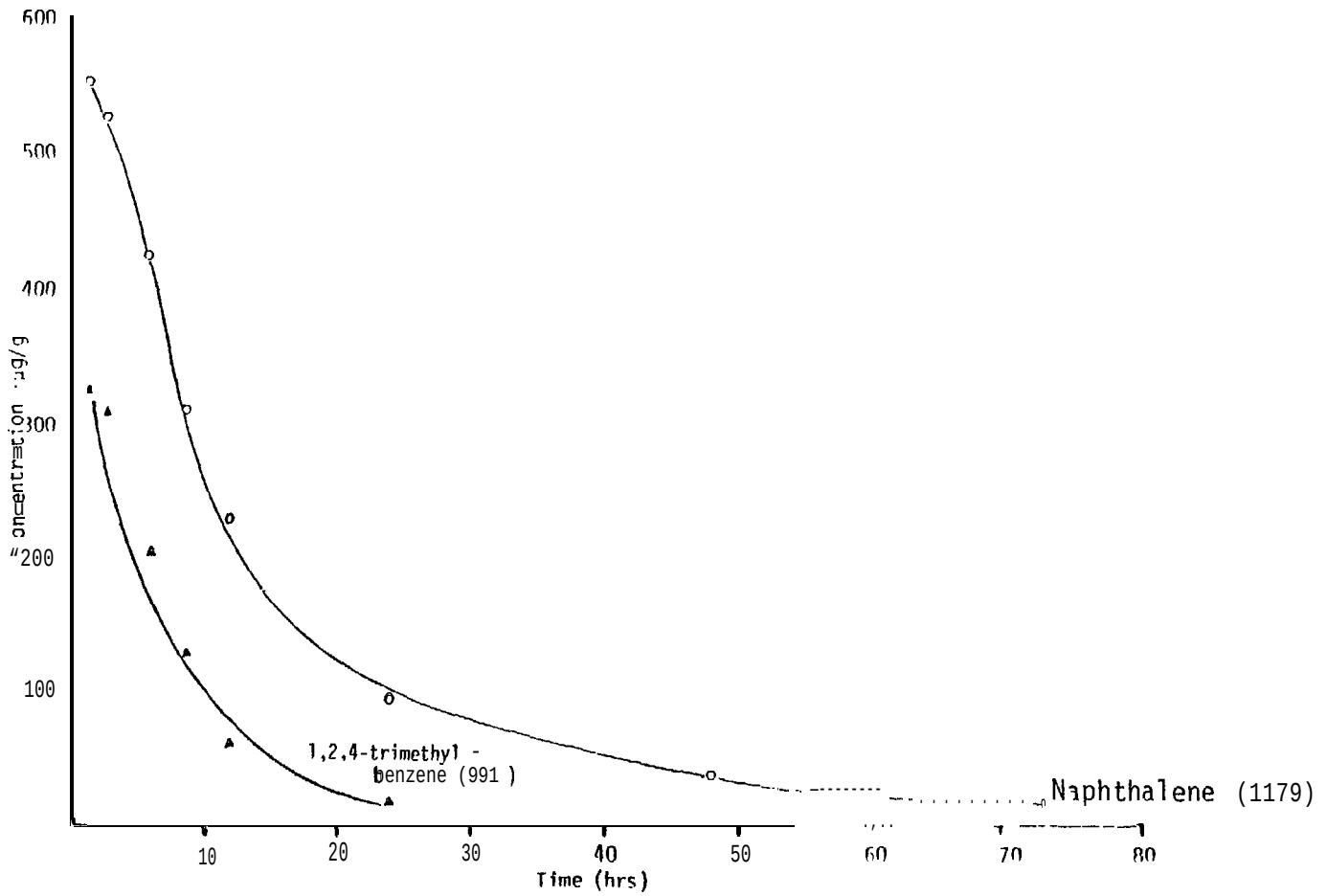



FIGURE 5-8. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

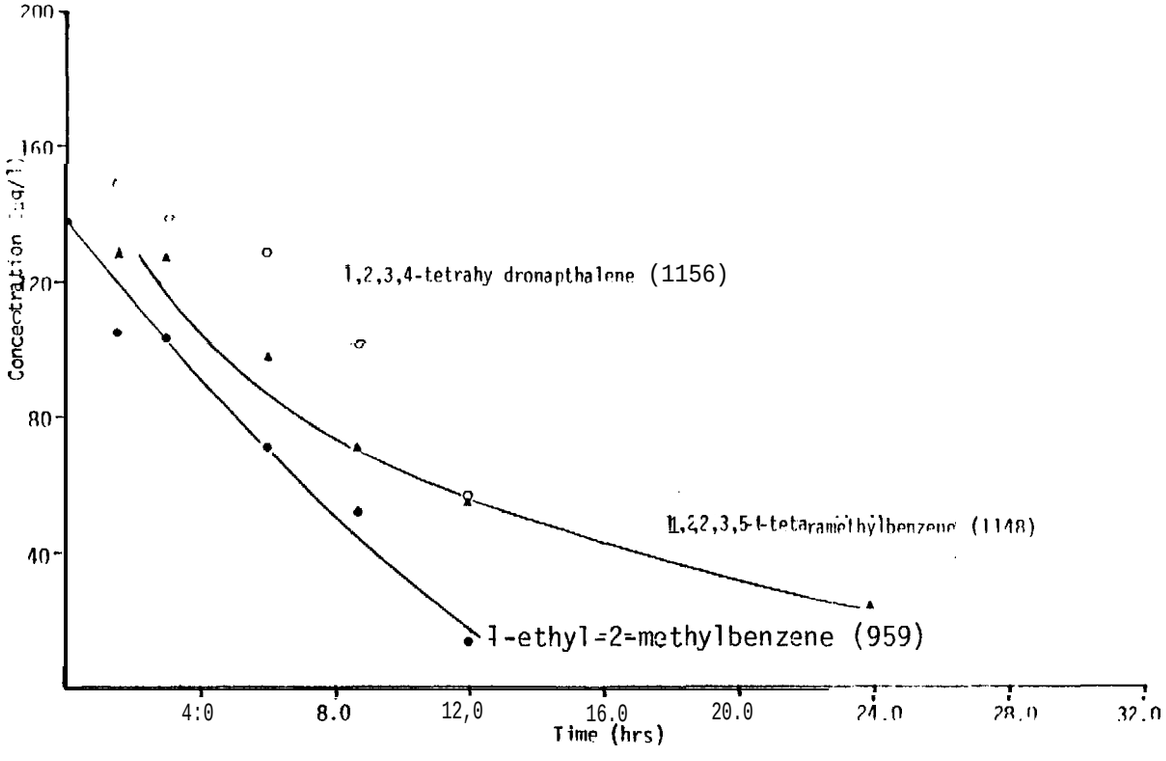



FIGURE 5-9. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

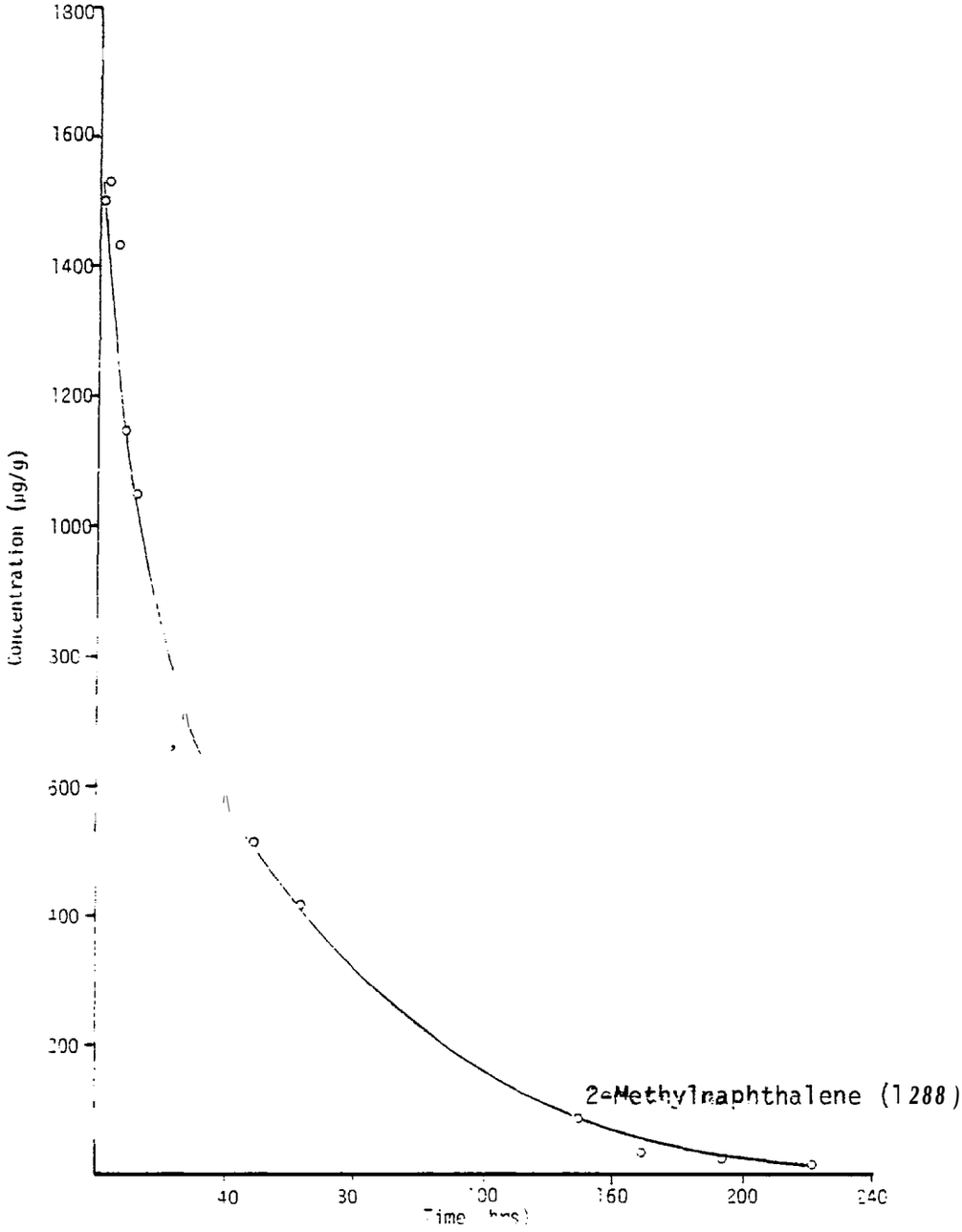



FIGURE 5-10. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

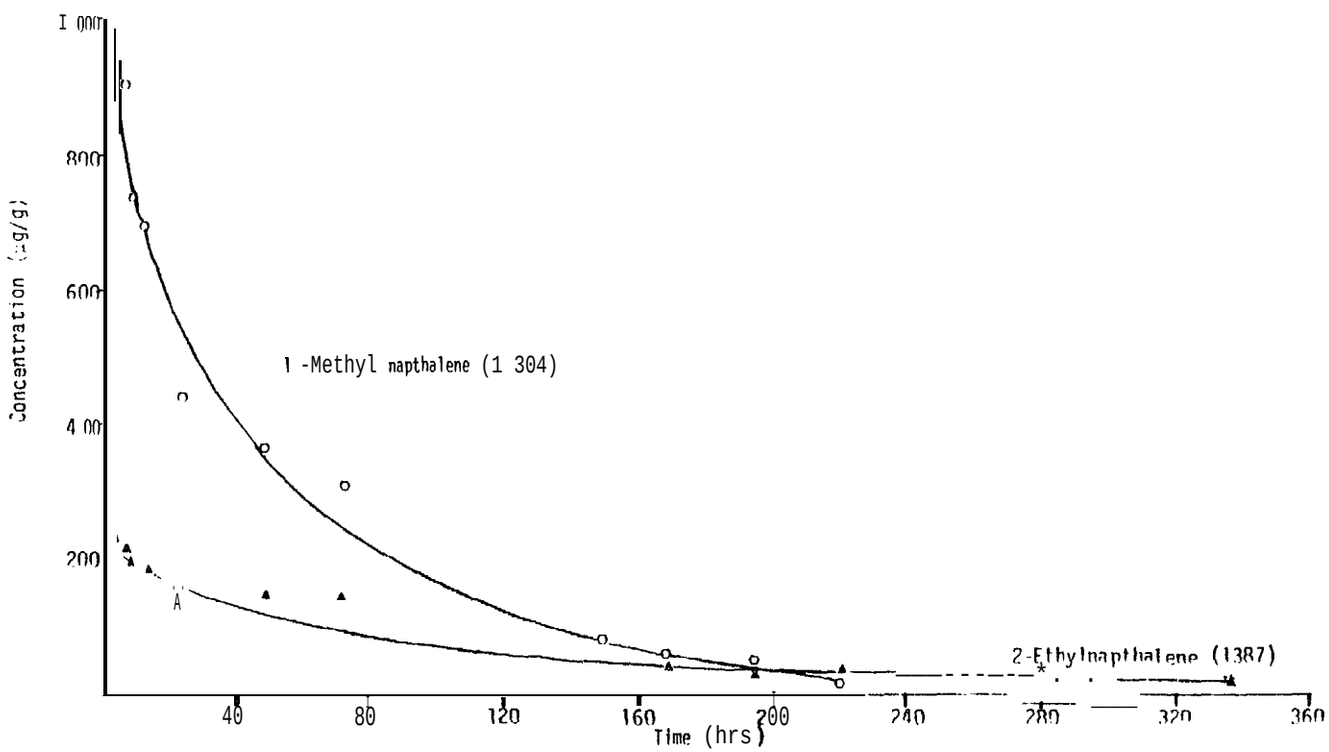



FIGURE 5-11. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

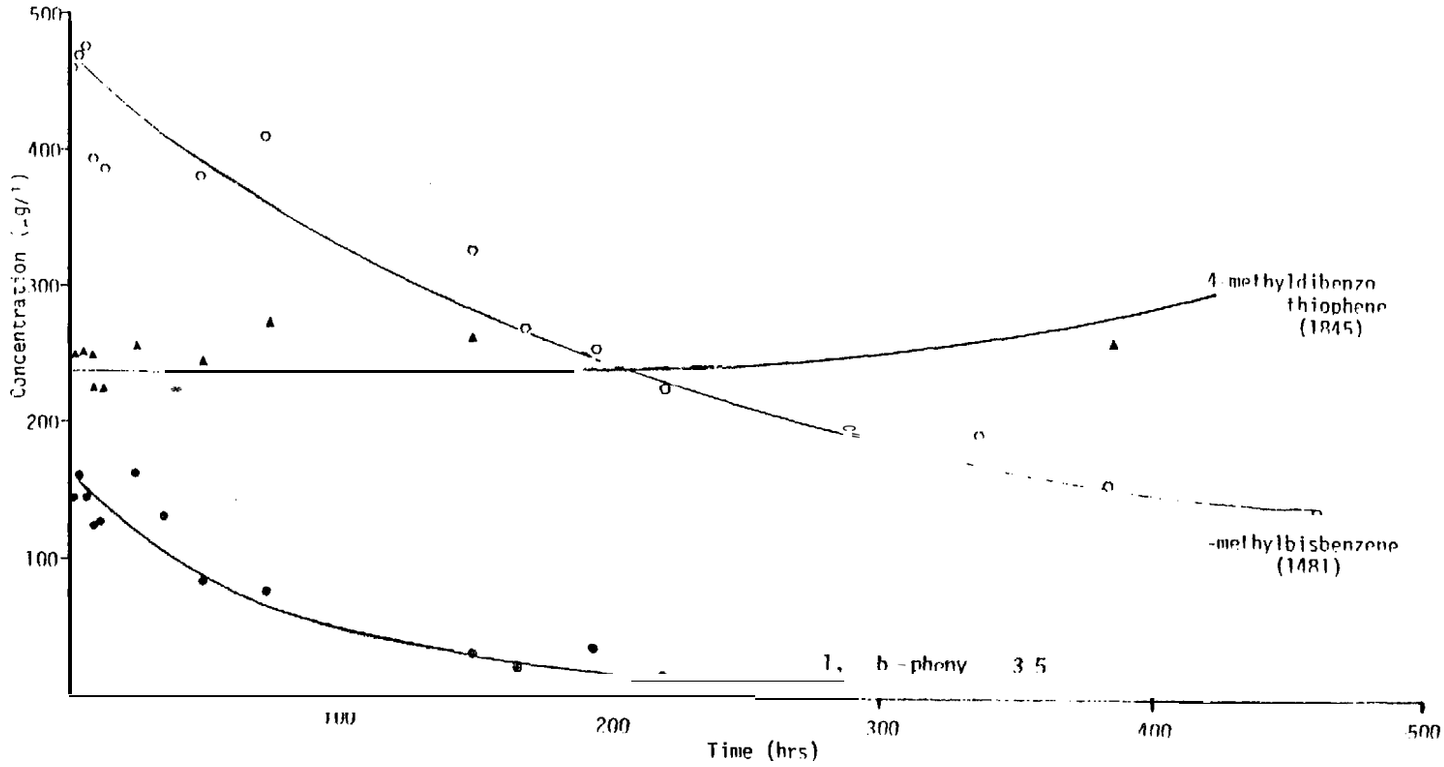



FIGURE 5-12. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

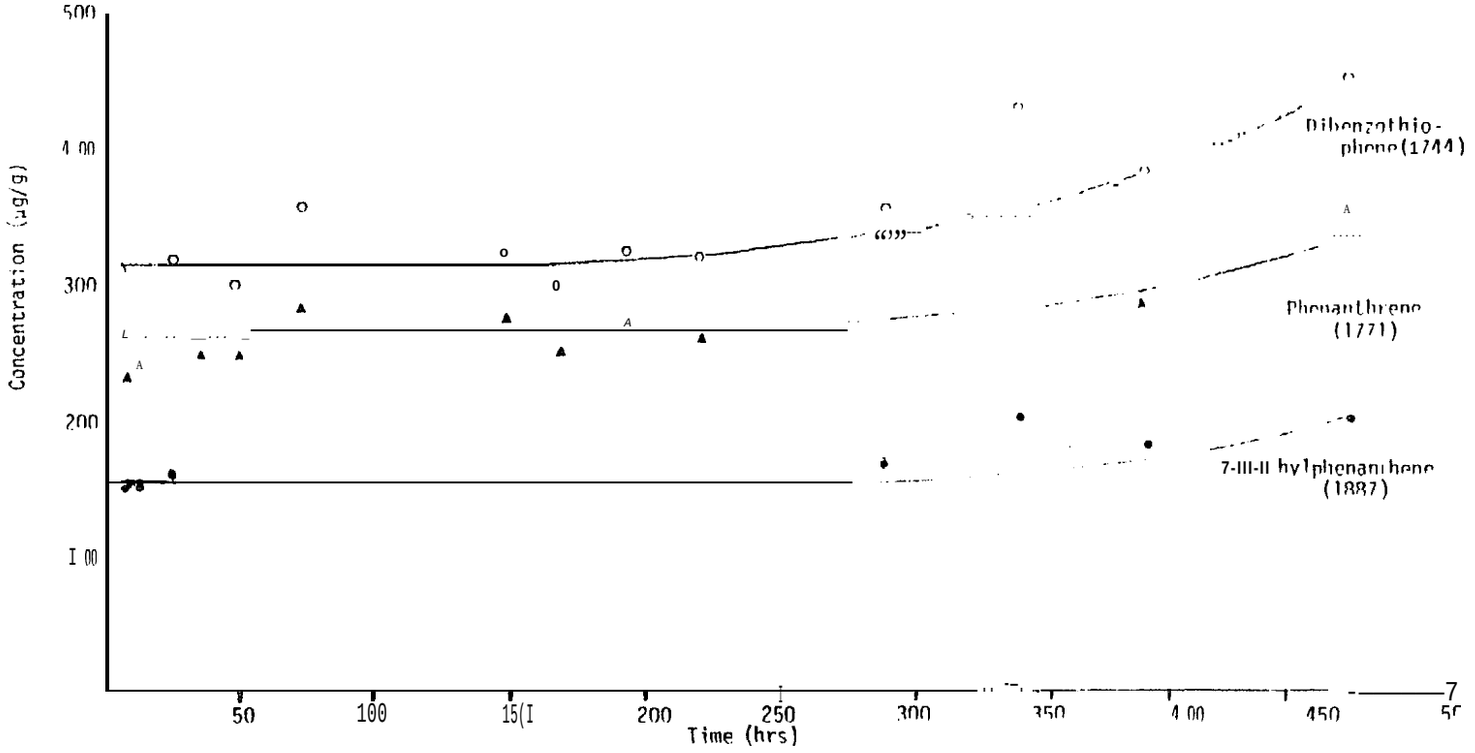



FIGURE 5-13. TIME-DEPENDENT CONCENTRATION IN OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

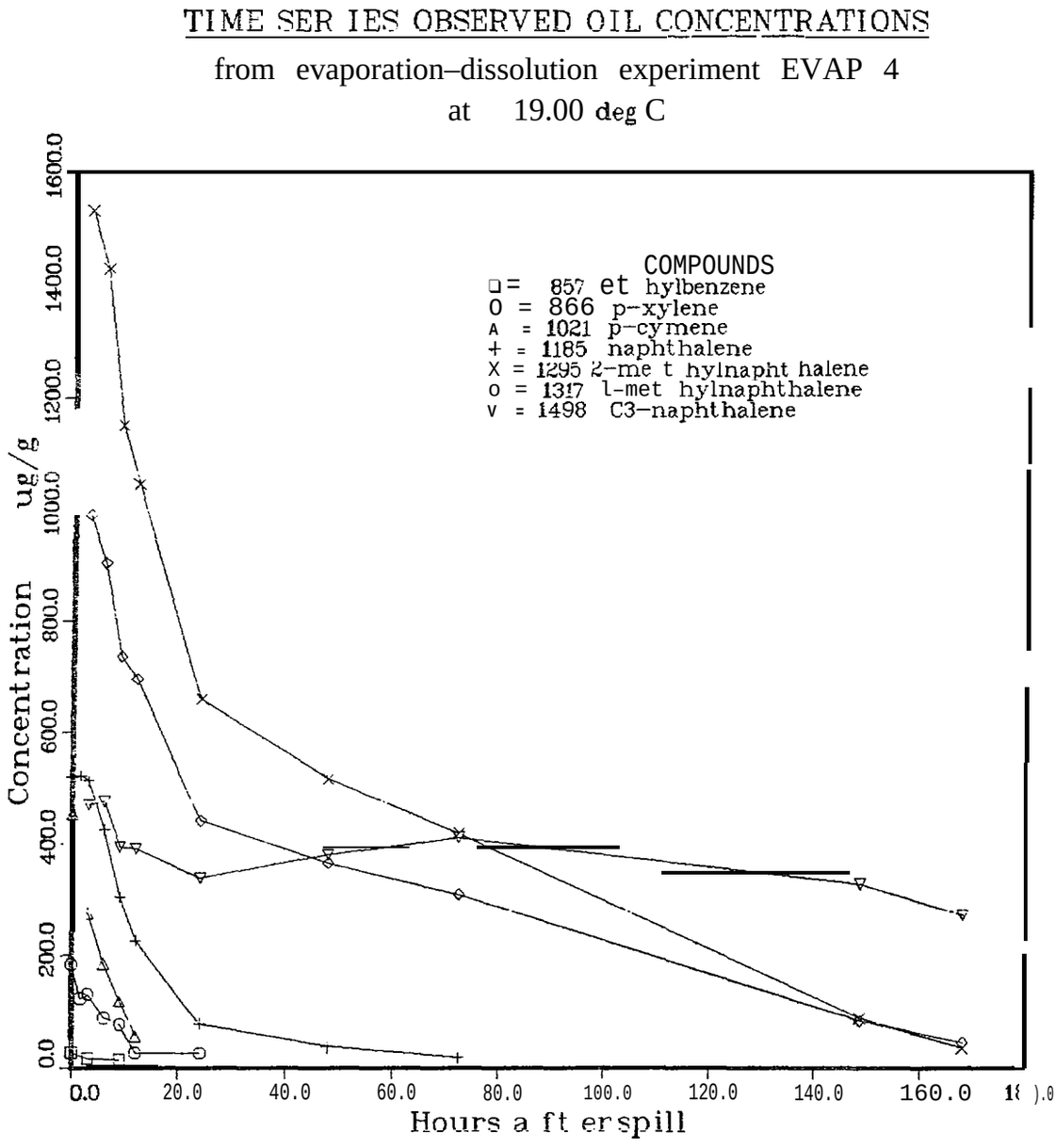



FIGURE 5-14. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN PRUDHOE BAY CRUDE OIL FEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT MIND. (E/ D-4 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

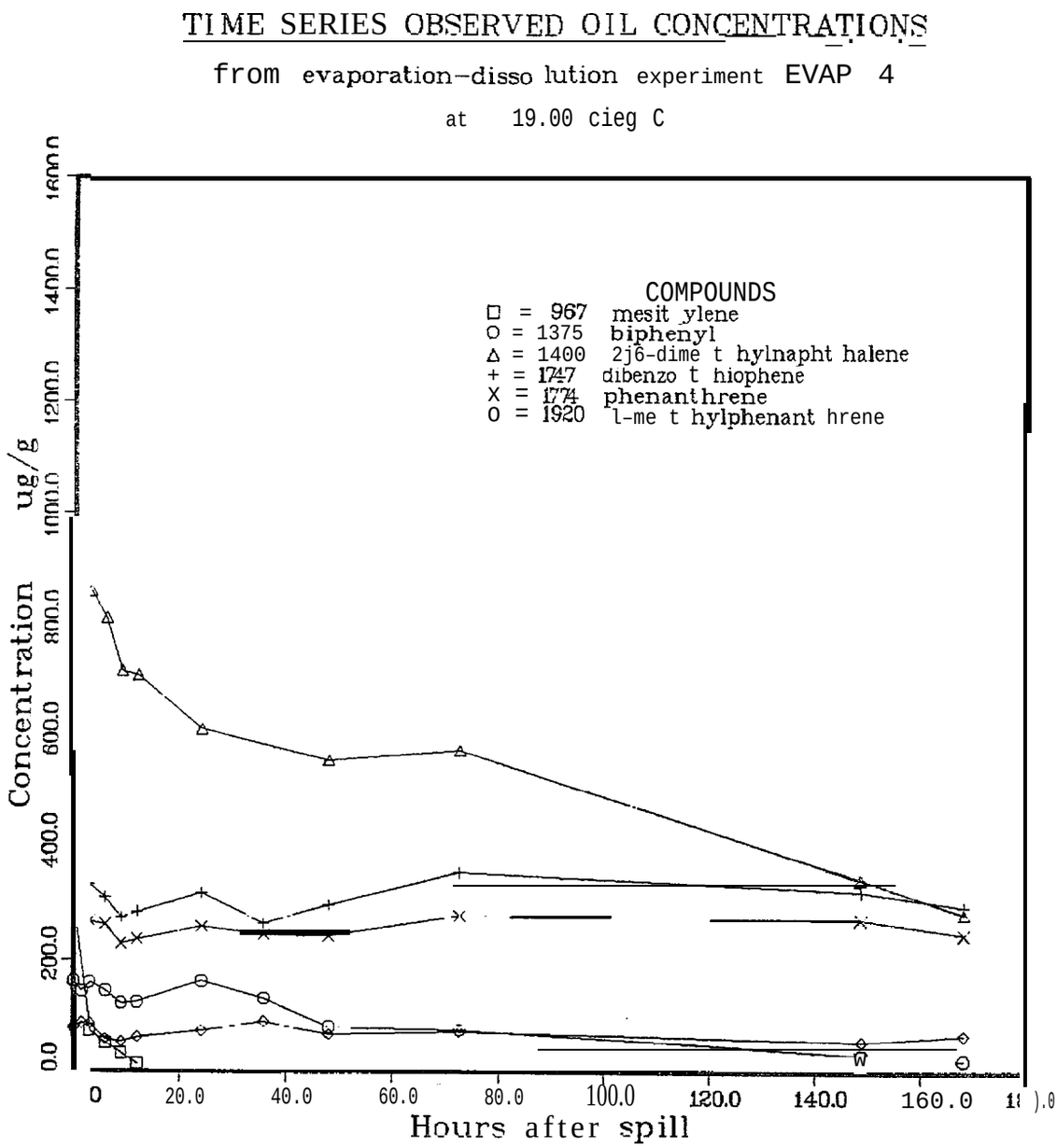



FIGURE 5-15. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC HIGHER MOLECULAR WEIGHT COMPONENT CONCENTRATIONS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND. (E/D-4 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

the more recently computer generated plots of the oil phase component concentrations from E/D-4.

The oil slick component concentration graphs (Figures 5-8 through 5-15 show the exponential decrease of the lower molecular weight components from the slick and the longer-term stability and residence of the higher molecular weight polynuclear aromatics, heterocyclic PNA's and their respective alkyl -substituted homologs.

The concentrations of lower molecular weight compounds such as ethylbenzene and 1,2-diethyl benzene were observed to decrease very rapidly in the first several hours, and after a period of 6 hours ethylbenzene (KOVAT 857) was no longer observed in the surface oil. Likewise, l-ethyl -2-methylbenzene (KOVAT 959) showed a very rapid decrease in concentration with no detectable material present after 12 hours (Figure 5-9). Evaporation and dissolution of 1,2,4-trimethyl benzene (KOVAT 991) were somewhat slower (Figure 5-8), but its exponential decay resulted in no detectable material after approximately 24 hours , and the concentration of its isomer, 1,2,3-trimethy lbenzene (KOVAT 1019) is seen to decrease rapidly in a 12-hour period. Tetramethylben zene (KOVAT 1148) was observed to decrease exponentially over the first 24 hours to the point where it was no longer observed (Figure 5-9). Tetrahydronaphthalene (KOVAT 1156) was also lost before 12 hours occurred and naphthalene decreased in an exponential fashion over a 74 hour period to where it was no longer detectable (Figures 5-8 and 5-q). The alkyl -substituted polynuclear aromatics showed longer residence times in the oil, with 2-methyl naphthalene (KOVAT 1288) and 1-methyl naphthalene (KOVAT 1304) present for 220 hours (Figures 5-10 and 5-11). They too showed an exponential decrease in concentration in the oil, and 1,1-biphenyl (KOVAT 1375) and 2-ethylnaphthalene (KOVAT 1387) showed similar effects as their concentrations dropped off exponentially to the point where they were no longer observed after 250 hours (Figures 5-11 and 5-12). The compounds with molecular weights above al kyl-substituted naphthalenes showed longer residence times in the oil, as this is illustrated in Figure 5-12 for 1,1-methylene his-benzene (KOVAT 1487) which was still present after

475 hours although its concentration had dropped by a factor of 4 in an exponential fashion during that period.

Dibenzothiophene, the major sulfur heterocyclic aromatic compound in Prudhoe Bay crude oil, did not show a significant decrease over a 500-hour period due to either evaporation or dissolution (Figure 5-13). In fact, the relative concentration of dibenzothiophene increased slightly in the weathered-oil-residue due to the loss of the lower molecular weight components. Phenanthrene (KOVAT 1771) also showed a slight increase in relative concentration as did the alkyl -substituted 4-methyl dibenzothiophene (KOVAT 1845) and 2-methyl phenanthrene (KOVAT 1887; Figure 5-13). Although these compounds do have limited water solubilities, as reported by CLARK and MACLEOD (1977), they are not readily dissolved from the oil into the water column and they are apparently not removedto any appreciable degreeby evaporation after the slick becomes diffusion controlled.

Water column concentrations of these same aromatic compounds are presented in Table 5-5 and Figures 5-16 through 5-21 show the manually plotted time-dependent concentration changes for several selected compounds. Figure 5-22 presents the computer generated plots of many of the same compounds for comparison. As was noted in detail in our November, 1980 Interim Quarterly Report, initial increases of concentrations of the lower molecular weight aromatics in the water column occur within the first 5 to 10 hours while higher molecular weight component concentrations peak at after a slightly longer period. Interestingly, after approximately 10 hours, exponential decreases in the water column concentrations occurred due to evaporative loss through air/sea exchange. While the methylene chloride extraction technique does not allow evaluation of benzene and toluene (due to hexane and benzene solvent interference during capillary chromatography), these concentrations can be determined by the purge and trap results as shown in Table 5-3 and Figure 5-6. It is possible with the methylene chloride extraction and subsequent fractionation procedure to quantify the water column and oil slick concentrations for other aromatics, ranging from ortho-, meta- and para-xylenes (l-2, 1-3, and

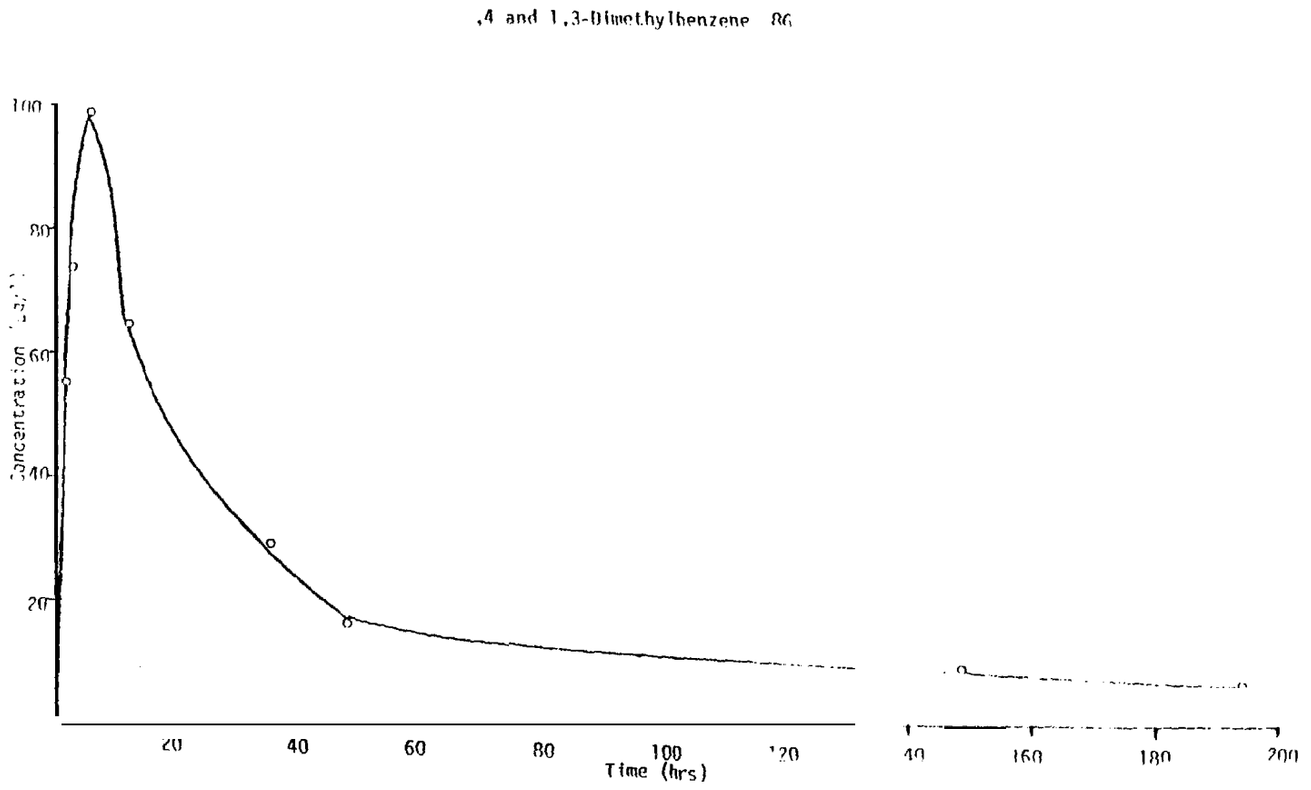



FIGURE 5-'6. TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

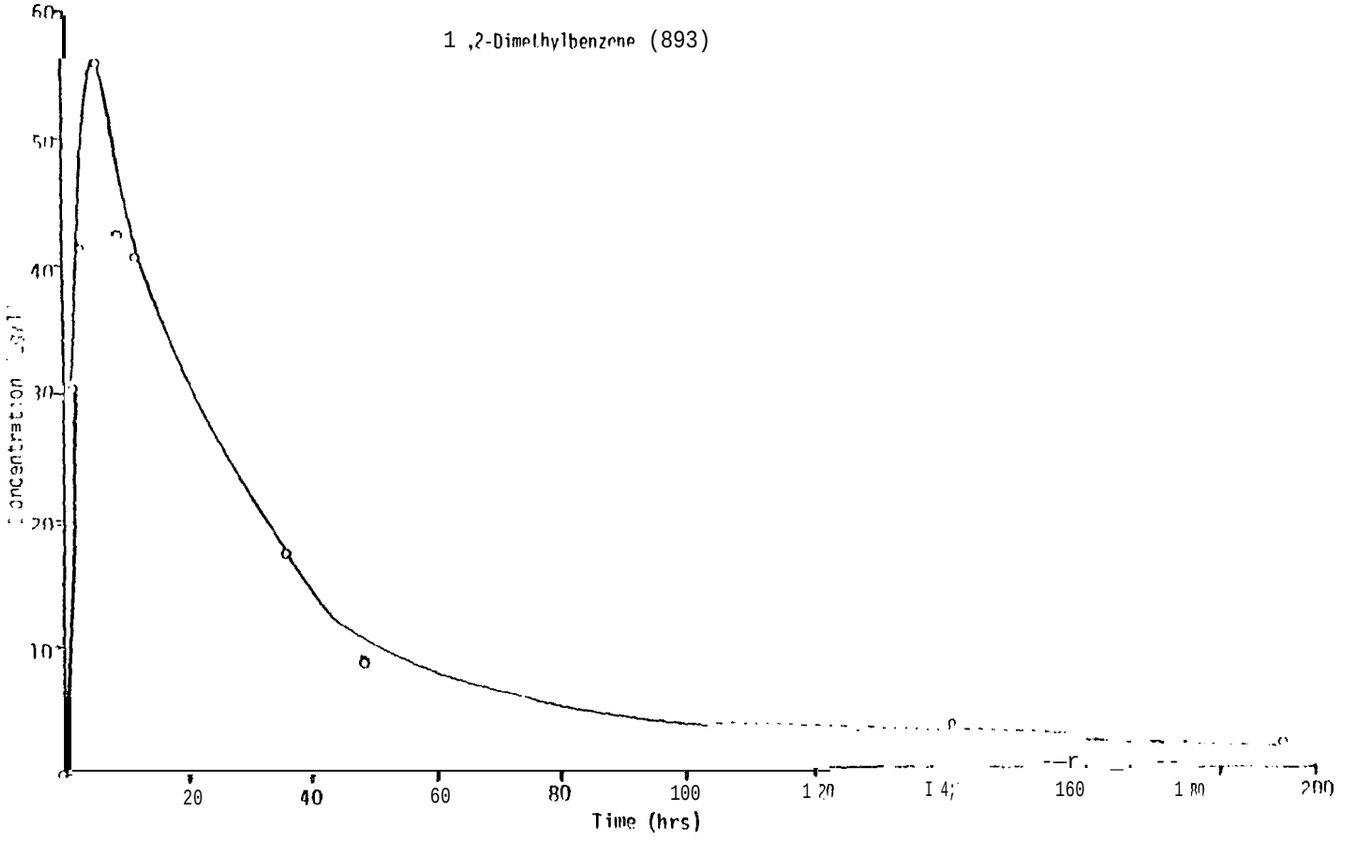



FIGURE 5-17. TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

Ethylbenzene (857)

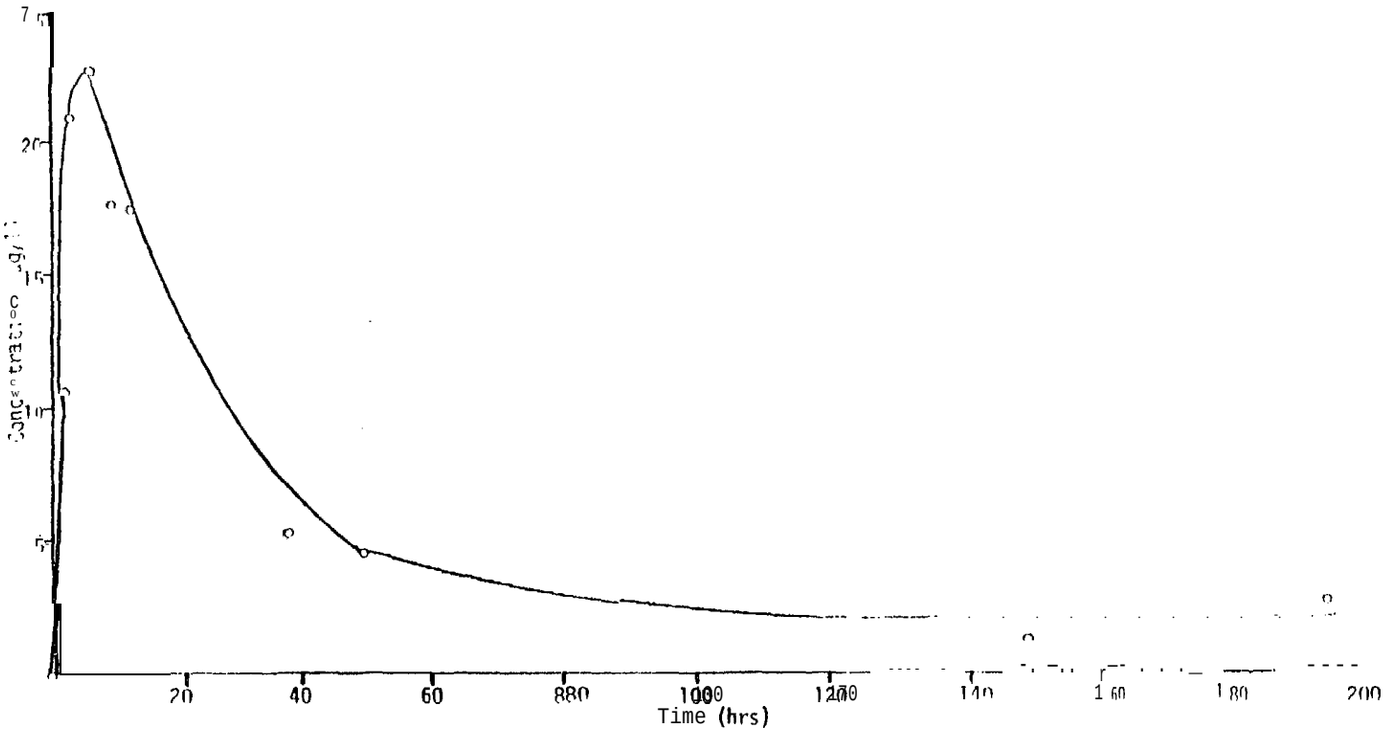



FIGURE 5-18. TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

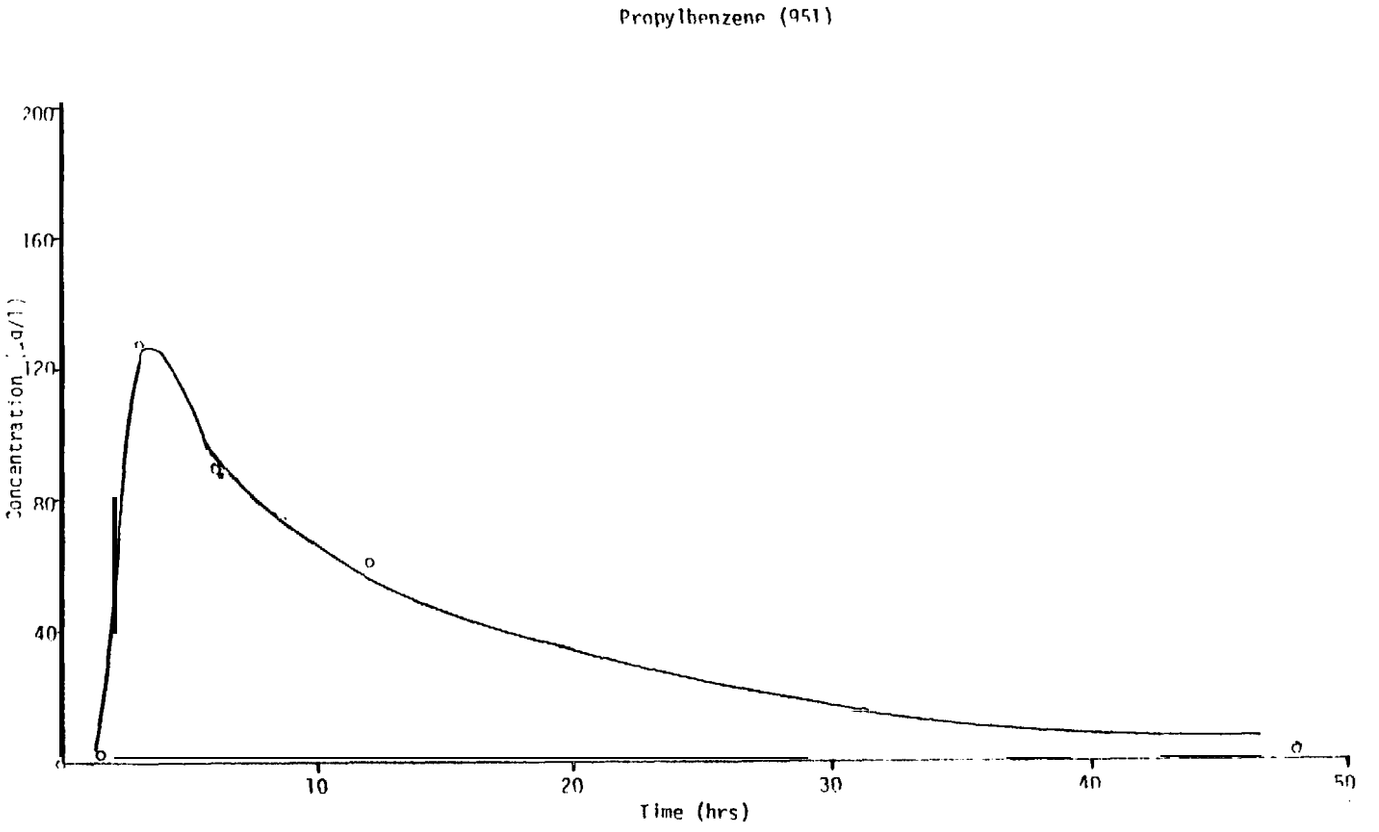
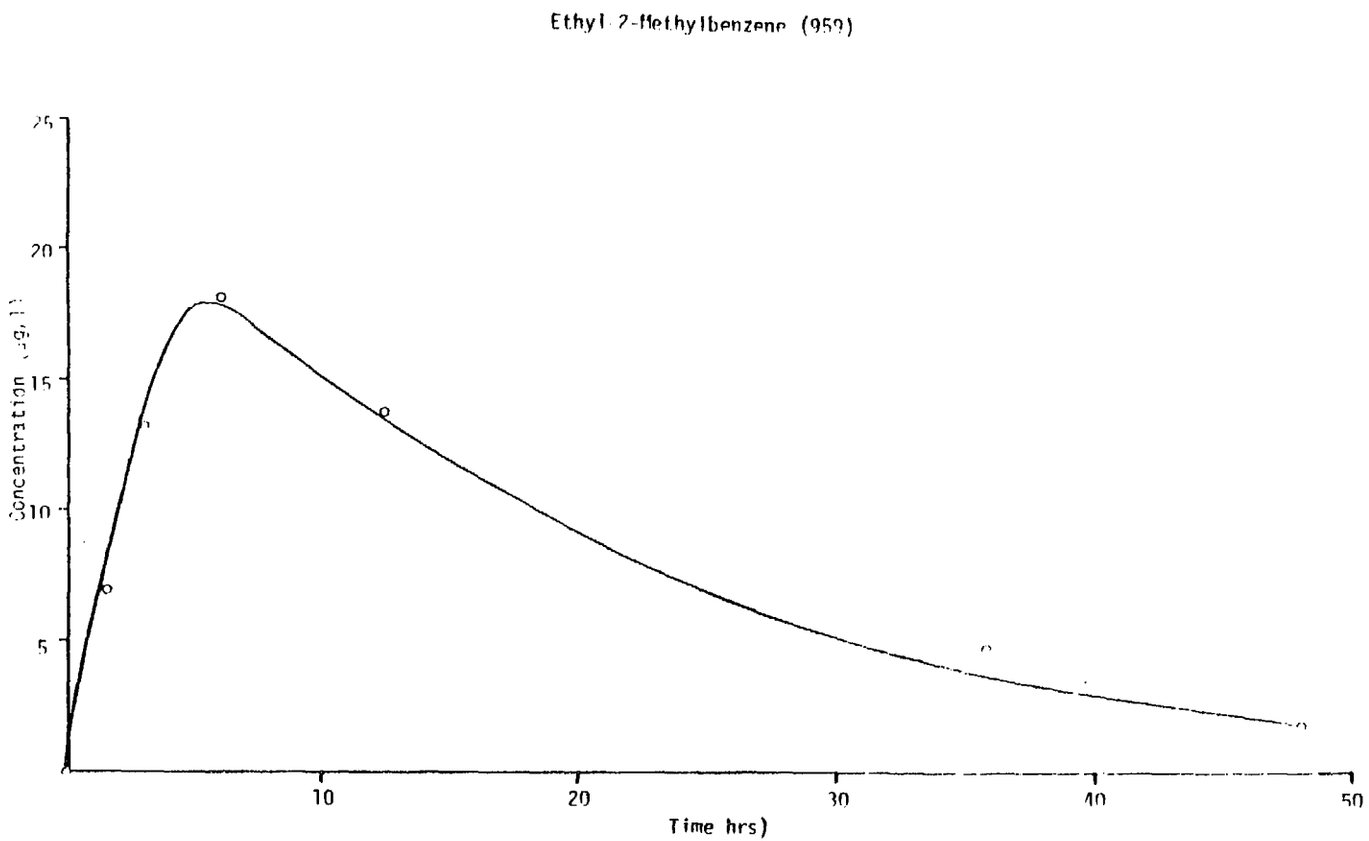



FIGURE 5-19. TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.




F GURE 5-20: TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

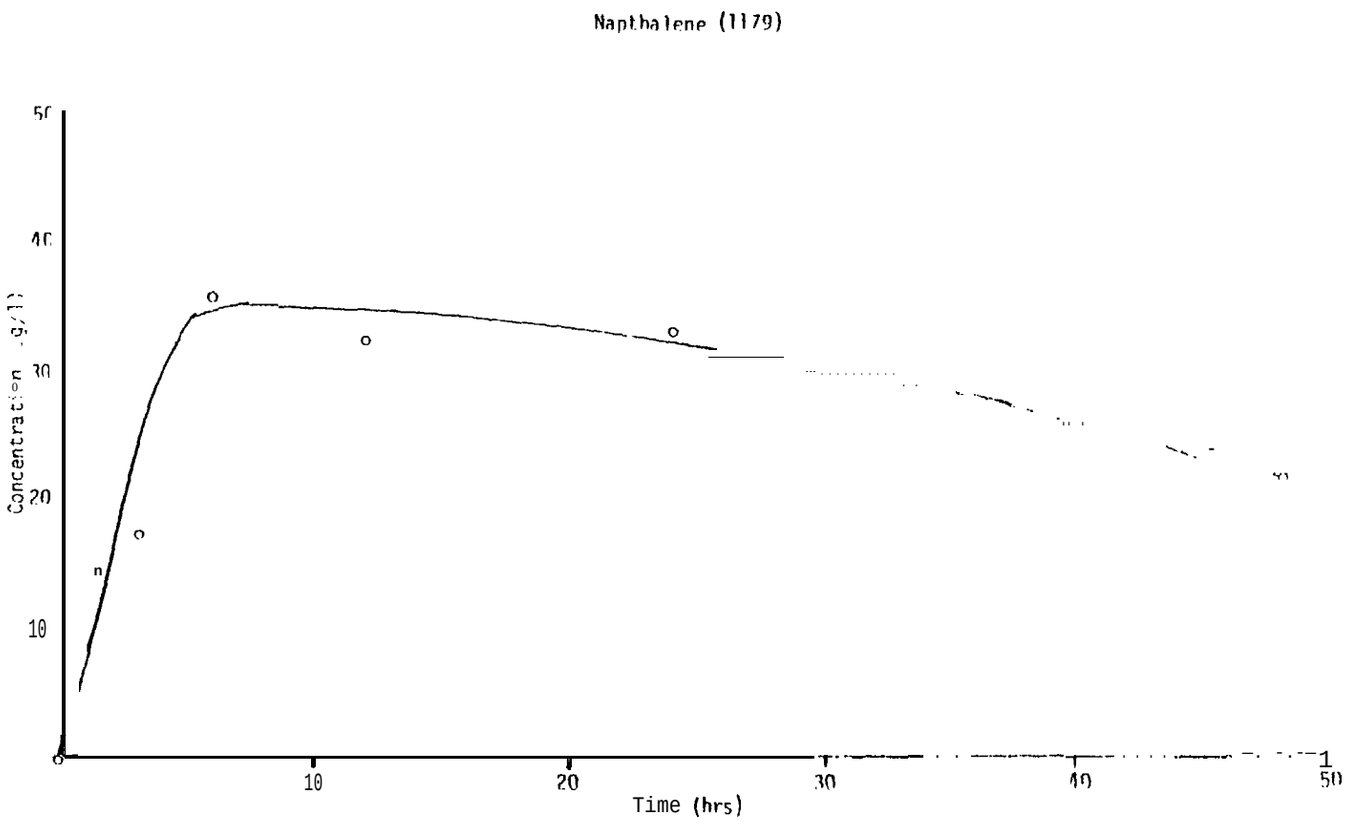



FIGURE 5-21. TIME-DEPENDENT CONCENTRATION IN THE WATER COLUMN WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND.

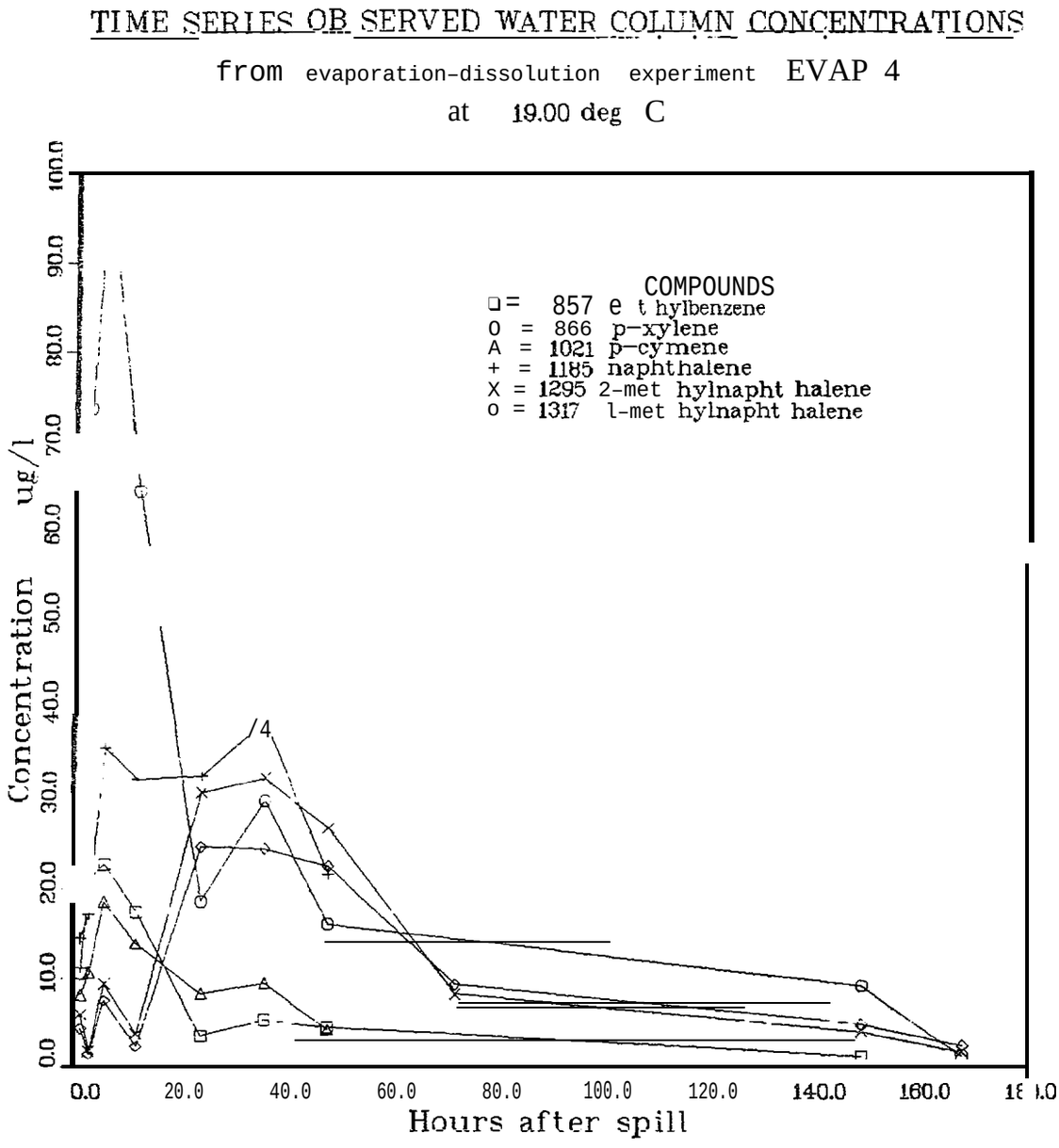



FIGURE 5-22. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN THE WATER BENEATH A PRUDHOE BAY CRUDE OIL SLICK WEATHERING AT 19°C UNDER INFLUENCE OF A 7 KNOT WIND. (E/D-4 DATA FROM EXP DATA BASE OF OIL FEATHERING YODEL).

1-4-dimethyl benzenes) through al kyl-substituted phenanthrenes. Figure 5-16 shows the time-dependent changes and concentrations of meta- and para-xylene with time. The initial buildup to 100 pm/1 in the first 5 hours was very similar to that observed when the purge and trap technique was used for similar measurements as reported in Figure 5-6. Validation of the comparability of the measurement techniques is provided by the similar values and trends obtained by these two significantly different methods (purge and trap FID GC Vs methylene chloride extraction, fractionation and FID chromatography). Likewise, concentration buildup and declines for ortho-xylene and ethyl benzene were similar when measured by both techniques. Figure 5-17 shows the time-dependent concentration changes in the water column for ortho-xylene, and these data also clearly parallel those observed for the other two isomers. Similar profiles are obtained for ethylbenzene, propylbenzene and 1-ethyl-2-methylbenzene in the subsequent Figures (5-18 through 5-20). Polynuclear aromatics starting with naphthalene show somewhat later concentration maxima and longer retention in the water column as shown by the data in Figures 5-21 and 5-22.

Each of the maximum concentrations reached during the initial stages of dissolution reflect the mole fraction of the component in the oil and the relative activity coefficients of the compound in the oil and the water. In almost all instances, however, the concentrations in the water column in the evaporation/dissolution chamber do not reach the higher values obtained during the closed system (separatory funnel) oil/seawater partition coefficient determinations described in the next section. This presumably reflects the rapid loss from the oil of the specific components due to evaporative processes and the concomitant decrease in overall mole fraction of these lower molecular weight materials in the oil. Finally, as these materials are ultimately removed from the oil slick reservoir itself, the water column concentrations undergo a decrease beneath the slick. In the case of the higher molecular weight. naphthalenes and alkyl -substituted naphthalenes, this decrease does not occur until 10 to 20 hours after the spill incident (20 hours for 1-methylnaphthalene, 35 hours for 2-methyl naphthalene, 35 hours for biphenyl). This is

presumably due to the longer residence time of these higher molecular weight materials in the oil causing their longer residence time in the water column beneath the slick.

During the initial evaporation/dissolution experiment using Prudhoe Bay crude oil, the oil was added from a height of 6-8" above the water and significant plunging of oil droplets into the water column was noted. While such droplet formation no doubt occurs in a real-spill event, such behavior significantly complicates development, of algorithms for evaporation and dissolution because of the greatly enhanced surface area of the oil droplets exposed to the water column. Development of dissolution algorithms to account for this droplet formation is much more complicated and is still underdoing evaluation at this time. Therefore, in subsequent evaporation/dissolution experiments, the oil was added via a horizontally placed transfer tube located 0.5 cm above the water surface. In this manner, the oil was observed to spread as a smooth slick over the water and significant 1 to 10-mm oil droplet dispersion was prevented. In that the algorithms for dissolution require input parameters such as the surface area of the oil slick exposed to the water, it was believed that this approach would provide much better experimental data to compare against computer predicted output for evaporation and dissolution weathering in the stirred tank experiments. Further, during the initial evaporation/ dissolution experiments using a 7 knot wind, 5 to 10-cm holes were "blown" in the surface slick. While such breakup of surface slicks in ocean systems is also known to occur, this behavior in the evaporation/ dissolution chamber complicates modeling of the observed results and generation of agorithms. For this reason, in subsequent evaporation/dissolution experiments, the wind speed was dropped to 1 knot such that buildup of volatile components would not occur in the air above the slick but that holes were not blown into the slick at the same time.

To evaluate these changes in the experimental procedure, a second 19°C evaporation/dissolution experiment was undertaken and Figures 5-23 and 5-24 present the computer plotted time-series observed oil concentrations from

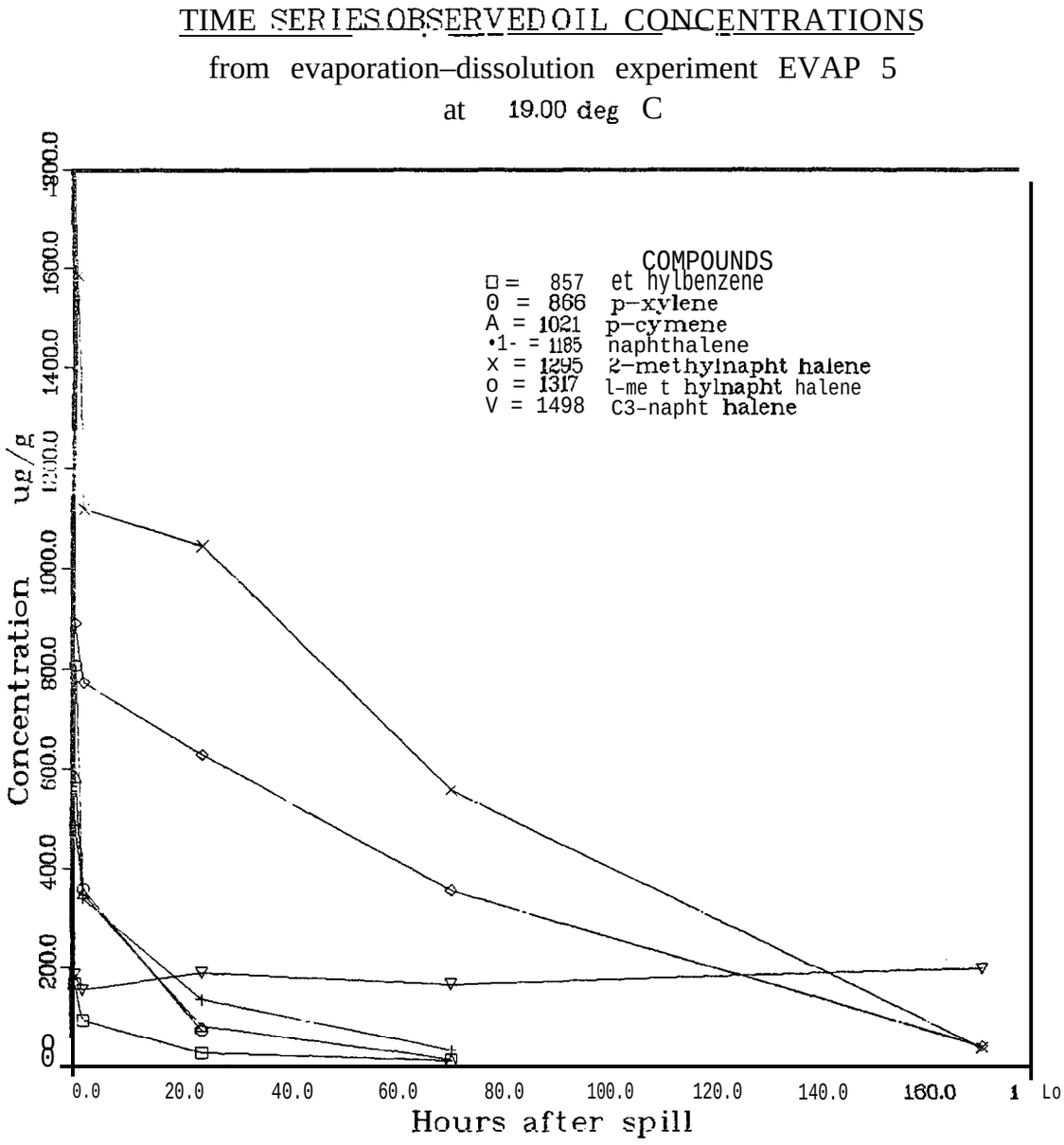



FIGURE 5-23. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 19°C UNDER INFLUENCE OF A 1 KNOT WIND. (E/D-5 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

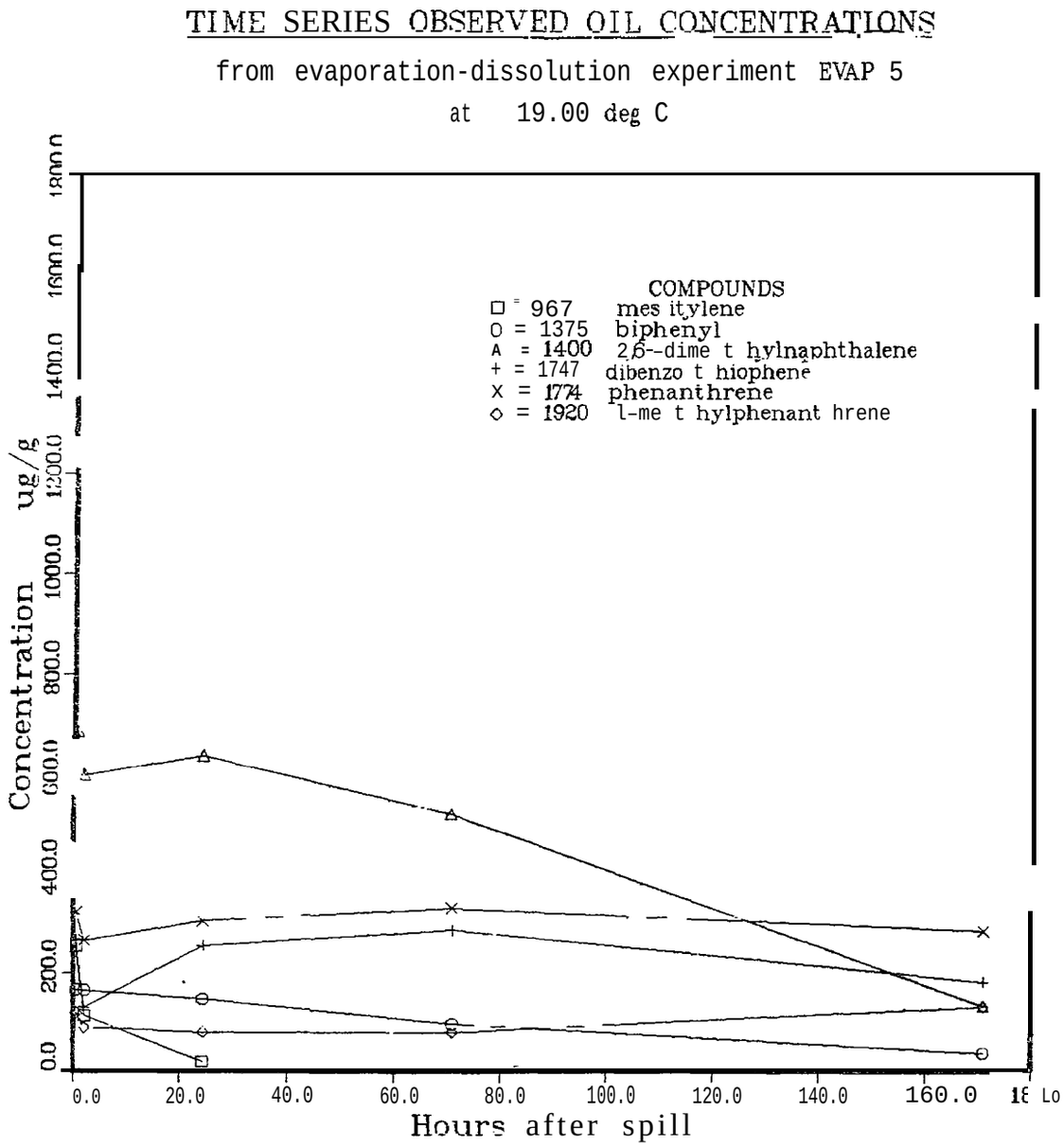



FIGURE 5-24. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN THE WATER BENEATH A PRUDHOE BAY OIL SLICK WEATHERINGAT 19°C UNDER INFLUENCE OF A 1 KNOT WIND. (E/D-5 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

that experiment. Quite clearly. the reduction in wind speed affects the rate of loss of the lower molecular weight components as can be seen by comparing Figures 5-23 and 5-14. Longer residence times of compounds from ethyl benzene through naphthalene are observed in the slick under these conditions. The residence time of higher molecular weight components such as mesitylene (Kovat 967) through 1-methyl phenanthrene are not drastically affected. That is, their residence time in the slick is significant over the 180 hours of experiment as would be anticipated. Reduction of the formation of oil in water dispersed droplets also significantly affects the amounts of hydrocarbons dissolved in the water column, as would be expected from the significantly decreased oil/water interracial surface area. Figure 5-25 presents the computer generated plot of the water column concentrations from evaporation/dissolution exp 5 where the oil was added to the evaporation/dissolution chamber with the horizontally positioned addition tube. Comparison of the data in Figure 5-22 with 5-25 shows that a factor of 2 to 3 decrease is observed in the water column concentrations as a result of this more gentle oil-addition procedure. As noted above, these modifications to the experimental procedure were necessitated by the requirement to maintain as carefully a controlled oil/water surface area as possible for verification of algorithms derived to predict dissolution phenomena. Results of observed vs predicted water column concentrations are presented in Section 5.1.5.

Rate constants are being determined at this time for the specific hydrocarbon compound concentration decreases from the slick. As these data become available, they will be compared to computer modeled output for verification of predicted behavior versus observed laboratory results as illustrated in Section 5.1.5.

Figures 5-26 and 5-27 present the gas chromatograms on the aliphatic and aromatic fractions of time series oil samples collected from an evaporation/dissolution experiment conducted under a 1-2 knot wind at 3°C (E/t-l-6). In this instance, time series samples were collected 30 minutes after the spill and at times 2 hours, 1 day, 3 days, 6 days, 12 days and 21

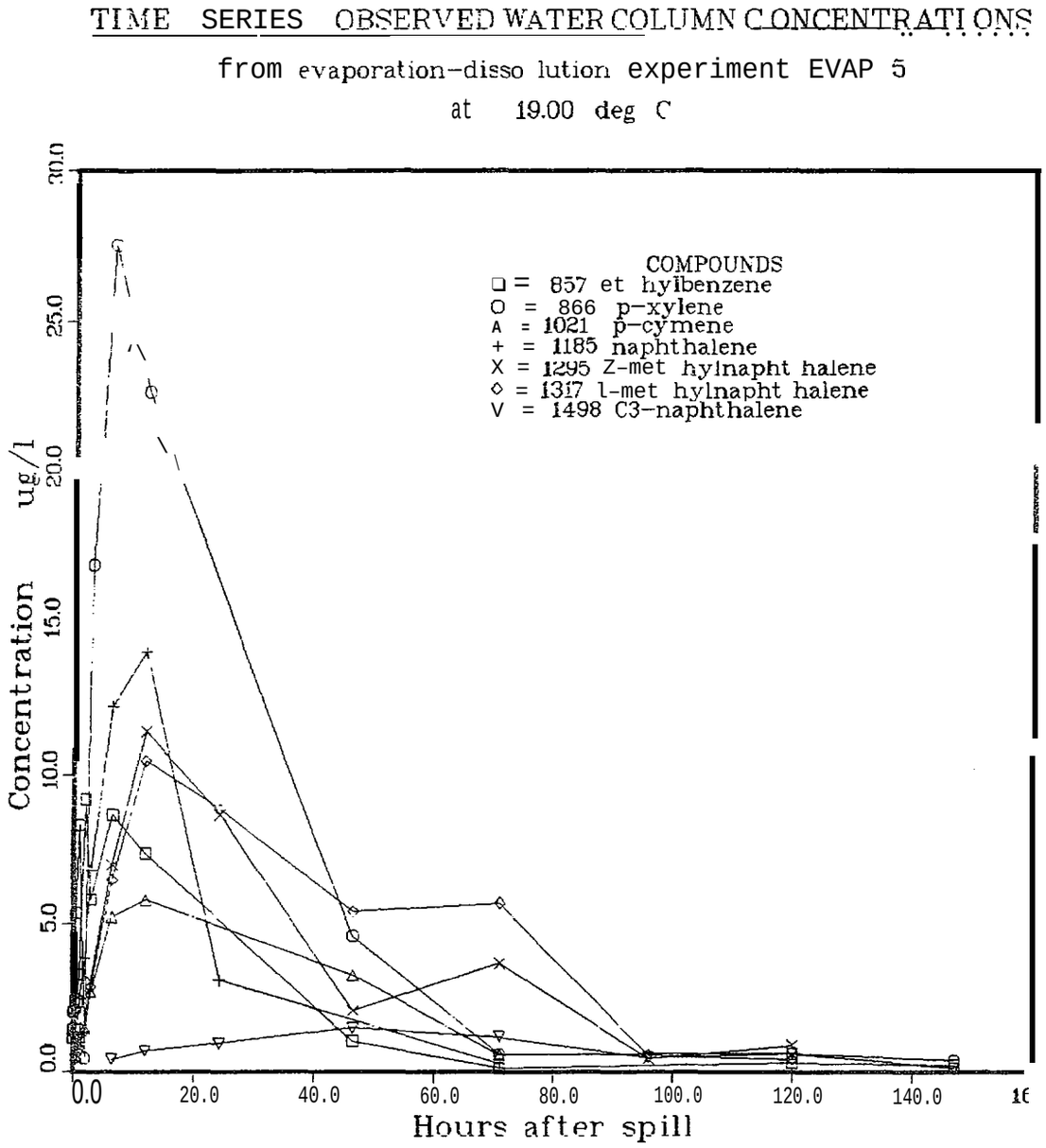



FIGURE 5-25. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN THE WATER BENEATH A PRUDHOE BAY CRUDE OIL SLICK WEATHERING AT 19°C UNDER INFLUENCE OF A 1 KNOT WIND. (E/D-5 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

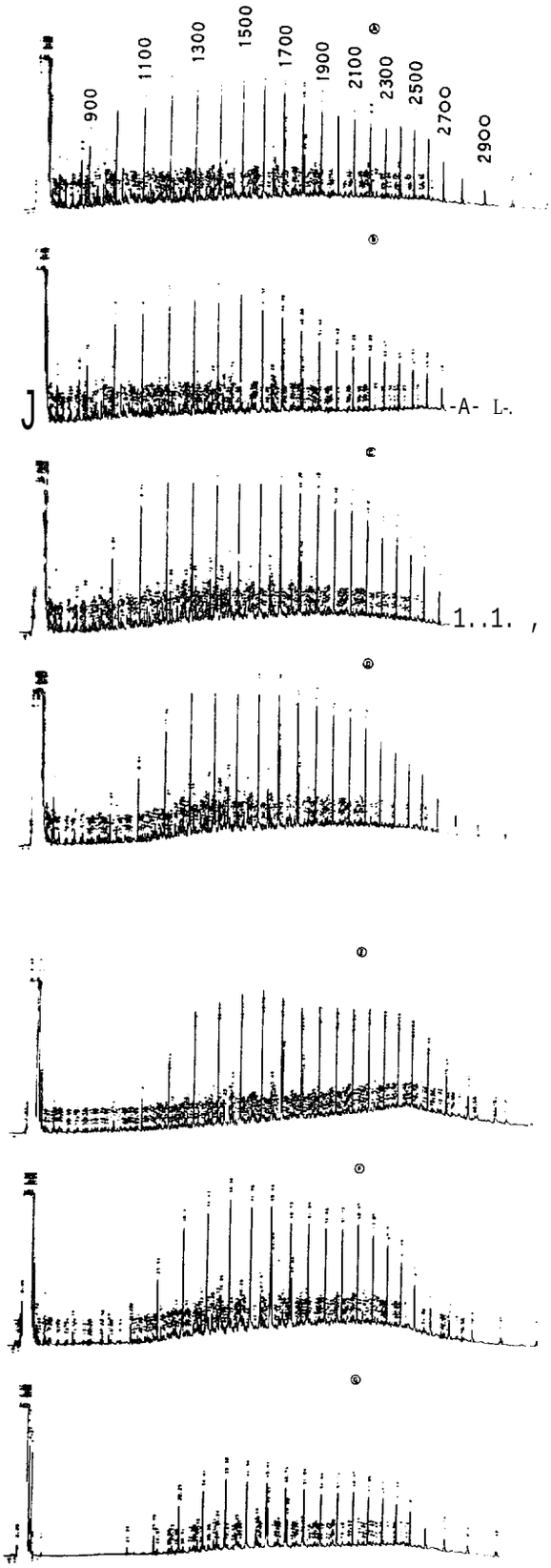



FIGURE 5-26. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF ALIPHATIC COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 3°C UNDER INFLUENCE OF A 1 KNOT HIND (E/D-6). TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 30 MINUTES; (B) 2 DAYS; (C) 1 DAY; (D) 3 DAYS; (E) 6 DAYS; (F) 12 DAYS; AND (G) 21 DAYS.

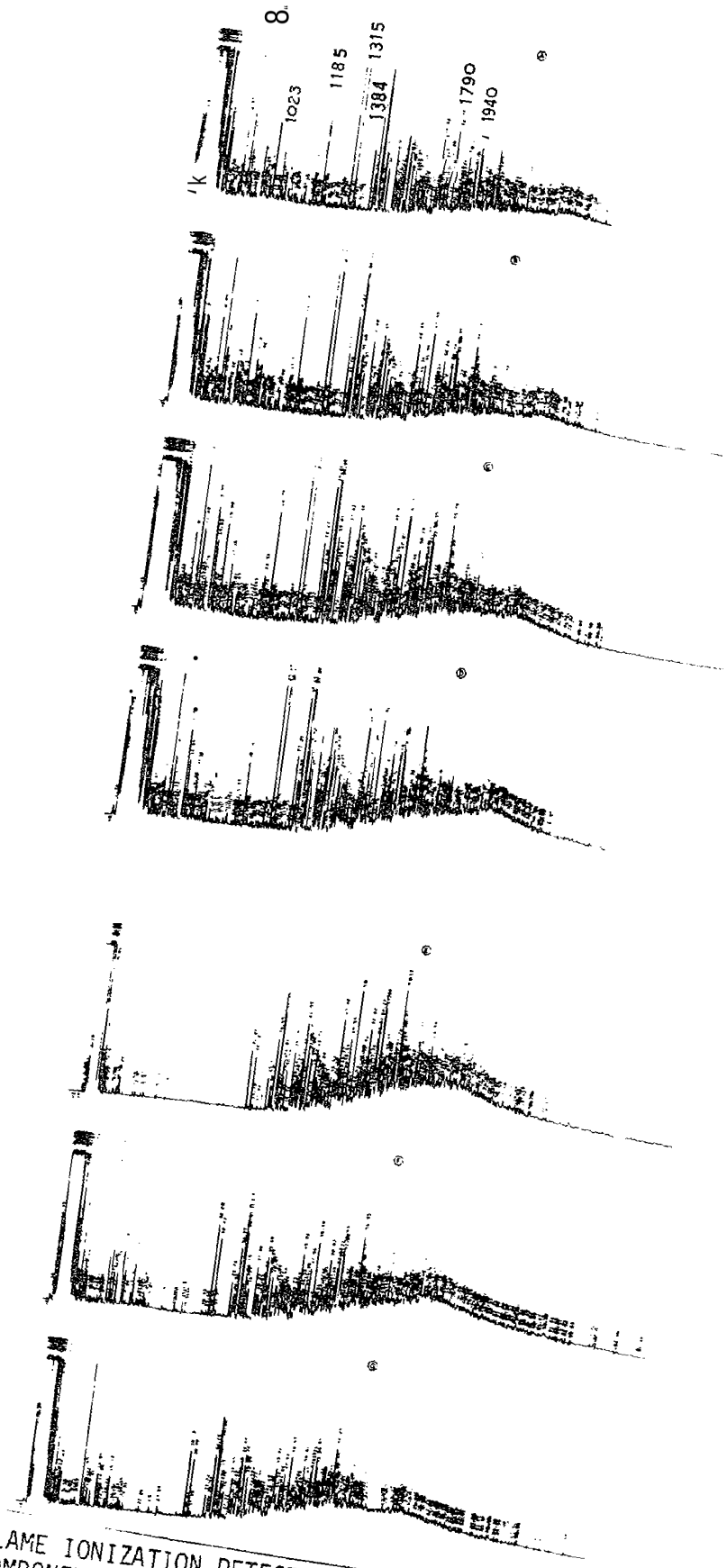



FIGURE 5-27. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF AROMATIC COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 3°C UNDER INFLUENCE OF A 1 KNOT WIND (E/D-6). TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 30 MINUTES; (B) 2 HOURS; (C) 1 DAY; (D) 3 DAYS; (E) 6 DAYS; (F) 12 DAYS; AND (G) 21 DAYS.

days following the initial spill event. On comparing these chromatograms to the chromatograms shown earlier in Figure 5-7, it can be seen that loss of lower molecular weight components due to volatilization is slightly inhibited at this lower temperature. This is perhaps best observed in examining the computer generated plots of specific compound concentrations in the oil vs time as shown in Figure 5-28 and 5-29.

Comparison of these latter figures to the computer plotted figures (5-23 and 5-24) for the 19°C experiment show significantly longer residence times of the intermediate molecular weight components compared to those lost at the higher temperature (note difference in time scales for Figures 5-28 and 5-29 vs 5-23 and 5-24). The lower molecular weight components (up to p-cymene) appear to be lost at approximately the same rates (after 60 hrs) in both experiments. The same relative increases in concentrations of higher molecular weight compounds such as dibenzothiophene, phenanthrene and methyl-phenanthrene can be observed in both experiments. Gas chromatograms for the time series water column samples obtained in the 3°C evaporation/dissolution experiment are presented in Figure 5-30. These chromatograms show the slow build-up of the relatively more water soluble lower and intermediate molecular weight alkyl-substituted aromatics in the water column. In this instance, however, the maximum water column concentrations are reached after approximately 50 hours and longer as shown by the computer plot of water column concentrations for this experiment (Figure 5-31). Obviously, many additional samples and chromatograms had to be obtained for generation of these plots but inclusion of additional chromatographic profiles in a report such as this is not practical. Clearly, however, the selected chromatograms and time-series concentration plots show the early water column buildup of the lower molecular weight compounds of interest such as toluene, ortho- and para-xylenes and alkyl -substituted benzenes. The higher molecular weight compounds such as naphthalenes and alkyl-substituted naphthalenes then reach maximum concentrations in the water column at 40-60 hours and then remain in the water column, not being lost through air/sea exchange and evaporation, for longer periods of time. It is quite interesting to compare the chromatographic profiles

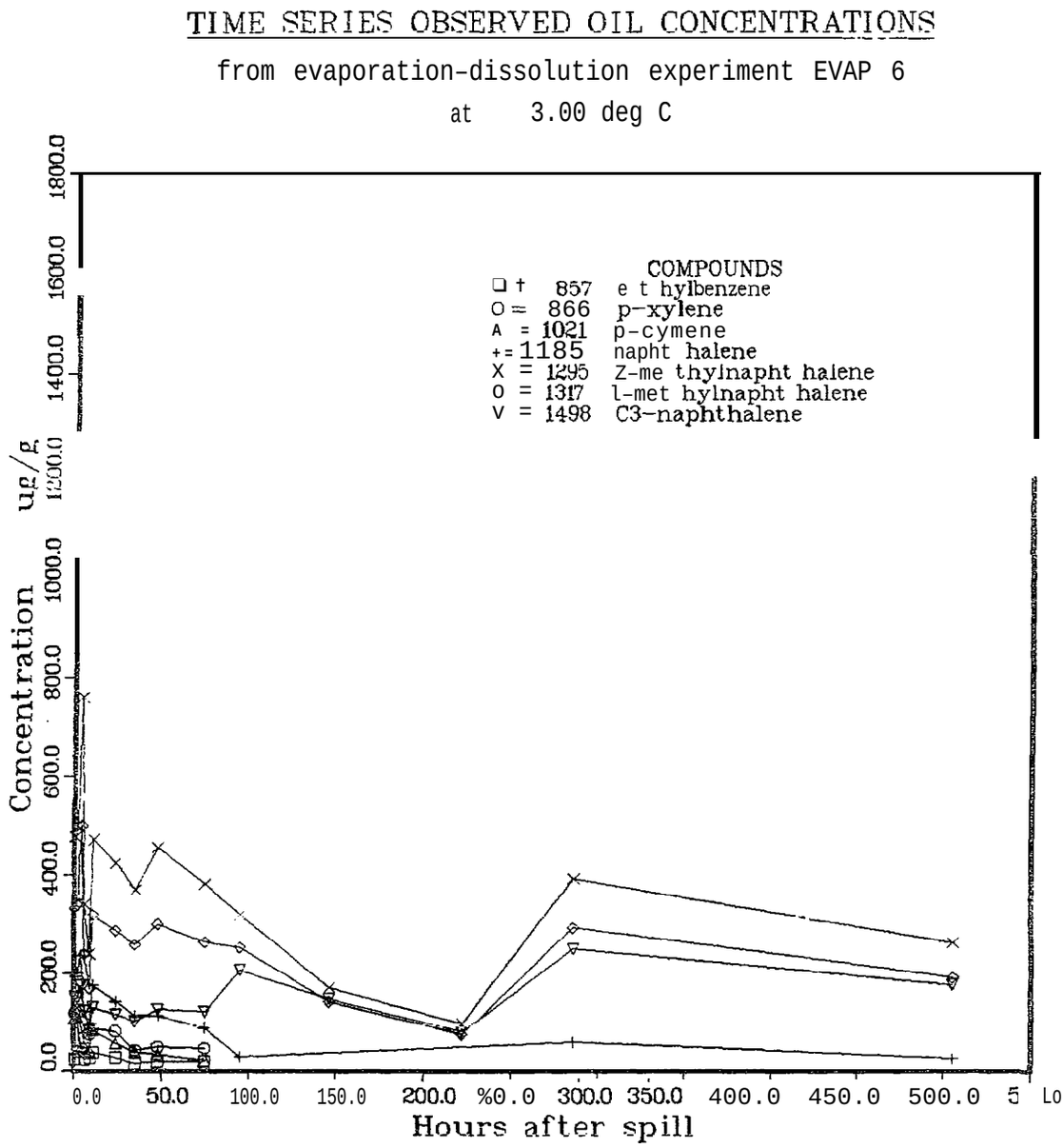



FIGURE 5-28. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATINS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 3°C UNDER INFLUENCE OF A 1 KNOT WIND. (E/D-6 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

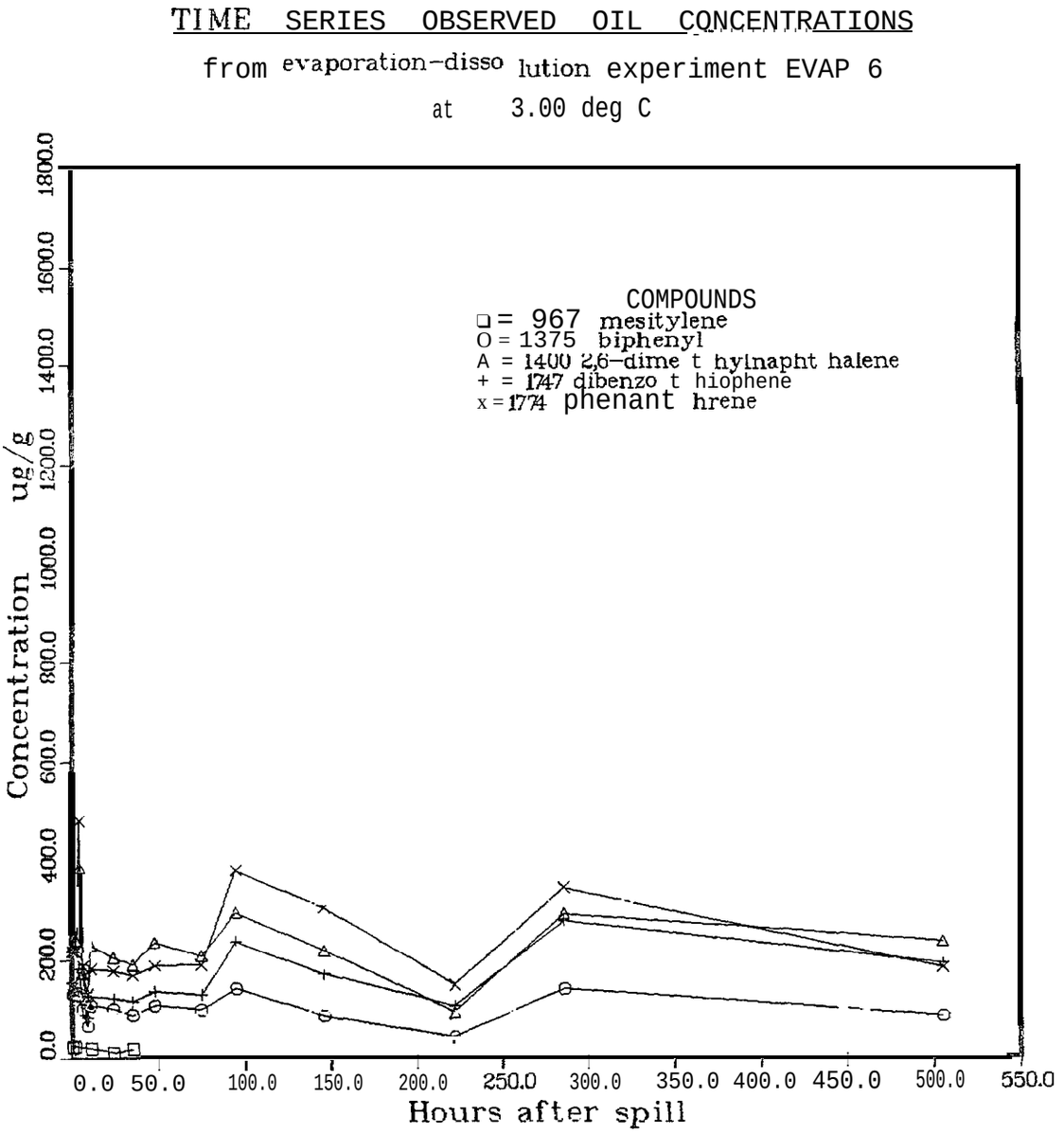



FIGURE 5-29. COMPUTER OPERATED TIME-SERIES PLOTS OF SPECIFIC HIGHER MOLECULAR WEIGHT COMPONENT CONCENTRATIONS REMAINING IN PRUDHOE BAY CRUDE OIL WEATHERING AT 3°C UNDER A INFLUENCE OF A 1 KNOT WIND. (E/D-6 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

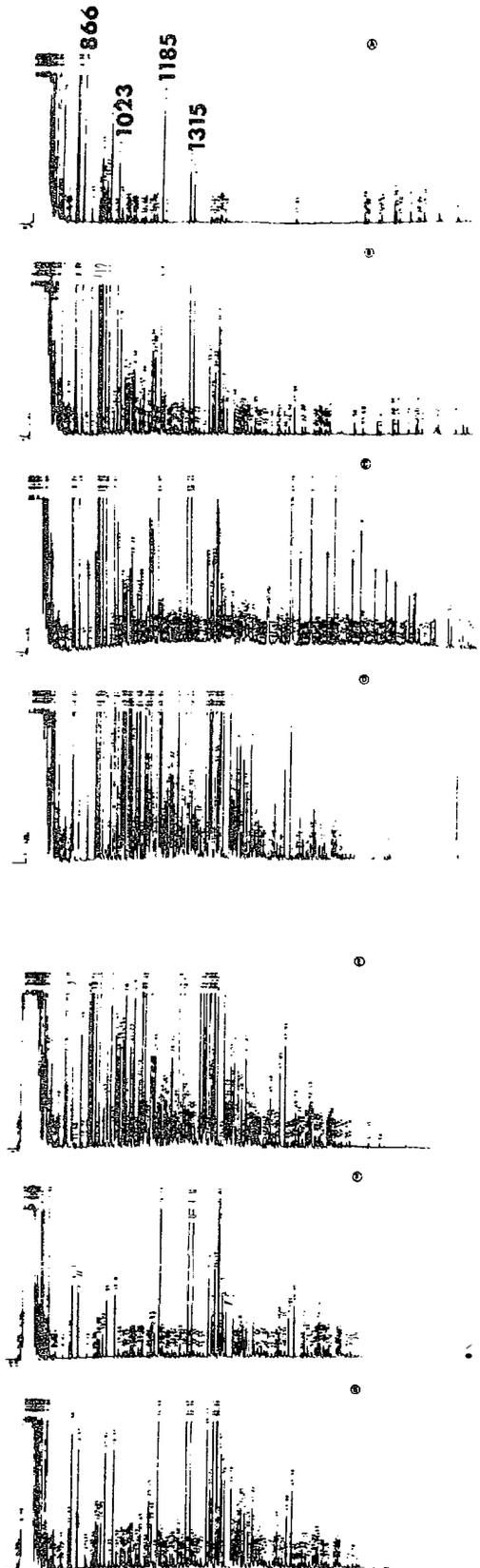



FIGURE 5-30. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF THE AROMATIC COMPONENTS REMAINING IN THE WATER COLUMN BENEATH A PRUDHOE BAY CRUDE OIL SLICK WEATHERING AT 3°C UNDER INFLUENCE OF A 1 KNOT WIND (E/D-6). TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 30 MINUTES; (B) 2 HOURS; (C) 1 DAY; (D) 3 DAYS (E) 6 DAYS; (F) 12 DAYS; and (G) 21 DAYS.

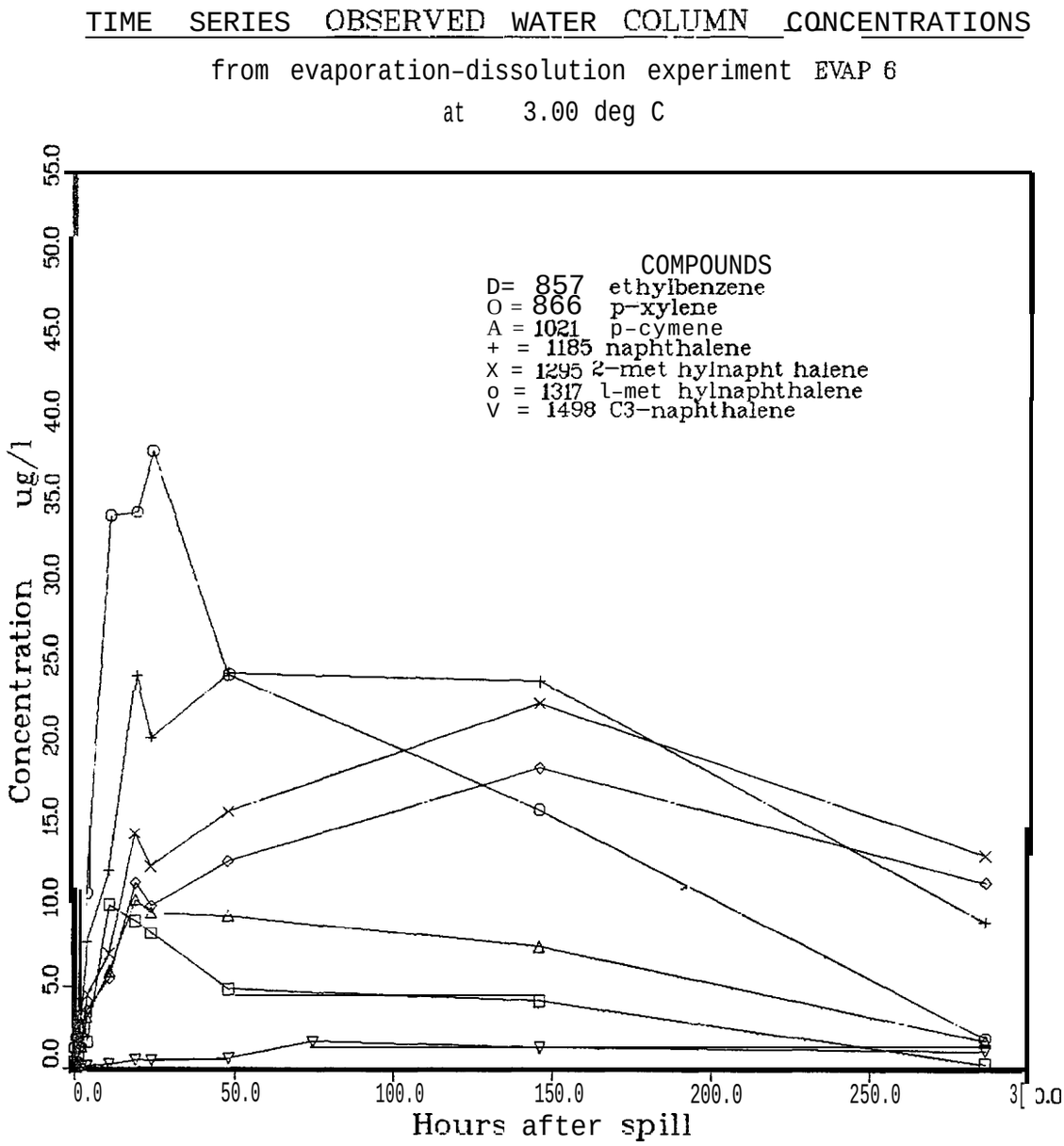



FIGURE 5-31. COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC AROMATIC COMPONENT CONCENTRATIONS REMAINING IN THE WATER COLUMN BENEATH A PRUDHOE BAY CRUDE OIL SLICK WEATHERING AT 3°C UNDER INFLUENCE OF A 1 KNOT WIND. (E/ D-6 DATA FROM EXP DATA BASE OF OIL WEATHERING MODEL).

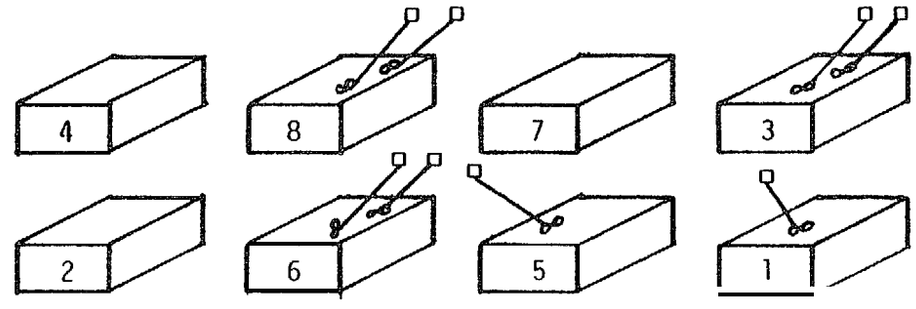
of the water column extracts (Figure 5.30) with the aromatic fractions of the oil sample extracts (Figure 5-27), in that the aromatics present in the water column are clearly skewed towards the lower molecular weight range. The lower molecular weight compounds in the oil are rapidly lost due to the combined effects of evaporation/dissolution such that, with time, only the higher molecular weight aromatic compounds remain in the slick up to the 21 days that this experiment was run.

### 5.1.2 Outdoor Evaporation/Dissolution Studies in Flow-Through Aquaria at Kasitsna Bay, Alaska

Part of the Summer 1980, Kasitsna Bay program involved construction of outdoor flow-through aquaria for long-term sub-arctic evaporation/dissolution and microbial degradation studies. Figure 5-32 presents a schematic diagram of the outdoor flow-through tank arrangement, and Figure 5-33 is a photograph of the outdoor flow-through tanks before installation of a cover to minimize fresh-water input from rain and snowfall. In September and October of 1980 four long-term microbial degradation experiments were begun: flow was maintained in two tanks where oil was allowed to weather in the presence and absence of Corexit 9527 (Tanks 3 and 7, respectively), and two tanks were maintained in a static condition where similarly treated oils were allowed to weather in the absence of continuous seawater flow (Tanks 5 and 2, respectively).

At the onset of the Spring, 1981 program, the four outdoor tanks were again examined and sampled, and two of the systems (Tanks 3 and 7) were left undisturbed to provide for continued longer term microbial degradation of the partially weathered oil over the summer months. Additional details on the results obtained from these and other long-term microbial degradation experiments are described in Section 5.2.

A more ambitious series of evaporation/dissolution experiments were then undertaken during the Spring 1981 program in these outdoor tanks using




Kas tsna Bay Revised New Exper menta P an 5-1-81

| Tank No. | Mousse | Oil | Turbulance | Corexit | Flow |
|---|---|---|---|---|---|
| 6 | + | - | + | + | + |
| 4 | + | - | - | - | + |
| 8 | + | - | + | - | + |
| 2 | + | - | - | + | + |
| 5 | - | + | + | + | + |
| 3 | - | 7 month old weathered oil | + | + | _ |
| 1 | - | + | + | - | + |
| 7 | - | 7 month old weathered oi | - | - | + |

FIGURE 5-32. SCHEMATIC DIAGRAM OF OUTDOOR FLOW-THROUGH TANK CONFIGURATION AT KASITSNA BAY, ALASKA THE MATRIX PRESENTS THE EXPERIMENTAL DESIGN AND TANK CONFIGURATION AS USED DURING THE SPRING/SUMMER 1981 FIELD PROGRAM.

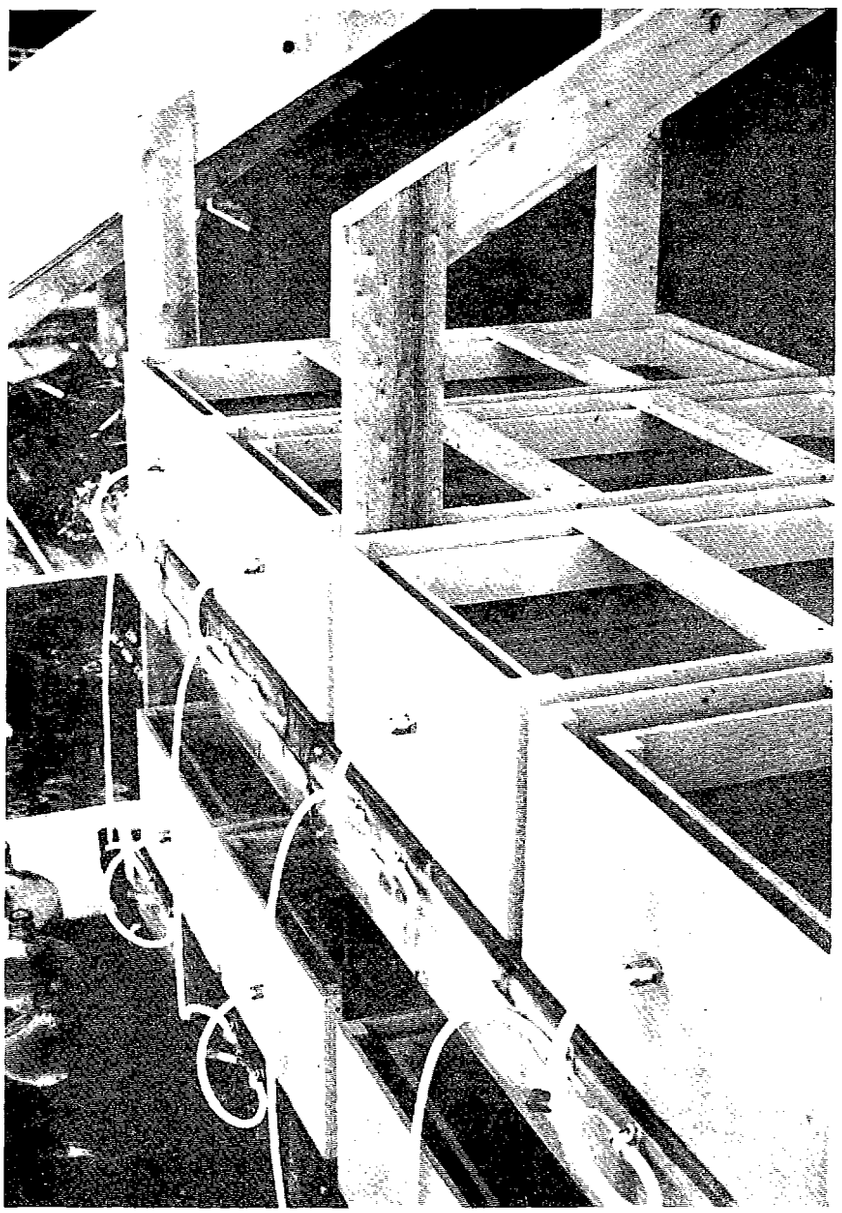


FIGURE 5-33. OUTDOOR FLOW-THROUGH OIL WEATHERING TANKSAT KASITSNA BAY, ALASKA BEFORE INSTALLATION OF A LEAN-TO COVER TO MINIMIZE FRESH WATER INPUT FROM RAIN AND SNOWFALL.

'the matrix design as presented in Figure 5-32. That is, evaporation/dissolution phenomena were examined with fresh Prudhoe Bay crude oil and artificially generated mousse in the presence and absence of turbulence and in the presence and absence of the dispersant Corexit 9527 as shown by the matrix design (Figure 5-32). Time-series photographs and chemical composition data were obtained on all of the experimental systems, and Table 5-6 presents the sampling times, the sample type (oil or water) and the chromatographic identifiers associated with each sample as required for computer data reduction.

Time-series capillary column chromatographic profiles were obtained on the oil fractions during the experimental runs at Kasitsna Bay and digitized data were recorded on magnetic tape and returned to La Jolla for incorporation into the data base for the oil weathering model. As in the evaporation/dissolution experiments in La Jolla, two types of water samples were obtained, with the first being 25-ml whole water samples in Pierce septum-capped vials for analysis of volatile organics by the purge and trap technique. In addition, 20 to 40-L samples of the discharged water from each tank were obtained and extracted with methylene chloride for later laboratory fractionation and GC and GC/MS analyses.

4s the data in Table 5-6 show, numerous samples were collected to provide quantitative data on evaporation/dissolution rates of oil under a wide variety of conditions; however, only three selected experiments are addressed in this report. Specifically, these include evaporation/dissolution results from: fresh oil in the presence of turbulence (Tank 1); artificially generated mousse in the presence of turbulence (Tank 8); and fresh crude oil plus Corexit in the presence of turbulence (Tank 5).

The importance of examining the evaporation/dissolution behavior of an artificially generated water-in-oil emulsion stemmed from the fact that significant increases in viscosity and specific gravity have been observed for many water-in-oil emulsions, and these increases have been shown to affect spreading, dispersion, interaction with suspended particulate material and

TABLE 5-5A OUTDOOR TANK #1 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0 hr, 1 hr, 7.5 hrs, 26 hrs, 53 hrs, 93 hrs, 150 hrs, 4 months, 6 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

```
LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 1
MEDIUM: WATER FRACTION TYPE: 2

                                TEMPERATURES      COREXIT  WIND
  HP-LABEL      HRS MINS  AIR   WATER    OIL   PRESENT  SPEED  MIXING  COMMENTS

87  9  AUG-21-1981 2880  0  15.00  11.00   .00    NO     .00  10.00  TANK 1 FRESH  OIL • TURB   PH2 F2 WATER   AFTER 4 MONTH

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA
MEDIUM: WATER FRACTION TYPE: 3

                                TEMPERATURES      COREXIT  WIND
  HP-LABEL      HRS MINS  AIR   WATER    OIL   PRESENT  SPEED  MIXING  COMMENTS

15  1  AUG-23-1981 2880  0  15.00  11.00   .00    NO     .00  10.00  TANK 1 FRESH  OIL + TURB   PH2 F3 WATER   AFTER 4 MONTH

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA
MEDIUM: OIL FRACTION TYPE: 0

                                TEMPERATURES      COREXIT  WIND
  HP-LABEL      HRS MINS  AIR   WATER    OIL   PRESENT  SPEED  MIXING  COMMENTS

34 13 MAY-03-1981   0  0  20.00  13.00   .00    NO     .00  10.00  TANK 1 TURB• FRESH OIL, TIMEZERO OIL        SAMPLE
52 25 AUG-10-1981 2880 0  15.00  11.00   .00    NO     .00  10.00  TANK 1 TURB + FRESH OIL=BRN  FLUID•FTEQ   4 MONTHS
135 15 SEP-11-1981 3600  0  15.00  11.00   .00    NO     .00  10.00  TANK 1 TURB + FRESH OIL=POOLED OIL SAMPLED  AFTER 5 MONTH
135  3 SEP-11-1981 3600  0  15.00  11.00   .00    NO     .00  10.00  TANK 1 TURB+FRESH OIL •  OIL SAMPLED   AFTER 5 MONTH

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 1
MEDIUM: FILM FRACTION TYPE: 0

                                TEMPERATURES      COREXIT  WIND
  HP-LABEL      HRS MINS  AIR   WATER    OIL   PRESENT  SPEED  MIXING  COMMENTS

58  9 SEP-29-1981 3600  0  15.00  11.00   .00    NO     .00  10.00  TANK 1 TURB + FRESH  OIL •  SURFACE FILM   AFTER 5 MONTH
```

TABLE 5-5 B OUTDOOR TANK #2 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0 hr, 1 hr, 7.5 hrs, 26 hrs, 53 hrs, 93 hrs, 150 hrs,
4 months, 6 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 2
MEDIUM: OIL FRACTION TYPE: 0

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 24 MAY-09-1981 | 0 | 0 | 20.00 | 13.00 | .00 | YES | .00 | .00 | TANK 2 □ olJsag* CORREXIT-TIME ZERO OIL SAMPLE |
| 93 | 24 MAY-06-1981 | 53 | 0 | .00 | 13.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE +CORREXIT-OIL SAMPLED AFTER 53 HOURS |
| 18 | 3 AUG-09-1981 | 2880 | 0 | 1s.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE +CORREXIT-OIL SAMPLE AFTER 4 MONTHS |
| 103 | 3 SEP-08-1981 | 3600 | 0 | 15.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE ● CORRCXIT . MOUSSE SAMPLED AFTER S MONTH |
| 16 | 2 APR-29-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE PLUS CORREXIT AFTER 6 MONTHS |
| 17 | 15 OCT-02-1981 | 4320 | 0 | 15.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE +CORREXIT-MOUSSE SAMPLED AFTER 6 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 2
MEDIUM: FILM FRACTION TYPE: 0

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 19 | 5 AUG-09-1981 | 2880 | 0 | 1s.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE +CORREXIT-SURFACE FILM AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 2
MEDIUM: WATER FRACTION TYPE: 1

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 75 | 25 AUG-20-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE +CORREXIT-PH2 F1WATER AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 2
MEDIUM: WATER FRACTION TYPE: 2

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 88 | 11 AUG-21-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE + CORREXIT-PH2 F2 WATER AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 2
MEDIUM: WATER FRACTION TYPE: 0

| | HP-LABEL | HRS | MINS | TEMPERATURES AIR | TEMPERATURES "Arc's | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| 46 | 27 APR-21-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | YES | .00 | .00 | TANK 2 MOUSSE PLUS CORREXIT H2O SAMPLE 6 MONTHS |

TABLE 5-5 C OUTDOOR TANK #3 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0 hr, 1 hr, 6 hrs, 24 hrs, 93 hrs, 150 hrs,
4 months, 6 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Feathering Model

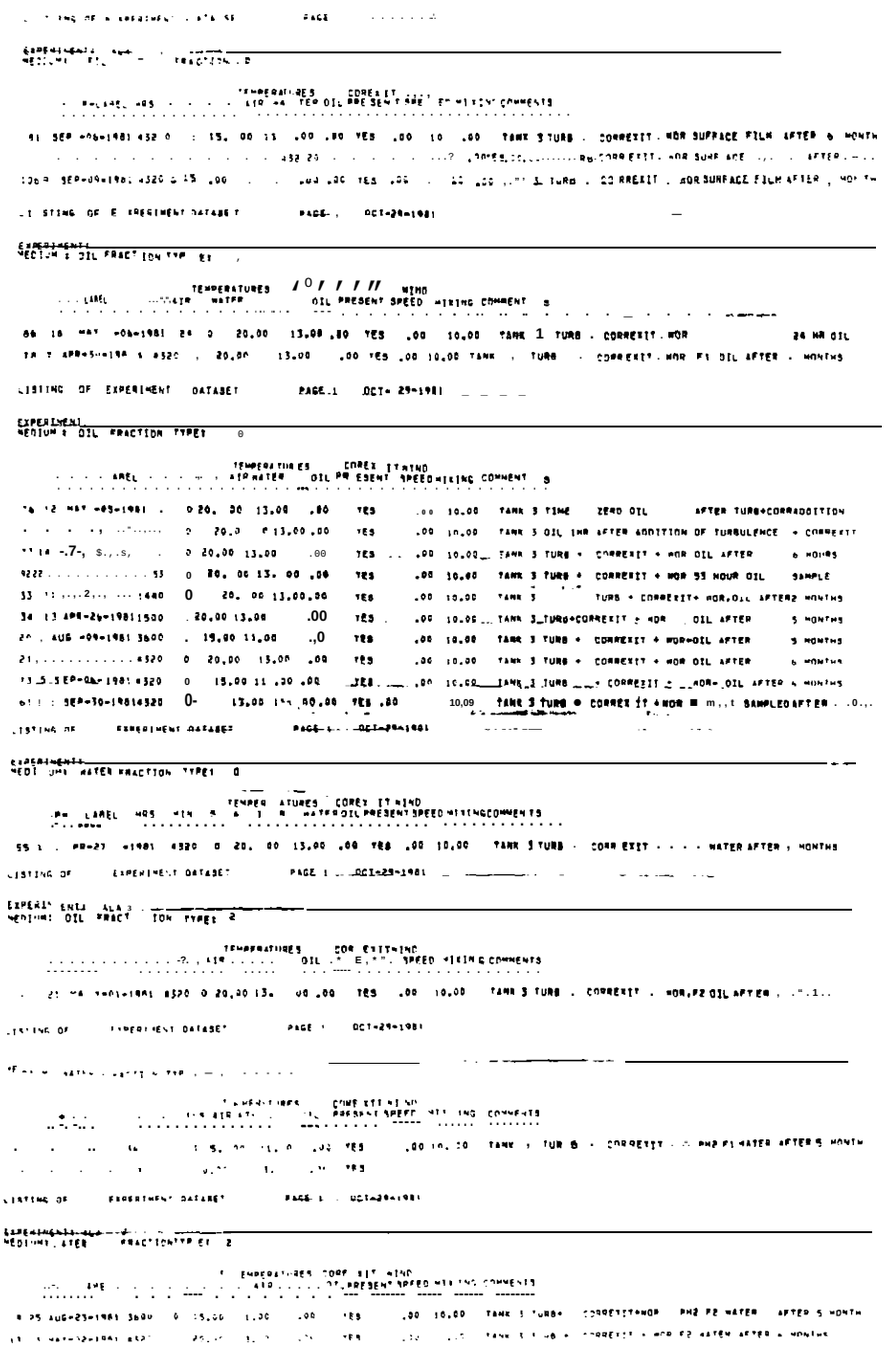


TABLE 5-6 D OUTDOOR TANK #4 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0hr, 1hr, 7.5 hrs, 26 hrs, 53 hrs, 93 hrs, 150 hrs,
4 months, 6 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA
MEDIUM: WATER FRACTION TYPE: 3

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 47 9 AUG-31-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY PH2 F3 WATER AFTER 4 MONTH |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA
MEDIUM: WATER FRACTION TYPE: 1

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 7a 4 , 6-20-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 8 MOUSSE ONLY-PH2 WATER, F1 , AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA
MEDIUM: OIL FRACTION TYPE: O

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS | |
|---|---|---|---|---|---|---|---|---|---|---|
| 21 10 MAY-10-1981 | 0 | 0 | 20.00 | 13.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY • TIME | ZERO OIL SAMPLE |
| 3a 29 AUG-10-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY-NORMAL | MOUSSE AFTER 4 MONTHS |
| 21 . AUG-09-1981 | 2880 | 0 | 1s.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY CRUSTY | ZERO OIL 4 MONTHS |
| 129 23 SEP-11-1981 3 | 3600 | o | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY . MOUSSE | UNDER CRUST AFTER 5 MONTH |
| 110 17 SEP-09-1981 5 | 3600 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY- STRANDED | CRUST SAMPLED AFTER 5 MONTH |
| 109 15 SEP-09-1981 | 3600 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 9 MOUSSE. ONLY. MOUSSE | SAMPLED AFTER 5 MONTHS |
| 7a 7 SEP-06-1981 | 3600 | o | 1s.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY . FLAKES | SAMPLED AFTER 5 MONTHS |
| 128 21 SEP-11-1981 | won | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY - MOUSSE | UNDERS TOE AFTER 5 MONTHS |
| 111 17 SEP-09-1981 5 | 3600 | 0 | 1s.00 | 11.00 | .00 | No | .00 | .00 | TANK 5 MOUSSE. ONLY-STRANDED | OIL CRUST AFTER 5 MONTH |
| 107 11 SEP-09-1981 | 3600 | o | 15.00 | 11.00 | .00 | MO | .00 | .00 | TANK 4 MOUSSE ONLY • CRUST | SAMPLED AFTER 9 MONTHS |
| 108 , 9 SEP-09-1981 5 | 3600 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY - UNDER | CRUST SAMPLED AFTER 5 MONTH |
| 63 15 SEP-30-1981 | 4320 | 0 | 15.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY - MOUSSE | SAMPLED AFTER 6 MONTHS |
| 64 17 SEP-30-1981 • | 320 | 0 | 1s.00 | 11.00 | .00 | NO | .00 | .00 | TANK 4 MOUSSE ONLY . CRUSTY | MOUSSE SAMPLED AFTER 6 MONTH |

TABLE 5-6E OUTDOOR TANK #5 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0 hr, 1hr, 8 hrs, 26 nrs, 53 hrS, 93 hrs, 150 hrs,
4 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

```
LISTING OF      EXPERIMENT DATASET      PAGE 1     OCT-29-1981

EXPERIMENT: ALA    5
MEDIUM: H2O        FRACTION TYPE: 0

                                   TEMPERATURES      COREX IT WIND
     HP-LABEL        HRS MINS  AIR    WATER    OIL  PRESENT SPEED □ 111N6 COMMENTS
     ------          ---------------------------------------------------------------
 • t 29 APR-27-1931-8520    0 20.00  13.00    .00    YES      .60 10.00   TANK 9  TURB  4 CORREXIT  +     PRESH OIL,     b MONTHS

LISTING OF      EXPERIMENT DATASET      PAGE 1     OCT-29-1981

EXPERIMENT: ALA    5
MEDIUM: OIL        FRACTION TYPE: 0

                                   TEMPERATURES      COREXIT  WIND
     HP-LABEL        HRS MINS  AIR    WATER    O I L  PRESENT SPEED MIXING COMMENTS
     ------          ---------------------------------------------------------------
 36 17 MAY-04-1981   0    0  20.00  13.00    .00    YES      .00 10.00  TANK 5 TURB  +  CORREXIT+FRESH OIL, TIME ZERO  OIL SAMPLE
 80 20 MAY-05-1981   8    0  20.00  13.00    .00    YES      .00 10.00  TANK 5 TURB  +  CORREXIT+FRESH OIL-8 HOUR OIL SAMPLE
 97 32 MAY-07-1981  53    0  20.00  13.00    .00    YES      .00 10.00  TANK 5 TURB  +  CORREXIT+FRESH OIL-53 HOUR  OIL SAMPLE

LISTING OF      EXPERIMENT DATASET      PAGE 1     OCT-29-1981

EXPERIMENT: ALA    5
MEDIUM: WATER      FRACTION TYPE: 1

                                   TEMPERATURES      COREXIT  WIND
     HP-LABEL        HRS MINS  AIR    WATER    OIL  PRESENT SPEED MIXING COMMENTS
     ------          ---------------------------------------------------------------
 79  3 AUG-20-1981 2880    0  15.00  11.00    .00    YES      .00 10.00  TANK 5 FRESH  OIL+CORREXIT+  TURB-PH2 F1 H2OAFTER 4 MONTH

LISTING OF      EXPERIMENT DATASET      PAGE 1     OCT-29-1981

EXPERIMENT: ALA    5
MEDIUM: WATER      FRACTION TYPE: 3

                                   TEMPERATURES      COREXIT  WIND
     HP-LABEL        HRS MINS  AIR    WATER    OIL  PRESENT SPEED MIXING COMMENTS
     ------          ---------------------------------------------------------------
 5s 5 ● w.31-lwl 2880    0  15.00  11.00    .00    YES      .00 10.00  TANK 5 FRESH  OIL + TURB    +  CORREXIT PH2 F3 H2O-4 MC
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TABLE 5-6F OUTDOOR TANK #6 OIL, WATER AND AIR SAMPLING TIMES

Blank, O hr, 1 hr, 6 hrs, 19 hrs, 30 hrs, 45 hrs, 100 hrs, 4 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 6
MEDIUM: OIL FRACTION TYPE: 0

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 22 16 MAY-19-1981 | 0 | 0 | 20.00 | 13.00 | .00 | YES | .00 | 10.00 | TANK 6 TURB + CORREXIT+MOUSSETI ME ZERO OIL SAMPLE |
| 56 9 AUG-12-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | 10.00 | TANKb MOUSSE● cOWWXt T+ TIIEO OIL AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPER IMENT: ALA
MEDIUM: ● hTER FR ACT ION TYPE: 1

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 11 29 AUG-23-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | 10.00 | TANK 6 MOUSSE + CORREXIT + TURB, PH2 WATER F1 AFTER 4 MO |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-30-1981

EXPERIMENT: ALA 6
MEDIUM: WATER FRACTION TYPE: 2

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 85 5 AUG-21-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | 10.00 | TANK 6 MOUSSE+ CORREXIT+TURB PH2 F2 WATER AFTER 4 MONTH |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

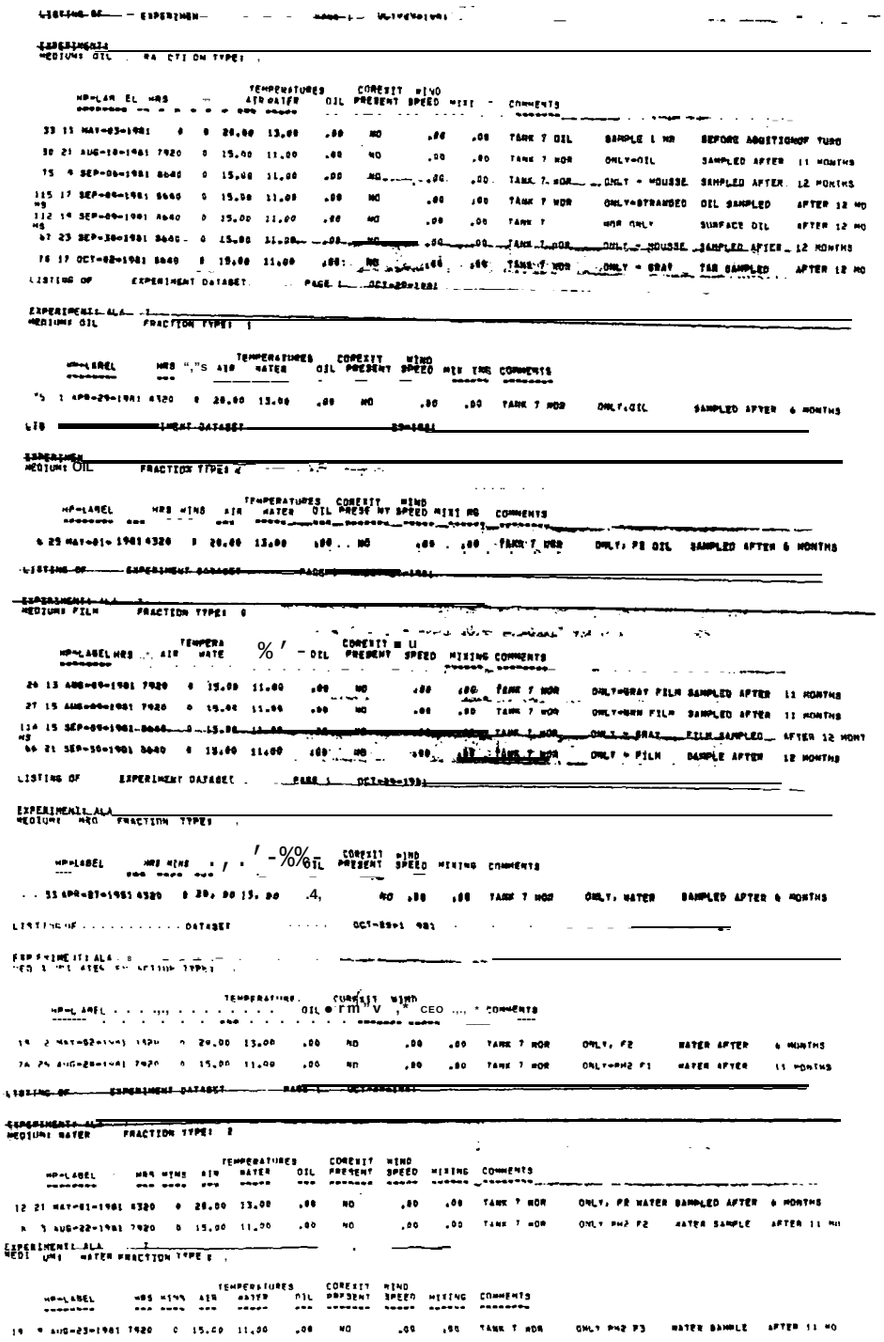
EXPERIMENT: ALA 6
MEDIUM: ATER FRACTION TYPE: 3

| HP-LABEL | HRS | MINS | TEMPERATURES AIR | WATER | OIL | COREXIT ● RESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 2 23 AUG-22-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | YES | .00 | 10*00 | TANK 6 ❑ OU8W4 CORREXIT+TURB PH2 F3 WATER AFTER 4 MONTH |

TABLE 5-6G OUTDOOR TANK #7 OIL, WATER AND AIR SAMPLING TIMES

6 months, 11 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model



| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LISTING OF | EXPERIMEN | | | | | | | | | | | | |
| EXPERIMENTS | | | | | | | | | | | | | |
| MEDIUM: OIL | | FRACTION TYPE: | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | EL | HRS | | AIR | WATER | OIL | PRESENT | SPEED | MIX | | COMMENTS | | |
| 33 | 11 | MAY-03-1981 | 0 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 OIL | SAMPLE 1 HR BEFORE ADDITION OF TURB |
| 38 | 21 | AUG-18-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=OIL SAMPLED AFTER 11 MONTHS |
| 75 | 4 | SEP-06-1981 | 8640 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY = MOUSSE SAMPLED AFTER 12 MONTHS |
| 115 | 17 | SEP-06-1981 | 8640 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=STRANDED OIL SAMPLED AFTER 12 MO |
| HS | | | | | | | | | | | | | |
| 112 | 14 | SEP-06-1981 | 8640 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 | HOR ONLY SURFACE OIL AFTER 12 MO |
| HS | | | | | | | | | | | | | |
| 67 | 23 | SEP-30-1981 | 8640 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY = MOUSSE SAMPLED AFTER 12 MONTHS |
| 76 | 17 | OCT-02-1981 | 8640 | 0 | 19.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY = GRAY TAR SAMPLED AFTER 12 MO |
| LISTING OF | | EXPERIMENT DATASET | | | | PAGE 1 | | OCT-20-1981 | | | | | |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: OIL | | FRACTION TYPE: 1 | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | MINS | AIR | WATER | OIL | PRESENT | SPEED | MIX | INS | COMMENTS | | |
| 75 | 1 | APR-29-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=OIL SAMPLED AFTER 6 MONTHS |
| LIS | | | | | | | | | | | | | |
| EXPERIMEN | | | | | | | | | | | | | |
| MEDIUM: OIL | | FRACTION TYPE: 2 | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | MINS | AIR | WATER | OIL | PRESENT | SPEED | MIX | MG | COMMENTS | | |
| 6 | 25 | MAY-01-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY: PR OIL SAMPLED AFTER 6 MONTHS |
| LISTING OF | | EXPERIMENT DATASET | | | | | | | | | | | |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: FILM | | FRACTION TYPE: 6 | | | | | | | | | | | |
| | | | | TEMPERA | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | | AIR | WATE | OIL | PRESENT | SPEED | MIXING | | COMMENTS | | |
| 26 | 13 | AUG-06-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=GRAY FILM SAMPLED AFTER 11 MONTHS |
| 27 | 15 | AUG-06-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=BRN FILM SAMPLED AFTER 11 MONTHS |
| 114 | 15 | SEP-06-1981 | 8640 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY = GRAY FILM SAMPLED AFTER 12 MONT |
| HS | | | | | | | | | | | | | |
| 66 | 21 | SEP-30-1981 | 8640 | 0 | 19.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY = FILM SAMPLE AFTER 12 MONTHS |
| LISTING OF | | EXPERIMENT DATASET | | | | PAGE 1 | | OCT-20-1981 | | | | | |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: H2O | | FRACTION TYPE: | | | | | | | | | | | |
| | | | | | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | MINS | | | OIL | PRESENT | SPEED | MIXING | | COMMENTS | | |
| 11 | 11 | APR-27-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY: WATER SAMPLED AFTER 6 MONTHS |
| LISTING OF | | DATASET | | | | | | OCT-20-1981 | | | | | |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: | | FRACTION TYPE: | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | | | | | | OIL | PRESENT | SPEED | | | COMMENTS | | |
| 19 | 2 | MAY-02-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY: F2 WATER AFTER 6 MONTHS |
| 76 | 24 | AUG-28-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY=PH2 F1 WATER AFTER 11 MONTHS |
| LISTING OF | | EXPERIMENT DATASET | | | | PAGE 1 | | OCT-20-1981 | | | | | |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: WATER | | FRACTION TYPE: 2 | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | MINS | AIR | WATER | OIL | PRESENT | SPEED | MIXING | | COMMENTS | | |
| 12 | 21 | MAY-01-1981 | 4320 | 0 | 20.00 | 13.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY: PR WATER SAMPLED AFTER 6 MONTHS |
| 8 | 3 | AUG-22-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY PH2 F2 WATER SAMPLE AFTER 11 MO |
| EXPERIMENTS ALA | | | | | | | | | | | | | |
| MEDIUM: | | WATER FRACTION TYPE 3 | | | | | | | | | | | |
| | | | | TEMPERATURES | | | CONSIST | WIND | | | | | |
| HP-LABEL | | HRS | MINS | AIR | WATER | OIL | PRESENT | SPEED | MIXING | | COMMENTS | | |
| 19 | 4 | AUG-23-1981 | 7920 | 0 | 15.00 | 11.00 | .00 | NO | | .00 | .00 | TANK 7 HOR | ONLY PH2 F3 WATER SAMPLE AFTER 11 MO |

TABLE 5-6H OUTDOOR TANK#8 OIL, WATER AND AIR SAMPLING TIMES

Blank, 0 hr, 1 hr, 6 hrs, 19 hrs, 30 hrs, 45 hrs, 100 hrs, 4 months

Computer listing of analyzed samples with reduced data in EXP data base of Oil Weathering Model

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 8
MEDIUM: OIL FRACTION TYPE: 0

| HP-LABEL | HRS | MINS | AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 59 1 1 AUG-12-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | TANK 8 MOUSSE +TURB-MOUSSE SAMPLED AFTER 6 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 8
MEDIUM: WATER FRACTION TYPE: 1

| HP-LABEL | HRS | MINS | AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 80 29 AUG-20-1981 | 2880 | 0 | 1s.00 | 11.09 | .00 | No | .00 | 10, WI | TANK 8 MOUSSE +TURB-PH2 F1 WATER AFTER 4 MONTHS |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: AL
MEDIUM: WATER FRACTION TYPE: 2

| HP-LABEL | HRS | MINS | AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 1S 33 AUG-23-1981 | 2880 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | TANK 8 MOUSSE +TURB PH2 F2 WATER SAMPLE AFTER 6 MONTH |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-29-1981

EXPERIMENT: ALA 8
MEDIUM: WATER FRACTION TYPE: 3

| HP-LABEL | HRS | MINS | AIR | TEMPERATURES WATER | OIL | COREXIT PRESENT | WIND SPEED | MIXING | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|
| 20 , 1 AUG-24-1981 | 2880 | 0 | .00 | .00 | .00 | NO | .00 | 10.00 | TANK 8 MOUSSE ● W*O PH2 F3 WATER SAMPLE AFTER 9 MONTH |

presumably evaporation/dissolution (PAYNE, 1981). TWARDUS (1980) indicated that no quantitative data existed on how mousse affects evaporation, but it was suspected that once mousse formation occurred, evaporation would occur at reduced rates. Similar predictions have been made by NOGATA and KONDO (1977), and, in our Spring 1981 experiments, attempts were made to quantify any differences in lower molecular weight volatile compound losses from fresh Prudhoe Bay crude oil and artificially (shaker table) generated mousse where evaporation was prevented duringmousse formation in a sealed teflon container. Specifically, in this experiment, a water-in-oil emulsion (or artificial mousse) was generated with fresh Prudhoe Bay crude oil by mixing 80 parts filtered seawater with 20 parts fresh oil in sealed teflon containers on a shaker table for 48 hours.

This fresh mousse was then poured onto the water surface in Outdoor Tank #8 and propeller driven turbulence was introduced to determine if differential rates of lower molecular weight hydrocarbon losses occurred in the more viscious water-in-oil emulsion compared to fresh Prudhoe Bay crude (Tank No. 1). As in the corresponding evaporation/dissolution chamber experiments in La Jolla, volatile compound concentrations were measured in the air 1 to 2 inches above the slick by pumping measured volumes of air through stainless steel columns packed with Tenax® at different time intervals following the spills. In both Tanks 1 and 8, turbulence was induced by propeller mixing. The water and air temperatures at the time of sampling were 6° and 6 to 12°C, respectively. After sampling, the Tenax® traps were capped with stainless Swagelok® fittings and stored at room temperature until FID GC analyses, using the procedures described in Appendix B. Backup columns in series with the front columns showed no breakthrough of lower molecular weight material 95+% recovery on the front traps. Interestingly, the qualitative appearance of the temperature programmed components of the volatiles from both systems were remarkedly similar (PAYNE, 1981), and the time-series data presented graphically in Figures 5-34A and 5-34B illustrate that essentially identical losses of lower molecular weight compounds ranging from butane to xylene were obtained for both the fresh oil and fresh mousse. The data in Figure 5-34C; however, show

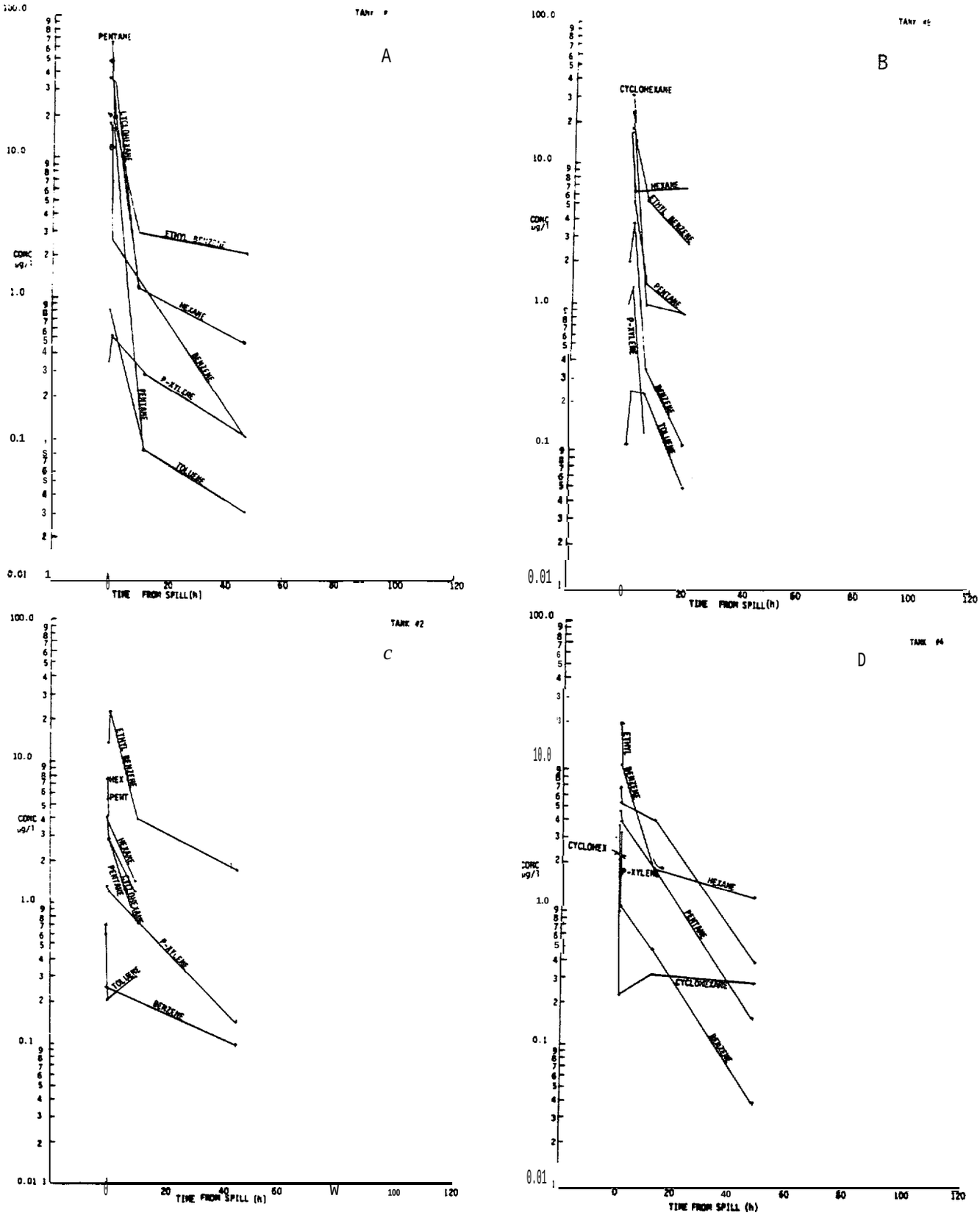



FIGURE 5-34. TENAX TRAP/FID GC DATA ON SUB-ARCTIC VOLATILE COMPONENT LOSS FROM PRUDHOE BAY CRUDE OIL AND MOUSSE ON FLOW-THROUGH SEAWATER ENCLOSURES IN KASITSNA BAY, ALASKA. A) FRESH OIL AND TURBULANCE; B) FRESH MOUSSE AND TURBULANCE; C) FRESH MOUSSE (NO TURBULENCE); D) FRESH MOUSSE AND COREXIT 9527 (NO TURBULANCE). WATER TEMP 6°C, AIR TEMP 6-13°C.

slightly longer retention of these compounds in mousse spread on seawater in the absence of turbulence. One of the static (non-propeller mixed) mousse systems (Tank 2) was also treated with Corexit 9527 immediately after the spill (Figure 5-34D), but this apparently did not affect evaporation loss compared to the non-dispersant treated control (Figure 5-34C).

Figure 5-35 presents selected time-series glass capillary gas chromatographic profiles obtained on the fresh oil samples in the flow-through tank in the presence of turbulence (Tank 1). The sampling points in Figure 5-35 are for times of: 1 hour, 26 hours, 4 months and 6 months. Figure 5-36 presents the time-series gas chromatographic profiles obtained on the artificially generated mousse in the presence of turbulence at sampling times 0, 30 hours and 4 months (Tank 8). Very similar losses of the lower molecular weight components below nC-9 appeared to have occurred in both the fresh oil and artificial mousse experiments however, slightly longer retention of lower molecular weight components is suggested in the artificial mousse case when examining the four month data (Figure 5-36C). Also, while only limited or no microbial degradation is suggested during the first 24 to 30-hour period, more significant microbial utilization of the aliphatics as opposed to the branched chain isoprenoids can be observed in the four month old samples from both the fresh crude and artificially generated mousse. In the fresh oil plus turbulence experiment, the nC-17/pristane and nC-18/phytane ratios dropped to 0.38 and 0.51, respectively after four months, and in the chromatogram of the four month old weathered mousse (Figure 5-36C) the nC-17/pristane and nC-18/phytane ratios dropped to 0.75 and 0.92, respectively. The values for these ratios in fresh Prudhoe Bay crude oil are 1.7 and 1.6, respectively. It should also be noted that after four months of weathering in both systems, the unresolved complex mixture had increased significantly. The effects of microbial degradation are even more striking in Figure 5-35D which presents the weathered sample from the fresh oil Plus turbulence tank after 6 months of weathering during the sub-arctic summer months from June through October, 1981. In the 6 months old sample (Figure 5-35D) the isoprenoid compounds, pristane (Kovat 1710) and phytane (Kovat 1815) dominate all of the other resolved components.

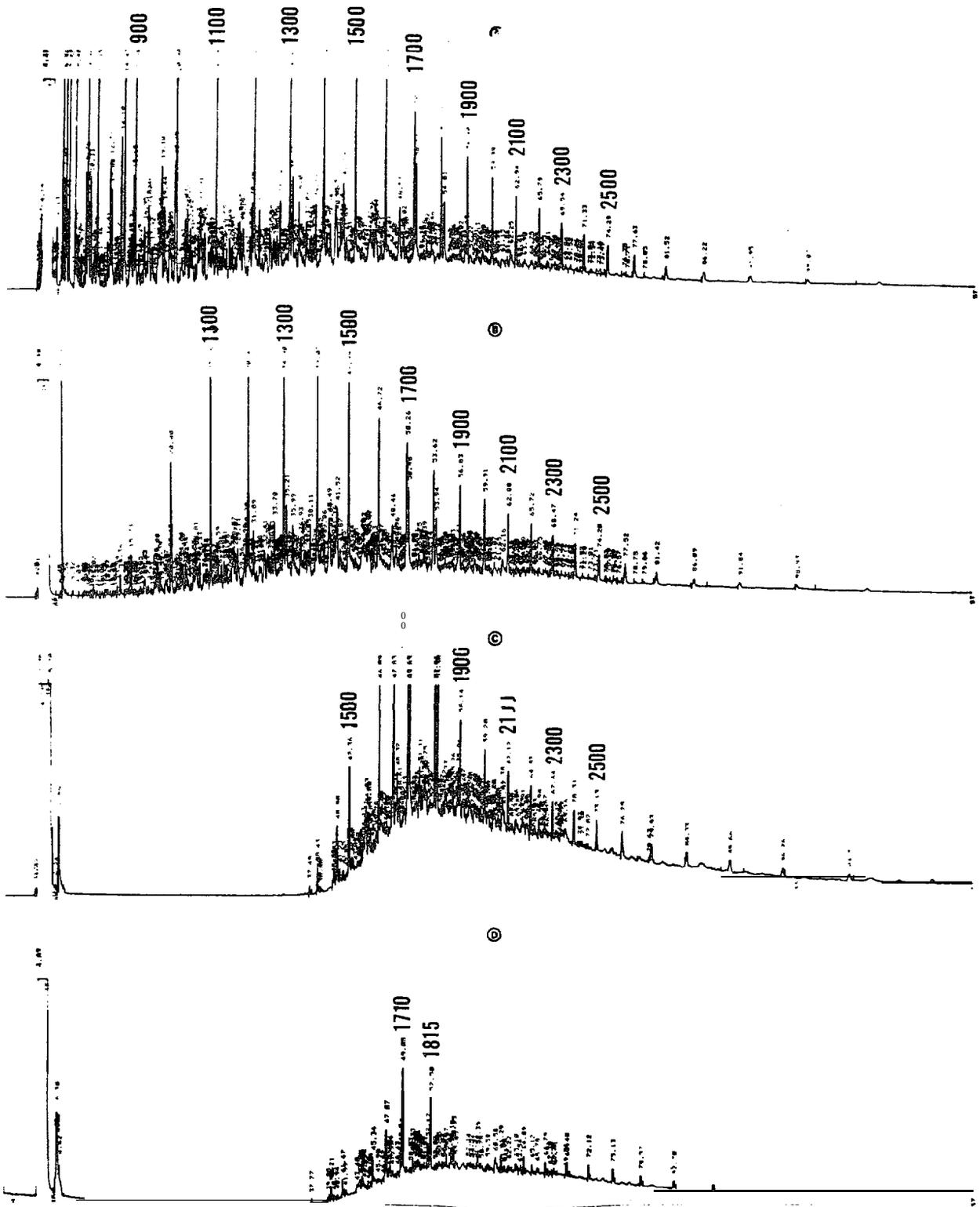



FIGURE 5-35. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON PRUDHOE BAY CRUDE OIL blathering IN THE PRESENCE OF PROPELLER DRIVEN TURBULENCE IN THE OUTDOOR FLOW-THROUGH AQUARIA (TANK #1) AT KASITSNA BAY, ALASKA. TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 1 HOUR; (B) 26 HOURS, (C) 4 MONTHS; AND (D) 6 MONTHS.

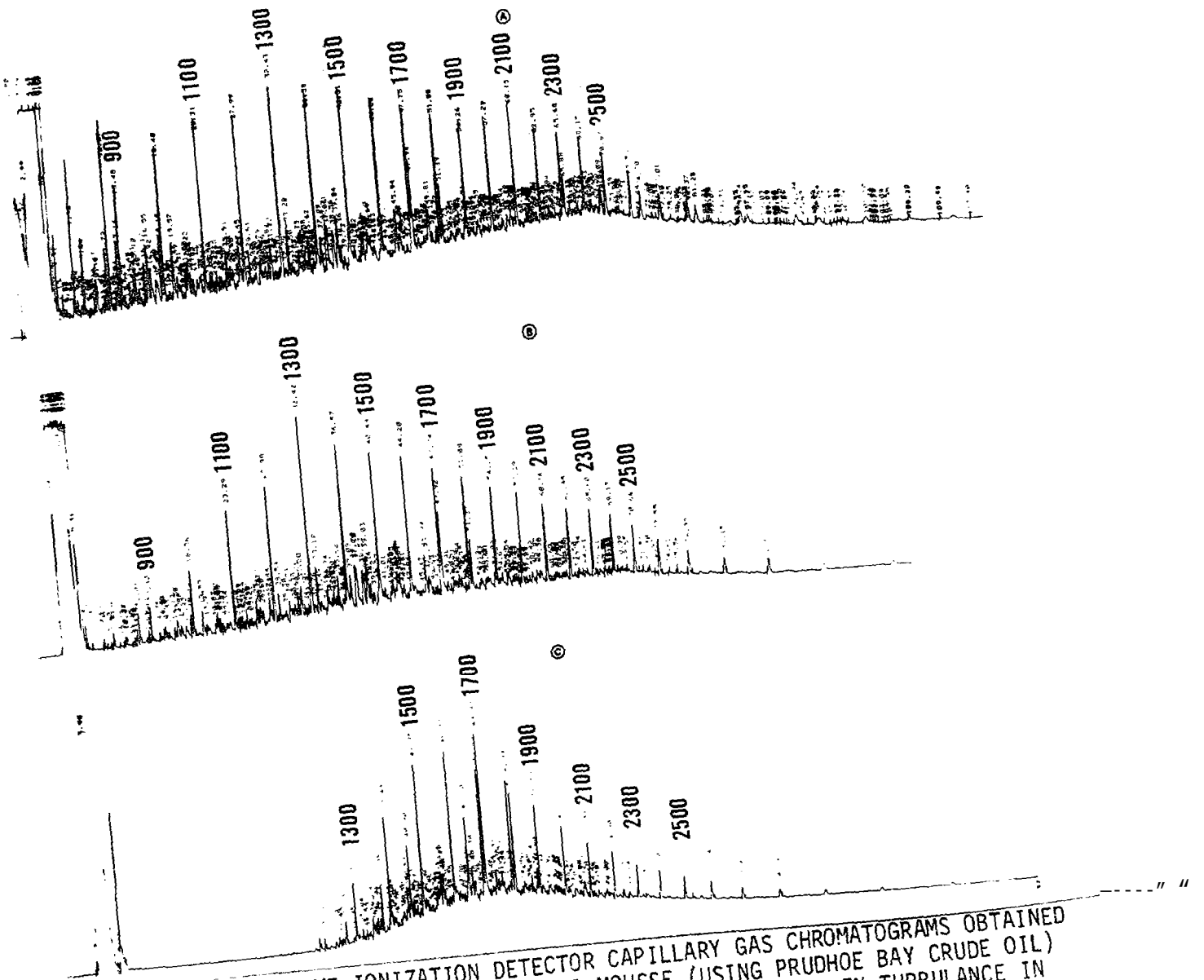



FIGURE 5-36. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON ARTIFICALLY GENERATED MOUSSE (USING PRUDHOE BAY CRUDE OIL) WEATHERING IN THE PRESENCE OF PROPELLER DRIVEN TURBULANCE IN THE OUTDOOR FLOW-THROUGH AQUARIA (TANK #8) AT KASITSNA BAY, ALASKA. TIME-SERIES SAMPLING POINTS AFTER THE "SPILL" (A) 5 MIN; (B) 30 HOURS; AND (C) 4 MONTHS.

Easier comparisons of the relative retention of the higher molecular weight components can be made by examination of the computer generated time-series concentration profiles obtained from capillary FID gas chromatographic analyses of the oil and mousse from the well-stirred tanks as shown in Figure 5-37. Kovat indices for the compounds in each plot are identified in the figures, and these data confirm that compounds in the range of nC-9 through nC-11 are preferentially retained in the mousse sample for longer periods of time (Figures 5-37A and C). Figures 5-38A and 5-38B show the time-series concentrations of components with Kovat indices ranging from 1300 to 2000 for the oil and artificially generated mousse samples, respectively. A similar relative increase in these higher molecular weight compound concentrations (in $\mu g/g$ oil) is noted for both the oil and mousse after approximately 25 hours, and this is due to the removal of significant mass of the oil by evaporation of the lower molecular weight components (compounds with molecular weights above nC-15 are not lost during this time frame). Absolute concentrations of the individual components in each of the mousse sample plots (on a $\mu g/g$ of mousse basis) are lower than those of the fresh oil because of the additional mass of seawater (80% by weight) in the water-in-oil emulsions.

Thus, in the presence of turbulence in these studies, the higher viscosity of the 80% water-in-oil mousse did not significantly affect evaporative loss of the lower molecular weight components boiling below xylene, but some reduction in evaporation was noted for intermediate molecular weight compounds (Kovat indices 800 to 1100) in the mousse. More significant differences were noted in the amounts of oil and fresh mousse that were dissolved and dispersed into the water column due to the turbulent regimes, and Table 5-7 presents selected time series water column concentrations for the two systems. The three orders of magnitude difference between the fresh oil and fresh mousse systems clearly reflects the latter's resistance towards dissolution and dispersion to droplets.

Figure 5-39 presents the glass capillary gas chromatograms on the time series oil samples from outdoor tank #5 from the Spring 1981 experiments

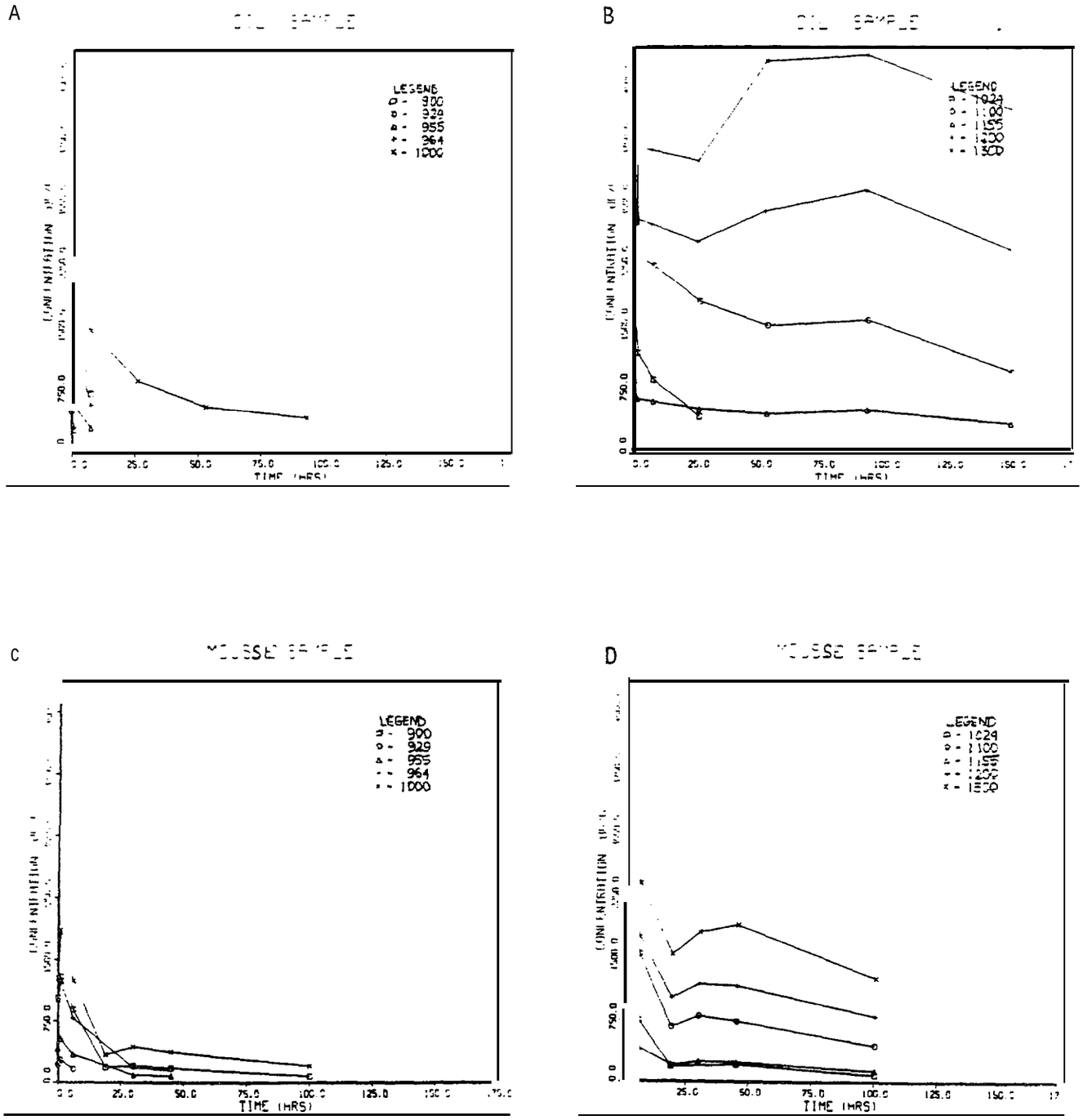



FIGURE 5-37. COMPUTER GENERATED PLOTS OF CAPILLARY FID-GC INTERMEDIATE MOLECULAR WEIGHT COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL AND MOUSSE WEATHERING UNDER SUB-ARCTIC CONDITIONS ON FLOW-THROUGH SEAWATER ENCLOSURES AT KASITSNA BAY, ALASKA. KOVAT INDICES ARE IDENTIFIED ON EACH PLOT. A AND B-FRESH PRUDHOE BAY CRUDE AND TURBULENCE; C AND D-FRESH PRUDHOE BAY MOUSSE AND TURBULENCE. TEMPERATURE AS IN FIGURE 5-3.4.

TABLE 5-7. TIME-SERIES WATER COLUMN CONCENTRATIONS (μg/l) OF DISSOLVED AND DISPERSED Hydrocarbons FROM FRESH PRUDHOE BAY CRUDE OIL AND MOUSSE WEATHERING ON FLOW-THROUGH SEAWATER ENCLOSURES (TURBULENT REGIME) AT KASITSNA BAY, ALASKA. (WATER TEMPERATURE 6°C , AIR TEMPERATURE 6-13°C). CONCENTRATIONS DETERMINED BY CAPILLARY TEMPERATURE-PROGRAMMED FID GAS CHROMATOGRAPHY.

| Fresh Oil | 0 hrs | 1 hrs | 7.5 hrs | 26 hrs | 53 hrs |
|---|---|---|---|---|---|
| Resolved Components | 7200 | 4740 | 1400 | 10110+ | 659 |
| Unresolved Complex Mixture | 3140 | 1460 | 420 | 447 | 114 |

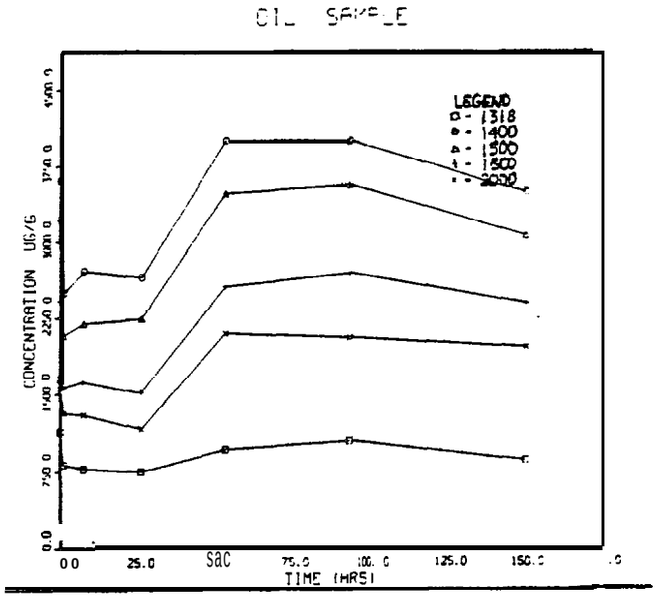
| Fresh Mousse* | 0 hrs | 1 hrs | 6 hrs | 19 hrs | 30 hrs | 45 hrs | 100 hrs |
|---|---|---|---|---|---|---|---|
| Resolved Components | 23 | 7 | 29 | 18 | 10 | 24 | 34 |
| Unresolved Complex Mixture | ND | ND | 12 | 45 | 37 | 69 | 59 |

*Water column concentrations corrected for total oil volume added as "mousse."

ND = none detected

+Possibly due to excessive oil droplet entrainment

A




B

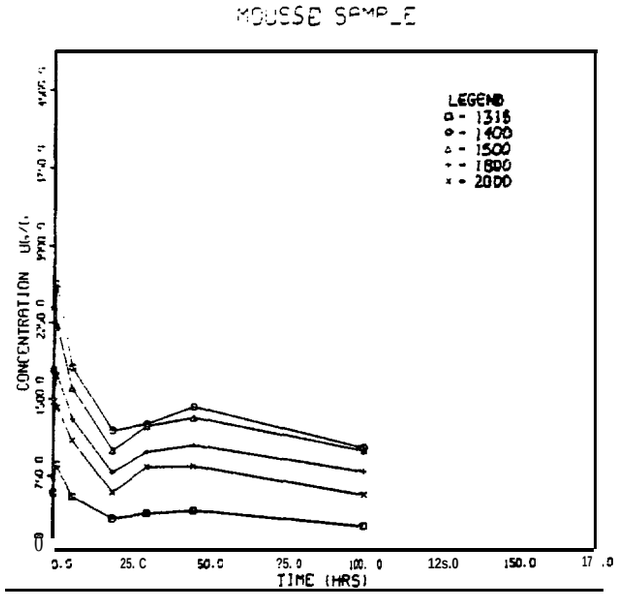



FIGURE 5-38. COMPUTER GENERATED PLOTS OF CAPILLARY FID-GC DATA ON HIGHER MOLECULAR WEIGHT COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL AND MOUSSE WEATHERING UNDER SUB-ARCTIC CONDITIONS ON FLOW-THROUGH SEAWATER ENCLOSURES AT KASITSNA BAY, ALASKA. KOVAT INDICES ARE IDENTIFIED ON EACH PLOT AND ENVIRONMENTAL CONDITIONS ARE AS IN FIGURE 5-34.

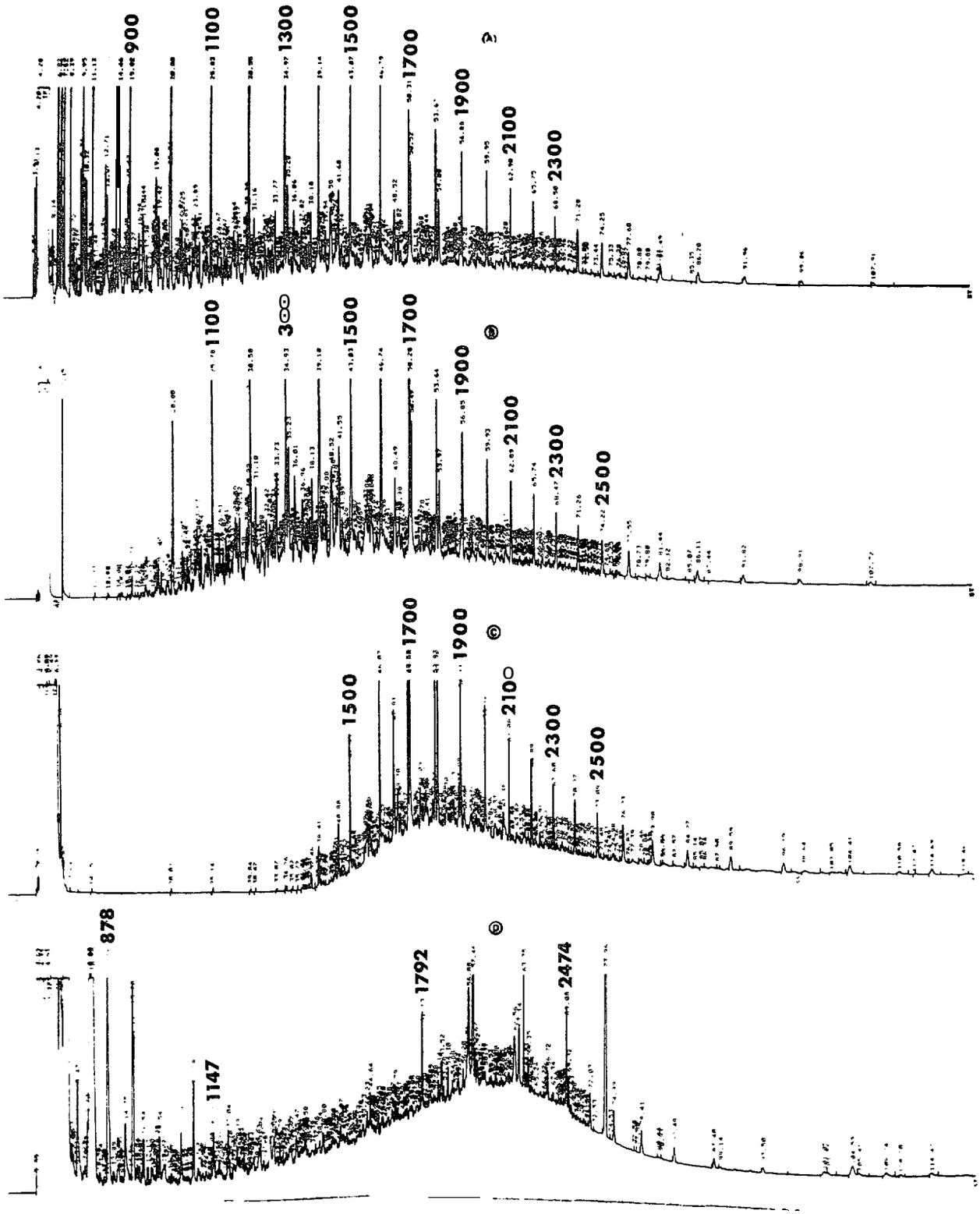



FIGURE 5-39. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON PRUDHOE BAY CRUDE OIL PLUS COREXIT (OIL:COREXIT = 20:1) WEATHERING IN THE PRESENCE OF PROPELLER DRIVEN TURBULENCE IN THE OUTDOOR FLOW-THROUGH AQUARIA (TANK #5) AT KASITSNA BAY, ALASKA. TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 1 HOURS; (B) 23 HOURS; (C) 4 MONTHS. CHROMATOGRAM D WAS OBTAINED ON THE POLAR (F3) FRACTION OBTAINED FROM AN ACIDIFIED WATER COLUMN SAMPLE AFTER 4 MONTHS OF IN SITU 'FEATHERING.

(fresh oil plus Corexit, 20:1, in the presence of turbulence). These data included to allow direct comparison to the fresh oil plus turbulence experiment in tank #1 over the same time frame as shown in Figure 5-35. As in the non Corexit fresh oil experiment, the most effective initial weathering mechanism was due to evaporation as compounds below Kovat indices 1000 were clearly lost during the first 24 hours. Visual observation of the water column extracts from this tank, however, also indicated that enhanced removal of oil into the water column occurred as a result of the dispersant. Water column extracts are undergoing analyses at this time.

4s noted above, the tanks were maintained in a flow-through condition during the period of April to October 1981 to allow indigenous microbial populations to be fully operative, and Figure 5-39C shows the chromatographic profiles obtained on the Corexit treated oil after 4 months of weathering. Interestingly, the chromatogram is nearly identical to the chromatogram in Figure 5-36C, the patchy mousse from stirred Tank 1 which was not treated with Corexit in April. As in the other case, most of the components below nC-14 have been removed by evaporation and dissolution processes during the warmer summer months, and the change in the nC-17/pristane and nC-18/phytane ratios to values of 1.1 and 1.0, respectively, illustrates the effects of microbial degradation. Surprisingly, the decrease in these ratios is not as great as that observed for Tank 1, although this is quite possibly due to the fact that the oil sample from Tank 5 was scraped from the side of the tank and not taken from the water surface. Unfortunately, some time during the four month weathering period between April and July, the water level in Tank 5 increased and overflowed and much of the oil was lost. After the water level was returned to the appropriate height in the outdoor tank, the stranded oil was then not subject to additional degradation from water-borne micro-organisms.

This observation is in line with similar findings by BLUMER et al. (1973) where they studied stranded oil on intertidal rocks from the beaches of Bermuda. In their studies, oil which was stranded in the upper intertidal zones away from the water showed only limited degradation due to bacterial processes, and weathering was limited to evaporation and photo-oxidation.

The chromatogram in Figure 5-39D shows the water column extract of the aromatic fraction under the oil after 4 months weathering during the spring and summer months. In that the tank overflowed sometime during that period, it might a priori be expected that more of the water soluble components would be lost due to air-sea exchange. Furthermore, since the tanks were maintained in a flow-through condition during this period, removal of water soluble components by advection might be anticipated. There are still significant levels of aromatic components remaining in the water column over this time period, although the lower molecular weight aromatics from benzene through naphthalene have been removed.

As noted in Table 5-6, additional time series (up to 150 hours) samples and chromatograms were obtained on the other outside tank experiments shown schematically in Figure 5-32. Some of these tank experiments are considered in Section 5.2.5 which deals with longer term microbial degradation results, and others are in various stages of analyses and computer data reduction. As such, they will not be discussed further here.

### 5.1.3 Outdoor Wave-Tank Experiments -- Kasitsna Bay

As noted above, the outdoor microbial degradation tanks were utilized for evaporation/dissolution experiments during the Spring 1981 program where turbulence was induced from propeller mixing. Even with this approach however, the turbulence regime was not entirely satisfactory and did not closely approximate that which would be observed in open ocean oil spill situations. Therefore, during the Summer 1981 program, a 2,500-L wave tank was designed and constructed on the outdoor platform supporting the trace organic geochemistry laboratory at Kasitsna Bay (Figure 5-40). The wave tank was equipped with a 7-foot diameter paddle-wheel at one end, with eight blades driven by a one horsepower electric motor via a chain/sprocket drive mechanism. To minimize contamination of water or oil samples from the construction materials of the tank itself, several precautions were taken. First, the tank was constructed of marine plywood and then coated with two coats of 2-part epoxy. After the

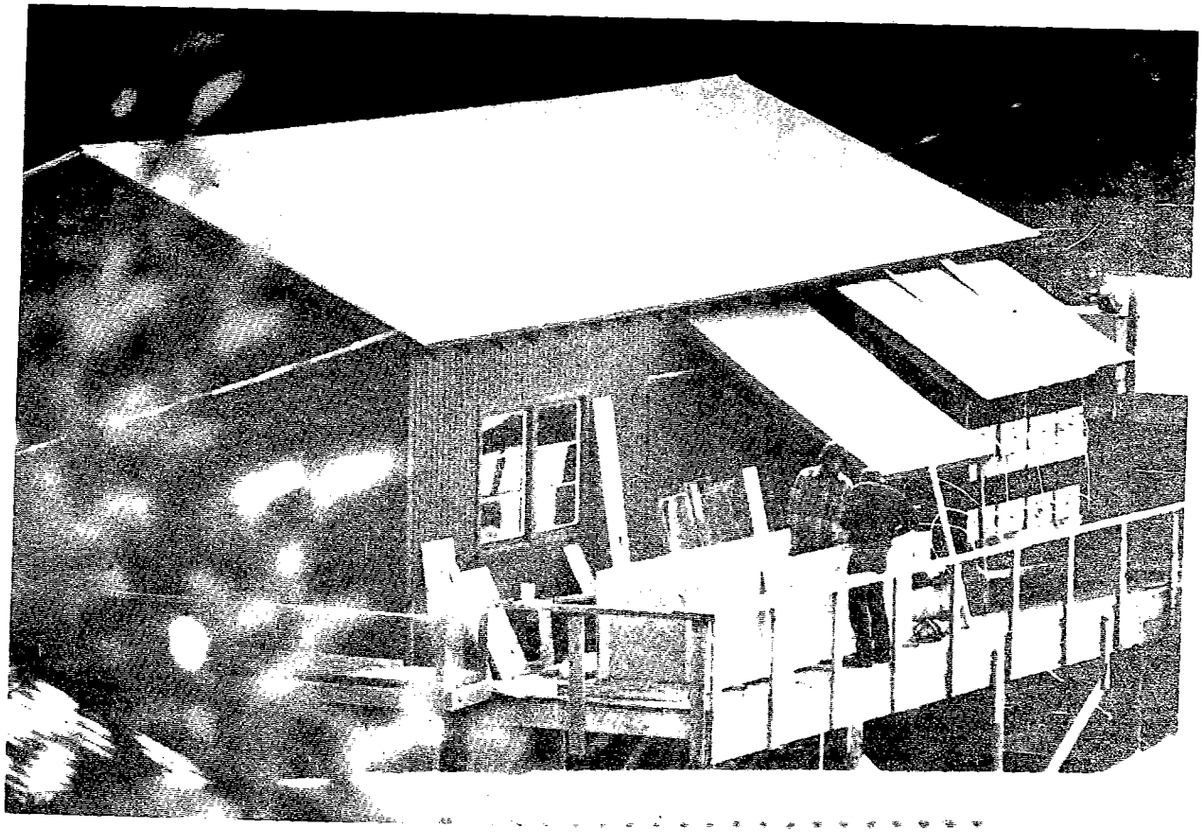


FIGURE 5-40. CONSTRUCTION OF THE 2,500 L WAVE TANK ON THE OUTDOOR PLATFORM ADJACENT TO THE ORGANIC GEOCHEMISTRY LABORATORY FACILITY AT KASITSNA BAY, ALASKA.

FIGURE 5-41. INITIATION OF 16.5 L "OIL SPILL" IN THE 2,500 L WAVE TANKAT KASITSNA BAY, ALASKA. SEA-WATER FLOW-THROUGH RATE OF 15 L/MIN PROVIDING A TANK TURNOVER RATE OF 1 TANK VOLUME PER 3 HOURS HAS BEEN MAINTAINED DURING THIS LONG-TERM EXPERIMENT. STANDING WAVES ARE GENERATED WITH THE PADDLE-WHEEL SHOWN AT THE FAR END OF THE FIGURE.

epoxy had cured for five days the tank was filled with seawater and the paddle wheel wave generation apparatus was actuated and allowed to run for 48 hours. At a reduced paddle-wheel speed of 12 rpm, 4 to 8 inch standing waves could be generated, and when progressing waves, slightly out of phase with the standing wave pattern randomly occurred, simulated wave breaking turbulence was obtained. With a seawater flow-through rate of 15 L/rein and a tank turnover of one tank volume per 3 hours, this then assured that any organics which would be leached from the cured 2-part epoxy would be flushed from the tank during this initial rinse process. Furthermore, before any actual oil weathering experiments were undertaken the tank was completely drained and then refilled with fresh seawater and allowed to run again for a period of 12 hours before initiation of the actual oil weathering studies in September 1981.

After the initial curing and check out of the tank system, 16 L of Prudhoe Bay crude oil (Figure 5-41), were spilled into the tank and extended weatheringwasthenallowedtooccur with samples being collected over a 21-day period as shown in Table 5-8. At each sampling point, Tenax® trapped air samples were obtained to monitor volatile hydrocarbon concentrations in the atmosphere at a distance of 3 to 4 inches above the slick, and 20-L water samples were obtained to measure the time dependent dissolution of lower molecular weight aromatic compounds under these more realistic open ocean conditions. Oil samples were also obtained for compound-specific concentration determinations in the resultant slick and mousse (Figure 5-42).

When the oil was initially spilled, significant quantities of 1 to 10-mm sized droplets of dispersed oil were noted in the water column (through a window installed in the side of the tank) and estimates of these dispersed oil concentrations are being obtained from examination of whole seawater extracts obtained at the time series intervals shown in Table 5-8. After approximately 12 hours the significant dispersion phenomena ceased and the oil accumulated at the far end of the wave tank away from the turbulence introduced by the paddles.

TABLE 5-8. COMPUTER LISTINGOF SAMPLES FROM WAVE TANK, KASITSNA BAY, ALASKA.

LISTING OF HISTORY DATASET PAGE 1 OCT-08-1981

EXPERIMENT: WAVE 1 PRINCIPAL INVESTIGATOR: DR
LOC PAGE: 78
STATUS: FIX
START DATE: SEP-09-1981
END DATE: OCT-08-1981

OIL WAS SPILLED IN A WAVE TANK THAT WAS CONSTRUCTED AT KASITSNA BAY, ALASKA TO DETERMINE LONG TERM EFFECTS OF TURBULENCE ON PRUDHOE BAY CRUDE.

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-08-1981

EXPERIMENT: WAVE 1
MEDIUM: OIL FRACTION TYPE: 1

| | HP-LABEL | HRS | WIND | AIR | WATER | OIL PRESENT | CONCENT | WIND SPEED | MIXING | COMMENTS | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 116 | 2 SEP-09-1981 | 0 | * | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | TIME ZERO | OIL | SAMPLE |
| 117 | 3 SEP-1 0-1981 | , | , | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 1 HOUR | OIL | SAMPLE |
| 118 | 5 SEP-10-1 981 | , | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 1 HOUR | OIL | SAMPLE |
| 119 | 7 SEP-1 0-1 981 | 0 | 0 | 15. 00 | 11. * | .00 | NO | .00 | 10.00 | WAVE TANK | 6 HOUR | OIL | SAMPLE |
| 121 | 9 SEP-10 -1981 | 12 | , | 15.00 | 11 .00 | . . . | NO | .00 | 10.00 | WAVE TANK | " " 12 HOUR | OIL | SAMPLE |
| 125 | 13 SEP-10-1981 | 24 | , | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 24 HOUR | OIL | SAMPLE |
| 131 | 27 SEP-11-1 981 | 36 | * | 15.00 | 11. * | .00 | 6a | .00 | 10.00 | WAVE TANK | 36 HOUR | OIL | SAMPLE |
| 136 | 1 SEP-11 -1981 | 48 | , | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | a m TANK | 48 HOUR | OIL | SAMPLE |
| 147 | 32 SEP-12-1981 | 72 | .8 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 3 DAY | OIL | SAMPLE |
| 161 | * SEP-15-1981 | 120 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 5 DAY | OIL | SAMPLE |
| 166 | 15 SEP-17-1981 | 172 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10. 00 | WAVE TANK | 7 DAY | OIL | SAMPLE |
| 16 | 21 SEP-20-1981 | 240 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 10 DAY | OIL | SAMPLE |
| 39 | 52 SEP-24-1981 | 336 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 14 DAY | OIL | SAMPLE |
| 85 | 11 OCT-08-1981 | 552 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 23 DAY | OIL | SAMPLE |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-08-1981

EXPERIMENT: WAVE 1
MEDIUM: AIR FRACTION TYPE: 0

| | HP-LABEL | HRS | WIND | AIR | WATER | OIL PRESENT | CONCENT | WIND SPEED | MIXING | COMMENTS | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 SEP-09-1981 | 0 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | TIME ZERO | AIR | SAMPLE |
| 0 | 0 SEP-1 0-1981 | 1 | 0 | 15. 00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 1 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-10-1 981 | 3 | 0 | 15.00 | 11.00 | .00 | NO | 0 | 10.00 | WAVE TANK | 3 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-10-1981 | 6 | 0 | 15.00 | 11.00 | .00 | NO | .99 | 10.00 | WAVE TANK | 6 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-10-1981 | 12 | * | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 12 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-10-1981 | 24 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 24 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-11-1981 | 36 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 36 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-11-1981 | 48 | * | 15. 00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 48 HOUR | AIR | SAMPLE |
| 0 | 0 SEP-12-1981 | 72 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 3 DAY | AIR | SAMPLE |
| 0 | 0 SEP-15-1981 | 120 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 5 DAY | AIR | SAMPLE |
| 0 | 0 SEP-17-1981 | 172 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 7 DAY | AIR | SAMPLE |
| 0 | 0 SEP-20-1981 | 240 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 10 DAY | AIR | SAMPLE |
| , | * SEP-24-1981 | 336 | 0 | 15.00 | 11. 00 | .00 | NO | .00 | 10.00 | WAVE TANK | 14 DAY | AIR | SAMPLE |
| 0 | 0 OCT-08-1981 | 504 | 0 | 15. 00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 21 DAY | AIR | SAMPLE |

LISTING OF EXPERIMENT DATASET PAGE 1 OCT-08-1981

EXPERIMENT: WAVE 1
MEDIUM: WATER FRACTION TYPE: 0

| | HP-LABEL | HRS | WIND | AIR | WATER | OIL | CONCENT PRESENT | WIND SPEED | MIXING | COMMENTS | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 SEP-09-1981 | 0 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | TIME ZERO | WATER | SAMPLE |
| 0 | 0 SEP-10-1981 | 1 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 1 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-10-1981 | 3 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 3 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-10-1981 | 6 | 0 | 15.00 | 11.00 | .00 | NO | .99 | 16. * | WAVE TANK | 6 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-10-1981 | 12 | 0 | 15.00 | 11.00 | .00 | NO | .99 | 10.00 | WAVE TANK | 12 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-10-1981 | 24 | 0 | 15.00 | 11.00 | .40 | NO | .00 | 10.00 | WAVE TANK | 24 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-11-1981 | 36 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 36 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-11-1981 | 48 | 0 | 15.00 | 11.00 | .*8 | NO | .00 | 10.00 | WAVE TANK | 48 HOUR | WATER | SAMPLE |
| 0 | 0 SEP-12-1981 | 72 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 3 DAY | WATER | SAMPLE |
| 0 | 0 SEP-15-1981 | 120 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 5 DAY | WATER | SAMPLE |
| 0 | 0 SEP-17-1981 | 172 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 7 DAY | WATER | SAMPLE |
| 0 | 0 SEP-20-1981 | 240 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 10 DAY | WATER | SAMPLE |
| 0 | 0 SEP-24-1981 | 336 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 14 DAY | WATER | SAMPLE |
| 0 | 0 OCT-08-1981 | 504 | 0 | 15.00 | 11.00 | .00 | NO | .00 | 10.00 | WAVE TANK | 21 DAY | WATER | SAMPLE |

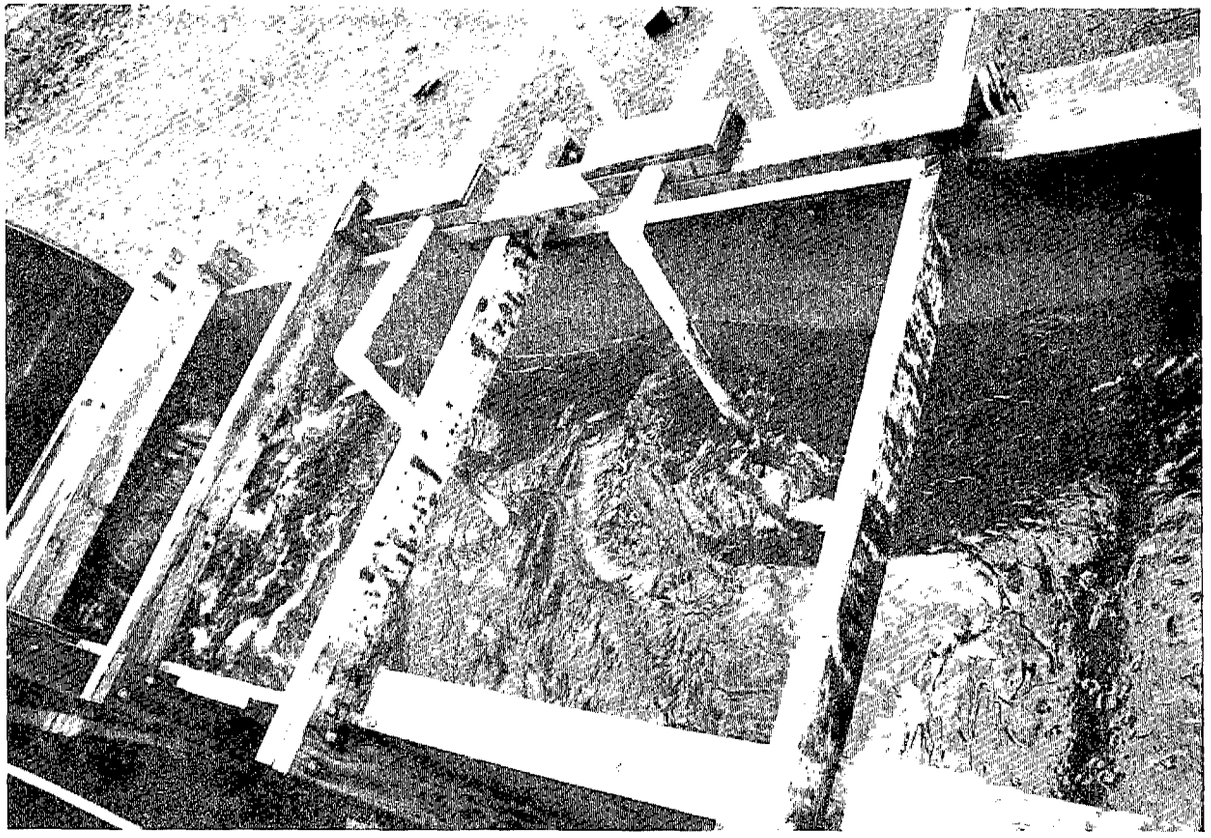


FIGURE 5-42. ACCUMULATED PRUDHOE BAY MOUSSE AT THE QUAISANT END OF THE WAVE TANK AFTER APPROXIMATELY 48 HOURS OF SUB-ARCTIC AMBIENT WEATHERING DURING SEPTEMBER 1981.

Figure 5-43 presents the flame ionization detector capillary gas chromatograms obtained on selected oil samples as a function of time. Clearly the removal of lower molecular weight aliphatics and aromatics due to evaporation/dissolution processes can be noted. While clear loss of the lower molecular weight components is evident from these chromatograms, adequate tracking of the individual compound concentrations can only be effectively completed with the utilization of the computer system. Each of the oil samples was analyzed at the Kasitsna Bay facility on the HP 5840 gas chromatograph which had been modified to allow fused silica capillary column analyses, and the digital output data were stored on magnetic tape. Upon return to the laboratory in La Jolla, CA, these tapes were then loaded into the DEC-10 computer system, and Figures 5-44 and 5-45 present computer generated compound concentrations (relative to nC-20) for selected aliphatic compounds in the whole crude oil samples. From these curves, quantitative rates for the losses of the lower molecular weight components are being obtained, and in the Section 5.1.5, predicted losses vs. observed behavior are discussed in detail. The approach of normalizing the compound speciffic data to nC-20 individual comppound concentrations on a $\mu g/g$ oil sample basis become difficult to interpret because of the factor of four increase in oil-in-water mass due to entrainment of water droplets during the formation of the stable emulsion. Evaporation and dissolution losses of n-C20 itself have been shown to be negligible during this time frame, and as such this compound can be used as an "internal standard" against which other component concentrations can be compared.

In conjunction with the oil and seawater sampling, larger volume samples of oil/mousse were obtained for density and viscosity determinations and Table 5-9 presents the kinematic viscosity data for a limited number of samples which have been worked up to date. Density and percent incorporated water data are being obtained at this time.

Although these data are still in the preliminary stages of development we anticipate that the results generated from the wave tank experiments will go further towards contributing to our overall understanding of combined

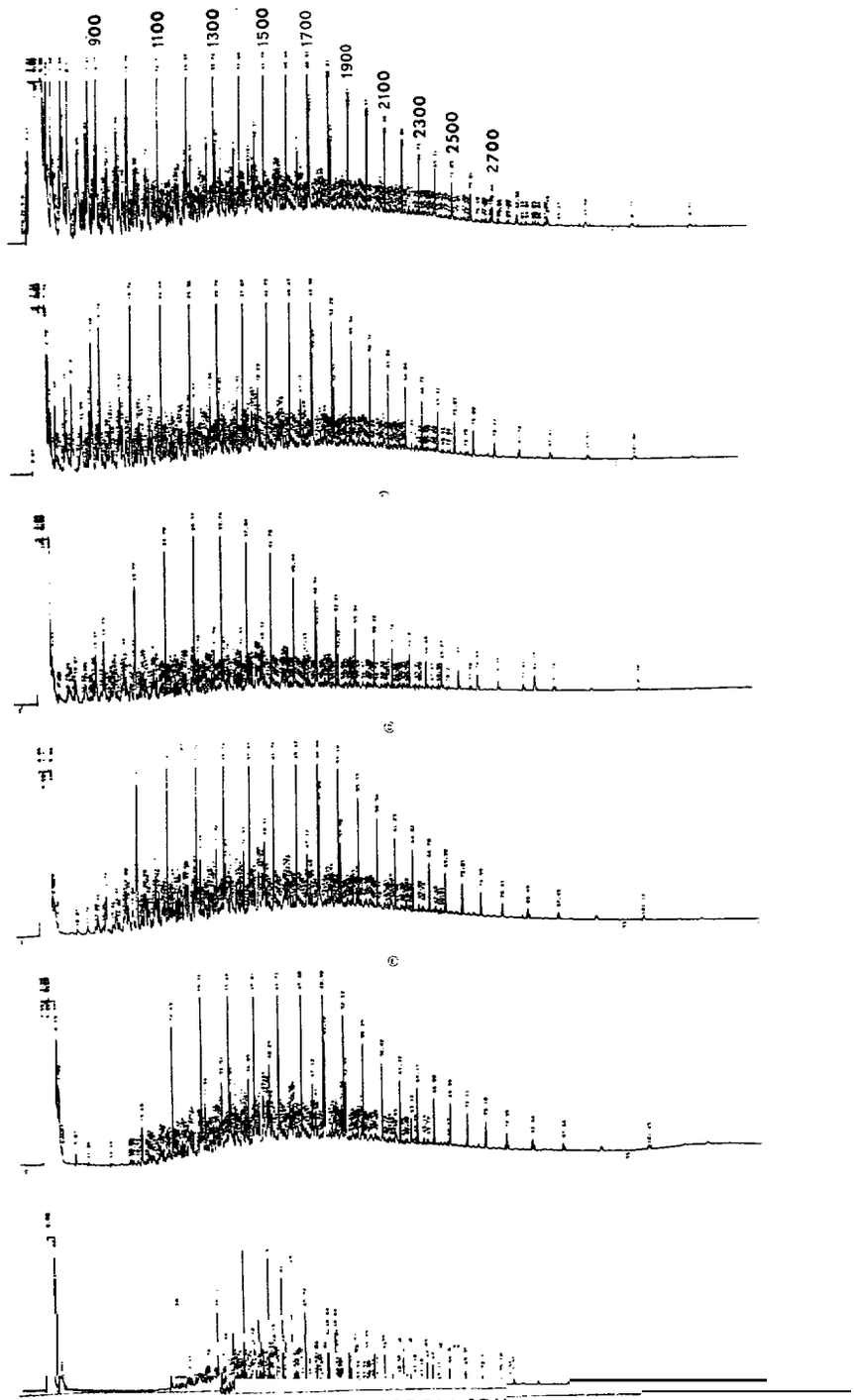



FIGURE 5-43. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON PRUDHOE BAY CRUDE OIL WEATHERING UNDER SUB-ARCTIC AMBIENT CONDITIONS IN THE 2,500 L WAVE TANK AT KASITSNA BAY. TIME-SERIES SAMPLING POINTS AFTER THE "SPILL": (A) 0 HOURS; (B) 6 HOURS; (C) 12 HOURS; (D) 48 HOURS; (E) 10 DAYS; AND (F) 23 DAYS.

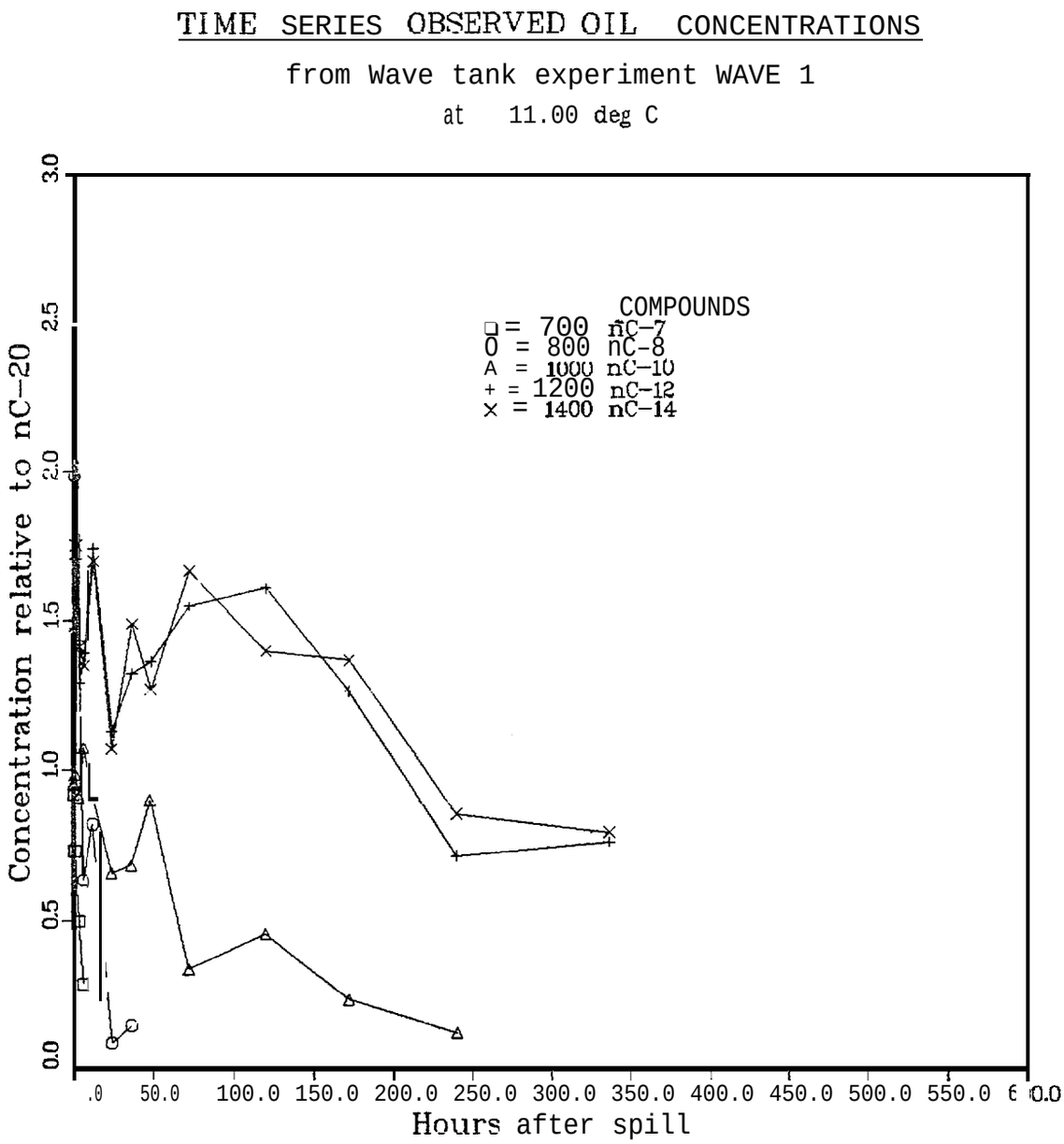



FIGURE 5-44, COMPUTER GENERATED TIME-SERIES PLOTS OF SPECIFIC COMPONENT CONCENTRATIONS REMAINING IN THE PRUDHOE BAY CRUDE OIL SLICK WEATHERING UNDER AMBIENT SUB-ARCTIC CONDITIONS IN THE 2,500 L WAVE TANK AT KASITSNA BAY. ALL CONCENTRATIONS HAVE BEEN NORMALIZED TO THE CONCENTRATION OF nC-20 AT EACH SAMPLING POINT.

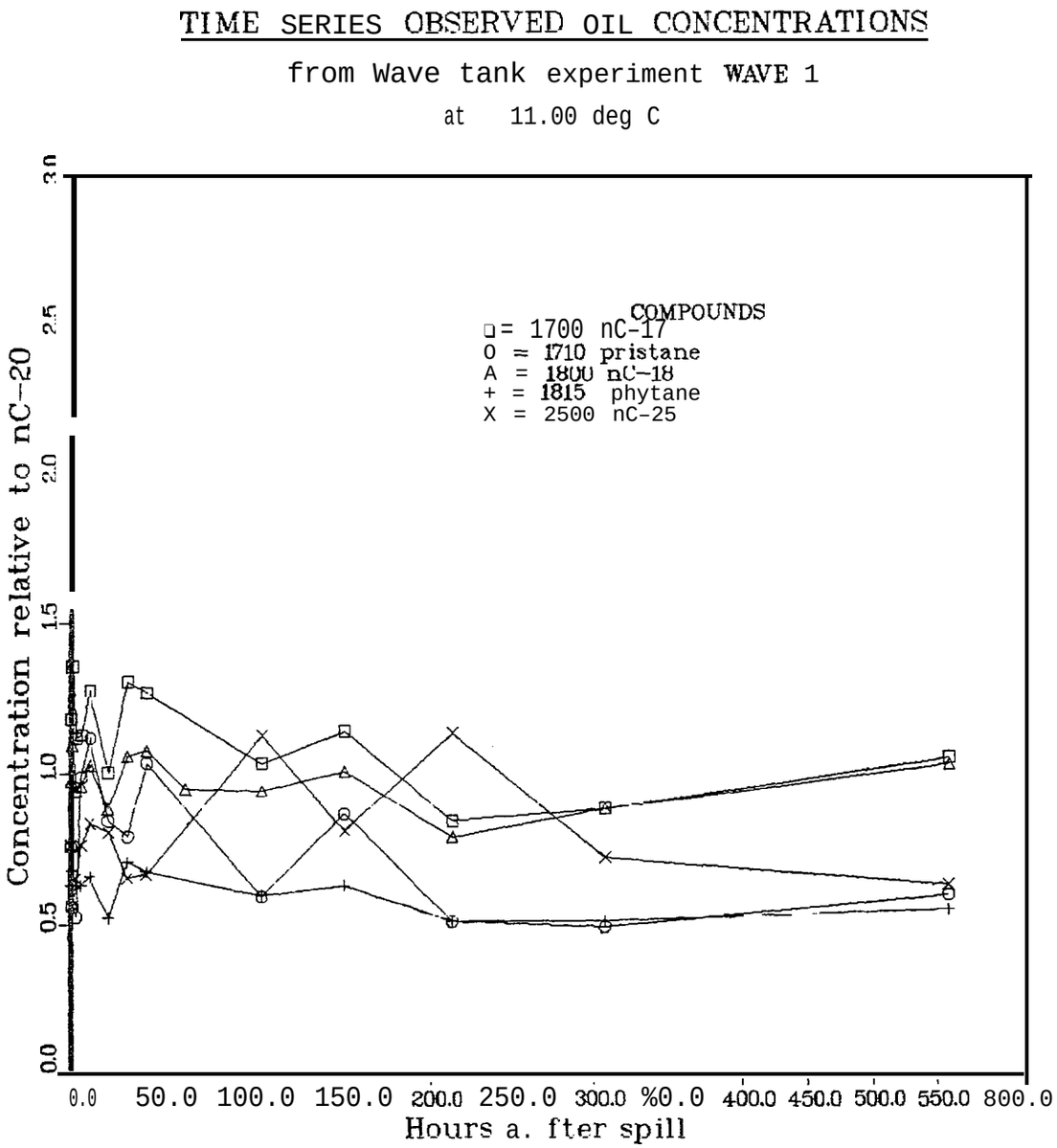



FIGURE 5-45. COMPUTER GENERATED TIME-SERIES PLOTS OF HIGHER MOLECULAR WEIGHT COMPONENT CONCENTRATIONS REMAINING IN THE PRUDHOE BAY CRUDE OIL SLICK WEATHERING UNDER AMBIENT SUB-ARCTIC CONDITIONS IN THE 2,500 L WAVE TANK AT KASITSNA BAY. ALL CONCENTRATIONS HAVE BEEN NORMALIZED TO THE CONCENTRATION OF nC-20 AT EACH SAMPLING POINT.

TABLE 5-9. KINEMATIC VISCOSITIES OF WAVE TANK MOUSSE*.

| Sampling Time | Viscosity @ 38°C (cSt) |
|---|---|
| Day 0 (fresh oil) | 21.2 |
| Day 2 | 432 |
| Day 5 | 709 |
| Day 13 | 2400 |
| Day 18 | 2615 |
| Day 27 | 2300 |

* in accordance with ASTM method D445

sub-arctic open ocean oil weathering processes than any other field experiment undertaken to date. That is, in this tank all of the interactive processes which affect, the chemical changes which occur to spilled petroleum can be allowed to act under as nearly natural conditions as possible. Specifically, the high water turn-over rate in the tank will facilitate microbial population changes from tidal cycling within Kasitsna Bay (GRIFFITH and MORIETA, 1980) to be reflected in microbial degradation processes. The position of the tank away from the protective walls of the geochemistry laboratory allows adequate sunlight exposure, and fresh water input from rain and snowfall are not affected.

During the first three weeks of the wave tank experiment, daily weather and integrated solar intensity measurements were taken (Table 5-10), and during our upcoming scheduled sampling trips to Kasitsna Bay in November and January, 1982, these measurement will be repeated. Biweekly air and water temperatures are being collected in the interim by NOAA resident laboratory manager. Because of the high turbulence in the tank and the relatively high watr turn-over rates, it is anticipated that the system will remain unfrozen during the winter months, therefore long-term weathering "open-ocean" effects during sub-arctic winter can also be evaluated. Longer term degradation of Prudhoe Bay mousse will also be possible and, as was noted above, time series samples for physical chemistry studies {viscosity, density, etc.) were collected along with samples for compositional analysis.

The edge effects from the tank walls serve to corral the test oil at one end of the tank. As a result, the oil slick appeared to behave very similarly at the oil water boundary to the edge of large open ocean oil spills such as the IXTOC-I blowout in the Gulf of Mexico (PAYNE et al., 1980). For example, at the edges of the continuous oil slick from the IXTOC spill, waves were observed to break over the oil, creating a significant dampening affect on the water surface. This wave action then either displaced the surface oil "mat" downward 4 to 5 inches, after which it resurfaced or it forced its way under the oil toward the center of the slick, where it folded over itself

TABLE 5-IQ. WEATHER OBSERVATIONS DURING WAVE TANK EXPERIMENTS -- KASITSNA BAY, ALASKA, SUMMER/FALL 1981.

| Date | Max. T | Min. T | Obsn. Temp. | Precip. | Radiation | Comments |
|---|---|---|---|---|---|---|
| 9/9/81 | -- | -- | 57°F | | (quantax $10^{20}$) | Clear |
| 9/10 | 60°F | 39°F | 45° F | | 8.0 | Cl ear |
| 9/1 ? | 56°F | 41 "F | 45° F | | 7.29 | Cl ear |
| 9/12 | 53°F | 40"F | 45°F | 0.05 in. | 5.5 | Overcast |
| 9/13 | 51°F | 40°F | 46°F | 0.06 | 5.0 | Overcast |
| 9/14 | 53°F | 44°F | 48°F | 0.09 | 3.43 | Overcast |
| 9/1 5 | 56°F | 45°F | 46°F | 0.45 | 7.68 | Overcast |
| 9/16 | 56°F | 45°F | 47° F | 0.42 | 5.36 | Overcast |
| 9/17 | 55°F | 45°F | 46°F | 0.53 | 5.05 | Overcast |
| 9/18 | 57°F | 46°F | 47°F | 0.31 | 4.96 | Overcast |
| 9/19 | 55°F | 45°F | 47°F | 0.62 | 5.63 | Overcast |
| 9/20 | 55°F | 46°F | 47° F | | 6.57 | Partly Cloudy |
| 9/21 | 55°F | 42°F | 45°F | | 6.95 | Partly Cloudy |
| 9/22 | 49°F | 36°F | 40"F | | 8.08 | Cl ear |
| 9/23 | 53°F | 45°F | 37°F | | 7.25 | Partly Cloud |
| 9/24 | 48°F | 38°F | 45° F | | 6.05 | Partly Cloudy |
| 9/25 | 48°F | 38°F | 35°F | | Missed | Snow Pellets |
| 9/26 | Missed | | | | | Rain |
| 9/27 | 50"F | 42°F | 45° F | 0.06 | 5.50 | Rain |
| 9/28 | 48°F | 36°F | 42° F | | 6.3 | Rain |
| 9/29 | 45°F | 35°F | 38° F | | 6.27 | Snow-No accumulation |
| 9/30 | 44°F | 35°F | 37°F | | 7.05 | Snow-No accumulation |

Observations made at 5:00 PM Local time

enhancing incorporation of water droplets (PAYNE, 1981). Similar behavior was observed in the wave tank.

As additional samples are obtained during the November and January, 1981 experiments, longer term weathering phenomena (combined microbial, photochemical, dispersion and emulsification processes) will be elucidated. Further, as the water samples obtained during the first 24 days are examined, estimates on the percent of the slick lost due to the initial dispersive action of the wave turbulence may be obtained. Ultimately, these data will be used in conjunction with predicted behavior from the oil weathering model for incorporation of dispersive phenomena into the overall oil mass-balance considerations. Examples of preliminary matches of predicted vs observed losses due to evaporation/dissolution are presented in Section 5.1.5.

### 5.1.4 Determination of Liquid/Liquid Partition Coefficients and Water Solubilities of Component Petroleum Hydrocarbons as a Function of Temperature

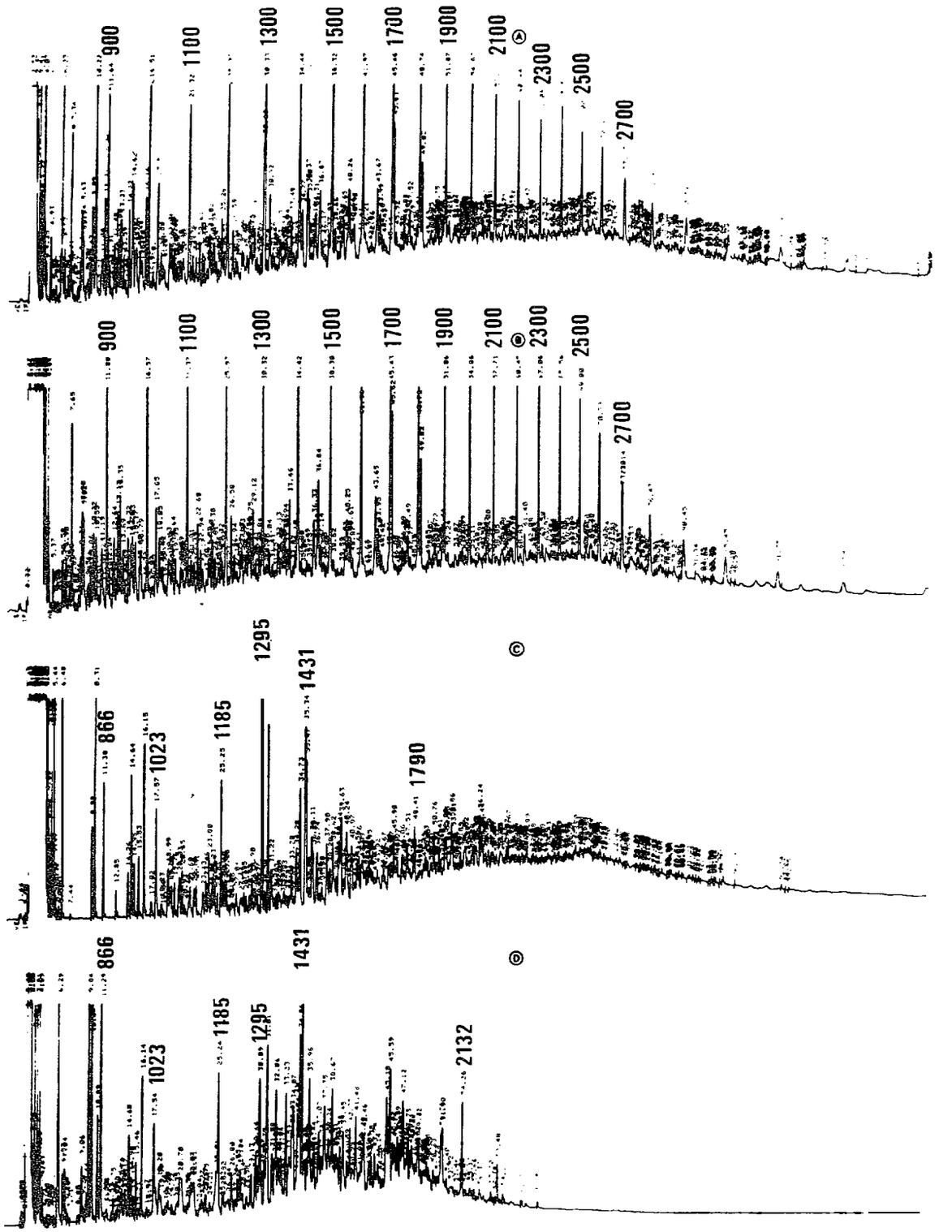
In order to adequately predict evaporation/dissolution phenomena with the oil weathering model, thermodynamic data in the form of equilibrium distribution coefficients are required to describe interphase mass transfer. These data are typically referred to as Henry's Law coefficients for evaporation or liquid-liquid partition coefficients (M-values) for dissolution. These data are used to describe how far from equilibrium the three phases are in terms of concentrations, and the departure from equilibrium measured on an arbitrary scale multiplied by the appropriate mass transfer coefficients yield the mass flux across the phase boundary from oil into the water and atmosphere.

To determine the liquid-liquid partition coefficients (M-values) for all of the components of interest in Prudhoe Bay crude oil, a series of equilibrium experiments were undertaken at 3, 13 and 23°C. In these experiments known volumes of oil and water were equilibrated in separatory funnels for 48 hours, with their phases being vigorously shaken at time zero and then allowed

to settle with occasional swirling over the first 24-hour period. Additional mixing (swirling) was done 13 hours before sampling and the phases were allowed to separate without further agitation. Water and oil phase samples were then removed and the samples were extracted with equal volumes of methylene chloride (800 ml).

During initial attempts at M-value determinations, a number of problems were encountered due to the formation of 1 to 5 $\mu$m micelles of dispersed oil in the water column phase, and this problem was discussed in depth in Appendix A. Incorporation of micelles into the aqueous phase led to anomalously high levels of "dissolved" petroleum hydrocarbons (exceeding volubility limits in some cases) in the aqueous phase. This micelle phenomenon yielded M-value partition coefficients which were anomalously low, and with these M-values initially predicted rates of dissolution of higher molecular weight components were too high. In addition to the microscopic examinations of the aqueous phases from these M-value experiments which confirmed the presence of micelles, indirect evidence of micelle formation was obtained by the presence of higher molecular weight n-alkanes in the aqueous phase. These compounds have extremely limited water solubilities (less than 0.$ $\mu$g/L for compounds with molecular weight greater than nC-18; SUTTON AND CALDER, 1974) and their presence in water column extracts were as evidence of micelle formation.

Because of these initial difficulties due to the oil-in-water dispersions, a number of additional M-value experiments were then undertaken where the oil and water phases were not as vigorously agitated. Figure 5-46 presents FID capillary gas chromatograms of (A) the whole unfractionated oil, (B) the aliphatic fraction of the surface oil , (C) the aromatic fraction of the surface oil, and (D) the unfractionated water column extract from under the slick. Initially, M-value determinations were attempted using L/C fractionated water column samples; however, only trace levels of aliphatic components were detected in the fractionated samples, and some breakthrough of the lower molecular weight aromatics (benzene, toluene, xylenes, and ethylbenzene)




'FIGURE 5-46. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OBTAINED ON SPECIFIC SAMPLES USED FOR COMPOUND SPECIFIC OIL/SEAWATER PARTITION COEFFICIENT (M VALUE) DETERMINATIONS. (A) UNFRACTIONED OIL; (B) ALIPHATIC FRACTION OF THE SURFACE OIL; (C) AROMATIC FRACTION OF THE SURFACE OIL AND (D) THE UNFRACTIONATED WATER COLUMN EXTRACT BENEATH THE SLICK. (KOVAT INDICES ARE SHOWN ABOVE MAJOR PEAKS).

during the liquid column chromatography was noted. This Phenomenon complicated ratio determinations for oil phase and water phase concentrations, so later M-value determinations were completed using unfractionated water column samples. In that the majority of components which are subject to dissolution are aromatic hydrocarbons, this procedure does not limit the data obtained. Figure 5-47 presents the reconstructed ion gas chromatogram of the water column extract, and Table 5-11 lists the identifications of the aromatic compounds of interest.

From this latest series of partition coefficient experiments, M-values for individual compounds at various temperatures were obtained, Table 5-12 presenting the calculated values for oil/seawater partitioning at 3 and 23°C. These values were obtained using a sub-program in the overall oil weathering model called M-VAL, which matches the oil phase and water phase specific compound concentrations by Kovat retention indices. Also shown in Table 5-12 are the identifications of selected compounds as determined by the GC/MS analysis of the water column and fractionated (F2) oil sample extracts.

These values are then used in the evaporation/dissolution oil weathering model as described in Section 4.0 of this report. The following Section 5.1.5 presents the results of predicted vs observed evaporation and dissolution behavior for specific compounds as measured in the evaporation/dissolution chamber at 23 and 3°C and in the wave tank experiments completed at Kasitsna Bay.

### 5.1.5 Predicted vs Observed Evaporation/Dissolution Results

As described in detail in the modeling section (4.0), two distinctly different modeling approaches are being taken in our efforts to predict oil weathering behavior. The component-specific model predicts individual compound concentrations in the slick as a function of time and the pseudo-compound (or fractional-distillate on cut) approach allows predictions of overall oil mass balance. Output data from the component-specific approach predicts time series concentrations in the slick, air and water column based on

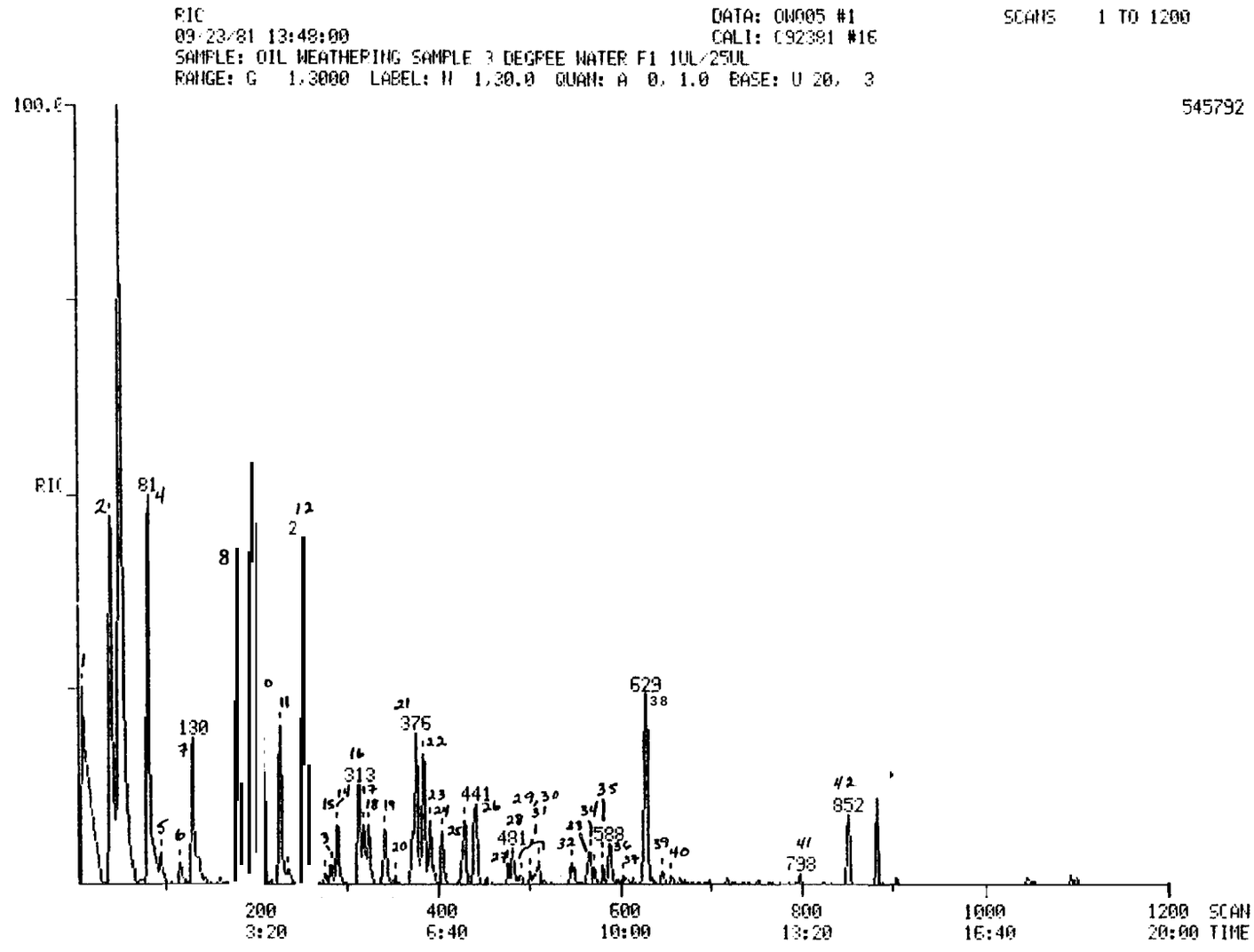



FIGURE 5-47. RECONSTRUCTED ION CHROMATOGRAM (RIC) FROM CAPILLARY GC/MS ANALYSES OF WATER COLUMN EXTRACTS FROM OIL/SEAWATER PARTITION COEFFICIENT EXPERIMENTS. IDENTIFICATIONS OF THE NUMBERED PEAKS IN THE CHROMATOGRAM ARE PRESENTED IN TABLE 5-11.

thermodynamic properties such as Henry's Law of constants, liquid-liquid partitioning coefficients and mass transfer coefficients.

Predicted vs observed water column concentrations for benzene, cyclohexane and toluene were generated in the evaporation/dissolution chamber and Preliminary results from these studies were described in our November 1980 Interim Quarterly Report. A much more sophisticated evaporation-dissolution model has since been generated, allowing prediction of specific compound concentrations in the water column beneath an oil slick.

A significant improvement in the model has come from the utilization of Henry's law coefficients in the calculation of the mass-transfer coefficient at the oil-air interface. Previously, only benzene, toluene and cyclohexane were modeled, and since these compounds all have similar volatilities, they behave in a similar manner. However, when considering compounds which are much less volatile (e.g., naphthalane), water column concentrations will peak much later than the concentrations of benezene, toluene, and cyclohexane. This is due to the fact that the less volatile compounds leave the oil-water phases much more slowly, allowing more time to transfer from the oil to the water phase. The equations being used to predict water and oil column concentrations are those presented in the November Quarterly (PAYNE et al., 1980), with changes being made only to the over-all mass transfer coefficient at the oil-air interface. Tables 5-13 through 5-24 present specific numerical output for six selected compounds examined in the evaporation and dissolution experiments at 3 and 21°C. The output presented in these tables is all the information needed to calculate the water and oil concentrations. The KW, KA, and KO values are individual-phase mass transfer coefficients; the M-value and Henry's law coefficient was derived from the Antoine vapor pressure equation and the constants, ANTA, ANTB, and ANTC are from REID et al. (1977). The quantities A through Z2 on the output are intermediate results used to calculate the final concentrations. For the water column concentrations:

$$y = Z1*EXP(D1*TIME) + Z2*EXP(D2*TIME)$$

TABLE 5-12. OIL/SEAWATER LIQUID-LIQUID PARTITION COEFFICIENTS (M-VALUES) DETERMINED AT 3 AND 23°C. (Continued).

M - Values Determined at 3° and 23° (continued)

| Kovats | M - Values | | | Compounds |
|---|---|---|---|---|
| | $3^{o}$oil/$3^{o}$-wat | $23^{o2}$-oil/$23^{o1}$-wat | $23^{o2}$-oil/$23^{o2}$-wat | |
| 1589 | 7,880 | 1,730 | 1,440 | |
| 1642 | 13,400 | 2,150 | 2,160 | |
| 1715 | 71,800 | ------ | 9,460 | methyl fluorene |
| 1743 | ------ | 8,030 | 6,950 | |
| 1841 | 9,760 | 5,270 | 4,080 | |
| 1867 | 30,100 | 11,900 | 10,800 | methyl dibenzothiophene |
| 2154 | ------ | 5,280 | 3,920 | |

TABLE 5-12. OIL/SEAWATER LIQUID-LIQUID PARTITION COEFFICIENTS (M-VALUES) DETERMINED AT 3 AND 23°C.

M - Values Determined at 3° and 23°

| Kovats | M - Values | | | Compounds |
|---|---|---|---|---|
| | 3°oil/3°-wat | 23°2-oil /23°1-wat | 23°2-oi' /23°2-wat | |
| 765 | 652 | 688 | 583 | tol uene |
| 859 | 2,660 | 2,690 | 2,250 | ethyl benzene |
| 867 | 3,030 | 3,060 | 2,550 | p-xyl ene |
| .992 | 2,730 | 2,260 | 1,900 | o-xyl ene |
| 923 | 8,840 | 8,520 | 7,310 | cumene |
| 953 | 13,400 | 14,645 | 14,800 | n-propyl benzene |
| 961 | 12,100 | 10,800 | 9,370 | ethyl methyl benzene |
| 967 | 14,900 | 13,600 | 11,800 | mesitylene |
| 979 | 10,800 | 9,350 | 7,840 | $C_3$ benzene |
| 992 | ------ | 11,200 | 9,080 | C3 benzene |
| 1021 | 14,800 ' | 5,830 | 9,660 | p-cymene |
| 1035 | 3,530 | 1,990 | 2,450 | naphthal ene |
| 1066 | 68,800 | ------ | 38,800 | $C_4$ benzene |
| 1086 | 10,740 | 4,290 | 2,530 | ethyl dimethyl benzene |
| 1121 | 57,300 | 6,530 | 12,600 | tetramethyl benzene |
| 1163 | ------ | 26,300 | 22,000 | naphthal ene |
| 1185 | 5,570 | 6,720 | 6,900 | naphthal ene |
| 1199 | ------ | 19,900 | 15,500 | $C_5$ benzene unsaturated |
| 1237 | ------ | 5,180 | 5,240 | 2-methyl naphthalene |
| 1284 | 3,900 | 1,110 | 1,070 | $C_6$ benzene |
| 1296 | 35,800 | 14,900 | 11,000 | 2-met hylnaphthal ene |
| 1316 | 30,400 | 5,320 | 4,830 | 1-methylnaphthal ene |
| 1338 | ------ | 4,690 | 4,060 | |
| 1343 | 10,100 | 951 | 951 | |
| 1371 | 3,210 | 466 | 424 | $C_7$ benzene |
| 1425 | 128,000 | ------ | 93,400 | dimethyl na phthal ene |
| 1428 | 67,000 | ------ | 23,200 | dimethylnaphthal ene |
| 1461 | ------ | 44,500 | 53,900 | |
| 1469 | 5,670 | 889 | 1,000 | n-octyl benzene |
| 1476 | 58,300 | 9,030 | 6,920 | C3 naphthalene |
| 1499 | ------ | 6,910 | 6,590 | |
| 1510 | 23,300 | 7,130 | 6,460 | 2-isopropylnaphtha lene |
| 1523 | 47,300 | 6,120 | 6,610 | |
| 1528 | ------ | 10,000 | 10,600 | l-isopropyl naphthalene |
| 1537 | 47,400 | 7,930 | 6,660 | trimethyl naphthalene |
| 1546 | 4,600 | 925 | 714 | |

TABLE 5-11. COMPOUNDS IDENTIFIED BY GC/MS ANALYSES OF WATER COLUMN EXTRACTS FROM OIL/SEAWATER PARTITION COEFFICIENT (M-VALUE) EXPERIMENTS.

| | |
|---|---|
| 1 | methyl chloride (solvent) |
| 2 | ethylbenzene |
| 3 | p-xylene |
| 4- | o-xylene |
| 5 | nonane |
| 6 | $C_9H_{16}$ |
| 7 | cumene |
| 8 | n-propylbenzene |
| 9 | ethyl methyl benzene |
| 10 | trimethylbenzene |
| 11,12 | $C_3$ benzenes |
| 13 | decane |
| 14,15 | $C_4$ benzenes |
| 16-18 | $C_3$ benzenes |
| 19 | unsaturated $C_3$ benzene |
| 20 | methyl isopropyl benzene |
| 21 | methylpropyl benzene |
| 22 | $C_4$ benzene |
| 23 | ethyl dimethyl benzene |
| 24-28 | $C_4$ benzenes |
| 29 | t-amylbenzene |
| 30 | $C_4$ benzene |
| 31 | tetramethylbenzene |
| 32,33 | unsaturated $C_4$ benzenes |
| 34 | $C_4$ benzene |
| 35 | $C_5$ benzene |
| 36 | tetralin |
| 37 | $C_5$ benzene |
| 38 | naphthalene |
| 39 | $C_2$ indane |
| 40 | unsaturated $C_5$ benzene (possibly a methyltetralin or a $C_2$ indane) |
| 41 | methyltetralin |
| 42 | Z-methyl naphthalene |
| 43 | 3-methylnaphthalene |

TABLE 5-13. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 854 ETHYLBENZENE.

```
STIRRED TANK MODEL FOR KOVAT 857,ETHYLBENZENE
INON THE KEYBOARD. KW =  3.000E+00 , KA =  1.506E+03 , KO =  1.000E+00 CM/HR
N (OIL/WATER) =  2.660E+03, HENRYS LAW (A 111/OIL) =  4.040E-03 DIMENSIONLESS , AT 3.000E+00 DEG C
ANTA =  1.602E+01, ANTO =  3.298E+03, ANTC = -5.995E+01
MOLE WT OF OIL = 2.880E+02 , DENSITY =  8.800E-01 GM/CC
VO =  2.000E+02 ML,  VW = 3.000E+04 ML
X/ZERO = 4.740E+02 MICROGRAMS/GRAM OF OIL ; AREA =  6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL =  2.997E+00 CM/HR
OVER-ALL KO AT OIL-AIR =  5.725E-02 CM/HR
A = -6.164E-02, B =  2.317E-05
C =  9.245E+00, D = -1.801E-01
E =  1.220E-01
D1 = -5.905E-02, D2 = -1.819E-01
C1 =  6.920E+00 , C2 =  4.671E+02
Z1 =  9.001E-02, Z2 = -V .001E-02
WATER CONCENTRATION PEAKS AT  9.109E+00 nouns
WHERE THE WATER CONCENTRATION =  3.501E-02, AND THE OIL CONCENTRATION =  9.312E+01
AND THE CONCENTRATION RATIO (OIL/WATER) =  2.660E+03
```

| noun | H20 | OIL |
|---|---|---|
| 0.20 | 2.144E-03 | 4.572E+02 |
| 0.40 | 4.186E-03 | 4.411E+02 |
| 0.60 | 6.130E-03 | 4.255E+02 |
| 0.00 | 7.979E-03 | 4.104E+02 |
| 1.00 | 9.738E-03 | 3.959E+02 |
| 1.20 | 1.141E-02 | 3.819E+02 |
| 1.40 | 1.300E-02 | 3.685E+02 |
| 1.60 | 1.451E-02 | 3.554E+02 |
| 1.80 | 1.594E-02 | 3.429E+02 |
| 2.00 | 1.729E-02 | 3.308E+02 |
| 2.25 | 1.889E-02 | 3.163E+02 |
| 2.50 | 2.037E-02 | 3.024E+02 |
| 2.75 | 2.176E-02 | 2.891E+02 |
| 3.00 | 2.306E-02 | 2.765E+02 |
| 3.25 | 2.426E-02 | 2.643E+02 |
| 3.50 | 2.537E-02 | 2.528E+02 |
| 3.75 | 2.640E-02 | 2.417E+02 |
| 4.00 | 2.736E-02 | 2.311E+02 |
| 4.25 | 2.824E-02 | 2.210E+02 |
| 4.50 | 2.905E-02 | 2.113E+02 |
| 6.00 | 3.263E-02 | 1.617E+02 |
| 8.00 | 3.475E-02 | 1.133E+02 |
| 10.00 | 3.487E-02 | 7.958E+01 |
| 12.00 | 3.374E-02 | 5.605E+01 |
| 14.00 | 3.188E-02 | 3.961E+01 |
| 16.00 | 2.964E-02 | 2.810E+01 |
| 18.00 | 2.724E-02 | 2.004E+01 |
| 20.00 | 2.482E-02 | 1.439E+01 |
| 22.00 | 2.248E-02 | 1.040E+01 |
| 24.00 | 2.026E-02 | 7.585E+00 |
| 26.00 | 1.819E-02 | 5.589E+00 |
| 211.00 | 1.629E-02 | 4.165E+00 |
| 30.(N) | 1.456E-02 | 3.144E+00 |
| 32.00 | 1.299E-02 | 2.406E+00 |
| 34.00 | 1.158E-02 | 1.868E+00 |
| 36.ON | 1.031E-02 | 1.472E+00 |
| 38.00 | 9.169E-03 | 1.177E+00 |
| 40.00 | 8.152E-03 | 9.552E-01 |
| 42.00 | 7.244E-03 | 7.853E-01 |
| 44.00 | 6.436E-03 | 6.545E-01 |

TABLE 5-14. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 867, P-XYLENE.

STIRRED TANK MODEL FOR KOVAT 867, P-XYLENE
FROM THE KEYBOARD, KW = -3.000E+00, KA = 1.500E+03 . KO = 1.000E+00CM/HR
M (OIL/WATER) = 3.030E+03, HENRYS LAW (AIR/OIL) . 4.032E-05 DIMENSIONLESS, AT 3.000E+00 DEG C
ANTA = 1.609E+01, ANTB = 3.347E+03, ANTC = -5.780E+01
MOLE WT OF OIL . 2.880E+02, DENSITY = 0.900 GM/CC
VO . 2.000E+02 ML., VW = 3.000E+04 ML
XZERO = 1.794E+03 MICROGRAMS/GRAM OF OIL, AREA = 6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL . 2.997E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 5.702E-02 CM/HR
A = -6.164E-02, B = 2.034E-05
C = 9.246E+00, D = -1.790E-01
E = 1.205E-01
D1 = -6.006E-02, D2 = -1.806E-01
C1 = 2.355E+01, C2 = 1.770E+03
Z1 = 3.029E-01, Z2 = -3.029E-01
WATER CONCENTRATION PEAKS AT 9.135E+00 HOURS
WHERE THE WATER CONCENTRATION , 1.160E-01, AND THE OIL CONCENTRATION = 3.538E+02
AND THE CONCENTRATION RATIO (OIL/WATER) , 3.030E+03

| noun | H20 | OIL |
|---|---|---|
| 0.20 | 7.126E-03 | 1.711E+03 |
| 0.40 | 1.391E-02 | 1.670E+03 |
| 0.60 | 2.030E-02 | 1.611E+03 |
| 0.80 | 2.653E-02 | 1.555E+03 |
| 1.00 | 3.238E-02 | 1.500E+03 |
| 1.20 | 3.794E-02 | 1.447E+03 |
| 1.40 | 4.322E-02 | 1.397E+03 |
| 1.60 | 4.824E-02 | 1.348E+03 |
| 1.00 | 5.300E-02 | 1.300E+03 |
| 2.00 | 5.752E-02 | 1.255E+03 |
| 2.25 | 6.203E-02 | 1.200E+03 |
| 2.50 | 6.779E-02 | 1.140E+03 |
| 2.75 | 7.242E-02 | 1.098E+03 |
| 3.00 | 7.673E-02 | 1.050E+03 |
| 3.25 | 8.074E-02 | 1.004E+03 |
| 3.50 | 8.446E-02 | 9.602E+02 |
| 3.75 | 0.791E-02 | 9.184E+02 |
| 4.00 | 9.110E-02 | 8.784E+02 |
| 4.25 | 9.404E-02 | 8.402E+02 |
| 4.50 | 9.675E-02 | 8.036E+02 |
| 6.00 | 1.087E-01 | 6.157E+02 |
| 0.00 | 1.159E-01 | 4.322E+02 |
| 10.00 | 1.163E-01 | 3.040E+02 |
| 12.00 | 1.126E-01 | 2.143E+02 |
| 14.00 | 1.065E-01 | 1.515E+02 |
| 16.00 | 9.901E-02 | 1.075E+02 |
| 18.00 | 9.100E-02 | 7.664E+01 |
| 20.00 | 8.294E-02 | 5.493E+01 |
| 22.00 | 7.510E-02 | 3.962E+01 |
| 24.00 | 6.769E-02 | 2.881E+01 |
| 26.00 | 6.078E-02 | 2.113E+01 |
| 28.00 | 5.443E-02 | 1.567E+01 |
| 30.00 | 4.863E-02 | 1.175E+01 |
| 32.00 | 4.338E-02 | 8.927E+00 |
| 34.00 | 3.865E-02 | 6.876E+00 |
| 36.00 | 3.440E-02 | 5.372E+00 |
| 38.00 | 3.059E-02 | 4.259E+00 |
| 40.00 | 2.719E-02 | 3.424E+00 |
| 42.00 | 2.416E-02 | 2.791E+00 |
| 44.00 | 2.145E-02 | 2.304E+00 |

TABLE 5-15. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1021, 1-METHYL-4-ISOPROPYLBENZENE.

ST I RRED TANK MODEL FOR KOVAT 1021, 1-METHYL-4- 1 SOPROPYLB
FROM THE KEYBOARD, KW = 3.000E+00 . KA = 1. 500E+03 . KO = 1. 000E+00 CM/HR
M ( u I L/ WATER ) = I.480E+04. HENRYS LAW (A IR/OI L) . 5.463E-06 DI MENS IONLESS . AT 3.000E+00 DEC C
ANTA = 7 . 594E+01 , ANTB = 3 539E+03 , ANTC = -7.0 10E+0 1
MOLE WT OF O I L = 2. 880E+02. DENS I TY = n. 800E-0 1 GM/CC
VO = 2.000E+02ML, VU = 3 : 000E+04ML
XZEHO = 4. 530E+02 MI CROGRAMS/GRAM OF OI L , AREA = 6. 170E+02 CM*CM
OVER-ALL KW AT WATER-OI L = 2.999 E+00 CM/HR
OVER-AI L KO AT oil,-AtN = o. 127E-03 CM/ HN
A = -6.169 E-02, U = 4.160E-06
c = 9,253E+00, D = -2.570E-02
R = 3.807E-02
D1 = -2.466 E-02, D2 = -6.273E-02
c1 = 4.406 E+02, C2 = 1.239E+01
Z1 = 4.959 E-02, Z2 = -4. 959E-02
WATER CONCENTRAT 10N PEAKS AT 2.453E+01 nouns
WHERE THE WATER CONCENTRATION = 1.644E-02. AND THE OIL CONCENTRATION = 2 .433E+02
AN D THE CONCENTRATIONRAT I O ( O I L/WATER ) = I . 480E+04

| noun | H20 | 011. |
|---|---|---|
| 0.20 | 3.743E-04 | 4. 507E+02 |
| 0 .40 | 7. 422E-04 | 4. 484E+02 |
| 0.60 | I . 104K-0:1 | 4.40 1E+02 |
| 0.80 | 1. 459E-03 | 4.438E+02 |
| 1.ON | 1.808E-03 | 4.41 5E+02 |
| 1.20 | 2.150E-03 | 4. 393E+02 |
| 1.40 | 2.467E-03 | 4. 370E+02 |
| 1.60 | 2.817E-03 | 4. 348E+02 |
| 1.80 | 3.142E-03 | 4. 325E+02 |
| 2.00 | 3.461E-03 | 4. 303E+02 |
| 2.25 | 3.852E-03 | 4. 276E+02 |
| 2.50 | 4.233E-03 | 4. 249E+02 |
| 2.75 | 4. 607E-03 | 4. 222E+02 |
| 3.00 | 4.97 1E-03 | 4. I 95E+02 |
| 3.25 | 5.320E-03 | 4. I 68E+02 |
| 3.50 | 5.676E-03 | 4. 1 4! E+02 |
| 3.75 | 6.0 I 6E-03 | 4. I I 5E+02 |
| 4.00 | 6. 348E-03 | 4. 089E+02 |
| 4.25 | 6, 672E-03 | 4. 063E+02 |
| 4. 50 | 6. 989E-03 | 4.037E+02 |
| 6.00 | 11. 735E-03 | 3.885E+02 |
| n.00 | 1 .0691,: -02 | 3.692E+02 |
| 10.00 | I ·227E-02 | 3.509E+02 |
| 12.00 | 1.353E-02 | 3.336E+02 |
| 14.00 | 1.451E-02 | 3.171E+02 |
| 16.00 | 1.525E-02 | 3.015E+02 |
| III. 00 | 1.578E-02 | 2.867E+02 |
| 20. on | 1.614E-02 | 2.726E+02 |
| 22.00 | 1.635E-02 | 2.593E+02 |
| 24.00 | 1.644E-02 | 2.466E+02 |
| 26.00 | 1 .641 E-02 | 2.345E+02 |
| 28.00 | 1. 630E-02 | 2.231E+02 |
| 30.00 | I.612E-02 | 2.122E+02 |
| 32.00 | I.587E-02 | 2.018E+02 |
| 34.00 | 1.557E-02 | 1.920E+02 |
| :14..00 | 1.523E-02 | 1.827E+02 |
| 38.00 | I.486E-02 | 1.738E+02 |
| 40 ON | 1.446E-02 | 1.653E+02 |
| 42.00 | 1.405E-02 | 1.573E+02 |
| 44. 00 | 1.362E-02 | 1.497E+02 |

TABLE 5-16. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1185, NAPHTHALENE.

STIRRED TANK MODEL FOR KOVAT 1185, NAPHTHALENE
FROM THE KEYBOARD, KW = 3.0001:+00, KA = 1.500E+03, KO = 1.000E+00 CM/HR
N (OIL/WATER) = 5.570E+03, HENRYS LAW (AIR/OIL) = 6.590E-07 DIMENSIONLESS, AT 3.000E+00 DEG C
ANTA = 1.614E+01, ANTB = 3.992E+03, ANTC = -7.130E+01
MOLE WT OF OIL = 2.880E+02, DENSITY = 0.800E-01 GM/CC
VO = 2.000E+02 ML, VW = 3.000E+04 ML
XZERO = 5.200E+02 MILLIGRAMS/GRAM OF OIL, AREA = 6.170E+02 CM*CM
OVER-ALL KU AT WATER-OIL = 2.998E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 9.807E-04 CM/HR
A = -6.167E-02, R = 1.107E-05
(: = 9.250E+00, 1) = -4.711E-03
N = 6.045E-02
D1 = -2.966E-03, D2 = -6.341E-02
C1 = 5.050E+02, C2 = 1.501E+01
Z1 = 9.524E-02, Z2 = -9.524E-02
WATER CONCENTRATION PEAKS AT 5.066E+01 HOURS
WHERE THE WATER CONCENTRATION = 7.812E-02, AND THE OIL CONCENTRATION = 4.351E+02
AND THE CONCENTRATION RATIO (OIL/WATER) = 5.570E+03

| HOUR | H2O | OIL |
|---|---|---|
| 0.20 | 1.144E-4XI | 5.195E+02 |
| 0.40 | 2.273E-03 | 5.190E+02 |
| 0.60 | 3.386E-03 | 5.185E+02 |
| 0.80 | 4.485E-03 | 5.181E+02 |
| 1.00 | 5.570E-03 | 5.176E+02 |
| 1.20 | 6.640E-03 | 5.171E+02 |
| 1.40 | 7.696E-03 | 5.166E+02 |
| 1.60 | 8.738E-03 | 5.162E+02 |
| 1.80 | 9.767E-03 | 5.157E+02 |
| 2.00 | 1.078E-02 | 5.152E+02 |
| 2.25 | 1.203E-02 | 5.146E+02 |
| 2.50 | 1.326E-02 | 5.141E+02 |
| 2.75 | 1.447E-02 | 5.135E+02 |
| 3.00 | 1.566E-02 | 5.129E+02 |
| 3.25 | 1.682E-02 | 5.124E+02 |
| 3.50 | 1.797E-02 | 5.118E+02 |
| 3.75 | 1.910E-02 | 5.112E+02 |
| 4.ON | 2.021E-02 | 5.107E+02 |
| 4.25 | 2.131E-02 | 5.101E+02 |
| 4.50 | 2.238E-02 | 5.096E+02 |
| 6.00 | 2.846E-02 | 5.063E+02 |
| 8.00 | 3.566E-02 | 5.022E+02 |
| 10.00 | 4.194E-02 | 4.982E+02 |
| 12.00 | 4.741E-02 | 4.943E+02 |
| 14.00 | 5.217E-02 | 4.906E+02 |
| 16.00 | 5.630E-02 | 4.870E+02 |
| 18.00 | 5.987E-02 | 4.835E+02 |
| 20.00 | 6.296E-02 | 4.801E+02 |
| 22.00 | 6.562E-02 | 4.768E+02 |
| 24.00 | 6.791E-02 | 4.736E+02 |
| 26.00 | 6.986E-02 | 4.704E+02 |
| 28.00 | 7.152E-02 | 4.673E+02 |
| 30.00 | 7.292E-02 | 4.642E+02 |
| 32.00 | 7.410E-02 | 4.612E+02 |
| 34.00 | 7.508E-02 | 4.583E+02 |
| 36.00 | 7.588E-02 | 4.554E+02 |
| 38.00 | 7.653E-02 | 4.525E+02 |
| 40.00 | 7.705E-02 | 4.497E+02 |
| 42.00 | 7.745E-02 | 4.469E+02 |
| 44.00 | 7.774E-02 | 4.441E+02 |

TABLE 5-17. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1295, 2-METHYLNAPHTHALENE.

STIRRED TANK MODEL FOR KOVAT 1293, 2-METHYLNAPHTHALENE
FROM THE KEYBOARD, KW = 3.000E+00, KA = 1.500E+03, KO = 1.000E+00 CM/HR
N (OIL/WATER) = 3.580E+04. HENRYS LAW (ATM/OIL) . 1.592E-07 DIMENSIONLESS , AT 3.000E+00 DEG C
ANTA = 1.627E+01 , ANTB = 4.237E+03, ANTC = -7.473E+01
MOLE WT OF OIL = 2.880E+02 . DENSITY = 8.800E-01 GM/CC
VO = 2.000E+02 ML, Vw = 3.000E+04 ML
XZERO = 1.260E+03 MICROGRAMS/GRAM OF OIL , AREA = 6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL = 1.000E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 2.388E-04 CM/HR
A = -6.169E-02, B = 1.723E-06
C = 9.254E+00, D = -9.931E-04
H = 6.122E-02
H1 = -7.334E-04, H2 = -6.196E-02
C1 = 1.253E+03, C2 = 5.384E+00
Z1 = 3.547E-02, Z2 = -3.547E-02
WATER CONCENTRATION PEAKS AT 7.246E+01 HOURS
WHERE THE WATER CONCENTRATION = 3.323E-02, AND THE OIL CONCENTRATION = 1.190E+08
AND THE CONCENTRATION IIA'I'10 (OIL/WATER) = 3.580E+04

| noun | H2O | OIL |
|---|---|---|
| 0.20 | 4.316E-04 | 1.260E+03 |
| 0.40 | 8.578E-04 | 1.259E+03 |
| 0.60 | 1.279E-03 | 1.259E+03 |
| 0.80 | 1.694E-03 | 1.259E+03 |
| 1.00 | 2.105E-03 | 1.259E+03 |
| 1.20 | 2.510E-03 | 1.259E+03 |
| 1.40 | 2.910E-03 | 1.258E+03 |
| 1.60 | 3.306E-03 | 1.258E+03 |
| 1.80 | 3.696E-03 | 1.258E+03 |
| 2.00 | 4.081E-03 | 1.258E+03 |
| 2.25 | 4.557E-03 | 1.257E+03 |
| 2.50 | 5.024E-03 | 1.257E+03 |
| 2.75 | 5.485E-03 | 1.257E+03 |
| 3.00 | 5.938E-03 | 1.256E+03 |
| 3.25 | 6.384E-03 | 1.256E+03 |
| 3.50 | 6.823E-03 | 1.256E+03 |
| 3.75 | 7.256E-03 | 1.255E+03 |
| 4.00 | 7.681E-03 | 1.255E+03 |
| 4.25 | 8.100E-03 | 1.255E+03 |
| 4.50 | 8.513E-03 | 1.255E+03 |
| 6.00 | 1.086E-02 | 1.253E+03 |
| 8.00 | 1.365E-02 | 1.251E+03 |
| 10.00 | 1.612E-02 | 1.248E+03 |
| 12.00 | 1.829E-02 | 1.246E+03 |
| 14.00 | 2.021E-02 | 1.244E+03 |
| 16.00 | 2.189E-02 | 1.242E+03 |
| 18.00 | 2.337E-02 | 1.240E+03 |
| 20.00 | 2.468E-02 | 1.238E+03 |
| 22.00 | 2.582E-02 | 1.236E+03 |
| 24.00 | 2.683E-02 | 1.234E+03 |
| 26.00 | 2.771E-02 | 1.232E+03 |
| 28.00 | 2.849E-02 | 1.230E+03 |
| 30.00 | 2.917E-02 | 1.228E+03 |
| 32.00 | 2.976E-02 | 1.226E+03 |
| 34.00 | 3.028E-02 | 1.224E+03 |
| 36.00 | 3.073E-02 | 1.223E+03 |
| 38.00 | 3.112E-02 | 1.221E+03 |
| 40.00 | 3.147E-02 | 1.219E+03 |
| 42.00 | 1.1761E-02 | 1.217E+03 |
| 44.00 | 1.2021E-02 | 1.215E+03 |

TABLE 5-18. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1317, 1-METHYLNAPHTHALENE .

STIRRED TANK MODEL FOn KOVAT 1317,1-METHYLNAPHTHALENE
FROM THE KEYBOARD, KW = 3. 0001:+00, KA = 1. 500E+03 , KO = 1.000E+00 CM/HR
M ( 01 L/WATER)= 3.040E+04, HENRYS LAW ( A 1R/O I 1,) = 1.204E-07DIMENS1 10NLESS AT 3. 000E+00 DEG (:
ANTA = 1.62 0E+01 , ANTB = 4.207E+03, ANTC = -7 .814E+01
MOLE WT OF O1 1. = 2.080E+02, DE NSITY = n.800E-0 I CM/CC
VO = 2.000 E+ 02 ML, Vw . 3.000E+04 MI.
X/ZERO = 7. 370E+02 M I CROGRAMS/GRAM OF 01 L, AREA = 6.170E+02 CM*CM
OV ER-ALL KW AT WATER-O1 L , 3.000E+00 CM/1111
OVER-ALL KO AT O1 L-AI R = 1.806E-04 (: M/HR
A = -6.169E-02, n = 2.029E-06
C = 9.254E+00; 0 = -II. 61 6E-04
II = (,.145E-02
D1 = -5.545E-04 , D2 = -6 .200E-02
C1 = 7.:133E+02 , C2 = 3.684E+00
Z1 = 2.434E-02 , Z2 = -2.434E-02
WATER CONCENTRATI ON PEAKS AT 7.676E+01 HOURS
WHERE THE WATER CONCENTRATI ON = 2.312E-02, AND THE OIL CONCENTRAT 10N = 7. 020E+02
AND THE C ON CENTRAT 10N RATIO (OIL/WATER ) = 3.040E+04

| noun | H20 | OIL |
|---|---|---|
| 0.20 | 2.973E-04 | 7.369E+02 |
| 0.40 | 5.909E-04 | 7.367E+02 |
| 0 60 | 8.808E-04 | 7.366E+02 |
| 0,410 | 1.167E-03 | 7.365E+02 |
| 1.00 | 1.4501,: -0:1 | 7.364E+02 |
| 1.20 | 1.729E-03 | 7.362E+02 |
| 1.40 | 2.005E-03 | 7.361E+02 |
| 1.60 | 2.277E-03 | 7.360E+02 |
| 1.80 | 2.546E-03 | 7.359E+02 |
| 2.00 | 2.812E-03 | 7.358E+02 |
| 2.25 | 3.139E-03 | 7.356E+02 |
| 2.50 | 3.461E-03 | 7.355E+02 |
| 2.75 | 3.779E-03 | 7.353E+02 |
| 3.00 | 4.091E-03 | 7.352E+02 |
| 3.25 | 4.398E-03 | 7.350E+02 |
| 3.50 | 4.70 1 E-03 | 7. 349E+02 |
| 3.75 | 4.999E-03 | 7, 347E+02 |
| 4. 00 | 5.292E-03 | 7. 346E+02 |
| 4.25 | 5.581E-03 | 7. 344E+02 |
| 4. 50 | 5.866E-03 | 7. 343E+02 |
| 6.00 | 7.481E-03 | 7. 334E+02 |
| 8.00 | 9.411E-03 | 7!323E+02 |
| 10.00 | 1.111E-02 | 7.:1 I 2E+02 |
| 12.00 | 1.261E-02 | 7.302E+02 |
| 14.00 | 1.393E-02 | 7.292E+02 |
| 16.00 | 1.510E-02 | 7.282E+02 |
| 1n. O() | 1.613E-02 | 7.272E+02 |
| 20·00 | 1.703E-02 | 7.263E+02 |
| 22·00 | 1.782E-02 | 7.254E+02 |
| 24.00 | 1.852E-02 | 7.245E+02 |
| 26 .00 | 1.914E-02 | 7.236E+02 |
| 28.00 | 1.968E-02 | 7.227E+02 |
| 30 .00 | 2.015E-02 | 7.218E+02 |
| 32.00 | 2.057E-02 | 7.209E+02 |
| :14.00 | 2.093E-02 | 7.201E+02 |
| 36 .00 | 2.125E-02 | 7.192E+02 |
| 38.00 | 2.153E-02 | 7.184E+02 |
| 40.00 | 2.177E-02 | 7.175E+02 |
| 42.00 | 2.198E-02 | 7.167E+02 |
| 44.00 | 2.216E-02 | 7.159E+02 |

TABLE 5-19. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 857, ETHYLBENZENE.

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STIRRED TANK MODEL FOR KOVAT  857, ETHYLBENZENE
FROM THE KEYBOARD, KW =  3.000E+00, KA =  1.500E+03, KO =  1.000E+00 CM/HR
H (OIL/WATER) =  2.400E+03, HENRYS LAW (AIR/OIL) =  1.232E-04 DIMENSIONLESS, AT  2.100E+01 DEG C
ANTA =  1.602E+01, ANTB =  3.298E+03, ANTC = -5.995E+01
MOLE WT OF OIL =  2.880E+02, DENSITY =  8.800E-01 GM/CC
VO =  2.000E+02 ML, VW =  3.000E+04 ML
XZERO =  4.740E+02 MICROGRAMS/GRAM OF OIL, AREA =  6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL =  2.996E+00 CM/HR
OVER-ALL KO AT OIL-AIR =  1.560E-01 CM/HR
A = -6.162E-02, B =  2.568E-05
C =  9.243E+00, D = -4.850E-01
R =  4.245E-01
D1 = -6.106E-02, D2 = -4.856E-01
C1 =  6.250E-01, C2 =  4.734E+02
Z1 =  2.867E-02, Z2 = -2.867E-02
WATER CONCENTRATION PEAKS AT  4.884E+00 HOURS
WHERE THE WATER CONCENTRATION =  1.860E-02, AND THE OIL CONCENTRATION =  4.464E+01
AND THE CONCENTRATION RATIO (OIL/WATER) =  2.400E+03
```

| HOUR | H2O | OIL |
|---|---|---|
| 0.20 | 2.305E-03 | 4.302E+02 |
| 0.40 | 4.369E-03 | 3.904E+02 |
| 0.60 | 6.215E-03 | 3.543E+02 |
| 0.80 | 7.862E-03 | 3.216E+02 |
| 1.00 | 9.329E-03 | 2.919E+02 |
| 1.20 | 1.063E-02 | 2.649E+02 |
| 1.40 | 1.179E-02 | 2.[illegible]E+02 |
| 1.60 | 1.282E-02 | 2.[illegible]E+02 |
| 1.80 | 1.372E-02 | 1.[illegible]E+02 |
| 2.00 | 1.452E-02 | 1.[illegible]E+02 |
| 2.25 | [illegible]537E-[illegible] | 1.593E+02 |
| 2.50 | [illegible]609E-[illegible] | 1.411E+02 |
| 2.75 | [illegible]670E-[illegible] | 1.251E+02 |
| 3.00 | [illegible]191-[illegible] | 1.108E+02 |
| 3.25 | [illegible]59E-[illegible] | 9.819E+01 |
| 3.50 | [illegible]91E-[illegible] | 8.702E+01 |
| 3.75 | [illegible]416-[illegible] | 7.712E+01 |
| 4.00 | [illegible]335-[illegible] | 6.835E+01 |
| 4.25 | [illegible]948E-[illegible] | 6.059E+01 |
| 4.50 | [illegible]35[illegible]E-01 | 5.371E+01 |
| 6.00 | [illegible]832E-02 | 2.613E+01 |
| 8.00 | [illegible]700E-02 | 1.011E+01 |
| 10.00 | [illegible]54E-02 | 4.023E+00 |
| 12.00 | 1.369E-02 | 1.695E+00 |
| 14.00 | 1.216E-02 | 7.939E-01 |
| 16.00 | 1.078E-02 | 4.352E-01 |
| 18.00 | 9.546E-03 | 2.839E-01 |
| 20.00 | 8.451E-03 | 2.130E-01 |
| 22.00 | 7.480E-03 | 1.740E-01 |
| 24.00 | 6.621E-03 | 1.485E-01 |
| 26.00 | 5.860E-03 | 1.293E-01 |
| 28.00 | 5.186E-03 | 1.137E-01 |
| 30.00 | 4.590E-03 | 1.003E-01 |
| 32.00 | 4.062E-03 | 8.865E-02 |
| 34.00 | 3.595E-03 | 7.842E-02 |
| 36.00 | 3.182E-03 | 6.938E-02 |
| 38.00 | 2.816E-03 | 6.140E-02 |
| 40.00 | 2.492E-03 | 5.434E-02 |
| 42.00 | 2.206E-03 | 4.809E-02 |
| 44.00 | 1.952E-03 | 4.256E-02 |

TABLE 5-20. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 867, P-XYLENE.

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STIRRED TANK MODEL FOR KOVAT 1367, P-XYLENE
FROM THE KEYBOARD, KW = 3.000E+00 . KA = 1.500E+03 . KO = 1.000E+00 CM/HR
N (OIL/WATER) = 2.800E+03, HENRYS LAW (AIR/OIL) = 1.220E-04 DIMENSIONLESS, AT 2.100E+01 DEG C
ANTA = 1.609E+01, ANTB = 3.347E+03, ANTC = -5.780E+01
MOLE WT OF OIL = 2.880E+02 , DENSITY = 8.600E-01 GM/CC
VO = 2.000E+02 ML, VW = 3.000E+04 ML
XZERO = 1.794E+03 MICROGRAMS/GRAM OF OIL , AREA = 6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL = 2.997E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 1.547E-01 CM/HR
A = -6.163E-02, B = 2.201E-05
C = 9.245E+00 , D = -4.806E-01
B = 4.199E-01
D1 = -6.115E-02, D2 = -4.811E-01
C1 = 2.073E+00 . C2 = 1.792E+03
Z1 = 9.404E-02; Z2 = -9.404E-02
WATER CONCENTRATION PEAKS AT 4.912E+00 HOURS
WHERE THE WATER CONCENTRATION = 6.0701E-02, AND THE OIL CONCENTRATION = 1.702E+02
AND THE CONCENTRATION RATIO (OIL/WATER) = 2.800E+03
```

| NOUN | H2O | OIL |
|---|---|---|
| 0.20 | 7.403E-03 | 1.630E+03 |
| 0.40 | 1.419E-02 | 1.480E+03 |
| 0.60 | 2.019E-02 | 1.345E+03 |
| 0.80 | 2.555E-02 | 1.221E+03 |
| 1.00 | 3.033E-02 | 1.110E+03 |
| 1.20 | 3.459E-02 | 1.008E+03 |
| 1.40 | 3.837E-02 | 9.156E+02 |
| 1.60 | 4.172E-02 | 8.318E+02 |
| 1.80 | 4.468E-02 | 7.556E+02 |
| 2.00 | 4.728E-02 | 6.865E+02 |
| 2.25 | 5.009E-02 | 6.009E+02 |
| 2.50 | 5.246E-02 | 5.400E+02 |
| 2.75 | 5.444E-02 | 4.790E+02 |
| 3.00 | 5.607E-02 | 4.240E+02 |
| 3.25 | 5.740E-02 | 3.769E+02 |
| 3.50 | 5.846E-02 | 3.344E+02 |
| 3.75 | 5.929E-02 | 2.967E+02 |
| 4.00 | 5.991E-02 | 2.632E+02 |
| 4.25 | 6.035E-02 | 2.335E+02 |
| 4.50 | 6.062E-02 | 2.072E+02 |
| 6.00 | 5.991E-02 | 1.014E+02 |
| 8.00 | 5.565E-02 | 3.946E+01 |
| 10.00 | 5.025E-02 | 1.371E+01 |
| 12.00 | 4.485E-02 | 6.569E+00 |
| 14.00 | 3.984E-02 | 3.010E+00 |
| 16.00 | 3.531E-02 | 1.593E+00 |
| 18.00 | 3.127E-02 | 1.000E+00 |
| 20.00 | 2.7071E-02 | 7.289E-01 |
| 22.00 | 2.449E-02 | 5.653E-01 |
| 24.00 | 2.167E-02 | 4.951E-01 |
| 26.00 | 1.918E-02 | 4.294E-01 |
| 28.00 | 1.697E-02 | 3.766E-01 |
| 30.00 | 1.502E-02 | 3.320E-01 |
| 32.00 | 1.329E-02 | 2.933E-01 |
| 34.00 | 1.176E-02 | 2.593E-01 |
| 36.00 | 1.041E-02 | 2.294E-01 |
| 38.00 | 9.208E-03 | 2.030E-01 |
| 40.00 | 8.1411E-03 | 1.796E-01 |
| 42.00 | 7.210E-03 | 1.589E-01 |
| 44.00 | 6.380E-03 | 1.406E-01 |

TABLE 5-21. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROMEVAPORATION/DISSOLUTION EXPERIMENTS. KOVAT 1021, 1-METHYL-4-ISOPROPYLBENZENE .

```
ST I RR ED TANKMODELFORKOVAT1021, 1-METHYL-4-ISOPROPYLB
FROM THE KEYBOARD , KW . 3.000E+00, KA = 1 . 500E+03, KO = 1.000E+00 CM/HR
N (0 I L/WATER ) = 7. 500E+03 , HENRYS LAW (AIR/OIL) = 2.040E-03 DIMENSIONLESS. AT 2. 100E+01 DEG C
ANTA = 1.594E+01 , ANTB = 3.539E+03 , ANTC = -7.010E+01
MOLE WT OF OIL = 2.8 80E+02. DENSITY = 0.800E-01 GM/CC
VO = 2. 000E+02 ML, Vw = 3. 000E+04 ML
XZERO = 4. 530E+02 MICROGRAMS/GRAM OF OIL, AREA = 6. 170E+02 CM*CM
OVER-ALL KW AT WATER-OIL = 2. 999E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 2.969E-02 CM/ HR
A = -6. 168E-02 , B = 0 223E-06
C = 9.251E+00, u = -9. 204E -02
R = 3.571E-02
D1 = -5.940E-02, D2 = -9. 512E-02
C1 = 2.886E+01 , C2 = 4.241E+02
Z1 = 1.043E-01 , Z2 = -1 .043E-01
WATER CONCENTRATION PEAKS AT 1 318E+01 HOURS
WHERE THE WATER CONCENTRATION = 1. 790E -02, AND THE OIL CONCENTRATION = 1. 342E+02
AND THE CONCENTRATION RATIO (OIL/WATER) = 7. 500E+03
```

| noun | H2O | OIL |
|---|---|---|
| 0.20 | 7. 336E-04 | 4. 447E+02 |
| 0. 40 | 1.445E-03 | 4.365E+02 |
| 0.60 | 2.134E-03 | 4.205E+02 |
| 0.80 | 2.802E-03 | 4.206E+02 |
| 1.00 | 3.448E-03 | 4. 129E+02 |
| 1.20 | 4.0751:-0:1 | 4.053E+02 |
| 1.40 | 4. 681E-03 | 3.978E+02 |
| 1 .60 | 5.268E-03 | 3.905E+02 |
| 1.80 | 5.836E-03 | 3.833E+02 |
| 2.00 | 6. 385E-03 | 3.763E+02 |
| 2.25 | 7. 046E-03 | 3.677E+02 |
| 2.50 | 7.680E-03 | 3.593E+02 |
| 2.75 | 8.287E-03 | 3.510E+02 |
| 3.00 | 8. 868E-03 | 3.430E+02 |
| 3.25 | 9.42414:-0:1 | 3.351E+02 |
| 3.50 | 9,956E-03 | 3.275E+02 |
| 3.75 | 1.046E-02 | 3.200E+02 |
| 4. 00 | 1.095E-02 | 3.127E+02 |
| 4.25 | 1 .1411: -02 | 3.055E+02 |
| 4.50 | 1.185E-02 | 2.985E+02 |
| 6 (m | 1.4091:-02 | 2.599E+02 |
| 8 .00 | 1.612E-02 | 2.161E+02 |
| 10.00 | 1.730E-02 | 1.798E+02 |
| 12.00 | 1.712E-02 | 1.496E+02 |
| 14.00 | 1.707E-02 | 1.246E+02 |
| 1 (,.00 | 1.755E-02 | 1.037E+02 |
| 18.00 | 1.698E-02 | 8.646E+01 |
| 20 ™ | 1.623E-02 | 7. 209E+01 |
| 22.00 | 1. 536 K-02 | 6.014E+01 |
| 24.00 | 1.443E-02 | 5.020E+01 |
| 26.00 | 1.347E-02 | 4.193E+01 |
| 211.41,1 | 1.250E-02 | :1,504 E+01 |
| 30.00 | 1.154E-02 | 2.931E+01 |
| 32.00 | 1.062E-02 | 2.453E+01 |
| :14.00 | 9.7:121.:-11:1 | 2.054E+01 |
| 36 ,00 | 8.493E-03 | 1,722E+01 |
| 38.00 | 8.165E-03 | 1.444E+01 |
| 40.00 | 7.369E-03 | 1.213E+01 |
| 42.00 | 6. 686E-03 | 1.019E+01 |
| 44.00 | 6.055E-03 | 8.570E+00 |

TABLE 5-22. STIRRED TANK MODEL COMPUTER PREDICTED MATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1185, NAPHTHALENE.

STIRRED TANK MODEL FOR KOVAT 1185, NAPHTHALENE
FROM THE KEYBOARD, KW = 3.000E+00, KA = 1.500E+03, KO = 1.000E+00 CM/HR
M (oil/water) = 6.800E+03, HENRYS LAW (AIR/OIL) = 2.996E-06 DIMENSIONLESS, AT 2.100E+01 DEG C
ANTA = 1.614E+01 ANTB = 3.992E+03 ANTC = -7.130E+01
HOLE WT OF OIL = 2.000E+02, DENSITY = 8.800E-01 GM/CC
VO = 2.000E+02 ML, VW = 3.000E+04 ML
XZERO = 5.200E+02 MILLIGRAMS/GRAM OF OIL, AREA = 6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL = 2.999E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 4.474E-03 CM/1111
A = -6.167P.-(VL, H = 9.070E-06
C = 9.251E+00, 1) = -1.516E-02
B = 4.999E-02
D1 = -1.342E-02 D2 = -6.141 E-02
C1 = 5.019E+02, C2 = 1.809E+01
Z1 = 9.4141,:-02, Z2 = -9.434E-02
WATER CONCENTRATION PEAKS AT 3.106E+01 HOURS
WHERE THE WATER CONCENTRATION = 4.902E-02, AND THE OIL CONCENTRATION = 3.333E+02
AND THE CONCENTRATION RATIO (OIL/WATER) = 6.800E+03

| HOUR | H2O | OIL |
|---|---|---|
| 0.20 | 9.360E-04 | 5.184E+02 |
| 0.40 | 1.850E-03 | 5.169E+02 |
| 0.60 | 2.765E-03 | 5.153E+02 |
| 0.80 | 3.659E-03 | 5.137E+02 |
| 1.00 | 4.539E-03 | 5.122E+02 |
| 1.20 | 5.405E-03 | 5.107E+02 |
| 1.40 | 6.258E-03 | 5.091E+02 |
| 1.60 | 7.098E-03 | 5.076E+02 |
| 1.80 | 7.925E-03 | 5.061E+02 |
| 2.00 | 8.738E-03 | 5.046E+02 |
| 2.25 | 9.738E-03 | 5.027E+02 |
| 2.50 | 1.072E-02 | 5.008E+02 |
| 2.75 | 1.168E-02 | 4.989E+02 |
| 3.00 | 1.262E-02 | 4.971E+02 |
| 3.25 | 1.354E-02 | 4.952E+02 |
| 3.50 | 1.445E-02 | 4.934E+02 |
| 3.75 | 1.534E-02 | 4.915E+02 |
| 4.00 | 1.620E-02 | 4.897E+02 |
| 4.25 | 1.706E-02 | 4.879E+02 |
| 4.50 | 1.789E-02 | 4.861E+02 |
| 6.00 | 2.256E-02 | 4.754E+02 |
| 8.00 | 2.793E-02 | 4.617E+02 |
| 10.00 | 3.245E-02 | 4.485E+02 |
| 12.00 | 3.623E-02 | 4.357E+02 |
| 14.00 | 3.935E-02 | 4.234E+02 |
| 16.00 | 4.191E-02 | 4.115E+02 |
| 18.00 | 4.396E-02 | 4.000E+02 |
| 20.00 | 4.559E-02 | 3.888E+02 |
| 22.00 | 4.684E-02 | 3.781E+02 |
| 24.00 | 4.777E-02 | 3.676E+02 |
| 26.00 | 4.841E-02 | 3.575E+02 |
| 28.00 | 4.881E-02 | 3.477E+02 |
| 30.00 | 4.899E-02 | 3.382E+02 |
| 32.00 | 4.900E-02 | 3.290E+02 |
| 34.00 | 4.885E-02 | 3.201E+02 |
| 36.00 | 4.857E-02 | 3.114E+02 |
| 38.00 | 4.817E-02 | 3.030E+02 |
| 40.00 | 4.768E-02 | 2.948E+02 |
| 42.00 | 4.711E-02 | 2.869E+02 |
| 44.00 | 4.647E-02 | 2.792E+02 |

TABLE 5-23. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS. KOVAT 1295, 2"METHYLNAPHTHALENE.

```
STIRRED TANK MODEL FOR KOVAT 1295, 2-14 ETHYLNAPHTHALENE
FROM THE KEYBOARD, KU =  3.000E+00 , KA =  1.500E+03 . KO =  1.000E+00 CM/HR
N (OIL/WATER) =  1,300E+04, HENRYS LA14 (AIR/OIL) =  8.402E-07 DIMENSIONLESS. AT  2.100E+01 DEG C
A NTA =  1.627E+01 , ANTB = 4. 237 E+03 . ANTC = -7. 47 5E+01
MOLE WT OF OIL =  2. 880E+02 , DENSITY = 0. 800E-01 GM/CC
VO =  2,000E+02 ML, Vw =  3. 000E+04 ML
S/ ERO = 1.260E+03 MICROGRAMS/GRAM OF OIL, AREA = 6.170E+02
OVER-ALL KW AT WATER-OIL =  2.999E+00 CM/HR                    C " * "
OVER-ALL KO AT OIL-AIR = 1.259E-03 CM/HR
A  = -6.169E-02, B =  4. 745E-06
C =  9.253E+00, D = -4. 595E-03
R =  3.1161 E-02
D1 = 3 , 836E -03 , D2 = -6. 244E-02
C1 =  1.244E+03, C2 =  1,632E+01
Z1 =  7.020E-01. Z2 = -1 .020E-01
WATER CONCENTRATION PEAKS AT  4. 760E+01 noms
WHERE THE WATER CONCENTRATION =  7.977E-02, AND THE OIL CONCENTRATION =  1.037E+03
AND THE CONCENTRATION RATIO ( OIL/WATER ) =  1,300E+04
```

| HOUR | H20 | OIL |
|---|---|---|
| 0.20 | 1.188E-03 | 1.259E+03 |
| 0.40 | 2.360E-03 | 1.258E+03 |
| 0.60 | 3.517E-03 | 1.257E+03 |
| 0.80 | 4. 658E-03 | 1.255E+03 |
| 1.00 | 5.785E-03 | 1.254E+03 |
| 1.20 | 6.896E-03 | 1.253E+03 |
| 1.40 | 7. 993E-03 | 1.252E+03 |
| 1.60 | 9.075E-03 | 1.251E+03 |
| 1.80 | 1.014E-02 | 1.250E+03 |
| 2.00 | 1.120E-02 | 1.249E+03 |
| 2.25 | 1.249E-02 | 1.247 E+03 |
| 2.50 | 1.377E-02 | 1.246E+03 |
| 2.75 | 1.503E-02 | 1.244E+03 |
| 3.00 | 1.626E-02 | 1.243E+03 |
| 3.25 | 1.74711 -02 | 1.242E+03 |
| 3.50 | 1.867E-02 | 1.240E+03 |
| 3.75 | 1.984E-02 | 1.239E+03 |
| 4.00 | 2.099E-02 | 1.237E+03 |
| 4.25 | 2.213E-02 | 1.236E+03 |
| 4.50 | 2.324E-02 | 1.235E+03 |
| 6.00 | 2.956E-02 | 1.227 E+03 |
| 8.00 | 3.703E-02 | 1.216E+03 |
| 10.00 | 4.354E-02 | 1.206E+03 |
| 12.00 | 4.920E-02 | 1.195E+03 |
| 14.00 | 5.412E-02 | 1.185E+03 |
| 16.00 | 5.838E-02 | 1.176E+03 |
| 18.00 | 6.205E-02 | 1.166E+03 |
| 20.00 | 6.522E-02 | 1.157E+03 |
| 22.00 | 6.793E-02 | 1.147E+03 |
| 24.00 | 7.025E-02 | 1.138E+03 |
| 26.00 | 7.221E-02 | 1.129E+03 |
| 28.00 | 7.387E-02 | 1.120E+03 |
| 30.00 | 7.525E-02 | 1.111E+03 |
| 32.00 | 7.640E-02 | 1.102E+03 |
| 34.00 | 7.733E-02 | 1.094E+03 |
| 36.00 | 7.808E-02 | 1.085E+03 |
| 38.00 | 7.867E-02 | 1.077E+03 |
| 40.00 | 7.911E-02 | 1.068E+03 |
| 42.00 | 7.94311-02 | 1.060E+03 |
| 44.00 | 7.963E-02 | 1.052E+03 |

TABLE 5-24. STIRRED TANK MODEL COMPUTER PREDICTED WATER COLUMN CONCENTRATIONS FROM EVAPORATION/DISSOLUTION EXPERIMENTS: KOVAT 1317, l-METHYLNAPHTHALENE.

STIRRED TANK MODEL FOR KOVAT 1317, 1 -METHYLNAPHTHALENE
FROM THE KEYBOARD, KW = 3.000E+00, KA = 1.500E+03, KO = 1.000E+00 CM/HR
M(OIL/WATER) = 5.000E+03, H ENRYS LAW(AIR/OIL). 6.661E-07 DIMENSIONLESS, AT 2.100E+01 DEG C
ANTA = 1.620E+01, ANTH = 4.207E+03, ANTC = -7.815E+01
MOLE WT OF OIL = 2.880E+02, DENSITY = 11.0001,:-01 CM/CC
VO = 2.000E+02 ML, VW = 3.000E+04 ML
XZERO = 7.370E+02 MICROGRAMS/GRAM OF OIL. AREA = 6.170E+02 CM*CM
OVER-ALL KW AT WATER-OIL = 2.998E+00 CM/HR
OVER-ALL KO AT OIL-AIR = 9.982E-04 CM/HR
A = -6.166E-02, B = 1.233E-05
C = 9,249E+00; H = -4.929E-03
R = 6.062E-02
D1 = -2.985E-03, D2 = -6.361E-02
c1 = 7.134E+02, C2 = 2.:IO:IY44?1
Z1 = 1.499E-01, Z2 = -1.499E-01
WATER CONCENTRATION PEAKS AT 5.046E+01 HOURS
WHERE THE WATER CONCENTRATION, 1.229E-01, AND THE OIL CONCENTRATION = 6.146E+02
AND THE CONCENTRATION RATIO (OIL/WATER) = 5.000E+03

| Noun | H2O | OIL |
|---|---|---|
| 0.20 | 1.806E-03 | 7.363E+02 |
| 0.40 | :1.51101,:-0:1 | 7.356E+02 |
| 0.60 | 5.346E-03 | 7.348E+02 |
| 0.IN) | 7.081E-03 | 7.341E+02 |
| 1.00 | 11.793E-03 | 7.334E+02 |
| 1.20 | 1.048E-02 | 7.327E+02 |
| 1.40 | 1.215E-02 | 7.320E+02 |
| 1.60 | 1.379E-02 | 7.313E+02 |
| 1.80 | 1.542E-02 | 7.306E+02 |
| 2.00 | 1.702E-02 | 7.299E+02 |
| 2.25 | 1.899E-02 | 7.291E+02 |
| 2.50 | 2.093E-02 | 7.282E+02 |
| 2.75 | 2.283E-02 | 7.274E+02 |
| 3.00 | 2.471E-02 | 7.265E+02 |
| 3.25 | 2.655E-02 | 7.257E+02 |
| 3.50 | 2.837E-02 | 7.249E+02 |
| 3.75 | 3.015E-02 | 7.240E+02 |
| 4.ON | 3.190E-02 | 7.232E+02 |
| 4.25 | 3.362E-02 | 7.224E+02 |
| 4.50 | 3.532E-02 | 7.216E+02 |
| 6.00 | 4.491E-02 | 7.168E+02 |
| 8.00 | 5.626E-02 | 7.107E+02 |
| 10.00 | 6.675E-02 | 7.049E+02 |
| 12.00 | 7.477E-02 | 6.993E+02 |
| 14.00 | 8.226E-02 | 6.939E+02 |
| 16.00 | 0,875E-02 | 6.886E+02 |
| 18.ON | 9.437E-02 | 6.836E+02 |
| 20.ON | 9.923E-02 | 6.786E+02 |
| 22.00 | 1.034E-01 | 6.739E+02 |
| 24.00 | 1.0701,:-0 1 | 6.692E+02 |
| 26.00 | 1.100E-01 | 6.646E+02 |
| 28.00 | 1.126E-01 | 6.601E+02 |
| :10.00 | 1.148E-01 | 6.558E+02 |
| 32.00 | 1.167E-01 | 6.515E+02 |
| 34.00 | 1.182E-01 | 6.472E+02 |
| 36.00 | 1.195E-01 | 6.431E+02 |
| 38.00 | 1.205E-01 | 6.390E+02 |
| 40.00 | 1.213E-01 | 6.349E+02 |
| 42.00 | 1.219E-01 | 6.309E+02 |
| 44.00 | 1.223E-01 | 6.270E+02 |

Figures 5-48 and 5-49 present the predicted water column concentrations at 21 and 3°C for the compounds presented in Tables 5-13 through 5-24. These figures clearly show the less volatile compounds persisting in the water column. This is what has been recently observed experimentally as shown in plots of observed component concentration (Figures 5-25 and 5-31). The experimental observations indicate that the naphthalenes tail-off much faster than predicted. This rapid tail-off could be due to some other degradation mechanism such as biological weathering (discussed in Section 5.2).

In general, the predicted time of occurrence of the peak water concentrations is quite good, but the peak concentrations do not always agree well. The prediction of the peak concentration is directly dependent on the initial concentration and the M-value. While our M-value data represent first-of-a-kind measurements, future determinations will no doubt yield improvements.

When utilizing the pseudo-component approach, characterization output from the oil weathering model is in the form of distillation cuts (pseudo-compounds) which remain in the oil slick as a function of time. Figure 5-50 presents time series plots of the predicted "distillation curves" from oil weathering at 13°C under natural environmental conditions, and Figure 5-51 presents normalized distillation curves for the "distillable components". Figures 5-52 and 5-53 present the observed hydrocarbon concentration distillation curves (real and normalized to total "distillable") generated from the wave tank gas chromatographic data discussed in the previous sections.

The observed distillation fraction curves were generated by summing all of the total resolved components in each chromatogram (as shown in Figure 5-43 in the previous section) by Kovat indices and then correlating these cumulative sums with the recorded boiling point for each n-alkane throughout the range of nC-7 through nC-28. These figures were generated using the program PBDIST which is an integral portion of the overall oil weathering model.

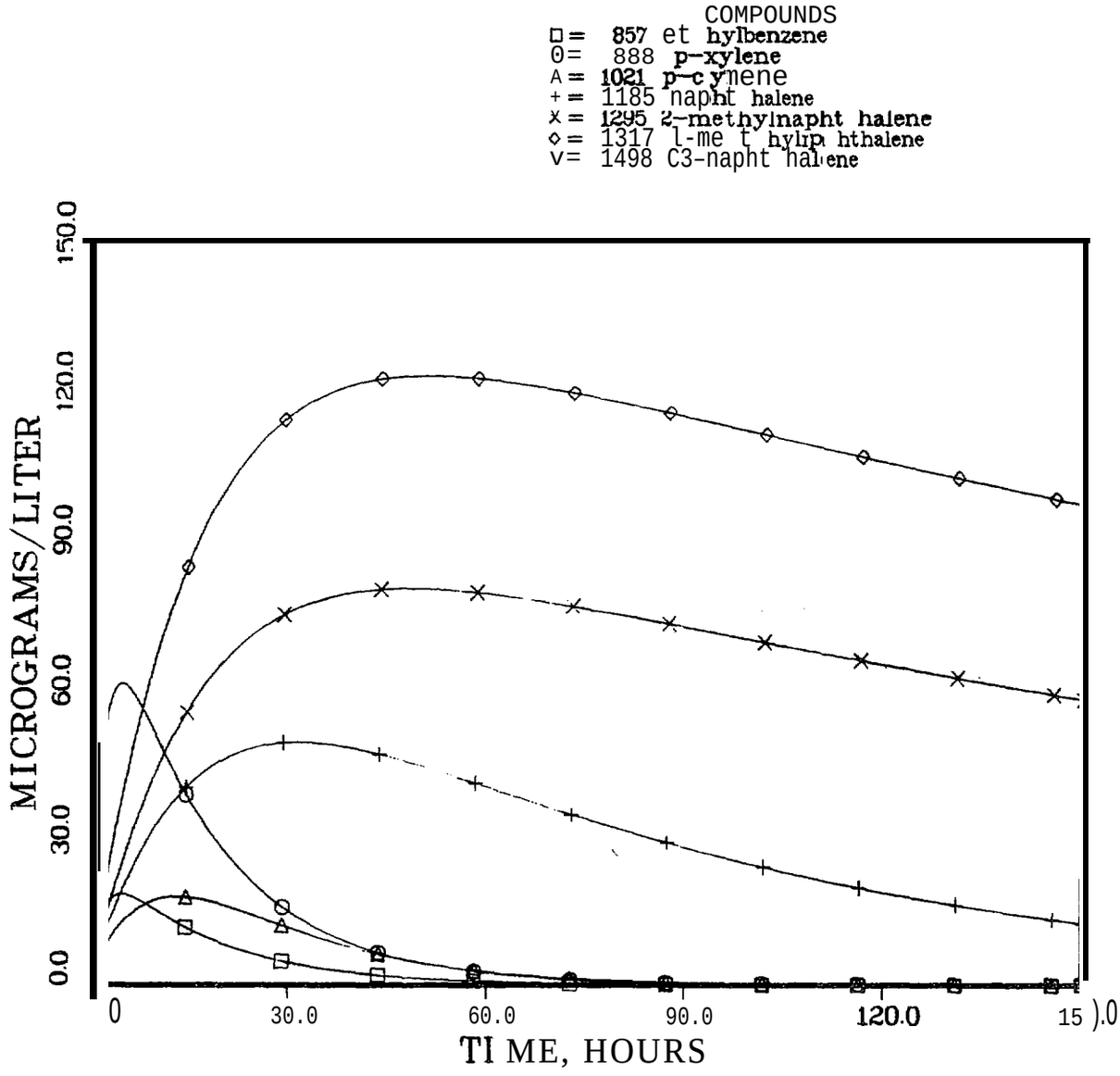



FIGURE 5-48. PREDICTED WATER COLUMN CONCENTRATIONS, STIRRED TANK MODEL AT 19°C.

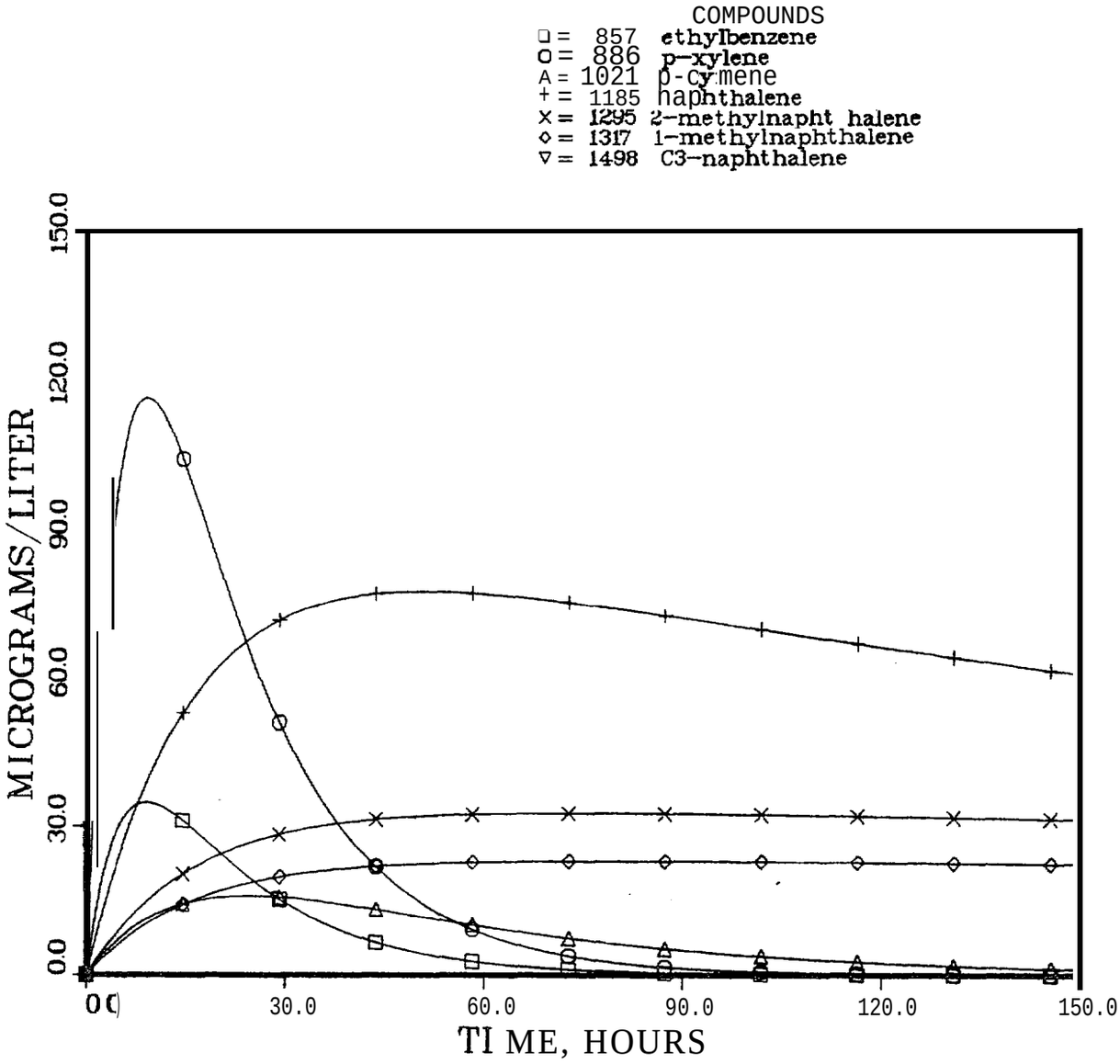



FIGURE 5-49. PREDICATED WATER COLUMN CONCENTRATIONS, STIRRED TANK MODEL AT 3"C.

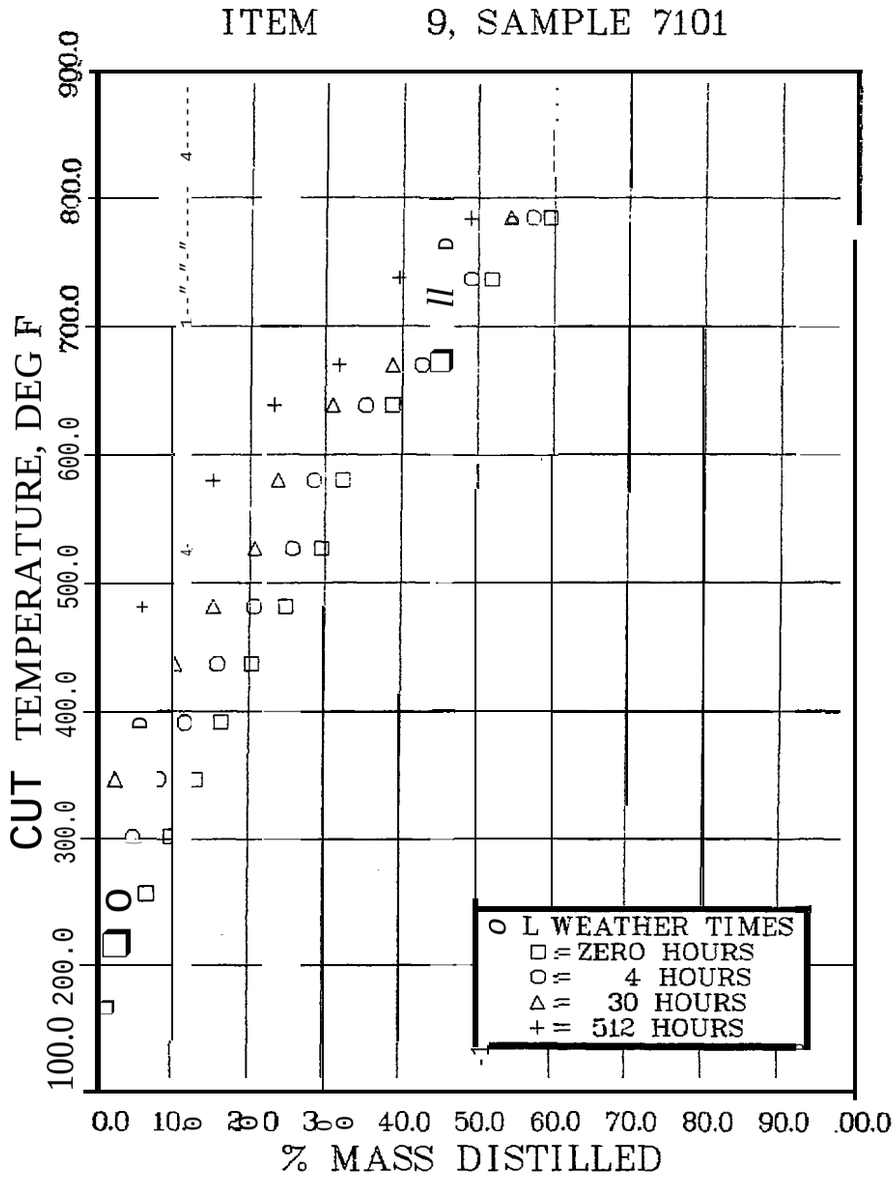



FIGURE 5-50. COMPUTER PREDICTED MASS BALANCE DISTILLATION CURVES FOR OIL WEATHERING IN THE WAVE TANK EXPERIMENT AT 55°F.

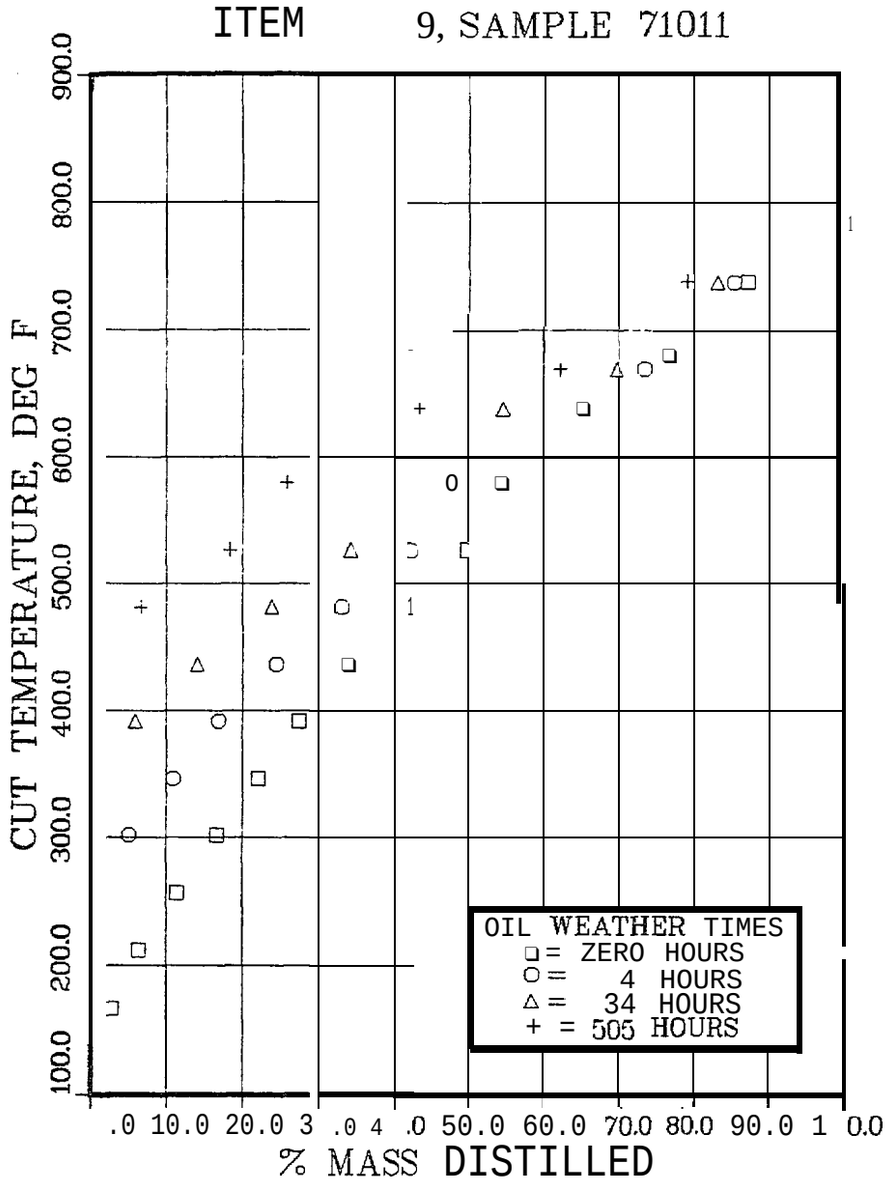



FIGURE 5-51. COMPUTER PREDICTED TOTAL DISTILLABLE BOILING POINT DISTRIBUTION CURVES FOR OIL WEATHERING IN THE WAVE TANK EXPERIMENT AT 55°F.

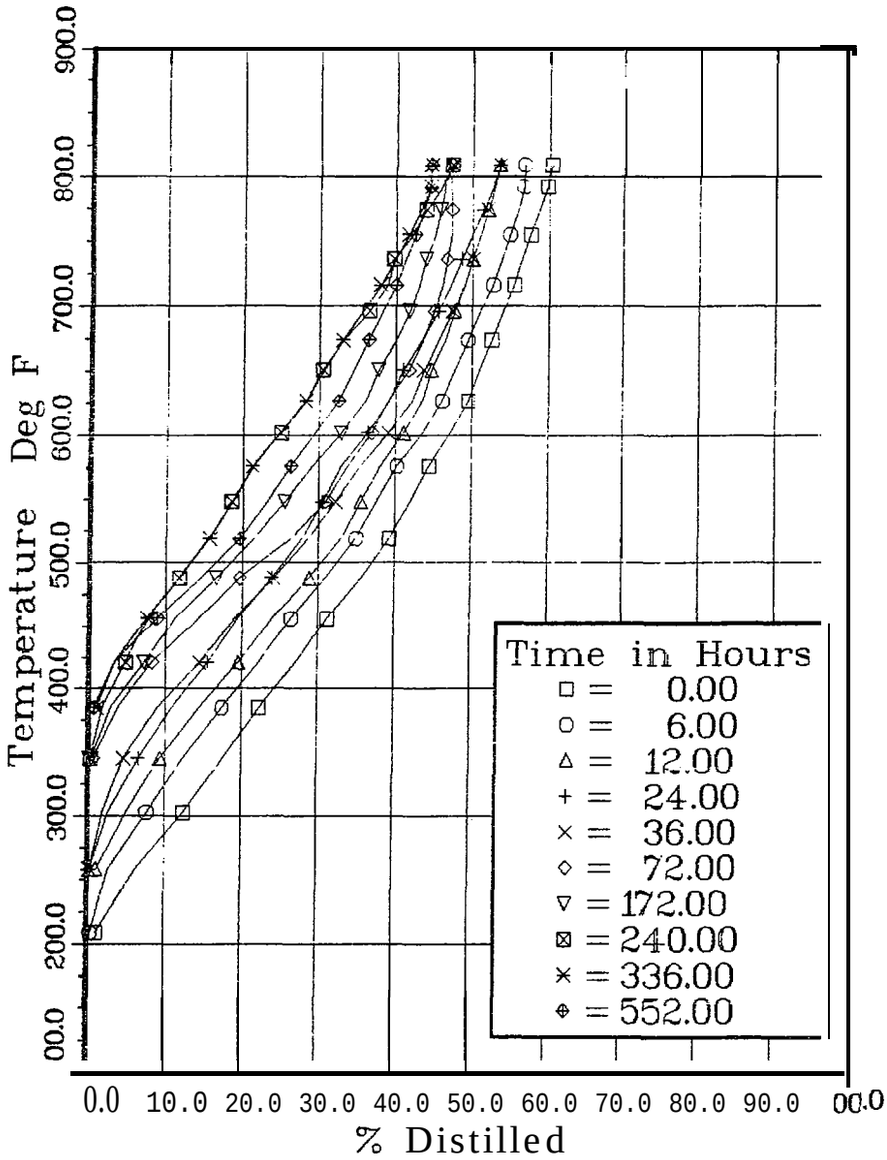



FIGURE 5-52. OBSERVED MASS BALANCE DISTILLATION CURVES GENERATED FROM GAS CHROMATOGRAPHIC DATA IN EXP DATA BASE FOR PRUDHOE BAY CRUDE OIL blathering IN THE WAVE TANK EXPERIMENT AT KASITSNA BAY, ALASKA.

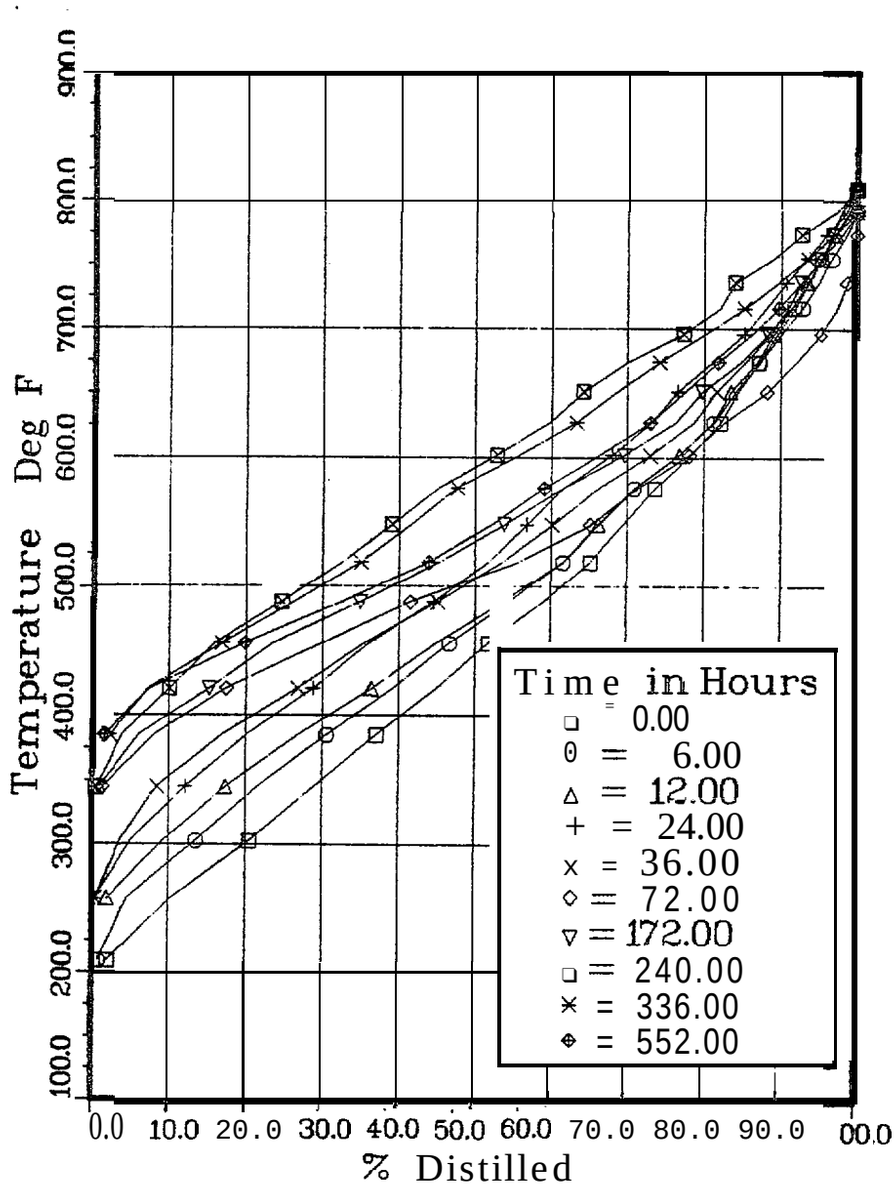



FIGURE 5-53. OBSERVED TOTAL DISTILLABLE BOILING POINT DISTRIBUTION CURVES GENERATED- GAS CHROMATOGRAPHIC DATA IN EXP DATA BASE FOR PRUDHOE BAY CRUDE OIL WEATHERING IN THE WAVE TANK EXPERIMENT AT KASITSNA BAY, ALASKA.

## 5.2 Microbial Degradation Studies

### 5.2.1 Summary of Year I Activities

The major themes of the microbial degradation studies being conducted in this program have been: (1) examination of the degradation of petroleum components in terms of specific compound susceptibility, (2) isolation and characterization of stable oxidized products arising from catabolic processes, and (3) quantification of the degree and rates of partitioning of these products into the air, oil and seawater phases (i.e., away from the slick-seawater interface).

To determine the extent of petroleum component partitioning attributable to the purely physical/chemical (i.e., abiotic) dissolution and evaporation processes occurring simultaneously with microbial degradation, it was our initial approach to create and maintain a biotic/abiotic contrast in flow-through seawater aquarium systems in order to limit microbial metabolic influence on slick disposition. As indicated in our November 1980 Interim Report, considerable difficulty was encountered in maintenance of such a contrast within the continuously flowing experimental systems. Continued efforts demonstrated that a significant microbial/abiotic contrast could not be maintained for longer than 6 to 8 days, and results suggested that the main problem in maintenance of such a contrast is one of the residence time for bacteria within the experimental systems. If the fraction of the indigenous marine bacteria which survive the sterilization attempts (by UV irradiation and $HgCl_2$ poisoning) cannot be flushed from the system at a rate substantially faster than the microbial population recovery dynamics (doubling times), repopulation and subsequential bacterial contamination of the "abiotic" experimental system is apparently inevitable.

Since the elevated flow rates utilized for the most recent sterilization attempts cannot be exceeded due to the analytically detrimental influence

on petroleum compound and oxidation product recoveries, such attempts to create and maintain this type of contrast were re-evaluated. A new experimental approach was developed, to facilitate continuation of the study of microbial degradation of crude petroleum. This new approach is quite viable with respect to the empirical needs of the overall modeling efforts, while at the same time alleviating the necessity for maintaining a biotic/abiotic contrast within the experimental system.

During the winter season of 1980-81, definitive microbial degradation studies were initiated with the continuous-flow experimental systems at Scripps Institution of Oceanography. The operational parameters for the aquaria included presence/absence of Corexit 9527, flow rates which provided approximately one tank volume change per 24 hours, and Prudhoe Bay crude petroleum at a volume ratio (oil-to-seawater) of about 1:200. Samples of the seawater effluent (20-40 liters) were taken at 0.5, 1, 2, 5, 10, 17, 24, 31, 38, 45 and 66 days, acidified (to PH 2.0) and $CH_2Cl_2$ extracted. The bulk extracts were fractionated by liquid/solid silica gel chromatography into aliphatic, aromatic and polar fractions. The polar fractions are expected to contain the majority of anticipated oxygenated products, and capillary GC-FID and GC/MS analyses of selected samples lend support to this hypothesis.

Seawater effluent extracts from weathered (Day 17) Prudhoe Bay crude and extracts of fresh crude were analyzed by capillary GC/MS. The aromatic fractions of the fresh crude and the weathered extracts (from two experimental systems) demonstrated strong qualitative resemblance; however, the polar fractions of fresh and weathered crude extracts were significantly different. Several tentatively identified compounds from the experimentally weathered crude extracts, which were absent in the corresponding fraction of fresh Prudhoe Bay crude, strongly suggest microbial degradation processes. These tentatively include benzenemethanol, 4-methyl benzenemethanol, 3-methylbenzoic acid, and a variety of phenols. Although the proposed mechanisms of microbial metabolism of petroleum hydrocarbons and the associated products are diverse, certain pathways have been delineated as being reasonably common with respect

to catabolism of aromatic compounds to hydroxylated and carboxylated moeities (JORDAN and PAYNE, 1980). Additional GC/MS characterization of both aromatic and polar fractions from Day 45 seawater effluent extracts were undertaken, and the results are discussed below (see oxidized Product Characterizations).

### 5.2.2 Continued Studies - Year II

Two areas of experimental effort have been undertaken: (1) the continuous-flow experiments were continued at Scripps Institution of Oceanography and at NOAA's Kasitsna Bay facility; and (2) the static tank experiments were conducted at SAI's La Jolla facility. Results to date will be presented below with major emphasis placed on the continuous-flow studies.

#### Continuous-Flow Studies

The continuous-flow experimental approach was designed with the intent of providing a dynamic characterization of marine microbial populations and their inherent metabolic capacity for degrading petroleum components as a function of interaction with petroleum. This can be described as the time-dependent response within the indigenous heterotrophic population towards a greater relative abundance of hydrocarbonoclastic (hydrocarbon-degrading) microbes, as indicated by a concomitant increase in degradation potential of the system as measured by increased $^{14}C$-labeled compound degradation. This has been empirically demonstrated by increases in the rates of mineralization to $^{14}CO_2$ of selected $^{14}C$-labeled hydrocarbons as a function of continued exposure to crude oil within the experimental aquariums. Additional components of the "response time" include (2) determinations of heterotrophic bacterioplankton growth rates from incorporation of tritium-labeled thymidine into deoxyribonucleic acid (DNA) and enumeration of bacterial cells by epifluorescence microscopy; and (3) determinations of overall metabolic activity by uptake of tritium-labeled leucine and glucose, and assays of relative metabolic activity by microautoradiography.

An EPA approved bacterial strain mixture (Petrobac®) was incorporated into the experimental scheme (as well as in the static tank study). This mixture was developed by Polybac Corporation (Allentown, PA, U.S.A.) for certain oil degradation applications and is composed of individual strains originating from conventional selective adaptation and mutation techniques to utilize specific compound types (e.g., hydrocarbons, phenols, etc.). The blend also contains "background" microbes which are capable of degrading major metabolizes from the socialized strains. It is of importance to note that this product was developed for degradation of oil in contact with a solid substrate (e.g., beach-stranded petroleum) and that Polyboc Corporation does not recommend its application to open water petroleum spills. However, their interest in the metabolic products arising from the interaction of the Petrobac® mixture with Prudhoe Bay crude petroleum under the given experimental conditions resulted in a high degree of cooperation between SAI and Polybac Corporation during the project.

It was also of interest to examine the influence of concentration levels of available dissolved inorganic nutrients ($PO_4^{-3}$, $NO_2^-$, $NO_3^-$, and $NH_3$) and dissolved oxygen upon microbial metabolic activities. To facilitate this, a nutrient solution was introduced (via a Peristaltic pump system) into two of the experimental aquariums to maintain elevated levels (with respect to incoming seawater) and aeration of the seawatersupplyingthesetwo tanks was Provided. The experimental matrix presented below delineates the combinations of nutrient and dissolved $O_2$ supplementation, as well as inoculation with the Petrobac® strains for each experimental system. A schematic of the overall system is presented in Figure 5-54 and the Figure 5-55 shows the completed flow-through system as utilized at SIO and Kasitsna Bay.

| Tank | Prudhoe Bay | Flow | Petrobac® | Nutrients/$O_2$ |
|---|---|---|---|---|
| 2 | + | + | + | + |
| 3 | + | + | | + |
| 5 | + | + | + | |
| 6 | + | + | | |

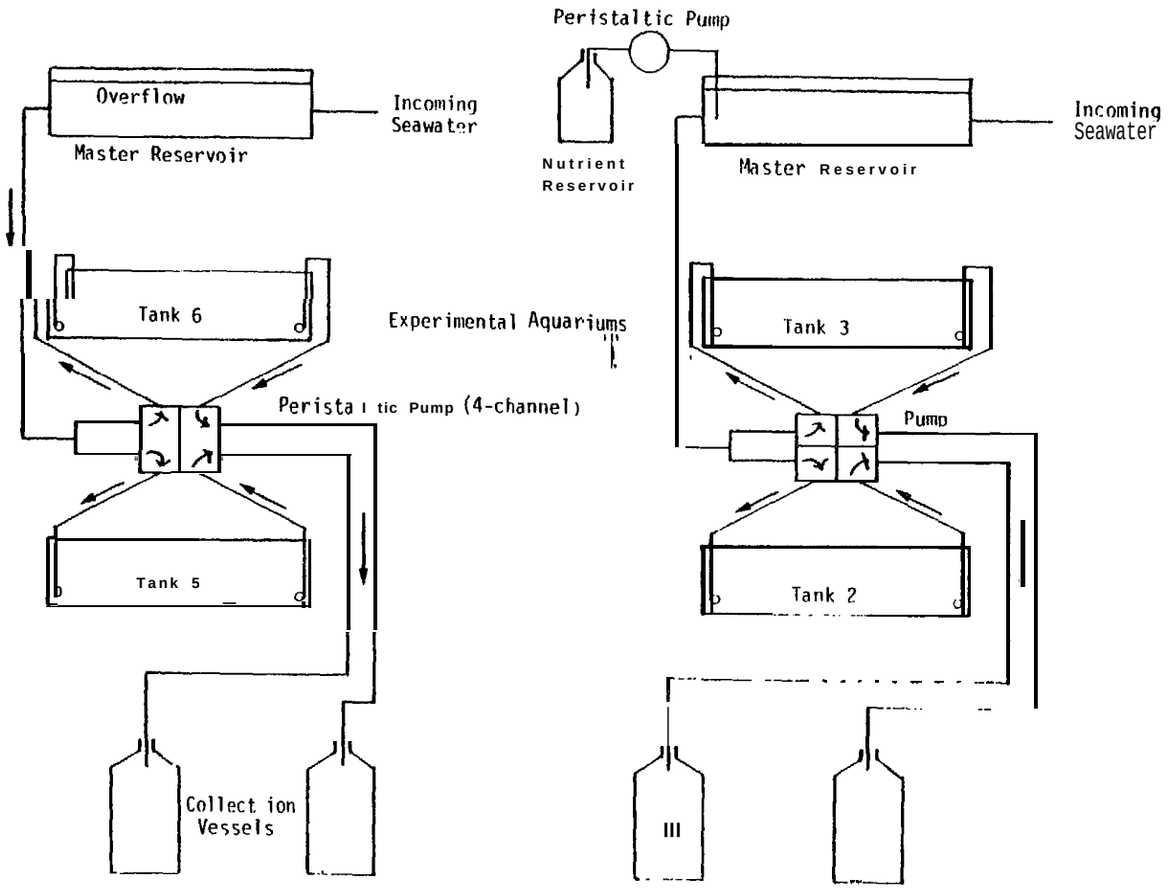



FIGURE 5-54. DIAGRAM AND PHOTOGRAPH OF THE CONTINUOUS-FLOW SEAWATER EXPERIMENTAL SYSTEMS AT SCRIPPS INSTITUTE OF OCEANOGRAPHY AND THE NOAA KASITSNA BAY FACILITY.

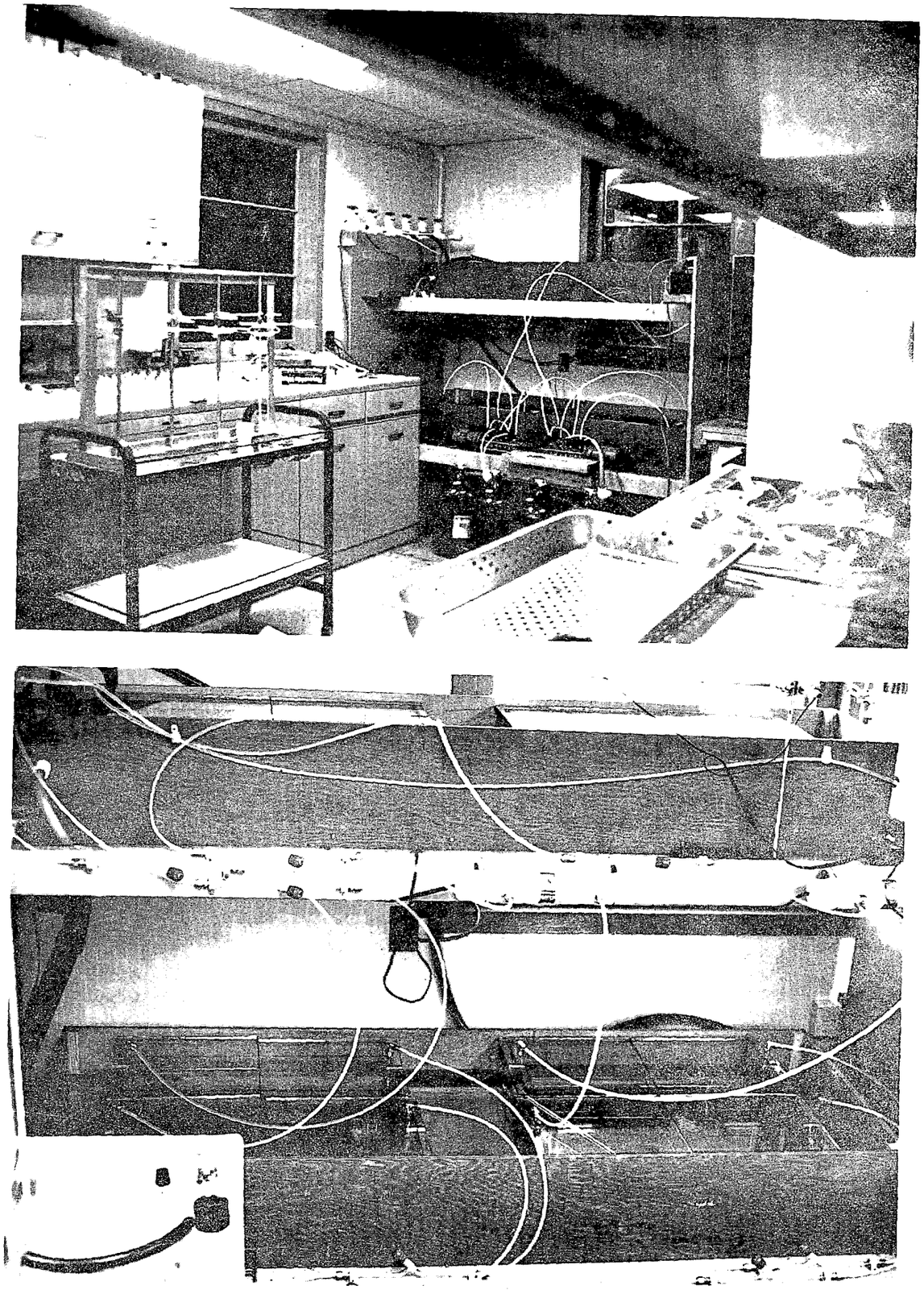


FIGURE 5-55. GENERAL VIEW OF CONTINUOUS-FLOW EXPERIMENTAL SYSTEM AT KASITSNA BAY, ALASKA FACILITY (TOP) AND CLOSEUP OF SYSTEM (BOTTOM) WITH ORIGINAL UV STERILIZATION UNITS.

Static-Tank Studv

The main purpose of the static tank experiment performed at SAI's La Jolla facility was to provide samples (seawater extracts and weathered oil) containing metabolic products arising from microbial degradation of Prudhoe Bay crude oil. Due to the inherent difficulty in recovering such oxidized products from continuously-flowing aquaria, small static seawater aquaria (30 liter) were set up with the following combinations of indigenous microbes, Petrobac® strains, fresh oil, artificially generated (shaker table) mousse, dissolved oxygen and nutrient supplementation (at two levels of nitrogen and Phosphorous):

| Tank | Indigenous Microbes | Petrobac® | Fresh Crude | Mousse | Aeration ($O_2$) | Nutrients |
|---|---|---|---|---|---|---|
| 1 | + | + | + | | + | + (1) |
| 2 | + | | + | | + | + (1) |
| 3 | + | + | + | | + | + (2) |
| 4 | + | | + | | + | + (2) |
| 5 | + | + | | + | + | + (1) |
| 6 | + | | | + | + | + (1) |
| 7 | + | + | | + | + | + (2) |
| 8 | + | | | + | + | + (2) |
| 9 | + | | + | | + | |
| 10 | + | | | | + | |

Nutrient levels were initiated at approximately (1) 10 $\mu$M nitrogen ($NH_4NO_3$-N) and 1 $\mu$M phosphorous ($KH_2PO_4$-P) ; and (2) 100 $\mu$M nitrogen ($NH_4NO_3$-N) and 10 $\mu$M Phosphorous ($KH_2PO_4$-P). Seawater samples for nutrient and pH determinations were taken weekly although the data are not available at the time of this writing. After approximately 50 days the seawater was removed from each

tank ( 30 liters), acidified to PH 2.0 and $CH_2Cl_2$ extracted. The remaining oil was also sampled and stored frozen for analysis. The samples from this experiment are being utilized for the portion of this program dealing with development of analytical methods for polar oxidized petroleum compounds.

### 5.'2.3 Oxidized Product Characterizations

The objective of this phase of the oil weathering modeling study is the identification of some of the major oxygenated petroleum compounds which can be found in the polar (F3) fraction in extracts of seawater with considerable exposure time to microbial weathering of surface slicks of Prudhoe Bay crude oil. This section presents the results of the GC/MS analyses of two such fractions. Figure 5-56 presents the reconstructed ion chromatogram (RIC) of the sample obtained from an outside aquarium oil weathering experiment from Kasitsna Bay and could thus include some photo-oxidation products; and Figure 5-57 presents the RIC from the same (polar) fraction from an indoor aquarium experiment conducted at SIO, and thus exposed only to a minimum of artificial light. Tables 5-25 and 5-26 present the tentative compound and functional group identities of the numbered peaks in Figures 5-56 and 5-57, respectively. The peak identifications on peaks of significant size were obtained by computer matching to the 30,000 compounds in the EPA/NIH library of our Finnigan 4021 GC/MS system. The search program selects five compounds which show the best mass spectra data fit with the unknown compound spectrum and gives an estimate of both fit and purity. The suggested compounds were screened to eliminate those compounds whose molecular weights or volatilities were not consistent with the relative GC retention time. In many cases the program produced several possible homologs of a suggested class of compounds, and we plan to use selected standards of various compound classes to pinpoint the assignment of such peaks. Table 5-27 presents lists of standards (by functional group class) which are being obtained for GC/MS retention time verification and expansion of the spectral library data base. At this time, most of the peaks existing from GC/MS analyses of selected fractions can be labelled

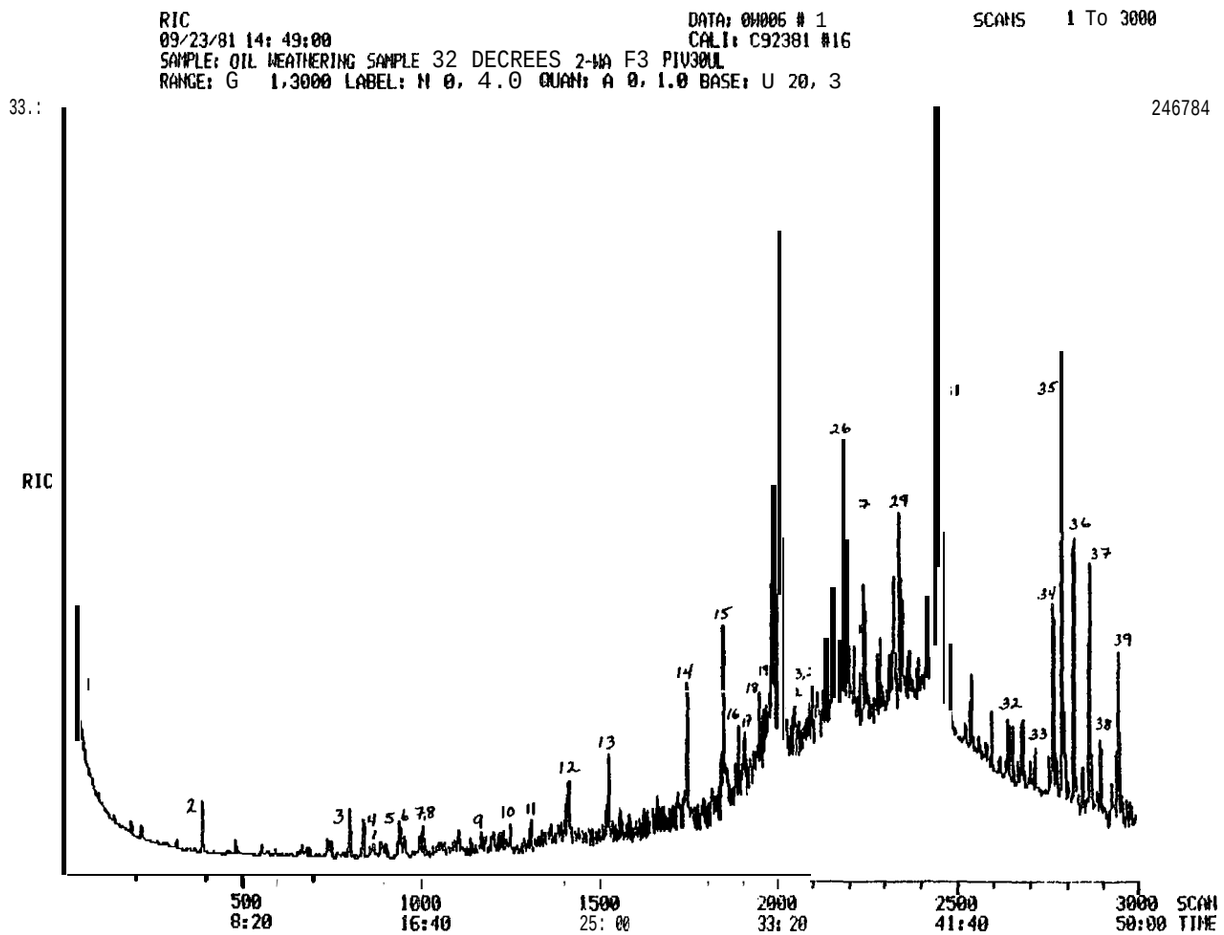



FIGURE 5-56. RECONSTRUCTED ION CHROMATOGRAM (RIC) FROM GC/MS ANALYSES OF THE POLAR (F3) WATER COLUMN EXTRACT OBTAINED FROM OUTDOOR FLOW-THROUGH TANK #2 FROM KASITSNA BAY, ALASKA. IDENTIFICATION OF THE NUMBERED PEAKS IN THE RIC ARE SHOWN IN TABLE 5-25.

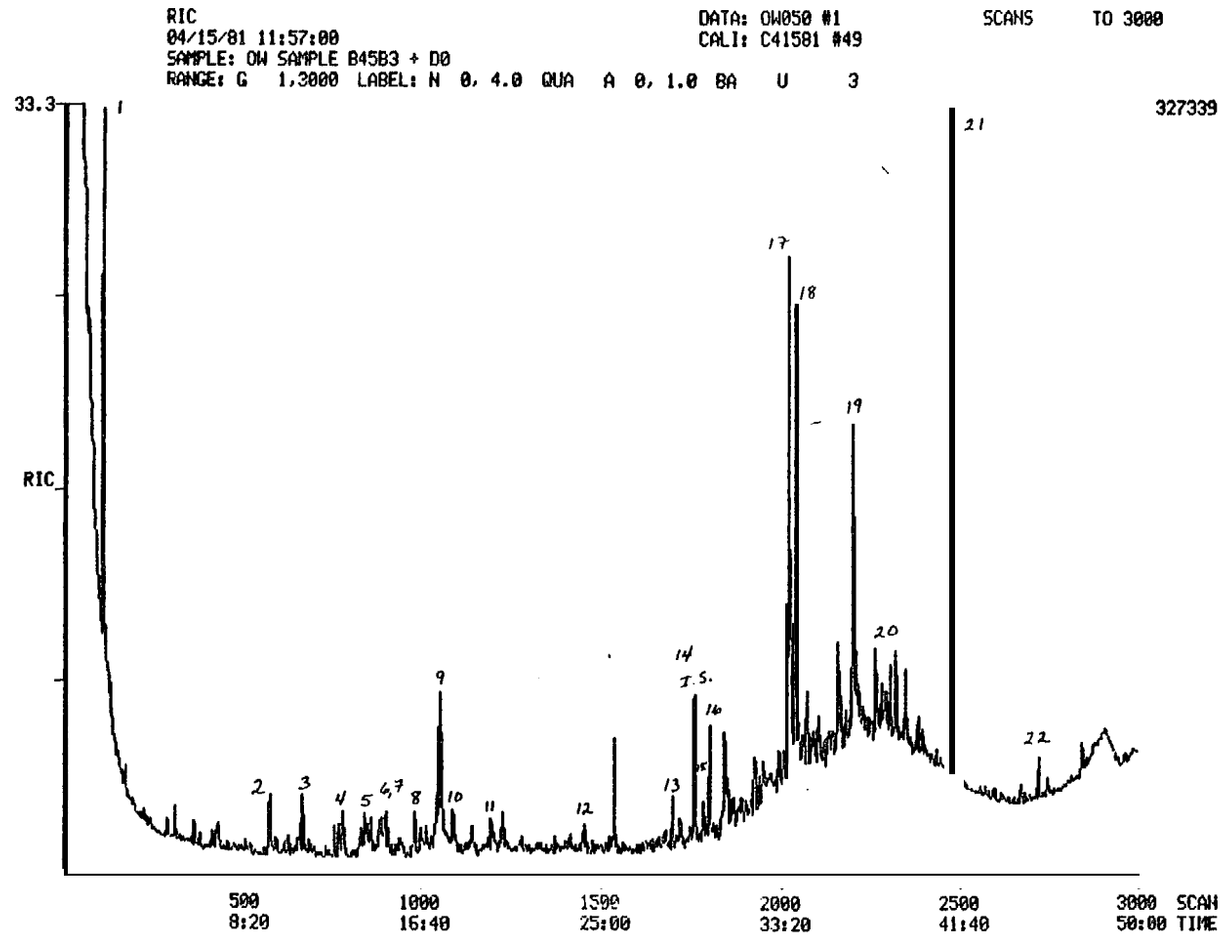



FIGURE 5-57. RECONSTRUCTED ION CHROMATOGRAM (RIC) FROM GC/MS ANALYSES OF POLAR (F3) WATER COLUMN EXTRACT OBTAINED FROM INDOOR FLOW-THROUGH TANK #3 AT SCRIPPS INSTITUTE OF OCEANOGRAPHY. IDENTIFICATIONS OF THE NUMBERED PEAKS IN THE RIC ARE SHOWN IN TABLE 5-25.

TABLE 5-25. TENTATIVE COMPOUND IDENTIFICATIONS FOR THE KASITSNA BAY POLAR (F3) FRACTION (see Figure 5-56).

| Peak No. | Scan No. | Tentative Identification |
|---|---|---|
| 1 | 38 | Low molecular weight ketone |
| 2 | 391 | $C_7$ - $C_8$ aldehyde |
| 3 | 807 | $C_9$ - $C_{10}$ aldehyde or alcohol |
| 4 | 846 | $C_3$ benzyl alcohol or $C_4$ phenol |
| 5 | 945 | $C_3$ benzyl alcohol or $C_2$ benzoic acid |
| 6 | 959 | o-(hydroxymethyl) benzoic acid |
| 7 | 1003 | $C_3$ benzyl alcohol or $C_2$ benzoic acid |
| 8 | 1011 | $C_{10}$ - $C_{11}$ aldehyde or alcohol |
| 9,10 | 1250(4) | $C_3$ benzoic acids |
| 11 | 1305 | $C_3$ tetrahydrobenzofuranone |
| 12 | 1415 | Fatty acid |
| 13 | 1523 | Dibenzylether |
| 14 | 1746 | Fatty acid |
| 15 | 1845 | Long chain aldehyde |
| 16 | 1888 | Fatty acid |
| 17 | ?902 | Long chain aldehyde |
| 18 | 1949 | Long chain alcohol |
| 19 | 1957 | Fatty acid, methyl ester |
| 20 | ---- | Unsaturated fatty acid |
| 21 | 1994 | Phthalate ester |
| 22-24 | 2006-?100 | Fatty acids |
| 25 | ---- | Long chain aldehyde/alcohol |
| 26,27 | 2187,2201 | Fatty acids |
| 28 | 2219 | Long chain alcohol |
| 29 | 2348 | Fatty acid |
| 30,31 | 2445,2456 | Phthalate esters |
| 32-39 | 2645-2951 | Steroids |

TABLE 5-26. TENTATIVE COMPOUND IDENTIFICATIONS FOR THE S10 POLAR (F3) FRACTION (see Figure 5-57).

| Peak No. | Scan No. | Tentative Identification |
|---|---|---|
| 1 | 42 | Cyclohexanone |
| 2 | 110 | p-Methylbenzyl alcohol |
| 3 | 680 | Methylacetophenone |
| 4 | 788 | 2,5-Dimethylbenzyl alcohol |
| 5 | 850 | o-Toluic acid |
| 6 | 909 | m-Toluic acid |
| 7 | 915 | p-Toluic acid |
| 8 | ---- | $C_2$ benzoic acid |
| 9 | ---- | Acrylate or crotonate ester |
| 10 | 1092 | 3,4-dimethylbenzoic acid |
| 11 | ---- | Acrylate or crotonate ester |
| 12 | ---- | Long chain fatty acid |
| 13 | 1698 | Fluorenone |
| 14 | ---- | D-10 phenanthrene (internal std.) |
| 15 | ---- | Long chain fatty acid |
| 16 | ---- | Acrylate or crotonate ester |
| 17 | ---- | Long chain unsaturated fatty acid |
| 18 | ---- | Long chain unsaturated fatty acid |
| 19 | ---- | Long chain saturated aldehyde or alcohol |
| 20 | ---- | Phthalate ester |
| 21 | ---- | $C_8$ phthalate ester (d.) |
| 22 | ---- | Steroid |

TABLE 5-27. STANDARDS CURRENTLY BEING OBTAINED AND ANALYZED TO PROVIDE RELATIVE RETENTION TIME AND QUADRUPLE MASS SPECTRAL DATA FOR INCORPORATION INTO THE FINNIGAN MASS SPECTRAL LIBRARY AND VERIFICATION OF OXIDIZED PRODUCT COMPOUND IDENTIFICATIONS.

Acids

normal acids: $C_3$ to $C_{12}$, $C_{14}$, $C_{16}$, and $C_{18}$
benzoic acid
2-ethylhexanoic acid
2-naphthoic acid
terephthalic acid
undecylenic acid

Alcohols

normal I-al kanols: $C_1$ to $C_{12}$, $C_{14}$ $C_{16}$, $C_{18}$, $C_{20}$, and $C_{22}$
straight chain, 2-alkanols: $C_3$ to $C_5$
2,3-butanediol
cyclohexanol
2-ethyl -1-butanol
2-methyl -1-butanol
3-methyl -1-butanol
2-methyl- -2-butanol
3-methyl -3-pentanol
4-methyl -2-pentanol
2-methyl -1-propanol
2-methyl -2-propanol
3-pentanol

Aldehydes

n-alkanals: $C_3$ - $C_{14}$
acrolein
benzaldehyde
glutaric dialdehyde
2-methylpropanal
3-methylbutanal

Esters

methyl esters of normal acids: $C_{10}$ - $C_{22}$
ethyl esters of normal acids: $C_2$ - $C_6$
propyl esters of normal acids: $C_2$ - $C_6$
methyl eicosenoate
methyl eicosadienoate
methyl eicosatrienoate
methyl erucate
methyl 2-hydroxydecanoate
methyl 2-hydroxydodecanoate
methyl 3-hydroxydodecanoate
methyl 2-hydroxyhexadecanoate
methyl 2-hydroxytetradecanoate

TABLE 5-27. STANDARDS CURRENTLY BEING OBTAINED AND ANALYZED TO PROVIDE RELATIVE RETENTION TIME AND QUADRUPOLE MASS SPECTRAL DATA FOR INCORPORATION INTO THE FINNIGAN MASS SPECTRAL LIBRARY AND VERIFICATION OF OXIDIZED PRODUCT COMPOUND IDENTIFICATIONS, (Continued).

methyl 3-hydroxytetradecanoate
methyl methacrylate
methyl 4-methyl hexadecanoate
methyl linolenate
methyl nervonate
methyl oleate
methyl palmitoleate

Ketones

normal 2-alkanones $C_3$ to $C_{13}$, $C_{15}$, $C_{17}$, and $C_{19}$
2,6-dimethyl-4-heptanone
2-heptanone
4-heptanone
isophorone
5-methyl-3-heptanone
5-methyl-2-hexanone
4-methyl-2-pentanone
3-pentanone

Phenols

4-t-butylcatechol
m-cresol
2,3-dihydroxynaphthalene
1,4-dihydroxynaphthalene
2,3-dimethylphenol
2,4-dimethyl phenol
4,6-dinitro-2-methylphenol
2,4-dinitrophenol
o-ethylphenol
p-ethylphenol
1-naphthol
2-naphthol
2-nitrophenol
4-nitrophenol
phenol
2,4,6-trimethylphenol

Phthalate Esters

di-n-alkyl: $C_1$ to $C_{12}$
butyl benzyl
di-(2-ethylhexyl)
di-isobutyl
di-isopropyl

only by possible compound class with a rather broad range of possible molecular weights. 411 GC/MS data from analyses of experimental samples are stored on 9-track magnetic tape, so additional compound searches and data manipulation can and will be completed as data on selected standards are obtained.

Both samples, from our flow-through tanks at Scripps Institution of Oceanography and at Kasitsna Bay showed an expected assortment of aldehydes, alcohols and acids. The reconstructed ion chromatogram from Kasitsna Bay showed almost twice as many significant peaks as that from S10, including a number of higher molecular weight compounds with GC/MS data consistent with several steroidal compounds. In this instance, however, none of the specific steroids selected from the library showed very close fit with the GC/MS data. With few exceptions there were no specific assignments to the peaks of the Kasitsna Bay extract. Only the compound class is assigned and several isomers and/or homologs must be considered.

In Particular, the Scripps sample does not show the diverse selection of steroidal possibilities in the high molecular weight region, although there is a small broad peak in that region of the chromatogram which could possibly be attributed to steroidal components. In this sample, several peaks show a reasonably good fit with specific compound assignments: p-methylbenzyl alcohol, the three toluic acids, and fluorenone, although the retention times of these peaks need to be checked against standards. In comparison, the polar extracts isolated from fresh oil samples show nothing in this region. (See Figures 3-1 through 3-4 in Section 3.0.)

It must be stressed that all of the compound and compound class assignments presented here must be considered as tentative only. In many cases, the GC/MS data are not highly convincing, and for many peaks the purity is not very high. The GC/MS data were obtained from a quadruple mass spectrometer, and thus, are not completely consistent with the GC/MS data of the library which were generated on magnetic sector instruments.

The glass capillary/gas chromatographic ($GC^2$) data have been compared with our set of existing standards which for the most part give only a rough guide to the expected retention times for the oxygenated compounds of interest. As noted above, additional standards have been selected (based on these initial compound identifications) and ordered to facilitate these analyses.

Additional work is continuing on the following projects: (1) analyses of additional polar fractions isolated from seawater extracts from the static tank experiments PIUS other flow-through experiments from both SIO and Alaska; (2) derivatization (methylation and/or trimethylsilylation) of the samples for clarification of assignment of alcohols, phenols, and acids; (3} selection and accumulation of suitable polar standards for $GC^2$ retention time calibration and for more precise GC/MS data comparison (generation of GC/MS data sets from known standards run on our quadrupole instrument); and (4) acquisition of additional MS library data (Wiley Interscience and in-house laboratory standards).

### 5.?.4 Results to Date - Continuous Flow Studies (S10 and Kasitsna Bay)

#### Sampling Design

The continuous-flow experimental aquarium systems at Scripps Institution of Oceanography (S10) and NOAA's Kasitsna Bay facility were set up (Summer 1981) and run for at least one week Drier to initiation of each experiment, to allow sufficient time for bacterial fouling, population buildup and stabilization of the microbial community within the aquariums. The tanks receiving the Petrobac® strains were inoculated with the bacterial slurry (prepared as needed from the dry spore-containing mix supplied by Polybac Corp.) each day until Day 7 after initiation of the experiments. After Day 7, the tanks were inoculated every other day for the remainder of the experimental time schedule.

The experimental aquaria and the incoming seawater were sampled for the radiolabeled substrate assays ($^{14}C$-hexadecane, $^{14}C$-methylnaphthalene, $^{14}C$-naphthalene; $H^3$-glucose, $H^3$-leucine, $H^3$-thymidine) on Days 0, 1, 2, 4, 5, 6, 7, 9, 12, 14, 16, 19, 21, 23, 26, 28, 30, 35, 42, 4g, and 56 at SIO and on the same schedule up to Day 30 at Kasitsna Bay. Samples for nutrients, epifluorescence and autoradiography assays were taken on Days 0, 1, 2, 4, 7, 14,, 71, and 28 for both experiments. Seawater samples (20 to 30 liters) for petroleum hydrocarbon and metabolic product analyses were taken on Days 1, 2, 5, Q, 16, 23, 30, 43 and 58 at SIO and up to Day 30 at Kasitsna Bay. To initiate each experiment, approximately 200 ml of Prudhoe Bay crude was added to each experimental aquarium shortly after sampling for the Day O assays listed above. Flow rates through the tanks were maintained by peristaltic pumps (Masterflex, Cole-Parmer Corp.) to provide a seawater throughput of about one tank volume ( 20 liters) per day.

## $^{14}C$-Hydrocarbon Degradation

One of the important "components" of the overall microbial response to input of crude oil into the marine environment relates to the ability of the naturally occurring heterotrophic microbes to utilize the petroleum as a food (organic carbon) source. This capacity is referred to as "degradation Potential", and can be inferred from the relative degree of mineralization (metabolism to $CO_2$) of representative petroleum hydrocarbons. Should selection within the heterotrophic fraction of the indigenous population favor an increase in relative abundance of hydrocarbon degraders, this should be reflected by a concomitant increase in degradation potential. One approach to empirically define this potential, which is sensitive and reproducible, involves exposing the microbes to a $^{14}C$-labeled petroleum hydrocarbon substrate, allowing sufficient time for degradation to occur with subsequent trapping of evolved $^{14}CO_2$ and quantification by liquid scintillation spectrometry. This approach has been taken in various forms in past studies (HARRISON et al. (1971); CAPARELLO and LA ROCK (1975); WALKER and COLWELL (1976); HODSON et al. (]977)), however experimental conditions in most cases have made it difficult

or totally infeasible to extrapolate results to a real spill situation. We have attempted to utilize the degradation potential approach with the continuously flowing seawater aquaria systems at S10 and Kasitsna Bay with the intention of providing empirical information that would be useful in modeling the impact of microbial degradation of spilled petroleum. Although caution must be taken in extrapolating results from a study utilizing such "controlled ecosystems" to open ocean spills, it is felt that our approach optimizes the ability to empirically describe the impact of oil upon various microbiological metabolic processes.

The degradation potential assay involves addition of a $^{14}C$-1abeled hydrocarbon substrate to seawater samples from the experimental aquaria and incoming seawater, incubation in stoppered vials for 24 hrs. at in situ temperatures, trapping of $^{14}CO_2$ and quantification by liquid scintillation spectrometry (details presented in Appendix B). The labeled substrates selected were $^{14}C$-hexadecane, $^{14}C$-methyl naphthalene, and $^{14}C$-naphthalene. The selection was based upon both availability and representation within the compounds and class types found in Prudhoe Bay crude, as well as other crude petroleums.

As indicated previously, the sampling points were concentrated at the beginning of each experiment to best detect and describe any degradation potential increase following input of Prudhoe Bay crude into the four experimental aquariums. The incoming seawater (from the master reservoirs) was also sampled at each time point. and assayed to check for "background" hydrocarbon degradation potential.

The data for the $^{14}C$-hydrocarbon degradation studies have been converted to q/liter-day and are presented graphically in Figures 5-58 for S10 results and Figure 5-59 for Kasitsna Bay, Alaska. The assumption made for data conversion is that trapping and detection of the $^{14}C$ carbon indicates loss of parent compound molecular structure even though total mineralization (to $CO_2$) cannot be deduced. The results from the SIO experiment demonstrate a dramatic increase in the amount of labeled substrate mineralized to $^{14}CO_2$

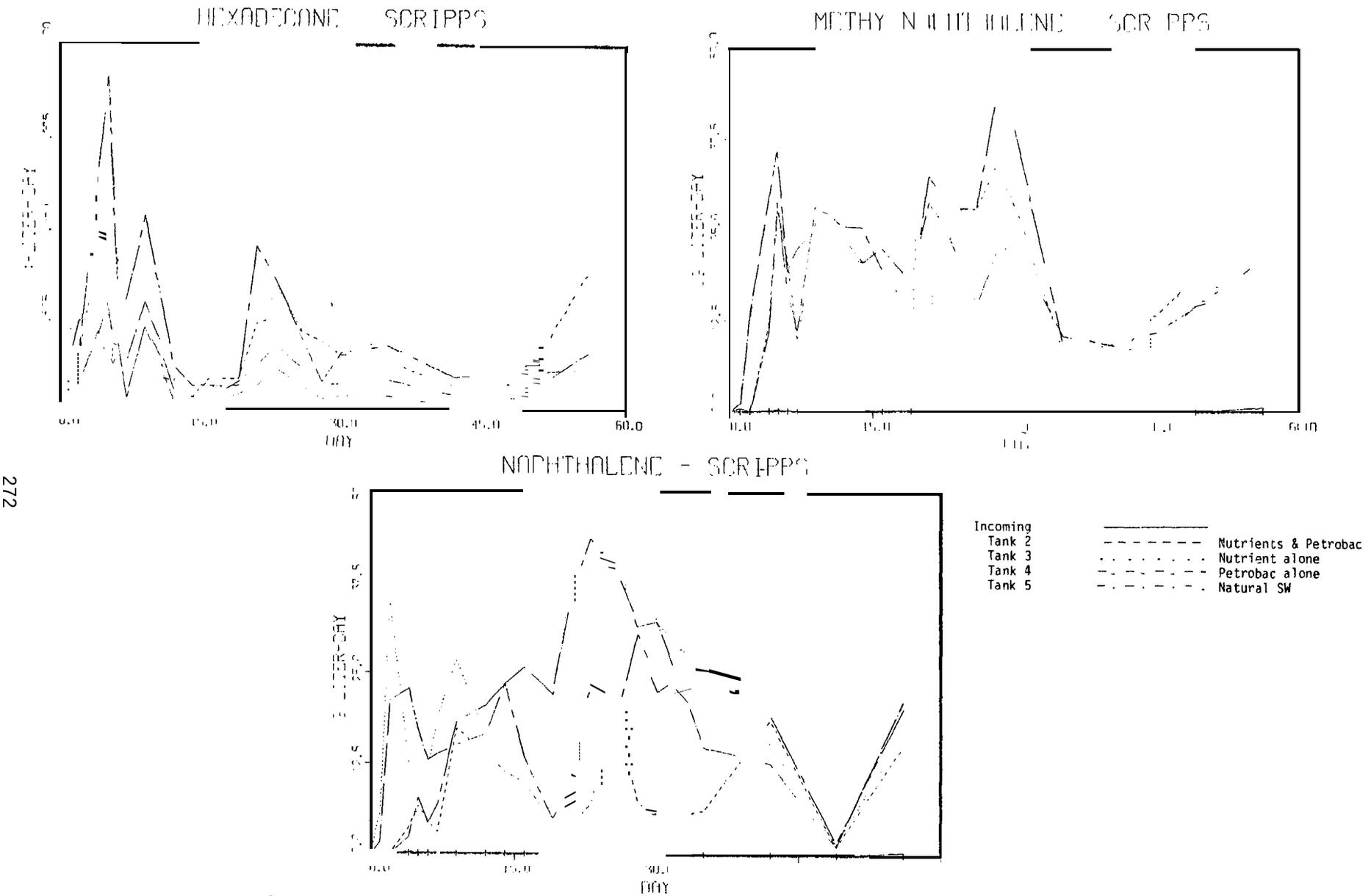



FIGURE 5-58. $^{14}C$-HYDROCARBON DEGRADATION DATA, SCRIPPS INSITUTION OF OCEANOGRAPHY, SUMMER 1981. DATA FOR EACH SUBSTRATE ARE DEPICTED FOR ALL EXPERIMENTAL AQUARIA AND INCOMING SEAWATER. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.

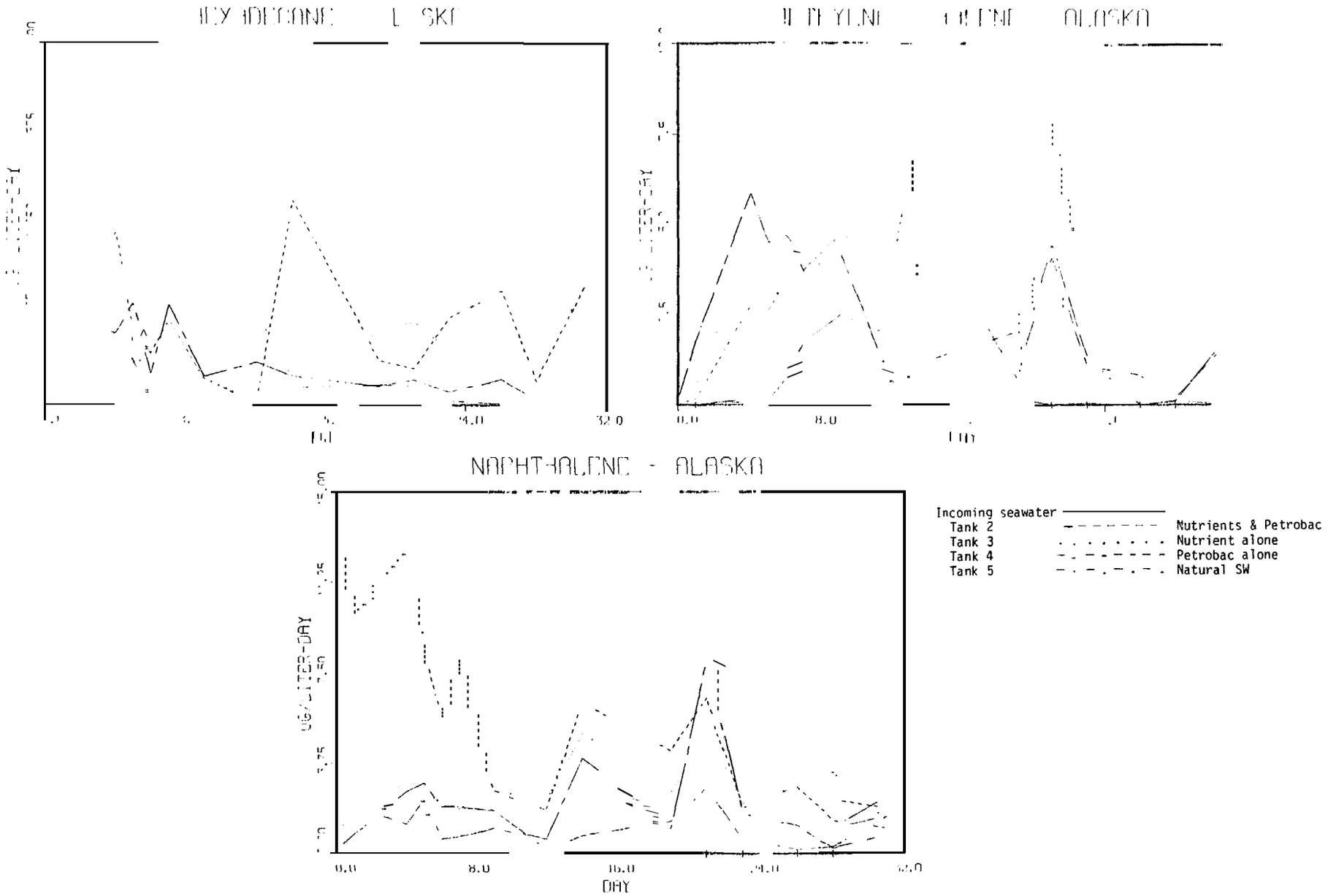



FIGURE 5-59. $^{14}C$-HYDROCARBON DEGRADATION DATA, KASITSNA BAY, ALASKA, SUMMER 1981. DATA FOR EACH SUBSTRATE ARE DEPICTED FOR ALL EXPERIMENTAL AQUARIA AND INCOMING SEAWATER. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.

within 48 hrs after introduction of oil for all three hydrocarbons. At Day 0, hexadecane was slightly degraded although no capacity was apparent for degrading the methylnaphthalene and naphthalene substrates for any of the samples. The incoming seawater never demonstrated any degradation capacity for the aromatic compounds until Day 56, although the hexadecane was degraded to some extent with the pattern (note Figure) being similar to the four experimental systems. Tanks 3 and 5 (both with indigenous microbes only) demonstrated slightly greater utilization of hexadecane over the course of the experiment, with a peakutilization of approximately 5% of the added labeled substrate (again note that percent degradation is based upon the label itself and not the entire compound). All experimental systems followed similar trends (incoming seawater included) with time with an overall degradation rate of roughly 1.5% of the added substrate during any given 24 hr incubation period.

In comparing the relative rates of degradation for radiolabeled hydrocarbon substrates, it must be emphasized that the loss of label ($^{14}C$) from the Parent molecule does not necessarily imply an "upper limit" on the amount of substrate which has been oxidized by microbes. In other words, certain metabolic conversions of the parent compound to other stable forms may occur without loss of the label. In this case, the degradation rate, as based upon detection and quantification of the last $^{14}C$ label, would be an underestimation of the actual amount of the original parent substrate "attached" by the microbial enzymatic systems, As will be noted below, the degradation data suggest that the hexadecane substrate was degraded at much lower rates than for either of the aromatic compounds. However, it is entirely possible that the mode of metabolic conversion for the aliphatic substrate renders the parent compound into stable forms (e.g., carboxylic acids, acetates) which may or may not undergo further mineralization during the 24-hr period of incubation.

Roth of the labeled aromatic hydrocarbon substrates were degraded at substantially higher rates (based on $^{14}CO_2$ production) compared to hexadecane for the SIO experiment. All four experimental aquaria seawater exhibited quite similar patterns for methyl naphthalene, with dramatic increases in the

amounts of substrate mineralization within 48 to 72 hrs to approximately 11%, with an average rate of roughly 6% per day over the 56 days of monitoring. Less consistency between experimental systems is apparent for the naphthalene data, although average degradation rates are comparable to those for methylnaphthalene. Two trends in the aromatic hydrocarbon substrates are worth noting: (1) the tanks inoculated with the Petrobac® mixture (tanks 2 and 5) responded more slowly than tanks with indigenous microbes alone, particularly noticable for the naphthalene data; and (2) in the case of naphthalene, the tanks with and without added Petrobac® exhibited similar trends, although the indigenous or "natural" tanks exhibited higher overall rates of substrate degradation.

The $^{14}C$-hydrocarbon data for the Kasitsna Bay experiment (Figure 5-59) demonstrated several similarities to the results from S10: (1) hexadecane was apparently utilized to a lesser extent than either methylnaphthalene or naphthalene; (2) the incoming seawater demonstrated very 1 ittle capacity for degrading any of the substrates; and (3) some similarities exist between experimental tanks for the two aromatic hydrocarbons, although to a lesser extent than with the S10 systems. Only in the case of methylnaphthalene was a definite increase apparent in rate of mineralization for all four tanks after introduction of Prudhoe Bay crude. Capacity to degrade hexadecane prior to oil introduction was demonstrated by samples from tanks 2 and 5 (which received Petrobac® inoculation) and for naphthalene in tank 2 only. Two additional trends which contrast the results from the S10 experiment are: (1) greater methylnaphthalene utilization for nutrient supplemented tanks (2 and 3) where nutrient supplementation had no apparent effect in S10 mineralization rate data; and (2) rates of substrate degradation were substantially lower in the Kasitsna Bay systems for all three hydrocarbons relative to the S10 experiment. This could be attributable to generally lower metabolic activities due to colder water temperatures, as they averaged 19 to 21°C during the course of the SIO study and 9 to 11°C for the Alaska study. The epifluorescence and autoradiography assays will provide an indication of relative mocrobial abundance and metabolic activity, respectively, between the S10 and Kasitsna Bay systems. However, these analyses are still underway at the time of this writing such that no definitive data are yet available.

## $^3$H-Labelled Substrate Uptake/Incorporation

To further assess the impact of spilled petroleum upon microbial heterotrophic activity, it is necessary to determine influences on heterotrophic production (growth rates), microbial biomass, general metabolic activity and relative metabolic activity (e.g., % metabolically active microbes within the heterotrophic population). The utilization of radiolabeled organic substrates at near ambient concentrations for determining rates of uptake and/or incorporation into cell biomass is a viable and sensitive empirical approach and has been pursued in past studies (AZAM and HOLM-HANSEN, 1973; HODSON et al., 1977; FUHRMAN et al., 1980; FUHRMAN and AZAM, 1980; GRIFFITHS and MORITA, 1981). The use of tritium-labelled organic compounds (sugars, amino acids, etc.) of high specific activities allows for direct measurement of uptake at near ambient concentrations ($10^{-8}$ to $10^{-9}$ M) and precludes the necessity of extrapolation using the Michaelis-Menten equation (as is needed when substrate concentrations are utilized which are greater than those normally found in the marine environment).

The incorporation of $^3$H-thymidine into bacterial DNA serves as a reasonable measure of DNA synthesis and cell production, although several assumptions and measurements are required for conversion of thymidine incorporation data into production estimates (FUHRMAN and AZAM, 1980). The level or rate of uptake (nmoles/liter-day) is converted to bacterial cell production rates (cells/liter-day) with an estimation of the DNA contentof natural marine bacteria. This conversion has been recently refined by FUHRMAN and AZAM (in press, 1981), into separate coefficients for the nearshore and offshore (> 10 km) waters studied (Southern California Bight). Estimations of average cell biomass by epifluorescence photomicroscopy allow for further data conversion from production rates (cells/liter-day) to organic carbon production (μg/C/liter-day). This is accomplished by determining cell size (volume) distributions and correlating the data to the amount of carbon per cell with a conversion factor developed by WATSON et al. (1977).

General metabolic activities have been determined by the $^3$H-glucose and $^3$H-leucine. The specific techniques utilized do not differentiate between substrate respired from that incorporated (assimilated) into cell biomass, and therefore the overall uptake cannot be used to estimate cellular production. However, FUHRMAN et al. (1980) found significant rank correlations between thymidine incorporation (mol/liter-day), thymidine turnover rates (%/hr), bacterial abundance or biomass (from epifluorescence microscopy) and glucose turnover rates(%/hr) in the euphotic zone of the Southern California Bight. Their results suggest that these methods may be comparable for assaying relative total bacterial activity between water samples.

An additional component of overall metabolic activity, in relation to the presence of crude petroleum, is that of relative or percent metabolic activity within the heterotrophic microbial population at any point in time. Although the epifluorescence microscopy yields information on bacterial abundance and biomass, it gives no indication of the metabolic state or relative activity. The latter type of information can be useful in the interpretation of the $^3$H-glucose, $^3$H-leucine, and $^3$H-thymidine assay data and is provided by microautoradiography. This approach gives indication of the percent metabolically active heterotrophs as determined from the fraction of cells which have taken up a radiolabelled organic substrate during a short period of incubation.

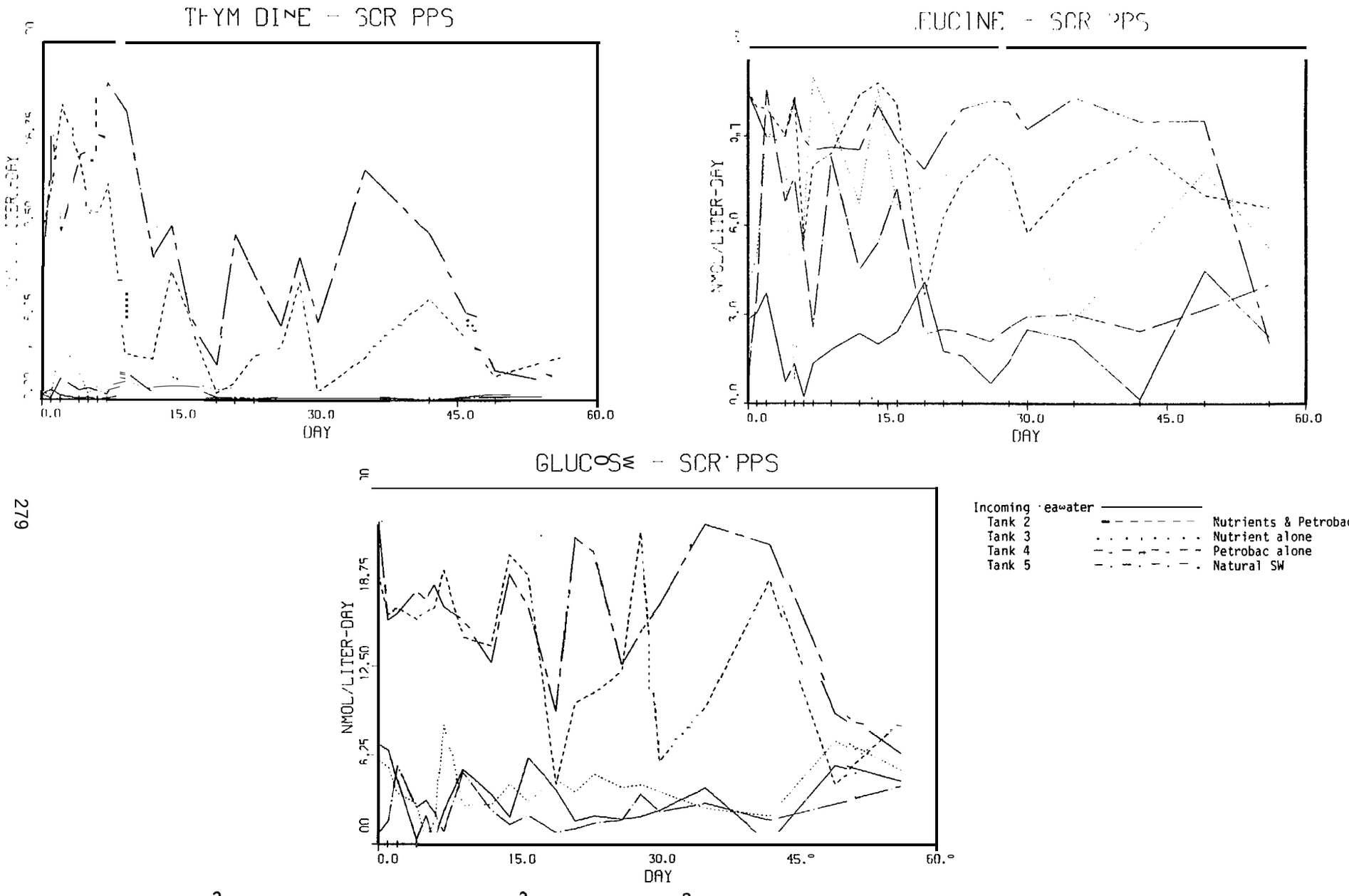
As details for the techniques mentioned above are presented in Appendix B, it will suffice here to briefly describe the procedures. The $^3$H-thymidine incorporation assay involves incubation of a seawater sample at in situ temperatures for uptake and subsequent incorporation into DNA of added labelled thymidine. The sample is filtered and the retained cells are extracted to remove non-incorporated label, and the amount of incorporated thymidine is determined by liquid scintillation spectrometry (LSC). The $^3$H-glucose and $^3$H-leucine uptake assays are very similar to the thymidine procedure except that no extraction step is performed to remove intracellular pools prior to quantification of retained label by LSC. In the epifluorescence techniques the cellular DNA is stained with a fluorescing dye, the sample is filtered and

the retained cells are counted and photographed under a phase contrast microscope fitted with an epifluorescent illuminator. The microautoragiography procedure is actually a combined autoradiography/epifluorescence technique in that cells are both radioactively and fluorescently labelled resulting from uptake of $^{3}$H-leucine and DNA staining with the fluorescent dye, respectively. The sample is filtered and the filter is treated with a photographic emulsion and developed. The cells having sufficient radioactivity from substrate uptake have silver grains associated with them, and comparison of total cells from epifluorescence examination to cells with associated silver grains indicates the percentage of active cells present at the time of sampling.

The $^{3}$H-thymidine incorporation, $^{3}$H-leucine uptake, and $^{3}$H-glucose uptake data for the S10 and Kasitsna Bay experiments are presented graphically in Figures 5-60 and 5-61, respectively. All data have been converted to uptake rates in nmoles/liter-day and are being normalized to uptake on a per bacterial cell basis at the time of this writing.

In the S10 thymidine incorporation experiments, all four experimental aquaria demonstrated similar patterns in terms of an initial increase in incorporation rates after introduction of oil, followed by a general decline and periodic fluctuations during the 56 days of monitoring. Higher rates of incorporation were apparent in the Petrobac® inoculated tanks (2, 5), which may be attributable to higher overall numbers of cells. The incoming seawater remained relatively inactive during the course of the experiment, and this may also be attributable to the relative abundance of bacteria (abundance data will be discussed below).

The leucine uptake data from the S10 experiment appear difficult to interpret due to the large fluctuations with time and between experimental systems. However, there is a significant difference between Petrobac® innoculated tanks (2, 5) and the tanks with "natural" microbes only (3, 6) in that the Petrobac® tanks demonstrated a slight decrease in leucine uptake after oil introduction whereas tanks 3 and 6 exhibited a sharp rise in uptake rates




GURE 5-60 $^{3}$H-THYMIDINE NCORPORATION, $^{3}$H-LEUCINE AND $^{3}$H-GLUCOSE UPTAKE DATA, SCRIPPS INSTITUTE OF OCEANOGRAPHY, SUMMER, 1981. DATA FOR EACH SUBSTRATE IS DEPICTED FOR ALL EXPERIMENTAL AQUARIUMS AND INCOMING SEAWATER. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.

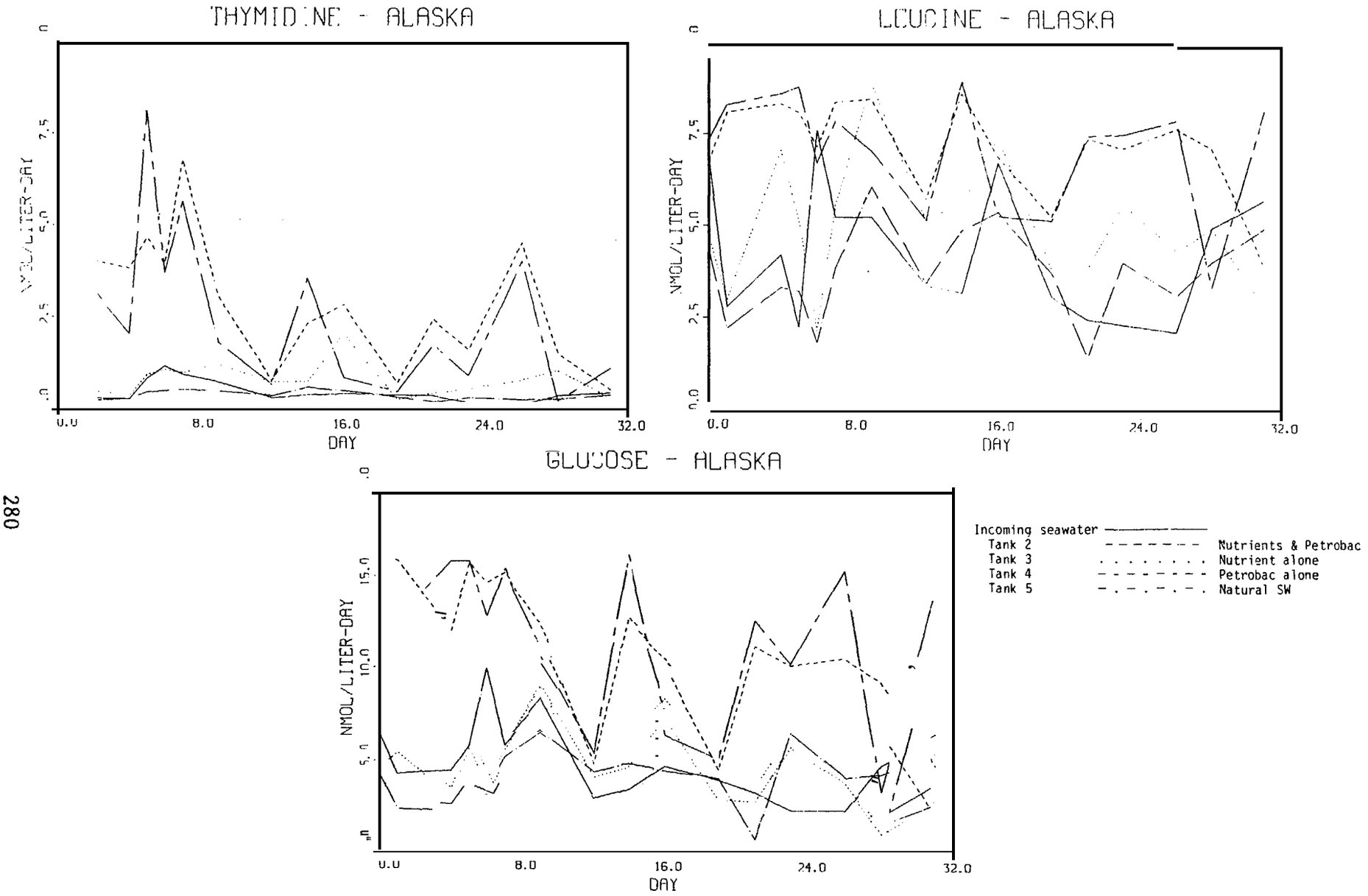



FIGURE 5-61. $^{3}$H-THYMIDINE INCORPORATION, $^{3}$H-LEUCINE AND $^{3}$H-GLUCOSE UPTAKE DATA, KASITSNA BAY, ALASKA, SUMMER, 1981. DATA FOR EACH SUBSTRATE IS DEPICTED FOR ALL EXPERIMENTAL AQUARIUMS AND INCOMING SEAWATER. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS

followed by declines. Some stability in trends among the systems is apparent after two weeks which in some cases paralleled trends of the incoming seawater.

The S10 glucose uptake data demonstrate a general decline in rates after oil introduction with exception to tank 6. The Petrobac® inoculated tanks (2, 5) exhibited higher rates of uptake over the course of the experiment and this may be attributable to higher bacterial abundance. Tanks 3 and 5 behaved verv similarly to the incoming seawater for this Particular substrate.

The thymidine incorporation data for the Kasitsna Bay experiment bear resemblances to the S10 results in that (1) a general increase in thymidine incorporation is apparent after oil introduction with roughly the same period of response, and (2) the Petrobac® inoculated aquaria demonstrated generally higher rates of incorporation. Epifluorescence data for the Kasitsna Bay experiment are not available at this time, so references to relative microbe abundance cannot be made.

The leucine uptake data for Kasitsna Bay are difficult to interpret, as was the corresponding S10 data, due to variance between systems. The Petrobac® innoculated tanks (2, 5) demonstrated no real impact from oil introduction and had generally higher levels of uptake. The tanks with "natural" microbes only exhibited a drop in uptake after oil introduction, however this drop was also apparent for the incoming seawater which supposedly had never been exposed to spilled petroleum.

The glucose uptake data from Kasitsna Bay bear resemblance to that from S10 in that (1) most systems demonstrated some decline in uptake and (2) the Petrobac® inoculated systems showed generally higher uptake rates, where the other experimental tanks (3, 5) more closely followed trends of the incoming seawater.

As indicated previously, bacterial abundance data from epifluorescence microscopy is available only from the S10 experiment at this time. Samples were taken for epifluorescence counts from each experimental aquarium and the incoming seawater every day for the first week and then on a weekly basis. The incoming seawater contained approximately $10^6$ cells/ml throughout the study and this was stable.

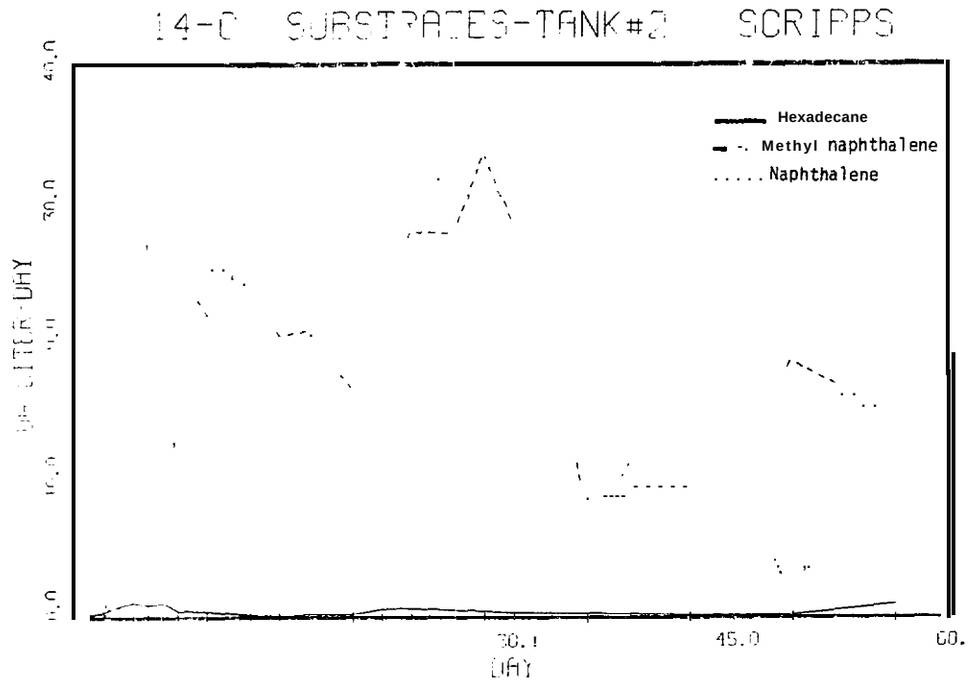
The tanks receiving Petrobac® inoculations (2, 3) averaged roughly 5 x $10^6$ cells/ml with tank 2 demonstrating the greatest variations including a large increase on Day 7 to 32 x $10^6$ cells/ml, followed by a decline to previous levels. The tanks with "natural" microbe populations (3, 6) contained approximately 2 x $10^6$ cells/ml and were relatively stable.

The epifluorescence photomicroscopy for counts and biomass determinations, as well as the microautoradiography for all remaining samples from the S10 and Kasitsna Bay are being completed at the time of this writing.

## Relations Between $^{14}C$ and $^{3}H$ Substrate Assay

To determine if any relationships exist between the degradation of the $^{14}C$-labelled hydrocarbons and uptake/incorporation of the $^{3}H$-labelled organic substrates, the data for each experimental system were plotted individually to include all substrates for the given experiment. The results from the S10 study are depicted in Figures 5-62 to 5-65, and for the Kasitsna Bay study in Figures 5-66 to 5-70.

As noted previously, a dramatic difference in degradation rates of hexadecane vs methylnaphthalene and naphthalene appears to exist for all experimental systems for both the SIO and Kasitsna Bay studies. The aromatic hydrocarbon substrates were degraded at significantly higher levels than the aliphatic compound, which seems to be in contrast to trends arising in many past studies (JORDAN and PAYNE, 1980). Both aromatic hydrocarbon substrates were degraded at comparable rates for all systems in each experiment, and the



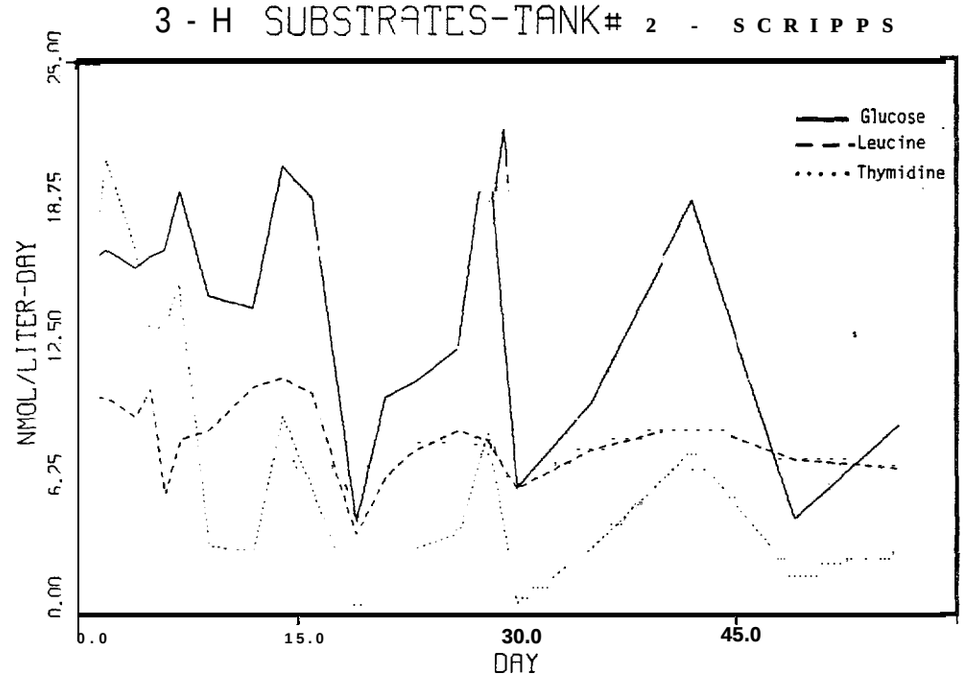
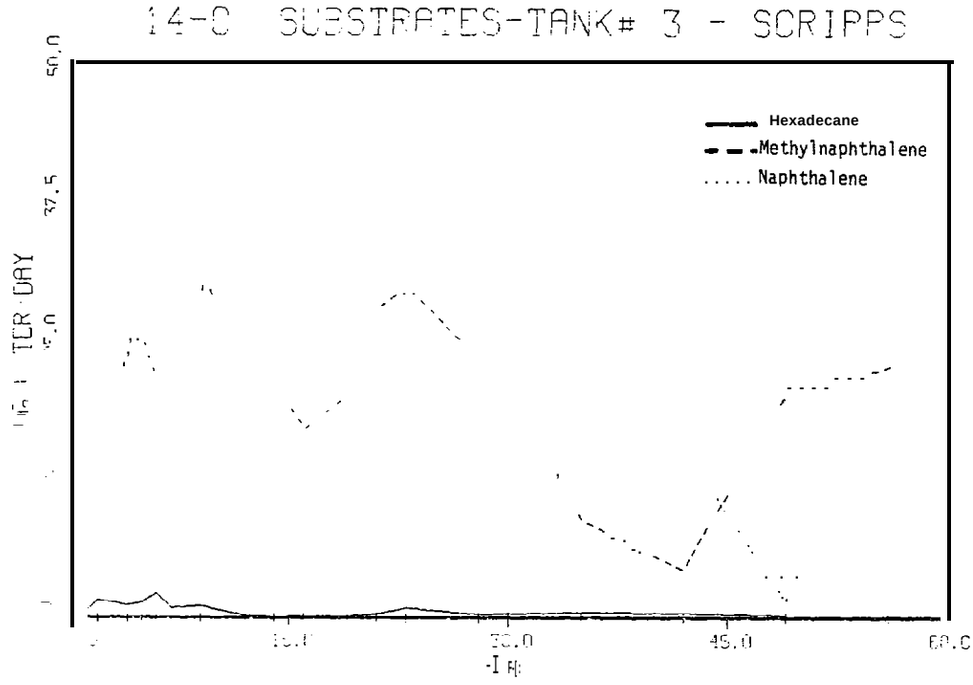
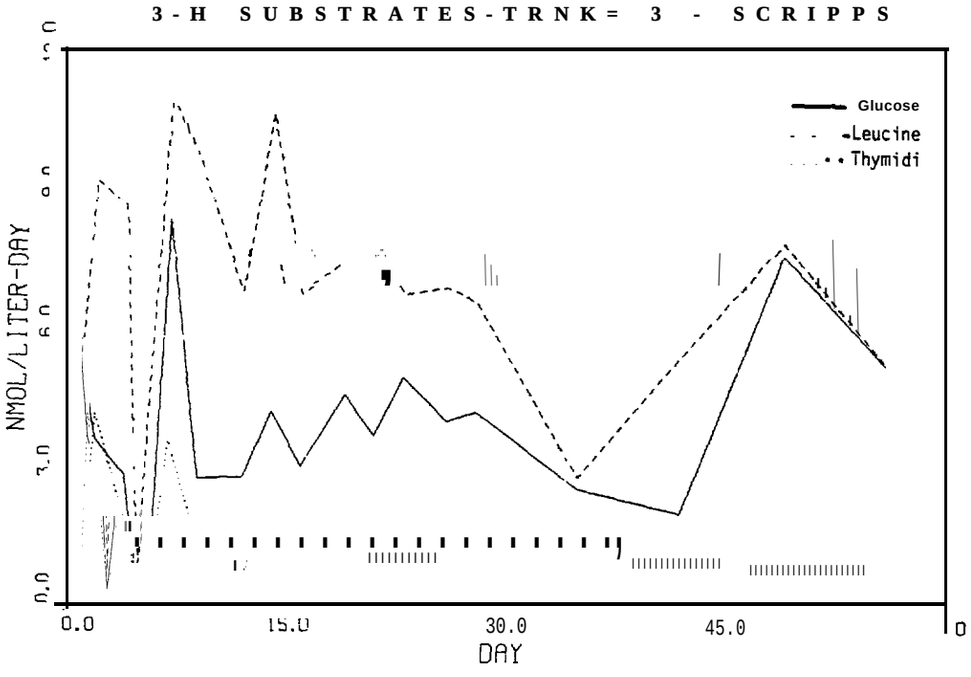
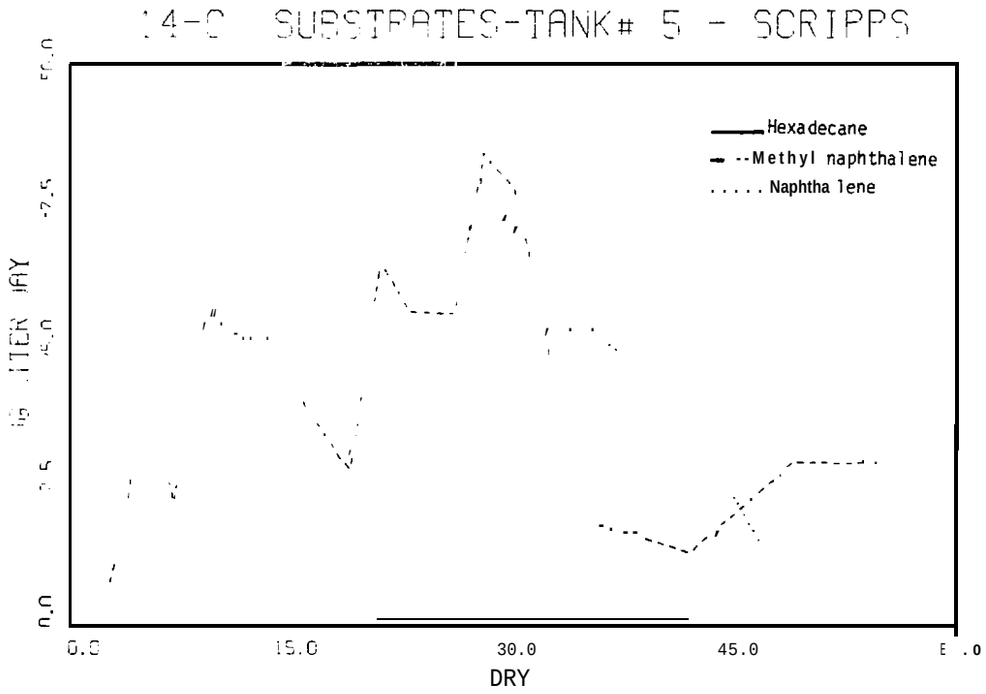




FIGURE 5-62. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK 2 (PETROBAC AND NUTRIENTS), SCRIPPS INSTITUTE OF OCEANOGRAPHY, SUMMER 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINT.




FIGU FIGURE 5-63. $^{14}$C-HYDROCARBON DEGRADATION AND $^{3}$H-SUBSTRATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK3 (NUTRIENTS ALONE), SCRIPPS INSTITUTE OF OCEANOGRAPHY, SUMMER 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



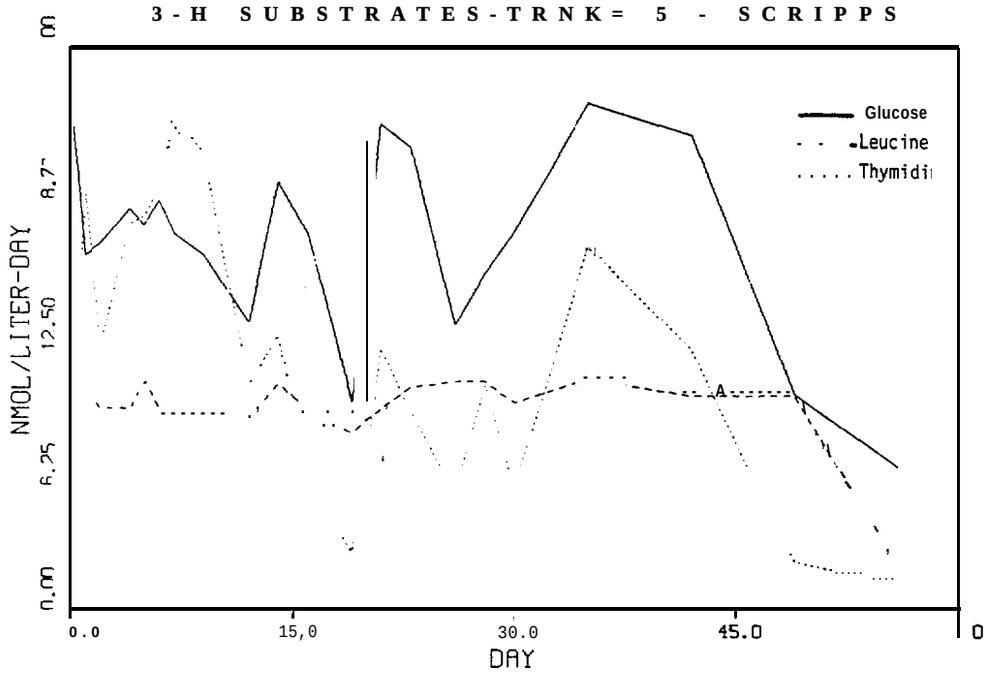
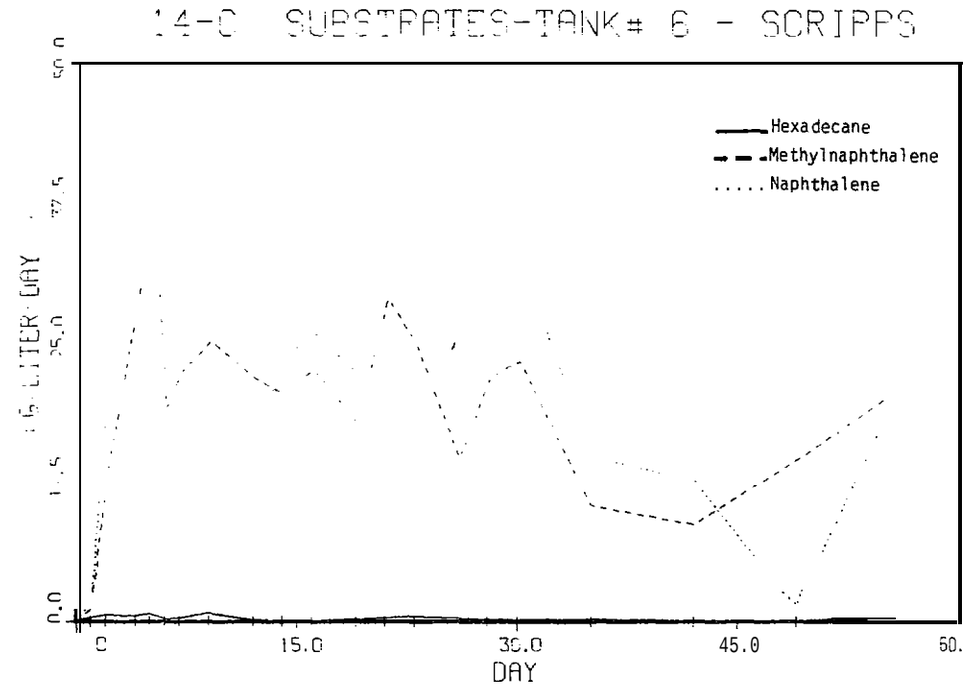




FIGURE 5-64. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK 5 (PETROBAC ALONE), SCRIPPS INSTITUTE OF OCEANOGRAPHY, SUMMER 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



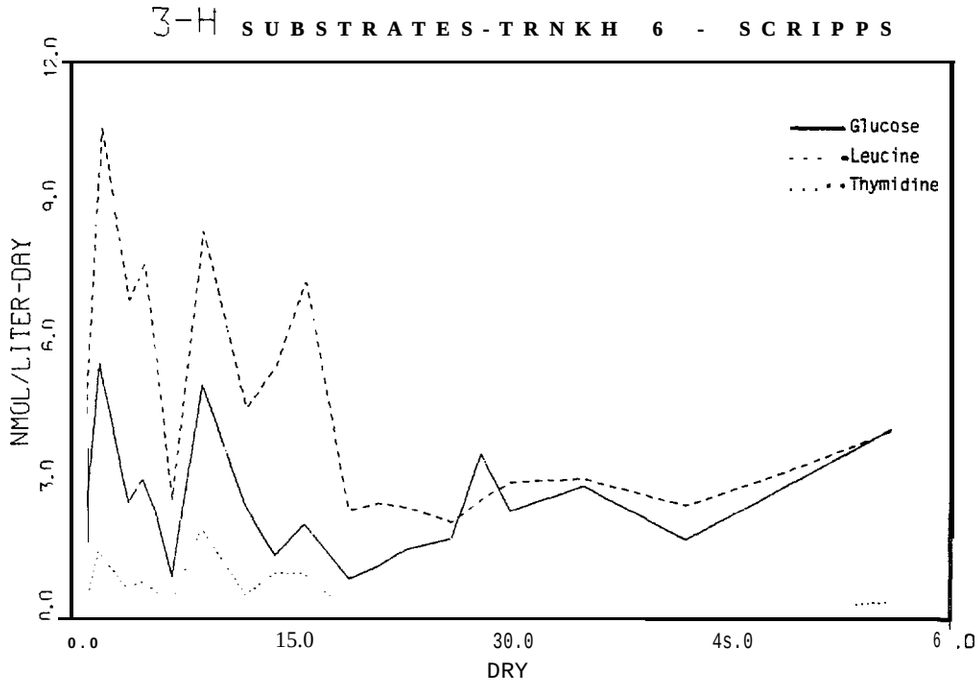
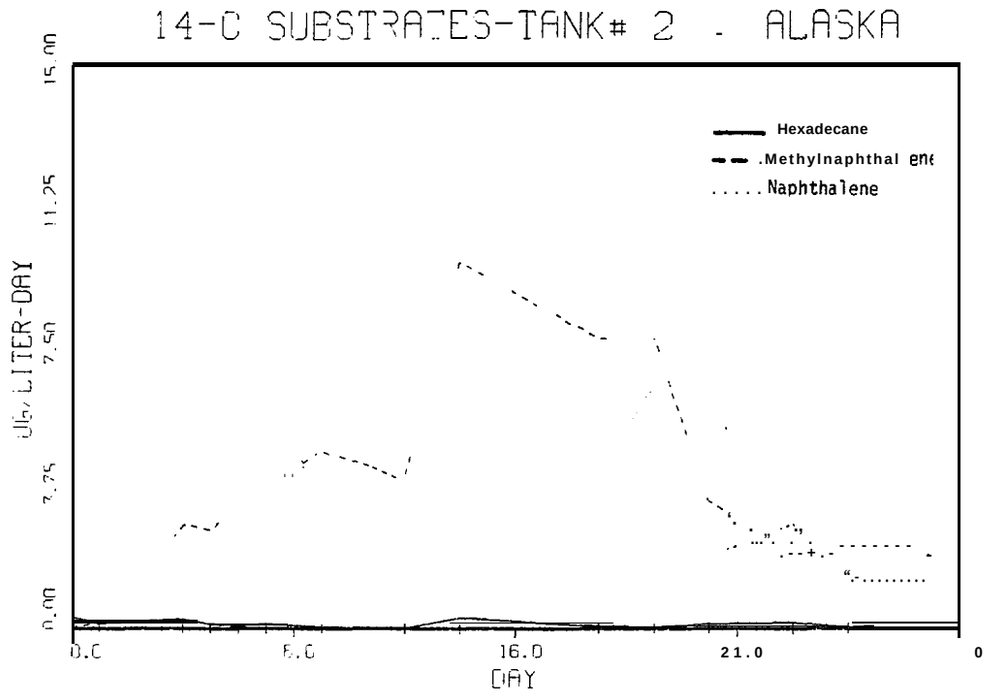




FIGURE 5-65. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/UPTAKE DATA FOR EXPERIMENTAL TANK 6 (NATURAL SEAWATER), SCRIPPS INSTITUTE OF OCEANOGRAPHY, SUMMER 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



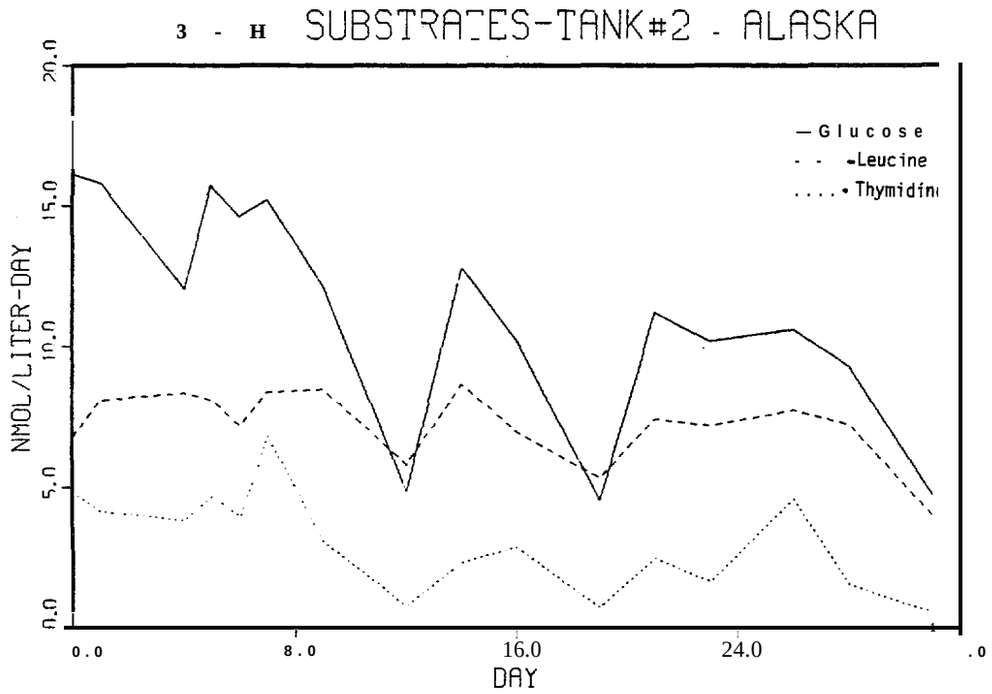
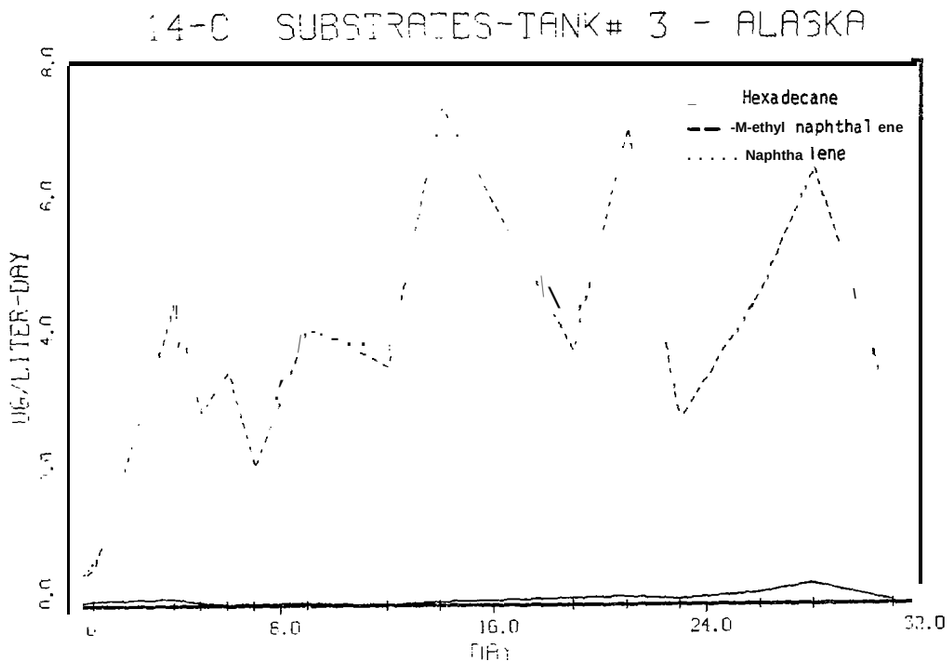




FIGURE 5-66. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/UPTAKE DATA FOR EXPERIMENTAL TANK #2 (PETROBAC AND NUTRIENTS), KASITSNA BAY, ALASKA, SUMMER, 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



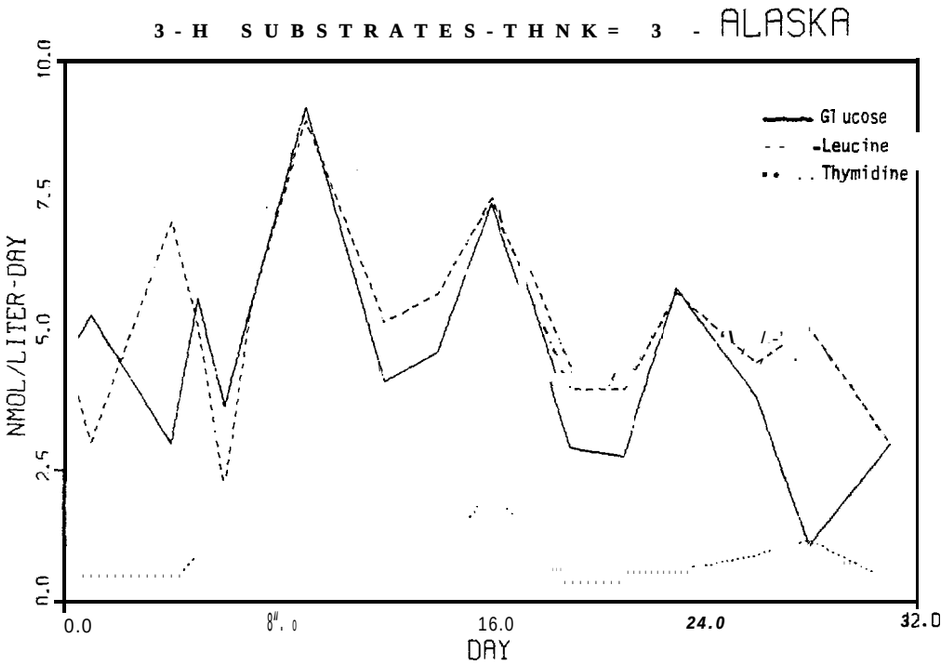
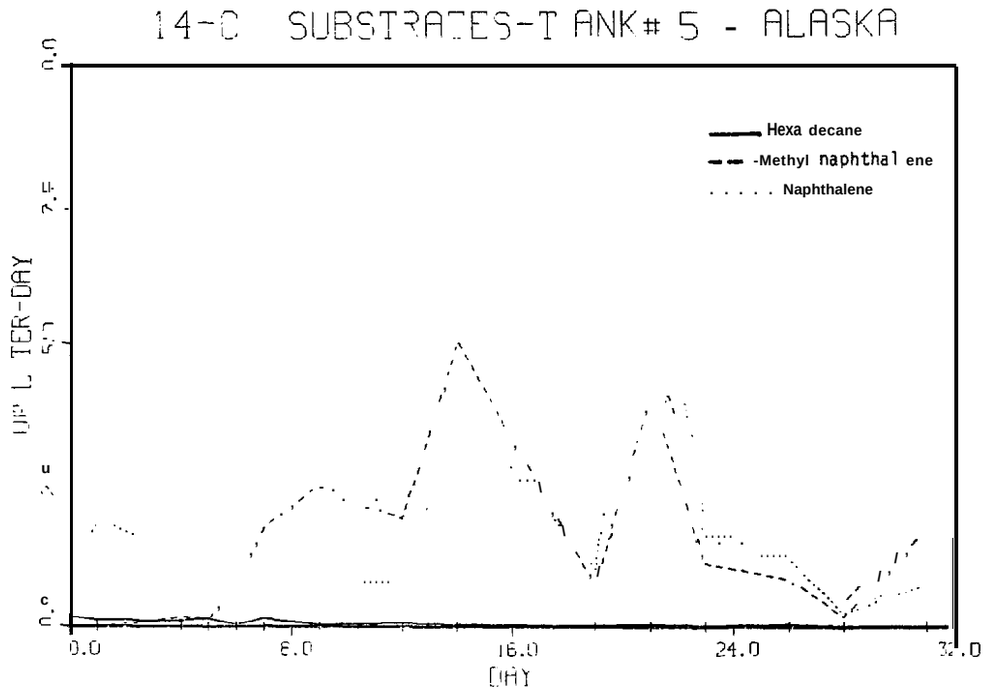




FIGURE 5-67. $^{14}$C-HYDROCARBON DEGRADATION AND $^{3}$H-SATURATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK #3 (NUTRIENTS ALONE), KASITSNA BAY, ALASKA, SUMMER, 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



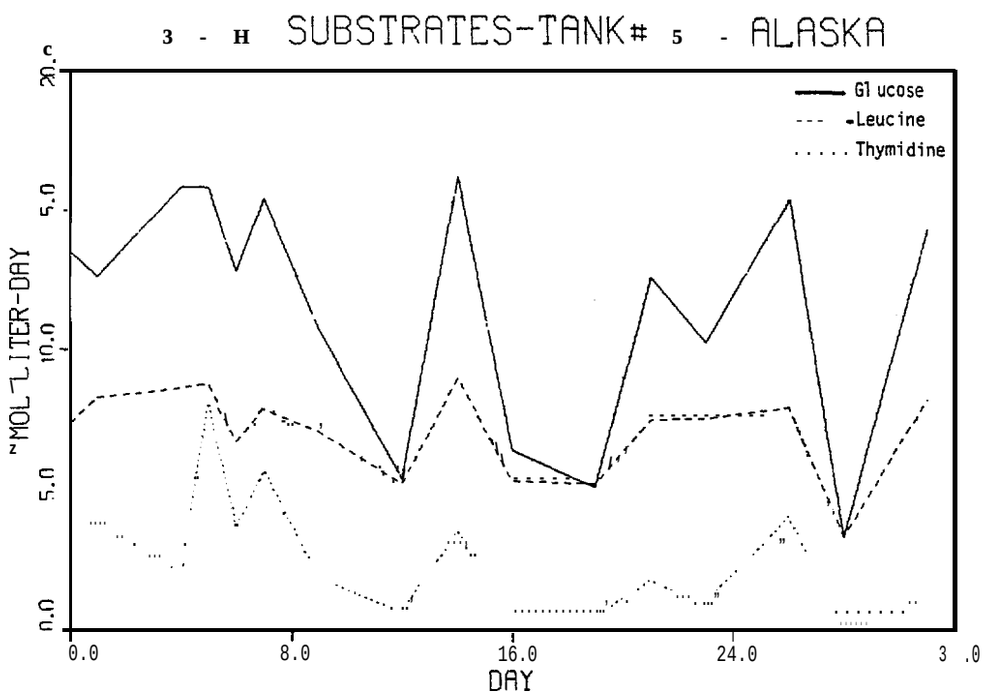
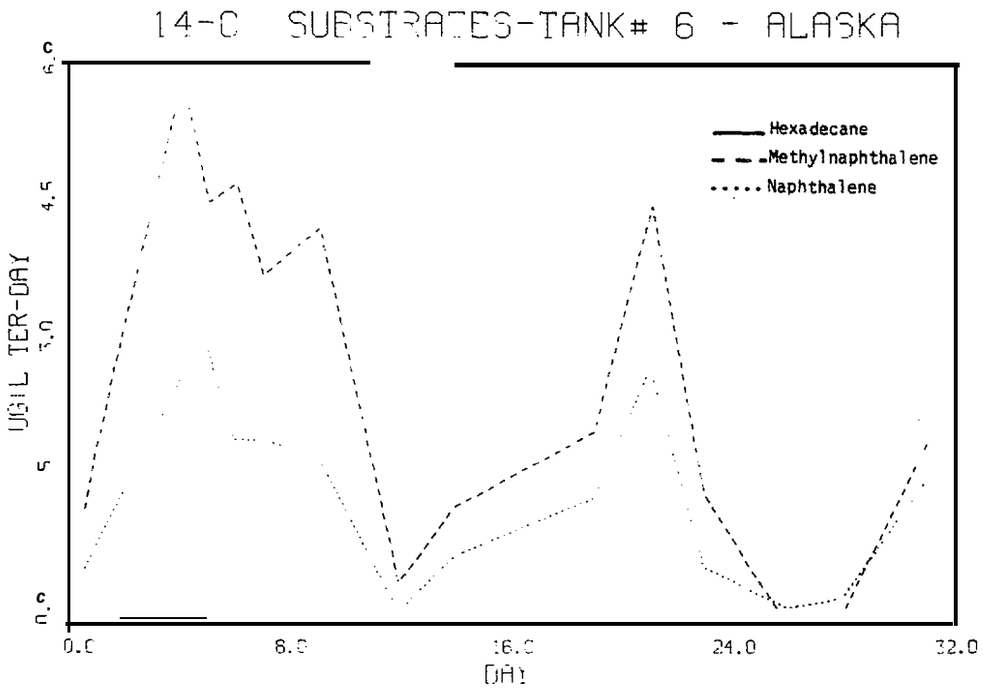




FIGURE 5-68. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK #5 (PETROBAC ALONE), KASITSNA BAY, ALASKA, SUMMER, 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



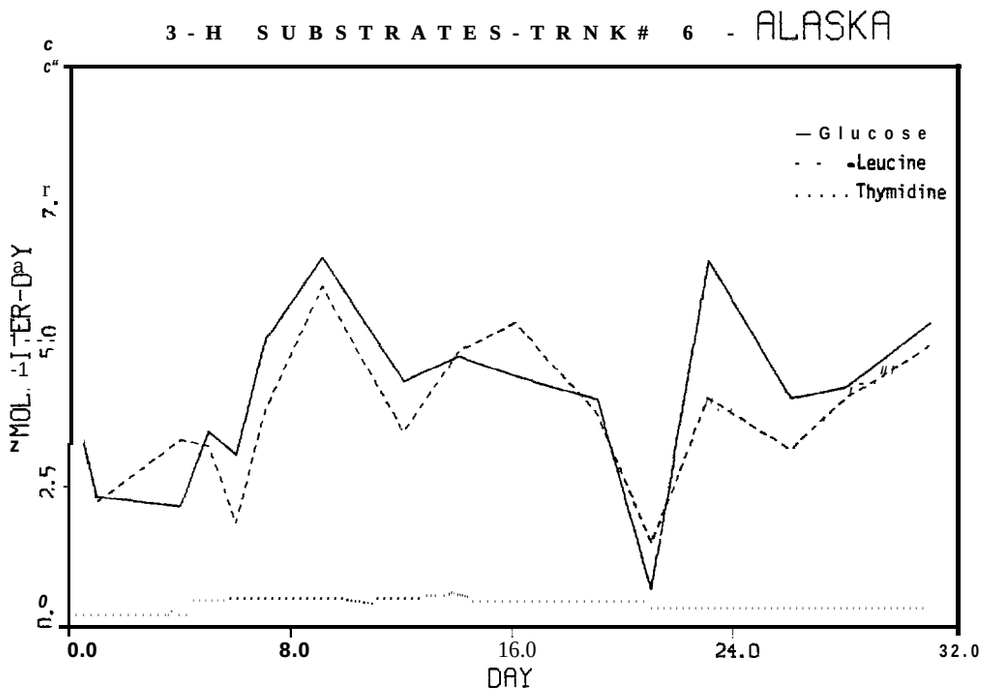
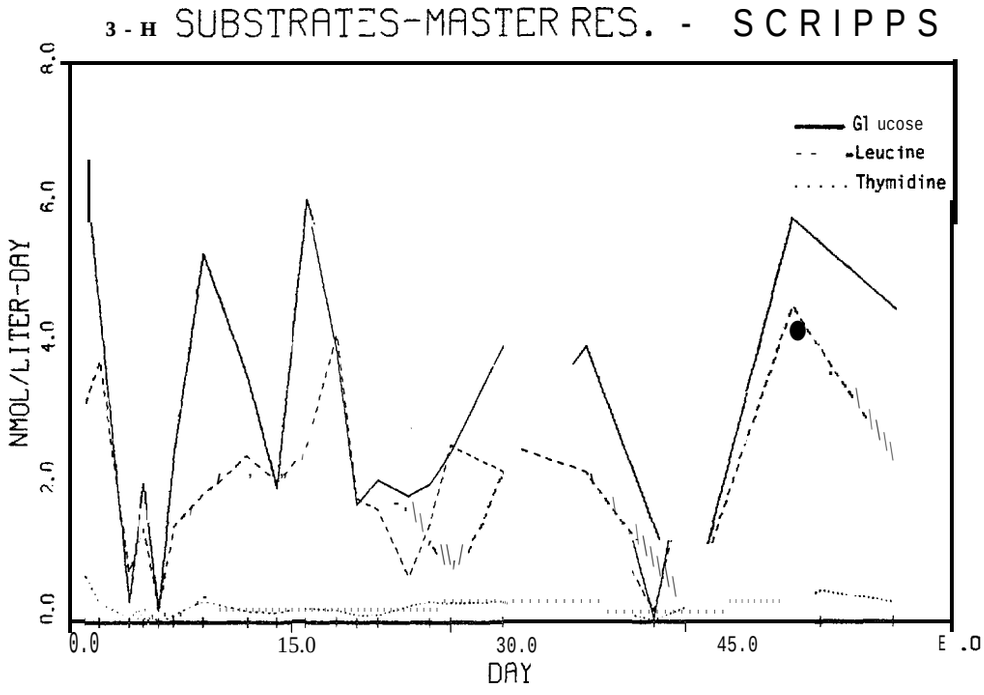




FIGURE 5-69. $^{14}C$-HYDROCARBON DEGRADATION AND $^{3}H$-SUBSTRATE INCORPORATION/ UPTAKE DATA FOR EXPERIMENTAL TANK #6 (NATURAL SEAWATER), KASITSNA BAY, ALASKA, SUMMER, 1981. VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.



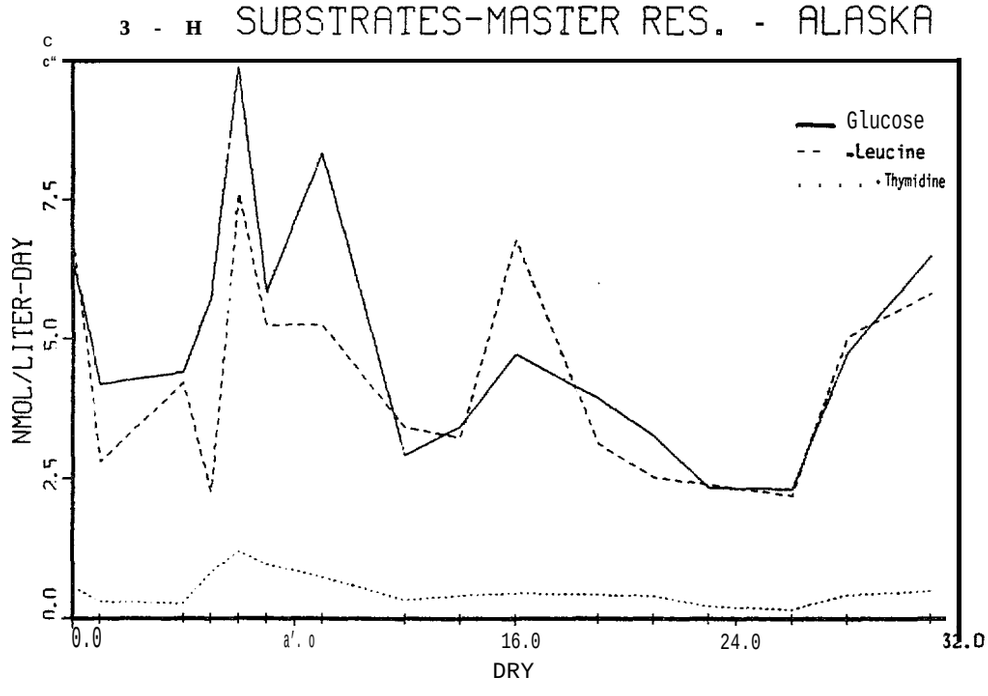




FIGURE 5-70. $^{3}$H-THYMIDINE INCORPORATION, $^{3}$H-GLUCOSE AND $^{3}$H-LEUCINE UPTAKE DATA FOR INCOMING SEAWATER (SCRIPPS INST. OF OCEANOGRAPHY AND KASITSNA BAY, ALASKA, SUMMER 1981). VERTICAL LINES ON ABSCISSA INDICATE SAMPLING POINTS.

patterns (relative rates) were also very similar between the two substrates in most cases. However, it must again be emphasized that the relative rates of degradation between labelled substrates, as based upon 10SS of the $^{14}C$ label, does not imply an upper limit on the actual amount of parent substrate undergoing metabolic conversion during the given period of incubation. This consideration could most certainly negate the apparent contrast in rates of degradation between the aliphatic and aromatic substances.

To further assess the soundness of utilizing data from this empirical approach for generating rates of degradation, it would be valuable to examine the partitioning of the parent labeled hydrocarbon substrate and associated metabolic products into the bacterial cell material and surrounding water column. This would be helpful in evaluating the apparent rate data for any given labelled substrate in that the approach would not rely solely upon loss of the $^{14}C$ label (to $^{14}CO_2$), and evidence of metabolic conversion of the parent compound" without loss of label can be obtained. To facilitate this evaluation in future experiments, we will determine the relative concentrations of labelled hydrocarbon substrate in the polar and nonpolar fractions of both cellular extracts and surrounding seawater (filtrate) for samples incubated with a given $^{14}C$-labelled hydrocarbon. The bacterial cells will be isolated by filtration and then the filter and filtrate will be extracted with the appropriate organic solvent. The polar and nonpolar fractionation can be accomplished with liquid solid (silica gel), column chromatography procedure, and the radioactivity for the fractions can be determined by liquid scintillation spectrometry. The polar fractions for both the cellular and water (filtrate) extracts should contain metabolized components and the nonpolar fractions should contain parent substrate. Since only the $^{14}C$ label will be detected, interference from other components (e.g., polar lipid material) is not a problem. The activity of all fractions together with the trapped $^{14}CO_2$ should provide for a mass balance determination for the amount of labelled hydrocarbon substrate originally added to the seawater sample.

In terms of relations between the $^{14}C$ and $^{3}H$-label led substrate trends, only in tanks 2 and 3 for the S10 study was a definite increase in hydrocarbon substrate degradation present which paralled increases in rates Of thymidine incorporation and glucose and leucine uptake after introduction of oil (Figures 5-62, 5-63). In most cases, no apparent impacts on the $^{3}H$-labelled substrate incorporation/uptake rates following oil introduction are obvious from the data. This is particularly true for the systems receiving the Petrobac® inoculations. It should be noted however, that the experimental aquaria in the Kasitsna Bay study demonstrated generally lower rates of $^{14}C$- and $^{3}H$-labelled substrate utilization (relative to the S10 study), and that "experimental noise" from variance inherent in the techniques may tend to obscure general trends unless they are highly prominant.

In summary, the trends which are most apparent in the data for the continuously-flowing experiments conducted at S10 and Kasitsna Bay are the following:

- the $^{14}C$-hexadecane appeared to be degraded at much slower rates than either $^{14}C$-methylnaphthalene or $^{14}C$-naphthalene (note previous statements on interpretation of relative rates).
- both aromatic hydrocarbon substrates were utilized at comparable rates with patterns (relative rates over time) following closely in most systems.
- generally lower rates of degradation were apparent for the Kasitsna Bay study relative to the SIO experiment.
- in most cases, dramatic increases in degradation rates for the $^{14}C$-hydrocarbon substrates occurred within 48 hrs. of oil introduction.
- nutrient supplementation had no apparent influence on degradation rates except for some slight evidence in the Kasitsna Bay study (note Figures 5-66 vs 5-68, and 5-67 vs 5-69).
- Increases in $^{3}H$-thymidine incorporation into cell DNA were apparent after oil introduction for the SIO data and to a much lesser extent for the Kasitsna Bay study.

- high variance in the $^{3}H$-glucose and $^{3}H$-leucine data exists for most experimental systems in both studies with no apparent impact from oil introduction except for some initial trends.

- only in two of the experimental aquaria (S10) was there a concomittant increase in both $^{14}C$-labelled and $^{3}H$-labelled substrate utilization after introduction of Prudhoe Bay crude.

Further Data Development - Relationships to Modeling Efforts

To evaluate the removal of petroleum components from the slick-seawater interface due to microbial degradation, certain extrapolations may be made from $^{14}C$-hydrocarbon degradation rate data. This approach will give an approximation of microbial ly-induced compound removal to help in development of the proper algorithms. The question to be answered by such approximations is one of relative significance (e.g., compared to dissolution, do microbes help to remove substantial amounts of organic carbon?). The existing rate data for the $^{14}C$-hydrocarbon substrates will be converted to total petroleum hydrocarbon compound rates by utilizing the relative abundance of hexadecane to aliphatic content and the relative abundance of methylnaphthalene and naphthalene to overall aromatic hydrocarbon content of Prudhoe Bay crude. This type of extrapolation is forced to assume that hexadecane is a "typical" aliphatic and that methylnaphthalene and naphthalene are "typical" aromatics in terms of biodegradability. This approach also says nothing for residual components; however, it will serve as a first-estimate of microbial impact upon overall dissolution. The $^{14}C$-substrate data will also be normalized to a "per cell" basis for estimation of uptake of organic carbon into the bacterial biomass. Completion of the epifluorescence analyses will be required for this, so estimates (e.g., mass of C/liter-day uptake) cannot be made at this time.

As previously indicated, the rates of degradation for a particular $^{14}C$-labelled hydrocarbon substrate are based upon the 1oss and subsequent detection of the label ($^{14}C$ in $^{14}CO_2$), and this may lead to an underestimation of the actual amount of parent material metabolized during the incubation period. Efforts are being undertaken to provide a basis for evaluating each

of the three substratus in terms of a mass balance approach. As described in Section 5.2.4, the approach can provide evidence of metabolic conversions without loss of the $^{14}C$ label and this would then infer an underestimation of the metabolism rate as based upon detection of $^{14}CO_2$. If a mass balance can de derived, then corrections can be made on existing $^{14}CO_2$ data for better estimations of degradation rates (with "degradation" defined as 1oss of parent compound molecular structure).

The $^{3}H$-thymidine data are being utilized to estimate bacterial secondary production by taking into account the average DNA content of cells and the average organic carbon content (related to cell volumes). These production estimates will be compared to organic carbon uptake estimates from the $^{14}C$-substrate data to see if organic carbon flux information can be derived.

### 5.2.5 Petroleum Hydrocarbon Analyses from Selected Flow-Through Microbial Degradation Experiments

#### Limited-Term Hydrocarbon Analyses -- SIO

Attention will be limited in this section to selected seawater extracts from the S10 study, as all petroleum hydrocarbon analyses by capillary gas chromatography for the SIO continuous-flow experiments have not been completed at this time. The chromatograms depicted in Figures 5-71 to 5-73 represent the aromatic (F2) and polar (F3) fractions (silica gel liquid--solid chromatographic fractionation) analyzed by fused-silica capillary gas chromatography with flame ionization (FID) detection. The fractions are from the $CH_2Cl_2$ seawater extracts for tanks 5 (Petrobac® inoculated) and 6 ("natural" microbes only) for several sampling points (Day 2, 5, 9, and 23 days).

The aliphatic (F1) fractions from all seawater samples analyzed to date for the S10 study contained only trace amounts of aliphatic hydrocarbons, which is to be expected since the less volatile higher molecular weight aliphatic compounds, which would have a longer retention in the oil slick, also

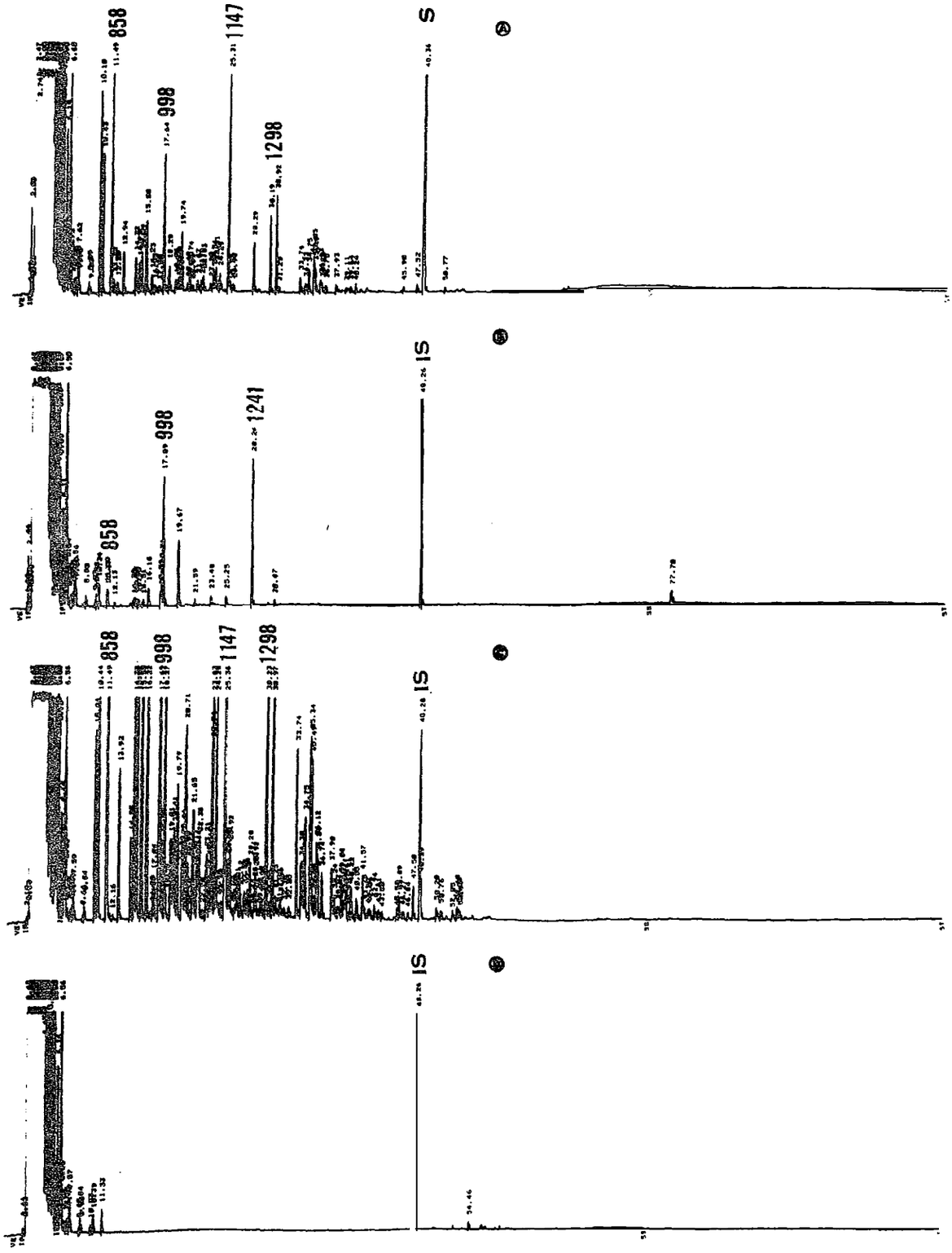



FIGURE 5-71, FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS FROM SCRIPPS INSTITUTE OF OCEANOGRAPHY WATER COLUMN AROMATIC FRACTIONS FROM TANKS 5 AND 6: (A) TANK 5, DAY 2; (B) TANK 5, DAY 5; (C) TANK6, DAY 2; AND (D) TANK6, DAY 5. (IS '-INTERNAL STANDARD) .

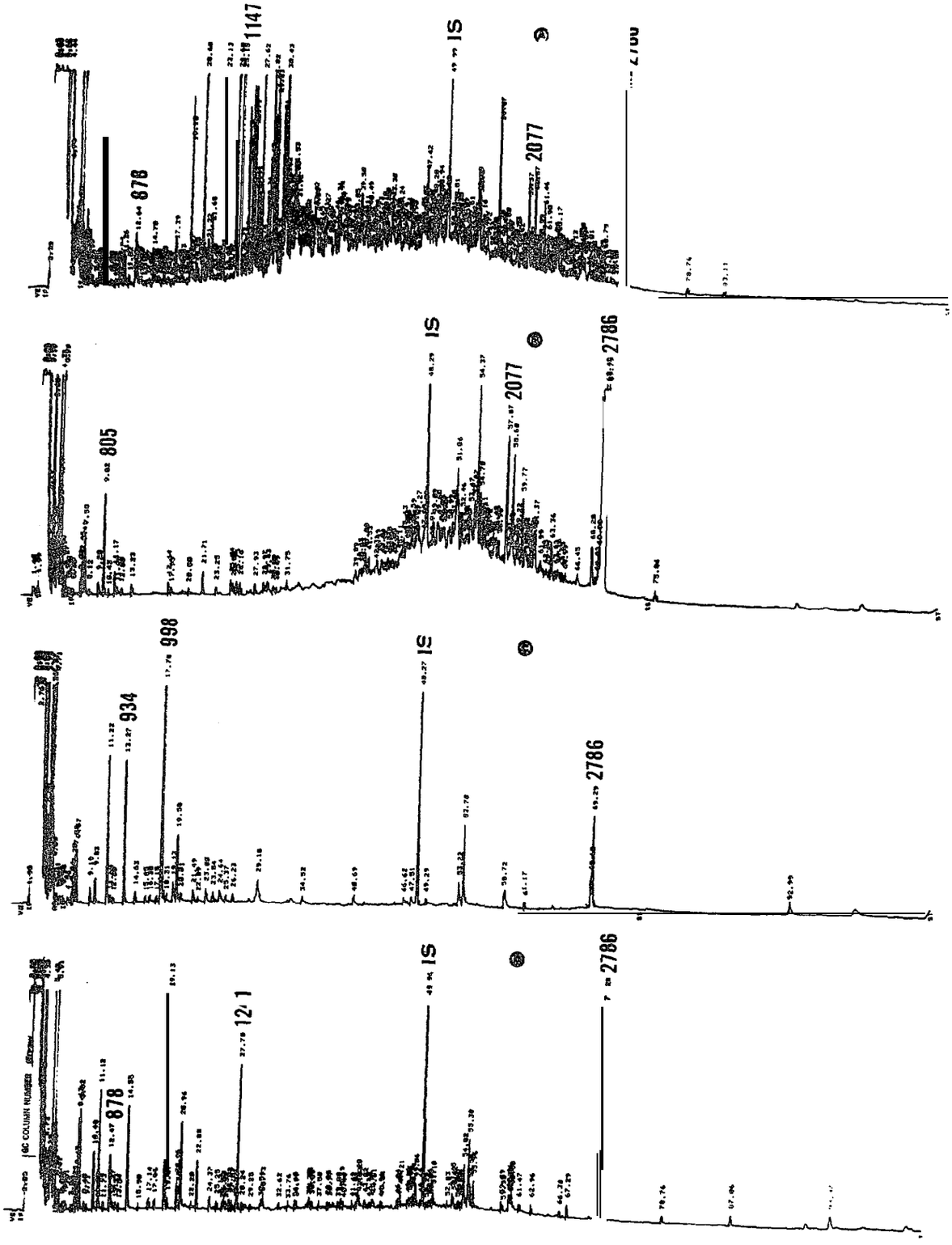



FIGURE 5-72. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS FROM SCRIPPS INSTITUTE OF OCEANOGRAPHY WATER COLUMN POLAR FRACTIONS FROM TANKS 5 AND 6: (A) TANK 6, DAY 2; (B) TANK 6, DAY 5; (C) TANK 5, DAY 2; AND (D) TANK 5, DAY 5. (IS = INTERNAL STANDARD).

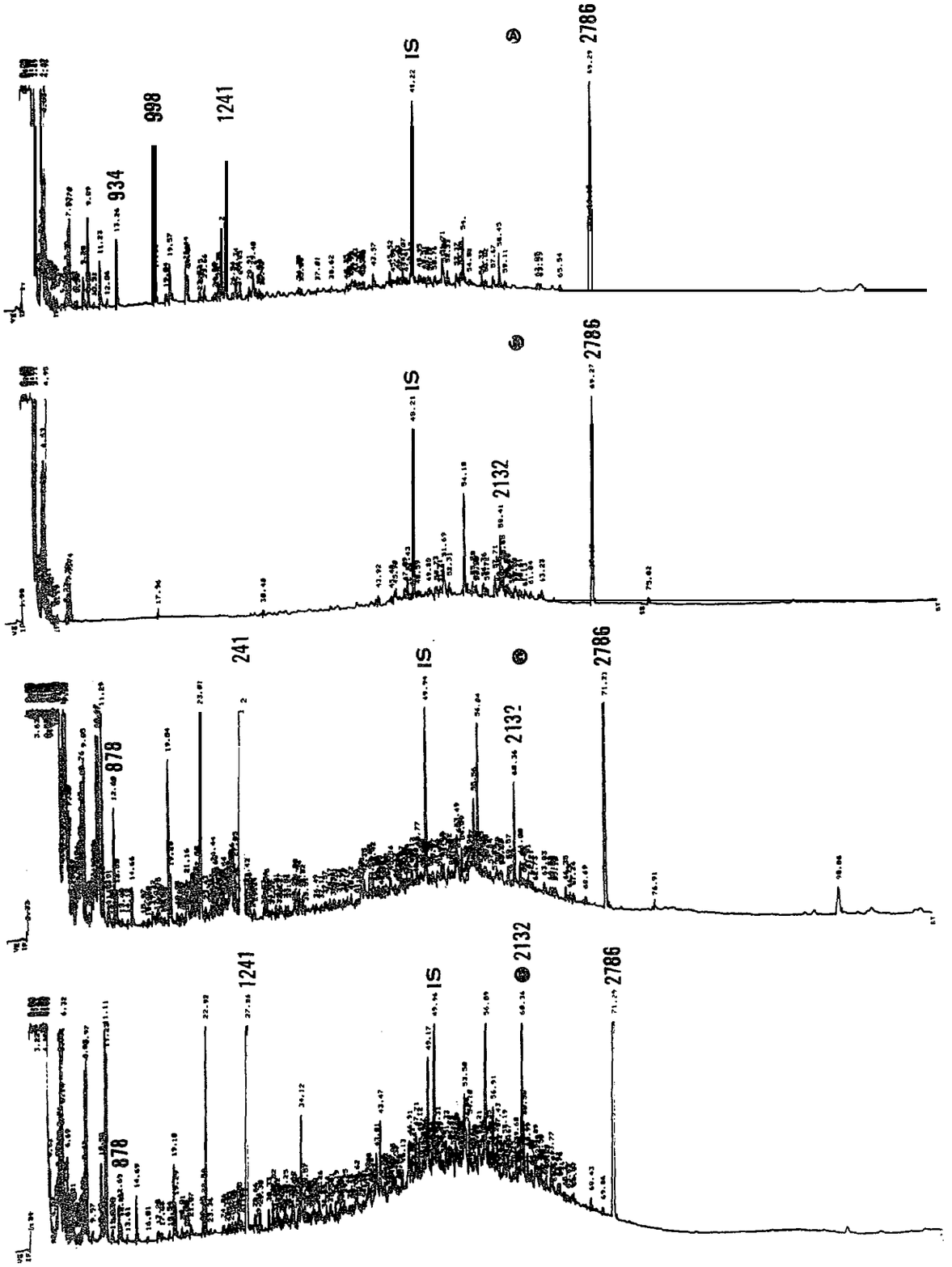



FIGURE 5-73. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS FROM SCRIPPS INSTITUTE OF OCEANOGRAPHY WATER COLUMN POLAR FRACTIONS FROM TANKS 5 AND 6: (A) TANK 5, DAY 9; (B) TANK 6, DAY 9; (C) TANK 5, DAY 23; AND (D) TANK 6, DAY 23. (IS = INTERNAL STANDARD).

have low solubilities relative to the more volatile (e. g., $CH_4$ to nC5) aliphatic components.

The chromatograms in Figure 5-71 demonstrate a time dependence of aromatic compounds passing into the water column. This can be noted by contrasting chromatograms from tank 5 for (A) Day 2 to (B) Day 5, and from tank 6 for (C) Day 2 to (D) Day 5. Chromatograms for corresponding fractions for sampling points prior to and after Days 2 and 5 are devoid of aromatic compounds. This quick "passage" of lighter molecular weight aromatics is most dramatic for the tank 6 fractions (chromatograms C and D) and the compounds present are most likely xylenes, alkyl benzenes, and alkyl naphthalenes.

Figures 5.72 and 5-73 depict chromatograms for polar (F3) fractions from tanks 5 and 6. It is of interest to note the differences between those for tank 6 (Figure 5-72) between (A) Day 2 and (B) Day 5, whereas the corresponding samples from tank 5 (chromatograms C and D) are quite similar. As was demonstrated by the $^{14}C$-labelled hydrocarbon degradation data (Figures 5-64 and 5-65), tank 6 degradation activity increased sharply during this time Period (Days 2 to 5) whereas tank 5 had a more delayed response to oil introduction. However, more complete identification of the compounds present in the tank 6 samples for these two sampling points is required to help substantiate or reject the potential correlation between the $^{14}C$-hydrocarbon degradation activities and the appearance of polar compounds in the extracts from these experimental systems.

After this time period, relatively few compounds were apparent in the polar fractions for these two aquaria until several weeks had passed since oil introduction. This is evidenced in the chromatograms in Figure 5-73 for Days 9 and 23. Although it should be noted that twice the volume of seawater was sampled and extracted for Day 23 as for Day 9, obvious differences exist between tank 5 and 6 Day-9 fractions (chromatograms A and B) and the corresponding fractions from Day 23 (chromatograms C and D). It is also of interest to note the fairly strong qualitative resemblance between the Day-23 samples for (C) tank Sand (D) tank 6.

This particular experiment was run for 56 days and analyses of remaining fractions from the S10 experimental aquaria are being completed at the time of this writing. Selected samples will be screened by GC/MS for oxidized products arising from microbial degradation of parent petroleum components.

Longer-term Hydrocarbon Analyses -- Kasitsna Bay

As noted in Section 5.1.2 of the evaporation/dissolution chapter, several long-term (6 months to 1 year) sub-arctic microbial degradation experiments were initiated in the outdoor tanks at the Kasitsna Bay laboratory in October, 1980. At that time, the tank configurations were set-up as shown below:

| | | |
|---|---|---|
| Tank 7 | Flow-through condition | Fresh oil |
| Tank 3 | Flow-through condition | Fresh oil + Corexit (20:1) |
| Tank 2 | Static condition | Fresh oil |
| Tank 5 | Static condition | Fresh oil + Corexit (20:1) |

During the Spring, 1981 program, after six months of weathering, oil and water column samples were obtained from the four tanks and the flow-through tanks 3 and 7 were maintained to continue longer term weathering studies. All of the remaining oil from the static tanks (2 and 5) was then removed and frozen for future analysis (if desired), and 40-L seawater samples were obtained, acidified, (to PH 2.0), extracted with $CH_2Cl_2$ and analyzed.

This section describes results of chemical analyses of the oil and water samples from these longer-term studies and presents additional results obtained from the 6 month to 1 year sampling period in the flow-through tanks 3 and 7. In addition, results are presented on summer (May through October) microbial degradation studies undertaken on fresh crude and artificially generated mousse in the presence and absence of turbulence and Corexit (as shown by the matrix diagram presented earlier in Section 5.1.2, Figure 5-32).

Two of the more significant findings of these longer term microbial degradation studies relate to the appearance of (1) clear seasonal trends in bacterial utilization and (2) differential microbial degradation with dependence on the status of the oil slick itself (e.g., stranded oil, mousse patches, surface slicks, oil droplets). As will be noted below, the chromatograms of samples collected after six months of ambient static tank weathering during the winter period from October 1980 through April 1981 showed only limited microbial degradation.

The significance of chromatographic analyses depicted in Figures 5-74 and 5-75 relates to a demonstration of the type of overall weathering which may occur during the subarctic winter season for oil stranded in an aquatic environment which experiences little flushing. This may be the case for an estuarine situation, where the water column beneath the slick is relatively stagnant. Limited evaporation would be expected due to the cold temperatures, and a "buildup" of the more water-soluble petroleum components in the underlying water column may occur. Microbial degradation of the oil slick and solubilized petroleum components in the water might also be limited due to cold water temperatures, as well as limitations in nutrient supplies from lack of water column flushing and subsequent nutrient replenishment.

Figure 5-74 depicts the aliphatic and aromatic fraction chromatograms obtained from oil samples which had weathered over the six months winter period. In this experiment, both the oil and water (in tank 2) were maintained in a static condition from October of 1980 to April 1981. In the aliphatic fraction (Figure 5-74A) n-alkanes are present down to nC-12, and the 17/pristane and 18/phytane ratios are approximately 1.79 and 1.85, respectively. These values are nearly identical to the corresponding ratios obtained from analysis of the starting oil and suggest limited microbial degradation during that time interval, in that isoprenoids are generally thought to be less biodegradable than their straight-chain counterparts (BLUMER et al., 1973). Furthermore, during the winter months, it is clear that loss of lower molecular weight components by evaporation processes was inhibited due to the colder subarctic

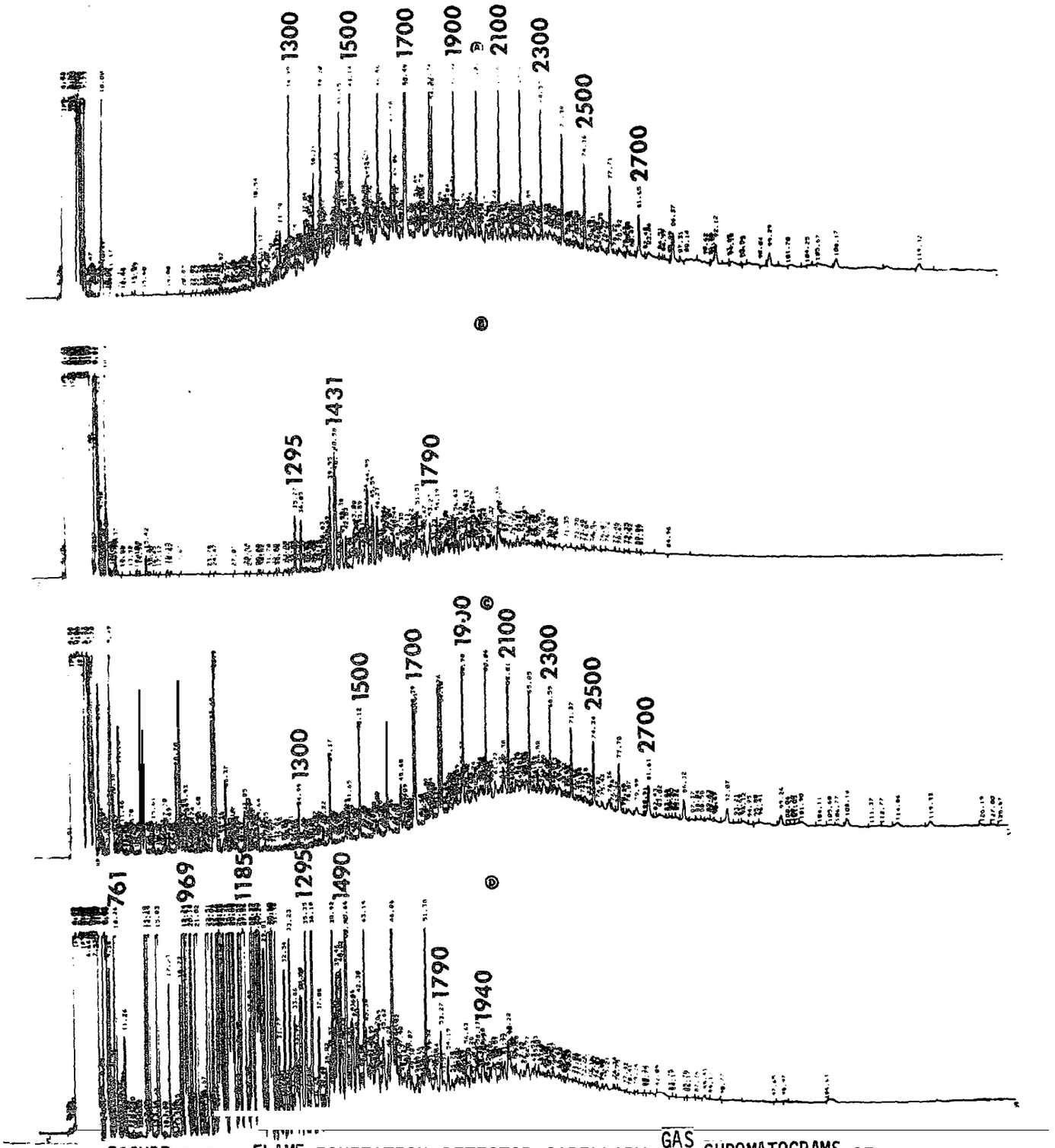
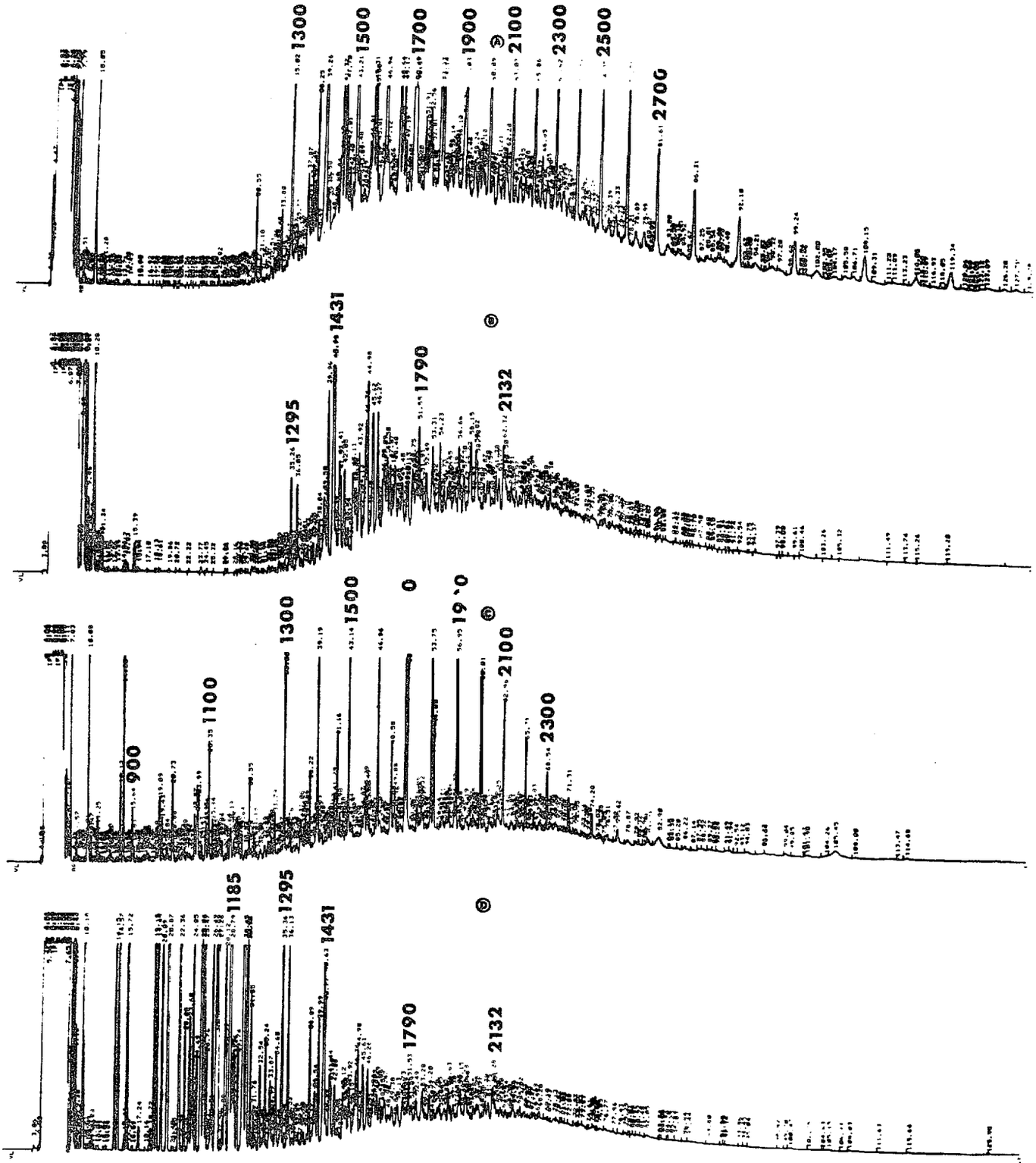



FIGURE 5-74. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF PRUDHOE BAY CRUDE OIL AND SEAWATER SAMPLES OBTAINED AFTER 6 MONTHS OF SUB-AMBIENT WEATHERING FROM OCTOBERTO APRIL 1981 UNDER STATIC (NO-FLOW) CONDITIONS (TANK 2). AAND B REPRESENT THE ALIPHATIC AND AROMATIC FRACTIONS OF THE OIL, RESPECTIVELY, AND C AND D REPRESENT THE ALIPHATIC AND AROMATIC FRACTIONS OF THE WATER COLUMN, RESPECTIVELY.




G M GA MA GRAM M M EA N N MA

temperature regimes. (Water temperatures were near 4°C when the experiments were initiated, and periodic freezing and thawing occurred during January and February, 1981.) Figure 5-74B shows the aromatic fraction of the oil, and this also shows that evaporation, and dissolution of compounds with Kovat indices less than 1200 has occurred from the surface oil slick. These more water soluble components are clearly evident in the acidified water extracts obtained from the water beneath the slick; Figure 5-74C and 5-74D depict the aliphatic and aromatic Tractions, respectively, of the acidified water column extract from the outdoor tank 2. While the capillary column is clearly overloaded, the presence of exceedingly highlevels of aromatic compounds in the water can be observed. Aromatic compounds present include benzene, toluene, xylenes, alkyl substituted naphthalenes, and phenanthrenes. The exceedingly high levels in the aromatic fraction also help to explain the limited breakthrough of some of these components into the aliphatic fraction (Figure 5-74C) during the liquid column chromatography.

In that the outdoor tank was stagnant during the six month period between October to April of 1981, these lower molecular components would not be readily removed by advection. However, they might a priori be expected to be lost due to the evaporative processes. One hypotheses to explain the lack of this anticipatedlossisthat the oil on the surface of the water formed a skin or cap which then prevented additional loss of these more water soluble aromatic compounds from the water column via evaporative processes. Similar observations were made by PAYNE, et al. (1980) during the sub-surface IXTOC-I blowout in theGulf of Mexico in 1979, where elevated levels of benzene, toulene, and xylenes were found in the water column. In that instance, it was also believed that the oil coating on the water acted as a cap to inhibit efficient air-Sea exchange and that removal of the compoundsby evaporation would only occur after advection of the water away from the slick (or wind driven movement of the slick itself).

Figure 5-75 presents the chromatograms of oil samples from the static tank experiment of oil plus Corexit (tank 5) after the same period of weathering. Qualitatively the chromatograms appear very similar to those in Figure

5-74, and it can be seen that during the winter months, most of the volatile components with molecular weights less than nC-12 (Kovat Index 1200) were lost (Figure 5-75). Figure 5-75b shows that the aromatic compounds with molecular weights less than the methyl naphthalenes were lost by evaporative and dissolution processes.

The aliphatic fraction of the acidified water column extract (Figure 5-75C) has higher levels of aliphatic compounds compared to the aliphatic fraction for the tank 2 water (Figure 5-74C), and this is presumably due to the influence of the dispersant.

Figure 5-75D shows the chromatogram obtained on the aromatic fraction of the water column extract from this tank, and as in the other case from the winter experiments, high levels of aromatic hydrocarbons are observed to remain in the water after six months of subarctic weathering. As noted before, this presumably reflects diffusion controlled processes limiting loss of these components through the viscous oil slick cover.

As noted above, outdoor tanks 3 and 7 were maintained in the flowing condition during the period of April through October 1981, and during this period, significant increases in microbial degradation of the oil in the tanks were noted. Further, in examining the oil from the different tanks, longer term oil weathering processes were observed to be clearly dependent on the status of the stranded or floating oil. Specifically, microbial degradation appeared to be primarily a surface phenomenon, and evidence of extensive microbial processes was limited to surface films emanating from larger oil/mousse patches.

Evidence of the differential weathering patterns observed in oil droplets versus surface film are presented in Figure 5-76. Figure 5-76A Presents the capillary column gas chromatogram (non-fractionated) obtained on oil droplets observed in outside tank 3 after eleven months of continuous weathering in the flow through system. Interestingly, compounds are present down to

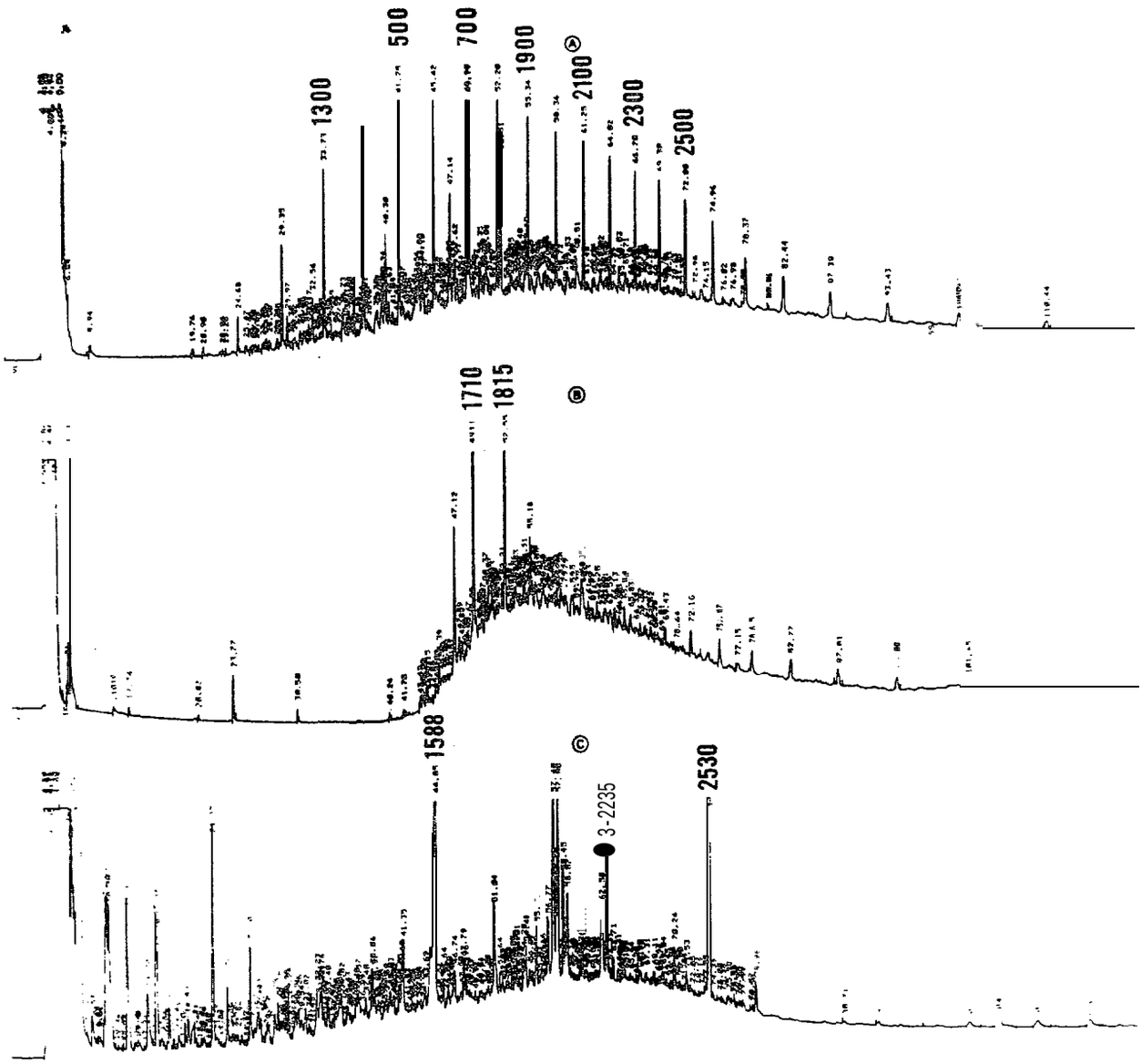



FIGURE 5-76. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF WEATHERED OIL AND WATER COLUMN SAMPLES AFTER 11 MONTHS OF CONTINUOUS SUB-ARCTIC WEATHERING (OCTOBER 1980 TO SEPTEMBER 1981) IN THE OUTDOOR FLOW-THROUGH AQUARIA (TANK 3): (A) OIL DROPLETS (ENTIRE EXTRACT); (B) SURFACE FILM EMINENTING FROM OIL PATCHES (ENTIRE EXTRACT); AND (C) ACIDIFIED SEAWATER EXTRACT.

Kovat indices 1100 showing limited evaporation from the interior of the droplet. In this instance, formation of a surface crust on the oil during the winter months, presumably limited further evaporation/dissolution losses and microbial activity over the summer.

Figure 5-76B, however, shows extensive evaporative and microbial degradation losses in the translucent film emanating from the larger patches of the oil in the outdoor tank. In this instance the only major resolved components remaining in the chromatogram are those of pristane and phytane and other possible isoprenoids. The chromatogram is also characterized by a relatively large unresolved complex mixture and higher molecular weight n-alkanes ranging from $nC_{23}$ through $nC_{29}$.

Figure 5-76C presents the chromatogram obtained from the acidified water extract after eleven months of natural weathering under the subarctic conditions. Clearly there are a number of polar compounds present in the sample extract and GC/MS analyses before and after derivitizations with diazomethane are underway at this time.

Figure 5-77A presents the FID capillary gas chromatogram for a large patch of floating mousse from tank 2 (artificial mousse and Corexit) after five months of weathering (May to September). Essentially complete loss of compounds below nC-13 due to evaporation and dissolution can be observed. From the appearance of the chromatogram, however microbial degradation is not readily apparent in this sample. This is believed to be due to the fact that the higher concentrations of relatively unweathered components making up the interior of the patch mask any selective microbial utilization of specific alkanes which might have occurred on the lower surface, which was exposed to the water column.

Figure 5-77B presents the chromatogram obtained on a sample of stranded mousse collected in September from the sides of tank 2, and this also shows

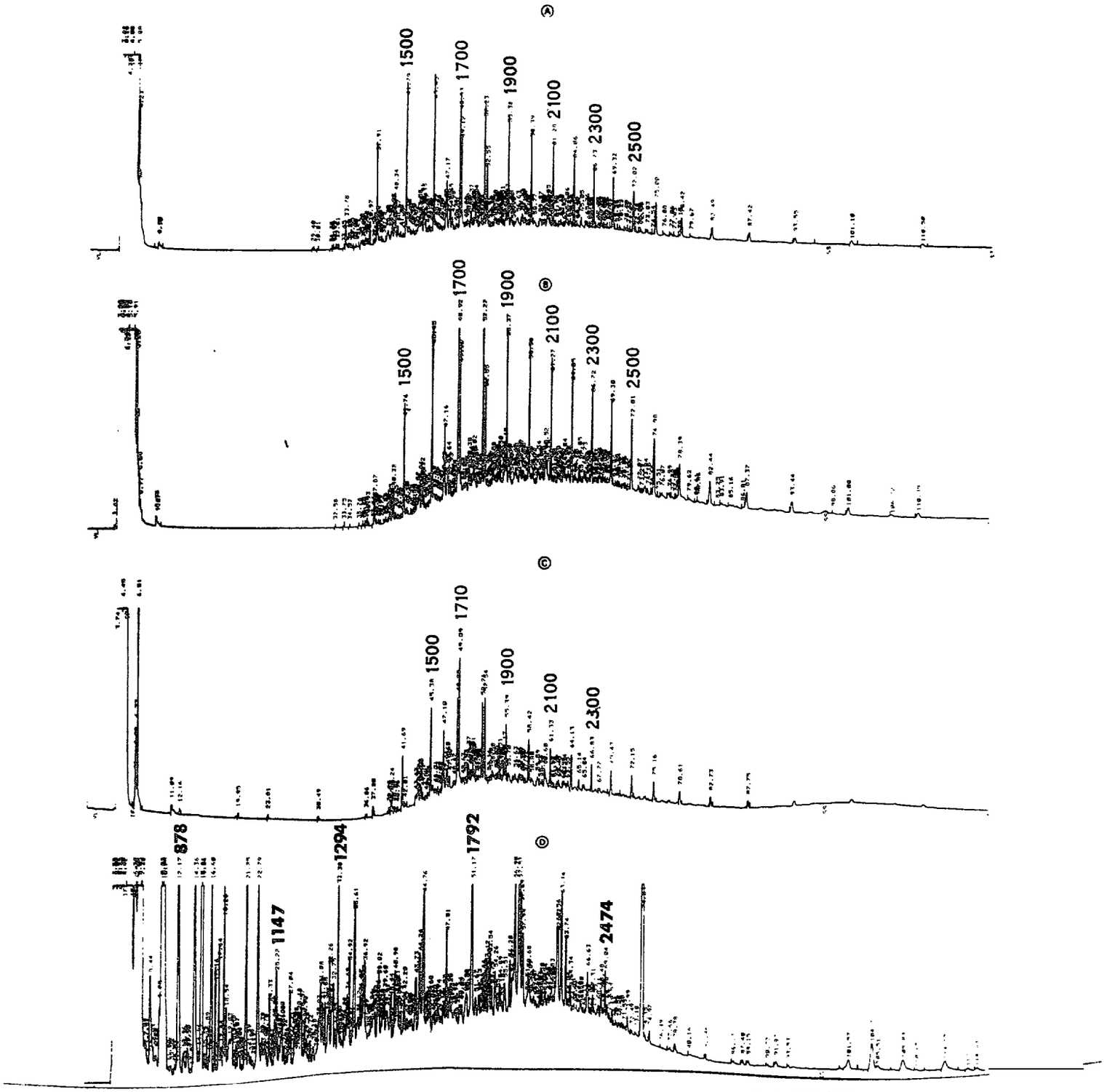



FIGURE 5-77. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS OF ARTIFICIALLY GENERATED PRUDHOE BAY MOUSSE PLUS COREXIT AFTER 5 MONTHS OF WEATHERING (MAY TO SEPTEMBER 1981) IN THE OUTDOOR FLOW-THROUGH AQUARIA (TANK 2) AT KASITSNA BAY, ALASKA: (A) ARTIFICIAL MOUSSE FLOATING ON THE WATER COLUMN; (B) STRANDED MOUSSE FROM THE SIDE OF THE CORRAL; (C) SURFACE FILM EMINENTING FROM MOUSSE PATCHES; AND (D) ACIDIFIED SEAWATER EXTRACTS.

only limited microbial degradation although a slight increase in loss of compounds below Kovat index 1400 is noted. This presumably reflects elevated temperatures encountered during atmospheric exposure.

Figure 5-77C shows the chromatogram obtained from a translucent film extending from the bulk of the mousse patch from tank 2. In this instance a loss of aliphatic and aromatic compounds below 1500 is evident and enhanced microbial degradation is suggested by the nC-17/pristane and nC-18/phytane ratios of 0.61 and 0.73, respectively.

Figure 5-77D shows the acidified water extract obtained from a 31.7 liter water sample obtained four months after the mousse was initially spilled in the flow through water system. This extract has been submitted to GC/MS analysis and Figure 5-56 (in Section 5.2.3) presents the reconstructed ion chromatogram obtained on that sample. The disparity in the appearance of the chromatogram in Figure 5-56 compared to Figure 5-770 can be attributed to inadvertent loss of lower molecular components before GC/MS analysis during transport to our La Jolla facility. An additional sea water extract of this tank was obtained after seven months of weathering and is undergoing extraction and fractionation at this time. Hopefully, this sample will provide sufficient material in this lower molecular weight range to facilitate GC/MS analysis. As noted earlier, the numbered peaks in Figure 5-56 have been tentatively identified by GC/MS. (Table 5-25 presents those compound identifications).

## 5.3 Oil/Suspended Particulate Material Interactions

### 5.3.1 Effects of Oil on SPM Settling Rates - La Jolla Studies

During the first half of this program, oil/suspended particulate material interactions were studied to determine adsorption/resorption rates at different temperatures and to determine the affects of these processes on sedimentation rates with various types of particulate material. These studies were undertaken with fresh Prudhoe Bay crude oil and Prudhoe Bay crude which

had undergone evaporati on/dissolution weathering for 48 hours. The presence and absence of the dispersant Corexit 9527 (10 parts oil to 1 part dispersant) were also incorporated as experimental variables, and three types of relatively pure sediments were utilized (carbonate, silica and deep basin clay; Table 5-28). Sedimentation rate determinations were made using a Cahn 2000 series sediment balance, and a particle size range of 4.0 $\phi$ to 9.0 $\phi$ (62 $\mu$m to 2 $\mu$m) was used.

The sediment material being analyzed was added to the stirred chamber shown in Figure 5-78, and aliquots were taken at times 0, 3 hours, 24 hours and 48 hours for analyses on the sediment balance. The data were then analyzed to yield final wet and dry weights of (settled) particulate and according to the Waddell settling equations to yield mean, median, skewness and kurtosis data on the grain size distribution.

<u>Waddell Settling formula</u>

$$T = \frac{K}{D^2}$$

T = time (minutes

D = diameter (microns)

$$K = \frac{0.3\ h\ v\ 10^8}{(d_s - d_l)\ g}$$

h = height of column of water

v = viscosity (poises)

ds = density (solid) g/ml

$d_l$ = density (liquid] g / m l

g = gravity in cm/sec

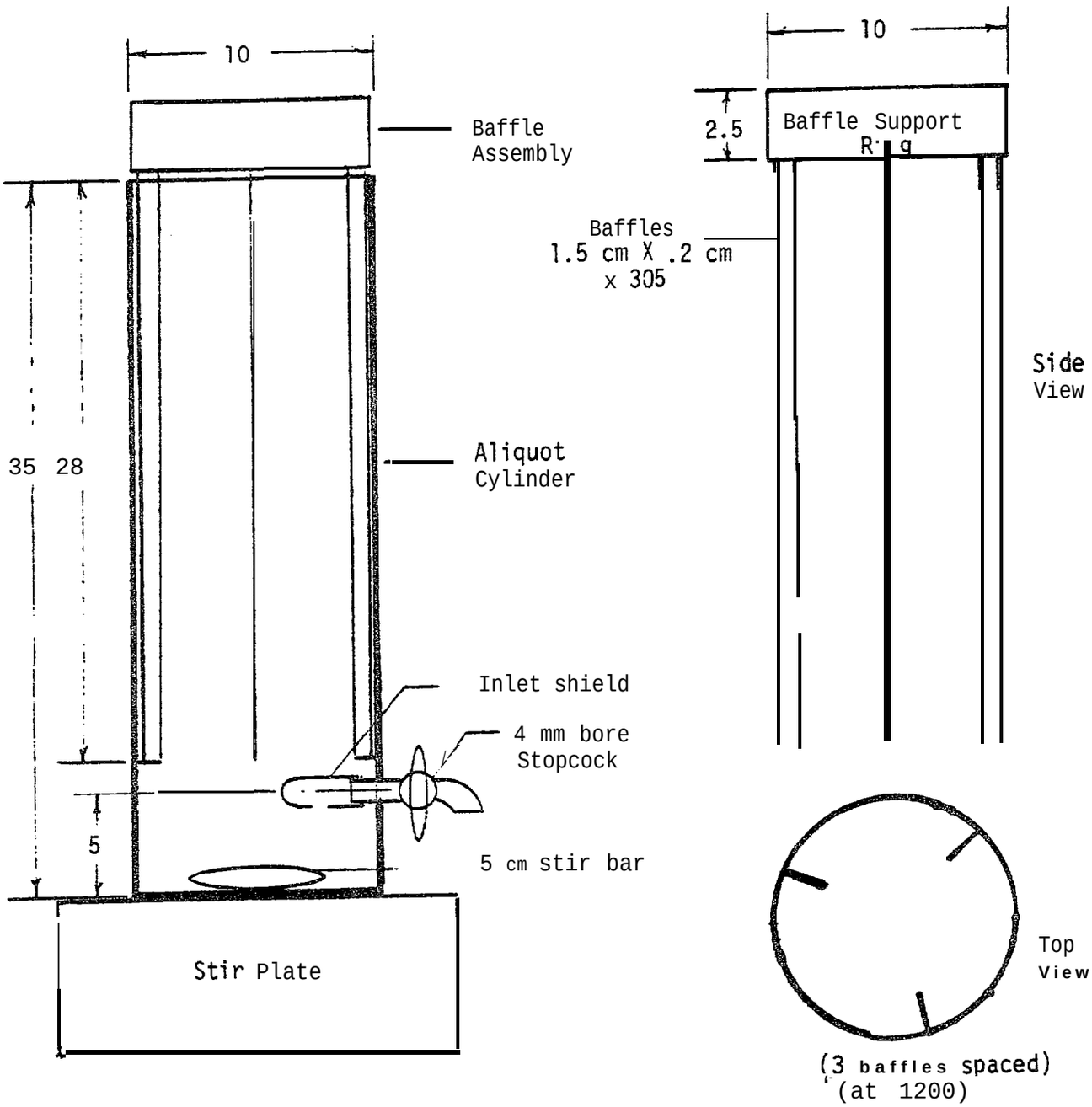
TABLE 5-28. GRAIN SIZE AND MAJOR METALLIC CATION ABUNDANCES FOR INITIAL OIL/SUSPENDED PARTICULATE MATERIAL EXPERIMENTS.

dispersive X-ray Analysis (SEM)

| Sample | Relative Atom % | | | | | |
|---|---|---|---|---|---|---|
| | Mg | Al | Si | K | Ca | Fe |
| Commercial Diatomite | - | - | 93 | - | 6 | 1 |
| Milled Foram Sand | 2 | 2 | 12 | - | 85 | 1 |
| San Nicolas Basin Clay | 2 | 6 | 48 | 3 | 35 | 6 |

Grain Size Information

| Sample | Median | Mean | Skewness | Kurtosis |
|---|---|---|---|---|
| Commercial Diatomite | 5.5 | 5.5 | + .03 | 1.0 |
| Milled Foram Sand | 5.4 | 5.9 | + .25 | .8 |
| San Nicolas Basin Clay | 5.5 | 5.8 | + .19 | 0.8 |




Note: All dimensions in cm.

FIGURE 5-78. ALIQUOT CYLINDER ASSEMBLY FOR OIL/SPM INTERACTION STUDIES.

Graphical Statistics

Skewness = $\frac{\phi 16 + \phi 84 - 2\phi 50}{2\,(\phi 84 - \phi 16)} + \frac{\phi 5 + \phi 95 - 2\phi 50}{2(\phi 95 - \phi 5)}$

Kurtosis = $\frac{\phi 95 - \phi 5}{2.44\,(\phi 75 - \phi 75)}$

Mean = $\frac{\phi 84 + \phi 16}{2}$

Median = $\phi$ size at 50% cumulative weight

Results from these initial studies were presented in detail in the September 1980 Interim Report, and therefore, will not be discussed in detail here. Essentially only very slight perturbations in SPM settling characteristics were observed as a result of oil, oil plus Corexit, and mousse interactions. Tables 5-29 and 5-30 present results from initial interaction studies completed with diatomite powder and deep basin clay (San Nicolas), respectively. From these results some subtle changes in the median and mean sediment size characteristics with both substrate types were observed for the oil-Corexit mixtures; however, oil alone did not have as significant an effect on these parameters. Table 5-31 presents a summary of the settling experiments using San Nicolas Basin sediment and oil and oil plus Corexit. Results of the first two runs with oil and the Corexit-oil mixture indicated minor interactions which can be detected in the settling rate data. The small increase in phi size (decrease in grain size) for both the median and mean and the decrease in settled weight percent are indicative of some buoyant force at work and/or of adsorption of oil , decreasing the effective density of the particles below a critical size (FEELY et al., 1978; BASSIN and ICHIYE, 1977). The largest settled weight differences occur in the oil/Corexit sediment experiments; however, the median, mean, skewness and kurtosis were not as drastically affected by the oil or oil plus Corexit interaction. Time-series changes in the phi size, skewness and final weight settled as a result of oil exposure are shown in Figure 5-79, and while the affect of exposure on all

TABLE 5-29. INITIAL INTERACTION. STATISTICAL EFFECTS OF DENSITY, DISPERSANT, AND SAMPLE WEIGHT ON DIATOMITE POWDER AT 23°C.

| Sample | Addition | ρ | Method of Injection | Dry Weight | Wet wt.* / Dry wt. | Median | Mean | Shewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|
| A | .01N Calgon | .997 | 30cc in cent. tube | 200 mg | .57 | 5.50 | 5.49 | +.03 | 1,04 |
| Run #4 | --- | 1.025 | 30cc in cent. tube | 200 mg | .51 | 5.37 | 5.41 | +.11 | 1.13 |
| Run #5 | --- | .997 | 40cc in cent. tube | 300 mg | .56 | 5.57 | 5.49 | -.38 | 1.06 |
| Run #6 | --- | 1.025 | 6cc in 10cc syringe | 160 mg | .50 | 5.47 | 5.50 | +.13 | 1.27 |
| Run #7 | Oil only | 1.025 | 30cc in cent. tube | 205 mg | .51 | 5.42 | 5.50 | +.98 | 1.11 |
| Run #8 | Oil-Corexit | 1.024 | 30 cc in cent. tube | 200.2 mg | .35 | 5.59 | 5.84 | +.16 | .78 |
| Run #9 | Oil-Corexit | .997 | 30cc in cent. tube | 204 mg | .52 | 5.50 | 5.50 | +.03 | 1.05 |
| Run #10 | Oil-Corexit | .997 | 30cc in cent. tube | 208 mg | .56 | 5.70 | 5.70 | +.03 | .98 |
| Run #11 | Oil-Corexit | .997 | separate addition of sediment and oil | 211 mg | .54 | 5.69 | 5.73 | +.08 | 1.05 |

* Ratio of sedimentation balance weight (weight of sediment in water)/dry weight of added sediment.

TABLE 5-30. STATISTICAL SUMMARY OF DEEP BASIN CLAY (SAN NICOLAS) AMBIENT TEMP (23°C), SEAWATER, MIXING TIME = 15 min.

| Date | Oil | 10:1 Corexit | (0-4) Run Rating | Median | Mean | Skewness | Kurtosis | Final Wt. | % Settle |
|---|---|---|---|---|---|---|---|---|---|
| 7/22/80 | --- | --- | 4.0 | 5.53 | 5.80 | +.19 | .75 | 108.9 | 10077 |
| 7/23/80 | --- | --- | 4.0 | 5.32 | 5.51 | +.21 | .89 | 105.5 | 1 00% |
| 7/21/80 | X | X | 2.5 | 4.89 | 5.31 | +.37 | .98 | 72.5 | 68% |
| 7/28/80 | X | X | 3.5 | 4.92 | 5.35 | +.35 | .95 | 71.9 | 67% |
| 7/24/80 | X | --- | 4.0 | 5.36 | 5.75 | +.26 | .87 | 91.7 | 86% |

Run Reproducibility

| | Mean | Skewness | Kurtosis | Final Wt. |
|---|---|---|---|---|
| Sediment | 5.66± 0.2 | .21 * .01 | .82 ± .1 | 107 ± 2.4 |
| Sediment-oil-Corexit | 5.33* 0.03 | .36 ± 0.1 | .97* .02 | 72.2 ± 0.4 |

TABLE 5-31. SUMMARY OF SAN NICOLAS BASIN SUSPENDED PARTICULATE MATERIAL AND FRESH PRUDHOE BAY CRUDE OIL INTERACTIONS.

| | CONDITIONS | | | STATISTICS | | | | |
|---|---|---|---|---|---|---|---|---|
| | Additive | temp. | time | median | mean | skewness | kurtosis | final weight recovered (wet) |
| 1. | none | 23°C | 0 | 5.25 | 5.47 | + .21 | .91 | 78.4 |
| 2. | oil | " | 3 hrs. | 5.50 | 5.69 | + .17 | .87 | 77.5 |
| 3. | oil | " | 24 hrs | 5.79 | 5.91 | + .11 | .94 | 74.3 |
| 4. | oil | " | 48 hrs. | 6.03 | 6.02 | + .005 | .90 | 71.5 |
| 5. | oil & corexit | " | 0 | 5.25 | 5.28 | + .90 | .75 | 44.70 |
| 6. | " " | " | 3 hrs. | 5.13 | 5.39 | + .28 | 1.05 | 26.32 |
| 7. | " " | " | 24 hrs. | 5.30 | 5.30 | + .08 | .85 | 34.05 |
| 8. | " " | " | 48 hrs. | 5.91 | 6.13 | + .12 | .81 | 31.15 |

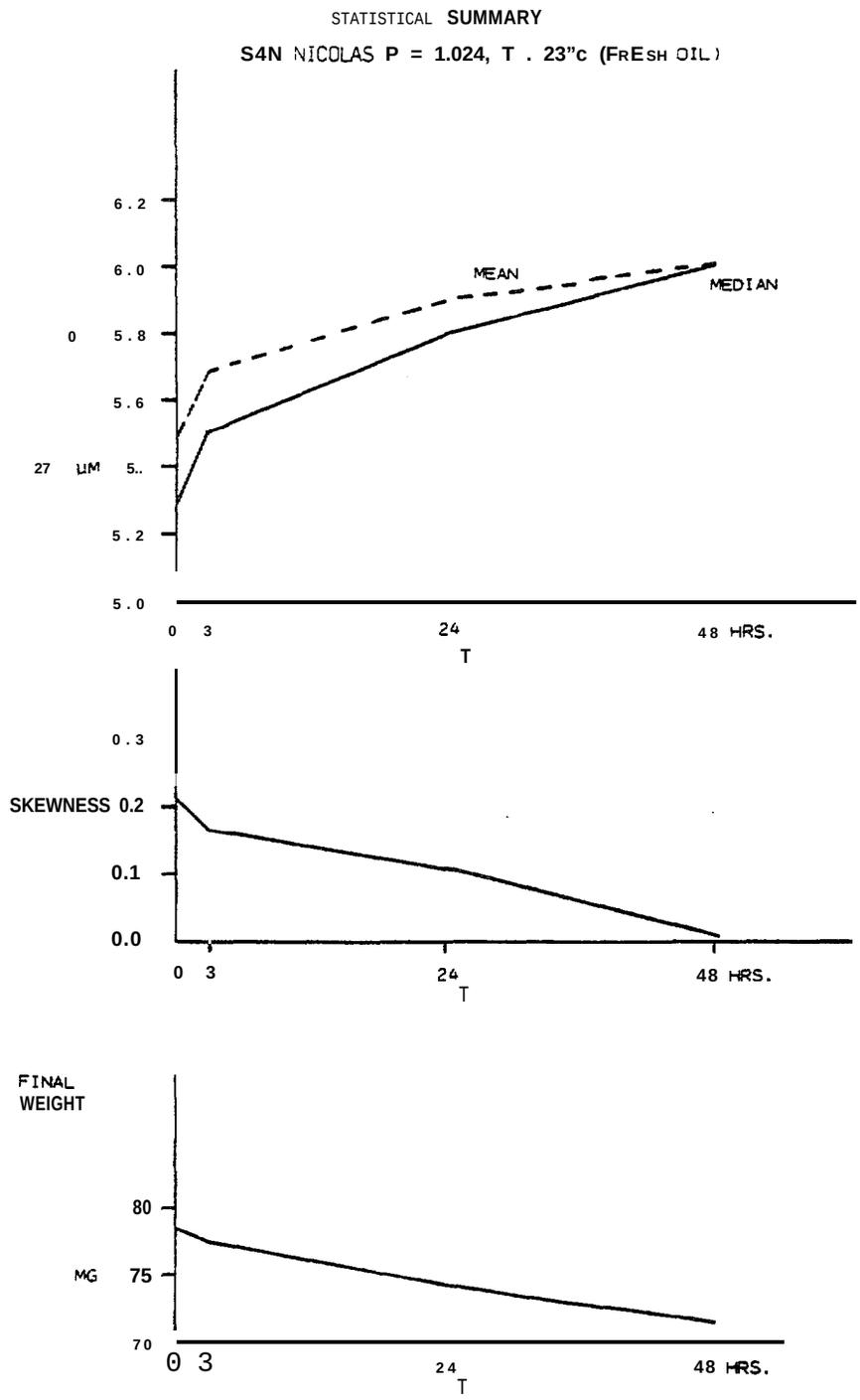



FIGURE 5-79. GRAPHICAL DISPLAY OF THE AFFECTS OF THE INTERACTION TIME FOR SAN NICOLAS BASIN SEDIMENT AND FRESH PRUDHOE BAY CRUDE OIL ON MAJOR STATISTICAL PARAMETERS (SEE TABLE 5-31). THE EFFECT OF TIME ON ALL THREE PARAMETERS IS STATISTICALLY SIGNIFICANT BUT NOT CONSIDERED TO BE MINOR.

three parameters is statistically significant, their overall perturbation to SPM characteristics were considered to be minor.

### 5.3.2 Detailed Analyses of Suspended Particulate Materials Characteristic of Lower Cook Inlet Alaskan Waters

As a result of the above findings, examinations of phi size and settling characteristics of oil/SPM mixtures were discontinued, and attention was instead directed towards the compound specific nature of the oil suspended particulate material interactions. Further, in an effort to satisfy environmental manager's needs with regard to oil/SPM interactions in Alaskan waters, attention was focused on the compound specific adsoprtion of petroleum hydrocarbon components onto sediments and fines representative of Lower Cook Inlet suspended particulars material.

Thus, during the Spring 1981 Kasitsna Bay program, studies were initiated to locate intertidal sites having significant deposits of sediment fines representative of Lower Cook Inlet suspended particulate material, and samples of these sediments were characterized as to their physical and compound specific oil retention properties. From the results of these initial investigations, two intertidal sites were selected as sources of divergent but representative samples of Lower Cook Inlet SPM. These sediments were then used for outdoor flow-through oil/SPM interaction experiments during the summer 1981 program at Kasitsna Bay.

Figure 5-80 presents a navigational chart for the Lower Cook inlet/ Shelikof Strait area, and Figure 5-81 shows expanded detail of the Kachemak Bay region. Sampling sites for initial SPM characterizations were selected using "Cook Inlet-southern part, navigational chart (1:200,000)-NOAA, C&GS 8554"; and, the unpublished Environmental Sensitivity Index (ESI) for Lower Cook Inlet (RUBY and MAIERO, 1979).

Suspended particulate material in Kachemak Bay was considered to have four primary sources:

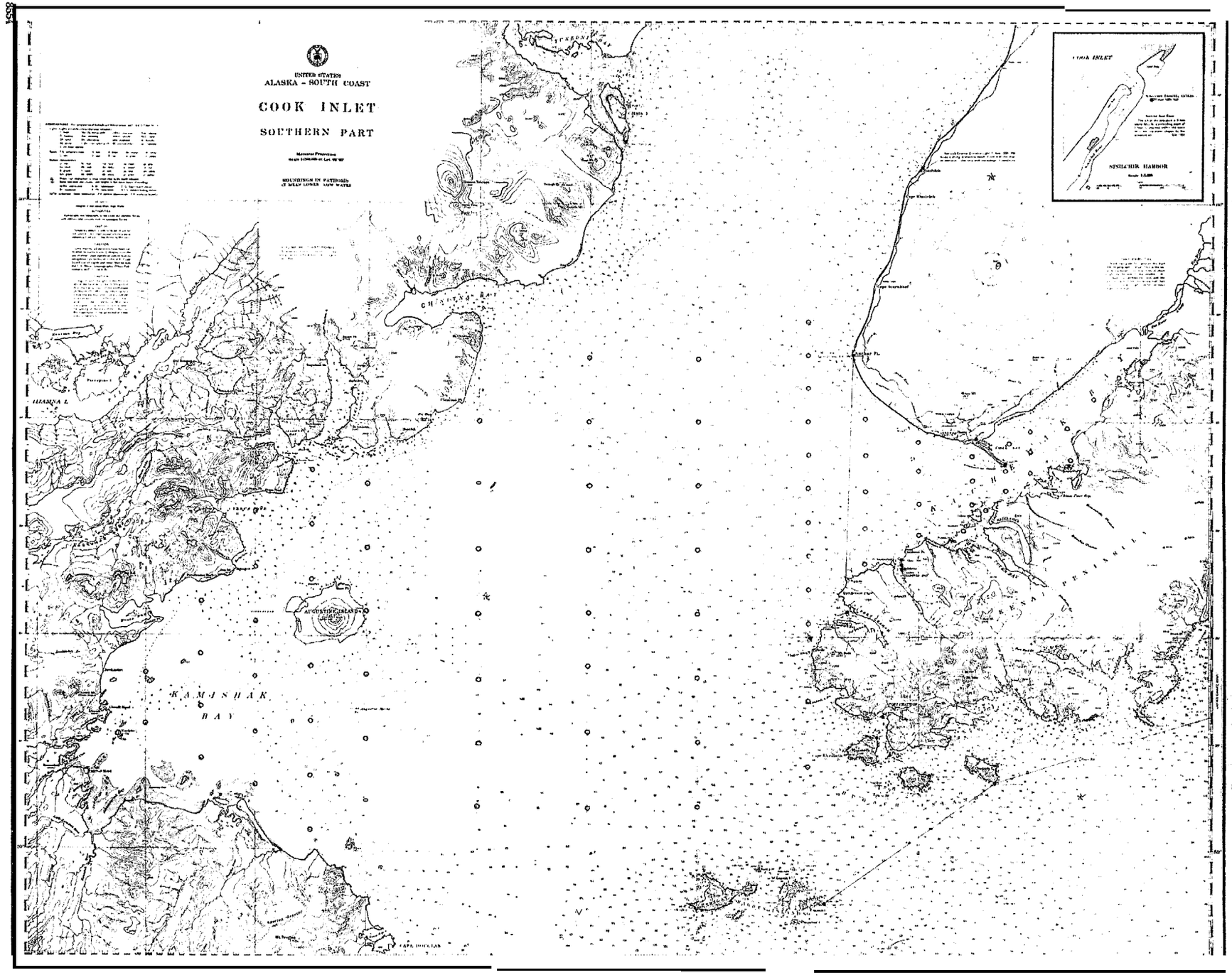



FIGURE 5-80. US DEPARTMENT OF COMMERCE COAST AND GEODETIC SURVEY, CHART #8554 OF THE LOWER COOK INLET REGION.

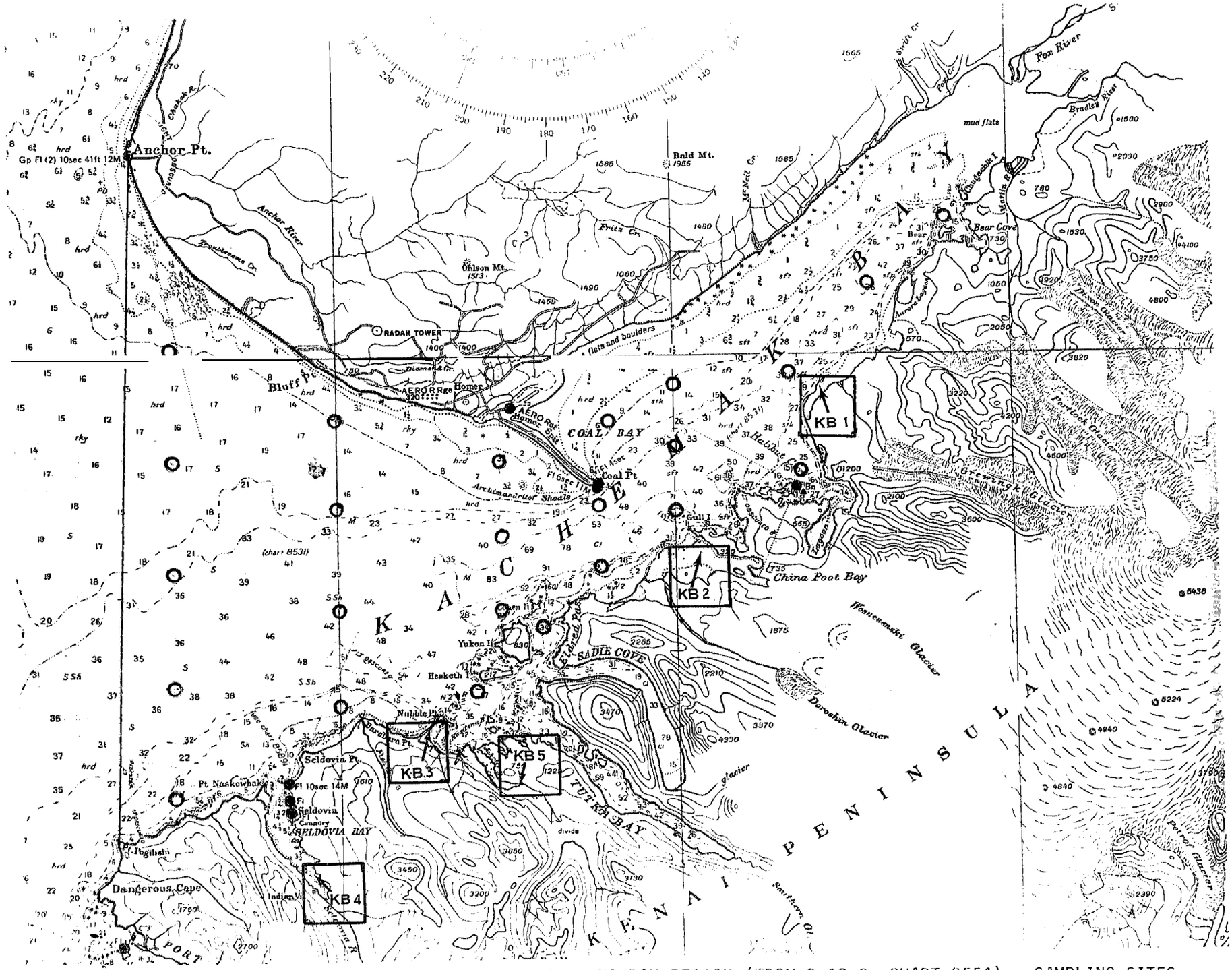



FIGURE 5-81 EXPANDED VIEW OF THE KACHEMAK BAY, KASITSNA BAY REGION (FROM C.&G.S. CHART 8554). SAMPLING SITES FOR OIL/SPM INTERACTION STUDIES AND INTERTIDAL OILED-CORRAL EXPERIMENTS ARE DENOTED AS: KB-1 GREWINGK GLACIER DELTA; KB-2 CHINA POOT BAY MUD FLATS; KB-3 COMPOSITE SEDIMENT; KB-4 SELDOVIA RIVER SALT MARSH PETROLEUM SEDIMENTS; KB-5 [illegible] OF INTERTIDAL MUD FLATS.

- Marine waters introduced to Kachemak Bay by tides and currents from Lower Cook Inlet (Gulf of Alaska and Shelikof Straits)
- Glacial melt waters
- Terrestrial sources-runoff
- Marsh detritus

A secondary source to any site was also considered to be resuspension of sediment through wind and wave scour and transport of sediments by tidal actions and long-shore and bottom currents.

The Spring 1981 sampling program was designed such that 3 sediment types which were representative of Lower Cook Inlet suspended particulate material could be obtained, and these included: pure glacial till, tidal flats supported primarily by marine deposits and tidal flats supported by marsh detritus and terrestrial runoff. To represent these sediment types, four primary sites were selected for sampling and these are shown on Figure 5-81 as KB-1, KB-2, KB-3 and KB-4. At each site, fine particulate and sediment floe were obtained from the upper 1 to 2 cm of deposits exposed during lower tidal excursions. Detailed descriptions of each site follow.

KB-1: Grewingk Glacier Delta and Melt Stream

This site is characterized as a large, protected, delta subject to tidal marine flushing and fresh water input from the Grewingk Glacier melt stream. The glacier is central and 3 to 4 miles southeast of the tidal flat which is bounded on the west by a wide gravel spit oriented southwest to northeast as formed by northeasterly moving tides and longshore currents in Kachemak Bay (Figure 5-81). Glacial sediments were found directly behind the tip of the gravel spit at the point that the glacial waters met the marine waters which were draining from the southern section of the flat. These deposits of glacial silt (2-5 mm thick) formed a mat which could be removed from underlying sediment, and samples of this material were obtained for oil/SPM characterization studies. The exposed surfaces of small to medium cobble in

the area were also covered with a similar mat of glacial silt, but quantitative sampling of this material was not possible. The richest glacial deposits were restricted to an area of approximately 800 meters$^2$ out of approximately 20,000 meters$^2$ inspected.

The influence of glacial melt waters served to increase biological Productivity as evidenced by large stands of Ulva sp. accompanied by significant numbers of amphipods. Filamentous brown algae were ubiquitous to the flat. Bird use of the area appeared moderate - evidence of bird tracks was lower than expected.

The glacial melt water was "milky" (bluish white) and had a fresh= bitter taste. The mouth of the delta (interface of drainage and receiving waters) was subject to erosion due to the meandering of the delta channel, and as such, the site at which samples were taken is considered to be geologically active. Little perturbation of the area was noted on re-occupying the station during the Summer 1981 field program; however, it was a'pparent that the sampling site may not remain in its present state for extended periods of time. Overall energy is low; however, localized disturbances may affect the subject sediment when incoming or outgoing tidal waters covering the flat are a few centimeters to a 1/3 meter deep (or depth equaling fetch height) so that wind driven waves can scour the bottom. This type of activity could make the placement of study plots difficult, and as a result of this instability and because of logistical considerations, extended oil/SPM interaction studies in the flow-through tanks at Kasitsna Bay facilities were not undertaken with this site as a source of SPM. Further discussions of the results of oil/SPM interaction studies using the substrate from KB-1 are presented in Section 5.3.4.

KB-2/China Poot Bay - Mud Flats

The area at which samples were taken is common to protected tidal flats in Lower Cook Inlet and Prince William Sound (RUBY and MAIERO, 1979). The sampling site is located on the southwest section of the flats, and this

site is protected from wave energy by a long, curved gravel spit forming the boundary between China Poot and Kachemak Bay (Figure 5-81). There is no source of fresh water immediately adjacent to the sampling site. The sources of sediment at this site are expected to be primarily of marine (i.e., outer bay) origin. The flat is very high in biological productivity - clams, polycheates and amphipods were abundant. It is apparent that benthic organisms are constantly reworking these sediments - fecal pellets and burrows were in profusion, and for the most part, the sediments appeared to be well oxidized with little or no evidence of $H_2S$.

The sampling area included "random" surficial samples taken from the sloping face of the flat (slope of 12:1 on the lower face to 23:1 on the upper face) and the flat, itself (average slope along transect of 75:1). The sediments on the slope face (to a depth of approximately 10 cm) consisted of a thin veneer of brown organic sediments in a consolidated mat having a thickness of 2 - 5 mm overlying black silt/sand homogeneous, well oxidized sediments. These sediments were well packed and did not yield to any degree to foot pressure. In comparison, the sediment composition on the flat proper was visually alike the sediments of the slope; however, the underlying black sediments were in a moderately reduced state (moderate $H_2S$ noted). Sample KB-2B was obtained from these reduced sediments while KB-2 was obtained on the 0-1 cm subsection from the slope face. Biological activity was higher on the flats compared to the slope face (evidence of siphon holes, etc.) and interstitial water was observed in each cross-section of sediment. The upper flat sediments were not as firm as those of the slope so that foot pressure could easily cause a depression. The reduced state (notable $H_2S$ present) may be a function of the ability of the flats to: drain quickly, increasing retention of organics (as opposed to wave action gently scouring the somewhat steeper slope with each tidal cycle), heating of the flats by solar energy (slope would be subject to direct sunlight during a limited portion of the sun's arc), and increased bacterial activity.

## KB-3, Kasitsna Bay - Composite Shell Fragments, Sand and Mud

The Kasitsna Bay sediment sample was taken from the interior of the bay along a tidal flat adjacent to Nubble Pt. (see Figure 5-81). The mud flats are located on the east side of a small spit located in the western interior of the Bay. Nave energy is minimized in this portion of the bay because of the short distance between spits; however, tidally generated currents appear significant. The sampling station lies at the foot of a sand/gravel beach having a moderate slope (1:17) to the high tide wrath and a steep slope (1:9) from the high tide to the maximum stem tide wrath on Nubble Pt.

The sediments on the protected flats consist of an unsorted matrix of sand, gravel and shell fragments bound tightly together with silts and organic materials. The nature of the components in the sediments indicate that material is transported to this area as a result of bottom scour (tidal) and longshore transport. Biological productivity is high. The flats were populated with vegetation stands of Ulva, Fucus and Enteromorpha accompanied by Mytilus, Balanus and numerous polycheates and amphipods. The holdfasts of the plants and byssal threads of the mussels appear to play a significant role in trapping sediments on the flats.

The sediments at this station were unique to the sediment samples collected during the spring season. Sediments sampled at other sites were fairly well sorted and somewhat homogeneous. Bottom scour did not seem to contribute to the sediment at the other stations and shell fragments were not as abundant. This station appears to contain representative composite of the components of the other stations sampled.

## KB-4, Seldovia Bay - Salt Marsh in Upper Bay

The sample from this station was taken in a submerged tidal channel in the Spartina sp. marsh at the head of Seldovia Bay. The marsh lies to the north of Seldovia River (Figure 5-81).

The sediments of the marsh are composed primarily of organic, decomposing detritus originating from the Spartina marsh. The normal cycle of the marsh is to die back in early winter and regrow in spring of the following year. When the marsh plants die back, the dead vegetative material is matted down, by wind and snow to form a thick vegetative cover over the flat. New shoots sprout from the rhizome mat in the spring pushing through the decomposing vegetative mat. In spring, the old vegetative mat decomposes introducing a significant amount of organic material to the marsh channels and flats in the vicinity of the marsh. Our sampling effort occurred during the stage of regrowth/decomposition.

The sampling station is adjacent to the mouth of Seldovia River. Incoming tides transport the fresh water runoff (overlying the denser marine wedge) onto the marsh so that terrestrial sediments may be deposited with marsh detritus. The transport of fresh water onto the marsh was confirmed during sampling as incoming tidal waters tasted totally fresh.

The marsh was rich in invertebrates and showed signs of heavy bird use (tracks).

Table 5-32 presents an overall description of the sediment/SPM samples collected at each site, and Table 5-33 presents size-compositional data derived from visual and microscopic observations of the samples collected from the four sites. From these examinations a pure form compositional diagram for the samples was prepared and is presented in Figure 5-82A. Figure 5-82B characterizes the sediments as far as suspected sediment source.

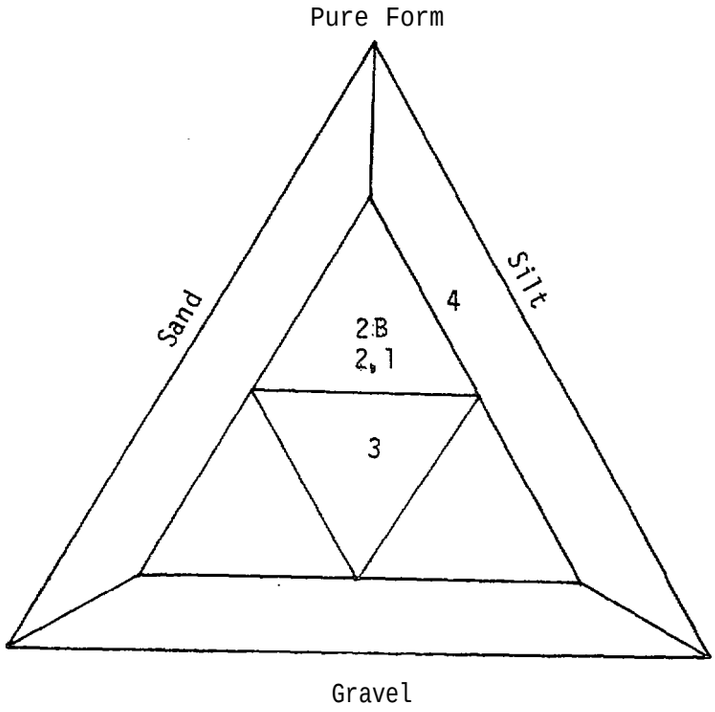
Immediately after these samples were collected, they were extracted and analyzed at the Kasitsna Bay facility for background biological and potential petroleum hydrocarbon content (from previous spill events). These analyses were completed at that time such that if the results had then indicated previous petroleum hydrocarbon contamination, alternative sampling sites could have been selected and sampled during the spring program before returning to

TABLE 5-32. OBSERVEI) CHARACTERISTICS AND OVERALL DESCRIPTIONS OF SEDIMENT/SPM SAMPLES COLLECTED DURING THE SPRING 1981 KASITSNA BAY FIELD PROGRAM.

| | 1 | 2 | 2B | 3 | 4 |
|---|---|---|---|---|---|
| ediment omponent | Glacial Silts<br>Fine sand<br>Gravel | silt<br>Fine sand | silt<br>Fine sand | Organics, S11 t<br>Fine-medium sand<br>Gravel, shel 1 frag. | Organics, Silt |
| ediment lassification | Sandy Silt | Sandy Silt | Silty Sand | Conglomerate | Detritus/Silt |
| '/00 | 0-5 | 15-30 | 15-30 | 15-30 | 0-5 |
| | Met:<br>Gray brown col or. Very fine sediments, easy to suspend - reins in in suspension easily. Silts gray wisen in suspension-settle portion brown.<br>Ory:<br>Blue gray color - Sample cements together when dry. Sufficient pressure needed to break sample apart. | Wet:<br>Green brown col or. Muddy - suspended easily, heavier fraction forms a "clay" on the bottom of the trap - Remains in suspension easily.<br>Ory:<br>Green gray co1 or fragments easily but needs sufficient pressure to reduce i t al 1 the way to powdared form. | Wet:<br>Brown black color. Silt suspended easily and sand (black) settles quickly. Sand forms the majority of the sample, silts remain in suspension easily.<br>Ory:<br>Gray black color. Very fine sand is black in color. Drying causes clumping rather than laying pow&r easily. | Wet:<br>Brown color. Silt and organics suspend easily. Organics appear to be a flock or mucoid sand, gravel and shel 1 fragments settle easily. Organics approx. 50% of sample.<br>Dry:<br>Brown gray col or. Sample cements together-difficult to break apart. Silt and organics act as a strong bonding agent. | Wet:<br>Brown color. Silt and plant fiber suspend easily. Fibers settle first followed by the very small sandy silt-a small fraction of the silt remains in suspension over B hours.<br>Dry:<br>Brown color. Drys as silt/ fiber matrix. Flakes when broken. Easy to powder. |

TABLE 5-33. SIZE COMPOSITIONAL DATA DERIVED FROM VISUAL AND MICROSCOPIC OBSERVATIONS OF SPM SAMPLES COLLECTED FROM INTERTIDAL SAMPLING SITES KB-1, KB-2, KB-2B, KB-3 AND KB-4 (SPRING 1981 KASITSNA BAY PROGRAM).

| | 1 | 2 | 2B | 3 | 4 |
|---|---|---|---|---|---|
| Cobble | | | | X | |
| Heavy Gravel | | | | x | |
| Medium Gravel | X | | | x | |
| Heavy Sand | | | | x | |
| Medium Sand | | | x . | x | |
| Light Sand | X | X | x | x | |
| Silt | X | X | X | X | X |
| Glacial Silt | X | ? | ? | ? | |
| Organics | | X | X | X | X |




1 - silts, sand - sandy silt (glacial )
2 - sand, silts - sandy silt (marine).
2B - silts, sand - silty sand (marine)
3 - organics, silt, sand, gravel - conglomerate (marine)
4 - organ ics, silt - silt (organic)

| | Glacial | Marine | Terrest. | Marsh |
|---|---|---|---|---|
| Glacial | 1 | 1 | | |
| Marine | | 2,2B,3 | 4 | |
| Terrest. | | | 4 | |
| Marsh | | | | |

FIGURE 5-82. (A) FIELD ESTIMATED SIZE COMPOSITIONAL DIAGRAM FOR SEDIMENT/SPM SAMPLES COLLECTED DURING THE SPRING PROGRAM; (B) SEDIMENTARY SOURCE DIAGRAM DERIVED FROM FIELD OBSERVATION DATA.

La Jolla. Particular attention was paid to the sediments from KB-4, the Seldovia River salt marsh, because of a Bunker C spill which occurred in Seldovia Bay (down stream) during 1978. Observations were completed during that spill event from vessels, aircraft and through the use of drift cards (MAIERO and MAYNARD, November 197$3), and the results of those studies had indicated that. the oil did not enter the upper end of the Bay. Fortunately, the capillary column gas chromatographic data confirmed that no prior contamination of that area (or any of the other sites) had occurred, and only trace levels of biogenic compounds were detected in any of the analyses. As a result, no additional field sampling was required during the spring program, and the frozen sediment samples were then shipped to La Jolla for additional characterization and initial oil/SPM interaction studies.

### 5.3.3 Additional Suspended Particulate Material Sample Characterization by Scanning Electron Microscopy

Upon returning to our laboratories in La Jolla, CA additional characterizations of the sediment/SPM samples were undertaken and these included: specific surface area determinations, scanning electron microscopy (SEM), dispersive X-ray compositional analyses and diffractive X-ray mineralogical analyses. The results of the SEM analyses are presented below; however, the X-ray diffraction studies have not been completed at this time so these data will be included in subsequent reports.

Each sample for SEM analyses was prepared by transferring a 55 to 57-mg sediment sample into 35 ml of deionized water. The sample was then shaken for 15 min on a wrist action shaker; this water was then transferred to a 50-cc plastic polyethylene centrifuge tube with a side arm to withdraw subsamples using a 3-cc syringe.

After bubbling with $N_2$ to insure SPM suspension, the sediment/water mixture was diluted twice and filtered through a 0.2 $\mu$m pore size nuclepore filter to yield 135 to 139 $\mu$g per filter. This filter was then sputter coated with gold for scanning electron microscopy analyses on a model 1S1 Super 111A

SEM. Figures 5-83 through 5-92 present two selected fields from each SPM sample as shown below.

Figure 5-83 - KB-1 Grewingk Glacial Till
Upper 0-5 mm of deposits removed from Glacier Delta

Figure 5-85 - KB-2A China Poot Bay
Upper 0-1 cm of deposits from intertidal mud flats

Figure 5-87 - KB-2B China Poot Bay
Lower 1-B cm composite from intertidal mud flats

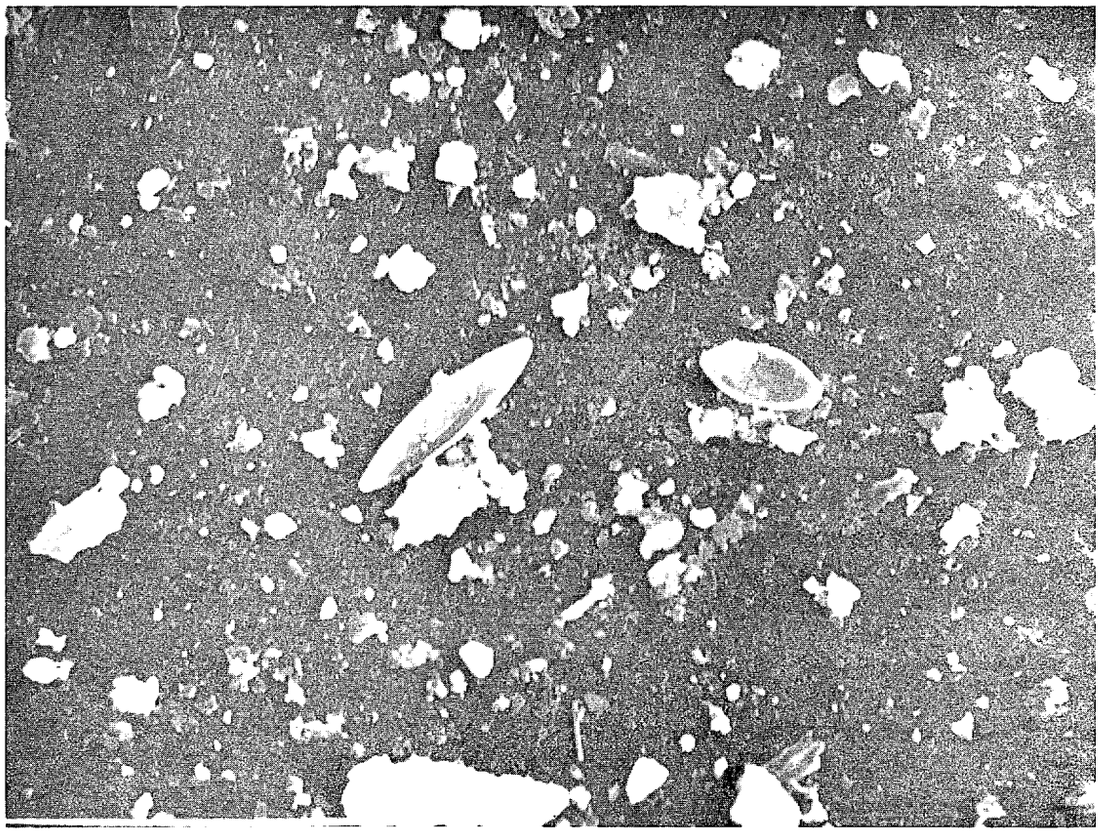
Figure 5-89 - KB-3 Kasitsna Bay
Upper 0-1 cm composite of sediment floe from protected mud flats

Figure 5-91 - KB-4 Seldovia River Estuary
Upper 0-1 cm composite of sediment/detrital floe from channel in Spartina sp. salt marsh

Following each set of SEM photomicrographs, a schematic diagram is presented which identifies the major components present.

Because the μg loading on each filter represents the same overall mass/filter area, direct compositional comparisons can be made for all the SPM samples. Thus, in Figure 5-83 it can be seen that diatoms and several larger clay fragments make up the majority of the sample by weight, while the majority of the surface is covered by less than 5- m clay fragments.

In Figure 5-85 of the surface 0 to l-cm sample from China Poot Bay, the upper photographs show several plant fragments, and large clay fragments while a significantly reduced level of less than 5 μm clay fragments compared



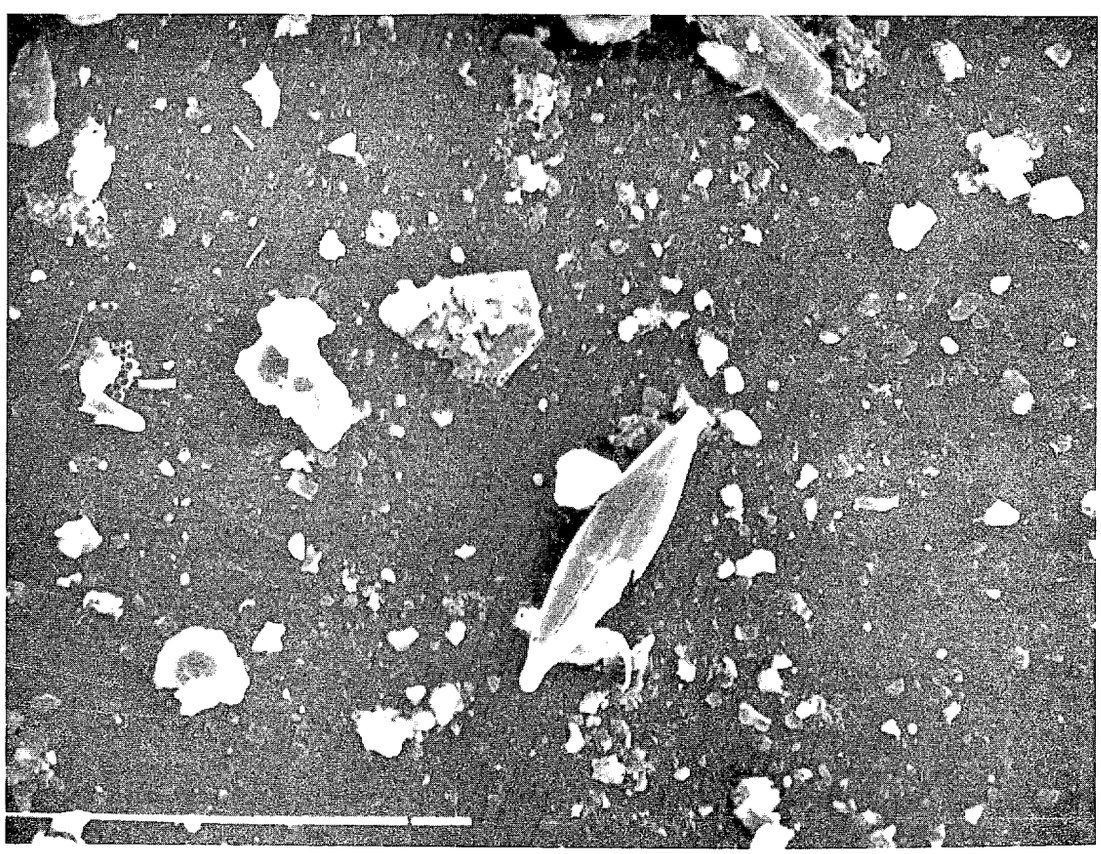


FIGURE 5-83 SCANNING ELECTRON MICROGRAPHS (1400X) OF KB-1-81 (Grewingh Glacier).

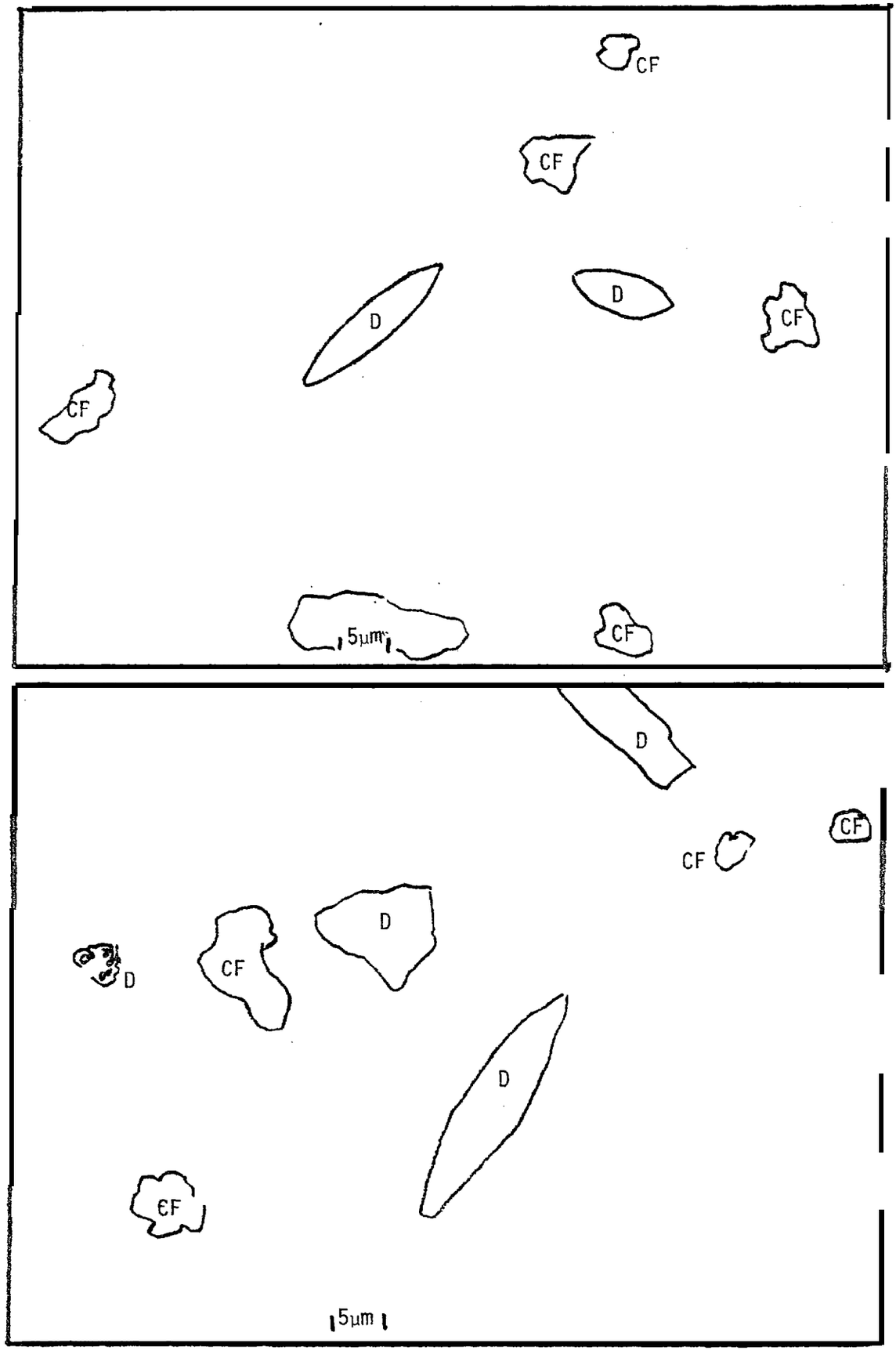



FIGURE 5-84 . IDENTIFICATION OF MAJOR COMPONENTS IN SEM PHOTO-MICROGRAPH OF KB-1-81 (Grewingh Glacier).

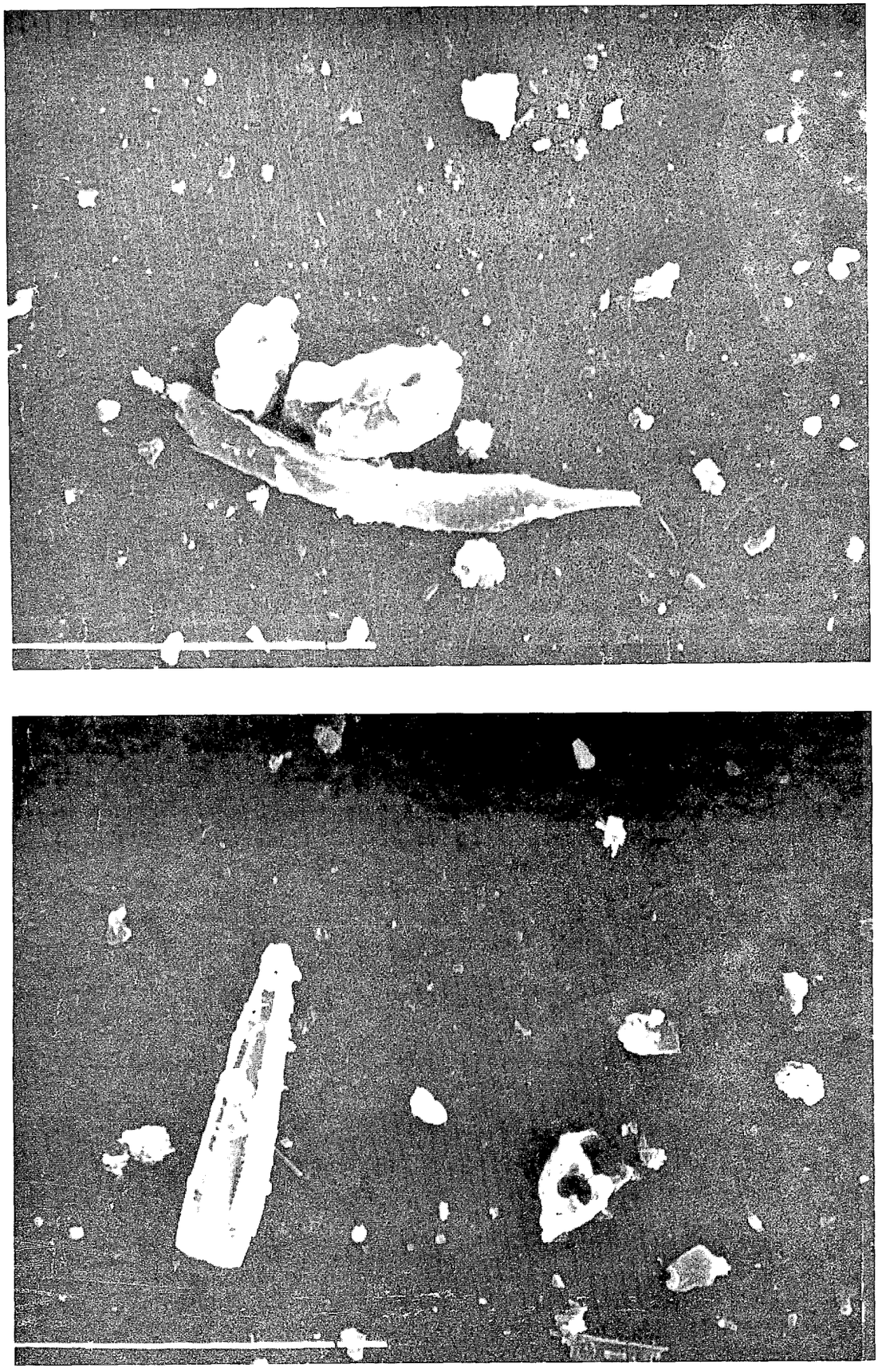
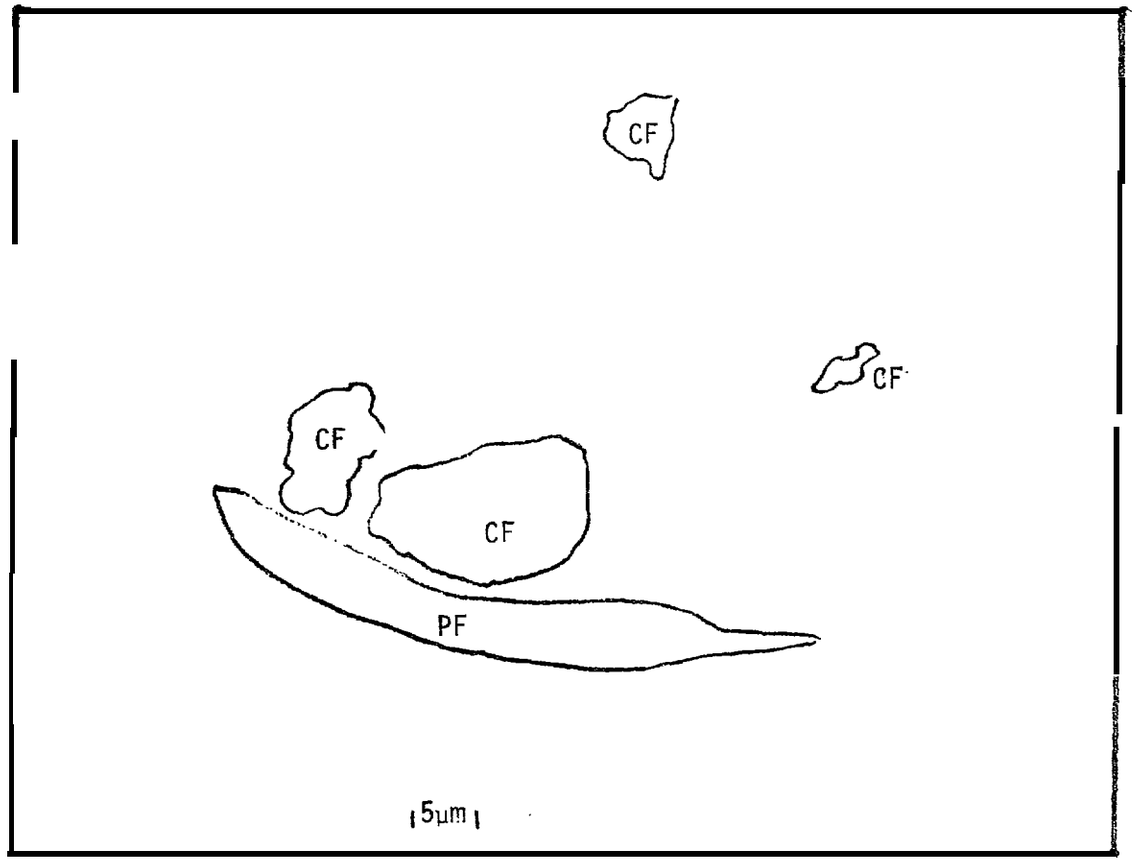


FIGURE 5-85 . SCANNING ELECTRON MICROGRAPHS (1400X) OF KB-2-81A (China Poot Bay 0-l cm).



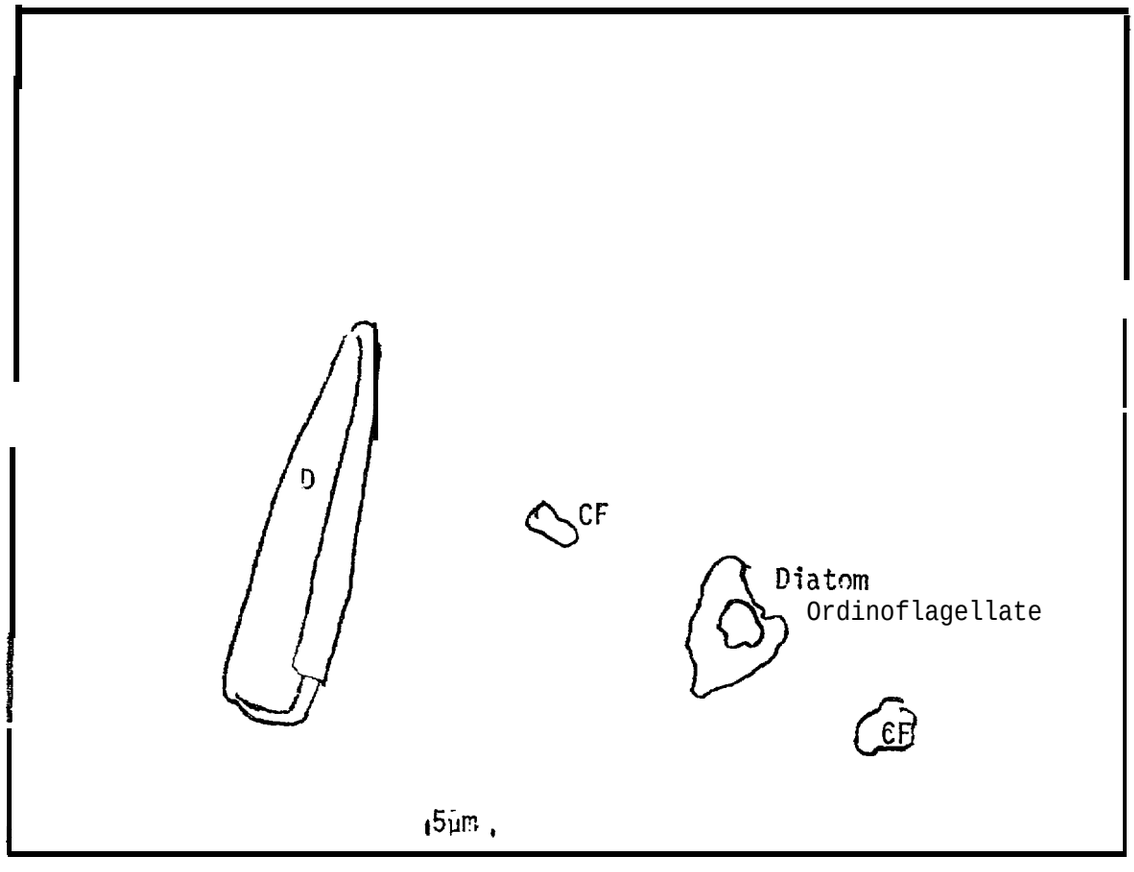




FIGURE 5-86. IDENTIFICATION OF MAJOR COMPONENTS IN SEM PHOTO-MICROGRAM OF KB-2-81A (China Poot Bay0-l cm).

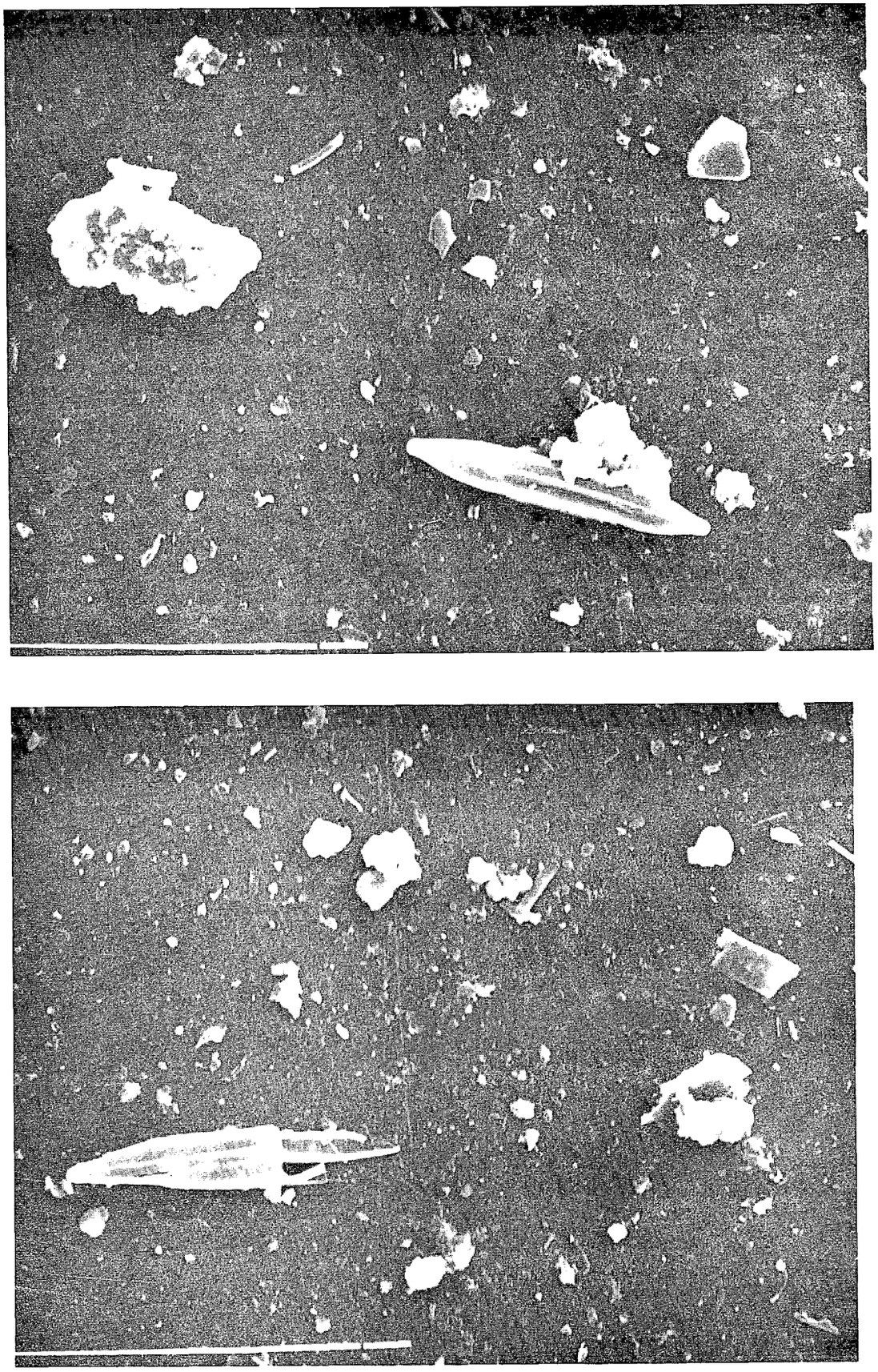
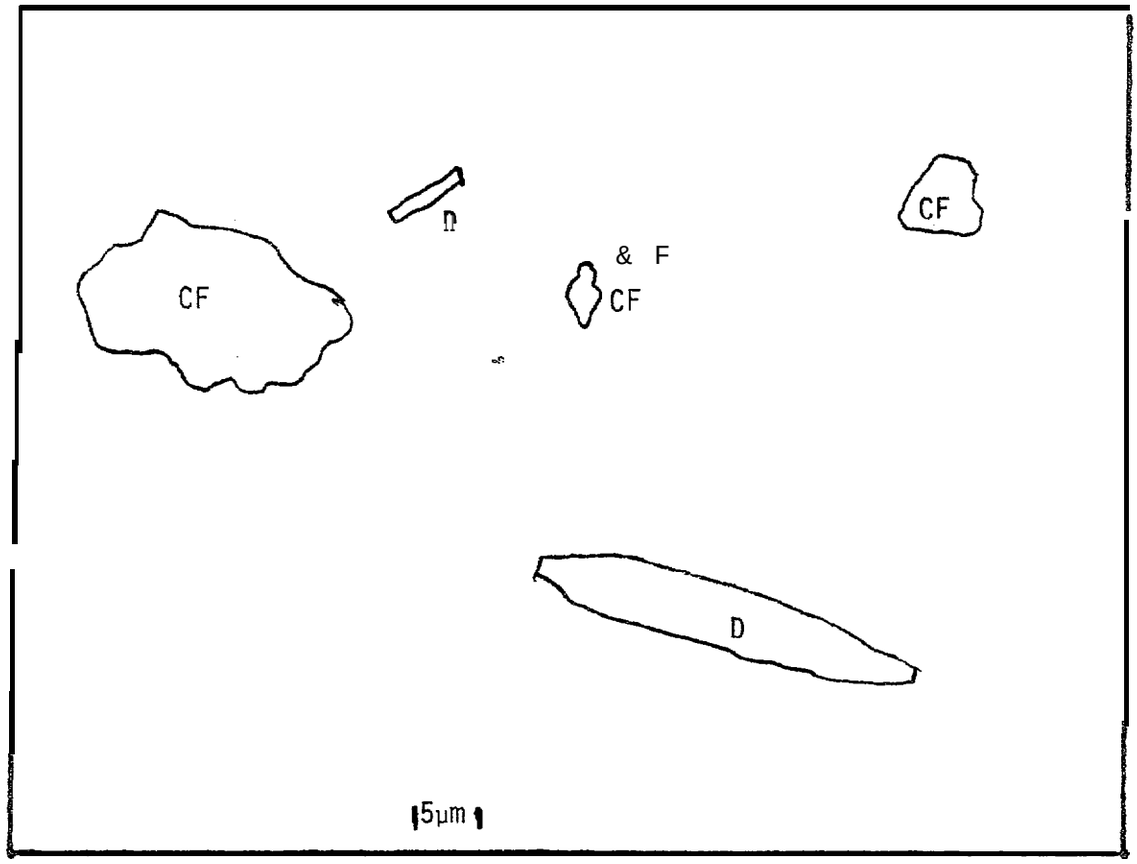


FIGURE 5-87. SCANNING ELECTRON MICROGRAPHS (1400X) OF KB-2-81B (China Poot Bay 1-8 cm).



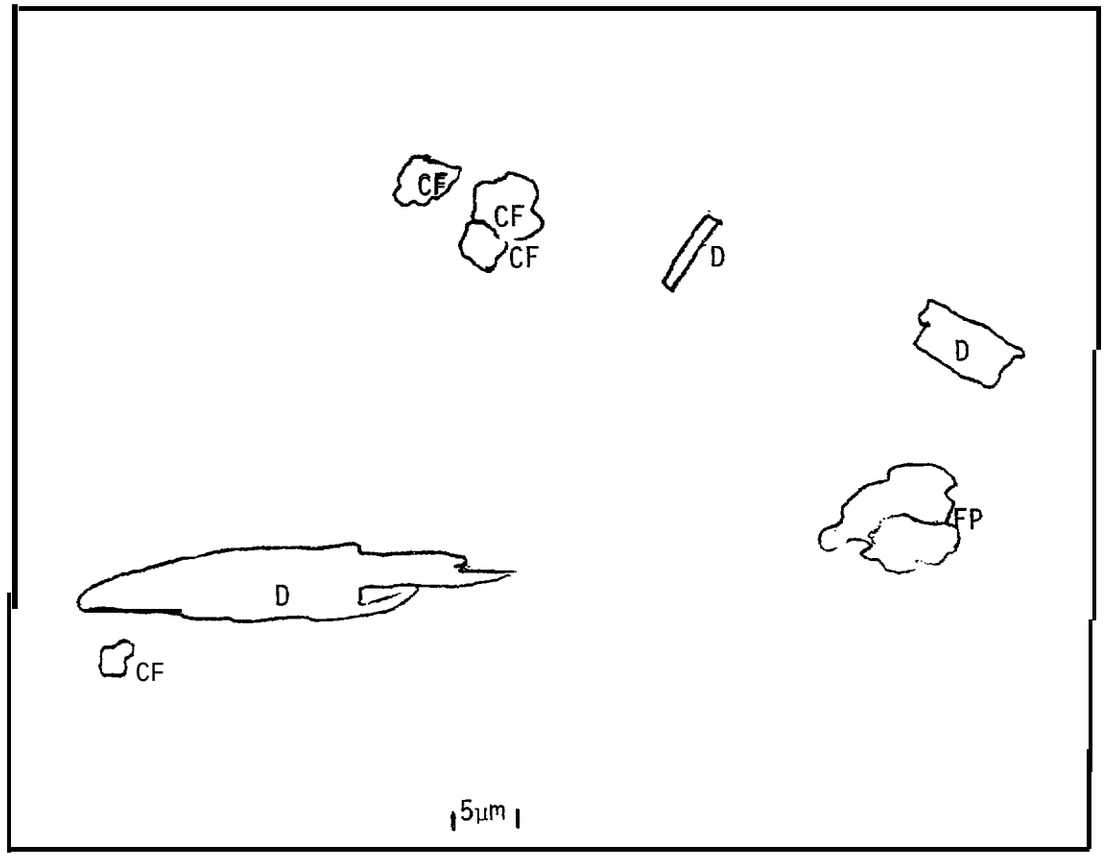




FIGURE 5-88 . IDENTIFICATION OF MAJOR COMPONENTS IN SEM PHOTO-MICROGRAM OF KB-2-81B (China Poot Bay 1-8 cm).

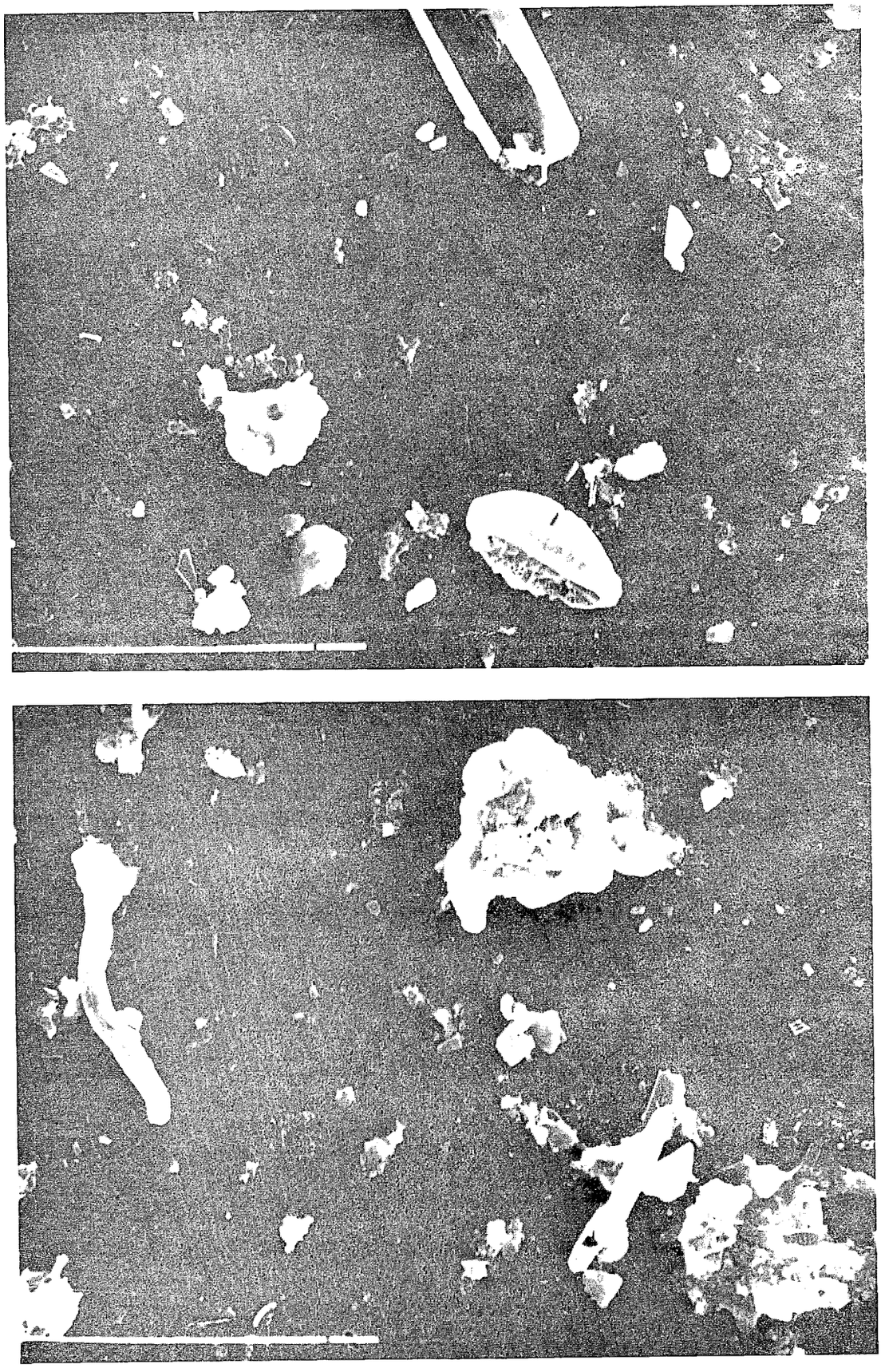


FIGURE 5-91. SCANNING ELECTRON MICROGRAPHS (1400X) OF KB-4-81 (Seldovia River Estuary).

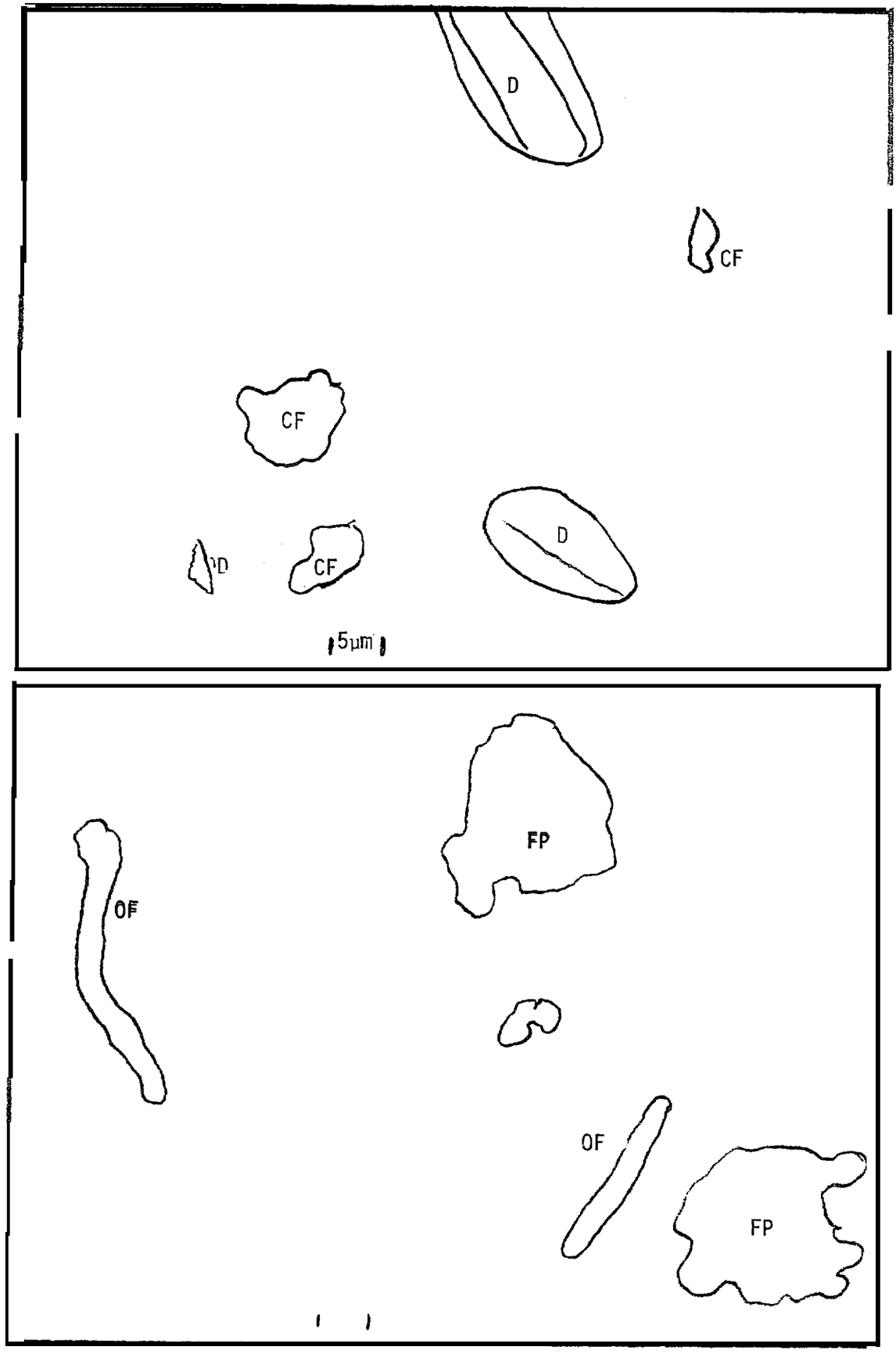



FIGURE 5-92. IDENTIFICATION OF MAJOR COMPONENTS IN SEM PHOTO-MICROGRAM OF KB-4-81 (Seldovia River Estuary).

to the sample from the Grewingk Glacier delta is observed. In the lower photograph for the 0 to 1-cm sample (Figure 5-85), a large diatom and a smaller fragment of what appears to be a diatom are present in addition to two larger clay flake fragments as shown in the schematics in Figure 5-86. The 1 to 8-cm depth sample from China Poot (Figure 5-87) shows a higher relative composition of clay <5 m fragments compared to the surface 0 to 1-cm sample, although the 1 to 8-cm sample is also characterized by several diatoms and clay fragments. In the second field from the 1 to 8-mm sample, another large diatom can be observed along with several fecal pellets and smaller diatom fragments mixed in with the ?ess than 5- m clay fragments.

In Figure 5-89 for KB-3 (Kasitsna Bay) the photographs show exceedingly high levels of diatom fragments and several clay fragments. In comparison to other sites sampled, there are significantly more diatom fragments at KB-3, however, here too several clay fragments in the 5 micron range can be observed.

The SEM photographs from KB-4 (Seldovia River Estuary) show very few clay fragments (Figures 5-91 and 5-92), and in general the samples are characterized by several large organic fragments, fecal pellets and a few diatoms.

Additional discussions of how the SEM characterizations correlate with hydrocarbon adsorption potential follow the next section on oil/SPM interactions (5.3.4), however, from the initial examination it is apparent that from a mineralogical standpoint, all five SPM types are basically from the same source which is believed to be terrestrial rock flour generated by glacial action, melting snow and river runoff. This is best represented by the SEM characterizations of the rock flour from the Grewi ngk Glacier (KB-1). The other sites selected then show various degrees of dilution of this rock flour material with other components. KB-3 (Kasitsna Bay) SPM was primarily diluted by silica tests from diatoms. KB-4 (Seldovia River Estuary) exhibited evidence of some of the same basic mineralogical material and was diluted by decaying organic plant material which was primarily derived from the Spartina

salt marsh. The two sediment samples from China Poot Bay (KB-2 and KB-2B) exhibited intermediate results in that the lower (1 to 8-cm subsection) showed extensive concentrations of' Terrestrial clay flakes with dilution by plant fragments and diatom skeletons. Interestingly, in this instance, the upper 0 to 1-cm sample contained fewer less than 5 $\mu$m sized clay flakes by weight and larger contributions from plant fragments and diatoms compared to the 1 to 8-cm samples.

### 5.3.4 Compound Specific Oil/SPM Partitioning Experiments

After the various sediment samples were characterized with regard to compositional makeup, a series of static equilibrium partitioning experiments were undertaken to evaluate their relative adsorption potential for individual components in Prudhoe Bay crude oil. From these results, two representative sediment samples showing the greatest and least affinity for crude oil adsorption were then to be selected for extended flow-through outdoor tank experiments in Kasitsna Bay during the Summer, 1981 program. Specifically, these Summer, 1981 experiments were designed to examine partitioning of oil components onto suspended particulate material as a function of the degree of subarctic evaporation and dissolution weathering.

For these initial oil/SPM characterization experiments, 20 grams of each sediment type were added to filtered seawater and the mixtures were agitated at 23° with magnetic stir bars. Care was taken in adjusting the stirring motors to insure that vortexinginthe samples did not occur, and 3.5 ml of fresh Prudhoe Bay crude oil were added to each beaker. The beakers were covered (watch glass) and the mixtures were allowed to stir for 4 days and then allowed to settle over an additional 12-hr period. At that time the sedimentary material from the bottom of each beaker was carefully siphoned under vacuum taking care to ensure that none of the sediment came into direct contact with the oil during removal. Similarly, 300-ml aliquots of the water beneath the oil slicks were removed for determination of water column burdens. The respective sediment and water column samples from each experiment were

then extracted and analyzed for petroleum hydrocarbon contamination along with unexposed sediment samples to determine background level hydrocarbon components present at each site.

Table 5-34 presents the total resolved component and UCM concentrations for the aliphatic and aromatic fractions from the sediment and water column extracts. Specific aromatic compound concentration burdens are also listed for the two phases examined in each experiment. From the data in the Table 5-34, it is possible to rank the sediments according to their overall adsorption efficiency for total and specific petroleum hydrocarbon components, and in the order of decreasing adsorption potential they are: KB-4 (Seldovia River salt marsh detritus); KB-1 (Grewingk Glacial till); KB-2A (China Poot Bay surface sediment]; KB-2B (China Poot Bay 1 to 8-cm sediment) and KB-3 (Kasitsna Bay composite sediments). These rankings were generated by examining the cumulative sum of the n-alkanes and total resolved and UCM component concentrations in the aliphatic fractions and the total resolved and UCM component concentrations observed in the aromatic fractions for each sediment type . Numerical rankings in the order of 1 through 5 were given to each sediment for each parameter described above, and these rankings were then summed to arrive at an overall total to reflect each sediment type's affinity for oil. Specific compound concentrations were also considered in this ranking, as were the relative water column concentrations above each sediment. That is, an inverse relationship was observed between particulate adsorption potential and the levels of hydrocarbons observed in the water above each sediment type, and this relationship was-also used in the overall rankings.

Figures 5-93 and 5-94 present the capillary gas chromatograms obtained on the sediment and water samples from the most adsorptive (Bay-4, Seldovia River salt marsh) and least adsorptive (Bay-3, Kasitsna Bay composite sediment) samples, respectively. Each figure is arranged as follows: Chromatogram "A" represents the aliphatic hydrocarbons in the oil-exposed sediments; Chromatogram "B" represents the background level of aliphatic hydrocarbons measured in the unexposed sample; Chromatogram "C" represents the aliphatic hydrocarbons in the water column extract; Chromatogram "D" represents

TABLE 5-34. RESULTS OF EQUILIBRIUM PARTITIONING OIL/SPM INTERACTION STUDIES (STATIC SYSTEM, 19°C).

| | AL IPHAT IC FRACTION** | | | | AROMATIC FRACTION*** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Ben zenes | | | Naphthal enes | | | | | Phenanthrenes | | |
| Samp 1 e * | Total Res | Total UCM | Total Σn-alk | Σn-alk / Branched | Total Res. | Total UCM | 1,4&1, 3-dimethyl (884) | ethyl (874) | naphthal ene (1 196) | 2-methyl (1305) | 1 -methyl (1322) | 2-ethyl (1404) | 2,3-dimethyl (1430) | 1,6,7 -trimethyl (1542) | phenanthrene (1788) | 2-methyl (1904) |
| K. Bay-1 Sediment | 340,000 | 73,000 | 26,000 | 0.08 | 46,000 | 42,000 | 15 | 62 | 40 | 630 | 400 | 103 | 440 | 290 | 570 | 390 |
| Aqueous Phase | 4,760 | 0 | 33 | 0.007 | 601 | 15 | 2.9 | 0.56 | 1.3 | 7.4 | 7.4 | 9.8 | 3.1 | 1.0 | 0.23 | - |
| K; Bay-2A Sediment | 795,000 | 18,000 | 16,000 | 0.02 | 385,000 | 7,100 | 46 | 270 | 90 | 550 | 310 | 96 | 240 | 143 | 200 | 83 |
| Aqueous Phase | 3,380 | 0 | 11 | 0.003 | 1,907 | 0 | 3.4 | 1.4 | 3.3 | 7.2 | 6.8 | 0.7 | 2.2 | 1.0 | | |
| K. Bay-2B Sediment | 6117,000 | 51,000 | 14,000 | 0.02 | 9.600 | 22,000 | | | | | | | | | | |
| Aqueous Phase | 170 | 0 | 17 | 0.1 | 2,720 | 0 | | | | | | | | | | |
| K. Bay-3 Sediment | 85,000 | 10,000 | 5,000 | 0.06 | 12,000 | 10,000 | 33 | 130 | 4 | 91 | 83 | 25 | 89 | 35 | 44 | - |
| Aqueous Phase | 5,840 | 0 | 8 | 0.001 | 512 | 0 | 2.0 | 0.74 | - | 0.63 | 4.4 | 0.28 | 2.3 | 0.28 | 0.53 | - |
| K. Bay-4 Sed i men t | 253,000 | 262,000 | 60,000 | 0.3 | 44,000 | 75,000 | 12 | 200 | 29 | 48 | 370 | 125 | 337 | 210 | 71 | - |
| Aqueous Phase | Not reduced - very low | | | | 2,180 | 0 | 2.9 | 0.46 | 0.16 | 0.49 | 1.3 | 0.12 | 2.2 | 0.34 | | - |

*K. Bay-1 --Grewingh Glacier Till - fine grained terrestrial plus diatoms, many flakes 5 μm and less
K. Bay-2A-China Poot Bay surface 1 cm - mostl y >5 μm terr plus some plant
K. Bay-28-China Poot Bay depth 1-8 cm - most material . 5 μm
K. Bay-3--Kasitsna Bay consol i dated sediment - 90% diatoms > 5 μm, some terr. ≤ 5 μm
K. Bay-4--Seldovia River salt marsh - organic plus fecal pellets

| Specific Surface Area | |
|---|---|
| | 9.1 |
| ⇓ | 8.2 |
| | 15.2 |
| " | 9.1 |
| " | 11.1 |

**Sediment concentration in μg/kg, water concentration in μg/l

● ** Sedinwnt concentration in μg/kg, water concentration in μg/l; numbers in parentheses are compound Kovatindices.

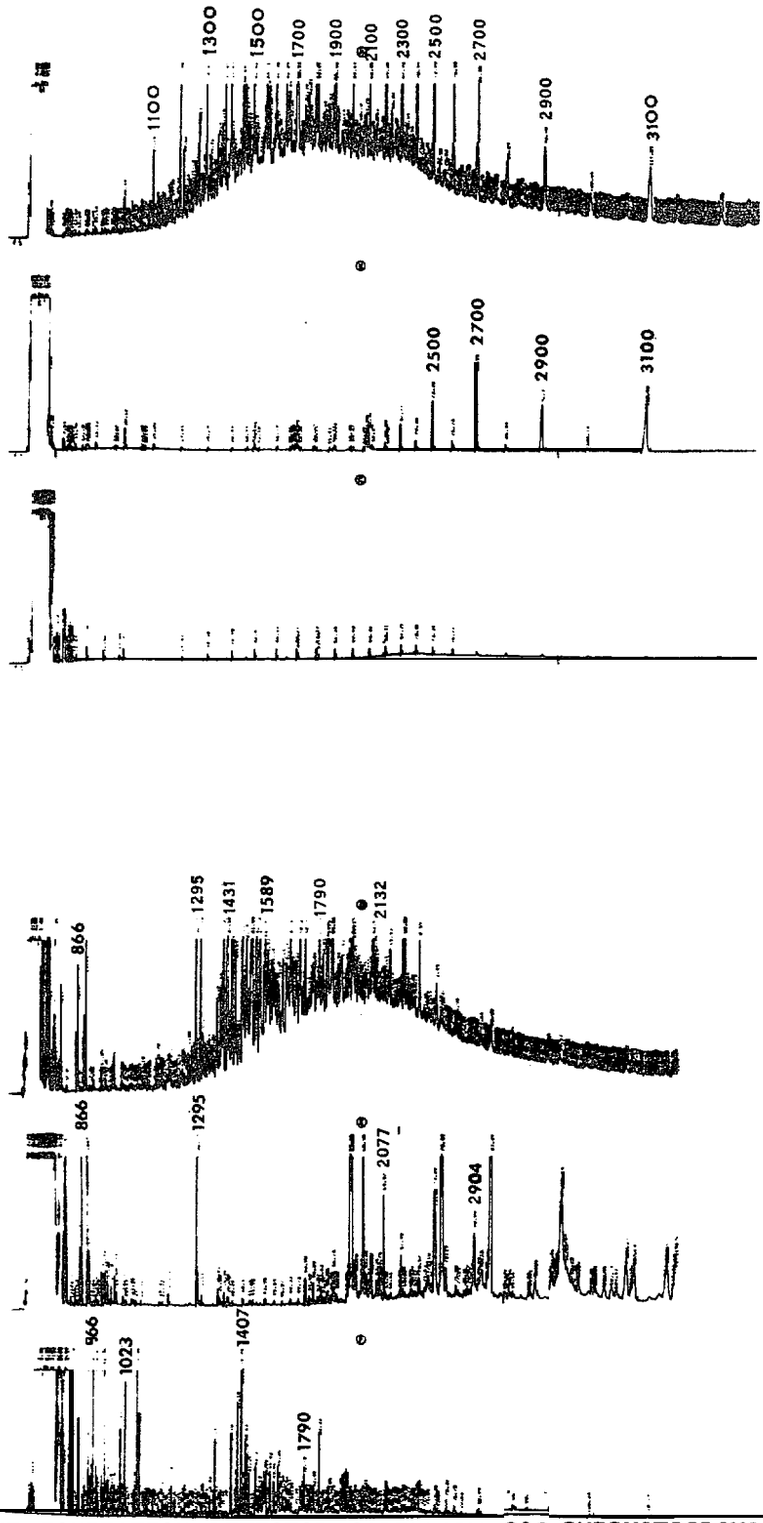



FIGURE 5-93. FLAME IONIZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS FROM KB-4 (SELDOVIA RIVER SALT MARSH) OIL/SPM INTERACTION STUDIES: (A) AL IPHATIC HYDROCARBONS IN THE OIL EXPOSED SEDIMENTS; (B) BACKGROUND LEVEL ALIPHATIC HYDROCARBONS MEASURED IN UN-EXPOSED SEDIMENT; (C) ALIPHATIC HYDROCARBONS IN THE WATER COLUMN EXTRACT; (D) AROMATIC HYDROCARBONS IN THE OIL EXPOSED SEDIMENTS; (E) BACKGROUND LEVEL AROMATIC HYDROCARBON COMPONENTS MEASURED IN THE UNEXPOSED SAMPLE; AND (G) AROMATIC HYDROCARBONS IN THE WATER COLUMN EXTRACT.

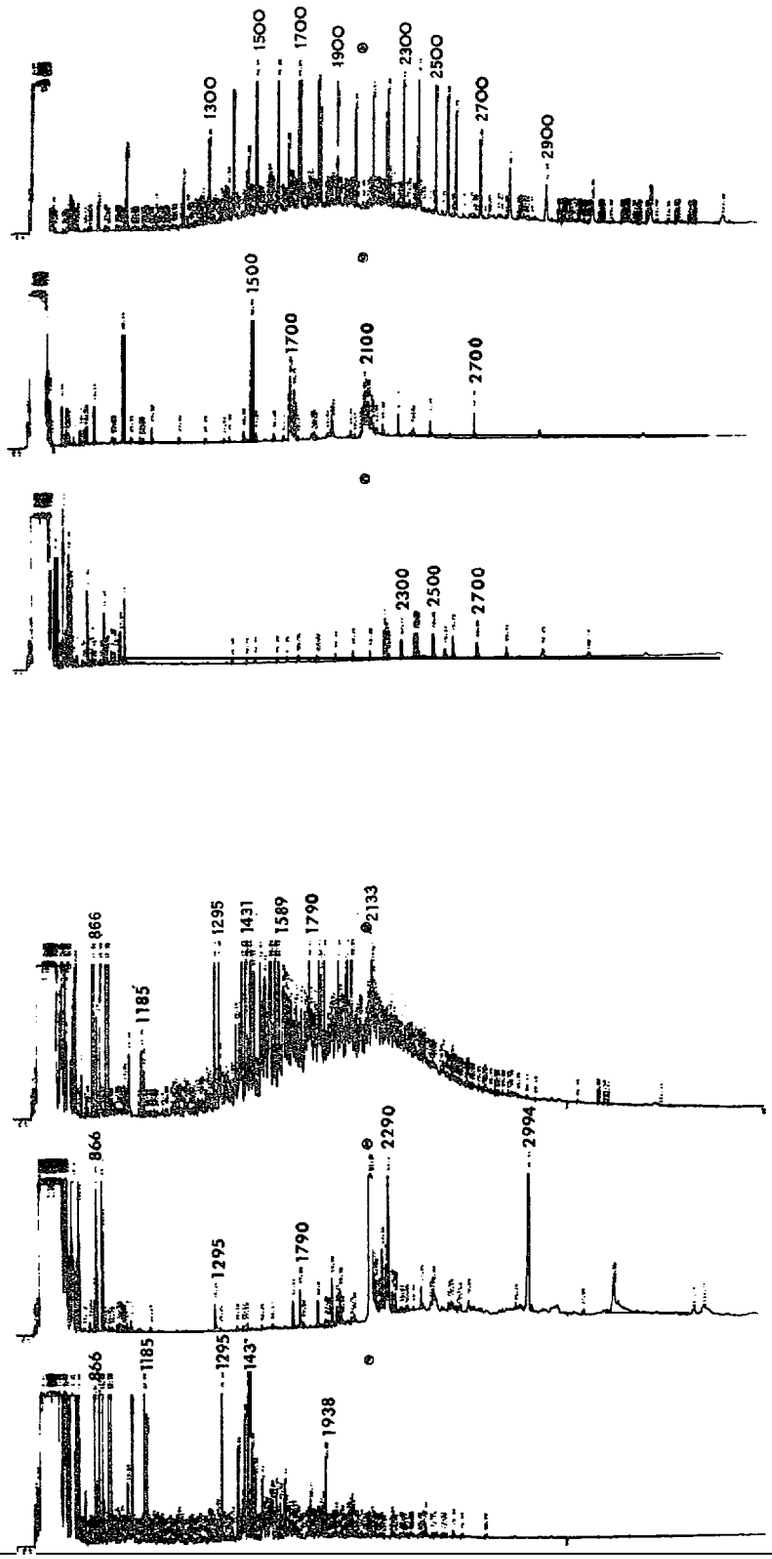



FIGURE 5-94. FLAME ION I ZATION DETECTOR CAPILLARY GAS CHROMATOGRAMS FROM KB-3 (KASITSNA BAY COMPOSITE SEDIMENT) OIL/SPM INTERACTION STUDIES: (A) ALIPHATIC HYDROCARBONS IN THE OIL EXPOSED SEDIMENTS; (B) BACKGROUND LEVEL ALIPHATIC HYDROCARBONS MEASURED IN UN-EXPOSED SEDIMENT; (C) ALIPHATIC HYDROCARBONS IN THE WATER COLUMN EXTRACT; (D) AROMATIC HYDROCARBONS IN THE OIL EXPOSED SEDIMENTS; (E) BACKGROUND LEVEL AROMATIC HYDROCARBON COY? PONENTS MEASURED IN THE UNEXPOSED SAMPLE; AND (G) AROMATIC HYDROCARBONS IN THE WATER COLUMN EXTRACT.

the aromatic hydrocarbons in the oil-exposed sediments; Chromatogram "E" represents the background level aromatic hydrocarbon components measured in the unexposed sample; and Chromatogram "G" represents aromatic hydrocarbons in the water column extract. Clearly, the most significant differences appear in considering the aliphatic fractions for the oil-exposed sediments, (Chromatograms A in Figures 5-93 and 5-94). The Seldovia River salt marsh sample shows a significant unresolved complex mixture and a suite of normal and branched hydrocarbons extending from nC-10 through nC-31. While this same suite of compounds is observed in the Kasitsna Bay sediments, the unresolved complex mixture is significantly smaller as is reflected in the reduced UCM data in Table 5-34. The aliphatic fraction chromatograms on the unexposed sediments showed some differences, with higher molecular weight odd numbered n-alkanes clearly predominating in the Seldovia River salt marsh sample. Specifically, nC-23, nC-25, nC-27 and nC-29 from plant wax components are clearly the most predominant feature in Figure 5-93B. Slightly higher aliphatic water column concentrations are observed in the samples from KB-3 compared to KB-4, and this reflects the inverse relationship noted above for SPM adsorption potential and water column hydrocarbon burdens.

The aromatic fractions of the contaminated sediments appear to be very similar, however, here again the unresolved complex mixture in the Seldovia River salt marsh sample is significantly larger, and higher levels of individual aromatic components with Kovat indices extending from 1400 to 1788 are noted with the organic-rich Seldovia River salt marsh SPM. The data in Table 5-34 also illustrate that a factor of 7 increase in total aromatic unresolved component concentrations is noted in comparing the Seldovia River and Kasitsna Bay sediment samples. The aromatic fractions of the uncontaminated sediments (Chromatograms E in Figures 5-93 and 5-94) show several significant differences, and in particular more higher molecular weight components can be observed in the sediment sample from the salt marsh. The large peaks near Kovat index 1900 to 2200 in the middle of both chromatograms are believed to be due to polyunsaturated components of biogenic origin; however, additional identifications of components in the aromatic fractions of the unexposed samples will not be available until additional GCMS analyses are undertaken.

Interestingly, the aromatic fraction of the water column components appear very similar for both samples. This largely reflects the higher compound-specific seawater solubilities for the lower molecular weight alkyl - substituted benzenes in the Kovat indices range of 700 to 874 and the limited solubilities of the alkyl-substituted naphthalenes in the Kovat index range of 1305 through 1542. It should be noted, in general, that the lower molecular weight aromatics do not specifically adsorbe onto the particulate material, but that they instead reside in the water column beneath the slick. Several lower molecular weight aromatics are suggested by the chromatogram in Figure 5-94D of the aromatic fraction of the sediment sample from KB-3; however, their presence may simply reflect inclusion of slightly greater volumes of water collected during siphoning off the sediment sample.

In terms of the overall oil affinity of the five selected SPM samples, several interesting correlations can be made between the composition data of the SPM as determined by scanning electron microscopy and the results from the glass capillary/gas chromatographic analyses. Specifically, the Seldovia Bay estuary SPM had the highest overall affinity for oil, and the SEM photos illustrate that this material was primarily composed of diatoms and larger (greater than 30 $\mu$m) organic fragments and fecal pellets. It also contains a few clay fragments which, as will be shown below, also have a very high affinity for oil.

The fine glacial rock flower or till from the Grewingk Glacial delta exhibited the next highest affinity for hydrocarbons, and in many instances, showed an equal or greater affinity for specific aromatic compounds compared to the organic rich detrital sediments from the Seldovia Bay estuary. The SEM photographs of this material show that the sampleis primarily very small clay fragments plus a relatively limited number of diatoms, which no doubt came from the marine input and flushing of the intertidal zone. The high affinity for oil in this instance, is believed to be due to the high surface area (on a surface area per weight basis) due to the profusion of fine clay fragments.

Because of this material's high affinity for oil and the fact that the near-shore waters in many areas in Alaska receive significant contributions of SPM from glacial till, this sample was considered to be ideal for extended long-term studies. Ironically, only small amounts of this relatively pure material could be obtained from intertidal sources near Kasitsna Bay, and where it was found, only limited amounts could be obtained by scrapping very thin belts or deposits from standing pools at the glacier delta. Because of the active geological nature of this site, however, a continued source of this material could not be depended upon. Further, the site was only accessible by whaler and as such, logistical and weather constraints were considered to be major obstacles which would prevent obtaining the necessary kilogram quantities of this material for inclusion in the flow-through oil/SPM interaction studies.

The SPM sample with the next highest affinity for oil was the surface 0 to 1-cm mat from China Poot Bay (K Bay-2A). The SEM photographs of this sample showed it to be primarily made up of clay and plant fragments with an occasional diatom skeleton. The 1 to 8-cm depth sample from this site also showed high affinities for aliphatic and aromatic components; and the SEM photographs in this case showed a higher concentration of the less than 5 $\mu m$ sized clay fragments with additional input and/or dilution from diatoms. The SPM sample from K Bay-3 (Kasitsna Bay) which showed the lowest affinity for adsorption, consisted almost exclusively of diatom fragments (by weight) with a few clay fragments in the less than 5 micrometer size range appearing in the background of the SEM photos.

The results of these initial oil/SPM interaction studies are in good agreement with the work of several other authors who have investigated oil/sediment interactions. Several of these similarities and one striking difference (dealing with a previous study on Glacial till) are considered in the following discussion.

With regard to similarities, GERRING et al. (1979) also reported the fractionation or partitioning of lower molecular weight aromatic compounds

(including up to 3-ring aromatics) into the dissolved phase before adsorption of the oil onto suspended particulate material and subsequent sinking, In test tank studies completed at the Marine Ecosystem Research Laboratory at. the University of Rhode Island, they found that the aromatic/aliphatic ratio in the sediment was much lower than that in the parent oil suggesting that preferential dissolution of lower molecular weight compounds may be occurring. Specifically, 2-34% of the higher molecular weight aliphatic, acyclic and greater than 3-ring hydrocarbons were absorbed onto the suspended particulates and sediments in contrast to 0.1% of the more water soluble naphthalene and methyl naphthalene components which were the predominant aromatic materials in the No. 2 fuel oils used in their studies.

WINTER (1978) also observed similar partitioning in studying two simulated oil spills and one mixture of aromatic compounds added to a test tank. The petroleum derived alkanes were approximately 10 times greater in the particulate fraction, and the lower molecular weight aromatics were at least 5 times more concentrated in the dissolved phase.

In samples of suspended particulate material collected along transects perpendicular to the South Texas OCS near Corpus Christi, PARKER and MACKO (1978) noted that the concentrations of higher molecular weight (nC-28 through nC-30) compounds remained relatively constant with distance from the shore while the total particulate hydrocarbon burdens decreased with increasing distance. These authors attributed this to the introduction and sorption of the hydrocarbons near the shore with subsequent movement of particulate bound oil with Deferential retention of the higher molecular weight compounds during weathering. Several higher molecular weight polynuclear aromatic hydrocarbons were also identified on the particulate material, and these included alkyl-substituted naphthalenes, phenanthrenes, dibenzothiophenes, fluoranthrene and pyrene. Concentrations of these materials were too low for quantitation; however, they could be detected by selected ion monitoring GC/MS. Similar partitioning of lower and higher molecular weight compounds have been

observed by DELAPPE et al. (1978) in a study designed to measure the partitioning of petroleum hydrocarbons among seawater particulate and the filter feeting Mytilus californianus.

PAYNE et al. (1980) and BOEHM and FIEST (1980) also observed a similar partitioning between lower and higher molecular weight compounds in the dissolved phase and suspended particulate material samples removed by filtration of large volume water samples obtained in the vicinity of the 1 XTOC-I blowout in the Gulf of Mexico.

In a laboratory study, MEYERS and QUINN (1973) found that the hydrocarbon adsorption efficiency (for the less than 44 μm particle sized fractions) decreased in the order of bentonite > kaolinite > illite > monmorillinite. Interestingly, when Meyers and Quinn treated sediment samples from Narragansett Bay with 30% peroxide to remove indigenous organic material, an increase in absorption potential was noted. These authors concluded that the organic material (which was presumably humic substances) presumably masked the sorption sites on the sediment thereby reducing the available surface area for adsorption of the organic compounds. SEUSS (1968), on the other hand, has suggested that a 3 to 4% organic material coating on clay will enhance sorption Processes by providing, in effect, a lipophillic layer to enhance non-polar hydrophobic binding. These results would be more in line with the results of our most recent studies in comparing the adsorption potential of the organic rich materials from the Seldovia River estuary (KB-4) to the composite diatom rich sediment samples from Kasitsna Bay (KB-3).

In a laboratory study ZURCHER et al. (1978) considered the dissolution, suspension, aglomeration and adsorption of fuel oil onto pure kaolinite. In their studies, as in ours, the dissolved water column samples showed significant levels of lower molecular aromatics in the benzene to methylnaphthalene range, and the adsorbed fraction contained n-alkanes and aromatics from Kovat indices 1400 through 3200. The clay minerals in this experiment were shown to adsorb about 200 mg of hydrocarbons per kilogram of dry material.

MEYERS and QUINN (1973) reported a similar value of 162 mg/kilogram for dry kaolinite. Our data, in Table 5-34, suggest values in line with these earlier determinations with a low of 122 mg/kilogram (total resolved and UCM from both the aliphatic and aromatic fractions) from the SPM samples from Kasitsna Bay (KB-3) to a high of 1.2 g/kilogram for the 0 to 1-cm subsample from the tidal mud flats from China Poot Bay (KB-2A).

While the results of these most recent oil/SPM interaction studies using representative samples from the lower Cook Inlet parallel the findings reported by previous investigators, they are somewhat contradictory to recent results reported by MALINKY and SHAW (1979). These authors examined the association of two lower molecular weight petroleum components and suspended sediments (primarily gracially derived sediments from the south central Alaska region) and concluded that sedimentation of oil by the adsorption to suspended mineral particles may not be a major pathway for the dispersion of petroleum in the marine environment. In that study, however, they used $^{14}C$-labelled decane and biphenyl at near saturation levels. In these experiments, the concentrations of the two hydrocarbons associated with the sediments was approximately 30% of the original aqueous concentration in parts per million. From loadings of permitted discharges in Port Valdez and measured sediments loads, the authors calculated that less than 3% of the oil released into the harbor could be associated with the sediment. Thus, the authors concluded that adsorption of hydrocarbons to suspended particulate material was not that significant, and that the role of suspended mineral particulate material may be far less significant in adsorption of polynuclear aromatic hydrocarbons in natural waters than is the role of total suspended matter. The applicability of their findings to real oil spills situations in natural environments may be limited, however, in light of the fact that they did not use a natural oil or even a water accommodated fraction of a natural oil, and by the fact that the compounds which were utilized have significantly higher water solubilities that the more toxic polynuclear aromatic hydrocarbons of interest. Clearly, the results of our studies on the glacially derived till from the Grewingk

Glacier show that it does have a high affinity for polynuclear aromatic hydrocarbons (see Table 5-34) and that the high surface area of the glacial till can provide an active site for oil adsorption and ultimate sedimentation.

### 5*3.5 Extension of Oil/SPM Interaction Studies During the Summer 1981 Program at Kasitsna Bay

After the initial characterization of the component specific affinity of the five representative SPM types, extended oil/SPM interaction studies were undertaken at Kasitsna Bay, Alaska during the Summer 1981 program. Unlike the previously completed experiment where oil was allowed to interact with suspended particulate material in a closed system, the more recent Alaska experiments were designed to look at the time-dependent partitioning of selected hydrocarbons onto SPM as other evaporative and dissolution processes were simultaneously occurring. That is, an overall SPM load was established in the flow-through seawater system in two of the outdoor tanks, and oil was then added to the tanks with turbulence induced by propeller mixing. The sediments chosen for these experiments were from KB-4, (Seldovia River Estuary) and KB-3 (Kasitsna Bay). As described previously" these had the greatest and least affinity for specific components in the static equilibration experiments completed before the onset of the Summer 1981 Alaska field program.

For the Kasitsna Bay field experiments, a separate input water reservoir was constructed for tanks 5 and 6 in the outdoor flow-through system (Figure 5-95). Aliquots of sediment were then added directly to the water in each side of the bifurcated reservoir (which was fed natural seawater) and a continuous supply of SPM burdened water was then fed into the outdoor tanks. One stirring motor was mounted on each side of the sediment/seawater reservoir to keep the finer grained sediment in suspension, and a peristaltic pump was used to feed the sediment laden water at a flow rate of 100 ml/minute to tanks 5 and 6, respectively. The sediment master reservoir contained 77 liters on each side, and weighed amounts of additional sediment was added periodically (every 3 to 10 hours) to maintain an overall sediment load in the master reservoir of 8.7 grams/l. When delivered to the 187 L experimental tanks at a

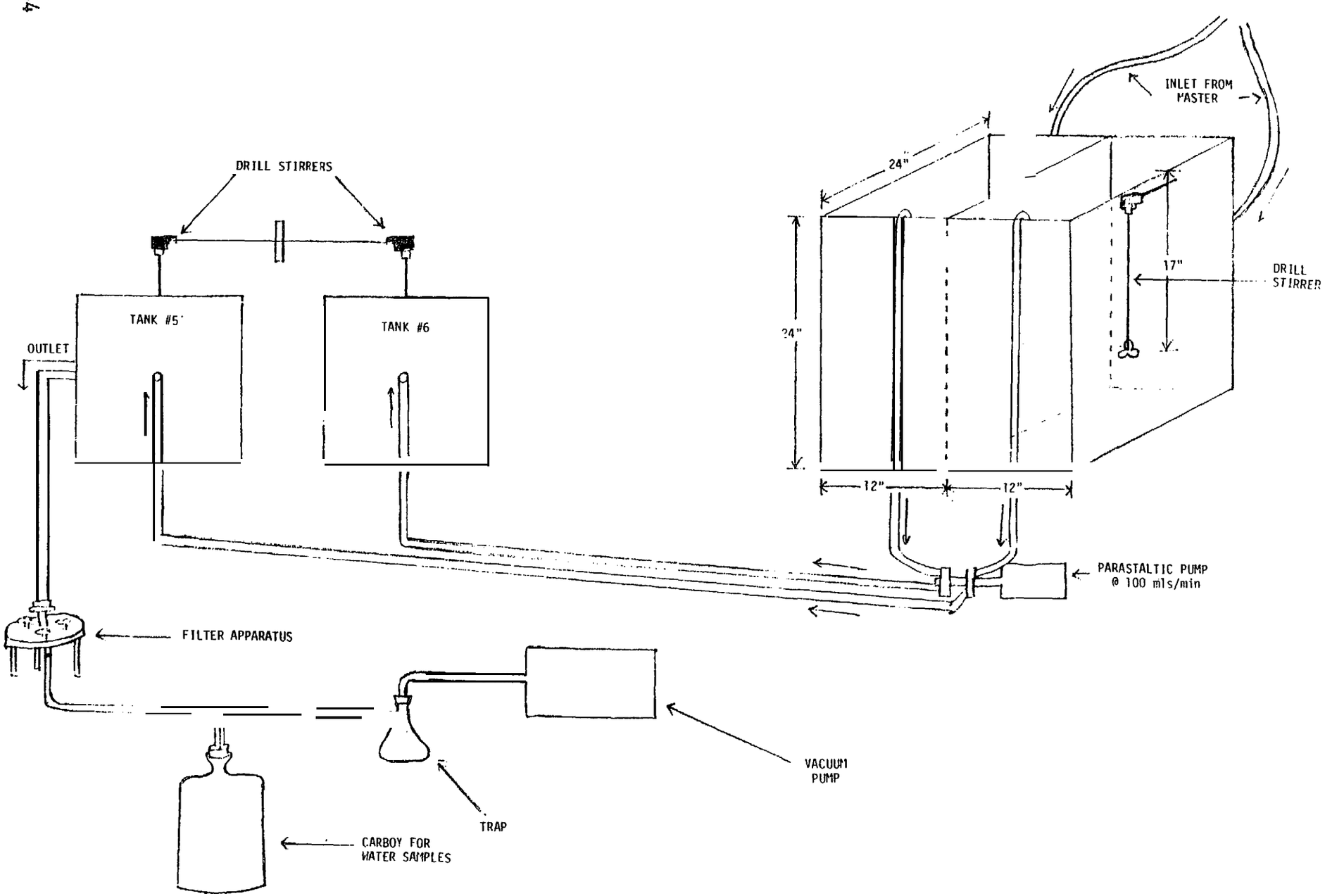



FIGURE 5-95. FLOW DIAGRAM FOR SPM STUDIES N ALASKA.

flow rate of 100 ml/min, ultimate SPM loads of 40 mg/L for Kasitsna Bay and 20 mg/L for the Seldovia sediments were maintained in the experimental chambers. Tank 6 received sediments from Kasitsna Bay, and tank 5 received sediments from the Seldovia River salt marsh. Oil was then spilled as before onto the experimental tanks, and agitation was maintained within the experimental tanks with two additional stirring motors.

During the experiment, water samples from the exhaust ports of the respective tanks were filtered through a 293-mm diameter, 0.45-micron kiln-fired glass fiber filter to remove the suspended particulate material, and the filtered water column samples were contained in a glass carboy for methylene chloride extraction and analysis of the dissolved phase (Figure 5-96).

Prior to each large volume (20 L) sample for chemical analysis, a smaller 50-ml aliquot was filtered through tared 2.5 cm, 0.45 micron millipore filter for determinations of SPM loading. After each chemistry sample was obtained, the 293 mm diameter glass fiber filter was removed and folded into kiln-fired aluminum foil (Figure 5-97) and frozen awaiting shipment to La Jolla for later extraction and analyses. Water column samples, were extracted with methylene chloride (3 x 250 ml) at the Kasitsna Bay facility (PAYNE et al., 1980) and the methylene chloride extracts were then reduced in volume using Kurderna-Danish concentrators and dried (water removal) by passage through $Na_2SO_4$ columns. The concentrates were then sealed in scintillation vials with foil-lined caps and shipped to La Jolla for analysis.

Tables 5-35 and 5-36 present the time series sampling points, sample matrix and sediment loading as measured gravimetrically from tanks 5 and 6 during the running of the oil/SPM interaction studies. The methylene chloride extracts from each of the time-series steps shown in the table and the frozen filters are Currently in storage at 3°C and -20°C, respectively, awaiting further extraction and analyses.

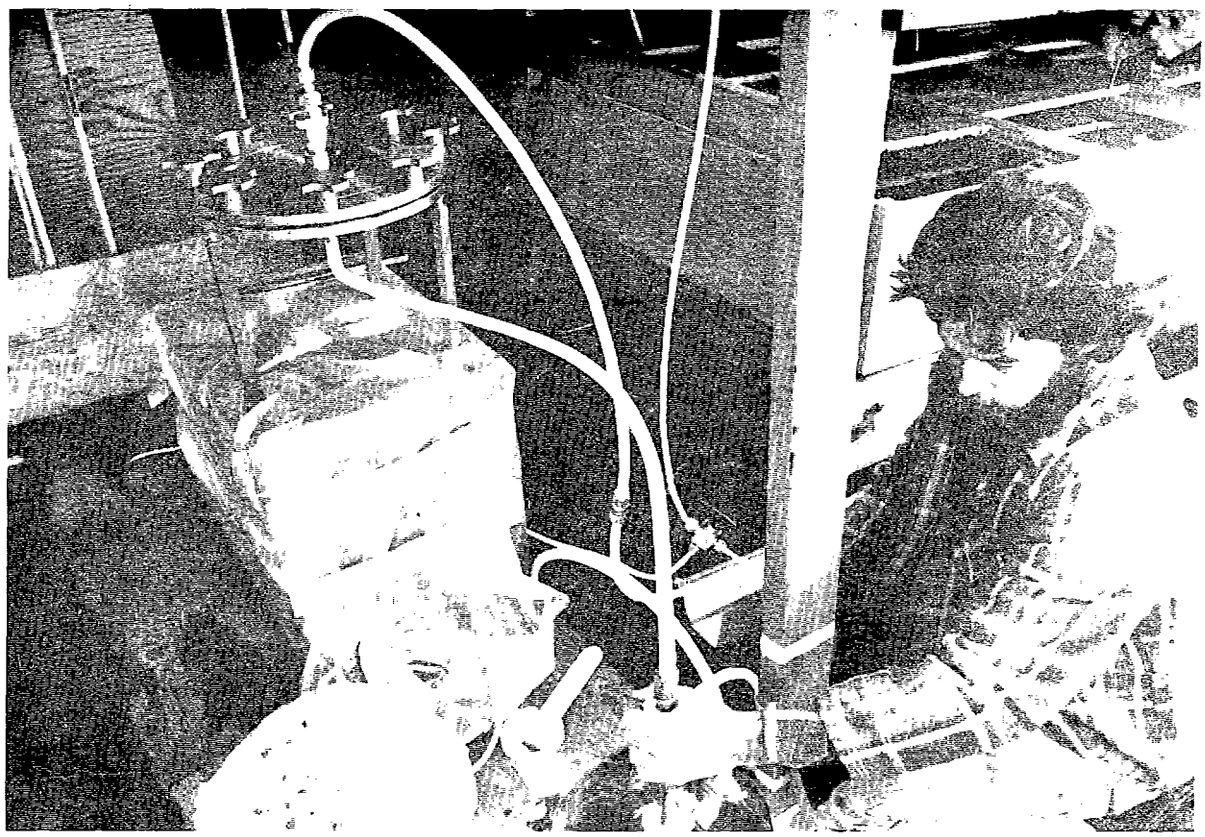


FIGURE 5-96. OUTDOOR TANKS AND FILTRATION SYSTEM USED FOR CONTINUOUS FLOW OIL/SPM INTERACTION STUDIES AT KASITSNA BAY, ALASKA. SUSPENDED PARTICULATE MATERIAL IS TRAPPED ON 293 mm DIAMETER KILN FIRED GLASS FIBER FILTERS MAINTAINED IN THE STAINLESS STEEL FILTER ASSEMBLY AND DISSOLVED HYDROCARBON COMPONENTS ARE EXTRACTED FROM THE WATER SAMPLES TRAPPED IN THE GLASS CARBOYS.

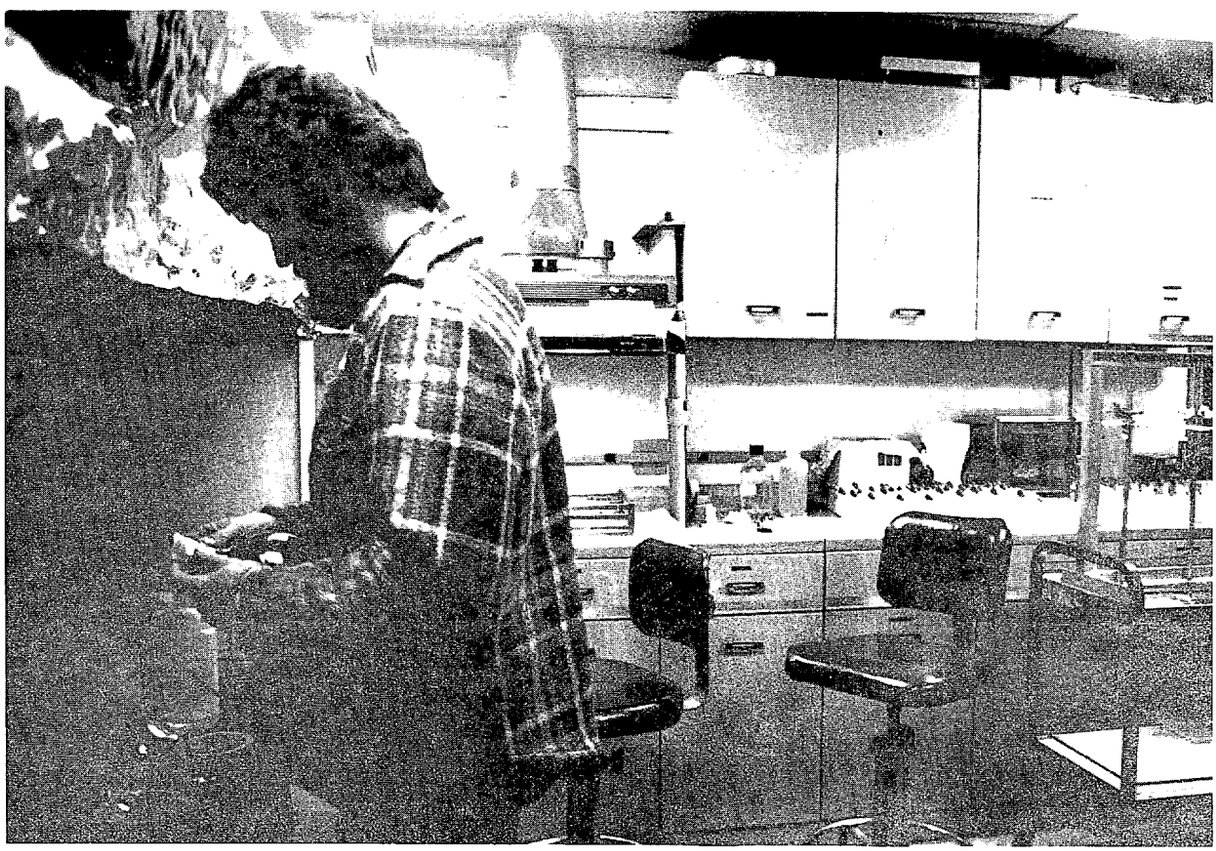


FIGURE 5-97. AFTER FILTRATION, FILTER SAMPLES WERE FOLDED INTO KILN-FIRED ALUMINUM FOIL AND FROZEN. WATER COLUMN SAMPLES WERE EXTRACTED WITH METHYLENECHLORIDE, DRIED OVER $Na_2SO_4$ CONCENTRATED (KD APPARATUS) AND SEALED IN FOIL CAPPED SCINTILLATION VIALS AND STORED AT 3°C. AT THE CONCLUSION OF THE SUMMER/FALL 1981 PROGRAM ALL SAMPLES WERE SHIPPED TO LA JOLLA FOR ADDITIONAL FRACTIONATION AND ANALYSES.

TABLE 5-35. SAMPLING TIMES AND SEDIMENT LOAD FOR FLOW-THROUGH OUTDOOR TANK SPM STUDIES USING SELDOVIA SALT MARSH SEDIMENT -- TANK 5 PARTICULATE MATERIAL, FILTERED SEAWATER AND OIL SAMPLES COLLECTED AT EACH TIME INDICATED.

| Date | Time | Cumulative Time | Sediment Load (mg/ℓ) |
|---|---|---|---|
| 9/20 | 1230 | 0 hrs | 19 |
| 9/20 | 1530 | 3 hrs | -- |
| 9/20 | 1830 | 6 hrs | 15 |
| 9/21 | 0030 | 12 hrs | 18 |
| 9/21 | 1230 | 24 hrs | 20 |
| 9/22 | 1230 | 2 days | 23 |
| 9/24 | 1230 | 4 days | 19 |
| 9/28 | 1230 | 8 days | 36 |

TABLE 5-36. SAMPLING TIMES AND SEDIMENT LOAD FOR FLOW-THROUGH OUTDOOR TANK SPM STUDIES USING KASITSNA BAY SEDIMENT -- TANK 6 PARTICULATE MATERIAL, FILTERED SEAWATER AND OIL SAMPLES COLLECED AT EACH TIME INDICATED.

| Date | Time | Cumulative Time | Sediment Load (mg/ℓ) |
|---|---|---|---|
| 9/20 | 1200 | 0 hrs | 36 |
| 9/20 | 1500 | 3 hrs | 40 |
| 9/20 | 1800 | 6 hrs | 39 |
| 9/21 | 0000 | 12 hrs | 37 |
| 9/21 | 1200 | 24 hrs | 39 |
| 9/22 | 1200 | 2 days | 39 |
| 9/24 | 1200 | 4 days | 32 |
| 9/28 | 1200 | 8 days | 30 |

From these experiments we hope to derive time-series oil/SPM partition coefficients for specific compounds as a function of the overall degree of oil weathering. While the results of the initial oil/SPM interaction studies may appear to duplicate some aspects of previously published work, it should be pointed out that the purpose of completing the static experiments in La Jolla was not to repeat the earlier studies, but to determine which two of the five representative Lower Cook Inlet sediment types should be utilized for the extended oil/particulate material interaction studies where evaporation and dissolution weathering perturbations to the process were included as part of the experimental design. Furthermore, several features of our approach are unique, and these factors are important to our understanding of longer term sub-arctic oil/SPM interactions. First, no other study has examined a cross section of suspended particulate material types from the Lower Cook Inlet area and looked at the compound specific partitioning to the material as a function of its source. Secondly, the time series oil weathering experiments conducted during the Summer 1981 program were designed to evaluate the affects of changes in oil viscosity on oil/particulate material interactions. Specifically, oils which have undergone evaporation and dissolution weathering do not tend to form micells and dispersions of oil-in-water to the same degree that fresh oils do. This was observed in our wave tank experiment where 1 to 10 mm diameter droplets were clearly present for the first 12 hours of weathering but not thereafter and in the flow-through outdoor tanks where turbulence was introduced by propeller mixing. In both cases, oil/micell formation and dispersions were shown to fall off rapidly after the first 12 to 24 hours. As a result of this behavior, availability of oil micells in the water column will change with time, and this will significantly affect the degree to which oil is available for particulate interactions and the rates of these processes.

Our experiments were designed to evaluate these factors such that a better understanding of their influence on oil-SPM interactions could be focused toward developing more accurate predictive capabilities on the effects of suspended particulate material on actively weathering oil.

### 5.3.6 Long Term Fate of Stranded Oil in Selected Intertidal Regimes in the Lower Cook Inlet Kachemak Bay/Shelikof Strait Area

As another but related aspect of the oil weathering program, SAI scientists participated in a collaborative effort with Drs. Griffiths and Morita (RU 190) to evaluate long-term weathering trends in sub-tidal sediments which had been contaminated with fresh and artificially weathered Cook Inlet crude oil. In that the results of those analyses detailed the long-term (up to 1 year) chemical weathering of sedimented oil, and are therefore relevant to the overall goals of this program, a copy of our report on the chemical analyses of the subtidal sediments has been included as Appendix C of this report.

In the Griffiths and Morita program, fresh and artificial y weathered* Cook Inlet crude oil samples were spiked into subtidal sediment quadrants, and these quadrants were then placed back into the subtidal regime in Kasitsna Bay and Sadie Cove. Three levels of spiking were utilized: 50 Parts per thousand (ppt), 1 ppt and 0.1 ppt (using both fresh and artificially weathered crude), and samples from these experiments were chemically analyzed at time 0 and after 1 year of natural weathering in the subtidal regime.

After one year, essentially no measurable hydrocarbon biodegradation took place in the sediments which had been spiked at the 50 ppt level with either fresh or previously weathered Cook Inlet crude oil. Additionally, GRIFFITHS and MORITA (1980) reported that from time-coarse experiments using sediments treated at the 50 part per thousand level with fresh crude oil, that affects of the crude oil on glucose uptake would continue for 3 to 5 years and the effects on nitrogen fixation would continue for an estimated 2 to 8 years.

At 1 ppt extensive degradation of the lower molecular weight aliphatic fraction was noted, but many of the aromatic components were not degraded.

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*Oil allowed to stand on seawater in static tanks for one week.

Statistically significant reductions in glucose uptake rates, nitrogen fixation rates, and redox potentials and a significant increase in respiration percentages were also noted. Interestingly, the effects on nitrogen fixation in the 1 to 50 ppt oil range were limited to fresh Cook Inlet crude. The weathered crude oil did not produce the same effects at these concentrations.

In the sediments treated with 0.1 ppt crude oil there was essentially 100% degradation of both the aliphatic and aromatic components after one year. No significant changes in glucose uptake or respiration rates were noted, and methane concentrations, $CO_2$ production rates, nitrogen fixation and denitrification rates were not significantly affected. There was, however, an 89% reduction in redox potential in the quadrants at this level and this finding was deemed to be important since redox potential is depressed after the crude oil has been degraded. It was suggested that the added carbon source plus the toxic effects of the oil itself caused in increased BOD in the system, and that this then further altered the sediment chemistry after the crude oil degraded.

Thus, while considerable data have been generated on the long-term fate and chemical weathering of oil in subtidal regimes in the Alaskan sub-arctic, no parallel set of data as yet exist on the rates and extents of the chemical weathering processes on stranded oil in sub-arctic intertidal zones. As part of this program then, a series of controlled intertidal oil-degradation experiments were initiated during the summer 1981 field study. The previously characterized sites, KB-1 through KB-4, plus an additional site (KB-5) at the head of Jakolof Bay (Figure 5-81), were thus revisited and a series of "controlled" intertidal sediment "oilings" were initiated.

At each of the sites a series of three 1 $m^2$ vented corrals were buried (Figure 5-98) in the intertidal sediments as the tide receded, and then each corral was "oiled" with 1.5 liters of fresh Prudhoe Bay crude oil (Figure 5-99). At each site a corral was placed in the upper intertidal zone at an elevation such that tidal flooding would occur only every 10 to 16 days during

FIGURE 5-98. INSTALLATION OF LOWER INTERTIDAL CORRAL FOR LONG-TERM STRANDED OIL STUDIES AT GREWINGK GLACIER (KB-1). DURING ALL CORRAL INSTALLATIONS, CARE WAS TAKEN TO ENSURE THAT THE SURFACE OF THE INTERIOR 1 $m^2$ PORTION OF THE TEST SITE WAS NOT DISTURBED.

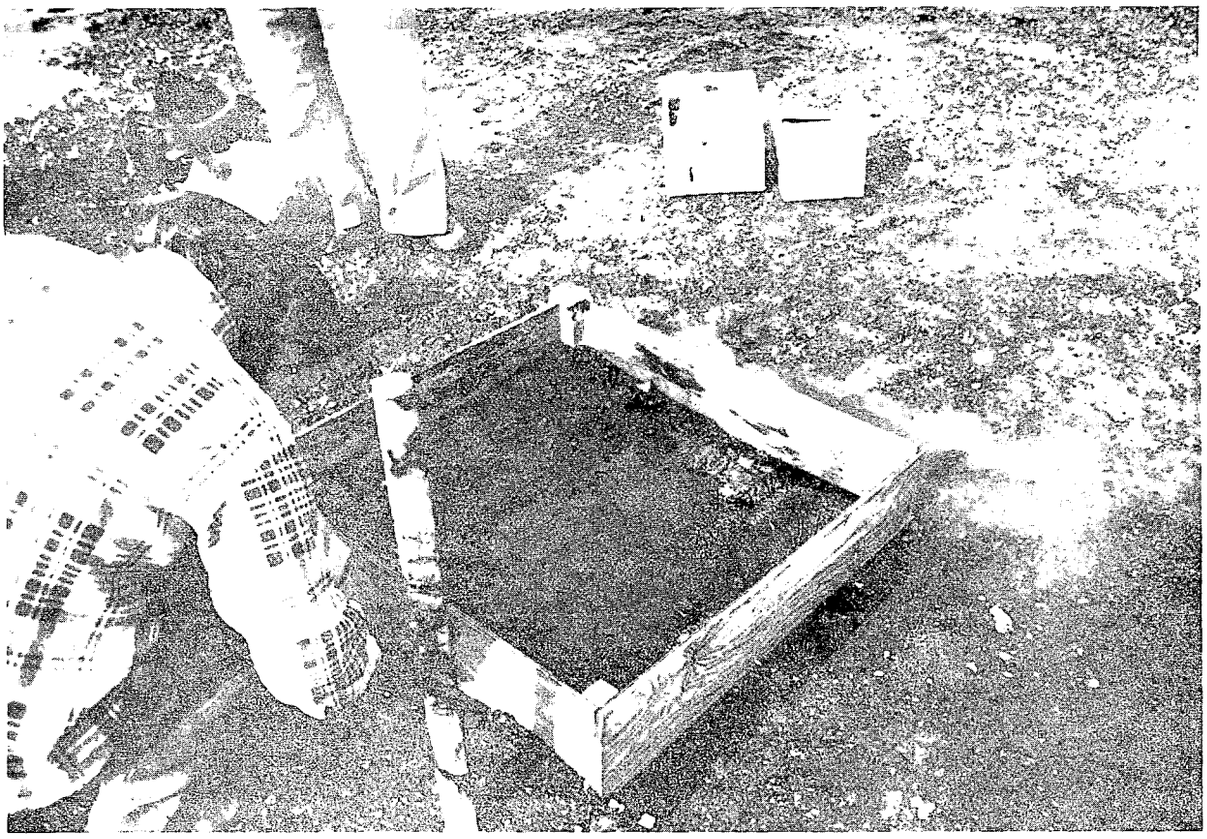

FIGURE 5-99. INTERTIDAL CORRAL AT CHINA POOT BAY (KB-2) 2 MINUTES AFTER 1.5 L ADDITION OF FRESH PRUDHOE BAY CRUDE OIL.

maximum tidal excursions (Figure 5-100). A second corral was then placed in the middle intertidal zone such that tidal action would be encountered daily, and finally, a third corral was buried in the lower intertidal zone such that during neep tides, the sediments would be continuously covered by seawater for several days. At three of the intertidal sites (specifically, KB-3, Kasitsna Bay; KB-4, Seldovia salt marsh; and KB-5, Jakolof Bay) additional quadrants were staked out adjacent to the intertidal corrals, and these sediments were "oiled" with 1.5 l of 10 day old weathered mousse from the wave tank experiments being run concurrently at the Kasitsna Bay facility.

By including naturally weathered mousse along with the fresh oil utilized in the experiments, the importance of open ocean weathering (specifitally removal of lower molecular weight aromatic components due to evaporation and dissolution processes) on intertidal sediment impact and recovery could also be evaluated. Further, in that mousse and weathered crude oils have higher viscosities and pour points than fresh crudes, the studies were intended to provide data on the difference in oil weathering as a function of the degree of penetration into the intertidal sediments.

No attempt was made to artificially mix the oil into the intertidal sediment, as the experiments were intended to simulate, as closely as possible, the effects of oil stranding after contamination during maximum tidal periods. Jakolof Bay was added to the other previously characterized sites, in that it is a location which experiences permanent shore-fast ice during several of the winter months. In this manner, it was hoped that the effects of this ice cover on intertidal oil weathering behavior could be examined. As shown by the scanninq electron microscope data and oil adsorption potential results from these sites, significantly different intertidal substrates representative several low energy intertidal regimes are encompassed in this study.

Table 5-36 presents the time series sediment samples which were obtained following the oiling at each site. Additional samplings are planned

FIGURE 5-110. INSTALLATION OF UPPER INTERTIDAL CORRAL AT JACKOLOF BAY (KB-5). THIS SITE IS TYPICAL OF ONE WHICH WOULD BE EXPOSED ONLY DURING SPRING TIDES, APPROXIMATELY EVERY 2 WEEKS.

during our upcoming winter 1981/1982 field efforts. Immediately after sampling, the sediment samples from each site were frozen, and they are currently awaiting extraction and analyses which will be undertaken during the next several months. During the installation of the quadrants extreme care was taken to avoid disturbing the center of the quadrant such that oil penetration would not be artificially enhanced. Also, at each site, vertical transect and detailed photographic data were obtained such that the degree of tidal exposure can be quantitated over the anticipated 6-12 month duration of these experiments.

Initially we had intended to select three intertidal areas which would be representative of three environments of significantly different long-range oil vulnerability as indicated by the associated Hayes/Gundlach Environmental Susceptibility Index (ESI) (GUNDLACH and HAYES, 1978; HAYES et al., 1976). This approach was modified, however, to examine the long-term weathering rates of oil in selectively different low-energy intertidal regimes as a function of sediment type, detrital input, fresh water availability and tidal exposure. Thus, while each of the intertidal sites selected could be classified with ESI indices values of 9 and 10 (sheltered tidal flats and/or marshes) subtle differences due to the topography at the selected sites (including fresh water input, extensive Spartina covering, possibility of wave scour, etc.) were included in the experimental design.

The purpose behind evaluation of differential hydrocarbon removal and oxygenated product formation is to determine if impact profiles can be generated as a function of the sub-arctic intertidal environment. These data will be useful to managers in oil spill predictions to assess long-term affects on different sub-arctic intertidal zones as a function of the energy regime and the sediment matrix. Correlation of these degradation rates with further refinement of numerical values (such as the Hayes/Gundlach index) will then be helpful in prediction and mapping ultimate long-term impacts for different intertidal zones. If oiled sediments from a particulate intertidal regime

were removed by storm activities and then redeposited in the nearshore subtidal region, potential rerelease of lower molecular weight aromatic compounds to the water column and/or inhibition of biotic activity as demonstrated by GRIFFITHS and MORITA (1980) in many of these sediments can take place. Knowledge of this potential behavior is felt to be important for long-term environmental impact assessment.

As noted above, data on 1 onger term intertidal weathering of stranded oil can be obtained by reoccupying the field sites during the winter programs. In this regard, the corrals and marker stakes (assuming that they have not been removed or damaged by prior storm activities) will be critical *in* relocating the specific oiled sites. Logistics for the winter and spring field sampling efforts are being coordinated with NOAA's Kasitsna Bay resident manager to ensure that our actual arrival dates most closely coincide with the appropriate winter weather and ice conditions.

## 5.4 Recent Inter-Laboratory Inter-Calibration Programs

SAI's laboratory has routinely participated in inter-calibration programs: (1) an inter-calibration program among the participating hydrocarbon laboratories in the Southern California OCS BLM program (PAYNE et al., 1979a); (2) the first NOAA/OCSEAP sediment inter-calibration program using Duwamish River samples (PAYNE et al., 1979b); and (3) a water column extract and mousse inter-calibration among the major laboratories involved in the NOAA RESEARCHER cruise to study the IXTOC-I blowout (PAYNE et al., 1980a). As part of the Multivariant Analysis of Petroleum Weathering Program, a more recent Duwamish II sediment inter-calibration program was completed in January 1981. In the BLM inter-calibration program, several different methods were utilized by the participating laboratories, but excellent inter-laboratory accuracy and precision were obtained. In the first OCSEAP inter-calibration program, our own laboratory evaluated three separate methods: Soxhlet extraction; shaker table extraction; and Soxhlet extraction using solvents recommended by Or. William MacLeod of NOAA/NMFS-Seattle. As in the previous inter-calibration

exercises, very good inter-method precision was obtained, and examination of our data and MacLeod's showed that essentially identical results were obtained in both laboratories.

In the most recent inter-calibration program, Duwamish II, a shaker table procedure for sediment extraction was used; however, the solvent systems were those which are typically utilized in our laboratory for hydrocarbon analyses. The results of our Duwamish II inter-calibration analysis are presented in Table 5-37. As the data indicate, fairly good precision was obtained, with coefficients of variations generally less than 20 percent for both the aliphatic and aromatic fractions. Figure 5-101 presents the relative concentrations of the polynuclear hydrocarbons obtained by our laboratory and by the NOAA/NMFS-Seattle laboratory. The profiles are nearly identical over a wide dynamic range, and the overall concentrations of amterials are well within one standard deviation. As the data suggest, very good agreement between our laboratory and the National Marine Fisheries Quality Control Laboratory is obtained. In general, when we conduct replicate analyses to evaluate laboratory precision, our results show that coefficients of variations for specific compounds at nanogram levels are near 20 percent or better.

TABLE 5-37. NOAA/NMFS INTERCAL BRAT ON RESULTS - DUWAMISH II, SC NCE APPLICATIONS, INC.

Concentration of areas (μg/g dry wt
Replicate No.

| Sample #: | 1 | 2 | 3 | $\bar{X}$ | CV* |
|---|---|---|---|---|---|
| Naphthalene | 57.5 | 37.4 | 49.8 | 48.2 | 21 |
| Benzothiophene | 0 | 0 | 0 | 0 | -- |
| 2-Methylnapthalene | 41.2 | 45.2 | 60.9 | 49.1 | 21 |
| -Methylnaphthalene | 16.6 | 15.8 | 19.5 | 17.3 | 11 |
| Biphenyl | 7.14 | 4.3 | 6.7 | 6.0 | 25 |
| 2,6-Dimethylnaphthalene | 46.0 | 59.2 | 76.7 | 60.6 | 25 |
| 2,3,5-Trimethylnaphthalene | 10.2 | 8.0 | 16.6 | 11.6 | 39 |
| Fluorene | 93.2 | 105. | 115. | 104. | 10 |
| Dibenzothiophene | 93.0 | 85.6 | 91.2 | 89.9 | 4 |
| Phenanthrene | 536. | 572. | 471. | 526. | 10 |
| Anthracene | 168. | 251. | 310. | 243. | 29 |
| 1-Methylphenanthr | 29.8 | 29.9 | 29.1 | 29.6 | 1 |
| | 1159. | 1127. | 1255. | 1180. | 6 |
| Pyrene | 731. | 771. | 941. | 814. | 14 |
| Benz (a) anthracene | 395. | 467. | 648 | 503. | 26 |
| Chrysene | 722. | 791. | 1076. | 863. | 22 |
| Benz (e) pyrene | 328. | 349. | 574. | 417. | 33 |
| (a) pyrene | 311. | 412. | 566. | 430. | 30 |
| Perylene | 263. | 284. | 355. | 300. | 16 |
| Aliquot Weight | 119.7 | 122.8 | 113.9 | 118.8 | 3.8 |
| Percent Dry Weight | 48.0 | 47.7 | 48.4 | 48.0 | .73 |

Concentrat on of n-alkanes (μg/g dry wt)
Replicate No.

| | 1 | 2 | 3 | $\bar{X}$ | CV* |
|---|---|---|---|---|---|
| $C_{14}$ | 152 | 138 | 242 | 177 | 32 |
| $C_{15}$ | 143 | 157 | 221 | 174 | 24 |
| $C_{16}$ | 146 | 147 | 213 | 167 | 23 |
| $C_{17}$ | 465 | 439 | 476 | 460 | 4 |
| Pristane | 433 | 438 | 466 | 446 | 4 |
| $C_{18}$ | 141 | 149 | 214 | 168 | 24 |
| Phytane | 191 | 189 | 264 | 215 | 20 |
| $C_{19}$ | 142 | 193 | 213 | 183 | 20 |
| $C_{20}$ | 131 | 133 | 200 | 155 | 25 |
| $C_{21}$ | 289 | 318 | 335 | 314 | 7 |
| $C_{22}$ | 183 | 161 | 189 | 178 | 8 |
| $C_{23}$ | 234 | 178 | 257 | 223 | 18 |
| $C_{24}$ | 242 | 302 | 297 | 280 | 12 |
| $C_{25}$ | 440 | 513 | 472 | 475 | 8 |
| $C_{26}$ | 340 | 371 | 393 | 368 | 7 |
| $C_{27}$ | 1159 | 1140 | 840 | 1046 | 17 |
| $C_{28}$ | 345 | 366 | 421 | 377 | 10 |
| $C_{29}$ | 857 | 834 | 768 | 820 | 6 |
| $C_{30}$ | 827 | 736 | 815 | 793 | 6 |
| $C_{31}$ | 1159 | 1349 | 1017 | 1175 | 14 |
| $C_{32}$ | 310 | 309 | 265 | 295 | 9 |

*Coefficient of variation - Standard Deviation/Mean

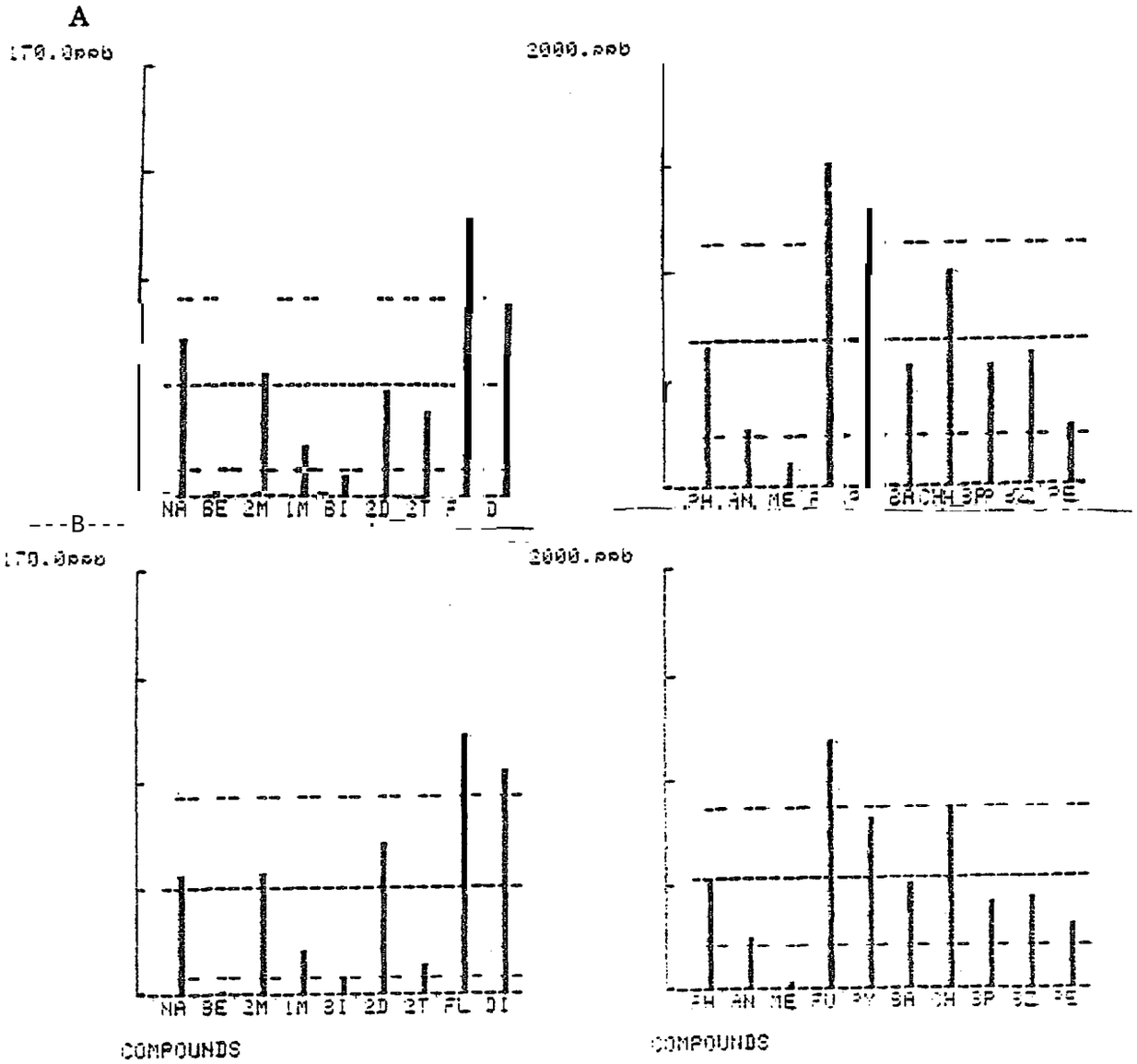


FIGURE 5-111. RELATIVE ABUNDANCE PLOTS FOR POLYNUCLEAR AROMATIC HYDROCARBONS DETECTED IN THE DUWAMISH 11 INTERCALIBRATION SAMPLES. (A) NOAA NATIONAL MARINE FISHERIES RESULTS AND (B) SCIENCE APPLICATIONS, INC. RESULTS. NOTE CHANGE IN CONCENTRATION SCALES BETWEEN DIBENZOTHIOPHENE (DI) AND PHENANTHRENE (PH); COMPOUND IDENTIFICATIONS FOR OTHER COMPONENTS ARE GIVEN IN TABLE 5-37.

## 6.0 CONCLUDING REMARKS AND RECOMMENDATIONS FOR UTILIZATION OF EXISTING AND FUTURE EXPERIMENTAL RESULTS FOR OIL WEATHERING MODEL DEVELOPMENT

Significant progress has been made in developing algorithms for evaporation and dissolution phenomena for both stirred tank and open ocean spill situations. With regard to the latter, both point source oil spills such as those resulting from tanker incidents and continuous source spill situations resulting from open ocean blowouts have been considered.

Our mathematical description of oil weathering in its present state considers evaporation using a pseudocomponent oil characterization, and evaporation and dissolution using a component-specific approach. This description will predict the mass of oil remaining in the slick as well as specific component concentrations in the oil and air and water columns. The major portion of these mathematical descriptions have been computerized, and the remainder are in the process of being coded and tested.

At this time, simulated oil spill mass balance and compound specific programs can be run for a variety of environmental situations. Further, the numerous experimental studies which have been completed provide a basis for comparing predicted and observed evaporation/dissolution behavior. In this regard the development of the GC data base system was critical in allowing compound-specific predicted vs observed concentrations. Predicted and observed results have been generated: (1) for stirred tank studies where water column and oil phase compound-specific data could be compared with computer predicted results, and (2) for oil distillation curves in order to compare predicted and observed mass balance for oil after varying stages of weathering. Specifically, predicted and observed mass balance distillation curves from the Kasitsna Bay wave tank experiments have beeri presented to illustrate the strength and application of the model and approach. Since a tremendous amount of information has been obtained from Kasitsna Bay field observations and measurements, it has been vital to properly design and implement the computer data base system for gas chromatographic data. Only by having this system developed and available could such field data be used directly for

verification and modification of the oil weathering model predictions. Specifically, from the combined results of La Jolla and Kasitsna Bay experiments, compound-specific data are now accessible (organized by Kovat retention indices) for generation of time-series observed concentration profiles for both the oil phase and water and air columns under a variety of environmental conditions.

Expansion and coupling of the existing dissolution algorithms to transport and dispersion models remains to be done; however, this is one of the topics which will be addressed in detail in upcoming NOAA-sponsored workshops on Oil Weathering Modeling and Transport which are scheduled to take Place in Seattle in January 1982. Coupling of the dissolution algorithms with dispersion process algorithms will then allow time-dependent hydrocarbon concentration predications in the water column for simulated spill situations. This information will be important to environmental managers in making more accurate biological impact assessments. Additional algorithm development is clearly needed to incorporate dispersion processes, particularly when dealing with fresh oils. As noted in the discussions of the wave tank experiments from Kasitsna Bay, information on the percent oil dispersed by wave action is being derived from whole-water sample extracts which were obtained during the first 12 to 24 hours of those experimental studies.

With regard to the status of the oil weathering model development, the following activities are scheduled for completion by January 1982:

1) Incorporation of modifications such that evaporation/dissolution behavior can be predicted for any of 800 crude oils on which composition data are currently available through the Bartlesville Energy Technology Center (BETC).

2) Additional model testing will be carried out after all pertinent mathematics have been programmed. The pseudo-component oil-weathering model will be applicable to any crude or oil cut, such as heavy naphtha or a gas oil, for which data are available. Component-specific predictions for any given oil or distillation product require only that the sample be fractionated into aliphatic, aromatic and polar constituents and analyzed by

capillary gas chromatography. With this analysis the initial oil-component concentrations can be entered into the GC database of the model and thereby used for time-series component concentration calculations.

3) Other pertinent testing of the model includes the prediction of concentrations of specific compounds in the water column. The toxicity of these compounds to marine life is directly related to exposure time and to concentration. Thus, the model will be tested to predict water and air column concentrations for which appropriate component specific data are available. Coupling of this predicted dissolution behavior with transport and dispersion models will then be undertaken.

4) Two other observable features of weathered oil - viscosity and mousse formation - are considered to be important because of the effects they have on mass transport from the slick. Therefore, existing information on these topics along with the results of experiments reported here will be used to develop viscosity and mousse formation predictions.

Dispersion, microbial degradation, suspended particulate material/oil interactions, photo-oxidation and auto-oxidation are other oil weathering processes known to occur. However, these are only now beginning to be understood in a mechanistic sense and their mathematical descriptions are still relatively primitive. Each of these processes is somewhat more complicated than bulk transport processes, since often complex chemical reactions affecting many compounds are involved, and there are very few accurate descriptions of chemical reactions to be used for pseudo-component models in the manner of the evaporation process model developed to date. The resulting mathematical models involve many variables and will require thorough experimentation, derivation, programming and testing.

As a result of our initial experimental activities and algorithm development, it has become clear that additional physical properties data are required, and compound-specific Henry's law constant and diffusivity determinations are being completed in our laboratories at this time. As noted above, additional modeling program needs include development of algorithms for modeling dispersion phenomena and expansion of viscosity correlations on water-in-oil emulsions beyond the current Mackay formulations, which predict water-in-oil emulsion viscosity as a function of water content (MACKAY, 1980).

While compound-specific oil characterizations have been completed on the four crude oils examined in this program, it is now believed that additional work on the asphalts and residual (non-distillable) fractions is required. This is particularly important with regard to mousse formation where the presence of asphalts, higher molecular weight waxes, and metal lo-porphyrin compounds have been implicated in the stabilization and formation of water-in-oil emulsions (PAYNE, 1981).

The microbial degradation experiments which have been conducted to date have produced data which allow calculation of total carbon flux into the water column as a result of bacterial processes; however, several additional experimental requirements have been defined as outlined below. Experiments conducted to evaluate the effects of nutrient supplementation on bacterial degradation rates have shown that only minimal effects are observed as a result of inorganic nutrient concentrations. An understanding of such information is necessary for development of algorithms for modeling microbial degradation behavior. Specifically, progress has been made in delineating which variables are important for development of algorithms for these processes and subsequent investigations are outlined at the end of this section.

The results of our oil/suspended particulate material interaction studies, which are being analyzed at this time, will better define the differences in adsorption and sedimentation of oil as a function of the degree of evaporation/dissoluti on weathering. With such information, it should be possible to develop algorithms for more accurate predictions of weathered oil/sedimentation behavior. In this regard, longer-term (two month and six month) data obtained from the flow-through wave tank experiments at Kasitsna Bay will be used to determine the density increases in open ocean mousse as a result of time dependent accommodation of suspended particulate material.

While initial photo-oxidation experiments were undertaken during the early phases of this program, detailed examinations of this complex phenomena have by design been postponed. Additional experiments need to be undertaken

to examine the increased flux of oil components to the water column as a result of photochemical oxidation processes.

The following synopses detail additional specific program areas and experimental requirements which need to be expanded upon in subsequent stages of this program.

Oil/Suspended Particulate Material Interactions

Experiments currently in progress are addressing the effects of time-dependent evaporation and dissolution "weathering" (viscosity change) on oil/SPM interactions. Additional collection and analyses of mousse and filtered water samples from the wave tank experiments currently in progress at Kasitsna Bay will yield data on the following:

ambient SPM loads from Kasitsna Bay,

density increases in 4 and 6 month old mousse due to accommodation and adsorption of SPM.

Parameters being considered for algorithm development for oil/SPM interactions include particulate load, particulate type, turbulence (as it affects dispersion of oil micelles), oil composition and viscosity (degree of weathering as it affects dispersion of micelles), and water temperature.

Water-in-Oil Emulsification (mousse formation)

Considerable progress has been made in developing correlations of percent water uptake and mousse viscosity (MACKAY, 1980). Wave tank experiments are underway to evaluate mousse formation from Prudhoe Bay crude oil as a function of chemical weathering (evaporation/dissolution, photo-oxidation, particulate adsorption and microbial degradation) and additional analyses are planned to further characterize the nondistillable residuum for percent asphalts, waxes and metal lo-porphyrins. Using this experimental approach as a

starting point, other parameters for modeling mousse formation include: oil composition (asphalt, wax and metallo-porphyrin content in addition to standard compositional data), turbulence regeim, water temperature, oil viscosity, presence of microbial and photo-oxidation products, SPM accretion and density variations.

## Microbial Degradation Studies

The utility of the $^{14}C$-labelled hydrocarbon substrate data for estimations of overall parent petroleum hydrocarbon removal from an oil slick due to microbial degradation is based upon two assumptions: (1) the degradation potential assay, which relies upon detection of $^{14}CO_2$, serves as an accurate indicator of total degradation (defined as loss of parent compound molecular structure); and (2) the hydrocarbon substrates utilized are "typical" in terms of the biodegradability of other compounds in their class (e.g., hexadecane is a typical aliphatic, naphthalene is a typical aromatic). To further assess the soundness of this approach, the following activities are being pursued:

determination of a mass balance for the $^{14}C$-labeled substrates (i.e. , how the parent compound and associated metabolites partition into the bacterial cell material and surrounding water column). This should provide an estimation of how accurate the detection of $^{14}CO_2$ is for defining total degradation.

incorporation of additional $^{14}C$-labeled hydrocarbon substrates into the degradation potential assay. Emphasis will be made on aromatics, potentially including such compounds as the PNAs benz(a)anthracene, benzo(a)pyrene, dibenz(a,h)anthracene, and dimethyl benz(a)anthracene.

parameters which are currently being evaluated for final development of algorithms for modeling microbial processes include microbial biomass, oil slick surface area, inorganic and organic nutrient concentrations, dissolved oxygen concentrations, water temperature, and inhibition of bacterial activity as a result of the toxicity of dissolved lower molecular weight aromatics.

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# APPENDIX A

## COMPUTER PREDICTED WEATHERING RESULTS, COMPUTER CODE LISTINGS AND COMPUTER CODE FLOW CHART

The results presented in this appendix are examples of calculated results (pages A-2 through A-30), the current code listing (pages A-31 through A-43), and code flow chart (pages A-44 through A-74). The code presented here is still in a state of development with work remaining to be completed on the mass-transfer coefficient section.

The example calculation is for Prudhoe Bay crude oil, item 9, sample 71011 (COLEMAN, 1978) with temperatures of 32 and 42°F at wind speeds of 10 and 40 knots. The mass-transfer coefficient used is that due to Mackay (MACKAY, 1973). The output from the calculation is self explanatory and details the weathering of 15 cuts of this particular crude through 500 hours. These results are summarized in Table A-1 and show the effects of wind and temperatures over 500 hours.

Table A-1

SUMMARY OF OIL-WEATHERING CALCULATIONS FOR PRUDHOE BAY CRUDE OIL AFTER 5(IO HOURS

| | | | | |
|---|---|---|---|---|
| Temperature, “F | 32 | 42 | 32 | 42 |
| Wind, Knots | 10 | 10 | 40 | 40 |
| Mass Fraction Remaining for cut # | | | | |
| 1 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 |
| 3 | 0 | 0 | 0 | 0 |
| 4 | 0 | 0 | 0 | 0 |
| 5 | 0 | 0 | 0 | 0 |
| 6 | 0.14 | 0.03 | 0 | 0 |
| 7 | 0.73 | 0.55 | 0.36 | 0.16 |
| 8 | 0.95 | 0.91 | 0.86 | 0.75 |
| 9 | 0.99 | 0.98 | 0.98 | 0.95 |
| 10 | 1 | 1 | 1 | 0.99 |
| 12 | 1 | 1 | 1 | 1 |
| 13 | 1 | 1 | 1 | 1 |
| 14 | 1 | 1 | 1 | 1 |

SUMMARY OF TDP CUTS CHARACTERIZATION FOR: PRUDHOE BAY, ITEM 9, SAMPLE 71011

| | TB | API | VOL | MW | TC | PC | VC | A | B | T10 | VIS | NC | NS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.670E+02 | 7.270E+01 | 2.123E+00 | 6.921E+01 | 9.310E+02 | 3.030E+01 | 3.802E+02 | 3.227E+00 | 1.976E-01 | 4.604E+02 | 4.144E-01 | 3 | [illegible] |
| 2 | 2.120E+02 | 6.420E+01 | 2.629E+00 | 1.015E+02 | 9.052E+02 | 3.654E+01 | 4.370E+02 | 3.311E+00 | 2.111E-01 | 4.959E+02 | 4.919E-01 | 3 | [illegible] |
| 3 | 2.570E+02 | 5.670E+01 | 3.539E+00 | 1.139E+02 | [illegible].040E+03 | 3.514E+01 | 4.860E+02 | 3.391E+00 | 2.228E-01 | 5.315E+02 | 6.006E-01 | 3 | [illegible] |
| 4 | 3.020E+02 | 5.160E+01 | 3.640E+00 | 1.278E+02 | [illegible].091E+03 | 3.365E+01 | 5.410E+02 | 3.493E+00 | 2.341E-01 | 5.677E+02 | 7.474E-01 | 3 | [illegible] |
| 5 | 3.470E+02 | 4.760E+01 | 3.741E+00 | 1.431E+02 | [illegible].139E+03 | 3.218E+01 | 6.015E+02 | 3.612E+00 | 2.448E-01 | 6.044E+02 | 9.433E-01 | 3 | [illegible] |
| 6 | 3.920E+02 | 4.520E+01 | 3.539E+00 | 1.607E+02 | [illegible].184E+03 | 3.062E+01 | 6.713E+02 | 3.767E+00 | 2.554E-01 | 6.420E+02 | 1.200E+00 | 3 | [illegible] |
| 7 | 4.370E+02 | 4.150E+01 | 4.348E+00 | 1.779E+02 | [illegible].230E+03 | 2.942E+01 | 7.396E+02 | 3.909E+00 | 2.643E-01 | 6.796E+02 | 1.555E+00 | 3 | [illegible] |
| 8 | 4.820E+02 | 3.780E+01 | 4.853E+00 | 1.960E+02 | [illegible].275E+03 | 2.834E+01 | 8.111E+02 | 4.059E+00 | 2.724E-01 | 7.176E+02 | 2.046E+00 | 3 | [illegible] |
| 9 | 5.270E+02 | 3.480E+01 | 5.056E+00 | 2.125E+02 | [illegible].323E+03 | 2.760E+01 | 8.766E+02 | 4.178E+00 | 2.789E-01 | 7.551E+02 | 2.003E+00 | 3 | [illegible] |
| 10 | 5.800E+02 | 3.060E+01 | 2.831E+00 | 2.365E+02 | [illegible].375E+03 | 2.649E+01 | 9.715E+02 | 4.366E+00 | 2.870E-01 | 8.006E+02 | 3.043E+00 | 3 | [illegible] |
| 11 | 6.300E+02 | 2.910E+01 | 6.572E+00 | 2.721E+02 | [illegible].422E+03 | 2.487E+01 | 1.113E+03 | 4.676E+00 | 2.971E-01 | 8.530E+02 | 5.262E+00 | 3 | [illegible] |
| 12 | 6.700E+02 | 2.620E+01 | 6.876E+00 | 2.872E+02 | [illegible].454E+03 | 2.443E+01 | 1.172E+03 | 4.787E+00 | 3.007E-01 | 8.007E+02 | 7.034E+00 | 3 | [illegible] |
| 13 | 7.300E+02 | 2.400E+01 | 6.067E+00 | 3.346E+02 | [illegible].508E+03 | 2.298E+01 | 1.360E+03 | 5.202E+00 | 3.102E-01 | 9.441E+02 | 1.803E+01 | 3 | |
| 14 | 7.850E+02 | 2.250E+01 | 7.402E+00 | 3.709E+02 | [illegible].544E+03 | 2.192E+01 | 1.504E+03 | 5.534E+00 | 3.160E-01 | 9.892E+02 | 3.768E+01 | 3 | 1 |
| 15 | 8.500E+02 | 1.140E+01 | 3.670E+01 | 6.000E+02 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 0.000E+00 | 1.810E+02 | 0 | 0 |

TB = NORMAL BOILING TEMPERATURE, DEG F
API = API GRAVITY
VOL = VOLUME PER CENT OF TOTAL CRUDE
MW = MOLECULAR WEIGHT
TC = CRITICAL TEMPERATURE, DEG RANKINE
PC = CRITICAL PRESSURE, ATMOSPHERES
VC = CRITICAL VOLUME, CC/MOLE
A AND B ARE PARAMETERS IN THE VAPOR PRESSURE EQUATION
T10 IS THE TEMPERATURE IN DEG R WHERE THE VAPOR PRESSURE IS 10 MM HG
VIS IS THE KINEMATIC VISCOSITY IN CENTISTOKES AT 122 DEG F
NC = ERROR CODE, SHOULD BE LESS THAN 20
NS = ERROR CODE, SHOULD BE EQUAL TO 1
IGNORE THE ERROR CODES FOR COMPONENT NUMBER 15

CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: PRUDHOE BAY, ITEM 9, SAMPLE 71011

VAPOR PRESSURE IN ATMOSPHERES AT 3.200E+01 DEG F

| | VP |
|---|---|
| 1 | 3.784E-02 |
| 2 | 1.086E-02 |
| 3 | 2.504E-03 |
| 4 | 5.643E-04 |
| 5 | 1.123E-04 |
| 6 | 1.955E-05 |
| 7 | 3.176E-06 |
| 8 | 4.635E-07 |
| 9 | 6.603E-08 |
| 10 | 5.303E-09 |
| 11 | 2.092E-10 |
| 12 | 3.826E-11 |
| 13 | 4.512E-13 |
| 14 | 1.364E-14 |

MEAN MOLECULAR WEIGHT OF THE CRUDE = 2.730E+02

OVER-ALL MASS-TRANSFER COEFFICIENTS

WIND SPEED = 1.000E+01 KNOTS, OR 1.853E+04 M/HR
INITIAL SLICK DIAMETER = 7.116E+02 M, OR AREA = 3.975E+05 M**2

OVER-ALL MASS-TRANSFER COEFFICIENT FOR CUMENE = 1.553E+01 M/HR

| CUT | M/HR | G-MOLES/(HR)(ATM)(M**2) | SPGR OF CUT |
|---|---|---|---|
| 1 | 1.663E+01 | 7.428E+02 | 6.929E-01 |
| 2 | 1.638E+01 | 7.317E+02 | 7.230E-01 |
| 3 | 1.618E+01 | 7.228E+02 | 7.519E-01 |
| 4 | 1.600E+01 | 7.148E+02 | 7.728E-01 |
| 5 | 1.584E+01 | 7.077E+02 | 7.901E-01 |
| 6 | 1.570E+01 | 7.011E+02 | 8.008E-01 |
| 7 | 1.558E+01 | 6.959E+02 | 8.179E-01 |
| 8 | 1.548E+01 | 6.914E+02 | 8.358E-01 |
| 9 | 1.540E+01 | 6.879E+02 | 8.509E-01 |
| 10 | 1.531E+01 | 6.837E+02 | 8.729E-01 |
| 11 | 1.520E+01 | 6.788E+02 | 8.811E-01 |
| 12 | 1.516E+01 | 6.771E+02 | 8.973E-01 |
| 13 | 1.506E+01 | 6.727E+02 | 9.100E-01 |
| 14 | 1.500E+01 | 6.701E+02 | 9.188E-01 |

FOR THIS SPILL OF 5.000E+04 BARRELS, THE MASS IS 7.062E+03 METRIC TONNES

VOLUME FROM SUMMING THE CUTS = 7.9E+03 M**3, OR 5.000E+04 BARRELS

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 4.8E+00 CENTISTOKES AT 122 DEG F

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 8.8E+00 AT T = 32.0 DEG F

COUNT THE CUTS IN THE FOLLOWING OUTPUT FROM LEFT TO RIGHT

THE INITIAL MOLES IN THE SLICK ARE:
1.305E+06 1.481E+06 1.048E+06 1.741E+06 634E+06 .395E+06 581E+06 1.637E+06 .601E+06 8.267E+05 683E+06
1.699E+06 1.305E+06 1.466E+06 4.791E+06

THE INITIAL MASSES IN THE SLICK ARE:
1.164E+08 1.504E+08 2.105E+08 2.225E+08 2.338E+08 2.242E+08 2.813E+08 3.209E+08 3.403E+08 1.955E+08 4.580E+08
4.080E+08 4.367E+08 5.438E+08 2.875E+09

STEP SIZE OF 163E-01 IS BASED ON CUT

TIME = 1.0E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
5.7E-01 8.5E-01 9.6E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 .0E+00 .0E+00 .0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.9E-01, AREA = 5.7E+05 M**2

TIME = 2.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
2.7E-01 6.9E-01 9.2E-01 9.8E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.8E-01, AREA = 7.1E+05 M**2

TIME = 3.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.1E-01 5.4E-01 8.6E-01 9.7E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.7E-01, AREA = 8.2E+05 M**2

TIME = 4.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
3.9E-02 4.0E-01 8.1E-01 9.5E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00

```
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.6E-01, AREA =  9.1E+05 M**2

TIME =  5.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.2E-02  2.9E-01  7.5E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.6E-01, AREA =  1.0E+06 M**2


STEP SIZE OF  1.500E-01 IS BASED ON CUT   2

TIME =  6.4E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
3.1E-03  2.0E-01  6.8E-01  9.2E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.5E-01, AREA =  1.1E+06 M**2

TIME =  7.4E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
7.9E-04  1.3E-01  6.2E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00    0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.5E-01, AREA =  1.2E+06 M**2

TIME =  8.5E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.8E-04  8.7E-02  5.6E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00   .0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.5E-01, AREA =  1.2E+06 M**2

TIME =  9.5E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
3.8E-05  5.6E-02  5.1E-01  8.6E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.4E-01, AREA =  1.3E+06 M**2

TIME =  1.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
7.3E-06  3.5E-02  4.6E-01  8.4E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.4E-01, AREA =  1.3E+06 M**2

TIME =  1.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.3E-06  2.2E-02  4.1E-01  8.2E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00   .0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.4E-01, AREA =  1.4E+06 M**2

TIME =  1.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
2.1E-07  1.3E-02  3.6E-01  8.0E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.4E-01, AREA =  1.5E+06 M**2

TIME =  1.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
3.2E-08  7.6E-03  3.2E-01  7.8E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.3E-01, AREA =  1.5E+06 M**2

TIME =  1.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
4.4E-09  4.3E-03  2.8E-01  7.6E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.3E-01, AREA =   .6E+06 M**2
```

```
STEP SIZE OF 3.835E-01 IS BASED ON COT 3

TIME =  1.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00 2.1E-03 2.4E-01  7.3E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.3E-01, AREA =  1.6E+06 M**2

TIME =  1.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.1E-03  2.01,:-0 I  7.1E-01  9.3E-01  9.9E-O I  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.3E-01, AREA =  1.7E+06 M**2

TIME =  1.8E+01 00110S, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  5.6E-04  1.7E-01  6.8E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1,0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.3E-01, AREA  =  1.7E+06 M**2

TIME = 2.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.8E-04  1.5E-01  6.6E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  t.0E+00  1.0E+00  1,0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.2E-01, AREA  =  1.8E+06 M**2

TIME = 2.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.3E-04  1.2E-01  6.4 F.-0 I 9.1E-01 9.8E-01  I.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1,0E+00  t.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.2E-01, AREA  =  1.8E+06 M**2

TIME = 2.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  6.4E-05 1.0E-01 : 6.1E-01:  9.1E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.2E-01, AREA  =  1.9E+06 M**2

TIME =  2.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.0E-05  8.6E-02  5.9E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MARS) REMAINING IN THE SLICK  =  9.2E-01, AREA  =  1.9E+06 M**2

TIME =  2.4E+01 NOUNS, MASS II'RAC71ON OF EACH CUT REMAINING:
0.0E+00  1.4E-05 7.2E-02  5.7E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.2E-01, AREA =  1.9E+06 M**2

TIME = 2.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  6.1E-06  (i.iJK-(ii! 5.4E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.2E-01, AREA =  2.0E+06 M**2

TIME =  2.6E+01 nouns, MAsS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.7E-06  4.9E-02  5.2E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  9.1E-01, AREA =  2.0E+06 M**2

TIME =  2.8E+01 NOUNS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.1E-06  4.0E-02  5.0E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
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1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.1E+06 M**2

TIME =  2.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.9E-07  3.3E-02  4.8E-01  8.6E-01  9.8E-01  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.1E+06 M**2

TIME =  3.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.0E-07  2.7E-02  4.6E-01  8.6E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.2E+06 M**2

TIME =  3.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  8.2E-08  2.2E-02  4.4E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.2E+06 M**2

TIME =  3.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.3E-08  1.7E-02  4.2E-01  8.4E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.2E+06 M**2

TIME =  3.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.3E-08  1.4E-02  4.0E-01  8.3E-01  9.7E-01  9.9E-01  1.0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.3E+06 M**2

TIME =  3.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  5.0E-09  1.1E-02  3.8E-01  8.3E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMA NING  N THE SLICK =  9.1E-01, AREA =  2.3E+06 M**2

TIME =  3.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  8.9E-03  3.6E-01  8.2E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.3E+06 M**2

TIME =  3.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  7.1E-03  3.4E-01  8.1E-01  9.6E-01  9.9E-01  1.0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  2.4E+06 M**2

TIME =  3.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  5.6E-03  3.3E-01  8.0E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  2.4E+06 M**2

TIME =  3.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  4.4E-03  3.1E-01  7.9E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING  N THE SLICK =  9.0E-01, AREA =  2.4E+06 M**2

TIME =  4.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.5E-03  2.9E-01  7.9E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   .0E+00  1.0E+00
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TIME = 1. 0E+02 HOURS , MASS FRACTI ON OF EACH CUT REMA I N ING ,
0 0E+00 0. 0E+00 9. 4E- 1 1   6.8E-03 3 .7 E-01 8. 4E-01   9.7E-01   1.0E+00   1.0E+00   1.0E+00   1.0E+00   1.0E+00   1.0E+00   1.0E+00
1 0E+00
FRACTION ( BASED ON MASS) REMA I N I NG I N THE SLICK =   8.7E-01 , AREA =   3.8E+06 M**2


STEP s 1 ZEOF   3. 222E+00 IS   BASED ON CUT  i i

TIME =   1.5 E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E +00  0.  0E+00  9.4E-05 1.6E-01  7.3E-01   9.6E-01   9.9E-01   1.0E+00   1.0E+00   1.0E+00   1.0E+00   1. 0E+00   1 .0E+00,
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SL ICE =   8.6E-01, AREA =   4.6E+06 M**2


TIME =   2.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
o.0E+00   0.0 E+00 0. 0E+00   5.6E-07   5.9E-02   6.1E-01   9.2E-01   9.9E-01   1.0E+00   1 .0E+00   1.0E+00   1 .0E+00   1.0E+00   1 0E+00
1.0E+00
FRACTION (B ASED  ON  MASS) REMAINING IN THE SLICK =   8.5E-01 . AREA =   5.:3E+06 M**2


TIME = 2.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAI NING:
0 0E+00   0.0E+00 O. 0E+00   1.6E-09   1.9E-02   5.0E-01   9.0E-01   9.8E-01   1.0E+00   1 . 0E+00   1.0E+00   1.0E+00   1.0E+00   1,0E+00
1.0E+00
FRACTION (nASEI)  ON  MASS) REMAI NING IN THE SL ICE =   8.5E-01 , AREA =   5 .9E+06 M**2


TIME =   3.1E+02 HOURS, MASS  FRACTION  OF EACH CUT REMAINING:
0. 0E+00  0. 0E+00  0. 0E+00  0.0E+00  5.2E-03  4. 0E-01   8.6E-01   9.6E-01   1.0E+00   1,0E+00   1.0E+00   1.0E+00   1.0E+00   1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING  I N  THE SLICK =   8.4E-01, AREA =   6.4E+06 M**2


STEP SIZE OF   1.078E+01 IS BASED ON  C U T   6

TIME = 3.6E+02 HOURS,  M A S S  FRACTION OF EACH CUT REMAINING:
0.0E+00   0.0E+00   0. 0E+00  0.0E+00   1.2E-03  3.1  E-01  8.3E-01  9.7E-01   1.0E+00   1. 0E+00   1.0E+00   1.0E+00   1. 0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON  M A S S)  REMAINING IN THE SLICK =   8.4E-01. AREA = 6.9E+06  M * * 2


TIME = 4.2E+02 HOURS,  M A S S  FRACTION OF EACH CUT RE MAI NING:
0. 0 E+00  0. 0E +00  0. 0E+00  0. 0E+00  2.4E-04  2.4E-01   7.9E-01   9.7E-01   1.0E+00   1.0E+00   1,0E+00   1.0E+00   1 .0E+00   1 .0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING  I N  THE SLICK  =   8.3E-01, AREA =   7.4E+06 M**2


TIME = 4.7E+02 HOURS,  M A S S  FRACTION OF EACH CUT REMAINING:
0.0E+00   0.0E+00   0  .6E+00  0.0E+00   4.5E-05   1.0E-01   7.6E-01   9.6E-01   9. 9E-01   1.0E+00   1.0E+00   1 .0E+00   1.0E+00   1 .0E+00
1.0E+00
FRACTION (BASED  ON  MASS) REMA I NING IN THE SL ICE =   0.:11:-01,  AREA =   7.9E+06 M**2


THE FINAL MASS FRACTIONS FOR THE SLICK  A T  5. 0E+02 HOURS ARE:
0.000E+00   0.000E+00   0.000E+00   0.000E+00   1.071E-05   1.488E-01   7.274E-01   9.549E-01   9.935E-01   9.995E-01   1.000E+00
1.000E+00   1.000E+00   1.000E+00   1.000E+00
FRACTION (BASED ON MASS) REMAINING  I N  THE SLICK =   8.3E-01,  AREA =   8.2E+06 M**2

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CRUDE OIL CHARACTERIZATION AND PSEUDOCOMP ONENT EVAPORATION MODEL
IDENTI FICATION: PRUDHOE BAY, ITEM 9, SAMPLE 71011

VA POR PRESSURE IN ATMOSPHERES AT 4.200 E+0 1 DEG F

| | VP |
|---|---|
| 1 | 5.192E-02 |
| 2 | 1.555E-02 |
| 3 | 3.960E-03 |
| 4 | 9.0''91: 04 |
| 5 | 1.878E-04 |
| 6 | 3.435E-05 |
| 7 | 5.860F-06 |
| 8 | 9.034E-07 |
| 9 | 1.356E-07 |
| 10 | 1.166E-08 |
| 11 | 5.055E-10 |
| 12 | 9.681E-11 |
| 13 | 1.297E-12 |
| 14 | 4.3401;-14 |

MEAN MOLECULAR WEIGHT OF TJJE CRUDE = 2.730E+02

OVER-ALL MASS-TRANSFER COEFFICIENTS

WIND SPEED = 4.000E+01 KNOTS, OR 7.412E+04 M/HR
INITIAL SLICK DIAMETER = 7.116E+02 M, OR AREA = 3.975E+05 M**2

OVER-ALL MASS-TRANSFER COEFFICIENT FOR CUMENE = 4.580E+01 M/HR

| CUT | M/HR | G-MOLES/(HR)(ATM)(M**2) | SPGR OF CUT |
|---|---|---|---|
| 1 | 4.903E+01 | 2.147E+03 | 6.929E-01 |
| 2 | 4.830E+01 | 2.114E+03 | 7.230E-01 |
| 3 | 4.771E+01 | 2.089E+03 | 7.519E-01 |
| 4 | 4.718E+01 | 2.066E+03 | 7.720E-01 |
| 5 | 4.671E+01 | 2.045E+03 | 7.901E-01 |
| 6 | 4.628E+01 | 2.026E+03 | 8.008E-01 |
| 7 | 4.594E+01 | 2.011E+03 | 8.179E-01 |
| 8 | 4.564E+01 | 1.998E+03 | 8.358E-01 |
| 9 | 4.541E+01 | 1.988E+03 | 8.509E-01 |
| 10 | 4.513E+01 | 1.976E+03 | 8.729E-01 |
| 11 | 4.481E+01 | 1.962E+03 | 8.811E-01 |
| 12 | 4.469E+01 | 1.957E+03 | 8.973E-01 |
| 13 | 4.440E+01 | 1.944E+03 | 9.100E-01 |
| 14 | 4.423E+01 | 1.936E+03 | 9.188E-01 |

FOR THIS SPILL OF 5.000E+04 BARRELS, THE MASS IS 7.062E+03 METRIC TONNES

VOLUME FROM SUMMING THE CUTS = 7.9E+03 M**3, OR 5.000E+04 BARRELS

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 4.8E+00 CENTISTOKES AT 122 DEG F

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 8.1E+00 AT T = 42.0 DEG F

COUNT THE CUTS IN THE FOLLOWING OUTPUT FROM LEFT TO RIGHT

THE INITIAL MOLES IN THE SLICK ARE:
1.305E+06 1.481E+06 1.848E+06 1.741E+06 1.634E+06 1.395E+06 1.581E+06 1.637E+06 1.601E+06 8.267E+05 1.683E+06
1.699E+06 1.305E+06 1.466E+06 4.791E+06

THE INITIAL MASSES IN THE SLICK ARE:
1.164E+08 1.504E+08 2.105E+08 2.225E+08 2.338E+08 2.242E+08 2.813E+08 3.209E+08 3.403E+08 1.955E+08 4.580E+08
4.080E+08 4.367E+08 5.430E+08 2.875E+09

CUT GOES AWAY N MINUTES, THEREFORE IT WAS DELETED AND THE CUTS RENUMBERED

STEP SIZE OF 9.445E-02 IS BASED ON CUT 1

TIME = 1.0E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
5.1E-01 8.4E-01 9.6E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.7E-01, AREA = 5.6E+05 M**2

TIME = 2.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
2.1E-01 6.7E-01 9.1E-01 9.8E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.5E-01, AREA = 6.9E+05 M**2

TIME = 3.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
6.8E-02 5.1E-01 8.6E-01 9.7E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.4E-01, AREA = 8.0E+05 M**2

TIME = 4.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.9E-02 3.7E-01 8.0E-01 9.5E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.4E-01, AREA = 8.9E+05 M**2

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STEP SIZE OF  1.447 E-O 1 I S BASED ON CUT 2

TIME =  5.2E+00 HOURS, MASS FRACTION OF EACH CUT REMA I N I NG:
4.9E-03  2.6E-01  7.4E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICE =  9.3E-01, AREA ,  9.7E+05 M**2

TIME =  6.2 E+00 HOURS, MASS FRACTI ON OF EACH CUT REMAINING:
1 1E-03  1.8E-01  6.8E-01  9.2E-01  9.911-0 1  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLI CK =  9.2E-01, AREA =  1.0E+06 M**2

TIME =  7.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
2.1E-04  1.2E-01  6.2E-01  9.1E-01  9.8E-01  1.0E+00  1.0E+00  f.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING I N THE SLICK =  9.2E-01, AREA =  1.1E+06 M**2

TIME =  8.2E+00 HOURS, MASS FRACTION OF  EACH CUT REMAINING:
3.7E-05  7.6E-02  5.6E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICE =  9.2E-01, AREA ,  1.2E+06 M**2

TIME =  9.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
5.8E-06  4.8E-02  5.0E-01  8.7E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAI NING IN THE SLICK =  9.1E-01, AnEA =  1.2E+06 M**2

TINE =  1.0E+01 nouns, MASS FRACTION OF EACH CUT REMAINING:
8.3E-07  2.9 E-02 4.5E-01  8.5E-01  9.7E-01  9.9E-o 1  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN TOE SLICK =  9.1E-01, AnEA =  1.3E+06 M**2

TIME =  1.1E+01 NOUNS, MASS FRACTION OF EACH CUT REMAIEING:
1 1 E-07  1.711-02 4.0E-01  8.3E-01  9.7E-01  9.9E-o 1  1.0E+00  1.0E+00  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION(BASED ON MASS) REMAINING IN TOE  SLICK =  9.1E-01, AnEA =  1.3E+06 M**2

TIME =  f.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.2E-08  1.0E-02 3.6E-01  8.1E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  1.4E+06 M**2

TIME =  1.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.3E-09 5.8E-03 3.1E-01  7.9E-01  9.6E-O 1  9.9E-01  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.5E+06 M**2

TIME =  1.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.2E-03  2.7E-01  7.7E-01  9.5E-01  9.91? -01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  f.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICE =  9.0E-01, AREA =  1.5E+06 M**2

STEP SIZE OF 3.759E-01 IS BASED ON CUT  3

TIME =  1.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.5E-03  2.3E-01  7.4E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLI CK =  9.0E-01, AREA =  1.6E+06 M**2

TIME =  1.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00 7.4E -04 2.0E-01  7.2E-01  9.4E-01  9.9E-0 1  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.6E+06 M**2
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TIME =  1.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.6E-04  1.7E-01  6.9E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.7E+06 M**2

TIME =  1.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.7E-04  1.4E-01  6.7E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.7E+06 M**2

TIME =  2.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  7.8E-05  1.2E-01  6.4E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.7E+06 M**2

TIME =  2.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.5E-05  9.9E-02  6.2E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.8E+06 M**2

TIME =  2.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.5E-05  8.3E-02  6.0E-01  9.1E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.8E+06 M**2

TIME =  2.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  6.6E-06  6.8E-02  5.8E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.9E+06 M**2

TIME =  2.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.8E-06  5.6E-02  5.5E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  1.9E+06 M**2

TIME =  2.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.2E-06  4.6E-02  5.3E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.0E+06 M**2

TIME =  2.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.7E-07  3.8E-02  5.1E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.0E+06 M**2

TIME =  2.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.9E-07  3.1E-02  4.9E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.0E+06 M**2

TIME =  2.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  7.2E-08  2.5E-02  4.7E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2. E+06 M**2

TIME =  3.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.8E-08  2.0E-02  4.5E-01  8.6E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.1E+06 M**2

TIME =  3.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.0E-08  1.6E-02  4.3E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.1E+06 M**2
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TIME =  3.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.8E-09  1.3E-02  4.1E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.2E+06 M**2

TIME =  3.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.0E-02  3.9E-01  8.4E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.2E+06 M**2

TIME =  3.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  8.1E-03  3.7E-01  8.4E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.2E+06 M**2

TIME =  3.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  6.4E-03  3.5E-01  8.3E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.3E+06 M**2

TIME =  3.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  5.0E-03  3.4E-01  8.2E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.3E+06 M**2

TIME =  3.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.9E-03  3.2E-01  8.1E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.3E+06 M**2

TIME =  3.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.1E-03  3.0E-01  8.1E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.4E+06 M**2


STEP SIZE OF  1.087E+00 IS BASED ON CUT   4

TIME =  4.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  2.0E-03  2.8E-01  7.9E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.4E+06 M**2

TIME =  4.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.6E-03  2.6E-01  7.9E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.5E+06 M**2

TIME =  4.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.2E-03  2.5E-01  7.8E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.5E+06 M**2

TIME =  4.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  9.5E-04  2.4E-01  7.7E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.5E+06 M**2

TIME =  4.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  7.4E-04  2.3E-01  7.6E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.5E+06 M**2

TIME =  4.7E+01 HOURS, MASS FRACTION OF EACH CUT REMA NING:
0.0E+00  0.0E+00  5.7E-04  2.1E-01  7.6E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
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FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01  AREA =  2.6E+06 M**2

TIME =  4.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  4.4E-04  2.0E-01  7.5E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  2.6E+06 M**2

TIME =  4.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.3E-04  1.9E-01  7.4E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  2.6E+06 M**2

TIME =  5.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  2.5E-04  1.8E-01  7.3E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  2.7E+06 M**2

TIME =  5.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.9E-04  1.7E-01  7.3E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  2.7E+06 M**2

TIME =  5.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.5E-04  1.6E-01  7.2E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  2.7E+06 M**2

TIME =  1.0E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.7E-11  6.0E-03  4.0E-01  8.5E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.4E-01, AREA =  3.7E+06 M**2


STEP SIZE OF  3.511E+00 IS BASED ON CUT   5

TIME =  1.5E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  7.7E-05  1.8E-01  7.5E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.3E-01, AREA =  4.5E+06 M**2

TIME =  2.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  3.8E-07  6.9E-02  6.4E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.2E-01, AREA =  5.2E+06 M**2

TIME =  2.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  9.0E-10  2.3E-02  5.3E-01  9.1E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.1E-01, AREA =  5.8E+06 M**2

TIME =  3.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  0.0E+00  6.8E-03  4.3E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.1E-01, AREA =  6.3E+06 M**2


STEP SIZE OF    160E+0  IS BASED ON CUT   6

TIME =  3.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  0.0E+00  1.8E-03  3.4E-01  8.5E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.0E-01, AREA =  6.7E+06 M**2

TIME =  4.2E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  0.0E+00  3.8E-04  2.6E-01  8.2E-01  9.7E-01   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
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FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   8.0E-01, AREA =  7.2E+06 M**2

TIME =   4. 8E+02 HOURS , MASS FRACTION OF EACH CUT REMAINING :
0.0E+00 0.0E+00 0.0E+00 0.0E+00 6.8E-05 2.0E-01 7.111E-01 9.6E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   7.91E-01 , AREA =   7.7E+06 M**2

THE FINAL MASS FRACTIONS FOR THE SLICK AT 5.0E+02  HOURS ARE:
0.000E+00  0.000E+00 0.000E+00 0.000E+00  2.299E-05  1.635E-01  7.581E-01  9.595E-01  9.965E-01  9.998E-01  1.000E+00
1.000E+00  1.0001E+00  1.000E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =   7.91E-01, AREA =  7.9E+06 M**2

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CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: PRUDHOE BAY, ITEM 9, SAMPLE 7101

VAPOR PRESSURE IN ATMOSPHERES AT 3.200 E+01 DEG F

| | VP |
|---|---|
| 1 | 3.704E-02 |
| 2 | 1.086E-02 |
| 3 | 2.504E-03 |
| 4 | 5.643E-04 |
| 5 | 1.123E-04 |
| 6 | 1.955E-05 |
| 7 | :1.17611-06 |
| 8 | 4.635E-07 |
| 9 | 6.603E-08 |
| 10 | 5.393E-09 |
| 11 | 2.092E-10 |
| 12 | 3.026E-11 |
| 13 | 4.512E-13 |
| 14 | 1.:1641,:-14 |

MEAN MOLECULAR WEIGHT OF TJJE CRUDE = 2.730E+02

OVER-ALL MASS-TRANSFER COEFFICIENTS

WIND SPEED = 4.000E+01 KNOTS, OR 7.412E+04 M/HR
INITIAL SLICK DIAMETER = 7.116E+02 M, OR AREA = 3.975E+05 M**2

OVER-ALL MASS-TRANSFER COEFFICIENT FOR CUMENE = 4.500E+01 M/HR

| CUT | M/HR | G-MOLES/(HR)(ATM)(M**2) | SPGR OF CUT |
|---|---|---|---|
| 1 | 4.903E+01 | 2.190E+03 | 6.929E-01 |
| 2 | 4.830E+01 | 2.157E+03 | 7.330E-01 |
| 3 | 4.771E+01 | 2.131E+03 | 7.519E-01 |
| 4 | 4.718E+01 | 2.108E+03 | 7.728E-01 |
| 5 | 4.671E+01 | 2.087E+03 | 7.901E-01 |
| 6 | 4.628E+01 | 2.067E+03 | 8.008E-01 |
| 7 | 4.594E+01 | 2.052E+03 | 8.179E-01 |
| 8 | 4.564E+01 | 2.039E+03 | 8.358E-01 |
| 9 | 4.541E+01 | 2.028E+03 | 8.500E-01 |
| 10 | 4.513E+01 | 2.016E+03 | 8.729E-01 |
| 11 | 4.481E+01 | 2.002E+03 | 8.811E-01 |
| 12 | 4.469E+01 | 1.997E+03 | 8.973E-01 |
| 13 | 4.440E+01 | 1.983E+03 | 9.100E-01 |
| 14 | 4.423E+01 | 1.976E+03 | 9.184E-01 |

FOR THIS SPILL OF 5.000E+04 BARRELS, THE MASS IS 7.062E+03 METRIC TONNES

VOLUME FROM SUMMING THE CUTS = 7.9E+03 M**3, OR 5.000E+04 BARRELS

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 4.8E+00 CENTISTOKES AT 122 DEG F

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 8.8E+00 AT T = 32.0 DEG F

COUNT THE CUTS IN THE FOLLOWING OUTPUT FROM LEFT TO RIGHT

THE INITIAL MOLES IN THE SLICK ARE:
1.305E+06 1.481E+06 1.840E+06 1.741E+06 1.634E+06 1.395E+06 1.581E+06 1.637E+06 .601E+06 8.267E+05 1.683E+06
1.699E+06 1.305E+06 1.466E+06 4.791E+06

THE INITIAL MASSES IN THE SLICK ARE:
1.164E+08 1.504E+08 2.105E+08 2.225E+08 2.338E+08 2.242E+08 2.813E+08 3.209E+08 3.403E+08 1.955E+08 4.580E+08
4.880E+08 4.367E+08 5.438E+08 2.075E+09

CUT COES AWAY IN MINUTES, THEREFORE IT WAS DELETED AND THE CUTS RENUMBERED

STEP SIZE OF 1.325E-01 IS BASED ON CUT 1

TIME = 1.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
6.1E-01 8.9E-01 9.8E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.7E-01, AREA = 5.7E+05 M**2

TIME = 2.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
3.2E-01 7.6E-01 9.4E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.6E-01, AREA = 7.0E+05 M**2

TIME = 3.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.4E-01 6.3E-01 9.1E-01 9.8E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.5E-01, AREA = 8.1E+05 M**2

TIME = 4.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
5.0E-02 5.1E-01 8.7E-01 9.7E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 .0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.4E-01, AREA = 9.0E+05 M**2

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TIME = 5. 3E+00 HOURS , MASS FRACTION OF EACH CUT REMAIN I NC :
2. I E-02 4. 0E-01  0, 2E-01  9, 6E-01  9. 9E-0I  I. 0E+00  I. 0E+00  1, 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
F RACTION (BASED O N  MASS) REMAINING IN THE SLICK =  9. 4E-01 , AREA =  9. 9E+05 M**2


STEP SIZE OF  I . 974E-01 IS BASED ON  C U T  2

TIME =  6. 5E+00 11OIJNS , MASS FRACTION OF EACH CUT REMAI N J NC :
5 .91,: -03 3. 0E-01  7. 7E-01  9. 5E-01  9. 9E-01  I. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00
FRACTION (BASED ON  M A S S)  R EMAINING IN THE SLI CK □  9. 3E -01 , AREA =  I . 1E+06 M**2


TIME  =  7. 7E+00 HOURS, MASS FRACTION  O F  EACH CUT REMAINING:
1. 5E-03 2. 2 E-01  7. 2E-01  9. 4E-01  9. 9E-01  I. 0E+00  I. 0E+00  I. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00
FRACTION (BASED  O N  MASS) REMAINING IN THE SLICK =  9. 3E-01 , AREA =  1. 2 E+06 M**2


TIME = 0. 9 E+00 HOURS, H A S S  FRACTION OF EACH CUT REMAINING:
3. 4E-04  1. 5E-01  6. 7E-01  9. 2E-01  9. 9E-01  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1, 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
FRACTION (nASJill  ON  MASS) REMAINING IN THE SLICK =  9. 2E-01 , AREA □  1. 2 E+06 M**2


TIME =  1. 0E+01 HOURS,  MASS FRACTION OF EACH CUT REMAINING:
7. J E-05  1. 1 E-0I  6. 2E-01  9. 1E-01  9. 8E-01  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00 t. 0E+00 I. 0E+00  1. 0E+00
FRACTION (BASED ON MASS) REMAINI NG  IN  THE SLICK □  9. 2E-01 , AREA =  1. 3E+06 M**2


TIME =  1. 1E+01 HOURS, MASS FRACTION OF EACH  C U T  REMAINING:
J  . 3E-05 7. 1E-02 5. 7E-01  8. 9E-01  9. 8E-0I  1. 0E+00  I. 0E+00  1. 0E+00 I, 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
FRACTION (BASED  O N  MASS) REMAINING IN THE SLICK =  9. 21,:-01, AREA =  1. 4E+06 M**2


TIME □  1. 2E+01 HOURS, N A S S  FRACTION  OF  EACH CUT REMAINING:
2. 3E-06  4. 7E-02  5. 2E-01  8. 0E-001  9. 8E-01  I. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00  t. 0E+00  1. 0E+00
FRACTION (BASED  O N  MASS) REMAINING IN  THE SLICK =  9. 1E-01 , AREA =  1. 4E+06 M**2


TIME =  1 .4E+01 Nouns,  MASS  FRACTION  OF  EACH CUT REMAINING:
3. 6E-07  3. 1E-02 4. 7 F.-O I 8. 6 E-01  9. 7E-01  1. 0E+00  I. 0E+00  1. 0E+00 I. 0E+00  I. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00
FRACTI ON (BASED  O N  MASS) REMAINING  IN  THE SLICK □  9. 1E-01 , AnEA =  1. 5E+06 M**2


TIME = 1. 5E+01  N o u n s ,  MASS FRACTION OF EACH CUT REMAINING:
5. 3E-08  1 .9E-02  4. 3E-01  8. 5E-01  9. 7E-01  I. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00  1, 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
FRACTION (BASED  O N  MASS) REMAINING  IN  THE SLICK =  9. 1E-01 , AREA =  I . 5E+06 M**2


TINE =  1. 6E+01  HOURS,  MASS FRACTI ON OF EACH CUT REMAINING:
7. I E-09  1. 2E-02 3. 9 E-0 I  n. 3E-0I  9. 7E-01  9 .911-0 I  I. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
FRACTI ON (BASED  O N  MASS) REMAINING IN THE SLICK =  9. 1E-01 , AREA =  1. 6E+06 M**2


TIME =  1. 7 E+01 NOUNS,  MASS  FRACTION  OF EACH CUT REMAINING:
0. 0E+00  7. 5E-03  3. 5E-01  8. 1E-01  9. 6E-01  9. 9E-01  I. 0E+00  1. 0E+00  1. 0E+00  1 .0E+00 1. 0E+00  1. 0E+00  1. 0E+00  I. 0E+00
FRACTION (BASED  O N  MASS)  REMAINING  IN  THE SLICK =  9. 0E-01 , AREA =  1. 6E+06 M**2


TIME =  1 .8E+01 HOURS, MASS FRACTI ON OF EACH CUT REMAINING:
0. 0E+00  4. 5E-03  3. 1E-01  7. 9E-01  9. 6E-01  9 9E-0 I  I. 0E+00  1. 0E+00  I. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00  1. 0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SL ICK  =  9. 01-01  , AREA =  I . 7E+06 M**2
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STEP SIZE OF  5.215E-01 IS BASED ON CUT   3

TIME =  2.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.5E-03  2.7E-01  7.8E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.7E+06 M**2

TIME =  2.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.6E-03  2.5E-01  7.6E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.8E+06 M**2

TIME =  2.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  9.6E-04  2.2E-01  7.4E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00  1.0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.8E+06 M**2

TIME =  2.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  5.0E-04  2.0E-01  7.3E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.9E+06 M**2

TIME =  2.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.5E-04  1.8E-01  7.1E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.0E-01, AREA =  1.9E+06 M**2

TIME =  2.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.1E-04  1.6E-01  7.0E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  1.9E+06 M**2

TIME =  2.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.2E-04  1.4E-01  6.8E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00    0E+00   .0E+00    0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.0E+06 M**2

TIME =  2.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  7.0E-05  1.3E-01  6.7E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00   .0E+00    0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.0E+06 M**2

TIME =  2.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.0E-05  1.1E-01  6.5E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00    0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.0E+06 M**2

TIME =  2.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.3E-05  9.9E-02  6.3E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00    0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.1E+06 M**2

TIME =  3.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.3E-05  8.8E-02  6.2E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00   .0E+00    0E+00   .0E+00    0E+00   .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.1E+06 M**2

TIME =  3.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  7.1E-06  7.7E-02  6.0E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.2E+06 M**2

TIME =  3.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.9E-06  6.8E-02  5.9E-01  9.1E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.2E+06 M**2
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TIME = 3.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.1E-06 6.0E-02  5.71:-01  9.1E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  J.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  0.91,:-0 1, AREA =  2.2E+06 M**2

TIME =  3.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAIN 1 Nc :
0.0E+00  1.1E-06 5.2E-02  17.61-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK  =  8.8E-01, AREA =  2.2E+06 M**2

TINE =  3.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  6.1E-07  4.5E-02  5.4E-01  9.011-0 1  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  t.0E+00  1.0E+00  1.0E+00  J.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.3E+06 M**2

TIME = 3.6E+01 HOURS, MASS FIIACTION OF EACH CUT REMAINING:
0.0E+00  3.2E-07  4.0E-02  5.3E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  I.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.3E+06 M**2

TIME =  3.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.7E-07 3.4E-02  5.1E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK ,  0. Nit-o 1, AREA = 2.3E+06 P1**2

TIME = 3.8E+01 I1OUJWJ, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  8.7E-08  3.0E-02  5.0E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.4E+06 M**2

TIMI,: =  3.9E+01 HOURS, MASS FOACTION OF EACH CUT REMAINING:
0.0E+00  4.5E-08  2.6E-02  4.9E-01  8.8E-0J  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1 .0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.4 E+06 M**2

TIME = 4.1E+01 NOUNS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.3E-08  2.2E-02  4.7E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  J.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA .  2.4E+06 M**2

TIME = 4.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.1E-08  1.9E-02  4.6E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FIIACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.5E+06 M**2

TIME = 4.3E+01 Nouns, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  5.7E-09  1.7E-02  4.5E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA  =2.5E+06 M**2

TIME = 4.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.4E-02 4.3E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.5E+06 M**2

TIME =  4.5E+01 110011s, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.2E-02 4.2E-01  n.6E-o1  4).8E-01  1.0E+00  1.0E+00  1.0E+00  1 .0E+00  1.0E+00  J.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.5E+06 M**2

TIME =  4.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.0E-02  4.1E-01  8.6E-01  9.iii?-o1  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN Tiii! SLICK =  8.8E-01, AREA =  2.6E+06 M**2
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TIME = 4.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  9.0E-03 4.0E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.0E-01, AREA =  2.6E+06 M**2

TIME =  4.8E+01 nouns.  MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  7.6E-03  3.8E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  11.ill;-ol, AREA =  2.6E+06 M**2

TIME =  4.9E+01 noons,  MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  6.5 E-03  3.7E-01  8.4E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 8.7E-01, AREA =  2.7E+06 M**2

TIME =  5.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  5.5E-03 3.6E-01  8.4E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AnEA = 2.7E+06 M**2

TIME = 5.1E+01 NOUNS,  MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  4.7E-03  3.5E-01 8.3E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01, AREA =  2.7E+06 M**2

TIME = 5.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  4.0E-03  3.4E-01  8.3E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00 I. 0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.7E-01. AnEA =  2.7E+06 PI**2

STEP SIZE OF  1.555E+00 IS BASED ON CUT  4

TIME =  1.0E+02 HOURS, MASS FRACTION OF EACH COT REMAINING:
0. 0E+00  0. 0E+00  2.2E-07 4.9E-02  5.9E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.5E-01, AREA =  3.7E+06 M**2

TIME = 1.5E+02 HOURS, MASS FRACTION OF EACH COT REMAINING:
0. 0E+00  0.0E+00  4.6E-13  3.7E-03  3.8E-01  0.6E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED on MASS) REMAINING IN THE SLICK =  8.4E-01, AREA = 4.5E+06 M**2

STEP SIZE OF 5.200E+00 IS BASED ON CUT 5

TIME =  2.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  1.4E-04 2. 2E-01  7.0E-01  9.6E-01  9. 9E-01  1. 0E+00  1.0E+00  1.0E+00  1. 0E+00  1. 0E+00 1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 8.3E-01, AREA =  5.2E+06 M**2

TIME =  2.6E+02 HOURS, MASS IVIACTION Or EACH CUT REMAINING:
0.0E+00  0. 0E+00 0.0E+00 3.8E-06  1.2E-01  7.1E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.3E-01, AREA =  5.8E+06 M**2

TIME =  3.1E+02 HOURS, MASS FRACTION OF EACH CUT R EMAINING:
0.0E+00  0.0E+00 0.0E+00 7.2E-00  5. 8E-02  6.3E-01  9.4E-01  9. 9E-01  1.0E+00  1. 0E+00  1 . 0E+00  1.0E+00  1 .0E+00 1 .0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.2E-01, AREA =  6.3E+06 M**2

TIME = 3.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0. 0E+00 9.4 E-10  2. 8E-02  5.6E-01  9.2E-01  9. 9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  n 2E-01,  AREA = 6.8E+06 M**2
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TIME = 4.2E+02  HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00 0.0E+00 0.0E+00  1.2E-02  4.9E-01  9.0E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.1E-01, AREA =  7.3E+06 M**2

TIME =  4.7E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00 0.0E+00 0.0E+00  0.0E+00  5.2E-03  4.3E-01  8.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.1E-01, AREA =  7.7E+06 M**2


STEP SIZE OF  1.778E+01 IS BASED ON CUT   6

THE FINAL MASS FRACTIONS FOR THE SLICK AT 5.1E+02 HOURS ARE:
0.000E+00  0.000E+00  0.000E+00  0.000E+00  2.242E-03  3.655E-01  8.642E-01  9.795E-01  9.983E-01  9.999E-01  1.000E+00
1.000E+00  1.000E+00  1.000E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.0E-01, AREA =  8.1E+06 M**2

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CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT EVAPORATION MODEL
IDENTIFICATION: PRUDHOE BAY, ITEM 9, SAMPLE 71011

VAPOR PRESSURE IN ATMOSPHERES AT 4.200E+01 DEG F

| | VP |
|---|---|
| 1 | 5.192)?-02 |
| 2 | 1.555E-02 |
| 3 | 3.968E-03 |
| 4 | 9.029E-04 |
| 5 | 1.878E-04 |
| 6 | 3.435E-05 |
| 7 | 5.868E-06 |
| 8 | 9.034E-07 |
| 9 | 1.356E-07 |
| 10 | 1.160E-08 |
| 11 | 5.055E-10 |
| 12 | 9.681E-11 |
| 13 | 1.297E-12 |
| 14 | 4.340E-14 |

MEAN MOLECULAR WEIGHT OF THE CRUDE = 2.730E+02

OVER-ALL MASS-TRANSFER COEFFICIENTS

WIND SPEED = 1.000E+01 KNOTS, OR 1.853E+04 M/HR
INITIAL SLICK DIAMETER = 7.116E+02 M, OR AREA = 3.975E+05 M**2

OVER-ALL MASS-TRANSFER COEFFICIENT FOR CUMENE = 1.553E+01 M/HR

| CUT | M/HR | G-MOLES/(HR)(ATM)(M**2) | STCR OF CUT |
|---|---|---|---|
| 1 | 1.663E+01 | 7.200E+02 | 6.929E-01 |
| 2 | 1.638E+01 | 7.171E+02 | 7.230E-01 |
| 3 | 1.618E+01 | 7.084E+02 | 7.519E-01 |
| 4 | 1.600E+01 | 7.005E+02 | 7.728E-01 |
| 5 | 1.584E+01 | 6.936E+02 | 7.901E-01 |
| 6 | 1.570E+01 | 6.872E+02 | 8.008E-01 |
| 7 | 1.558E+01 | 6.820E+02 | 8.179E-01 |
| 8 | 1.548E+01 | 6.776E+02 | 8.358E-01 |
| 9 | 1.540E+01 | 6.742E+02 | 8.509E-01 |
| 10 | 1.531E+01 | 6.701E+02 | 8.729E-01 |
| 11 | 1.520E+01 | 6.653E+02 | 8.811E-01 |
| 12 | 1.516E+01 | 6.636E+02 | 8.973E-01 |
| 13 | 1.506E+01 | 6.593E+02 | 9.100E-01 |
| 14 | 1.500E+01 | 6.567E+02 | 9.188E-01 |

FOR THIS SPILL OF 5.000E+04 BARRELS, THE MASS IS 7.062E+03 METRIC TONNES

VOLUME FROM SUMMING THE CUTS = 7.9E+03 M**3, OR 5.000E+04 BARRELS

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 4.8E+00 CENTISTOKES AT 122 DEG F

KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE CUTS = 8.1E+00 AT T = 42.0 DEG F

COUNT THE CUTS IN THE FOLLOWING OUTPUT FROM LEFT TO RIGHT

THE INITIAL MOLES IN THE SLICK ARE:
1.305E+06 1.481E+06 1.848E+06 1.741E+06 634E+06 .395E+06 581E+06 .637E+06 .601E+06 a267E+05 1.683E+06
1.699E+06 1.305E+06 1.466E+06 4.791E+06

THE INITIAL MASSES IN THE SLICK ARE:
1.164E+08 1.504E+08 2.105E+08 2.225E+08 2.338E+08 2.242E+08 2.813E+08 3.209E+08 3.403E+08 1.955E+08 4.580E+08
4.880E+08 4.367E+08 5.438E+08 2.875E+09

STEP SIZE OF 8.651E-02 IS BASED ON CUT 1

TIME = 1.0E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
4.7E-01 8.0E-01 9.5E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 .0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.9E-01, AREA = 5.7E+05 M**2

TIME = 2.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.7E-01 6.0E-01 8.8E-01 9.7E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.7E-01, AREA = 7.0E+05 M**2

TIME = 3.1E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
5.1E-02 4.2E-01 8.0E-01 9.5E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 9.6E-01, AREA = 8.1E+05 M**2

TIME = 4.2E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
1.3E-02 2.8E-01 7.2E-01 9.3E-01 9.9E-01 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00 1.0E+00

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1.0E+00
FRACT ION (BASED ON MASS ) REMA I NING I N THE SLI CK =   9.6E-0 i , AREA =   9. I E+05 M**2


STEP SIZE OF  I . 169F.-O 1 IS BASED ON CUT 2

TIME =   5.3E+00 HOURS, MASS FRACTION OF EACH cUT REMAINING:
2,41:-03  1.7E-01  6. 4E-0 i  9.0E-01  9. 8E-0 i  1.0E+00  I.0E+00  I.0E+00  1. 0E+00  1.0E+00  1.0E+00  1.0E+00  I . 0E+00  1.0E+00
I 0E+00
FRACTION (BASED ON MASS) REMA I NING IN  TOE SLICK =   9.5E-01 , AREA =   1 .0E+06 M**2


TIME =   6.3E+00 HOURS, MASS FRACTION OF EACH CUT REMAINING:
4.2E-04  1.0E-01  5.6E-01  u. 8E-0 i  9.7E-01  I.0E+00  I.0E+00  I.0E+00  I.0E+00  1. 0E+00  1.0E+00  1.0E+00  1.0E+00  I.0E+00
1.0E+00
FRACTION (BASED ON  MASS)  REMAINING IN THE SLICK =   9.5E-01 . AREA =   1.1E+06 M**2


TIME = 7.4E+00 HOURS, MASS FRACTION OF EACH  C U T  REMAINING:
6.4E-05  5. 8E-02 4.9E-01.5E-01  9.7E-01      9. 9E-01  I.0E+00  1.0E+00  1.0E+00 1. 0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
I.0E+00
FRACTION (BASED  ON MASS) REMAINING IN THE  SLICK =   9.4 E-01 , AREA =   1.1E+06 M**2


TIME = 8.4E+00 HOURS, MASS FRACTION OF  EACU  CUT REMAINING:
8.6E-06  3.2E-02  4.2E-01  8.2E-01  9. 6E-0 i  9.9 E-01  1.0E+00  I.0E+00  1. 0E+00  1.0E+00  1. 0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON  MASS)  REMAINING IN THE  SLICK =   9.4 E-01 , AREA =   1.2E+06 M**2


TIME = 9.5E+00 nouns, MASS FRACTION  OF  EACH  CUT REMAINING:
1.0E-06  1.7E-02  3.6E-01 7.9E-01    9.5E-01  9.9E-01  I.0E+00  1.0E+00  1.0E+00  I.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED  ON MASS) REMAINING IN TJIE  SLICK = 9.4 E-01 , AnEA =   1.3E+06 M**2


TIMI? □   1.1E+01 HOURS, MASS FRACTION  OF  EACH  CUT REMAINING:
I .1E-07  8.7E-03  3. 0E-01 7.6E-01  9.5E-01  9. 9E-0 i  I.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1· 0E+00 I .0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING  IN  TOE  SLICK =   9.3E-01 , AREA =   1.3E+06 M**2


TIME =   1.2E+01 HOURS, MASS FRACTION OF EACH  CUT  REMAINING:
9. 8E-09  4.3E-03  2.5E-01  7.3E-01  9.4E-01  9.9E-01  I.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0Γ+00  1.0E+00  1.0E+00
1.0E+00
FRACTI ON (BASED OR MASS) REMAIKI NG  IN  THE SLICK = 9.3E-01 , AREA = 1.4E+06  P I * * 2


STEP SIZE OF  2.813E-01 IS BASED  UN  C U T  3

TIME =   1.3E+01 HOURS, MASS FRACTION OF EACH CUT REM AINING:
0.0E+00  2.0E-03  2.1E-01  7. 0E-0 i  9. 3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
I.0E+00
FRACTION (BASED  O N  MASS) REMAINING IN THE SLICK =   9.3E-01 , AREA =   1.4E+06 M**2


TIME =   1.4E+01 HOURS, MASS FRACTION  O F  EACH CUT REMAINING:
0.0E+00  8.9E-04  1.7E-01  6.7E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  t.0E+00  1. 0E+00
1.0E+00
FRACTION (nASEI) ON MASS) REMAINING IN THE SLICK =   9.2E-01 , AREA =   1.5E+06 M**2


TIME =   I .5E+01 HOURS, MASS FRACTION OF EACH  C U T  REMAINING:
0. 0E+00  3.0E-04  1.4E-01  6.4E-01 9. 1E-01  9.8E-01  1.0E+00  I.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  I.0E+0C
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1.0E+00
FRACTION (BASED ON MASS) REMAINING  N THE SLICK =  9.2E-01, AREA =  1.6E+06 M**2

TIME =  1.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.6E-04  1.1E-01  6.1E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION  BASED ON MASS) REMAINING IN THE SLICK =  9.2E-01, AREA =  1.6E+06 M**2

TIME =  1.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  6.2E-05  8.7E-02  5.8E-01  8.9E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.2E-01, AREA =  1.7E+06 M**2

TIME =  1.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  2.4E-05  6.8E-02  5.5E-01  8.8E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING    THE SLICK =  9.2E-01, AREA =  1.7E+06 M**2

TIME =  1.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  9.0E-06  5.3E-02  5.2E-01  8.7E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =   .8E+06 M**2

TIME =  2.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  3.3E-06  4.1E-02  4.9E-01  8.6E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  1.8E+06 M**2

TIME =  2.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.2E-06  3.2E-02  4.6E-01  8.5E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING  N THE SLICK =  9.1E-01, AREA =  1.8E+06 M**2

TIME =  2.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.0E-07  2.4E-02  4.3E-01  8.4E-01  9.7E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  1.9E+06 M**2

TIME =  2.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.3E-07  1.8E-02  4.1E-01  8.3E-01  9.7E-01  9.9E-01   .0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  1.9E+06 M**2

TIME =  2.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.3E-08  1.4E-02  3.8E-01  8.2E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00   .0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.0E+06 M**2

TIME =  2.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  1.4E-08  1.0E-02  3.6E-01  8.1E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  9.1E-01, AREA =  2.0E+06 M**2

TIME =  2.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  4.3E-09  7.3E-03  3.4E-01  8.0E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00   .0E+00  1.0E+00
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```
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01, AREA =   2.0E+06 M**2

TIME = 2.8E+0 I NOUNS, MASS FRACTION OF EACH CUT REMAINING:
n.0E+00  0.0E+00 5.7E-03 3.14:-01  7.9E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  I.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   0.01,:-01 , AREA =   2.1E+06 M**2

TIME = 3.0S+01 NOUNS, MASS FRACTION 0% EACH CUT REMAINING:
0.0E+00  0.0E+00 4.2E-03 2.9E-01  7.0E-01  9.6E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01, AREA =   2.1E+06 M**2

TIME = 3.1E+01 NOUNS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.1E-03 2.7E-01  7.6E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01. AREA =   2.2E+06 M**2

TIME =  3.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  2.2E-03 2.5E-01  7.5E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01, AnEA =   2.2E+06 M**2

STEP SIZE OF 7.6991? -01 1S BASED ON CUT 4

TIME =  3.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.6E-03  2.4E-01  7.4E-01  9.5E-01  9.91<-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9. OK-01 , AnEA = 2.2E+06 M**2

TIME =  3.4E+01 NOONS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00 0.0E+00  1.0E-03  2.11-01  7.3E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01, AREA =  2.3E+06 M**2

TIME =  3.6E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  6.6E-04  1.91,:-01  7.1E-01  9,41,:-01  9.9 K-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   9.0E-01, AREA =  2.3E+06 M**2

TIME = 3.7E+01 NOUNS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00 4.1E-04  1.7E-01  7.0E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN "THE? SLICK =   8.9E-01, AREA =  2.4E+06 M**2

TIME =  3.9E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  2.5E-04  1.5E-01  6.1111-01  9.3E-01  9.91,:-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   11.91-01, AREA =  2.4E+06 M**2

TIME =  4.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.5E-04  1.4E-01  6.7E-01  9.3E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00 1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =   8.9E-01, AREA =  2.5E+06 M**2
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```
TIME =  4.2E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  9.2E-05  1.2E-01  6.5E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.5E+06 M**2

TIME =  4.4E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  5.5E-05  1.1E-01  6.3E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00   .0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.5E+06 M**2

TIME =  4.5E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.2E-05  9.8E-02  6.2E-01  9.2E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.6E+06 M**2

TIME =  4.7E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.9E-05  8.7E-02  6.0E-01  9.1E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.6E+06 M**2

TIME =  4.8E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  1.1E-05  7.7E-02  5.9E-01  9.1E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.7E+06 M**2

TIME =  5.0E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  6.3E-06  6.8E-02  5.7E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.9E-01, AREA =  2.7E+06 M**2

TIME =  5.1E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.6E-06  6.0E-02  5.6E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.7E+06 M**2

TIME =  5.3E+01 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  2.0E-06  5.2E-02  5.4E-01  9.0E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.8E-01, AREA =  2.8E+06 M**2


STEP SIZE OF  2.252E+00 IS BASED ON CUT   5

TIME =  1.0E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  3.0E-16  3.0E-04  1.9E-01  7.4E-01  9.5E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.6E-01, AREA =  3.8E+06 M**2

TIME =  1.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  2.9E-07  4.5E-02  5.7E-01  9.1E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.5E-01, AREA =  4.6E+06 M**2

TIME =  2.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  7.6E-11  8.3E-03  4.2E-01  8.6E-01  9.8E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
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I.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.4E-01, AREA =  5.3E+06 M**2


STEP SIZE OF  7.316E+06 IS BASED ON CUT  G

TIME ,  2.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00 0. 0E+00 0.0E+00 0. 0E+00  1.2E-03 3.0E-01  8.1E-01  9.7E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK = 8.4E-01, AREA =  5.9E+06 M**2

TIME = 3.1E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00 0.0E+00  1.5E-04  2.0E-01  7.6E-01  9. 6E-01 9.9E-01  1.6E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.3E-01, AREA =  6.4E+06 M**2

TIME =  3.6E+02 HOURS, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00  0.0E+00  0.0E+00  1,4E-05  1.3E-01  7.1E-01  9.5E-01  9.9E-01  1, 0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.3E-01, AREA =  6.9E+06 M**2

TIME  =  4.1E+02 Nouns, MASS FRACTION OF EACH CUT REMAINING:
0.0E+00  0.0E+00 0. 0E+00 0.0E+00  1 2E-06  0.4E-02  6.6E-01  9.4E-01  9.9E-01  1.0E+00  1.0E+00  1.0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.2E-01, AREA =  7.3E+06 M**2

TIME = 4.6E+02 NOONS, MASS FRACTION OF EACH CUT REMAINING:
0 .0E+00 0.0E+00 0. 0E+00  0.0E+00 8.1E-08 5.2E-02  6. 1E-01  9.3E-01  9. 9E-01  1.0E+00  1.0E+00 1. 0E+00  1.0E+00  1.0E+00
1.0E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.2E-01, AREA =  7.7E+06 M**2

THE FINAL MASS FRACTIONS FOR THE SLICK  AT  5.1E+02 NOUNS ARE:
0 000E+00  0. 000E+00  0.000E+00  0.000E+00  4.020E-09  3.190E-02  5. 551E-01  9.139E-01  9.866E-01  9.989E-01  1.000E+00
1.000E+00  1.000E+00  1.000E+00  1.000E+00
FRACTION (BASED ON MASS) REMAINING IN THE SLICK =  8.2E-01, AREA =  8.1E+06 M**2

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CODE LISTING: OCTOBER 1981

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00010  c        ***** CUTVAP . FOR *****
00020  C
00030  C        GET YOUR OUTPUT FROM CUTVAP , OUT/F I LE : FORTRAN
00040  C
00050           REAL*4MW, MW1, KH, HTC1 ,MTC3, MASS. MOLES
00060           COMMON /COIL/ MW1,TC1,VC1,PC1,CNUM1 , VIS1
00070           COMMON /SPILL/ MTC3(30) ,VP(30) ,VLOC(30),RHO(30),Z, TERM2
00080        1,MW(30)
00090           COMMON / PCODE/IOU
00100           DIMENSION TB(30),API(30),A(30),B(30),TBL(30),APIL(30),VC(30)
00110        1,TC(30),PC(30),CNUM(30),TI0(30),HVAPI(30),HVAPZ(30)
00120        2,VOLL(30),VOL(30),MOLES(30),MTC1(30),VIS(30),VISE(30)
00130        3,VLOCK(30),SPGR(30),NC(30) ,NS(30)
00140           DIMENSION ANAME1(10) , ANAME2(10)
03150           OATA  ANAME2/'NORTH','SLOP', 'E CRU','DE    ',6*'      ' /
00160           DATA TBL/137.5,196.,228.,256.,20:1. ,X04. 5,327 . 5,004.,:100.5
00170        1,405.,426.3,449.5,470.,490.,509.5,528.,547.5,567.5,586.,602.
00180        2,621.,641.,650.,7*0./
00190           DATA APIL/71.6,59.7,55.,53.8,49.6,49.6,47.3,46.,44.,38.6
00200        1,38.8,37.2,35.4,33.9,33. 1.32?31.8,31.6,30.7,29.6,28.,26.9
00210        2,14.6,7*0./
00220           D A T A [illegible] ,2.,1.9,2.,2.,2.,2.,2.,2.
00230        1 ,2.,2.,2.,2.,2.1,2.,2.,1.0,55.,7*0./
00240           YI(X)=((1.-X)**0.38)/(X*X)
00250           OPEN (UNIT=32,DIALOG='DSED:CUTVAP . OUT')
00260           IOU=32
00270           APIBL=25 .7
00280           TYPE 501
00290  501      FORMAT(1X,'ENTER TTIE NUMBER OF TOP CUTS TO BE CHARACTERIZED
00300        1 ON I2')
00310           TYPE 502
00320  502      FORMAT (1X,'IF YOU HAVE NO INPUT DATA JUST ENTER 99. )
00330           TTPK: 503
00340  503      FORMAT(1X,'A 99 ENTRY WILL USE THE L IBRARY EXAMPLE')
00350           ICODE=1
00360           ACCEPT 504, NCUTS
00370  504      FORMAT(I2)
00380           IF(NCUTS.NE.99) CO TO 505
00390           ICODE=2
00400           NCUTS=23
00410           APIB=APIBL
00420           DO 507 I=1,10
00430           ANAME1(I)=ANAME2(I)
00440  507      CONTINUE
00450           CO TO 333
00460  505      TYPE 516
00470  516      FORMAT(1X,'ENTER THE IDENTIFICATION OF THE CRUDE ')
00480           ACCEPT 517, (ANAME1(I),I=1,10)
00490  517      FORMAT (10$1.)6)
00500           TYPE 521
00510  521      FORMAT(1x, 'ENTER THE BULK API GRAVITY' )
00520           ACCEPT 11, APIB
00530  333      DO 900 I=1,NCUTS
00540           COTO (80,81 ),ICODE
00550  no       TYPE 10, I
00560  10       FORMAT(1X,'ENTER THE BOILING POINT AT 1 ATM TB IN DEG F
00570        1 FOR COT' ,I3)
00580           ACCEPT 11 , TB(I)
00590  11       FORMAT(F10.0 )
00600           TYPE 12, I
00610  12       FORMAT(1 X,'ENTER API GRAVITY FOR CUT' ,I3)
00620           ACCEPT 11, API(I)
00630           TYPE 13, I
00640  13       FORMAT(1X,'ENTER VOLUME PER CENT FOR CUT',I3)
00650           ACCEPT 11, VOL(I)
00660           CO TO 900
```

```
01     TB(I)=TBL(I)
       API(I)=APIL(I)
       VOL(I)=VOLL(I)
900    CONTINUE
C
C      DISPLAY THE CUTS BACK TO THE USER.
C
       TYPE 681
681    FORMAT(/,1X,'CUT',5X,'TB',9X,'API',9X,'VOL')
       DO 700 I=1,NCUTS
       TYPE 699, I,TB(I),API(I),VOL(I)
699    FORMAT(1X,I2,3(2X,1PE10.3))
700    CONTINUE
       TYPE 701
701    FORMAT(1X,'DO YOU WANT TO CHANGE ANY?')
712    ACCEPT 702, ANS
702    FORMAT(A1)
       IF(ANS.EQ.'N') GO TO 713
       TYPE 703
703    FORMAT(1X,'ENTER THE DATA POINT NUMBER TO BE CHANGED ON I2')
       ACCEPT 504, N
       TYPE 704
704    FORMAT(1X,'ENTER 1 TO CHANGE TB, 2 FOR API, 3 FOR VOL%')
       ACCEPT 705, IC
705    FORMAT(I1)
       TYPE 706
706    FORMAT(1X,'ENTER THE CHANGED DATA')
       GO TO (707,708,709), IC
707    ACCEPT 11, TB(N)
       GO TO 710
708    ACCEPT 11, API(N)
       GO TO 710
709    ACCEPT 11, VOL(N)
710    TYPE 711
711    FORMAT(1X,'DO YOU WANT TO CHANGE ANYMORE?')
       GO TO 712
C
C      ALWAYS RENORMALIZE THE INPUT VOLUMES TO 100%.
C
713    VTOTAL=0.
       DO 720 I=1,NCUTS
       VTOTAL=VTOTAL+VOL(I)
720    CONTINUE
       DO 721 I=1,NCUTS
       VOL(I)=100.*VOL(I)/VTOTAL
721    CONTINUE
C
C      NOW CHARACTERIZE ALL THE CUTS EXCEPT THE LAST ONE WHICH IS
C      THE BOTTOM OF THE BARREL.  USE A VAPOR PRESSURE OF 0. AND A
C      MOLECULARE WEIGHT OF 600.
C
       MW(NCUTS)=600.
       VP(NCUTS)=0.
       NV=1
       NC1=NCUTS-1
       DO 1000 I=1,NCUTS
       APIN=API(I)
       TBN=TB(I)
       IF(I.EQ.NCUTS) NV=2
       CALL CHAR(APIN,TBN,AN,BN,NSN,NV)
C
C      THE CHARACTERIZATION SUBROUTINE RETURNS THE LOG10 OF THE
C      KINEMATIC VISCOSITY (CENTISTOKES) AT 122 DEG F.
C
       VISK(I)=10.**VIS1
       VLOGK(I)=ALOG(VISK(I))
```

```
      GO TO (61,1000), N V
61    NS(I)=NSN
      A(I)=AN
      B(I)=BN
      MW(1)=MW1
      TC(1)=TC1
      TC(I)=TC(I)+459.
      VC(I)=VC1
      PC(I)=PC1
      CNUM(I)=CNUM1
C
C     FIND THE TEMPERATURE AT WHICH THE VAPOR PRESSURE IS 10 MMHG
c     BY US ING NEWTON-RAPHSON WITH TB AS THE FIRST GUESS.
(:
      NC(I)=0
      YTEN=ALOG10(0.01315/PC(I))
      X=(TB(I)+459.)/TC(I)
140   EX=EXP(-20.*(X-B(I))**2)
      Y=-A(I)*(1.-X)/X-EX
      YOBJ=Y-YTEN
      VP(I)=PC(I)*10.**Y
      TEST=ABS(VP(I)-0.01315)
      IF(TEST.LT.0.001315) GO TO 150
      NC(I)=NC(I)+1
      IF(NC(I).GT.20)GO TO 160
      DY=A(I)/(X*X)+40.*(X-B(I))*EX
      n1=YOBJ-NY*X
      X=-B1/DY
      GO TO 140
C
C     UNSUCCESSFUL EXIT FROM NEWTON-RAPHSON
(:
160   TYPE 161, I,X,Y
161   FORMAT(1X,'T10  FAILURE FOR',I4,' AT T = ',1PE10.3,' WHERE
     1 LOG10(P) = ',1PE10.3)
      GO TO 9999
C
c     SUCCESSFUL EXIT FROM NEWTON-RAPHSON
C
150   T10(I)=X*TC(I)
C
C     CALCULATE THE HEAT OF VAFORIZATION AT 10 MMHG WITH THE
C     CLAPEYRON EQUATION AND USE WATSONS METHOD FOR THE
C     VAPOR PRESSURE BELOW 10 MMHG.
C
      TR2=T10(I)/TC(I)
      EX=92.12*(TR2-B(I))*EXP(-20.*(TR2-B(I))**2)
      HVAP=1.987*T10(I)*T10(I)*(2.303*A(1)/(TR2*TR2)+EX)/TC(I)
      HVAP1(I)=HVAP/MW(I)
      HVAPZ(I)=HVAP/(1.-TR2)**0.38
1000  CONTINUE
C
c     END OF TBP CUTS CHARACTERIZATION
c
      WRITE (10U,162) (ANAME1(I),I=1,10)
162   FORMAT(1H1,'SUMMARY OF TBP CUTS CHARACTERIZATION FOR: •
     1,10A5)
      WRITE (10U,163)
163   FORMAT(/,8X,'TB',8X,'API',8X,'VOL',9X,'MW',9X,'TC',9X,'PC'
     1,9X,'VC',10X,'A',10X,'B',8X,'T10',8X,'VIS',5X,'NC NS')
      DO 169 I=1,NCUTS
      WRITE(10U,164) I,TB(I), API(I), VOL(I), MW(I),TC(I), PC(I),VC(I)
     1,A(I),B(I),T10(I), VISK(I), NC(I), NS(I)
164   FORMAT(1X,I2,11(1X,1PE10.3),2(1X,I2))
169   CONTINUE
      WRITE (10U,180)
```

```
01990   180     FORMAT(//,1X,'TB = NORMAL BOILING TEMPERATURE, DEG F')
02000           WRITE (IOU,181)
02010   181     FORMAT(1X,'API = API GRAVITY')
02020           WRITE (IOU,182)
02030   182     FORMAT(1X,'VOL = VOLUME PER CENT OF TOTAL CRUDE')
02040           WRITE (IOU,183)
02050   183     FORMAT(1X,'MW = MOLECULAR WEIGHT')
02060           WRITE (IOU,184)
02070   184     FORMAT(1X,'TC = CRITICAL TEMPERATURE, DEG RANKINE')
02080           WRITE (IOU,185)
02090   185     FORMAT(1X,'PC = CRITICAL PRESSURE, ATMOSPHERES')
02100           WRITE (IOU,186)
02110   186     FORMAT(1X,'VC = CRITICAL VOLUME, CC/MOLE')
02120           WRITE (IOU,187)
02130   187     FORMAT(1X,'A AND B ARE PARAMETERS IN THE VAPOR PRESSURE
02140         1 EQUATION')
02150           WRITE (IOU,191)
02160   191     FORMAT(1X,'T10 IS THE TEMPERATURE IN DEG R WHERE THE VAPOR
02170         1 PRESSURE IS 10 MM HG')
02180           WRITE (IOU,192)
02190   192     FORMAT(1X,'VIS IS THE KINEMATIC VISCOSITY IN CENTISTOKES
02200         1 AT 122 DEG F')
02210           WRITE (IOU,188)
02220   188     FORMAT(1X,'NC = ERROR CODE, SHOULD BE LESS THAN 20')
02230           WRITE (IOU,189)
02240   189     FORMAT(1X,'NS = ERROR CODE, SHOULD BE EQUAL TO 1')
02250           WRITE (IOU,190) NCUTS
02260   190     FORMAT(1X,'IGNORE THE ERROR CODES FOR COMPONENT NUMBER  ,I2)
02270   999     TYPE 153
02280   153     FORMAT(1X,'ENTER T IN DEG F FOR VP CALCULATION')
02290           ACCEPT 11, XSAVE
02300           TK=(XSAVE-32.)/1.8+273.
02310           IF(XSAVE.LT.0.) GO TO 999
02320           XPRINT=XSAVE
02330           XSAVE=XSAVE+459.
02340   C       CALCULATE THE VAPOR PRESSURE AT THE INPUT TEMPERATURE.
02350   C
02360   C       AT THIS POINT IF THE INPUT TEMPERATURE IS LESS THAN THE
02370   C       10 MMHG TEMPERATURE USE THE WATSON-CLAPEYRON EQUATION.
02380   C
02390   C       THE WATSON-CLAPEYRON EQUATION IS:
02400   C
02410   C       LN(P2/P1) = (HVAPZ/(R*TC))*INTEGRAL
02420   C
02430   C       WHERE P1 = PRESSURE AT TR1, P2 = PRESSURE AT TR2, HVAPZ IS
02440   C       THE HEAT OF VAPORIZATION AT ABSOLUTE ZERO,
02450   C       R = 1.987 BTU/(LBMOLE, DEG R),
02460   C       TC = CRITICAL TEMPERATURE AND INTEGRAL = VAPORIZATION
02470   C       INTEGRAL BETWEEN TR1 AND TR2.
02480   C
02490           WRITE (IOU,1001)
02500   1001    FORMAT(1H1,'CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT
02510         1 EVAPORATION MODEL')
02520           WRITE (IOU,1002) (ANAME1(I),I=1,10)
02530   1002    FORMAT(1X,'IDENTIFICATION: ',10A5,/)
02540           WRITE (IOU,1003) XPRINT
02550   1003    FORMAT(1X,'VAPOR PRESSURE IN ATMOSPHERES AT ',1PE10.3,' DEG F'
02560           WRITE (IOU,1004)
02570   1004    FORMAT(/,12X,'VP',/)
02580           DO 2000 I=1,NC1
02590           X=XSAVE
02600           IF(X.LT.T10(I)) GO TO 144
02610           X=X/TC(I)
02620           EX=EXP(-20.*(X-B(I))**2)
02630           Y=-A(I)*(1.-X)/X-EX
02640           VP(I)=PC(I)*10.**Y
```

```
02650          GO TO 1999
02660   144    TR1=X/TC(1)
02670   C
02680   c      DO INTEGRAL BY SIMPSONS RULE WITH 21 POINTS
02690   C
02700          TR2=T10(I)/TC(1)
02710          DH=(TR2-TR1)/20.
02720          RESULT=Y1(TR1)
02730          TR=TR1
02740          DO 142 K=1,10
02750          TR=TR+DH
02760          RESULT=RESULT+4.*Y1(TR)
02770          TR=TR+DH
02780          RESULT=RESULT+2.*Y1(TR)
02790   142    CONTINUE
02800          TR=TR+DH
02810          RESULT=RESULT+4.*Y1(TR)
02820          TR=TR+DH
02830          RESULT=DH*(RESULT+Y1(TR))/3.
02840          P1=-4.33-HVAPZ(I)*RESULT/(1.987*TC(1))
02850          VP(I)=EXP(P1)
02860   1999   WRITE(1 OU,168)I,VP(I)
02870   168    FORMAT(1X,I2,5X,1PE10.3)
02880   2000   CONTINUE
02890          TYPE 550
02900   550    FORMAT(1X,'THE TBP CUTS HAVE BEEN CHARACTERIZED')
02910          TYPE 551
02920   551    FORMAT(1X,'DO YOU WISH To WEATHER THIS CRUDE?')
02930          ACCEPT 702, ANS
02940          IF(ANS.EQ.'N') GO TO 9999
02950          TYPE 552
02960   552    FORMAT(1X,'ENTER THE SPILL SIZE In BARRELS')
02970          ACCEPT 11, BBL
02980          TYPE 553
02990   553    FORMAT(1X,'ENTER WIND SPEED IN KNOTS PER HOUR')
03000          ACCEPT 11, WINDS
03010          TYPE 111
03020   111    FORMAT(1X,'ENTER NUMBER OF norms FOR oil, WEATHERING TO OCCUR')
03030          ACCEPT 11, X2
03040   C
03050   c      NOW CALCULATE THE IN ITIAL GRAM MOLES FOR EACH COMPONENT TO
03060   C      GET THE INTEGRATION STARTED.
03070   C
03080          BM=0.159,knu14
03090          TMOLES=0.
03100          DO 570 I=I,NCUTS
03110          SPGR(I)=141.5/(API(I)+131.5)
03120          AMASS=7532.*SPGR(I)*BBL*VOL(I)
03130          MOLES(I)=AMASS/MW(I)
03140          TMOLES=TMOLES+MOLES(I)
03150          BIO(I)=100.*MOLES(I)/(BM*VOL(I))
03160   570    CONTINUE
03170   C
03180   c      CALCULATE THE MEAN MOLECULAR WEIGHT OF THE CRUDE
03190   C
03200          SUM=0.
03210          DO 170 I=1,NCUTS
03220          SUM=SUM+MOLES(I)
03230   170    CONTINUE
03240          WTMOLE=0.
03250          DO 171 I=1,NCUTS
03260          WTMOLE=WTMOLE+MW(I)*MOLES(I)/SUM
03270   171    CONTINUE
03280          WRITE(1 OU,172) WTMOLE
03290   172    FORMAT(/,1X,'MEAN MOLECULAR WEIGHT OF THE CRUDE = ',1PE10.3)
03300   C
```

```
C         CALCULATE AN AREA IN THE SAME WAY IT WILL BE CALCULATED
C         AS THE SLICK WEATHERS.
C
          Z=0.02
          VOLUM=0.
          DO 666 I=1,NCUTS
          VOLUM=VOLUM+MOLES(I)/RHO(I)
666       CONTINUE
          AREA=VOLUM/Z
          DIA=SQRT(AREA/0.785)
C
C         CONVERT WIND SPEED TO M/HR.
c
          WINDM=1632.9*WINDS
C
C         THE MASS TRANSFER COEFFICIENT IS CALCULATED ACCORDING TO TWO
c         WAYS: MTC1 IS ACCORDING TO MACKAY AND BASED ON CUMENE WITH
C         A MOLECULAR WEIGHT OF 120. KH IS CUMENE'S MASS TRANSFER
C         COEFFICIENT. THESE ARE OVER-ALL MASS-TRANSFER COEFFICIENTS.
C
          TERM1=0.015*WINDM**0.70
          TERM2=DIA**(-0.11)
C
c         KH INCLUDES THE SCHMIDT NUMBER FOR CUMENE.
C
          KH=TERM1*TERM2
          WRITE (IOU,560)
560       FORMAT(1H1,'OVER-ALL MASS-TRANSFER COEFFICIENTS')
          WRITE (IOU,561)WINDS,WINDM
561       FORMAT(/,1X,'WIND SPEED = ',1PE10.3,' KNOTS. ON ',1PE10.3
     1,' M/HR')
          WRITE (IOU,616) DIA, AREA
616       FORMAT(1X,'INITIAL SLICK DIAMETER = ',1PE10.3,'M, On AREA = '
     1,1PE10.3,' M**2')
          WRITE (IOU,562) KH
562       FORMAT(/,1X,'OVER-ALL MASS-TRANSFER COEFFICIENT FOR CUMENE = '
     1,1PE10.3,' M/HR',/)
          WRITE (IOU,579)
579       FORMAT(3X,'CUT',12X, 'M/HR',7X,'G-MOLES/(HR)(ATM)(M**2)',
     1,3X,'SPGR OF CUT')
          TEMP=(0.2E-05)*TK
          DO 564 I=1,NC1
          MTC1(I)=KH*0.93*SQRT((MW(I)+29.)/MW(I))
C
c         MTC3(I) IS THE OVER-ALL MASS-TRANSFER COEFFICIENT DIVIDED
C         BY R*T. R=82.06E+06(ATM)(M**3)/(G-MOLE)(DEG K)
c
          MTC3(I)=MTC1(I)/TEMP
          WRITE (IOU,566) I, MTC1(I), MTC3(I), SPGR(I)
566       FORMAT(2X,I3,3(10X,1PE10.3))
564       CONTINUE
          SPGRB=141.5/(API+131.5)
          MASS=0.1582*BBL*SPGRB
          WRITE (IOU, 565) BBL, MASS
565       FORMAT(/,1X,'FOR THIS SPILL OF ',1PE10.3,' BARRELS, THE
     1 MASS IS ',1PE10.3, ' METRIC TONNES')
          VOLUMB=VOLUM/0.169
          WRITE (IOU,581) VOLUM,VOLUMB
581       FORMAT(/,1X, 'VOLUME FROM SUMMING THE CUTS = ',1PE8.1,' M**3
     1, OR ',1PE10.3,' BARRELS')
C
c         CALCULATE THE VISCOSITY OF THE CRUDE AT 122 DEG F AND THE
C         ENTERED ENVIRONMENT TEMPERATURE.
C
          VISMIX=0.
          DO 571 I=1,NCUTS
```

```
03970          VISMIX=VISMIX+MOLES(I)*VLOGK(I)/TMOLES
03980   571    CONTINUE
03990          VISMIX=EXP(VISMIX)
04000          WRITE (10U,572) VISMIX
04010   572    FORMAT(/,1X,'KINEMATIC VISCOSITY OF THE BULK CRUDE FROM
04020         THE CUTS = ',1PE8.1,' CENTISTOKES AT 122 DEG F')
04030          VISMIX=0.
04040          DO 573 I=1,NCUTS
04050          VIS(I)=VISK(I)*EXP(1923.*(1 /XSAVE-0.001721
04060          VLOG(I)=ALOG(VIS(I))
04070          VISMIX=VISMIX+MOLES(I)*VLOG(I)/TMOLES
04080   573    CONTINUE
04090          VISMIX=EXP(VISMIX)
04100          WRITE (10U,574) VISMIX,XPRINT
04110   574    FORMAT(/,1X,'KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE
04120         CUTS = ',1PE8.1,' AT T = ',0PF5.1,' DEG F',/)
04130          NEQ=NCUTS
04140   C
04150   C      PRINT EVERY XP TIME INCREMENT.
04160   C
04170          XP=1.
04180          X1=0.
04190          MOLES(NCUTS+1)=AREA
04200          CALL BRKG4(MOLES,X1,X2,XP,NEQ)
04210          TYPE 590
04220   590    FORMAT(1X,'DO IT AGAIN?')
04230          ACCEPT 702, ANS
04240          IF(ANS.EQ.'Y') GO TO 999
04250   9999   CONTINUE
04260          END
04270          SUBROUTINE CHAR(API,TB,A,B,NS,NV)
04280          REAL*4 MW1
04290          COMMON /COIL/ MW1,TC1,VC1,PC1,CNUM1,VIS1
04300          DIMENSION C(2,6),T(2,6),P(4),V(2,6)
04310          DATA ((C(I,J),J=1,6),I=1,2)/6.241E+01,-4.595E-02,-2.836E-01
04320        1,3.256E-03,4.578E-04,5.279E-04
04330        1,4.260E+02,-1.007,-7.449,1.38E-02,1.047E-03,2.621E-02/
04340          DATA ((T(I,J),J=1,6),I=1,2)/4.055E+02,1.337,-2.662,-2.169E-03
04350        1,-4.943E-04,1.454E-02
04360        1,412.2,1.276,-2.865,-2.088E-03,-3.707E-04,2.880E-02/
04370          DATA P/1.237E-02,0.2516,4.039E-02,-4.024E-02/
04380          DATA ((V(I,J),J=1,6),I=1,2)/ -0.4480,-9.344E-04,0.01583
04390        1,-5.219E-05,5.268E-06,1.536E-04
04400        1,-0.6019,1.793E-03,-3.159E-03,-5.1E-06,9.067E-07,3.522E-05/
04410   C
04420   C      THIS SUBROUTINE CHARACTERIZES A CUT OF CRUDE OIL WITH RESPECT
04430   C      TO VAPOR PRESSURE.  THE INPUT REQUIRED IS API GRAVITY AND THE
04440   C      BOILING POINT AT 1 ATMOSPHERE.  THE OUTPUT IS A SWITCH NS
04450   C      WHERE NS=1 MEANS THE VAPOR PRESSURE EQUATION CAN BE USED DOWN TO
04460   C      10 MM HG AND NS=2 MEANS THE CLAPEYRON EQUATION SHOULD BE USED.
04470   C
04480   C      THE VAPOR PRESSURE EQUATION IS:
04490   C
04500   C      LOG10(PR) = -A*(1.-TR)/TR - EXP(-20*(TR-B)**2)
04510   C
04520   C      WHERE PR = REDUCED PRESSURE, TR = REDUCED TEMPERATURE AND
04530   C      A AND B ARE RETURNED BY THIS SUBROUTINE.
04540   C
04550   C      API = GRAVITY, TB = BOILING POINT AT 1 ATMOSPHERE IN DEG F.
04560   C      CALCULATE CRITICAL TEMPERATURE AND MOLECULAR WEIGHT.
04570   C
04580          API2=API*API
04590          TB2=TB*TB
04600          CROSS=API*TB
04610   C
04620   C      CALCULATE THE VISCOSITY OF THE CUT.
```

```
C
      I=1
      IF(API.GT.35.) I=2
      VIS1=V(I,1)+V(I,2)*TB+V(I,3)*API+V(I,4)*CROSS+V(I,5)*TB2
     +V(I,6)*API2
      GO TO (99,101), NV
99    I=1
      IF(TB.GT.500.) I=2
      MW1=C(I,1)+C(I,2)*TB+C(I,3)*API+C(I,4)*CROSS+C(I,5)*TB2
     1+C(I,6)*API2
      TC1=T(I,1)+T( ,2)*TB+T( ,3)*AP +T  ,4)*CROSS+T(I,5)*TB2
     1+T(I,6)*API2
      TCK=(TC1+459 )/1.8
C
C     CALCULATE THE VISCOSITY OF THE CUT.
C
      I=1
      IF(API.GT.35.) I=2
      VIS1=V(I,1)+V(I,2)*TB+V(I,3)*API+V(I,4)*CROSS+V(I,5)*TB2
     +V(I,6)*API2
C
C     CALCULATE THE CARBON NUMBER
C
      CNUM1=(MW1-2.)/14.
      X=ALOG10(CNUM1)
C
C     CALCULATE B FOR THE VAPOR PRESSURE EQUATION
C
      BPRIME=P(1)+X*(P(2)+X*(P(3)+X*P(4)))
      B=BPRIME-0.02
C
C     CALCULATE THE CRITICAL VOLUME  CC/GMOLE
C
      VW=1.88+2.44*CNUM1
      VC1=VW/0.044
C
C     CALCULATE THE CRITICAL PRESSURE IN ATMOSPHERES
C
      PCP=20.8*TCK/(VC1-8.)
      PC1=PCP+10.
      TR=(TB+459.)/(TC1+459.
      PR=1./PC1
      NS=1
      IF(TR.LE.B) GO TO 100
      A=(ALOG10(PR)+EXP(-20.*(TR-B)**2))*TR/ TR-1
      GO TO 101
100   NS=2
101   RETURN
      END
      SUBROUTINE BRKG4(Y,X1,X2,XP,NEQ)
      REAL*4 K1,K2,K3,K4,MTC3,MW,MWU
      COMMON /SPILL/ MTC3(30),VP(30),VLOG(30),RHO(30 ,Z,TERM2
     ,MW(30)
      COMMON /PCODE/ IOU
      COMMON /TALK/ NEQ1
      DIMENSION Y(30),YARG(30),K1(30),K2(30),K3(30),K4(30)
      DIMENSION YSAVE(30),YF(30),YMSAVE(30),YN(30),MWU(30)
C
C     RUNGA-KUTTA 4-TH ORDER NUMERICAL INTEGRATION FOR SIMULTANEOUS
C     DIFFERENTIAL EQUATIONS.  SEE C.R. WYLIE. PAGES 108-117 OR
C     D. GREENSPAN. PAGES 113-115.
C
C     THIS SUBROUTINE DOES THE PRINTING, THE INITIAL AND FINAL VALUES
C     ARE ALWAYS PRINTED.  PRINT THE RESULTS EVERY XP INCREMENT
C     IN X.
C
```

```
C       THE USER MUST WRITE SUBROUTINE FXYZ WHICH CALCULATES THE
C       K1, K2, K3, AND K4 VECTORS AS A FUNCTION OF X AND THE
C       CURRENT Y VECTOR.  INTEGRATION FOLLOWS THE REFERENCES AND
C       WAS TEST ON PROBLEM 5, PAGE 116 IN WYLIE.
C
C       THE FIRST NCUTS POSITIONS IN THE Y VECTOR ARE THE MOLES
C       OF THE COMPONENTS, POSITION NCUTS+1 IS THE AREA OF THE
C       SLICK.
C
        NEQ1=NEQ+1
        NS=1
        IN=1
        IKEEP=1
        TOTAL=0.
        TSAVE=0.
        DO 30 I=1,NEQ
        YSAVE(I)=Y(I)
        YMSAVE(I)=Y(I)*MW(I)
        MWU(I)=MW(I)
        TSAVE=TSAVE+YMSAVE(I)
        TOTAL=TOTAL+Y(I)
30      CONTINUE
        NDEL=0
        NFAST=0
        X=X1
        XW=X+XP
        WRITE (IOU,933)
933     FORMAT(/,1X,'COUNT THE CUTS IN THE FOLLOWING OUTPUT FROM LEFT
       TO RIGHT',/)
        WRITE (IOU,931)
931     FORMAT(1X,'THE INITIAL MOLES IN THE SLICK ARE:')
        WRITE (IOU,900) (Y(I),I=1,NEQ)
900     FORMAT(1(1X,1PE10.3))
        WRITE (IOU,932)
932     FORMAT(/,1X,'THE INITIAL MASSES IN THE SLICK ARE:')
        WRITE (IOU,900) (YMSAVE(I),I=1,NEQ)
        WRITE (IOU,902)
902     FORMAT(/)
C
C       CALCULATE DY/DX AND SET THE STEP SIZE TO APPROXIMATE
C       A 5% CHANGE IN THE MOST RAPIDLY CHANGING Y.  WHEN THIS
C       Y DECREASES BY A FACTOR OF 20, RESET THE STEP SIZE
C       ACCORDING TO THE NEXT Y.
C       SOME Y'S WILL CHANGE SO FAST THAT THEY WILL BE GONE
C       IN A FEW MINUTES.  THESE ARE DELETED BEFORE INTEGRATION
C       STARTS AND NOTED ON THE PRINTED RESULTS.
C
899     NFAST=NFAST+1
890     CALL FXYZ(X,Y,K1,NEQ)
        H=0.05*Y(NFAST)/K1(NFAST)
        YOLD=Y(NFAST)
        H=ABS(H)
        H2=H/2.
        GO TO (801,898), IN
801     IF(H.GT.0.05) GO TO 806
C
C       Y(NFAST) CHANGES TOO FAST TO CALCULATE, DELETE IT AND MOVE
C       EVERYBODY ONE SPACE TO THE LEFT.
C
C       WHEN YOU MOVE THE AREA BE SURE TO SUBTRACT THE CONTRIBUTION
C       OF THE CUT JUST DELETED.
C
        ISTART=1
        NFAST=1
        NDEL=NDEL+1
        NEQ=NEQ-1
```

```
      AD=Y(I)/RHO(I)/Z
      DO 850 I=1,NEQ
      I1=I+1
      Y(I)=Y(I1)
      VP(I)=VP(I1)
      MTC3(I)=MTC3(I1)
      YSAVE(I)=YSAVE(I1)
      VLOG(I)=VLOG(I1)
      RHO(I)=RHO(I1)
      MWU(I)=MWU(I1)
      YMSAVE(I)=YMSAVE(I1)
850   CONTINUE
      Y(NEQ+1)=Y(NEQ+2)-AD
      WRITE (IOU,849) NDEL
849   FORMAT(1X,'CUT ',I2,' GOES AWAY IN MINUTES, THEREFORE IT WAS
     DELETED AND THE CUTS RENUMBERED',/)
      GO TO 890
886   IN=2
      NEQ1=NEQ+1
898   WRITE (IOU,871) H,NFAST
871   FORMAT(/,2X,'STEP SIZE OF ',1PE10.3,' IS BASED ON CUT ',I3,/)
897   IF(X.LT.XW) GO TO 901
      XW=X+XP
      YTOT=0.
      TMASS=0.
      DO 31 I=1,NEQ
      YF(I)=Y(I)/YSAVE(I)
      YTOT=YTOT+Y(I)
      YM(I)=Y(I)*MWU(I)
      TMASS=TMASS+YM(I)
      YM(I)=YM(I)/YMSAVE(I)
31    CONTINUE
      WRITE (IOU,432) X
432   FORMAT(2X,'TIME = ',1PE8.1,' HOURS, MASS FRACTION OF EACH
     CUT REMAINING:')
      WRITE (IOU,911) (YM(I),I=1,NEQ)
911   FORMAT(14(1X,1PE8.1))
C
C     WHEN THE FRACTION REMAINING OF COMPONENT I GETS LOW,
C     SET ITS VAPOR PRESSURE AND MOLES EQUAL TO ZERO.
C
      DO 631 I=ISTART,NEQ
      IF(YF(I).GT.1.0E-08) GO TO 631
      IKEEP=I+1
      VP(I)=0.
      Y(I)=0.
631   CONTINUE
      ISTART=IKEEP
      CONE=TMASS/TSAVE
      WRITE (IOU,922) CONE,Y(NEQ1)
922   FORMAT(2X,'FRACTION (BASED ON MASS) REMAINING IN THE SLICK
     = ',1PE8.1,', AREA = ',1PE8.1,' M**2')
      WRITE (IOU,902)
C
C     INCREASE XP TO 50 HOURS AFTER 50 HOURS OF WEATHERING.
C
      GO TO (701,901), NS
701   IF(X.LT.50.) GO TO 901
      NS=2
      XP=50.
C
C     TAKE A STEP IN TIME
C
90    XARG=X
      DO 10 I=1,NEQ1
      YARG(I)=Y(I)
```

```
06610   101     CONTINUE
06620           CALL FXYZ(XARG,YARG,K1,NEQ)
06630           XARG=X+H2
06640           DO 102 I=1,NEQ1
06650           YARG(I)=Y(I)+H*K     /2
06660   102     CONTINUE
06670           CALL FXYZ(XARG,YARG,K2,NEQ)
06680           DO 103 I=1,NEQ1
06690           YARG(I)=Y(I)+H*K2(I)/2.
06700   103     CONTINUE
06710           CALL FXYZ(XARG,YARG,K3,NEQ)
06720           XARG=X+H
06730           DO 104 I=1,NEQ1
06740           YARG(I)=Y(I)+H*K3(I)
06750   104     CONTINUE
06760           CALL FXYZ(XARG,YARG,K4,NEQ)
06770           DO 105 I=1,NEQ1
06780           Y(I)=Y(I)+H*(K1(I)+2.*(K2( )+K3( ))+K4( ))/6.
06790   105     CONTINUE
06800   C
06810   C       RECALCULATE THE OVER-ALL MASS-TRANSFER COEFFICIENTS OUTSIDE
06820   C       THE DERIVATIVE SUBROUTINE.  THE DIAMETER DEPENDENCE IS VERY
06830   C       SLOW.  TERM2 IS THE OLD DIA**(-0.11).  SO DIVIDE THE OLD
06840   C       COEFFICIENT BY TERM2 AND MULTIPLY IN THE NEW ONE.
06850   C
06860           DIA=SQRT(Y(NEQ1)/0.785)
06870           TNEW=DIA**(-0.11)
06880           ADJUST=TNEW/TERM2
06890           DO 115 I=1,NEQ
06900           MTC3(I)=MTC3(I)*ADJUST
06910   115     CONTINUE
06920           TERM2=TNEW
06930           IF(X.GE.X2) GO TO 106
06940           X=XARG
06950           TEST=ABS(Y(NFAST)/YOLD)
06960           IF(TEST.LT.0.01) GO TO 899
06970           GO TO 897
06980   106     WRITE (IOU,930) X
06990   930     FORMAT(1X,'THE FINAL MASSES FOR THE SLICK AT ',1PE8.1
07000         1,' HOURS ARE:')
07010           TMASS=0.
07020           DO 913 I=1,NEQ
07030           YM(I)=Y(I)*MWU(I)
07040           TMASS=TMASS+YM(I)
07050           YM(I)=YM(I)/YMSAVE(I)
07060   913     CONTINUE
07070           GONE=TMASS/TSAVE
07080           WRITE (IOU,900) (YM(I),I=1,NEQ)
07090           WRITE (IOU,922) GONE,Y(NEQ1)
07100           RETURN
07110           END
07120           SUBROUTINE FXYZ(XARG,MOLES,K,NEQ)
07130           REAL*4 MOLES,K,MTC3,MW
07140           COMMON /SPILL/ MTC3(30),VP(30),VLOC(30),RHO(30),Z,TERM2
07150         1,MW(30)
07160           COMMON /TALK/ NEQ1
07170           DIMENSION MOLES(30),K(30)
07180   C
07190   C       THE THICK AREA IS MOLES(NEQ+
07200   C
07210           SUM=0.
07220           DO 100 I=1,NEQ
07230           SUM=SUM+MOLES(I)
07240   100     CONTINUE
07250           DO 200 I=1,NEQ
07260           K(I)=MTC3(I)*MOLES(NEQ1)*VP(I)*MOLES(I)/SUM
```

```
07270          K(I)=-K(I)
07280    200   CONTINUE
07290          VOL=0 .
07300          DO 300 I=1,NEQ
07310          VOL=VOL+MOLES(I)/RHO(I)
07320    300   CONTINUE
07330          Z=VOL/MOLES(NEQ1)
07340          K(NEQ1)=(5.4E+05)*(Z**1.33)*MOLES(NEQ1)**0.33
07350          RETURN
07360          END
```

CODE FLOW CHART; OCTOBER 1981

<Entry: MAIN>

```
C       ***** CUTVAP.FOR *****
C
C       GET YOUR OUTPUT FROM CUTVAP.OUT/FILE:FORTRAN
C
      REAL*4 MW,MW1,KH,MTC1,MTC3,MASS,MOLES
      COMMON /COIL/ MW1,TC1,VC1,PC1,CNUM1,VIS1
      COMMON /SPILL/ MTC3(30),VP(30),VLOC(30),RHO(30),Z,TERM2
     1,MW(30)
      COMMON /PCODE/ IOU
      DIMENSION TB(30),API(30),A(30),B(30),TBL(30),APIL(30),VC(30)
     1,TC(30),PC(30),CNUM(30),TI0(30),HVAPI(30),HVAPZ(30)
     2,VOLL(30),VOL(30),MOLES(30),MTC1(30),VIS(30),VISK(30)
     3,VLOCK(30),SPGR(30),NC(30),NS(30)
      DIMENSION ANAME1(10),ANAME2(10)
      DATA ANAME2/'NORTH',' SLOP','E CRU','DE   ',6*'     '/
      DATA TBL/137.5,196.,226.,256.,283.,304.5,327.5,354.,380.5
     1,405.,426.5,449.5,470.,490.,509.5,528.,547.5,567.5,586.,602.
     2,621.,641.,650.,7*0./
      DATA APIL/71.6,59.7,55.,53.8,49.6,49.6,47.3,46.,44.,38.6
     1,38.8,37.2,35.4,33.9,33.1,32.2,31.8,31.6,30.7,29.6,28.,26.9
     2,14.6,7*0./
      DATA VOLL/1.5,2.1,2.,2.,2.,1.,2.,1.9,2.,2.,2.,2.,2.,2.
     1,2.,2.,2.,2.,2.1,2.,2.,1.8,55.,7*0./
      YI(X)=((1.-X)**0.38)/(X*X)
      OPEN(UNIT=32,DIALOG='DSKD:CUTVAP.OUT')
      IOU=32
      APIBL=25.7
      TYPE 501
  501 FORMAT(1X,'ENTER THE NUMBER OF TBP CUTS TO BE CHARACTERIZED
     1 ON 12')
      TYPE 502
  502 FORMAT(1X,'IF YOU HAVE NO INPUT DATA JUST ENTER 99')
      TYPE 503
  503 FORMAT(1X,'A 99 ENTRY WILL USE THE LIBRARY EXAMPLE')
      ICODE=1
      ACCEPT 504, NCUTS
  504 FORMAT(I2)
      IF(NCUTS.NE.99)  GO TO 505
```

```
      ICODE=2
      NCUTS=23
      APIB=APIBL
```

```
      DO 507 I=1,10
```

```
      ANAME1(I)=ANAME2(I)

      NU

      GO TO 333

  505 TYPE 516
  516 FORMAT(1X,'ENTER THE IDENTIFICATION OF THE CRUDE')
      ACCEPT 517, (ANAME1( ),I=1,10)
  517 FORMAT(10A5)
      TYPE 521
  521 FORMAT(1X,'ENTER THE BULK API GRAVITY')
      ACCEPT 11, API8

  333 DO 900 I=1,NCUTS

      GO TO (80,81), ICODE

   80 TYPE 10, I
   10 FORMAT(1X,'ENTER THE BOILING POINT AT 1 ATM TB IN  EG F
     I FOR CUT',I3)
      ACCEPT 11, TB(I)
   11 FORMAT(F10.0)
      TYPE 12, I
```

```
      TYPE 701
  701 FORMAT(1X,'DO YOU WANT TO CHANGE ANY?')

  712 ACCEPT 702, ANS
  702 FORMAT(A1)
      IF(ANS.EQ.'N')  GO TO 713

      TYPE 703
  703 FORMAT(1X,'ENTER THE DATA POINT NUMBER TO BE CHANGED ON 12')
      ACCEPT 504, N
      TYPE 704
  704 FORMAT(1X,'ENTER 1 TO CHANGE TB, 2 FOR API, 3 FOR VOLX')
      ACCEPT 705, IC
  705 FORMAT(I1)
      TYPE 706
  706 FORMAT(1X,'ENTER THE CHANGED DATA')
      GO TO (707,708,709), IC

  707 ACCEPT 11, TB(N)
      GO TO 710

  708 ACCEPT 11, API(N)
      GO TO 710

  709 ACCEPT 11, VOL(N)
```

```
710 TYPE 711
711 FORMAT(1X,'DO YOU WANT TO CHANGE ANYMORE?')
    GO TO 712

C
C       ALWAYS RENORMALIZE THE INPUT VOLUMES TO 100%.
C

713 VTOTAL=0.

    DO 720 I=1,NCUTS

    VTOTAL=VTOTAL+VOL(I)

720 CONTINUE

    DO 721 I=1,NCUTS
```

```
      VOL( I )= 100 .*VOL( I )/VTOTAL

  721 CONT I NUE

C
C       N O W  CHARACTER I ZE ALL THE CUTS EXCEPT THE LAST ONE WH I CH IS
C       THE BOTTOM OF THE BARREL..  USE  A  VAPOR PRESSURE OF 0 . AND A
C       MOLECULARE WEIGHT OF 600.
C
      MW(NCUTS) = 606 .
      VP(NCUTS)=0.
      NV=1
      NC1=NCUTS-1

      DO 1000 I = 1 , NCUTS

      API N=API( I )
      TBN=TB( I )
      IF( I . EQ . NCUTS) NV = 2
      CALL CHAR(API N, TON, AN, BN,NSN, NV)
C
C       THE CHARACTER I ZATION SUBROUTINE RETURNS THE LOG10 OF THE
C       KINEMATIC VISCOSITY (CENTISTOKES) A T 122 DEG F.
C
      VI SK( I )=10.**VIS1
      VLOCK( I )=ALOG(VISK( I ))
      C( ) TO (61 ,1000) , NV

   61 NS( I )=NSN
      A( I )=AN
      B( I )=BN
      MW( I )=MW1
      TC( I )=TC1
      TC( I )=TC( I )+459.
      VC( I )=VC1
      PC( I )=PC1
```

```
      CNUM(I)=CNUM1
C
C       FIND THE TEMPERATURE AT WHICH THE VAPOR PRESSURE IS 10 MMHG
C       BY USING NEWTON-RAPHSON WITH TB AS THE FIRST GUESS.
C
      NC(I)=0
      YTEN=ALOG10(0.01315/PC(I))
      X=(TB(I)+459.)/TC(I)

  140 EX=EXP(-20.*(X-B(I))**2)
      Y=-A(I)*(1.-X)/X-EX
      YOBJ=Y-YTEN
      VP(I)=PC(I)*10.**Y
      TEST=ABS(VP(I)-0.01315)
      IF(TEST.LT.0.001315)  GO TO 150

      NC(I)=NC(I)+1
      IF(NC(I).GT.20)  GO TO 160

      DY=A(I)/(X*X)+40.*(X-B(I))*EX
      BI=YOBJ-DY*X
      X=-BI/DY
      GO TO 140

C
C       UNSUCCESSFUL EXIT FROM NEWTON-RAPHSON
C

  160 TYPE 161, I,X,Y
  161 FORMAT(1X,'T10 FAILURE FOR',I4,' AT T = ',1PE10.3
     1 LOG10(P) = ',1PE10.3)
      GO TO 9999
```

```
C
C       SUCCESSFUL EXIT FROM NEWTON-RAPHSON
C

  150 T10(I)=X*TC(I)
C
C       CALCULATE THE HEAT OF VAPORIZATION AT 10 MMHG WITH THE
C       CLAPEYRON EQUATION AND USE WATSONS METHOD FOR THE
C       VAPOR PRESSURE BELOW 10 MMHG.
C
      TR2=T10(I)/TC(I)
      EX=92.12*(TR2-B(I))*EXP(-20.*(TR2-B(I))**2)
      HVAP=1.987*T10(I)*T10(I)*(2.303*A(I)/(TR2*TR2)+EX)/TC(I)
      HVAPI(I)=HVAP/MW(I)
      HVAPZ(I)=HVAP/(1.-TR2)**0.38

C
C       END OF TBP CUTS CHARACTERIZATION
C
      WRITE (IOU,162) (ANAME1(I),I=1,10)
  162 FORMAT(1H1,'SUMMARY OF TBP CUTS CHARACTERIZATION FOR: '
     1,10A5)
      WRITE (IOU,163)
  163 FORMAT(/,8X,'TB',8X,'API',8X,'VOL',9X,'MW',9X,'TC',9X,'PC'
     ,9X,'VC',10X,'A',10X,'B',8X,'T10',8X,'VIS',5X,'NC NS')

      DO 169 I=1,NCUTS
```

```
      WRITE (IOU,164) I,TB(I),API(I),VOL(I),MW(I),TC(I),PC(I),VC(I),A(I)
     1,B(I),T10(I),VISK(I),NC(I),NS(I)
  164 FORMAT(1X,I2,11(1X,1PE10.3),2(1X,I2))

  169 CONTINUE

      Will TE (IOU,180)
  180 FORMAT(//,1X,'TB = NORMAL BOILING TEMPERATURE, DEG F')
      WRITE (IOU,181)
  181 FORMAT(1X,'API = API GRAVITY')
      WRITE (IOU,182)
  182 FORMAT(1X,'VOL = VOLUME PER CENT OF TOTAL  CRUDE")
      WRITE (IOU, 183)
  183 FORMAT(1X,'MW = MOLECULAR WE IGHT')
      WRITE (IOU,184)
  184 FORMAT(1X, 'TC = CRITICAL TEMPERATURE, DEG RANK INE')
      WRITE (IOU,185)
  185 FORMAT(1X,'PC  =  CRITICAL PRESSURE,ATMOSPHERES')
      WRITE (I OU, 106)
  186 FORMAT(1 X,' VC = CRITICAL VOLUME, CC/MOLE')
      WRITE (I OU,187)
  187 FORMAT(1X,'A AND n ARE PARAMETERS IN THE VAPOR PRESSURE
     1 EQUATION')
      WRITE (IOU,191)
  191 FONHAT(IX,'TIO IS TUE TEMPERATURE IN DEG R WHERE THE VAPOR
     1 PRESSURE IS 10 MM HG')
      WRITE (I OU,192)
  192 FORMAT(1X,'VIS IS TRE KINEMATIC VISCOSITY IN CENTISTOKES
     I AT 122 DEC F')
      WRITE (I OU,188)
  188 FORMAT(1X,'NC=ERROR CODE,SHOULD BE LESS TRAN 29')
      WRITE (I OU, 189)
  189 FORMAT(1X, 'NS = ERROR CODE, SHOULD BE EQUAL TO 1')
      WRITE (IOU,190) NCUTS
  190 FORMAT(1X,'IGNORE THE ERROR CODES FOR COMPONENT NUMBER ',12)

  999 TYPE 153
  153 FORMAT(1X,'ENTER T IN DEG F FOn VP CALCULATION')
      ACCEPT 11 , XSAVE
      TK=(XSAVE-32.)/1.8+273.
      IF(XSAVE.LT.0.) GO TO 999
```

```
      XPRINT=XSAVE
      XSAVE=XSAVE+459.
C       CALCULATE THE VAPOR PRESSURE AT THE INPUT TEMPERATURE.
C
C       AT THIS POINT IF THE INPUT TEMPERATURE IS LESS THAN THE
C       10 MMHG TEMPERATURE USE THE WATSON-CLAPEYRON EQUATION.
C
C       THE WATSON-CLAPEYRON EQUATION IS:
C
C       LN(P2/P1) = (HVAPZ/(R*TC))*INTEGRAL
C
C       WHERE P1 = PRESSURE AT TR1, P2 = PRESSURE AT TR2, HVAPZ IS
C       THE HEAT OF VAPORIZATION AT ABSOLUTE ZERO.
C       R = 1.987 BTU/(LBMOLE, DEG R),
C       TC = CRITICAL TEMPERATURE AND INTEGRAL = VAPORIZATION
C       INTEGRAL BETWEEN TR1 AND TR2.
C
      WRITE (IOU,1001)
 1001 FORMAT(1H1,'CRUDE OIL CHARACTERIZATION AND PSEUDOCOMPONENT
     1 EVAPORATION MODEL')
      WRITE (IOU,1002) (ANAME1(I ,I=1,10)
 1002 FORMAT(1X,'IDENTIFICATION: ',10A5,/)
      WRITE (IOU,1003) XPRINT
 1003 FORMAT(1X,'VAPOR PRESSURE IN ATMOSPHERES AT  ,1PE10.3   DEG F')
      WRITE (IOU,1004)
 1004 FORMAT(/,12X,'VP',/)

      DO 2000 I=1,NC1

      X=XSAVE
      IF(X.LT.T10(I))  GO TO 144

      X=X/TC(I)
      EX=EXP(-20.*(X-B(I))**2)
      Y=-A(I)*(1.-X)/X-EX
      VP(I)=PC(I)*10.**Y
      GO TO 1999

  144 TR1=X/TC(I)
```

```
C
C       DO INTEGRAL BY SIMPSONS RULE WITH 21 POINTS
C
        TR2=T10(I)/TC(I)
        DH=(TR2-TR1)/20.
        RESULT=YI(TR1)
        TR=TR1

        DO 142 K=1,10

        TR=TR+DH
        RESULT=RESULT+4.*YI(TR)
        TR=TR+DH
        RESULT=RESULT+2.*YI(TR)

  142 CONTINUE

        TR=TR+DH
        RESULT=RESULT+4.*YI(TR)
        TR=TR+DH
        RESULT=DH*(RESULT+YI(TR))/3.
        P1=-4.33-HVAPZ(I)*RESULT/(1.987*TC(
        VP(I)=EXP(P1)

 1999 WRITE (IOU,168) I,VP(I)
  168 FORMAT(1X,I2,5X,1PE10.3)

 2000 CONTINUE
```

```
      WRITE (IOU,172) WTMOLE
  172 FORMAT(/,1X,'MEAN MOLECULAR WEIGHT OF THE CRUDE = ',1PE10.3)
C
C       CALCULATE AN AREA IN THE SAME WAY  T WILL BE CALCULATED
C       AS THE SLICK WEATHERS.
C
      Z=0.02
      VOLUM=0.

      DO 666 I=1,NCUTS

      VOLUM=VOLUM+MOLES(I )/RHO(I)

      AREA=VOLUM/Z
      DIA=SQRT(AREA/0.785)
C
C       CONVERT WIND SPEED TO M/HR.
C
      WINDM=1852.9*WINDS
C
C       THE MASS TRANSFER COEFFICIENT IS CALCULATED ACCORDING TO TWO
C       WAYS:  MTC1 IS ACCORDING TO MACKAY AND BASED ON CUMENE WITH
C       A MOLECULAR WEIGHT OF 120.  KH IS CUMENE'S MASS TRANSFER
C       COEFFICIENT.  THESE ARE OVER-ALL MASS-TRANSFER COEFFICIENTS.
C
      TERM1=0.015*WINDM**0.78
      TERM2=DIA**(-0.11)
C
C       KH INCLUDES THE SCHMIDT        FOR CUMENE.
C
      KH=TERM1*TERM2
      WRITE (IOU,560)
  560 FORMAT(1H1,'OVER-ALL MASS-TRANSFER COEFFICIENTS'
      WRITE (IOU,561) WINDS,WINDM
  561 FORMAT(/,1X,'WIND SPEED = ',1PE10.3,' KNOTS, OR ',1PE10.3
     1,' M/HR')
```

```
C
C       CALCULATE THE MEAN MOLECULAR WEIGHT OF THE CRUDE
C
      SUM=0.

      DO 170  =1,NCUTS

      SUM=SUM+MOLES(I)

      WTMOLE=0.

      DO 171  I=1,NCUTS

      WTMOLE=WTMOLE+MW(I)*MOLES(I)/SUM

   71 CONTINUE
```

```
      WRITE (IOU,616) DIA,AREA
  616 FORMAT(1X,'INITIAL SLICK DIAMETER = ',1PE10.3,' M, OR AREA = '
     1,1PE10.3,' M**2')
      WRITE (IOU,562) KH
  562 FORMAT(/,1X,'OVER-ALL MASS-TRANSFER COEFF CIENT FOR CUMENE = '
     1,1PE10.3,' M/HR',/)
      WRITE (IOU,579)
  579 FORMAT(3X,'CUT',12X,'M/HR',7X,'G-MOLES/(HR)(ATM)(M**2)'
     1,3X,'SPGR OF CUT')
      TEMP=(8.2E-05)*TK

      DO 564 I=1,NC1

      MTC1(I)=KH*0.93*SQRT((MW(I)+29.)/MW(I))
C
C       MTC3(I) IS THE OVER-ALL MASS-TRANSFER COEFFICIENT DIVIDED
C       BY R*T.  R=82.06E+06 (ATM)(M**3)/(G-MOLE)(DEG K)
C
      MTC3(I)=MTC1(I)/TEMP
      WRITE (IOU,566) I,MTC1(I),MTC3(    SPGR
  566 FORMAT(2X,I3,3(10X,1PE10.3))

  564 CONTINUE

      SPGRB=141.5/(API8+131.5)
      MASS=0.1502*BBL*SPGRB
      WRITE (IOU,565) BBL,MASS
  565 FORMAT(/,1X,'FOR THIS SPILL OF ',1PE10.3,' BARRELS, THE
     1 MASS IS ',1PE10.3,' METRIC TONNES')
      VOLUMB=VOLUM/0.159
      WRITE (IOU,581) VOLUM,VOLUMB
  581 FORMAT(/,1X,'VOLUME FROM SUMMING THE CUTS = ',1PE8.1,' M**3
     1, OR ',1PE10.3,' BARRELS')
C
C       CALCULATE THE VISCOSITY OF THE CRUDE AT  22 DEG F AND THE
C       ENTERED ENVIRONMENT TEMPERATURE.
C
      VISMIX=0.
```

```
      DO 571 I=1,NCUTS

      VISMIX=VISMIX+MOLES(I)*VLOGK(I)/TMOLES

  571 CONTINUE

      VISMIX=EXP(VISMIX)
      WRITE (IOU,572) VISMIX
  572 FORMAT(/,1X,'KINEMATIC VISCOSITY OF THE BULK CRUDE FROM
     1 THE CUTS = ',1PE8.1,' CENTISTOKES AT 122 DEG F')
      VISMIX=0.

      DO 573 I=1,NCUTS

      VIS(I)=VISK(I)*EXP(1923.*(1./XSAVE-0.001721)
      VLOG(I)=ALOG(VIS(I))
      VISMIX=VISMIX+MOLES(I)*VLOG(I)/TMOLES

      VISMIX=EXP(VISMIX)
```

```
      WRITE (IOU,574) VISMIX,XPRINT
  574 FORMAT(/,1X,'KINEMATIC VISCOSITY OF THE BULK CRUDE FROM THE
     1 CUTS = ',1PE8.1,' AT T = ',0PF5.1,' DEG F',/)
      NEQ=NCUTS
C
C       PRINT EVERY XP TIME INCREMENT
C
      XP=1.
      X1=0.
      MOLES(NCUTS+1)=AREA
      CALL BRKG4(MOLES,X1,X2,XP,NEQ)
      TYPE 590
  590 FORMAT(1X,'DO IT AGAIN?')
      ACCEPT 702, ANS
      IF(ANS.EQ.'Y')  GO TO 999

 9999 CONTINUE

      END
```

No source errors
9 K CORE USED

<Entry: CHAR>

```
      SUBROUTINE CHAR(API,TB,A,B,NS,NV)
      REAL*4 MW1
      COMMON /COIL/ MW1,TC1,VC1,PC1,CNUM1,VIS1
      DIMENSION C(2,6),T(2,6),P(4),V(2,6)
      DATA ((C(I,J),J=1,6),I=1,2)/6.241E+01,-4.595E-02,-2.836E-01
     1 ,1.256E-03,4.578E-04,5.279E-04
     2 ,4.268E+02,-1.007,-7.449,1.38E-02,1.047E-03,2.621E-02/
      DATA((T(I,J),J=1,6),I=1,2)/4.055E+02,1.337,-2.662,-2.169E-03
     1,-4.943E-04,1.454E-02
     2,412.2,1.276,-2.865,-2.800E-03,-3.707E-04,2.888E-02/
      DATA P/1.237E-02,0.2516,4.039E-02,-4.024E-02/
      DATA((V(I,J),J=1,6),I=1,2)/-0.4488,-9.344E-04,0.01583
     1,-5.219E-05,5.268E-06,1.536E-04
     2,-0.6019,1.793E-03,-3.159E-03,-6.1E-06,9.067E-07,3.522E-05/
C
C        THIS SUBROUTINE CHARACTERIZES A CUT OF CRUDE OIL WITH RESPECT
C        TO VAPOR PRESSURE.  THE INPUT REQUIRED IS API GRAVITY AND THE
C        BOILING POINT AT 1ATMOSPHERE.  THE OUTPUT IS A SWITCH NS
C        WHERE NS=1 MEANS THE VAPOR PRESSURE EQUATION CAN BE USED DOWN TO
C        10 MM HG AND NS=2 MEANS THE CLAPEYRON IMIUATION SHOULD BE USED.
c
c        THE VAPOR PRESSURE EQUATION IS:
C
C        LOG10(PR) = -A*(1.-TN)/TR - EXP(-20*(TR-B)**2)
C
C        WHERE PR = REDUCED PRESSURE, TR = REDUCED TEMPERATURE AND
C        A AND B ARE RETURNED BY THIS SUBROUTINE.
C
C        API = GRAVITY, TB = BOILING POINT AT 1ATMOSPHERE IN DEG F.
C        CALCULATE CRITICAL TEMPERATURE AND MOLECULAR WEIGHT.
C
      API2=API*API
      TB2=TB*TB
      CROSS=API*TB
C
C        CALCULATE THE VISCOSITY OF THE CUT.
C
      I=1
      IF(API.GT.35.)  I=2
      VIS1=V(I,1)+V(I,2)*TB+V(I,3)*API+V(I,4)*CROSS+V(I,5)*TB2
     1+V(I,6)*API2
      GO TO (99,101), NV
```

```
   99 I=1
      IF(TB.GT.500.)  I=2
      MW1=C(I,1)+C(I,2)*TB+C(I,3)*API+C(I,4)*CROSS+C(I,5)*TB2
     1+C(I,6)*API2
      TC1=T(I,1)+T(I,2)*TB+T(I,3)*API+T(I,4)*CROSS+T(I,5)*TB2
     1+T(I,6)*API2
      TCK=(TC1+459.)/1.8
C
c        CALCULATE THE VISCOSITY OF THE CUT.
C
```

```
      I=1
      IF(API.GT.35.)  I=2
      VIS1=V(I,1)+V(I,2)*TB+V(I,3)*AP +V( ,4 *CROSS+V( ,5)*TB2
     1+V(I,6)*API2
C
C       CALCULATE THE CARBON
C
      CNUM1=(MW1-2.)/14.
      X=ALOG10(CNUM1)
C
C       CALCULATE B FOR THE VAPOR PRESSURE EQUATION
C
      BPRIME=P(1)+X*(P(2)+X*(P(3)+X*P(4)))
      B=BPRIME-0.02
C
C       CALCULATE     CRITICAL VOLUME, CC/GMOLE
C
      VW=1.88+2.44*CNUM1
      VC1=VW/0.044
C
C       CALCULATE THE CRITICAL PRESSURE IN ATMOSPHERES
C
      PCP=20.8*TCK/(VC1-8.)
      PC1=PCP+10.
      TR=(TB+459.)/(TC1+459.)
      PR=1./PC1
      NS=1
      IF(TR.LE.B)  GO TO 100
      A=(ALOG10(PR)+EXP(-20.*(TR-B)**2))*TR/(TR-1.)
      GO TO 101
  100 NS=2
  101 RETURN

      END
```

```
No source errors.
8 K CORE USED
```

<Entry: BRKG4>

```
      SUBROUTINE BRKG4(Y,X1,X2,XP,NEQ)
      REAL*4 K1,K2,K3,K4,MTC3,MW,MWU
      COMMON /SPILL/ MTC3(30),VP(30),VLOC(30),RHO(30),Z,TERM2
     1,MW(30)
      COMMON /PCODE/ IOU
      COMMON /TALE/ NEQ1
      DIMENSION Y(30),YARG(30),K1(30),K2(30),K3(30),K4(30)
      DIMENSION YSAVE(30),YF(30),YMSAVE(30),YM(30),MWU(30)
C
C       RUNGA-KUTTA 4-TH ORDER NUMERICAL INTEGRATION FOR SIMULTANEOUS
C       DIFFERENTIAL EQUATIONS.  SEE C.R. WYLIE, PAGES 108-117 OR
C       D. GREENSPAN, PAGES 113-115.
C
C       THIS SUBROUTINE DOES THE PRINTING, THE INITIAL AND FINAL VALUES
C       ARE ALWAYS PRINTED.  PRINT THE RESULTS EVERY XP INCREMENT
C       IN X.
C
C       THE USER MUST WRITE SUBROUTINE FXYZ WHICH CALCULATES THE
C       K1, K2, K3, AND K4 VECTORS AS A FUNCTION OF X AND THE
C       CURRENT Y VECTOR.  INTEGRATION FOLLOWS THE REFERENCES AND
C       WAS TEST ON PROBLEM 5, PAGE 116 IN WYLIE.
C
C       THE FIRST NCUTS POSITIONS IN THE Y VECTOR ARE THE MOLES
C       OF THE COMPONENTS, POSITION NCUTS+1 IS THE AREA OF THE
C       SLICK.
C
      NEQ1=NEQ+1
      NS=1
      IN=1
      IKEEP=1
      TOTAL=0.
      TSAVE=0.

      DO 30 I=1,NEQ

      YSAVE(I)=Y(I)
      YMSAVE(I)=Y(I)*MW(I)
      MWU(I)=MW(I)
      TSAVE=TSAVE+YMSAVE(I
      TOTAL=TOTAL+Y(I)
```

```
   30 CONTINUE

      NDEL=0
      NFAST=0
      X=X1
      XW=X+XP
      WRITE (IOU,933)
  933 FORMAT(/,1X, ' COUNT THE CUTS I NTHEFOLLOWING  OUTPUT FROM LEFT
     1 TO RIGHT',/)
      WRITE (IOU,931 )
  931 FORMAT(1X, 'TOE INITIAL MOLES IN THE SLICK ARE: " )
        WRITE (IOU,900) (Y(I), I=1, NEQ)
  900 FORMAT( 11(1X,1PE10. 3))
      WRITE (I OU,932)
  932 FORMAT(/, 1X, 'THE INITIAL MASSES IN TOE SLICK ARE:')
      WRITE (100,900) (YMSAVE( I), I=1, NEQ)
      WRITE (I OU,902)
  902 FORMAT(/ )
C
C       CALCULATE DY/DX AND SET ITIE STEP SIZE TO APPROXIMATE
C       A 5% CHANGE IN THE MOST RAPIDLY CHANGING Y.   WHEN THIS
C       Y DECREASES BY A FACTOR OF 20, RESET THE STEP SIZE
C       ACCORDING TO THE NEXT  Y.
C       SONE Y'S WILL CHANGE SO FAST TOAT THEYWILL BE cONE
C       IN A FEW MINUTES.  THESE ARE DELETED BEFORE INTEGRATION
C       STARTS   AND NOTE) ON TOE PRINTED RESULTS.
C

  899 NFAST=NFAST+1

  890 CALL FXYZ(X, Y, K1, NEQ)
      H= 0.05*Y(NFAST)/K1 (NFAST)
      YOLD= Y ( NFAST )
      H= ABS(H)
      H2=H/2.
      GO TO (801,898), IN

  801 IF(H.GT. 0.05) GO TO 006
```

```
C
C       Y(NFAST) CHANGES TOO FAST TO CALCULATE, DELETE IT AND MOVE
C       EVERYBODY ONE SPACE TO THE LEFT.
C
C       WHEN YOU MOVE THE AREA BE SURE TO SUBTRACT THE CONTRIBUTION
C       OF THE CUT JUST DELETED.
C
      ISTART=1
      NFAST=1
      NDEL=NDEL+1
      NEQ=NEQ-1
      AD=Y(1)/RHO( )/Z

      DO      =1,NEQ

      I1=I+1
      Y(I)=Y(I1)
      VP(I)=VP(I1)
      MTC3(I)=MTC3(I1)
      YSAVE(I)=YSAVE(I1)
      VLOC(I)=VLOC(I1)
      RHO(I)=RHO(I1)
      MWU(I)=MWU(I1)
      YMSAVE(I)=YMSAVE(I1)

      Y(NEQ+1)=Y(NEQ+2)-AD
      WRITE (IOU,849) NDEL
  849 FORMAT(1X,'CUT ',I2,' GOES AWAY IN MINUTES  THEREFORE IT WAS
     1 DELETED AND THE CUTS RENUMBERED',/)
      GO TO 890
```

```
806 IN=2
    NEQ1=NEQ+

890 WRITE (IOU,871) H,NFAST
871 FORMAT(/,2X,'STEP SIZE OF ',1PE10.3,' IS BASED ON CUT ',I3,/)

897 IF(X.LT.XW)  GO TO 901

      XW=X+XP
      YTOT=0.
      TMASS=0.

      DO 31 I=1,NEQ

      YF(I)=Y(I)/YSAVE(I)
      YTOT=YTOT+Y(I)
      YM(I)=Y(I)*MWU(I)
      TMASS=TMASS+YM(I)
      YM(I)=YM(I)/YMSAVE(I)

   31 CONTINUE
```

```
      WRITE (IOU,432) X
  432 FORMAT(2X,'TIME = ', PE8.1          MASS FRACTION OF
       CUT REMAINING:')
      WRITE (IOU,911) (YM(I    =1
  911 FORMAT(14(1X,1PE8.1))
C
C       WHEN THE FRACTION REMAINING OF COMPONENT I GETS LOW,
C       SET ITS VAPOR PRESSURE AND MOLES EQUAL TO ZERO.
C

      DO 631 I=ISTART,NEQ

      IF(YF(I).GT.1.0E-08)  GO TO 631

      IKEEP=I+1
      VP(I)=0.
      Y(I)=0.

  631 CONTINUE

      ISTART=IKEEP
      CONE=TMASS/TSAVE
      WRITE (IOU,922) CONE,Y(NEQ1)
      FORMAT(2X,'FRACTION (BASED ON MASS) REMAINING IN THE SLICK
     1 = ',1PE8.1,', AREA = ',1PE8.1,' M**2')
      WRITE (IOU,902)
C
C       INCREASE XP TO 50 HOURS AFTER 50 HOURS OF WEATHERING.
C
      GO TO (701,901), NS
```

```
  701 IF(X.LT.50.)  GO TO 901

      NS=2
      XP=50.
C
C       TAKE A STEP IN TIME
C

   90' XARC=X

      DO 101 I=1,NEQ1

      YARC( )=Y(I)

      CALL FXYZ(XARG,YARG,K1,NEQ)
      XARG=X+H2
```

```
      DO 102 I=1,NEQ1

      YARG(I)=Y(I)+H*K1(I)/2.

  102 CONTINUE

      CALL FXYZ(XARG,YARG,K2,NEQ)

      DO 103 I=1,NEQ1

      YARG( )=Y(I)+H*K2(I)/2.

  103 CONTINUE

      CALL FXYZ(XARG,YARG,K3,NEQ)
      XARG=X+H
```

```
      DO 104 I=1,NEQ1

      YARG(I)=Y(I)+H*K3(I)

  104 CONTINUE

      CALL FXYZ(XARG,YARG,K4,NEQ)

      DO 105 I=1,NEQ1

      Y(I)=Y(I)+H*(K1(I)+2.*(K2(I)+K3(I))+K4(I))/6.

  105 CONTINUE

C
C       RECALCULATE THE OVER-ALL MASS-TRANSFER COEFFICIENTS OUTSIDE
C       THE DERIVATIVE SUBROUTINE.  THE DIAMETER DEPENDENCE IS VERY
C       SLOW.  TERM2 IS THE OLD DIA**(-0.11).  SO DIVIDE THE OLD
C       COEFFICIENT BY TERM2 AND MULTIPLY IN THE NEW ONE.
C
      DIA=SQRT(Y(NEQ1)/0.785)
      TNEW=DIA**(-0.11)
      ADJUST=TNEW/TERM2
```

```
      DO 115 I=1,NEQ

      MTC3(I)=MTC3(I)*ADJUST

    1

      TERM2=TNEW
      IF(X.GE.X2)  GO TO 106

      X=XARG
      TEST=ABS(Y(NFAST)/YOLD)
      IF(TEST.LT.0.01)  GO TO 899

      GO TO 897

  106 WRITE (IOU,930) X
  930 FORMAT(1X,'THE FINAL MASSES FOR THE SLICK AT   1PE8.
     1,' HOURS ARE:')
      TMASS=0.
```

```
0>)>>>>>>>>>>>>>>>>>>:      DO 913 I=1,NEQ
.                    1
<
.
.
.
.
.
<
.
.
.
<<<
.
0<_________________
                     913 CONTINUE

                     YM(I)=Y(I)* MWU(I )
                     TMASS=TMASS+ YM ( 1 )
                     YM(I)=YM(I)/YMSAVE(I) '

                     GONE= TMASS/TSAVE
                     WRITE (10U,900) (YM(I), I=1, NEQ)
                     WRITE (10U,922) GONE,Y(NEQ1)

                     RETURN

                     END
```

No source errors.
8 K CORE USED

<Entry: FXYZ>

```
      SUBROUTINE FXYZ(XARG,MOLES,K,NEQ)
      REAL*4 MOLES,K,MTC3,MW
      COMMON /SPILL/ MTC3(30),VP(30),VLOC(30),RHO(30),Z,TERM2
     1,MW(30)
      COMMON /TALK/ NEQ1
      DIMENSION MOLES(30),K(30)
C
C       THE THICK AREA IS MOLES(NEQ+1).
C
      SUM=0.

      DO 100 I=1,NEQ

      SUM=SUM+MOLES(I)

  100 CONTINUE

      DO 200 I=1,NEQ

      K(I)=MTC3(I)*MOLES(NEQ1)*VP(I)*MOLES(I)/SUM
      K(I)=-K(I)

      CONTINUE
```

```
      DO 300 I=1,NEQ

      VOL=VOL+MOLES(I)/RHO(I)

  300 CONTINUE

      Z=VOL/MOLES(NEQ1)
      K(NEQ1)=(7.4E+05)*(Z**1.33)*MOLES(NEQ1)**0.33

      ETU1

      END
```

No source errors.
0 K CORE USED

APPENDIX B

METHODS FOR MICROBIAL DEGRADATION STUDIES

## $^{14}$C-Hydrocarbon Mineralization Assay

Three $^{14}$C-labeled hydrocarbon substrates were utilized for the determination of hydrocarbon degradation potential, defined here as the percent mineralization to $^{14}CO_2$ : n(1-$^{14}$C) hexadecane (53.6 mCi/mmol , Amersham), (1(4,5,8)-$^{14}$C) naphthalene (5 mCi/mmol, Amersham), and (1(4,5,8)-$^{14}$ C) methylnaphthalene (5 mCi/mmol, Bionuclear). Working solutions were prepared with hexane or benzene as solvents to give 0.1 $\mu$Ci/ $\mu$l activities, stored at 4°C, and assayed weekly for radioactivity to insure consistency in the concentrations of substrates. Seawater aliquots (50 ml) from each of the experimental tanks and the incoming seawater were transferred to 100 ml sterile serum bottles and spiked with 0.5 $\mu$Ci of the $^{14}$C-labeled hydrocarbons, one compound per sample with each sample prepared in duplicate. Controls were killed with 1 $\mu$M $HgCl_2$ prior to spiking with the labeled compound.

The spiked seawater samples were capped with sleeve stoppers and incubated in the dark for 24 hours at in situ temperatures in a seawater bath, After the incubation period the stoppers were replaced with identical stoppers fitted with a polypropylene "center well" containing a 25-mm by 30-mm rectangle of Whatman No. 1 filter paper folded into an accordian-pleated array and wetted with 200 $\mu$l of 1N NaOH. The samples were then acidified to pH 2.0 by injection of 0.5 ml of 1 N $H_2SO_4$ (through the sleeve stopper) with a hypodermic syringe. After 2 hours the filter paper was transferred to a second 100 ml serum bottle containing 1 ml of 1N $H_2SO_4$ which was quickly capped with a sleeve stopper fitted with a center well (as before) and a wick which had been wetted with 200 $\mu$l of phenethylamine.

After 12-14 hours the phenethylamine wicks were transferred to a scintillation vial containing 10 ml of Beta-Phase cocktail (West Chem Products) and assayed for radioactivity on a Beckman LS100C scintillation counter.

The resulting counts for duplicates were averaged and corrected for the control counts prior to further data treatment. The data (in counts per minute) were converted to $\mu$g/liter·day by the following equation.

$$\mu g/\ell \cdot day = (cpm)\left(\frac{1\ dpm}{0.9\ cpm}\right)\left(\frac{1\ \mu Ci}{2.22 \times 10^6\ dpm}\right)\left(S.A.^{-1}\right)\left(m.w.\right)\left(\frac{1000\ ml}{1\ \ell}\right)\left(\frac{1}{50\ ml}\right)\left(\frac{1}{day}\right)$$

where a counting efficiency of 90% was utilized, SA is the specific activity in $\mu$Ci/$\mu$ mole, and M.W. is the molecular weight of the particular labeled substrate.

References: WATSON et al. (1971); CAPARELLO and LA ROCK (1975); WALKER and COLWELL (1976); HODSON et al. (1977).

## $^3$H-Thymidine Incorporation

Thymidine (methyl -$^3$H) solutions were stored as supplied (20 Ci/mmol, New England Nuclear) in 70% aqueous ethanol for maximum stability. Working solutions were prepared by evaporating to dryness the appropriate volume under a stream of dry filtered air and reconstituting with distilled water. These solutions were stored at 4°C and checked weekly for radioactivity.

Duplicate seawater aliquots (10 ml) from each experimental aquarium and the incoming seawater were spiked with 5nM of labeled thymidine and incubated in the dark at in situ temperatures for 1 hour. Incubation uptake was terminated by filtration through a 25-mm dia. type HA membrane (0.45 $\mu$m nominal pore size, Millipore Corp.). After filtration the vacuum was stopped and 10 ml of ice-cold (< 5°C) filtered (sterile) seawater was added to cool the filter. This was filtered through and the vacuum was stopped priorto addition of 15 ml ice-cold (< 5°C) 5% trichloroacetic acid (TCA) to extract the soluble thymidine pools from the cells. Temperature control is critical during the extraction as a temperature rise above 10"C for TCA will hydrolyse DNA and allow incorporated label to solubilize and pass through the filter. After

3 min. the vacuum was started and the filter was rinsed twice with ~5 ml ice-cold 5%, TCA, and then placed in a scintillation vial . Ethyl acetate (1 ml) was added to dissolve the filter; 10 ml of Beta-Phase cocktail was added and the radioactivity was assayed by liquid scintillation spectrometry.

The resulting counts for duplicates were averaged and corrected for Poisoned controls (1 $\mu$M $HgCl_2$) and a counting efficiency of 35%. The data were converted to nmoles/liter day of incorporation by the formula:

$$\text{n moles}/\ell\cdot\text{day} = (\text{cpm})\left(\frac{1\ \text{dpm}}{0.35\ \text{cpm}}\right)\left(\frac{1\ \text{Ci}}{2.22 \times 10^{12}\ \text{dpm}}\right)\left(\frac{1\ \text{m mol}}{20\ \text{Ci}}\right)\left(\frac{10^6\ \text{n mol}}{\text{m mol}}\right)\left(\frac{24\ \text{hr}}{\text{day}}\right)\left(\frac{1}{0.015\ \ell}\right)\left(\frac{1}{1\ \text{hr}}\right)$$

References: FUHRMAN and AZAM (1980); FUHRMAN et al. (1980); FUHRMAN and AZAM (in press, 1981)

## $^3$H-Leucine and $^3$H-Glucose Uptake

The procedure for both substrates was identical except for the amino acid leucine, in that a larger sample was prepared such that an aliquot could be saved and preserved for the autoradiography procedure (details in this section).

Working solutions of $^3$H-Leucine (60 Ci/mmol, New England Nuclear) were prepared by diluting an aliquot of the stock solution into distilled water. The $^3$H-Glucose solutions (30 Ci/mmol, New England Nuclear) were prepared by evaporating an aliquot under a stream of dry, filtered air followed by reconstitution in distilled water. All solutions were stored at 4°C and assayed weekly for radioactivity to check stability.

Each experimental aquarium and the incoming seawater was sampled in duplicate and controls were killed with 1 M $HgCl_2$ prior to addition of radiolabeled substrate. To each sample (10 ml for $^3$H-Glucose; 15 ml for $^3$H-Leucine) 50 $\mu$l (1.5 $\mu$Ci) of radiolabeled compound was added, followed by incubation for 2 hr. in the dark at in situ temperature.

The incubation was terminated by sample filtration through a I-1A membrane (0.45 $\mu$m nominal pore size, Millipore Corp.), followed by several washes with filter-sterilized seawater to remove any nonincorporated label. After filtration, each filter was placed in a scintillation vial, and 1 ml Ethyl acetate added to dissolve the membrane. After approximately 10 min., 10 ml of Beta-Phase cocktail was added and the sample assayed for radioactivity by liquid scintillation spectrometry. Duplicates were averaged and corrected for control blanks, and the resulting counts were converted to uptake in nmoles/liter day with the formula:

$$\text{n moles}/\ell\cdot\text{day} = \text{cpm}) \left(\frac{1 \text{ dpm}}{0.35 \text{ cpm}}\right)\left(\frac{1 \text{ Ci}}{2.22 \times 10^{12} \text{ dpm}}\right)\left(\text{S.A.}^{-1}\right)\left(\frac{10^6 \text{ n mol}}{\text{m mol}}\right)\left(\frac{24 \text{ hr}}{\text{day}}\right)\left(\frac{1}{2 \text{ hr}}\right)\left(\frac{1}{0.015\,\ell}\right)$$

where a counting efficiency of 35% was utilized and S.A. is the specific activity (in Ci/mmol) for the labeled substrate.

References: AZAM and HOLM-HANSEN (1973); FUHRMAN et al . ( 1980).

## Epifluorescence Enumeration

Seawater samples (10-15 ml) from each experimental aquarium and the incoming seawater were immediately preserved with 4% filter-sterilized formalin (buffered with $Na_2B_4O_7$), and the cellular DNA was stained to fluoresce with Acridine orange (0.01%, 2 min.) prior to filtration. The Nucleopore polycarbonate filters were stained prior to use with Irgalan black (to eliminate autofluorescence) and a type AA (0.8 $\mu$m, Millipore) membrane was

used as a back filter to distribute the vacuum evenly. After filtration, the filter was mounted on a microscope slide with a cover slip affixed with paraffin oil. Blanks were prepared in a similar fashion except that filter-sterilized seawater (GS, 0.2 $\mu$m, Millipore Corp.) was preserved and stained.

The slides were examined by epifluorescence microscopy and counted in a random fashion by grids. All counts for each grid were averaged (10 grids per slide) for duplicate slides and the data converted to cells x $10^6$/ml seawater.

References: HOBBIE et al. (1977); FUHRMAN and AZAM (1980).

Autoradiography Assay

The micro-autoradiographic technique provides for simultaneous examination by phase contrast microscopy of bacterial cells stained with acridine orange and labeled with developed silver grains. The method of preparation provides for orientation of bacteria between the photographic emulsion and the microscope objective to prevent visual interference by the silver grains.

The 5 ml aliquots from the $^3$H-leucine uptake assays (preserved with 4% formalin) were stained with sterile-filtered 0.01% acridine orange for 1 min., followed by filtration through a 0.2 $\mu$m pore size nucleospore membrane (25 mm dia.). A type AA filter (0.8 $\mu$m, Millipore) was used as a back filter for even vacuum distribution. The filter was rinsed with sterile, filtered, distilled water, and kept damp for subsequent transfer of cells onto the surface of a mounted gelatin-coated coverslip. (Details of the gelatin-coated coverslip preparation are presented elsewhere - see References below).

Resulting autoradiograms were prepared in total darkness with Kodak NTB2 Nuclear track emulsion coating, dried, and exposed at 4°C. After the appropriate exposure time, the autoradiograms were developed, fixed and further prepared as detailed elsewhere (see References below). Bacteria were

counted by epi fluorescence microscopy and silver gain clusters were counted by transmitted phase contrast microscopy.

References: MEYER-REIL (1978); FUHRMAN and AZAM (in press, 1981).

## METHODS FOR HYDROCARBON ANALYSES AND PHOTOCHEMICAL/MICROBIAL OXIDATION PRODUCT CHARACTERIZATION

### Volatile Hydrocarbon Analyses

Volatile hydrocarbons are sampled from the air above the slick in the evaporation/dissolution chamber (or the flow-through outdoor tanks in Alaska) by vacuum-pumping measured volumes of air through 1/8 in. ID x 12 in. long stainless tubes packed with Tenax® GC polymer. For each sample, two tubes are connected in series with Swagelok fittings, and prior to and immediately after sampling, all tubes are sealed with Swagelok endcaps and plugs. Sampling is achieved by use of a Gast Mfg. Corp. vacuum pump attached to the Tenax® traps via flow regulators and flexible Teflon tubing. Air velocities above the slick in the evaporation/dissolution chamber are measured with a Kurz air velocity meter 4m above the oil/seawater interface.

Before each sample is obtained, the Tenax® trap's flow velocity is checked with a bubble flow meter. Approximately 60 second samples are generally obtained at flow rates ranging from 20 to 30 ml/min; thus, sample volumes ranged from 20-30 ml.

Water samples for analysis of dissolved lower-molecular-weight aliphatic and aromatic hydrocarbons are taken in Pierce septum-capped vials for subsequent purge and trap analysis by GC/MS techniques similar to those developed by Bellar and Lichtenberg (1974) and others.

Following collection, the water samples are refrigerated (no preservatives are added), and they are maintained at 3°C until analysis. Capped stainless-steel Tenax® traps are stored at ambient temperature until analysis.

The Tenax® air samples are analyzed by heat resorption followed by Flame Ionization Detector (FID) gas chromatography on a Hewlett Packard 57330A

instrument or gas chromatography/mass spectrometry (GC/MS) using a Finnigan 4021 quadruple instrument. The heat resorption is accomplished by installing the Tenax® traps in a Tekmar liquid sample concentrator (LSC-2) interfaced to the injection port system of either the FID GC or GC/MS (PAYNE et al., 1980b).

At the time of resorption (5 min. at 180°C at 20 ml/min He flow) the gas chromatographic column (packed 6 ft. x 22 mm I.D. SP-1000) and oven are cryogenically cooled to 30°C. Following resorption, the oven is programmed rapidly (30°C/min) to 100°C and then from 100°C to 200°C at 10°C/min. The final temperature of 200°C is held for the duration of the chromatographic run. A GC column flow rate of 20 ml/min He is also used and the injector temperature is held at 200°C.

The effluent from the gas chromatography is then analyzed by FID on the HP-GC or it is passed through a glass jet separator for enrichment and then directly into the ion source of the GC/MS (operated in the electron impact-mode at 300°C). Spectra are acquired by operating the ion source at 70eV from 35 to 300 amu in 1.95 sec. A hold time of 0.05 sec is used to allow the electronics to stabilize before the next scan. The ion source is tuned for maximum sensitivity with perfluorotributylamine and the ion fragments at m/e 69 and m/e 219 are calibrated to give a 2.5:1 ratio; the electron multiplier is operated at 1600V with the preamplifier gain at $10^{-7}$ amps/volt. GC/MS data acquisition is initiated at the moment of resorption. Typically, 900-1000 scans are acquired for each data file.

The water samples stored in Pierce vials are allowed to come to room temperature and 5-ml aliquots are withdrawn and injected into the purge device of the LSC-2. Before purging in mass spectrometry operations, 100 ng each of three internal standards, dichlorobutane (m/e 55), bromochloromethane (m/e 130), and bromochloropropane (m/e 77) are added. This allows correction of recovered values for matrix effects and corrects for differences in ionization potential, lens voltage, etc., among runs. Instrumental conditions are identical to those described for Tenax® column analysis.

Before analyses with either instrument, response factors are determined for 10-12 target aliphatic and aromatic compounds of interest by spiking several known mixed standards into salt water blanks which are then analyzed as samples (PAYNE et al., 1980b).

Higher Molecular Weight Petroleum Hydrocarbon Analyses

Water sediment and oil/mousse samples are analyzed by procedures which basically involve: 1) extraction, 2) fractionation into aliphatic, aromatic and polar constituents by liquid/solid ($SiO_2$) column chromatography and analysis by FID capillary gas chromatography and capillary gas chromatography/mass spectrometry. Specific details with regard to these analytical Procedures (including instrument calibrations, sensitivity, data reduction, etc.) are presented in Appendix C to this report (Methods Section, Page 4 of "Chemical Weathering of Petroleum Hydrocarbons in Sub-Artic Sediments : Results of Chemical Analyses of Naturally Weathered Sediment Plots Spiked with Fresh and Artificially Weathered Cook Inlet Crude Oil").

Water samples from the flow-through seawater systems are collected in 20-liter carboys and pH was adjusted to 2.0. Three hundred-fifty ml of methylene chloride is then added to each carboy (approximately 200 ml of methylene chloride. goes into solution on the first addition) and the mixture is stirred vigorously for 3 minutes. The methylene chloride is removed by pressurizing the carboys with $N_2$ and forcing the methylene chloride through a stainless steel syphon tube into a separator funnel. This procedure is repeated two more times. The methylene chloride extract is concentrated to 100 ml in K-D concentrators and then passed through sodium sulfate to remove the residual water. The anhydrous methylene chloride extract is then concentrated to 2 ml and solvent-exchanged to hexane. The concentrate is then fractionated on silica gel using the three fraction schemes describedin Appendix C, page 4 of "Chemical Weathering of Petroleum Hydrocarbons in Sub-Artic Sediments: Results of Chemical Analyses of Naturally Weathered Sediment Parts Spiked with Fresh and Artificially Weathered Cook Inlet Crude Oil".

APPENDIX C

# CHEMICAL WEATHERING OF PETROLEUM HYDROCARBONS IN SUB-ARCTIC SEDIMENTS: RESULTS OF CHEMICAL ANALYSES OF NATURALLY WEATHERED SEDIMENT PLOTS SPIKED WITH FRESH AND ARTIFICALLY WEATHERED COOK INLET CRUDE OILS

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## OBJECTIVES

The primary goal of this program was to examine the biological and chemical impact of fresh and weathered crude oil after its incorporation into sub-arctic sedimentary regimes. The experiments that were used in this program were designed by Dr. Robert Griffith and his colleagues at Oregon State University to study one-year time series changes in biological productivity, recruitment and recolonization as a function of the chemical composition of the oil within the sedimentary study plots.

In an effort to assist Dr. Griffith in this program, the Environmental Chemistry and Geochemistry Division of Science Applications, Inc. (SAI) undertook detailed chemical analyses of the sediment samples used in these experiments. Specifically, hydrocarbon profiles (concentrations) were determined in control and experimental sedimentary plots which had been spiked with three different levels of fresh and artificially weathered Cook Inlet Crude Oil. These sediments were examined: first, after the initial spiking, and second, after one year of natural weathering in the sedimentary regime at Kasitsna Bay, Alaska. Additional studies were also undertaken in Sadie Cove, Alaska, where oiled sediments were spiked with Chiton and starch before deployment into the field, to determine if biotic weathering processes were controlled by limited nutrient concentrations.

Results of the hydrocarbon analyses from these experiments are presented in this section.

## IMPLICATIONS FOR OFF-SHORE OIL AND GAS DEVELOPMENT

Many investigators have long suspected that spilled oil on the water surface or in the water column does not constitute as great an environmental threat as oil which has been incorporated into sedimentary regimes. ironically, in the case of most major oil spills and laboratory studies, the sediments have been found to be the ultimate repository or sink for the bulk of the higher molecular weight components in the released oil (Jordan and Payne, 1980, D'Oxouville et al., 1979; Meyers, 1978; Mayo et al., 1978; Gearing et al., 1979; Winters 1978; Meyers and Quinn 1973; Zurcher and Thuer 1978; Bassin and Ichiye 1977). Once incorporated into the sediments, many of the unweathered toxic components of oil are retained unaltered for extended periods (Teal et al., 1978; Mayo et al., 1978) causing a variety of long term pertibations to plants, organisms and the physical (areobic vs. an aerobic) nature of the sediment itself. If contaminant concentrations reach high enough levels, the biological productivity of an entire area may be completely destroyed immediately after the spill impact, and residual toxic levels may prevent recolonization of native species for a number of years (American Institute of Biological Sciences, 1978). This is a significant problem in areas of high productivity or in sedimentary regimes critical to the survival of juvenile species. Alternately, competing species with different degrees of tolerance to oil could opportunistically recolonize an area, thus further altering the biological balance at the spill site for years.

In these experiments, we attempted to determine the levels or concentrations of oil in sub-Arctic sediments that could cause limited recovery or long term damage to an area. We also sought to determine concentrations and conditions under which specific compounds in the complex hydrocarbon mixture are selectively removed due to biotic and abiotic processes after incorporation of oil into the sediments. The results of these studies indicate that spiked levels of oil approaching 50 parts per thousand (ppt) (total oil wt/wt) cause extensive and significant long term damage to sub-Arctic sediments, and that little or no significant additional weathering (removal of toxic components) occurs at least up to one year following initial exposure. This was observed when both fresh and artificially weathered crude oils were spiked into the sedimentary matrix at the 50 ppt level. Similar trends were observed at the 1 ppt level, but some evidence of selective lower molecular weight hydrocarbon degradation after one year was found. The experimental results also suggest that at levels of oil approaching 50 ppt, the biotic utilization of specific hydrocarbon components is not inhibited by limited nutrient levels but rather by the toxicity of the oil itself.

A recommendation which can be drawn from these results is that in oil spill prevention, mitigation, and clean-up efforts, every attempt should be made to prevent oil from reaching sub-Arctic sediments partitularly in low energy nearshore subtidal regimes where high biological productivity is observed.

## METHODS

Techniques for artificially weathering Cook Inlet Crude Oil and subsequent spiking, homogenization, and deployment of sediment into the experimental trays for in situ weathering are described elsewhere. Subsamples of the spiked and control sediments from the experimental trays were frozen at the initiation of the experiment and again after one year in the field. All frozen sediment samples were shipped on ice to SAI's Trace Environmental Chemistry Laboratory in one lot on 17 October 1980, where they were subsequently stored at -4°C until analyses were begun.

### Extraction

Each sediment sample was extracted using a shaker-table procedure which is similar to that described by Payne et al. (1978) and Brown et al. (1980) and which has been shown to yield comparable results to Soxhlet extraction (MacLeod and Fischer, 1980; and Payne et al., 1979). Briefly, the thawed sediment was placed in tared 500 ml Teflon jars and a wet weight was determined. Approximately 50 ml of methanol was added to the sediment for water removal, and the jars were sealed and agitated on a shaker table for 15 minutes. The jars were then centrifuged at 3000 rpm for 20 minutes at room temperature and the supernatant was decanted off and saved, and the drying procedure was repeated. After the second drying step, 150 ml of methylene chloride ($CH_2Cl_2$) and methanol (65:35 v/v) were added to the jars and agitation

was continued for 12 hours. The samples were centrifuged, the supernatant saved, and the procedure was repeated with the agitation occurring for a period of 6 hours. The methanol-water washes and the methanol-methylene chloride extracts were combined in a separator funnel and back extracted with 400-500 ml of saturated sodium chloride in distilled water which had been previously extracted with hexane. The lower layer ($CH_2Cl_2$) was removed and the water phase was back extracted with three additional 100 ml aliquots of $CH_2Cl_2$. The combined $CH_2Cl_2$ extracts were concentrated to approximately 100 ml using a Kuderna-Danish (K-D) apparatus, and dried by passage through a column of sodium sulfate followed by additional elution with $CH_2Cl_2$. The dried extract was concentrated to about 10 ml using a K-D apparatus arid solvent exchanged (3x) into hexane, followed by solvent reduction to 1-2 ml in preparation for column chromatography.

## Liquid Column Chromatography

To fractionate the sediment extracts, a three-part fractionation scheme was employed to separate the aliphatic, aromatic, and polar compounds (Payne, et al., 1980). A 10 mm I.D. x 23 cm long column with a 16 ml pore volume was packed with 1.5 cm of activated copper at the base of the column (to remove elemental sulfur), followed by a hexane slurry of 60/200-mesh silica gel that had been cleaned with $CH_2Cl_2$ and activated at 210°C for 24 hours. The elution scheme was as follows:

| Fraction/Solvent | Amount | Compound Class |
|---|---|---|
| 1. Hexane | 30 ml | Aliphatic hydrocarbons |
| 2. Hexane:Benzene 50:50 | 45 ml | Aromatic hydrocarbons |
| 3. 50% $CH_3OH$ ,n $CH_2Cl_2$ | 60 ml | Polar compounds |

## Gas Chromatographic Analysis

All gas chrmatographic results were obtained on a Hewlett-Packard 5840A gas chromatography equipped with an 18835A glass capillary inlet system and flame ionization detector. The microprocessor-based instrument was interfaced to a Texas Instruments Silent 700 ASR data terminal equipped with casette tape drive, allowing permanent storage of calibration data, retention times, and peak areas required for the data reduction system.

A 30-meter J&W Scientific Co. SE-54 wall-coated open tubular fused silica capillary column was utilized for the desired chromatographic separations. Temperature programming used with this column included:

| | |
|---|---|
| Initial Temperature | 50°C for 5 minutes |
| Program Rate | 3.5°C/min |
| Final Temperature | 275° for 60 minutes |

The injection port and detector were maintained at 280° and 350°C, respectively. All injections were made in the splitless mode of operation with an injection port backflush 1 minute into the run.

Constant injection volumes of 1.0 μl were analyzed automatically using a Hewlett-Packard model 7671A Automatic Liquid Sampler, increasing precision substantially relative to manual injection.

## Gas Chromatogram Data Reduction

Hydrocarbon concentrations for individual resolved peaks in each gas chromatogram were calculated on a DEC-10 System Computer using the formula given in equation 1. This particular example is of the program used for seawater analysis. Operator-controlled modification of the DEC-10 program allows similar data reduction on sediments, tissues, or individual oil (mousse) samples.

$$\mu g \text{ compound X/L seawater} = (A_X) \times (R.F.) \times \left[\frac{P.I.V. + 2}{Inj.S.Vol.} \cdot \frac{Pre\text{-}C.S.\ Vol.}{Post\text{-}C.S.Vol.} \cdot \frac{100}{\%NSL \text{ on LC}} \times \frac{100}{\%DW/FW} \times \frac{1}{\text{liters}}\right] \quad (1)$$

where:

| | |
|---|---|
| Ax | = the area of peak X as integrated by the gas chromatograph (in arbitrary GC area units) |
| R.F. | = the response factor (in units of μg/GC area unit) |
| P.I.V. + 1 | = the post-injection volume (in μl) from which a 1-μl aliquot had been removed for analysis by GC (measured by syringe immediately following sample injection) |
| Inj.S.Vol. | = the volume of sample injected into the GC (always 1.0 μl as measured by an HP Automatic Liquid Sampler) |

| | | |
|---|---|---|
| Pre-C.S.Vol. & Post-C.S. Vol. | = | the total solvent volumes before and after an aliquot is removed for gravimetric analysis on a Cahn electrobalance |
| %NSL on LC | = | the percent of sample non-saponifiable lipid used for $SiO_2$ column chromatography |
| %DW/FW | = | the percent dry weight of wet weight in the sediment tissue, or oil sample being analyzed |
| liters | = | liters of seawater initially extracted (or grams wet weight of oil or sediment). |

During analysis of the extracts, the 5840A gas chromatography was recalibrated after every 8 to 10 injections, and individual response factors were calculated for all detected even and odd n-alkanes between $nC_8$ and $nC_{32}$. Concentrations of other components (e.g., branched and cyclic) that eluted between the major n-alkanes were calculated by linear interpolation of the adjacent n-alkane response factors and the unknown compound peak's KOVAT index. By incorporating the post-injection volume (PIV) into the calculation, the amount of hydrocarbons measured in the injected sample were converted to the total hydrocarbon concentration in the sample.

Unresolved complex mixtures (UCM's) were measured in triplicate by planimetry; the planimeter area was converted to the gas chromatograph's standard area units at a given attenuation and then quantitated using the average response factors of all the n-alkanes occurring within the range of the UCM, as shown in equation 2.

$$\frac{\mu g\ UCM}{liter} = Area_p \times (Conf.\ F) \times \frac{S.\ Att.}{Ref.\ Att.} \times (\overline{R.F.}_{a-b}) \times [\ldots] \qquad (2)$$

where:

| | |
|---|---|
| Area | = UCM area in arbitrary planimeter units, |
| Conv. F. | = a factor for converting arbitrary planimeter units to GC area units at a specific GC attenuation, |
| S. Att. and Ref. Att. | = the GC attenuation at which the sample chromatogram was run and the reference attenuation to determine the conversion factor (Conv. F.), respectively, |
| $R.F._{a\ b}$ | = the mean response factor for all sequential n-alkanes (with carbon numbers a to b) whose retention times fall within the retention time window of the UCM, and |
| [...] | = the same parameters enclosed in brackets in equation 1. |

Confirmation of KOVAT index assignment to n-alkanes was done by computer correlation with n-alkane standard retention times and direct data-reduction-operator input.

Assignment of a KOVAT index to each branched or cyclic compound eluting between the n-alkanes was done by interpolation using the unknown compound and adjacent n-alkane retention times. Assignment of KOVAT indices to peaks in the aromatic fraction was made by direct correlation of unknown peaks with retention times from the n-alkane and aromatic standard runs completed prior to sample injection (Payne, et al., 1978b).

Capillary Gas Chromatography Mass Spectrometry

Selected extractable organic compounds previously analyzed by fused silica capillary column-FID GC were also subjected to fused silica capillary gas chromatography/mass spectrometry (GC/MS). A 30-meter J&W Scientific Co. SE-54 capillary column (0.25-mm I.D. with a film thickness of 25 µm was used to achieve chromatographic separation in a Finnigan 4021 quadruple mass spectrometer. The capillary system was operated in the splitless (Grob-type) mode. The static time upon injection was 0.8 min, after which time the injection port was backflushed with the split and septum sweep flows at a combined rate of 35 ml/min. Linear velocity was set at 35 cm/see, which gave a flow rate of 1.18 ml/min. The GC was programmed to remain isothermal at 30°C for 1.5 min following injection, elevated at 4°C/min from 30 to 160°, and 8°C/min from 160-275°, after which the oven was held isothermally at 275°C for approximately 20 minutes.

The flexible fused silica column was routed directly into the ion source of the mass spectrometer, which was operated in the electron impact mode at 70eV with the lens potentials optimized for maximum ion transmission. The quadruple offset and offset programs were adjusted to yield a fragmentation ratio for perfluorotributylamine m/e 69-to-219 of 4:1. This tuning yields quadruple electron impact spectra that are comparable to magnetic sector electron impact spectra, thereby allowing optimal matches in the computer search routines used in the INCOS data system that scans the quadruple rods from 35-475 amu in

0.95 sec. A hold time of 0.05 sec between scans allows the electronics to stabilize prior to the next scan. The mass spectrometer was tuned at the beginning of each day using perfluorotributylamine. A calibration was accomplished with a routine diagostic fit of 2% mass accuracy. Prior to analysis of samples, standard mixtures of n-alkanes, pristane, phytane, and mixed aromatic hydrocarbons were injected.

## RESULTS AND DISCUSSION

### Time Zero Samples

Figure 1 presents the FID capillary gas chromatograms obtained on the control sediment samples taken from Kasitsna Bay at the beginning of the spiked sediment experiments. The most characteristic feature in the aliphatic fraction chromatogram, A, is the predominance of odd numbered n-alkanes in the molecular weight range of $nC_{21}$ to $nC_{29}$, (RT 56.53; 62.12; 67.03; 71.93; 78.77) reflecting biogenic input. The sample also contains very low levels of $nC_{17}$ and pristane (RT 44.55; 44.75) and $nC_{18}$ and phytane (RT 47.40; 47.83). The three major components at retention times 31.21, 35.77 and 43.08 are internal spikes and a GC recovery standard (triisopropylbenzene, 31.21; n-decylcyclohexane, 43.08; and hexamethylbenzene, 35.77, respectively). There is no apparent evidence of any petroleum contamination and there appears to be a small cluster of branched and unsaturated biogenic hydrocarbons between $nC_{20}$ and $nC_{21}$. The aromatic fraction chromatogram, B, from this

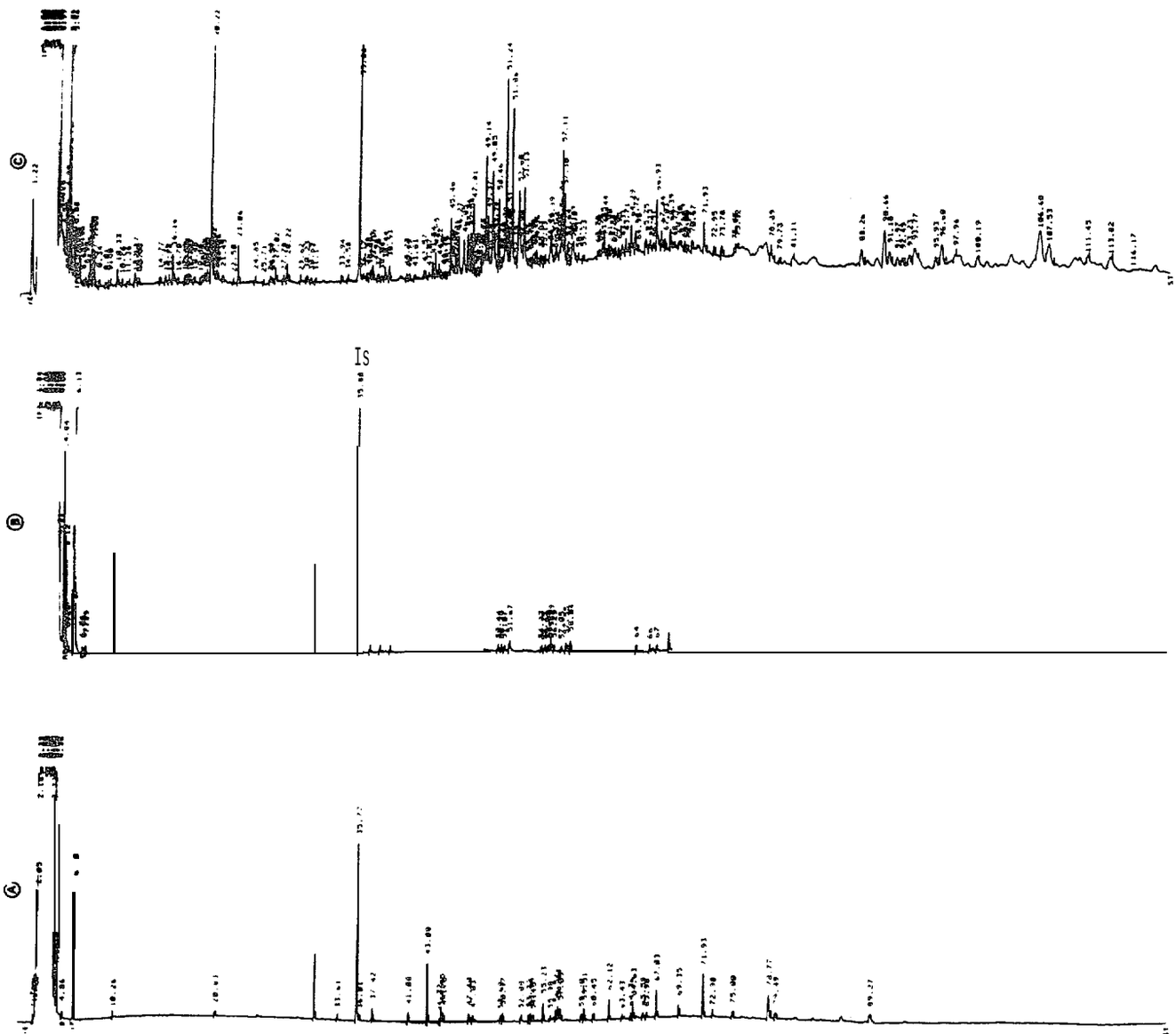



Figure 1. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction; B, the aromatic fraction and C, the polar fraction extracts obtained from time zero control sediment samples from Kasitsna Bay.

sample shows very little contamination of any kind, with only sub-nanogram per gram-dry-weight components present. The polar fraction chromatogram, C, does show evidence of several polar materials which are currently underoing analysis by GC/MS. From GC/MS analyses of similar sediment samples, the identities of these peaks are suspected to be long chain fatty acid esters of biogenic origin.

Tables 1 and 2 present the reduced quantitative data obtained from the capillary FID gas chromatographic runs of these and all the other sediment samples analyzed as part of this program. The data in Tables 1 and 2 illustrate several interesting quantitative aspects which should be considered when interpreting the results. First, the background levels of hydrocarbons in the control samples from Kasitsna Bay at times zero and one year were both extremely low. In neither case was an Unresolved Complex Mixture (UCM) present, and the highest hydrocarbon concentration in these two samples was only six micrograms per gram dry weight. The odd to even n-alkane ratios for these samples (1 and 625) were high, ranging from 5.2 to 7.9, reflecting predominance of the odd n-alkanes of biogenic origin.

Figures 2 and 3 present gas chromatograms of the hexane and benzene fractions from the fresh Cook Inlet crude oil and the artificially weathered Cook Inlet crude oil used to spike the sediment samples, respectively. Figure 2A clearly shows a high degree of complexity in the lower molecular weight range from $nC_8$ through $nC_{12}$,

Table 1. Reduced Aliphatic Hydrocarbon Data Derived from Flame Ionization Detector Capillary GC Analyses

| Sediment Sample | OSU ID No | Time in Field (years) | Total Resolved ug/g | Total UCM* ug/g | Σ n-alkanes ug/g | Σ even n-alkanes ug/g | Σ odd n-alkanes ug/g | pristane + phytane / n-alkanes | odd alk / even alk | pristane / nC17 | phytane / nC18 | pristane / phytane | n-alk / branched |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KASITSNA BAY CONTROL | 1 | 0 | 5.89 | 0. | 2.76 | 0.449 | 2.31 | o 0157 | 5.15 | 0.758 | 0. | 4-- | 0.883 |
| KASITSNA BAY CONTROL | 625 | 1 | 1.22 | o. | 0.533 | 0.06 | n 473 | n | 7.86 | n | 0. | 0. | 0. 776 |
| FRESH CRUDE SPIKE 50ppt | 5 | 0 | 2840. | 4090. | 1460. | 742. | 722. | 0 0749 | 0.973 | 0.681 | 0.343 | 2.63 | 1 06 |
| FRESH CRUDE SPIKE 1ppt | 4 | 0 | 83.3 | 154. | 52.8 | 24 2 | 28.6 | 0 055 | 1.18 | 0.630 | 0.411 | 2.18 | 0.690 |
| FRESH CRUDE SPIKE 0.1ppt | 3 | 0 | 11.3 | 12.8 | 5.03 | 2.11 | 2.92 | n 596 | 1.39 | 0.601 | 0.380 | 2.40 | 0.803 |
| WEATHERED CRUDE SPIKE 5( | 7 14 | 0 | 1530. | 3020. | 945. | 460. | 485. | 0 104 | 1.06 | 0.721 | 0.326 | 2.15 | 1.62 |
| WEATHERED CRUDE SPIKE I | 12 | 0 | 62.2 | 136. | 40.3 | 19.3 | 21.0 | n 0871 | 1.09 | 0.645 | 0.371 | 2.27 | 1.84 |
| FRESH CRUDE SPIKE 50ppt | 628 | 1R | 2430. | 174n. | 1080. | 560. | 515. | 0.0861 | 0.921 | 0. 761 | 0.354 | 2.63 | 0.796 |
| FRESH CRUDE SPIKE 50ppt | 629 | 1R | 2700. | 3770. | 1250. | 645. | 605. | 0 0799 | 0.934 | 0. 7FJ0 | 0.386 | 2.43 | 0.860 |
| FRESH CRUOE SPIKE 50ppt | 630 | 1R | 2060. | 3010. | 95(-I . | 494. | 458, | 0 0832 | 0.927 | 0.708 | 0.357 | 2.41 | 0. 862 |
| FRESH CRUDE SPIKE 1 ppt | 631 | I | 21.3 | 98.1 | 10.9 | 4.89 | 6.04 | n 144 | 1.24 | 1.28 | 0.709 | 2.40 | 1.06 |
| FRESH CRUDE SPIKE 0.1ppt | 634 | 1 | 3.29 | 13.1 | 1.09 | 0.179 | 0.917 | n 0320 | 5 IFI | 0.800 | 0. | 3-- | 0.496 |
| WEATHERED CRUDE SPIKE 50 | 637 | I | 1530. | 3710. | 949. | 449. | 499. | 0.109 | 1.11 | 0. 926 | 0.463 | 2.40 | 1.64 |
| WEATHERED CRUDE SPIKE 1 | 640 | i | 14.3 | 319. | 2.81 | 0. | 2.81 | 0 | 2-- | 0. | 0. | 0. | 0.243 |
| SADIE COVE CONTROL | 206 | 0 - | 26.1 | 0. | 10.7 | 1.37 | 9.33 | 0 | 6.81 | 0. | 0. | 0. | 0.773 |
| SADIE COVE OIL & STARCH | 782 | 1 | 3760. | 5200. | 1605. | 837. | 768. | 0.071 | 0.917 | 0.762 | 0.391 | 2.55 | 0.743 |
| SADIE COVE OIL | 779 | 1 | 4730. | 6100. | 1920. | 98.3. | 932. | n o r m | 0.948 | 0.880 | 0,420 | 2.75 | 0.681 |
| SADIE COVE OIL & CHITIN | 780 | 1 | 4700. | 6670. | 1986. | 1070. | 968. | 0 0630 | 0.951 | 0.626 | 0.345 | 2.14 | 0.732 |
| COOK INLET CRUDE OIL | | | | | | | | | | | | | |
| FRESH | | N.A. | 84000 | 77600 | 33000 | 18300 | 14700 | 0.0703 | o. 804 | 0.673 | 0.331 | 2.41 | 0.648 |
| WEATHERED | | N.A. | 38700, | 54500. | 24500. | 11600. | 12900. | IT, 0989 | 1.17 | 0.654 | 0.380 | 2.23 | 1.73 |

*UCM = Unresolved Complex Mixture

Table 2. [{educed Aromatic Hydrocarbon Data Derived from Flame Ionization Detector Capillary GC Analyses.

| Sediment Sample | OSU ID No | Time in Field (years) | Total Resolved ug/g | Total UCM* ug/g | Naphthalene (1185)** | 7 Methyl-naphthalene (1295) | 1 Methyl-naphthalene (1313) | Biphenyl (1381) | 2,6 Dimethyl naphthalene (1404) | Fluorene (1586) | Phenan-threne (1786) | Anthracene | 1 Methyl-phenanthrene | fluoranthene | Pyrene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KASITSNA BAY CONTROL | 1 | 0 | 3.08 | 0. | nd | nd | nd | nd | nd | nd | 0.0262 | nd | nd | nd | 0.0392 |
| KASITSNA BAY CONTROL | 625 | 1 | 1.212 | 0. | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| FRESH CRUDE SPIKE 50ppt | 5 | A | 1460 | 1740 | 58 0 | 137 | 94.9 | 16.2 | 65 4 | 32.5 | 56.6 | nd | 18.0 | nd | nd |
| FRESH CRUDE SPIKE 1ppt | 4 | 0 | 12.2 | 22.3 | 0 163 | 0 960 | u 570 | o 0418 | 0 469 | o 120 | 0.190 | nd | 0 0658 | nd | nd |
| FRESH CRUDE SPIKE o 1ppt | 3 | 0 | 0.0289 | 0.0259 | o.00025 | 0.00064 | 0.[)0037 | nd | 0 0032 | nd | 0.00032 | n d | nd | 0.01321 | 0.00012 |
| WEATHERED CRUDE SPIKE 50 | 14 | 0 | 210 | 824. | nd | 5.59 | 4.77 | nd | 11.1 | 4.88 | 8.65 | nd | nd | 1,47 | nd |
| WEATHERED CRUDE SPIKE 1 | 12 | 0 | 10.7 | 40,62 | 0.152 | 0.513 | 0.334 | nd | 0.467 | 0.150 | 0.255 | nd | nd | nd | 0.0316 |
| FRESH CRUDE SPIKE 50ppt | 628 | 1 | 463. | 1235. | 15.3 | 39.6 | 23.7 | 1.48 | 19.2 | 4.84 | 6.7 | nd | 2.48 | 1.00 | nd |
| FRESH CRUDE SPIKE 50ppt | 629 | 1 | 428. | 880 | 13,3 | 35,2 | 21.0 | 1.17 | 17.9 | 4.27 | 5.98 | nd | 2.40 | 0.840 | nd |
| FRESH CRUDE SPIKE 50ppt | 630 | 1 | 300 | 2020. | 9.75 | 30.4 | 18.6 | nd | 17.5 | 4.44 | 7.15 | nd | 2,95 | nd | nd |
| FRESH CRUDE SPIKE 1ppt | 631 | 1 | 9.33 | 29.7 | 0.163 | 0.517 | (7.433 | 0.0311 | 0 383 | 0.107 | 0.129 | nd | 0.0621 | nd | nd |
| FRESH CRUDE SPIKE 0.1ppt | 634 | 1 | 2.23 | 3.98 | nd | 0.0257 | nd | nd | 0.0321 | nd | 0.0307 | nd | nd | nd | 0.0185 |
| WEATHERED CRUDE SPIKE 5 0 | 637 | 1 | 288. | 901. | nd | 5.19 | 4.07 | nd | 9.58 | 3.71 | 6.80 | nd | nd | nd | nd |
| WEATHERED CRUDE SPIKE 1 | 640 | 1 | 12.28 | 51.84 | 0 u429 | 0.243 | 0.134 | 0.0234 | 0.420 | 0.195 | 0.137 | nd | 0.116 | 0.032 | 0.0297 |
| SADIE COVE CONTROL | 206 | 0 | 2.92 | 0 | nd | nd | nd | nd | nd | nd | 0.10258 | nd | nd | 0,02803 | 0.21073 |
| SADIE COVE OIL & STARCH | 782 | 1 | 781. | 2010. | 22 7 | 51.0 | 29.5 | 1.21 | ?2.2 | 4.50 | H.37 | nd | 2.64 | nd | nd |
| SADIE COVE OIL | 779 | 1 | 872. | 2440. | 32.6 | 75 0 | 43,2 | nd | 32.3 | 6.27 | 10.2 | nd | 5.71 | 2.04 | nd |
| SADIE COVE OIL & CHITIN | 780 | 1 | 1070. | 1660. | 33.8 | 77.8 | 45.7 | 1.80 | 31.0 | 6,24 | 9.99 | nd | 6.66 | nd | nd |
| COOK INLET CRUDE OIL | | | | | | | | | | | | | | | |
| FRESH | | N.A. | 34700. | 41600. | 484. | 1110. | 644. | nd | 540. | nd | 190. | nd | nd | nd | nd |
| WEATHERED | | N.A. | 15400 | 31400. | nd | nd | nd | nd | 223. | 102. | 235. | nd | nd | nd | nd |

* Unresolved complex mixture.
* Kovat indices in parentheses,
nd = not detected,

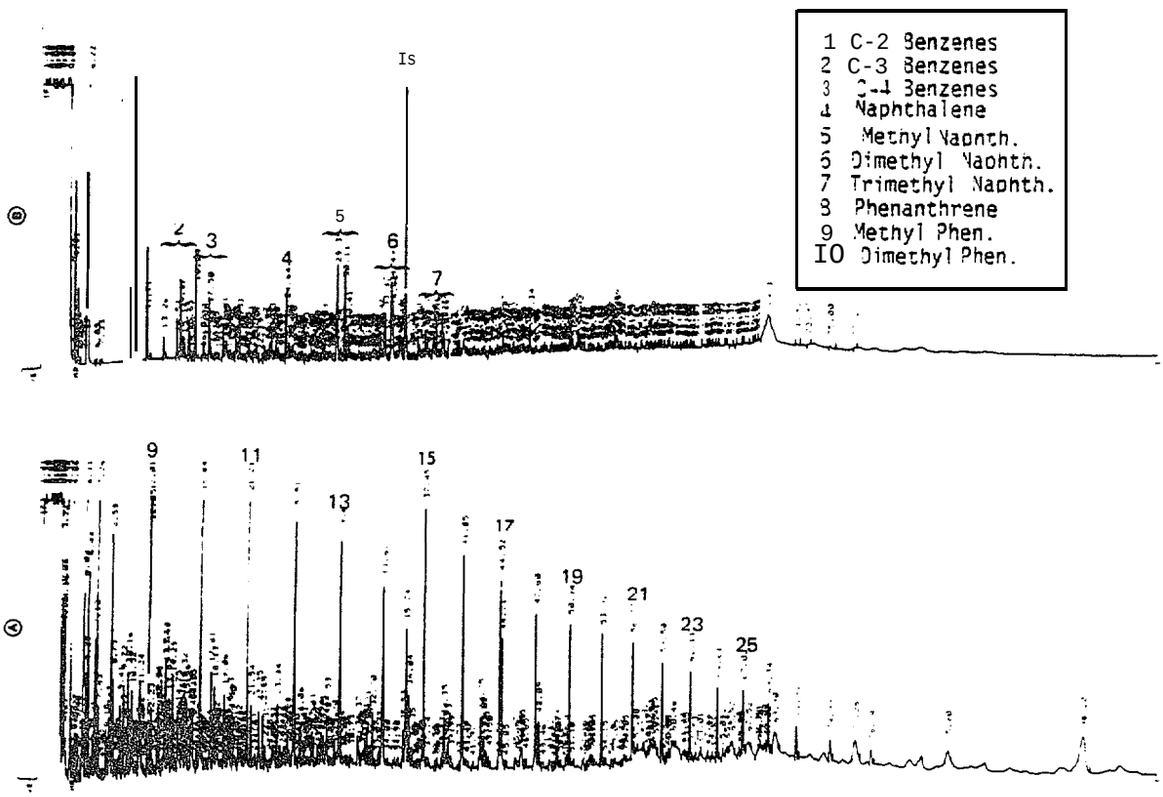



Figure 2. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction, and B, the aromatic fraction extracts obtained on the fresh Cook Inlet Crude Oil used to spike the Kasitsna Bay sediment samples.

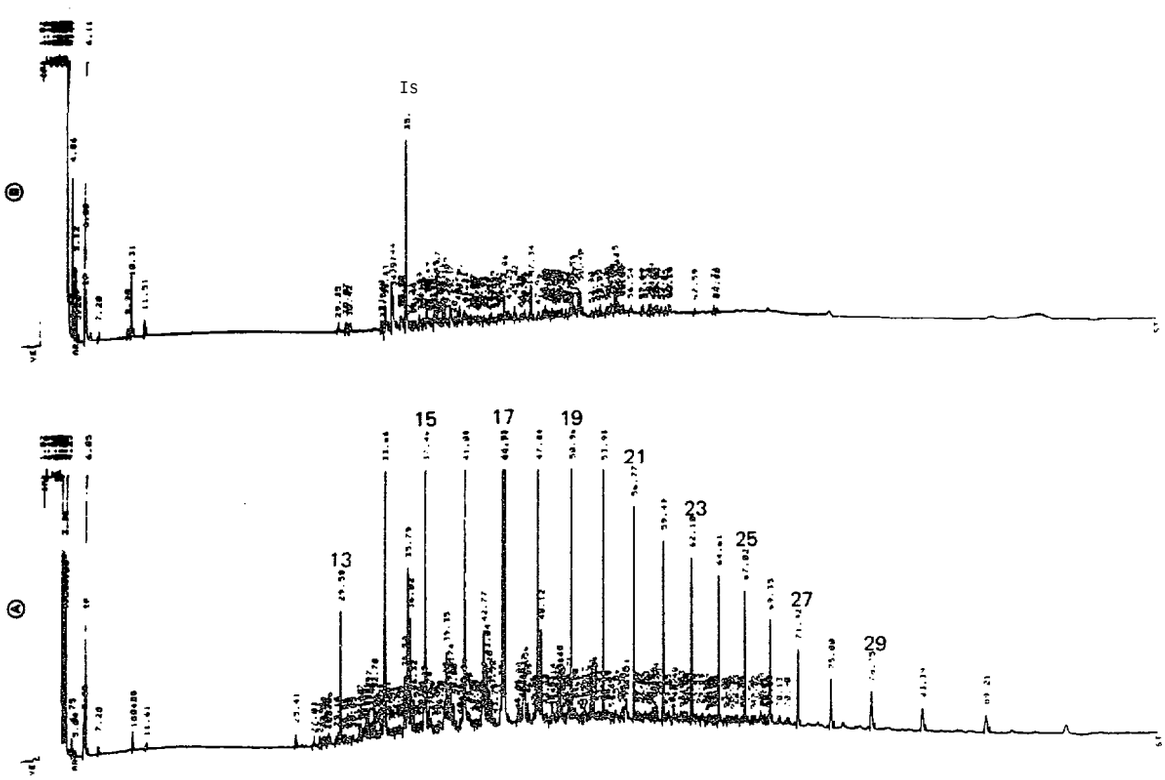



Figure 3. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction, and B, the aromatic fraction extracts obtained from the Artificially Weathered Cook Inlet Crude Oil used to spike the Kasitsna Bay sediment samples.

although the aliphatic fraction is characterized in general, by n-alkanes from $nC_8$ through $nC_{32}$. The aromatic fraction shows a number of lower molecular weight aromatic compounds in the range of KOVAT index 800 to KOVAT index 1500 (RT 10.09 to 35.79). These compounds were identified by GC/MS as alkyl substituted benzenes such as xylenes, ethylbenzene, trimethylbenzene and propylbenzenes. The large peak at RT 35.79 is the GC internal standard hexamethylbenzene. Also in this sample are peaks identified as napthalene (RT 24.64}, 2-methylnapthalene (RT 29.38), l-methylnapthalene (RT 30.11), 2,6-dimethylnapthalene (RT 33.87), and several low level alkyl substituted phenanthrenes, as shown by the data in Table 2.

Figure 3 shows the gas chromatograms of artificially weathered crude oil used to spike the sediment samples. Clearly the aliphatic fraction, Figure 3A, shows loss of the lower molecular weight n-alkanes below $nC_{13}$; however, the higher molecular weight materials are present at approximately the same ratios as in the starting crude oil. This is illustrated by the consistency in the pristane/phytane, pristane/$nC_{17}$, and phytane/$nC_{18}$ ratios for the fresh and weathered crude oils, as shown by the data in Table 1. The aromatic fraction of the artificially weathered crude shows nearly complete dimunition of the lower molecular weight hydrocarbons below dimethylnapthalene; however, there still are several higher molecular weight polynuclears present. These are primarily phenanthrene at RT 47.34 (KOVAT 1790), l-methylphenanthrene at RT 51.97 (KOVAT 1933), and fluoranthene at RT 55.45 (KOVAT 2070). Higher

molecular weight compounds such as benz(a)anthracene, benzo(e)pyrene, benzo(a)pyrene and perylene are not apparently present in either the starting or weathered Cook Inlet crude oil to an appreciable degree.

Figure 4 shows the gas chromatograms of the aliphatic, aromatic and polar fractions obtained on the Kasitsna Bay time zero sample spiked with fresh crude oil at 1.0 ppt. The chromatograms obtained on the sediments spiked at 50 ppt were essentially identical in appearance to those in Figure 4, and thus the heavier spiked sample's chromatograms are not shown here. Further, the concentrations of crude oil in the 50 ppt samples were at such a high level that only approximately 2% of the extractable materials could be effectively applied to the liquid chromatography columns for separation into aliphatic, aromatic and polar fractions. This allowed accurate quantitation of the materials but did not figuratively show the presence of the lower molecular weight compounds to the same degree as the lower level spiked samples where the entire sample could be fractionated and analyzed without prior dilution.

With regard to the chromatograms in Figure 4, the aliphatic fraction, A, is nearly identical to the aliphatic fraction of the starting fresh Cook Inlet Crude oil shown in Figure 2. This is reflected qualitatively in the chromatograms presented in the figures and also quantitatively by the pristane/phytane, pristane/$nC_{17}$ and phytane/$nC_{18}$ ratio data presented in Table 1. 'he suite 'f $nC_{20}$-$nC_{21}$ branched/unsaturated compounds in the background control sample are completely masked in the spiked sediment samples. The aromatic fractions of the spiked

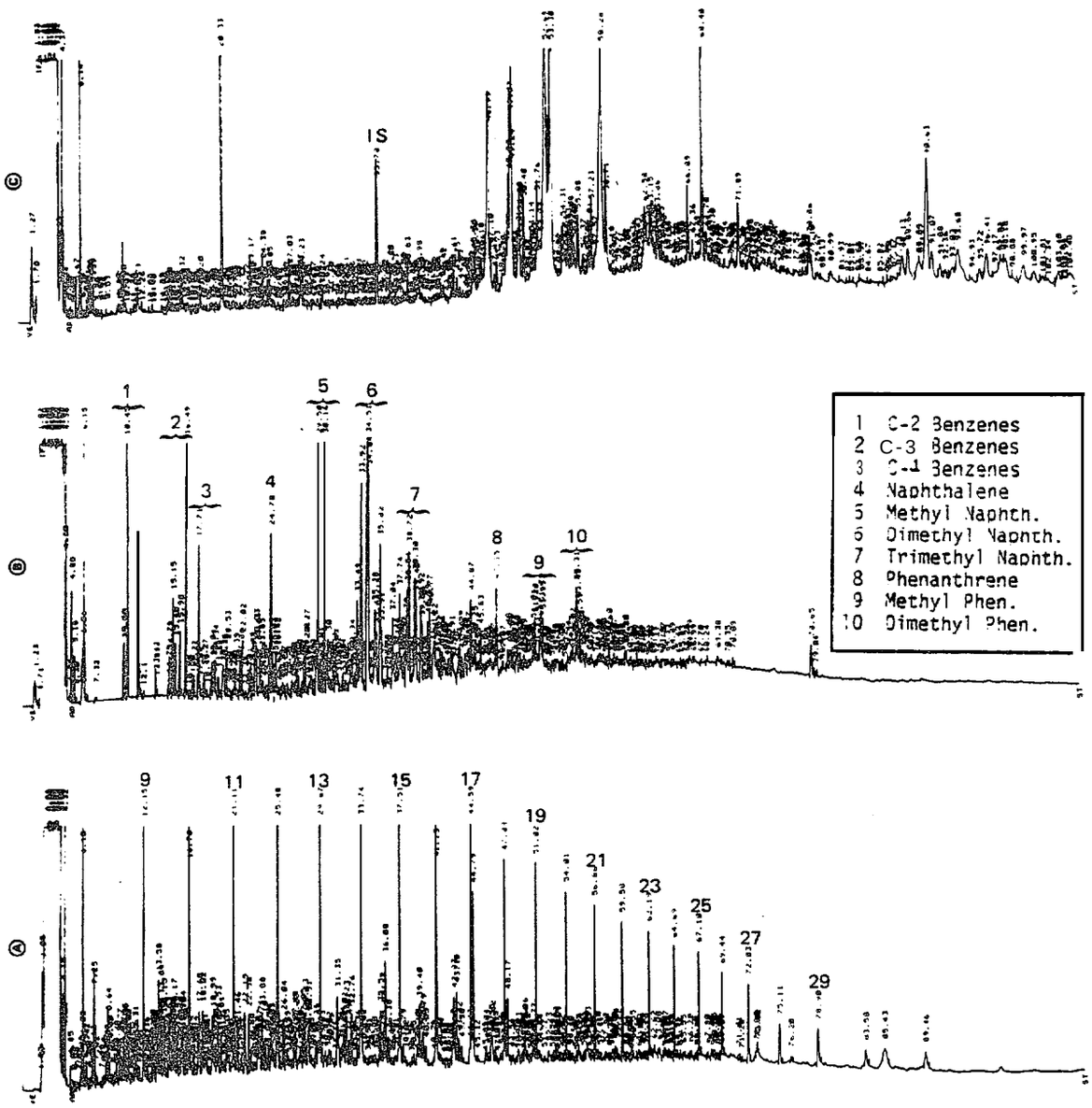



Figure 4. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction, B, the aromatic fraction, and C, the polar fraction extracts obtained from time zero Kasitsna Bay sediment samples which had been spiked with fresh Cook Inlet Crude Oil at 1 ppt.

sample show many of the same aromatic compounds in the napthalene (KOVAT 1185) to pyrene (KOVAT 2124) range and the alkyl-substituted aromatic compounds at KOVAT indices 800 to1012 as in the starting crude oil. The polar fraction of the fresh spiked sediment at time zero shows many of the same biogenic compounds as in the Kasitsna Bay control sediment. This is particularly true of the compounds between retention times 46.99 and 68.40. These compounds are present at a greater apparent concentration in the spiked sediment sample; however, examination of reduced chromatographic data output shows that this primarily reflects a smaller final sample extract volume resulting in more material being loaded on the fused silica capillary column.

Figure 5 presents the capillary chromatograms obtained on the time zero sediment samples spiked with artificially weathered crude oil, The chromatograms are qualitatively very similar to those shown in Figure 3 which presented the weathered Cook inlet crude used to spike the sediment samples. Aliphatics are virtually absent below $nC_{13}$ as are aromatic compounds with KOVAT indices below 1300. A number of higher molecular weight polynuclear aromatic compounds can be identified in the weathered crude, and these are 2-methylnaphthalene at 29.38, 1-methylnapthalene at 30.11, 2,6-dimethylnapthalene at 33.88, fluorene at 40.61, phenanthrene at 47.41, 1-methylphenanthrene at 51.85 and fluoranthene at 55*45. There appear to "be no polynuclear aromatic hydrocarbons with molecular weights greater than chrysene in the time zero artificially weathered sediment sample.

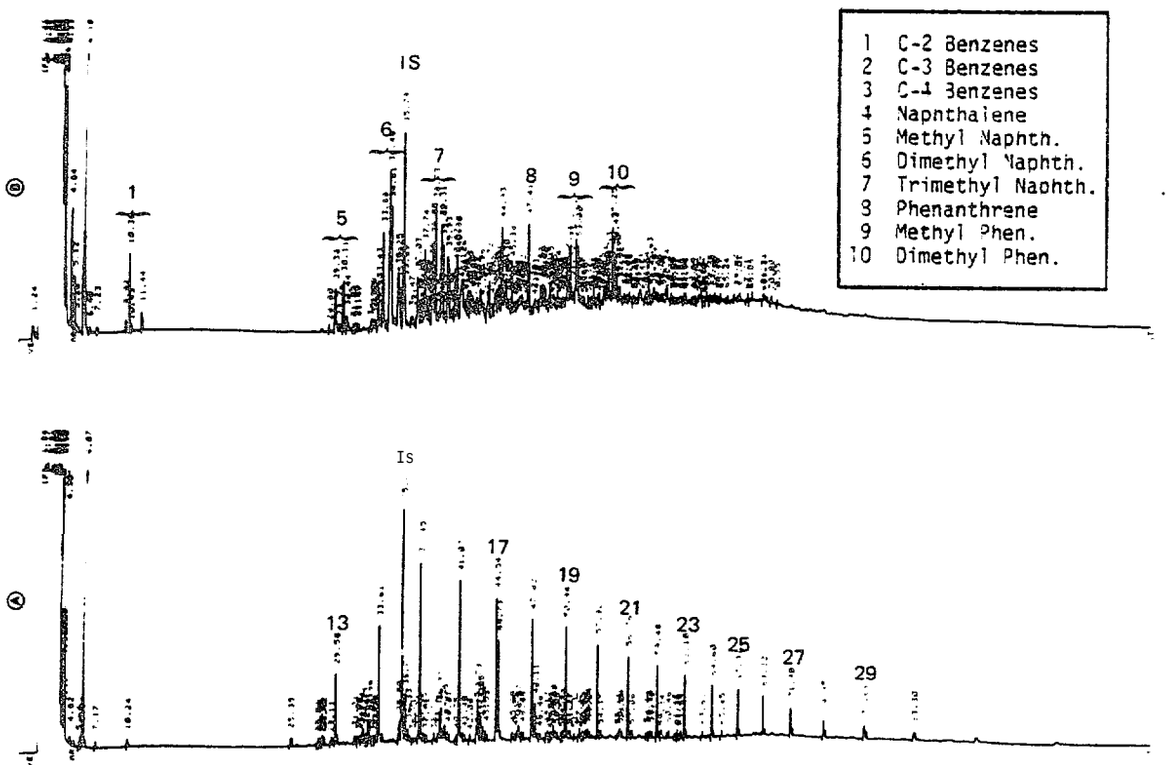



Figure 5. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction and B, the aromatic fraction extracts obtained from time zero Kasitsna Bay sediment samples spiked with Artificially Weathered Cook Inlet Crude Oil at 50 ppt.

Time One Year Samples

Each sediment sample was spiked and placed in a sediment tray; the sediment samples were deployed at various depths in Kasitsna Bay and Sadie Cove. After one year of exposure the trays were retrieved and subsamples of the sediments were collected. Figure 6 shows the chromatograms obtained on the aliphatic fraction of A, the 50 ppt fresh crude oil spiked into the sediment at time zero, and B, C, and D, the triplicate samples examined after one year of natural weathering. Several features are significant in this figure. The first and most obvious feature is the lack of any appreciable weathering of the oil at this high level of concentration. This is reflected in the qualitative appearance of the chromatograms and in the data presented in Table 1. Specifically, the lower molecular weight n-alkanes from $nC_8$ through $nC_{12}$, and the branched and cyclic compounds occurring between KOVAT index 900 and 1000 appear to be nearly identical in all four samples.

Figure 7 graphically presents the concentration abundance of the n-alkanes in the 50 ppt spiked sediment sample at time zero and again after one year of weathering in Kasitsna Bay. Note that in addition to the concentrations of the time zero and one year samples being very similar, the overall trends showing decreases in the higher molecular weight compounds are nearly identical for both samples, illustrating the lack of any appreciable selective weathering.

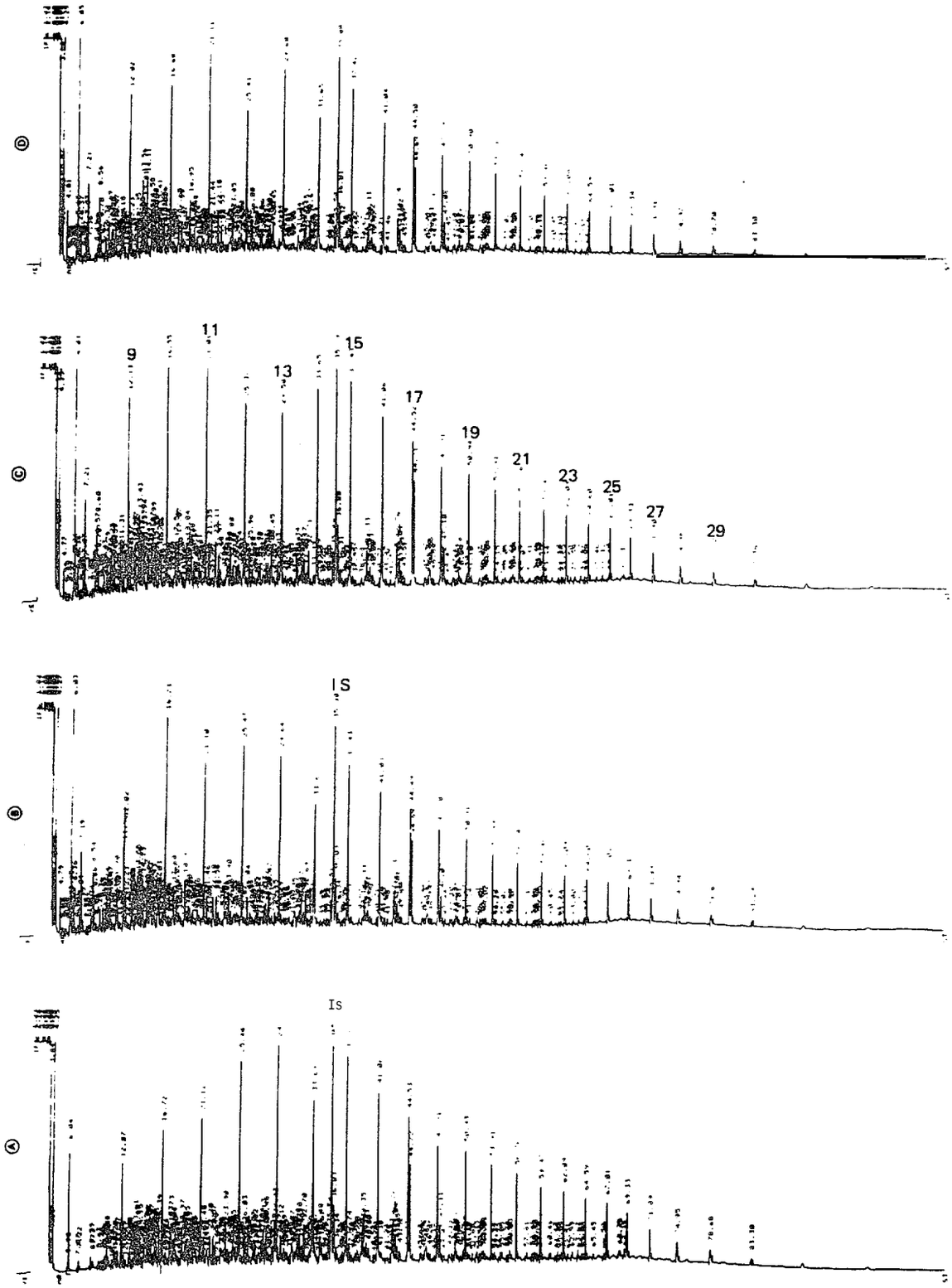



Figure 6. Flame ionization Detector capillary gas chromatograms of: A, the aliphatic fraction of the 50 ppt fresh Cook Inlet Crude Oil spiked into the sediment at time zero, and B, C, and D, the aliphatic fractions of the triplicate samples examined after one year of natural weathering in Kasitsna Bay.

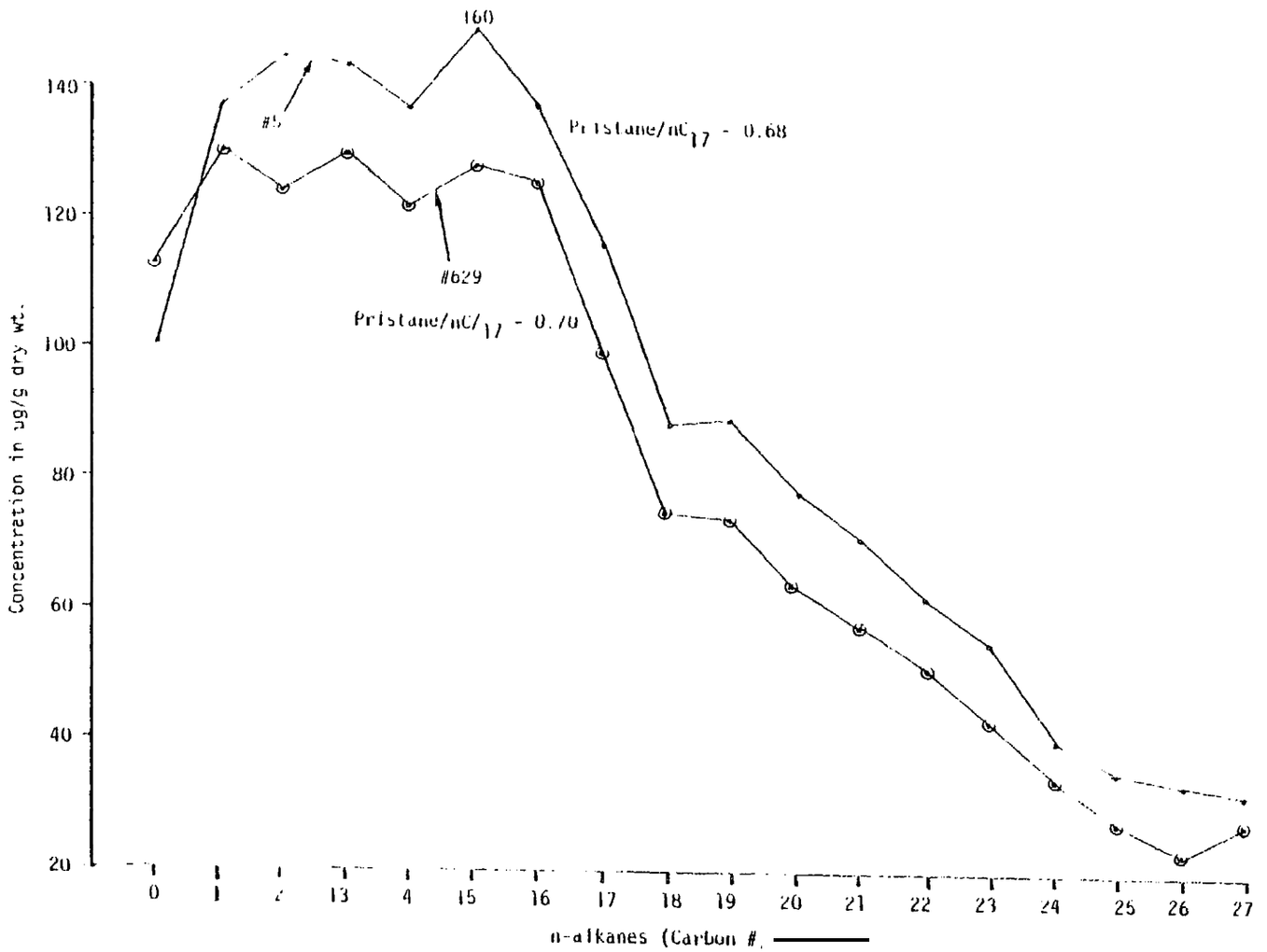



Figure 7. Concentration abundance of the n-alkanes in a sediment sample spiked with 50 parts per thousand fresh crude illustrating the time zero sample (•) and sample after one year of weathering (⊙).

The similarity of the pristane/$nC_{17}$ and phytane/$nC_{18}$ ratios, as observed qualitatively in Figure 6 and Table 1, also illustrates the lack of any appreciable biotic or abiotic weathering in these samples. The chromatographic profiles are essentially superimposable, reflecting the homogeniety of the initial spiked sediment, the replicability of the weathering process in the field and the precision of the analytical method. Individual values for these three fractions are presented in Table 1, and the agreement of such features as the total n-alkanes, sum of the odd n-alkanes, even n-alkanes, pristane/phytane ratios, etc., is worthy of consideration.

Figure 8 presents the gas chromatograms of the aromatic fractions obtained on the 50 ppt fresh Cook Inlet-spiked sediment at time zero (A) and the replicate fractions (B, C and D) obtained from analyses of the triplicate sediment samples after one year of natural weathering. As in Figure 6, there does not appear to be any selective weathering of the individual components present; however, examination of the reduced data in Table 2 and Figure 9 shows that some decreases in aromatic hydrocarbon concentrations did occur after 1 year. The apparent lower levels of material in chromatogram A (Figure 8) only reflect a larger final sample extract volume from which an aliquot was removed for analysis by GC. Figure 9A presents a graphical representation of the concentrations of eight selected aromatic compounds in the fresh 50 ppt

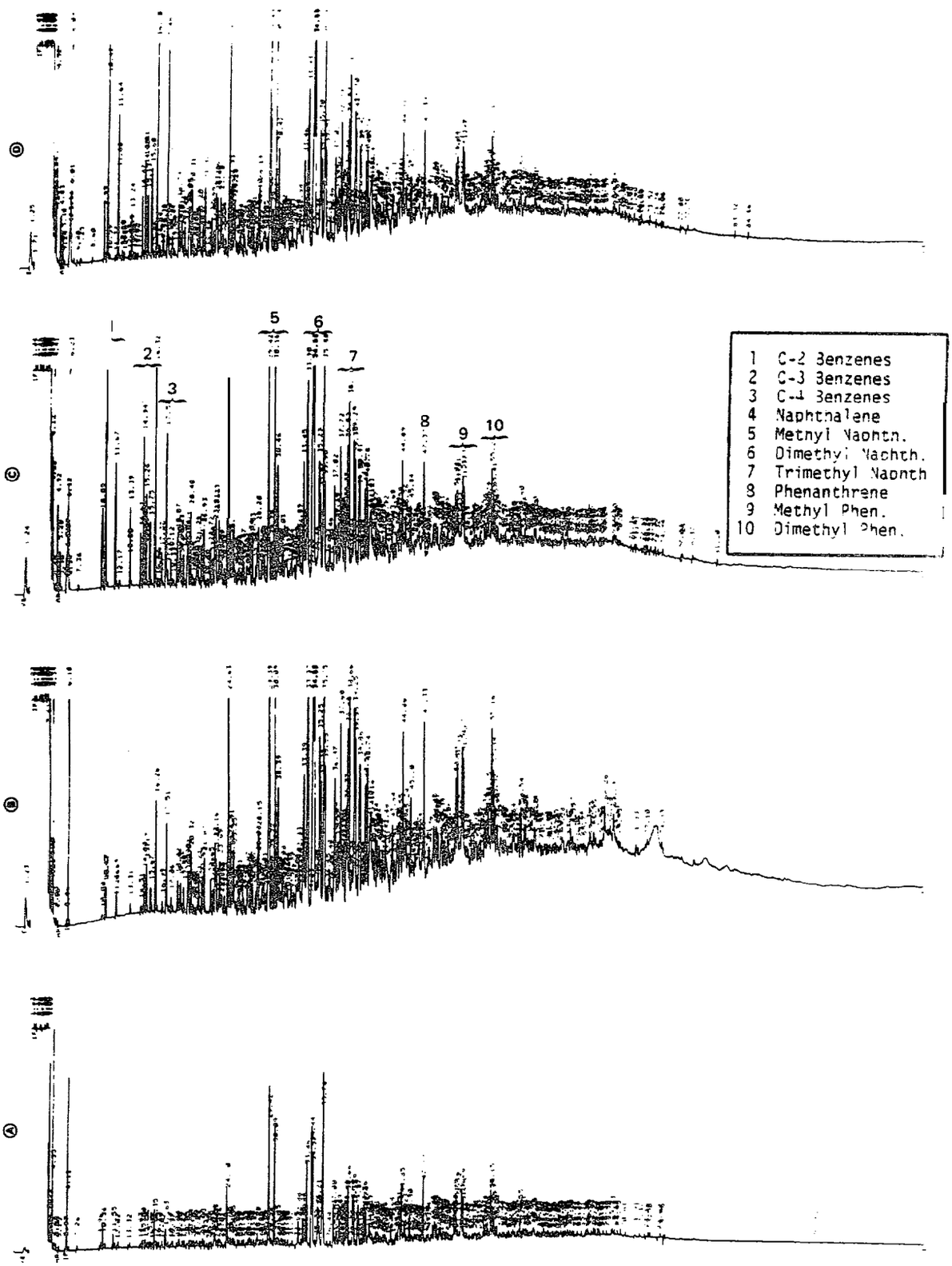



Figure 8. Flame Ionization Detector gas chromatograms of: A, the aromatic fraction of the 50 ppt fresh Cook Inlet Crude Oil spiked into the sediment at time zero and B, C, and D, the aromatic fractions of the triplicate samples examined after one year of natural weathering in Kasitsna Bay.

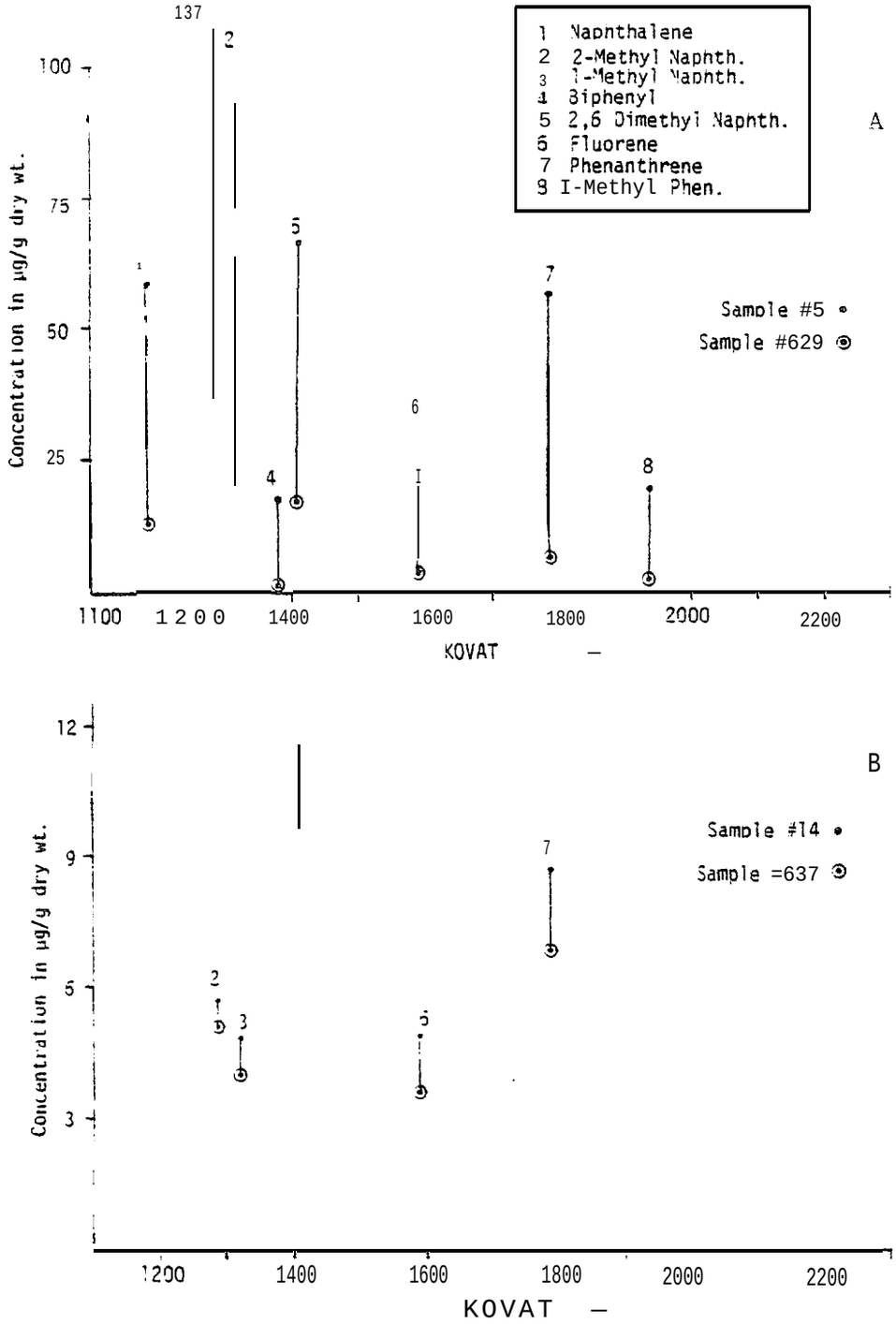



Figure 9. Concentration abundance of selected aromatic hydrocarbons from a 50 parts per thousand spike of fresh crude (Top) showing the time zero sample (•) and sample after one year of weathering (⊙), and bottom, a 50 ppt spike of artificially weathered crude at time zero (·) and after one year of weathering (⊙).

spiked sediments at time zero and time one year. While time zero levels of individual aromatic compounds ranged from 50 to 137 micrograms per gram dry weight (for napthalene through 2,6-dimethylnapthalene), after one year these compounds were present at concentrations ranging from 15 to 40 micrograms per gram dry weight. The decreases in aromatic compounds from Kovat indices 1100 to 1500 were greater than the decreases in aromatics with Kovat indices ranging from 1500 to 2000. This presumably reflects two things: 1) the greater volatility and water volubility of the lower molecular weight aromatic compounds, and 2) the lower relative abundance of the higher molecular weight aromatics in the crude oil 'co begin with.

Figure 9B shows the relative losses of aromatic hydrocarbons in the artificially weathered crude oil spiked into the Kasitsna Bay sediments at time zero and time one year. This figure illustrates that much smaller relative changes occurred over the one year period after the oil was spiked into the sediment. That is, the starting concentrations of aromatic compounds such as 2-methylnaphthalene through phenanthrene ranged between only 6 and 12 micrograms per gram dry weight of sediment when artificially weathered crude was used to spike the sample at time zero. These levels were not significantly reduced after one year of weathering in the sediments of Kasitsna Bay: the most significant weathering occurred while the oil was "artificially weathered" on the surface of a

salt water aquarium before the oil was spiked into the sediment. Nevertheless, once these compounds are introduced into the sediments, they are not as rapidly removed as they would be from simple dissolution in the starting oil itself.

Figure 10 presents the gas chromatograms of the aliphatic and aromatic fractions obtained on the 1 ppt fresh-crude oil spiked sediment after one year of weathering in Kasitsna Bay. In comparison with Figure 4 which shows the starting 1.0 ppm spiked material, it is clear that significant weathering of the sample has occurred. This is reflected first in the significantly greater relative loss of the lower molecular weight alkanes below $nC_{13}$, presumably due to a combination of biological and abiotic (dissolution) processes. Evidence of biochemical degradation is shown in examining the pristane/$nC_{17}$ and phytane/$nC_{18}$ levels in the aliphatic fraction in Figure 10 compared to the aliphatic fraction in Figure 4, and by examining the numerical values for these ratios in Table 1. Clearly the straight chain alkanes have been preferentially removed relative to the branched chain isoprenoids. The overall levels of other aliphatic hydrocarbons are also significantly reduced as illustrated qualitatively in Figure 10 and by the data in Table 1. Figure 11 graphically presents the concentration abundance of n-alkanes in the 1.0 ppt fresh crude oil sediment spike at time zero and after one year of natural weathering. Clearly all of the lower molecular weight alkanes below $nC_{18}$ are reduced by a factor of from 2 to 5 and the higher molecular weight n-alkanes are reduced by at Least a factor of 2 compared to the sample taken at time zero. For the 1 ppt sample the total

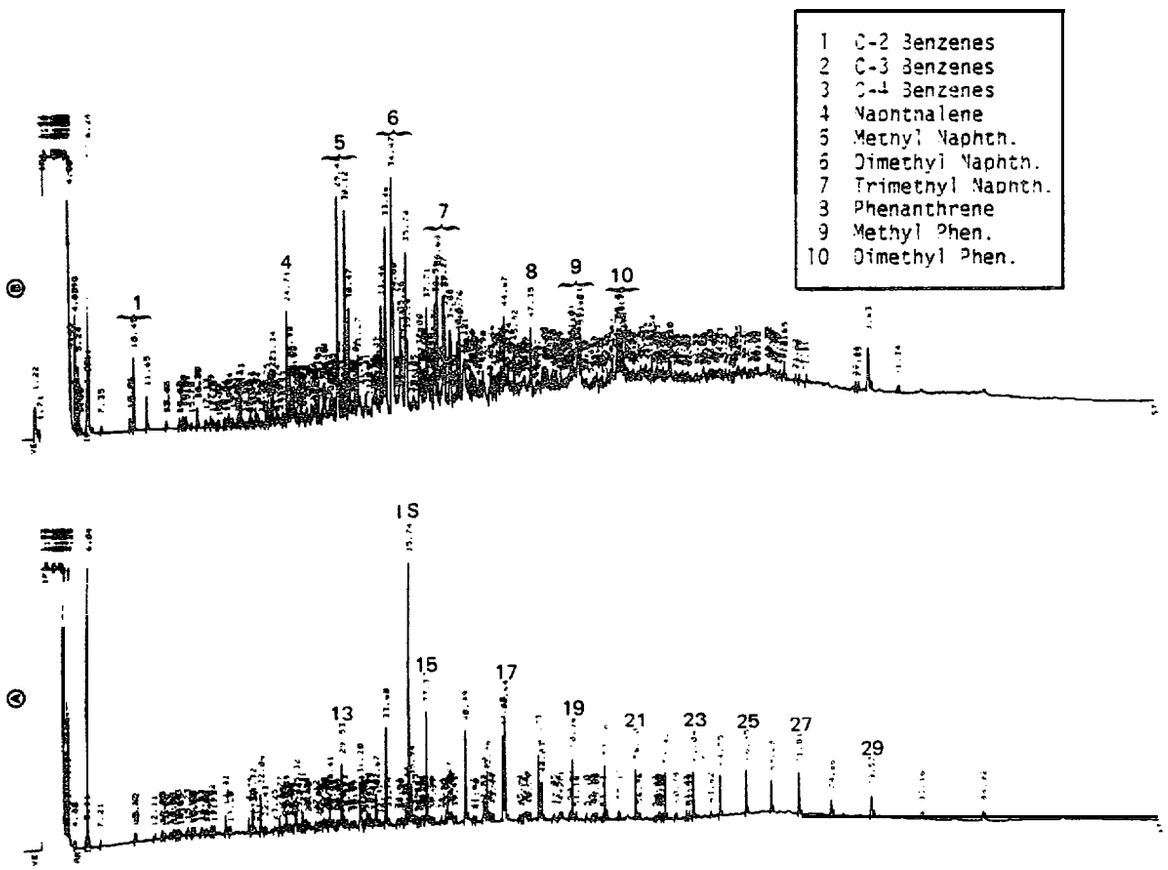
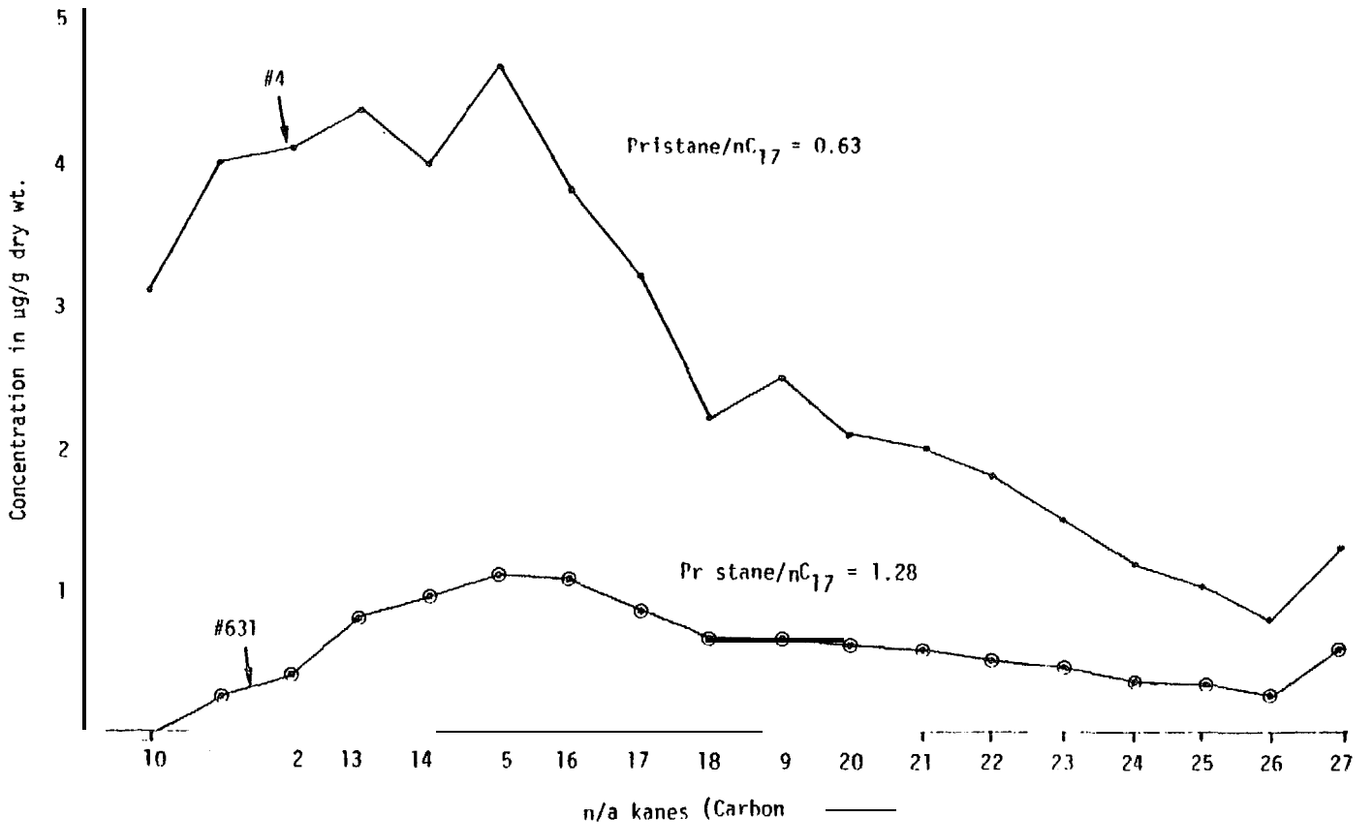



Figure 10. Flame Ionization Detector gas chromatograms of: A, the aliphatic fraction and B, the aromatic fraction extracts obtained from 1 ppt fresh Cook Inlet Crude Oil spiked sediments after one year of weathering in Kasitsna Bay.




F gure 11 Concentration abundance of the n-alkanes for a sediment oil spike of 1.0 part per thousand fresh crude illustrating the time zero sample (•) and sample after one year of weathering (⊙).

resolved hydrocarbons decreased from 83 to 21 μg/g dry weight during the year of exposure and the unresolved complex mixture decreased from 154 to 98 μg/g dry weight.

The aromatic fraction data in Figure 10B show somewhat less degradation compared to the aliphatic fraction. Compounds with molecular weights less than naphthalene (KOVAT < 1185) are obviously removed due to a combination of biological and abiotic factors (dissolution and evaporation); however, compounds with molecular weights greater than l-methylnapthalene (KOVAT > 1315) appear to be present in relatively identical concentrations compared to the starting materials. That is, while overall levels are slightly reduced as illustrated by the data in Table 2, the relative concentrations of the individual polynuclear aromatics are very similar in the time zero and time one year samples. This is also reflected quite obviously by the qualitative appearance of the aromatic fractions shown in Figures 4B and 10B, respectively, and by the data presented in Figure 12A. Figure 12A graphically presents the relative concentration abundance of selected aromatic hydrocarbons from the 1 ppt spike of fresh crude oil at time zero and after one year. Clearly while the relative range of concentrations of all of the compounds in the time zero and one year samples are lower compared to the 50 ppt sample shown in Figure 9A, the overall concentrations of the time zero and naturally weathered 1 ppt samples are still relatively similar. This is particularly true of the higher molecular weight compounds, bi-phenyl, fluorene, phenanthrene and

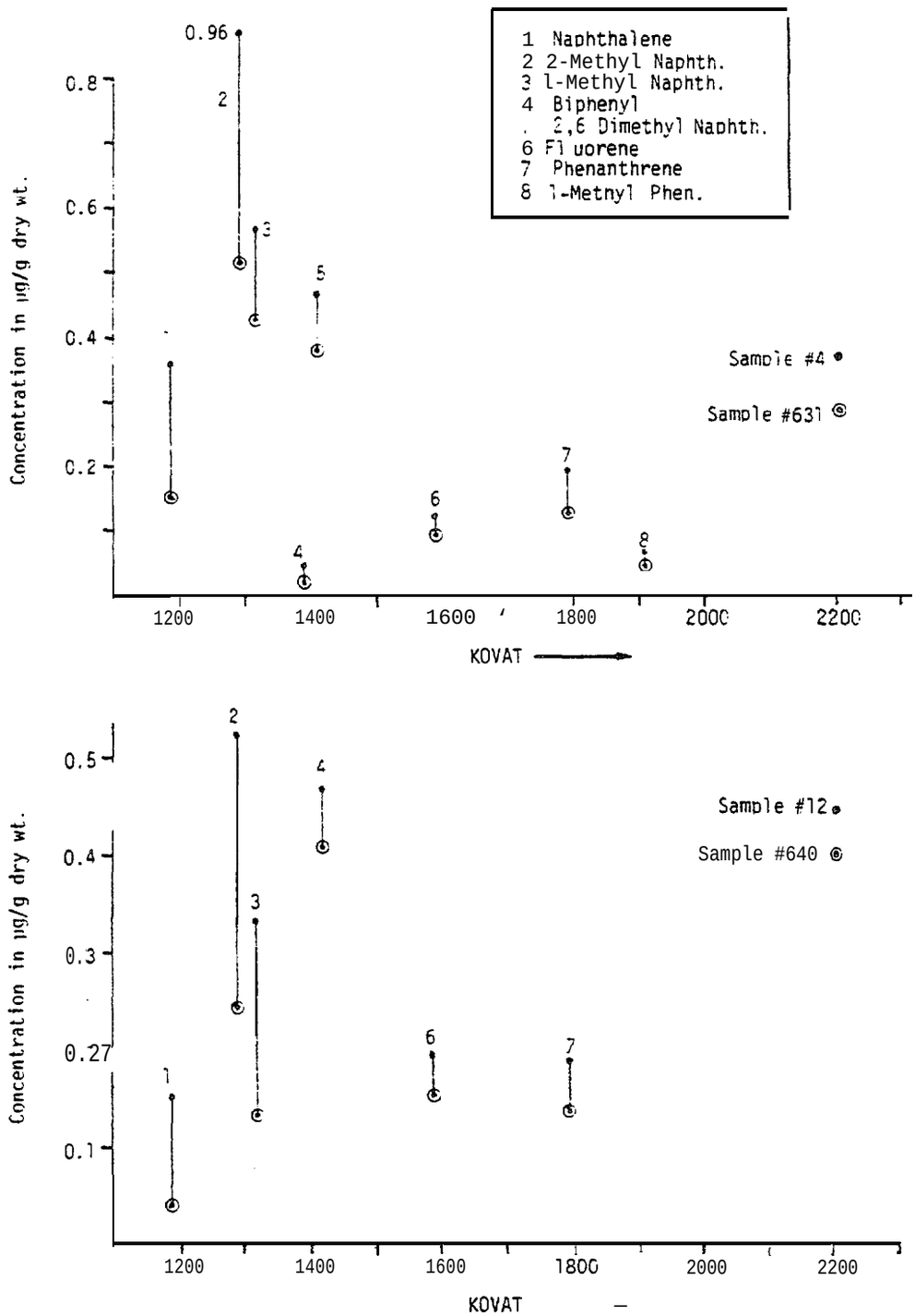



Figure 12. Concentration abundance of selected aromatic hydrocarbons from a 1.0 part per thousand spike of fresh crude (Top) showing the time zero sample (•) and sample after one year of weathering (⊙). Bottom shows a 1.0 ppt spike of artificially weathered crude for the time zero sample (•) and sample after one year of weathering (⊙).

l-methylphenanthrene. As in Figure 9A and B, the relative concentrations of artificially weathered aromatic compounds from the 1.0 ppt sample shown in 12B show that concentrations are in the same range in the artificially weathered sample as in the fresh sample after it had been weathered for a full year.

Clearly, while biological degradation of the aliphatic hydrocarbons (primarily n-alkane) occurred at the 1 ppt level, concomitant degradation of the higher molecular weight polynuclear aromatics compounds with molecular weights above that of methylnapthalene did not occur at a significant level.

This lack of degradation of higher molecular weight PNA's at the 1.0 ppt level is also illustrated in Figure 13, which presents the aromatic fraction chromatograms of: A) the 1 part per thousand fresh crude spiked into the sediment at time zero; B) the aromatic fraction obtained from the 1 ppt sediment after one year of in situ weathering in Kasitsna Bay; and C) the aromatic fraction of the 1 ppt sediment spiked with artificially weathered crude oil after one year of additional weathering in Kasitsna Bay. Clearly, examination of chromatograms 13A and B shows that some loss of the lower molecular weight alkyl substituted benzenes at retention times 10.45, 11.68, 15.15, 15.90, 16.49 and 17.71 has occurred due to either evaporation or dissolution. Compounds with molecular weights greater than that of 1-methylnapthalene at retention time 29.41 (B) are present in nearly identical relative concentrations. The chromatogram in 13C shows that the same compounds were also

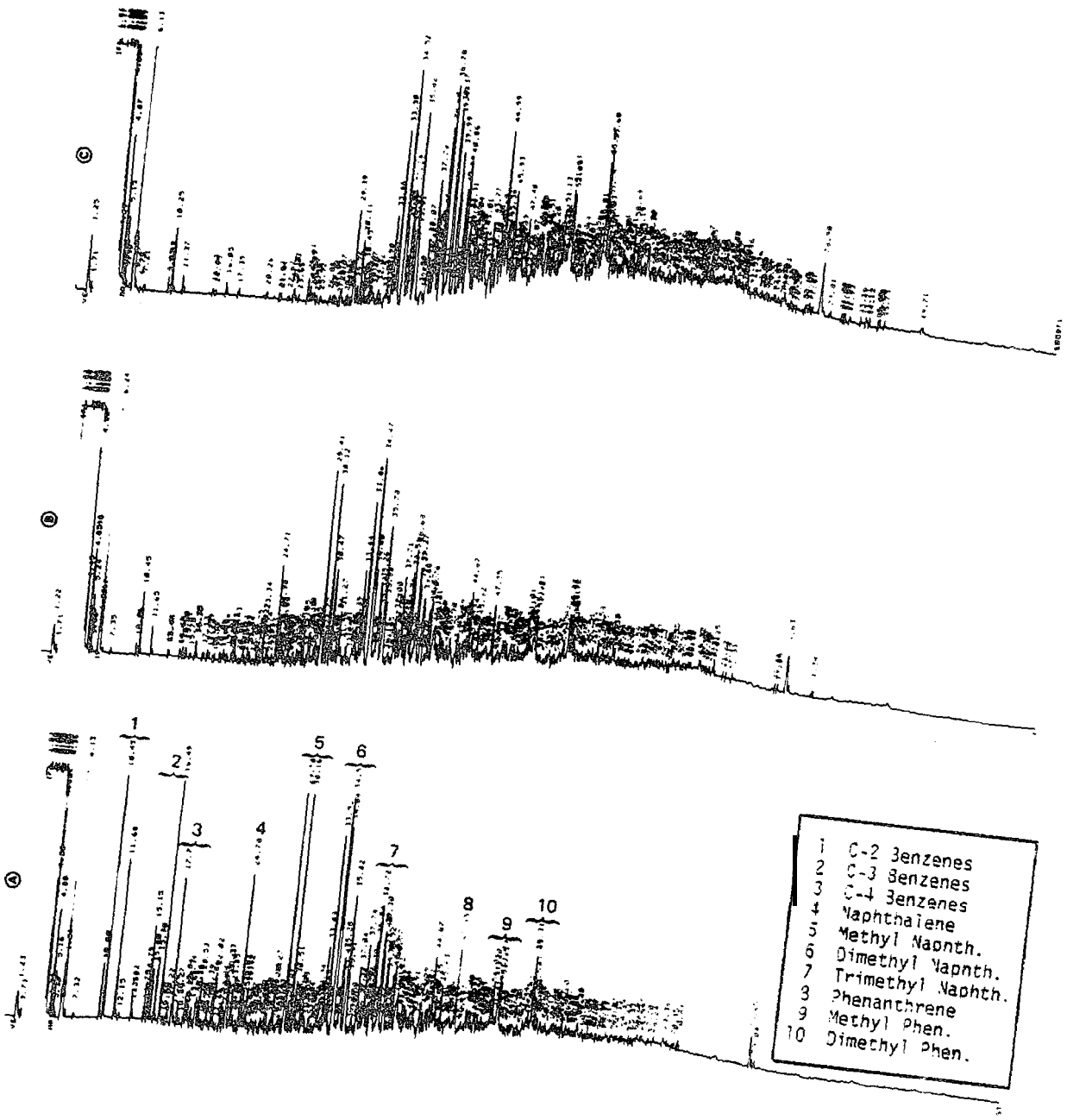



Figure 13. Flame ionization Detector gas chromatograms of extracts of the aromatic fractions obtained from:
ppt fresh crude oilat time zero;
after one year of natural weathering in the Kasitsna Bay and C, the ppt sediment sample spiked with artificially weathered crude oil
after one year of additional weathering in Kasitsna Bay,

present in the "artificially weathered" oil which was spiked into the sediment after an additional year of natural weathering. This suggests that although many lower molecular weight aromatic compounds are removed from natural weathering of spilled oil while the oil is still at the surface, once the less water soluble and volatile higher molecular weight PNA's are incorporated into the sediment, additional degradative processes are extremely slow. Thus, while the relatively non-toxic aliphatic hydrocarbons are significantly degraded by biological processes in the sediments at 1 ppt, the more toxic aromatic compounds appear to be longer lived when introduced to the sediment from either fresh or weathered crude oil at similar levels.

Figure 14 presents the aliphatic, aromatic and polar fraction chromatograms obtained on the 0.1 ppt fresh crude oil spiked into the sediment at time zero (a) and after one year of weathering in the sediments of Kasitsna Bay (b, aliphatic fraction; c, aromatic fraction; d, polar fraction). Clearly, almost all of the n-alkanes in the starting oil are no longer present in the sediment after one year of weathering. In fact, the only compounds of any significance in the aliphatic fraction of the fully weathered sediment are higher molecular weight odd n-alkanes, $nC_{23}$, $nC_{25}$, $nC_{27}$, and $nC_{29}$. These same compounds are also predominant in the fresh crude sample shown in Figure 14A. That is, instead of seeing a regular decrease in higher molecular weight n-alkanes from $nC_{22}$ through $nC_{32}$, the odd carbons at 23, 25 and 27 from biogenic input are clearly present. These are the only compounds which

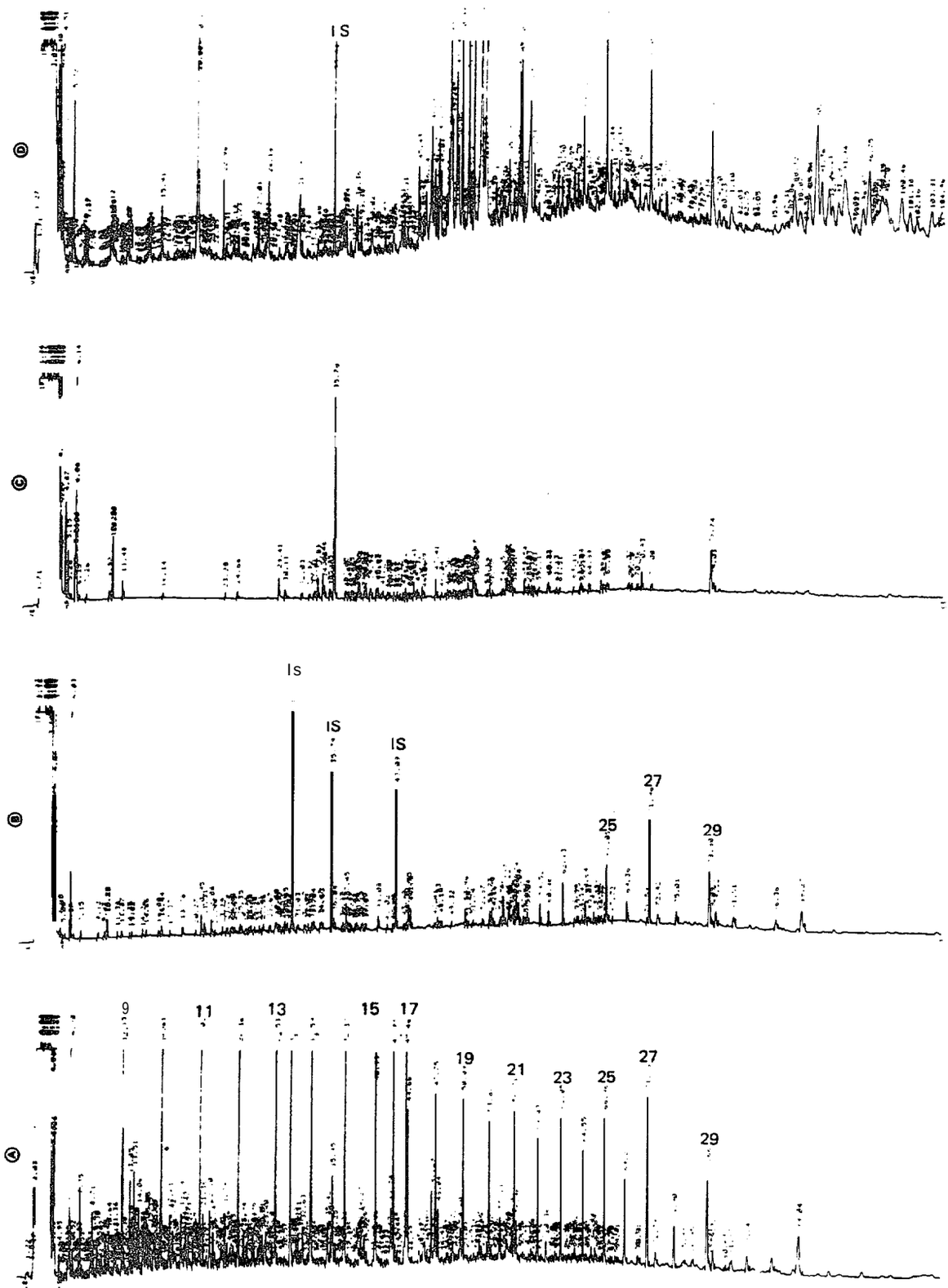



Figure 14". Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction of the sediment spiked with 0.1 ppt Fresh Crude Oil at time zero and B, the aliphatic fraction, C, the aromatic fraction, and D, the polar fraction extracts obtained on the 0.1 ppt Fresh Crude Oil spiked sample after one year of Natural Weathering in Kasitsna Bay.

remain in the sediment after one year, although there is some evidence that several unsaturated compounds between KOVAT indices 1900 and 2200 are present in Figure 14B. The aromatic fraction 14C shows only extremely low levels of residual materials with some evidence of pyrene perhaps remaining in the sediment at retention time 78.70. This compound was not detected in the starting crude oil to an appreciable degree, however, so its presence may reflect input from some other source. GC/MS characterization of the compounds in the polar fraction, 14D, is being completed at this time.

Figure 15 shows the chromatograms of the aliphatic and aromatic fractions of the 50 ppt artificially weathered crude oil spiked into the sediment after one year of additional degradation in the sediment plots in Kasitsna Bay. Comparison of the sediments spiked with the weathered crude oil at time zero, as shown in Figure 5, shows little or no change in the oil composition after one year of additional weathering. This is perhaps better illustrated in Figure 16, which presents the concentration abundance of the n-alkanes in the sediment spike at 50 ppt of the artificially weathered crude oil in the time zero sample and after one year of additional natural weathering. The data illustrate that all compounds below the level of $nC_{14}$ are drastically reduced in both the starting material and the residual oil isolated after one year of natural weathering; however, the higher molecular weight compounds are not significantly altered. The corresponding data for the aromatic fraction of the 50 ppt spike of artificially weathered crude are shown in Figure 9B. These

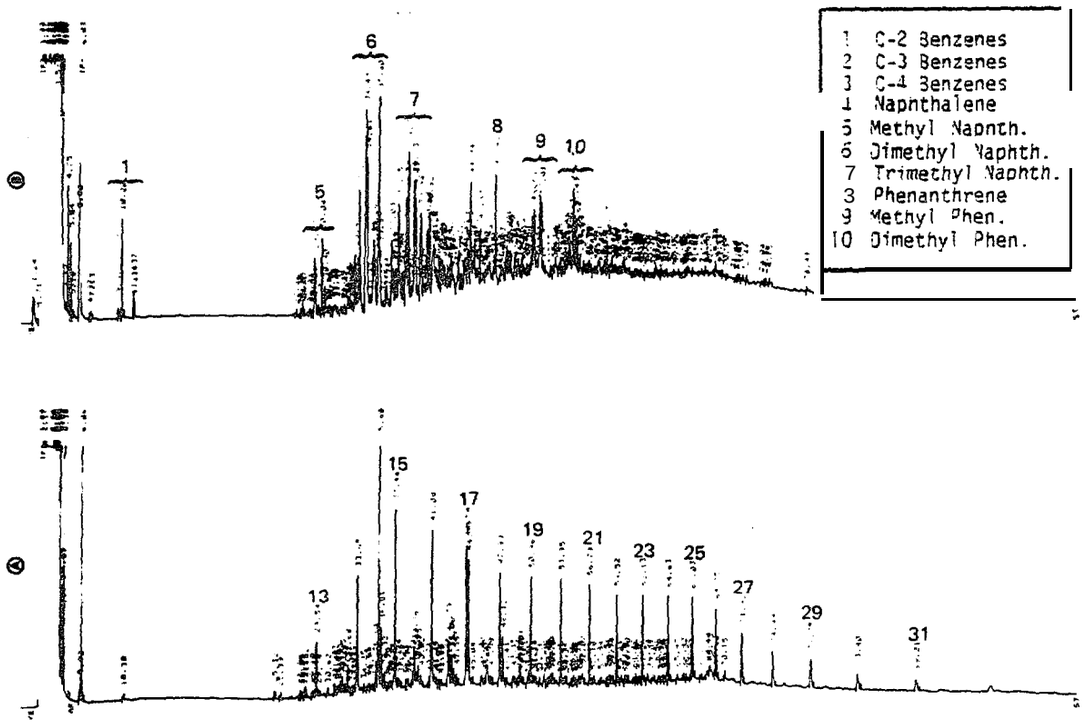



Figure 15. Flame Ionization Detector capillary gas chromatograms of: A, the aliphatic fraction and B, the Aromatic fraction extracts obtained from the time one year Kasitsna Bay sample spiked with Artificially Weathered Cook Inlet Crude Oil at 50 ppt.

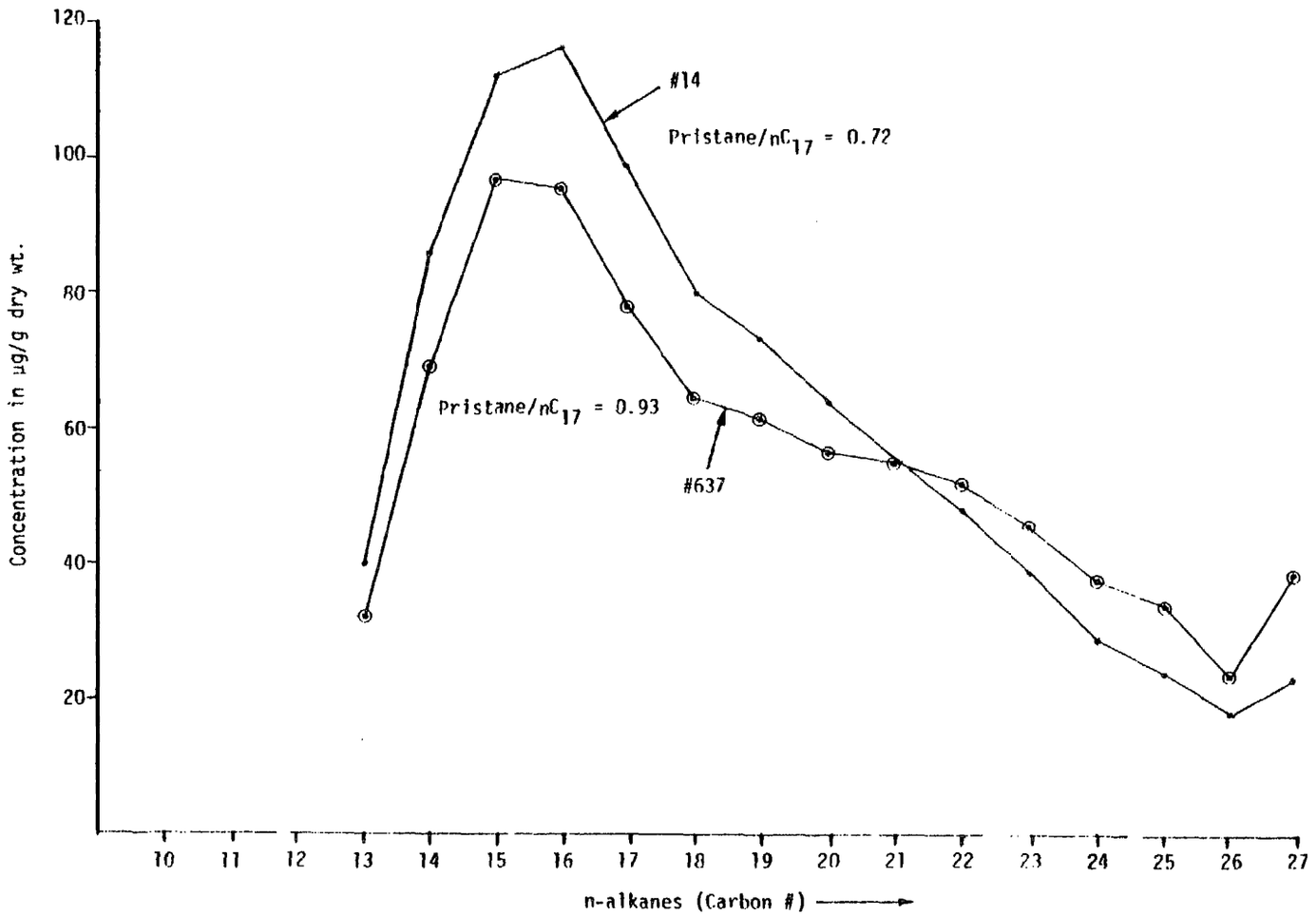



Figure 6. Concentration abundance of the n-alkanes for a sediment oil spike of 50 parts per thousand artifically weathered crude illustrating the time zero sample (•) and sample after one year of weathering (⊙).

show that while the overall concentrations of the lower molecular weight mono and di-cyclic aromatic compounds were reduced in the weathered crude oil compared to the fresh crude oil, once the artifically weathered oil reached the sediment, further degradation and loss of the aromatic compounds did not occur.

When 1.0 ppt weathered crude oil was spiked into the sediments, much greater degradation and loss of the lower molecular weight n-alkanes occurred as illustrated by the data in Figure 17. In Figure 17 the loss of lower molecular weight aliphatic compounds can clearly be observed in the artificially weathered oil as it was spiked into the sediments. The sample collected after one year of weathering at Kasistna Bay contained essentially no aliphatic hydrocarbons below $nC_{24}$. This was very similar to the case when 1.0 ppt fresh crude oil was spiked into the sediments and similar decreases in the aliphatic fraction were observed. The data in Figure 12B, however, show that the relative concentrations of aromatics in the 1.0 ppt weathered crude did not decrease significantly over the year period after the oil was introduced into the sediment. Quite clearly from these results, after fresh or weathered oil is incorporated into the sub-Arctic sedimentary regime at concentrations greater than 1.0 ppt, only limited additional degradation of the aromatic fraction occurs, at least in periods up to one year.

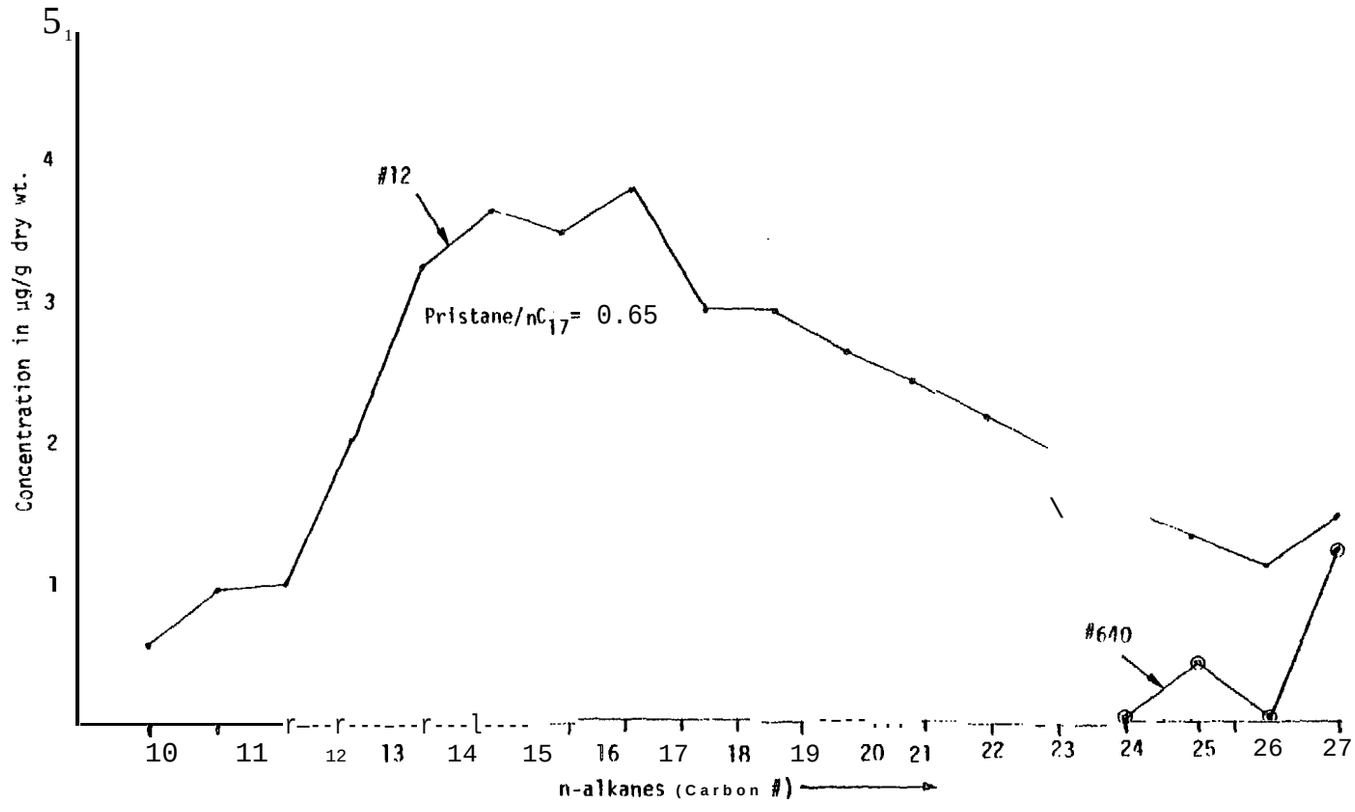



Figure 17. Concentration abundance of the n-alkanes for a sediment oil spike of 1.0 parts per thousand artifically weathered crude illustrating the time zero sample (•) and sample after one year of weathering (⊙).

Sadie Cove Oil/Nutrient Spiked Experiments

Figure 18 presents the aliphatic fraction chromatograms obtained on a) the 50 ppt oil plus starch b) 50 ppt oil alone and c) 50 ppt oil plus Chiton samples from Sadie Cove. The three chromatograms are essentially identical showing that little or no degradation of the oil occurred at the 50 ppt level. This is also reflected quantitatively by comparing the numbers in Table 1 for samples No.s 782, 779 and 780. These data suggest that the total reoslved hydrocarbons and unresolved complex mixtures are essentially identical in the three samples. Other similarities include the odd/even hydrocarbon ratios, the ratio of the sum of pristane plus phytane to the total n-alkanes, and the pristane/ $nC_{17}$ and phytane/$nC_{18}$ ratios. Essentially, these data suggest that at the 50 ppt level degradation is not nutrient limited. Figure 19 presents the aromatic fraction chromatograms obtained on the same three Sadie Cove sediment samples: a) oil plus starch, b) oil alone and c) oil plus Chiton. As the data in Table 2 illustrate, the aromatic compounds which were identified appear to be essentially the same in all three samples, although there may be some decrease in the levels of aromatic compounds in the oil and starch sample (a). Replicate analyses would be required to determine if the subtle difference in overall aromatic compound levels is statistically significant. Alternatively, it may be prudent to examine 1.0 ppt oil spikes in the presence and absence of nutrients to determine if enhanced aromatic hydrocarbon degradation can be induced to lower overall hydrocarbon levels where the inherent toxicity may be reduced.

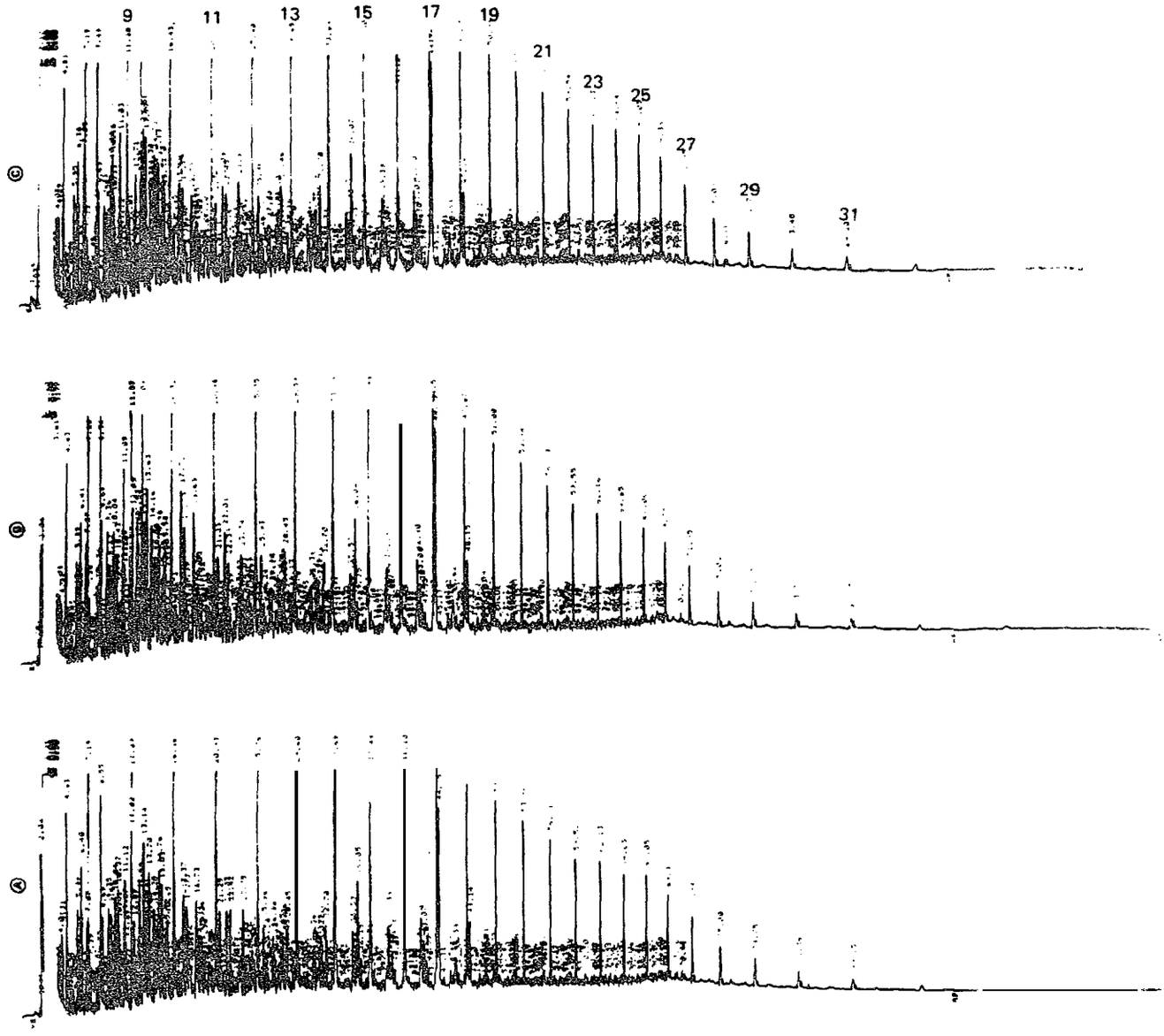



Figure 18. Flame Ionization Detector capillary gas chromatograms of aliphatic fraction extracts obtained on: A, 50 ppt fresh Oil plus starch, B, 50 ppt fresh Oil alone, and C, 50 ppt fresh Oil plus Chitin after one year of natural weathering in the sediments of Sadie Cove.

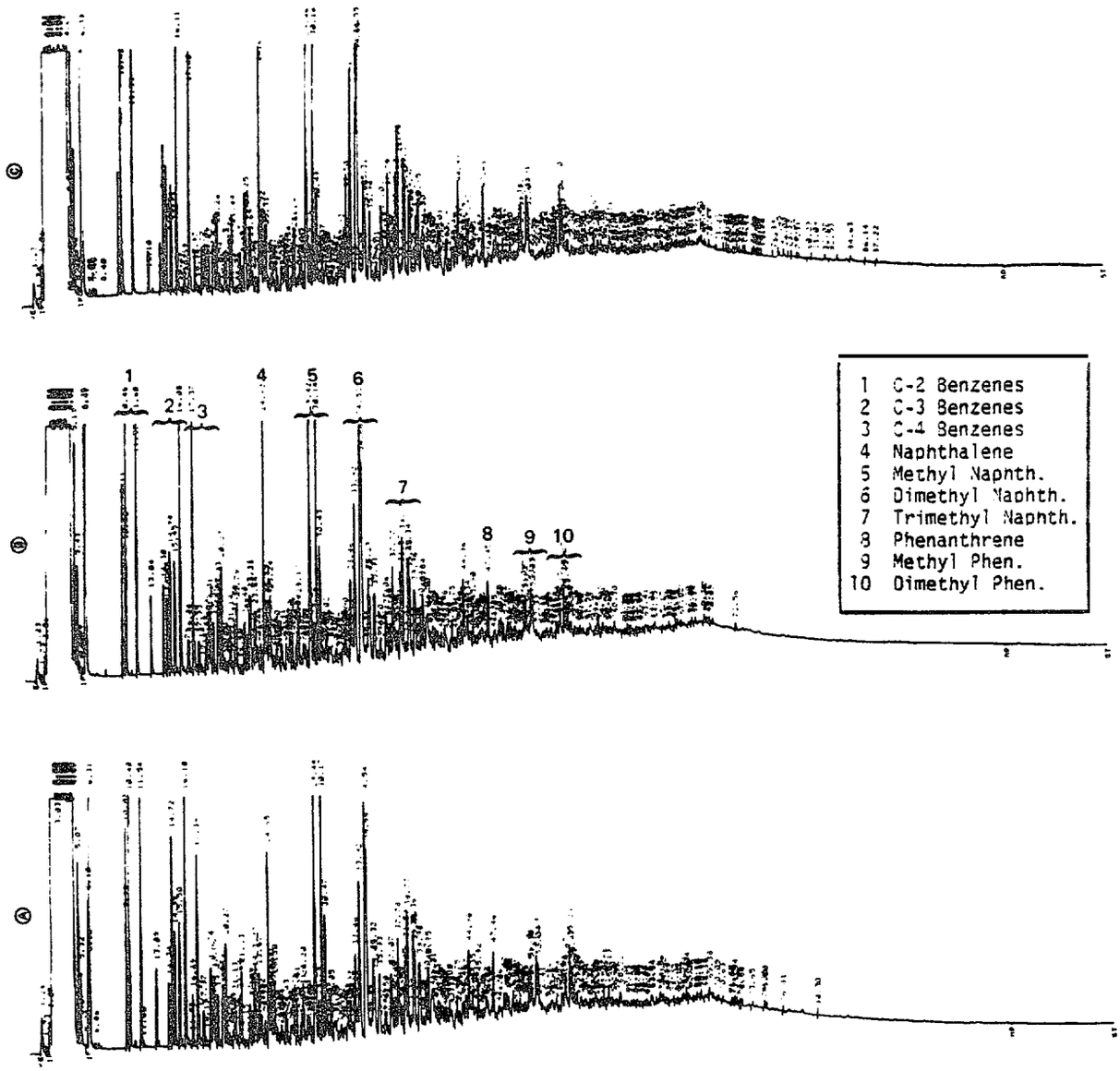



Figure 19. Flame Ionization Detector capillary gas chromatograms of aromatic fraction extracts obtained on: A, 50 ppt fresh Oil plus starch, B, 50 ppt Oil alone, and C, 50 ppt fresh Oil plus Chitin after one year of natural weathering in the sediments of Sadie Cove.

SUMMARY

The results presented here support the conclusion that in a major oil spill event in the sub-Arctic marine environment, the most significant weathering of the oil will occur at the air/sea interface or in the water column before the oil is incorporated into the sedimentary regime. This is particularly true in fine-grain sediment matrices in low-energy environments. Once levels of fresh and weathered Cook Inlet Crude oil reached concentrations in excess of 1 ppt in the sediment plots examined in the study, very little additional weathering or loss of higher molecular weight aromatic hydrocarbons occurred. At spiked levels of 50 ppt with both fresh and weathered crude oil, nearly complete inhibition of microbiological utilization or selective removal of aliphatic hydrocarbons was also observed, especially for those sediments spiked with fresh crude. Recovery of biological activity and selective utilization of aliphatic hydrocarbons did occur in the samples spiked with fresh and weathered crude at 1 ppt, and in the 0.1 ppt spiked samples, there was little or no evidence of either aliphatic or aromatic petroleum hydrocarbon contamination after one year. At that time, the 0.1 ppt spiked samples appeared to contain only the same biogenic hydrocarbons observed in the non-spiked control sediment samples from Kasitsna Bay.

In the study plots which were spiked with 50 ppt oil plus added nutrients (starch and Chitin), there was no evidence of any enhanced biotic recovery or selective hydrocarbon utilization with either fresh or weathered crude oil. This suggests inhibition of biological processes

from the high levels of toxic aromatic compounds in the oil itself rather than inhibition from limited nutrient concentrations. To more accurately address the role of added nutrients in oil degradation, detailed analyses should be completed on lower spiked oil concentrations in the presence and absence of nutrients. Also, experiments to assess the role of dissolved oxygen, grain-size, the energy (tidal and wave) input to the sedimentary environment, total organic carbon content and other factors such as total bio-mass, could be considered in future studies.

From the results obtained on the fresh and weathered crude oils and the sediment samples examined in this program, it appears that the maximum amount of weathering and removal (dissolution and evaporation) of toxic components can be achieved if spill clean up and treatment efforts are designed to prolong the time that the oil remains on the water surface or suspended in the water column. This may suggest limited use of dispersants or detergents in certain spill situations, particularly if damage to coastal zones is not imminent. Containment and recovery of the residual higher molecular weight materials should take precedence over other strategies such as chemical dispersal which may result in higher sub-tidal sediment loadings.

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